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A study of Low C/N Ratio Waste Water Treatment Using Fluidized Bed Bioreactor

Kai Li, *The University of Western Ontario*

Supervisor: Dr. Jesse Zhu, *The University of Western Ontario*
Joint Supervisor: Dr. George Nakhla, *The University of Western Ontario*
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Abstract

In wastewater treatment field, one of the severe challenges is the handling of ammonia-rich wastewater with a low C/N ratio. The failure of nitrogen treatment can lead to adverse ecological and biological effects including depletion of dissolved oxygen, eutrophication, toxicity to aquatic life, and reduction in the suitability of water for reuse. Conventionally, extra organic carbon dosing is required in treating low C/N wastewater. Alternately, partial nitrification is of interest as an emerging technology for its' lesser need of organic carbon addition and cost savings in aeration. In this study, a lab-scale partial nitrification fluidized bed bioreactor (PNFBR) and a pilot-scale circulating fluidized bed bioreactor (CFBBR) were investigated for the treatment of ammonia-rich synthetic wastewater and low C/N ratio domestic wastewater, respectively.

The results of the this study demonstrated that the PNFBR is capable of handling synthetic wastewater with exceptionally high ammonia concentrations (up to 400 mg NH_4^+-N/L) at the maximum nitrogen loading rate (NLR) of 0.8 kg N/(m^3·d) without dosing extra carbon source. By controlling dissolved oxygen of 1.31 mg/L in the system, partial nitrification was observed at a hydraulic retention time (HRT) of 18 hours. The effluent of PNFBR achieved a NO_2^--N /NH_4^+-N ratio of 1.27, which can be utilized as appropriate

influent of anaerobic ammonium oxidation (anammox) process towards complete nitrogen removal.

Additionally, domestic wastewater with Low C/N (2.8) ratio was treated in a pilot-scale CFBBR at various OLRs (organic loading rates) ranging from 0.06 to 0.44 kg COD/m^3-d and NLRs (Nitrogen loading rates) ranging from 0.03- 0.07 kgN /(m3·d). Glucose was dosed to provide enough carbon source. The CFBBR was able to achieve a 84% reduction in carbon and a 90.5% reduction in nitrogen, with the effluent TN < 20mg/L, COD < 60mg/L.

Key words: wastewater, fluidized bed bioreactor, partial nitrification, biological nitrogen removal.

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List of Nomenclature

Q_c — Carbon source influent flowrate

Q_{D-D} — Recycling from downer to downer

Q_{D-R} — Recycling from downer to riser

Q_{inf} — Influent flowrate

Q_{R-R} — Recycling from riser to riser

List of Abbreviations

AAOB   Anaerobic Ammonia Oxidation Bacteria

Alk   Alkalinity

Anammox   Anaerobic ammonium oxidation

AOB   Ammonium oxidizing bacteria

BOD   Biochemical oxygen demand

CFBBR   Circulating fluidized bed bioreactor

HDPE   High-density polyethylene

HRT   Hydraulic retention time

NH_4-N   Ammonia nitrogen

NO_2-N   Nitrite nitrogen

NO_3-N   Nitrate nitrogen

NOB   Nitrite oxidizing bacteria

PNFBR   Partial nitrification fluidized bed bioreactor

sCOD   Soluble chemical oxygen demand

SDNR   Specific denitrification rate

SN   Soluble total nitrogen

SNR   Specific nitrification rate

SRT   Sludge retention time

TCOD   Total chemical oxygen demand

TN   Total nitrogen

TSS   Total suspended solid

VSS   Volatile suspended solid

1. Introduction

1.1 Rationale

The discharge of nitrogen has been strictly controlled in natural water bodies in the last two decades in wastewater treatment plants because eutrophication can be stimulated by nitrogen as well as phosphorus. Biological nitrogen removal processes have been applied widely throughout the world, however, it is difficult to improve N removal rates when treating low C/N (carbon/nitrogen) ratio wastewater, such as landfill leachate and sludge digester liquor with high ammonia concentration exceeding 1000mg/L, because extra organic matter is needed. In addition, this high level of ammonium makes it difficult to be biologically nitrified due to the ammonia toxicity to nitrifiers and the extensive oxygen requirement for nitrification.

Generally, the nutrients removal efficiency is relatively low when the influent C/N is lower than 5. Low C/N wastewater can also be found in domestic wastewater in developing countries due to incomplete sewage systems. Being held in an anaerobic tank before entering the city's sewers system can result in ammonia accumulation converted from nitrogen fraction in the organic matter. In this study, the C/N ratio of this domestic wastewater tend to remain as low as 2.8 with the ammonia concentration 4 times greater than normal municipal wastewater.

Partial nitrification and anaerobic ammonia oxidation (anammox) processes, as the emerging biological nitrogen removal processes, are eliciting the interest of researcher for the treatment of ammonia rich wastewater due to the low biomass production, as well as low oxygen and organic demands.

The fluidized bed bioreactor has gained wide industrial applications including water and wastewater treatment. Unlike conventional suspended growth processes, the microorganisms are attached on media, such as sand or plastic particles. These 'bioparticles" are suspended in the reactors due to a force provided by the up-flow liquid. The high concentration of biomass results in a significant decrease in bioreactor volume requirements.

1.2 Objectives

The objectives of this thesis are as follows:

1) Achieve partial nitrification in a fluidized bed bioreactor (PNFBR) with effluent nitrite to ammonia ratio of 1.3:1 at limited dissolved oxygen (DO) and alkalinity (Alk) condition, so that the effluent of PNFBR can be used as the influent of an anaerobic ammonia oxidation (anammox) process for further nitrogen removal (not included in this study).

2) Investigate low C/N municipal wastewater treatment using a circulating fluidized bed

bioreactor (CFBBR) in Guangzhou Institute for Energy Conversion (GIEC), China. Optimize the operation condition by adjusting extra carbon dosing and fluidization velocity to meet the discharge standard

1.3 Scope of the thesis

This thesis mainly focuses on the high ammonia and low C/N ratio wastewater treatment using fluidized bed bioreactors. Chapter 2 provides a literature review on the principles and applications of conventional and emerging nitrogen removal technologies. Chapter 3 discusses the operation and performance of the partial nitrification fluidized bed bioreactor for ammonia-rich wastewater treatment. Chapter 4 focuses on the performance of the circulating fluidized bed bioreactor for domestic wastewater treatment in China.

2. Literature Review

2.1 Introduction

Nitrogen is a necessary nutrient for the growth of aquatic and terrestrial plant life and is an essential fertilizer. The presence of high levels of nitrogen in waterways can stimulate the rapid growth of aquatic plants and microorganisms, such as algae. This process is referred to as eutrophication. The increased presence of plants and microorganisms in a receiving water body deprives the water of dissolved oxygen, increases the turbidity of the water, and decreases its suitability for reuse.

Eutrophication is not only toxic to aquatic life, but also to human beings. Too much nitrogen, as nitrate, in drinking water can be harmful to young infants. When a child consumes the nitrate-contaminated water, the nitrate compound is converted to nitrite in the infant's digestive tract and transported throughout their body. A portion of these the nitrite ions make their way to the host's circulatory system. Once inside the system, the nitrite ions bond to iron in the blood cells, which prevents the cells from obtaining oxygen. The deprivation of oxygen throughout the children's body causes their skin to turn blue and their major organs begin to loose functionality. A prolonged insufficient oxygen supply to the brain can cause paralysis and can eventually lead to death (Gerardi, 2002).

Nitrogen in raw municipal wastewaters is predominantly in the form of organic nitrogen, ammonia (-III) and to a much lesser extent as nitrate (+V) and nitrite (+III). Ammonia and organic nitrogen are often lumped together and measured as Total Kjeldahl Nitrogen (TKN). For municipal wastewater, about 60% to 70% of the TKN is NH4-N. Although nitrogen recovery for wastewater is an emerging alterative to this problem, biological nitrogen removal (BNR), is still the most economically feasible and effective treatment for municipal and industrial wastewaters (Ahn, 2006).

2.2 Conventional Biological Nitrogen Removal (BNR) Technology

BNR processes have been developed for one century, and involve two steps: nitrification and denitrification. The main objective of the BNR processes is the conversion of ammonia and organic nitrogen to nitrogen gas, which is then released to the atmosphere due to its low solubility and thus is removed from the water. BNR processes can be divided into the conventional processes and emerging processes (Section 2.4), which are discussed further below.

2.2.1 Conventional BNR Processes: Nitrification

Nitrification is the term used to describe the two-stage biological processes in which ammonia is oxidized to nitrate under strict aerobic conditions (Metcalf & Eddy, 2003). In the first stage, the oxidation of ammonia is performed by ammonia-oxidizing bacteria (AOBs), which oxidize ammonia (NH_4^+) to nitrites (NO_2^-). In the second stage, a second

type of nitrifying species, nitrite-oxidizing bacteria (NOBs), are responsible for the oxidation of nitrites (NO_2^-) to the nitrates (NO_3^-), which has less toxic to waterbody. In these two stages, reactants ammonia or nitrite are used as an energy source and electron donors, while molecular oxygen is used as an electron acceptor. The stoichiometry of biological nitrification is as follows:

Equations 2.1-2.3: Stoichiometry of Nitrification

$$AOBs: \quad 2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O \qquad\qquad (2.1)$$

$$NOBs: \quad 2NO_2^- + O_2 \rightarrow 2NO_3^- \qquad\qquad (2.2)$$

$$Total\ oxidation\ reaction: \quad NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O \qquad\qquad (2.3)$$
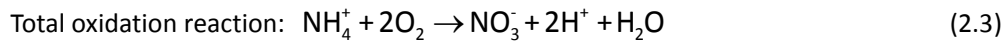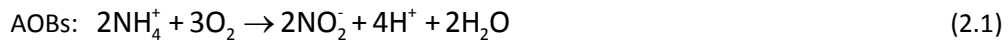
According to the equations above, for each g of ammonia-nitrogen (NH_4^+-N) converted to nitrate-nitrogen (NO_3^-N), 4.57 g of O_2 is required, with 3.43 g O_2/g N and 1.14 g O_2/g N in each stage, respectively. Since this process generates acid, alkalinity is needed to neutralize the solution. The full nitrification reaction can be approximated by Equation 2.4.

Equation 2.4: Stoichiometry of Nitrification With Alkalinity

$$NH_4^+ + 2HCO_3^- + 2O_2 \rightarrow NO_3^- + 2CO_2 + 3H_2O \qquad\qquad (2.4)$$

Based on Equation 2.4, the amount of alkalinity required to carry out the reaction is 7.14

g of alkalinity as CaCO₃ per g of ammonia-nitrogen converted.

The reaction above releases energy, which can be utilized by AOBs and NOBs for synthesis of new cells. In addition, these reactions likes nitrification, also comsume oxygen while generate H^+ and nitrite as an intermediate product. Equations for the biochemical conversion of ammonia to nitrate with cell synthesis for AOBs and NOBs are as follows (USEPA., 1993):

Equations 2.5-2.7: Biochemical Conversion of Ammonia to Nitrate for Cell Synthesis

AOBs: $55\,NH_4^+ + 76\,O_2^- + 109\,HCO_3^- \rightarrow C_5H_7O_2N^* + 54\,NO_2^- + 57\,H_2O + 104\,H_2CO_3$ (2.5)

NOBs: $400\,NO_2^- + NH_4^+ + 4\,H_2CO_3 + HCO_3^- + 195\,O_2 \rightarrow C_5H_7O_2N^* + 400\,NO_3^- + 3\,H_2O$ (2.6)

Overall Reaction:

$NH_4^+ + 1.83\,O_2 + 1.98\,HCO_3^- \rightarrow 0.021\,C_5H_7O_2N^* + 0.98\,NO_3^- + 1.041\,H_2O + 1.88\,H_2CO_3$ (2.7)
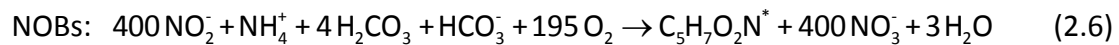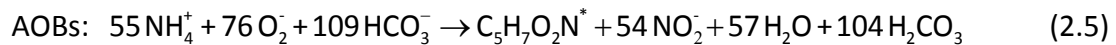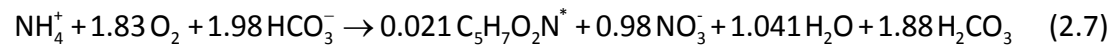
$C_5H_7O_2N^*$ is used to represent synthesized bacterial cells.

AOBs can be roughly divided into two categories (Gallert and Winter, 2005):

1) Autotrophic AOBs, such as Nitrosomonas, Nitrosococcus and Nitrosospira, Nitrosolobus, and Nitrosovibrio. These bacteria convert ammonium (NH4+) or ammonia (NH3) to nitrite and grow by consuming inorganic nitrogen and carbon compounds under aerobic conditions.

2) Heterotrophic AOBs, such as Arthrobacter, Flavobacterium and Thiosphaera. Unlike autotrophic AOBs, the heterotrophic AOBs can use both organic and inorganic nitrogen as substrate. So Heterotrophic nitrification can be defined as the oxidation

of ammonium/ammonia or of organically bound nitrogen of the oxidation state 3 to hydroxylamine, and subsequently nitrite by heterotrophic bacteria under aerobic conditions (Papen, 1998). However, heterotrophic AOBs have much less ammonia oxidation rate than autotrophic AOBs ($1/10^3$ – $1/10^6$). In biological nitrogen removal, autotrophic AOBs play a more important role.

Characteristics of different autotrophic AOB and NOB species are presented in tables 2.1-2.2

Table 2.1 Characteristics of different AOB species

Parameters	Nitrosomonas	Nitrosococcus	Nitrosospira	Nitrosolobus	Nitrosovibrio
Shape	Coccus	Coccus	Spiral	-	Spiral
Size/μm	(0.7-1.5)× (1.0-2.4)	(1.5-1.8)× (1.7-2.5)	(0.3-0.8)× (1.0-8.0)	(1.0-1.5)× (1.0-2.5)	(0.3-0.4)× (1.1-3.0)
pH	7.0-8.5	6.0-8.0	6.5-8.5	6.0-8.2	7.5-7.8
Temperature/℃	5-40	2-40	20-35	15-30	25-40

Table 2.2 Characteristics of different NOB species

Parameters	Nitrobacter	Nitrospina	Nitrococcus	Nitrospira
Shape	Rod	Rod	Spherical	Spiral
Size/μm	(0.6-0.8)× (1.0-2.0)	(0.3-0.4)× (2.7-6.5)	1.5-1.8	0.3-0.4
pH	6.0-7.5	6.5-7.0	6.8-8.0	6.5-7.0
Temperature/C	5-10	25-30	15-30	25-30

2.2.2 Conventional BNR Processes: Denitrification

Denitrification is an anoxic process, where nitrate serves as an electron acceptor and is converted into inert nitrogen gas (N_2) by facultative heterotrophic bacterial species such as pseudomonas and clostridium. Unlike the nitrification process, denitrification uses organic matter as electron donor and nitrite or nitrate as an electron acceptor instead of oxygen. The common carbon sources are: acetate, glucose, sugar, methanol and a variety of food and beverage waste. All these biodegradable organic matter can be represented by chemical formula $C_{10}H_{19}O_3N$ (U.S. EPA, 1993), and the reaction can be simplified by Equation 2.8.

Equation 2.8: Stoichiometry of Heterotrophic Denitrification

$$C_{10}H_{19}O_3N + 10\,NO_3^- \rightarrow 5\,N_2 + 10\,CO_2 + 3\,H_2O + NH_3 + 10\,OH^- \tag{2.8}$$
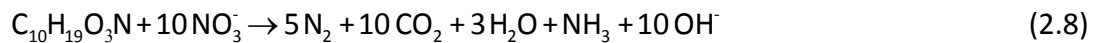
However, the denitrification reactions with different carbon source are all slightly different. For example, when acetate is used as carbon source, the reaction stoichiometry is in accordance with equation 2.9:

Equation 2.9: Denitrification using Acetate as Carbon Source

$$5\,CH_3COOH + 8\,NO_3^- \rightarrow 4\,N_2 + 10\,CO_2 + 6\,H_2O + 8\,OH^- \tag{2.9}$$
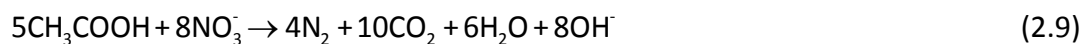
According to the above equations, for every mol of nitrate consumed, 1 mol of alkalinity is produced. In another word, for every gram of nitrate consumed by the organisms, 3.57 grams of alkalinity as CaCO3 is produced. In consideration of alkalinity consumption

in nitrification reaction (7.14g alk as CaCO₃/ gN), half of alkalinity is recovered in the denitrification process.

Equations 2.10: Denitrification using Acetate as Carbon Source with Cell Synthesis

$$0.819\,CH_3COOH + NO_3^- \rightarrow 0.068\,C_5H_7NO_2 + HCO_3^- + 0.301\,CO_2 + 0.902\,H_2O + 0.466\,N_2 \quad (2.10)$$

The factors affect denitrification process is presented in Table 2.3.

Table 2.3 Optimums operational conditions for denitrification process

Parameters	Value
Temperature	20-40C
Dissolved oxygen	< 0.2 mg/L
Free nitrous acid	<0.01mg/L
pH	7.0-7.5
SRT/d	3-6days

2.3 Conventional BNR Processes

2.3.1 Suspended Growth

The Ludzack Ettinger process is a two-step suspended growth nitrification/denitrification process, which has a history of more than 50 years. Nonetheless, denitrificaiton reaction is limited greatly by RAS recycle ratio. Therefore, Modified Ludzack Ettinger (MLE) process, one of the most common BNR processes was designed by Barnaed (1973). The main difference between MLE and original Ludzack Ettinger process is that it provides an internal recirculation from oxic zone to anoxic zone, which contains rich nitrate to

conduct denitrificaiton reaction. As a result, both higher denitrifiaciton rate and better whole nitrogen removal efficiency can be achieved.

Inf. → Pre-Anoxic → Oxic (nitrification) → Clarifier → Eff.

Return Activated Sludge (RAS)

WAS
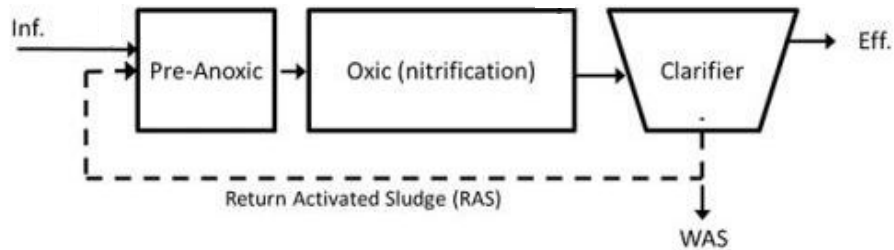
Fig. 2.1 Ludzack Ettinger Process Schematic

Nitrate rich mixed liquor recirculation

Inf. → Pre-Anoxic → Oxic (nitrification) → Clarifier → Eff.

Return Activated Sludge (RAS)

WAS
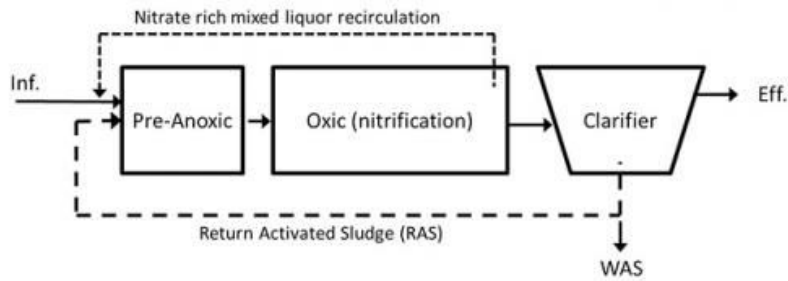
Fig. 2.2 Modified Ludzack Ettinger (MLE) Process Schematic

Table 2.4 MLE system parameters (Hafez, H. et al, 2010):

System Parameters	Unit	Value
pH	/	6.0-8.0
HRT	h	4-8
SRT	d	7-20
MLSS	mg/L	2000-3000
NLR	kg/(m^3·day)	0.06
TN removal	%	75%-80%
RAS of influent	%	50-100

Advantages:

The MLE is a well-known and relatively easy-to-operate system with low capital and operation cost and a strong ability to resist shock loading. In the MLE process, nitrification or denitrification, as well as organic matter such as COD removal can be achieved at the same time.

Limitations:

Firstly, Nitrogen-removal capability is a function of internal recycle. In order to improve nitrogen removal efficiency, the internal recycle ratio has to be increased, thus increasing operating costs. Secondly, the internal recycle flow from the oxic zone contains DO, making it difficult to maintain the desired anoxic condition, which will decrease the denitrification efficiency. Thirdly, it is difficult to achieve 90% or above nitrogen removal efficiency. In addition, it also has large building footprint and infrastructure requirements.

2.3.2. Sequencing Batch Reactor (SBR)

SBRs are considered as fill and draw version of the conventional activated sludge process. In general, the systems have 5 steps as shown in Figure 2.3, which are carried out in sequences as follows:

(1) Fill. The reactor is filled with wastewater by opening inlet valve, while non-aerated mixing is provided by mechanical means.

(2) React.   During this stage, aeration of the mixture by mechanical pumps or by supplying air into diffusers located at the bottom of the tank to promote nitrification reactions.

(3) Settle. During this stage, no aeration or mixing is provided and the produced sludge is settled to the bottom of the reactor. Under these conditions, denitrification predominantly occurs during the anoxic fill.

(4) Decant. The outlet valve is opened during this stage and the treated liquid supernatant exits the tank as effluent. No mixing or aeration is applied so that further denitrification can still proceed.

(5) Idle. This is a period that provides time for one SBR reactor to finish its filling stage before switching to another.

Normally the wastewater treatment plant needs at least 2 tanks to maintain continuous flow, so that one is in stages (1), while another goes through stages (2)-(4). For a typical cycle, 3, 2, 0.5, 0.5 hours are required respectively.
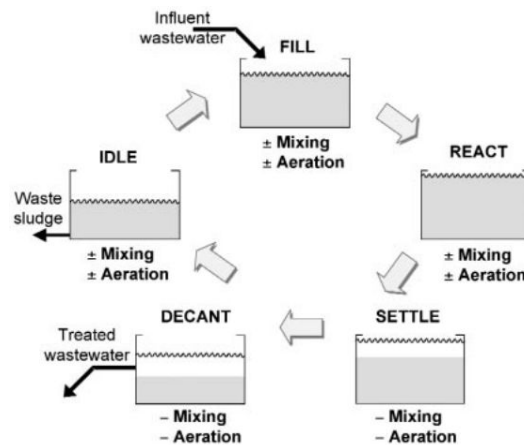
Fig. 2.3 SBR Schematic

Table 2.5 SBR system parameters (Gustavsson, D.J, et al, 2008)

System Parameters	Unit	Value
pH	/	6.0-8.0
HRT	h	15-40
SRT	d	10-30
MLSS	mg/L	3000-5000
NLR	kg/(m^3·day)	0.6-0.65
TN removal	%	91%-95%

Advantages:

- The process is flexible, easy to operate and also simplified because there is no requirement of final clarifiers or returned activated sludge pumping.

- Quiescent settling can provide better solids separation (low TSS concentration in effluent).

- Low capital cost and small footprint is required, applicable for different sized treatment plant.

Limitations:

- More complex for design and process control.

- Higher maintenance on the unit as well as increased operational cost is required for instruments and monitoring devices.

- Equalization of batch effluent prior to filtration and disinfection maybe needed.

2.3.3 Attached Growth Processes

In an attached growth system, microorganisms are grown in a biofilm that is attached to the surface of a solid support medium (Chen et al., 2006). This process in which the individual microorganisms are immobilized, is also called a fixed film process. Wastewater treatment processes are based on the use of two types of attached growth; static biofilms such as trickling filters, particulate biofilms such as fluidized bed bioreactors. Advantages of biofilm processes are primarily due to the active biomass built up and maintained in the reactor through attachment to solid surfaces. Thus, fixed-film processes allow the accumulation of high biomass concentrations, which facilitate large volumetric loadings and maintain good effluent quality. Moreover, biofilm reactors are mainly useful when slow growing microorganisms like nitrifiers have to be kept in a wastewater treatment process. The biofilm surface area in these reactors does not typically exceed 200 m^2/m^3 (van Loosdrecht *et al.,* 1993).

2.3.4 Trickling Filters (TF)

Trickling filters have been used to treat wastewaters in decades. They consist of a non-submerged fixed bed bioreactor of rocks, coke, lava, or plastic as media over which wastewater flows downward. The use of a carrier media promotes attached growth operations wherein a layer of biofilm to grow on the bed of media. The diameter of the

media is typically 3- 10 cm and has a depth of TRICKLING FILTERS reactor is 1-6 meter. The waste streams is sprayed from the top of the reactor through feed pipes, then 'trickles' down through the media where it is then collected and removed at the bottom of the reactor. Aerobic conditions are maintained by spraying, diffusion, or by air ejected through the bed. Because the bacteria are growing on the inert media, they can grow much larger than they could from a suspended growth process. The maximum biomass thickness is normally controlled by hydraulic dosage rate, type of media, type of organic matter, temperature and nature of the biological growth. As a layer of aerobic microorganisms thickens through microbial growth, oxygen cannot penetrate the medium face, and anaerobic organisms develop. As the biological film continues to grow, the microorganisms near the surface lose their ability to cling to the medium, and a portion of the slime layer falls off the filter. This process is known as sloughing. The sloughed solids are picked up by the underdrain system and transported to a clarifier for removal from the wastewater (EPA,2000).
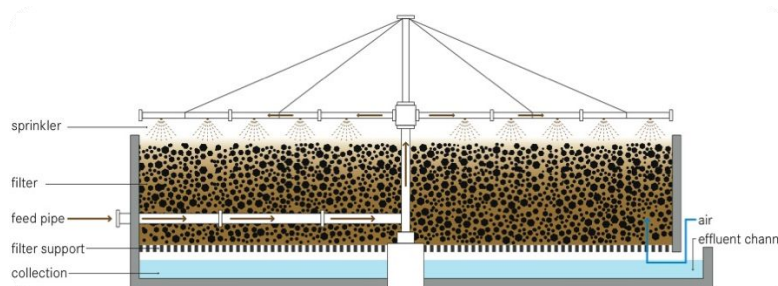
Fig. 2.4 Trickling Filters Process Schematic

Table 2.6 Trickling filters system parameters (Dai, Y. et al, 2013)

System Parameters	Unit	Value
pH	/	6.0-8.0
Temperature	^oC	8-28
Hydraulic loading	m^3/m^2-d	1-10 (nitrification)
HRT	h	7-20
NLR	$kgNH_3$-$N/(m^3 \cdot day)$	0.03-0.25
NH_3-N removal	%	90-98
Recirculation ratio	/	100%

Advantages:

Trickling filters system is a process with relatively low level of technology, easy operation and low cost of the system is one of comparative advantages. Besides, compared to suspended growth systems, the advantages of an trickling filters system include more effective of treating high concentrations of organics, lower requirement of energy consumption and less sludge production. So trickling filters system is applicable for communities with small or medium sizes.

Limitations:

TRICKLING FILTERS system is not considered to achieve nitrification rather than denitrification, that means nitrogen can not be removed completely in this process. In

addition, under high organic loadings, the growths of slime will cause plugging, of the void spaces between the medium, thus, limiting volume of void spaces in medium. It also restricts the air circulation and the amount of oxygen available for the nitrifier. Additional treatment may be needed to meet more stringent discharge standards.

2.3.5 Fluidized Bed Bioreactor

When a liquid flows upwards through a bed of granular particles, the particles are subjected to hydraulic drag forces. These drag forces cause the bed to expand and when the drag forces totally counteract with the force of gravity, the particles become suspended in the stream of flowing liquid. This state is called fluidization and reactors with fluidized beds have gained wide industrial applications including water and wastewater treatment. The use of fluidized bed reactors in biological treatment of water and wastewater has been traced back to the 1940s in the UK (Pugh, 1945 cited by Sutton and Mishra, 1994) when it was used for ammonia removal. Most water and wastewater applications of fluidized bed reactors use either activated carbon or sand as media. Microorganisms attach to the surface of the media forming a biofilm. The biofilm derives its energy from nutrients contained in the bulk water. Soluble matter diffuses into the biofilm while particulate matter is degraded either by attachment to the biofilm surface or by extra-cellular enzymes (Arvin and Harremoes, 1990). The fluidized bed configuration has a number of features, which are useful in the context of biological wastewater treatment, in general, and ammonia removal in particular.

The classical circulating fluidized bed system consisting predominantly of two fluidized bed bioreactors, an anoxic-riser and an aerobic-downer. The nitrification and denitrification processes can be achieved simultaneously with continuous circulation of the liquid between the two columns. The fluids (both raw wastewater and recycle flow) enter from the bottom of the riser and exit at the top of the downer. The solids or particles, which are covered by the biofilm, are recycled between the downer and the riser. The air is normally injected at the bottom of the downer.

The circulating fluidized bed bioreactor (CFBBR) is a slight modification on classical circulating fluidized bed system given above. In CFBBR, the particles keep fluidization in the riser and downer separately, while fluids circulate. The two reactors are operated between the slugging and the turbulent flow regimes Chowdhury . et al, 2009.
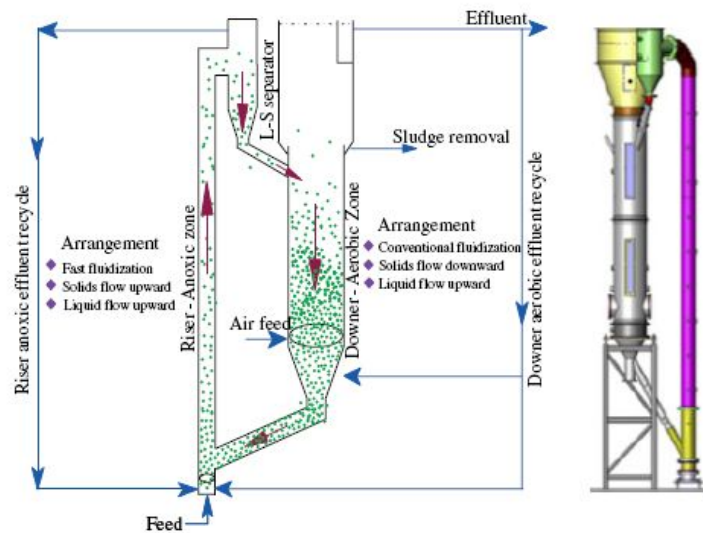
Fig. 2.5 Circulating fluidized bed bioreactor process schematic

Table 2.7 CFBBR system parameters (Chowdhury . et al, 2009)

System Parameters	Unit	Downer	Riser
pH	/	7.0-8.0	7.0-8.0
Temperature	^{o}C	22	22
HRT	h	1.6	0.5
DO	mg/L	>2	0
TN removal	%	85	

2.4 Emerging Biological Nitrogen Removal: Partial Nitrification (PN)

In the interest of reducing energy and chemical addition, scientists are pursing more effective BNR methods. In the past decade, several emerging ideas based on the theory have been developed, such as partial nitrification, anammox   (Jetten, 1999 and Fux, 2002), and the combinational processes of these two technologies, such as Canon (Gong, 2002), Sharon (Shalini, 2012). These technologies provide a more cost effective and energy saving way through interrupting and altering the conventional nitrogen cycle. Several shortcuts or byproducts are involved in these new methods (Ahn, 2006). These methods improve the nitrogen removal rate by providing higher biomass concentration and mass transfer rate in the reactor and the primary nitrogen circulation is not impacted (WEF, 2011).

The novelty of these emerging BNR is mainly due to the following two aspects:

1) The improvement and optimization of new technology- for example, the partial nitrification is an improved process based on the conventional nitrification process.

2) The discovery, development and application of new bacteria. For example, the discovery of Anaerobic Ammonia Oxidation Bacteria (AAOB) leads to the development of the anammox process.

- Reduction of oxygen demand by up to 25 %

- Reduced demand of organic matter for denitrificartion by 40%

- Reduced biomass production by 40% during denitrification

The PN process is not only the fundamental step of emerging BNR, but it also is the rate-limiting step. Therefore increasing the efficiency of PN process is crucial to the success emerging BNR processes. However, PN only changes the presences form of nitrogen, and does not remove it from the wastewater completely. To achieve biological nitrogen removal, a combination of PN with other process is needed. The anammox process is ideal as undertake downstream process following PN.

Table 2.8: Economical comparison between the conventional and emerging BNR processes (Fux and Siegrist, 2004)

Parameter	Unit	PN-anammox	Nitrification-Denitrfication			
Reactor Volume	m^3	75/55/150[*]	75/190[**]			
Sludge Yield	g COD/g COD	-	0.2	0.2	0.4	0.4
Investment	€/kg N	1.3	1.35	1.35	1.35	1.35
Operation	€/kg N	1.15	1.25	1.35	1.25	1.35
Energy	€/kg N	0.15	0.25	0.35	0.25	0.35
Maintenance/analysis	€/kg N	0.7	0.7	0.7	0.7	0.7
Replacement	€/kg N	0.3	0.3	0.3	0.3	0.3
Chemicals	€/kg N	0.05	0.3	0.5	0.4	0.65
Sludge disposal	€/kg N	0	0.15	0.3	0.45	0.75
Total	€/kg N	2.5	3.05	3.5	3.45	4.1

[*]Buffer tank / Partial nitrification / anammox

[**]Buffer tank / nitrification and denitrification

2.4.1 Principles of Partial Nitrification

In 1998, Delft University of Technology successfully developed SHARON$^{@}$ technology which combines partial nitrification with denitrification (Hellinga et al., 1998; Mulder et al, 2001). After that, Delft developed a variety of other emerging BNR processes (Gallet al., 2007; Garrido et al., 1997).

PN actually is the first step in the convention nitrification process (**Equations** 2.1-2.3). It involves only biological oxidation of ammonia to nitrite by AOBs with limited oxygen and alkalinity. The goal of partial nitrification wastewater treatment is to create conditions in

the bioreactor that promote the growth of AOB populations to produce high concentrations of nitrites in the bioreactor's effluent by suppressing further biological conversions of the nitrite to nitrate.

The PN process produces energy (-260.2 kJ $\cdot$ mol $^{-1}$ NH_4^+ -N) (Gallet al., 2007), which can be utilized by AOBs for their growth. This reaction involves two steps:

In the first step, ammonia is converted to hydroxylamine by AOBs with the essential enzyme ammonia monooxygenase (AMO). Then AOBs use hydroxylamine oxidoreductase (HAO) to transform hydroxylamine to nitrite. The CO2 is used by the autotrophic nitrifiers as a carbon source for biomass growth according to the Calvin cycle (Kantartzi et al., 2006).

Equation 2.11 Partial Nitrification Pathway

$$NH4 + \xrightarrow{AMO} NH_2OH \xrightarrow{HAO} NO_3^- \tag{2.11}$$

Partial Nitrification is not very difficult to achieve by pure culture's AOB. However, in the wastewater treatment, the use of pure cultures is not feasible economically because of interference by indigenous microorganisms. Thus mixed culture are employed, wherein NOBs play a big role, which affects AOBs. The main reasons are as follows:

1) The end product of AOBs, such as nitrite, is the substrate of NOBs. Also, AOBs are depended on the presence of NOBs for eliminating the toxic NO2, it therefore aids in the defence against the toxicity of NO2 by preventing its accumulation or formation of toxic by-products such as NO that can inhibit bacterial enzymes (Sudarno et al., 2010).

2) NOBs and AOBs have similar yields, growth and decay rates (Table 2.9), and are thus difficult to separate.

2.4.2 Characteristics of Partial Nitrification

In partial nitrification, ammonia is not only energy source, but also involved in cell synthesis reaction as the nitrogen source. According to Equation 2.3, the theoretical cell yield of AOBs is 0.15 g VSS /g-NH_4^+-N, although the actual yield is even lower, only one-tenth of heterotrophic bacteria for the following reasons: 1) Substrate consumption for cell growth is quite low. Only 14% of the electrons released from general Ammonia oxidation are used for cell growth, much less than 60-70% for the heterotrophic bacteria, (Rittmann and McCarty, 2001). 2) High energy consumption of synthesis. Assimilation needs to consume a lot of reducing powers and ATP (Gallert and Winter, 2005). Low cell yield causes slow cell growth, which makes partial nitrification difficult to start-up and achieve stable operation.

The hydrogen ion is produced during the reaction, which rapidly lowers pH. Since the optimum growth conditions for AOBs are neutral to slightly alkaline (7.0 to 8.5), substantial changes in pH can cause a huge impact on the partial nitrification process.

Ammonia in the water can be divided into free ammonia (NH3, or FA) and ammonium ion (NH_4^+), as shown in Equation 2.12).

Equation 2.12 Ionization Equilibrium between FA and NH_4^+

$$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^- \tag{2.12}$$
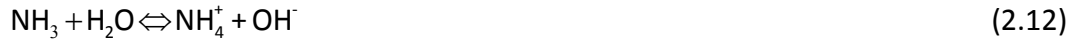
Monod kinetics are commonly used to describe microbial kinetics in general and can be also used to describe the growth of AOBs. In the absence of inhibition (or low inhibition), the growth kinetics for ammonia oxidation reaction can be described by equation 2.9:

Equation 2.13 Growth Kinetic of AOBs

$$r^{AOB} = r_{max}^{AOB} \bullet \frac{S_{O_2}}{S_{O_2} + K_{O_2}^{AOB}} \bullet \frac{S_{NH_3}}{S_{NH_3} + K_{NH_3}^{AOB}} \bullet \frac{S_{TIC}}{S_{TIC} + K_{TIC}^{AOB}} \tag{2.13}$$

The kinetics of Nitrosomonas europaea in pure culture kinetics are shown in Figure 2.6 (Kantartzi et al., 2006), with the parameters listed in Table 2.9.
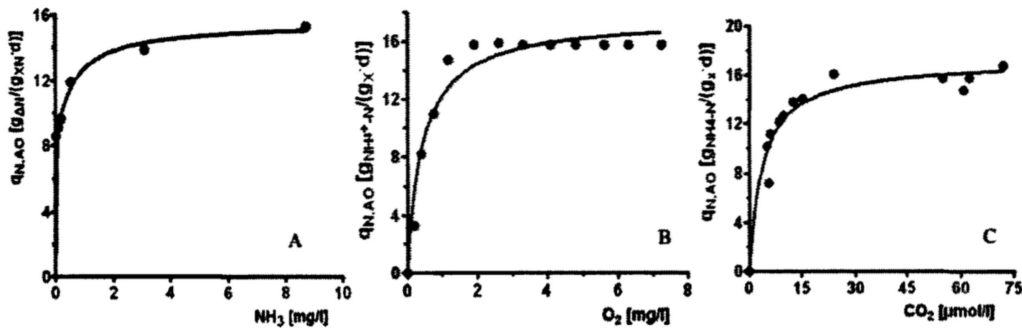
Figure 2.6 Kinetic Curves for Nitrosomonas europaea in different pure culture

A:NH3 is the limiting substrate B:O2 is limiting substrate C：CO2 is limiting substrate

2.4.3 Optimization of Partial Nitrification

The basic goal of the partial nitrification process is to achieve nitrite accumulation.

Accordingly, optimization strategies focus on increasing the population and activity of AOBs rather than NOBs. The impact process parameters for AOBs and NOBS are discussed below:

1) Dissolved Oxygen (DO). DO control is the most common method for PN process. The Monod half-saturation constant of DO for AOBs and NOBs are 0.3 mg O2/ L and 1.1 mg O2/ L at 30C, respectively (Wiesmann, 1994). Since AOBs' half –saturation DO centenarian is much larger than NOBs', NOBs' activity dropped significantly at low DO conditions. The critical DO concentration for AOBs to produce nitrite is 1.7mg O2/L (Ruiz et a1, 2003.); nitrite accumulation is more feasible when the DO decreases lower than 1 mg/L, whereas when the DO is greater than 1mg/L, the activity of NOBs begins to recover (Chuang et al., 2007, Sliekers et al., 2005)

2) Free Ammonia (FA). AOBs have higher FA tolerance than NOBs. Generally speaking, when FA concentration is 0.1-1.0 mg N/L, NOB activity is inhibited (Abeling and Seyfried, 1992; Anthonisen et al., 1976). But the FA inhibition concentration varies for the different NOB species. For example, Nitrospira's FA inhibition concentration is 0.04-0.08 mg N/L (Philips et al. 2002), some researchers indicate that in some cases for Nitrobacter, no free ammonia inhibition was detected even at concentrations up to 33 mg N/L (Blackburne et al., 2007). AOB's tolerance concentration of FA is normally 10-150 mg N/ L at 30 C (Anthonisen et al.,1976), which corresponds to 70 -300mgN/L at temperature of 30 ± 5 C and pH between 6.5 – 8 (Van et al., 2007).

It is also reported that NOB can adapt to FA inhibition. After acclimation, NOB can improve their tolerance of FA, which decrease nitrite accumulation rate. Wong-Chong and Loehr (1978) observed that NOBs acclimated to FA could tolerate concentrations as high as 40 mg NH3-N/L, while unacclimated ones were inhibited at concentrations of 4.6 mg NH3-N/L. Turk and Mavinic (1989) observed NOBs acclimated to FA could tolerate concentrations of 11.4 mg NH3-N/L after 58 days' acclimation at temperature of 20 C and pH between 7.0-7.2, while unacclimated ones were inhibited at concentrations of 4.6 mg NH3-N/L.

A higher FA concentration is needed to enhance FA inhibition of NOB, however, AOBs might get inhibited at that point. In general, the FA concentration is recommended to keep at 5-10 mg N/L (Chung et al., 2006).

3) Total Inorganic Carbon/ Alkalinity . Tokutomi et al., (2010) used studied partial nitrification at temperature of 30 C and pH between 7.5-8.0 with the influent ammonia of 455-1303 mg N/L, using NaOH and NaHC03 to adjust alkalinity, alternately. The results show that partial nitrification can be achieved under the presence of NaHCO3, even when DO > 2mg/L. but with the addition of NaOH, nitrite nitrogen accumulation decreased.

Equation 2.14 Reaction Stoichiometry of PN with 50% NH3 conversion

NH_4^+ + HCO3 $^-$ + 0.75 O_2 → 0.5 NH_4^+ + 0.5 NO_2^- + CO2 + 1.5 H_2O

(2.14)

According to equation 2.14, alkalinity computation in this process is 50% of the full nitrification.

4) Temperature. The activation energy for AOB and NOB are 68 kJ/mol, and 44kJ/ mol respectively (Hellingaet al., 1998), therefore, AOB are more sensitive to temperature changes than NOB (Figure 2.7). Grunditz and Dalhammar (2001) reported optimum temperatures for Nitrosomonas and Nitrobacter of 35 ^{0}C, 15-30 ^{0}C respectively, and therefore control the temperature at 35 ^{0}C can enhance the performance of the PN process.
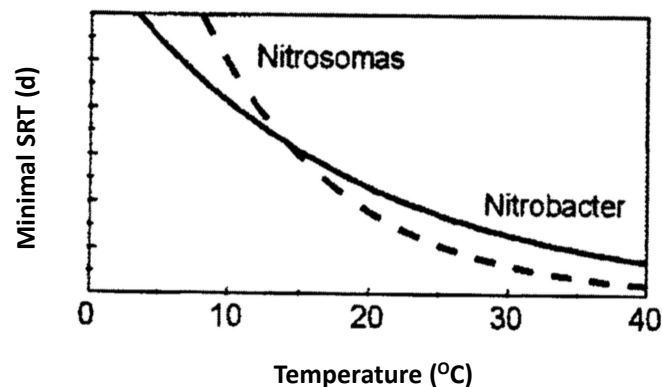
Figure 2.7 Influence of temperature on the minimal SRT for nitrification sludge

(Van Kempen et al., 2001)

If the reaction temperature is raised from room to 30-40 °C, AOBs' growth will be greater than the NOB, hence NOBs can be washed out by controlling by SRT. However, some AOBs will also be washed out during the SRT control, which can decrease volumetric removal rates. In SHARON process, nitrite accumulation is more than 90%, while

volumetric removal rates are less than 1.0 kgN.m/d.

5) Inhibition. Adding specific inhibitors may also selectively inhibit NOBs' activity. The inhibitors commonly used are chlorate, cyanate, azide and hydrazine (Phillips et al., 2002). Xu et al. (2011) reported that in aerobic granular sludge systems, PN process can be achieved successfully with nitrite accumulation rate of 92.95% by adding 5 mMKClO3. However, KclO3 is prohibitively expensive, given the high cost of its practical application to wastewater treatment.

More kinetic coefficient for AOB and NOB are presented in table 2.9.

Table 2.9 The complete list of kinetic coefficients for AOB and NOB at 30C

	Features	AOB	NOB
Y	Yield coefficient (mgVSS/mgN-d)	0.33	0.083
Ks	Half-max-rate concentration (mgN/L)	1.5	2.7
b	Decay coefficient (d-1)	0.32	1.7
μ_{max}	The maximum specific growth rates(d-1)	1.03	0.77-1.03
Ki,FA	Inhibition concentration (mgFA/L)	10-150	0.1-1
Ki,FNA	Inhibition concentration (mgFNA/L)	0.5	0.1
$K_{m,O2}$	Half-saturation constant for O_2 (mg O_2/L)	0.3	1.1
$K_{m,CO2}$	Half-saturation constant for CO_2 (mg C/L)	21.4	-
$K_{m, N}$	Half-saturation constant for N (mg N/L)	0.47	8.9
Cell Synthesis Energy	%	14	10
pH	/	7.0-8.5	6.0-7.5
T	C	35	15-30

2.4.4 Application of Partial Nitrification

The Technical University of Delft developed the SHARON process in the 1990's. Its purpose is to remove nitrogen from high strength ammonia liquors, like anaerobic digestion liquor, by nitrification of ammonia to nitrite followed by denitrification. In this process, the hydraulic retention time (HRT) is equal to the solids retention time (SRT) without applying solids separation. A combination of high temperature (35 °C) and a short aerobic HRT (2.5 days) favors AOBs and disadvantages NOBs. The stoichiometry of the SHARON process is given by the following equations (Ahn, 2006).

Equation 2.15 Stoichiometry of SHARON Process

$$NH_4^+ + 0.75O_2 + HCO_3^- \rightarrow 0.5\ NH_4^+ + 0.5NO_2^- + CO_2 + 1.5H_2O \qquad (2.15)$$
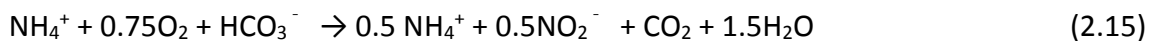
The first full-scale SHARON reactor was built in Dokhaven Wastewater Treatment Plant, Rotterdam, Netherland. A 1800m^3 continuous stirred tank reactor (CSTR) with capacity of 32.5 m^3/h is constructed to treat reject water. The average ammonia concentration of influent is 1230 mg N/L, and the nitrogen loading rate is 0.5 kgN/m^{3}d. The nitrite/ammonium ratio in the effluent and ammonium conversion are 1.1 and 53% at pH of 7,respectively, while nitrate in the effluent is almost zero. This system has an intermittent aeration supply with 600 kg O$_2$/h of flow rate, with aerobic and anoxic phases lasting for one day each. Methanol is added as carbon source and electron donor for denitrification.
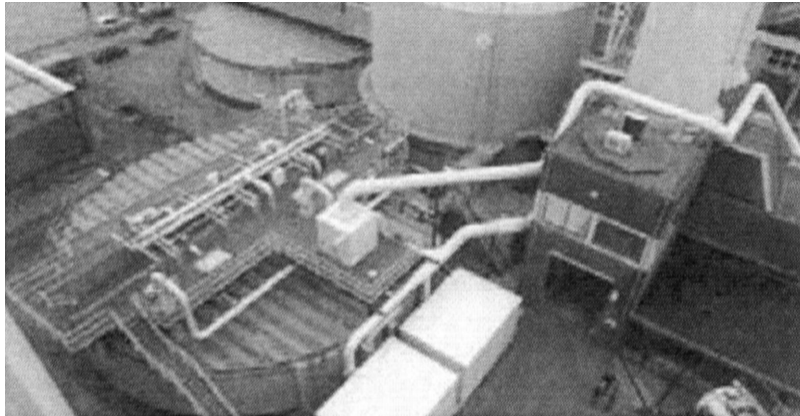
Figure2.8 The SHARON reactor (Grontmij ,2006)

2.5 Emerging Biological Nitrogen Removal: Anaerobic ammonium oxidation (anammox)

The anammox process is based on energy conservation from anaerobic NH_4^+ oxidation with NO_2^- as electron acceptor without addition of external carbon source (Jetten et al., 1999). The main carbon source for the growth of anammox bacteria is CO_2 (van de Graaf et al., 1996).

2.5.1 Principles of The Anammox Process

The anammox Process integrates ammonia oxidation and nitrite reduction reactions under an anaerobic condition, which is completed by autotrophic Anaerobic Ammonia Oxidation Bacteria (AAOB) (Equation 2.16). This reaction can be further broken down into the redox half-reactions that occur within the cell (Equations 2.17-2.19). Equations

2.20 &2.21 show the cell synthesis and overall reaction, respectively.

Equation 2.16 Stoichiometry of anammox process

$$NO_2^- + 2NH_4^+ \rightarrow N_2 + 2H_2O \qquad (2.16)$$

Equations 2.17-2.19 Redox reactions of anammox process

$$NO_2^- + 2H^+ + e \rightarrow NO + H_2O \qquad (2.17)$$

$$NO + NH_4^+ + 2H^+ + 3e \rightarrow N_2H_4 + H_2O \qquad (2.18)$$

$$N_2H_4 \rightarrow N_2 + 4H^+ + 4e \qquad (2.19)$$
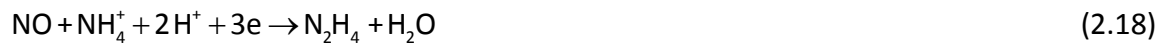
Equation 2.22 Cell synthesis in anammox process

$$2.3NO_2^- + HCO_3^- + 0.8H_2O \rightarrow 0.2H^+ + 2.1NO_3^- + CH_2O_{0.5}N_{0.15} \qquad (2.20)$$
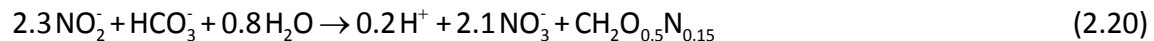
Equation 2.23 Stoichiometry of overall anammox with cells synthesis

$$NH_4^+ + 1.32NO_2^- + 0.066HCO_3^- + 0.13H^+ \rightarrow 1.02N_2 + 0.26NO_3^- + 2.03H_2O + 0.066CH_2O_{0.5}N_{0.15}$$
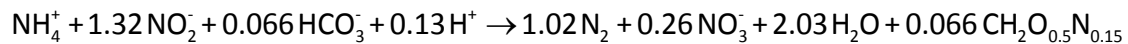
Some AOBs can also achieve anaerobic ammonium oxidation, such as Nitrosomonas eutropha (Bock et al., 1995), albeit a very low rate of $0.2 - 0.4$ g $N.g^{-1}VSS.d^{-1}$ (Noophan et al., 2009). This process produces nitrite and NO in the presence of NO_2 as oxidizer, and hence, it is fundamentally different from the anammox process and will not be discussed here.

The principle of anammox process is mainly as follows:

1) Bacteria. AAOB has very low growth rate ($0.0027h^{-1}$) and yield (0.066mg VSS/ NH4-N)

(Strous et al., 1998). Thus, long start-up times are needed for anammox process. The startup time for the first full-scale reactor was 3.5 years (Van der Star et al., 2007).

2) Process Conditions. AAOB are very sensitive to environment, so some main factors should be controlled under the condition:

- pH: 6.7-8.3.

- Temperature: 6-43 C (Strous et al., 1999b, Thamdrup and Dalsgaard, 2002).

- DO: Lower than 0.5% of air saturation (Strous et al., 1997b.)

2.5.2 Characteristics of AAOBs

So far, known AAOB includes: Candidatus Brocadia anammoxidans, Candidatus Kuenenia Stuttgartiensis, Candidatus Brocadia Fulgida, Candidatus Scalindua Sorokinii, Candidatus Scalindua Wagneri, Candidatus Scalindua Brodae (Jetten et al., 2005) and Candidatus anammoxoglobus Propionicus (Kartal et al., 2007b). All species of AAOBs have their own adaptability to their environment, and normally, only one of them dominates at each specific operating conditions (Van der Star et al., 2008).

AAOB can coexist with AOB and denitrifying bacteria. For example, AAOB are strict anaerobic bacteria, while AOB can consume oxygen to make anaerobic condition for AAOB (Tsushima et al., 2007b). Denitrifying bacteria can produce nitrite, which is substrate for AAOB (Meyer et al., 2005). This relationship is presented in Figure 2.9.
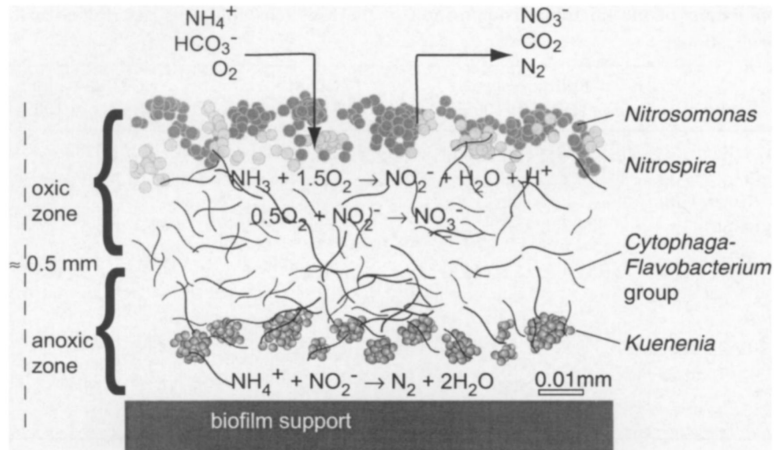
Figure2.9 The Bacterial distribution on the biofilm (Egli et al. ,2003)

2.5.3 Stoichiometry Characteristic of the anammox Process

The stoichiometry of the anammox process can be affected by many factors, but the biomass yield and NH4:NO2:NO3 ratio are the two main factors people concern (table 2.10).

Table 2.10 Performance of anammox processes

Sp.Max. Conversion (KgN/m³/d)	NH4:NO2:NO3	Biomass yield g VSS/ g N	Specific sludge activity gN/ g VSS.d	Reference
26(37℃)	1:1.2:0.33	0.16-0.26	1.6	Tsushima et al., 2007b
11.5(37℃)	1:1.22:0.36	/	0.58	Isaka et al., 2007b
9.5 (30-40℃)	1:1.31:0.25	/	/	Van der Star et al., 2007
0.71 (35℃)	1:1.22:0.22	0.07	0.45	Trigo et al., 2006
1.0 (32-33℃)	1:1.32:0.26	0.158	0.91	Strous et al., 1998

Changes the ratios of various inorganic nitrogen forms in influent may affect the effluent

water quality. Figure 2.10 shows the nitrogen removal rates and nitrogen removal

efficiencies are 1.2 kg-N/(m^3 .day) and 50% (NH$_4^+$ /NO$_2^-$; 0.75–0.85),   1.3 kg-N/(m^3 .day)

and 55% (0.95–1.05), 1.5 kg-N/(m^3 .day) and 63% (1.15–1.25), respectively at a fixed

HRT of 8 hours and a fixed influent nitrogen concentration of 800 mg N/L .
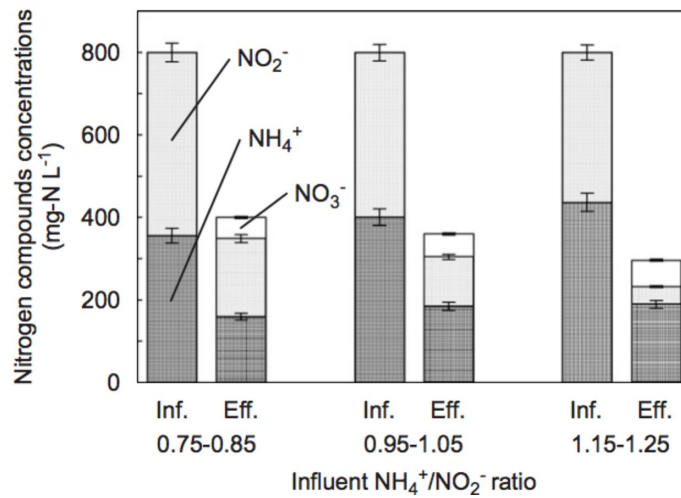
Figure2.10 Nitrogen concentrations in influent and effluent at different influent

NH$_4^+$-N/NO$_2^-$-N (Tsushima et al., 2007b)

2.5.4 Kinetics

The reported AAOB growth rates of 0.028d^{-1} to 0.39d^{-1} (Table 2.11) are not only quite

low, but also highly variable depending on the predominant AAOB species (Isaka et al.,

2006).

The decay rate is another important factor, which affects AAOBs' growth. Not too many

researchers have studied the decay rate of AAOB. The value of decay rate is about 0.001 d^{-1}, which is much less than AOB and NOB. Normally, the seed for the anammox process is from nitrifying and denitrifying activated sludge. Thus a starvation period during startup may promote the enrichment of AAOB.

Table 2.11 Growth and decay rates of different microorganisms

Type	T (^{O}C)	Decay rate (d^{-1})	Growth rate (d^{-1})	Decay rate/ growth rate (%)	Reference
AAOB	20	0.01	0.028	3.6	Han et al., 2002
	35	0.0048	/	/	Scaglione et al., 2009
	35	0.0011	0.08	1.4	Dapena-Mora, 2004b
	37	/	0.128-0.193	/	Tsushima et al., 2007a
	37	/	0.39	/	Isaka et al., 2007a
	32	/	0.072	/	Strous et al., 1998
AOBs	10	0.05	0.35	14.3	Gujer et al., 1999
	20	0.15	1	15	
	23	0.185	1.109	16.7	Hwang et al., 2009
	24	0.191	1.189	16.1	
NOBs	10	0.1	1	10	Gujer et al., 1999
	20	0.2	2	10	

2.5.5 Applications of the Anammox Process

The first full-scale anammox Reactor was built in Dokhaven Wastewater Treatment Plant, Rotterdam, Netherland in 2002 (Van der Star et al., 2007). It is a 70 m^3 internal

circulation (IC) anaerobic reactor with a design nitrogen loading rate of 7.1 N/m^3.d. This reactor takes the effluent from SHARON process with nitrite to ammonia ratio of 1:1 for further treatment (Mulder et al., 2001). The effluent of this anammox reactor is recycled where to provide enough hydraulic surface loading rate and sheer force for formulation of granular sludge. The startup time of this reactor was about 800 days. After 3-year operation, it finally reached full capacity and stabilized. The maximum nitrogen-loading rate for this reactor was 9.5 kg N m^{-3}.d^{-1}. This reactor can achieve 90% of TN removal in a pH range between 7-8 and temperature range of 30- 40 C.
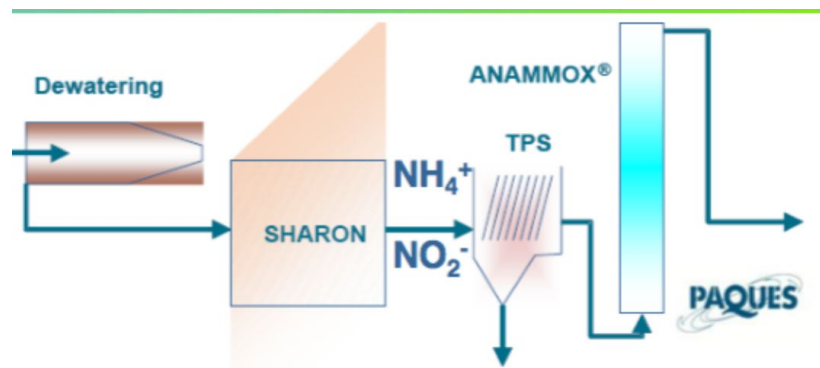
Figure2.11 A combined SHARON- Anammox Process in Dokhaven WWTP

Table 2.12 Performance of anammox and single-reactor nitritation·-anammox processes (Vander Star et a1..2007)

Process	Location	Reactor Type	Volume (d⁻¹)	Area Conversion (gN/m².d)	Sp.Max. Conversion (KgN/m³/d)
anammox Process	NL	Granular sludge reactor	100		1
	JP		58		3
	NL		5		4
	DE	Moving bed	67	5	1
	SE		2	0.5	0.1
	CH	SBR	2.5		2
Single-reactor nitrification-anammox peocess	NL	Bubble column	600		1.2
	AT	SBR	500		0.6
	CH		400		0.4
	GB	RDC	240	7	1.7
	DE		80	2	0.6
	CH		33	2	0.4
	DE	Moving bed	102	6	1
	SE		4	2	0.5

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3. Partial Nitrification using Fluidized Bed Bioreactor (PNFBR)

3.1 Objective of PNFBR

The objective of this study was to achieve partial nitrification of the ammonia-rich synthetic wastewater without organic matter in a fluidized bed bioreactor (PNFBR) with nitrite to ammonia ratio of 1.3:1 of effluent at limited dissolvef oxygen (DO) and alkalinity (Alk) condition. The effluent of PNFBR can be used as the influent of anaerobic ammonia oxidation (anammox) process for further nitrogen removal. In order to achieve partial nitrification, the PNFBR was operated at a certain condition, which favors ammonium oxidizing bacteria (AOB) over nitrite oxidizing bacteria (NOB).

3.2 Materials and Methods

3.2.1 Experimental Set Up

A lab-scale PNFBR (shown in Figure 3.1) was designed and built to treat synthetic wastewater with high concentration of ammonia and no organic matter. The temperature PNFBR was controlled by a water bath system. An on-line dissolved oxygen probes were placed at the bottom of the reactor and connected to a dissolved oxygen control system. The oxygen was provided from air line with a fine bubble air diffuser on top of the reactor (shown in Figure 3.2). A thermometer and a pH sensor were placed at the middle of the reactor.

The PNFBR was developed using a 10.4 L cylindrical Plexiglas's column with a height of

1.7 m and a diameter of 8.9 cm . A 4 L water level balancer was attached to the column, which allows the liquid to circulate to the bottom of PNFBR to achieve fluidization. In addition,aeration was supplied from the top of the column and a separator was used to stabilize the PNFBR by preventing air entering and damaging the circulating pump. A 40L container was used as a feeding tank, from which influent were pumped to the bottom of the column by a peristaltic pump. The PNFBR dimensions are summarized in the Table 3.1.
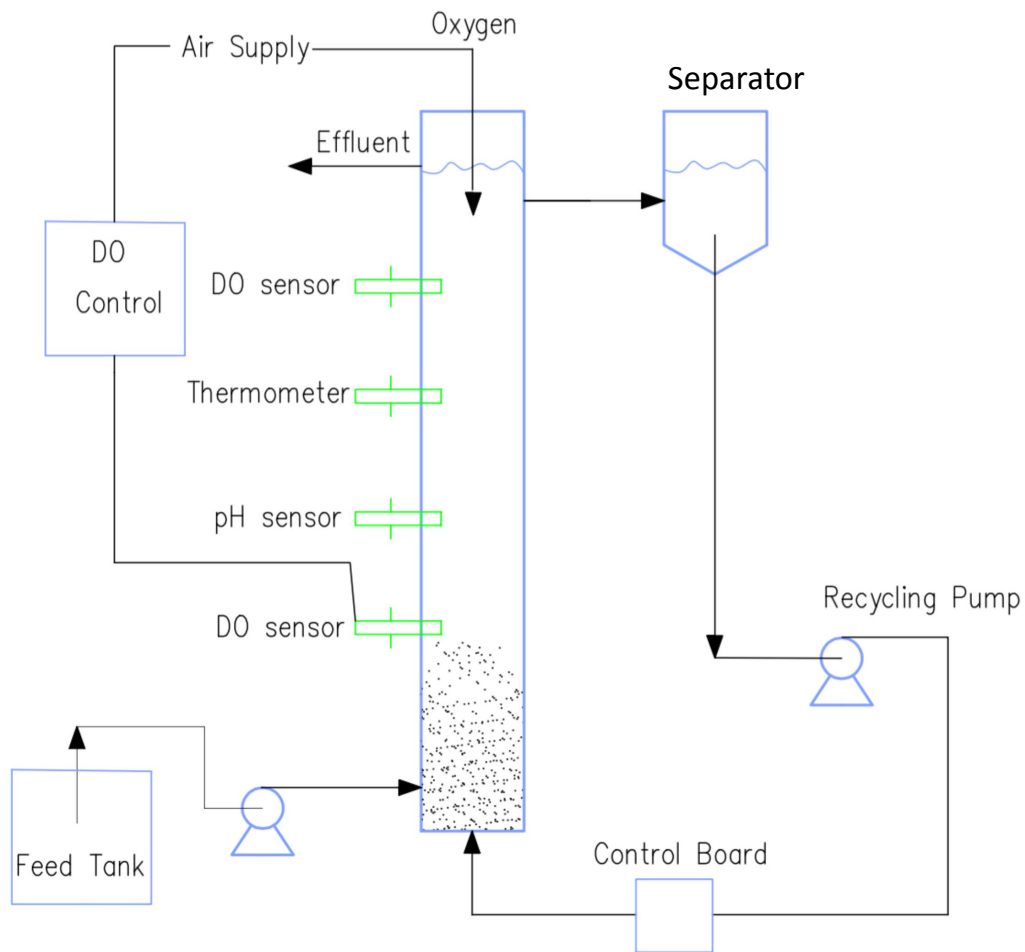
Figure 3.1 Schematic of PNFBR
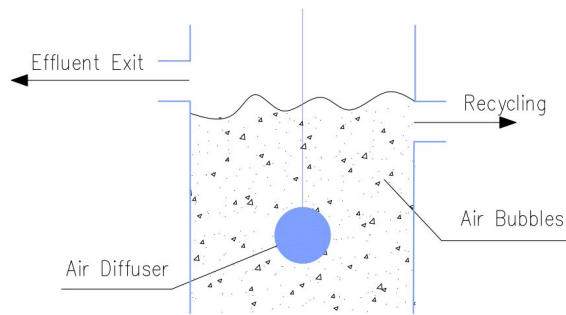
Figure 3.2 Schematic of Aeration

Approximately 2 kilograms HDPE (high-density polyethylene) particles with a range of diameters of 600 – 850 μm (Figure 3.3), were added into the reactors, which occupied 20% volume of the 10.4L Column. The media characteristics are detailed in Table 3.2.

The effluent of PNFBR can be used as influent of anammox process for further treatment (Not included in this study). The system was operated at 35°C with the average DO concentration approximately 1.5 mg/L and a pH of 7.5-8.

Figure 3.3 HDPE media

Figure 3.4 hydraulic control panels
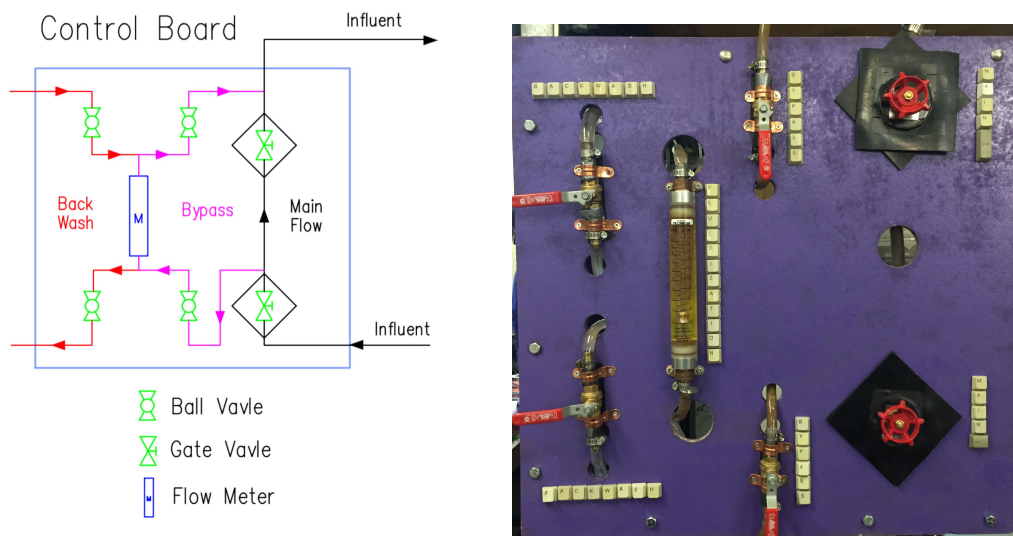
Table 3.1 PNFBR Parameters

Parameter	Value	Unit
Total Reactor Volume	14.4	L
Clarifier	4	L
Column Volume	10.4	L
Column Diameter	3.5	Inch
DO	1.3-1.7	mg/L
Temperature	35	^{O}C
pH	7.5-8	
HRT	12-18	h
Loading rate	22.5-30	L/d
Q_R	2.5-3	LPM
Bed Expansion	20%	
Concentration of Feed	100-400	mg NH_4-N/L
Alkalinity/ NH4-N ratio	5	mg CaCO3/L

Table 3.2 Particles Parameters

Parameter	Value	Unit
Type	HDPE	
Weight	2	kg
Compacted bed height	34	cm
Compacted media volume	2.1	L
Diameter	600-850	μm
Wet bulk density	1230	Kg/m^3
Dry bulk density	810	Kg/m^3

3.2.2 Synthetic Waste water composition

The synthetic wastewater used in this study consisted mainly of NH4Cl, NaHCO3 and some other trace element, as shown in Table 3.3.

Table 3.3 Composition of Synthetic Wastewater

Composition	Concentration	Unit
NH_4Cl	100-400	mg N/L
$NaHCO_3$	500-2000	mg N/L
KH_2PO_4	0.025	mg/L
$CaCl_2 \cdot 2H_2O$	0.14	mg/L
$MgSO_4$	0.3	mg/L
Trace Element	1.5	ml/L
EDTA	15	mg/L
ZnSO4·7H2O	0.43	mg/L
CoCl2	0.24	mg/L
MnCl2	0.99	mg/L
CuSO4·H2O	0.25	mg/L
NaNoO4·H2O	0.22	mg/L
NiCl·6H2O	0.19	mg/L
H3BO4	0.014	mg/L

3.2.3 Analytical Methods

The influent and effluent samples were collected daily and analyzed for various water quality parameters including Ammonia Nitrogen (NH4-N), Nitrite Nitrogen (NO2-N), Nitrate Nitrogen (NO3-N), and alkalinity. Additionally, biomass attachment was measured and recorded every two weeks.

In order to measure the biomass attachment, approximately 10 g media were collected from PNFBR, which were then sonicated (Model 75HT, ETL Laboratory Investigating Inc., New York) for 3 hours at 30 C. This process was performed in order to detach the biomass from the particle. The VSS content of the detached biomass was measured using standard methods (APHA, 1992). To measure the dry mass of the particles, they were left to dry at room temperature for 1-2 days.

3.3 Results and Discussion

3.3.1 PNFBR Startup

The Partial Nitrification Fluidized Bed Bioreactor was seeded with mixed liquor suspended solids (MLSS), originally obtained from the Adelaide Water Pollution Control Plant as return activated sludge (RAS), and subsequently enriched with AOBs in a 20L batch reactor for 30 days. This AOBs enrichment culture was able to convert approximately 100 mg/L NH4-N to 60mg/L NO2-N and 40mg/L NO3-N at a biomass

concentration of 1000 mg/L Volatile Suspended Solids (VSS), during almost 10 hours corresponding to a specific ammonia oxidation rate of 0.1 mg NH_4-N/(mg VSS.h)

After seeding with 15L sludge, the PNFBR was recirculated without feeding for 2 days to enhance biomass attachment. Limited aerobic conditions were maintained by controlling the amount of air supplied to the reactor.

3.3.2 PNFBR Operation

The experimental study included 4 phases over a period of 77 days as follows:

- **Phase 1 (25 days)**:

  The system was started at the feeding rate of 30 L/d during phase 1. The ammonia concentration in the influent was 100 mg NH4-N/L and the alkalinity/ammonia ratio was controlled as 5:1. Liquid flow rate was 3 L/min, corresponding to superficial liquid velocities of 8mm/s. The HRT and the temperature were 12 hours and 35C, respectively. DO in the PNFBR was controlled at 1.31 ± 0.20mg/L.

  The results show that the effluent NH_4^+-N was 42 mg/L, and PNFBR achieved average ammonia removal of 57.2% at nitrogen loading rate of 0.2kg N/($m^3 \cdot$d). The NO_2^--N and NO_3^--N in the effluent were and 37.1 mg/L and 7.3 mg/L, corresponding to conversion efficiency of 37.7% and 7.4%, receptivity. The average effluent NO_2^-N / NH_4^+-N ratio was 0.88. The alkalinity consumption during this phase was 273 mg $CaCO_3$/L, corresponding to alkalinity / NH_4^+-N consumption ratio of 4.9.

- **Phase 2 (18 days):**

In this phase, the influent ammonia concentration was doubled to 200mg/L with 1000mg/L alkalinity as $CaCO_3$, while the feeding rate was still 30L/d. The liquid flow rate was 3 L/min, corresponding to superficial liquid velocities of 8mm/s. The HRT and the temperature were 12 hours and 35C, respectively. DO in the PNFBR was controlled at 1.29 ± 0.20mg/L.

The results show that the effluent NH_4^+-N was 94 mg/L, and PNFBR achieved average ammonia removal of 52.8% at nitrogen loading rate of 0.4kg $N/(m^3 \cdot d)$. The NO_2^--N and NO_3^--N in the effluent were and 85.7 mg/L and 9.8 mg/L, corresponding to production rate of 43.0% and 5.0%, respectively. The average effluent NO_2^-N / NH_4^+-N ratio was 0.95. The alkalinity consumption during this phase was 528 mg $CaCO_3$/L, corresponding to alkalinity / NH_4^+-N consumption ratio of 5.0.

- **Phase 3 (14 days):**

In this phase, the influent ammonia concentration was doubled to 400mg/L with 2000mg/L alkalinity as $CaCO_3$, while the feed flow rate was still 30L/d. The liquid flow rate was 2.7 L/min, corresponding to superficial liquid velocities of 7.3mm/s. The HRT and the temperature were 12 hours and 35C, respectively. DO in the PNFBR was controlled at 1.71 ± 0.20mg/L.

The results show that the effluent NH_4^+-N was 223 mg/L, and PNFBR achieved average ammonia removal of 44.1% at nitrogen loading rate of 0.8kg $N/(m^3 \cdot d)$. The NO_2^--N and NO_3^--N in the effluent were and 148 mg/L and 9.5 mg/L, corresponding

to production rate of 38.1% and 2.5%, respectively. The average effluent NO_2^--N / NH_4^+-N ratio was 0.68. The alkalinity consumption during this phase was 775 mg $CaCO_3$/L, corresponding to alkalinity / NH_4^+-N consumption ratio of 4.38.

- **Phase 4 (14 days):**

In this phase, the influent ammonia concentration was still 400mg/L with 2000mg/L alkalinity as $CaCO_3$. However, the HRT was increased from 12 hours to 18 hours, corresponding to feed flow rate of 22.5L/d. The liquid flow rate was 2.5 L/min, corresponding to superficial liquid velocities of 6.7 mm/s. DO in the PNFBR was controlled at 1.35 ± 0.20mg/L.

The results show that the effluent NH_4^+-N was 167 mg/L, and PNFBR achieved average ammonia removal of 57.1% at nitrogen loading rate of 0.53 kg N/(m³·d). The NO_2^--N and NO_3^--N in the effluent were and 211 mg/L and 15 mg/L, corresponding to production rate of 53% and 3.8%, respectively. The average effluent NO_2^--N / NH_4^+-N ratio was 1.27. The alkalinity consumption during this phase was 1090 mg $CaCO_3$/L, corresponding to alkalinity / NH_4^+-N consumption ratio of 4.7.
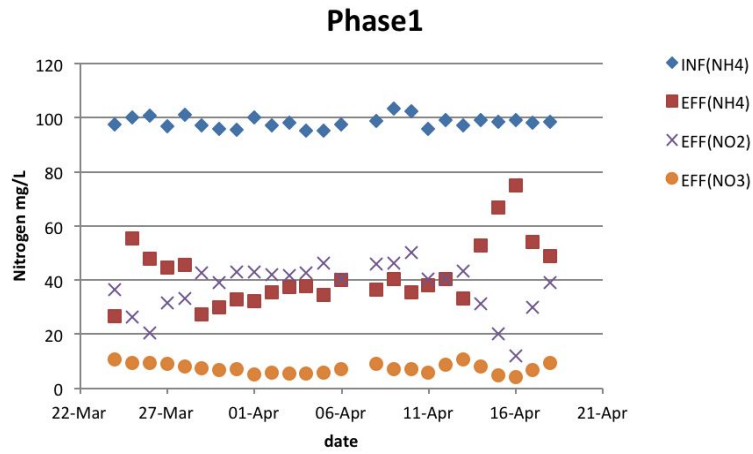
Phase1

Figure 3.5 Results on Phase 1
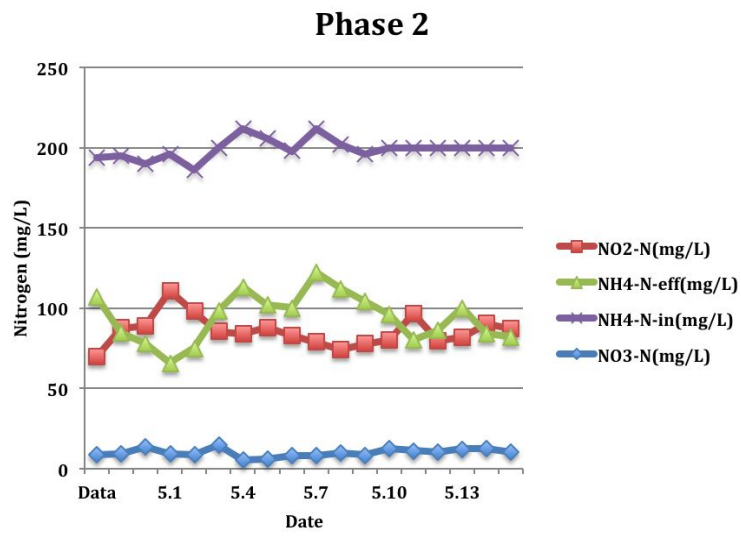
Phase 2

Figure 3.6 Results on Phase 2
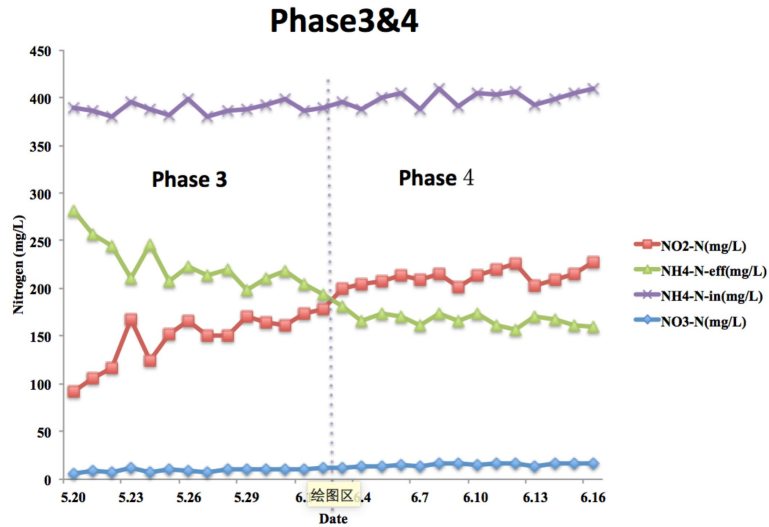
Figure 3.7 Results on Phase 3&4

Table 3.4 Operational Condition and performance data of PNFBR

Parameter	Unit	Phase 1	Phase 2	Phase 3	Phase 4
NH4-N-In	mg/L	98.3 ± 2.1	199 ± 6.3	399 ± 6	399 ± 7
NH4-N-Eff	mg/L	42.0 ± 11.5	94 ± 14.5	223 ± 24	167 ± 7
NO2-N	mg/L	37.1 ± 9.8	85.7 ± 9.3	148 ± 26	211 ± 9
NO3-N	mg/L	7.3 ± 1.8	9.8 ± 2.4	9.5 ± 1.6	15 ± 1.7
NO2/NH4 in Effluent	/	0.88	0.95	0.68	1.27
Free ammonia	mg /L	4.3	9.5	22.6	16.9
NLR	kg NH$_4$- N/m^3.d	0.2	0.4	0.8	0.53
DO	mg/L	1.31 ± 0.20	1.29 ± 0.20	1.71 ± 0.35	1.35 ± 0.5
pH	/	-	8.04 ± 0.04	8.09 ± 0.20	7.97± 0.18
HRT	hours	12	12	12	18
T	^{O}C	35	35	35	35
Alkalinity Consumption	mg CaCO3/L	273 ± 77	528 ± 108	775 ± 137	1090 ± 190
△Alkalinity/NH4	/	4.88	5.0	4.38	4.7

3.3.3 Performance of PNFBR

During the first 5 days of the start-up period, NH4-N removal efficiency was lower than 50% of the influent ammonia due to the biomass acclimatization at the NLR of 0.2kg/m^3.d. Afterwards NH4-N removal increased to a stable level above 65% in approximately 2 weeks. During this time, NO2-N concentration in the effluent started to increases steadily approaching 50% on April 14th (day 17) with average NO2-N/NH4-N ratio of 1.2, which is close to required ratio for anammox (1.3). NO3-N in the effluent shows a slow decreasing trend from 10% to 5% of the influent ammonia. The PNFBR performance dropped sharply in the last 5 days of phase 1, due to an unexpected increase in temperature (moving from 35 C to higher than 40 C), which reduced AOB's activity. After fixing the problem, the system went back to normal again. The average NO2-N/NH4-N in phase 1 was 0.88.

After partial nitrification environment was established in the PNFBR, the NLR was increased gradually by changing the influent NH4-N concentration in the feeding. The influent flow rate was kept at about 30 L/d while the NH4-N concentration was increased from 100mg/L to 200mg/L, and approached 400mg/L in the end, corresponding to NLR rising from 0.2kg/m^3.d to 0.4 kg/m^3.d (phase 2) and 0.8 kg/m^3.d (phase 3&4). The purpose of this exercise was to determine the max NLR of PNFBR. The

average NO2-N/NH4-N ratio in effluent was 0.95 and 0.68, during phase 2 and phase 3, respectively.

In order to achieve the target NO2-N/NH4-N ratio of 1.3, a longer HRT (from 12h to 18h) was applied in phase 4. Thus, the NO2-N/NH4-N ratio in the effluent averaged at 1.27 at the NLR of 0.53 kg/m^3.d.

3.3.4 Discussions

- **Free ammonia (FA) affects on PNFBR**

The AOB and NOB are inhibited at FA concentration of 10-150 mg/L and 0.1 – 1.0 mg/L, respectively (Abeling and Seyfried, 1992; Anthonisen et al., 1976). FA concentration can be calculated according to Equation 3.1.

Equation 3.1 FA concentration calculation in the PNFBR (Sukru and Mohamed, 2007)

$$FA\ (mg/l) = \frac{17}{14} \frac{\sum NH_4\text{-}N\ (mg/l) \times 10^3}{(k_b/k_w) + 10^{pH}}$$

where k_b/k_w = e6344/(273 + T)

In this study, the calculated concentration of FA was 4.3 – 22.6 mg/L for the NLR of 0.2 and 0.8 kg NH4-N/m^3.d, respectively. FA concentration in the PNFBR was considerable high to inhibit NOB selectively, and it also seems to be a determining factor for NO2-N accumulation in the PN. As a result, the NOB was inactivated in the PNFBR, while AOB was still functioning.

- **Dissolve Oxygen (DO) affects on PNFBR**

The recommended DO level for PR is XXX. The DO concentration in the PNFBR were 1.31 ± 0.20, 1.29 ± 0.20, 1.71 ± 0.35, 1.35 ± 0.5 mg/L with average NO2/NH4 ratio in effluent 0.88, 0.95, 0.68, 1.27 during phase 1-4, respectively. In this study, the worst performance of PNFBR occurred at phase 3 with highest DO concentration. However, NO2-N accumulation and partial nitrification still happened even when DO concentration in PNFBR was as high as 1.7 mg/L. Also, An et al (2008) observed 80% NO2-N/NH4-N ratio at the high DO (higher than 2mg/L) concentration in a membrane bioreactor. This indicates that the DO might not be the limited pace for partial nitrification because of the high concentration of FA.

- **Nitrogen Balance of PNFBR**

The nitrogen in PNFBR mainly exists in the forms of NH_4^+-N, NO_2^--N and NO_3^--N. Considering of the simultaneous inflows and outflows by a same peristaltic pump, the nitrogen balance over PNFBR system is presented in equation 3.2

Equation 3.2 Nitrogen mass balance in PNFBR

$$\mathrm{Nitrogen\,Balance} = \frac{Eff_{NH_4^+\text{-}N + NO_2^-\text{-}N + NO_3^-\text{-}N}}{Inf_{NH_4^+\text{-}N + NO_2^-\text{-}N + NO_3^-\text{-}N}} \times 100\%$$

The results indicate an increasing trend of nitrogen balance during phase 1 – 4, which are 88%, 91%, 96% and 98%, respectively. The nitrogen imbalance may have been caused by the existence of heterotrophic bacteria in the system, which consume nitrate

and nitrite. Also, the population of heterotrophic bacteria was gradually decreased during the experiment due to the low carbon source.

3.3.5 Biomass in PNFBR

The partial nitrification was mainly achieved by biomass attached on the particles. Based on bio-particles attachment tests, shown in Table 3.5, the biomass attachment increased from 1.5 mg VSS/ g particles to 2.3 mg VSS/ g particles during the whole phases, corresponding to total biomass increase in the PNFBR from 3 g to 4.6 g.

Table 3.5 The characteristic of Bio-particles

Parameter	Phase 1	Phase 4
Bio-particles attachment	1.5 mg VSS/ g Particles	2.3 mg VSS/ g Particles
Particle weight	2 kg	2 kg
$W_{Biomass}$	3 g	4.6 g

It was observed that a layer of granular sludge was formed above the bio-particles in this PNFBR (Figure 3.8). The thickness and biomass concentration of this granular sludge layer both increased from 1.5 centimeter to 2.5 centimeter, and from 1.3 g/L to 1.6g/L, respectively, corresponding to total biomass increase in the PNFBR increased from 80 mg to 300 mg. The characteristics of this granular sludge layer is presented are Table 3.6.

Figure 3.8 Granular sludge formed in PNFBR

Table 3.6 The characteristic of granular sludge layer

Parameter	Phase 1	Phase 4
Thickness	1.5 cm	2.5 cm
VSS	1.3 g/L	1.6 g/L
Volume	62 ml	189 ml
$W_{biomass}$	80 mg	300 mg

It is evident from the data of tables 3.5 & 3.6 that the attached biomass increased by 53.3% from phase 1 to phase 4, while the granular sludge increased by 275% during the same period. This result showed that the growth rate of attached biomass was only 20% of the granular biomass. However, the total attached biomass was 3 g, which was still 15 times more than 300 mg of granular biomass.

Nitrification tests were conducted during the first and the last phase of this study to examine nitrification kinetics of the attached and granular biomass of the PNFBR. The 0.5 L batch reactors were equipped with magnetic stirrers and aerobic diffusers (purging air to maintain dissolved oxygen).

The results are presented in Figure 3.9 & 3.10, and Table 3.7
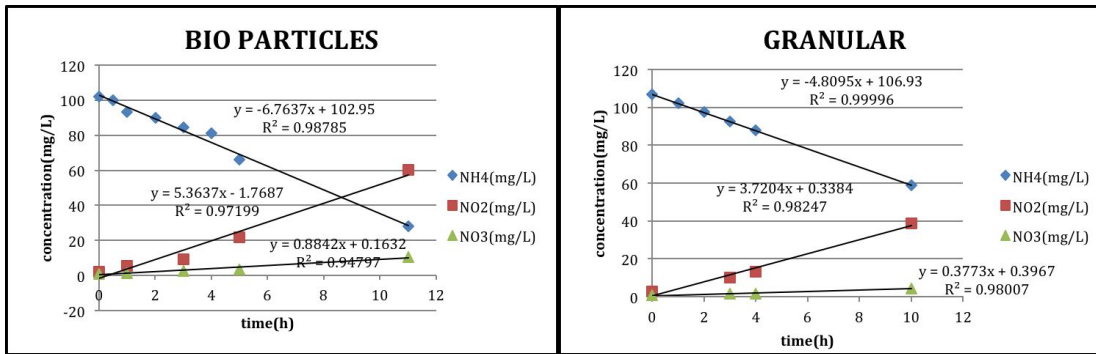
Figure 3.9 Specific Nitrification Test for a) Bio-particles; b) Granular biomass on Phase 1

Table 3.7 Specific Ammonia uptake, nitritation and nitration rates

Parameter	Phase 1		Phase 4	
	Bio-particles	**Granular**	**Bio-particles**	**Granular**
Samples Wight	12 g dry particles	10 ml	8.25 g dry particles	12 ml
Concentration	1.5 mg VSS/g particles	1300 mg/L	2.3 mg VSS/g particles	1575 mg/L
Reactor Volume (ml)		500		
*r $_{NH4-N}$ mg NH$_4$-N/(mg VSS.h)	0.188	0.185	0.198	0.180
*r $_{NO2-N}$ mg NO$_2$-N/(mg VSS.h)	0.149	0.143	0.179	0.156
*r $_{NO3-N}$ mg NO$_3$-N/(mg VSS.h)	0.027	0.038	0.026	0.026

*r$_{NH4-N}$ = NH4-N uptake rate × Container volume / biomass weight

*r$_{NO2-N}$ = NO2-N production rate × Container volume / biomass weight

*r$_{NO3-N}$ = NO3-N production rate × Container volume / biomass weight
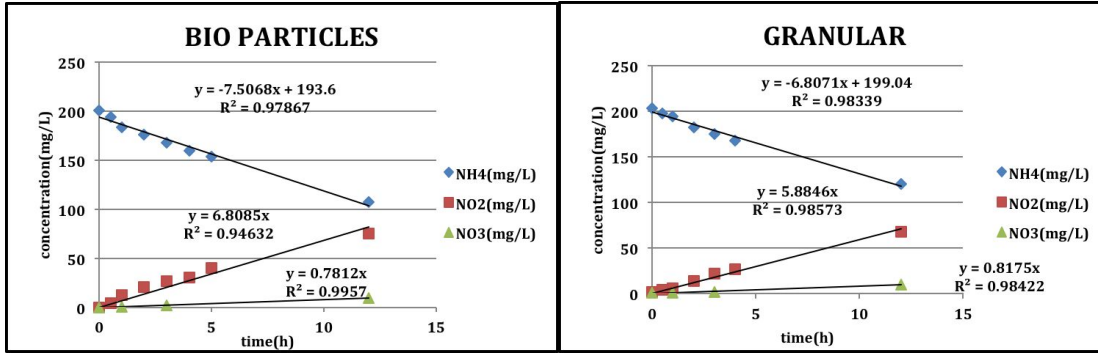
Figure 3.10 Specific Nitrification Test for a) Bio-particles; b) Granular biomass in Phase 4

From the phase 1 to phase 4, the specific nitrification rate of attached biomass and granular biomass changed from 0.188 to 0.198 mg NH_4-N/(mg VSS.h), 0.185 to 0.180 mg NH_4-N/(mg VSS.h), respectively; The specific nitrite production rate of attached biomass and granular biomass slightly increased from 0.149 to 0.179 mg NO_2-N/(mg VSS.h), 0.143 to 0.156 mg NO_2-N/(mg VSS.h), respectively, corresponding to growth of 20% and 9%, respectively; The specific nitrate production rate of attached biomass and granular biomass decreased from 0.027 to 0.026 mg NO_3-N/(mg VSS.h), and from 0.038 to 0.026 mg NO_3-N/(mg VSS.h), respectively.

The results of the batch tests indicate the followings:

a) For the attached biomass, the activity of AOB increased by 20%, while the activity of NOBs maintained almost at the same level. For the granular biomass, the activity of AOB increased by 9%, while the activity of NOBs decreased by 32% significantly.

b) At the end of this study, attached biomass shows less difference of activity with granular biomass (15% higher in specific nitrite production rate and same specific nitrate

production rate).

c) Even though adequate oxygen and alkalinity were provided, most of the ammonia was still converted to nitrite (77%-90%) instead of being further oxidized to nitrate (10%-23%). This result implied that the population of NOBs is much less than AOBs.

3.4 Summary and Conclusions

1) The PNFBR was able to achieve partial nitrification at 35 C with influent ammonia concentration from 100mg/L to 400mg/L during four phases:

- **100 mg NH_4^--N/L.** PNFBR was able to achieve effluent NO_2^--N/ NH_4^--N ratio of 0.88 with HRT of 12 hours and DO of 1.31mg/L.

- **200 mg NH_4^--N/L.** PNFBR was able to achieve effluent NO_2^--N/ NH_4^--N ratio of 0.95 with HRT of 12 hours and DO of 1.29mg/L.

- **400 mg NH_4^--N/L.** PNFBR was able to achieve effluent NO_2^--N/ NH_4^--N ratio of 0.68 with HRT of 12 hours and DO of 1.71mg/L.

- **400 mg NH_4^--N/L.** PNFBR was able to achieve effluent NO_2^--N/ NH_4^--N ratio of 1.27 with HRT of 18 hours and DO of 1.31mg/L.

2) Only 9% of the influent NH_4^+-N was converted to NO_3^--N in PNFBR. Additionally, a conversion rate of 13% was observed in the specific nitrification tests where adequate oxygen and alkalinity were provided. These results showed that only small amount of

NOBs existed in the system.

3) The maximum nitrogen loading rate and nitrogen conversion rate at reliable operation condition were 0.53 kgN /m^3.d,and 1.7 kgN/m^3, respectively.

Conclusions: This research achieved a good result for partial nitrification using fluidized bed bioreactor. The effluent from this PNFBR can be directly used as the influent of anammox process by controlling temperature, DO level and alkalinity.

3.5 References

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4. Circulating Fluidized Bed Bioreactor (CFBBR)

4.1 System Information

4.1.1 Reactor Description

A pilot- scale Circulating Fluidized Bed Bioreactor was designed and built to treat municipal wastewater from an apartment building in the Guangzhou Institute for Energy Conversion (GIEC), Guangzhou, China. This CFBBR (2.6m height, 2.4m depth and 0.4 m width) was divided into two reactors: an aerobic downer (933L) and an anaerobic riser (341L). The wastewater was pumped from a holding tank underneath the building to the bottom of the riser, and then left the system at the top of downer after treatment. In order to achieve downer to downer and downer to riser circulation, the recycling liquids from downer was pumped to a tank (50 L) and then divided into two steams with main flow entering pipe distributor in the downer and the rest was pumping to pipe distributor in the riser. It should be noted that particles were not circulated. The oxygen was provided with 4 dome fine bubble diffusers in the downer (at roughly 2 meter height).

The details of reactor parameters can be found in Table 4.1 and Figure 4.1.

Table 4.1 Characteristics of reactor and particles

Parameters	Downer	Riser
Reactor volume (m^3)	1	0.34
Reactor area (m^2)	0.32	0.16
Reactor height (m^2)	2.6	2
Particles type	HDPE	HDPE
Particles (kg)	242	96
Pecked bed height (cm)	105	88
Particle media diameter (mm)	1.1	1.1
True density (kg/m^3)	1230	1230
Dry bulk density (kg/m^3)	810	810
U_{mf}, minimum fluidization velocity (cm/s)	0.29	0.29
U_t, particle terminal velocity (cm/s)	6.9	6.9
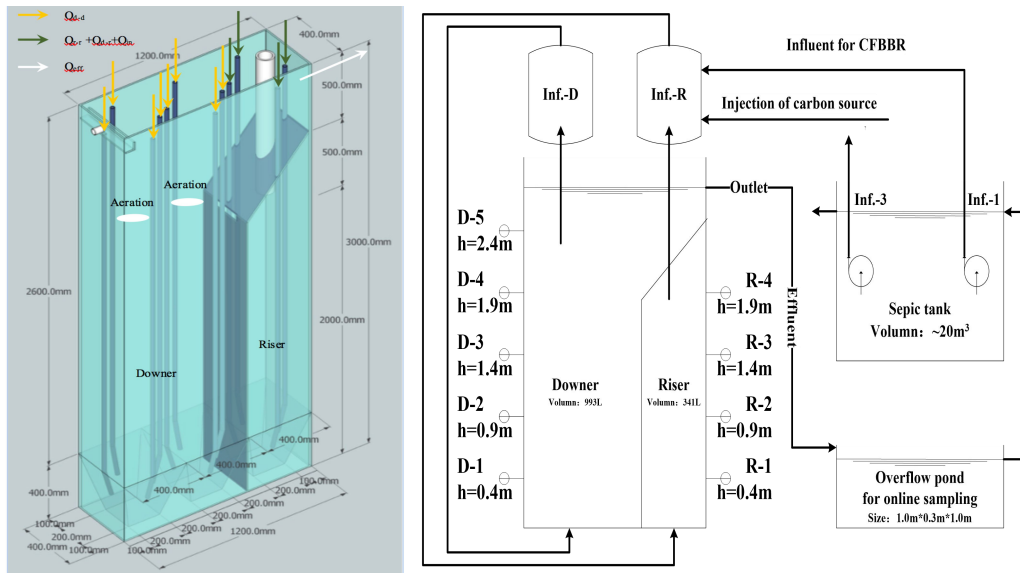
Fig4.1 Diagram for CFBBR at GIEC

4.1.2 Measurement and Analyses

Wastewater flows and airflow were measured with flow meters. DO were measured on-line with DO sensors. The routine analysised parameters for influent and effluent streams were total and soluble chemical oxygen demand (TCOD and SCOD) concentrations; total and soluble (TBOD5 and SBOD5); total and volatile suspended solids (TSS and VSS); total and soluble total nitrogen (TN and SN); alkalinity and pH; concentrations of nitrate (NO_3^- -N), nitrite (NO_2^- -N), ammonia (NH_4^+-N) and; dissolved oxygen (DO). Biomass concentrations on the carrier as reflected by VSS, were also measured.

TSS, VSS, BOD5 were analyzed according to the Standard Methods (APHA, 1992). TCOD, and SCOD, were measured using HACH methods and investigating kits (HACH Odyssey DR/2800) based on potassium dichromate oxidation and spectrophotometric determination. Soluble sample was obtained by applying filter paper with a pore size of 0.45 um. Alkalinity was measured by titration with 0.02 N H2SO4 in accordance with the Standard Method No. 2320 (APHA, 1992).

Biomass attachment was measured every week. The VSS content of the detached biomass was measured using standard methods (APHA, 1992) and the sonicated particles were weighted after drying at room temperature for 1 d.

4.1.3 Influent characteristics

The Influent wastewater was originated from a ten-floor apartment building, consisting

of apartments (with kitchen), students' dormitory (without kitchen) and a cafeteria. The domestic wastewater moved from the building to an unmixed anaerobic holding tank with a HRT < 1day before entering the CFBBR. Based on the influent wastewater characteristics presented in table 4.2, the influent wastewater contained high concentration of ammonia and low COD/ nitrogen ratio when compared with the typical municipal wastewater.

Table 4.2 The characteristic of influent

TN	SN	NH$_4$-N	NO$_3$-N	NO$_2$-N	Alkalinity
mg/L	mg/L	mg/L	mg/L	mg/L	mgCaCO$_3$/L
130.6±33.2	118.4±30.6	103.1±26.4	0.5±0.5	0.018±0.017	525.4±128.3
TCOD	**SCOD**	**TBOD$_5$**	**SBOD$_5$**	**TSS**	**VSS**
mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
271.0±79.8	193.7±49.1	83.3±26.7	58.7±26.9	37.6±32.8	28.6±19.0
SN/TN		**SCOD/TCOD**	**SBOD$_5$/TBOD$_5$**		**VSS/TSS**
0.9±0.1		0.7±0.1	0.7±0.2		0.8±0.2
TBOD$_5$/TCOD		**SBOD$_5$/SCOD**	**TCOD/NH$_4$-N**		**Alk/NH$_4$-N**
0.28±0.12		0.29±0.15	2.8±0.5		5.1±1.0

4.1.4 Effluent Objectives

The targeted effluent quality from this CFBBR is mandated by the Chinese standards (Discharge standard of pollutants for municipal wastewater treatment plant) as summarized in table 4.3.

Table 4.3 Chinese standards for municipal wastewater effluent (annual average daily value)

Parameters	Value	Unit
COD	60	mg/L
NH3-N	8(15*)	mg/L
TN	20	mg/L

* when T <12C

Considerating the low COD/nitrogen ratio in this project, extra organic matter in the form of glucose was needed. Typically, the required COD/ nitrogen ratio is around 5, however, in this case, the target COD/nitrogen ratio of 8:1 was used to ensure complete denitrification and facilitate regularly compliance with the TN limit.

Equation 4.1 Stoichiometric relationships of denitrification with glucose (Vít Matějů et al., 1992)

$$C_6H_{12}O_6 + 2.8\ NO^-_3 + 0.5\ NH^+_4 + 2.3H^+ \rightarrow\ 0.5\ C_5H_7NO_2 + 1.4N_2 + 3.5\ CO_2 + 6.4H_2O$$
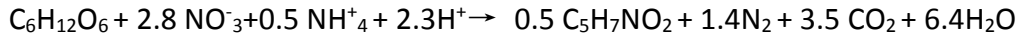
4.2 System Start-Up and Operation

Before the start-up of CFBBR, approximately 1.5 m^3 RAS, which was taken from the Datansha Municipal Wastewater Treatment Plant, Guangzhou, China, were seeded into the system. The Datansha WWTP, with a capacity of 165,000 m^3/d, mainly handles residential sewage (90%) and serves for 1.5 million populations (Jian Li et al., 2010).

This RAS with 3.7 g /L of TSS and 2.8 g /L of VSS was introduced into the CFBBR and circulated between the downer and riser for 2 days without feeding. The aerobic and anoxic conditions were maintained in downer and riser respectively, to promote initial

biomass growth on particles.

The operational conditions and performance of CFBBR in the 7 phases are presented in Tables 4.4 – 4.13, which depict the influent and effluent characteristics.

4.2.1 Phase 1 ((day 1 – day34)

The system was started with a feeding rate of 275 L/d during phase 1 without any additional carbon source. The operational conditions and water quality data are summarized in table 4.4 & 4.5, respectively. Liquid recycling rates in the downer and riser were 166 m^3/d and 34 m^3/d, respectively, corresponding to superficial liquid velocities of 6mm/s and 2.5mm/s, respectively. The downer-to-riser recirculation rate was controlled at approximately 198 L/d, which was less than the fluent flow rate of 275L/d and was negligible compared to the internal recirculating rates in the downer and riser. The HRT of the downer and riser were 60 hours and 19 hours respectively. DO in the downer was maintained higher than 6 mg/L, while airflow rate was kept at 1 m^3/h. The average temperature in the reactor was 19 C.

Table 4.4 Operational Conditions in Phase 1

Parameters	Value	Unit
Particles weight	145/60	kg
Q_{Inf}	275	L/d
Q_C	0	g/L
Q_{D-R}	198	L/d
Q_{R-R}	34	m^3/d
Q_{D-D}	166	m^3/d

The results show that the CFBBR achieved high ammonia removal efficiency of 99.7%. However, the average effluent TCOD and TN concentrations were 92mg/L and 94 mg/L, which were higher than the Chinese effluent regulations of 60mg/L and 20mg/L, respectively. Also, the effluent nitrate was as high as 47mg/L. These results indicate CFBBR has good nitrification, but poor denitrification due to lack of organic matter (COD/N ratio =2.78).

Table 4.5 CFBBR results in Phase 1

Parameter	Unit	Influent	Effluent	Removal	C/N ratio
TCOD	mg/L	333 ± 54	92 ±6.2	72.5%	
TN	mg/L	153 ± 17	94 ± 14.5	61.6%	
NH3-N	mg/L	120 ± 9	0.4 ± 0.2	99.7%	2.78
NO3-N	mg/L	0.6 ± 0.4	47 ± 12	/	
Alk	mg CaCO3/L	565 ± 42	21 ± 2.3	534	

4.2.2 Phases 2-4 (day 35 – day 66)

The phases 2-4 with influent flow rate of 400L/d, 600L/d and 550L/d, respectively, were discussed together due to the similar operational conditions and fluctuating influent flow rate. Organic matter in the form of glucose was added using a peristaltic pump during these period to improve denitrification. The glucose concentration corresponded to 388 mg/L COD based on the influent flow rate.

The internal recycling rates in the downer and riser were 151 m^3/d and 24.5 m^3/d,

respectively, corresponding to superficial liquid velocities of 5.5 mm/s and 1.8 mm/s. The downer-to-riser recirculation rate was increased sharply from 198 L/d to 1111 L/d, which was 2 times as fluent flow rate of 570L/d. The HRT of downer and riser were decreased to 36 hours and 11 hours respectively. DO in the downer was maintained higher than 5mg/L, while airflow rate was kept at 2.0 m^3/h. the average temperature is the reactor was 24.6 C.

According to Table 4.6 & 4.7, TN and TCOD removal efficiency improved from 61.6% to 73.9%, and 72.5% to 75.6%, respectively. However, the effluent of 42mg TN/L and 72 mg COD/L still did not meet the regulations. The COD/N ratio of 4.39 was not enough for complete denitrification, hence, more organic matter was needed.

Table 4.6 Operational conditions in Phases 2-4

Parameters	Value	Unit
Particles weight	145/60	kg
Q_{Inf}	570	L/d
Q_C	388	g/L
Q_{D-R}	1111	L/d
Q_{R-R}	24.5	m^3/d
Q_{D-D}	151	m^3/d

Table 4.7 CFBBR results in Phases 2-4

Parameter	Unit	Influent	Effluent	Removal	C/N ratio
TCOD	mg/L	712 ± 59	79 ± 43.4	75.6%	
TN	mg/L	162 ± 19	42 ± 28	73.9%	
NH3-N	mg/L	128 ± 10	4.1 ± 0.9	96.8%	4.39
NO3-N	mg/L	0.8 ± 0.1	30 ± 18	/	
Alk	mg CaCO3/L	656 ± 29	34 ± 9	622	

4.2.3 Phase 5 (day 70 – day 83)

This is a recovery phase from the accidently washout of 45kg particles from riser to downer due to a sudden increase in riser-to-riser circulating from 24.5m³/d to approximately 80 m³/d at day 67. High biomass in the downer shocked the CFBBR by decreasing DO to less than 1mg/L in the downer. In order to recover the system, several changes were made as follows: 1) added more particles to the riser, thus the overall particles in the downer and riser were increased from 145 kg and 60 kg to 192 kg and 68 kg, respectively; 2) reduced the influent flow rate from 570mg/L to 275mg/L; 3) Increased air flow rate from 2.0 mg/L to 2.5 mg/L.

Liquid flow rates in the downer and riser were 165 m³/d and 48 m³/d, respectively, corresponding to superficial liquid velocities of 6mm/s and 3.5mm/s, respectively. The downer-to-riser recirculation rate was 800L/d, which was 3 times the influent flow rate of 275L/d. The HRT of downer and riser were 60 hours and 19 hours respectively. After 3

days recovery, DO in the downer went up to 5-6mg/L again, while airflow rate was kept

at 2.5m^3/h. the average temperature in the reactor was 28 C.

Based on table 4.9, High TN and TCOD removal efficiency (85.4% and 92.9%) were

achieved with COD/nitrogen ratio of 5.41. The effluent TN and TCOD were 12mg/L and

51mg/L, respectively, which met the regulation of 20 mg/L and 60 mg/L.

Table 4.8 Operational conditions in Phase 5

Parameters	Value	Unit
Particles weight	192/68	kg
Q_{Inf}	275	L/d
Q_C	550	g/L
Q_{D-R}	800	L/d
Q_{R-R}	48	m^3/d
Q_{D-D}	165	m^3/d

Table 4.9 CFBBR results in Phase 5

Parameter	Unit	Influent	Effluent	Removal	C/N ratio
TCOD	mg/L	898 ± 49	51 ± 13	85.4%	
TN	mg/L	166 ± 9	12 ± 3	92.9%	
NH3-N	mg/L	130 ± 6.6	0.2 ± 0.1	99.8%	5.41
NO3-N	mg/L	0.3 ± 0.3	7.4 ± 4	/	
Alk	mg CaCO3/L	680 ± 29	117 ± 27	563	

4.2.4 Phase 6 (day 84- day 97)

During this phase, the influent flow rate was increased from 275 m³/d to 575 m³/d. The downer-to-riser recirculation rate was increased sharply from 800 L/d to 1849 L/d. Liquid flow rates in the downer and riser were 165 m³/d and 49 m³/d, respectively, corresponding to superficial liquid velocities of 6mm/s and 1.8 mm/s. The HRT of downer and riser were decreased to 36 hours and 11 hours respectively. DO in the downer was maintained higher than 6 mg/L, while airflow rate was kept at 3 m³/h. The average temperature in the reactor was 29 C.

According to table 4.10 & 4.11, although influent flow rate was doubled, CFBBR still achieved high TN and TCOD removal efficiency of 83.5% and 90.5%, receptivity, with an initial COD/nitrogen ratio of 5.88. The effluent TN and TCOD were 12mg/L and 45mg/L, respectively, which met the regulation of 20 mg/L and 60 mg/L.

Table 4.10 Operational conditions in Phase 6

Parameters	Value	Unit
Particles weight	192/68	kg
Q_{Inf}	575	L/d
Q_C	550	g/L
Q_{D-R}	1849	L/d
Q_{R-R}	49	m³/d
Q_{D-D}	165	m³/d

Table 4.11 CFBBR results in Phase 6

Parameter	Unit	Influent	Effluent	Removal	C/N ratio
TCOD	mg/L	723 ± 49	45 ± 13	83.8%	
TN	mg/L	123 ± 9	12 ± 3	90.5%	
NH3-N	mg/L	98 ± 6.6	0.1 ± 0.1	99.8%	5.88
NO3-N	mg/L	0.4 ± 0.1	8.4 ± 0.9	/	
Alk	mg CaCO3/L	501 ± 29	110 ± 27	392	

4.2.5 Phase 7 (day 98- day 130)

In order to get higher treatment capacity of 800m^3/d, more particles were added into both downer and riser. The downer-to-riser recirculation rate was increased correspondingly from 1849L/d to 2837L/d, which was 3 times as fluent flow rate. Liquid flow rates in the downer and riser were 171 m^3/d and 44 m^3/d, respectively, corresponding to superficial liquid velocities of 6mm/s and 1.8 mm/s, respectively. The HRT of downer and riser were increased to 26 hours and 8 hours respectively. DO in the downer was maintained higher than 6mg/L, while airflow rate was kept at 4m^3/h. the average temperature in the reactor was 29 ℃.

According to table 4.12 & 4.13, CFBBR achieved high TN and TCOD removal efficiency of 77.8% and 90.5%, receptivity with COD/nitrogen ratio of 6.26. The effluent TN and TCOD were 15mg/L and 42mg/L, respectively, which can finally meet the regulation of 20 mg/L and 60 mg/L.

Table 4.12 Operational conditions in Phase 7

Parameters	Value	Unit
Particles weight	242/96	kg
Q_{Inf}	800	L/d
Q_C	480	g/L
Q_{D-R}	2837	L/d
Q_{R-R}	44	m^3/d
Q_{D-D}	171	m^3/d

Table 4.13 CFBBR results in Phase 7

Parameter	Unit	Influent	Effluent	Removal	C/N ratio
TCOD	mg/L	708 ± 31	42 ± 17	77.8%	
TN	mg/L	113 ± 17	15 ± 5	90.5%	
NH3-N	mg/L	89 ± 7.5	1.7 ± 0.3	99.8%	6.26
NO3-N	mg/L	0.5 ± 0.3	11.4 ± 5.8	/	
Alk	mg CaCO3/L	458 ± 33	72 ± 37	387	

The overall results show that the CFBBR was able to treat 800m^3/d of domestic

wastewater to meet the Chinese effluent standard.

4.3 Performance Assessment

4.3.1 Nitrogen Removal

The CFBBR removed 61.6%, 73.9%, 92.9%, 90.5% and 90.5% of TN at influent flow rate

of 275, 570, 275, 570, 800 L/d, and influent COD/N ratios of 2.78, 4.39, 5.41, 5.88, and

6.26 respectively. Figures 4.2-4.4 shows the variation of influent and effluent TN, NO3-N and NH4-N concentrations during the different phases of this study. Influent and effluent NO2-N concentrations were negligible with a value of less than 0.3mg/L. A significant change of nitrogen removal efficiency was observed at the same HRT with increased COD/N ratios. For the first 6 phases, the nitrogen removal efficiency increased from 72.5 to 92.9% at influent flow rate of 275 L/d, when COD/N ratios increased from 2.78 to 5.41. In the last phase, the nitrogen removal efficiency was 90.5% at an feeding rate of 800 L/d with COD/N ratio of 6.26. The CFBBR effluent can readily achieve 15 mg TN /L at nitrogen loading of 0.07 kg N/(m^3.d)，which was below the Chinese effluent regulation of TN of 20mg/L.

The influent NH4-N was nitrified in the downer, where DO level was higher than 5mg/L. Even though the average influent NH4-N was as high as 103mg/L through out this study, the CFBBR was always able to achieve high NH4-N removal efficiency (96.8-99.8%) with a range of nitrogen loading from 0.03 to 0.07 kg N/(m^3.d).

The NO3-N generated in downer was recycled to the riser and denitrified at the anoxic environment with the extra dosing of carbon source. The effluent NO3-N decreased from 47 to 7.4mg/L and 30 to 8.4 mg/L at influent flow rate of 275 and 570 m^3/d, when COD/N ratios increased from 2.78 to 5.41 and from 4.39 to 5.88, respectively. In the last phase, the effluent NO3-N concentration achieved 11.4mg/L at influent feeding rate of 800m^3/d with COD/N ratio of 6.26.

4.3.2 Organic Removal

The original influent COD/N was 2.8, which was less than denitrification requirement. Therefore, extra organic matter in the form of glucose was added in to the CFBBR after phase 1 to ensure complete denitrification. Figure 4.5 shows the performance of the system in removing COD from domestic wastewater at different phases. The CFBBR removed 72.5, 75.6, 85.4, 83.8 and 77.8% at influent flow rate of 275, 570, 275, 570, 800 L/d, with influent COD/N ratios of 2.78, 4.39, 5.41, 5.88, and 6.26 respectively. Even though the average influent COD concentrations were 271 mg/L and kept almost same throughout this study, a significant change in effluent COD concentrations was observed with variation of organic dosing and organic loading rates (OLRs). The effluent COD decreased from 92 to 42 mg/L when OLR increased from 0.06 to 0.44 kg COD/(m^3.d).,The effluent TCOD of last 3 phases were 51, 45, 42mg/L which met the Chinese effluent standard of 60mg N/L, whereas 92mg/L and 79mg/L left in the effluent in the first 4 phases, due to low COD/N ratio.
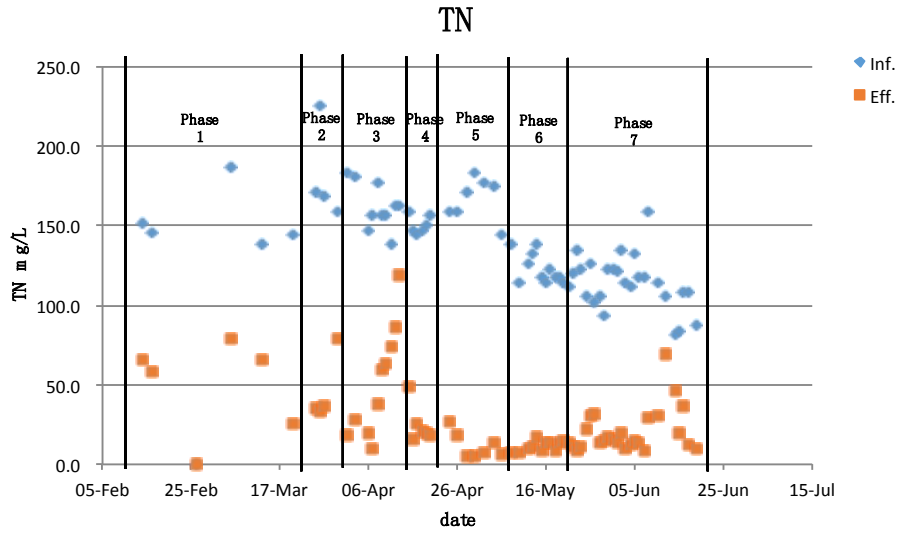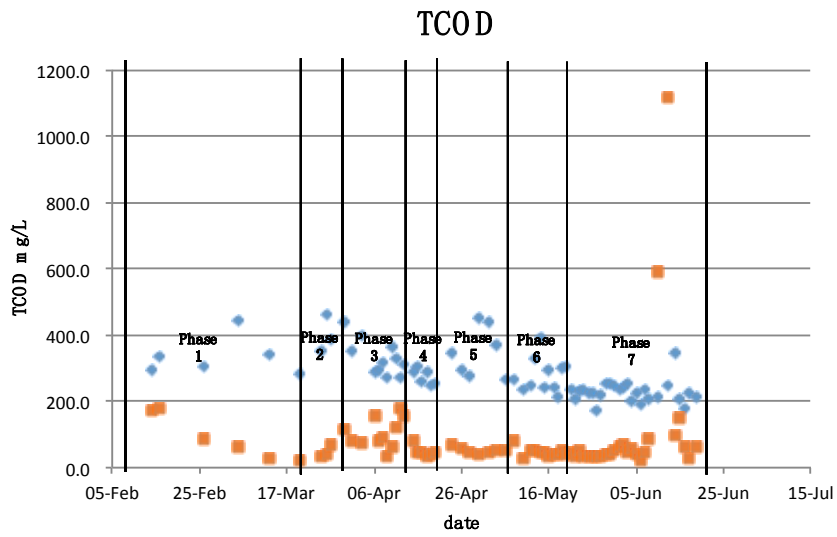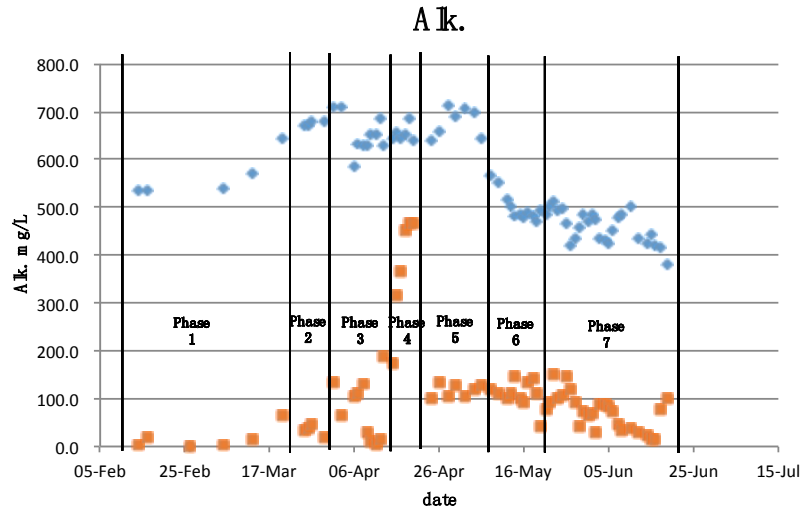
Fig4.2 TN in influent and effluent in CFBBR
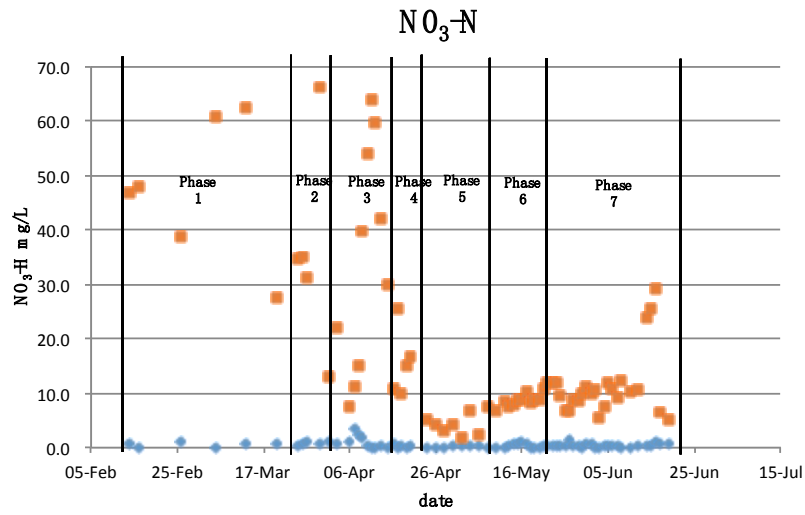
Fig4.3 NO3-N in influent and effluent in CFBBR
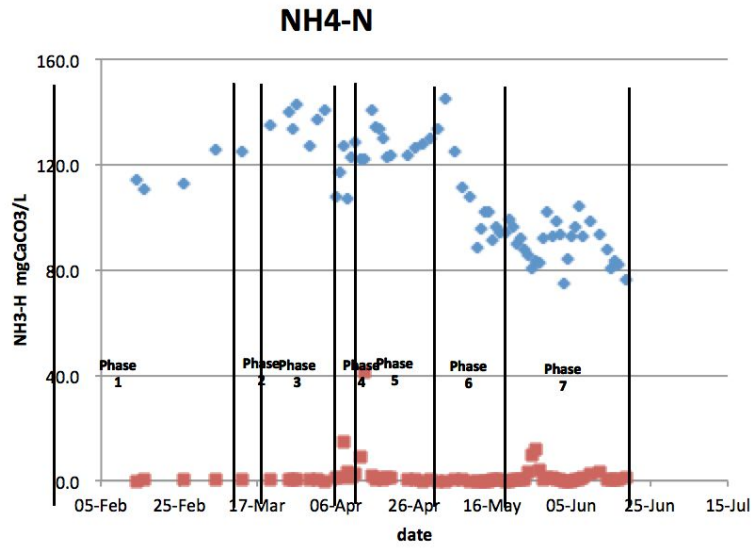
Fig4.4 NH4-N in influent and effluent in CFBBR

Fig4.5 TCOD in influent and effluent in CFBBR

Fig4.6 Alkalinity in influent and effluent in CFBBR

4.3.3 Biomass

The biomass attachment results are shown in Table 4.14. During the first 5 phases, no obvious biomass growth on particles was observed, and the biofilm starts to form quickly at phase 7.

Table 4.14 biomass attachment on particles

| Biomass attachment	Phase 1	Phase 2	Phase 3	Phase 4	Phase 5	Phase 6	Phase 7
Riser mg VSS/g particles	0.3	0.8	0.7	0.5	0.8	2.6	14.4
Downer mg VSS/g particles	0.3	0.1	0.2	0.7	1.2	0.6	2.8

4.3.4 Specific Nitrification and Denitrification

Batch tests were conducted during the last phase of this study to examine nitrification/

denitrification kinetics of the attached biomass of the CFBBR. The 0.5 L batch reactors were equipped with magnetic stirrer and aerobic (purging air to maintain dissolved oxygen) and anoxic (maintained airtight to avoid intrusion of oxygen from air). The results of duplicated specific nitrification and denitrification tests for attached biomass in phase 7 are shown in Figures 4.7-4.8 and Tables 4.15-4.16:

- **Specific nitrification test**

The results showed the attached biomass had nitrification rate of 0.1 kg N/(m^3.d) with average specific nitrification rates of 0.05 g N/(g VSS.d). A nitrification rates of 0.4–0.5 kg N/(m^3.d) was reported by Fdez-Polanco et al. (1994) and Sen and Dentel (1998) when they used a lab-scale FBBRs to treat MWW, with an influent NH4–N concentrations of 30-47mg/L. From previous work from Dr. Nakhla and his co-workers, Nabin (2008) observed specific nitrification rates of 0.09 g N/(g VSS.d) in a lab-scale liquid–solid circulating fluidized bed bioreactor (LSCFB) with average influent NH4–N concentrations of 23mg/L.
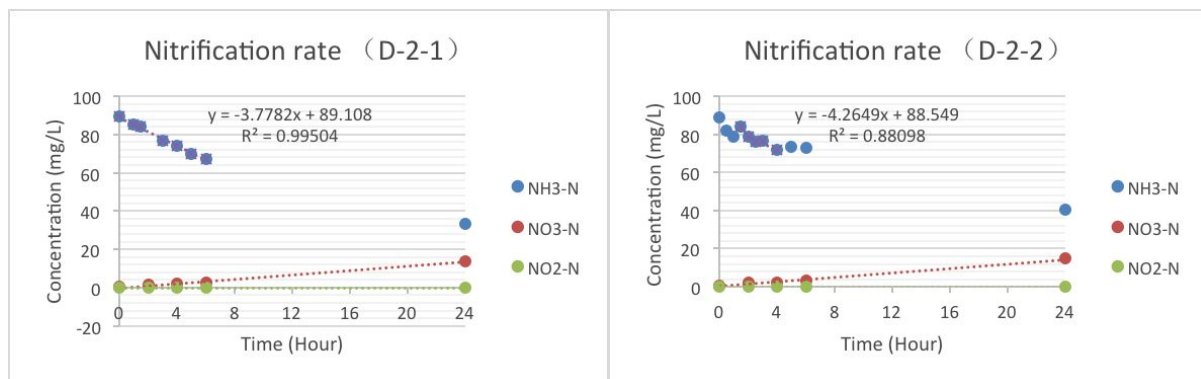
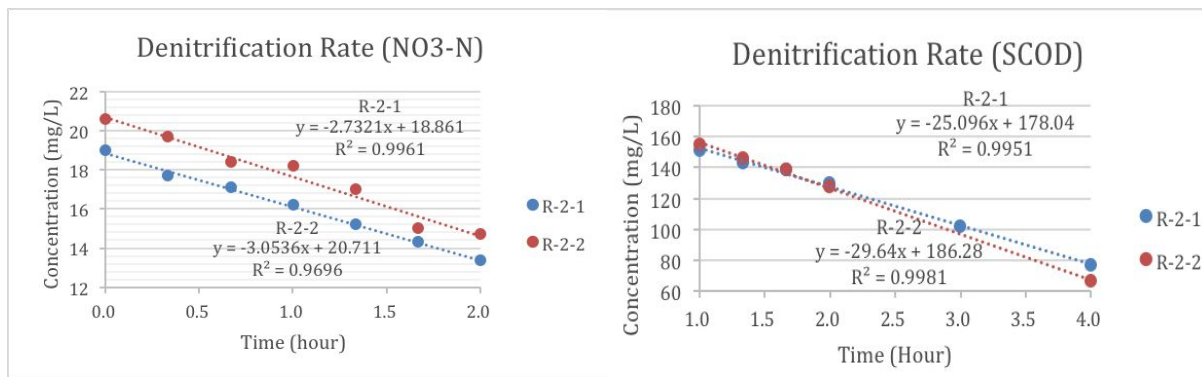**Figure 4.7** Duplicate Specific Nitrification test for bio-particles in Downer

Table 4.15 Specific Nitrification test

Parameters	Unit	D-2-1	D-2-2
Nitrification Rate	(mg N/L.h)	3.77	4.26
Initial Attached VSS	(mg)	223	227
Specific Nitrification Rate	(g N/g VSS.d)	0.04	0.05
Final Biomass	(mg)	142	148
Biomass Yield	(mg VSS/mg NH4-N)	0	0
Alk/N ratio	g CaCO3/g N	6.1	5.0

- **Specific denitrification test**

The results showed the attached biomass had denitrification rate of 0.1 kg N/(m^3.d) with average specific denitrification rates of 0.14 g N/(g VSS.d) with initial F/M ratio of 0.59 g COD/ (g VSS.d). Nabin (2008) observed specific denitrification rates of 0.23-0.43 g N/(g VSS.d) with initial F/M ratio of 0.41-0.83 g COD/ (g VSS.d) in a lab-scale liquid–solid circulating fluidized bed bioreactor (LSCFB).

Figure 4.8 Duplicate Specific Denitrification test for bio-particles in Riser

Table 4.16 Specific Denitrification test

Parameters	Unit	R-2-1	R-2-2
Denitrification Rate	(mg NO_3-N/L.h)	2.7	3.1
COD Consumption Rate	(mg SCOD/L.h)	25.1	29.6
Initial Attached VSS	(mg)	260.4	258.3
Specific Denitrification Rate	(g NO_3-N/g VSS.d)	0.13	0.14
Specific COD Consumption Rate	(g SCOD/g VSS.d)	1.16	1.38
Final Biomass	(mg)	264.3	239.5
Biomass Yield	(mg VSS/mg NH4-N)	0.2	0
Intial C/N ratio	g COD/g NO_3-N	9.2	9.7

4.4 Summary and Conclusions

The CFBBR was operated at 7 phases to treat domestic wastewater and detailed organic and nitrogen kinetics were conducted to enhance understanding of this process. The followings are principal conclusions drawn from the results of this study:

The CFBBR was able to achieve Chinese effluent standard with TN less than 20mg/L and TCOD less than 60mg/L at nitrogen and organic loading rates of 0.07 kg N/(m^3.d) and 0.44 kg COD/(m^3.d), corresponding to an influent flow rate of 800 L/d and HRT 34 hours, respectively.

The specific nitrification tests showed attached biomass had nitrification rate of 0.1 kg

N/(m^3.d) with average specific nitrification rates of 0.05 g N/(g VSS.d). The specific nitrification tests show the attached biomass had denitrification rate of 0.1 kg N/(m^3.d) with average specific denitrification rates of 0.14 g N/(g VSS.d) with initial F/M ratio of 0.59 g COD/ (g VSS.d).

Conclusions: This pilot CFBBR system demonstrated its effectiveness as a compact water treatment technology capable of nitrifying high concentration ammonia domestic wastewater. With extra organic carbon addition, the system can conduct sufficient denitrification process to reduce total nitrogen effluent concentrations of the system to meet Chinese municipal effluent discharge regulations of <60 mg COD/L and <20 mg TN/L.

4.5 References

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5. Conclusions

5.1 Summary and conclusions

The results of this study demonstrate the fluidized bed bioreactors' effectiveness as a compact wastewater treatment technology capable of treating high influent ammonia concentration and low COD/ ammonia nitrogen wastewater.

The lab-scale PNFBR can treat ammonia rich-synthetic wastewater by controlling temperature, DO level and alkalinity. The effluent from this partial nitrification process can be directly used as the influent of anammox process.

The pilot CFBBR system demonstrated its effectiveness as a compact wastewater treatment technology capable of nitrifying high concentration ammonia domestic wastewater. With extra organic carbon addition, the system can sufficiently denitrify to reduce total nitrogen effluent concentrations of the system to meet municipal effluent discharge regulations of <60 mg COD/L and <20 mg TN/L.

5.2 Recommendations and Future Work

Since the PNFBR system was able to achieve the synthetic wastewater treatment with NH4-N level (400mg/L), I would recommend to continue this study with higher NH4-N level, such as 800mg/L, which is closer to landfill leachate or sludge digester liquor.

Secondly, Investigating the activities of AOB and NOB in both attachment and granular

biomass can not only help operators understand and analyse the performance of PNFBR

better, but also optimize the operational conditions accordingly.

For CFBBR system, I would recommend to continue this system with higher influent

flowrate.

Curriculum Vitae

Kai Li
Male

Education

2013-Present   **Master in Engineering Science, Chemical and Biochemical Engineering**
University of Western Ontario, London, Ontario

2007-2011   **Bachelor of Engineering, Chemical Engineering**
Shenyang University of Chemical Technology, Shenyang, China

Research Experience

2013-Present   **Graduate Research**, Department of Chemical and Biochemical Engineering, University of Western Ontario

Work Experience

2014-2015   **Teaching Assistant**, Department of Chemical and Biochemical Engineering, University of Western Ontario
- Course: Biochemical Reaction Engineering

Scholarship

2013-2014   **Research Engineer**, Ekologix Canada, NSERC Industrial
- Evaluation and interpretation of the performance of an aeration/mixing technology for a full-scale wastewater treatment process