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Comparative Study of a Novel Membrane Bioreactor System for Biological Nutrient Removal with Conventional Systems

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Comparative Study of a Novel Membrane Bioreactor System for Biological Nutrient Removal with Conventional Systems

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Abstract

This comparative study evaluated a novel membrane bioreactor (NMBR) for biological nutrient performance and membrane fouling with conventional BNR systems i.e. anaerobic/anoxic/aerobic (A^2O) process and University of Capetown (UCT) modified MBR process (UMBR). Comparison of the NMBR and A^2O process, conducted at hydraulic retention time (HRT) of 8 hr and solids retention time (SRT) of 10 days using synthetic wastewater (SWW) and municipal wastewater (MWW), revealed that NMBR achieved lower effluent phosphorus than the A^2O with 0.2 vs 1.2 mg/L (SWW) and 0.8 vs 1 mg/L (MWW) as well as 20% lower sludge production. The study also substantiated that NMBR intermediate clarifier assisted chemical oxygen demand (COD), nitrogen, and P removals. Furthermore, the NMBR achieved 0.3 m/L lower effluent dissolved organic nitrogen (DON) than A^2O and the DON reduction by membrane averaging 0.4 mg/L.

The second comparative study with NMBR and UMBR process, tested at an HRT of 6 hr and SRT of 10 days using two different strength of MWW, indicated that effluent nitrate and P concentrations were lower in the NMBR than the UMBR by as much as 1-1.7 and 0.3 mg/L, respectively. Sludge P fractionation substantiated that poly-P content increased from 27-37% to 57-59% of the total phosphorus (TP) and P uptake by denitrifying phosphate accumulating organisms (DPAO) accounted for 37-40% of the total uptake in both systems.

Both MBR systems showed similar membrane fouling trends with similar fouling rate of 4.4×10^{-2} LMH/kPa·h. A statistical analysis confirmed that soluble microbial product impacts membrane fouling more significantly than floc size, the bound protein/total protein ratio and bound extracellular polymeric substance (EPS). The

biofilm layer deposited on the membrane caused denitrification of as much as 1.5 mg N/L, which was primarily impacted by dissolved oxygen and transmembrane pressure, triggering membrane fouling.

Another study of the impact of denitrification on membrane fouling propensity, using three different sludges i.e. conventional activated sludge (CAS), ordinary heterotrophic organisms (OHO) and DPAO, indicated that DPAO denitrification decreased cake layer resistance by 53% compared to an increase of 220 and 150% in CAS and OHO denitrification. The reduction in cake layer resistance for DPAO denitrification was associated with the increase in hydrophobicity and decrease in carbohydrate/protein ratio in bound EPS of DPAO after denitrification, with the reverse trend observed with CAS and OHO.

Therefore, the contributions of this study are summarized as followings:

1. Identification of the role of the intermediate clarifier in the NMBR
2. Confirmation of the advantages & disadvantages of the NMBR relative to conventional systems
3. Extensive characterization of membrane foulants in BNR systems
4. Delineation of the fact that contrary to common belief, DPAO reduces fouling

Keywords

Membrane bioreactor, biological nutrient removal, enhanced biological phosphorus removal, denitrifying phosphate accumulating organism, membrane fouling, dissolved organic nitrogen, P fractionation.

Co Authorship

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I dedicate this piece of work to them.

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List of Abbreviations and Symbols

Am	membrane area (m^2)
BCA	bicinchoninic acid
$bEPS_{pro}$	bound EPS protein
$bEPS_{car}$	bound EPS carbohydrate
BNR	biological nutrient removal
BSA	bovine serum albumin
CAS	conventional activated sludge
COD	chemical oxygen demand (mg/L)
DO	dissolved oxygen (mg/L)
DON	dissolved organic nitrogen (mg/L)
DPAO	denitrifying phosphate accumulating organism
EBPR	enhanced biological phosphorus removal
EPS	extracellular polymeric substances (mg/g VSS)
FR	fouling rate ($L/m^2\ h^2\ kPa$) or (LMH/kPa h)
GAO	glucogen accumulating organism
HRT	hydraulic retention time (h)
Jp	permeate flux (L/m^2 h) or (LMH)
Lp	permeability (L/m^2 h kPa) or (LMH/kPa)
MBR	membrane bioreactor
MFI	modified fouling index (10^3 s/L^2)
MLSS	mixed liquor suspended solids (g/L)
MLVSS	mixed liquor volatile suspended solids (g/L)
MWW	municipal wastewater
NMBR	novel MBR
OHO	ordinary heterotrophic organism
P	transmembrane pressure (kPa)
PAO	phosphate accumulating organism
PCA	perchloric acid
PLC	programmable logic control
Qp	permeate flow (L/h)
rDON	recalcitrant dissolved organic nitrogen (mg/L)
SCOD	soluble chemical oxygen demand (mg/L)
SMP	soluble microbial products (mg/L or mg/gVSS)
SMP_{pro}	SMP protein
SMP_{car}	SMP carbohydrate
SRT	solid retention time (day)
STKN	soluble total kjeldahl nitrogen (mg/L)
SVI	sludge volume index (ml/g)
SWW	synthetic wastewater
T	time (h)
$tEPS_{pro}$	total EPS protein
$tEPS_{car}$	total EPS carbohydrate
TCOD	total chemical oxygen demand (mg/L)
TMP	transmembrane pressure (kPa)

TKN	total kjeldahl nitrogen (mg/L)
TP	total phosphorous (mg/L)
TSS	total suspended solids (g/L)
UASB	upflow anaerobic sludge blanket
UCT	university of cape town
UMBR	UCT MBR
VFA	volatile fatty acid (mg/L)
VSS	volatile suspended solids (g/L)
Y_{obs}	observed yield (gVSS/gCOD)

1.0 Introduction

1.1 Background

Biological nutrient removal (BNR) is becoming increasingly critical due to severe contamination of water bodies and more stringent guidelines for nitrogen (N) and phosphorus (P). N and P are the primary cause of eutrophication in receiving waters. BNR is an economic process compared to physical and chemical technology. Recently, BNR systems have started to employ membrane technology for a final solid separation. Membrane bioreactor (MBR) adapted BNR processes have reported various advantages compared to conventional system activated sludge employing final clarifier. MBR process benefits are small foot print of installation and perfect capture of biomass while final clarification has often experienced serious operational problems i.e. sludge bulking, pinfloc and rising sludge.

BNR capacity in MBR was characterized by higher nitrification rate and low sludge yield due to perfect retention of sludge and colloids as well as operation at long solids retention time (SRT). However, the application has been restricted due to membrane fouling, which increases maintenance cost. Primary foulants such as extracellular polymeric substances (EPS) and soluble microbial product (SMP), generated from biomass activity or present in incoming wastewater deteriorate permeability.

Nakhla and Patel (2008) patented a novel MBR (NMBR) process for BNR, characterized by the employment of an intermediate clarifier placed after the anaerobic

tank and membrane utilization in aerobic tank. It presented several advantages such as low sludge yield and high content of denitrifying phosphate accumulating organisms (Patel et al., 2005)

Although the system has been optimized in previous studies (Patel et al., 2005), it should be required to assess this system with conventional systems. It was also necessary to identify the role of the intermediate clarifier in BNR improvement. In addition, membrane fouling which is essential to understand MBR system operation has not been investigated.

1.2 Goal of the research

The primary objective of the current study is to evaluate the NMBR BNR capacity through comparative performances with conventional BNR systems firstly with final clarifier and secondly with membrane i.e. A^2O and UCT. The specific goals are as follows;

1. To investigate fate of COD, nitrogen, phosphorus and solids in the system and delineate contribution of each process to BNR performance.

2. To assess the role of intermediate clarifier, final clarifier and membranes in nutrient removal.

3. To thoroughly comprehend the fouling mechanisms in membrane assisted BNR systems and investigate fouling parameters i.e. SMP, EPS and their component relationship.

4. To investigate the potential role of the membrane biofilm layer in BNR performance and determine its impact on membrane fouling, as well as evaluating the fouling propensity of different denitrifying organisms.

1.3 Thesis overview

Chapter 2 describes literature pertinent to the research study and chapter 3 demonstrates all the material and methods used in this study.

Chapter 4 thoroughly deals with the role of intermediate clarifier in NMBR BNR performance.

Chapter 5 discusses the comparative study with A^2O in terms of COD, N and P fate for synthetic wastewater and municipal wastewater.

Chapter 6 demonstrates the comparison of effluent DON in the MBR and conventional system and emphasizes the beneficial role of membrane in decreasing DON.

Chapter 7 elaborates on phosphorus fractionation in the two membrane assisted BNR systems studied here as well as BNR performance for different municipal wastewaters.

Chapter 8 discusses membrane fouling in the two tested MBR systems for BNR including denitrification phenomena in biofilm layer of membrane.

Chapter 9 demonstrates diverse denitrification related fouling propensity related to different denitrification pathway in BNR system.

Chapter 10 summarized the major findings and conclusions of this study followed by engineering significance in Chapter 11.

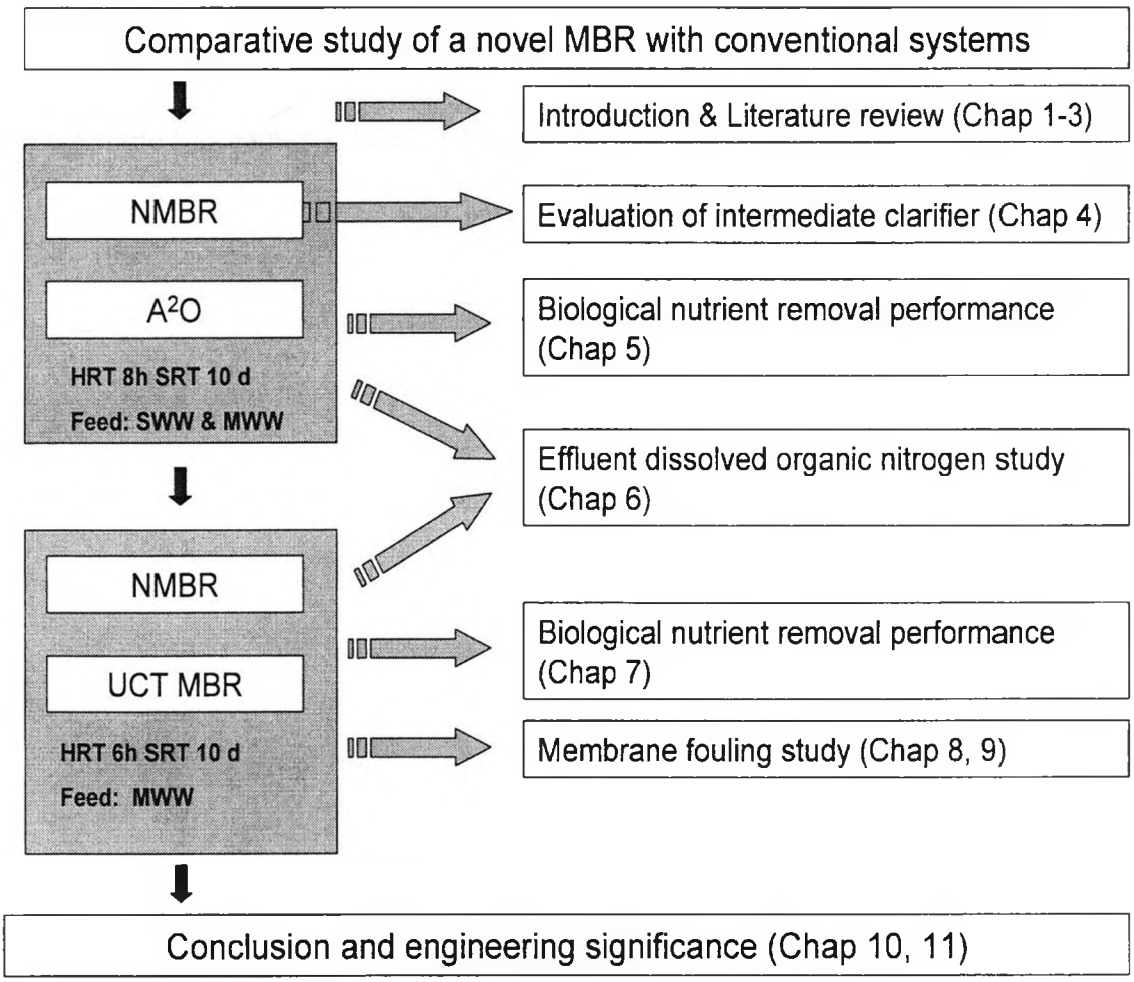


Figure 1.1 Schematic overview of the study.

1.4 References

Nakhla G.; Patel J. (2008) Treatment of Wastewater Containing Phosphorus and Nitrogen. US Patent No. US 7,326,343 B2 dated Feb 5.

Patel J.; Nakhla G.; Margaritis A. (2005) Optimization of biological nutrient removal in a membrane bioreactor system. *J Environ. Eng.* **131,** 1021-1029.

2.0 Literature review

2.1 Principles of biological nutrient removal

2.1.1 Nitrogen removal

Nitrogen in wastewater can be transformed and removed by biologically mediated nitrification and denitrification as well as nitrogen uptake for cell synthesis. Nitrification is oxidation of ammonia to nitrite and nitrate using oxygen and carbon dioxide as electron acceptor and carbon source, respectively. Ammonia can be converted from organic nitrogen through deamination and ammonification. Two autotrophic organisms are key involved organisms i.e. Nitrosomonas and Nitrobacter.

Nitrosomonas

$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+ + \text{New cells}$ Eq (2.1)

Nitrobacter

$2NO_2^- + O_2 \rightarrow 2NO_3^- + \text{New cells}$ Eq (2.2)

Nitrification is influenced by SRT, temperature,. and dissolved oxygen, ambient pH, and presence of toxic compounds. Nitrifiers are slow growing organisms necessitating longer SRT. Temperature change from 20 to 10°C causes more than 60% reduction in nitrification rate and the optimum pH for the reliable operation is 6.8-7.4. (Randall et al., 1992)

Denitrification is the process of nitrate reduction to nitrogen gas by microorganism under anoxic conditions i.e. absence of dissolved oxygen. It requires readily biodegradable COD serving as carbon source and follows Eq. (2.3).

$$NO_3^- + rbCOD \rightarrow N_2\ (gas) + CO_2 + H_2O + OH^- + New\ cells \qquad Eq\ (2.3)$$

Like any biodegradation process, the type of organic matter and temperature strongly impact the rate. Biological nitrogen removal can reduce energy requirement compared to the BOD removal only because denitrification consumes organic carbon. Denitrifying organisms are divided into two groups, one capable of dissimilating nitrates to nitrogen gas directly and other producing nitrogen gas via nitrate, nitrite and nitrous oxides. Moreover, incorporation of denitrification reduces sludge yield because denitrifying organisms obtain less energy from utilizing oxidized nitrates as an electron acceptor compared to dissolved oxygen.

Factors impacting denitrification are oxygen, pH, temperature, and organic carbon. With presence of oxygen, denitrification is significantly inhibited. Denitrification can be inhibited at DO concentration of 0.2 mg/L and above (Metcalf and Eddy, 2003). Denitrification rate increases with temperature. Denitrifiers are sensitive to pH greater than 8. It was observed that nitrite accumulated at pH 8.5 while nitrous oxide increased at pH 5. Optimum nitrate removal occurs at pH 7.5. The type of organic carbon also affects denitrification. Thus, readily biodegradable COD (rbCOD) increases denitrification rate more than slowly biodegradable COD. Isaac and Henze (1995) tested denitrification

under carbon limiting and excess carbon using acetate. At C/N ratio of below 1.86 mgC/mgN the denitrification rate was 1.9 mgN/gVSS/h compared to 3.4 mgN/gVSS/h with a C/N ratio of 7.5 mgC/mgN. Tam et al (1992) tested three carbon sources i.e. acetate, methanol and glucose to evaluate denitrification rates and observed that acetate is the most efficient and achieved the highest nitrogen removal rate. Biochemically, organic carbon is utilized via the glycolytic pathway and tricarboxylic acid (TCA) cycle (Gaudy and Gaudy, 1980). Acetyl Co-A is easily formed from acetate while methanol or glucose requires several intermediates to enter the TCA cycle.

Recently, due to stringent effluent total nitrogen concentrations as low as 3 mg/L, significant emphasis has been exerted on refractory nonbiodegradable dissolved organic nitrogen in effluent (efDON). According to an intensive review by Pehlivanoglu-Mantas and Sedlak (2006), efDON accounts for up to 80% of the total nitrogen in nitrification-denitrification process effluents. Based on data collected from seven plants in USA, Pagilla et al (2006) also reported that the percentage of efDON ranged from 20-85% of the effluent 5 mg/L TN.

Reduction of efDON is challenging due to the complexity of its nature. Awobamise et al (2007) tested the biodegradability of efDON during 30 days and observed that out of initial DON of 1 mg/L, biodegradable DON increased in the first 20 days from less than 0.1 to 0.5 mg/L, indicating that 50% of DON is not removed by biological processes. This is consistent with the observation by Urgun-Demirtas et al. (2007) where 18-61% of efDON was bioavailable in the first 14 days. Pagilla et al.

(2006) observed that the molecular weight (MW) of DON ranged from 1 to 1000 kD, with the low MW compounds biodegradable. Thus, various physical or chemical treatments attempted for breaking the chain of high MW DON compounds, revealed the feasibility of anion exchange, coagulation, ozonation, advanced oxidation to some extent (Pehlivanoglu-Mantas and Sedlak, 2006), though their application is usually limited to industrial wastewaters.

Parkin and McCarty (1981) suggested that SRT can be a key parameter for controlling efDON because more influent DON is biodegraded at longer SRTs. However, increased biomass endogenous respiration increases DON, suggesting the occurrence of an optimal SRT. O'Shaughnessy et al. (2006) also reported that longer SRT and higher temperature within ranges of 10-17 days and 5-17°C, respectively led to efDON reduction.

2.1.2 Phosphorus removal

Phosphorus removal occurs via biological metabolism and natural P precipitation with cations i.e. Ca, Mg, Al present in wastewater. Relatively low P removal occurs via cell synthesis and P precipitation, with phosphorus removal achieved by mostly phosphate accumulating organism (PAO) which is capable of storing P within the cell to as high as 10% by weight of solids compared to 2 % in activated sludge. P removal occurs through two steps i.e. P release and uptake. PAO releases under anaerobic conditions i.e. absence of nitrate or dissolved oxygen. Concomitantly, PAO store volatile fatty acid (VFA) as intracellular products i.e. poly hydroxylbutyrate (PHB). Key

requirement for reliable P removal is sufficient VFA in the anaerobic zone and sufficient DO in aerobic zone.

Usually P uptake occurs in the aerobic tank using dissolved oxygen as electron acceptor but also can be observed by nitrate reduction in the anoxic tank by denitrifying phosphate accumulating organisms (DPAO). Thus P removal achieved by wasting sludge during cyclic metabolism in anaerobic conditions (P release and VFA consumption (PHB production)) and subsequent anoxic and/or aerobic conditions (P uptake, PHB oxidation and cell synthesis)

In enhanced biological phosphorus removal (EBPR) systems, the role of DPAO can be significant in both P and nitrogen removal. Bortone et al (1996) reported that DPAOs using the Dephanox system allowed a constant high efficiency of P removal even operating with low COD/TKN ratio wastewater. Hu et al (2002) concluded that the most important factor influencing the occurrence of DPAOs and associated anoxic P uptake is the nitrate load to the main anoxic reactor, i.e. if the nitrate load is large enough or exceeds the heterotrophic denitrifiers' potential of the anoxic reactor, then DPAOs are stimulated in the system.

A summary of the pertinent BNR reactions is presented in Table 2.1.

Table 2.1 Summary of BNR reactions

Process step	Major process and organisms
Anaerobic tank	PAO: P release and PHB synthesis OHO: Fermentation
Pre-anoxic tank	OHO: Nitrate, BOD reduction DPAO: P, nitrate reduction and PHB degradation
Aerobic tank	OHO: BOD removal, ammonification Autotrophs: ammonia reduction via nitrification
Post-anoxic tank	OHO: Nitrate reduction using cellular substrate or external carbon i.e. methanol PAO: P uptake and PHB degradation

2.1.3 Factors for successful P removal operation

1) VFA concentration

It is widely accepted that an anaerobic/aerobic sequence is a necessity to initiate and sustain EBPR. However, to ensure reliable removal of ortho-phosphorus to less than 0.1 mg/L, sufficient VFA is required to form intracellular storage products (e.g. PHBs) (Filipe et al., 2001). rbCOD fermentation in the anaerobic zone can enhance VFA content of municipal wastewater. Most VFA present in municipal wastewater is acetic acid and propionic acid.

2) Nitrate inhibition

Nitrate presence in the anaerobic zone causes shortage of rbCOD for PAO because heterotrophic organisms use nitrates as a terminal electron acceptor.

3) Secondary P release

Secondary P release occurs when P rich sludge is sustained at long anaerobic retention time. The released P is not related to PHB synthesis, and accordingly it is not removed in subsequent aerobic zone. (Barnard et al., 2006) In addition, it requires more VFA addition.

4) Competing organisms

The most widely reported competitor to PAO is glycogen accumulating organism (GAO). GAO also takes up VFA in anaerobic condition without P release. However, the energy produced via glycogen degradation, compared to poly-P degradation in PAO. Thus, in presence of GAO, P release and uptake is diminished and effluent P deteriorates. Several studies on controlling GAO observed that influent VFA type influenced GAO metabolism (Oehmen et al., 2005). GAO activity can be also inhibited by operational conditions of temperature below 30 °C and pH 8 (Barnard et al., 2006)

2.1.4 Typical BNR systems

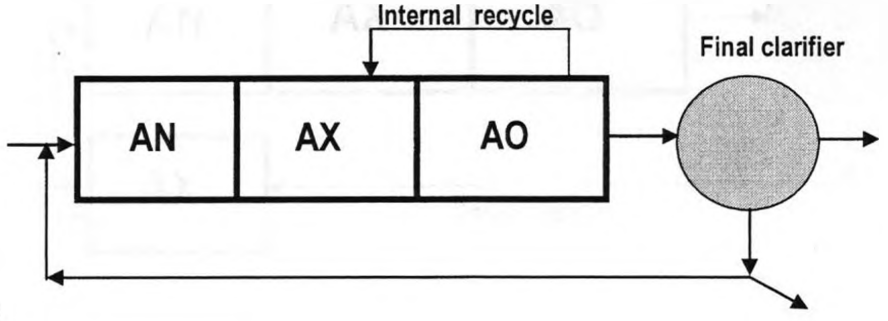
Figure 2.1 represents typical BNR systems which all share a common feature where nitrified mixed liquor from the aerobic tank is recycled to the anoxic tank for reducing nitrates (Henze et al., 2008). A^2O system, the patented product of Air Products and Chemicals (Allentown, PA, USA), was characterized by the sequence of anaerobic/anoxic/aerobic tank in order to remove nitrates and P. However, nitrates in recycled sludge from the clarifier to the anaerobic tank can reduce P removal due to rbCOD consumption. The UCT system (Figure 2.1b), developed by University of Cape Town, consists of three main bioreactors i.e. anaerobic, anoxic and aerobic tank. Influent wastewater is fed to anaerobic zone for enhancing P release using raw wastewater VFA. The following anoxic tank is designed to reduce nitrates generated from the aerobic tank. The system can achieve high P removal efficiency but requires high pumping energy due to large internal recycles comprising three recirculation lines including two internal recycle from the anoxic to the anaerobic and from the aerobic and the anoxic tank as well as settled sludge from the final clarifier to the anoxic tank to eliminate nitrate inhibition in the anaerobic tank.

The Bardenpho system (Figure 2.1c), comprised of sequences of anaerobic/anoxic/aerobic/anoxic/aerobic tank, was developed during 1970s. The main features of this system are two anoxic zones for enhancing overall denitrification. The first anoxic tank was designed to utilize carbon source in wastewater while the second anoxic tank denitrifies under endogenous respiration. Another merit of the system is low

nitrate introduction to anaerobic tank decreasing rbCOD utilization by ordinary heterotrophs. Thus, it can achieve low sludge production as well as rich P sludge but requires high BOD/P ratio influent and high pumping energy. However, the Bardenpho system has several limitations. It has little operational flexibility indicating that P removal mainly depends on the incoming wastewater characteristics. In addition, significantly low denitrification rates in the second anoxic tank do not assist nitrate removal at low wastewater C/N ratio but deteriorate P removal due to secondary P release.

The Johannesburg process (Figure 2.1d) is characterized by the prevention of nitrate introduction to anaerobic tank due to denitrification in the first anoxic stage with endogenous respiration. However, it prevents nitrate introduction to the anaerobic tank only when the influent COD/TKN ratio is high.

Besides these systems, BNR can be achieved by sequencing batch reactors (SBR), oxidation ditch and two sludge process i.e. Dephanox.



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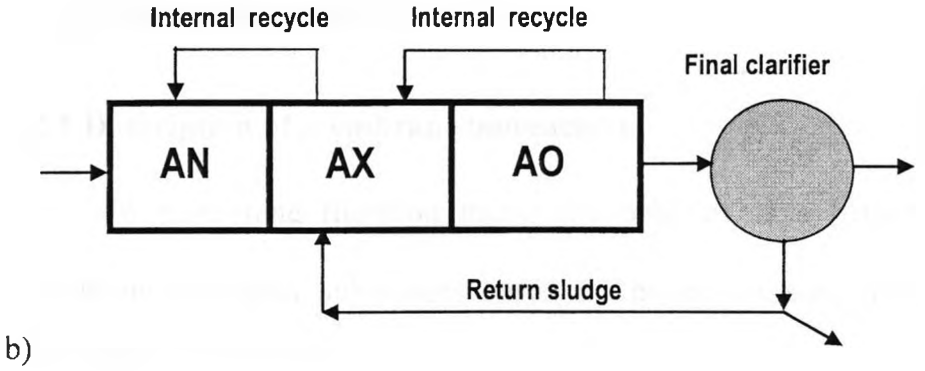

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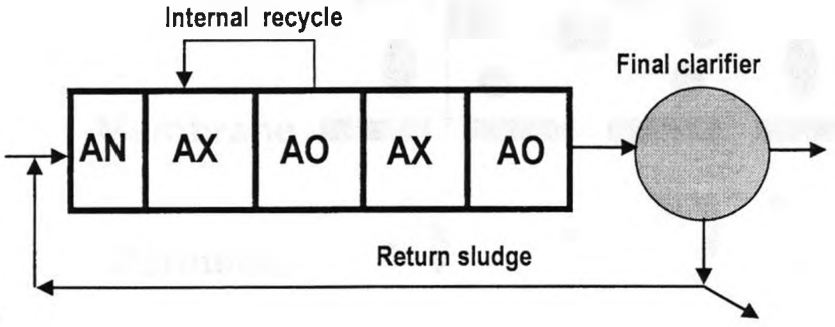

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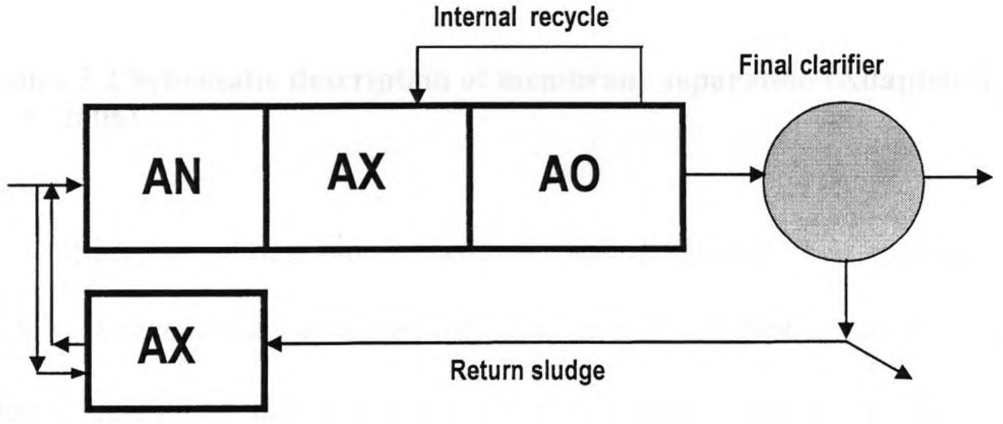

d)

Figure 2.1 biological nutrient removal systems (a) A^2O (b) UCT (c) Modified Bardenpho™ (d) Johannesburg (AN: anaerobic, AX: anoxic, AO: aerobic tank)

2.2 Membrane bioreactors

2.2.1 Description of membrane bioreactors

In membrane filtration membrane behaves as a barrier between two phases. Membrane separates substances based on molecular size. TMP is driving force for permeation. (Figure 2.2)

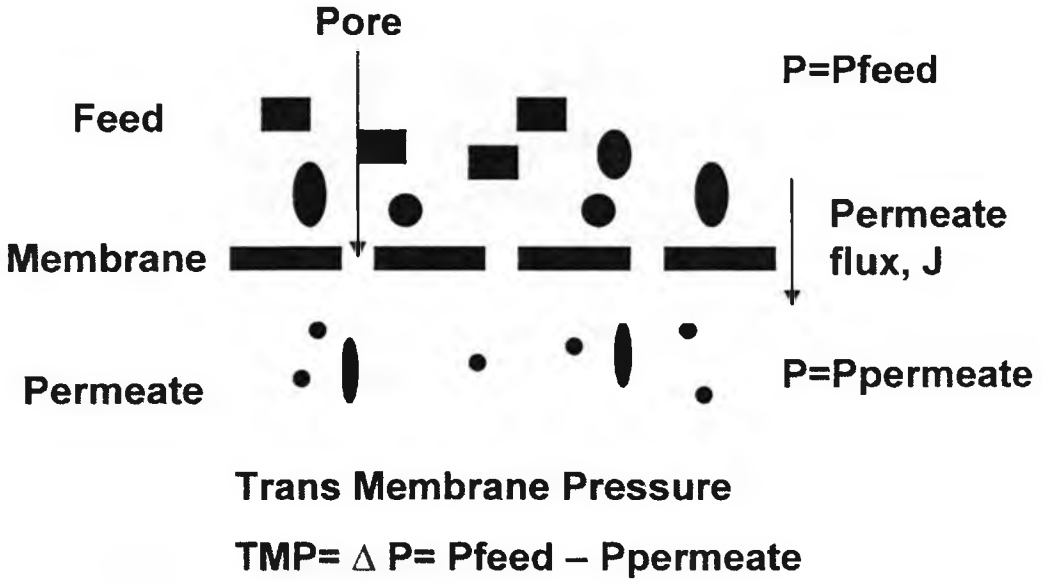

Figure 2.2 Schematic description of membrane separation (Adapted from Evenblij et al., 2006)

Since membrane bioreactors have been developed, their application is increasing rapidly. A recent study indicated that more than 2200 MBR installations in operation and under construction and 258 full scale MBR plants (mostly for municipal wastewater treatment) have been constructed (Yang et al., 2006). Figure 2.3 illustrates the differentiation of membrane type depending on the separation capability and molecular weight cut off. The unit of Da represents the mass of a hydrogen atom. Reverse osmosis

has very small pore size which is the most selective membrane. It can reject monovalent ions i.e. sodium and chloride. Normally, reverse osmosis operates at very high pressure as much as 700 psi while other membranes operate at relatively lower pressure with larger pore size. Ultrafiltration is applied for wastewater treatment to capture solids and microorganisms (Judd and Judd, 2006).

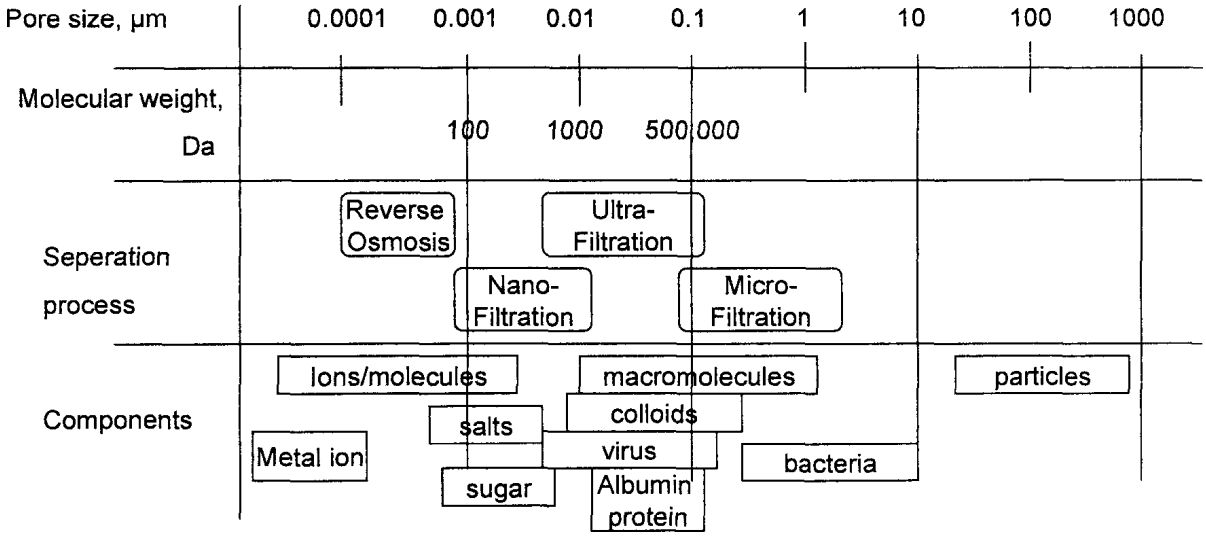

Figure 2.3 Classification of membrane

The advantages and disadvantages of MBR relative to conventional system are summarized in Table 2.2. MBR characteristics compared to conventional activated sludge system are operation at high concentration as much as 10 g/L and perfect capture of sludge, thus reducing bioreactor hydraulic retention time (HRT) and foot print. However high of biomass concentrations decrease oxygen transfer efficiency and operational cost including maintenance are relatively higher than conventional systems. For examples, Davies et al (1998) reported that MBR operational cost is around 1.5-2 times

conventional systems based on 2000 person equivalent (p.e.) and 40000 p.e. capacity, respectively.

Table 2.2 Advantages and disadvantages of MBR systems

Advantage	Disadvantage
• Excellent effluent quality • Low sludge production • Shorter start-up time • Feasible for treating extreme condition wastewater • Small foot print	• Membrane fouling • High operational cost • Complicated controlling system

Membranes are incorporated in activated sludge systems in two ways (Fig 2.4) although practically there is no strict differentiation. Submerged membranes are simple and save energy compared to cross flow side stream MBR which require high pump recirculation rates. In addition, submerged MBR benefits relatively less fouling due to air bubbling agitation while external MBR is easier for chemical cleaning.

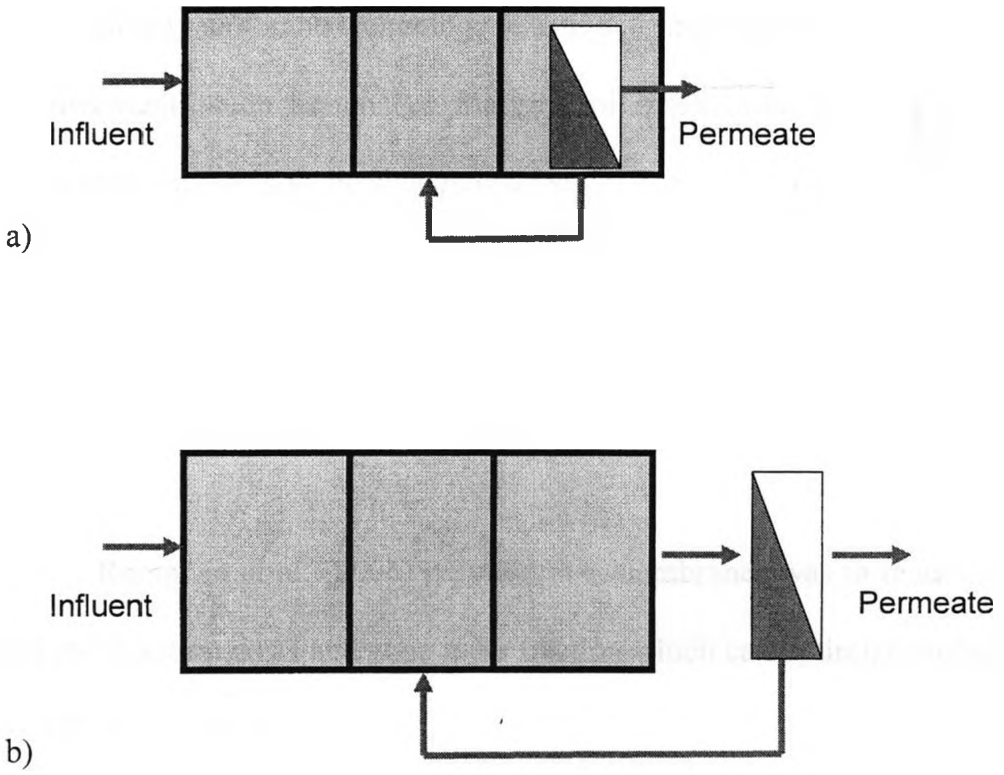

Figure 2.4 Membrane separation configuration (a) internal membranes (or submerged) (b) external membranes (or side stream)

2.2.2 MBR BNR performances

Membrane assisted BNR processes exhibited superior nutrient removal capability over conventional BNR process. In BNR configurations, final clarification was primarily considered for solids separation. However, depending on the sludge blanket retention, the clarifier assisted partially in nitrogen removal due to denitrification within the sludge blanket, at the cost of higher effluent suspended solids (Siegrist et al., 1995; Monti et al., 2006).

Since membrane technology substituted final clarification in BNR systems several improvements such as smaller footprint of installation, lower sludge production and better nitrification have been achieved (Monti et al., 2006). Monti et al. (2006) observed a 15% lower sludge yield in the MBR system than in the identically operated conventional system with a final clarifier in pilot scale comparisons at the same HRT of 10 h and solids residence time (SRT) of 12 d.

Ramphao et al. (2006) reported that membranes was to reduce sludge thickening and stabilization costs and zone mass fraction which can optimize biological nitrogen and phosphorus removal.

Some of the reported advantageous MBR operating conditions i.e. long solids resident time (SRT) and low sludge production are not necessarily conducive to enhanced biological phosphorus removal (EBPR). The sparse literature on EBPR in MBRs is controversial. Lesjean et al. (2002) operated a University of Cape town (UCT) adapted MBR process on a wastewater with COD:N:P ratios of 100:7:1 at an HRT of 18-21 h and SRT of 15 d, and achieved effluent P below 0.1 mg/L without chemical addition, attributing the high P removal primarily to EBPR, with retention of solids and colloids by the membrane as secondary.

On the other hand, Fleischer et al. (2005) operated a 6-stage pilot MBR on primary effluent with COD:N:P ratio of 100:13:2 at an HRT of 8.4 h and SRT of 19 to 23 d, and maintained effluent P of 2 mg/L, decreasing to 0.1 mg/L at an alum dose of 2.7

mole Al/mgTP. Mouthon-Bello and Zhou (2006) operated a pilot anoxic/anaerobic/aerobic MBR system at HRTs of 5.8 and 7.9 h, and SRTs of 20 and 50 d on two municipal wastewaters (MWW) characterized by COD:N:P ratios of 100:17:3.4 and 100:17:1.6, respectively and interestingly found that despite a longer SRT in the latter case, P in the membrane tank decreased from 1.8 to 0.7 mg/L, with permeate concentrations of 0.5 and 0.1 mg/L. The aforementioned authors concluded that EBPR did not occur and attributed P removal to precipitation by the relatively high influent metals and particulates rejection by the membrane. Furthermore, Monti et al. (2006) in a comparative assessment of EBPR in a conventional and membrane-assisted UCT pilots treating primary effluent at HRTs of 7-12 h and SRT of 12 d, that when the influent VFA were limiting, because of the lower yield in the MBR, the conventional system exhibited better soluble P removal.

2.3. Membrane fouling

2.3.1 Membrane Fouling mechanisms

Although MBR process is reliable in terms of perfect capture of solids in the system, membrane fouling has restricted its practical application and increased operational costs (Le-Clech et al., 2006).

Figure 2.5 presents the major mechanism of fouling SMP and EPS accumulated on membrane surfaces. Pore clogging occurs due to colloidal and cell debris. Deposition of sludge cake on membrane surfaces increases transmembrane pressure and decrease permeability. Some of foulants are easily removed, thus called reversible fouling,

compared to irreversible fouling caused by deposition of organic and inorganic components into membrane pores.

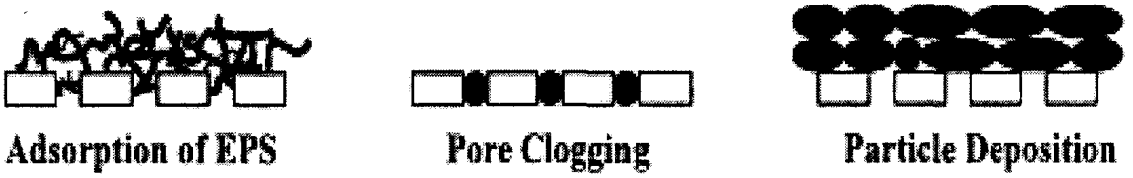

Figure 2.5 Mechanism of biofouling in membrane separation bioreactors. (adapted from Liao et al., 2004)

2.3.2 Fouling factors

Table 2.3 categorizes fouling factors. Membrane fouling occurs through interaction among the various factors. Extensive research on membrane fouling has unveiled the impact of many operational conditions such as HRT, SRT, dissolved oxygen (DO), temperature and aeration as well as sludge characteristics i.e. particle size, viscosity (Le-Clech et al, 2006).

Table 2.3 Fouling impact factors

Fluid Mechanics	Shear stress on membrane
Membrane module	Fiber packing density, space distance
Membrane material	Hydrophobicity, surface charge, pore size
Operating conditions	pH, HRT, SRT, Food to microorganism ratio, ion strength
Sludge properties	EPS, Particle size, hydrophobicity, surface charge,

Several studies reported that MLSS concentration impact on membrane fouling is not significant at 4-12 g/L and even no direct relationship was observed (Bouhabila et al., 1998). Lim and Bai, (2003) observed that small particles tend to decrease filterability.

Membrane material impact on fouling was presented by Yamato et al (2006) which observed that polyvinylidene fluoride membrane was better than polyethylene membrane in terms of reducing irreversible fouling. According to Chang et al. (2001) hydrophobic membrane formed more cake layer than hydrophilic membrane as the membrane pore size was same.

Membrane fouling is also influenced by use of suspended carrier. Yang et al. (2006) investigated membrane fouling through comparative study with/without suspended carrier and observed that membrane fouling was lower in membrane system with addition of suspended carrier.

MBR configuration can also influence fouling propensity. According to Chae et al (2006) which studied fouling difference between an anoxic/aerobic series MBR and a vertical submerged MBR, the former showed greater fouling tendency than the latter.

Membrane fouling is related to microbiology. Choi et al. (2006) observed that non dominant species in activated sludge deposited on the membrane causing irreversible

fouling. Meng et al (2006) studied that bulking sludge showed greater fouling tendency than normal sludge due to irregular shape of flocs and higher EPS and sludge viscosity.

The influence of F/M ratio on the irreversible and reversible fouling rate in a wide range of MLSS concentration was conducted by Watanabe et al. (2006). They observed irreversible fouling rate increased with F/M ratio at low MLSS concentration of 2-3g/L but reversible fouling rate increased with F/M ratio at high MLSS concentration of 8-12g/L. The former case was associated with accumulation of dissolved organic carbon in mixed liquor while the latter was related to increased viscosity in high concentration of MLSS.

SRT is also impacting factor on membrane. Bouhabila et al. (1998) observed that membrane fouling was greater at SRT of 30 days compared to 10 and 20 days. But at extreme low SRT i.e. 2 days fouling drastically increased compared to 10 days (Trussell et al., 2006).

Several studies stressed the effect of DO concentration on biofilm formation. Jin et al (2006) tested DO concentration impact on fouling observing that at low DO fouling increased 7.5 times as high DO fouling due to reduced porosity by low DO biofilm.

Figure 2.6 describes the formation of EPS and SMP. EPS is polymer formed through microbial activity. It consists of protein and polysaccharides as well as lipids and nucleic acids. EPS play an important role in floc formation and protection. EPS can be formed through substrate utilization and biomass metabolism. Bound EPS in floc can be

subsequently hydrolyzed to soluble form, which is called SMP. SMP can be also formed through substrate utilization. Thus, SMP can be produced via two pathways i.e. utilization associated production (UAP) and biomass associated production (BAP).

SMP production is influenced by operational conditions such as SRT, HRT, temperature, and F/M ratio.

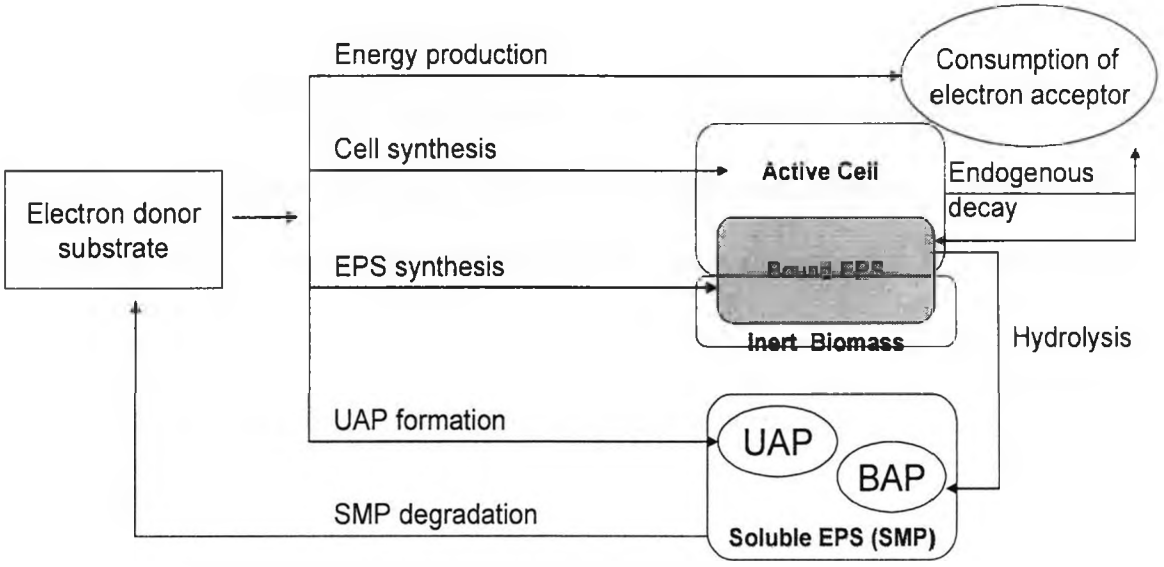

Figure 2.6 EPS and SMP formation (adapted from Laspidou and Rittmann, 2002)

It is generally established that the main fouling factors are EPS and SMP, particularly SMP which are often cited as the primary foulants. Nonetheless the published findings present various contradictory conclusions on foulants due to the complexity of microbial systems. Lesjean et al. (2004) addressed that SMP is a more important factor than EPS. Le-Clech et al. (2006) suggested that carbohydrate in SMP is related to fouling. On the contrary, Drews et al. (2007) observed that SMP was not a governing factor in membrane fouling at influent COD as high as 1200 mg/L. Lee et al. (2003) observed poor

relationship between EPS and fouling but it was suggested that EPS composition is a more important factor than EPS concentration.

2.3.3 Fouling control

Membrane fouling can be mitigated via physical or chemical methods. Physical cleaning includes permeate relaxation and backwashing. Relaxation is the state of pausing filtration while backwashing refers to reversing permeate flow direction. Both methods are effective in recovering permeability. Psoch and Schiewer (2006) tested the influence of membrane cleaning in three ways i.e. only air sparging, only backflushing and combination of air sparging and backflushing and observed that the combination protocol presented lowest overall resistance and highest permeability.

However, physical cleaning effectiveness decreases as irreversible fouling accumulates in membrane, thus necessitating chemical cleaning. Recommended chemical agents are NaOCl and citric acid for organic and inorganic fouling, respectively according to protocol provided by membrane suppliers. Normally, maintenance cleaning for maintaining design permeability employs 0.01 wt.% NaOCl for 30 min at every 3-7 days while recovery cleaning is carried out at 0.2-0.5 wt.% NaOCl or 0.2-0.3 wt.% citric acid although the specific protocol varies from a plant to another. (Le-Clech et al., 2006)

2.3.4 Membrane fouling characteristics in BNR systems

Compared to various studies on MBR employing single reactor for biochemical oxygen demand removal and nitrification, the studies on membranes employed for BNR have been sparse (Lesjean et la., 2002; Mouthon-Bellow and Zhou, 2006; Fleischer et al., 2005; Kang et al., 2007). Recently, typical fouling studies with membrane coupled BNR have been reported (Drews et al., 2007; Ahmed et al., 2007; Chae et al., 2006; Lyko et al., 2008).

Some of findings are in agreement with the observations from conventional MBR systems. For instance, the positive impact of longer SRT on fouling was observed by Ahmed et al. (2007) with anoxic-aerobic SBR system at SRTs of 20-100 days. It is also consistent with the finding of Liang et al. (2007) using single stage MBR system at the different SRTs of 10, 20 and 40 days. Chae et al. (2006) confirmed that HRT is inversely proportional to EPS and particle size. Lyko et al. (2008) observed that membrane performance of full scale system deteriorated as temperature dropped to as low as 4 °C. However, several particular observations that distinguished MBR applications for BNR from single oxic MBR are noteworthy. Ahmed et al. (2008) conducted an investigation of feed composition impact on biomass community and fouling in SBR systems, and concluded that more rapid fouling was observed with propionate or methanol based feed than with acetate or glucose-rich feed. However, relatively higher content of phosphorus accumulating organisms and improvement of phosphorus removal was observed with

acetate or methanol rich substrates than with glucose or propionate substrate, suggesting that an acetate feed is optimal for BNR-based MBR processes as a proper external carbon source for assisting both fouling mitigation and EBPR performance.

Geilvoet et al. (2006) performed filtration test with denitrification and nitrification tank sludge samples and observed better filterability in the nitrification tank samples. According to the study by Rosenberger et al. (2006), an MBR system with post-denitrification exhibited lower fouling propensity than pre-denitrification, revealing that the reason was not because of denitrification scheme but because of SMP accumulation.

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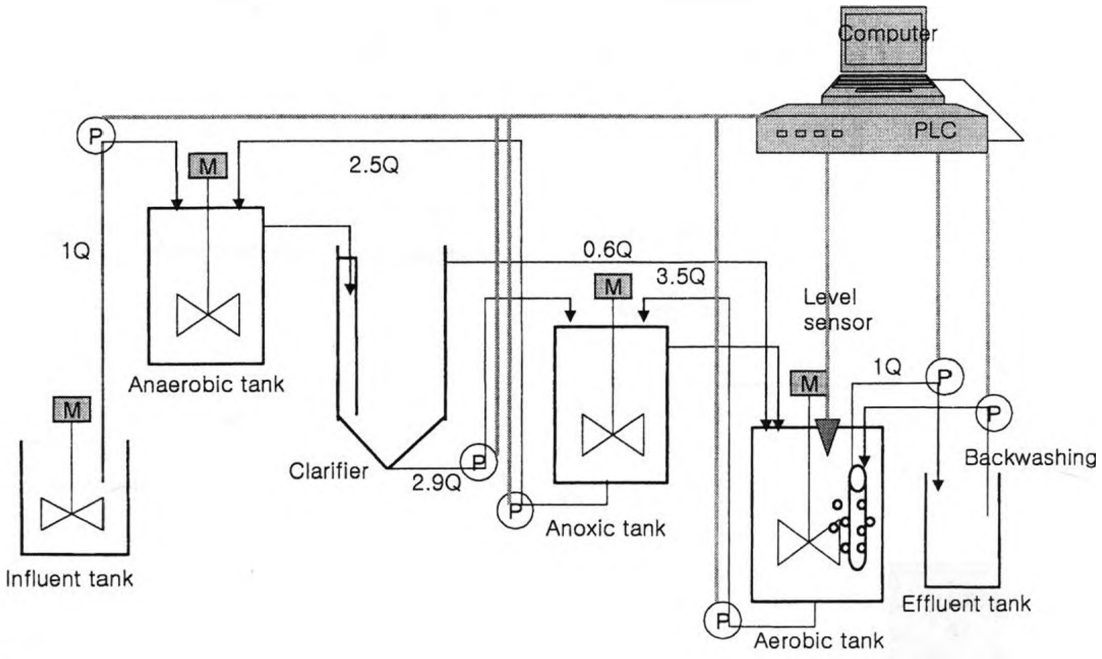
3.0 Material and Methods

3.1 System description

The laboratory scale MBR process, patented in North America (Nakhla and Patel, 2008), consists of four units made of acrylic plastic: anaerobic reactor, clarifier, anoxic reactor and aerobic reactor. A schematic diagram of the system is shown in Fig 3.1a. Influent wastewater is fed into the anaerobic tank along with internal recycled sludge from anoxic tank at 250% of the raw wastewater flow rate. The effluent from the anaerobic tank goes into the clarifier in which the sludge is concentrated to enter anoxic tank while the supernatant flows by gravity to the aerobic tank. Aerobic sludge is recycled to the anoxic tank for denitrification at 3.5 times the influent flow. A hollow membrane ultrafilter (Fig 3.1b) with a pore size of 0.04 μm and surface area of 0.09 m^2 (Zenon Environmental System Inc., Oakville, ON, Canada) is placed in the aeration tank and operated at flux of 12 $L/m^2/h$.

The conventional A^2O system illustrated in Figure 3.1c consists of three tanks and a clarifier. Internal recirculation from the aerobic to the anoxic tank and sludge recycle from the clarifier to the anaerobic tank were set at 350 and 70%, respectively, of influent wastewater flow rate.

UCT MBR (UMBR) consists of anaerobic, anoxic, and aerobic tanks (Fig 3.1d). The recycled sludge streams were from anoxic tank to anaerobic and from aerobic tank to anoxic at the rate of 2.5 and 3.5 times the influent flowrate.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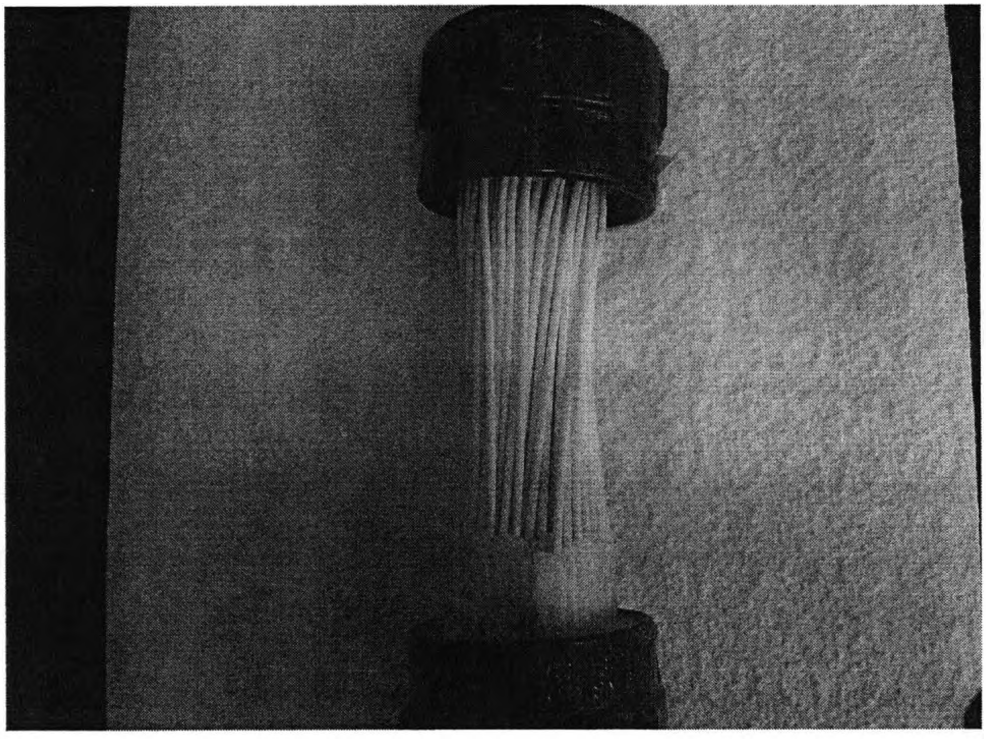
PLC
P
M
2.5Q
1Q
0.6Q
3.5Q
Level
sensor
Anaerobic tank
Clarifier
2.9Q
Anoxic tank
Influent tank
Aerobic tank
Effluent tank
Backwashing

a)



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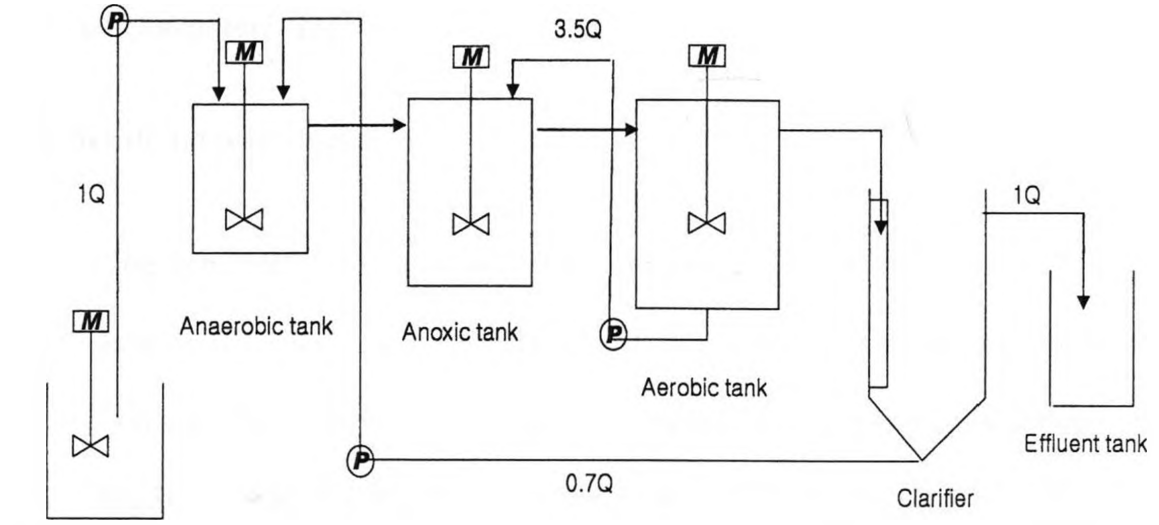

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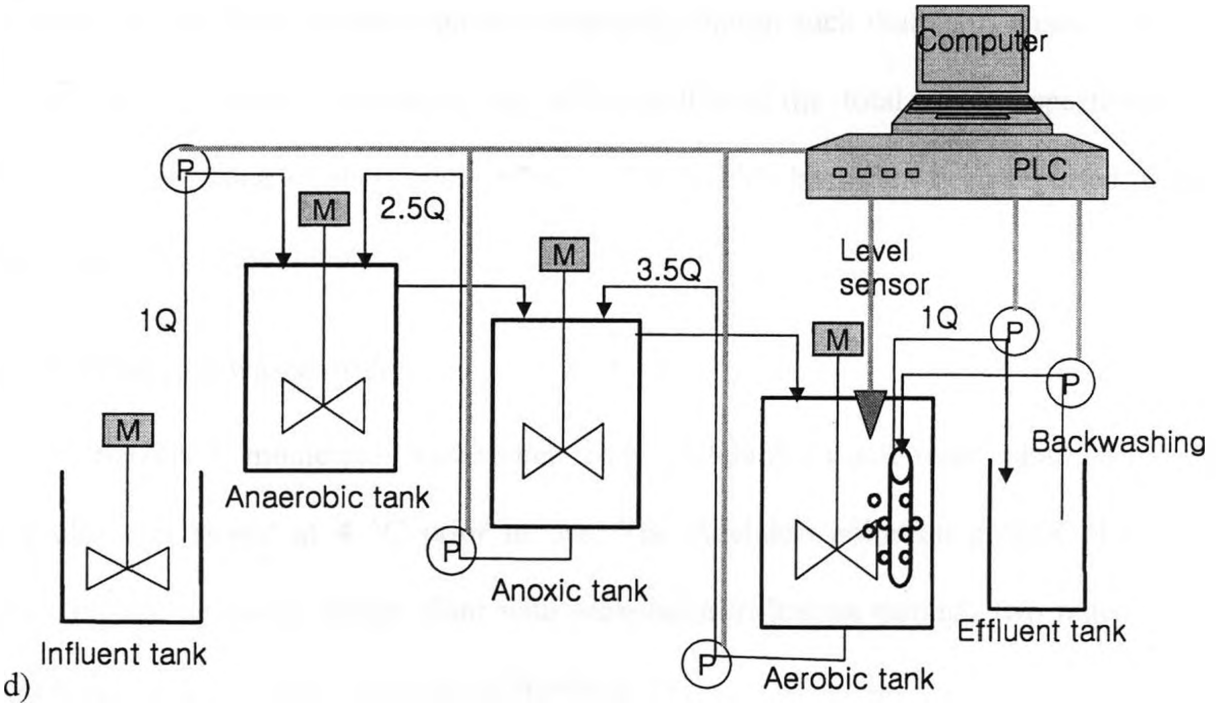

d)

Figure 3.1 System description (a) NMBR (b) hollow fiber membrane (c) A^2O (d) UMBR (Q, P and M denote flowrate, pump and mixer, respectively).

3.2 Feed characteristics

3.2.1 Synthetic wastewater

The synthetic feed (in mg/L) was composed of sodium acetate (128), glucose (143), peptone (83), ammonia chloride (97.3), potassium phosphate monobasic/dibasic (11/13), sodium bicarbonate (280) and trace metals. The trace metals added were (in mg/L): $MgSO_4$ (69.6), $CuSO_4 \cdot 5H_2O$ (0.06), $MnCl_2 \cdot 4H_2O$ (0.24), $NaMoO_4 \cdot 2H_2O$ (0.06), $CoCl_2 \cdot 6H_2O$ (0.24), $ZnCl_3$ (0.3). The feed was prepared nearly once a day and used without storage. This composition was purposely chosen such that short chain VFA and readily biodegradable COD constituted 30% and 40% of the total COD, respectively, to avoid any limitation of short chain VFA to PAO which has often been reported in real wastewater treatment plants.

3.2.2 Municipal wastewater

Screened municipal wastewater from Adelaide wastewater plant (London, Canada) was stored at 4 °C prior to use. The Adelaide pollution control plant is a conventional activated sludge plant with seasonal nitrification through two independent sections with a total rated capacity of 36,400 m^3/d.

3.3 System operation

3.3.1 Start-up and SRT control

Both systems were inoculated with activated sludge from Adelaide wastewater plant (London, Canada) and mixed with anaerobic sludge from an upflow anaerobic

sludge blanket (UASB) system to expedite start-up. Following start-up and commissioning, SRT was controlled by wasting sludge corresponding to 10% of reactor volume from each reactor on daily basis. The solids in the clarifier were also accurately accounted for by emptying the clarifier and mixing its contents.

3.3.2 NMBR vs A^2O comparative study

Both systems were operated at an influent flowrate of 66 L/d corresponding to a bioreactor HRT of 8 h using SWW and MWW, which was within operational condtions of conventional systems. Although MBRs are operated at much longer SRTs, the SRT of 10 d was selected to ensure fair comparison at conditions typical of the conventional A^2O. Both the new MBR and A^2O processes were tested at the anaerobic, anoxic and aerobic biomass fractions corresponding to respective bioreactor volumes of 5/5/12 L. Temperature and pH in the bioreactors of both systems were 21-24 °C and 7-7.5, respectively. Dissolved oxygen (DO) was maintained 0.8-2 mg/L in the aerobic reactor. The system was run for a total of 320 d, with 150 d using SWW and 170 d using MWW or 15 and 17 turnovers of the SRT.

3.3.3 NMBR vs UMBR comparative study

Both systems were operated at a bioreactor HRT of 6 h (an influent flowrate of 88 L/d) and a SRT of 10 d and compared at anaerobic, anoxic, aerobic bioreactor volumes of 5, 5, and 12 L, respectively. However, due to filtration decline as a result of membrane

fouling, actual flow was within 10% of the design flowrate. The systems were controlled by a programmable logic control (MicroLogix 1100, Allen-Bradley, USA) which also recorded the change of transmembrane pressure (TMP). To prevent overflow, the water level in the membrane tanks was controlled by a level sensor and controller (GEMS® ELS-100/opto-PAK). The filtration mode was composed of 50 min of continuous filtration, 4 min of relaxation and 1 min of backwashing. Backwash flowrate was set at 60 mL/min, corresponding to a flux of 12 $L/m^2/h$. The system was run for a total of 300 d or 30 turnovers of the mean SRT. During the first 150 days, the system was fed with settled MWW. However, after 150 days the MWW was supplied without settling and supplemented with 30 mg/L of acetic acid to supply sufficient VFA for P release of PAO in anaerobic zone and enhance P removal.

3.3.4 Membrane cleaning

Membranes were cleaned by soaking in a 200 ppm NaOCl solution for 6 h and washing with clean water as TMP reached a maximum of 57 kPa as recommended by the supplier.

3.4 Analytical methods

3.4.1 General parameters

Samples of the influent and each process effluent stream i.e. anaerobic, anoxic, aerobic stage and clarifier were collected and analyzed for total suspended solids (TSS), volatile suspended solids (VSS), sludge volume index (SVI) and total/soluble Kjeldahl

nitrogen (TKN/STKN) using Standard Methods (APHA, 1998). Total/soluble COD (TCOD/SCOD), NH_3, NO_3, NO_2, Total/soluble phosphorus (TP/SP) were measured using HACH methods and test kits (HACH Odyssey DR/2500). Soluble parameters were determined after filtration through a 0.45 μm filter paper.

A DO meter (YSI, Model 50) was used in monitoring dissolved oxygen in reactor. pH and oxidation reduction potential (ORP) were measured in each reactor with a pH meter (Thermo Orion, Model 330) and ORP meter (WTW Gmbh and Co.KG, Model Multi 340i), respectively.

3.4.2 VFA analysis

Volatile fatty acids (VFAs) in the wastewater were analyzed by a gas chromatograph (GC Varian 3800, Varian Canada Inc., Mississauga, Canada), equipped with a flame ionization detector and a fused silica column. Filtered samples were injected into the column (CP-Sil 5 CB) at 250 °C detector temperature with 1/10 split ratio. Column temperatures were maintained at 110 °C for 0.5 min, 130 °C for 4 min and 165 °C for 2 min with temperature increase at the rate of 20 °C/min.

3.4.3 Fouling parameter analysis

Particle size distribution was determined by Malvern Mastersizer 2000 (Malvern Instruments Ltd., Worcestershire, United Kingdom) using laser diffraction measurement on samples in suspension. In principle, particles are passed though a focused laser beam

and these particles scatter light at an angle being inversely proportional to their size. The angular intensity of the scattered light is measured by a series of photosensitive detectors. EPS extraction from mixed liquor samples was conducted by a method using DOWEX (Sigma-Aldrich 91973) as a cationic exchange resin (CER), which was added to the samples at the ratio of 75g CER/g dry VSS and stirred at 600 rpm for 2 hr (Frølund et al., 1996). The treated EPS sample was subsequently centrifuged at 12,000×g for 15 min (Sorvall® RC-5B Refrigerated Superspeed Centrifuge). SMP sample from mixed liquor was collected after centrifugation at 12,000×g for 15 min and filtration through 0.45 μm filer paper. Extraction and centrifugation was carried out at 4 °C to avoid biomass activity. EPS and SMP were determined by summing carbohydrate and protein.

Bound EPS was determined by subtracting SMP from EPS. Carbohydrate was measured according to the method of Dubois et al. (Dubois et al., 1956) with glucose as the standard. Protein was determined by micro bicinchoninic acid (BCA) protein assay (Pierce, Rockford, USA) using standard solution of bovine serum albumin (BSA), which was modified from Lowry et al. (Lowry et al., 1951) method.

3.5 Batch test

3.5.1 P release and uptake

P release and uptake rates were determined by batch tests, wherein 1L of mixed liquor was centrifuged at 3000×*g* (Beckman Coulter, Allegra 6 centrifuger, USA) for 5 min with the supernatant replaced with nutrient-rich distilled water. After N_2 sparging to

remove oxygen, 30-40 mg/L acetic acid was spiked and pH was adjusted to 7.1±0.1. Samples were collected every 15 min during the first 3 h for monitoring VFA and P concentration. As P release was completed, half of mixed liquor was transferred to another bottle for supplying oxygen for P uptake. For anoxic P uptake, excess nitrate were added into the initial anaerobic bottle. Samples from the two bottles were collected every 15 min for monitoring P and nitrate reduction. DPAO content was estimated from batch tests according to Meinhold et al. (1999), where the aerobic P uptake rate by non-DPAO is calculated by subtracting the anoxic P uptake rate (q_{ax}) from aerobic P uptake rate (q_{ao}), with the anoxic P uptake rate in anoxic conditions by DPAO assumed at 80% of their aerobic P uptake rate. Thus, the DPAO content can be obtained from Eq (3.1).

$$\frac{DPAO}{non-DPAO} = \frac{q_{ax}/0.8}{q_{ao,cor}} \qquad \text{Eq. (3.1)}$$

3.5.2 P fractionation

P fractionation was done according to the method of de Haas et al. (2000) which relies on the principle that extraction of biomass with perchloric acid (PCA) and NaOH recovers metal phosphates (orthophosphates), and biologically bound polyphosphates, respectively. The supernatants from sequential centrifugation of 50 mL of the mixed liquor at 3000×g for 5 min prior to and after addition of 10 ml of 0.9% NaCl solution represents loosely adsorbed phosphorus on biomass. Subsequently, the biomass was extracted three times with PCA followed by NaOH. PCA extraction was done by adding 20 mL 0.5 M PCA in the sludge pellet and shaking at 0-3°C for 5 min, followed by

centrifuging and supernatant removal while NaOH extractions were conducted using 20 mL 1M NaOH for 30 min, 15min and 15min. The final residue of biomass pellets after extractions was resuspended with 50 mL of distilled water. TP in initial sludge, initial supernatant, the two extracts i.e. PCA and NaOH and residue were analysed while ortho-P in initial supernatant and two extracts was measured after filtering through 0.45 μm filter paper. Recovery was determined as the ratio of the sum of TP obtained in rest of steps and initial TP in sludge according to Eq (3.2). Ortho-P in the two extracts is chemical bound P while non-orthoP in TP is mostly biologically formed P, or complex P.

$$\text{Recovery (\%)} = \frac{\text{TP in supernatant} + \text{TP in PCA extract} + \text{TP in NaOH extract} + \text{TP in residue}}{\text{TP in mixed liquor}} \times 100$$

Eq (3.2)

3.6 References

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4.0 The beneficial role of intermediate clarification in a novel MBR based process for biological nitrogen and phosphorus removal

4.1 Introduction

BNR systems have been widely used for simultaneously reducing nitrogen (N) and phosphorus (P) from municipal wastewaters. In BNR configurations, final clarification was primarily considered for solids separation. However, depending on the sludge blanket retention, the clarifier assisted partially in nitrogen removal due to denitrification within the sludge blanket, at the cost of higher effluent suspended solids (Siegrist et al., 1995; Monti et al., 2006).

Since membrane technology substituted final clarification the BNR system has presented several improvements such as smaller footprint of installation, lower sludge production and better nitrification (Monti et al., 2006). Recently, a novel MBR system has been developed as shown Fig 3.1a. (Nakhla and Patel, 2008; Patel et la., 2005) The salient feature of the system is the placement of a clarifier following the anaerobic tank, the concentrated biomass of which is sent to the anoxic tank while the ammonia-rich supernatant is treated in an aerobic tank employing submerged ultrafiltration membranes. The main advantages are lower sludge yield, higher denitrification potential, and higher P removal compared to conventional BNR systems.

The comparative performance of this novel MBR configuration with other systems is presented in Table 4.1. Notwithstanding the various operational conditions, it is evident from Table 4.1 that the system (Patel et al., 2005) performance with respect to P and N removal is better than the DEPHANOX system (Sorm et al., 1998; Bortone et al., 1996) Johannesburg process (Bortone et al., 1996), the University of Cape Town (UCT) process (Monti et al., 2006), and the modified UCT employing membrane (Monti et al., 2006). By comparison with the four Anaerobic-Anoxic-Oxic (A^2O) processes (Ma et al., 2005; Pai et al., 2004; Peng et al., 2006; Wang et al., 2006), this novel system produced lower final effluent phosphorus and nitrogen concentration than average of the four.

Table 4.1 also indicates that membrane-assisted BNR systems achieved final effluent concentrations of ammonia and chemical oxygen demand (COD) well below the conventional systems. However, a conventional BNR system can achieve lower effluent nitrates than an MBR system, due to the extra denitrification in the final clarifier, as reflected by the findings of Monti et al. (2006) who reported that 3 mg/L nitrates reduction in the final clarifier led to a lower final effluent nitrates concentration than the MBR.

Although a final clarifier is designed for good sludge settling and subsequently, maintaining stable biomass concentrations in the system, the operational failure due to pin floc or filamentous organisms' proliferation causes the discharge of high effluent suspended solids, necessitating incorporation of an additional bioreactor e.g. selector. In this application, intermediate clarifier is not restricted by sludge settling problem. In

addition, it should be highlighted that the main purpose of intermediate clarifier is to adsorb soluble and colloidal COD to biomass, which enhances the denitrification efficiency in the anoxic tank. Thus, the hydraulic retention time can be also relatively shorter than the final clarifier.

Table 4.1 Performance comparison from references.

Process & Reference	Feed*	HRT (hr)	SRT (days)	Effluent (mg/L)				
				TCOD (SCOD)	TKN (NH_4-N)	NO_3-N	TN	TP (SP)
UCT [c] (Monti et al., 2006)	MWW	10	12	43 (22)	5 (0.1)	5	10	1 (0.2)
DEPHANOX [a] (Sorm et al., 1998)	MWW	23	10	34 (20)	6 (1.2)	12	18	0.6 (0.4)
DEPHANOX [a] (Bortone et al., 1996)	MWW	23	10	26 (13)	5 (1.5)	21	26	0.9 (0.5)
JHB [b] (Bortone et al., 1996)	MWW	18	20	30 (11)	4 (0.5)	17	21	2.7 (1.7)
A^2O [d] (Ma et al., 2005; Pai et al., 2004 ; Peng et al., 2006 ; Wang et al., 2006)	SWW	9	11	18	2 (1)	7	9	0.3
MBR [c] (Monti et al., 2006)	MWW	10	12	20	1 (0.1)	9	10	0.1
Novel MBR [e] (Patel et al., 2005)	SWW	12	20	3	0.5 (0.4)	6	7	0.2

*MWW (municipal wastewater) SWW (synthetic wastewater)

[a]1:1.6:1.5, [b]1:3.4:4.5, [c]1:2.5:5.5, [d]1:0.8:2.2, [e]1:1:2 [Volume ratio anaerobic : anoxic : aerobic tank]

Compared to the broad knowledge on the role of final clarifier, the relevant study on the intermediate clarifier is very rare and its role is uncertain. It must be emphasized that although the DEPHANOX process is well known for adopting an intermediate clarifier among BNR systems, the fate of nutrients in the intermediate clarifier has not been delineated. Thus, this study aims at the elucidation on its role in terms of phosphorus and nitrogen removal through the novel MBR system employing an intermediate clarifier.

4.2 Materials and methods

4.2.1 System description

It is given chapter 3.1.

4.2.2. System operation

The MBR system was operated at bioreactor HRT of 8 h (an influent flowrate of 66 L/d) and a SRT of 10 d and compared at two different biomass fractions of 0.25/0.25/0.5 for anaerobic, anoxic and aerobic zone, respectively, denoted as MBR_P (the subscript P represents patent) and the typical fractions of 0.16/0.2/0.64 denoted as MBR_C (the subscript c represents conventional), corresponding to bioreactor volumes of 5/5/12 L and 3.5/4.5/14 L. Temperature and pH observed in both systems were 21-24 °C and 7-7.5, respectively. Dissolved oxygen (DO) was maintained 0.8-2 mg/L in the aerobic reactor. The system was run for a total of 150 d or 15 turnovers of the SRT approximately, with 80 d in Run 1. The SWW, system start-up and membrane cleaning are given in chapter 3.2.1, 3.3.1 and 3.3.4, respectively.

4.2.3 Analytical methods

It is given in chapter 3.4.1.

4.3 Results and discussion

4.3.1 Overall performance and mass balances

Table 4.2 shows the steady state effluent quality in the two runs. Steady state data was collected after 3 turnovers of the mean SRT. Data was found to fit normal distribution using the statistical software (Minitab 13.1) and hence the standard deviations of the data are reported in Table 4.2. Influent total COD concentration was 290-320 mg/L while steady state effluent MBR soluble COD concentrations were close at 5-9 mg/L during the two runs. The effluent NO_3-N concentrations from MBR_P and MBR_C averaged 7.9 and 7.6 mg/L respectively, while the effluent ortho P were 0.2 and 0.4 mg/L corresponding to 96 and 91% removal efficiency, with an average feed TP of 4.6 mg/L. Influent TSS, contributed by peptone, averaged 30 mg/L and anaerobic, anoxic and aerobic sludge were maintained at 2.3-2.5, 2.3-2.6 and 2.4-2.6 g SS/L for both runs, respectively.

Steady-state mass balances and the contribution of various removal mechanisms as a percentage of the total influent COD are presented in Table 4.3. The aerobic COD consumption obtained from the difference between the measured OUR and oxygen demand for nitrification in the aerobic tank was found to be 2.3-2.4 g/d. On the other hand, COD consumption through denitrification was calculated using Eq 4.1 (Metcalf and Eddy, 2003) and the biomass yields (Y_{obs}) of 0.17 and 0.16 g VSS/g COD for MBR_P

and MBR_C respectively. Nitrogen recovery was very close to 100% and nitrogen removed through denitrification accounted for 55-56% of the influent total nitrogen during the runs. The phosphorus mass balance between influent P and the combined P in effluent and in wastage also shows high closure.

$$\text{COD consumption through denitrification} = \frac{2.86}{1-1.42\times Y_{obs}} \quad (4.1)$$

Table 4.2 Steady state influent and effluent quality obtained from two runs

(All units are in mg/L except where stated otherwise.)

Parameter	Influent	Run 1	Run 2
		MBR_P_eff	MBR_C_eff
TCOD	310 ± 10 (15)	-	-
SCOD	250 ± 8 (15)	9 ± 4 (6)	5 ± 3 (9)
TKN	33 ± 1 (14)	-	-
STKN	28 ± 2 (14)	0.5 ± 0.2 (6)	0.4 ± 0.2 (9)
NH_4-N	24 ± 0.3 (25)	0.1 ± 0.03 (10)	0.1 ± 0.04 (15)
NO_3-N	-	7.9 ± 0.4 (10)	7.6 ± 0.8 (15)
NO_2-N	-	0.3 ± 0.2 (10)	0.2 ± 0.1 (15)
TP	4.6 ± 0.1 (27)	-	-
PO_4-P	-	0.2 ± 0.1 (10)	0.4 ± 0.1 (15)
SS	30 ± 9 (25)	-	-
SVI (mL/g)	-	150 ± 19 (8)	180 ± 15 (11)
Operational Conditions			
Parameter		MBR_P	MBR_C
System MLSS (g/L) *		2.4 ± 0.1 (10)	2.5 ± 0.1 (15)
TP in VSS (%)		6.5 ± 0.3 (10)	6.0 ± 0.5 (12)
Sludge yield (g VSS/g COD)		0.16 (R^2 =0.96)	0.17 (R^2 =0.98)
VSS/TSS		0.79 ± 0.02 (10)	0.79 ± 0.02 (15)
OUR (mg O_2/L/h)		35 ± 2.4 (5)	34 ±2.8 (8)

- Numbers within parenthesis are the number of samples, R^2 is the correlation coefficient of the linear relationship between cumulative VSS produced versus cumulative COD removed computed as liquid influent–liquid effluent COD.
- MBR_P were assigned 5/5/12L for anaerobic, anoxic and aerobic size respectively, correspondingly 1.8h/1.8h/4h of HRT compared to 3.5/4.5/14L in MBR_C at 1.3h, 1.6h and 5.1h.

Table 4.3 Mass balance in COD, Nitrogen and P

* All units are in % of feed except where stated otherwise.

	MBR_P			MBR_C		
	COD	N	P	COD	N	P
Influent (g/d)	20.2	2.31	0.303	20.2	2.31	0.303
Wastage [a]	31	18	94	30	18	87
Effluent	3	25	4	2	24	9
Aerobic	11	N/M	N/M	12	N/M	N/M
Denitrification						
Anaerobic [b]	2	4	N/M	0.4	1	N/M
Anoxic [b,c]	23	50	N/M	25	53	N/M
Clarifier [b]	1	2	N/M	0.4	1	N/M
Total closure [d]	71	99	98	70	97	96

- N/M represents not measured

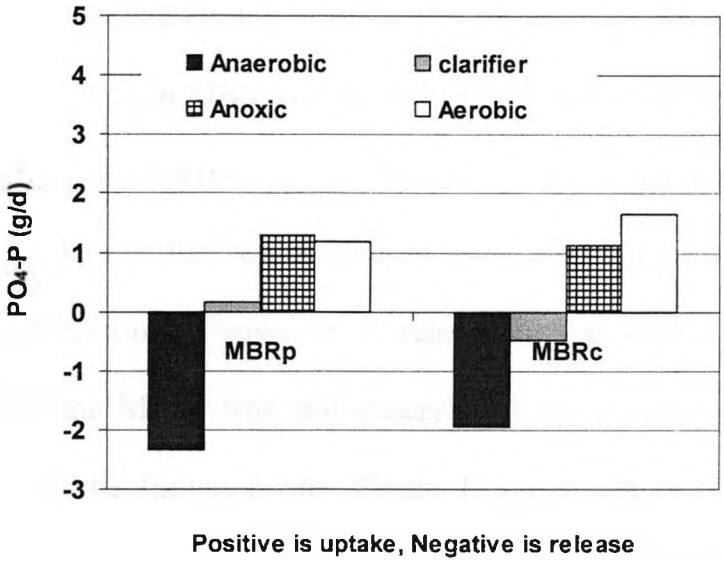
a Wasted VSS is 4.5-4.6 g/d corresponding to 10% of VSS in the system.

b Calculated values based on Eq 4.1 and mass balance for COD and N, respectively

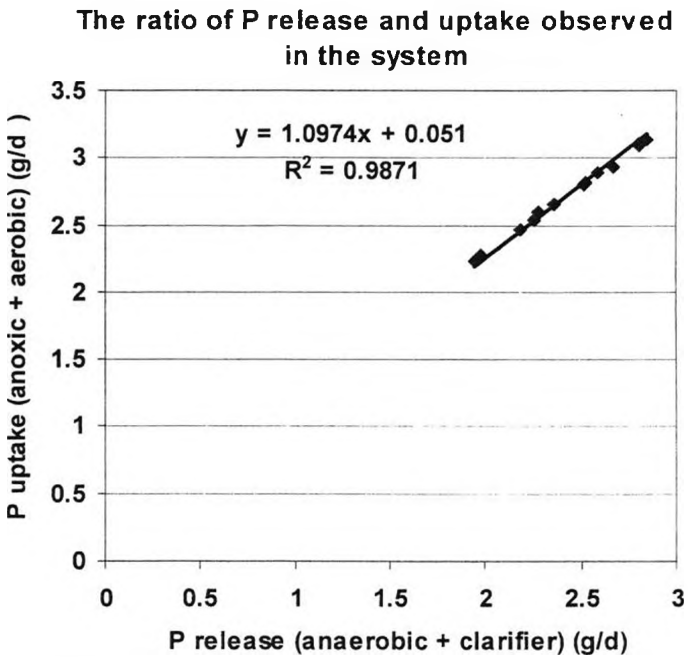
c DPAO denitrification accounts for 0.64 and 0.62g NO_3-N/d for MBR_P and MBR_C, respectively, out of denitrified nitrogen.

d Closure means the overall percentage of COD, N or P removed from the system out of influent. P mass balance closure: (P in effluent + P in wastage)/Influent P

4.3.2 P removal



a)

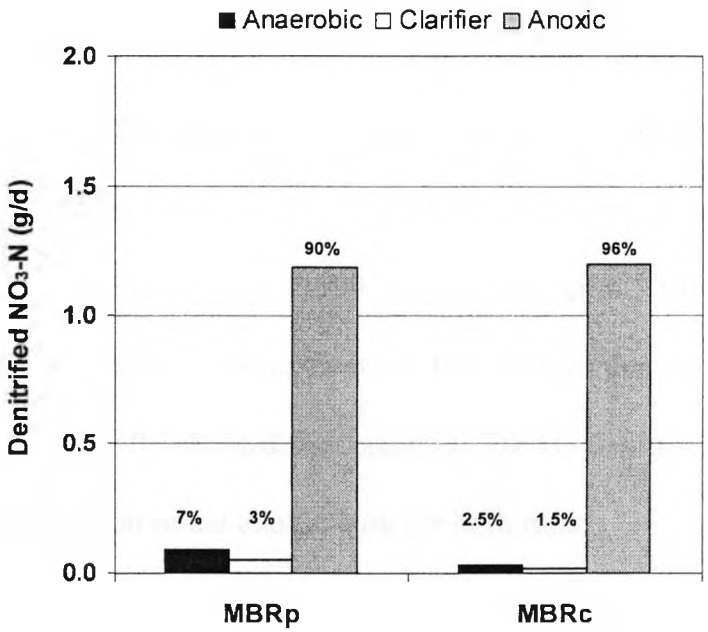


b)

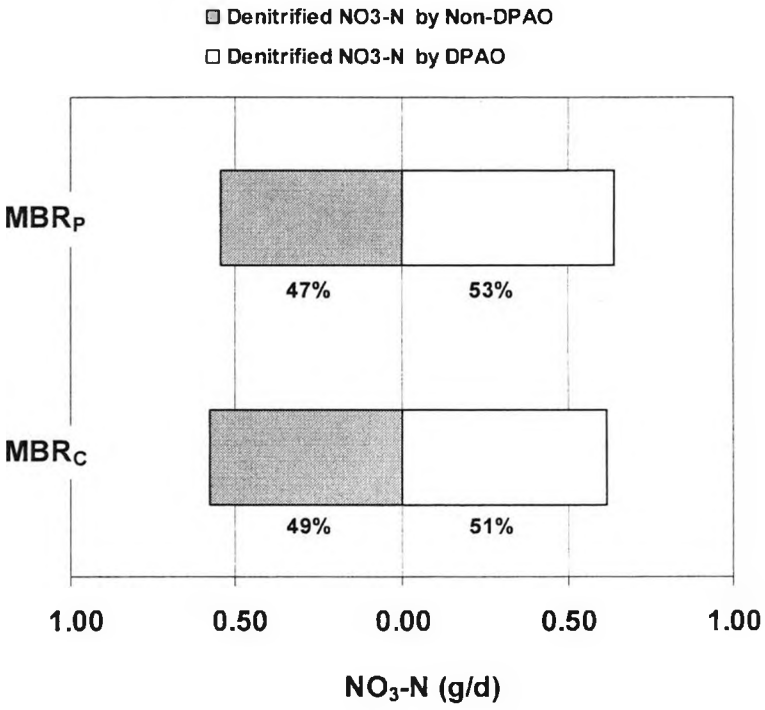
Figure 4.1 (a) The fate of orthophosphate and (b) the ratio of P release/uptake.

Figure 4.1a shows the anaerobic P release rates of 2.3 and 2.0 g/d in MBR_P and MBR_C, respectively. The effect of nitrates on PAOs in the anaerobic reactor appeared insignificant, as the denitrified nitrates in the anaerobic tanks averaged 0.02 g NO_3-N/d in MBR_C and 0.09 g NO_3-N/d in MBR_P as shown in Fig 4.2a respectively while released P was 2.0-2.3 g PO_4-P/d. With respect to P in the MBR_P, it is apparent that a P uptake of 0.16 g/d occurred in the clarifier, which appears to be associated with denitrification of 0.05 g NO_3-N/d. Interestingly, however, P release in the MBR_C with 30% shorter anaerobic HRT than the MBR_P was still observed in the clarifier, i.e. "an extended" anaerobic phase as will be discussed later. Figure 4.1a also demonstrates the anoxic and aerobic P uptake in each run. It appears that average anoxic P uptake accounted for 52 and 41% of the overall P uptake in MBR_P and MBR_C, respectively. Figure 4.1b displays the ratio of P release to uptake on a mass basis in the system. It clearly shows that the ratio is 1.1 which is close to the typical range of 1.15-1.2 suggested by Wentzel et al (1985).

4.3.3. Nitrogen Removal



a)



b)

Figure 4.2 (a) The fractionation of denitrification and(b) pattern of denitrification in the anoxic tank.

Denitrification occurred in the anaerobic tank, the clarifier and the anoxic tank as seen from Fig 4.2a. As mentioned earlier, denitrification can be accompanied by the anoxic P uptake by DPAOs (Fig 4.2b). The amount of nitrates removed by DPAOs relative to P uptake has been reported and the average of 0.52 g NO_3-N/g P (Patel et al., 2006; Hu et al., 2002; Lee et al., 2001; Meinhold et al., 1999; Murnleitner et al., 1997) was used to estimate the contribution of DPAOs to denitrification. It is evident that P was removed in the anoxic tank at a mass rate of 0.7-1.3 g/d. Accordingly, DPAO denitrification accounts for 51-53% of total denitrification in the anoxic tank for both runs.

4.3.4. The beneficial role of the intermediate clarifier

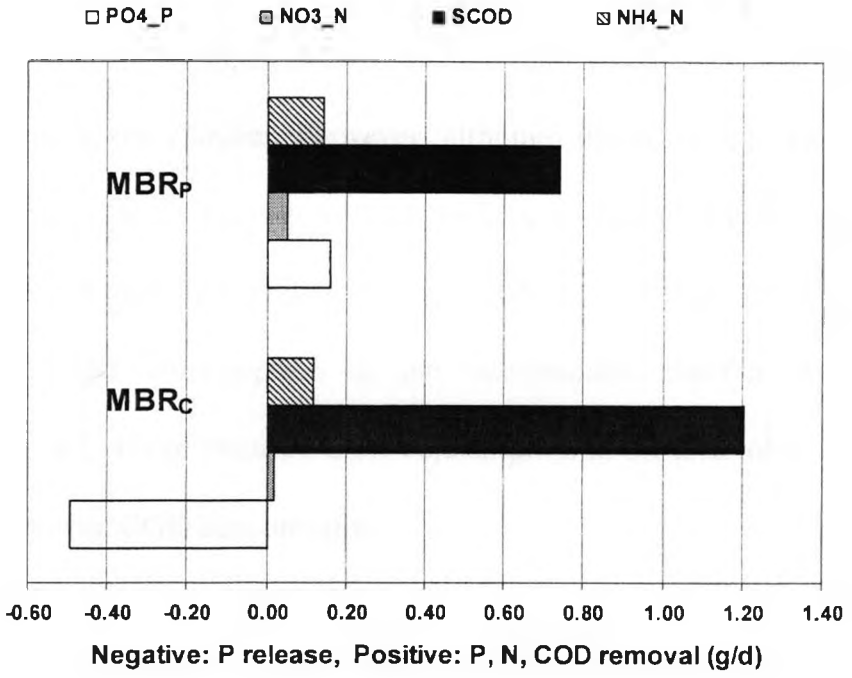


Figure 4.3 The variation of soluble carbon, nitrogen and phosphorus in the clarifier.

Figure 4.3 presents the variation of the soluble organics and nutrients in the intermediate clarifier. COD was removed through fermentation of particulate COD, adsorption, denitrification and sequestration by PAO. It was observed that COD reduction was 0.74 and 1.21 g/d for MBR_P and MBR_C, respectively. Using the sludge yields of 0.16 and 0.17 gVSS/gCOD in Eq 4.1, the estimated COD consumption for the denitrification was 0.19 and 0.08 g/d for MBR_P and MBR_C. The calculated COD sequestered by PAO in the MBR_C, was 0.98 g/d using a ratio of 2 g COD/g P release. (Smolders et al., 1994)

Thus, average COD reduction due to P and N in the MBR_C was 1.06 g/d, indicating that 0.15 g/d was removed by COD adsorption to biomass. On the contrary, the estimated adsorbed COD in the MBR_P was 0.55 g/d which accounts for the 73% of the SCOD removal in the clarifier. However, although the adsorbed COD is higher in the MBR_P, it seems that it was not used as carbon source in the following anoxic tank because effluent nitrates were higher in the MBR_P than MBR_C. The data from Table 4.3 indicate that COD consumption in the intermediate clarifier was 0.07-0.21 g/d corresponding to 2-4% of the total COD consumption in the anaerobic or anoxic tank and 3-8% of the aerobic COD consumption.

The fate of COD in the intermediate clarifier appeared quite different as compared to the final clarifier. Generally, final clarifiers play the role of solids separation and the nature of COD in the place is slowly biodegradable or non biodegradable. Some of clarifiers can be utilized for denitrification through hydrolysis and endogenous respiration occurring in the sludge blanket. (Koch et al., 2001) On the contrary, the type of COD consumed in the intermediate clarifier was mainly readily biodegradable, which is used by anoxic heterotrophic organisms and PAOs. Some of the COD can also disappear through fermentation. Usually, anoxic heterotrophic organisms and DPAOs grow at 20 % lower yield than aerobic heterotrophic organisms and PAOs, respectively. Hence, these two organisms' activity can assist to reduce sludge production. (Gujer et al., 1995)

With respect to ammonia nitrogen, it was observed that ammonia was removed in the clarifier at the rate of 0.12-0.14 g/d (Fig 4.3). Based on 0.05 g NO_3-N/d denitrified and the sludge yield of 0.16 g VSS/ g COD, and using the typical nitrogen content in the sludge of 8%, the estimated nitrogen uptake for biomass synthesis is 0.002 g/d (= 0.2 gCOD/d×0.16gVSS/gCOD×0.08), which is negligible compared to the observed removal. Thus, a plausible mechanism of the reduction can be chemical precipitation i.e. struvite formation ($MgNH_4PO_4 \cdot 6H_2O$). To commence the reaction two conditions should be met i.e. pH and ambient solution concentration. pH range can be widely implemented from 7 to 10 which covers the ambient clarifier pH of 7-7.3 in this study (Zeng et al., 2006). The concentrations of Mg^{2+}, PO_4^{3-} and NH_4^+ were 0.16, 0.5 and 0.75mM, respectively for the MBR_P. It exceeds the solubility product of struvite of $10^{-13.3}$ at 20 °C (Ohlinger et al.,1998). The decline of the ammonia nitrogen can assist the overall nitrogen removal even though the reduction is not significant at 0.5 mg/L correspondingly to 2% of the influent nitrogen.

As for the fate of ortho P in the intermediate clarifiers of MBR_P and MBR_C, as previously mentioned, it was observed that P removal occurred at the rate of 0.16 g/d in the MBR_P while P was released at the rate of 0.49 g/d in the MBR_C. The data clearly indicates that P reduction in the MBR_P occurred through two pathways i.e. chemical precipitation (struvite) and denitrification. The contribution of DPAOs to P removal in the MBR_P is 0.1 g P/d, of which 0.06 g P/d can not be justified on the basis of biological uptake implying chemical precipitation.

P release in the MBR_C is directly associated with the rbCOD reduction. An argument can be made that the extra P release may be due to a metabolic phenomenon i.e. secondary release dissociated VFA consumption, which cannot be removed in the subsequent anoxic or aerobic stages. To verify the nature of the P release, using the well established P model in Eq. (4.2), P balance can be determined. (Meinhold et al., 1999)

$$\text{P uptake} = a\text{P release} + \text{P (metabolic)} \qquad (4.2)$$

$$\text{Effluent P} = \text{influent P} - (a\text{-}1)\ \text{P release} - \text{P(metabolic)}$$

where, a=1.15-1.2,

P (metabolic) can be obtained from the calculation as follows; Y_{obs} (0.17 g VSS/g COD) × COD consumption (305 mg/L × 66 L/d × g/ 1000 mg) × P content in non-PAO organism (0.015 mg P/mg VSS) = 0.05 g P/d (0.78 mg P/L in the basis of influent flowrate).

The ratio of P release and uptake in this study, obtained from the plot of P release rate versus P uptake rate (Fig 4.1b) is 1.097 g/g. Use Eq (4.2) parameter values of 4.6 mg/L, 1.097, 36 mg/L and 0.78 mg/L for influent P, a, total P release and P (metabolic), respectively, yields effluent P of 0.3 mg/L close to the experimental value of 0.4 mg/L, thus confirming that the P release in the clarifier is definitely part of P release associated with VFA consumption.

To evaluate the intermediate clarifier contribution to the overall P removal in the MBR_C, the effluent P predicted without including intermediate clarifier P release according to Eq (4.2), using same P uptake/release ratio of 1.097 and average anaerobic P release of 29 mg/L, increases from 0.3 to 0.9 mg/L.

4.4 Conclusions

The goal of this study was to clarify the function of the intermediate clarifier of the novel MBR by investigating the fate of nutrients in the clarifier as well as biological nutrient removal performance at two different anaerobic HRT conditions. Within the HRT and SRT investigated in this study of 8 hours and 10 days for the treatment of wastewater characterized by average COD, TKN and P concentrations of 310, 33 and 4.6 mg/L, respectively, the following conclusions can be drawn:

1. The new MBR system achieved effluent nitrate and P concentrations of 7.6-7.9 and 0.2-0.4 mg/L, respectively.
2. Anoxic P uptake accounted for 41-55% of the total P uptake. The contribution of DPAOs to denitrification in the anoxic tank was at 51-53% of the total denitrification.
3. The roles played by the intermediate clarifier in runs 1 and 2 are different. COD and nitrogen were removed through COD adsorption, sequestration, denitrification in both runs. However, while in run 1, P was removed through P uptake, in run 2, P was released due to insufficient preceding anaerobic HRT of 1.3 h, relatively 30% shorter than run 1.

4. The intermediate clarifier affected 3-8% COD reduction relative to the aerobic tank and 2% ammonia removal of the influent nitrogen.
5. An estimate of the contribution of intermediate clarifier indicates that effluent P increased from 0.3 to 0.9 mg/L without extra P release in the MBR_C clarifier.

The intermediate clarifier enhanced P removal and denitrification as compared to the conventional BNR. Thus, from a practical perspective, the capital cost of the intermediate clarifier should be weighed against the cost of additional chemical P removal and associated increased sludge treatment costs.

4.5 References

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5.0 Comparative Performance of A^2O and a novel MBR based Process for Biological Nitrogen and Phosphorus Removal

5.1 Introduction

BNR systems have been widely used for removing nitrogen and phosphorus as well as organic matter from wastewater because of cost effectiveness and energy savings. Due to readily biodegradable COD (rbCOD) limitations in municipal wastewaters (MWW), several systems that use DPAOs in BNR process such as the external nitrification process (Bortone et al., 1996) have demonstrated their ability to achieve soluble effluent P of 0.5 mg/L at low influent carbon to nitrogen ratio of 3.8:1.

Today, BNR systems have employed membranes instead of final clarification and reported several advantages such as reduction of footprint and increase of nitrification rate. Monti et al. (2006) observed 15% lower sludge yield in the MBR system than in the identically operated conventional system with a final clarifier in pilot scale comparisons at the same HRT of 10 h and solids residence time (SRT) of 12 d.

Recently, a new MBR system for biological nutrient removal has been developed as shown in Figure 3.1a (Nakhla and Patel, 2006). The salient feature of the system is the placement of a clarifier following the anaerobic tank. The concentrated biomass in the clarifier is sent to the anoxic tank while supernatant is treated in an aerobic tank employing submerged ultrafiltration membranes. The main advantages are lower sludge yield, higher denitrification potential and higher P removal compared to conventional

BNR systems. It must be asserted that even though this MBR system is similar in configuration to the DEPHANOX system (Bortone et al., 1996), it is a single sludge as opposed to the two-sludge DEPHANOX system, which employs fixed film processes for nitrification.

Typical MBRs operate at biomass concentrations of 8-15 g/L and long SRTs while conventional BNR systems operate at SRTs as low as 5-10 d, and mixed liquor suspended solids (MLSS) concentration of 3-4 g/L. Thus, the comparison between BNR systems employing clarifiers and submerged membranes (Monti et al, 2006) at similar operational conditions of HRT and SRT rather than the typical design conditions are evidently very sparse in the literature. Monti et al. (2006) observed that the MBR assisted BNR system achieved better P removal than conventional BNR system at the two tested HRTs of 7 and 10 h while slightly lower effluent nitrates were observed in the conventional system due to additional denitrification in the final clarifier.

The primary aim of this study is to compare the BNR capacity of this novel patented membrane assisted BNR system (Nakhla and Patel, 2008) with that of a conventional anaerobic-anoxic-oxic (A^2O) system. The focus of this study is on delineating differences in denitrification and biological P removal mechanisms rather than the role of clarifiers and membranes, which has been studied in a 2.2 m^3 pilot-scale plant by Monti et al. (2006).

5.2 Materials and methods

5.2.1 System description

It is given in chapter 3.1.

5.2.2 System operation

Both systems were operated at an influent flowrate of 66 L/d corresponding to a bioreactor HRT of 8 h. Although MBRs are operated at much longer SRTs, the SRT of 10 d was selected to ensure fair comparison at conditions typical of the conventional A^2O. Both the new MBR and A^2O processes were tested at the anaerobic, anoxic and aerobic biomass fractions corresponding to respective bioreactor volumes of 5/5/12 L. Temperature and pH in the bioreactors of both systems were 21-24 °C and 7-7.5, respectively. Dissolved oxygen (DO) was maintained 0.8-2 mg/L in the aerobic reactor. The system was run for a total of 150 d, with 80 d using SWW and 70 d using MWW or 8 and 7 turnovers of the SRT. The used feed and membrane cleaning are given chapter 3.2 and 3.3.4.

5.2.3 Analytical method

It is given in chapter 3.4.1 and 3.4.2.

5.2.4 Dynamic test

Excess NO_3-N (45 mg/l) was spiked in the feed to assess the impact of abrupt low TCOD/Nitrogen ratio (4.5:1) on denitrification capacity for 16 hrs. Hourly samples of

various process effluents for both systems were collected over a period of 16 hours following the spike, and analyzed for nitrates.

5.3 Results and Discussion

5.3.1 Overall performance (SWW Run)

Table 5.1 shows the steady state effluent quality during the SWW and MWW runs. Steady state data was collected after 3 turnovers of the SRT. Data was found to fit normal distribution using the statistical software (Minitab 13.1) and hence the standard deviations of the data are reported in Table 5.1. During the SWW run, influent total COD concentration was 290-320 mg/L while steady state effluent MBR and A^2O system soluble COD concentrations were close at 5-9 mg/L during the run. Overall nitrogen removal efficiencies were 74 and 75% for MBR and A^2O system, respectively with complete nitrification. Influent TSS, contributed by peptone, averaged 30 mg/L and the effluent solids were 15.9 mg/L in the A^2O due to high SVI of 210 mL/g respectively combined with denitrification in the sludge blanket. Total suspended solids in the systems including the clarifier were maintained at 59 and 63 g in the MBR and the A^2O, respectively, during the entire period. Anaerobic, anoxic and aerobic sludge were maintained at 2.3-2.5, 2.3-2.6 and 2.4-2.6 g SS/L for both systems, respectively. The biomass fraction for anaerobic, anoxic and aerobic tank was maintained 0.22-0.23, 0.22-0.24 and 0.53-0.56 for MBR and A^2O, thus resulting in a higher anoxic COD uptake, and a lower yield. Sludge production calculated as the slope of the cumulative VSS produced versus cumulative COD removed was 20% lower in MBR than in A^2O. Monti et al. (2006) observed a 15% higher yield in the conventional system than the MBR system, using municipal wastewater at HRTs of 7 and 10 h and SRT of 12 d.

Table 5.1 Steady state influent and effluent quality obtained from SWW and MWW run (All units are mg/L except where stated otherwise)

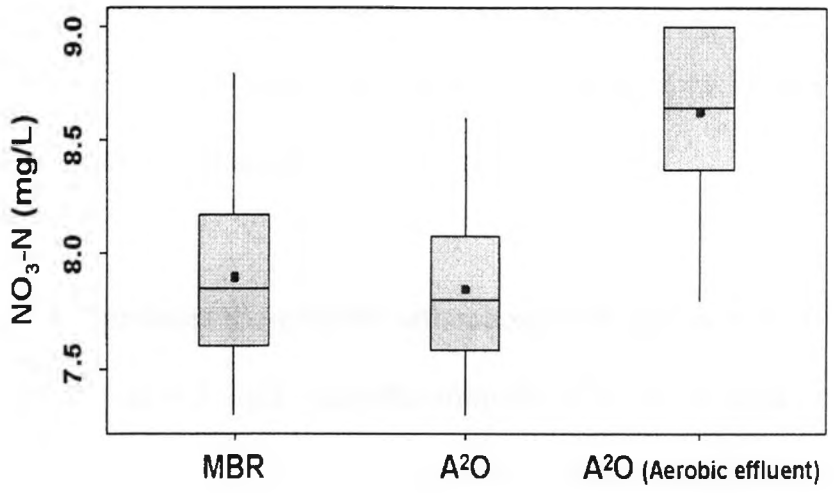
Parameter	Influent (SWW)	MBR_eff	A^2O_eff	Influent (MWW)	MBR_eff	A^2O_eff
TCOD	310 ± 10 (15)[+]	-	21± 4 (9)	340 ± 22 (15)	-	28 ± 5 (15)
SCOD	250 ± 8 (15)	9 ± 4 (6)	5 ± 1 (9)	118 ± 15 (12)	15 ± 3 (18)	14 ± 2 (15)
VFA	100 ± 5 (15)	-	-	33 ± 2.5 (7)	-	-
TKN	33 ± 1.0 (14)	-	2.0 ± 1.3 (9)	37 ± 2.4 (7)	-	3.5 ± 0.4 (7)
STKN	28 ± 2.0 (14)	0.5 ± 0.2 (6)	0.7 ± 0.2 (9)	25 ± 3.1 (7)	1.5 ± 0.3 (10)	1.8 ± 0.2 (7)
NH_4-N	23.9 ± 0.3 (25)	0.1 ± 0.03 (10)	0.1 ± 0.03 (15)	18 ± 2 (14)	0.2 ± 0.1 (23)	0.3 ± 0.1 (18)
NO_3-N	-	7.9 ± 0.4 (10)	7.8 ± 0.6 (15)	0.5 ± 0.2 (5)	7.8 ± 0.4 (19)	7.8 ± 0.3 (18)
NO_2-N	-	0.3 ± 0.2 (10)	0.2 ± 0.1 (15)	-	0.2 ± 0.1 (17)	0.3 ± 0.1 (15)
TP	4.6 ± 0.1 (27)	-	1.4 ± 0.5 (15)	4.0 ± 0.1 (8)	-	1.3 ± 0.3 (18)
PO_4-P	-	0.2 ± 0.1 (10)	1.2 ± 0.4 (15)	2.5 ± 0.2 (11)	0.8 ± 0.2 (20)	1 ± 0.3 (18)
SS	30 ± 9 (25)	-	15 ± 7 (15)	115 ± 10 (14)	-	18 ± 2 (18)
SVI (mL/g)	-	150 ± 19 (8)	210 ± 17 (11)	-	164 ± 15 (6)	193 ± 21 (8)

Operational Conditions				
Parameter	MBR	A^2O	MBR	A^2O
System SS (g) *	59 ± 4 (10)	63 ± 3 (15)	59 ± 5 (20)	66 ± 4 (15)
System VSS (g) *	47 ± 4 (10)	52 ± 3 (15)	45 ± 4 (20)	52 ± 4(15)
TP in VSS (%)	6.5	4.8	4.9	4.3
Sludge yield (gVSS/g COD)	0.16 (R^2 = 0.96)	0.21 (R^2 = 0.98)	0.13 (R^2= 0.98)	0.16 (R^2= 0.98)

[+] Mean±standard deviation (the number of samples)

* SS and VSS were calculated over all reactor compartments

- R^2 is the correlation coefficient of the linear relationship between cumulative VSS produced versus cumulative COD removed computed as liquid influent–liquid effluent COD.



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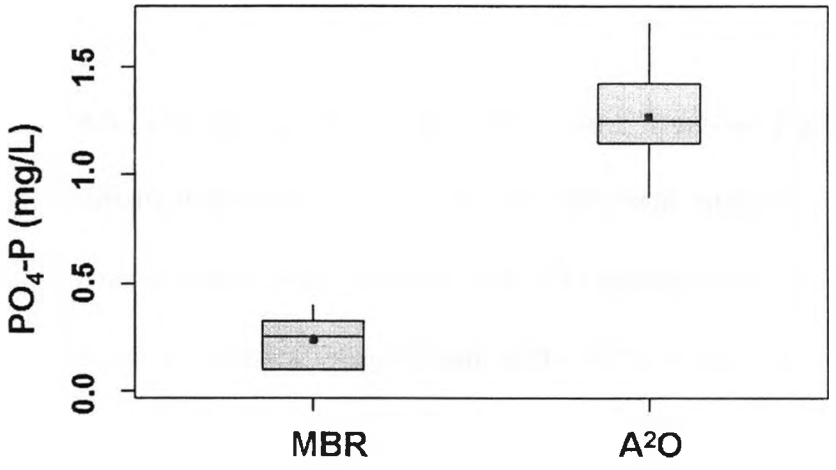


b)

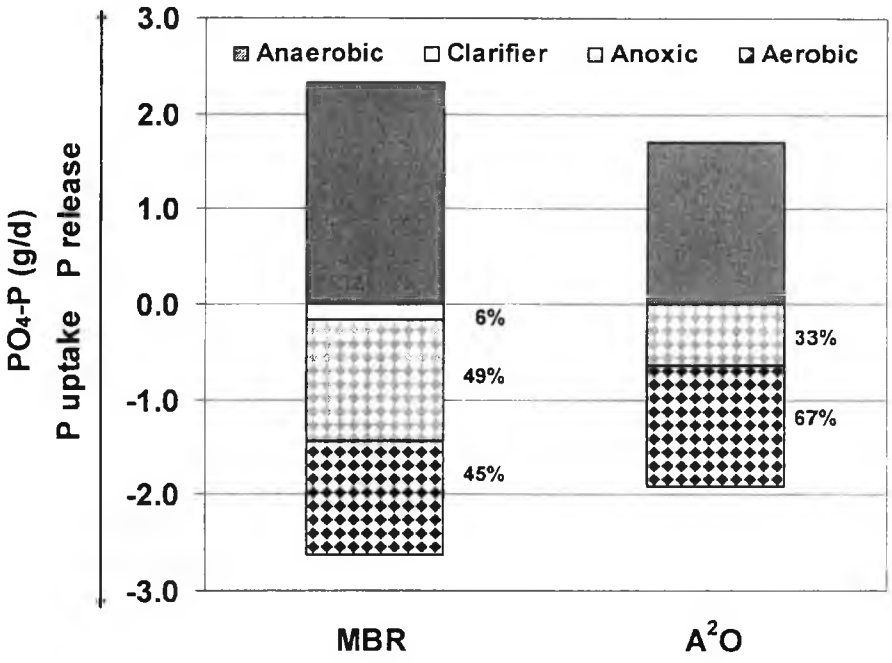
Figure 5.1 Box graph for (a) effluent nitrogen and (b) phosphorus during SWW run (Percentiles are shown: Minimum, 25th, 75th and Maximum. The horizontal line and the dot inside the box represent the median and the average, respectively).

Figure 5.1 represents the statistical distribution of effluent nitrates and orthophosphates in the both systems using the statistical software (Minitab 13.1). As depicted in Figure 5.1a, average effluent NO_3-N concentrations from MBR and A^2O are similar at 7.8 mg/L. There are evident statistical differences between the A^2O final effluent and aerobic effluent nitrates concentrations with the final effluent as much as 2 mg/L lower than the aerobic effluent.

Figure 5.1b represents the effluent orthophosphates during run. The MBR steady state effluent ortho-P was 0.2 mg/L outperforming the A^2O of 1.2 mg/L, with an average influent TP concentration of 4.6 mg/L. It emphatically highlights the statistically significant differences in effluent orthophosphates between two systems. The A^2O process not only produced higher effluent orthophosphates than the MBR but also more widely variable (0.9-1.7 vs 0.1-0.4 mg/L).

A paired T-test, comparing the value of the means from two related samples and determining their statistical difference, was used for statistical analysis conducted on the nitrates and phosphates between MBR effluent and A^2O aerobic effluent. It indicated that observed differences were statistically significant at the 95% confidence level. .

5.3.2 P removal



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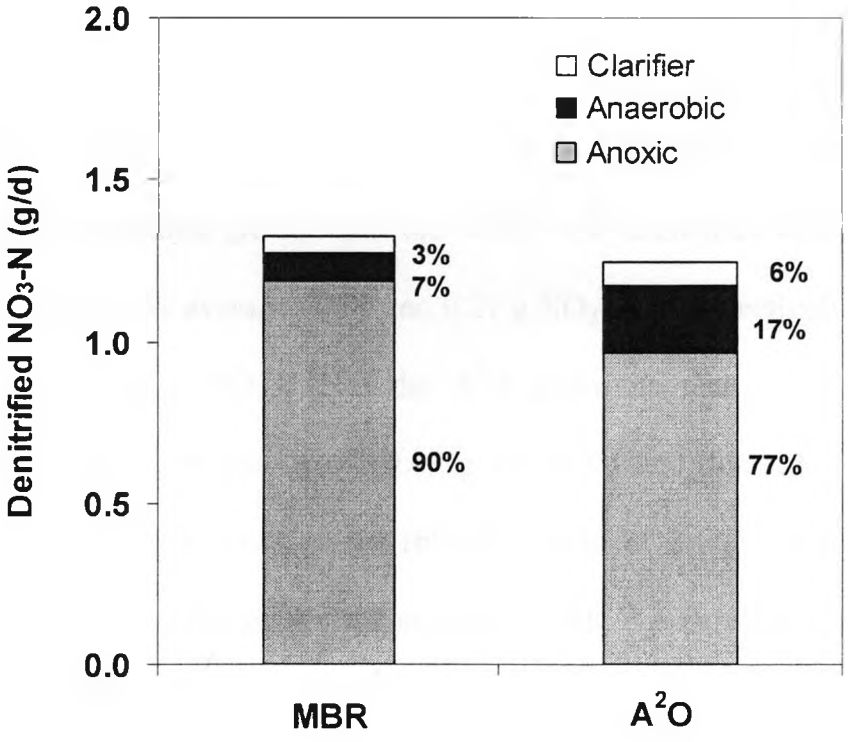

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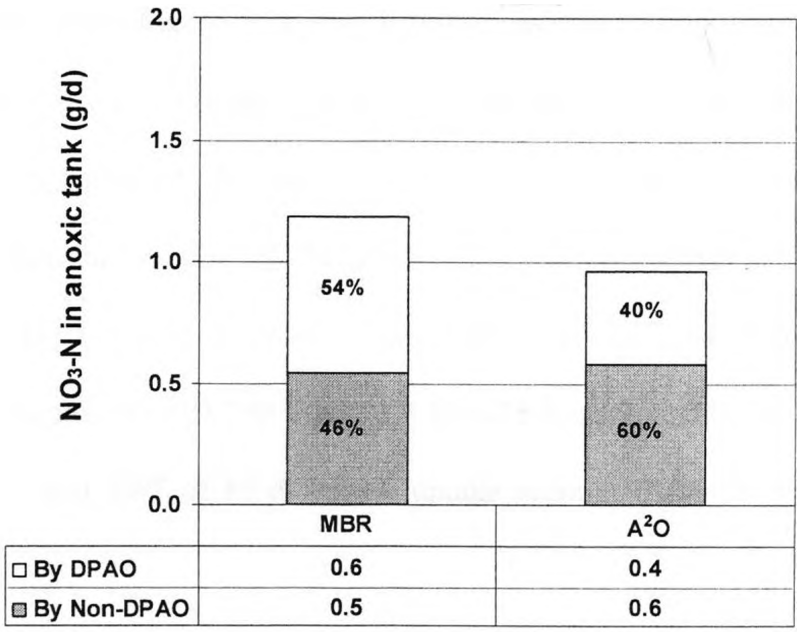


Figure 5.2 (a) The fate of orthophosphate (b) fractionation of denitrification and (c) denitrification in anoxic tank in both systems during SWW run.

As apparent from Figure 5.2a, P release was higher in the MBR system than in the A^2O system, at 2.3 and 1.7 g/d respectively. The effect of nitrates on PAOs in the A^2/O anaerobic reactor appeared greater than the MBR. The denitrified nitrates in the MBR and A^2O anaerobic tanks averaged 0.09 and 0.21 g NO_3-N/d, respectively. The additional denitrification of 0.12 g NO_3-N/d in the A^2O anaerobic tank relative to the MBR anaerobic tank would consume about 0.48 g rbCOD/d and decrease P release by an estimated 0.24 g PO_4-P/d based on the rbCOD/P ratio of 2:1 (Smolders et al., 1994), which may affect PAO activity. On the contrary, MBR P removal was promoted by an extra P uptake of 0.2 g/d in the intermediate clarifier simultaneously with the denitrification of 0.1 g NO_3-N/d..

It appears from Figure 5.2a that P uptake in the MBR is higher than the A^2O system. Average anoxic P uptake accounted for 49 and 33% of the overall P uptake in MBR and A^2O respectively. Despite the difference between this system and external nitrification system such as the DEPHANOX, the enhanced DPAO activity is consistent with the findings of Hu et al. (2002) who observed that in a BNR treating strong municipal wastewater (TCOD 750 mg/L, TP 13.6-28.9 mg/L and TKN 45-82.5 mg/L) at an HRT of 25 h and SRT of 10 d, anoxic uptake accounted for 38-70% of the total P uptake.

An argument can be made that due to recycled dissolved oxygen to the anoxic zone, some of the P can be removed by PAOs. Although an oxygen demand for P uptake of 0.32 g O_2/g P has been proposed by Smolders et al (1995), it is hard to expect PAO activity associated with recycled oxygen in anoxic condition because rapid DO consumption occurs mainly due to ordinary heterotrophs oxidizing readily biodegradable COD, rather than PAO using relatively slowly biodegradable intracellular products. It thus presumes that anoxic P uptake was mostly associated with DPAOs which concomitantly remove nitrates.

5.3.3. Nitrogen Removal

The contribution of the anaerobic, the clarifier and the anoxic tank to overall denitrification is shown in Figure 5.2b. It is noteworthy that a relatively higher extent of denitrification was observed in the clarifier of the A^2O than MBR. For further

understanding of the denitrification pathways occurring in the anoxic tank, the relationship between nitrates removal and phosphorus uptake in anoxic tank is presented in Figure 5.2c. The amount of nitrates removed by DPAOs relative to P uptake has been reported and the average of 0.52 g NO_3-N/g P (Murnleitner et al., 1997; Meinhold et al., 1999; Lee et al, 2001; Hu et al., 2006; Patel et al., 2006) was used to estimate the contribution of DPAOs to denitrification. Accordingly, DPAO denitrification accounts for 54 and 40% of the total denitrification mass rates in the MBR and A^2O respectively based on the anoxic P uptake of 1.3 and 0.6 g/d.

5.3.4 Role of Intermediate Clarifier and Impact of Anaerobic HRT

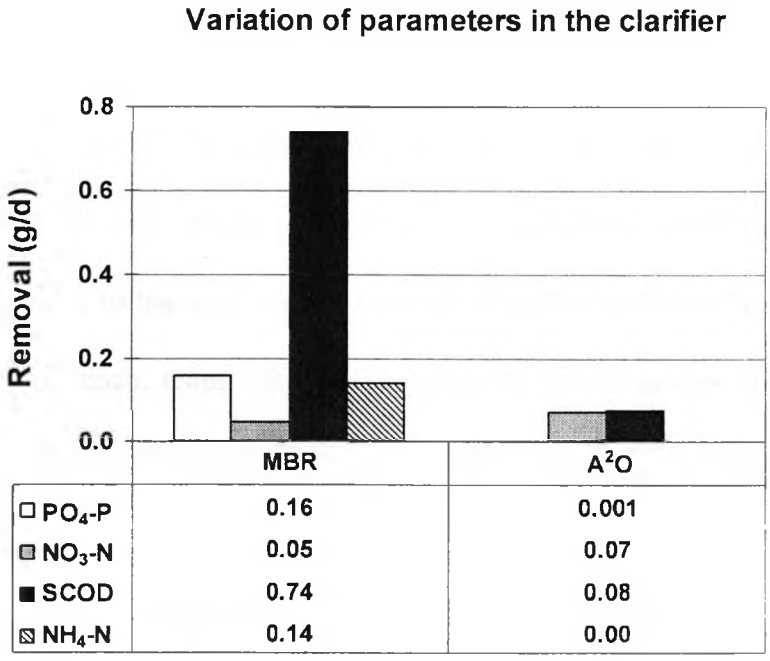


Figure 5.3 The variation of soluble carbon, nitrogen and phosphorus variation in the clarifier during SWW run.

Figure 5.3 presents the steady-state variation of mass removal rates of soluble COD, ammonia, nitrates, and phosphates in MBR intermediate clarifier and A^2O final clarifier. The estimated amounts of COD required for denitrification for the MBR and A^2O systems using Eq. 5.1 (Metcalf and Eddy, 2003) were 3.7 and 4.0 g COD/g NO_3-N respectively.

$$\text{COD consumption through denitrification} = \frac{2.86}{1-1.42\times Y_{obs}} \qquad (5.1)$$

For the analysis of the data of Figure 5.3, the aforementioned ratio of P uptake to nitrate denitrified of 1.92 g PO_4-P/g NO_3-N was used. Similarly, the ratio of VFA_{COD} sequestered to P release of 2 g COD/g PO_4-P (Smolders et al., 1994) was adopted. It has been reported that 7-10 mg COD is required for 1 mg P removal (Metcalf and Eddy, 2003) and the typical ratio of P uptake to P release is 1.15-1.2 (i.e. net P removal is 0.15-0.2 times P release) close to the relationship between P uptake and P release proposed by Wentzel et al. (1985). Hence, using 10 and 0.2 from the above ranges and dividing the required COD per P removal by the net P release yields 2 mg COD/mg P release .

Compared to only denitrification in the A^2O final clarifier, the role of MBR intermediate clarifier in the fate of various nitrogen and phosphorus species can be elucidated on the basis of the detailed data depicted in Figure 5.3. For the MBR, the estimated COD used for denitrification is 0.19 g SCOD/d, far below the observed value of 0.74 g SCOD/d. This clearly highlights the role of biosorption in the soluble COD

removal, which accounted for 74% of the SCOD removal in the clarifier. The estimated contribution of DPAOs to P removal in the MBR is 0.1 g P/d and hence 0.06 g P/d can not be justified on the basis of biological uptake since the total P uptake was 0.16 g P/d. Concomitantly, ammonia was also removed with orthophosphates implying that chemical precipitation of ammonium phosphate salts i.e. struvite may have occurred. Stuvite is a function of pH and solution concentration. Zeng and Li (2006) reported that pH can be implemented in a wide range of 7-10 although higher pH expedites the reaction. Magnesium concentration in the feed was 0.58 mM and factoring the dilution by recycle streams was 0.16 mM in the clarifier. For the MBR, the ambient PO_4^{3-} and NH_4^+ concentrations were 0.5 mM and 0.75 mM respectively; thus not only exceeding the solubility product of struvite at 20 °C of $10^{-13.3}$ (Ohlinger et al., 1998) but also closely approaching the P:Mg molar ratio of 4:1-5:1 which is favorable for phosphate precipitation at 18-20 °C (Maurer et al., 1999).

5.3.4 Comparative performance under limiting influent VFAs

An extended comparative study between the two systems was conducted using municipal wastewater with low VFA. As shown in Table 5.1, the VFA concentration in the MWW averaged 33 mg/L about a third of the SWW. Although apparent from Table 5.1, the overall nitrogen removal efficiencies in the two systems appear close at 74 and 73% for the MBR and the A^2O, respectively, in fact the observed effluent total soluble nitrogen comprising STKN, nitrates and nitrites were statistically different at the 95% confidence level, with the MBR achieving around 0.3 mg/L lower values. It is

noteworthy that the combined denitrification in the anoxic and anaerobic tank in the MBR on a mass basis still exceeded the A^2O, at 1.16 and 1.1 g/d, respectively. Furthermore, the overall P removal efficiencies in the two systems were at 80 and 75% for MBR and A^2O respectively, with the MBR achieving 0.2 mg/L lower effluent orthophosphates than the A^2/O while the difference was statistically significance at the 95% confidence level. This enhanced P and N removal in the MBR is attributed to better fermentation of particulate COD as elaborated upon further.

Table 5.2 presents that the fate of orthophosphate and VFA in the anaerobic tank is quite different between the two systems. P release rate was higher in the MBR than the A^2O at 0.34 and 0.18 g/d, respectively. Anaerobic tank VFA consumption averaged 0.11 and 0.55 g/d for the MBR and A^2O respectively. Moreover, 0.22 g VFA/d was consumed in the intermediate clarifier. It should be emphasized that VFA consumption was not attributed to methanogenesis involving the conversion of VFA to methane gas because the anaerobic oxidation reduction potential (ORP), measuring the relative amounts of oxidized or reduced matter, ranged from -100 to -150 mV, well below the -300 mV ambient in anaerobic systems (Gerardi, 2003). Theoretically, VFA consumption for P release and denitrification is based on the 2 mg VFA_{COD}/mg P (Smolders et al., 1994; Yagci et al., 2005) and Eq. 5.1 respectively.

Thus, the estimated VFA consumption in the intermediate clarifier was 0.22 g/d, quite comparable to the experimental measurement. On the other hand, the estimated VFA consumption in the MBR and A^2O anaerobic tanks was 1.28 (=3.5×0.16+2×0.34)

and 0.88 (=3.7×0.14+2×0.18) g/d, respectively, much greater than the 0.11 and 0.55 g/d observed experimentally. The discrepancy between the measured and theoretical VFA consumption is expected to be met by fermentation of particulate organics (Barker and Dold, 1997). Thus, fermentation likely contributed to an estimated 1.17 and 0.33 g/d of VFA generation, clearly pointing to a much higher fermentation capacity in the MBR anaerobic tank relative to the A^2O tank.

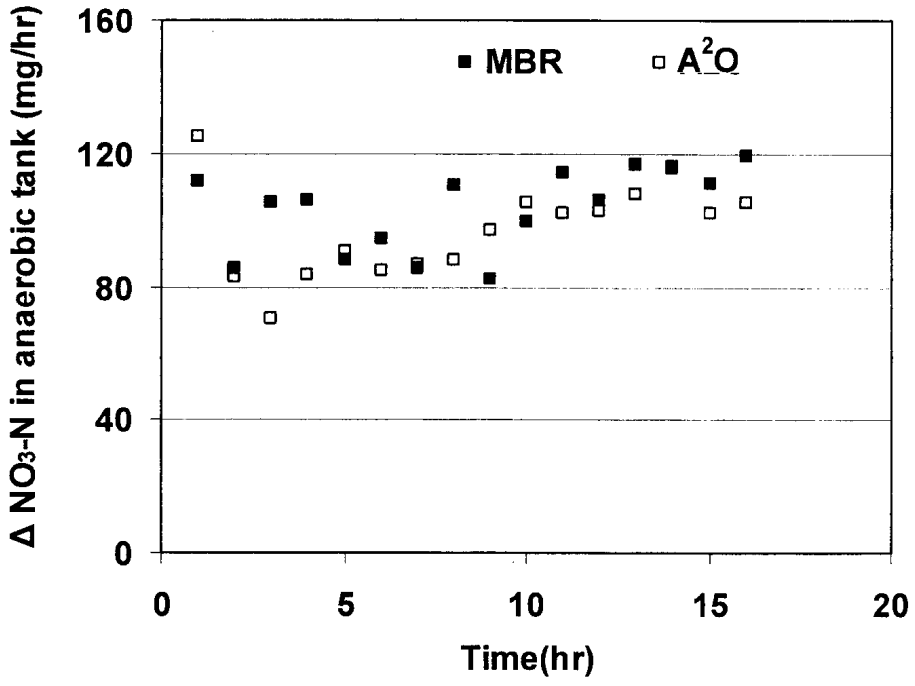
Interestingly, in this run it was observed that P was still released in the intermediate clarifier of the MBR system and contributed to increase total P release in the MBR from 0.34 to 0.42 g/d. Contrasted with the SWW run wherein the intermediate clarifier affected anoxic P removal (Figure 5.3) in the MWW it is thus evident that in the MWW the clarifier behaved as a secondary anaerobic zone, where further P release occurs concomitantly with VFA uptake. This phenomenon is associated with the nature of the municipal wastewater specifically, requiring longer hydrolysis and fermentation time than the acetate-rich SWW. Accordingly, some of readily biodegradable and fermentable COD might escape from the anaerobic zone and get sequestered in the intermediate clarifier. It is therefore hyphothesized from the SWW and MWW run that the intermediate clarifier affected denitrification, ammonia removal, and SCOD removal both by biosorption and sequestration by PAOs.

Table 5.2 Nutrient mass balances obtained from MWW run

	MBR_ Anaerobic	MBR_ Clarifier	MBR_ Anoxic	A^2O_ Anaerobic	A^2O_ Anoxic
P release (g P/d)	0.34	0.08	-	0.18	-
Denitrification (g NO_3-N/d)	0.16	0.01	1	0.14	0.96
VFA consumption (g VFA_{COD}/d)	0.11	0.22	-	0.55	-
Theoretical VFA consumption* (g VFA_{COD}/d)	1.28	0.2	-	0.88	-

* Calculated as VFA consumption for P release (2 mg VFA_{COD}/mg P) and denitrification (Eq. 5.1)

5.3.5 Dynamic test



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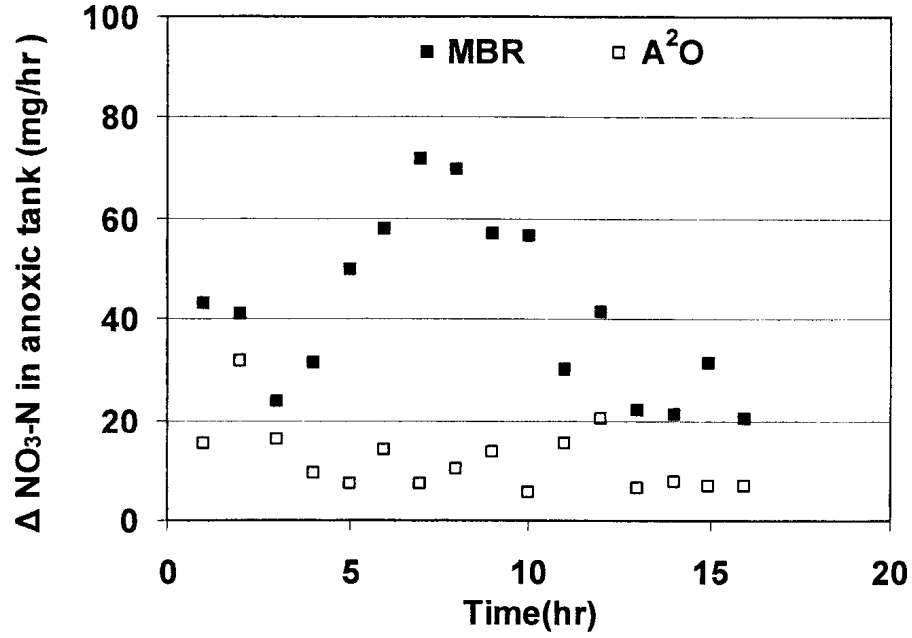

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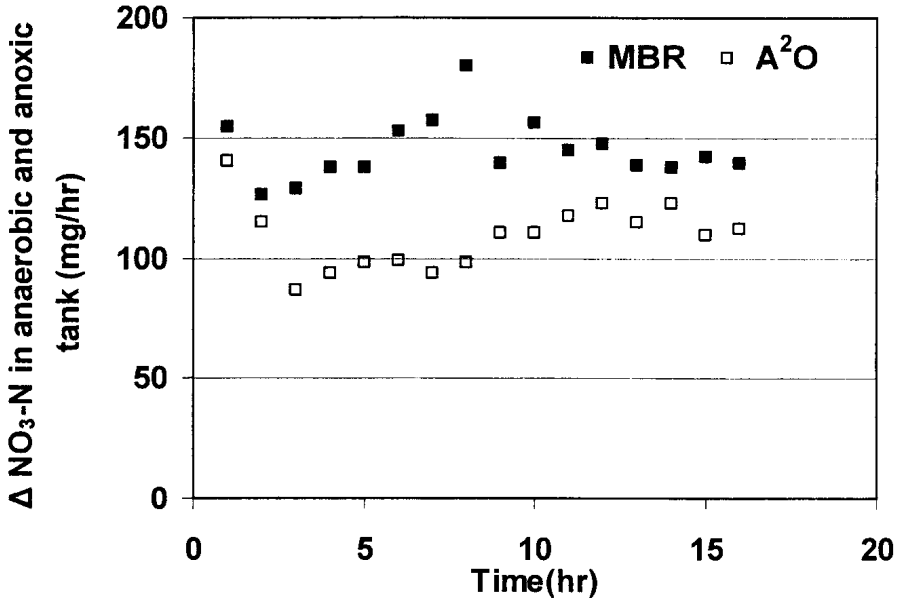

c)

Figure 5.4 Denitrification profile during dynamic test in SWW run in (a) anaerobic tank, (b) anoxic tank and (c) overall denitrification.

In order to investigate the denitrification capacity of each system during SWW run, a dynamic experiment was conducted on MBR and A^2O at an influent COD: nitrogen ratio of 4.5:1 by spiking nitrates in the feed while maintaining the same influent COD. Figure 5.4a depicts the mass denitrification rates in the anaerobic tank, calculated as the mass of nitrates removed divided by the anaerobic HRT. The mass of nitrates removed at any given time (t) is computed as the difference in concentration at time t and time (t-1) multiplied by the volume of the anaerobic tank. Although both systems had high denitrification rates in the anaerobic tank during the test, the denitrification rate was on average 6 mg NO_3-N/hr higher in the MBR than in the A^2O.

The denitrification rate in the anoxic tank, presented in Figure 5.4b, clearly shows much higher denitrification in the MBR than the A^2O. The maximum denitrification rate reached 72 mg NO_3-N/hr in the MBR as opposed to 31 mg NO_3-N/hr in the A^2O. It is evident from Figure 5.4c also that the overall denitrification rate during the test was higher in the MBR than in the A^2O system at an average of 145 vs 109 mg NO_3-N/hr. Statistical analysis using a paired T-test conducted on the overall denitrification rate between MBR and A^2O indicated that observed differences were statistically significant at the 99% confidence level.

5.4 Conclusions

Within the HRT and SRT investigated in this study of 8 hours and 10 days for the treatment of wastewater characterized by COD, TKN and P concentrations of 310, 33,

and 4.6, respectively in the SWW and 340, 37 and 4.0 mg/L, respectively, in the MWW, the following conclusions can be drawn.

1. The MBR system outperforms the A^2O system in phosphorus removal. Anoxic P uptake in the MBR system accounted for the 49% of the total P uptake as compared to the 33% in the A^2O during SWW run.

2. The contribution of DPAOs to denitrification in the anoxic tank was much higher at 54% of the total denitrification in the MBR system as compared to the 40% in the A^2O. The MBR system yield was 20% lower than the A^2O system.

3. The MBR intermediate clarifier assisted nitrogen, COD and P removal through denitrification, COD adsorption and P release or uptake while the A^2O final clarifier facilitated nitrogen and COD reduction through denitrification. The fate of orthophosphate in the clarifier differed depending on the feed VFA, with P uptake in VFA-rich wastes and P release in VFA-limited influents. The MWW results emphasized the better fermentation of COD in the MBR relative to the A^2O.

4. The dynamic shock loading tests clearly demonstrates that MBR has better denitrification capacity than the A^2O.

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6.0 Impact of membranes on refractory dissolved organic nitrogen

6.1. Introduction

Concern with dissolved organic nitrogen in effluent (efDON) from biological nutrient removal plants is increasing due to stringent total nitrogen effluent quality requirements. According to an intensive review by Pehlivanoglu-Mantas and Sedlak (2006), efDON accounts for up to 80% of the total nitrogen in nitrification-denitrification process effluent. Based on data collected from seven plants in USA, Pagilla et al (2006) also reported that the percentage of efDON ranged from 20-85% of the effluent 5 mg/L TN.

Reduction of efDON is challenging due to the complexity of its nature. Awobamise et al (2007) tested the biodegradability of efDON during 30 days and observed that out of initial DON of 1 mg/L, biodegradable DON increased in the first 20 days from less than 0.1 to 0.5 mg/L, indicating that 50% of DON is not removed by biological processes. This is consistent with the observation by Urgun-Demirtas et al. (2007) where 18-61% of efDON was bioavailable in the first 14 days. Pagilla et al. (2006) observed that the molecular weight (MW) of DON ranged from 1 to 1000 kD, with the low MW biodegradable. Thus, various physical or chemical treatments attempted for breaking the chain of high MW DON compound, revealed the feasibility of anion exchange, coagulation, ozonation, advanced oxidation to some extent (Pehlivanoglu-Mantas and Sedlak, 2006), though their application is usually limited to industrial wastewaters. Parkin and McCarty (1981) suggested that SRT can be a key

parameter for controlling efDON because more influent DON is biodegraded at longer SRTs. However, increased biomass endogenous respiration increases DON, suggesting the occurrence of an optimal SRT. O'Shaughnessy et al. (2006) also reported that longer SRT and higher temperature within ranges of 10-17 days and 5-17°C, respectively led to efDON reduction.

MBRs have demonstrated superior performance over the conventional biological wastewater treatment process in terms of better nitrification, perfect capture of solids and colloidal organic matter. Several MBR performance with respect to efDON are presented in Table 6.1. Apparently efDON is associated with SRT. As SRT varied at 15 to 26 d (Lesjean et al. 2002) and 20 to 50d (Mouthon-Bello and Zhou, 2006) efDON decreased with increasing SRT not only in terms of concentration but also as % of TN in both cases. However, from the table the average efDON from three BNR systems was 1.8 mg/L, which seems relatively high compared to the less than 1 mg/L efDON observed in 68% of the 188 tested Maryland and Virginia wastewater plant samples (Pagilla et al., 2007).

Despite the few reports tabulated above, the advantages of MBR systems on efDON are not thoroughly delineated, particularly as they relate to the relative contribution of membranes and long SRTs. In this study, a comparative assessment of MBR and a conventional BNR system at identical SRTs was undertaken with special focus on investigating the impact of membrane on efDON to shed light on the membrane role in DON reduction.

Table 6.1 MBR process efDON from references

	Configuration[a]	Feed type[b]	SRT (d)	HRT (h)	TN (mg/L)	DON (mg/L)	DON (%)
Lesjean et al. (2002)	AN-AX-AO (Pilot-scale)	MWW (1000/70/11)	15	21	9	2.6	29
			26	18	11	1.7	15
Mouthon-Bello and Zhou (2006)	AX-AN-AO (Pilot-scale)	MWW (360/61/9)	20	6	10	3.3	33
			50	8	12	2.1	18
Monti et al. (2006)	AN-AX-AO (Pilot-scale)	MWW (380/35/4)	12	10	11	0.7	7
			12	7	12	0.6	5
Ersu et al. (2008)	AN-AX-AO (Lab-scale)	SWW (510/43/11)	25	10	6	1.4	23

a AN:anaerobic AX:anoxic AO:aerobic
b MWW (municipal wastewater) SWW (synthetic wastewater), numbers within parenthesis are TCOD/TN/TP in mg/L

6.2 Materials and methods

6.2.1 System description

It is given in chapter 3.1.

6.2.2 System operation

The first comparative study with runs 1 and 2, aimed primarily at assessing the role of membranes and impact of influent wastewater characteristics on efDON, was conducted using synthetic wastewater (SWW) and municipal wastewater (MWW) at total HRT of 8 hrs in the NMBR and A^2O systems. The second study with run 3 was carried out using MWW in the NMBR and UMBR at an HRT of 6 hrs. The entire experimental plan consisted of three runs at a SRT of 10 days. The feed, system start-up and membrane operation are given in chapter 3.2, 3.3.1 and 3.3.4, respectively.

6.2.3 Analytical methods

It is given in chapter 3.4.1.

6.3 Results and discussion

Table 6.2 summarizes the influent and effluent nitrogen characteristics. Data was found to fit normal distribution using the statistical software (Minitab 13.1) and hence the standard deviations of the data are reported in Table 6.2. Briefly, the SWW used during the first run was characterized by average TCOD, TKN and TP concentrations of 310, 33 and 4.6 mg/L, respectively, comparable with the MWW (used in runs 2 and 3) of 280, 30 and 4.0 mg/L. The systems were operated for around 500 days including the MWW run of 350 days. Total influent organic nitrogen concentrations in the SWW and MWW were around 10 and 17 mg/L, respectively with DON concentrations of 4 and 7 mg/L, respectively. However, particulate organic nitrogen in the SWW was mostly biodegradable. Comparing the efDON in NMBR and A^2O between the SWW and MWW runs evidently shows that efDON increased by as much as 0.8 mg/L during the MWW run, with an average of 0.7 mg/L.

Table 6.2 Pseudo-steady state influent and effluent quality obtained from the entire runs.

		Run1 (Days 1-150)			Run2 (Days 151-360)		Run3 (Days 360-500)	
	Feed SWW	NMBR	A^2O	Feed MWW	NMBR	A^2O	NMBR	UMBR
TKN	33±1.0 (14)	-	1.6±0.4 (11)	30±4 (27)	-	3.0±0.4 (12)	-	-
Soluble organic N[1]	4±2 (14)	0.3-0.5 (11)	0.5-0.8 (11)	7±3 (27)	0.8-1.2 (12)	1.2-1.6 (12)	0.4-1.35 (13)	0.4-1.46 (13)
NH_4-N	24±0.3 (25)	0.1±0.03 (25)	0.1±0.03 (25)	17±2 (34)	0.2± 0.1 (40)	0.3±0.1 (40)	0.2 ± 0.2 (25)	0.1 ± 0.1 (26)
NO_3-N	-	7.8±0.6 (25)	6.6±0.5 (25)	0.5± 0.2 (5)	8.2± 0.7 (40)	7.5± 0.7 (40)	6.8±2.1 (24)	8.5±2 (20)
NO_2-N	-	0.3±0.2 (25)	0.2±0.1 (25)	-	0.2±0.1 (32)	0.3±0.1 (32)		

* Numbers within parenthesis are the number of samples
[1] EfDON is expressed as the range of 10^{th} and 90^{th} percentiles.

It is also apparent from Table 6.2 that the 10^{th}-90^{th} percentile spread in run 2 at an overall HRT of 8 hours were 0.8-1.2 mg N/L, as compared to 0.4-1.35 mg N/L in run 3 at an overall HRT of 6 hours. Equally important from a compliance standpoint, the efDON even from a membrane system can reach 1.3-1.5 mg N/L, thus implying that in order for a 3 mg N/L total limit to be met, total inorganic nitrogen has to be below 1.5 mg/L. Furthermore, the observed variation in efDON of about 1 mg/L in MWW emphasizes the need for real-time control of total inorganic nitrogen, a difficult feat to achieve in cold climates due to much slower nitrification and denitrification kinetics.

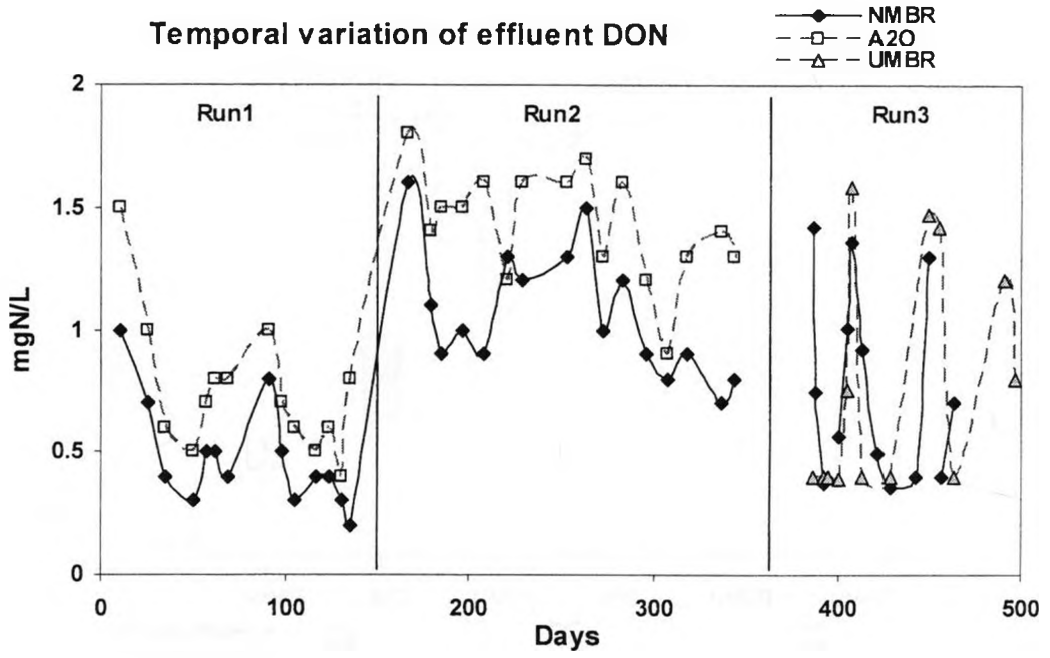

Figure 6.1 Temporal variation of efDON during the runs.

Figure 6.1 presents the temporal variation of efDON during the entire runs. Apparently, during the first run with SWW, most efDON in both NMBR and A^2O were less than 1 mg/L while in the MWW runs efDON varied relatively widely from 0.4 to 1.6 mg/L. Interestingly, it appears that the trend of efDON was fairly cyclical over the time which is consistent with the observation by O'Shaughnessy et al. (2006). During first run using constant SWW feed, efDON fluctuated within 0.4 mg/L. In run 3 the cyclical pattern was more evident in both NMBR and UMBR systems varying by as much as 1.1 mg/L. It may be associated with the fact that DON accumulates and disappears in the system over the SRT turnovers similar to the cyclical behavior of soluble microbial products observed by Holakoo et al (2007) and Shin and Kang (2003) in glucose-fed bioreactors.

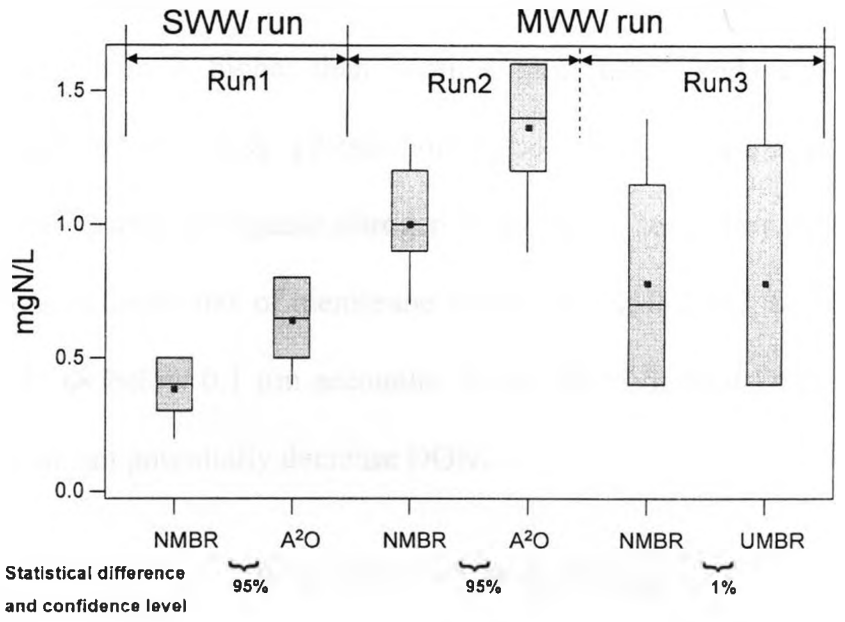

Figure 6.2 Box graph for efDON during the runs (Percentiles are shown: Minimum, 25th, 75th and Maximum. The horizontal line and the dot inside the box represent the median and the average, respectively)

Figure 6.2 shows the statistical distribution of the pseudo-steady state efDON data during the runs. The NMBR achieved average efDON during the SWW run of 0.4 mg/L compared to 0.7 mg/L in A^2O, with a 10th to 90th percentile range of 0.3-0.5 and 0.5-0.8 for NMBR and A^2O, respectively. The major finding is the positive impact of membrane process on reducing efDON. Obviously, the results demonstrate that NMBR achieved lower efDON than the A^2O. The two comparisons reveal that NMBR achieved 57-70% lower efDON than A^2O. Statistical analysis conducted in each case showed that the differences were statistically significant at higher than 95% confidence level. Furthermore, it is also evident that efDON varied more widely for the A^2O relative to the

MBR. This noticeable difference is associated with physical blockage of membrane pores or cake layer. It has been reported that mostly DON molecular weight distribution is less than 1000 kDa, which is higher than nominal molecular weight cut-off 300 kDa of membranes used in this study (Westerhoff et al., 2006). Pagilla et al (2008) also differentiated the species of organic nitrogen in the seven secondary effluent samples by filtering through different size of membrane filters i.e. 0.1, 0.2, 0.3, 0.45 and 1.2 μm and observed that DON below 0.1 μm accounted for 40-95 % of total DON. It suggests that MBR application can potentially decrease DON.

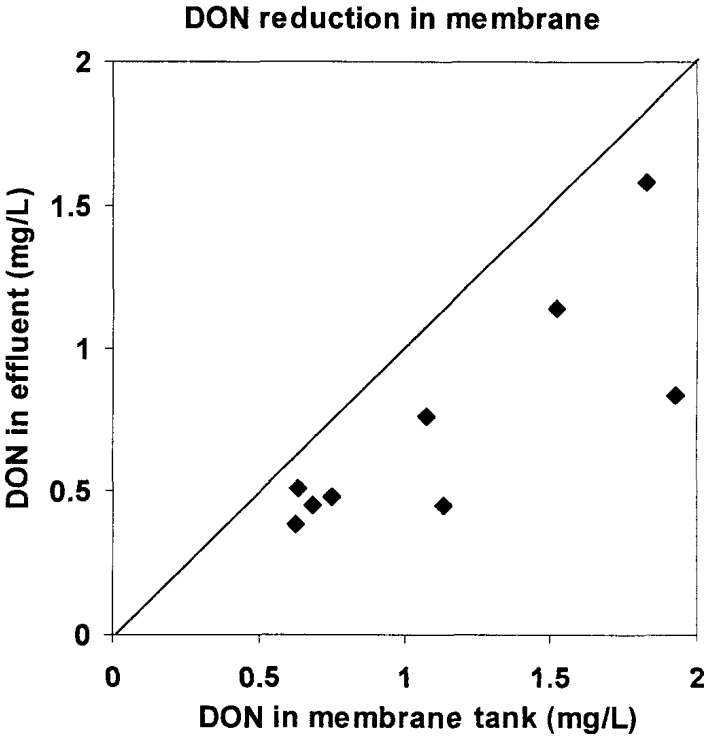

Figure 6.3 DON reduction between membrane tank and permeate during run 3

During run 3 both NMBR and UMBR systems achieved similar efDON as low as 0.4 mg/L with an average of 0.8 mg/L. Figure 6.3 demonstrates that the observed DON reduction between the aeration tank and the permeate in both NMBR and UMBR during

run 3 was as high as 1 mg/L but averaged 0.4 mg/L, corresponding to an average 35% of DON in aerobic tank, which is consistent with the difference between NMBR effluent and A^2O effluent in run 2 of 0.35 mg/L. Although the significant rejection of efDON by membrane was observed in this study, further investigation on the nature of efDON i.e. recalcitrant or biodegradable is warranted.

6.4 Summary and conclusions

Within the HRT and SRT ranges investigated in this study of 6-8 hours and 10 days for the treatment of wastewater characterized by COD, TKN and P concentrations of 310, 33 and 4.6 mg/L, respectively, in the SWW and 280, 30 and 4 mg/L, respectively in the MWW the following conclusions can be drawn.

- Comparing the efDON between the NMBR and A^2O, the NMBR produced 0.3 mg/L lower during the MWW and SWW runs, reflecting the positive impact of membrane.
- DON reduction by membrane was significant at an average of 35% of the aeration tank DON in NMBR and UMBR systems.
- During both SWW and MWW runs, despite constant operating and feed conditions, efDON followed a cyclical pattern over time, varying by as much as 1.1 mg/L. This may be indicative of simultaneous generation and biodegradation.
- During the MWW run, efDON in both NMBR and A^2O systems increased by as much as 0.8 mg/L, and 0.7 mg/L on average above the SWW run.

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7.0 Phosphorus Fractionation in Membrane-Assisted Biological Nutrient Removal Processes

7.1 Introduction

Several attempts were made to implement the MBR technology in BNR processes (Lesjean et al., 2002; Fleischer et al., 2005; Monti et al., 2006; Mouthon-Bello and Zhou, 2006). Some of the reported advantageous MBR operating conditions i.e. long solids resident time (SRT) and low sludge production are not necessarily conducive to enhanced biological phosphorus removal (EBPR). The sparse literature on EBPR in MBRs is controversial. Lesjean et al. (2002) operated a University of Cape town (UCT) adapted MBR process on a wastewater with COD:N:P ratios of 100:7:1 at an HRT of 18-21 h and SRT of 15 d, and achieved effluent P below 0.1 mg/L without chemical addition, attributing the high P removal primarily to EBPR, with retention of solids and colloids by the membrane as secondary.

On the other hand, Fleischer et al. (2005) operated a 6-stage pilot MBR on primary effluent with COD:N:P ratio of 100:13:2 at an HRT of 8.4 h and SRT of 19 to 23 d, and maintained effluent P of 2 mg/L, decreasing to 0.1 mg/L at an alum dose of 2.7 mole Al mg^{-1}TP. Mouthon-Bello and Zhou (2006) operated a pilot anoxic/anaerobic/aerobic MBR system at HRTs of 5.8 and 7.9 h, and SRTs of 20 and 50 d on two municipal wastewaters (MWW) characterized by COD:N:P ratios of 100:17:3.4 and 100:17:1.6, respectively and interestingly found that despite a longer SRT in the

latter case, P in the membrane tank decreased from 1.8 to 0.7 mg/L, with permeate concentrations of 0.5 and 0.1 mg/L. The aforementioned authors concluded that EBPR did not occur and attributed P removal to precipitation by the relatively high influent metals and particulates rejection by the membrane.

Furthermore, Monti et al. (2006) in a comparative assessment of EBPR in a conventional and membrane-assisted UCT pilots treating primary effluent at HRTs of 7-12 h and SRT of 12 d, that when the influent VFA were limiting, because of the lower yield in the MBR, the conventional system exhibited better soluble P removal. All the aforementioned studies focussed on P removal with no detailed assessment of the contribution of different P removal mechanisms i.e. chemical precipitation, anoxic and aerobic EBPR, and membrane retention. Thus the primary objective of this study is to evaluate the relative contribution of various P removal mechanisms in MBRs, a feat complicated by the wide variations in influent volatile fatty acids and metal concentrations in municipal wastewaters. Furthermore, as the work of Monti et al. (2006) has highlighted the challenges of maintaining stable EBPR at short HRTs of about 7 h, this study pushes the envelop of HRTs down to 6 h with the demonstration of stable EBPR.

This paper discusses the findings of a comparative study involving a novel membrane assisted BNR process (Nakhla and Patel, 2008) and UCT process coupled with membranes, with the former MBR system characterised by employment of an intermediate clarifier between the anaerobic and the anoxic tank in order to concentrate

biomass, on which rich organic matter is adsorbed in the anaerobic phase and, subsequently, utilize it for denitrification in anoxic phase, thus enhancing denitrification and EBPR (Kim and Nakhla, 2008).

7.2 Materials and methods

7.2.1 System description

It is given in chapter 3.1.

7.2.2 System operation

It is given in chapter 3.3.3-3.3.4. The system was run for a total of 300 d or 30 turnovers of the mean SRT. During the first 150 days (phase I), the system was fed with settled MWW. However, after 150 days (phase II) the MWW was supplied without settling and supplemented with 30 mg/L of acetic acid to enhance P removal.

7.2.3. Analytical methods

It is given in chapter 3.4-3.5.

7.3 Results and discussions

7.3.1 Overall performance

Table 7.1a shows the steady state effluent quality, collected after 3 turnovers of the SRT, during phases I and II. Data was found to fit normal distribution using the statistical software (Minitab 13.1) and hence the standard deviations of the data are reported in Table 7.1. Influent total COD concentration averaged 250 and 440 mg/L for

phases I and II, respectively while steady state effluent MBR and UMBR COD concentrations were close at 13-20 mg/L during the two phases. Average VFA in feed was 30 mg/L in phase I as compared to 70 mg/L in phase II.

Effluent nitrates averaged 6.8 and 7.6 mg/L in the NMBR for phase I and II, respectively compared to 8.5 and 8.6 mg/L in the UMBR. Overall nitrogen removal efficiencies were 73-80 and 70-77% for NMBR and UMBR, respectively with influent total nitrogen of 31 and 44 mg/L for phases I and II respectively. Overall P removal efficiencies were higher in NMBR than UMBR i.e. 57% vs 54% in phase I and 94% vs 91% in phase II, with lower effluent P in the NMBR i.e. 1.5 vs 1.4 mg/L in phase I and 0.5 vs 0.8 mg/L in phase II . Total suspended solids in the NMBR and UMBR systems in phase I were 56 and 51 g in respectively but increased to 88 and 82 g in phase II. Sludge production calculated as the slope of the cumulative VSS produced versus cumulative COD removed was close in both systems at 0.28 and 0.25 gVSS/gCOD in phase I and II, respectively.

Table 7.1 (a) Steady state influent and effluent quality obtained from the two systems (All units are in mg/L except where stated otherwise).

Parameter	Phase I			Phase II		
	Influent	NMBR	UMBR	Influent	NMBR	UMBR
TCOD	250±100 (25)*	-	-	440±150 (19)	-	-
SCOD	64±40 (25)	13±4 (22)	12±5 (22)	180±80 (19)	14±7 (19)	18±6 (19)
VFA	30±5 (10)	-	-	70±5 (8)	-	-
TKN	29±5 (20)	-	-	43±5 (10)	-	-
STKN	20±4 (15)	0.6±0.5 (13)	0.8±0.7 (13)	31±5 (10)	0.8±0.5 (10)	1.1±0.5 (10)
NH_3-N	16±3 (20)	0.2±0.2 (25)	0.1±0.1 (26)	21±2 (19)	0.2±0.2 (19)	0.2±0.2 (19)
NO_3-N	-	6.8±2.1 (24)	8.5±2 (20)	-	7.6±2.1 (19)	8.6±2.2 (19)
NO_2-N	-	0.1±0.1 (21)	0.1±0.1 (21)	-	0.1±0.1 (15)	0.1±0.1 (15)
TP	3.5±1.5 (14)	-	-	8.7±2 (19)	-	-
PO_4-P	2.1±0.7 (18)	1.5±0.6 (23)	1.6±0.5 (23)	4±1.5 (19)	0.5±0.2 (19)	0.8±0.3 (19)
SS	120±60 (23)	-	-	270±90 (19)	-	-

Operational conditions				
Parameter	NMBR	UMBR	NMBR	UMBR
System SS^+ (g)	56±10 (23)	51±15 (23)	88±25 (15)	82±20 (15)
System VSS^+ (g)	44±7 (22)	40±8 (21)	64±7 (15)	58±7 (15)
Membrane tank SS (g/L)	2.5±0.6 (24)	2.5±0.7 (24)	4±1.3 (15)	4±1.2 (15)
Sludge yield, Y_{obs} (g VSS/g COD)	0.27	0.28	0.25	0.25
VSS/TSS	0.78	0.78	0.73	0.74
P content in sludge (% of VSS)	3.1	2.7	6.3	5.9
OUR (mgO_2/L/h)	32±3 (6)	30±4 (6)	43±3 (5)	42±3 (5)

* Mean± standard deviation (the number of samples)

\+ SS and VSS were calculated over all reactor compartments

(b) Mass balance in COD, Nitrogen and P (All units are in % of feed except where stated otherwise).

	Phase I						Phase II					
	NMBR			UMBR			NMBR			UMBR		
	COD	N	P	COD	N	P	COD	N	P	COD	N	P
Wastage	36	29	52	35	29	42	30	29	90	32	28	85
Effluent	6	25	45	7	28	56	4	21	7	4	25	12
Aerobic	25	-	-	24	-	-	15	-	-	16	-	-
Denitrification	16	40	-	18	37	-	21	44	-	19	42	-
Closure (%)	83	94	97	84	94	98	70	94	97	71	95	97

7.3.2. Mass balances

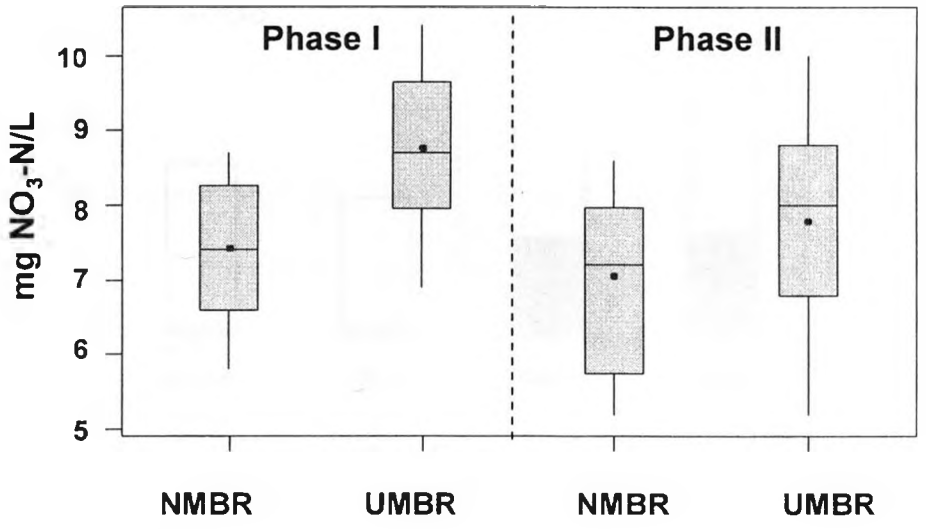
COD mass balance, calculated according to Barker and Dold (1995), is presented in Table 7.1b. The COD oxidized aerobically was estimated by the difference between the measured OUR and the oxygen demand for nitrification. COD consumption through denitrification was calculated using Eq (7.1) (Metcalf & Eddy, 2003):

$$\text{COD consumption through denitrification} = \frac{2.86}{1 - 1.42 \times Y_{obs}} \qquad (7.1)$$

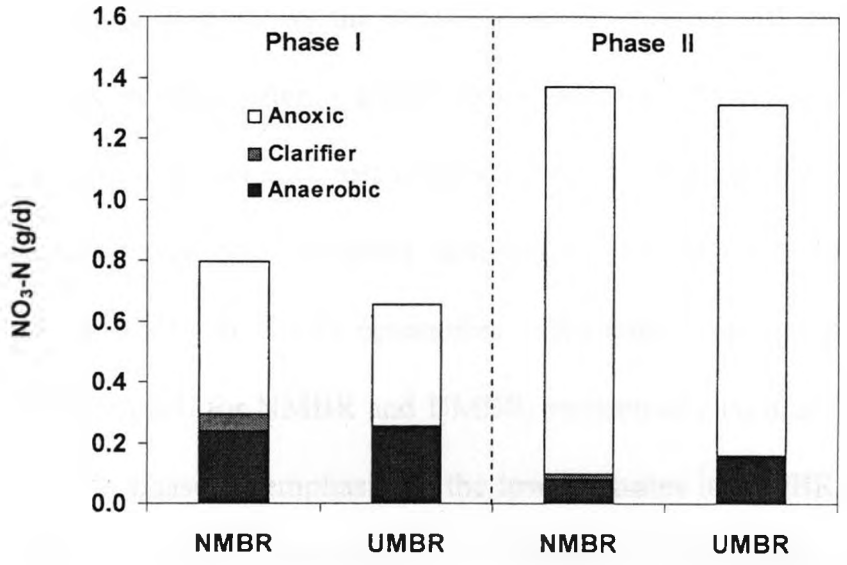
Total COD recoveries in both systems were 82-84% and 71-73% in phases I and II, respectively. Overall low recovery is associated with COD loss through hydrolysis of slowly biodegradable COD consisting of particulate, colloidal material and complex

organic matters requiring breakdown prior to utilization and subsequent fermentation in the anaerobic and anoxic tanks (Barker and Dold, 1997), with lower recovery in phase II due to increased fermentation in the anaerobic tank, as reflected by average ORP values of -200 mV compared to -130 mV in phase I. Aerobic COD consumption was higher than anoxic COD removal in phase I but lower in phase II, substantiating the reduced sludge yield in phase II of 0.28 vs 0.25 gVSS/g COD. Nitrogen removal through denitrification in both systems accounted for 31-38% and 41-44% during phase I and II, respectively with consistently higher values in the NMBR. In phase I effluent P was significantly high in both systems but in phase II over 85% of P was removed through sludge waste stream.

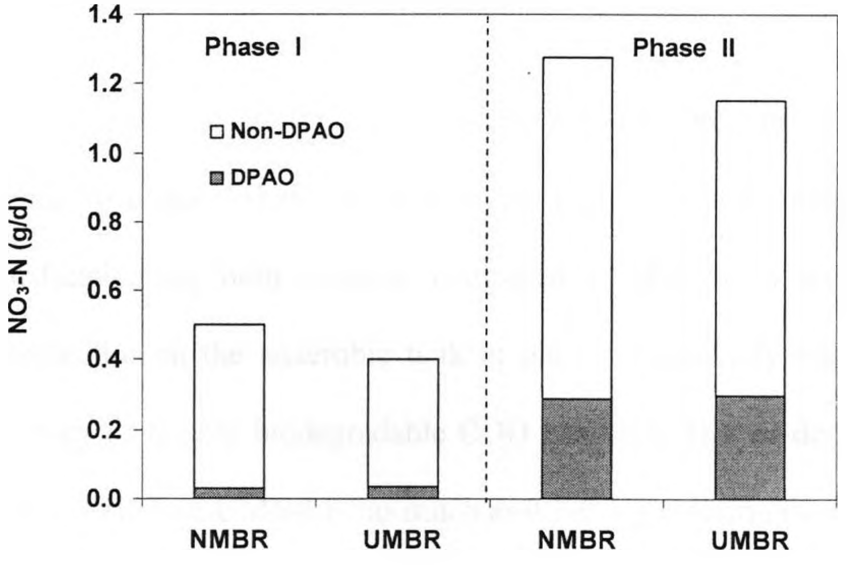
7.3.3. Nitrogen removal



a)



b)



c)

Figure 7.1 (a) Statistical distribution of effluent nitrates (Percentiles are shown: Minimum, 25th, 75th and Maximum. The horizontal line and the dot inside the box represent the median and the average, respectively) (b) denitrification pattern (c) fractionation of anoxic denitrification.

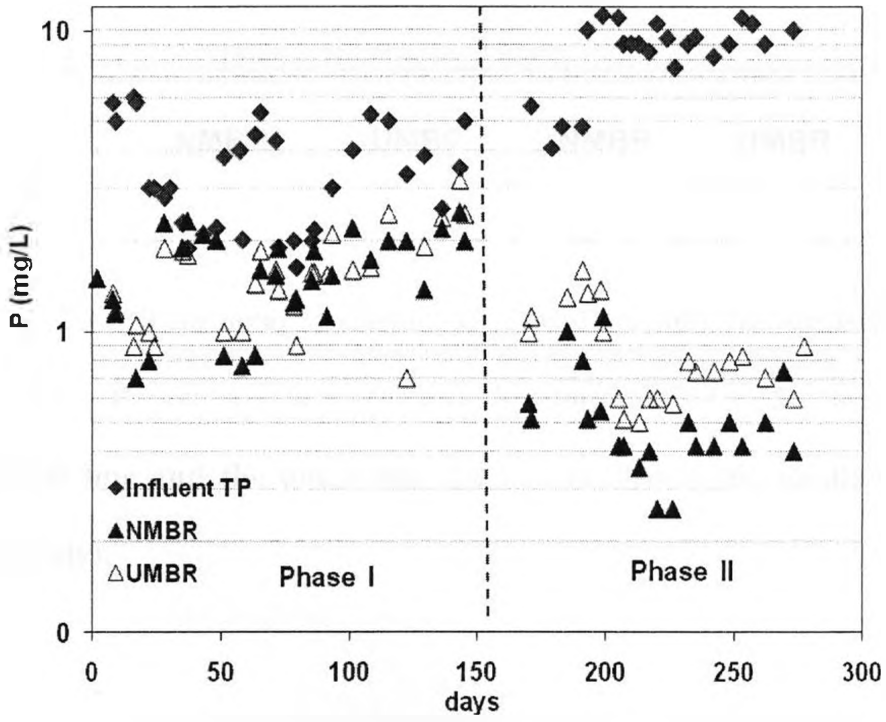
Figure 7.1a shows the statistical distribution of effluent nitrate concentration in both MBR systems after 3 turnovers of the mean SRT in phases I and II. Statistical analysis using a paired T-test conducted on the nitrates between NMBR and UMBR effluent indicated that observed differences were statistically significant at the 95% confidence level. The 25-75 percentiles of the data in phase I ranged from 6.5-8.1 mg/L and 7.9-9.5 mg/L for NMBR and UMBR, respectively compared to 5.8-8 mg/L and 6.8-8.7 mg L in phase II, emphasizing the lower nitrates in NMBR relative to UMBR by as much as 1-1.7 mg/L. Interestingly both MBR permeate nitrates were 0.5-1 mg/L lower than in the aerobic tank due to denitrification in the membrane biofilm, accounting for 10-15% of the nitrates in the aerobic tank in both systems.

Figure 7.1b presents denitrification mass rates in various processes of both systems. In phase I denitrification in the anoxic tank accounted for 62% of the total denitrification for both systems, compared to 88-93% in phase II. Relatively higher denitrification in the anaerobic tank in phase I negatively impacted EBPR due to the deficiency of readily biodegradable COD (rbCOD). Higher denitrification was achieved in the NMBR than UMBR by as much as 0.1-0.2 g/d during the two phases.

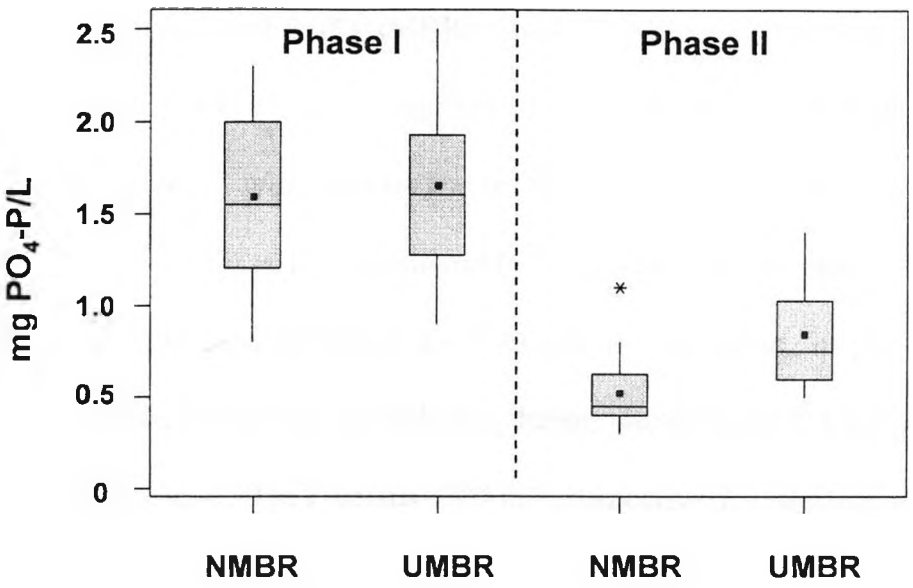
Figure 7.1c displays the fractionation of denitrification by the two different responsible microorganisms i.e. ordinary heterotrophs and DPAOs. Denitrification by DPAOs accounted for 6-9% and 22-26% in phase I and II, respectively. Nitrate reduction by DPAO was estimated based on the ratio of required nitrates per P removal i.e.0.59

gN/gP as determined from the batch tests elaborated upon further. Although on mass basis, both systems were similar at 0.04 g/d in phase I and 0.3 g/d in phase II, the percentage contribution of DPAOs to denitrification in the NMBR was lower due to the higher denitrification mass rates.

7.3.4 Phosphorus removal



a)



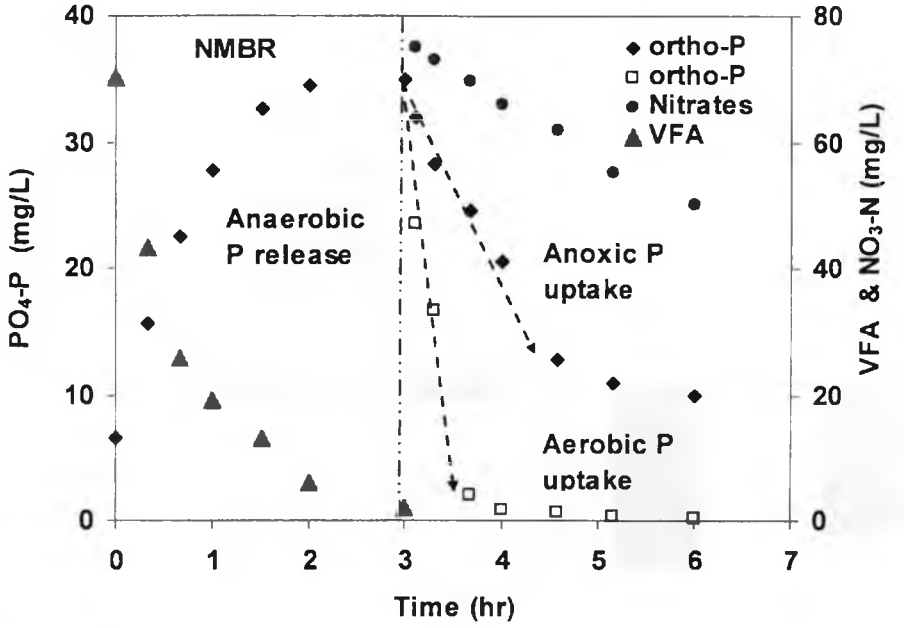
b)

Figure 7.2 (a) Temporal variation of phosphate and (b) statistical distribution of effluent P (Percentiles are shown: Minimum, 25th, 75th and Maximum. The horizontal line and the dot inside the box represent the median and the average, respectively).

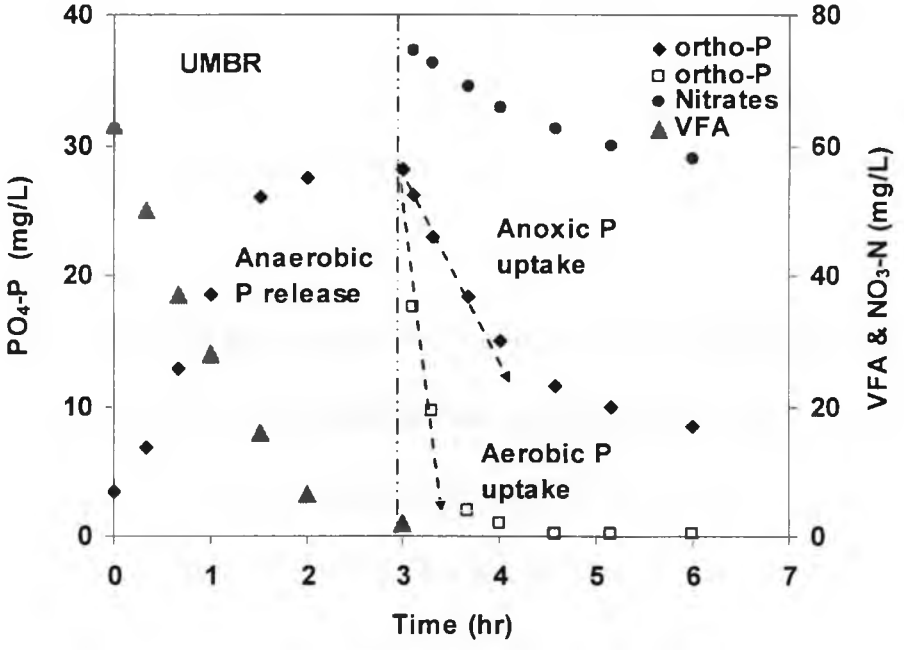
Figure 7.2a represents the temporal variation of P removal during phases I and II. Influent TP averaged 3.5 and 8.7 mg/L in phase I and II respectively. Effluent P was hardly below 1 mg/L during phase I which relied on the incoming 30 mg/L VFA present in wastewater with VFA/TCOD ratio of 0.12 and VFA/P ratio of 8.5. However, in phase II starting day 170, since 30 mg/L VFA were supplemented effluent P decreased well below 1 mg/L even at influent TP as high as 10 mg/L. VFA/TCOD and VFA/TP in phase II was 0.16 and 8.1, respectively. Thus, P deterioration in phase I can be justified by the

lower VFA/TCOD ratio and lower RBCOD availability due to denitrification in the anaerobic tank. The additional denitrification in the anaerobic tank was 0.25 g/d for both systems in phase I and 0.08 (NMBR) vs 0.16 (UMBR) g/d in phase II, consuming rbCOD of 1.1 g/d and 0.4 vs 0.7 g/d using Eq (7.1), corresponding to P release requirement of 0.5 g/d and 0.16 vs 0.3 g/d based on the rbCOD/P ratio of 2.2 obtained from the batch tests. The 0.5 gP/d in phase I is considerably higher than the measured P release of 0.05 g/d indicating significant hindrance to PAO activity. However, in phase II, the addition of VFA enhanced P removal. In addition, during phases I and II ORP in the anaerobic zone were different at -130 mV versus -200 mV, respectively, reflecting the more fermentative environment in phase II.

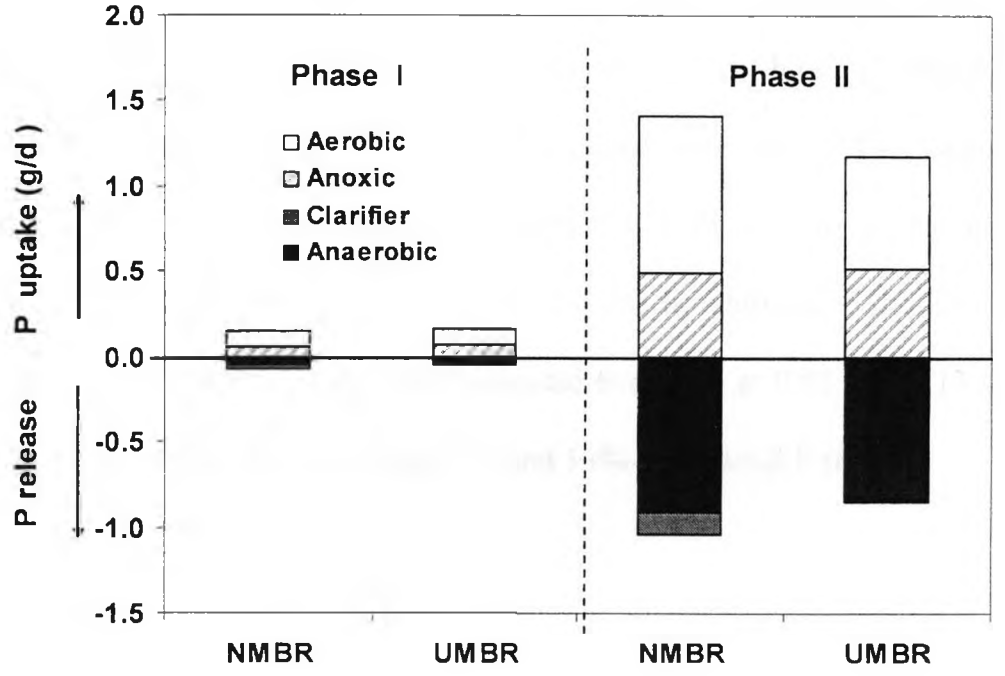
Figure 7.2b depicts the statistical distribution of effluent P after three turnovers of mean SRT, with 25-75 percentiles of 1.2-2 mg/L and 1.3-1.9 mg/L in the NMBR and UMBR, respectively. Statistical analysis on the effluent phosphates between two systems indicated that observed differences were statistically significant at 99% confidence level in phase II and relatively insignificant at 70% in the phase I. Phase II data demonstrates that when VFAs are not limiting, not only lower P was achievable in NMBR system as reflected by 25-75 percentiles of 0.4 to 0.6 mg/L compared to 0.6-1 mg/L in UMBR, but also more stable EBPR .


NMBR
ortho-P
ortho-P
Nitrates
VFA
Anaerobic
P release
Anoxic P
uptake
Aerobic P
uptake
PO4-P (mg/L)
VFA & NO3-N (mg/L)
Time (hr)
0
10
20
30
40
0
20
40
60
80
0
1
2
3
4
5
6
7

a)


UMBR
ortho-P
ortho-P
Nitrates
VFA
Anaerobic
P release
Anoxic P
uptake
Aerobic P
uptake
PO4-P (mg/L)
VFA & NO3-N (mg/L)
Time (hr)
0
10
20
30
40
0
20
40
60
80
0
1
2
3
4
5
6
7

b)



c)

Figure 7.3 (a) NMBR P profile during batch test (b) UMBR P profile during batch test (c) P mass release and uptake during phase I and II.

Figures 7.3a and b reflect the higher P release and uptake rates in the NMBR than the UMBR in phase II. P uptake/release ratios were 1.2 and 1.1 in NMBR and UMBR, respectively. $VFA_{consumption}/P_{release}$ ratio was 2.2-2.3 which is fairly coincident with the literature (Smolders et al., 1994). This test also clearly confirms anoxic denitrification by DPAO. The required NO_3-N per P removal was 0.59. The P release and uptake profiles facilitate estimation of DPAO content of total PAO using the method of Meinhold et al (1999). Initial aerobic and anoxic P uptake rate (q_{ao}, q_{ax}) in the NMBR is 12.6 and 4 mg P/gVSS/h vs 10.3 and 3.8 mg P/gVSS/h in the UMBR, respectively. According to Eq (3.1), the DPAO content of both systems was 40% of PAO.

Figure 7.3c presents the P release and uptake during both phases. Apparently, P uptake and release in phase I was similar in both systems; however, phase II shows that the NMBR achieved higher P release and uptake than the UMBR. Anoxic P uptake accounted for 37-44% of the total P uptake in both systems which agree with the estimated aforementioned DPAO content of 40%. In addition, it should be emphasized that intermediate clarifier positively impacted P release at 0.02 and 0.13 g/d in phase I and II, respectively, corresponding to 32 and 13% of the total P release.

7.3.5 P fractionation

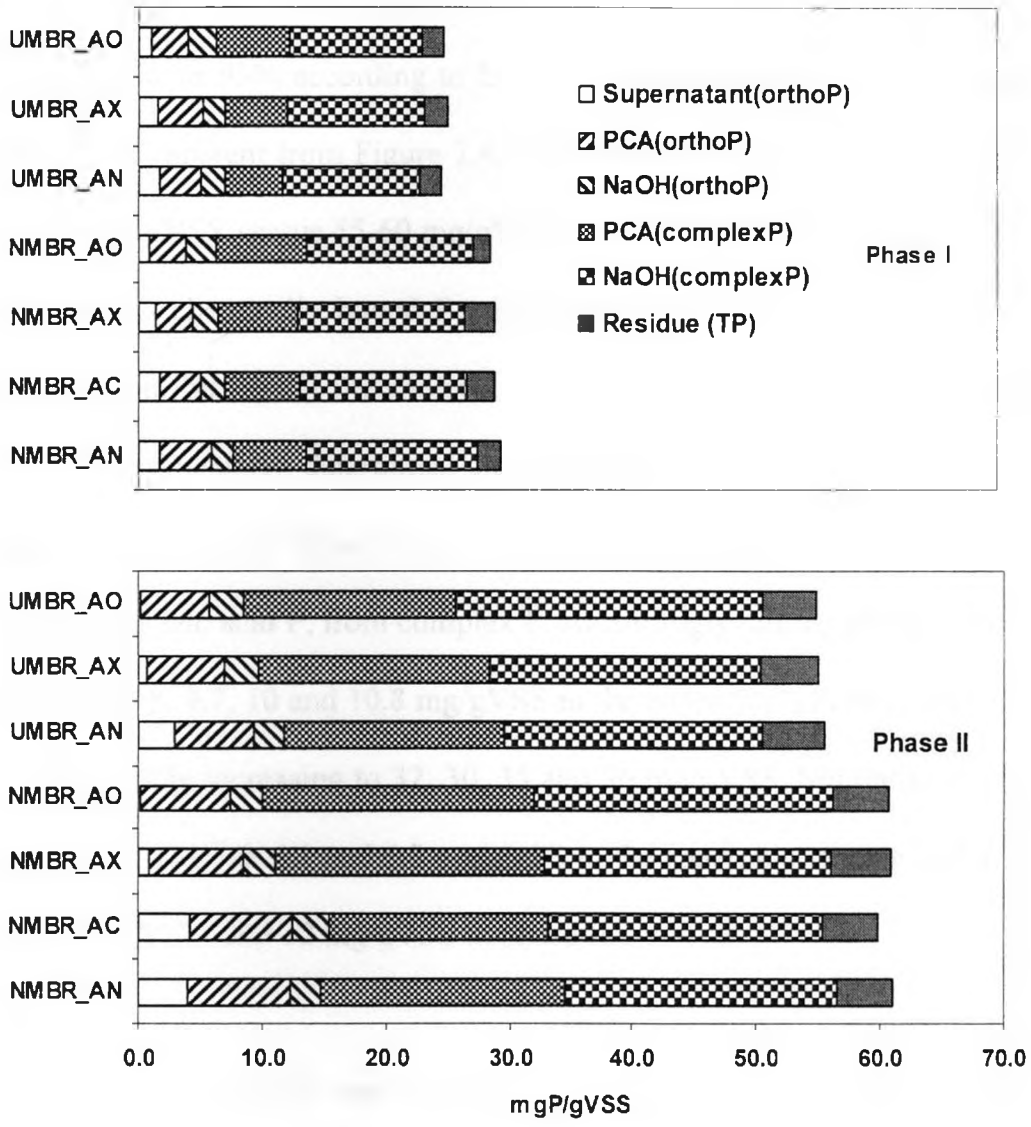


Figure 7.4 P fractionation during phase I and II. (AN-anaerobic, AC-clarifier, AX – anoxic, AO-aerobic).

Figure 7.4 compares the average phosphate fractionation in phases I and II of triplicates conducted in each phase after 4, 9, and 12 turnovers of the mean SRT. Total P recovery was over 95% according to Eq. (3.2) and residue TP was less than 10% of the initial TP. As apparent from Figure 7.4, the P content was lower in phase I than phase II i.e. 25-30 mg/gVSS versus 55-60 mg/gVSS. The ortho-P extracted from PCA and NaOH step represents chemically bound P with Mg or Ca while complex P is mostly poly-P originated from biological metabolism. Although complex P contains nucleic acid P it was not experimentally determined but assumed as 10 mg/g because it is relatively constant for sludge (de Haas et al., 2000). Thus, poly-P was reasonably estimated by subtracting nucleic acid P, from complex P. Accordingly, during phase I, stored poly-P in NMBR was 9.8, 9.7, 10 and 10.8 mg/gVSS in the anaerobic, clarifier, anoxic and aerobic tank, respectively increasing to 32, 30, 35 and 36 mg/gVSS. Similarly, in phase I poly-P in the UMBR was 5.9, 6.1 and 6.8 mg/gVSS in the anaerobic, anoxic and aerobic tank as compared to 29, 31 and 32 mg/gVSS in phase II.

Chemical bound P was 17-22% of the total P in phase I for both systems but dropped to 7% in phase II while poly-P accounted for 27-37% and 57-59% in phases I and II, respectively, reflecting the high PAO contribution in phase II. In addition, the poly-P increase in phase II substantiates that P deterioration in phase I was due to limited influent VFA rather than potentially GAO presence. The small poly-P in phase I also indicates that P removal in phase I occurred mainly through biomass synthesis and the observed TP content of 27-31 mg/gVSS in NMBR and UMBR closely matches the non-PAO P content of 30 mg/gVSS (Wentzel et al., 1990).

Scrutiny of the poly-P change in the anaerobic reactor or clarifier and anoxic reactor in phase II clearly indicates that DPAO contributed to P uptake and nitrate reduction, as evidenced by the poly-P increase in anoxic tank at 2-5 mg/gVSS. The NMBR achieved higher aerobic poly-P than UMBR at 36 versus 32 mg/gVSS in phase II, confirming that the lower effluent P in NMBR is due to EBPR.

7.4 Conclusions

Within the HRT and SRT investigated in this study of 6 hours and 10 days for the treatment of wastewater characterized by COD, TKN and P concentrations of 250, 29 and 3.5 mg/L, respectively in the low strength MWW and 440, 43 and 8.7 mg/L, respectively in the high strength MWW, the following conclusions can be drawn:

1. The NMBR outperformed the UMBR in nitrogen and phosphorus removal using both low and high strength MWW with effluent nitrate of 6.8-7.6 versus 8.5-8.6 mg/L and effluent ortho P of 0.5-1.5 versus 0.8-1.4 mg/L.
2. Anoxic P uptake in the NMBR and UMBR were close at 37-40% of total P uptake. The contribution of DPAO to denitrification was 22-26% in both systems. DPAO content in both systems was estimated at 40% of PAO from batch test.
3. A batch test on P release and uptake yielded P uptake/release ratios of 1.1-1.2 with $VFA_{consumption}/P_{release}$ ratio of 2.2-2.3 and $NO_3\text{-}N_{reduction}/P_{uptake}$ ratio of 0.59 in both systems.
4. Chemical P fractionation indicated that mostly P removal in both systems occurred through EBPR in phase II, although chemically bound P accounted for 7% of TP removal. Stored poly-P concentrations in the aerobic mixed liquor in phase II were 36 and 32 mg/gVSS for NMBR and UMBR. The relatively higher poly-P in the anoxic tank compared to anaerobic tank confirmed anoxic P uptake by DPAO.

7.5 References

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8.0 Comparative studies on membrane fouling between two membrane based BNR systems

8.1 Introduction

The widespread employment of membrane technology to wastewater treatment has assisted nutrient removal performance (Monti et al., 2006). Although MBR process is reliable in terms of perfect capture of solids in the system, membrane fouling has restricted its practical application and increased operational costs (Le-Clech et al, 2006). So far, extensive research on membrane fouling have unveiled the impact of many operational conditions such as HRT, SRT, dissolved oxygen (DO), temperature and aeration as well as sludge characteristics i.e. particle size, viscosity (Le-Clech et al, 2006).

Today, it is generally accepted that the main fouling factors are extracellular polymeric substances (EPS) and soluble microbial product (SMP) which are mostly by-products of microbial activity, particularly SMP which are often cited as the primary foulants. Nonetheless the published findings present various contradictory conclusions on foulants due to the complexity of biological treatment nature. Lesjean et al. (2004) addressed that SMP is a more important factor than EPS. Le-Clech et al. (2006) suggested that carbohydrate in SMP is related to fouling. On the contrary, Drews et al. (2007) observed that SMP was not a governing factor in membrane fouling at influent COD as high as 1200 mg/L. Lee et al. (2003) observed poor relationship between EPS

and fouling but it was suggested that EPS composition is a more important factor than EPS concentration.

Compared to various studies on MBR employing single reactor for biochemical oxygen demand removal and nitrification, the studies on membranes employed for BNR have been sparse (Lesjean et la., 2002; Mouthon-Bellow and Zhou, 2006; Fleischer et al., 2005; Kang et al., 2007). Membrane assisted BNR system is quite different from single stage system in terms of microbiological community and operational conditions such as recycle stream and required oxygen.

Recently, typical fouling studies with membrane coupled BNR has been reported (Drews et al., 2007; Ahmed et al., 2007; Chae et al., 2006; Lyko et al., 2008). Some of findings are in agreement with the observations from conventional MBR systems. For instance, the positive impact of longer SRT on fouling was observed by Ahmed et al. (2007), testing at 20, 40, 60 and 100 days with anoxic-aerobic SBR system. It is consistent with the finding of Liang et al. (2007) using single stage MBR system at the different SRTs of 10, 20 and 40 days. Chae et al. (2006) confirmed that HRT is inversely proportional to EPS and particle size. Lyko et al. (2008) observed that membrane performance of full scale system deteriorated as temperature dropped to as low as 4 °C.

However, several particular observations that distinguished MBR applications for BNR from single oxic MBR can be addressed. Ahmed et al. (2008) conducted an investigation of feed composition impact on biomass community and fouling in SBR

system, and concluded that the rapid fouling was observed with propionate or methanol based feed than with acetate or glucose dominant feed. However, relatively higher content of phosphorus accumulating organisms and improvement of phosphorus removal was observed with acetate or methanol dominant substrate than with glucose or propionate substrate, suggesting that a combined feed of acetate and methanol can be utilized in BNR-based MBR process as a proper external carbon source for assisting both fouling and EBPR performance.

Geilvoet et al. (2006) performed filtration test with denitrification and nitrification tank sludge samples and observed better filterability in the nitrification tank samples. According to the study by Rosenberger et al. (2006), an MBR system with post-denitrification presented better fouling trends than pre-denitrification, revealing that the reason was not because of denitrification scheme but because of present SMP.

Despite aforementioned studies there is still a paucity of knowledge on how EPS in BNR systems influence membrane fouling by operational conditions. Although MBR processes favor higher MLSS and longer SRT, these conditions are adverse for biological phosphorus removal because P removal efficiency improves at shorter SRT of the range of 7-16 days (Wentzel et al., 1997). In this study, to enhance biological phosphorus removal, two MBRs were operated at relatively lower HRT and SRT compared to other aforementioned studies i.e. 25 days (Lyko et al., 2008), 60 days (Chae et al., 2006), 20-100 days (Ahmed et al., 2007) and 30 days (Drews et al., 2007). Thus, this study primarily focuses on membrane fouling investigation from two MBR-based biological

nitrogen and phosphorus removal systems with typical operational conditions of BNR process.

The other major contribution of this work is a detailed study of the role of biofilm deposited on the membrane in denitrification and its impact factors such as TMP, COD reduction, biomass and DO. Whereas membrane biofilm studies focused on the fouling propensity in the MBR, the research on the beneficial role of the biofilm layer for nutrient removal has been rarely reported. According to Kang et al. (2007) a decline of nitrates between membrane tank and permeates took place due to denitrification in the film layer. However, the impact factors for the occurrence still need to be explored.

Therefore, the purpose of this study is two-fold; the investigation of the factors affecting membrane fouling and the elucidation of the role of membrane biofilm denitrification.

8.2 Materials and methods

8.2.1 System description

It is given in chapter 3.1.

8.2.2 System operation

It is given in chapter 3.3.3 and the study was conducted during a total of 120 d or 12 turnovers of the mean SRT approximately using settled MWW.

8.2.3 Analytical methods

It is given in 3.4.1 and 3.4.3 .

8.3. Results and discussions

Table 8.1 presents overall effluent quality from the two systems. Steady state data collected from 4 turnovers of the mean SRT indicates that average influent COD, nitrogen and phosphorus were 250, 29 and 3.5 mg/L, respectively. The average effluent COD, nitrogen and P concentrations from the NMBR were 13, 8 and 1.5 mg/L respectively as compared to 12, 9 and 1.6 mg/L respectively from the UMBR. The total suspended solids in the systems were 56 and 51 g for the NMBR and UMBR, respectively, and both membrane tank mixed liquor suspended solids concentrations were 2.5 g/L. Standard deviations of the data were obtained from testing for normal distribution of data using a statistical software (Minitab 13.1).

8.3.1. Fouling characteristics

Membrane permeate flux, permeability and fouling rate were calculated according to Eq. (8.1)-(8.3).

$$\text{Flux: } J_P \text{ (LMH or L/(m}^2\text{ h))} = \frac{Q_p}{A_m} \tag{8.1}$$

$$\text{Permeability: } Lp \text{ (LMH/kPa or L/(m}^2\text{ h kPa))} = \frac{J_p}{\Delta P} \tag{8.2}$$

$$\text{Fouling rate: } FR \text{ (LMH/kPa·h or L/(m}^2\text{ h}^2\text{ kPa))} = \frac{L_p}{\Delta t} \tag{8.3}$$

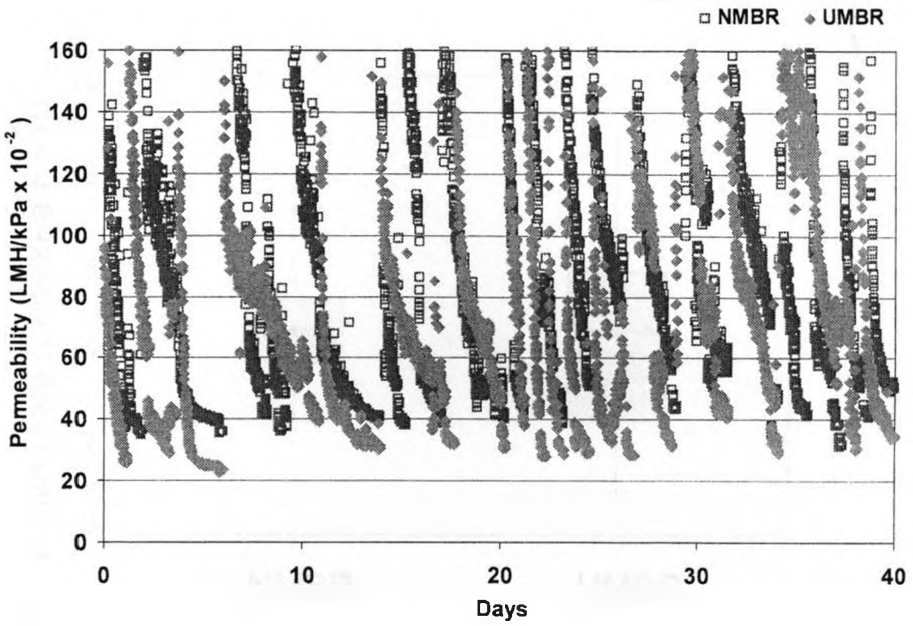
Q_P: Permeate flowrate (L/h) A_m: Membrane surface area (m^2)

ΔP: Transmembrane pressure (kPa) Δt : time (h)

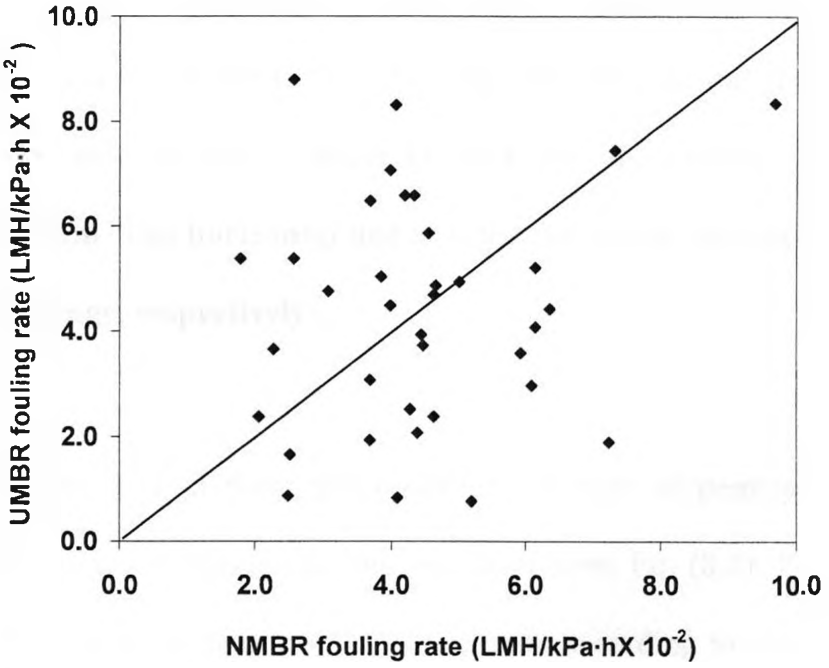
Table 8.1 Steady state influent and effluent quality obtained from two systems

(All units are in mg/L except where stated otherwise.)

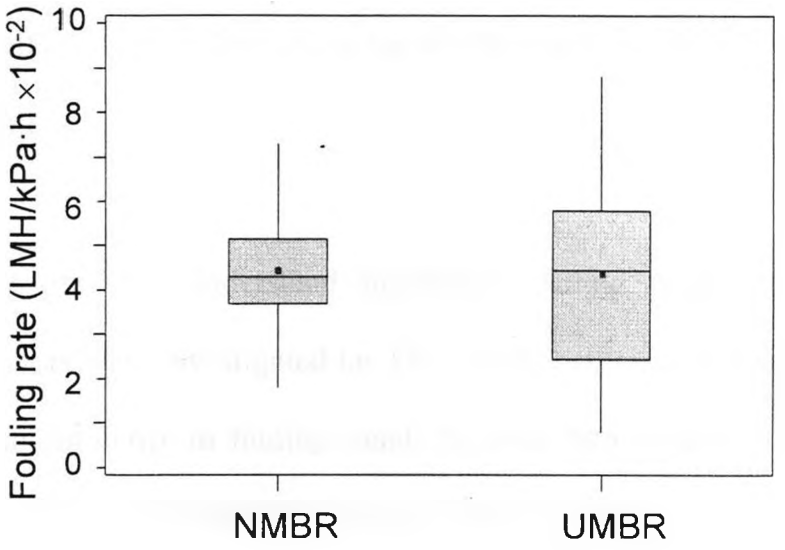
Parameter	Influent	NMBR_eff	UMBR_eff
TCOD	250 ± 100 (25)	-	-
SCOD	64 ± 30 (25)	13 ± 4 (22)	12 ± 5 (22)
TKN	29 ± 5 (20)	-	-
STKN	20 ± 4 (15)	0.6 ± 0.5 (13)	0.8 ± 0.7 (13)
NH_3-N	16 ± 3 (20)	0.2 ± 0.2 (25)	0.1 ± 0.1 (26)
NO_3-N	-	6.8 ± 2.1 (24)	8.5 ± 2 (20)
NO_2-N		0.1± 0.1 (21)	0.1 ± 0.1 (21)
TP	3.5 ± 1.5 (14)	-	-
PO_4-P	2.1 ± 0.7 (18)	1.5 ± 0.6 (23)	1.6 ±0.5 (23)
SS	120 ± 60 (23)	-	-
SVI (mL/g)	-	148 ± 56 (23)	135 ± 52 (23)
Operational conditions			
Parameter		NMBR	UMBR
System SS (g)		56 ± 10 (23)	51 ± 10 (23)
System VSS (g)		44 ± 7 (22)	40 ± 8 (21)
Membrane tank SS (g/L)		2.5±0.6 (24)	2.5 ± 0.7 (24)
Sludge yield, Y_{obs} (g VSS/g COD)		0.27 (R^2 =0.96)	0.28 (R^2 =0.97)
VSS/TSS		0.78	0.78
Aeration (L/min)		5	5
Membrane area (m^2)		0.31	0.31


NMBR
UMBR
Permeability (LMH/kPa x 10^{-2})
160
140
120
100
80
60
40
20
0
0
10
20
30
40
Days

a)


UMBR fouling rate (LMH/kPa·h X 10^{-2})
10.0
8.0
6.0
4.0
2.0
0.0
0.0
2.0
4.0
6.0
8.0
10.0
NMBR fouling rate (LMH/kPa·hX 10^{-2})

b)



c)

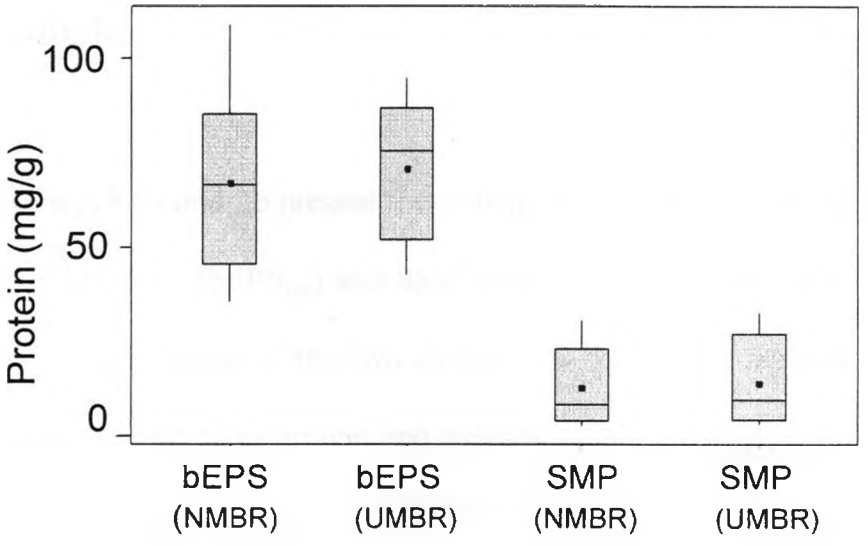
Figure 8.1 (a) Temporal variation of permeability during the run (b) comparison of fouling rate between two systems during the run and (c) statistical distribution of fouling rate in two systems (Percentiles are shown: Minimum, 25th, 75th and Maximum. The horizontal line and the dot inside the box represent the median and the average, respectively).

Figure 8.1a displays the temporal variation of permeability in both NMBR and UMBR systems during the run calculated from Eq. (8.2). Fouling rate was determined from the slope of permeability versus time according to Eq. (8.3) during the first 1.5-2 days. Figure 8.1b presents a comparison of the overall fouling rate between two systems and the relationship is dispersed. Statistical analysis using T-test shows that the statistical differences between two fouling rates are insignificant at the 95% confidence level. Figure 8.1c also statistically shows the similarity in fouling rates between two systems

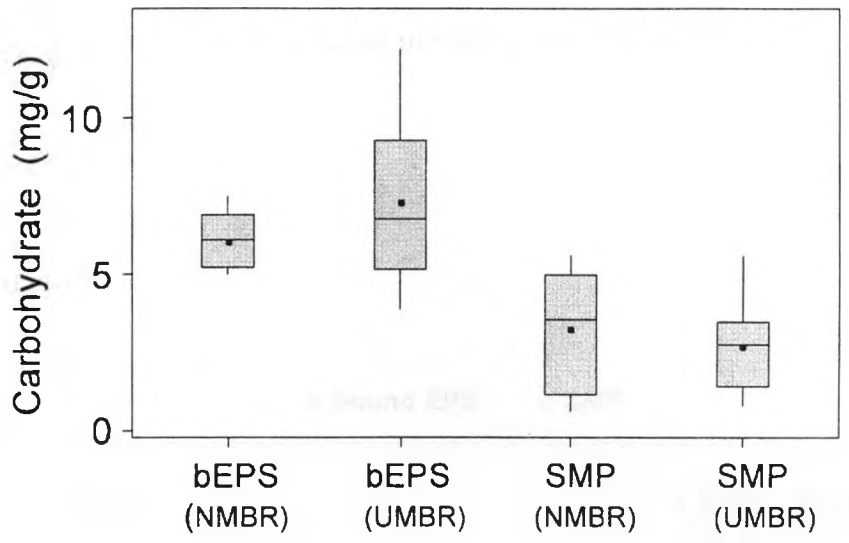
with average of 4.4×10^{-2} LMH/kPa·h even though UMBR varied more widely than NMBR. Statistically observed 25 percentile to 75 percentile fouling rates were between 3.8×10^{-2}-5.2×10^{-2} LMH/kPa·h for NMBR compared to 2.5×10^{-2}-5.9×10^{-2} LMH/kPa·h for UMBR.

In order to understand membrane fouling propensity several possible fouling indicators were investigated i.e. EPS, SMP, particle size distribution, and SVI. However, due to similarity in fouling trends between two systems, the combined data from two systems were evaluated for fouling characteristics.

EPS and SMP



a)

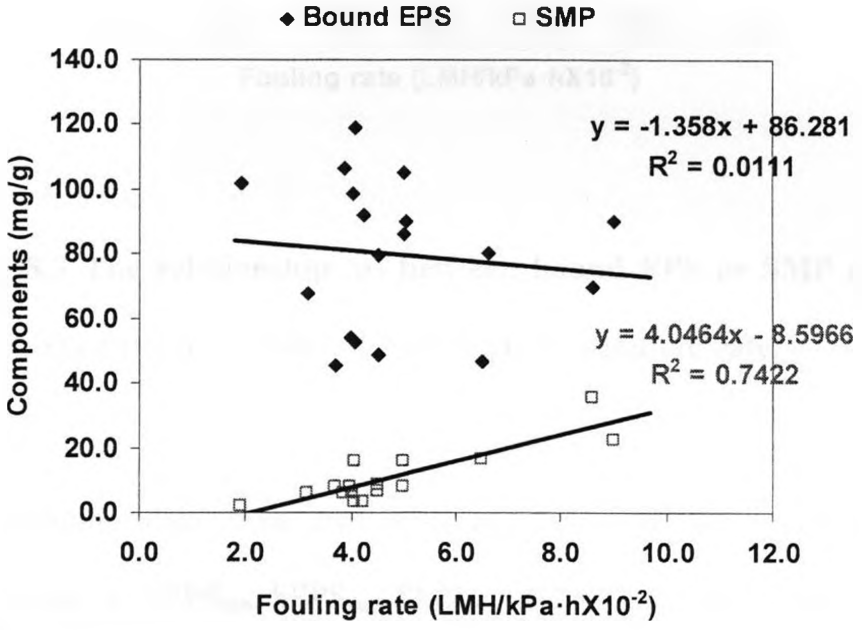


b)

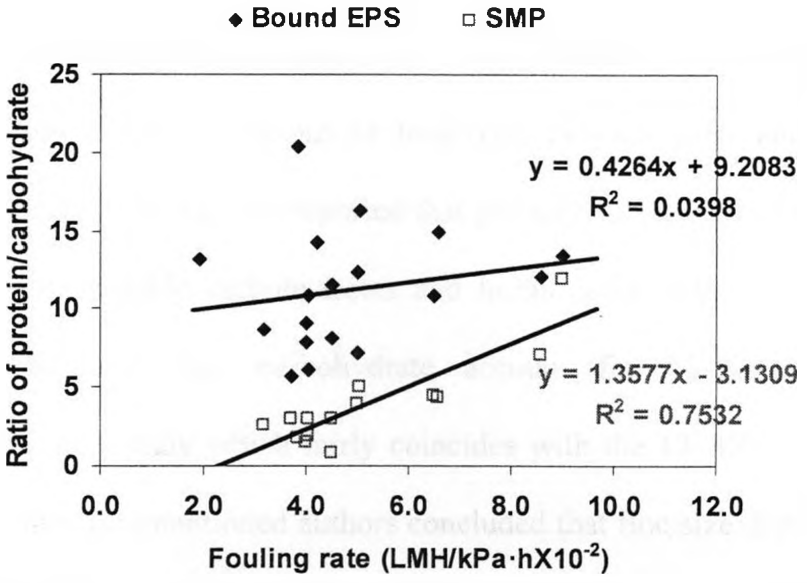
Figure 8.2 Statistical distribution of (a) protein and (b) carbohydrate in the mixed liquor of both systems (Percentiles are shown: Minimum, 25th, 75th and Maximum. The horizontal line and the dot inside the box represent the median and the average, respectively)

Figures 8.2a and 2b present the statistical distribution of bound EPS protein ($bEPS_{pro}$) and carbohydrate ($bEPS_{car}$) and SMP protein (SMP_{pro}) and carbohydrate (SMP_{pro}) in the aerobic mixed liquor of the two systems. In this study, the content of humic acid was negligible compared to protein and carbohydrate. Statistically, the 25th -75th percentile of the data of $bEPS_{pro}$ and $bEPS_{car}$ for NMBR were 46-84 and 5-6 mg/gVSS, respectively similar to the 57-85 and 5-8 mg/gVSS in UMBR, respectively. Similarly, the SMP_{pro} and SMP_{car} data for NMBR and UMBR ranged between 5-20 and 2-5 mg/gVSS or 10-35 and 2-6 mg/L respectively. The average $bEPS_{pro}$ and $bEPS_{car}$ for the NMBR and UMBR were

70 and 6 mg/gVSS respectively while SMP_{pro} and SMP_{car} are 13 and 4 mg/gVSS. Thus, apparently no statistical differences in $bEPS_{pro}$ and $bEPS_{car}$ were observed between the two systems similar to the trend in SMP_{pro} and SMP_{car}.



a)



b)

Figure 8.3 The relationship (a) between bound EPS or SMP and fouling rate (b) between the ratio of protein/carbohydrate and fouling rate.

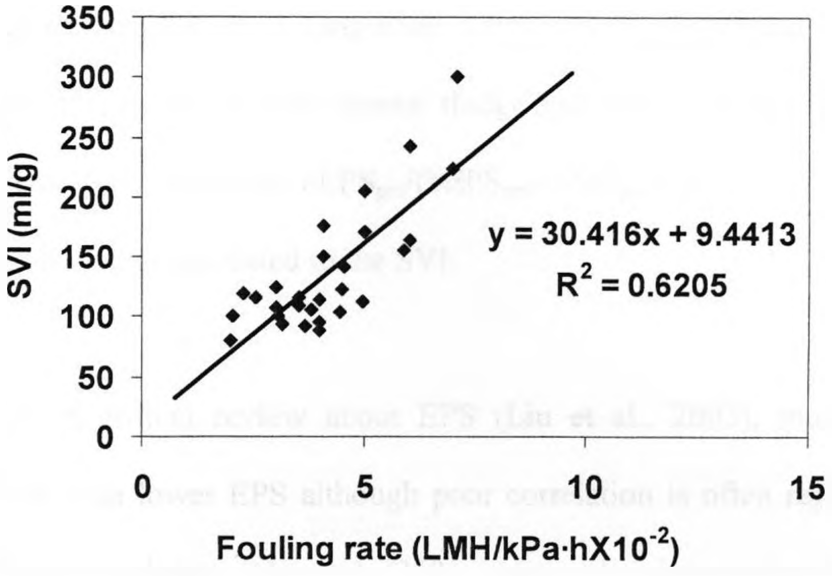
Combining data from two systems, the correlation between the four fouling components i.e. $bEPS_{pro}$, $bEPS_{car}$, SMP_{pro}, SMP_{car} and fouling rate was observed, but no relationship was found (Figure not included). However, Fig 8.3a clearly indicates that the fouling rate is more related to SMP than bEPS, consistent with the observations of Rosenberger and Kraume (2002) and Le-Clech et al. (2006).

Some researches emphasized that the composition of EPS/SMP affects fouling formation (Al-Halbouni et al., 2008). Figure 8.3b presents the relationship between fouling rate and the ratio of protein/carbohydrate in bound EPS and SMP. It appears that the fouling rate is fairly associated with the ratio of protein/carbohydrate in SMP. Thus, it

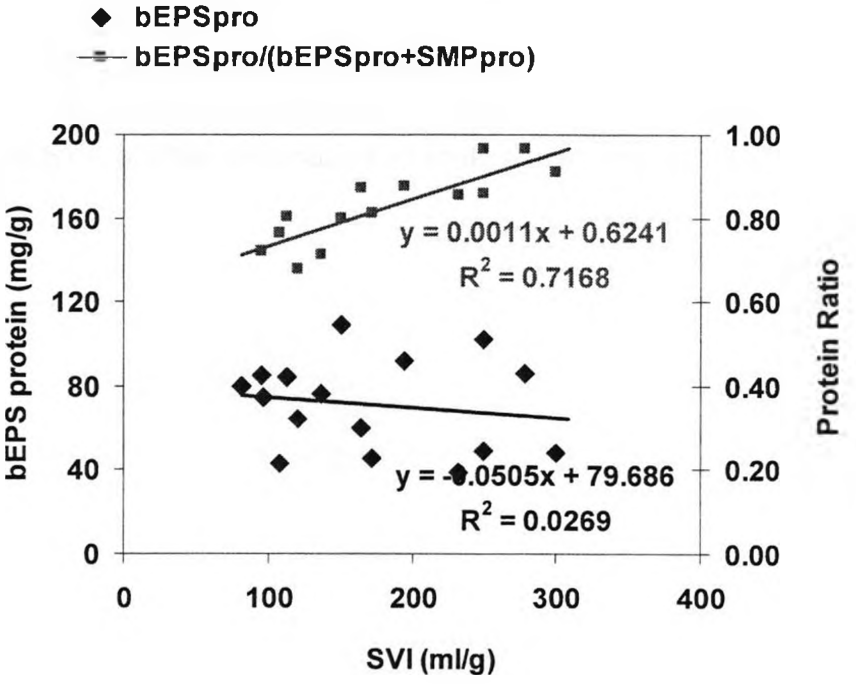
may indicate that protein is a controlling factor for membrane fouling in this study, contrary to the finding of Geng et al. (2007), which is very similar to current study in terms of operational conditions i.e feed type, characteristics and system configurations (HRT 7 hr, SRT 12 d), who reported that primary substances observed on the membrane surface were soluble carbohydrates and humic acids rather than proteins. It must be asserted however that carbohydrate account for 23-50% of the SMP in the aforementioned study which fairly coincides with the 13–43% content in this study. In addition, the aforementioned authors concluded that floc size distribution and the amount of soluble EPS (SMP) are the most important fouling properties while the bound EPS and zeta potential and relative hydrophobicity were not closely associated with membrane fouling. The observed floc size, bound EPS, bound protein, soluble carbohydrate and protein were 140-150 μm, 1-10 mg/gVSS, 25-35 mg/gVSS, 8-20 mg/L and 4-7 mg/L, respectively.

From Fig 8.3a, it can be suggested that SMP is more responsible for membrane fouling than EPS. Moreover, Fig 8.3b presents that the main foulant in SMP is protein rather than carbohydrate over a range of protein/carbohydrate ratio of 3-12. Metzger et al. (2007) assessed the effect of different filtration modes using a combination of relaxation and backwashing with hydrophilic polymeric membranes and observed that proteins are more tightly and irreversibly attached to the membrane than carbohydrates. This may explain why the ratio of protein in SMP is closely associated to the fouling rate.

Sludge volume index and particle size distribution



a)

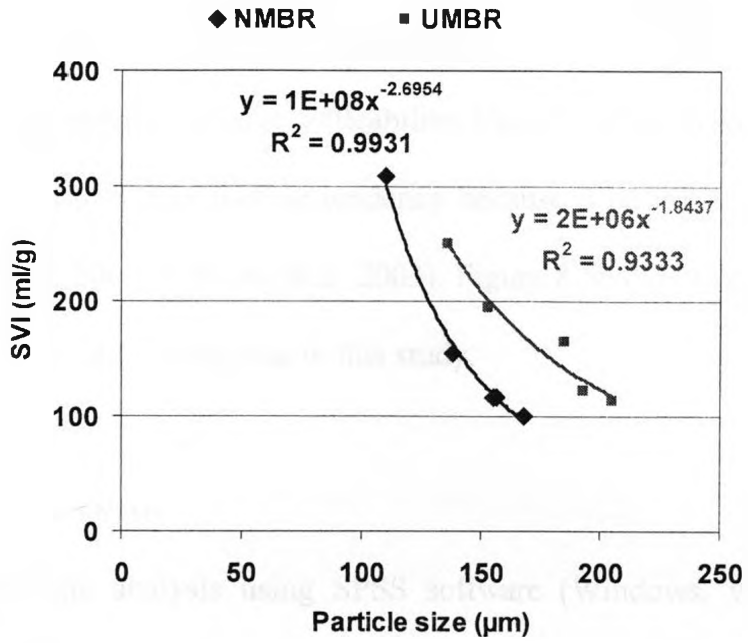


b)

Figure 8.4 The relationship (a) between SVI and fouling rate (b) between SVI and bound protein or the ratio of $bEPS_{pro}/(bEPS_{pro}+SMP_{pro})$.

During the study, SVI varied widely from 80 to 300 ml/g in the two systems. Figure 8.4a displays that SVI increased with increasing fouling rate. This may confirm the findings of Chang et al. (Chang et al., 1999) who observed that higher fouling correlates to higher SVI by testing with normal sludge and bulking sludge. Figure 8.4b also presents fair relationship between $bEPS_{pro}/(bEPS_{pro}+SMP_{pro})$ and SVI whereas the amount of $bEPS_{pro}$ is clearly unrelated to the SVI.

From a critical review about EPS (Liu et al., 2003), mostly sludge settleability improves with lower EPS although poor correlation is often reported depending on the operational conditions. Ng et al. (2005) observed a clear reciprocal relationship between EPS and SVI. Moreover, Martinez et al. (2004) observed that higher bound protein increased SVI compared to little impact of carbohydrate and lipid. From this aspect, Fig 8.4b may provide new information on this issue, in that bound protein in itself is not related to SVI, but the distribution of proteins between the solids and liquid impacts SVI.



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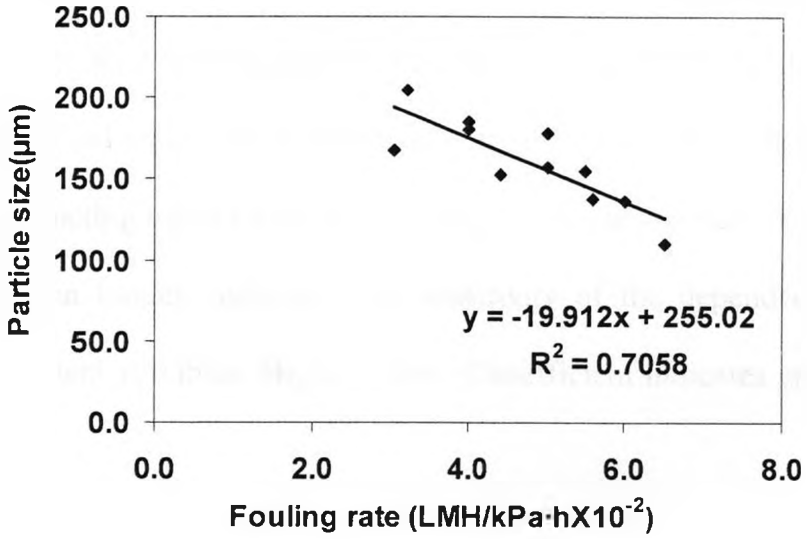


b)

Figure 8.5 The relationship (a) between SVI and particle size (b) between fouling rate and particle size.

Figure 8.5a indicates the relationship between SVI and particle size from the two systems. Excellent fit was established between two parameters. It confirms that bigger floc size improves sludge settleability. Usually, it has been accepted that smaller floc size is related to higher fouling tendency because it increase pore blocking resistance (Geng and Hall, 2007; Lim and Bai, 2003). Figure 8.5b clearly confirms that indeed lower floc size increased fouling rate in this study.

Statistic analysis

Statistic analysis using SPSS software (Windows, version 14) was conducted to investigate the impact of several fouling parameters on membrane fouling. Multiple regression analysis assesses how the dependant variables affect the independent variable. However, all the independent variables are expressed in different units necessitating standardized regression coefficients of the variables. Thus, the beta coefficient, calculated by subtracting mean value and dividing by the standard deviation, is used to interpret the regression model, indicating the sensitivity of the dependent variable to each of the independent variables. Higher value of coefficient indicates greater impact on dependant variable.

This analysis conducted with the dependant variable i.e. fouling rate and the four chosen independent variables including bEPS (mg/g), SMP (mg/g), $bEPS_{pro}/(bEPS_{pro}+SMP_{pro})$ and particle size (μm), characterized a statistical relationship between fouling rate and the four components in Eq. (8.4) at R^2 of 0.85 and 95% confidence level.

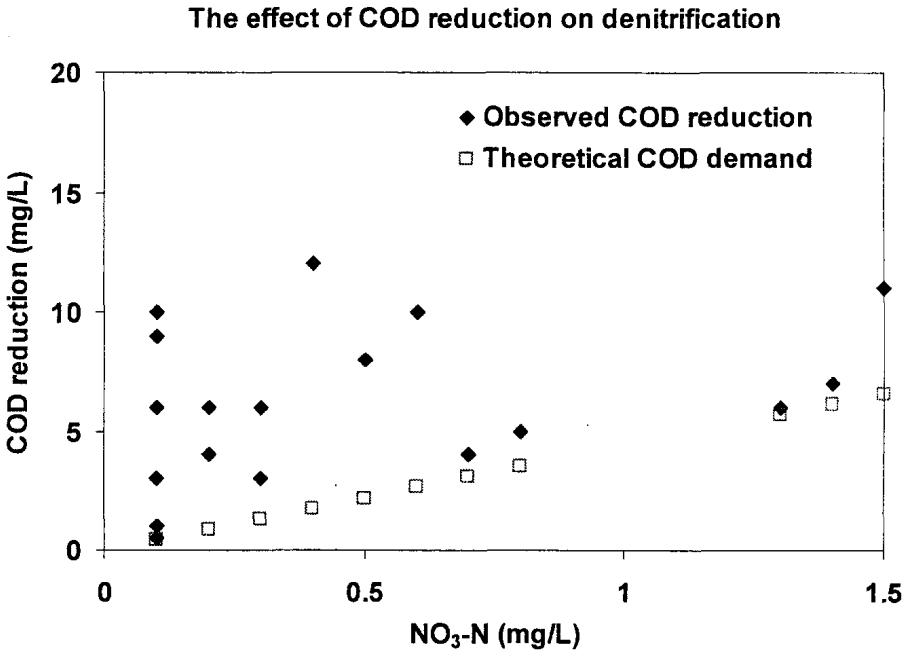
Fouling rate=4.6 + 0.11 SMP - 0.02 particle size + 2.53 protein ratio – 0.0004 bEPS (8.4)

The beta coefficients are -0.01, 0.15, -0.34 and 0.48 for bEPS, protein ratio, particle size and SMP, respectively with positive values indicating positive relationship and negative values indicate inverse relationship with fouling rate. According to the beta coefficients, the effect of SMP on membrane fouling was greater than the other three parameters. Particle size and protein ratio also affected fouling rate albeit more significantly by the former than the latter while bound EPS had negligible influence. Hence, this statistical approach confirms that SMP is the primary fouling factor although floc size and protein ratio also increased fouling.

8.3.2. Membrane fouling associated with denitrification

Denitrification in the biofilm is very often observed in large flocs or fixed film systems as DO profile drops through the film layer. However, rarely has it been reported in MBR systems and a single paper addressed the occurrence. So far, studies on MBR denitrification tended to focus on simultaneous nitrification and denitrification by controlling dissolved oxygen and increasing floc size (Holakoo et al., 2007). However, the current study observed nitrate reduction in the membrane biofilm similar to the findings of Kang et al. (2007), who revealed that the type of biomass in suspension and biofilm is identical, and that organic compounds less than 1 kDa in size are utilized for

denitrification. However, it should be emphasized that the aforementioned study is quite different from this present study in terms of SRT, MLSS and aeration protocol. They operated the system at a SRT of 60 days and MLSS of 7 g/L with intermittent aeration which is 6 times longer SRT and 2.8 times higher MLSS than this study. However, despite the difference in operating conditions the reduction of nitrates across the membrane is 1.5 mg/L similar to the observation in this study.



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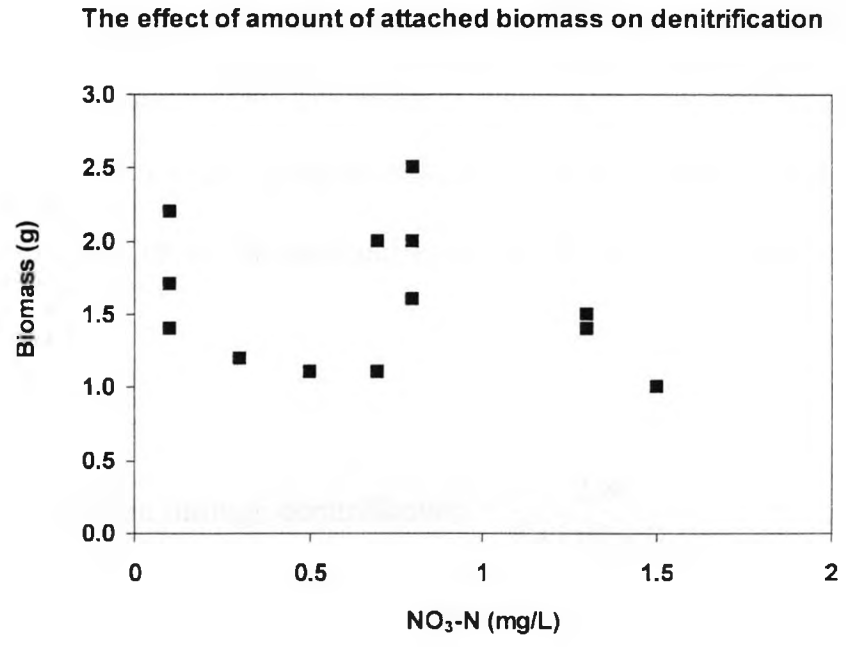
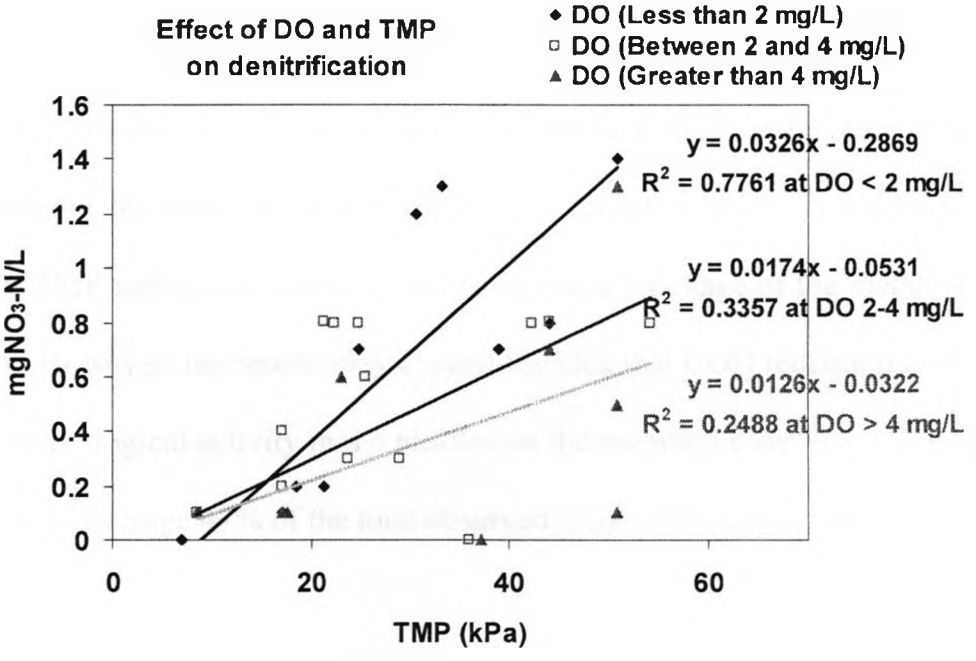


b)



c)

Figure 8.6 Denitrification impact factors: (a) COD reduction (b) attached biomass (c) DO and TMP.

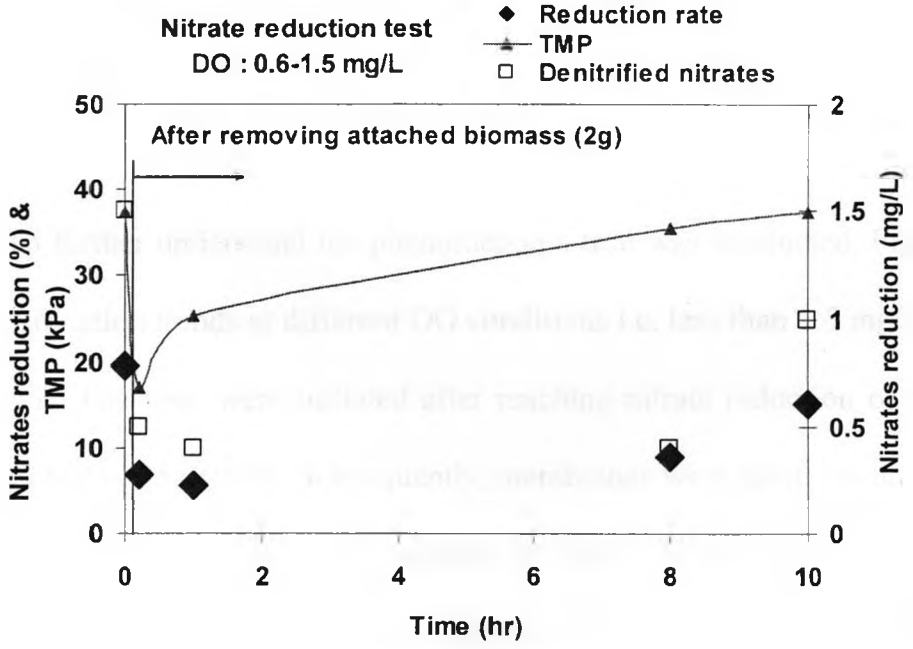
During the run, the observed nitrate reduction was 1 mg/L on average corresponding 10-15% of the nitrate in the membrane tank. Figure 8.6a displays how the amount of COD reduction (based on SCOD) between membrane tank and permeates affects the nitrate reduction. The graph includes theoretical COD demand for denitrified nitrates, calculated using Eq. (8.5) (Metcalf and Eddy, 2003) and the biomass yield (Y_{obs}) from Table 8.1.

$$\text{COD consumption through denitrification} = \frac{2.86}{1-1.42\times Y_{obs}} \qquad (8.5)$$

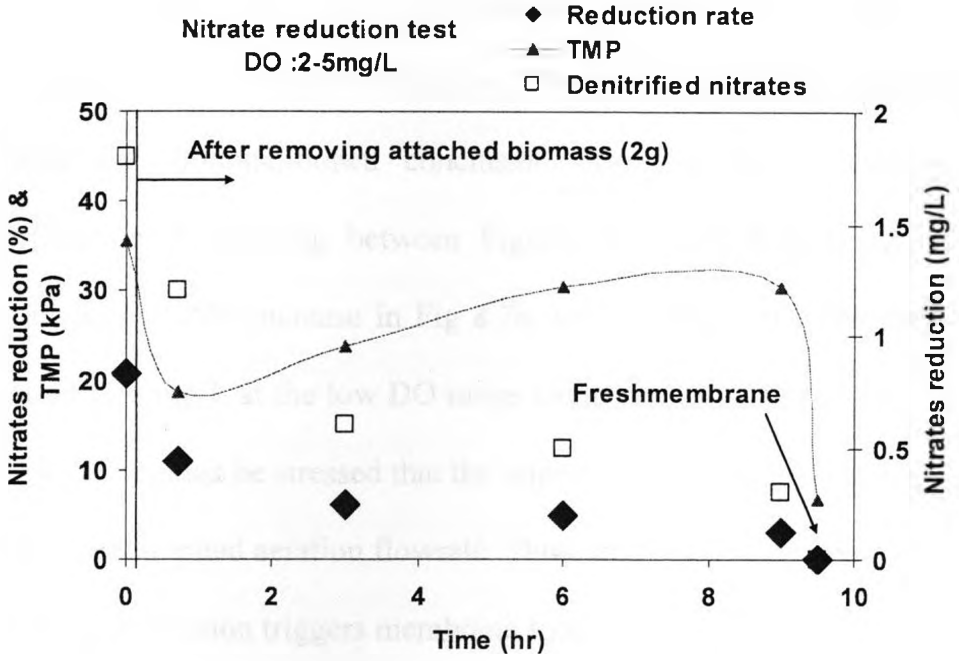
It appears that not only did the observed COD reduction varied widely by as much as 12 mg/L but also it was not related to nitrate reduction. However, apparently theoretical COD consumption was lower than observed COD reduction, indicating COD is not limiting factor for the observed denitrification. Normally it has been agreed that COD reduction (or SMP reduction) is mostly due to physical blockage of the membrane pores or cake layer. However, the results may expand the idea that COD reduction is also partly resulting from biological activity in the biofilm on the membrane surface. In this study, it accounted for on average 47% of the total observed COD reduction across the membrane.

Figure 8.6b presents the relationship between the amount of attached biomass on the membranes and denitrification. The amount of biomass was 1-2.5 g but there is no direct relationship between two parameters, indicating that denitrification was not limited by the observed amount of biomass.

Figure 8.6c depicts the relationship between denitrification and TMP with combined data from the two systems because this occurrence is dependant on biofilm deposited on the membrane surface. At first glance, it spreads out with wide range of TMP. Thus, it was sorted according to the ambient DO. It should be emphasized that DO in the aerated MBR was not manipulated and aeration was constantly supplied at 5 L/min. In the case of less than 2 mg O_2/L, higher denitrification correlated with higher TMP with regression coefficient (R^2) of 0.77. However, at more than 2 mg O_2/L, nitrates reduction was poorly related to the TMP change with R^2 of 0.24. This trend clearly indicates that DO is a governing factor impacting denitrification, which in turn increases membrane fouling and TMP at constant flux.



a)



b)

Figure 8.7 The nitrates reduction test on different DO conditions: (a) 0.6-1.5 mg/L (b) 2-5 mg/L.

To further understand the phenomenon a trial was conducted. Figure 8.7 depicts two denitrification trends at different DO conditions i.e. less than 1.5 mg/L and the other at 2-5 mg/L. The tests were initiated after reaching nitrate reduction of around 1.5 mg/L at high TMP of 35-40 kPa. Subsequently, membranes were taken out and washed with clean water to remove the attached biomass on the membrane surface, followed by placing back to the tank for additional filtration. Nitrate reduction and TMP were regularly monitored over the time. The results suggest interesting information on the impact of denitrification within biofilm on TMP. Initial nitrate reduction rate prior to removing biomass layer was 20% of the ambient nitrate concentration in the MBR tank. But after

cleaning, it dropped to below 10%. However, comparing two graphs by DO conditions, the reduction rate increased with raising TMP only at lower DO presented in Fig 8.7a. It confirms the aforementioned conclusion that low DO is essential for enhanced denitrification. Comparing between Figures 8.7a and 8.7b in terms of fouling and denitrification, TMP increase in Fig 8.7a was 20 kPa as the observed nitrate reduction increased to 1 mg/L at the low DO range compared to 12 kPa and 0.5 mg/L respectively in Fig 8.7b. It must be stressed that the impact of air scouring is same in both case due to the identical supplied aeration flowrate. Thus, this observation may verify that membrane biofilm denitrification triggers membrane fouling.

Generally, it has been accepted that membrane fouling occurs through three steps i.e. adsorption, pore clogging, cake formation (Liao et al., 2004). Although the biomass layer was removed, TMP did not drop below 15 kPa, exhibiting the fouling due to SMP pore clogging. Recent studies regarding denitrification and membrane fouling addressed that denitrification causes fouling deterioration. Ma et al. (2006) observed that anoxic-aerobic condition showed higher fouling rate than aerobic conditions owing to smaller floc size. Jang et al. (2006) stated that worse fouling was observed in denitrification than in nitrification due to increased SMP and decreased floc size after denitrification. Drews et al. (2007) also observed that SMP increased with decreasing nitrates in post-denitrification BNR system. Thus, it may conclude that biofilm denitrification increases membrane fouling.

8.4 Summary & Conclusion

Within the HRT and SRT investigated in this study of 6 hours and 10 days for the treatment of wastewater characterized by COD, TKN and P concentrations of 250, 29 and 3.5 mg/L, respectively, the following conclusions can be drawn.

1. There is no significant difference between two membrane-BNR systems in terms of membrane fouling with average fouling rate 4.4×10^{-2} LMH/kPa·h in both.
2. Membrane fouling was relatively more related to SMP than bound EPS. Protein/carbohydrate ratio in SMP was associated with fouling rate.
3. SVI was fairly related to the ratio of bound protein/total protein compared to poor relationship with the amount of bound protein. SVI and particle size showed excellent relationship. It was also confirmed that particle size was inversely proportional to fouling rate.
4. A statistical analysis using multiple regression characterized the significance of four fouling parameters from the greatest to the lowest i.e. SMP, particle size, the ratio of bound protein/total protein and bound EPS.
5. Nitrate reduction occurred in the biofilm of membrane at an average 1 mgN/L. Primary factor impacting denitrification was ambient DO rather than amount of attached biomass and COD reduction. In addition, it appears that denitrification triggered membrane fouling.

8.5 References

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9.0 Membrane fouling propensity of denitrifying organisms

9.1 Introduction

It has been widely established that EPS and SMP are primary membrane foulants. Although membrane application mainly focused on CAS in the last decade, membranes have been recently applied to BNR systems (Lesjean et al., 2006; Fleischer et al., 2005; Monti et al., 2006). The fouling propensity in BNR systems is different from single aerobic reactor systems because of microbial diversity. Literature on the membrane fouling during denitrification is rather sparse. Geilvoet et al. (2006) concluded that the filterability of nitrifying sludges is better than denitrifiying sludges. Ma et al. (2006) stated that the sequence of anoxic and aerobic conditions increases fouling relative to single aerobic conditions because of smaller flocs. Jang et al. (2006) attributed the increased fouling in denitrification relative to nitrification to SMP increase and floc size reduction. Drews et al. (2007) reported that denitrification increased fouling due to SMP increase. Kim and Nakhla (2008) also observed that denitrification in membrane biofilms increased trans-membrane pressure.

All aforementioned studies have employed ordinary heterotrophic organisms (OHO) for denitrification. In BNR systems, denitrification can occur through OHO and DPAO. While OHO require external carbon for nitrate reduction, DPAO utilize intracellular carbon to remove P and nitrate simultaneously (Kim and Nakhla, 2008).

Thus, denitrification by DPAO is favourable for the treatment of low C/N wastewater. Since recently enhanced biological phosphorous removal (EBPR) processes have employed membranes (Drews et al., 2007; Monti et al., 2006), to the extent of our knowledge there is no study on membrane fouling propensity that differentiated between the two different denitrifying microbial populations. Thus, the main focus of this study is to compare OHO and DPAO denitrification in terms of fouling characteristics using BNR sludge and conventional activated sludge (CAS).

9.2. Materials and Methods

9.2.1 Experimental design

Batch tests were conducted with 3 liters of BNR sludge collected from aeration tank of a lab-scale EBPR system operating for more than 1.5 years on degritted municipal wastewater from the Adelaide wastewater plant (Kim and Nakhla, 2008) and CAS from Adelaide WWTP (London, Canada) The mixed liquor was centrifuged at 3000×*g* (Beckman Coulter, Allegra 6 centrifuger, USA) for 5 min with the supernatant replaced with nutrient-rich distilled water. After N_2 sparging to remove oxygen, 50-60 mg/L acetic acid based on the VFA/P release ratio of 2 (Smolders et al., 1994) was spiked to enrich internal cellular carbon storage in the PAO and pH was adjusted to 7.1±0.1. Samples were collected every 15 min during the first 3 h for monitoring VFA and P concentration. As P release was completed, 1L of mixed liquor was splitt in two bottles: bottle A for OHO and bottle B for DPAO denitrification. Subsequently, excess nitrates at a concentration of 20-22 mg NO_3-N/L were added into both bottles while 30 mg/L of

acetic acid was spiked in bottle A for OHO denitrification. Samples from the two bottles were collected every 15 min for monitoring P and nitrate reduction. CAS sludge samples were prepared according to the same procedure as the BNR sludge except for the P release step, which was omitted. Tests were repeated four times over a period of 8 weeks. While bottle B represented denitrification by DPAOs using intracellular carbon, denitrification in bottle A was due to both DPAO and OHO utilising the external carbon added. As elaborated upon, this resulted in a very rapid denitrification rate, with complete denitrification achieved in bottle A within 2 hours as compared to 5 hours in bottle B. Thus, to evaluate the contribution of DPAOs in the mixed sample (bottle A), following the exhaustion of the added carbon, a second nitrate spike at a dose of 10 mg NO_3-N/L, was performed, referred to henceforth as DPAO in heterotrophic test, or DPAO-H. This also prolonged the test duration in bottle A to match bottle B, in effect minimizing biases due to different endogenous respiration rates between the two tests. Samples of BNR sludges at the end of the P release stage, at the end of the OHO denitrification in bottle A, at the end of the second spike in bottle A, and at the end of the DAPO denitrification in bottle B, as well as the initial and final (after denitrification) CAS samples were collected for MFI determination, and foulants characterization i.e. SMP and BEPS carbohydrates and proteins.

9.2.2 Analytical methods

Batch filtration tests were conducted to measure the Modified Fouling Index (MFI) (Schippers and Verdouw, 1980) using a stirred batch cell (Amicon ,USA) to

measure the permeate volume with an ultrafiltration (UF) membrane (nominal molecular weight cut-off point of 300 kDa) under constant pressure. Two samples were applied to fractionate the membrane foulants into the soluble and suspended solids (SS) components. Soluble sample were prepared after centrifuging the mixed liquor at 12,000 g for 15 min and filtering the supernatant through a 0.45 μm filter paper. 300 ml of mixed liquor and soluble sample were filtered through UF membranes under constant pressure of 10 psi (69 kPa) with monitoring the flow rate as a function of time. A plot of the t/V versus V graph (t in seconds and V in liters) was constructed where the slope ($\tan\alpha$) of the straight part of the curve was calculated. MFI is found from the following Eq (9.1) and is corrected for the pressure and temperature of 210 kPa and 20° C, respectively.

$$MFI = \frac{\eta_{20}}{\eta} . \frac{\Delta P}{210} . \tan\alpha \qquad (9.1)$$

Where: η_{20} = viscosity at 20° C, η = viscosity at the water temperature, ΔP = pressure applied in kPa,

The MFI for the SS component (MFIss) is calculated by subtraction of the soluble component from the mixed liquor, denoting MFIsol.

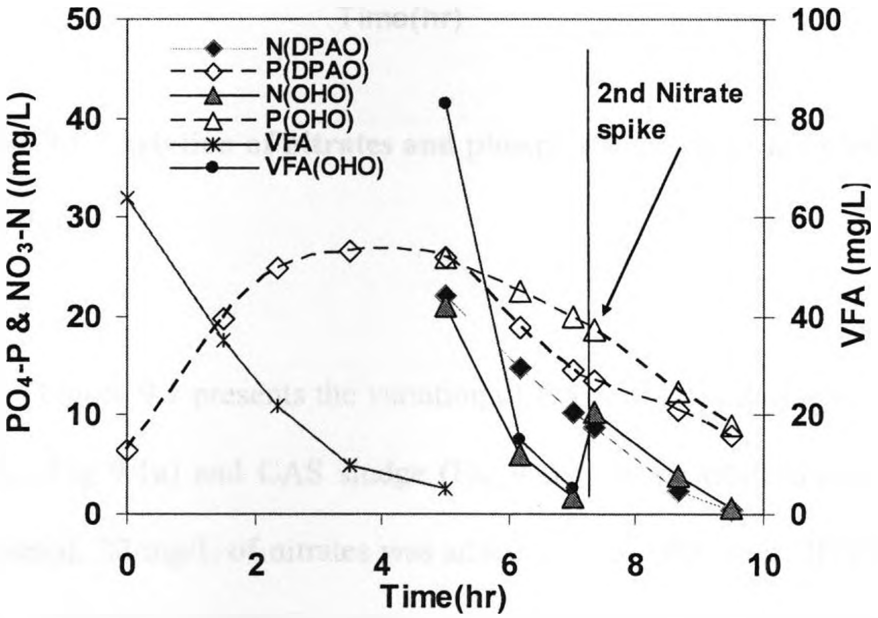
A hydrocarbon-hexane extraction was used to measure the hydrophobicity in the sludge, EPS, and SMP as protein and carbohydrate. The procedure is as follows: a 50 ml sample was agitated for 10 min, with 50 ml n-hexane, in a separating funnel. After 10 min, when the phases were completely separated, of the 50-ml aqueous phase, only 40 mls of the aqueous solution were transferred to glassware prior to protein and carbohydrate analysis. The relative hydrophobicity is expressed in Eq (9.2) as the ratio of

the aqueous phase concentration after emulsification (S_e) to that of the initial sample concentration (S_i):

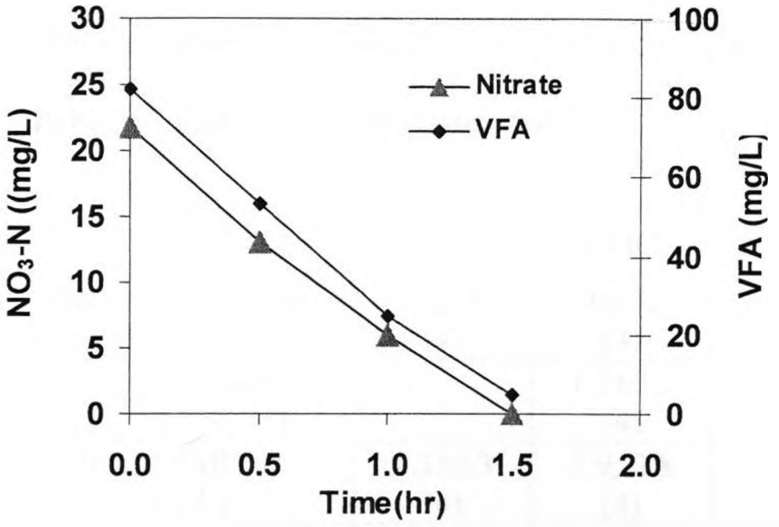
Relative hydrophobicity (%) = 100 (1- Se/Si) (9.2)

9.3. Results and discussions

9.3.1 batch test



a)



b)

Figure 9.1 Variation of nitrates and phosphates during batch test (a) BNR sludge (b) CAS sludge

Figure 9.1 presents the variation of P and nitrates during the batch test with BNR sludge (Fig 9.1a) and CAS sludge (Fig 9.1b). In the BNR sludge, after P release was completed, 22 mg/L of nitrates was added in both OHO and DPAO bottles and external carbon at 80 mgCOD/L, as acetic acid, were added to the OHO bottle Nitrates in OHO were rapidly reduced within 2 hrs similar to CAS denitrification. Following the second nitrate spike in the OHO batch, denitrification continued but at relatively slow rate due to rbCOD completion.

Compared to the denitrification using external carbon in the OHO batch, DPAO denitrification was slower because it utilized internal cellular carbon i.e. poly-hydroxylbutyrate (PHB). P uptake occurred simultaneously with denitrification in both the OHO and DPAO bottles. P removed was 6 and 12 mg/L in OHO and DPAO bottle,

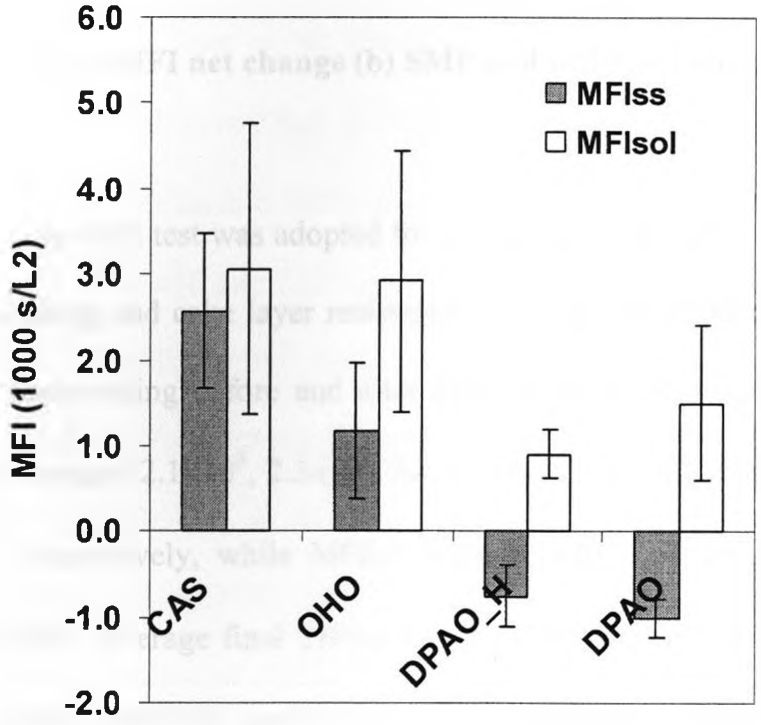
respectively. However, after the second nitrate spike in OHO bottle, DPAO contributed more to denitrification, as evidenced by a P drop from 20 to 7 mg/L.

Table 9.1 Summary of the batch test

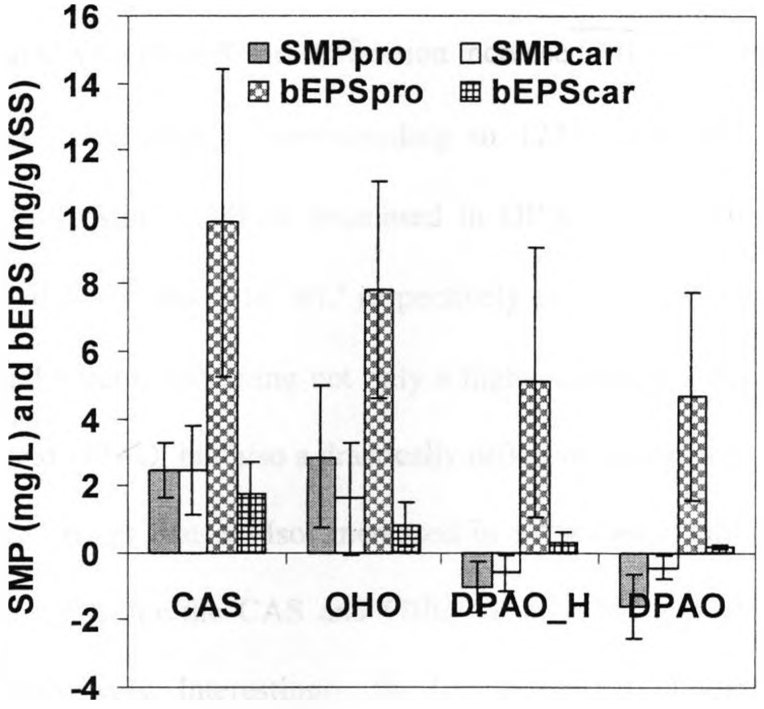
	CAS	OHO	DPAO_H	DPAO
Denitrification rate (mgN/gVSS hr)	6±2.5 (4)	4±0.2 (4)	0.9±0.2 (2)	1.5±0.1 (4)
P uptake rate (mgP/gVSS hr)	-	1.2±0.3 (4)	1.8±0.2 (2)	1.9±0.2 (4)
Initial SMPcar (mg/L)	2.3±0.3 (4)	1.9±0.8 (4)	1.7±0.5 (2)	1.3±0.5 (4)
Initial SMPpro (mg/L)	14±3 (4)	19±4 (4)	21±6 (2)	18±6 (4)
Initial bEPScar (mg/gVSS)	4±1 (4)	3±1 (4)	3±1 (2)	2.5±1 (4)
Initial bEPSpro (mg/gVSS)	43±4 (4)	35±9 (4)	28±2 (2)	29±5 (4)
Final SMPcar (mg/L)	5±1 (4)	3.5±2 (4)	1±0.1 (2)	1±0.4 (4)
Final SMPpro (mg/L)	17±2 (4)	22±3 (4)	20±5 (2)	16±5 (4)
Final bEPScar (mg/gVSS)	6±1 (4)	4±2 (4)	4±1 (2)	3±1 (4)
Final bEPSpro (mg/gVSS)	53±3 (4)	43±10 (4)	33±2 (2)	34±3 (4)
Initial MFIss (10^3 s/L^2)	2.1±0.1 (4)	2.3±1 (4)	3±1.2 (2)	2.2±1.2 (4)
Initial MFIsol (10^3 s/L^2)	2.1±1.2 (4)	2.3±0.7 (4)	1.9±0.8 (2)	2±0.5 (4)
Final MFIss (10^3 s/L^2)	4.7±0.8 (4)	3.5±1.4 (4)	2.2±0.8 (2)	1.2±1.0 (4)
Final MFIsol (10^3 s/L^2)	5.2±1.3 (4)	5.2±2.1 (4)	2.8±0.5 (2)	3.5±1.1 (4)
MLVSS (g/L)	2.4	2.2	2.2	2.2
P content in sludge (% of VSS)	2	5.5	5.5	5.5
Sludge yield (Y_{obs})	0.56	0.25	0.25	0.25

Table 9.1 summarizes the test results. Standard deviations of the data were obtained from testing for normal distribution of data using a statistical software (Minitab 13.1). Denitrification rate was 6, 4, 0.9, 1.5 mgN/gVSS hr for the CAS, OHO, DPAO-H and DPAO respectively. P removal rate was relatively higher in 2 mgP/gVSS hr in DPAO compared to 1.2 and 1.8 mgP/gVSS hr in OHO and DPAO-H, respectively. P content in sludge in BNR was 5.5% compare to 2% in CAS. Overall, initial SMPpro and SMPcar were 14-21 mg/L and 1.3-2.3 mg/L while initial bEPSpro and bEPScar were 28-43 mg/gVSS and 2-4 mg/gVSS. Final SMPpro and SMP car were 16-22 mg/L and 1-5 mg/L whereas final bEPSpro and bEPScar were 33-53 mg/gVSS and 3-6 mg/gVSS.

9.3.2 MFI test



a)



b)

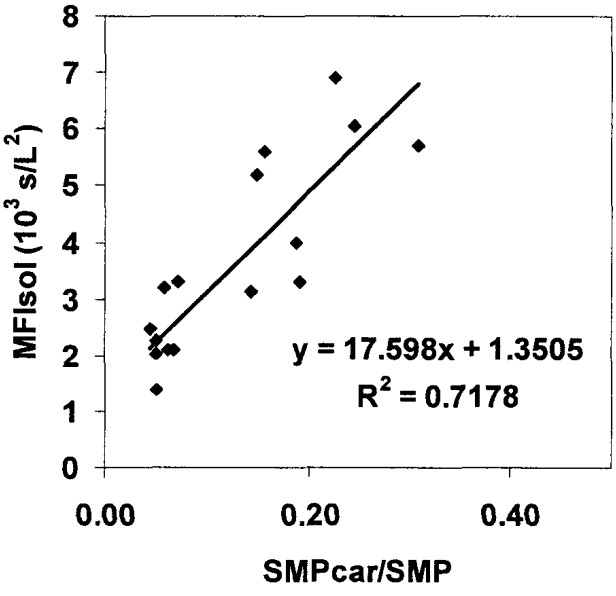
Figure 9.2 (a) MFI net change (b) SMP and bEPS net change

The MFI test was adopted for assessing the two primary fouling mechanisms i.e. pore blocking and cake layer resistance (Kim and Jang, 2006), with the initial and final values representing before and after denitrification. As apparent from table 9.1, initial MFIss averaged 2.1×10^3, 2.3×10^3, 3×10^3 and 2.2×10^3 s/L^2 for CAS, OHO, DPAO-H and DPAO, respectively, while MFIsol were 2.1×10^3, 2.3×10^3, 1.9×10^3 and 2.0×10^3 s/L^2 respectively. Average final MFIss were 4.7×10^3, 3.5×10^3, 2.2×10^3, and 1.2×10^3 s/L^2 for CAS, OHO, DPAO-H and DPAO respectively while final MFIsol averaged 5.2×10^3, 5.2×10^3, 2.8×10^3 and 3.5×10^3 s/L^2.

Figure 9.2a illustrating the net MFI change during denitrification conspicuously reflects that CAS and OHO denitrification increased MFIss by an average of 2.6×10^3 and 1.2×10^3 s/L^2 respectively corresponding to 123% and 52% of the initial values. . However, interestingly MFIss decreased in DPAO-H and DPAO denitrification at an average of 0.8×10^3 and 1×10^3 s/L^2 respectively corresponding to 27% and 40% reduction of the initial values, indicating not only a higher cake resistance in CAS and OHO than DPAO-H and DPAO, but also a drastically different denitrification impact on membranes. Figure 9.2b shows that MFIsol increased in all 4 cases, with the highest increases of 150% and 135% for the CAS and OHO versus 47% and 75% for the DPAO-H and DAPO, respectively. Interestingly, the final soluble MFI for both the CAS and OHO sludges were identical at 5.2×10^3 s/L^2, while the DPAO-H and DPAO were within 20% at $2.8\text{-}3.5\times10^3$ s/L^2. Jang et al. (2006) tested the impact of denitrification on fouling propensity and observed that denitrification with and without external carbon source increased both MFIss and MFIsol by as much as 14×10^3 and 11×10^3 s/L^2, respectively, corresponding to 460 and 120 % of the initial values. However, although the net change of MFIsol is consistent with the literature, the negative net change of MFIss in DPAO is quite intriguing. Furthermore, it appears that the trend was evidently related to the extent of DPAO contribution to denitrification, in that the net change in MFIss decreased in order from CAS to OHO, DPAO-H, and DPAO. Noting that the OHO sample in fact reflects the combination of OHO and DPAO, it is not surprising that the change in MFIss in the OHO was well below the CAS sludge. It is also noteworthy that the net MFI (MFIss+MFIsol) change in DPAO-H and DPAO is quite lower than the two other cases, with CAS final resistance was much higher than the BNR sludge.

9.3.3 SMP and bEPS change

Figure 9.2b illustrates the net change of SMP and bEPS components in each case. It is interesting to note that SMP in DPAO-H and DPAO decreased by on average 2 mg/L, but increased by 4.5-5 mg/L on average in the CAS and OHO sludges. bEPS net change, calculated as the difference between the initial and final sum of bEPSpro and bEPScar, were 12, 9, 6, 5 mg/gVSS for CAS, OHO, ODPAO and DPAO, respectively. However, it seems that the SMP and bEPS changes alone can not rationalize the net change in MFIsol and MFIss. For instance, although DPAO decreased SMP, MFIsol increased. Similarly, bEPS increased in DPAO but MFIss decreased.



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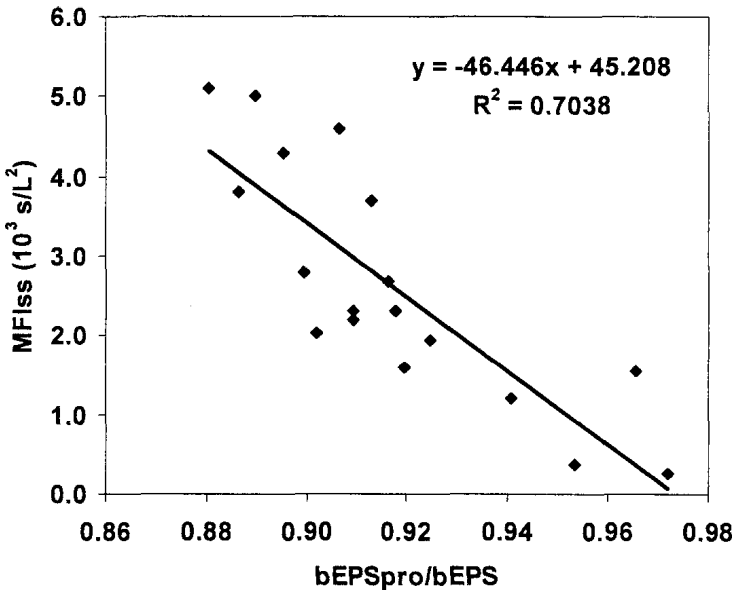


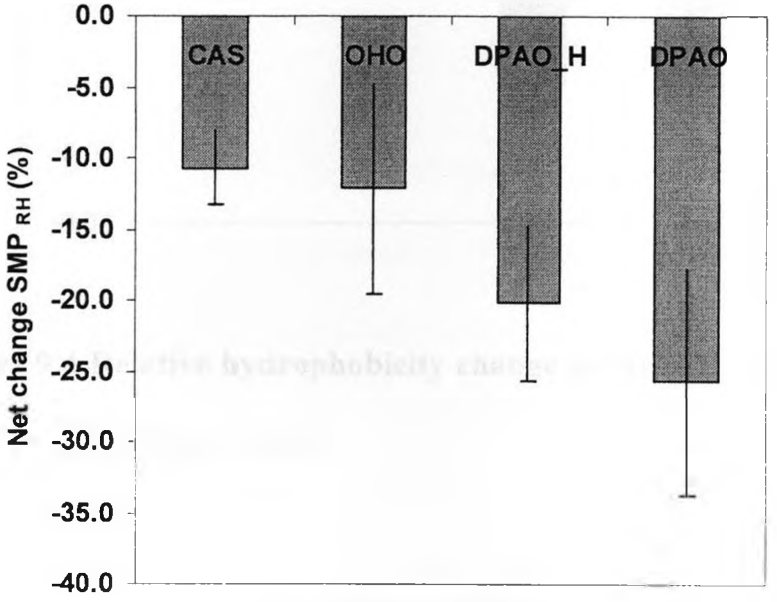
b)

Figure 9.3 Relationship between (a) MFIsol and SMPpro/SMP (b) MFIss and bEPSpro/bEPS

Figure 9.3 presents the relationship between fouling parameters i.e. SMP and bEPS and MFI values. From Fig 9.3a, it appears that SMPcar/SMP ratio was closely associated with MFIsol, suggesting that carbohydrate content in SMP is the predominant factor impacting MFIsol. It has been reported that denitrification-associated membrane fouling was due to SMP increase (Jang et al., 2006; Drews et al., 2007). However, this study evidently indicates that denitrification-associated membrane fouling especially, pore blocking resistance, is governed by the nature of SMPs, in this case carbohydrate content rather than the concentration of SMP. Figure 9.3b shows that the MFI is inversely correlated with the ratio of bEPSpro/bEPS, indicating that as protein in bEPS increased ,

suspended solids fouling resistance decreases or conversely as bEPScarb increased fouling resistance increased.

9.3.4 Relative hydrophobicity



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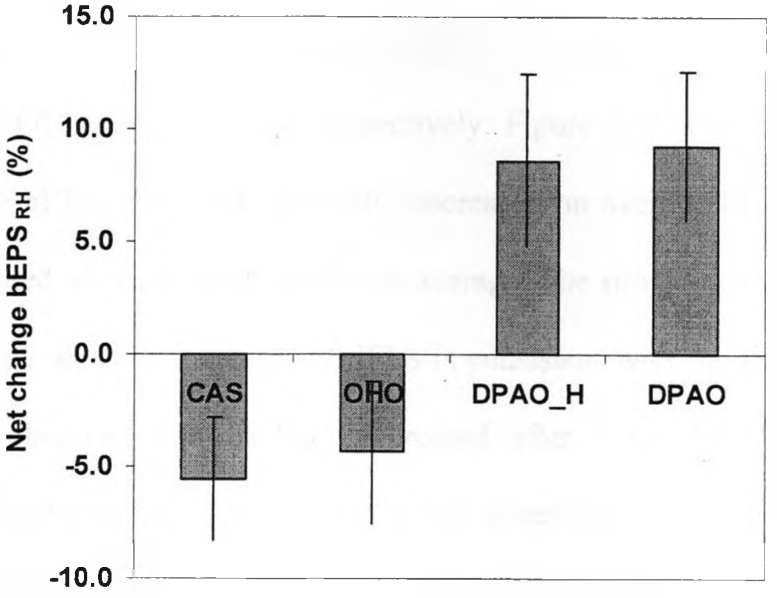

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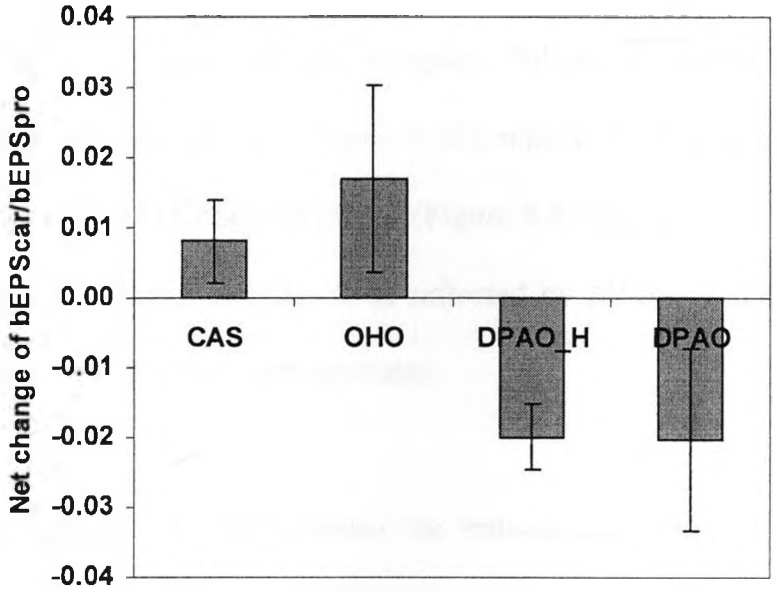

c)

Figure 9.4 Relative hydrophobicity change in (a) SMP and (b) bEPS (c) net change of bEPScar/bEPSpro ratio

In order to investigate the difference between the MFI results, relative hydrophobicity was conducted. Figure 9.4a presents the relative hydrophobicity change in SMP. Net change of SMP_{RH} was greatest in DPAO at average 25% compared to 10, 12 and 20% in CAS, OHO and DPAO-H, respectively. Figure 9.4b shows the net change of $bEPS_{RH}$. While $bEPS_{RH}$ in CAS and OHO decreased on average by 5-6%, DPAO-H and DPAO exhibited an increase of 8-10% on average. The simultaneous decrease in CAS and OHO $bEPS_{RH}$ with the increase in MFIss is consistent with the finding of Jang et al. (2006), who observed that $bEPS_{RH}$ decreased after CAS denitrification and subsequently, increased membrane fouling due to floc deterioration. Conversely, the increase in relative hydrophobicity of bEPS in DPAO-H and DPAO occurred simultaneously with the decrease in MFIss. According to an extensive review of EPS by Raszka et al. (2006) the

constituents of bEPS impact hydrophobicity, with protein increasing hydrophobicity. In the DPAO-H and DPAO samples, following denitrification, MFIss decreased, bEPSpro/bEPS increased (Figure 9.3b), relative hydrophobicity increased (Figure 9.4b), and the ratio of bEPScar/bEPSpro (Figure 9.4c) decreased. All of this evidently indicates that the cake layer resistance, as reflected by MFIss, is more strongly impacted by the proteins in bEPS than carbohydrates.

Liao et al. (2001) tested the influence of SRTs on the EPS and observed that protein was lower while carbohydrate was significantly higher at SRTs of 4 days than at 9 days, suggesting that excess carbohydrate was accumulated as EPS rather consumed for sludge growth, implying that without external carbon OHO may consume carbohydrates in EPS since they are more readily biodegradable than proteins and subsequently bEPScar/bEPSpro ratio decreased, whereas OHO with external carbon increased bEPScar/bEPSpro ratio because some of carbon was converted to carbohydrates.

This study compared the fouling propensity caused by different denitrification pathways, while most studies on the impact of denitrification on membrane fouling were conducted using conventional sludge rather than BNR sludge which is more diverse in microorganisms. Conclusively, it can be stated that DPAO denitrification increased hydrophobicity of floc compared to decrease in OHO and CAS, resulting in lower cake layer resistance

9.4 Summary & Conclusions

Based on the findings of this denitrification-associated fouling propensity tests using CAS, BNR sludges (OHO and DPAO), the following conclusions can be drawn.

1. MFIss increased by 150-220% in CAS and OHO but decreased in DPAO denitrification by 53% indicating the lower cake layer resistance in DPAO whereas MFIsol increased in all cases.
2. SMP increased by average 4.5-5 mg/L after CAS and OHO denitrification compared to 2 mg/L reduction in DPAO denitrification. bEPS increased in all cases by as much as 5-12 mg/gVSS but DPAO bEPS net change was the lowest.
3. Relative hydrophobicity in the sludge indicated that DPAO denitrification increased $bEPS_{RH}$ by 8-10% on average compared to a decrease in OHO and CAS samples by 5-6% suggesting that $bEPS_{RH}$ change caused MFIss reduction in DPAO. The $bEPS_{RH}$ change was caused by a change in protein content of bEPS, presumably associated with carbohydrate utilization in bEPS during denitrification in the absence of available external carbon.
4. Comparing denitrification fouling between CAS and BNR sludge, CAS exhibited much higher fouling propensity as evidenced by increased MFI, SMP and bEPS production.

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10.0 Conclusions

Based on the finding of two consecutive lab scale comparative studies between NMBR and conventional systems within the HRT and SRT ranges investigated in this study of 6-8 hours and 10 days for the treatment of wastewater characterized by COD, TKN and P , the following conclusions are drawn;

1. NMBR biological P removal capacity is better than A^2O with effluent P concentration of 0.2 vs 1.2 mg/L (with SWW) and 0.8 vs 1 mg/L (with MWW) as well as higher DPAO denitrification at 54% vs 40% of the total denitrification. Sludge production was 20% lower in NMBR than A^2O.

2. NMBR intermediate clarifier acted as anaerobic or anoxic zone depending on the hydraulic retention time of the preceding anaerobic tank and subsequently, enhanced overall P and nitrogen removal whereas the A^2O final clarifier facilitated nitrogen and COD reduction through denitrification

3. NMBR achieved lower effluent nitrates and ortho P than UMBR, using both low and high strength MWW, 6.8-7.6 versus 8.5-8.6 mg/L and 0.5-1.5 versus 0.8-1.4 mg/L, respectively with similar DPAO content at 40% in both systems. P fractionation in NMBR and UMBR indicated that P removal occurs mostly via PAO metabolism with a 7% of total P removal attributed to chemical precipitation.

4. The effluent DON from three different systems i.e. NMBR, A^2O, UMBR demonstrated that NMBR process achieved 0.3 mg/L lower than the A^2O process but compared to the UMBR. DON reduction by membrane averaged 35% of the ambient aeration tank concentration.

5. Membrane fouling studies with two membrane assisted BNR processes under same feed and operational conditions demonstrated similar fouling rate in both, with a permeability of 4.4×10^{-2} LMH/kPa·h. Fouling rate was more associated with SMP and protein/carbohydrate ratio than bound EPS. The significance of fouling parameters was characterized from the greatest to the lowest i.e. SMP, particle size, the ratio of bound protein/total protein and bound EPS.

6. Denitrification within the biofilm layer in membrane reduced nitrates by on average 1 mgN/L. The denitrification was more influenced by ambient DO rather than amount of attached biomass and COD reduction. Denitrification also increased membrane fouling.

7. Denitrification related fouling studies indicated significant different fouling propensity between ordinary heterotrophic organisms (OHO) and denitrifying phosphate accumulating organisms (DPAO). Compared to 150-220% increase in cake layer resistance in the former, the latter caused 53% decrease while both cases increased pore blocking resistance after denitrification. The different fouling behaviour was associated with EPS hydrophobicity change after denitrification, wherein relative hydrophobicity of bound EPS in DPAO increased 10% compared to a decrease in OHO by 5%.

11.0 Engineering significance and recommendations

This study on a novel MBR process evaluation presented several significant points.

1) The role of intermediate clarifier is beneficial to enhance P removal efficiency. It indicates that the capital cost of the intermediate clarifier should be weighed against the cost of additional chemical P removal and associated increased sludge treatment costs.

2) NMBR achieved 20% lower sludge production compared to the conventional A^2O system with clarifier at 0.13-0.16 vs 0.16-0.21 gVSS/gCOD. The sludge reduction also decreases the cost of waste sludge treatment and handling.

3) The DON reduction by membrane, accounting for 35% of the ambient membrane tank concentration, and nitrate reduction of 0.5-1 mg/L within membrane biofilm layer may decrease the amount of chemical dosage required for removing inorganic nitrogen to meet total effluent nitrogen of 3 mg/L. In addition, denitrification by DPAO may reduce external carbon dosage.

The following areas warrant further investigation.

a) Investigation of system performance by changing mixed liquor internal recirculation

b) Determination of the nature of effluent DON and its biodegradability

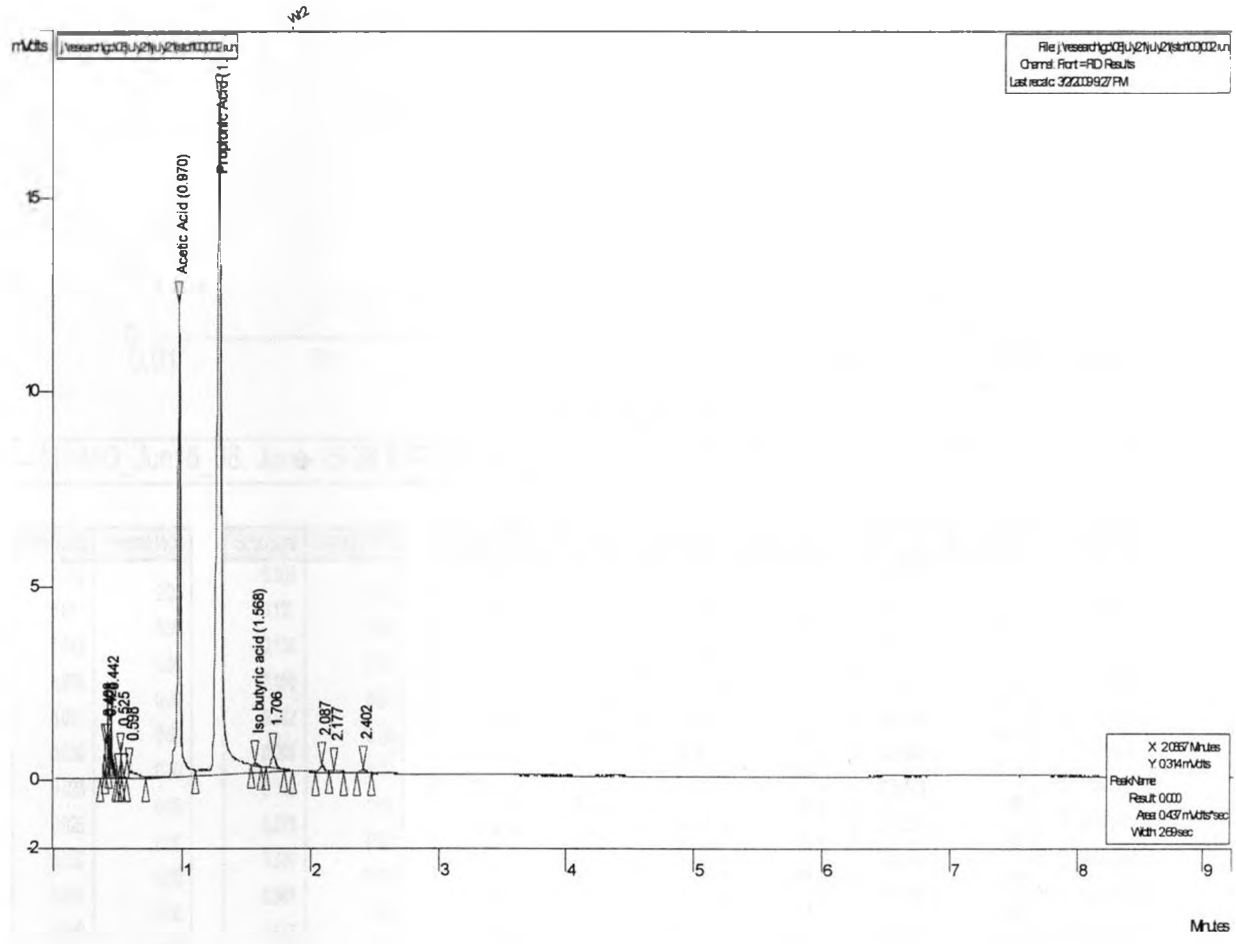
c) Identification of the molecular weight distribution of the SMP

d) Evaluation of the denitrification associated membrane fouling propensity in the continuous system rather than in off-line batch studies.

Appendix A

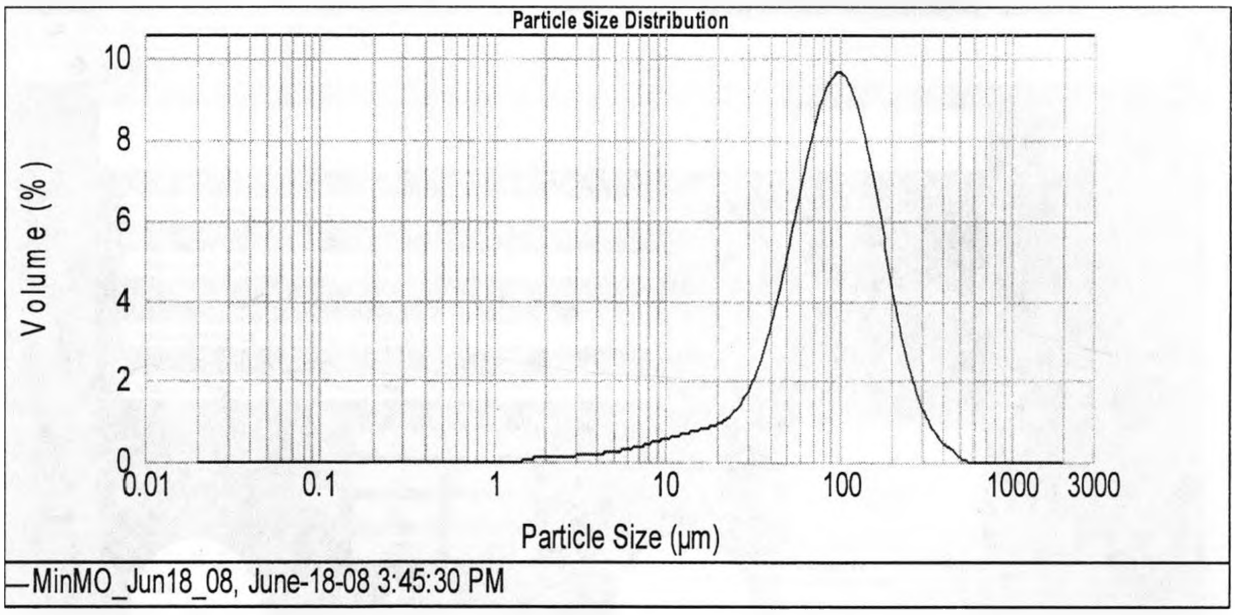
Gas chromatograph diagram

VFA standard curve



Appendix B

Particle size distribution



Size (µm)	Volume In %
0.010	0.00
0.011	0.00
0.013	0.00
0.015	0.00
0.017	0.00
0.020	0.00
0.023	0.00
0.026	0.00
0.030	0.00
0.035	0.00
0.040	0.00
0.046	0.00
0.052	0.00
0.060	0.00
0.069	0.00
0.079	0.00
0.091	0.00
0.105	

Size (µm)	Volume In %
0.105	0.00
0.120	0.00
0.138	0.00
0.158	0.00
0.182	0.00
0.209	0.00
0.240	0.00
0.275	0.00
0.316	0.00
0.363	0.00
0.417	0.00
0.479	0.00
0.550	0.00
0.631	0.00
0.724	0.00
0.832	0.00
0.955	0.00
1.096	

Size (µm)	Volume In %
1.096	0.00
1.259	0.00
1.445	0.01
1.660	0.07
1.905	0.08
2.188	0.09
2.512	0.10
2.884	0.12
3.311	0.14
3.802	0.16
4.365	0.19
5.012	0.23
5.754	0.27
6.607	0.33
7.586	0.40
8.710	0.47
10.000	0.54
11.482	

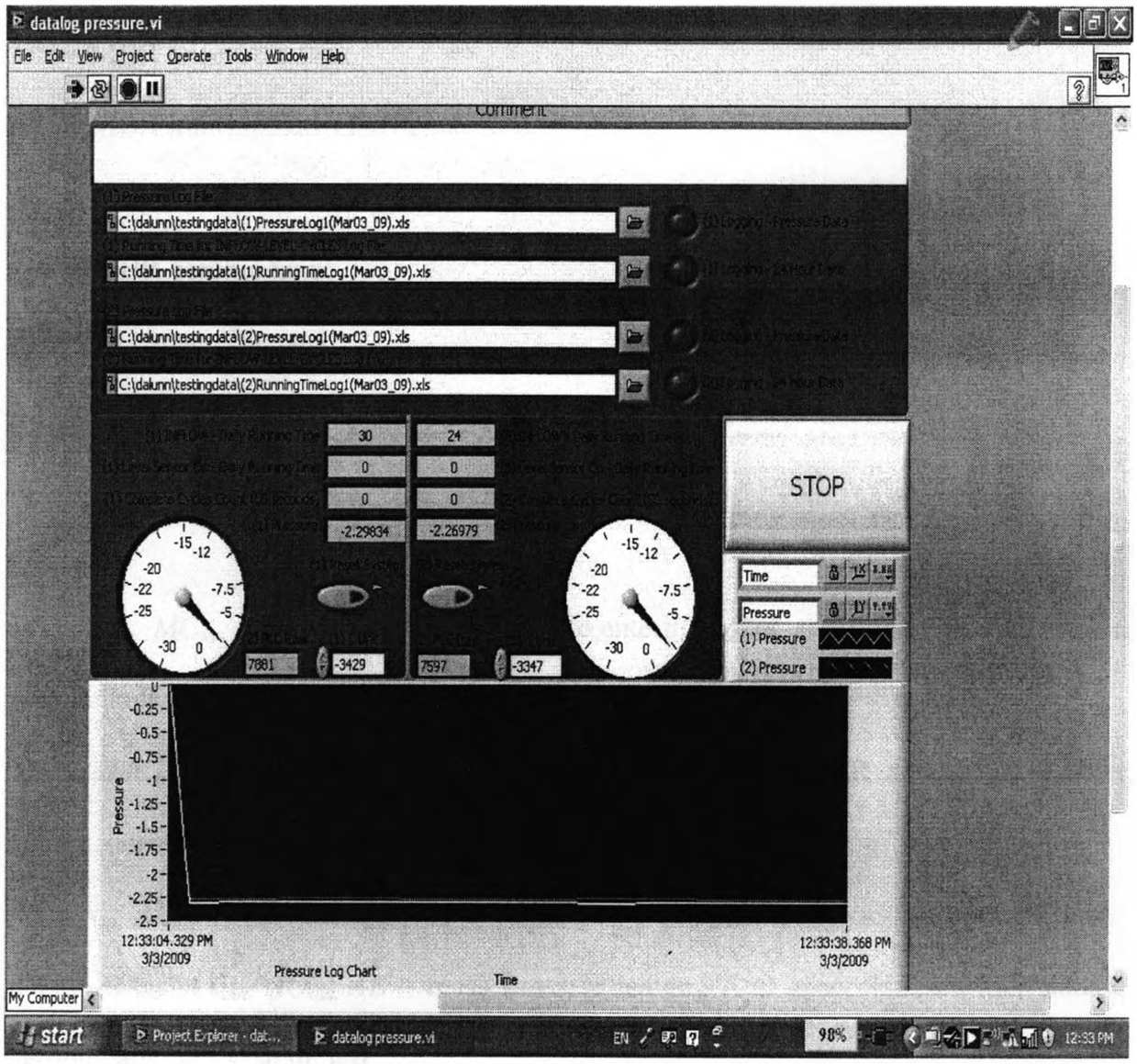
Size (µm)	Volume In %
11.482	0.60
13.183	0.66
15.136	0.71
17.378	0.78
19.953	0.88
22.909	1.06
26.303	1.36
30.200	1.82
34.674	2.48
39.811	3.34
45.709	4.39
52.481	5.54
60.256	6.69
69.183	7.69
79.433	8.41
91.201	8.70
104.713	8.53
120.226	

Size (µm)	Volume In %
120.226	7.90
138.038	6.89
158.489	5.67
181.970	4.37
208.930	3.18
239.883	2.15
275.423	1.38
316.228	0.83
363.078	0.48
416.869	0.29
478.630	0.06
549.541	0.00
630.957	0.00
724.436	0.00
831.764	0.00
954.993	0.00
1096.478	0.00
1258.925	

Size (µm)	Volume In %
1258.925	0.00
1445.440	0.00
1659.587	0.00
1905.461	0.00
2187.762	0.00
2511.886	0.00
2884.032	0.00
3311.311	0.00
3801.894	0.00
4365.158	0.00
5011.872	0.00
5754.399	0.00
6606.934	0.00
7585.776	0.00
8709.636	0.00
10000.000	

Appendix C

Labview screen reading transmembrane pressure from PLC



Appendix D

Mass balance calculations

Nomenclature

MN = MBR anaerobic tank

MC = MBR intermediate clarifier

MX = MBR anoxic tank

MO = MBR aerobic tank

AN = A^2O anaerobic tank

AX = A^2O anoxic tank

AO = A^2O aerobic tank

MT, MN_{in}, MC_{in}, MX_{in}, MO_{in} = mass flowrate entering MBR anaerobic, clarifier, anoxic, aerobic tank, g/d

MN_{out}, MC_{out}, MX_{out}, MO_{out}, ME = mass flowrate leaving MBR anaerobic, clarifier, anoxic, aerobic tank, and system, g/d

AT, AN_{in}, AX_{in}, AO_{in}, = mass flowrate entering A^2O anaerobic, anoxic, aerobic tank, g/d

AN_{out}, AC_{out}, AX_{out}, AO_{out}, AE = mass flowrate leaving A^2O anaerobic, clarifier, anoxic, aerobic tank and system, g/d

V = Volume, L

MN_{De} = Denitrified NO_3-N in MBR anaerobic tank, g N/d

MX_{De} = Denitrified NO_3-N in MBR anoxic tank, g N/d

MT_{De} = Total denitrified NO_3-N in MBR, g N/d

MW = MBR sludge wastage , g/d

AN_{De} = Denitrified NO_3-N in A^2O anaerobic tank, g N/d

AX_{De} = Denitrified NO_3-N in A^2O anoxic tank, g N/d

AT_{De} = Total denitrified NO_3-N in A_2O, g N/d

AW = A^2O sludge wastage, g/d

OUR = Oxygen uptake rate, mg O_2/L.h

MO_{oxi_COD} = Total oxidized COD during aerobic zone, g/d

MT_{De_COD} = Total oxidized COD during denitrification, g/d

4.57 = Equivalent coefficient, mg O_2 / mg N

2.86 = Equivalent coefficient mg O_2 / mg N

1.42 = COD equivalent coefficient, mg COD / mg VSS

Calculation on the mass balance

I. Calculation for denitrification

1) Denitrified NO_3-N in anoxic zone, g/d

$MX_{De} = MX_{in,\ NO3\text{-}N} - MX_{out,\ NO3\text{-}N}$

2) Denitrified NO_3-N in anaerobic zone, g/d

$MN_{De} = MN_{in,\ NO3\text{-}N} - MN_{out,\ NO3\text{-}N}$

3) Total denitrified NO_3-N in the system, g/d

$MT_{De} = MX_{De} + MN_{De}$

4) TKN of MBR effluent, ME_{TKN}, g/d

5) NO_3-N of MBR effluent, $ME_{NO3\text{-}N}$, g/d

6) Nitrogen in waste sludge , MW_N, g/d

TKN in waste sludge (MW_{TKN}, g/d) + NO3-N in waste sludge ($MW_{NO3\text{-}N}$, g/d)

$MW_{TKN} = 0.1 * MWvss$

7) Influent TKN, MI_N, g/d

8) Total nitrogen leaving system, MT_{out_N}, g/d

$MT_{out\_N} = ME_{TKN} + ME_{Nitrate} + MW_N$

II. Calculation for COD mass balance

1) Total generated NO_3-N, $MT_{gen\_nitrate}$,g/d

$MT_{gen\_nitrate} = MT_{De} + ME_{NO3\text{-}N}$

2) Oxidized COD in aerobic, MO_{oxi_COD}, g/d

$MO_{oxi\_COD} = OUR * V_{MO} * 24 - 4.57 * MT_{gen\_nitrate}$

3) Oxidized COD during denitrification, MT_{De_COD}

$MT_{De\_COD} = 2.86 / (1-1.42*Y_H) * MT_{De}$

4) Oxidized COD by recycled DO(MO_{DO}) in anoxic, MT_{DO_COD}

$MT_{DO\_COD} = 1 / (1-1.42*Y_H) * MO_{DO}$

5) Total oxidized COD, MToxi_COD, g/d

$MToxi\_COD = MO_{oxi\_COD} + MT_{De\_COD}$

6) Effluent TCOD, ME_{TCOD}, g/d

7) COD in waste sludge, MW_{COD}, g/d

$MW_{COD} = 1.42 * MWvss$

8) COD leaving the system, MT_{out_COD}, g/d

$MT_{out\_COD} = MT_{oxi\_COD} + ME_{TCOD} + MW_{COD}$

9) Influent COD, MT_{in_COD}, g/d

10) COD balance, %

$\% = MT_{out\_COD} / MT_{in\_COD}$

III. Example of calculation

System = MBR, Influent flowrate = 66L/d, Wastage = 4.4 gVSS/d

Influent TCOD = 310 mg/L Influent TKN = 35 mg/L

OUR = 36 mg O_2/L/h, V_{MO} = 12 L, DO = 1.5 mgO_2/L, Y_H = 0.16 mg VSS/mgCOD

	Influent	MN	MC	MX	MO	ME
SCOD (mg/L)	255	21	15	7	8	7
NO_3-N (mg/L)	-	1	0.8	1.5	7.3	7.3

Total denitrified nitrate in the system (MT_{De}) = MX_{De} + MN_{De} = 1.22 g/d

Total generated NO_3-N, $MT_{gen\_nitrate}$ = 1.7 g/d

TKN of MBR effluent, ME_{TKN} = 0.08 g/d

NO_3-N of MBR effluent, $ME_{NO3\text{-}N}$ = 0.48 g/d

Nitrogen in waste sludge, MW_N = 0.45 g/d

Total nitrogen leaving system, MT_{out_N} = 2.24 g/d

Influent TKN, MI_N = 2.31 g/d

→ Nitrogen balance % = MT_{out_N} / MI_N = 97 %

Oxidized COD in aerobic, MO_{oxi_COD} = 36 * 12 * 24 / 1000 – 4.57 * 1.7 = 2.56 g/d

Oxidized COD during denitrification, MT_{De_COD} = 2.86 / (1-1.42Y_H)* MT_{De} = 4.53 g/d

Oxidized COD by recycled DO(MO_{DO}) in anoxic, MT_{DO_COD}

= 1 / (1-1.42Y_H)* MO_{DO} = 0.45 g/d

Total oxidized COD, MToxi_COD = $MO_{oxi\_COD} + MT_{De\_COD} + MT_{DO\_COD}$

$= 2.56 + 4.53 + 0.45 = 7.54$ g/d

Effluent TCOD, $ME_{TCOD} = 0.5$ g/d

COD in waste sludge, $MW_{COD} = 6.33$ g/d

COD leaving the system, $MT_{out\_COD} = 7.54 + 0.5 + 6.33 = 14.3$ g/d

Influent COD, $MT_{in\_COD} = 20.46$ g/d

➔ COD balance % = $MT_{out\_COD} / MT_{in\_COD} * 100 = 70$ %

Appendix E

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