DOMESTIC WASTEWATER TREATMENT EMPLOYING A NOVEL BAFFLED OSMOTIC MEMBRANE BIOREACTOR-MICROFILTRATION HYBRID SYSTEM

by

NIRENKUMAR PATHAK

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School of Civil and Environmental Engineering
Faculty of Engineering and Information Technology
University of Technology Sydney (UTS)
New South Wales, Australia

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CERTIFICATE OF AUTHORSHIP/ORIGINALITY

I, Nirenkumar Bansidhar Pathak declare that this thesis, is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Civil and Environmental Engineering – FEIT at the University of Technology Sydney.

I certify that this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledge within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. This research is supported by the Australian Government Research Training Program. In addition, I certify that all information sources and literature used are indicated in the thesis.

Signature of candidate:

Production Note:
Signature removed prior to publication.

(Nirenkumar Pathak)

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3. **Pathak, N.,** Chekli, L., Wang, J., Kim, Y., Phuntsho, S., Li, S., Ghaffour, N., Leiknes, T. & Shon, H. 2017, Performance of a novel baffled osmotic membrane bioreactor-microfiltration hybrid system under continuous operation for simultaneous nutrient removal and mitigation of brine discharge, Bioresour Technol, 240, pp. 50-8.
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Conference papers and presentation

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LIST OF ABBREVIATIONS

AL-DS	Active layer facing draw solution
AL-FS	Active layer facing feed solution
AOB	Ammonia oxidizing bacteria
AS	Activated sludge
BNR	Biological nutrient removal
CEOP	Cake-enhanced osmotic pressure
CLSM	Confocal laser scanning microscopy
COD	Chemical oxygen demand
CP	Concentration polarization
CTA	Cellulose triacetate
DI	Deionised
DOC	Dissolved organic carbon
DS	Draw solution
ECP	External concentration polarization
EDGs	Electron donating groups
EDX	Energy dispersive X-ray spectroscopy
EPS	Extracellular polymeric substances
EWGs	Electron withdrawing groups
FDFO	Fertilizer drawn forward osmosis
FS	Feed solution
HA	Humic acid
HRT	Hydraulic retention time

ICP	Internal concentration polarization
LC-MS	Liquid chromatography mass spectroscopy
LC-OCD	Liquid chromatography-organic carbon detection
LMH	Litres per square meter per hour
MBR	Membrane bioreactor
MD	Membrane distillation
MF	Microfiltration
MLE	Modified Ludzak–Ettinger (MLE)
MLSS	Mixed liquor suspended solids
NaOAc	Sodium acetate
NF	Nanofiltration
NOB	Nitrite oxidizing bacteria
OCT	Optical coherence tomography
OLR	Organic loading rate
OMBR	Osmotic membrane bioreactor
OMBR-MF	Osmotic membrane bioreactor-microfiltration
OMPs	Organic micro-pollutants
PA	Polyamide
PAOs	Phosphorous accumulating organisms
PES-MF	Polyether sulfone-microfiltration
PPCPs	Pharmaceutical and personal care products
PRO	Pressure retarded osmosis
RO	Reverse osmosis
RSF	Reverse salt flux

RSFS	Reverse salt flux selectivity
SBR	Sequencing batch reactor
SEM	Scanning electron microscopy
SMP	Soluble microbial products
SND	Simultaneous nitrification and denitrification
SOA	Ammonium sulphate
SOUR	Specific oxygen uptake rate
SRSF	Specific reverse salt flux
SRT	Solid retention time
SWRO	Seawater reverse osmosis
TDS	Total dissolved solids
TDS	Total dissolved solids
TFC	Thin-film composite
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorous
TrOCs	Trace organic contaminants
TS	Total solids
UF	Ultrafiltration

Abstract

A novel baffled osmotic membrane bioreactor microfiltration (OMBR-MF) hybrid system was proposed for the domestic wastewater treatment with specific focus on nutrient and organic micropollutant (OMPs) removal. This baffled OMBR-MF hybrid system was first applied in laboratory scale conditions to treat simulated wastewater. Insertion of baffles in the aerobic reactor, created separate oxic and anoxic zones. In particular, simultaneous nitrification and denitrification (SND) was achieved in a single baffled OMBR-MF hybrid system. Thus, this reactor design enables both aerobic and anoxic processes reduce the process footprint and energy costs associated with pumping the mixed liquor in-between the oxic and anoxic tanks and chemical dosing costs for pH adjustment. The bioreactor was operated under four different oxic-anoxic cycle time at constant flux operation employing thin film composite-forward osmosis (TFC-FO) and polyether sulfone-microfiltration (PES-MF) membranes. At 65 d sludge retention time (SRT) 86-92 % COD, 63-76 % TN and 57-63 PO_4-P % removal was achieved during Run 1 to Run 4 in a bioreactor. The oxic-anoxic cycle time of 0.5-1.5 h appeared to be an appropriate choice for the process. Incorporation of MF membrane effectively alleviated salinity build up in the reactor, allowing stable operation of the system.

Based on outstanding SND performance using baffled OMBR-MF hybrid system test at different oxic-anoxic conditions long-term OMBR-MF hybrid system performance was evaluated at optimum oxic-anoxic (0.5-1.5 h) cycle time. The process performance was evaluated in terms of water flux, salinity build up in the bioreactor, organic and nutrient removal and microbial activity using synthetic reverse osmosis (RO) brine as draw solution (DS). The incorporation of MF membrane was effective in maintaining a reasonable salinity level (612–1434 mg/L) in the reactor which resulted in a much lower flux decline (i.e. 11.48–6.98 LMH) as compared to previous studies. An average of 8.56 LMH FO flux was achieved during 38 days of continuous operation. The stable operation of the osmotic membrane bioreactor–forward osmosis (OMBR-FO) process resulted in an effective removal of both organic matter (97.84%) and nutrient (phosphate 87.36% and total nitrogen 94.28%), respectively. The dissolved oxygen profile during aerobic-anoxic cycle confirmed < 0.5 mg/L oxygen favourable for denitrification.

To further investigate novel baffled OMBR-MF system performance in particular the efficiency of OMPs removal under unique redox environment (oxic-anoxic conditions) were evaluated. The performance of OMBR-MF system was examined employing three different draw solutes (DS), and three model OMPs. The DS employed in this study were sodium chloride (NaCl), potassium chloride (KCl) and sodium acetate (CH_3COONa). Three model organic micropollutants used were caffeine, atenolol and atrazine respectively. The highest forward osmosis (FO) membrane rejection was attained with atenolol (100%) due to its higher molar mass and positive charge. With inorganic DS caffeine (94–100%) revealed highest removal followed by atenolol (89–96%) and atrazine (16–40%) respectively. All three OMPs exhibited higher removal with organic DS as compared to inorganic DS. Significant anoxic removal was observed for atrazine under very different redox conditions with extended anoxic cycle time. This can be linked with possible development of different microbial consortia responsible for diverse enzymes secretion. Overall, the OMBR-MF process showed effective removal of carbonaceous matter, nutrient and organic micropollutants (OMPs).

Membrane biofouling is an inevitable phenomenon in any membrane process. Therefore real-time membrane fouling characterization without affecting continuous operation would be helpful in devising efficient antifouling strategy. Further, real wastewater exhibits entirely different foultants and very diverse bacterial community. So, it would be more interesting to study foulant and microbial interaction with membrane employing real wastewater. So, in order to study the biofouling development on forward osmosis membranes optical coherence tomography (OCT) technique was employed. On-line monitoring of biofilm growth on a flat sheet cellulose triacetate forward osmosis (CTA-FO) membrane was conducted for 21 days with three different draw solutes. Further, the process performance was evaluated in terms of water flux, organic and nutrient removal, microbial activity in terms of soluble microbial products (SMP) and extracellular polymeric substance (EPS), and floc size. The measured biofouling layer thickness was in the order sodium chloride (NaCl) > ammonium sulfate (SOA) > potassium dihydrogen phosphate (KH_2PO_4). Very high organic removal (96.9 ± 0.8%) and reasonably good nutrient removal efficiency (85.2 ± 1.6% TN) was achieved. The sludge characteristics and biofouling layer thickness suggest that less EPS and higher floc size were the governing factors for less fouling.

Osmotic membrane bioreactor for wastewater treatment is very attractive and emerging process. It has shown very promising results for organic, nutrient and trace organics removal. With current technological advances, employing hybrid OMBR-MF have potential to produce fresh water at less cost than conventional desalination/water recovery technologies (i.e. ultrafiltration/RO systems). Main benefits of using baffled OMBR-MF hybrid system are better removal efficiency in terms of nutrient and micropollutants, saving in energy and pH adjustment costs, reduced process piping costs as SND takes place in single reactor and more flexible treatment unit.

The major challenges of OMBR to be a techno-economically viable technology are developing a high performance low cost forward osmosis membrane with higher flux and high selectivity with less internal concentration polarization (ICP) effect, and the availability of suitable draw solutions (to explore other divalent organic DS with lower RSF and lower fouling propensity and to compare their performance in baffled OMBR-MF system). It would be interesting to address microbial community dynamics in oxic and anoxic zone in the baffled bioreactor to elucidate its impact on nutrient and OMPs removal.

Besides, most of studies of OMBR have been performed at lab-scale. Therefore, more studies both in pilot and in full-scale plants are necessary to gain knowledge to achieve a better OMBR performance. In order to commercialise OMBR, full scale benchmarking and efficient process controls intensification are major challenges. Looking to the present progresses in FO membrane development (outer selective hollow fiber and nanomaterials made) in order to meet similar flux of existing porous membranes and very high performance of FO membranes in rejection of nutrients and micropollutants as compared to MF/UF membranes, OMBR can become techno- economically viable alternative for waster reuse applications in near future.

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CHAPTER 1

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INTRODUCTION

1 Introduction

1.1 Research background

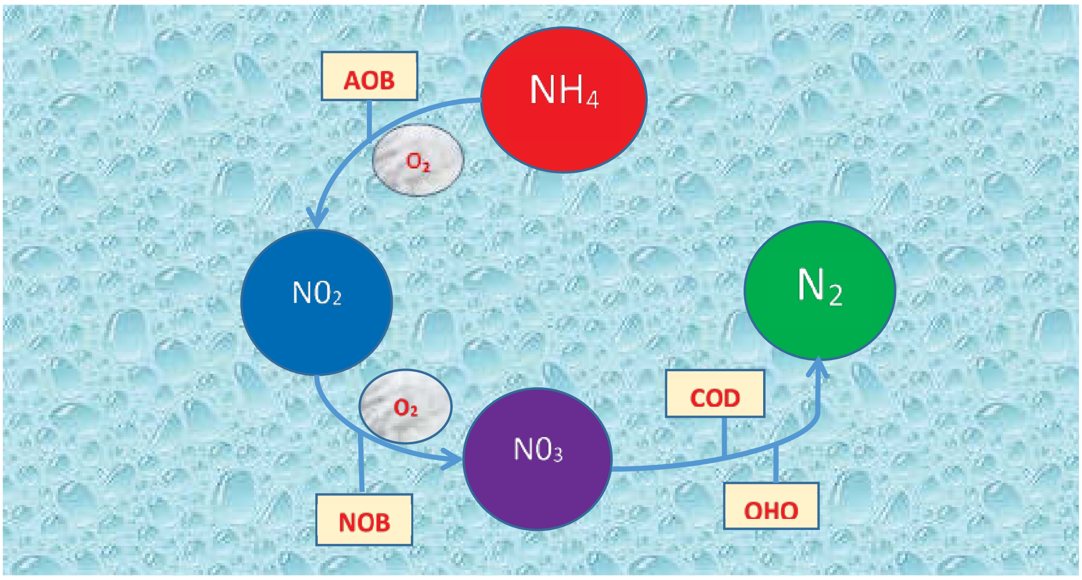
Water is one of the most ubiquitous resources and can be either consumed directly or used in applications such as irrigation, industrialisation and power generation (Wu et al., 2013b). Global consumption of water is doubling every 20 years, more than twice the rate of population growth. According to the United Nations more than one billion people on the earth already lack access to fresh drinking water. Further, as per United Nations predictions, between two and seven billion people will face water shortages by the year 2050 (Wu et al., 2013b). Increasing population numbers, a changing climate, intensive agricultural practices, economic growth and urbanisation will undoubtedly continue to make the issue of water scarcity a global priority for years to come. Therefore, topic of wastewater recycle and reuse in domestic, manufacturing and agriculture is gaining increasing attention around the world (Upen Bharwada, 2011). Wastewater reuse is reliable and a cost-effective approach for environmental protection. Therefore, significant efforts have been dedicated to develop new as well as to improve existing technologies for wastewater reuse (Luo et al., 2017a).

Membrane based technology could play a vital role in solving the water scarcity issues through alternative sources such as saline water sources and wastewater reclamation (Phuntsho et al., 2012). Forward osmosis (FO) is a simple and spontaneous process that has recently been engineered and adapted to various water treatment applications (Cath et al., 2009). The lesser and reversible fouling in comparison to other pressure driven processes such as nanofiltration (NF) and reverse osmosis (RO) are attractive features of FO (Lutchmiah et al., 2014). One of the promising options is to integrate submerged FO membrane with bioreactor known as osmotic membrane bioreactor (OMBR) has recently been proposed for advanced wastewater treatment and reuse (Achilli et al., 2009, Luo et al., 2017a). OMBRs can be engineered for clean water extraction, nutrient and trace organic chemical removal and toxic organic compounds biodegradation from wastewater and the FO membranes in OMBR have low fouling propensity (Lu and He, 2015, Holloway et al., 2015a). However, a key concern with OMBRs is elevated bioreactor salinity caused by retention of dissolved solutes from the influent wastewater and diffusion of draw solutes from the FO draw solution into the bioreactor by a phenomenon known as reverse salt flux (RSF) (Morrow et al., 2018b, Luo et al., 2015a). Increased bioreactor salinity may result in decreased water flux, greater membrane fouling, and sub-optimal biological carbon and nitrogen removal due to adverse impacts on the microbial activity and population structure in the bioreactor (Morrow et al., 2018a, Wang et al., 2017c, Yap et al., 2012).

The primary nutrients which should be removed to prevent deterioration of water bodies are carbon, nitrogen and phosphorous. Carbon is not considered difficult to remove biologically (Rasool et al., 2014). The nutrients (N and P) are essential elements of life, but when they are released to the environment in excessive amounts severe problems arise (Dafne Crutchik et al., 2017, Mosquera-Corral, 2016). Excessive nitrogen discharged from sewage and industrial wastewater has many adverse effects on the environment. which includes promotion of eutrophication, toxicity to aquatic organisms and depletion of dissolved oxygen in receiving water bodies due to bacterial oxidation of ammonia to nitrate (He et al., 2009, Zhang and Chen, 2009). Moreover, nitrates in wastewater streams have raised concerns due to severe impacts on human and animal health (Rasool et al., 2014). Therefore, wastewater discharge standards for nitrogen have become more stringent due to severe eutrophication and environment pollution (Guadie et al., 2013). In the Australian directive on treated wastewater, the maximum allowable total nitrogen concentration is 5 mg/L TN for discharge into the aquatic ecosystem (EPA, 2005) (Shrestha, 2013).

To accomplish removal of carbon and nitrogen species, conventional activated sludge systems typically rely on physical separation of different zones (e.g., aerobic, anoxic, and anaerobic zones) within multiple reactors (Morrow et al., 2018a). Biological nitrification–denitrification is one of the most economical processes for nitrogen removal from municipal wastewaters (Gupta and Gupta, 2001). Because of different environmental conditions of nitrifiers and de-nitrifiers, total nitrogen removal in wastewater treatment plants is most commonly achieved in a two-stage system (He et al., 2009). Nitrogen removal is achieved by aerobic nitrification and anoxic denitrification using autotrophic nitrifying and heterotrophic denitrifying bacteria (Figure 1.1). Nitrification is performed by two different nitrifying bacteria communities, and thus, nitrification is considered as a two-step process. Ammonia Oxidizing Bacteria (AOB) firstly oxidize ammonium to nitrite and Nitrite Oxidizing Bacteria (NOB) perform the nitrate formation (nitratation). Thus two separate reactors are required to provide different environments for the two kinds of bacteria in nitrogen removal process (Fu et al., 2009a).

Simultaneous nitrification and denitrification (SND) is a process that nitrification and denitrification simultaneously occur in a single bioreactor under low DO (Dissolved Oxygen) condition (< 0.5 mg/L) (Baek and Kim, 2013). For continuously operated plants, nitrogen removal obtained in a single tank can save the cost of a second tank, simplify the overall process design, low operating dissolved oxygen (DO) requirement and by effectively maintaining neutral pH can reduce chemical cost, and less sludge production compared to conventional treatment plants (Baek and Kim, 2013, Dey, 2010, Feng et al., 2011, Yoo et al., 1999). Also, possibility of upgrading production compared to conventional treatment plants (Baek and Kim, 2013, Dey, 2010, Feng et al., 2011, Yoo et al., 1999). Also, possibility of upgrading extended aeration conventional activated sludge treatment by conversion into SND system can be a reasonable approach that can help meet stringent nitrogen discharge limits (Dey, 2010).



*** Ammonia Oxidizing Bacteria (AOB); Nitrite Oxidizing Bacteria (NOB)**

Figure 1.1 Nitrogen transformation.

Besides, trace organic contaminants (TrOCs) have been widely detected in sewage and sewage impacted water bodies at concentrations of up to several µg/L (Phan et al., 2014). Although a number of studies have reported better and more stable removal of the moderately biodegradable TrOCs by MBR than CAS, little improvement is generally reported in case of hydrophilic and resistant TrOCs (Phan et al., 2014, Tadkaew et al., 2011). In this context, OMBR can offer better removal of TrOCs. Further, different redox conditions may promote the growth of different microbial consortia thus significantly influencing TrOC biodegradation (Phan et al., 2014). It has been hypothesised that under varying aerobic and anoxic conditions in a single reactor, it would be interesting to see TrOCs removal which has been rarely reported in the literature.

In line with above mentioned research gaps we have examined total nitrogen and trace organic removal in a single reactor inserting baffles to partition reactor in oxic and anoxic zones respectively. Simulated sea water reverse osmosis brine has been proposed as a draw solution which can be safely discharged into the sea after dilution in OMBR-MF hybrid process (Figure 1.2). Due to FO flux decline with time and mitigate salinity build up we have operated MF membrane in parallel with FO membrane in the bioreactor. Incorporation of MF membrane further helped in mitigation salinity build up and achieving almost complete nitrification. Other OMBR studies reported that ammonia-oxidizing bacteria, which are responsible for ammonia removal via nitrification, are particularly sensitive to salinity and sharp decreases in nitrification efficiency have been reported for bioreactors with salinities ranging from 2 to 15 g/L NaCl (Morrow et al., 2018b). Thus, combining MF membrane with FO helped in maintaining constant hydraulic retention time and decrease in salinity build up in the bioreactor enhancing nitrification and total nitrogen removal. Finally, non-destructive optical coherence tomography (OCT) technique was employed for the first time to analyse FO membrane fouling in dynamic environment by capturing real time images in OMBR-MF hybrid system.

1.2 Objectives and scope of the research

The baffled OMBR-MF hybrid process is proposed in this study. This research aims to carry out series of lab scale experimental investigation on the effects of the various operating parameters, effects of different draw solutes, and reactor configuration on the carbonaceous organic, nutrient and organic micropollutant removal. Also, fouling nature and characteristic will be studied employing various techniques.

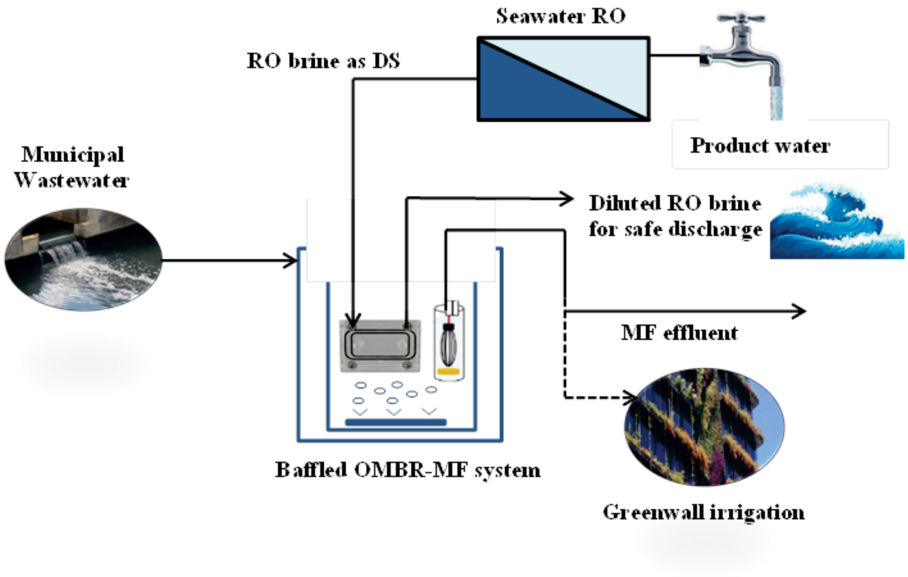


Figure 1.2. Conceptual diagram of the seawater reverse osmosis (SWRO) brine baffled osmotic membrane bioreactor (OMBR) hybrid process.

Therefore, the specific objectives of the study can be summarised into different segments:

- Demonstrate the concept of baffled OMBR-MF hybrid system in sewage treatment and evaluate optimum operating oxic–anoxic cycle time for organic and total nitrogen removal.
- Evaluate baffled OMBR-MF hybrid system for sewage treatment with SWRO brine as DS in long-term operation.
- Assess baffled OMBR-MF hybrid system performance for organic micropollutant (OMPs) removal from municipal wastewater under different redox environment.

- Examine biofouling phenomena of FO membrane in real-time using non-destructive and in-situ optical coherence tomography (OCT) technique.

1.3 Outline of the Thesis

This thesis is structured into eight main chapters, and each chapter gives a particular aspect. Chapter 1 introduces research background, objectives and scope of the research.

Chapter 2 provides background information by way of a literature review on an emerging process of forward osmosis and main parameters affecting its performance and fouling phenomena and antifouling strategies characteristics in OMBR operation. Nitrogen removal fundamentals and nitrogen removal techniques are discussed. Also, OMBR performance in terms of carbonaceous matter and nutrient removal has been discussed.

The materials, description of methodologies used for the study and the analytical methods are presented in Chapter 3 under the title Materials and Methodology.

Chapter 4 focuses on the baffled OMBR-MF hybrid system performance to achieve simultaneous nitrification and denitrification (SND) under four different set of operating conditions. From this study, the optimum oxic-anoxic cycle time was obtained employing SWRO brine as a DS.

Chapter 5 describes long-term baffled OMBR-MF system performance in terms of FO water flux, salinity build up and TN removal treating simulated municipal wastewater.

Chapter 6 is on TOrC removal in a single baffled OMBR-MF hybrid system assessed under oxic-anoxic conditions.

Chapter 7 analyses typical FO membranes fouling during OMBR-MF hybrid system employing in-situ and non-destructive optical coherence tomography (OCT) technique for the first time in dynamic environment with real sewage and different DS.

Research outcomes and recommendations for future research are given in Chapter 8.

CHAPTER 2

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LITERATURE REVIEW

2 Literature review

2.1 Water scarcity a global problem

In our era, water, the natural resource with no substitute, is under unprecedented increasing demand (Stefan, 2017). As of April 2017, the world's population is believed to have reached 7.6 billion and it is predicted to increase to 10 billion by the year 2056 Figure 2.1(a). Providing clean and affordable water to meet human needs is a grand challenge of the 21st century (Qu et al., 2013). Created from population growth, urbanization and higher standards of living, industrial expansion and agriculture, and regional imbalances will continue to increase the water demand globally, thus to diminish the fresh water availability (Stefan, 2017).

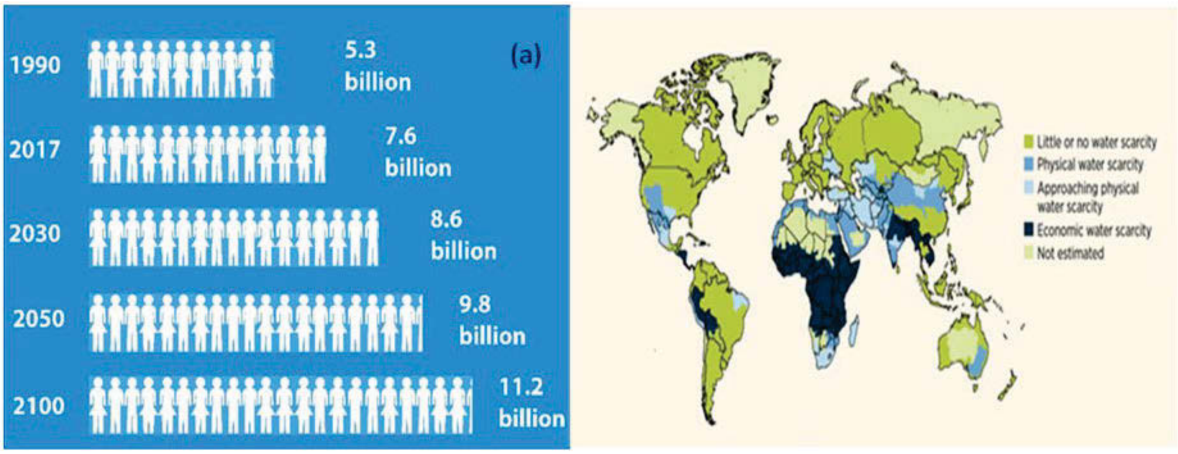

Figure 2.1. (a) Global population and (b) Global physical and economic water scarcity (2012) (WWAP, 2012).

By 2025, it was estimated that 50% of the world's population will be living in water-stressed areas (WHO, 2014) (Zhang et al., 2016). Water stress is when annual water supplies drop below 1,700 m^3 per person. When annual water supplies drop below 1,000 m^3 per person, the population faces water scarcity, and below 500 m^3 is termed absolute scarcity. Water scarcity can be divided into two mechanisms: (i) physical (absolute) water scarcity and (ii) economic water scarcity Figure 2.1 (b) (Molden, 2013). The former is the situation caused by a lack of enough water to meet all demands to make ecosystems function effectively. And the latter is originated from a lack of the investment in water infrastructure to meet the water demand for human activity. Therefore, freshwater resources are getting scarcer due to the impacts of global warming, and rapid and extensive industrialization and urbanization (Rijsberman, 2006).

The many problems worldwide associated with the lack of clean, fresh water are well known: 1.2 billion people lack access to safe drinking water, 2.6 billion have little or no sanitation, millions of people die annually—3,900 children a day—from diseases transmitted through unsafe water or human excreta (Shannon et al., 2008, Stefan, 2017). Approximately one-half of the world's population depends on polluted water sources and ca. one billion people consume agricultural products originating from lands irrigated with raw or inadequately treated wastewater (Stefan, 2017). The increasing divergence between water resources and demands all over the world highlights the need for more reliable and resilient water supplies to reach an appropriate resources/demand balance (Li, 2017).

2.2 Water reclamation

Under an average economic growth scenario and if no efficiency gains are assumed, global water demand will increase 53% by 2030, up to 6.9 trillion m^3 per year (Linares et al., 2017). Along with the growing demand for fresh water, there is also an increase in the amount of wastewater that needs to be treated adequately to meet public health and environmental discharge regulations. This problem is more significant along coastlines, where today, more than 3 billion people live, and it is likely that by 2025 this number will double (Linares et al., 2013). As a result of these trends, over the last two decades, wastewater recovery for direct and indirect planned reuse has become a more common practice, with an increasing number of studies that compare various technologies that can treat and recover secondary wastewater effluent (Linares et al., 2013). In response to water scarcity trends, engineering solutions to augmentation of the existing supplies were implemented in various geographies around the world. Examples include seawater desalination, wastewater recycling, and bulk water transfer between catchments (Stefan, 2017). Today, around 80% of all wastewater is discharged into the world's waterways where it creates health, environmental and climate-related hazards. Urbanisation further exacerbates this challenge with increasing wastewater generation, while at the same time using more of Earth's dwindling resources (2018). The overarching goal for the future of reclamation and re-use of water is to capture water directly from most under-exploited resources such as industrial or municipal wastewaters and restore it to potable quality (Shannon et al., 2008). Water from industrial or domestic use contains energy, water, organics, phosphates, nitrogen, cellulose, rare earths, and other resources. Technologies are increasingly making resource recovery from wastewater commercially feasible, including bio-gas, fertiliser, paper, metals, plastics and, perhaps most importantly, it is a source of 'new' water (2018).

According to the 2017 water reuse statistical survey, rising water shortage over the globe is a driver that is relied upon to reinforce showcase wastewater development. Global markets for wastewater-recycling and reuse technologies during the period from 2012 to 2016 increased from nearly $15.7 billion to $18.3 billion, equivalent to a compound annual growth rate (CAGR) of 19.6%. Further, hike in market trend is expected to increase from $ 18.3 billion in 2016 to $21.4 billion in 2021, reflecting a five-year CAGR of 13.6% (Figure 2.2).

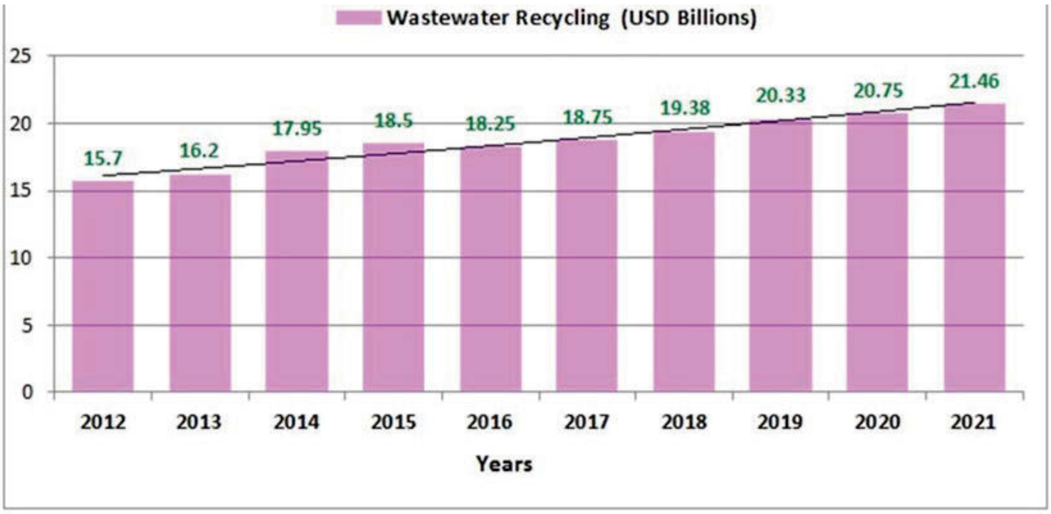

Figure 2.2. Global market for wastewater recycling and reuse technologies (Recycling Expo, 2018).

Current infrastructure for wastewater treatment, as well as for the production of safe and readily available water is difficult to keep pace with the increasingly stringent regulation and growing demand for high quality reclaimed water, in both developed and developing country. In recent years, membrane technologies have started to play a vital role in solving water scarcity on the planet, which is in close association with global climate change. The major reasons are that membranes allow not only effective separation of various contaminants from water sources to achieve the required quality, but also exploration of water resources from non-traditional sources such as wastewater and seawater for direct or indirect portable reuse (Li, 2017). However, reclaimed water requires advanced treatment due to the presence of a plethora of low molecular weight, neutral molecules such as nitrosamines, 1,4-dioxane, disinfection byproducts, endocrine disruptors, etc. which pass through the membrane filtration steps (Stefan, 2017). Hence, water treatment technology featured with high efficiency and low cost is urgently required (Zhang et al., 2016). Forward osmosis is one of the emerging technologies.

2.3 Forward osmosis membranes

The relatively high energy demand to operate conventional pressure driven membrane processes (NF, RO) still remains a challenge to be managed (Li, 2017) As alternatives to reverse osmosis (RO), forward osmosis (FO) has received considerable interest for water and energy related applications in recent years (Li et al., 2016). Forward osmosis (FO) is a novel low-energy and a natural osmotically-driven membrane process, in which the driving force for separation is the difference in chemical potential between a concentrated draw solution and a broad range of aqueous solutions (Dong et al., 2014, Li, 2017). FO uses a semi-permeable membrane which is placed between a feed solution (FS) with low osmotic pressure and a draw solution (DS) with high osmotic pressure. Water flows from the FS side to the DS side across the FO membrane automatically under the difference of natural osmotic pressure and, at the same time, salts and contaminants in the FS are being rejected (Sun et al., 2016, Zhao et al., 2012).

FO membrane has a few advantages, these being: 1. low energy consumption because of the use of osmotic pressure instead of hydraulic pressure as the driving force (Nguyen et al., 2016a) ; 2. high rejection of various contaminants due to small pore radius (mean radius of 0.25−0.30 nm) (Lu and He, 2015), thus increasing the quality of the product water; 3. low fouling propensities resulting from the dense and tight surface structure of the FO membrane (Nguyen et al., 2016b, Nguyen et al., 2016a); 4. simple operation of membrane cleaning, and high permeability recovery (Li et al., 2016). As a result, FO exhibits great promise to address the global issues regarding water resource shortage and environmental pollution via effective wastewater treatment and reclamation (Sun et al., 2016).

In the past decade, FO has been used for seawater desalination, during oil and gas production for fracking and produced water volume minimisation, the food industry for stream concentration, industrial and municipal wastewater treatment as well as for purifying water in emergency situations (Dong et al., 2014, Li, 2017).

2.3.1 Mass transfer to the FO membrane

Despite the possible new approaches and the benefits of using a FO process, FO still has limitations, such as relatively low water flux, solute diffusion from the DS into the FS (and vice versa), concentration polarisation (CP), and membrane fouling (Chun et al., 2017). The water transport in FO can be expressed by the general equation (Lee et al., 1981):

$$J_W = \mathrm{A}(\sigma \Delta\pi - \Delta P) \tag{2.1}$$

Where A is the water permeability coefficient of the membrane, σ is the reflection coefficient, Δπ is osmotic pressure difference across the membrane and ΔP is the applied hydraulic pressure. The difference (σΔπ-ΔP) represents the effective driving force (Cath et al., 2006a, Zhao et al., 2012). An equation (Equation 2.2) for the flux of osmosis membranes when a low concentrated solution is facing the thin-film side of the membrane, and the porous support (mesh) is facing a high concentrated solution was derived by (Loeb et al., 1997).

$$J_W = \frac{1}{k} \ln\left(\frac{\pi_{\mathrm{Hi}}}{\pi_{\mathrm{Low}}}\right) \tag{2.2}$$

Where Jw is the osmotic water flux (LMH), K is the solute resistivity of the membrane ($m^2 \cdot h \cdot L{-1}$), πHi is the osmotic pressure in the high concentrated solution (bar), and

πLow is the osmotic pressure in the low concentrated solution (bar). Loeb's equation can be slightly modified and applied to model the flux decline of the dilution experiment. One of the most critical problems is the significantly lower water flux obtained in experimental study than that estimated with the osmotic pressure difference (Wei and Tang, 2015). Two factors significantly impeding osmotically-driven membrane filtration performance are concentration polarization (CP) and reverse permeation of draw solutes (Chun et al., 2017). Theoretically, a semipermeable membrane would reject any dissolved draw solute into the feed solution. Real membranes are not perfectly semipermeable, and a small amount of salt will permeate the membrane in forward osmosis process. One effect of this salt permeation is to reduce the effective osmotic pressure difference across the membrane (Lee et al., 1981). Reverse salt transport not only reduces the driving force, but may also enhance membrane fouling, and have inhibitory or toxic effects on the microbial community in the membrane bioreactor systems. Therefore, it is essential to understand the mass transport in osmotically-driven membrane systems to understand fouling (Chun et al., 2017).

Concentration polarization is a common and inevitable phenomenon in both pressure driven and osmotically driven membrane processes (Zhao et al., 2012). Concentration polarization (CP) occurs when the difference in salt concentration across the active later is different than the difference in concentration in the bulk solutions itself which results in much lower water flux than expected (Cath et al., 2006a). The special flow pattern in the FO as well as other osmotically driven membrane processes leads to lower-than-expected water flux is often attributed to a concentration polarization layer build-up within the membrane support. Specifically, two types of concentration polarization (CP) phenomena – external CP and internal CP – can take place in osmotic-driven membrane processes as discussed below (Cath et al., 2006a). CP can refer to the formation of a concentration layer at the membrane surface, defined as external concentration polarization (ECP), or in the porous structure of asymmetric membranes, defined as internal concentration polarization (ICP); both reduce the driving force of the osmotic process, and thus, the water flow through the membrane decreases. ECP can be controlled by several hydrodynamic techniques such as increasing the cross-flow velocity (Linares et al., 2017).

When the feed is placed against the support layer of an asymmetric membrane (as in PRO applications), water enters the porous support layer and diffuses across the active layer into the draw solution. The salt in the feed freely enters the open structure as it is transported into this layer by convective water flow. The salt cannot easily penetrate the active layer from the support layer side and therefore increases in concentration within the porous layer. This is referred to as concentrative ICP (McCutcheon and Elimelech, 2006). When the feed solution is against the active layer and the draw solution is against the backing layer, as in the case of FO desalination, the ICP phenomenon now occurs on the permeate side. We refer to this as dilutive ICP since the draw solution is diluted by the permeate water within the porous support of the membrane(McCutcheon and Elimelech, 2006). It can be clearly seen in Figure 2.3**.** that the osmotic pressure difference between the bulk feed and bulk draw solution (Δπ bulk) is higher than the osmotic pressure difference across the membrane (Δπm) due to external CP and that the effective osmotic pressure driving force (Δπeff) is even lower due to internal CP (Cath et al., 2006a).

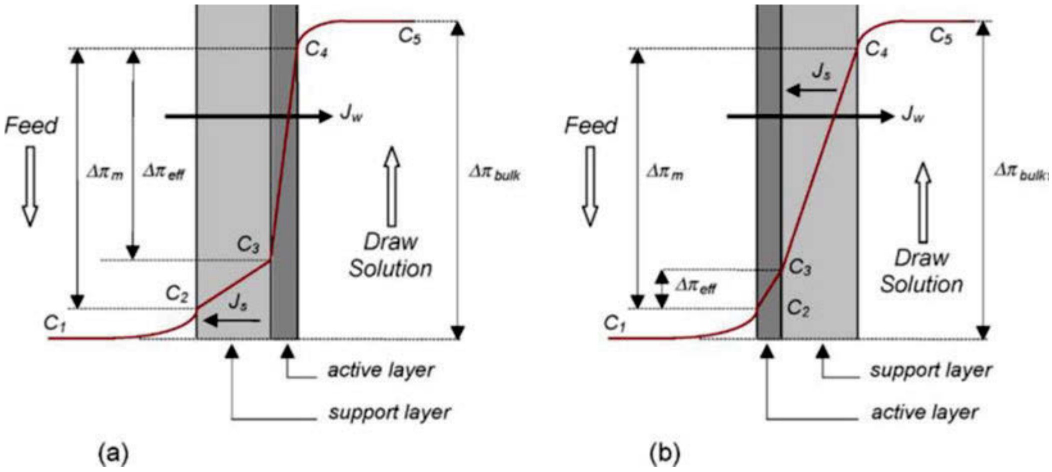

Figure 2.3. Concentrative internal CP and (b) dilutive internal CP across a composite or asymmetric membrane in FO Adapted from (Cath et al., 2006a).

The ICP phenomenon was first modelled by (Lee et al., 1981) in the context of pressure retarded osmosis. A simplified version of ICP model was later developed by (Loeb et al., 1997) for forward osmosis:

$$J_W = K_m \ln \mathrm{A}\left(\frac{\pi_{draw} - J_W + \mathrm{B}}{\pi_{feed} + \mathrm{B}}\right) \quad \text{(AL-DS, concentrative ICP)} \qquad (2.3)$$

$$J_W = K_m \ln \mathrm{A}\left(\frac{\pi_{draw} + \mathrm{B}}{\pi_{feed} + J_W + \mathrm{B}}\right) \quad \text{(AL-FS, diluted ICP)} \qquad (2.4)$$

where Jw is the volumetric flux of water; Km is the mass transfer coefficient for the membrane porous support layer; A and B are the water permeability and solute permeability of the rejection layer, respectively; and $\boldsymbol{\pi}_{\text{draw}}$ and $\boldsymbol{\pi}_{\text{feed}}$ are the osmotic pressure of the draw solution and that of the feed water, respectively (Xiao et al., 2011).

The earliest FO studies found that ICP could reduce the water flux by more than 80% (Zhao et al., 2012). ICP is very minimally affected by changing the hydraulic conditions in the membrane cell, but it is affected by the orientation of the dense layer of the membrane. Other studies refer to the overall performance of the membranes and concludes that the optimal configuration to prevent membrane damage is with the active layer facing the feed solution, reducing the ICP in the support layer, because the direction of the water flow is opposite to the concentration of the bulk draw solution into this layer; this configuration is also effective against membrane fouling (Linares et al., 2017).

2.3.2 FO Membrane material

Membrane properties significantly impact membrane transport behaviour, especially the water permeability and feed solute passage (Shon et al., 2016e). The ideal FO membrane should have high water permeability and salt rejection, should be thin without a porous support layer to remove the ICP effects, and should also have good mechanical strength. However, providing a thin membrane without support layers is a big challenge since it does not provide adequate mechanical strength to carry the water flow inside the membrane module (Yip et al., 2010). FO membranes currently available in the market include asymmetric cellulose triacetate (CTA) and polyamide thin-film composite (TFC) materials (Luo et al., 2016b). However, commercially available membranes lack one or more of the above-mentioned characteristics, thereby inhibiting their application to an FO process (Shon et al., 2016e).

Most existing FO and OMBR studies were performed with cellulose triacetate (CTA) based FO membranes are from Hydration Technology Innovations (HTI, Albany, OR). These membranes consist of a CTA active layer embedded in a thin polyester mesh for mechanical support. The hydrophilic nature of cellulose renders these membranes readily wettable. Thus, CTA FO membranes can simultaneously achieve high water permeability and excellent fouling resistance (Luo et al., 2016b). However, it was shown that CTA membranes are vulnerable to hydrolysis and biological degradation (Hou et al., 2016).

The existing CTA FO membrane has low working pH range, low pure water permeability and low salt rejection which are a cause of concern for FO process (Yip et al., 2010). For example, a commercial asymmetric CTA membrane specifically designed for FO process is chemically stable only within a small pH range from 4 to 7 such that the membrane will hydrolyse when it is exposed to an ammonium bicarbonate draw solution (Shon et al., 2016e).

TFC FO membranes comprise a thin, selective polyamide active layer on a porous supporting layer and are reported to have much higher water flux and better solute rejection than the existing CTA FO membrane. In addition, TFC membranes possess high chemical and biodegradation resistance and high mechanical strength (Hou et al., 2016). Indeed, the thick and dense support layer used for TFC-RO is not suitable for FO process as it causes severe ICP. Recent development of new membrane materials has resulted in the fabrication and commercialisation of polyamide TFC membranes. The innovative claim for this TFC has been the modification of the support layer which is significantly thinner and also highly porous considerably reduces the ICP making it suitable for FO applications (Hunt, 2007). In particular, the hollow fibre thin film composite FO membrane is a significant breakthrough since flat sheet membranes are more complicated for the design of spiral-wound modules accommodating two different and independent flows in the module separately. Moreover, conventional asymmetric single-skinned FO membranes face a dilemma of either experiencing more severe dilutive ICP in AL-FS or having much higher fouling propensity in AL-DS. In order to resolve this issue (Wang et al., 2010) proposed a novel membrane structure design for FO applications comprising a highly porous sublayer sandwiched between two selective skin layers via phase inversion. This typical sandwiched structure, has a primary selective layer to reject the draw solute and a relatively loose secondary selective layer to reject feed foulants (Duong et al., 2014). Double skinned FO membrane could mitigate the adverse influence of internal concentration polarization (ICP) by preventing the salt and other solutes in the draw solution from penetrating into the membrane porous support (Wang et al., 2010, Wang et al., 2016c). (Qi et al., 2012) synthesized a first novel crosslinked layer-by-layer (LbL) forward osmosis (FO) membranes with a double-skinned design. They reported that the double-skinned LbL membranes demonstrated much better antifouling performance compared to the single-skinned counterpart. To further improve the membranes performances in terms of water permeability and antifouling characteristics in another study, (Song et al., 2015) developed novel CNT incorporated double-skinned FO membranes by interfacial polymerization.

Modelling study form Tang et al. (2011) revealed that double-skinned TFC membranes have minimum effect on eliminating the ICP occurred in the membrane support layer, and lower water flux was obtained compared to single-skinned TFC membrane (Ong et al., 2017). Although the formation of a second skin layer in this prototype FO membrane may induce additional water transport resistance and decrease water permeation flux, the adverse effect of the internal concentration polarization can be significantly mitigated (Wang et al., 2010).

A flurry of membrane development work has been carried out to improve FO membrane properties focusing on minimizing ICP and achieving higher water permeate flux and solute rejection (Shon et al., 2016e). Biomimetic membranes, based on aquaporins, have the potential to further advance FO and OMBR processes. Aquaporins are water-channel proteins in biological cell membrane. Each aquaporin channel is capable of transporting up to 3x10^9 water molecules per second through a single aquaporin subunit (promote very high water flux rates) and absolute rejection of all other solutes (Engelhardt et al., 2018). By introducing aquaporins into polymeric membranes, the permeability-selectivity trade-off of conventional TFC membranes could be considerably overcome. Li et al. (2017c) reported that incorporating aquaporin proteins into the polyamide selective layer of a hollow fiber TFC FO membrane could largely increase the membrane water flux while reduce the reverse salt flux. Nevertheless, there is a dearth in current literature on the performance of biomimetic FO membranes in OMBR operation, where the biocompatibility of these newly developed membranes is challenged. Table 2.1 below shows comparison of CTA , TFC and Aquaporin membrane (Luo et al., 2018b).

Table 2.1 Key properties of the aquaporin and two conventional membranes. Adapted from (Luo et al., 2018b)

Parameters	Aquaporin	CTA	TFC
Pure water permeability (L/m^2 h-bar)	2.09 ± 0.02	0.84 ± 0.03	2.50 ± 0.25
Salt (NaCl) permeability (L/m^2 h)	0.07 ± 0.01	0.32 ± 0.06	0.19 ± 0.03
Membrane structural parameter(µm)	301 ± 36	575 ± 28	245 ± 35
Observed NaCl rejection (%)	99.9 ± 0.1	92.0 ± 1.4	98.0 ± 0.2
Contact angel (°)	74.5 ± 8.9	60.4 ± 5.2	42.3 ± 3.2
Zeta potential at pH 8 (mV)	-16.4 ± 2.3	-4.5 ± 0.4	-14.2 ± 0.5

2.4 Osmotic membrane biological reactors (OMBRs)

Osmotic membrane bioreactors (OsMBRs) are a recent breakthrough technology designed to treat wastewater (Nguyen et al., 2017). Osmotic membrane bioreactor (OMBR) that combined FO membrane separation and conventional active sludge process emerged in recent (Li et al., 2016). Compared to conventional MBR that employs hydraulically driven membrane processes, such as microfiltration and ultrafiltration, OMBR retains the inherent advantages of both membrane bioreactor (MBR) and FO such as better product water quality, high removal of trace organic chemicals, low fouling propensity and higher fouling reversibility and low energy cost (Li et al., 2016, Luo et al., 2018a). The better retention of organic matter by FO may lead to 1) improved biological degradation of recalcitrant organics due to the prolonged retention time for organic matter, 2) reduced dissolved organic content in treated effluent, and 3) a likely enhanced removal for micropollutants (Xiao et al., 2011). OMBRs can be engineered for clean water extraction, nutrient recovery, and toxic organic compounds biodegradation from wastewater (Qiu and Ting, 2014b). Research in recent years reported more novel aspects of this process in achieving facilitated phosphorus recovery, bioenergy recovery and enhanced removal of emerging pollutants (Qiu et al., 2016). However, there are still some drawbacks associated with this new technology including salt accumulation, forward osmosis (FO) membrane fouling and draw solution (DS) regeneration (Cicek et al., 1999). Table 2.2 shows comparison of conventional MBR and emerging osmotic membrane bioreactor (OMBR)(Upen Bharwada, 2011).

2.4.1 OMBR operational and configuration for water reclamation

A common OMBR includes a bioreactor, a FO separation unit and a DS system that makes possible the regeneration of the DS or the provision of fresh DS. An OMBR is a hybrid of the FO membrane process for water extraction, aeration process for the cultivation of activated sludge to treatment wastewater contaminants and lastly, a pressurized filtration stage such as RO or NF system for drinking water recovery and draw solute regeneration. Water is extracted from the impaired water source such as domestic wastewater and causing dilution of the draw solution. Using a pressurized filtration stage such as RO or NF system in the downstream, product water is obtained and draw solution is regenerated as well (Shon et al., 2016d). OMBR can be operated either in osmotic dilution mode or in combination with an additional process to re-concentrate draw solution and produce reusable water (Figure 2.4).

Table 2.2 Comparison of conventional MBR and OMBR (Upen Bharwada, 2011).

MBR	OMBR
MF or UF membranes are employed. Comparatively less rejection is obtained than FO.	FO membrane cab achieve similar rejection as RO.
In MBR 30%-75% TOC removal efficiencies can be achieved.	In OMBR process the FO membrane with a 98% TOC removal efficiency allows the downstream RO to operate in longer cycles.
In MBR removal of P can be achieved by addition of flocculants followed by larger particle flocs filtration or rejection through membrane.	The OMBR system rejects P more cost effectively because the removal is based on size exclusion without flocculation.
In MBR fouling is major issue and cleaning cost is significant.	The OMBR offers ultralow fouling characteristics and less cleaning cost due to lack of hydraulic pressure across the membrane.
In MBR system design has evolved to continually improve the economy of energy required for scouring, backwashing and aeration.	In OMBR fine bubble diffusion for oxygen transfer and a longer interval between backwashing and cleaning also should require less energy.
In MBRs total energy estimate is 2-4 kWh/m^3 water treated.	In OMBR total energy estimate is 2.80 kWh/m^3 water treated.

In the osmotic dilution mode, draw solution, such as seawater and fertilizers, can be discharged or reused directly and the extraction of clean water is not necessary (Ansari et al., 2016), thereby allowing OMBR to consume much less energy than conventional MBR. When the production of clean water is needed, a desalination process, such as RO or membrane distillation (MD), is commonly integrated with OMBR (Holloway et al., 2015b). The desalination process subsequent to OMBR can provide an additional barrier to further improve the product water quality. On the other hand, high contaminant removal by OMBR can prevent the downstream membrane process from severe fouling (Song et al., 2018). As shown in Figure 2.4, an OMBR has three unique characteristics as a wastewater treatment process as followings: (1) a biological process, (2) a physicochemical process with high selectivity for both organic and inorganic pollutants, and (3) an energy efficient process (Kim, 2014). The non-porous nature of the semi permeable FO membranes allows to reject 98% of total organic carbon (TOC) in the OMBR system (Achilli et al., 2009). The high removal of TOC reduces the amount of soluble organics within the diluted draw solution, the contaminants majorly responsible for the fouling of the RO process downstream (Shon et al., 2016d). Cornelissen et al. (2011) reported that OMBR-RO could reduce the capital cost of wastewater reuse by 25% compared to conventional MBR-RO using the UF membrane. Cost saving achieved by OMBR-RO depends on the assumption that the cost and water permeability of the FO membrane are comparable to those of the UF membrane (Luo et al., 2017b).

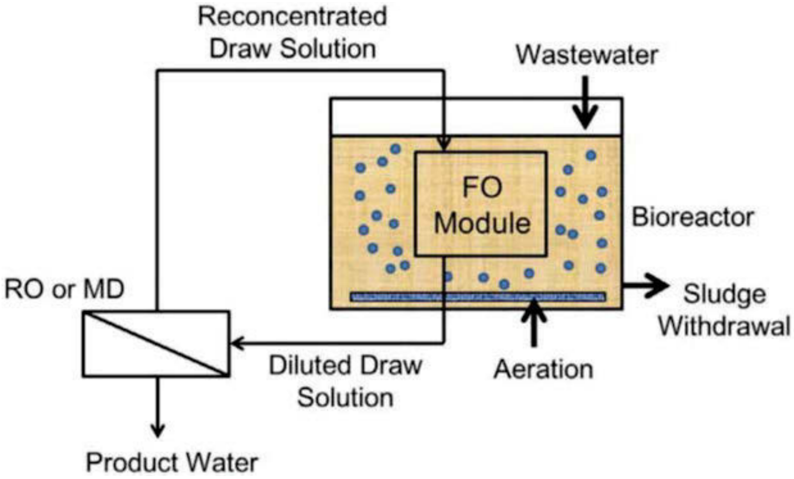

Figure 2.4. OMBR hybrid system for wastewater treatment and reuse. Adapted from (Song et al., 2018).

OMBRs are also divided into two configurations. Figure 2.5 demonstrates two representative OMBR configurations, cross-flow and submerged OMBR in accordance with the position of membrane cells. Cross-flow type features the effect of fouling reduction, while submerged type possesses a higher effective membrane area than other configurations. Several sensors (pH, conductivity, weight, water level, etc.,) are installed for the monitoring of water and other molecules transported in OMBR systems. Recently, the device for supplemental draw solute supply is also required to maintain constant draw solution concentration during long term experiments, which can eliminate the over estimation of flux decline (Shon et al., 2016b).

2.4.2 Salt accumulation in OMBR

Osmotically driven membrane processes such as OMBR are an emerging technologies that show promise in water and wastewater treatment (Phillip et al., 2010). Due to the use of FO membranes in OMBR, salt accumulation will occur in the bioreactor due to two mechanisms: 1) retention of solutes from the feed water, and 2) reverse diffusion of solutes from the high concentration draw solution solution (Cath et al., 2006b, McCutcheon and Elimelech, 2006, Xiao et al., 2011). In OMBR process most of the colloidal and dissolved solids will retain inside the bioreactor. This provides the desired high level of separation, but also leads to salt accumulation to the feed side with potentially adverse impacts on the biological treatment and the operation (Lay et al., 2010). This issue is important, because elevated feed salinity can have consequences in the form of a diminished driving force, membrane scaling if the precipitation limit of the relevant salts is exceeded, and when FO is integrated with a bioreactor, the elevated salinity will have further impacts in physicochemical and biological ways (Lay et al., 2012). The second phenomenon for OMBRs is known as reverse salt flux (RSF), solute diffusion from the DS into the feed, may pose greater limitation on future implementation of OMBR and other osmotic processes (Achilli et al., 2010, Hancock and Cath, 2009). An ideal semipermeable membrane would prevent any dissolved draw solute from permeating into the feed solution. However, no membrane is a perfect barrier, and a small amount of dissolved solute will be transported across the membrane (Phillip et al., 2010). This "reverse salt transport" is expected to occur because of the difference in solute concentration between the DS and the reactor solution (Achilli et al., 2009, Achilli et al., 2010). The reverse salt transport in turn enhances salt accumulation, while reducing the effective driving force due to a lowered net osmotic pressure across membrane and an increased ICP (Hancock and Cath, 2009, Hancock et al., 2011, Yap et al., 2012). Results show that reverse transport of solutes through commercially available FO membranes range between 80 mg to nearly 3,000 mg per liter of water produced. Divalent feed solutes have low permeation rates (less than 1 mmol/m^2-hr) while monovalent ions and uncharged solutes exhibit higher permeation (Hancock and Cath, 2009). Thus, reverse salt transport (RSF) from the DS not only results in a reduced driving force, but may also ave inhibitory or toxic effects on the microbial community inside the reactor (Achilli et al., 2009).

It could also mean additional economic costs for replenishment of the lost draw solutes, and further consideration is needed if the draw solute is of environmental concern (Lay et al., 2012). Increased bioreactor salinity may result in decreased water flux, greater membrane fouling, altering biomass characteristics and bacterial community structure, thereby deteriorating biological carbon and nitrogen removal (Morrow et al., 2018a, Song et al., 2018).

Nevertheless, a major technical challenge to OMBR application is the lack of appropriate draw solutions that could reduce salt accumulation and membrane fouling during long-term operation (Nguyen et al., 2016a). NaCl and $MgCl_2$ may be the best inorganic DS for most water and wastewater applications including OMBR, for their relatively low molecular weight, high solubility, high osmotic pressure that can be given by this solution, easily and economically separated and recycled, and previous interest or utilization in FO research. However, salinity build-up is more severe for OMBR using such inorganic draw solutions, due to their relatively high reverse permeation (Devia et al., 2015, Makki and Zghair, 2014, Achilli et al., 2010, Song et al., 2018).

For instance, Holloway et al. (2014) used NaCl salt as the DS for an OMBR system and achieved 96% and 99% removal of chemical oxygen demand (COD) and phosphate with high water flux (5.72 L/m^2 h), respectively. Nevertheless, as monovalent ions (Na^+ with hydrated radius of 0.18 nm and Cl^- with hydrated radius of 0.19 nm could easily pass through the FO membrane (membrane pore of 0.37 nm), TDS concentration in the bioreactor increased approximately 8 g/L after 40 days (Nguyen et al., 2015).

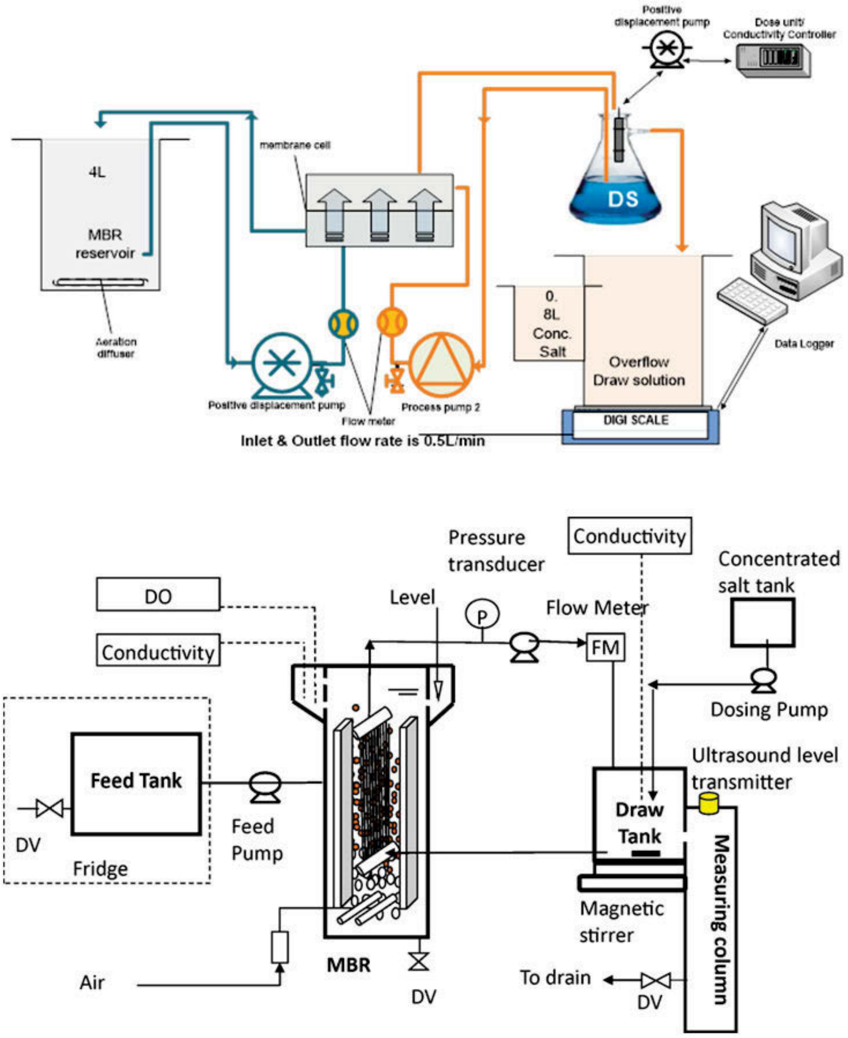

Figure 2.5 Schematic diagram of OMBR: (a) Cross-flow type and (b) submerged type. Adapted from (Shon et al., 2016b) (a) Alturki et al. (2012) and (b) Zhang et al. (2012b).

Moderate to high mixed liquor TDS values have been acknowledged to confer adverse impacts onto bacterial populations that were not acclimatized to highly saline environments. Salt concentrations exceeding 1% have demonstrated the ability to invoke bacterial plasmolysis and/or loss of metabolic activities (Shon et al., 2016c). Ammonia-oxidizing bacteria, which are responsible for ammonia removal via nitrification, are particularly sensitive to salinity and sharp decreases in nitrification efficiency have been reported for bioreactors with salinities ranging from 2 to 15 g/L NaCl. Notably, Holloway et al. (2015b) observed NH_4-N accumulation for about 3 weeks due to high salinity build up (3-8 g/L) in the bioreactor. Elevated salt concentrations had adversely affected microbial community and salinity build up (up to 8 g/L) was the major cause for loss of nitrification. In the same study in next the phase when the system was operated with UF membrane in parallel to FO better NH_4-N removal was achieved (recovery of nitrification) throughout the operation due to low salinity level (1 g/L) employing UF subsystem. Kinetics studies have suggested that nitrogen and phosphorus removal efficiency dropped to 20% and 62%, respectively, when salt concentration was 5% NaCl in the bioreactor (Nguyen et al., 2016b).

2.4.3 Salt accumulation mitigation strategies

Recently, Chang et al. (2017) reported that various researchers have proposed a number of tactics to overcoming the challenge of salinity build-up for sustainable OMBR operation, including regular sludge wastage (Wang et al., 2014a, Wang et al., 2014b), the use of organic or ionic organic draw solutions to prevent salt reversal (Bowden et al., 2012, Ansari et al., 2015), and integration of a porous membrane (e.g. microfiltration (MF) and ultrafiltration (UF) membrane) with OMBR (Holloway et al., 2015b, Holloway et al., 2015a, Wang et al., 2014a, Wang et al., 2014b). Development of new salts (mixtures) or the use of alternative draw solutions instead of conventional ones are emerging as another effective strategy that promises to alleviate the salinity content (Siddique et al., 2017). By applying a group of novel DS (organic and surfactant) with inorganic salt, (Nguyen et al., 2015, Nguyen et al., 2016a) achieved a reduction in reverse salt flux and thus a resultant lower salt accumulation (Qiu et al., 2016). The use of draw solutions with divalent ions would imply lower reverse salt flux. However, it is known that draw solutions containing divalent ions yield lower water fluxes than draw solutions containing monovalent ions at similar osmotic pressure. This is due to the lower diffusivity coefficients of the divalent ions in comparison with those of the monovalent ions (Soler-Cabezas et al., 2018).

Wang et al. (2014a) found that lower SRT was helpful in lowering the accumulated reversed salt. However, in an OMBR system with an operating SRT of 10 days, the bioreactor salinity still increased substantially. Moreover, a short SRT resulted in a low sludge concentration, e.g., the mixed liquor suspended solid (MLSS) was in the range of 1.02 ± 0.10 g/L in the OMBR at SRT of 10 d, which could reduce the performance of an OMBR (Bell et al., 2016, Zhu et al., 2017, Aftab et al., 2017).

Qiu et al. (2016) noted that another promising strategy in controlling salt accumulation is the integration of a microfiltration (MF) or ultrafiltration (UF) unit into a OMBR to develop a hybrid MF/UF-OMBR process as shown in Figure 2.6 (Holloway et al., 2014, Qiu et al., 2015). By applying this approach, (Holloway et al., 2015b, Holloway et al., 2014) showed a stable operation of a pilot UF-MBR treating raw domestic wastewater over a period of four months. Removal to below the detection limit was reported by Holloway et al. (2014) for 15 out of 20 TrOCs investigated in their pilot plant study (Bell et al., 2016). Long-term evaluations of the UF-MBR revealed that the bioreactor salinity could be maintained at relatively low concentrations (1.5 g/L total dissolved solids (TDS)), thereby maintaining the driving force (salinity difference between the bioreactor and DS) for water flux across the FO membrane and limiting any inhibition of the microbial community responsible for carbon oxidation, nitrification/denitrification, and phosphorous removal. In addition to reducing bioreactor salinity, the hybrid UF-OMBR system would produce two different reuse streams: non-potable water (through the UF membrane) and potable water (through the FO and RO membranes) (Holloway et al., 2016). Nutrients can be recovered from the UF permeate as fertilizers or other beneficial products, while the water can be utilized for landscape irrigation (Holloway et al., 2016, Chang et al., 2017).

However, Fane et al. (2015) emphasized that previously mentioned strategies cannot completely address the issue of salinity build-up in OMBR. Indeed, the development of novel FO membranes with low salt permeability is the most effective to control salinity build-up (Luo et al., 2018b).

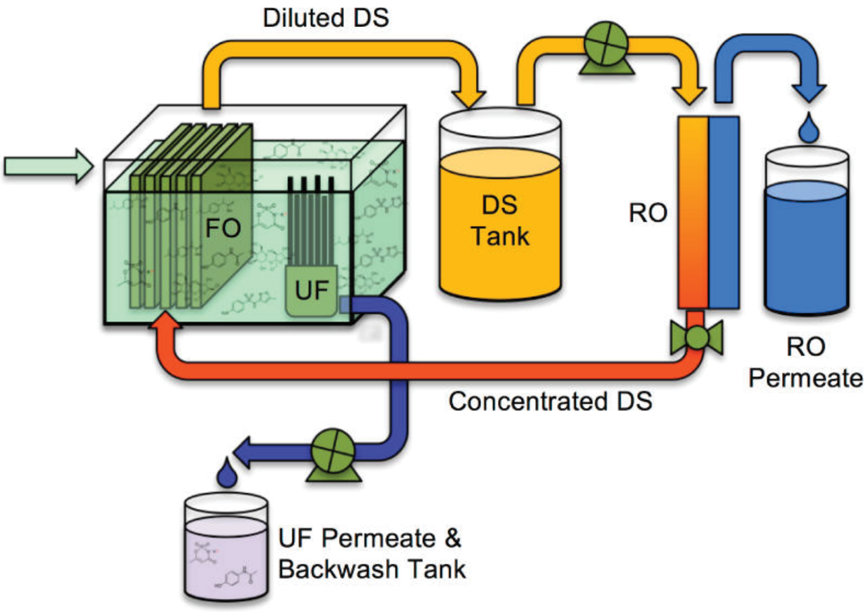

Figure 2.6. A schematic of an integrated UF-MBR system. Adapted from (Holloway et al., 2014).

2.4.4 Membrane fouling in OMBR

Membrane fouling is a key issue for all membrane processes, as it has adverse effect on the membrane performance and results in the increase of operational cost (Sun et al., 2017). However, no matter it is OMBR or direct FO concerned, the performance of the FO membrane is adversely affected by membrane fouling (Sun et al., 2016).

Understanding the fouling behaviour in the FO processes is particularly important because both sides of the FO membrane are in constant contact with impaired waters: the active layer with impaired water and the support layer with synthetic or natural DSs (e.g., seawater or brine) (Chun et al., 2017). Membrane fouling in osmotically driven membrane processes can be classified into four major groups according to the characteristics of foulants:

- Colloidal fouling – deposition of colloidal particles on the membrane;
- Organic fouling – deposition and adsorption of macromolecular organic compounds on the membrane;
- Inorganic scaling – precipitation or crystallization of sparingly dissolved inorganic compounds on the membrane; and
- Biofouling – adhesion and accumulation of microorganisms, and development of biofilm on the membrane (She et al., 2016). In any membrane technology, biofouling control is considered as a major challenge because all other types of fouling are fairly readily avoided by either chemical and physical pre-treatment. However, biofouling formation only requires a few colonies to be developed with microorganisms present in all water systems which tend to adhere to surfaces and multiply on any surface in contact with the water even in an oligotrophic environment (Chun et al., 2017).

Membrane fouling is very complex phenomenon which is affected by the wastewater composition, the operational condition and the property of membrane (structure or material) (Onoda, 2016, Bell et al., 2016). In fact, it has been demonstrated by previous publications that FO membrane fouling played a significant role in water flux decline in OMBRs (Yuan et al., 2015, Wang et al., 2014a). Zhang et al. (2012b) attributed 45% of the total flux decline to FO membrane fouling during the long-term OMBR operation

(Wang et al., 2016c). Salt accumulation also increases the ionic strength of the wastewater, which may increase bacterial adhesion to the membrane and change the membrane surface charge (zeta potential). Coday et al. (2015) demonstrated that increasing ionic strength reduced the negative charge of FO membranes, which can potentially affect membrane fouling propensity and the bidirectional diffusion of ionic constituents across the membrane (Bell et al., 2016, Soler-Cabezas et al., 2018). The reverse diffusion of draw solutes might also affect the fouling tendencies of FO processes. RSF was reported to contribute significantly to flux decline through accelerated CEOP (cake enhanced osmotic pressure), in which the draw salts diffused were captured by the fouling layer and thus accelerated CEOP as shown in Figure 2.7. The accumulation of draw solutes in the cake layer from RSF in FO membrane fouling results in a greater loss of driving force in FO (Kim et al., 2015, Morrow et al., 2018b). Divalent ions are considered to be major contributors to fouling due to bridging between the divalent ions and organic matter, resulting in more severe membrane fouling (Bell et al., 2016).

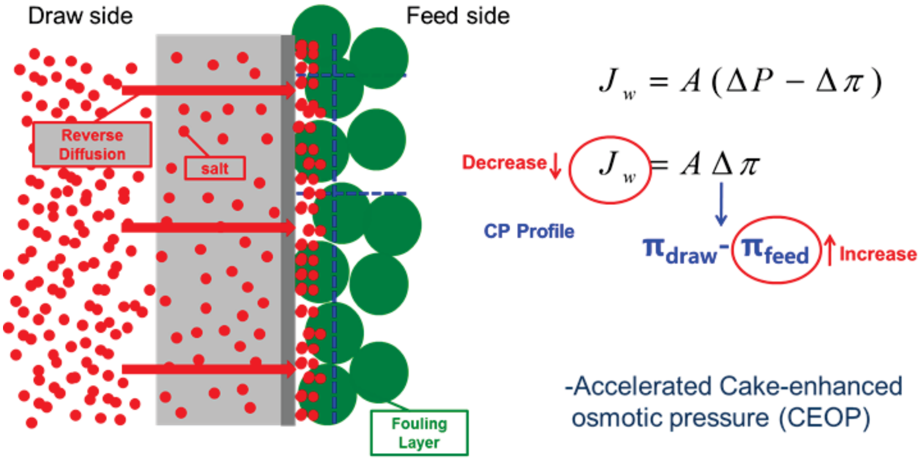

Figure 2.7. Schematic illustration of cake enhanced osmotic pressure. Adapted from (Lee et al., 2010a).

Bell et al. (2016) compared the fouling behaviour of two different FO membranes, cellulose triacetate membranes and polyamide thin film composite (TFC) membranes. This group of authors published that TFC membranes were more prone to fouling during a long-term OMBR study (Luján-Facundo et al., 2017). FO fouling is generally more pronounced when the active rejection layer is facing the draw solution (AL-DS), since this orientation is prone to severe internal pore clogging in the porous membrane support layer (Zhang et al., 2012b). Membrane fouling, concentration polarization (both ICP and ECP) and reverse solute diffusion (RSD) are interrelated closely to each other in ODMPs and can be modeled using the osmotic-resistance filtration model (She et al., 2016). Therefore, greater attentions should be paid to FO membrane fouling mechanisms and its mitigation methods in order to further enhance the water flux in OMBRs.

2.4.5 Foulant characterization and antifouling strategies

Membrane fouling hinders the efficiency and productivity of OMBR by decreasing permeate flux, membrane selectivity and service lifetime (Luo et al., 2018a). As a result, it is important to visualize and characterize the spatial distribution and transport of key membrane foulants in OMBR. This fouling characteristics provide insights in the design of pre-treatment process, the formulation of operational procedure, and fouling mitigation strategies (Luo et al., 2018a, Chun et al., 2017). In practical OMBR applications, the membrane is often fouled by a mixture of different types of foulants from natural or industrial wastewaters and the membrane fouling can be identified using a series of tools (She et al., 2016).

Some of the common microbiological characterisation techniques include adenosine triphosphate (ATP) measurements, EPS quantification, and application of confocal laser scanning microscopy (CLSM). Based on these surface characteristics, it has been found that the propensity for fouling increases for membranes that are highly charged, more hydrophobic, and rougher (Chun et al., 2017). A number of optical and nonoptical imaging techniques have been developed previously for use in the study of biofilm structure and development. These techniques include, surface-enhanced Raman spectroscopy (SERS), light microscopy, electron microscopy, transmission electron microscopy (TEM) 3D visualization, infrared spectroscopy, reflectance spectroscopy, optical fluorometry, nuclear magnetic resonance imaging NMRI, atomic force microscopy AFM, and photoacoustic spectroscopy (Xi et al., 2006).

To observe the morphology of the foulants on the membrane, CLSM and SEM are applied. In addition, a FTIR spectrophotometer is used (Zhang et al., 2012b) for the characterization of the composition of biopolymers in the cake layer (Shon et al., 2016a). Confocal laser scanning microscopy (CLSM) combined with multiple fluorescence labeling is one of the best approaches for nondestructive in situ examination of FO membrane biofouling induced by EPS and bacterial cells, which could obtain the structure, distribution and function of biofouling constituents at the microscale (Wang et al., 2016c). Some other emerging and non-invasive fouling characterisation methods include Ultrasonic time-domain reflectometry (UTDR), Nuclear magnetic resonance (NMR) microscopy, electrical impedance spectroscopy (EIS), radio activation analysis, computerised axial tomography (CAT), small-angle neutron scattering (SANS) and electrochemical methods (Chun et al., 2017). Optical coherence tomography (OCT) imaging is increasingly applied in the field of membrane research used to visualize biofilms at the mesoscale (mm-scale) (West et al., 2016). OCT is an optical technique that employs near-infrared light of relatively long wavelength so that a deeper detection with micrometer-resolution can be achieved (Gao et al., 2013). Xi et al. (2006) were first to demonstrate that OCT techniques have the potential for noninvasive, label-free, real-time and in-situ characterization of biofilm thickness and structure without stopping the operation of the membrane filtration unit. Therefore, OCT imaging provides a quantitative, high resolution, spatially-resolved means to capture volumetric imaging of the biofilm in a non-destructive way (Dreszer et al., 2014). Table 2.3 shows summary of techniques used to identify biofilm structure.

To mitigate membrane fouling, various techniques are employed. The membrane fouling which can be recovered by air scrubbing or wiping by sponge is called as reversible fouling, and which cannot be recovered is called as irreversible fouling (Onoda 2016). In OMBR, osmotic backwashing is an effective mean for removing foulants from the membrane surface (Achilli et al. 2009; Yap et al. 2012). During osmotic backwashing water diffuses from the draw solution side to the feed side of the membrane, thereby dislodging attached organic particles and dissolving inorganic foulants from the membrane surface (Holloway, Achilli & Cath 2015). Due to the complexity and time intensive nature of osmotic backwashing, it is important to mitigate FO membrane fouling to minimize the frequency of FO membrane cleaning in OMBR operations (Bell, Holloway & Cath 2016).

Table 2.3. Methods for evaluation of membrane structure. Adapted from (Shon et al., 2016a)

Instruments	**Advantages/disadvantages**
CLSM	• Not only the presence and the viability of the biofilm consortium but also biofilm/substrate interactions can be investigated. • Visualize the 3D structure of biofilms • Optical sectioning of thick biological structures with no out-of-focus disturbance • Fixation step is needed to enhance the permeability of the cell for the gene probes. • Thereby the 3D information is partly lost due to shrinking of the biofilm. Without staining, imaging is not possible so is • Without staining, imaging is not possible so is less suitable for online monitoring.
AFM	• The tip of the probe gives information on the surface contours of the sample. • Direct visualization of intact hydrated specimens at high magnification. • It cannot elucidate internal biofilm structures.
OCT	• Optical signal acquisition and processing method allowing extremely high-quality, micrometer-resolution, 3D image from within optical scattering media (or reflecting structure) • Non-invasive
SEM	• The surface topology of the biofilms can be examined at a high magnification. • Shrinking problem due to dehydration and fixation of samples
TEM	• Cross-section gives useful information about the spatial relationships of microorganism within the biofilm matrix. • Sample preparations result in the inclusion of artifacts.
MRI	• Sequences of NMR measurements in the presence of magnetic fields with linear gradient are carried out and a certain space resolution is derived. Finally the generation of 2D images of a sample is possible.

ATR-Spectroscopy	- Limited to a thin layer
FTIR Spectroscopy	- Scanning of the IR absorption in a sample at different wavelengths yields a characteristic "fingerprint" of certain wavelengths in which the radiation has been absorbed stronger than in other ones. - Sufficient to monitor the formation of biofilms thicker than 0.05 mm. - Reported work was limited to pure cultures of Pseudomonas fluorescens

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To recover the irreversible fouling, it needs the chemical cleaning. Due to the low fouling tendency of FO membrane, studies on chemical cleaning of FO membrane are limited. With regard to the fouled cellulose triacetate (CTA) FO membrane, Valladares Linares et al. (2013) have used 1% Alconox and 0.8% sodium ethylenediaminetetraaceticacid (EDTA) to remove the organic foulants, while Yoon et al. (2013) applied 100 mg/L

NaClO for eliminating biofouling (Wang et al., 2017b). Cleaning solutions (Alconox, EDTA, and NaOCl) that have been determined to work well for CTA FO membranes are not compatible with polyamide-based, TFC FO membranes.

Exposure to Alconox and EDTA increases the water flux and RSF through the TFC membrane due to changes in the polymeric structure of the membrane. As an alternative to detergents and EDTA, the polyamide TFC membrane can be cleaned with a basic solution (NaOH) followed by an acid (HCl) mixture without compromising the integrity of the membrane active or support layers (Holloway et al., 2015a).

Nevertheless, the chemical cleaning damages the membrane, because the cost increases and the adverse effect on the environment by the treatment and disposal of spent chemicals are concerned, the frequency of chemical cleaning must be minimized (Onoda, 2016).

2.5 Nutrient removal

Nitrogen and phosphorus are essential elements of life, however, excess nitrogen and phosphorus continuously release into the environment during naturally occurring processes (e.g. weathering, leaching, erosion) and anthropogenic activities (e.g. surface run-off from agricultural and livestock activities, wastewater treatment plants, etc.) (Dafne Crutchik et al., 2017). The presence of excessive amounts of innocuous nutrients can also upset the balance of aquatic ecosystem through eutrophication (Cai et al., 2013). Eutrophication may lead to rapid plant growth and algal bloom in natural water bodies due to nutrient overloading; this leads to oxygen depletion resulting in deterioration of water quality and endangering of aquatic life (Ruiz et al., 2014) (Praveen and Loh, 2016).

The eutrophication problem is expected to increase due to the increasing population, agricultural intensification and industrialization (Dafne Crutchik et al., 2017).

Nevertheless, eutrophication can be reversed by reducing the nutrients load to water bodies. One such solution is to decrease the load of nutrients discharged from wastewater treatment plants. Thus, efficient and reliable nutrients removal and/or recovery technologies are required (Dafne Crutchik et al., 2017). Nitrogen and phosphorus removal/recovery from wastewater can be achieved by biological or physical-chemical processes. The selection of nutrients removal/recovery technologies is determined by the nitrogen and phosphorus concentrations, and consequently the cost-effectiveness of the process (Dafne Crutchik et al., 2017).

Biological nutrient removal (BNR) is a relatively low-cost, reliable and effective means to remove total nitrogen and total phosphorus from wastewater through the use of microorganisms under different environmental conditions in the treatment process (Shrestha, 2013, METCALF and Eddy, 2003). Thus both aerobic and anoxic environments should prevail in order to remove nitrogen (Hai et al., 2014b).

During the complex biological phosphorous removal process, measurable chemical transformations occur, both in the wastewater and within sludge biomass. As shown in Figure 2.8 biological phosphorous removal process is achieved by enriching polyphosphate-accumulating organisms (PAOs) in alternating anaerobic/aerobic wastewater treatment systems. Under anaerobic conditions, PAOs are able to take up easy-biodegradable organic carbon with energy supplied from polyphosphate degradation. Under the subsequent aerobic conditions, PAOs take up excess phosphorus from wastewater. Wasting the phosphorus rich biomass following uptake, excess phosphorus removal from wastewater is achieved (Wu and Rodgers, 2010).

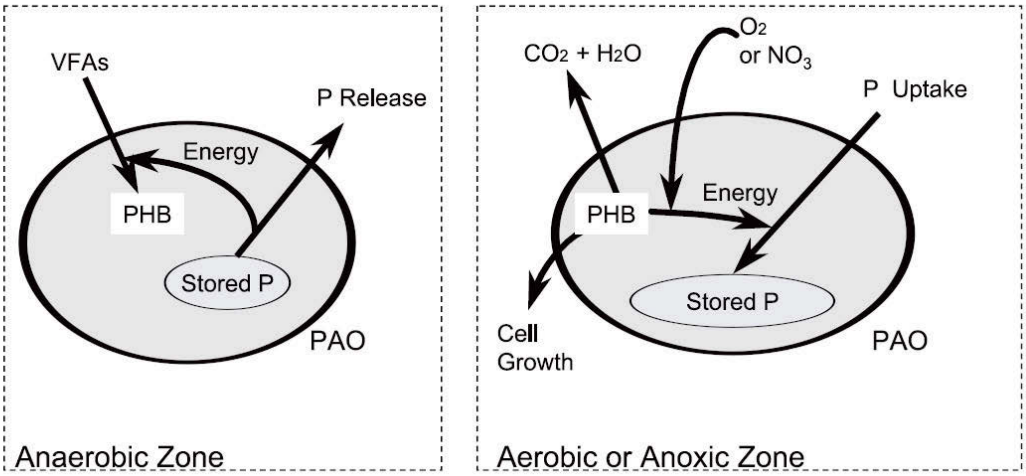


Figure 2.8 Biological phosphorous removal. Adapted from (Jeyanayagam, 2005).

2.5.1 Nitrogen removal

Nitrogen is an essential nutrient for plants and animals. Approximately 80 percent of the Earth's atmosphere is composed of nitrogen, and it is a key element of proteins and cells. Wastewater generated from municipal, industrial and agricultural processes mostly contain nitrogen (Shrestha, 2013). The per capita contribution of nitrogen in domestic wastewater is about one-fifth of that for biochemical oxygen demand (BOD). Total nitrogen in domestic wastewater typically ranges from 20 to 70 mg/L for low to high strength wastewater (Moore, 2010, Tchobanoglous, 2003). Discharge limit for nitrogen are country specific. Technology based nutrient limits are now prevalent or being promulgated in Europe and Asia including more recently in large population centres of China and India. The typical design requirements for total nitrogen is 10 mg/L, regardless of the strength of wastewater and of the carbon/nitrogen ratio. More stringent nitrogen limits are applied to sensitive estuarine systems, with limits as low as 3–4 mg N/L for total nitrogen. Ammonia requirements are more variable and are as low as 1 mg N/L or not specified in many cases (Li, 2017).

Biological nitrogen removal in wastewater treatment occurs by two primary mechanisms: 1) biomass synthesis (nitrogen assimilation) and sludge wasting, and 2) two main separated but complementary processes called nitrification and denitrification able to achieve high levels of nitrogen removal (Dafne Crutchik et al., 2017, Moore, 2010).

2.5.1.1 Nitrification

Nitrification in an activated sludge (AS) systems is defined as the biological oxidation of the ammonium present in wastewater to its most oxidized form (nitrate). In AS systems, this process is performed by two different nitrifying bacteria communities, and thus, nitrification is considered as a two-step process. Ammonia Oxidizing Bacteria (AOB) firstly oxidize ammonium to nitrite (nitritation, equation 2.1) and Nitrite Oxidizing Bacteria (NOB) perform the nitrate formation (nitratation, equation 2.2). The nitrification process has the following stoichiometric equations (Wiesmann, 1994) (Dafne Crutchik et al., 2017, Wiesmann, 1994).

$$NH_4^+ + 3/2\ O_2 \xrightarrow{\textbf{AOB}} NO_2^- + H_2O + 2H^+ \ (\textit{Nitrosonomas spp., Nitrosospira spp}) \qquad (2.1)$$

$$NO_2^- + 1/2\ O_2 \xrightarrow{\textbf{NOB}} NO_3^- \ (\textit{Nitrobacter spp., Nitrospira spp.}) \qquad (2.2)$$

Stoichiometrically the oxygen requirements for the first and second reactions are 3/2 x 32/14 = 3.43 and 1/2 x 32/14 = 1.14 mgO_2/mgN. Hence the stoichiometric conversion of ammonia to nitrate, both expressed as N, requires 2 x 32/14 = 4.57 mgO_2/mgN utilized. Taking into account the ammonia utilized for synthesis of nitrifier cell mass, the oxygen requirement per mgN nitrified is slightly less, with reported values down to 4.3 mgO_2/mgN (Grady Jr et al., 2011).

It is important to take into account the affectations or inhibitions in the nitrification process. Temperature, pH, free ammonia (FA) and free nitrous acid (FNA) or the lack of inorganic carbon presence are one of the most deeply studied parameter that could affect this process (Dafne Crutchik et al., 2017). Table 2.4 summarizes the operational parameters favouring nitrification. Generally, increasing temperature, mean retention time, substrate nitrogen, and a sufficiently high sludge retention time t_{RX} are beneficial for nitrifying bacteria. They result in sufficient MLVSS. A sludge age of t_{RX} > 4–6 days is needed to achieve nitrification. The presence of healthy and adequate nitrifying bacteria is the basic requirement for successful nitrification (Wiesmann et al., 2006).

Table 2.4 Operational parameters influencing nitrification. Adapted from (Wiesmann et al., 2006)

Parameters	Optimal range and remarks
Oxygen concentration	2-3 mg/L O_2, limits nitrification
pH	pH 7.2-8.0, pH < 5.5 and > 9.0 critical
Temperature	28-32° C, temperature < 5 and > 40° C critical
Ammonia concentration	Inhibits Nitrosomonas > 10 mg/L, Nitrobacter > 0.1 mg/L
Ammonium ion concentration	Inhibits Nitrification > 400-500 mg/L
Solid retention time	> 4-6 days, increases with decreasing temperature
Hydraulic retention time	>10 h at low temperatures
Mixed liquor suspended solids	>2 g/L MLVSS
F/M ratio	~ 0.5 g NH_4-N /g MLVSS recommended

2.5.1.2 Denitrification

The following step inside de nitrogen removal is the denitrification. Denitrification is the reduction of nitrate to nitrogen gas (N_2), which is removed from the system achieving the wastewater nitrogen removal (Dafne Crutchik et al., 2017). Most denitrifying organisms are facultative aerobic chemoorgano-heterotrophic bacteria which make up approximately 80% of the bacteria within an activated sludge environment (Wiesmann et al., 2006). This process is composed of different steps (Equation 2.3) starting with nitrate reduction to nitrite, followed by nitrite reduction to nitric oxide and nitrous oxide and finally to nitrogen gas (Gujer, Henze, Takahashi & van Loosdrecht 1999) (Dafne Crutchik et al., 2017). Under anoxic conditions nitrite and nitrate serve as electron acceptors instead of O_2 and organic substrates as electron donors for ATP production at very low oxygen concentration (Wiesmann et al., 2006).

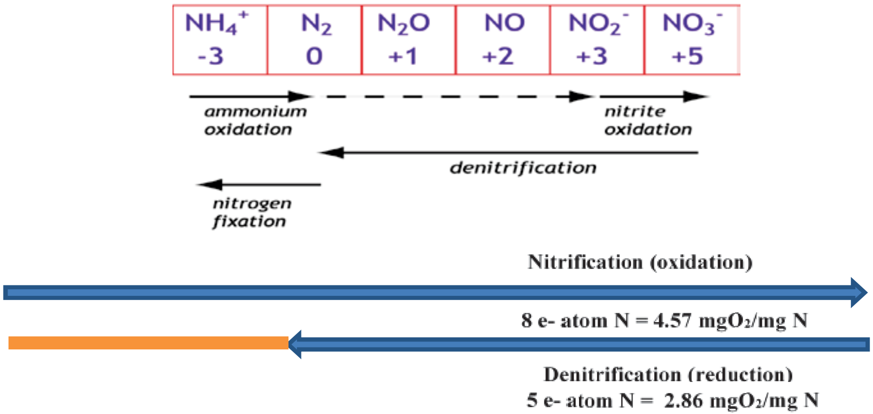
$$NO3^- \longrightarrow NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2 \qquad (2.3)$$

The benefits of denitrification include (i) reduction in nitrate concentration which ameliorates the problem of rising sludge from denitrification in the secondary settling tank, (ii) recovery of alkalinity and (iii) reduction in oxygen demand (Henze et al., 2008). With regard to reduction in oxygen demand, under anoxic conditions, nitrate serves as electron acceptor instead of dissolved oxygen in the degradation of organics (COD) by facultative heterotrophic organisms. The oxygen equivalent of nitrate is 2.86 $mgO_2/mgNO_3$-N which means that 1 mg NO_3-N denitrified to N_2 gas has the same electron accepting capacity as 2.86 mg of oxygen. In nitrification to nitrate, the ammonia donates 8 electrons (e-)/mol, the N changing from an e- state of -3 to +5. In denitrification to N_2, the nitrate accepts 5 e-/mol, the N changing from an e- state of +5 to 0. Because 4.57 mgO_2/mgN are required for nitrification, the oxygen equivalent of nitrate in denitrification to N_2 is 5/8 x 4.57 = 2.86 $mgO_2/mgNO_3$-N (Table 2.5). Therefore, for every 1 mg NO_3-N denitrified to N_2 gas in the anoxic zone, during which about 8.6 mgCOD is utilized, 2.86 mg less oxygen needs to be supplied to the aerobic zone. Because the oxygen requirement to form the nitrate from ammonia is 4.57 $mgO_2/mgNO_3$-N, and 2.86 $mgO_2/mgNO_3$-N is "recovered" in denitrification to N_2 gas, a maximum of 2.86/4.57 or 5/8ths = 0.63 of the nitrification oxygen demand can be recovered. A comparison of the nitrification and denitrification reactions is given in Table 2.5 (Henze et al., 2008).

Thus, nutrient removal may also reduce a treatment plant's overall operating costs. When aerobic biological treatment processes must nitrify wastewater, denitrifying the effluent (converting nitrate-nitrogen to atmospheric nitrogen) can recover lost oxygen and alkalinity, thereby saving aeration energy. Denitrification also can reduce or eliminate the need for chemicals to maintain an optimum pH for biological treatment. Finally, biological nutrient removal (BNR) may produce a sludge with better settling properties than the sludge produced via conventional treatment (Agency, 2007). Denitrification needs certain favourable conditions, such as the presence of organic substrate, very low dissolved oxygen concentration, correct pH and temperature (Wiesmann et al., 2006). Table 2.6 summarizes the operational factors favouring denitrification.

Table 2.5 Comparison of nitrification and denitrification processes. Adapted from (Grady Jr et al., 2011)

	Nitrification	Denitrification
Form	Ammonia (NH_4+)	Nitrate (NO_3^-)
Function	Electron donor	Electron acceptor
Half reaction	Oxidation	Reduction
Organisms	Autotrophs	Heterotrophs
Environment	Aerobic	Anoxic



Nitrification: 4.57 mgO_2/mg NH_4-N nitrified to NO_3-N
Denitrification: 2.86 mgO_2 recovered/ mg NO_3-N denitrified to N_2 gas
Therefore, denitrification allows at best 62.5 % (5/8 or 2.86/4.57) recovery of the nitrification

2.6 Nitrogen removal process configurations

Biological nutrient removal (BNR) from wastewater may be performed by adopting various process configurations. Some BNR systems are designed to remove only TN or TP, while others remove both (Münch et al., 1996, USEPA, 2007).

USEPA 2007 report on categorised Biological Nutrient Removal (BNR) process configurations as follows:

- Modified Ludzack-Ettinger (MLE) Process – continuous-flow suspended-growth process with an initial anoxic stage followed by an aerobic stage; used to remove TN.

Table 2.6 Operational parameters influencing denitrification. Adapted from (Wiesmann et al., 2006)

Parameters	Optimal range and remarks
Organic carbon	Main control parameter, ratio of 3:1 (organics as COD to NO_2 and NO_3) is optimal for complete denitrification, and above 3:2 causes increase in NO_2 and NO_3.
Oxygen concentration	Inhibits denitrification, obvious inhibition of denitrification at > 0.2 mg/L O_2 concentration.
pH	Affects enzymatic activity of denitrifying bacteria, 7.0 < pH optimum < 7.5.
Temperature	Denitrification rate increases with increasing temperature until 35°C; very low rate below 5°C.
Redox potential	+50 to -50 mV, above +50 mV aerobic conditions dominate.

- A/O Process – MLE process preceded by an initial anaerobic stage; used to remove both TN and TP.
- Step Feed Process – alternating anoxic and aerobic stages; however, influent flow is split to several feed locations and the recycle sludge stream is sent to the beginning of the process; used to remove TN.
- Modified Bardenpho Process – Bardenpho process with addition of an initial anaerobic zone; used to remove both TN and TP.
- Bardenpho Process (Four-Stage) – continuous-flow suspended-growth process with alternating anoxic/aerobic/anoxic/aerobic stages; used to remove TN.
- Sequencing Batch Reactor (SBR) Process – suspended-growth batch process sequenced to simulate the four-stage process; used to remove TN (TP removal is inconsistent).

- Modified University of Cape Town (UCT) Process – A/O Process with a second anoxic stage where the internal nitrate recycle is returned; used to remove both TN and TP.
- Rotating Biological Contactor (RBC) Process – continuous-flow process using RBCs with sequential anoxic/aerobic stages; used to remove TN.
- Oxidation Ditch – continuous-flow process using looped channels to create time sequenced anoxic, aerobic, and anaerobic zones; used to remove both TN and TP (USEPA, 2007).

2.6.1 Modified Ludzak–Ettinger (MLE) process

The primary process for biological nitrogen removal consists of an aerobic stage for nitrification and an anoxic stage for denitrification shows a two stage biological nitrogen removal system (Ludzack and Ettinger 1962) called a modified Ludzak–Ettinger (MLE) process (Figure 2.9). They were the first to propose a single sludge nitrification–denitrification process using biodegradable organics in the influent wastewater (Wiesmann et al., 2006). The Modified Ludzack-Ettinger configuration is composed of an anoxic and aerobic tanks and a secondary settler. The influent wastewater is first fed to the anoxic tank for denitrification and next to the aerobic zone for nitrification. An internal recycle flow from the aerobic tank to the head of the anoxic tank provides an extra nitrate for denitrification. After these two processes (anoxic and aerobic), the wastewater goes to the secondary settler for a clarification (Boucher et al., 2009). The MLE process involves recycling activated sludge and a portion of an activated sludge basin’s effluent back to the first (anoxic) tank. The recycled nitrate is converted to nitrogen gas in the anoxic tank (2014).

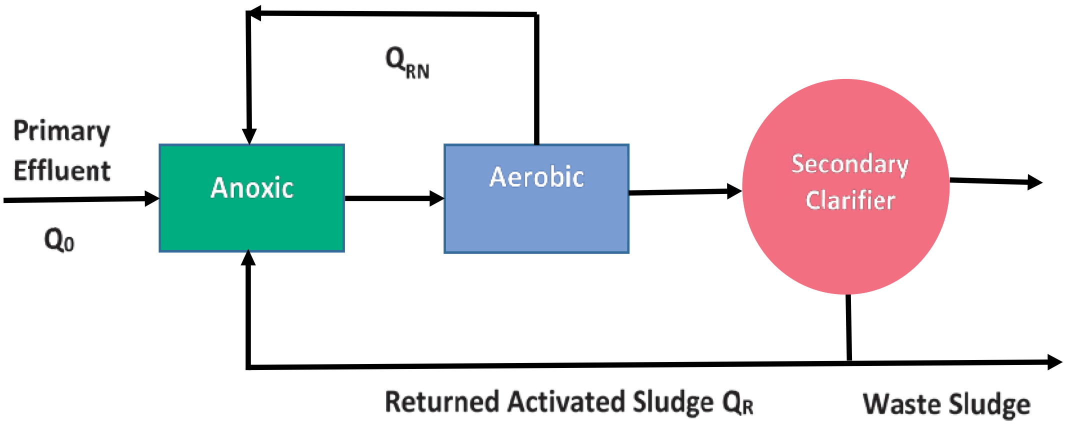


Figure 2.9 Modified Ludzak–Ettinger (MLE) process. Adapted from (Wiesmann et al., 2006).

One drawback of this process is the remaining NO_3^- which is discharged after formation because a typical maximum recycle flow rate is Q_{RN}~ $5(Q_0+Q_R)$. At higher Q_{RN}, the energy consumption for pumping is too high, resulting in high operational costs without a noticeable increase in N removal. This process enables excellent nitrification and a good degree of denitrification down to 4–8 mg/L total nitrogen (Wiesmann et al., 2006).

2.6.2 Step feed process

Anoxic zones can be established in a conventional step feed process to increase mixed-liquor concentrations in the early stages, resulting in a four-stage BNR step-feed process with a 30 to 40% longer SRT than that of a conventional plug-flow arrangement (Figure 2.10). If the anoxic and oxic reactors are the same size, a four-stage system should have an influent flow split of about 15:35:30:20% so the F:M ratio will be the same in each step. Each stage should have its own influent controls. The flow into the last step is critical because the nitrate produced there will not be reduced (Agency, 2007). The step-feed system can be operated with an anoxic zone in each pass to produce 6-8 mg/L TN. Step-feed also offers other advantages, such as lower solids loading to the final clarifiers, higher SRT for the same tank volume, and prevention of solids washout during high-flow conditions by using the first pass for sludge reaeration (Jeyanayagam, 2005).

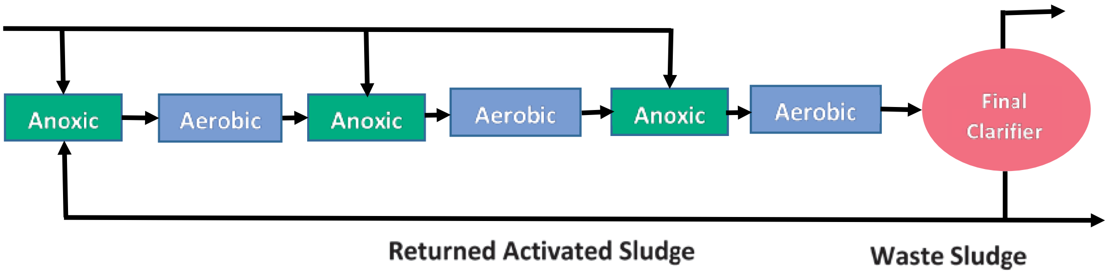


Figure 2.10 Step Feed Process. Adapted from (Grissop, 2010).

2.6.3 Bardenpho process (Four-stage)

A four stage Bardenpho process is a MLE process with an additional set of anoxic and aerobic tanks added to remove nitrate that is inefficient for an MLE process to remove. Additional BOD or methanol does not need to be added to the last anoxic tank to reduce effluent nitrate, but methanol addition will further improve nitrate removal. The breakdown of the activated sludge releases BOD that can be used to remove nitrate, but the breakdown also releases ammonia. Consequently, the ammonia released is converted in the last aerobic tank. Additionally, the last aerobic tank is generally necessary to prevent additional denitrification or anaerobic conditions in the secondary clarifiers (2014). The denitrification process is directly related to the fraction of mixed liquor suspended solids recycle. A Bardenpho process is used for plants to attain a low effluent TN. It can achieve removal rates of 90% and concentrations in the range of 3 - 5 mg/L TN (Noons, 2014). A process flow diagram is shown in Figure 2.11.

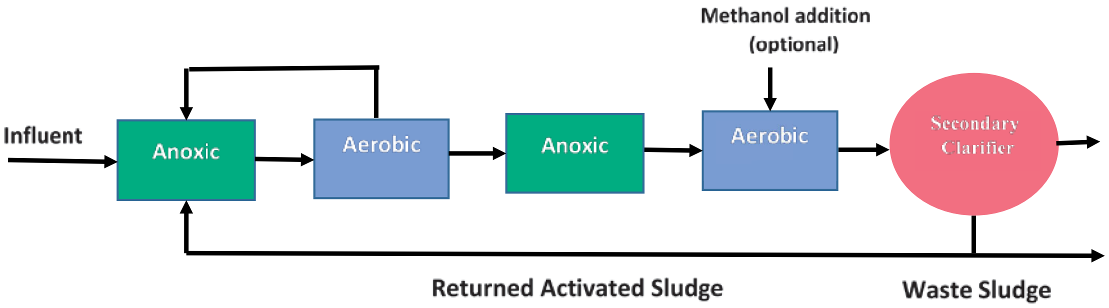


Figure 2.11 Four-stage Bardenpho process. Adapted from (Grissop, 2010).

2.6.4 Sequencing batch reactor (SBR) process

The Sequencing batch reactors (SBR), unlike all continuous BNR systems, operates as a time-orientated activated sludge system. Flow, energy input, and tank volume are varied according to a pre-determined, periodic, operating strategy (Münch et al., 1996). SBR are easy to operate and capable of producing 6-8 mg/L TN with proper cycle times. The use of SBRs eliminates the need for final clarifiers; however, effluent equalization would be required to avoid sizing the downstream disinfection system for peak decant flow rates (Jeyanayagam, 2005). A conventional SBR, which is designed to remove CBOD, consists of four phases: fill, react, settle, and decant (Figure 2.12). To denitrify wastewater, the fill phase is adjusted to “mixed fill”, in which the influent is stirred (but not aerated). At facilities with effluent nitrate limits less than 5 mg/L, a second anoxic phase may be added after the react cycle, and a carbon source (e.g., methanol) may be added to enhance denitrification before the settling and decant phases (Agency, 2007).

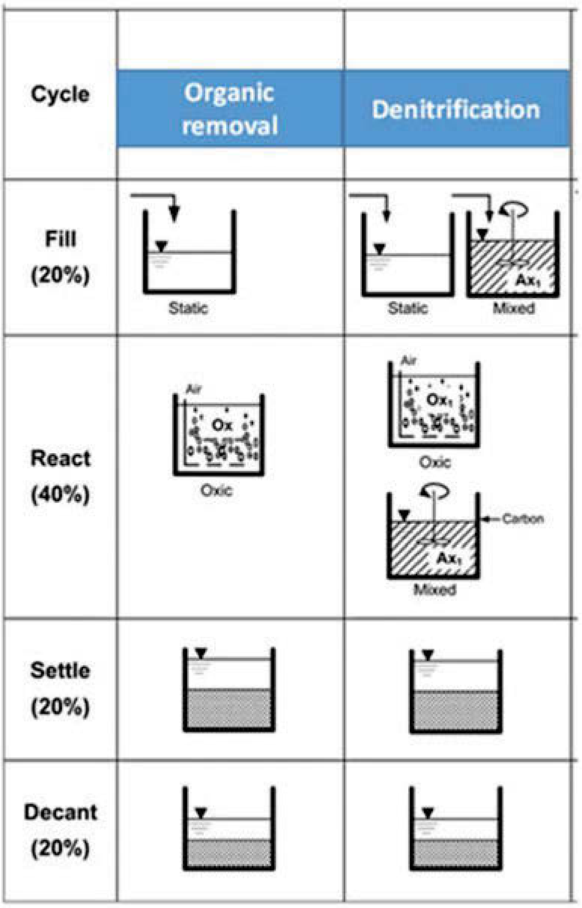


Figure 2.12 Sequencing batch reactor processes. Adapted from USEPA (Agency, 2007).

2.7 Membrane bioreactor (MBR) in nutrient removal

Membrane bioreactors (MBRs) are rapidly gaining in popularity and are a promising technology for future wastewater treatment (Kimura et al., 2008). The integration of a biological nutrients removing (BNR) process with membrane bioreactors (MBRs) is becoming increasingly popular due to its various advantages in wastewater treatment, e.g., flexibility of operation, ability to attain higher sludge age and, consequently, less sludge production, and higher nitrification and denitrification rates (Ahmed et al., 2008). For this reason, MBR has been widely applied to remove organic pollutants as well as nutrient in wastewater (Song et al., 2010). An MBR offers good nitrification conditions because of the high retention of sludge allowed. Therefore, even slowly growing nitrifying bacteria have an excellent chance to establish themselves in the aerated tank (Wiesmann et al., 2007).

Biological nitrogen removal has been achieved by two types of MBR systems: the single-reactor type MBR and the modified Luzack-Ettinger (MLE)-type MBR. The single-reactor-type MBR introduced the alternating aerobic and anoxic conditions to a submerged MBR system by intermittent aeration in the aerobic tank for simultaneous removal of carbon and nitrogen (Yuan et al., 2008). However, to minimize the membrane fouling, filtration operation in this type of MBR is limited during only the aeration period. To make up for this drawback, the MLE-type MBR (a membrane coupled anoxic/oxic process), was developed for continuous filtration operation and removal of carbon and nitrogen simultaneously. The MLE type MBR is composed of a continuous aerated MBR and a separated anoxic tank, in which the mixed liquor was recycled continuously from aerobic zone to anoxic zone (Yuan et al., 2008). Nitrogen removal with preliminary denitrification and with post-denitrification is in operation with MBRs (Wiesmann et al., 2007). In MBR processes reported for TN removal, the pre-denitrification configurations with anoxic zone is always the preferred since the endogenous use of wastewater carbon is possible (Figure 2.13) (Lee et al., 2010b). In anoxic/oxic process, organic matter is mainly consumed in anoxic stage, which apparently resulted in lower competition between nitrifiers and heterotrophs in the next aerobic stage (Fu et al., 2009a).

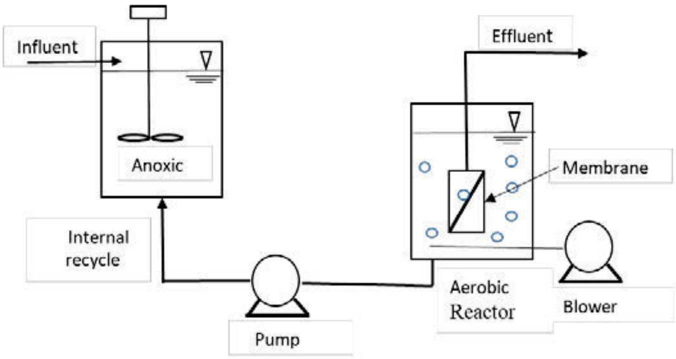


Figure 2.13 Nutrient removal in submerged MBR with preliminary denitrification. Adapted from (Lee et al., 2010b).

In the submerged MBR configuration, to maintain aerobic conditions in the biological reactor and to control membrane fouling, air is blown. This deters the formation of anoxic zones in the reactor, which is essential for denitrification (Basu et al., 2014). On the other hand, separate anoxic compartment impair the beauty of integrated MBRs such as small footprint or ease of operation (Kimura and Watanabe, 2005a). To overcome this limitation, Watanabe and Kimura (2006) introduced the simple concept of baffled membrane bioreactor (BMBR). This involves insertion of baffles in the biological tank, creating separate aerobic and anoxic chambers. The membrane modules are immersed in the aerobic chamber (Basu et al., 2014). Thus, simultaneous nitrification and denitrification (SND) slso called aerobic denitrification, transpires when the two microbial reactions occur at the same time in the same reactor (Holman and Wareham, 2005).

Figure 2.14 shows the concept of the baffled MBR (BMBR). The aeration bubbler is placed inside the baffles. In the operation of the BMBR, membrane filtration is carried out in the constant flow rate mode and the feed rate of the raw wastewater is set at a higher value than that of filtration. When the liquid level is higher than the top of the baffles (Figure 2.14 (a)), the whole reactor is vigorously mixed by aeration and kept aerobic. Addition of the raw wastewater is stopped when the liquid level reaches the set highest level. Then, the liquid level goes down due to membrane filtration and eventually goes beyond the top of the baffles. From this point, the reactor is divided into two zones. The outer zone is going to be anoxic due to oxygen consumption by biomass while the inner zone is going to be kept aerobic due to aeration (Figure 2.14 (b)). When the liquid level reaches the set lowest level, addition of the raw water is initiated and the liquid level is allowed to rise.

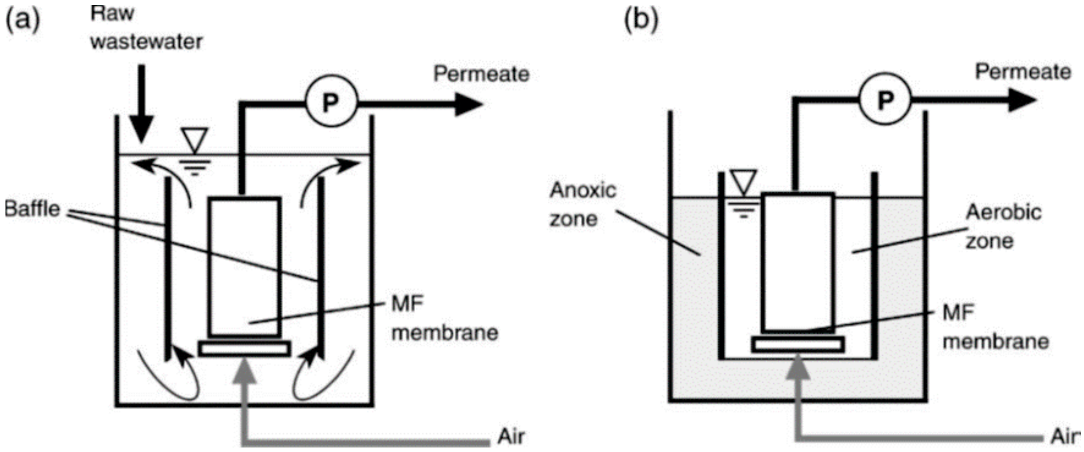


Figure 2.14 Concept of the baffled membrane bioreactor (BMBR). Adapted from (Kimura et al., 2007a).

Eventually, the liquid level exceeds the top of the baffles and the outer zone is going to become aerobic again due to vigorous mixing provided by aeration (Figure 2.14 (a)). Thus, in the BMBR, aerobic and anoxic conditions are alternatively created in the outer zone at a constant interval and therefore improvement in the nutrient removal is expected in comparison to just integrated MBRs, which is principally aerobic (Kimura et al., 2007a, Kimura and Watanabe, 2005a).

2.8 Organic micropollutant removal

Recently, emerging contaminants such as micro-pollutants presence in water poses significant challenge to regulators, engineers and scientific community (Besha et al., 2017). So, ubiquitous contamination by endocrine-disrupting chemicals (EDC), pharmaceutically active compounds, personal care products (PCP), disinfection by-products and industrial chemicals in surface water, groundwater, and reclaimed water is of increasing concern (Coday et al., 2014). Organic micropollutants (OMPs) are a diverse range of emerging organic chemicals (Table 2.7) of either anthropogenic or natural origin (Figure 2.15).

Organic micro-pollutants (OMPs) occur ubiquitously in treated and untreated domestic wastewater at concentrations in the range of a few nanograms per liter (ng/L) to several micrograms per liter (µg/L) (Alturki et al., 2012, Coday et al., 2014, Luo et al., 2015b). While the impacts of anthropogenic organic micropollutants on the environment and humans are not fully elucidated to date, negative effects have been reported for laboratory bioassay tests and real-life test organisms (Luo et al., 2017b, Altmann et al., 2015, Besha et al., 2017). Exposure routes may include dermal contact and consumption of potable water and aquatic and agricultural products (Coday et al., 2014).

However, conventional wastewater treatment plants (WWTPs) incompletely remove emerging pollutants present at low concentrations, moreover, some soluble microbial products (SMPs) formed in activated sludge may be more toxic and/or more mutagenic than original organic compounds (Shon et al., 2006). Thus, WWTPs become point sources of complex contamination of receiving water bodies. Recent trends towards indirect potable water reuse in many metropolitan and arid areas around the world provide further impetus for the effective treatment of trace chemical contaminants (Alturki et al., 2012).

Table 2.7. Classes of emerging compounds. Adapted from (Barceló, 2003)

Compound class	**Examples**
	Pharmaceuticals
Veterinary and human antibiotics	Trimethoprim, erythromycin
Analgesics and anti-inflammatory drugs	Codein, ibuprofen, acetaminophen, acetylsalicylic acid, diclofenac, fenoprofen
Psychiatric drugs	Diazepam
Lipid regulators	Bezafibrate, clofibric acid, fenofibric acid
Beta-blockers	Metoprolol, propranolol, timolol
X-ray contrast media	Lopromide, iopamidol, diatrizoate
Steroids and hormones (contraceptives)	Estradiol, estrone, estriol, diethylstilbestrol
	Personal care products
Fragrances	Nitro, polycyclic, and macrocyclic musks
Sunscreen agents	Benzophenone, methylbenzylidene camphor
Insect repellents	N,N-Dimethyltoluamide (DEET)
Antiseptics	Triclosan, chlorophene
Surfactants and surfactant metabolites	Alkylphenol ethoxylates, alkylphenols (nonylphenol and octylphenol), alkylphenol carboxylates
Flame retardants	Polybrominated diphenyl ethers (PBDEs), tetrabromo bisphenol A, tris(2-chloroethyl)phosphate (TCEP)
Industrial additives and agents	Chelating agents (EDTA), aromatic sulfonates
Gasoline additives	Dialkyl ethers, methyl 4-butyl ether (MTBE)
Disinfection by-products	Iodo-THMs, bromoacids, bromoacetonitriles, bromoaldehydes, cyanoformaldehyde, bromate, NDMA

Figure 2.15 Sources of representative trace organic compounds.

Employing MBR technique a significant portion of suspended solids, organic pollutants, and even salinity could be removed from the wastewater, there are still some challenges to be addressed. For instance, the emerging micro pollutants were difficult to be completely removed by MBR equipped with UF membrane (Wang et al., 2016a, Wang et al., 2017b). On the other hand, RO is an energy intensive treatment technology, which cannot be affordable in some developing countries where coincidently water demand is also high, such as in the Middle East and North Africa (MENA) (Ghaffour, 2009). It is therefore crucial to develop a novel technology capable of removing emerging micro pollutants at low energy cost.

The removal of trace pollutants from wastewater by OMBRs is also a promising strategy. In principle, OMBRs can be applied for removing TOrCs as a combined result of FO membrane rejection and biological degradation (Figure 2.16). FO membrane could achieve excellent rejection of a wide range of TrOCs (Wang et al., 2016a). The removal of trace organics by OMBR was reported (Yap et al., 2012) to be 80% for organics with molecular weight higher than 266 g mol/1, whereas the removal of low molecular weight (<266 g mol/1) appeared to be mostly due to biological degradation (Alturki et al., 2012).Specifically, hydrophilic and/or charged organic compounds with higher molecular weight can generally be effectively rejected by FO membranes mainly via size exclusion, electrostatic exclusion and adsorption to membranes (Wang et al., 2016a). Holloway et al. (2014) illustrated the effectiveness of using biological and membrane treatment for TOrC removal—it was demonstrated that 19 of 20 measured TOrCs in real wastewater were completely removed and rejected by the biological and membrane barriers.

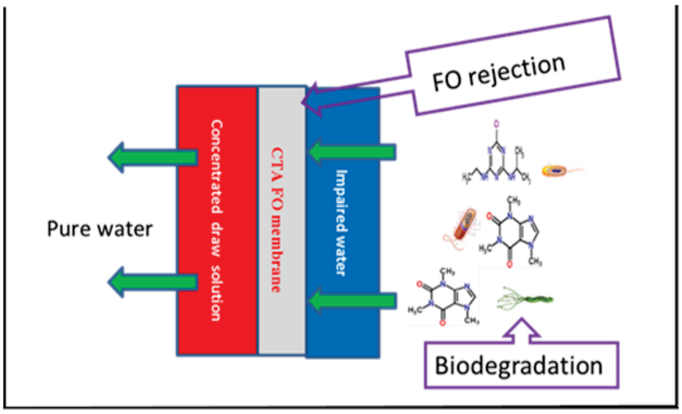


Figure 2.16 Organic micropollutant removal mechanism in OMBR.

2.9 Conclusions

This chapter comprehensively reviews forward osmosis as an emerging technology for wastewater reclamation when combined with bioreactor. FO membrane material, salt accumulation and fouling issues are extensively studied. Also, mitigation techniques for salinity buildup and fouling removal has been discussed. Recently nutrient and organic micropollutant removal are given more consideration in both developed and developing countries specifically imposing stringent limit for total nitrogen removal. Conventional nitrogen removal technologies consume more space, chemical and energy. Therefore

MBR technologies with total nitrogen removal and wastewater reclamation in a single reactor is more attractive alternative. Osmotic membrane bioreactor can successfully employed for water reclamation from various resources including municipal and industrial wastewaters. However, the FO operation has some limitation such as reverse salt diffusion of draw solute and draw solution regeneration requirement. Also, reverse salt diffusion of draw solute often has a negative effect on membrane fouling. Seawater reverse osmosis brine or fertilizer DS can be employed as a DS and after osmosis dilution diluted SWRO brine can be safely discharged to the sea or fertilizer DS can be utilised for fustigation after suitable dilution. Therefore, simultaneous nitrification and denitrification (SND) can be achieved for total nitrogen removal in singe OMBR employing baffles. Moreover, it would be interesting to evaluate OMP removal in different redox condition in a single reactor. Effect of salinity build up on the microorganisms and process performance should be investigated. Based on literature review it appears that scope exists to assess not extensively employed a novel, real time and non- destructive OCT monitoring technique for FO membrane fouling examination.

CHAPTER 3

UNIVERSITY OF TECHNOLOGY SYDNEY

Faculty of Engineering & Information Technology

EXPERIMENTAL INVESTIGATIONS

3 Experimental investigations

3.1 Introduction

The experimental work covers performance evaluation of baffled osmotic membrane bioreactor microfiltration (OMBR-MF) hybrid system and a comprehensive investigation of the nutrient removal, organic micropollutant removal in baffled OMBR-MF hybrid system and fouling characterization of the forward osmosis membrane. Experiments were conducted with various draw solution to elucidate the driving force – flux relationship. FO membranes were evaluated using inorganic and organic DS and with simulated or real sewage as a feed solution (FS). Basic membrane properties such as salt rejection and water permeability for the commercial FO membranes were determined by the RO process. Descriptions of the FO membrane module and general working and operation for novel baffled osmotic membrane bioreactor microfiltration (OMBR-MF) hybrid system are deliberated in this chapter. Other analytical techniques employed during course of the study are discussed. Descriptions of the experimental procedures specific to certain work but not included in detail within this chapter can be found in their respective chapters. The laboratory scale experiments were conducted in four different sets of experiments. The flow chart in Figure 3.1 describes the order of different activities and their interrelation which were carried out during the research time. First two laboratory experiments were performed in School of Civil and Environmental Engineering, University of Technology, Sydney, Australia. The organic micropollutant removal and fouling characterization study was performed at Water Desalination and Reuse Center (WDRC), King Abdullah University of Science and Technology (KAUST), Saudi Arabia.

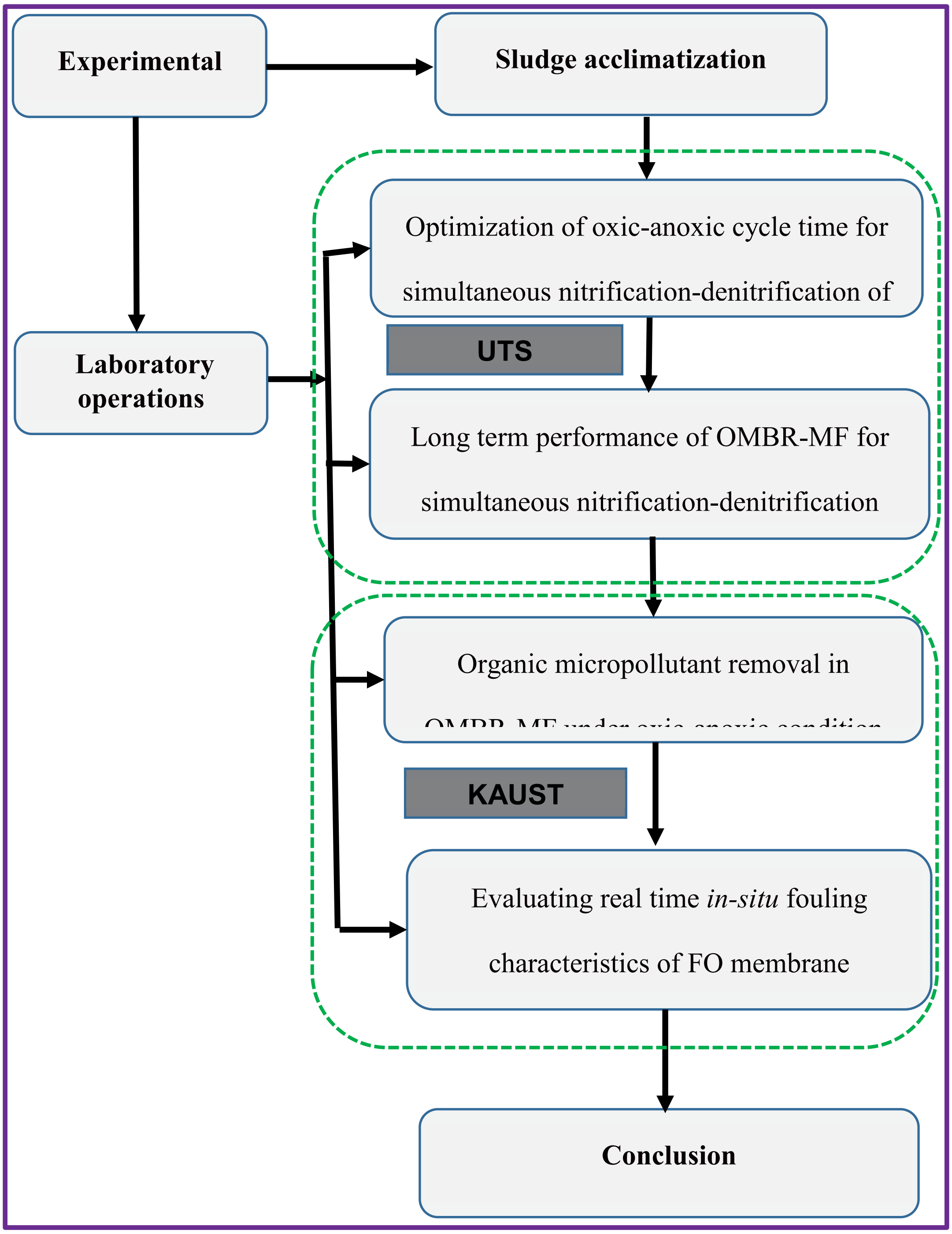


Figure 3.1 Flow chart of the research activities.

For oxic-anoxic cycle time optimization and long term performance of baffled OMBR-MF studies the seed sludge was collected from the recycled water facility at Central Park, Sydney, Australia. Sludge acclimatization is one of the essential components to provide preferably active biomass growth inside the bioreactor so that this biomass can perform well in the wastewater treatment process. The sludge was acclimatized for a month prior to adding into the baffled OMBR-MF system. Baffled OMBR-MF hybrid system working and operating parameters are discussed in the section 3.2.5.

3.2 Experimental Materials

3.2.1 Feed solutions for the baffled OMBR-MF experiments

Simulated and real wastewater as a feed solutions (FS) were used for the lab-scale investigation. In order to provide a continuous source of completely biodegradable organic pollutants and maintain the constant feed concentration, synthetic wastewater was used. The influent water consisted of 300 mg/L glucose, 50 mg/L yeast, 15 mg/L KH_2PO_4, 10 mg/L $FeSO_4$, 60 mg/L $(NH_4)_2SO_4$, and 30 mg/L urea. This wastewater contains glucose as the main carbon source and ammonium sulphate and potassium phosphate as the main source of nutrient. The synthetic wastewater prepared daily and had concentrations of total organic carbon (TOC), ammonium nitrogen (NH_4-N), total nitrogen and phosphate (PO_4-P) of 100, 16, 28 and 3.5 mg/L, respectively. For fouling characterization experiments real wastewater was employed.

3.2.2 Draw solutions for the OMBR-MF experiments

For OMBR-MF study described in chapter 4 and chapter 5 simulated sea water reverese osmosis brine (SWRO) was employed as a draw solution. DS were prepared by dissolving 64 g/L (1.1 M NaCl) sodium chloride in deionized (DI) water. Osmotic pressure and diffusivity were obtained by OLI Stream Analyzer 3.2 (OLI System Inc., Morris Plains, NJ, USA). For 1.1 M NaCl, electrical conductivity and osmotic pressure are 91.26 mS/cm and 51.78 atm, respectively. In addition to the SWRO Brine draw solutes, other draw solutes such as SOA, KH_2PO_4, KCl and Na-acetate were also used in the experiments in

Chapter 6 and 7 for the purpose of making comparative studies. The details of such DS are provided in those respective chapters.

3.2.3 Forward osmosis (FO) and microfiltration (MF) membrane characteristics

The FO membranes used in this study were a flat-sheet TFC polyamide (PA) membrane (Toray, Korea) and Hydration Technology Innovations made Cellulose triacetate CTA (HTI, Albany, OR, USA) respectively. Membranes were stored in distilled water at 4°C prior to use, and were oriented AL-FS (active layer facing feed solution) during the experiments with the feed solution being the OMBR mixed liquor. The TFC membrane chemistry is proprietary, though it is believed that the TFC membrane has embedded polyester screen support and a negatively charge surface (Luo et al., 2016b). The total effective FO membrane area was 264 cm^2. The MF membrane was supplied by Uniqflux Membranes LLP, India and was made of polyethersulfone (PES) with a nominal pore size of 0.33 μm and an effective surface area of 1000 cm^2. The characteristics of this membrane are shown in Table 3.1.

3.2.4 Forward osmosis (FO) membrane module

The submerged FO membrane module was custom designed and fabricated. Two stainless steel plates were attached to each side of the stainless steel block. The two FO membrane coupons were secured in place on each side of the stainless steel block with the stainless steel plates and then fixed using bolts and nuts. The channel in the membrane module ran through the stainless steel block having a width of 11 cm, a length of 12 cm, and a depth of 0.5 cm. Mesh spacers were used on DS side to provide additional support to the membrane and promote mixing of DS. Two ¼” nozzles were provided on each side of the stainless steel plates allowing DS to flow through the channel (Figure 3.2).

Table 3.1 Characteristics of FO and MF membranes used in this study

Characteristics	**TFC FO membrane**	**CTA FO membrane**	**MF membrane**
Membrane area m^2	0.0264	0.0264	0.1
Material	TFC PA*	CTA	PES*
Geometry	Flat sheet	Flat sheet	Hollow fibre
Supplier	Toray, Korea	HTI, USA	Uniqflux Membranes LLP, India
A LMH/bar*	1.63	1.17	NA
B LMH*	0.65	0.98	NA
S (μm)	312	473	NA
Outer diameter	NA	NA	1.0 mm
Module working length	NA	NA	15.5 cm
Pore size	NA	NA	0.33 μm
Fiber no. of membrane	NA	NA	210

*TFC PA: Thin film composite polyamide, PES: Polyether sulphone, LMH: Litres per cubic meter per hour, Hydration Technology Innovations (HTI) (Albany, OR, USA)

3.2.5 Laboratory-scale OMBR-MF experimental set-up

A laboratory-scale baffled OMBR-MF system was used in this study and a schematic of the system is shown in Figure 3.3. This hybrid system consisted of a feed solution reservoir, a plexiglass bioreactor with a submerged plate and-frame FO membrane cell and a hollow fiber MF membrane module, a concentrated DS reservoir and a diluted DS reservoir. The bioreactor tank (i.e., 24.5 cm length * 15.5 cm width * 40 cm height) had an effective volume of 11.5 L. On the three inside walls of the tank, plexiglass partition of 25 cm length was running from top to 5 cm above the bottom of the tank thus making hollow baffle box inside the tank with a the size of 18.5 cm length, 12.5 cm width and 25 cm height. The baffles were bent at approximately 30° angle in the end (3.5 cm length) to avoid dead zone formation and to attain thorough mixing of biomass. The volume ratio of the outer tank to the inner tank was approximately 1.9 when the water level was at the top of the inserted baffles (Figure 3.4). By changing the position of the level controller, the oxic and anoxic cycle times can be adjusted accordingly. The concept and operating details of the baffled reactor is discussed elsewhere (Kimura et al., 2007a).

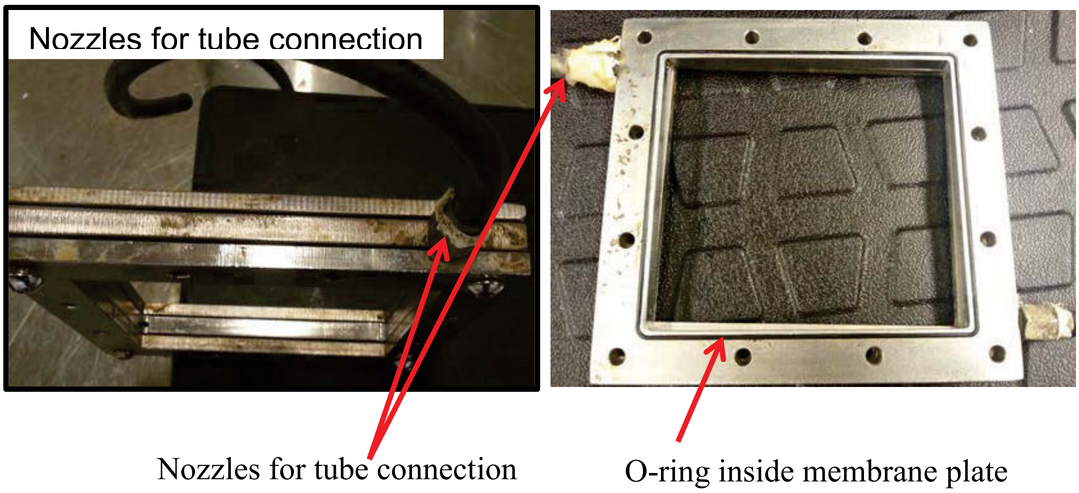


Figure 3.2 Membrane module.

A plate-and-frame membrane module was prepared using commercial TFC FO membranes (Toray, Korea) and the module was immersed in the bioreactor tank for osmotic filtration. FO membrane samples were suspended vertically and parallel to the MF membrane module. The air diffuser was installed inside the oxic chamber of the bioreactor for oxygen supply at 2-3 litres per minute (LPM) air-flow rate thus subjected both membranes to air scouring. The MF membrane, operated continuously, was driven by a peristaltic pump (Longer BT100 2 J). The MF permeate flux was changed manually in accordance with the change of FO water flux in order to maintain stable oxic and anoxic cycle times during the entire operation.

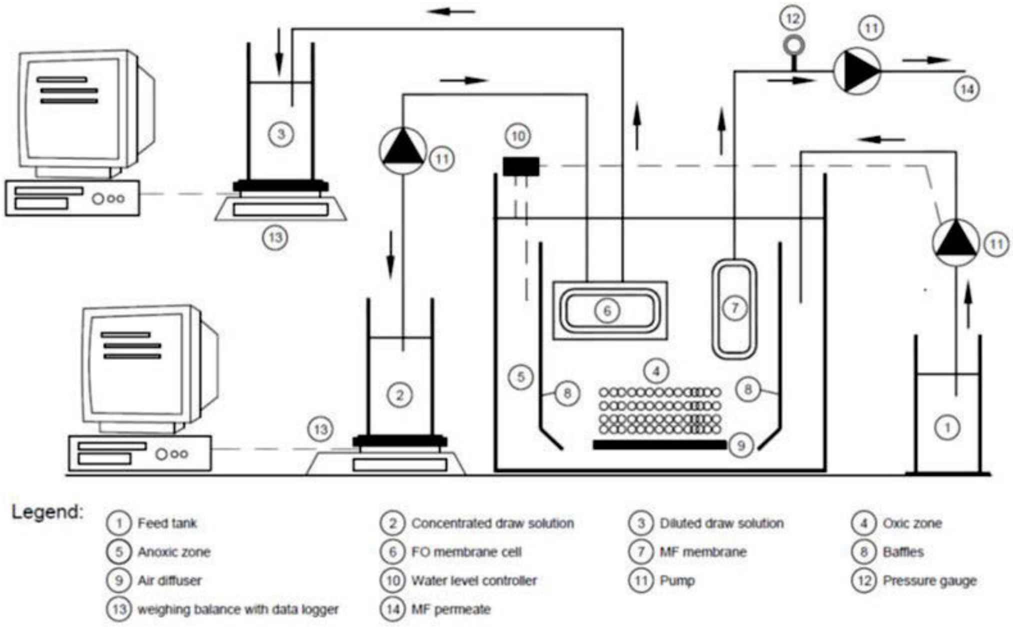


Figure 3.3 OMBR-MF hybrid system experimental set-up.

A high resolution (±0.1 kPa) pressure sensor (Keller, Reinacherstrasse, Basel, Switzerland) was installed to record the trans-membrane pressure (TMP). Both of the concentrated and diluted DS reservoirs were placed on the weighing balance (Adam PGL 15001) and connected to a computer. The weight difference between the diluted and used to adjust the oxic-anoxic cycle time as well as to regulate the feed pump (peristaltic pump Longer WT600 2J) to feed synthetic wastewater to the bioreactor.

The OMBR-MF hybrid system was continuously operated under similar conditions at a constant temperature of 22 ± 1 °C. The mixed liquid suspended sludge (MLSS) was adjusted to 4700 mg/L initially. Throughout baffled OMBR-MF operation, the sludge retention time (SRT) was controlled at 115 days by daily wasting 100 mL of mixed liquor from the bioreactor. The hydraulic retention time (HRT) for baffled OMBR + MF combined system was set at 30.25 h. A 1.1 M NaCl DS was used as simulated reverse osmosis (RO) brine. The concentrated DS was refilled twice a day and the diluted DS tank was emptied. The salt accumulation in the bioreactor was determined by monitoring the conductivity of the mixed liquor with a conductivity meter. The pH, total dissolved solids (TDS) and conductivity of the mixed liquor, permeate and DS were measured regularly (HACH, Germany). No membrane cleaning was conducted for both FO and MF membrane during the entire operation.

3.3 Analytical Methods

3.3.1 Measurement of water flux

The experimental water flux Jw (L/m^2 h) was calculated by measuring the net increase in diluted DS volume with time as follows:

$$J_W = \frac{\text{Increase in diluted draw solution volume (L)}}{\text{Time (h)} \times \text{membrane area } (\text{m}^2)} \qquad (3.1)$$

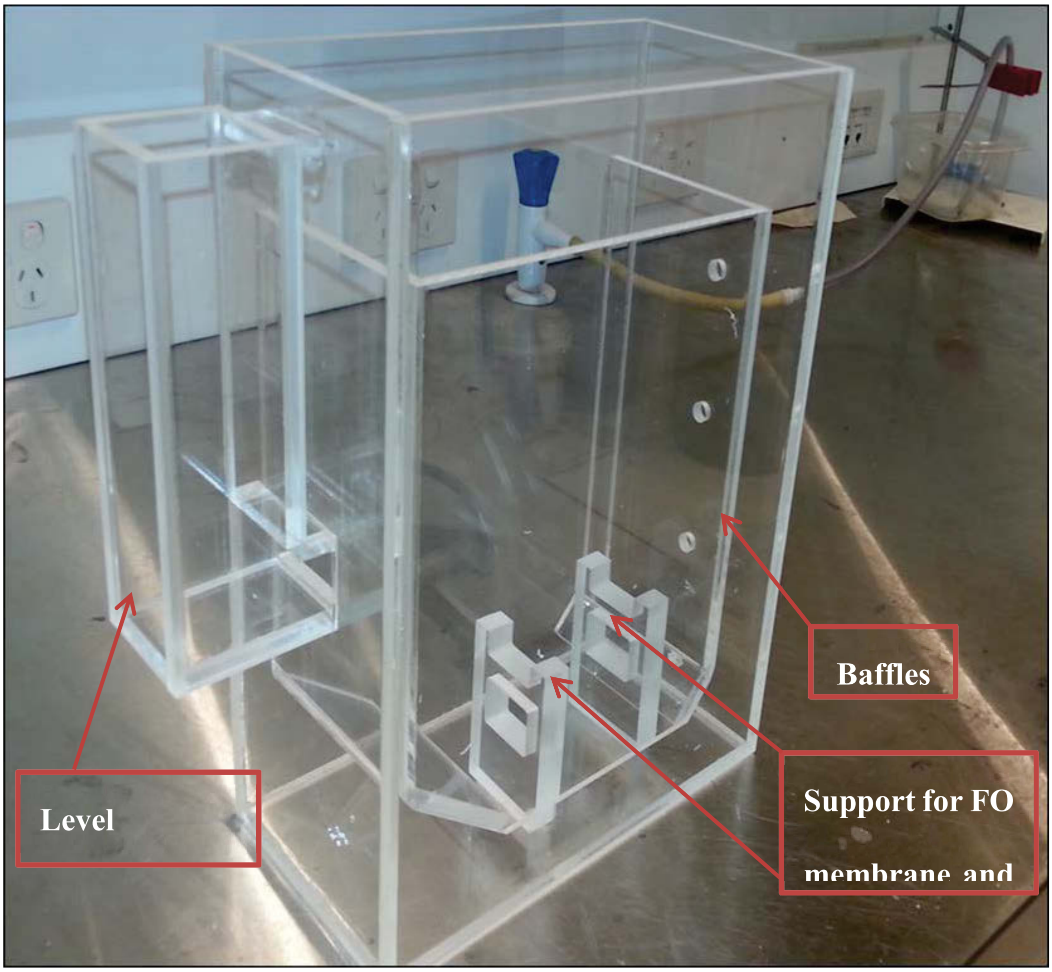


Figure 3.4 Baffled reactor for laboratory experiments.

3.3.2 Basic water quality parameters

COD, NO_2-N, NO_3-N, NH_4-N, TN and PO_4-P were measured using photometric method (Spectroquant Cell Test, NOVA 60, Merck) (Figure 3.5 (a)). Before measurement, samples were filtered using at 0.45µm filters. The pH, total dissolved solids (TDS) and conductivity of the mixed liquor, permeate and DS were measured using HACH make (Germany) portable meter with multiple probes. The concentration of dissolved oxygen was measured by using a DO meter (Vernier, USA). A high resolution (±0.1 kPa) pressure sensor (Keller, Reinacherstrasse, Basel, Switzerland) was installed to record the trans-membrane pressure (TMP).

3.3.3 Specific oxygen uptake rate (SOUR)

YSI 5300 Biological Oxygen Monitor was used to measure the SOUR according to the APHA, AWWA, WEF (1998) (Figure 3.5 (b)). The oxygen consumption measurement can be achieved through the use of oxygen electrode with oxygen permeable Teflon membrane. The voltage generated from the reaction is proportional to the oxygen concentration of the sample and produces oxygen uptake during a period of 2 – 20 min (Shrestha, 2013).

Figure 3.5 (a) Spectroquant Cell Test, NOVA 60, Merck and (b) Biological Oxygen Monitor.

3.3.4 MLSS and MLVSS

The mixed liquid suspended solids (MLSS) and mixed liquid volatile suspended solids (MLVSS) of the mixed liquor in the OMBR were determined according to the APHA, AWWA, WEF (1998). The MLSS and MLVSS were measured by filtering the mixed liquor sample through a GFC Whatman’s 1.2 μm filter paper. The retained solid residue on the filter paper was dried by placing in an oven at 105 ºC for 2 h followed by desiccation for 20 min and finally weighted to calculate the MLSS. Then the dried residue on the filter paper was again heated in a furnace at 550 ºC for 20 min followed by desiccation for 20 min and weighted to calculate MLVSS. The MLSS measuremnt procedure is shown in Figure 3.6.

Figure 3.6 MLSS analysis procedure. Adapted from (Sanchez Huerta, 2016).

3.3.5 Total organic carbon (TOC)

The efficiency of the baffled OMBR-MF in the removal of organic matter was analyzed through the measurement of the total organic carbon (TOC) which was assessed using a Multi N/C 2000 analyzer (Analytik Jena AG) at UTS lab (Figure 3.7) and TOC-V-CSH, Shimadzu, Japan at KAUST lab respectively. TOC analyser operates using a 680°C combustion catalytic oxidation method. Before measurement, samples were filtered using Whatman® GMF filters at 0.45 μm. This machine measures the total organic carbon (TOC), however, since all samples were filtered at 0.45 μm, the measured values correspond to only the dissolved faction. The analysis was performed according to EPA standards (EPA/600/R-09/122). Standards were prepared with potassium hydrogen phthalate (KHP), per the manufacturer's recommendations. For calibration, a standard stock solution of KHP was prepared at 1000ppm, and further dilutions from 0.5-5.0 ppm made from the aforementioned stock solution (Mines, 2012).

Figure 3.7 Total organic carbon (TOC) analyser.

3.3.6 Floc size mesurement

Mean particle size of the sludge flocs was measured by using a particle size analyzer (Malvern Mastersizer, UK).

3.3.7 Soluble microbial product (SMP) and extracellular polymeric substances (EPS) quantification

The concentrations of the soluble microbial product (SMP) and extracellular polymeric substances (EPS) in the mixed liquor were measured according to the procedures outline below. Sample of mixed liquor was collected from OMBR and centrifuged at 9,000 rpm for 10 min, then the supernatant was filtered through a 0.45 µm filter. The filtrate was then measured for the soluble microbial product (SMP) (Ng and Ng, 2010). The cation exchangr resin (CER-Dowex) and formaldehyde-NaOH method was used to extract the extracellular polymeric substances (EPS) from the sludge (Zhang et al., 1999) respectively. The extracted samples were analysed for protein (PN) and polysaccharide (PS) concentrations, following the modified Lowry method (Sigma, Australia) and Anthrone-sulfuric acid method (Raunkjær et al., 1994)(Raunkjær et al., 1994), respectively. Standard curves of PN and PS were developed using various concentrations of Bovine Serum Albumin (BSA) and glucose, respectively. Specifically, the microassay technique was employed using the enhanced protocol method described in the product literature. Absorbance was measured at 650 nm and 630 nm for PN and PS respetively using a UV/Visible Spectrophotometer. Before measurement, samples were filtered using Whatman® GF/B filters at 1.2 μm.

3.3.8 SEM-EDX analysis

The surface and cross-sectional morphologies of pristine and fouled membrane samples were observed by scanning electron microscopy (SEM) and an energy diffusive X-ray (EDX) analyzer (SEM, Zeiss Supra 55VP, Carl Zeiss AG, Germany) (Figure 3.8). The membrane was dried at vacuumed condition then samples were flash frozen in liquid nitrogen before fracturing. For the membrane with a backing fabric a sharp razor was used for a decent cut. Samples taken from each membrane were coated with gold using Balzers Sputter Coater (SCD 050, BAL-TEC, Germany). The SEM images were carried out at an accelerating voltage of 10 kV, and different image magnifications at various areas were obtained for each sample.

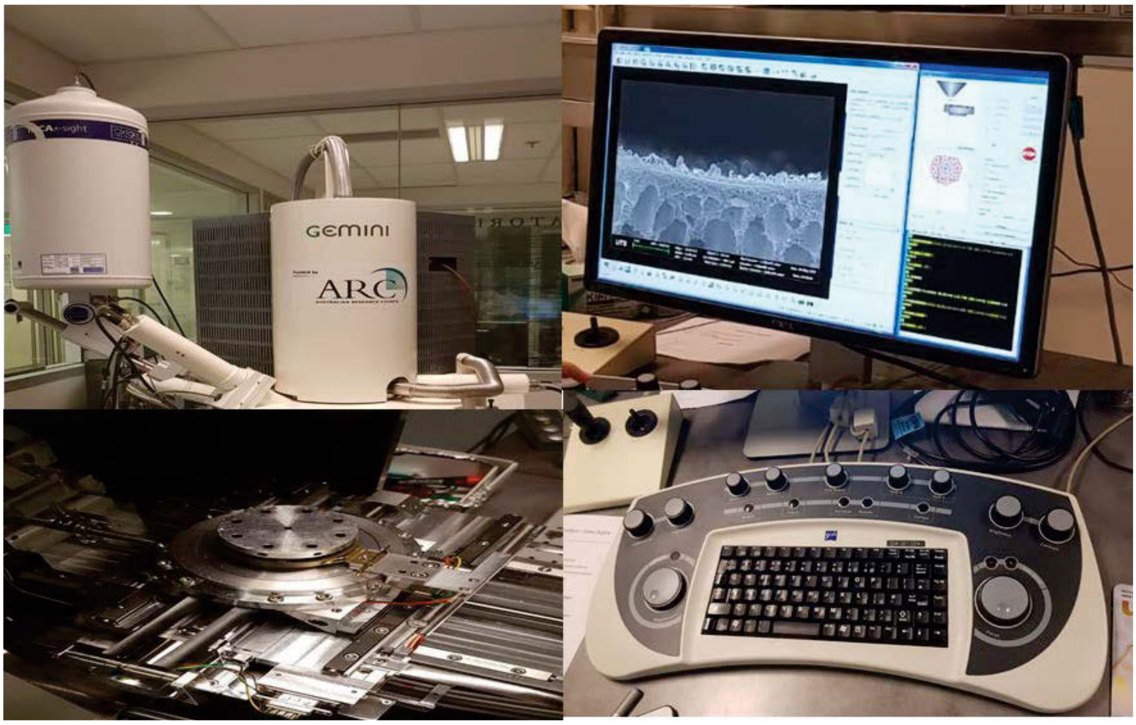


Figure 3.8 High-resolution Schottky field emission scanning electron microscope (SEM Zeiss Supra 55 vp).

CHAPTER 4

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SIMULTANEOUS NITRIFICATION-DENITRIFICATION USING BAFFLED OSMOTIC MEMBRANE BIOREACTOR-MICROFILTRATION HYBRID SYSTEM AT DIFFERENT OXIC-ANOXIC CONDITIONS

4 Simultaneous nitrification-denitrification using baffled osmotic membrane bioreactor-microfiltration hybrid system at different oxic-anoxic conditions

4.1 Introduction

With rapidly growing world population, climate change and extensive industrialization, pressure is increasing on the limited fresh water resources (Kim et al., 2017, Phuntsho et al., 2012). Increasing water scarcity has led to advancement of many technologies enabling use of alternative non-conventional water sources, such as domestic wastewater. This can help ease water demand in water stressed regions by wastewater reclamation and ultimately protecting our fragile environment (Kieniewicz, 2006, Luo et al., 2016a).

In recent years, membrane bioreactors (MBRs) have been extensively used for municipal and industrial wastewater treatment. MBRs offer several distinct advantages compared to the most commonly used secondary treatment by the conventional activated sludge (CAS) process, providing high-quality effluent, smaller foot print and less sludge yield (Wang et al., 2011, Cornelissen et al., 2008). Existing MBR systems use large pore size membranes (either microfiltration or ultrafiltration) (Visvanathan et al., 2000). While these membranes can effectively retain both particulate matter and some pathogenic agents, they are not able to retain low molecular weight organic compounds. For these compounds, the retention time is the same as the hydraulic retention time, which is usually very short in a typical MBR process. As a result, conventional MBR is only effective for the removal of most but not all trace organic contaminants. Besides, membrane fouling and high energy consumption are the two major obstacles of membrane bioreactors (MBR) processes. In order to overcome the membrane fouling issues, an innovative osmotic membrane bioreactor (OMBR) has gained interest in recent years. The OMBR works on the principle of natural osmosis and hence consumes much less energy as compared to MBR (Cornelissen et al., 2008, Achilli et al., 2009, Nguyen et al., 2015). Besides, OMBR process is able to remove most of the pollutants including most micropollutants from the wastewater not generally removed by the conventional MBR process since OMBR uses a nonporous membrane with rejection almost similar to reverse osmosis process (Praveen et al., 2016). In OMBRs, wastewater flows across an FO membrane from the activated sludge (or bioreactor) to the concentrated draw solution driven by osmotic pressure difference which offers several excellent advantages such as low fouling tendency, less pumping energy requirement and high retention for a wide range of pollutants (Yuan et al., 2015).

Although, OMBR process has many benefits over the conventional MBR, there are still major technical challenges that need to be solved, such as salt accumulation due to reverse salt flux and internal concentration polarization (ICP) (Wang et al., 2014b). The accumulation of solute in the bioreactor both due to the reverse salt transport of draw solutes and high rejection of feed solutes cause an elevated salinity condition in the OMBR bioreactor, that subsequently reduces the osmotic pressure difference or driving force between the feed and permeate side and hence FO flux decline. Moreover, salt accumulation can cause inhibition to bacterial viability and microbial consortia in the bioreactor (Wang et al., 2014a) which can undermine the biological treatment process. Various approaches have been tested in order to mitigate the salinity build up, including operating at short sludge retention time (SRT) (Wang et al., 2014a). However, biological ammonia removal in the OMBR cannot be completed at low SRT since the nitrifying bacteria population would decrease due to their relative long generation time. Moreover, accumulation of ammonium ions will likely cause ammonia to diffuse across the FO membrane at high concentrations, ultimately leading to the deterioration of permeate water quality (Wang et al., 2014a, Yap et al., 2012). Therefore, incorporation of a MF/UF filtration unit has been proposed to mitigate salinity build up during long-term OMBR operation. The MF/UF membranes could let the salts pass through but retain the activated sludge (Holloway et al., 2015a, Wang et al., 2014b) and in a way draining the salinity away from the bioreactor.

Further, the use of simulated seawater reverse osmosis (SWRO) brine as a draw solution (DS) is another novel aspect of the system. Literature review shows that seawater reverse osmosis (SWRO) concentrate causes the potential harm of brine discharge to the receiving sea water due to its too high salinity compared to point of discharge (Abualtayef et al., 2016, Tularam and Ilahee, 2007a). Seawater brine concentrate depends on the recovery rate of SWRO plant. At 50% recovery rate about 70 g/L concentrated RO brine can be obtained. The RO concentrate waste disposal is serious concern due to high levels of TDS and other contaminants. Therefore, OMBR could be a viable alternative to alleviate RO brine concentration. Thus employing SWRO brine as a DS can alleviate any adverse effects on the marine ecosystem (Qiu et al., 2015, Tularam and Ilahee, 2007a). In this context, forward osmosis-membrane bioreactor (FO-MBR) is presented as an innovative and viable technique to mitigate RO brine discharge.

Discharge of nitrogen (N) and phosphorus (P) in water bodies are known to be the major nutrients responsible for eutrophication issues in the environment, therefore, nutrient removal from wastewater is essential before final environmental discharge. Reports in literatures have shown that simultaneous nitrification and denitrification can be achieved in the same reactor vessel, a phenomenon defined as simultaneous nitrification and denitrification (SND). This has become an attractive technology for N removal as SND eliminates the need for separate nitrification and denitrification reactors as employed in conventional secondary treatment. Subsequently no mixed liquor recycle pump is needed, providing simpler reactor designs with smaller footprint (Yang and Yang, 2011, Pathak et al., 2017). Nutrient removal may also reduce a treatment plant's overall operating costs. Nitrification increases aeration needs and chemical consumption for pH adjustment by alkaline chemicals dosage. On the contrary, denitrification recovers lost oxygen and alkalinity. In addition to energy cost saving for aeration, denitrification eliminates need for chemicals to maintain optimum pH. Finally, biological nutrient removal (BNR) may produce a sludge with better settling properties than the sludge produced via conventional treatment (Agency, 2007).

Kimura and Watanabe (2005a) proposed a baffled membrane bioreactor by inserting baffles into a conventional submerged bioreactor and creating alternating aerobic and anoxic conditions to facilitate SND without sludge recirculation. The inner zone of the baffles maintained aerobic conditions through aeration, whereas the outer zone alternated between aerobic and anoxic conditions (Kimura and Watanabe, 2005a). The baffled MBR gives the advantage of a smaller footprint (e.g. no additional anoxic tank) and the baffle design eliminates mixing of the anoxic biomass and sludge recycle between the oxic and anoxic tanks (Kimura et al., 2007a).

This study assesses a hybrid osmotic membrane bioreactor microfiltration (OMBR-MF) process for SND using baffles in the bioreactor to treat municipal wastewater. The single-stage reactor design employed combines oxic and anoxic treatment thereby reducing space requirements and offers energy cost savings for continuous aeration and sludge recycling while achieving SND. A thin film composite (TFC) forward osmosis (FO) membrane and a microfiltration (MF) membrane were operated in parallel in a bioreactor. A laboratory-scale hybrid MF-OMBR was operated under four different oxic-anoxic conditions. Flux decline, organic and nutrients removal, extracellular polymeric substances (EPS) production and variation in mixed liquor suspended solids (MLSS) were measured. Besides this literature reports that as compared to the HTI made CTA–FO membrane, Toray made TFC–FO membrane has higher water flux, lower reverse salt transport and better resistance to hydrolysis and biological degradation (Hou et al., 2016). To date there are limited studies on OMBRs using TFC–FO membrane, thus, the objective of this study is to appraise TFC–FO membrane performance in the OMBR-MF hybrid process using simulated RO brine as draw solution (Hu et al., 2017).

4.2 Experimental

The experiments were carried out according to the procedures descried in chapter 3. Laboratory scale experimental set-up (Figure 3.3) and general operational procedure are shown in chapter 3. Membrane module and baffled reactor used in this experiment are shown in Figure 3.2 and Figure 3.4 respectively. Synthetic wastewater as a feed and simulated SWRO brine preparation details are provided in Chapter 3.

4.2.1 Operating conditions in the OMBR-MF hybrid system

The operating conditions are shown in Figure 4.1. The operation protocol of OMBR-MF study is shown in Table 4.1.

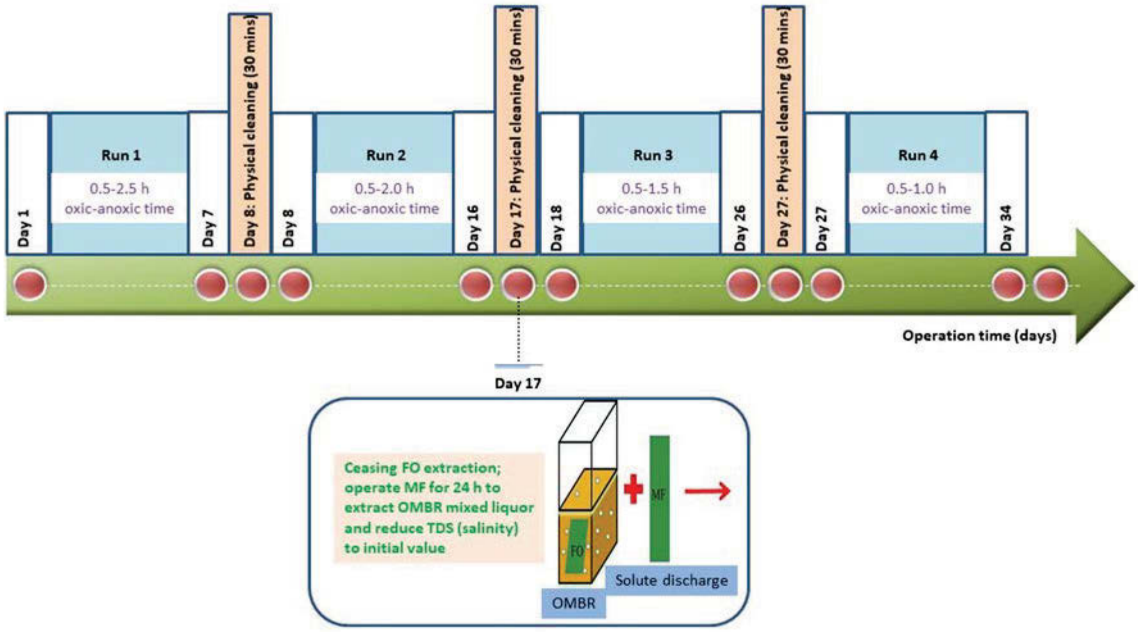


Figure 4.1 Operational protocol of the hybrid OMBR-MF system at different oxic-anoxic cycle time.

In this study 32 h HRT and 65 d SRT has been set. The HRT and SRT can be decoupled in OMBRs because water is processed through the membrane but solids are retained during filtration. In general, OMBR studies should extend the SRT beyond 10 days, which is the minimum for establishing good nitrification. Further, at SRTs longer than 80 days the dewaterability of the sludge get reduced (Yap et al., 2012). Therefore in this study 65 d SRT has been maintained. Another reason for longer SRT was to allow sludge perform better nitrification under elevated salinity environment. Thus, without losing much biomass from the system this can easily be achieved.

Table 4.1 Operating conditions in the OMBR-MF hybrid system

Parameters	Description
FO Membrane orientation	FO mode (AL-FS)*
Reactor volume	11.5 L
Draw solution (DS) concentration	1.1 M NaCl
DS Flowrate	10 ml/min @5.8 rpm*
MLSS*	3 -5.5 g/L
Aerobic cycle time	0.5 h
Anaerobic cycle time	2.5, 2, 1.5 and 1 h
HRT* FO-MF hybrid system	32 h
SRT*	65 d
F/M* Ratio	0.1 d^{-1}
Air Flow rate	3 LPM*

*AL-FS: active layer feed side, rpm: revolution per minute, MLSS: mixed liquor suspended solids, HRT: hydraulic retention time, SRT: sludge retention time, F/M: food to microorganism ratio, LPM: litres per minute.

Also, based on published reports of OMBR hydraulic retention time (HRT) appears to be long in OMBR studies. This can be attributed to relatively low FO flux in OMBR. Holloway et al. (2015a) in review article reported that lowest HRT was set at 1.4 d in OMBR study. In our study HRT was set at 1.33 d. In the same review other HRT values were varying too much in the range 2-19 d respectively. This was due to increased salinity caused rapid flux decline. In our study HRT was always remained 1.33 d and constant due to parallel MF operation to alleviate salinity and maintain constant HRT.

Total retention time in the reactor is 32 h is the hydraulic retention time. HRT has been calculated as the sum of all reactor volumes (V) divided by effluent flow rate (Q). Here flowrate is taken as a sum of FO and MF flowrates respectively. This hydraulic retention time (HRT) is not similar to the oxic-anoxic retention time. The oxic-anoxic cycle time was set by adjusting distance between two legs of the level controller. This has more relevance with how long aeration is applicable in oxic and anoxic zone respectively. When oxic-anoxic cycle time was adjusted to 0.5-1.0 h means whole reactor was assumed to be in oxic conditions for 0.5 h and for remaining 1.0 h outer zone of the reactor was assumed to be in the anoxic conditions thereby facilitating denitrification.

4.3 Results and discussion

4.3.1 Flux performance and salt accumulation at different oxic-anoxic conditions

Figure 4.2 shows variations in water flux over time for both FO and MF membranes and also salinity increase rate in the OMBR-MF hybrid system. The MF membrane was operated from day 1 to mitigate salinity build up in the reactor. In the OMBR–MF study during Run 1, initial FO water flux was 10.7 LMH but decreased to 6.8 LMH after 7 days of continuous operation. At the same time salinity increased steeply from 0.55 to 1.81 g/L. In another OMBR study with TFC FO membrane, water flux decreased from 15.3 LMH to 5 LMH while the bioreactor salinity increased up to 5 g/L during the first week of operation since the OMBR was operated without MF membrane (Wang et al., 2016c). Run 2 operations showed a more stable flux varying between 8.75 - 6.8 LMH and somewhat stable salinity around 2.5 g/L. Before commencing the subsequent runs under different oxic-anoxic cycle times, the FO membrane was physically cleaned with DI water followed by gentle cleaning with a sponge ball.

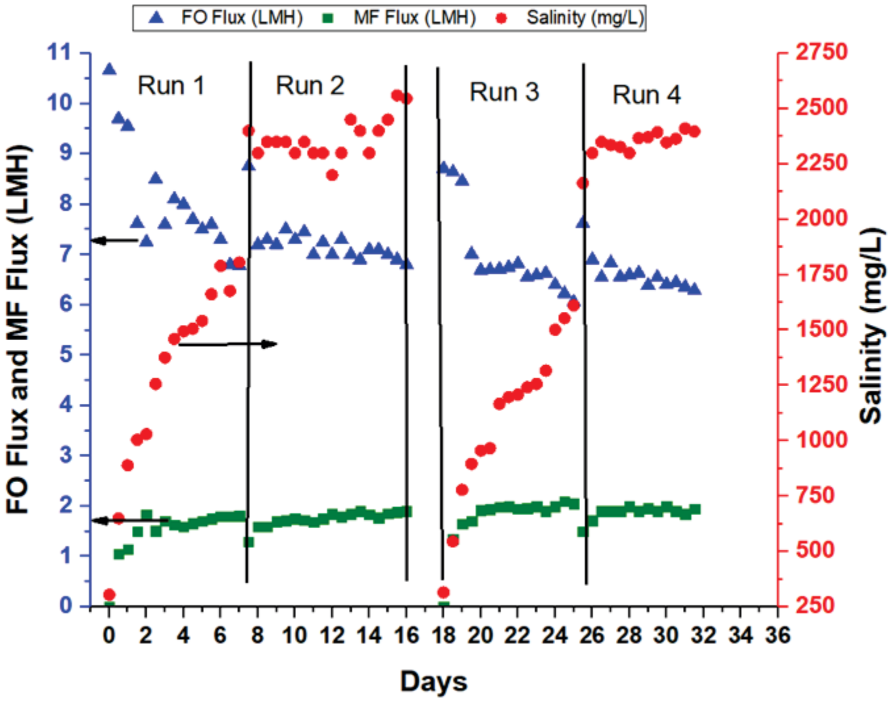


Figure 4.2 Flux and salinity variation at different oxic-anoxic conditions (Feed: synthetic wastewater; draw solution: simulated RO brine; temperature: 20 ± 5°C; membrane orientation: active layer facing the feed solution; 7 days operation for each oxic-anoxic cycle).

Then OMBR-MF operation was then resumed to continuously examine the flux behaviour in the Runs 3 and 4. As shown in operational protocol (Table 4.2), on day 16 after completion of Run 2 physical cleaning was performed to the FO membrane. Besides, MF membrane was solely operated for 24 h in order to bring down salinity to initial TDS levels and then resuming operation at initial salinity. In the beginning of the Run 3, 8.71 LMH initial FO flux was observed which was about 18.3% lower than initial FO flux during Run 1. The FO flux varied between 8.71 -6.06 LMH during Run 3 and a steady salinity build up was observed from 0.32 - 1.6 g/L. Likewise in Run 4 flux varied between 7.62 - 6.19 LMH with salinity increasing to 2.4 g/L. MF membrane flux increased with time in the range 1.05-2.1 LMH during Run 1 to 4 in order to maintain constant HRT which also helped in overall salinity build up alleviation in the reactor to some extent (2.5 g/L). As can be seen in Figure 4.2, salinity build up appears stable during Run 2 and 4 as compare to salinity increased in Run 1 and 3. This is due to relatively higher FO flux and simultaneous reverse salt flux which induced higher salinity build up during Run 1 and 3 respectively. Again this can be correlated to very fresh FO membrane in Run 1 and bleeding off excess salt from the reactor when commencing with Run 3.

The reason for stable salinity level during Run 2 and 4 could be initial low FO flux as compared to Run 1 and 3 which can be attributed to relatively less reverse salt flux keeping salinity level stable. However, due to high salt accumulation from Run 1 and Run 3 actual salinity during Run 2 and Run 4 are higher than Run 1 and 3 respectively. As stated above overall salinity during OMBR-MF operation was upto 2.5 g/L. Thus the salinity build up during the operation of the OMBR-MF system was relatively low in comparison of earlier OMBR studies and hence did not adversely affected biological activity in the reactor. Luo et al. (2016a) reported 8 g/L salt accumulation in 30 d OMBR operation with 0.5 M NaCl DS. Wang et al. (2014a) also reported in their OMBR study around 25 g/L salinity increase within 30 d operation when 1 M NaCl DS was used. Zhang et al. (2012b) also reported 5.5 g/L salinity built-up in OMBR study with 0.5 M NaCl 30 d operation. Further, the result obtained here compares favourably with a stable mixed liquor conductivity of approximately 5 mS/cm was observed during OMBR operation with continuous MF extraction (Luo et al., 2015c).

From Figure 4.2, it is clear that the flux decline trend was highest for Run 1 and Run 3. The FO flux decline could be related to the salt accumulation (as indicated by rapid TDS increase) and membrane fouling due to accumulation of MLSS, on the membrane surface when submerged in the bioreactor. The FO flux decline during OMBR operation has also been reported by other researchers (Wang et al., 2014a). However, adding MF membrane in the MF-OMBR system helped to maintain higher FO flux as compared to other OMBR studies. Wang et al. (2014b) had also reported that by incorporation of MF membrane could mitigate OMBR flux decline achieving 2.75 times higher permeate water flux than that in normal OMBR operation. Compared to Runs 1 and 3, the flux decline was not significantly high for Runs 2 and 4 which is likely due to low initial flux.

4.3.2 Total organic carbon removal

The OMBR-MF system was operated over 33 d applying four different conditions (Runs 1- 4). Biological process performance of the baffled OMBR-MF hybrid system was evaluated with regards to the removal carbonaceous organics and nutrients, biomass production, and biological activity. TOC removal is expressed as concentrations in the reactor supernatant, MF permeate and FO permeate respectively compared to feed concentrations. TOC removal variation during Run 1 to Run 4 in reactor supernatant, MF permeate and FO permeate was 86.1-92.3 %, 89.0-93.9 % and 98.3-98.6 % respectively (Figure 4.2**).** The OMBR FO channel was characterized by a very high TOC removal efficiency (98 %) during all four experimental runs. Hu et al. (2017) and Qiu and Ting (2013) also reported around 98% TOC removal efficiencies obtained from the TFC-FO permeate using NaCl DS. Recently, Wang et al. (2014a) reported 96% TOC removal with TFC FO membranes due to high rejection by the membrane in combination with bacterial biodegradation, which is in agreement with previously reported OMBR results. In this study, TOC removal in the bioreactor is shown to be affected by the oxic-anoxic cycle times; 86 % TOC removal observed in Run 1, 88 % in Run 2, on average 92 % Run 3 and 4 respectively. TOC concentrations in the MF permeate were observed to steadily decrease from 10.3 to 5.9 mg/L over the course of all runs. The increase in MF membrane rejection can be attributed to the better sludge acclimatization (heterotrophic bacteria proliferation) under continuous operation of bioreactor as well as pore blocking and fouling of MF membrane.

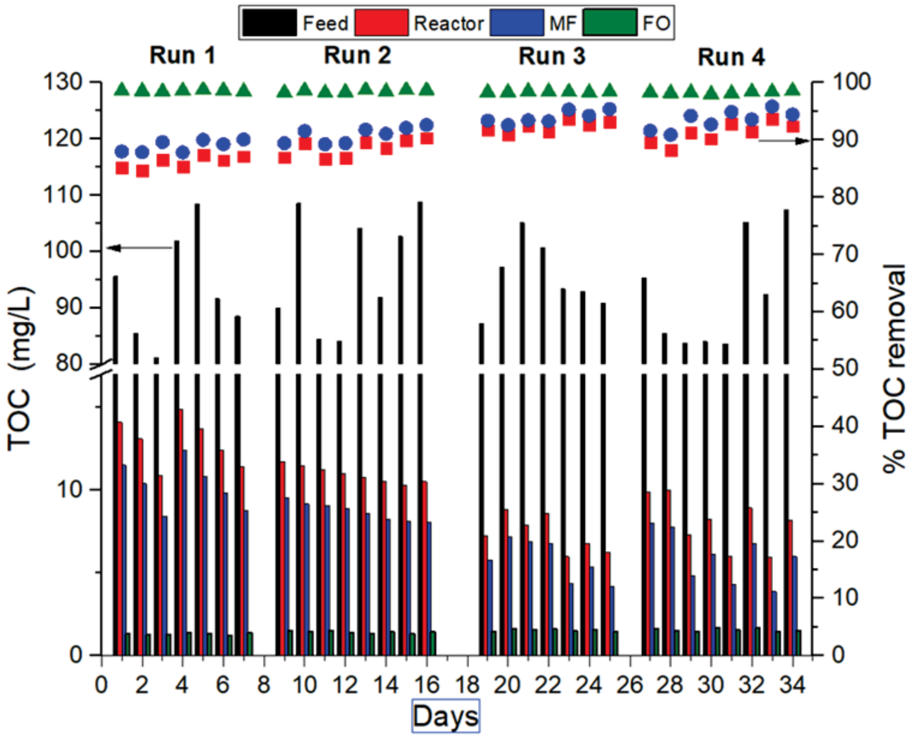


Figure 4.3 Variation of TOC concentration in the influent, bioreactor, MF and FO effluents and TOC removal in OMBR-MF hybrid system. Experimental conditions are as described in Fig. 4.2.

4.3.3 Nitrogen removal

In this baffled OMBR-MF system, nitrification is carried out in the aerobic chamber when the MLSS level is above the top of the inserted baffles (Figure 3.3) the autotrophic nitrifying bacteria oxidize ammonia to nitrate. On the other hand, denitrification occurs in the outer anoxic chamber when the liquid level is low and the heterotrophic denitrifiers releases nitrogen gas by nitrate ion reduction (Xu et al., 2014, Belli et al., 2015).

Apparently, the duration of the oxic-anoxic condition, would have a great impact on the treatment performance especially in terms of the nitrogen removal.

Figure 4.4 shows the TN concentrations in the influent, bioreactor supernatant, MF permeate and FO permeate as well as the removal efficiencies observed during all operating periods. As shown in Figure 4.4, significant differences between TN concentrations in the influent and treated water was found during the different oxic-anoxic cycle times tested. Higher TN removal can be related to denitrification occurring in the outer zone of the hybrid baffled MF-OMBR. The TN removal observed in the baffled MF-OMBR was due to the co-existence of heterotrophic and autotrophic micro-organisms in the bioreactor (Kimura and Watanabe, 2005a). The average effluent TN concentration decreased with the decrease of the anoxic time (Run 1-3). It is likely that at constant HRT, as the anoxic cycle time reduced, more nitrates circulated to the anoxic zone, where the denitrifying bacteria could have removed nitrate by denitrification, and denitrification efficiency was increased, thus leading to an improved nitrogen removal performance.

At the average influent TN concentration of 27.5 mg/L, the average reactor mixed liquor TN concentrations at Run 1 to 4 were 10.1, 8.9, 6.5 and 8.1 mg/L, respectively. Average nitrogen removal efficiencies during 1-4 were 62.8, 67.5, 76.1 and 71.2 %, respectively (Figure 4.4). The nitrogen removal efficiency of the OMBR operated with short anoxic cycle times (e.g. 1.5 h, Run 3, 1.0 h Run 4) was higher 76.1 and 71.2 % than that with thelonger anoxic cycle times (e.f. 2.5 h Run 1, 2.0 h Run 2). Further, in the effluents of all the four different operational Runs, on an average 0.1 mg/L of NO_2-N was observed. The very low NO_2-N concentration in the effluent and mostly NO_3-N presence in the treated effluent suggested that nitrification was almost perfectly completed (data not shown).

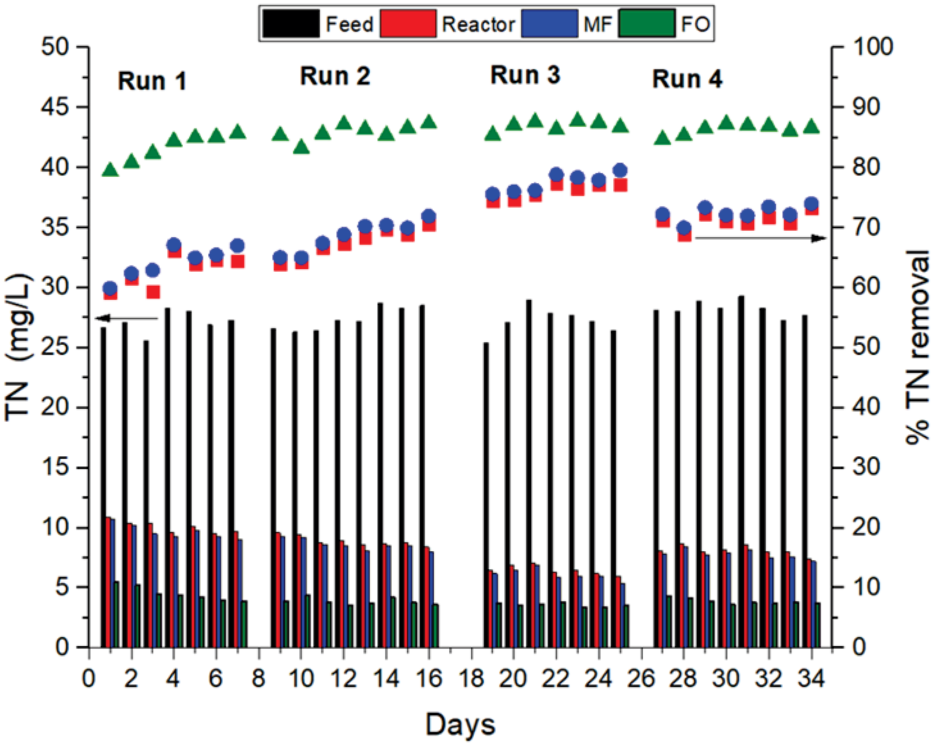


Figure 4.4 Variation of TN concentration in the influent, bioreactor, MF and FO effluents and TN removal in OMBR-MF hybrid system Experimental conditions are as described in Fig. 4.2.

This can be attributed to the 65 d longer SRT in the bioreactor was favourable for enrichment of nitrifying bacteria and nitrification could not have been the rate-determining step in this process (Wu et al., 2013a). Consequently, in OMBR-MF hybrid system , the degree of the denitrification in the anoxic environment decides TN removal efficiency (Ahn et al., 2003b). Garardi et al. (2007) has reported that activated sludge comprise of almost 80% of facultative anaerobes which are capable of denitrification. In the present study the treatment performance of the baffled MF-OMBR was influenced by the duration of oxic-anoxic cycle time. The TN removal varied from 63 to 76 % at different oxic-anoxic cycle time without addition of external carbon source.

However, specifically in Run 4 (0.5-1.0 h oxic-anoxic cycle time) less TN removal efficiency was obtained as compared to Run 3 (0.5-1.5 h oxic-anoxic cycle time). Due to short anoxic time in Run 4 it was believed that mixed liquor must have circulated more frequently between interior oxic zone and exterior anoxic zone in such a manner that dissolved oxygen could not be depressed enough to support sufficient denitrification as compared to Run 3 (Kimura et al., 2007a). Nah et al. (2000) previously reported that when the oxic-anoxic cycle time was shortened low TN removal efficiency was observed indicating that length of the anoxic period may not be enough for complete denitrification. It has been reported that high DO concentration in the anoxic chamber would stoichiometrically compete for the available substrate in the feed as well as kinetically influence the denitrifying bacteria (Tan and Ng, 2008). Plósz et al. (2003) also demonstrated that oxygen entering a bioreactor affects denitrification metabolically. In Run 3 best TN removal efficiency was achieved. So, 0.5-1.5 h oxic-anoxic cycle time may be considered as optimum. This cycle time led to sufficient diffusional limitation of DO. This favourable condition might have obtained satisfactory removal of available nitrate that transferred from aerobic zone.

Efficiency of creating of an anoxic environment in the baffled OMBR-MF process is demonstrated by dissolved oxygen (DO) measurements in the anoxic zone. Figure 4.5 shows the DO profile in outer zone of the baffles, roughly in middle of the anoxic zone about 12 cm down from the tip of the baffle. The measured values shown in Figure 4.5 were obtained on day 4, 16, 22 and 33 when good removal of nitrogen was observed, representing each Run 1 to 4 respectively.

Actually, the reactor was operated in a continuous mode. The oxic and anoxic cycle time was controlled by employing level controller connected to the feed pump in series. As per the desired cycle time the long leg of the level controller was extended inside the exterior of the baffle zones. When liquid level used to reach the lower edge of the level controller feed pump automatically operated and pumped the feed water into the reactor. When liquid level reached to the another short leg above the tip of the baffles, pump stopped. Thus, the distance between the level controller decides the time of oxic and anoxic cycle accordingly. Actually in all four runs during the OMBR-MF operation, oxic cycle time was set 0.5 h. Anoxic cycle time was varying from 2.5 h to 1.0 h respectively.

As can be seen in Figure 4.5, at time ($t = 0$ min) a wastewater pump has started and thus wastewater was fed to the reactor. When mixed liquor in the baffled OMBR reached above the baffle box at desired height, the level controller sensor activated and then feed pump stopped automatically. After 30 min, the water level again reached to the tip of the baffles (end of aerobic cycle time). Efficient denitrification requires formation of a decent anoxic environment in the outer compartment of the baffled reactor. In this baffled OMBR-MF study, a favourable anoxic condition was accomplished in the exterior chamber (DO < 0.5 mg/L as shown in Figure 4.5).

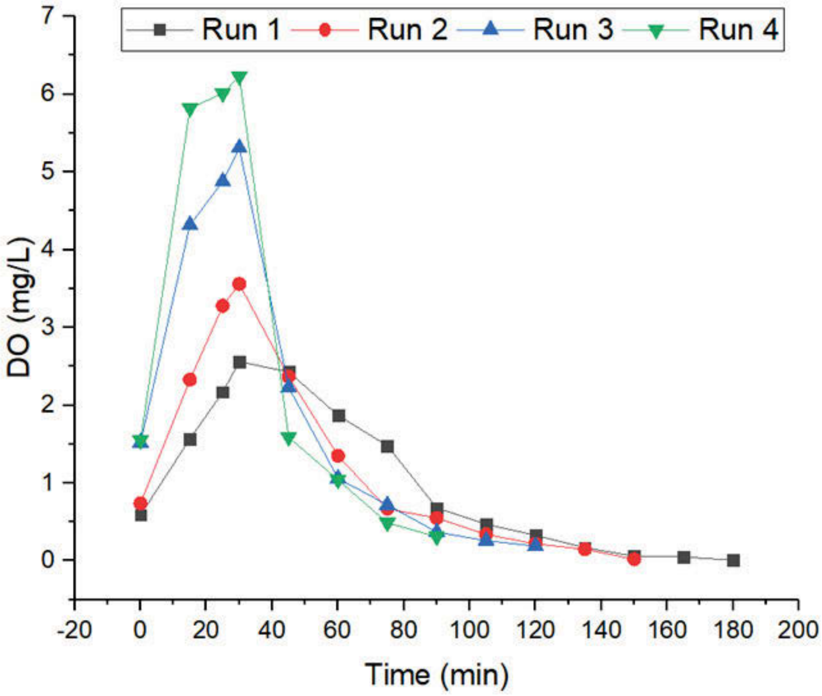


Figure 4.5 Dissolved oxygen variation in OMBR-MF system during oxic-anoxic cycle time.

The data shown in Fig. 4.5 indicate that the interior zone worked as an aerobic reactor for 0.5 h in the total operation time during all rums. DO concentration variation was probably caused by the fact that wastewater feeding was carried out from the top of the reactor in anoxic zone. Therefore heterotrophic bacteria might have consumed DO with time at varying degree. This might have led to changing DO concentration in the anoxic zone.

Further, nitrogen removal efficiency also depends on the influent COD/TN. The higher the COD/TN, the better the nitrogen removal was achieved. In this study COD/TN ratio was maintained around 12. Besides, the pH variations was dependent on the extent of the nitrification and denitrification occurred. In this study, pH variation was always observed within neutral pH from 6.9 to 7.42. So, daily pH adjustment was not essential thus saved chemical cost, due to the characteristics of the baffled reactor process configurations.

Other reports also suggested that the alkalinity produced through denitrification in anoxic zone was enough for the requirement of nitrification in oxic zone (Ge et al., 2010).

4.3.4 Phosphorous removal

Biological phosphorus removal is realised by creating conditions favourable for the growth of Phosphate Accumulating Organisms (PAOs). These microorganisms are responsible for the accumulation of excess phosphate in their cells if short chain Volatile Fatty Acids (VFAs), especially acetate, are available as feedstock. An initial anoxic zone allows the PAOs to take up VFAs into their cells and most usually store them in the form of polyhydroxyalkanoates (PHA). PAOs are basically the only bacteria able to store substrate in a first anoxic condition and oxidise them in a second aerobic phase. In wastewater treatment systems, when there are alternating anoxic and aerobic conditions, the PAOs release the orthophosphate in the anoxic/anaerobic part of the cycle and then collect a greater amount of it in the aerobic part of the cycle (Biswas et al., 2011). Earlier a study was undertaken to examine the potential of a laboratory-scale SBR for removal of phosphorous from wastewater employing two combinations of reaction periods, viz. anoxic–oxic (A/O) and anoxic–oxic–anoxic (A/O/A) (Kundu et al., 2014). Thus, Biological phosphorous removal effectively takes place when phosphorous releases in anoxic conditions and is accumulated at a high rate in the aerobic phase. In the baffled OMBR, sludge mixture was exposed to oxic and anoxic conditions at particular time interval during Run1-4, and biological phosphorus removal might have occurred to some extent. In the present study, the observed low DO concentration in the anoxic zone might have proliferated PAOs as described above which would have favoured phosphorous release. During aerobic condition phosphorous uptake by bacteria might have occurred.

Thus, phosphorus removal was expected to be achieved in a similar way as was observed and reported by Kimura and Watanabe (2005a).

PO_4-P removal in the various stages of the baffled OMBR-MF system show a removal of 57.1- 63.1 % in the reactor, 61.1-66.1 % in the MF permeate and 97.9-98.3 % in the FO permeate for all four runs (Figure 4.6). A stable and effective removal of PO_4-P (> 98 %) in FO processes is seen throughout the operating period. Wang et al. (2016a) et al. reported that with regard to the phosphates removal in OMBRs, the TP concentration was generally observed very low in the permeate as a result of the high rejection of phosphorus by FO membrane. For instance, Holloway et al. (2007) reported an excellent phosphate removal efficiency of 99% with the FO membrane.

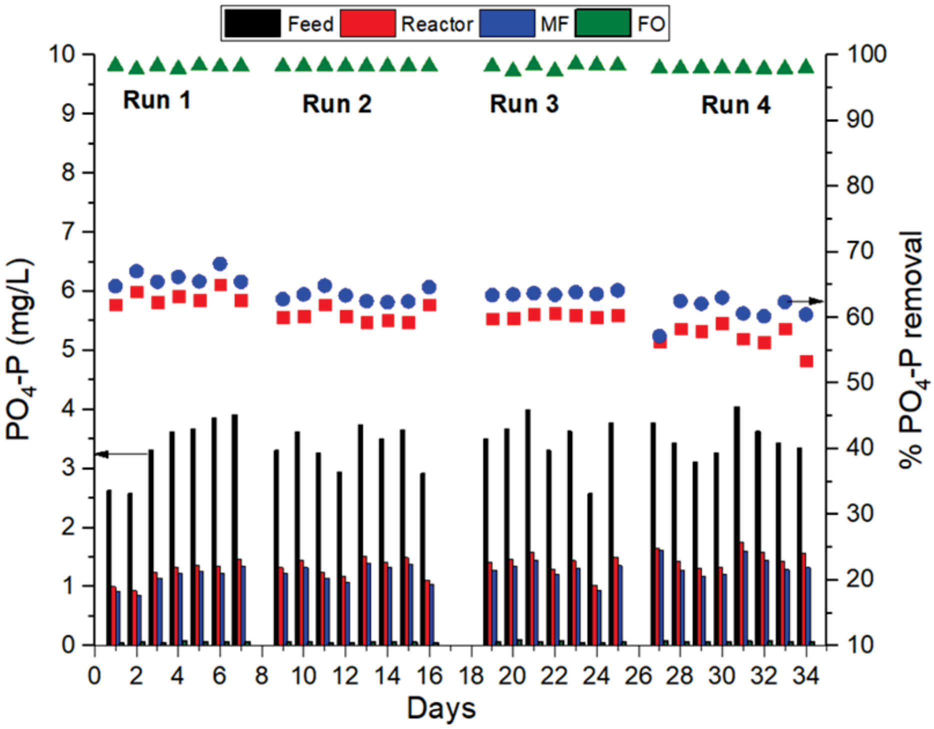


Figure 4.6 Variation of phosphate concentration in the influent, bioreactor, MF and FO effluents and phosphate removal in OMBR-MF hybrid system Experimental conditions are as described in Fig. 4.2.

During Run 1 highest PO_4-P removal was achieved in the bioreactor. This can be attributed to the prolonged anoxic time which resulted in very low DO concentration (0.17-0.02 mg/L) during last 30 minutes of anoxic cycle time. This might have released phosphorous and during oxic period phosphorous uptake would have realised followed by regular wasting of the sludge might have realised PO_4-P removal in the bioreactor.

Further, previous MBR report suggests that longer SRT adversely affects the biological phosphorus removal capability of the bioreactor and it might be responsible for low sludge yield, limiting phosphate uptake by new cellular material (Cosenza et al., 2012). Also, in the baffled OMBR-MF system, possibly under longer anoxic cycle time in Run 1 and 2, denitrifying-polyphosphate-accumulating organisms (DPAO) might have contributed to denitrification of NO_3-N using available substrate. Several studies have suggested that PAOs are more efficient in enhanced phosphorus uptake in oxic environments than anoxic, and phosphorus removal can be reduced by excessive anoxic phosphorus uptake (Brown et al., 2011). In addition, previous studies reported that when phosphorus is assimilated under anoxic conditions, P assimilation in oxic conditions decreases by up to 60% (Ekama and Wentzel, 1999).

In this study, during the OMBR operation it was observed that biomass clung to the outer baffle wall as well to the inside wall of the reactor in anoxic zone. Specifically, when switching over to anoxic cycle, the low DO concentration in the anoxic zone might have created anaerobic condition inside of the biomass that attached to the wall and phosphorous release would possibly have occurred. This also helped to achieve biological P removal from the reactor.

Another possible explanation for the good removal of phosphorus is precipitation with inorganic substances. In present study, salting out might have occurred and some potassium phosphate in the reactor from feed wastewater may have precipitated out with the salt transported in the reactor from draw solution. Thus, regular sludge withdrawal might have achieved phosphorus removal through biomass and settled phosphorus discharge from dead zones.

Compared with the conventional OMBR, the total removal efficiency of MF-OMBR system should be represented by the combination of MF effluent and diluted draw solution. The combined TOC/TN/TP removal efficiency of the system could be obtained using Equation 4.1 (Wang et al., 2014b):

$$C_{mix(t)} = \frac{C_{MF(t)}V_{MF(t)} + C_{FO(t)}V_{FO(t)}}{V_{MF(t)} + V_{FO(t)}} \qquad (4.1)$$

Where, $C_{mix(t)}$ is the TOC/nutrient in the mixed effluents (i.e., MF effluent and diluted DS) (mg/L), C_{MF} is the TOC/nutrient concentration in the MF membrane effluent (mg/L), C_{FO} is the TOC/nutrient concentration in the diluted draw solution (mg/L), V_{MF} is the volume of the MF membrane effluent (L), while V_{FO} was calculated based on the weight change of the draw solution due to the flux decline of FO membrane (L).

The combined (MF+FO) TOC removal efficiency for Run 1 to Run 4 were 94.3, 94.8, 96.1 and 95.7 % respectively. Combined PO_4-P removal efficiency observed were 83.8, 81.1, 80.3 and 78.1 % for Run 1 to Run 4 respectively. Similarly, combined TN removal efficiency during Run 1 to Run 4 were 74.7, 77.4, 82.1 and 78.8 % respectively.

For MF membrane average TOC, TN and TP rejection were 22.5, 4.3, and 18.4 % respectively. For FO membrane average TOC, TN and TP rejection were 83.8, 52.5, and 94.4 % respectively.

4.3.5 Biomass activity in baffled OMBR-MF system

The nature of fouling to the FO membrane was substantially influenced by the fractionation of SMP and bEPS in the bioreactor. Figure 4.6 shows the comparison of soluble microbial products (SMPs) and bound bEPSs concentrations of the baffled OMBR operated under different oxic-anoxic cycle times (Run 1-4). SMP analyses from the bioreactor show not much variation in protein content but carbohydrate concentrations being higher corresponding to during longer anoxic cycles (e.g. Run 1 vs. 2). SMP concentrations were generally found to be higher for the longer anoxic cycle times (e.g. 14.1 mg/L @ 2.5 h, 11.2 mg/L @ 2.0 h, 8.2 mg/L @ 1.5 h, 9.4 mg/L @ 1.9 h). Tan and Ng (2008) have reported that high SMP concentrations in MBR induced rapid membrane fouling. The higher SMP and EPS concentration measured in Run 1 may explain the higher membrane fouling tendency observed.

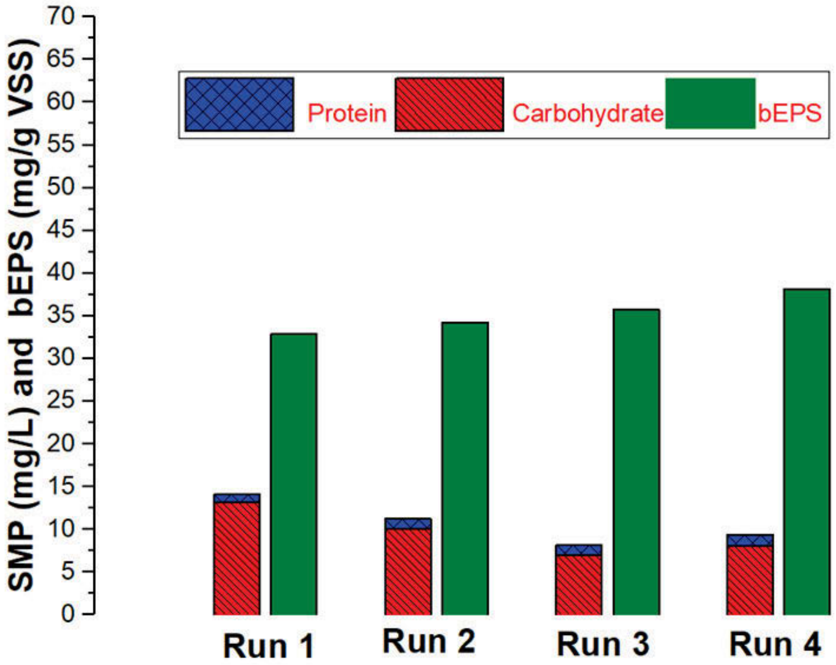


Figure 4.7 Soluble and bound extracellular polymeric substances variation in the OMBR.

MLSS and MLVSS were increased from 3.8 to 5.3 g/L and 3.3 to 4.6 g/L respectively during entire OMBR-MF study. Further, superior retention capacity of FO membrane can be attributed to the increased sludge retention by membrane thereby increasing SRT and less sludge removal. Zhang et al. (2015) reported that longer SRT is favourable for less sludge production. A similar trend during OMBR-MF operation was also observed in our study at 65 d SRT. MLVSS/MLSS ratio was found varying in the range 0.84-0.88 in this study. The decrease in the MLVSS/MLSS ratio has also been observed in another OMBR study (Alturki et al., 2012). Rosenberger et al. (2005) investigated MLSS and membrane fouling relationship. They reported that fouling potential was less pronounced with increased MLSS when MLSS concentration was lower than 6 g/l. In present study also MLSS was increased yet less than 6 g/L. This can be attributed to weak fouling of FO membrane and merely physical cleaning had contributed to higher flux recovery after two weeks of operation.

However, literature on the membrane fouling during denitrification is rather sparse. Zhou et al. (2013) reported that keeping a higher level of dissolved oxygen (DO) concentration in the mixed liquor can help in eliminating SMP based on both experimental measurements and modelling simulation. Geilvoet et al. (2006) performed filtration test with denitrification and nitrification tank sludge samples and observed better filterability in the nitrification tank samples. As a general trend, a high bioreactor DO leads to a better filterability and a lower fouling rate (Jiang et al., 2008). Kim and Nakhla (2010) found that denitrifying phosphorous accumulating organisms (DPAO) could consume the storage intracellular carbon during the endogenous denitrification, and thus result in formations of SMP and EPS. Bound EPS was found varying from 29.9 to 38.1 mg/gVSS in increasing order from Run 1 to 4. This can be ascribed to increase in biomass concentration with time. A 32.3 mg/g VSS bEPS was measured at 90 d SRT in aerobic MBR study (Zhang et al., 2015) which was less than present SND study. Paetkau and Cicek (2011) investigated nitrogen removal for a conventional, aerated membrane bioreactor and low oxygen, simultaneous nitrification–denitrification (SND) membrane bioreactor (SND-MBR). The SND-MBR was associated with higher transparent exopolymer substances (TEPS) values greater fouling rates. Both TEPS and sCOD were elevated during the unstable denitrification period. However, in present study, bEPS were higher in Run 2 and 4 as compared to Run 1 and 3. This can also be attributed to relatively high TDS concentration (salinity) in the mixed liquor. Wang et al. (2014a) compared the bEPS under similar operating conditions and feed wastewater for conventional OMBR and hybrid MF-OMBR. Higher bEPS in regular OMBR can be linked to the excessive salinity build up which was found approximately ten times higher than hybrid MF-OMBR. In this study, MF membrane incorporation helped to alleviate the salinity build up thereby reduced EPS release.

4.4 Conclusions

This study investigated TOC and nutrient removal in a baffled OMBR-MF system under four different oxic-anoxic conditions. In a reactor 0.5-1.5 h oxic-anoxic conditions (Run 3) has achieved best 92 % TOC, 76 % TN and 63 % phosphate removal. Combining MF membrane effectively maintained salinity build upto 2.5 g/L in the reactor. High SRT (65 d) favoured nitrifying bacteria to proliferate and denitrification was the rate limiting step for SND process. SMP data showed that anoxic cycle time has pronounced effect on membrane biofouling so it is important to set operating conditions in order to prevent fouling.

CHAPTER 5

UNIVERSITY OF TECHNOLOGY SYDNEY

Faculty of Engineering & Information Technology

PERFORMANCE OF A NOVEL BAFFLED OSMOTIC MEMBRANE BIOREACTOR MICROFILTRATION HYBRID SYSTEM UNDER CONTINUOUS OPERATION FOR SIMULTANEOUS NUTRIENT REMOVAL AND MITIGATION OF BRINE DISCHARGE

5 Performance of a novel baffled osmotic membrane bioreactor-microfiltration hybrid system under continuous operation for simultaneous nutrient removal and mitigation of brine discharge

5.1 Introduction

With rapidly growing world population, the water scarcity issue is becoming critical and affects drinking water supplies, energy, food production, industrial output, and the quality of our environment at a global scale (Phuntsho et al., 2011). Hence, the emphasis on developing alternative approaches to supply 'fit for purpose' water is emerging. Therefore, an alternative water supply systems are becoming a visible practice in many water stressed regions (Memon and Ward, 2014). A paradigm shift is already taking place and low grade water such as grey water and sewage are now increasingly seen as a viable source of water, nutrient and energy rather than a waste (Wang et al., 2016b, Memon and Ward, 2014). However, there are still many challenges faced in wastewater treatment processes, especially in relation to nutrient and trace organic removal (Nguyen et al., 2016a). In particular, nutrient removal is very important for water reuse, especially in water supply for outdoor use, to prevent water quality deterioration via eutrophication. This phenomenon is mainly caused by the presence of nitrogen and phosphorus in wastewater effluents, leading to algal blooms, oxygen deficiency, and ultimately an increased mortality of the aquatic species (Mun et al., 2011, Devia et al., 2015).

Conventional techniques for N and P removal from wastewater are based on physical and chemical methods. These techniques are not economical and do not facilitate nutrients recycle and reuse (Praveen and Loh, 2016). Fan et al. (1996) reported that perfect nitrification could be achieved in the mrmbrane bioreactor (MBR) system. In order to achieve simultaneous nitrification-denitrification, a continuous aerated submerged MBR system for nitrification with a separated anoxic tank for denitrification was developed

(Ahn et al., 2003a). The energy required for sludge recirculation and mixing in an anoxic tank accounts for 10–20% of the total energy consumption in a common MBR. This is in addition to the energy usage for aeration to mitigate membrane fouling which represents up to 60–70% of the total operating energy in MBRs (Kurita et al., 2015). To overcome these shortcomings, researchers introduced the alternating anoxic and oxic conditions in a submerged MBR by intermittent aeration for total nitrogen removal. However, in the intermittently aerated MBR, filtration operation is limited to the aeration periods, mainly to prevent membrane fouling (Song et al., 2010).

In recent years, more studies have shown that nitrification and denitrification could occur concurrently in one single reactor under aerobic conditions with low dissolved oxygen, through the so-called simultaneous nitrification and denitrification (SND) process. SND relies on concurrent aerobic NH_4-N oxidation and anoxic denitrification under identical operating conditions (Fu et al., 2009b). Kimura and Watanabe (2005b) have proposed a baffled membrane bioreactor, in which baffles are inserted in a submerged MBR, and the level of water in the reactor is controlled to facilitate simultaneous nitrification/denitrification without sludge recirculation. The inner zone of the baffles maintains an aerobic condition because of aeration, whereas the outer zone alternates between aerobic and anoxic conditions (Kimura and Watanabe, 2005b). Thus, a baffled MBR offers advantages such as small footprint (no additional anoxic tank) and baffle design substitutes stirring of anoxic biomass and sludge recycle between oxic and anoxic tank. The baffles inserted in the MBR create circulation flows in the membrane tank and vigorously mix the biomass. This also improves the efficiency of mechanical cleaning (Kimura et al., 2007b).

More recently, osmotic membrane bioreactors (OMBRs) have attracted growing interests in the field of low strength domestic/municipal wastewater treatment (Wang et al., 2016d). OMBR can potentially produce high quality reclaimed water for potable reuse, irrigation, or direct discharge in environmentally sensitive areas (Luo et al., 2015b). OMBR have many advantages such as higher quality pure water, low and reversible fouling compared to pressure-driven membrane processes, minimum cleaning and energy efficient in the absence of any hydraulic pressure in comparison to the traditional membrane bioreactors (MBRs) (Wang et al., 2016c, Luo et al., 2017b).

However, OMBR also has some limitations such as salinity build-up (i.e. accumulation of dissolved salts inside the bioreactor), internal concentration polarization and the energy associated with the DS recovery process (Nguyen et al., 2016a). In order to mitigate the salinity build up, various approaches have been tested including operating at short SRT (Wang et al., 2014b). However, ammonia removal via biological treatment in the OMBR cannot be completed at low SRT since the nitrifying bacteria population would decrease due to their relative long generation time. In this case, the concentration of ammonia would accumulate in the mixed liquor and negatively impact on the microorganisms in the OMBR. Moreover, diffusion of high concentration ammonia across the FO membrane eventually leads to the deterioration of permeate quality (Yap et al., 2012, Wang et al., 2014b). Therefore, for long-term operation of the OMBR, incorporation of microfiltration (MF)/ultrafiltration (UF) membrane (Holloway et al., 2014, Holloway et al., 2015a) has been suggested as a promising option. MF/UF are also helpful to mitigate salinity build up because these membranes could let the salts pass through but retain the activated sludge (Wang et al., 2014a).

The amount of concentrate produced from a desalination plant is a factor of the desalination recovery rate. Literature review shows that the concentrate produced from seawater reverse osmosis (SWRO) plants have up to two times more salt concentration than the receiving water since they generally operate at 50% recovery rate (Tularam and Ilahee, 2007b). As reported by Abualtayef et al. (2016) the potential harm of brine to the environment yields from either its higher than normal salinity compared to point of discharge, or due to pollutants that otherwise would not be present in the receiving waterbody. In addition to the destructive saline properties of the concentrate, in the case of thermal desalination, the brine is usually hotter than the local recipient water body, a circumstance that has also been shown to cause further environmental damage, especially to fragile ecosystems such as corals. Due to these negative effects, direct disposal to seawater of RO concentrates is doomed to disappear (Perez-Gonzalez et al., 2012).

There are a few actual regulations, standards, or guidelines for brine discharges around the world particularly in the developed countries like the US, Australia and Israel. There is substantial variation in the specifics of the regulations, but almost all share two key elements: a salinity limit and a point of compliance expressed as a distance from the discharge. Jenkins et al. (2012) reviewed RO concentrate discharge regulations and standards which have been applied around the world. These range from salinity increments within 1 parts per thousand (ppt), 5%, or absolute levels such as 40 ppt. These limits typically apply at the boundary of a mixing zone whose dimensions are of order 50 to 300 m around the discharge (Jenkins et al., 2012). In contrast, inland plants have to solve the problem of concentrate disposal without the possibility of their discharge to seawater, so the development of other management options is an urgent demand (Perez-Gonzalez et al., 2012). Although the TDS values of RO concentrates from brackish water desalting are significantly less than seawater TDS, they are typically greater than 10,000 mg/L, which makes them more compatible with ocean water than fresh waters. In this scenario OMBR could be a viable alternative. In this context, forward osmosis-membrane bioreactor (FO-MBR) is presented as an innovative technique to mitigate RO brine discharge. The FO-MBR process may also demonstrate a lower membrane fouling propensity than pressure-driven membrane processes such as conventional MBR. Membrane fouling in FO is relatively low, more reversible and can be minimized by optimizing hydrodynamics (Zhao et al., 2012).

The present study investigates for the first time the performance of an integrated osmotic and microfiltration membrane bioreactor system for municipal wastewater treatment employing baffles in the reactor. Thus, the single-stage reactor design employed here combines aerobic and anoxic processes to reduce the footprint and decrease energy costs of continuous aeration and sludge recycling in order to achieve simultaneous nitrification-denitrification. The process performance was investigated in terms of water flux and salinity build up, organic and nutrient removal and microbial activity using simulated RO brine as a DS. Further, as pointed out in several reviews (Wang et al., 2016b, Yap et al., 2012) cellulose triacetate- forward osmosis (CTA-FO) membranes were predominantly utilized in early OMBRs studies. However, the loss of membrane rejection of CTA-FO membranes due to its biodegradation has been a major concern. In contrast, thin film composite (TFC) membranes possess better chemical/biological stability and separation properties. In spite of the increased interest in OMBR, there are limited reports of their operation with TFC membranes to investigate feasibility of this technology. Hence, a newly developed TFC FO membrane (Toray Korea) has been employed in the current study.

5.2 Experimental

The experiments were carried out according to the procedures descried in chapter 3. Laboratory scale experimental set-up (Figure 3.3) and general operational procedure are shown in chapter 3. The FO and MF membrane characteristics are detailed in Table 3.1. FO membrane module and baffled reactor used in this experiment are shown in Figure 3.2 and Figure 3.4 respectively. Synthetic wastewater as a feed and simulated SWRO brine preparation details are provided in Chapter 3.

5.2.1 Operating conditions in the OMBR-MF hybrid system

The operating conditions are listed in Table 5.1. No membrane cleaning was conducted for both FO and MF membrane during the entire operation (i.e. 38 days).

5.2.2 Mass balance in baffled OMBR-MF hybrid system

A detailed mass balance of the OMBR-MF hybrid system is also presented in Figure 5.1 and equations 5.1 to 5.11 to provide a better understanding of the salt accumulation phenomena occurring in the bioreactor. The OMBR–MF hybrid system consists of a flat sheet FO membrane submerged in the bioreactor. In order to enhance biological activity in OMBR, high retention of sludge (suspended solids including microbes) and low retention of salts in the bioreactor was simultaneously satisfied with incorporation of MF membrane (Figure 5.1).

Feed wastewater flows into the bioreactor with a constant flow rate (Q_{in}) and a salt concentration (C_{in}). It is assumed that pure water penetrates through the FO membrane, and salts, organic matters, and microbes are retained and accumulated in the bioreactor. These concentrated materials (i.e., sludge) are discharged with a flow rate (Q_s) and a salt concentration (Cs). Continuous aeration in the bioreactor may result in complete mixing of salts, and the salt concentrations in the sludge (C_s) and the bioreactor (C_{ml}) are thus assumed to be identical. Draw solution (DS) enters the inside of the flat sheet membrane channel with a flow rate (Q_c) and a salt concentration (C_c) to make osmotic pressure difference between the inside and the outside (i.e., the bioreactor) of the flat sheet membrane channel. Drawing pure water out of feed wastewater via FO membranes, DS becomes diluted and is discharged from OMBR with a flow rate (Q_d) and a salt difference between the inside and the outside (i.e., the bioreactor) of the flat sheet membrane channel. Drawing pure water out of feed wastewater via FO membranes, DS becomes diluted and is discharged from OMBR with a flow rate (Q_d) and a salt concentration (C_d) respectively.

Table 5.1 Operating conditions in the OMBR-MF hybrid system

Parameters	Description
FO Membrane orientation	FO mode (AL-FS)*
Reactor volume	11.5 L
Draw solution (DS) concentration	1.1 M NaCl
DS Flowrate	10 ml/min @5.8 rpm*
MLSS*	4.7 -6.1 g/L
Aerobic cycle time	0.5 h (0.5 cm above baffle)
Anaerobic cycle time	1.5 h (1.5 cm below baffle)
HRT* **FO-MF hybrid system**	30.25 h
SRT*	115 d
F/M* Ratio	0.1 d^{-1}
Air Flow rate	2 LPM*

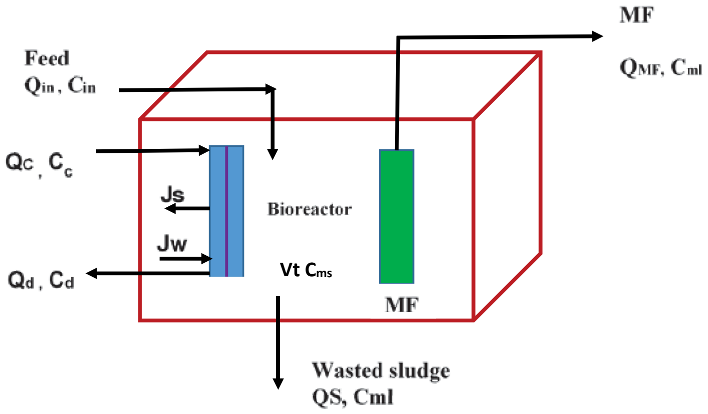


Figure 5.1 Mass balance in the baffled OMBR-MF system.

Feed wastewater flows into the bioreactor with a constant flow rate (Q_{in}) and a salt concentration (C_{in}). It is assumed that pure water penetrates through the FO membrane, and salts, organic matters, and microbes are retained and accumulated in the bioreactor. These concentrated materials (i.e., sludge) are discharged with a flow rate (Qs) and a salt concentration (C_s). Continuous aeration in the bioreactor may result in complete mixing of salts, and the salt concentrations in the sludge (C_s) and the bioreactor (C_{ms}) are thus assumed to be identical. Draw solution (DS) enters the inside of the flat sheet membrane channel with a flow rate (Q_c) and a salt concentration (C_c) to make osmotic pressure difference between the inside and the outside (i.e., the bioreactor) of the flat sheet membrane channel. Drawing pure water out of feed wastewater via FO membranes, DS becomes diluted and is discharged from OMBR with a flow rate (Q_d) and a salt concentration (C_d) respectively.

At a steady state, mass balance for water and salts in the bioreactor is described as:

$$Q_{in} + Q_c = Q_d + Q_{MF} + Q_S \qquad (5.1)$$

$$Q_{in}\, C_{in} + Q_c\, C_c = Q_d\, C_d + Q_{MF}\, C_{ml} + Q_S\, C_m \qquad (5.2)$$

The salt accumulation in the bioreactor remains a challenge to the further development of a novel osmotic membrane bioreactor (OMBR) for wastewater treatment and reuse. During OMBR operation, the salt accumulation could occur due to the effective rejection of salts from the influent by high retention forward osmosis (FO) membranes and the reverse diffusion of solutes from the draw solution. The increased salt concentration could adversely affect microbial activity in the bioreactor and thus deteriorate the membrane and treatment performance of OMBR to some extents. Therefore, it is essential to estimate salt accumulation inside the bioreactor.

In order to solve earlier derived mass balance equations water flux (Jw) and solute flux (Js) has to be calculated as follows (Chou et al., 2010, Xiao et al., 2011) :

$$J_{W} = A\,(\Delta\pi_{eff} - \Delta P) \tag{5.3}$$

$$J_S = \frac{B\,J_W}{A\beta R_g T} \tag{5.4}$$

Relation between *Jw* and *Js* can be expressed as follows:

$$\frac{Js}{Jw} = \frac{B}{A\beta R_g T} \tag{5.5}$$

Where Jw is the volumetric water flux (LMH); JS is the solute flux (gMH); A is the pure water permeability of FO membrane; B is solute permeability; $\Delta\pi_{eff}$ is effective osmotic pressure drop considering internal and external concentration polarization (ICP and ECP); ΔP is pressure difference between DS and feed sides; β is the van't Hoff coefficient (β = 2 for NaCl); Rg is the universal gas constant (=8.31 J/mol K); and T is the absolute temperature. Eq. (5.5) suggests that if more water permeates, more salt also diffuses through the membrane. The solute flux is proportional to water flux, implying that $\frac{Js}{Jw}$ can be replaced by a constant value for a given membrane and a given solute. This ratio does not depend on the DS concentration, FS concentration, or the membrane orientation. A low $\frac{Js}{Jw}$ ratio is generally preferred, as severe solute reverse diffusion can promote FO membrane fouling and deteriorate FO performance.

Water balance around the OMBR-MF hybrid system can be expressed as :

Water fed to OMBR = FO permeate+ MF permeate + water wasted through sludge (5.6)

This can be expressed as follows:

$$Q_{in} = J_w A_{FO} + Q_{MF} + Q_s \tag{5.7}$$

Here, Q_{in} (L/h), Q_{MF} (L/h) and Qs (L/h) are the volumetric flow of the feed, the MF system, and the waste sludge respectively; and J_w is pure water flux through FO membrane and A_{FO} is the FO membrane area (m^2).

However, under unsteady-state condition mass will be accumulated over time. The derivation of an unsteady-state solute mass balance (solute mass variation with time) can be written as:

Accumulation = solutes from influent + solutes from RSF - solutes to the sludge (5.8)

Equation 5.8 can be mathematically expressed as follows:

$$V_t \frac{dC_{ms}}{dt} = Q_{in}C_{in} + J_W A_{Fo} - Q_{MF}C_{ms} - Q_s C_{ms} \tag{5.9}$$

Where, V_t is the bioreactor volume and $\frac{dC_{ms}}{dt}$ is change in solute concentration inside the reactor mixed liquor with time.

Now, by inserting terms from Equation 5.5 and Equation 5.6 into Equation 5.9, we get

$$V_t \frac{dC_{ms}}{dt} = (J_w A_{FO} + Q_{MF} + Q_s) C_{in} + \frac{B}{A\beta R_g T} J_w A_{FO} - (Q_{MF} C_{ms} + Q_s) C_{ms} \qquad (5.10)$$

Here, Q_{MF} can be calculated as product of MF flux (J_{MF}) and MF membrane area (A_{MF}) respectively.

Hydraulic retention time (HRT) of OMBR is calculated as the sum of all reactor volumes (V_t) divided by effluent flow rate.

$$\mathrm{HRT} = \frac{V_t}{J_w A_{FO} + J_{MF} A_{MF} + Q_S} \qquad (5.11)$$

Similarly, sludge retention time (SRT) in OMBR is calculated as the sum of all reactor volumes (V_t) divided by sludge wasted (Qs)

$$\mathrm{SRT} = \frac{V_t}{Q_S} \qquad (5.12)$$

Further, MF permeate flow at operating HRT of the OMBR-MF system becomes:

$$Q_{MF}(t) = \frac{V_t}{\mathrm{HRT}} - \frac{V_t}{\mathrm{SRT}} - J_w . A_{FO} \qquad (5.13)$$

Having considering HRT and SRT effects Equation 5.9 can be rearranged as follows:

$$\frac{dC_{ms}}{dt} = \frac{1}{\mathrm{HRT}} \left(C_{in} + \frac{B}{A\beta R_g T} \right) - \frac{1}{\mathrm{SRT}} \left(C_{ms} + \frac{B}{A\beta R_g T} \right) - \frac{J_{MF} A_{\mathrm{MF}}}{V_t} (C_{ms}) \qquad (5.14)$$

Hence, time-dependent salt accumulation in the OMBR can be determined by coupling Equation 5.14 that explains the contribution of both RSF (reverse salt flux) and the solute inflow from the influent towards salt accumulation in OMBR-MF hybrid system. The RSF is represented by the term B/AβRgT in Equation 5.14 has molar concentration unit.

5.3 Results and discussion

5.3.1 Water flux and salinity build up in the baffled OMBR-MF hybrid system

The OMBR-MF hybrid system was operated at constant DS concentration of approximately 64 g/L (i.e., 1.1 M NaCl). Water flux of both FO and MF membranes as well as TDS concentration in terms of mg/L NaCl as a function of time over the course of the OMBR-MF experiments are shown in Figure 5.2. From the beginning of baffled OMBR-MF operation, MF was operated to mitigate the salinity build up in the reactor. Initial FO flux was 11.9 LMH and this flux varied in the range of 11.54-6.98 LMH during the 38 days of continuous operation. During the first five days of operation, more than 9.5 LMH FO flux was observed and then decreased by 1 LMH during the first three weeks of operation. In between 18 to 30 days, the FO flux fluctuated around 8 LMH. In the final phase of the OMBR-MF operation, FO flux gradually decreased to around 7 LMH. Overall, an average of 8.56 LMH FO flux was achieved during the 38 days of continuous operation. The decrease in the FO water flux could be related to the internal concentration polarization (ICP) effect, salt accumulation and biofoulants accumulation on the membrane surface due to MLSS in the reactor. The FO flux decline during OMBR operation has also been reported by other researchers (Wang et al., 2014a).

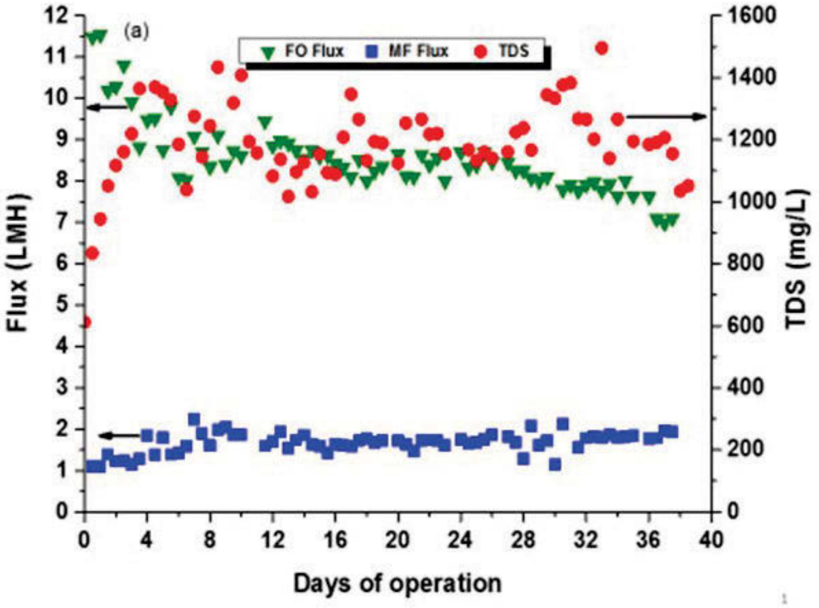


Figure 5.2 Variation of water flux and reactor salinity in baffled OMBR-MF (Feed: synthetic wastewater; draw solution: simulated RO brine; temperature: 20 ± 5°C; membrane orientation: active layer facing the feed solution; 38 days continuous operation).

Recently, Wang et al. (2016c) observed that the water flux in the OMBR with TFC FO membrane quickly reduced from about 15.3 LMH to approximately 8.0 LMH during the first 8 days of operation. The FO flux slightly decreased to the final value of about 3.0 LMH while 22 mS/cm mixed liquor conductivity was reached at the end of the operation. In another continuous OMBR study an average 9 LMH flux was achieved over 30-day examination. However, in order to maintain 9 LMH flux, backwashing was performed at 14, 21 and 28 days respectively (Achilli et al., 2009). In the present study, no membrane cleaning was performed during the 38 days of continuous operation and almost similar average flux (8.56 LMH) was obtained. Moreover, (Holloway et al., 2015b) operated OMBR with UF membrane and reported that during the first three weeks, when OMBR was operated without UF membrane, flux declined considerably (down to 4.2 LMH) and thereafter, by incorporation of UF membrane, FO flux was found to increase and remain stable (4.8 LMH) for the rest of the study. In another MF-OMBR study byWang et al. (2014b), the MF membrane was continuously operated under constant flux at 5 LMH but significant FO flux decline was reported during the first 30 days of operation after which almost stable FO flux (5.5 LMH) was obtained. In the present study, even though MF membrane was operated in parallel to FO, the FO flux decline was gradual and relatively slow. Nevertheless, MF was operated at very low flux (1.1-2.4 LMH) while high FO flux was continuously achieved (average of 8.56 LMH). This also could be attributed to the high permeability of TFC PA membrane in comparison to the above cited studies that employed CTA membrane.

As reported by Luo et al. (2016a), salinity build-up in the bioreactor is an intrinsic phenomenon associated with OMBR operation and the rate of solute diffusion through the membrane depends on membrane selectivity, diffusion coefficient of the solute and on the concentration difference across the membrane (Nguyen et al., 2016a, Holloway et al., 2015a). In practice, to prevent the inhibition of the microbial community activities due to reverse salt flux, the maximum bioreactor tank salinity must not exceed 2 g/L (Holloway et al., 2014, Nguyen et al., 2015). In this study, during the course of operation, the conductivity, TDS and pH (data not shown for pH) in the reactor, FO and MF permeates were measured regularly. Results showed that, due to simultaneous operation of MF membrane with FO, the TDS value did not increase significantly and remained almost stable in the mixed liquor (612-1434 mg/L). The salt permeating through the MF membrane was also helpful to maintain a high driving force between concentrated DS and mixed liquor. It could be seen that the trend of salinity (in terms of EC) variation of the reactor mixed liquor and MF permeate was similar (Figure 5.3) indicating that the incorporation of MF membrane to discharge the soluble salt could effectively decrease the salinity and further alleviate the salt accumulation in the OMBR.

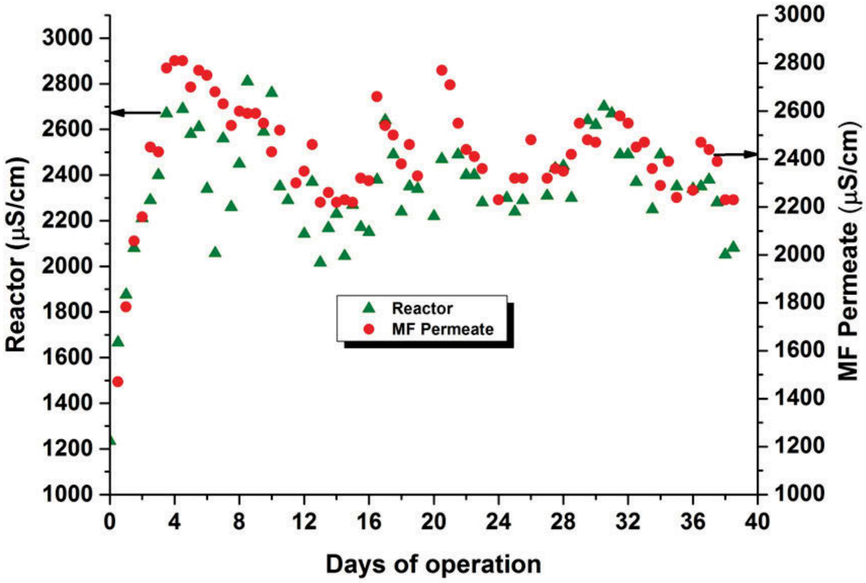


Figure 5.3 Variations of electrical conductivity (EC) in the reactor and MF effluent (Testing conditions are shown in Figure 5.2).

The measured TDS concentration in the bioreactor changed from 612-1434 mg/L corresponding to 1.24-2.92 mS/cm during the first week of study and then after, an average TDS of less than 1200 mg/L was obtained during the rest of investigation time. This salinity range is well below the value reported in previous studies where a stable mixed liquor conductivity of approximately 5 mS/cm was observed during OMBR operation with continuous MF extraction (Qiu et al., 2015, Luo et al., 2016a, Wang et al., 2014b). Further, the result obtained here compares favourably with Luo et al. (2015b) work as they reported that after a small increase in the first week, the mixed liquor conductivity stabilized at approximately 400 mg/L after incorporation of MF membrane.

Similarly, (Holloway et al., 2015b) observed that TDS reached a peak concentration (approximately 8000 mg/L) during OMBR testing without UF membrane. This could be attributed to the small hydrated radius of monovalent ions (Na with a hydrated radius of 0.18 nm and Cl with a hydrated radius of 0.19 nm) which could easily pass through the FO membrane (membrane pore size: 0.37 nm) (Nguyen et al., 2016a). In the previous study, as soon as the UF subsystem was operated in parallel to OMBR, the TDS concentration rapidly declined and remained constant at approximately 1000 mg/L until the end of the UFO-MBR investigation. After incorporation of UF membrane, a stable FO flux of 4.8 LMH was achieved over the duration of the investigation without a single membrane cleaning (Holloway et al., 2015b). Finally, in their work on OMBR, Alturki et al. (2012) observed a rapid increase in the mixed liquor conductivity from 0.27 to 8.27 mS/cm within seven days without housing the submerged MF/UF membrane in the bioreactor (Alturki et al., 2012). It should be emphasized that during the 38 days of baffled OMBR-MF test runs, both the FO and MF membranes were not offered any physical cleaning nor backwashing. The authors believe that during long-term operation, FO biofouling could significantly affect the OMBR-MF hybrid system performance. In order to mitigate biofouling of FO membrane different cleaning techniques can be adopted. The first one could be the physical cleaning of the FO membrane. For this cleaning strategy, OMBR operation should be stopped and FO membrane module should be taken out from the system followed by cleaning with deionised water (DI) and then gentle cleaning with sponge ball. Since fouling layer in FO process is not compact (no applied pressure) (She et al., 2016), one step cleaning can recover the desired initial flux. When the flux recovery is not satisfactory then chemical cleaning can be performed. As reported by Holloway et al. (2015a), chemically enhanced osmotic backwashing is conducted by replacing the draw solution with a very low salinity base (NaOH) or acid (HCl) cleaning solutions, which are continuously recirculated on the draw solution side of the membrane.

5.3.2 Total organic carbon and phosphate removal

Biological process performance of the baffled OMBR-MF hybrid system was assessed with regards to the removal of basic contaminants (i.e. TOC, NH_4-N, TN, and PO_4-P), sludge production, and biological activity. TOC removal in reactor mixed liquor, MF permeate and diluted draw solution (FO) was 91.31 %, 93.51 % and 97.84 % respectively. The average TOC concentration in the feed, reactor, MF permeate and FO was 96.55 mg/L, 8.55 mg/L, 6.25 mg/L and 2 mg/L respectively (Figure 5.4 (a)). The removal of TOC from the OMBR FO channel was over 97% during the entire experimental period. As in the previous study Qiu and Ting (2013) noted that the overall removal rate of organic matter constantly reached up to 98% and the TOC in the DS was less than 5.0 mg/L during OMBR operation. Recently, Wang et al. (2016a) also achieved 96% TOC removal with TFC membrane when treating 140 mg/L fed TOC, with an average of 5.2 mg/L TOC reached in FO permeate.

In the current study, higher TOC removal has been achieved in both reactor and FO permeate as compared to (Wang et al., 2016c). Thus, biological degradation contributed greatly to reduce the concentration of TOC, overcoming the concentration process caused the FO membrane rejection. In the diluted DS and in the MF permeate, TOC concentration further decreased due to the FO and MF membrane rejection, respectively. Nevertheless, the reverse draw solute flux undesirably impacted the biological treatment of OMBR. In fact, TOC concentration in the bioreactor increased slightly at the beginning of OMBR operation (day 7 and 9 respectively). This observation

P) removal is consistent with that reported by (Luo et al., 2016a, Luo et al., 2016b) and could be attributed to the high rejection of almost all the organic matter by the FO membrane, which caused a significant accumulation of non-degradable or/and refractory dissolved organic matter (DOM) within the bioreactor (Qiu and Ting, 2013).

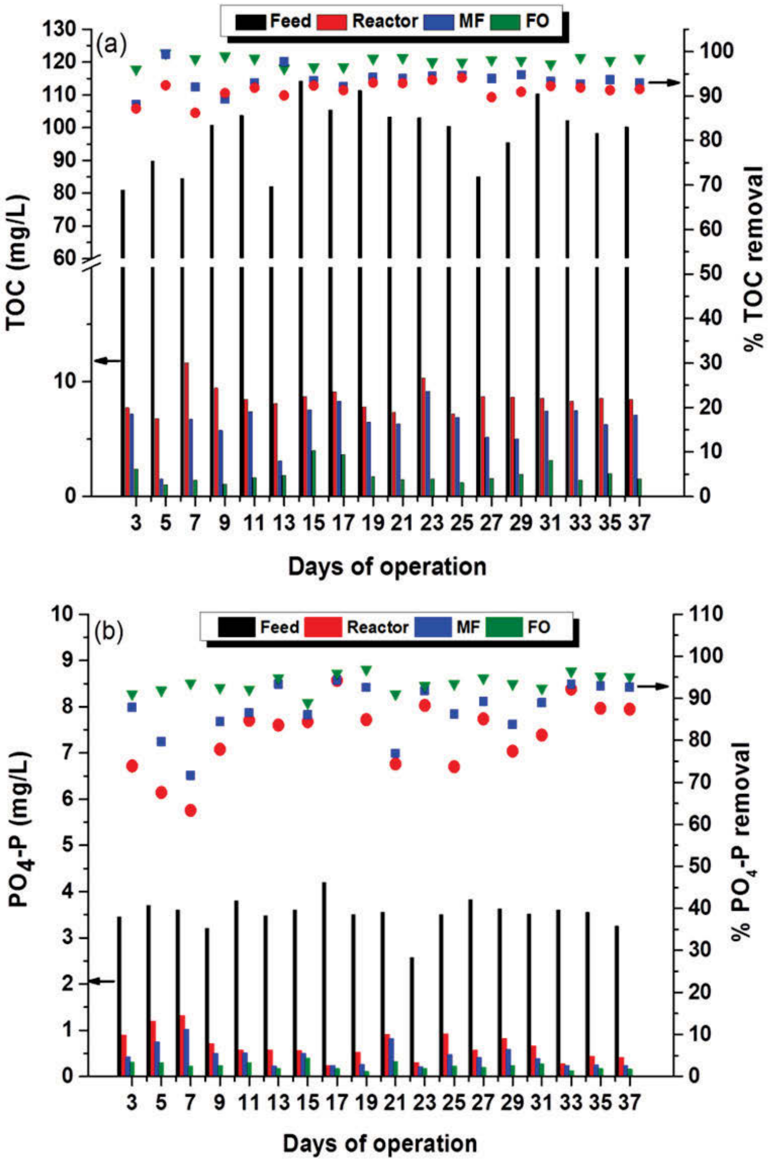


Figure 5.4 Performance of baffled OMBR-MF for (a) TOC removal, (b) phosphate (PO_4-P).

It has been reported that, during OMBR operation, increase salinity in the bioreactor could inhibit the metabolic activity of biomass and plasmolysis causing the release of intracellular constituents and soluble microbial products (Wang et al., 2014a). This study also showed that the presence of high TDS can interfere with the oxygen transfer and affect the biological metabolism thereby reducing the capacity of the reactor to sustain shock loads. The incorporation of MF membrane in the present study successfully kept a salinity level well within the control (Figure 5.2) leading to high TOC removal efficiency (Figure 5.4(a)).

Phosphate can be eliminated by two different mechanisms: assimilation and luxury uptake (Rosenberger et al., 2002). The baffled OMBR-MF system showed very stable and effective performance in achieving high removal of PO_4-P with 81.22 %, 87.36 % and 93.46 % removal efficiency achieved in reactor, MF and FO processes (Figure 5.4 (b)). A relatively high and stable phosphorous removal was observed corresponding to the average 0.23 mg/L obtained in FO permeate. In the baffled OMBR, mixed liquor suspension is cyclically exposed to aerobic and anoxic conditions, and enhanced biological phosphorus removal might have occurred to some extent. In the present study, the observed low DO concentration in the anoxic zone can have created a pseudo-anaerobic condition which would have favoured phosphorous release. During aerobic condition phosphorous uptake by bacteria could have happened. Thus, phosphorus removal can be achieved similarly to what was observed by (Kimura and Watanabe, 2005b). Another possible explanation for the good removal of phosphorus is precipitation with inorganic substances. Aggregates of phosphorus and inorganic substances would settle in dead zones of the bottom of OMBRs (Rosenberger et al., 2002). In present study, salting out might have occurred and some potassium phosphate in the reactor from feed wastewater may have precipitated out with the salt transported in the reactor from draw solution. Thus, regular sludge withdrawal might have achieved phosphorus removal through biomass and settled phosphorus discharge from dead zones. Guo et al. (2008) achieved more than 98% of PO4-P removal in sponge-submerged membrane bioreactor. The explanation given was due to the sponge providing a good anoxic condition around the surface of the sponge and the anaerobic condition inside the sponge which makes the aerobic submerged membrane bioreactor able to achieve a higher removal efficiency of PO_4-P (Guo et al., 2008). In our study, during the OMBR operation it was observed that biomass clung to the outer baffle wall as well to the inside wall of the reactor in anoxic zone. Specifically, when switching over to anoxic cycle, the low DO concentration in the anoxic zone might have created anaerobic condition inside of the biomass that attached to the wall and phosphorous release would possibly have occurred. Qiu et al. (2015) reported 97.9% of phosphate phosphorus (PO_4−P) rejection by the FO membrane in a hybrid microfiltration-forward osmosis membrane bioreactor (MF-FOMBR). In two studies by Nguyen et al. (2015 and 2016), their OMBR systems achieved more than 99% and more than 98% phosphate (PO_4-P) removal respectively. Moreover, Holloway et al. (2007) also showed that very high rejection of phosphate (99.6-99.9 %) by the FO membrane could be attained during concentration of anaerobically digested sludge centrate. Indeed, the FO membrane can almost completely reject PO_4 –P due to its negative charge and the relatively large radius diameter (0.49 nm) of the orthophosphate ion, which is the dominant phosphate species under the conditions tested (Aftab et al., 2015; Praveen and Loh, 2016).

The polyphosphate accumulating organisms are susceptible to saline conditions, and the increased osmotic pressure within their cells due to salt accumulation could diminish their phosphate accumulating capacity (Lay et al., 2010). Kinetics studies have suggested that nitrogen and phosphorus removal efficiency dropped to 20% and 62%, respectively, when salt concentration was 5% NaCl in the bioreactor (Nguyen et al., 2016a). However, in this study, PO_4-P build-up in the bioreactor was not observed which can be attributed to reasonably low salinity as compared to other OMBR reports.

5.3.3 Nitrogen removal

In the proposed baffled OMBR-MF hybrid system, nitrification is carried out in the whole chamber when the liquid level was above the top of the inserted baffles (Figure 3.4) while denitrification proceeds in the outer (anoxic) zone when the liquid level was low. Figure 5.5 (a) shows the removal of NH_4–N during baffled OMBR-MF continuous operation. Initially, 97% of NH_4–N was removed by the reactor, which then decreased down to 80% after 3 days of operation as shown by the NH_4–N concentration increase observed in the reactor.

The stability of nitrification was thus affected since the increase in supernatant NH_4–N concentrations on day 7 (12.5 mg/L) and day 9 (8.9 mg/L) significantly affected effluent concentrations. The drop in the NH_4–N removal could be attributed to the effect of salinity on biomass. Additionally, the ammonia-oxidizing bacteria (AOB) are generally slow growing and more sensitive to changes in environmental conditions such as temperature and salinity (Qiu and Ting, 2013). Therefore, the activity of the AOB and nitrite-oxidizing bacteria (NOB) could easily be inhibited by elevation of salinity (non-halophilic bacteria) which hampered the biological conversion of NH_4–N (Ye et al., 2009). Ye et al. (2009) also showed that a high salinity of 1.02 (W/V%) can be detrimental to the survival of many AOB and other bacteria.

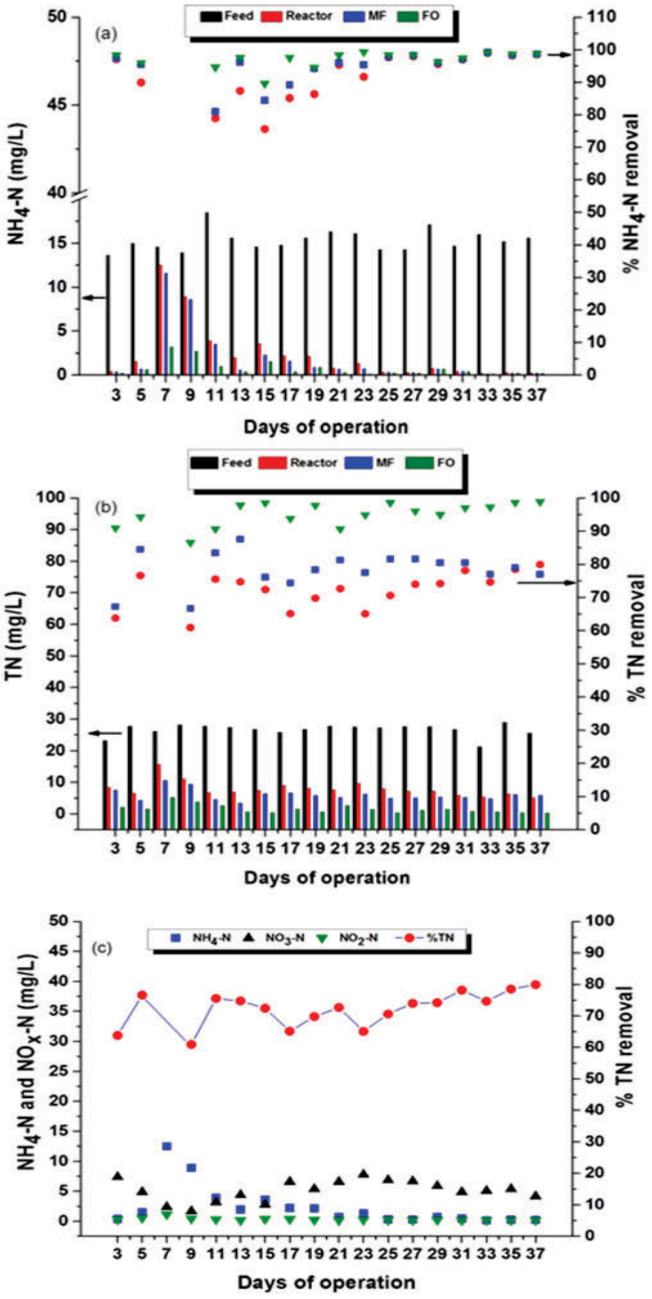


Figure 5.5 Performance of baffled OMBR-MF system for (a) NH_4-N removal, (b) total nitrogen removal, (c) variation of NH_4-N, NO_2-N, NO_3-N and TN removal in the bioreactor.

Besides, the survival bacteria were also shown to be strongly inhibited. Consequently, the NH_4-N removal efficiency decreased greatly. When the salinity level in the bioreactor was then stabilised after 11 days, the nitrifiers regained their potential to remove NH_4–N and as a result the nitrifying activity was restored. In fact, after 19 days of operation, the supernatant NH_4–N concentration decreased significantly and the conversion of NH_4–N finally recovered to more than 97% till the end of the study.

Furthermore, although nitrifiers are slow growing bacteria, the proposed baffled OMBR-MF with a prolonged HRT of 30.25 hours and 115 days SRT was favourable for the relative long generation time of the nitrifying bacteria allowing better removal efficiencies. Aftab et al. (2015b) also observed similar behaviour in their study when targeting NH_4–N removal. In current study, the average NH_4–N concentration of 0.84 and 0.46 mg/L in the MF permeate and diluted DS was obtained respectively. Wang et al. (2016c) achieved about 97% NH_4–N removal in mixed liquor and 99% NH_4–N removal in FO permeate respectively. Most of the OMBR studies reported almost perfect nitrification. However, in this study complete nitrification has not been observed. It is worthwhile to note that in order to achieve simultaneous denitrification, air flow rate was kept quite low during baffled OMBR-MF operation. Therefore, in addition to salinity effect, low air flow rate might have created limited oxygen supply and non-homogeneous aeration; hence complete nitrification might have been compromised. In fact, Kurita et al. (2015) studied a baffled MBR and observed that, due to reduced aeration rate, the supply of oxygen to the biomass was apparently not sufficient; resulting in limited nitrification and an increased concentration of NH_4–N in the treated water. This result can also be correlated to the aerobic-anoxic cycle time (30 min-90 min, respectively). In fact, due to prolonged anoxic cycle time, denitrification performance possibly would have been improved though offset by the increase of NH_4–N. However, during the second and third week of baffled OMBR-MF operation, reasonably high but unstable removal was observed and then from 20 day onwards, more than 95% NH_4-N removal in mixed liquor was achieved.

Total nitrogen concentration in the treated water was apparently lower than that in the feed water (Figure 5.5 (b)). This reduction in TN was accomplished by denitrification due to the creation of anoxic conditions associated with the insertion of the baffles. Hence, the TN removal was well achieved under elevated salinity conditions and overall TN removal rate reached 94.28% in the diluted DS (FO permeate). Considering the all system, 70.38% of average TN removal could be achieved by the reactor (biological process) without recirculation of mixed liquor for 38 days continuous operation. Indeed, removal of nitrogen was significant without addition of external carbon, indicating the effectiveness of the proposed baffled OMBR-MF hybrid system. The stability of nitrification was thus affected since the increase in supernatant NH_4–N concentrations on day 7 (12.5 mg/L) and day 9 (8.9 mg/L) significantly affected effluent concentrations. The drop in the NH_4–N removal could be attributed to the effect of salinity on biomass. Additionally, the ammonia-oxidizing bacteria (AOB) are generally slow growing and more sensitive to changes in environmental conditions such as temperature and salinity (Qiu & Ting 2013). Therefore, the activity of the AOB and nitrite-oxidizing bacteria (NOB) could easily be inhibited by elevation of salinity (non-halophilic bacteria) which hampered the biological conversion of NH_4–N (Ye et al. 2009). Ye et al. (2009) also showed that a high salinity of 1.02 (W/V%) can be detrimental to the survival of many AOB and other bacteria. Besides, the survival bacteria were also shown to be strongly inhibited. Consequently, the NH_4-N removal efficiency decreased greatly( )( )( ). When the salinity level in the bioreactor was then stabilised after 11 days, the nitrifiers

Figure 5.5 (c) shows the changes in concentration of NH_4–N, NO_2-N, and NO_3-N in the mixed liquor during the operation. Denitrification allows maintaining a relatively low NO_3–N concentration with an average concentration of 5.12 mg/L in mixed liquor supernatant within the 38 days of operation. TN removal efficiency is also plotted in Figure 5.5 (c). In the aerobic bioreactor, TN consumption occurs mainly through microbial assimilation. At the same time, nitrification converts NH_4–N to nitrite (NO_2-N) and then nitrate (NO_3-N) under aerobic conditions (Luo et al., 2016b). Incomplete nitrification is usually manifested by the detection of both NH_4–N and NO_x-N in the bioreactor. From Figure 5.5 (c), it is clearly seen that the removal of nitrogen in the baffled OMBR-MF was limited by nitrification especially during the first week of operation. However, considerably good denitrification has been achieved throughout the operation. Overall, TN removal was considerably high in this study.

Figure 5.5 (c) shows that, when NO_3-N concentration in the mixed liquor increases, the T-N in the treated water also increases and TN removal efficiency decreases. Also, in the baffled OMBR-MF system, the high rejection of the FO membrane prolonged the retention time of NO_2–N and NO_3–N within the bioreactor, which also facilitated the removal of NO_2–N and NO_3–N to nitrogen during the anoxic cycle. One explanation for the better TN removal performance was the improvement in the creation of an anoxic environment. This was confirmed by dissolved oxygen (DO) measurements in the anoxic zone. Figure 5.6 shows the DO profile in outer zone of the baffles at two different depths in the aerobic and anoxic zone, respectively. The measured values shown in Figure 5.6 were obtained on day 31, when good removal of nitrogen was observed. As can be seen in Figure 5.6, at time (t= 0 minute) a wastewater pump has started and thus wastewater was fed to the reactor. When water level in the reactor reached on top of the inserted baffles at desired height, the level controller sensor activated and then feed pump stopped automatically. After 30 min, the water level had dropped back to the top of the inserted baffles (end of aerobic cycle time). In order to achieve efficient denitrification in the system, creation of a good anoxic condition in the exterior zone of the reactor is essential. Further, the denitrification is the limiting step in the removal of nitrogen in the operation. In present work, a good anoxic condition was achieved in the outer zone (DO < 0.5 mg/L as shown in Fig. (4)). The experimental data also confirmed that the outer zone worked as an anoxic reactor for a long period in the total operation time which probably explained the superior denitrification performance of the proposed baffled OMBR-MF system. Furthermore, the experimental results also proved that the creation of an anoxic environment could be achieved even in the bottom part of the reactor at 18 cm depth (Fig. (4)). This was probably due to the high concentration of MLSS (4.7-6.1 g/L) which eventually promoted better denitrification. Several studies have indicated the negative effect of salinity on MLSS (as low as 1 g/L MLSS) which adversely led to poor MLVSS/MLSS ratio as low as 0.45 (Wang et al., 2014a). Finally, in the current study, a reasonably high C/N ratio of about 14 has been maintained in baffled OMBR-MF system which is favourable enough to prevail better denitrification and reduction of total nitrogen for baffled OMBR-MF hybrid system.

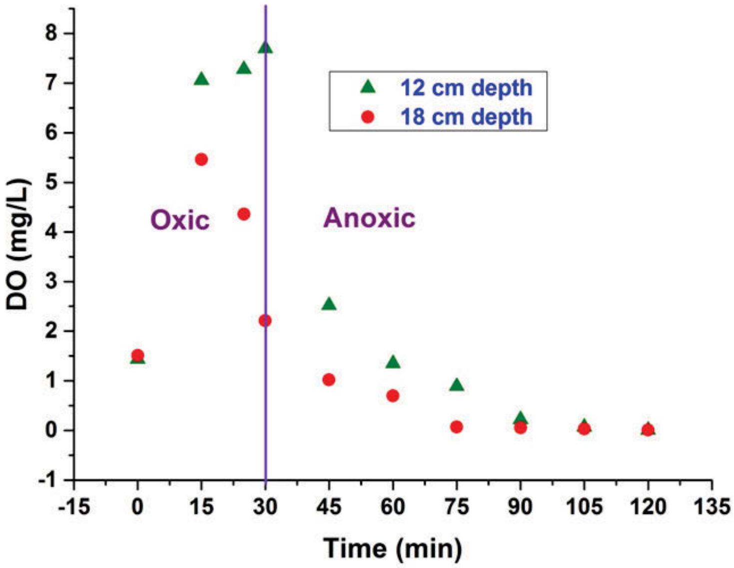


Figure 5.6 Dissolved oxygen (DO) profile with aerobic-anoxic cycle time in baffled OMBR-MF hybrid system.

5.3.4 Biomass activity

Water extraction by the MF membrane from OMBR mixed liquor did not significantly impact biomass characteristics (Figure 5.7). Since very little excess sludge was discharged everyday (i.e. 115 days SRT) from the bioreactor, the MLSS concentration improved with time during the operation. In the later stage (21-38 days), the growth rate of MLSS was steady about 6 g/L due to low sludge organic loading. The MLSS concentration in the reactor varied from 4.7 to 6.1 g/L over the 38 days of continuous operation. Some studies (Li et al., 2016) demonstrated that high salinity in the mixed liquor adversely impacts on the MLSS. For example, Wang et al. (2016c) operated OMBR, employing both CTA and TFC membranes, at 0.76 g/L stable MLSS and the MLVSS/MLSS ratio dropped down to 41% within 33 days operation. This finding was correlated with the increase salinity level in the reactor; (reaching up to 20 mS/cm), clearly showing the adverse effect of salinity on microbial activity. In another study, (Luo et al., 2016b) noted that a small but noticeable decrease in MLSS concentration was observed during OMBR operation with 0.5 M NaCl as a DS and yet at infinite SRT conditions.

Alturki et al. (2012) reported that build-up of salinity level up to 4.13 g/L of NaCl led to a gradual decrease in the ratio of MLVSS over MLSS from 0.87 to 0.66 after seven days of operation. The decrease in the MLVSS/MLSS ratio indicates that biological activity of the reactor may have deteriorated over time (Alturki et al., 2012). Further, an increase in the osmotic stress could result in the dehydration and plasmolysis of bacterial cells and thus reduce their viability (Luo et al., 2016a). However, in the present work, the relatively low salt concentration (< 1.5 g/L over the entire operating time) in the bioreactor enabled the normal growth of the microbial community due to continuous salt bleeding by MF membrane and daily withdrawn mixed liquor (100 mL) from the bioreactor. Thus, high concentration of active biomass as well as a stable and high (i.e. above 0.84) MLVSS/MLSS ratio was maintained during the operation (Figure 5.7).

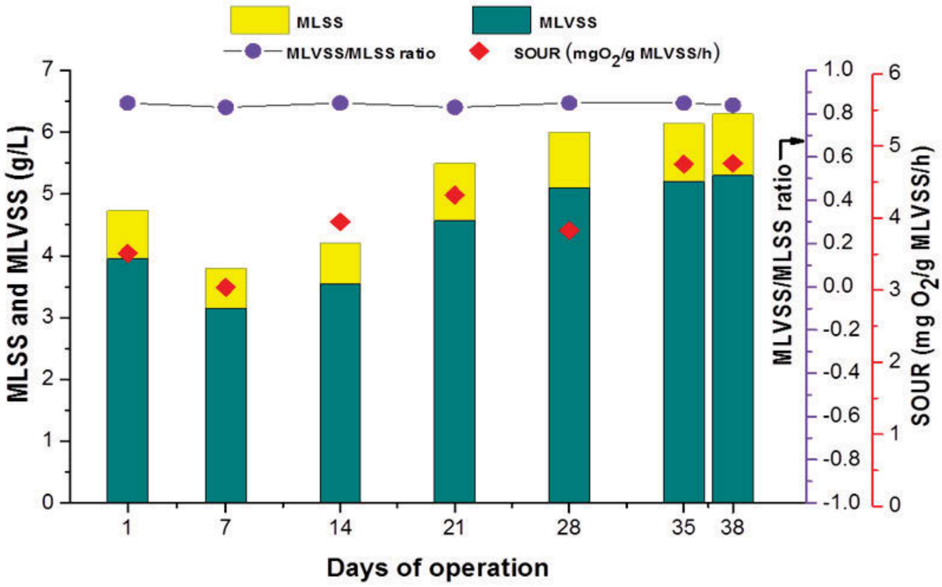


Figure 5.7 Variation of MLSS, MLVSS concentrations and MLVSS/MLSS ratio and SOUR in baffled OMBR-MF hybrid system with time in bioreactor. Mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) concentrations were analysed based on Standard Method 2540 (APHA, 1998). SOUR was determined based on Standard Method 1683 (APHA, 1998) to indicate biomass activity. Experimental conditions are shown in Fig. 5.2.

The Specific Oxygen Uptake Rate (SOUR), also known as the oxygen consumption or respiration rate, is defined as the milligram of oxygen consumed per gram of volatile suspended solids (VSS) per hour. Biomass activity was evaluated by determining the specific oxygen uptake rate (SOUR) of activated sludge in OMBR. The specific oxygen uptake rate (SOUR) has been widely used to understand the effect of a higher concentration of materials including salt on the activity of biomass in various aerobic processes (Choi et al., 2007). In this study, respiration test of the activated sludge showed a significant decrease in the SOUR from an initial 4.51–3.03 mg O_2/g MLVSS/h during the first week of baffled OMBR-MF hybrid system, suggesting a deterioration of biological activity (Fig. 5.7). This observation is in good agreement with previous studies (Wang et al., 2014b, Luo et al., 2015a), and could be ascribed to the inhibition on biomass growth and activity with salinity increase (Luo et al., 2017b). Luo et al. (2015a) noted that the SOUR of the biomass in the control-MBR was stable at approximately 2.8 mg O_2/g MLVSS h during the experiment. However, a lower SOUR value (2–2.5 mg O_2/g MLVSS h) was observed in the saline-MBR with increasing the NaCl concentration from 10 to 16 g/L. Lay et al. (2010) also confirmed the adverse impact of salinity build-up on the microbial activity during biological treatment. In our long term OMBR operation, after first week biomass growth (indicated by the MLSS and MLVSS concentrations) and activity (indicated by the sludge SOUR) were relatively high in this study. This increased SOUR level can be attributed to the fact that due to continuous MF membrane operation in present study, salt accumulation in the reactor was not abruptly increased as reported in other OMBR studies. This probably provided sufficient time and favourable conditions for microorganisms to proliferate well. Actually, as can be seen in Figure 5.7, in the following weeks, measured SOUR was well within the optimum range prescribed for MBR operation (i.e. 3-5 mg O_2/g MLVSS/h) while the salinity level in the bioreactor was stabilised (Figure 5.7).

5.3.5 Fouling behaviour

Figure 5.8 (a) shows the image of FO membrane before and after (fouled) 38 days of continuous operation. No significant foulant deposition has been observed on the membrane surface. Since the baffled OMBR-MF system was operated with the membrane active layer facing the feed side (AL-FS mode), foulant build up occurs on the active layer, where it could easily be removed by hydraulic shear force due to continuous aeration (Mi and Elimelech, 2008). This is different from what occurs with microporous membranes in traditional MBR, where the initial foulant deposition takes place within the porous structure of the membranes, and hydraulic shear forces cannot effectively remove the foulant (Qiu and Ting, 2013). Figure 5.8 (b) shows SEM images of both pristine and fouled TFC membranes, respectively. It could be observed from SEM images that the surface of pristine TFC FO membrane is rougher and more rugged (valley like structure-Magnification x 5000). As shown in SEM observation for fouled membrane, compared with the original membrane, the active layer of fouled membrane surface was almost fully covered with a rather thin and compact gel-like fouling layer. The foulant layer was 2.38 μm thick as deduced from the SEM image. This is smaller than the typical thickness of 20–50 μm fouling layer found in MBRs (Lay et al., 2011). It is worthwhile to note that the fouling layer on the FO membrane surface was very thin, and it had only a small effect on the water flux during the entire operation time.

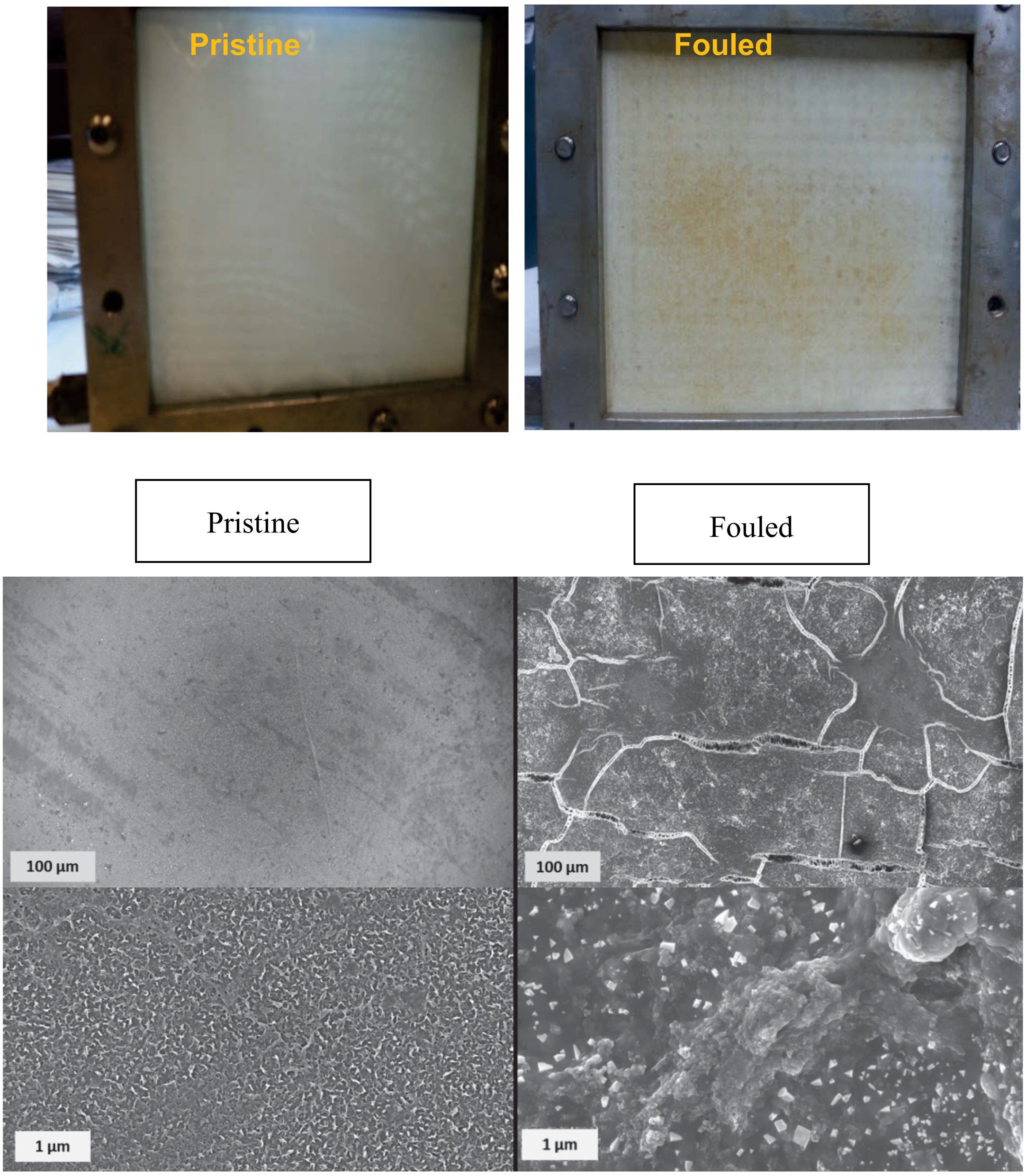
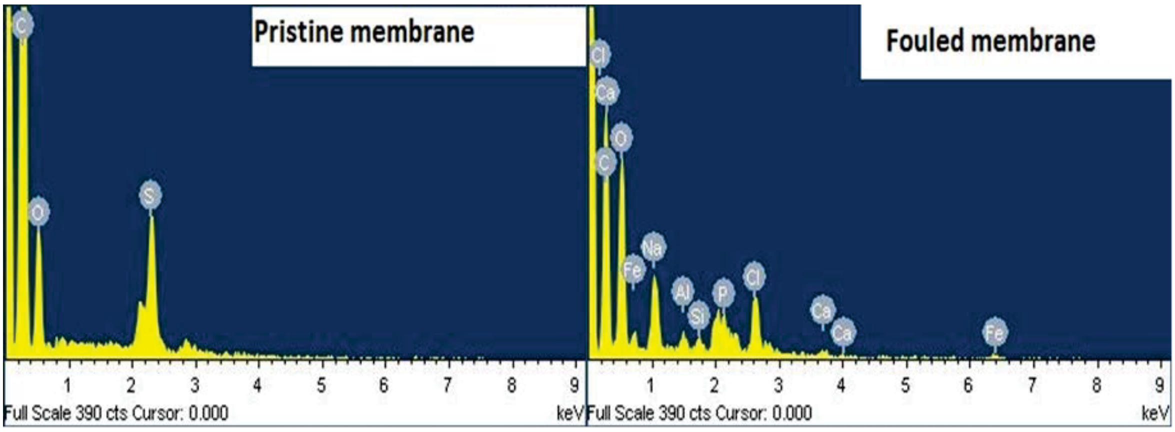


Figure 5.8 (a) Picture of the FO membrane before and after baffled OMBR-MF hybrid operation, and (b) SEM images of active layer of the pristine membrane and fouled membrane (morphology of flat-sheet membrane at 100x (top) and enlarged at 5000x (bottom) respectively.

The EDX analysis for both pristine and fouled membrane (Figure 5.9) was also performed. From EDX analysis of pristine membrane, it can be seen that the TFC FO membrane surface mainly includes C, O and S. On the other hand, many inorganic elements such as

Na, Ca, Fe, Al, Cl, P and Si were observed on the fouled membrane surface. The source for many of those inorganic elements was most probably the synthetic wastewater (e.g. Fe, P). The presence of Na and Cl could be correlated to the reverse salt diffusion from the DS.



	Pristine membrane		**Fouled membrane**	
Element	**Weight%**	**Atomic%**	**Weight%**	**Atomic%**
C	75.01	82.66	44.22	59.02
O	16.95	14.02	28.36	28.42
S	8.04	3.32	--	--
Na	--	--	5.25	3.66
Al	--	--	0.96	0.57
Si	--	--	1.04	0.60
P	--	--	2.06	1.07
Cl	--	--	7.93	3.59
Ca	--	--	1.33	0.53
Fe	--	--	8.85	2.54
Total	100		100	

Figure 5.9 EDX spectrum with element composition from the active layer of the pristine and fouled membrane cake layers formed using simulated RO brine draw solution.

5.4 Conclusions

Primary findings drawn from this study can be summarized as follow:

- The performance of a novel baffled OMBR-MF hybrid system was examined for water flux, salinity build up and nutrient removal specifically SND was successfully achieved in a single reactor.
- An average of 8.56 LMH FO flux was achieved during 38 days of continuous operation.
- MF membrane incorporation alleviated salinity build up and hence better performance was achieved.
- The dissolved oxygen profile during the aerobic-anoxic cycle confirmed < 0.5 mg/L oxygen favourable for denitrification.
- More than 97 % TOC, 87 % PO_4-P and 94% TN removal was achieved from OMBR-FO channel.

CHAPTER 6

UNIVERSITY OF TECHNOLOGY SYDNEY

Faculty of Engineering & Information Technology

ASSESSING THE REMOVAL OF ORGANIC MICROPOLLUTANTS BY A NOVEL BAFFLED OSMOTIC MEMBRANE BIOREACTOR-MICROFILTRATION HYBRID SYSTEM

6 Assessing the removal of organic micropollutants by a novel baffled osmotic membrane bioreactor-microfiltration hybrid system

6.1 Introduction

With rapidly growing world's population, climate change and extensive industrialization pressure is increasing on the limited fresh water resources (Kim et al., 2017). Increased water scarcity led to advancement of many technologies that utilize alternative water sources, such as domestic sewage. This can help in protecting environment and ease water paucity by indirect and direct reuse of impaired water (Luo et al., 2016a). Nevertheless, wastewater treatment processes facing some issues, specifically regarding organic micropollutant removal (Nguyen et al., 2016a). Removal of OMPs from wastewater by current physico-chemical technologies is prohibitively expensive (Singhal and Perez-Garcia, 2016). Wastewater treatment facilities using conventional activated sludge treatment are ineffective and inconsistent of degrading the wide range of organic micropollutants that could potentially pose risks to humans and the environment (Holloway et al., 2014, Singhal and Perez-Garcia, 2016).

Therefore, main concern to reclaimed water application is unpredictable and usually limited OMPs removal by traditional wastewater treatment processes (Luo et al., 2016a). Novel OMPs removal or destruction options are activated carbon, ultraviolet (UV) disinfection and advanced oxidation processes (AOP). Also, membrane bioreactor (MBR), reverse osmosis (RO), nanofiltration (NF) and more recently, forward osmosis (FO) have been used extensively. In various studies it was found that the removal efficiency mostly depends on OMPs hydrophilicity, surface charge, and bio degradability (Besha et al., 2017, Coday et al., 2014, Luo et al., 2016a). Advanced treatment processes based on MBR technologies can achieve higher and more consistent micropollutants removal compared to conventional systems (Besha et al., 2017). It has been investigated that MBR process efficiently remove moderately biodegradable and hydrophobic OMPs to conventional process (Park et al., 2015). Although MBR effectively removes some of the OMPs like ibuprofen, it cannot be used as an absolute barrier to effectively remove some poorly biodegradable OMPs (Alturki et al., 2012, Besha et al., 2017). In fact, MBR could not remove hydrophilic OMPs very well due to their persistent nature and low bio-adsorption on sludge (Luo et al., 2017b). Further, it has been demonstrated that during MBR treatment, hydrophobic trace organic contaminants can adsorb to the MLSS, resulting in a longer retention time in the bioreactor, hence leading to enhanced removal efficiency. However, current MBR systems are not effective for the removal of some persistent and hydrophilic trace organic contaminants (Tadkaew et al., 2011). Therefore, in this study we have selected three representative compounds caffeine, atenolol and atrazine. Caffeine shows resistance to biodegradation in the beginning of the treatment but most commonly found stimulant, atenolol has higher molecular weight so easy to remove by FO membrane and Atrazine is most persistent as well as shows low FO rejection. An environmental and health significance of those compounds are described as follows.

Caffeine (3,7-dihydro-1,3,7-trimethyl-1h-purine-2,6-dione) has been coined the most commonly consumed stimulant by humans (Moore et al., 2008). The common sources of caffeine are coffee, tea, soft and energy drinks, and caffeine supplements (stimulants), which explain why it is usually detected at high concentration in raw sewage (Luo et al., 2014). It has been reported that an estimated global average consumption of 70 mg caffeine/person/d. An unknown portion of this consumption makes its way through wastewater-treatment plants globally, and some caffeine will inevitably be deposited into aquatic receiving systems. Caffeine concentrations resulting in lethal and sublethal effects on aquatic organisms were greater than those detected in surface waters globally (Moore et al., 2008).

Gaudet-Hull et al. (1994) found that caffeine concentrations in water were high enough to affect Xenopus laevis egg development when exposed for 96 hours (LC50 = 0.22 to 0.37 mg/mL). The mutagenic potential of caffeine in lower organisms, such as bacteria and fungi, and in mammalian cells in the absence of an exogenous metabolic activation system. Apart from the mutagenic effects, it is important to point out that caffeine toxicity in humans has been associated with irritability, insomnia, nervousness, diuresis, muscle twitching, cardiovascular disorders and gastrointestinal disturbances (Fernandes et al., 2017). Notwithstanding,, the continuous introduction of caffeine may cause subtle effects acting as a pseudo-persistent pollutant for its continuous release in the environment and little is known about its chronic effects (OECD, 2002)(Zarrelli et al., 2014).

Atenolol, a beta-blocker, is commonly found in wastewater, treated effluent, and in the open environment. Studies have shown that atenolol can affect the function of vital cellular activities in fish. Environmentally relevant concentrations of atenolol have been shown to cause the reduction of hemoglobin in trout (Steinbach et al., 2013). The production of glucose in trout has also been shown to be greatly decreased when in an environment with concentrations as low as 0.01 nM. These effects from atenolol have the possibility of decreasing the overall fitness of fish exposed to even small concentrations(Campbell, 2017).

Atenolol had slight stimulatory consequences on E. coli (p ¼ 0.12, q ¼ 0.36) and HEK293 (p ¼ 0.093, q ¼ 0.63) cell proliferation. This drug binds to b-adrenergic receptors in human cells, enhancing several metabolic functions including carbohydrate oxidation and glycogenolysis (Pomati et al., 2007). These receptors are commonly found in the kidneys, which explains the specific response observed here on HEK293. Although the toxicity of atenolol as the individual compound is negligible, it shows a synergistic effect when atenolol is mixed with other β-blockers in the environment (Xu, 2017).

Atrazine is one of the chloro-triazines, which also include simazine and cyanazine (Ribaudo and Bouzaher, 1994). Atrazine is slightly to moderately toxic to freshwater fish and slightly to highly toxic to freshwater invertebrates (IRED, 2006). For aquatic environments reported half-lives were much longer. In an anaerobic aquatic study, atrazine's overall half-life, water half-life, and sediment half-life were given as 608, 578, and 330 days, respectively (IRED, 2006).

The Environmental Protection Agency (EPA) has officially classified atrazine as a possible human carcinogen (class C). Some information indicates that atrazine causes cancer in rats receiving high doses over the course of their lifetimes (Ribaudo and Bouzaher, 1994). Whether the effects seen in animals are relevant to humans is disputed, but a few recent epidemiological studies have found associations between atrazine levels in drinking water and increased levels of birth defects. In one study, researchers found that babies conceived in the months with the highest atrazine levels in drinking water are the most likely to suffer from birth defects. Lazorko-Connon and Achari (2009) reported that with the few studies conducted on the effects of atrazine to humans, the herbicide is being implicated for increases in various cancers including ovarian, prostate, breast, and non-Hodgkin's lymphoma. Other studies have found that atrazine exposure increases the chance of having an underweight, small, or premature baby and the risk of miscarriage (2011). It can be concluded that the presence of atrazine in different spheres of environment causes severe effects on human health. These range from those on nervous system, immune system, kidney, heart and liver as well as on hormones and enzymes (Pathak and Dikshit, 2011).

More recently research effort has been dedicated to the development of an innovative osmotic membrane bioreactor (OMBR) process, which uniting activated sludge process with forward osmosis (FO) membrane (Luo et al., 2015b, Nguyen et al., 2015). FO membrane appeared as a robust alternative for the indirect and direct potable reuse applications and a good barrier to OMPs in the bioreactor thereby aiding their consequent biodegradation (Coday et al., 2014). OMBRs have many advantages such as higher quality product water, lower fouling propensity than conventional membrane processes and better energy efficiency. However, the salt accumulation in the mixed liquor due to the reverse salt flux (RSF) from the draw solution (DS) and the osmotic concentration of the feed solution leads to a reduced driving force for permeate flux and also affect the biological activity inside the reactor (Lay et al., 2010, Luo et al., 2015a, Nguyen et al., 2015, Pathak et al., 2017, Qiu and Ting, 2013).

Nitrogen compounds are nutrients limiting sewage treatment and they can cause a variety of problems, including a reduction in concentrations of dissolved oxygen in water sources which can lead the death of fish and also bring about eutrophication (Derakhshan et al., 2018). Nitrogen removal by simultaneous nitrification/denitrification (SND) requires a separate anoxic tank in the process with circulation of the mixed liquor from the anoxic tank and membrane tank in a MBR plant. Circulation of the mixed liquor suspension accounts for 10-15% of total energy consumption in current MBRs. Kimura et al. (2007a) proposed a baffled membrane bioreactor that can eliminate the energy needed for the mixed liquor circulation. In our previous work, Pathak et al. (2017) successfully demonstrated the performance of a novel baffled OMBR in which baffles are inserted in the reaction tank and feed water is drawn through FO membranes. By utilizing this method, SND can be promoted in a single reactor. As a result, sludge recirculation pump and anoxic tank mixer can be omitted (Pathak et al., 2017).

This paper investigated the technical feasibility of a baffled OMBR-MF hybrid system for wastewater treatment applications, in particular the efficiency of OMPs removal under oxic-anoxic conditions. This study also evaluated carbonaceous organic removal and nutrient removal in a baffled OMBR-MF system employing inorganic and organic draw solutes. The baffled OMBR-MF system performance was investigated in terms of permeate flux and salt accumulation, analysing growth of biofouling layer and microbial activity using confocal laser scanning microscopy (CLSM), extracellular polymeric substances (EPS) and floc size analysis respectively. Lastly, three model OMPs were analysed to evaluate the feasibility for wastewater reuse.

6.2 Experimental

The experiments were carried out according to the procedures descried in chapter 3. Laboratory scale experimental set-up (Figure 3.3) and general operational procedure are shown in chapter 3. The CTA-FO and MF membrane characteristics are detailed in Table 3.1. FO membrane module and baffled reactor used in this experiment are shown in Figure 3.2 and Figure 3.4 respectively.

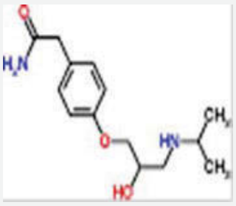
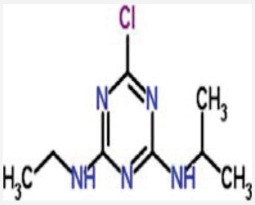
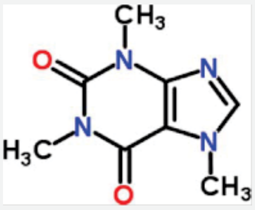
6.2.1 Feed solution

Synthetic wastewater was used as a feed solution and details of feed solution preparation are provided in Chapter 3. In lab-scale baffled OMBR-MF hybrid system three OMPs removal was examined. Atenolol, atrazine and caffeine were supplied by Sigma Aldrich (Saudi Arabia). All three OMPs commonly exist in sewage and considered as persistent to conventional activated sludge process. Atenolol is a beta-blocker retaining both electron donating groups (-OR, -CH) and electron withdrawing group (-$CONH_2$). Similarly atrazine is a herbicide also has electron donating group (-NHR) and electron withdrawing group (-Cl). Wei et al. (2016) reported that caffeine being a stimulant and its removal was too less in the beginning and it would need longer adaptation time even though cyclic structure has strong electron donating group (-R). Their key properties are provided in Table 6.1. Stock solution with a final concentration of 3 g/L (i.e., 1 g/L for each OMP) was prepared by dissolving 3 mg of OMP compounds (i.e., 1 mg for each OMP) in 1 mL of pure methanol. The stock solution was then stored in a refrigerator at 4 °C prior to the experiments.

6.2.2 Draw solutions

The DS employed in this study were prepared to make 0.75 M by dissolving respective salts of three different chemicals sodium chloride (NaCl), potassium chloride (KCl) and sodium acetate (CH_3COONa or NaOAc) in deionized (DI) water. The chemicals used in this study were reagent grade procured from Sigma-Aldrich, Saudi Arabia. NaCl and KCl were selected as inorganic DS and NaOAc was chosen as organic DS to compare the performance of baffled OMBR between inorganic and organic draw solutes. NaCl is commonly used inorganic ionic salt draw solute in most of all OMBR studies. KCl is inorganic salt with high water flux. These solutes are ideal for minimizing ICP and creating high osmotic pressures. Both NaCl and KCl possess high solubilities in water and no toxicity. The use of organic based draw solutes such as salts of NaOAc exhibits significantly lower reverse salt flux than that for inorganic DS. Additionally, organic DS are biodegradable and do not contribute toward salinity build-up in the bioreactor (Yap et al., 2012, Achilli et al., 2010, Bowden et al., 2012). Thermodynamic properties of DS were determined at temperature of 20 ºC using OLI Stream Analyzer (OLI System Inc., Morris Plains, NJ, USA) and provided in Table 6.2. The osmotic pressure of 0.75 M NaCl, KCl and NaOAc were 34.08, 32.45 and 30.38 atm respectively. The corresponding diffusivities were 1.32×10-9 m^2/s, 1.61× 10-9 m^2/s and 1.07×10-9 m^2/s for NaCl, KCl and NaOAc respectively.

Table 6.1 Physicochemical properties of OMPs used in this study

	Atenolol	**Atrazine**	**Caffeine**
Structure[a]			
Application	Beta-blocker	Herbicide	Stimulant
Formula	$C_{14}H_{22}N_2O_3$	$C_8H_{14}ClN_5$	$C_8H_{10}N_4O_2$
Molecular weight	266.3 Da	215.7 Da	194.2 Da
Charge	Positive	Neutral	Neutral
pKa[a]	9.6	1.7	10.4
Log Kow[a]	0.16	2.61	−0.07

6.2.3 OMBR-MF hybrid system operational protocol

The OMBR-MF hybrid system was operated from day 1 to 7, day 10 to 16 and day 19 to 25 using KCl, NaCl and NaOAc DS respectively. At end of each run FO operation was ceased and reactor was operated solely with MF membrane in order to reduce salinity to initial value. In the beginning of each run new CTA-FO membrane and new DS was employed.

Table 6.2 Characteristics of draw solution (DS) used in OMBR-MF system

Chemicals	**Potassium chloride**	**Sodium chloride**	**Sodium acetate**
Formula	KCl	NaCl	CH_3COONa
Molecular weight (g/mol)	74.6	58.5	74.6
Concentration (M)	0.75	0.75	0.75
Osmotic pressure (atm)	32.45	34.08	30.38
Diffusivity ($\times 10^{-9}$ m^2/s)	1.61	1.32	1.07
Viscosity (cP)	0.99	1.07	1.31

Thermodynamic properties were determined at temperature of 20 ºC by using OLI Stream Analyzer.

6.3 Analytical methods

General analytical methods have been reported in section 3.3 in Chapter 3. Specific analytical techniques employed in this study have been discussed in the following sections of this chapter.

6.3.1 LC-MS for organic micropollutants measurement

OMPs analysis was performed by following same protocol as mentioned in previous work (Wei et al., 2016). For each OMP analysis 50 ml sample was aliquoted. This OMP sample was spiked with the corresponding isotopes and then concentrated using solid phase extraction device (Dione Autotrace 280) (Figure 6.1). The prepared samples were then injected at flow rate of 1 mL/min and filtrated through Cartridge Filters Oasis® HLB 6cc (500mg) from Waters Cartridge Filters Oasis® HLB are specialized in the extraction of organic compounds, as they are made from two monomers N-vinylpyrrolidone (hydrophilic) and lipophilic divinylbenzene (hydrophobic) which provide them with a high capacity for the retention of organic compounds. After the sample was extracted and concentrated by SPE, the 10 mL eluted sample was vaporized and further concentrated into 1mL sample by a Turbo Vap® concentration workstation at 39°C and under Nitrogen gas atmosphere. Once the compounds were retained inside the cartridge filter, they were eluted through organic solvents (MeOH and 10% MeOH in MTBE) at 1 mL/min flow rate. All the reagents and solvents used for processing and extracting the samples are analytical grade (>99% purity) and HPLC purity.

The organic micropollutants quantification was carried out through a Liquid Chromatograph Agilent Technologies® 1260 Infinity coupled with a Mass Spectrometer AB SCIEX QTRAP 550 equipped with a Luna 5u C18 (2) 100 A Phenomenex® column (No. 00F-4252-E0) (Figure 6.1) with dimensions of 150 x 4.60 mm and 5 μm pore size. A sample volume of 20μL was injected in each run at 0.8 mL/min flow rate. The mobile phase used was a positive phase composed by A) 0.1% Formic Acid in Extra Pure Water and B) 0.1% Formic Acid in Methanol (as the Formic Acid donates only one H+ enhancing the ionization of molecules); the mobile phase gradient involved 65% A held for 0.5 min, then stepped down to 50% at 0.51 min and decreased linearly to 5% at minute 8. It is held at 5% for 6 mins, then stepped up to 65% A for an equilibration step of 4 min, giving a total running time of 18 mins. The quantification analysis and data process was carried on through the software Analysit® Instrumental Control and Data processing Software Version 1.6 by AB Sciex (Sanchez Huerta, 2016).

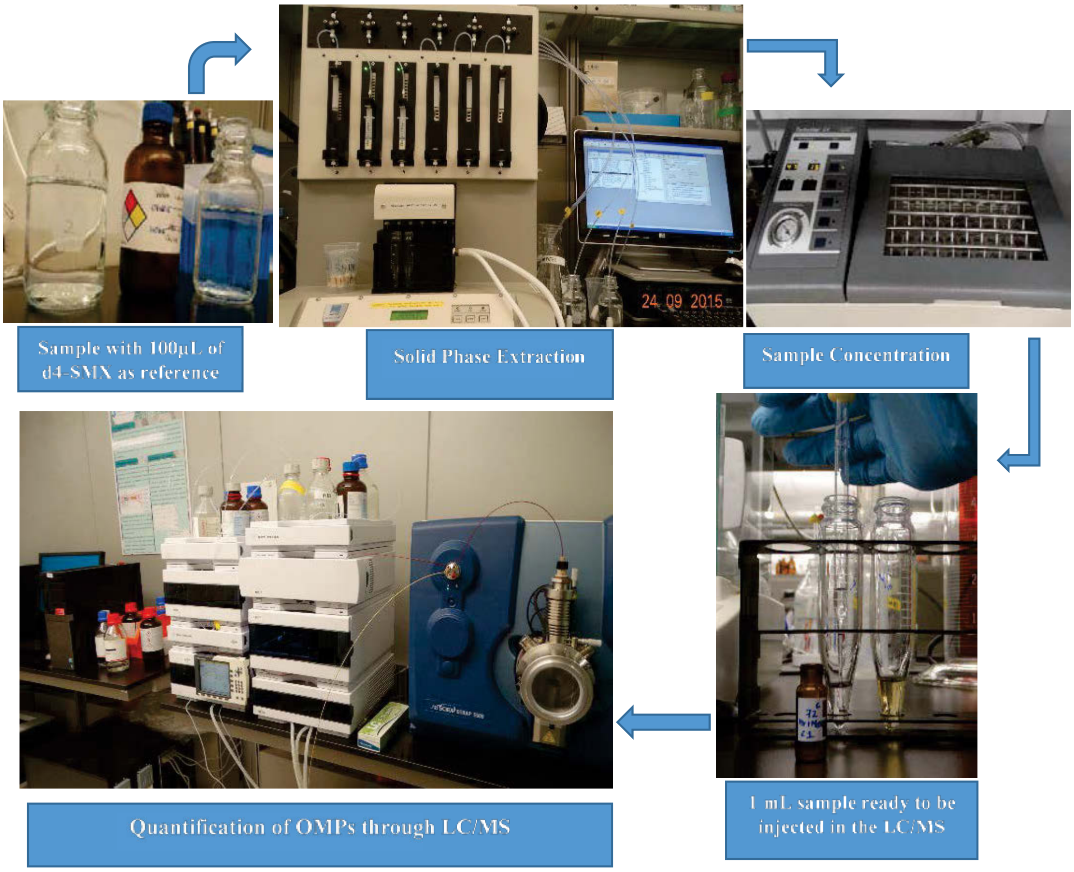


Figure 6.1 Sample preparation and quantification of OMPs in LC/MS. Adapted from (Sanchez Huerta, 2016).

6.3.2 Organic micropollutants removal efficiency

OMPs removal in the reactor and MF can be obtained using Eq. (1). Since FO utilized DS, OMPs removal in FO should be calculated in a different way using Eq. (2) (Cui et al., 2014).

$$\boldsymbol{R_{OMPs}} = \left(\mathbf{1} - \frac{\boldsymbol{C_{OMPs}}}{\boldsymbol{C_{OMPs,f}}}\right) \times \mathbf{100\%} \tag{6.1}$$

$$\boldsymbol{R_{FO,OMPs}} = \left(\mathbf{1} - \frac{\boldsymbol{C_{D,OMPs} \times V_D / V_P}}{\boldsymbol{C_{OMPs,f}}}\right) \times \mathbf{100\%} \tag{6.2}$$

Where, R_{OMPs} is the removal efficiency for organic micropollutants in the reactor or MF membrane, $R_{FO,OMPs}$ is the removal efficiency for organic micropollutants in FO, C_{OMPs} is the concentration of OMPs in the MF permeate or the reactor (mmol/L), $C_{D,OMPs}$ is the concentration of OMPs in DS (mmol/L), $C_{OMPs,f}$ is the concentration of organic micropollutants in feed solution (mmol/L), V_D is the volume of DS (L) and V_P is the volume of the FO permeate (L).

6.3.3 Liquid chromatography-organic carbon detection (LC-OCD)

Liquid chromatography-organic carbon detection (LC-OCD) developed based on size-exclusion chromatography (SEC) was utilized to characterize the water-soluble organic carbon (OC) such as polysaccharides and proteins found in EPS.

Characterisation of dissolved organic carbon (DOC) composition in the reactor mixed liquor and foulant solution samples was carried out using the LC-OCD (Figure 6.2). The LC-OCD (Model 8, DOC-LABOR, Germany) with a size exclusive chromatography (SEC) column filled with Toyopearl resin (HW-50S) technique employed in this work provided more detailed information on all hydrophilic fractions (such as biopolymers including polysaccharides and proteins, humic substances, building blocks, and low molecular weight substances) (Wei & Amy, 2013).

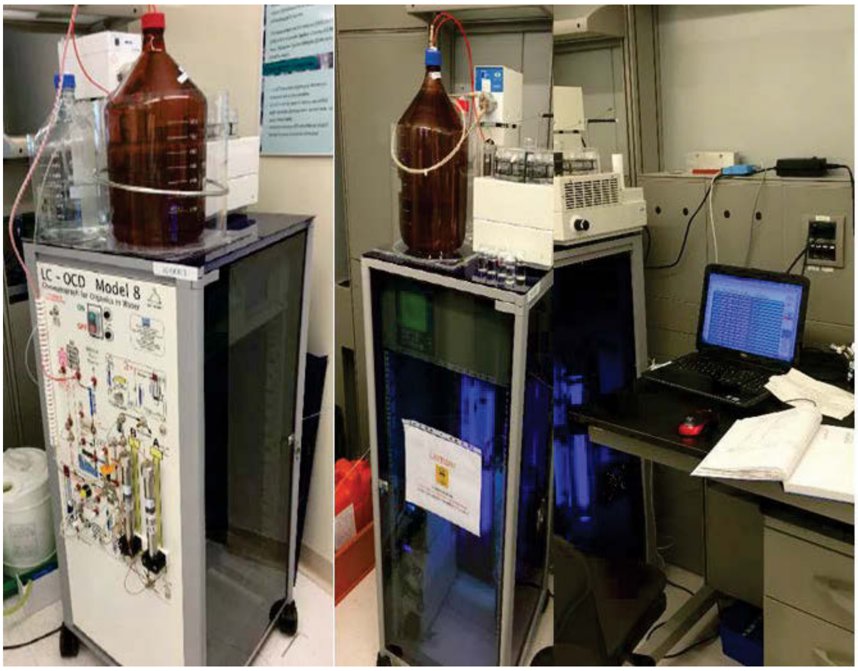


Figure 6.2 Liquid chromatography-organic carbon detection (LC-OCD) analysis.

A LC-OCD (Model 8, DOC-LABOR, Germany) with a size exclusive chromatography (SEC) column filled with Toyopearl resin (HW-50S) was used to characterize the fractions of sludge water according to the molecular weight (MW) corresponding to the retention (or elution) time in SEC column as follows: biopolymers (including polysaccharides, proteins, and aminosugars) with MW>20 kDa (retention time of 26–38 min), humic substances (HS) with MW of 500–1000 Da (retention time of 40–46 min), building blocks (i.e., breakdown products of humics) with MW of 300–500 Da (retention time of 46–53 min), low molecular weight (LMW) acids and HS with MW<350 Da (retention time of 53–57 min) and LMW neutrals (including monooligosaccharides, alcohols, aldehydes, ketones) with MW<350 Da (retention time >57 min). One sample flowed into 3 detectors (UVD, OCD, OND) sequentially, where the UVD measured the spectral adsorption coefficient at 254 nm, the OCD oxidized all organic matter in a thin film UV reactor and measured OC in terms of the produced CO_2 by a non-dispersive infrared detector, the OND oxidized organic nitrogen into nitrate and measured nitrate using UVD at 220 nm. The quantitative results on the whole sample and all fractions could be obtained through the pre-established calibration curves using standard substances (Wei and Amy, 2013).

6.3.4 Confocal laser scanning microscopy (CLSM)

The fouled FO membranes were removed from the bioreactor at the end of each experimental run with all three DS. For each sample, the membrane was cut into 1.0 cm x 1.5 cm membrane coupons to ensure the representativeness of results. The fouled membrane samples were stained with a mixed dye for both live and dead bacteria (LIVE/DEAD BacLight from Molecular Probes company), which consisting of SYTO 9 and Propidium iodide dyes. After staining, the membrane coupons were kept at ambient temperature under dark for half an hour.

CLSM analyses were conducted on an up-right CLSM platform (LSM 710, Zeiss), applying 488 nm and 620 nm argon laser for laser line excitation. As the top morphology of the FO membrane could change when it dries, and thus influences the biofilm observation, membrane samples in a wet state were directly placed on a glass slide for analyses after rinsing with PBS solution. After visualization of the biofilm, the corresponding thicknesses at two locations of each sample were estimated via the “Z-stack” function within the ZEN software of the Zeiss LSM 710 (Li et al., 2017b) SHENG. Three dimensional reconstructions were obtained with ZEISS confocal software (ZEN 2012).

6.4 Results and discussion

6.4.1 Process performance of OMBR-MF hybrid system

Figure 6.3 illustrates the variation of FO and MF water flux as a function of time for each draw solution and salt accumulation in the mixed liquor. Among the three different DS, KCl produced the highest permeate flux (7.95-6.5 LMH (litres per square meter per hour)) followed by NaCl (7.46-6.0 LMH) and then NaOAC (7.1-2.6 LMH) at a similar molar concentration. This can be attributed to the osmotic pressure difference and corresponding diffusivity of the different DS tested.

At 0.75 M DS concentration, the osmotic pressure of NaCl is 34.1 bar and for KCl is 32.5 bars, respectively. However, the diffusivity of KCl (1.61×10^{-9} m^2/s) is much higher than NaCl (1.32×10^{-9} m^2/s), which justifies the higher initial water flux for KCl DS (7.95 LMH) than other two DS NaCl (7.46 LMH) and NaOAc (7.06 LMH). Furthermore, the viscosity of KCl is also less than NaCl. NaOAc has a lower osmotic pressure and diffusivity and higher viscosity, which is linked to the lowest initial water flux among the three DS employed in this study. Moreover, it has been reported that the small diffusions coefficient of NaOAc was responsible for severe internal concentration polarisation within the FO membrane support layer thus lowering the water flux (Luo et al., 2016a). A significant permeate flux decline within seven days of the experiment was observed for NaOAc DS.

The normalised water flux of all three DS is shown in Figure 6.4 (a), where a decrease with time is observed for all three DS. The flux decline trend is much quicker for NaOAc DS followed by KCl and NaCl, respectively. The SRSF from the draw side to the feed is another significant and unique aspect in osmotically driven membrane operations (Alturki et al., 2012). Specific reverse salt flux (SRSF) is defined as the ratio of reverse salt flux (RSF) of draw solutes and water flux is a valuable parameter for DS performance in FO process. Independent of the concentration, the values of SRSF remain relatively constant for each salt. Lower values of SRSF indicate minimum salt loss or less reverse transport of solute (Achilli et al., 2010, Bowden et al., 2012, Siddique et al., 2017). SRSF of NaCl, KCl and NaOAc were 0.74, 1.14 and 0.26 g/L respectively (Data adapted from Siddique et al. (2017); Bowden et al., (2012) and Achilli et al. (2010)). The SRSF value is the lowest for NaOAc (0.26 g/L) among the three DS. Basically, organic DS NaOAc showed very low RSF due to its large molar mass and so lower diffusion coefficient. Much lower salt accumulation in a reactor with NaOAc can be linked to low water flux exhibited by organic DS as compared to other two inorganic DS NaCl and KCl. The rapid flux declined can also be attributed to the severe membrane fouling. NaOAc being an organic DS, can support the microbial growth on the membrane surface thereby promoting an additional barrier to the water permeation. In another OMBR study, it was also observed that using NaOAc as an organic DS the RSF from draw side to the reactor could provide carbon source (acetate) for bacteria which contributed to severe FO membrane fouling. Further, in comparison to inorganic DS NaCl less salt accumulation was noticed in the reaction tank for NaOAc DS (Luo et al., 2016). The SRSF is the highest for KCl manifested by the increased salinity in the bioreactor followed by NaCl DS. The hydrated diameter for K is lower than Na (Achilli et al., 2010) which also leads to more SRSF (1.14 g/L) for KCl as compared to other two Na based DS. As a result NaCl showed relatively less flux decline and salinity increase in the bioreactor during one week process.

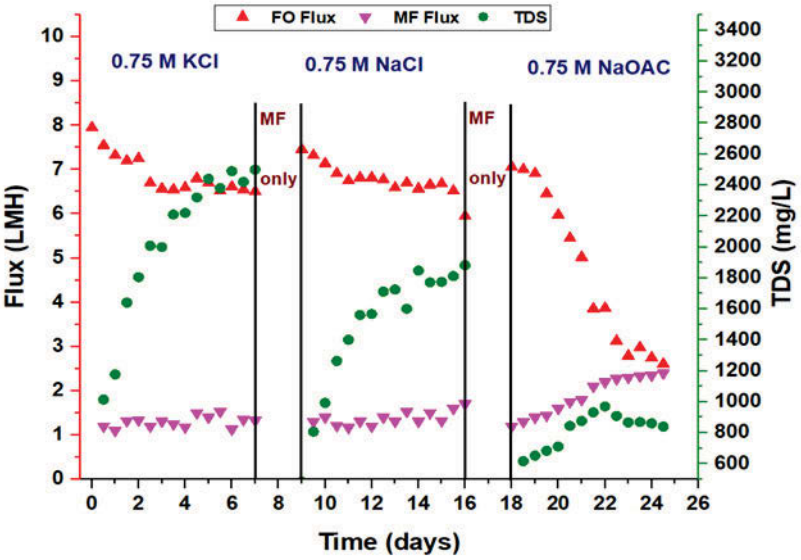


Figure 6.3 Variations of water flux with time in baffled OMBR-MF hybrid system (feed: synthetic wastewater; draw solution: 0.75 M KCl, 0.75 M NaCl and 0.75 NaOAc; temperature: 22 ± 5°C; membrane orientation: active layer facing the feed solution; 7 days operating time for each draw solution; SRT 70 d).

In this experiment reactor TDS increased from about 470-2500 mg/L for KCl, 485-1882 mg/L for NaCl followed by NaOAc at 476-971 mg/L (Figure 6.4 (a)). The lower TDS increase was observed for NaOAc due to its low SRSF (0.26 g/L) as compared to KCl (1.14 g/L) and NaCl (0.75 g/L). Lower RSF which allowed less amount of NaOAc to accumulate in the bioreactor. Moreover, NaOAc is an organic DS so it can easily be consumed by microbes. NaOAc is widely used as an external carbon source in wastewater treatment specifically to enhance denitrification. This means biomass is capable of oxidising acetate (electron donor) more readily and use carbon and energy for metabolism which is not possible with other inorganic DS. Thus, the combined effects of low RSF (0.26 g/L) as well as consumption of acetate ion as a substrate by microbes led to less salinity build up when NaOAc was employed as DS. For the 0.75 M NaCl employed, salinity increased from 0.49 g/L to 1.88 g/L which is similar to observations in another OMBR study reporting a salinity increase from 0.17 g/L to 4.13 g/L in one week OMBR operation with 1 M NaCl (Alturki et al., 2012). In the present study, incorporation of a MF membrane unit was therefore done to alleviate salt accumulation in the mixed liquor.

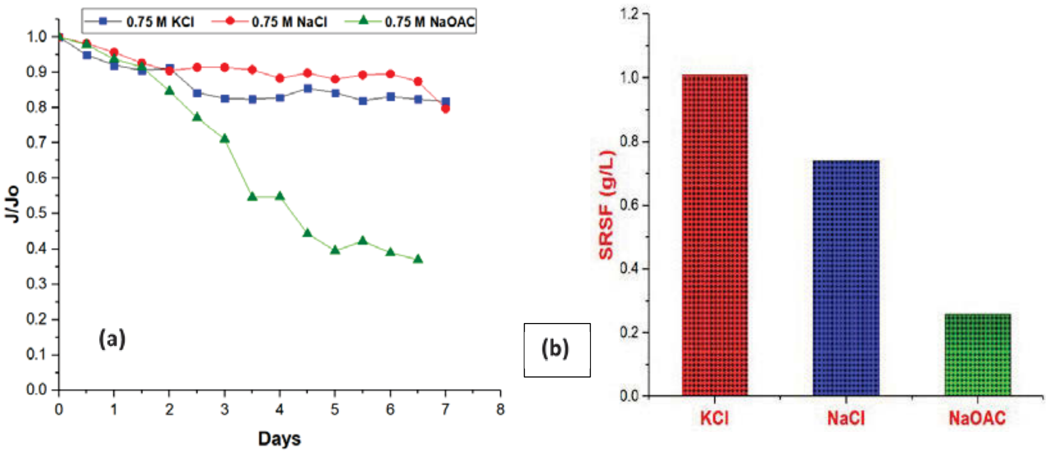


Figure 6.4 (a) Normalised flux decline as a function of time of treated water and (b) SRSF in OMBR with three different DS (Testing conditions are shown in Figure 6.3).

6.4.2 Organic-micropollutants (OMPs) removal

The removal of organic micropollutants is mainly directed by the interaction between physical rejection by the FO membrane and biological degradation in the reactor (Eyvaz et al., 2016). Figure 6.5 shows the rejection rate of OMPs in oxic and anoxic reactors as well as by MF and FO membranes during one week of continuous operation. The OMBR-MF hybrid system exhibited excellent removal for all OMPs ranging between 93-100 % respectively. These results are in agreement with previous OMBRs studies showing high removal of OMPs by this system (Holloway et al., 2014, Luo et al., 2017b). In fact, due to great rejection by FO membrane followed by adsorption onto the biomass which provides extended detention time in the OMBR tank might have facilitated improved biodegradation of OMPs (Wang et al., 2016).

Results show that the highest FO membrane rejection was attained with atenolol (100 %) employing all three DS. Atenolol possess highest molar mass (266.3 g/mol) compared to the other two OMPs can be attributed to highset rejection (Kim et al., 2017). Alturki et al. (2012) reported in their OMBR study that almost all OMPs having larger than 266 g/mol molar mass revealed outstanding removal efficiency. Wang et al. (2016a) noticed that typically hydrophilic OMPs with more than 200 g/mol molar mass could be effectively detained by FO membrane. They attributed this improved OMPs removal either due to the size exclusion or adsorption phenomena. Moreover, atrazine and caffeine have neutral charge while atenolol has positive charge (Kim et al., 2017). Holloway et al. (2014) also noticed high FO rejection for atenolol with similar CTA membrane for sewage treatment in bench scale and pilot scale studies. Under neutral pH and ambient conditions of this study CTA FO membrane remained relatively unchanged. However, positively charged atenolol has higher molar mass and hydrated diameter as compared to two neutral OMPs employed in this study. Thus, steric hindrance would have predominantly affected OMPs transfer and rejection (Holloway et al., 2014, Kim et al., 2017). Moreover, it has been postulated that membrane fouling leads to membrane pore blocking. This further inhibited OMPs partitioning through the membrane due to its adsorption to the biofouling layer (Holloway et al., 2014). This can be attributed with the results obtained in present study as a thick biofilm for NaOAc > NaCl > KCl provided high rejection of all three studied OMPs, respectively.

Due to high retention capacity of FO membrane, OMPs could have detained in the reactor for much longer than actual HRT. Subsequently, the increased retention time could facilitate further biological degradation (Alturki et al., 2012). Caffeine is readily and completely biodegradable compound (Dorival-García et al., 2013) and it showed high removal in bioreactor more than 94 % with all three DS. Trinh et al. (2016) have examined effect of salinity shock on OMPs removal efficiency in MBR study. They have observed that in 24 h time after introducing the salinity shock of 20 g/L, 97 % caffeine removal efficiency was achieved. Authors have reported that caffeine removal was slightly reduced under high salinity conditions. In another MBR study caffeine removal efficiency was found to range between 96–99% regardless of its exposure to simulated hazardous events such as ammonia shock or aeration failure (Phan et al., 2015a). Higher caffeine removal can be related to the fact that caffeine is easily biotransformable compound and its biotransformation is thus maintained by the subset of organisms or metabolic processes not impacted by the shocks (Trinh et al., 2016, Phan et al., 2015a). When KCl DS was employed anoxic zone achieved higher caffeine removal 98 % as compared to oxic zone (94 %). Atenolol showed more than 90 % removal for both oxic and anoxic in this study with all three DS. Employing NaCl DS in anoxic zone 96 % atenolol removal was obtained as compared to 89 % in oxic zone. Other literatures also reported that MBRs achieved high and stable removal (>90%) of eight pharmaceuticals and personal care products (PCPs) including atenolol and caffeine (Phan et al., 2015b, Trinh et al., 2016, Phan et al., 2015a). Atenolol and caffeine are hydrophilic and thus biodegradation is thought to be the major removal mechanism during biological treatment processes (Phan et al., 2015b). Phan et al. (2014) also reported good removal of the atenolol and caffeine which can be attributed to the existence of anoxic tanks. Park et al. (2009) reported that in a constructed wetland relatively high atenolol (95 %) removal efficiency was achieved. The presence of amide functional group in atenolol is thought to make it amenable to biodegradation via mediated hydrolysis reactions under anoxic conditions, as the pond was relatively stagnant with longer hydraulic residence time. In our study DO level variation with extended anoxic conditions might have created favourable conditions for higher micropollutant removal.

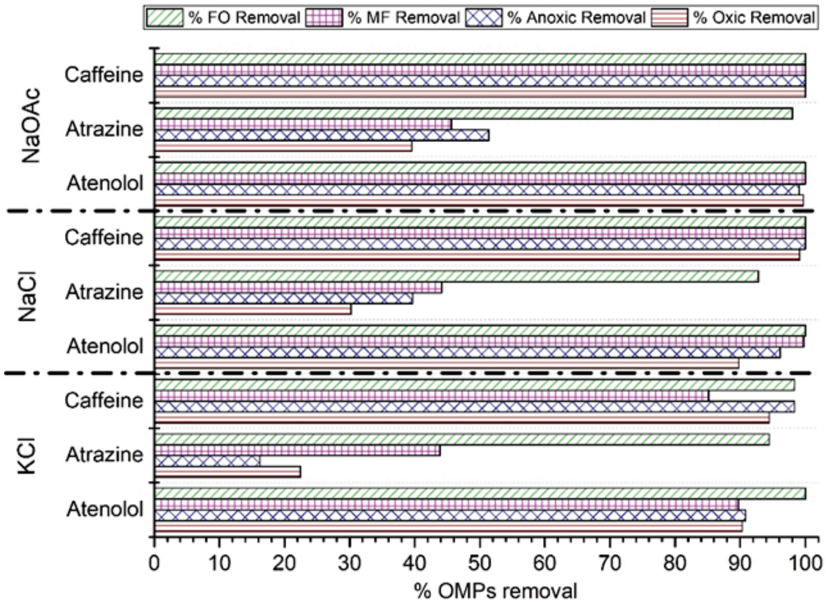


Figure 6.5 Variations of OMPs removal in baffled OMBR-MF hybrid system using different DS. Experimental conditions are as described in Fig. 6.3.

Atrazine removal in the oxic and anoxic reactors varied in the range of 22-40% and 16-51% respectively for all three DS. Further, in comparison to caffeine and atenolol inferior removal of atrazine can also be attributed to its persistent nature towards biodegradation. Alturki et al. (2012) examined OMPs removal using OMBR and they reported that certain micropollutants such as diuron, triamterene, simazine including atrazine were too persistent to biodegradation and less than 50% removal efficiency could have been achieved. Luo et al. (2015a) previously reported that low removal of OMPs could be referred either to the absence of electron donating group (EDG) or presence of strong electron withdrawing group (EWG), such as –Cl, -NH_2 and –NO_2 bonds attached to benzene ring structure. Atrazine possess halide (-Cl) the electron withdrawing functional group attached to the cyclic ring responsible for inferior biological process performance in our study (Luo et al., 2017a). Phan et al. (2014) in their MBR study observed < 20 % atrazine removal when operated at internal recirculation ratio of 3 and at 25 d SRT. They also reported that atrazine and ametryn are both triazine compounds, but only ametryn was well removed (80%), possibly because of the presence of –Cl (strong EWG) in atrazine but not in ametryn. Despite its recalcitrant nature, due to their extended retention in the bioreactor, biodegradation was still the most prevalent removal mechanism of hydrophilic atrazine in OMBR–MF hybrid system.

When NaCl and NaOAc DS was employed, 40% and 51% atrazine removal was observed in the anoxic zone in the baffled reactor compared to 30% and 39 % removal in oxic zone respectively. In this study due to the extended anoxic period (1.5 h) relatively better anoxic conditions prevailed evidenced by too low DO concentration in anoxic zone of baffled OMBR (DO profile was shown in our previous work). Hai et al. (2014a) reported that near-anoxic conditions (DO = 0.5 mg/L) can be a favourable operating regime for the removal of the persistent OMPs such as carbamazepine possess strong EWG groups such as N=O and NH_2 which was similar like halide (-Cl) group in atrazine. In another study Derakhshan et al. (2018) elucidated very high (74 %) biodegradation of atrazine in the anoxic moving bed biofilm reactor under nitrate reduction conditions. They reported that atrazine biodegradation was improved (74 %) in the presence of nitrates in comparison with absence of nitrate that showed only 10 % atrazine removal. In addition atrazine and nitrate compete for reduction by denitrifying bacteria, nonetheless both molecules simultaneously reduced though denitrifying bacteria prefer nitrate to atrazine as an electron acceptor. Also, anoxic mixed biofilm culture was suitable for the atrazine degradation therefore atrazine removal mechanism in this system was co-metabolism. In our study relatively high atrazine removal in anoxic zone could also be attributed to the existence of attached biomass on to the outer baffle wall as well to the inside wall of the reactor in anoxic zone. Further, oxic-anoxic cycle variation must have created very different DO levels in the baffled reactor with extended anoxic cycle time. This might have created different redox conditions that could be responsible for the growth of different microbial consortia inside attached biomass leading to the excretion of diverse enzymes. Thus, varying degree of biodegradation was observed with atrazine micropollutant in oxic and anoxic zones respectively (Phan et al., 2014). Future work has been planned to address microbial community dynamics in oxic and anoxic zone in the baffled bioreactor to elucidate its impact on OMPs removal.

Moreover, FO alone, or in combination with biodegradation, can be used to reject a broad range of OMPs. The rejection mechanisms of OMPs by FO involve a complex combination of mechanisms, including steric hindrance, electrostatic repulsion, solubility and diffusivity in the membrane, and hydrophilic−hydrophobic forces between the solutes and membrane. FO rejection performance also depends on operating and physiochemical conditions on both sides of the membrane (Coday et al., 2014). Table 6.3 shows the FO rejection in this baffled OMBR-MF study.

Results from above studies showed that Caffeine and Atenolol were well rejected by FO membranes. However, FO membrane could not well reject Atrazine. One of the reason for poor Atrazine rejection could be too low initial bioreactor concentration. Apart from its persistent nature comparatively low molecular weight (215 Da) of Atrazine is also contributing factor.

Table 6.3 FO rejection performance for selected OMPs

Draw solution	**Caffeine**	**Atenolol**	**Atrazine**
	FO Rejection %		
KCl	> 90	> 67.57	> 7.33
NaCl	BDL	> 67.58	> 12.25
NaOAc	BDL	BDL	> 3.80

- BDL is below detection limit which is 25 ng/L for LCMS instrument.

Linares et al. (2011) investigated the rejection of 13 OMPs by a similar FO membrane. Rejection of hydrophilic ionic contaminants was between 92.9% and 98.6%. On the other hand, rejection of neutral compounds such as caffeine varied significantly from 40% to 95.2%. In our study we obtained similar results except Atrazine employing FO membranes. Alturki et al. (2012) has reported that atrazine like OMPs showed negligible removal in FO-MBR study. Similar low atrazine removal about 30 % was reported by Xie et al. (2014) in their FO study employing 2 µg/L feed solution.

6.4.3 Carbonaceous organics and phosphorous removal

The hybrid OMBR-MF system, with an integrated MF unit to alleviate salt accumulation resulted in an almost complete removal in terms of TOC regardless of DS used due to the high retention characteristics of the FO membrane, longer HRT and SRT (Figure 6.6). Average concentrations of TOC in the diluted KCl, NaCl and NaOAc DS were 1.59 ± 0.60, 1.95 ± 0.47 and 1.27 ± 0.27 mg/L, respectively, representing removal efficiencies of 98, 98 and 99 %. Other OMBR studies have reported 98-99 % global TOC removal. As FO membrane has very high pollutant selectivity, insignificant seepage of TOC into the DS was noticed during the OMBR process (Achilli et al., 2009, Qiu and Ting, 2014a, Tan and Ng, 2008). In our study, a similar performance by OMBR process was achieved.

The OMBR performance in terms of phosphate (PO_4-P) removal was evaluated for all three DS (Figure 6.7). Due to the high retention properties of the FO membrane, substantial enrichment of phosphate within the bioreactor was anticipated for each DS. An accumulation was reported in other OMBR studies and related to the effective FO membrane rejection based on a negatively charged and large hydrated diameter of the ortho-phosphate ion (Luo et al., 2016a). With an average influent phosphate concentration of 3.53 ± 0.29 mg/L, the concentration in the mixed liquor was found to be 1.13 ± 0.16 mg/L (). However, the salinity build-up in the case of the inorganic DS generated a detrimental condition for phosphorous accumulating organisms (PAOs). It is generally hypothesized that salt accumulation within the cells not only adversely affects the sensitivity of PAOs but also reduces the phosphate accumulating ability of microbes increasing the osmotic stress within the cells (Luo et al., 2016a, Lay et al., 2010). A reasonable overall phosphate removal (68%) in mixed liquor under strict anoxic conditions was the result of higher biomass activity. Aftab et al. (2015a) also reported a lower accumulation of phosphate due to increased microbial activity resulting in higher phosphate consumption, this latter fulfilling the nutrient demand of PAOs with the incorporation of MF membrane. The FO process achieved more than 97 % removal of phosphate for each DS due to excellent rejection offered by FO membrane.

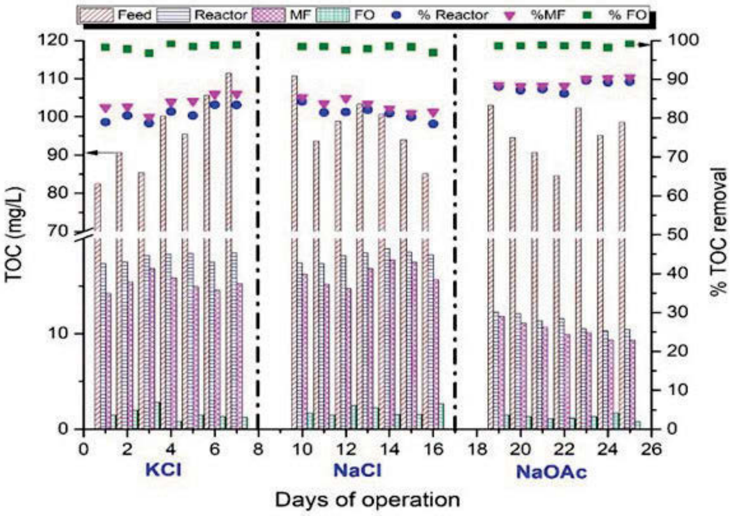


Figure 6.6 Variation of TOC concentration in the feed, bioreactor, MF and FO effluents and TOC removal in OMBR-MF hybrid system using different DS. Experimental conditions are as described in Fig. 6.3

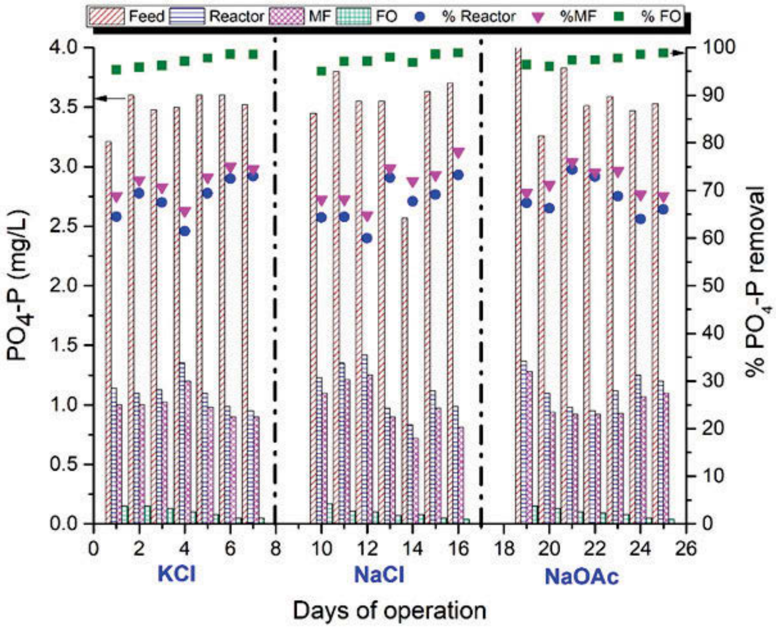


Figure 6.7 Variation of PO_4-P concentration in the feed, bioreactor, MF and FO effluents and PO_4-P removal in OMBR-MF hybrid system using different DS. Experimental conditions are as described in Fig. 6.3.

6.4.4 Simultaneous nitrification-denitrification (SND) in OMBR-MF hybrid system

Nitrification of ammonia in domestic wastewater is first required before it can be further denitrified into molecular nitrogen. However, nitrification remains a limiting step in SND process due to high DO and longer SRT requirement (Kimura and Watanabe, 2005a, Tan and Ng, 2008). Figure 6.8 (a) and (b) show the removal of NH_4-N and TN for all three DS at the same molar concentration. Nitrification is a very sensitive process, as the nitrifying microbes involved in the process are slow growing and highly susceptible to the process conditions such as DO concentration and increased salt concentration (Lay et al., 2010). Permeate quality showed that more than 98% of NH_4-N removal was achieved for all DS. Almost complete nitrification was achieved in this study and can be attributed to sufficient oxygen availability and maintaining longer SRT of 70 d. Hence limitation in nitrification was not observed (Tan and Ng, 2008). The trend of NH_4-N build-up was observed for inorganic draw solutes in previous studies with high saline stress in the bio-tank (Luo et al., 2015b, Qiu and Ting, 2013). Recently Siddique et al. (2017) noticed NH_4-N accumulation in the bioreactor using inorganic DS. The main reason for NH_4-N accumulation was reported as high salinity (7-10 g/L) build up in the reactor. Holloway et al. (2015b) also observed NH_4-N accumulation for about 3 weeks due to high salinity build up (3-8 g/L) in the bioreactor. Elevated salt concentrations had adversely affected microbial community and salinity build up (up to 8 g/L) was the major cause for loss of nitrification. In the same study in next the phase when the system was operated with UF membrane in parallel to FO better NH_4-N removal was achieved throughout the operation due to low salinity level (1 g/L) employing UF subsystem. In contrast to the previous results (Holloway et al., 2015b, Siddique et al., 2017) a high removal of NH_4-N within the bioreactor was observed (Figure 6.8 (a)) throughout the operation with both the inorganic and organic DS. Compared to other OMBR studies, incorporating MF membrane in the bioreactor mitigated salinity build-up (0.9 to 2.4 g/L), and good nitrification was achieved due to the high SRT and sufficient aeration employed in the present study. In another OMBR-MF hybrid study salinity build up to 5 mS/cm in the bioreactor was effectively controlled by combing MF membrane in comparison to 50 mS/cm in the conventional OMBR without MF membrane. In this study 98 % NH_4-N removal was achieved using CTA-FO membrane (Wang et al., 2014b).

Overall TN removal efficiencies in the reactor were 73 % at a low aeration rate of 2-3 L air/min. TN removal was > 84 % in the FO permeate for all DS. Remarkable denitrification achieved in the baffled OMBR-MF hybrid system was possibly due to the FO membrane rejection of nitrite/nitrate species, which prolonged their retention in the bioreactor, thus facilitating their removal during the anoxic cycle under very low DO concentration.

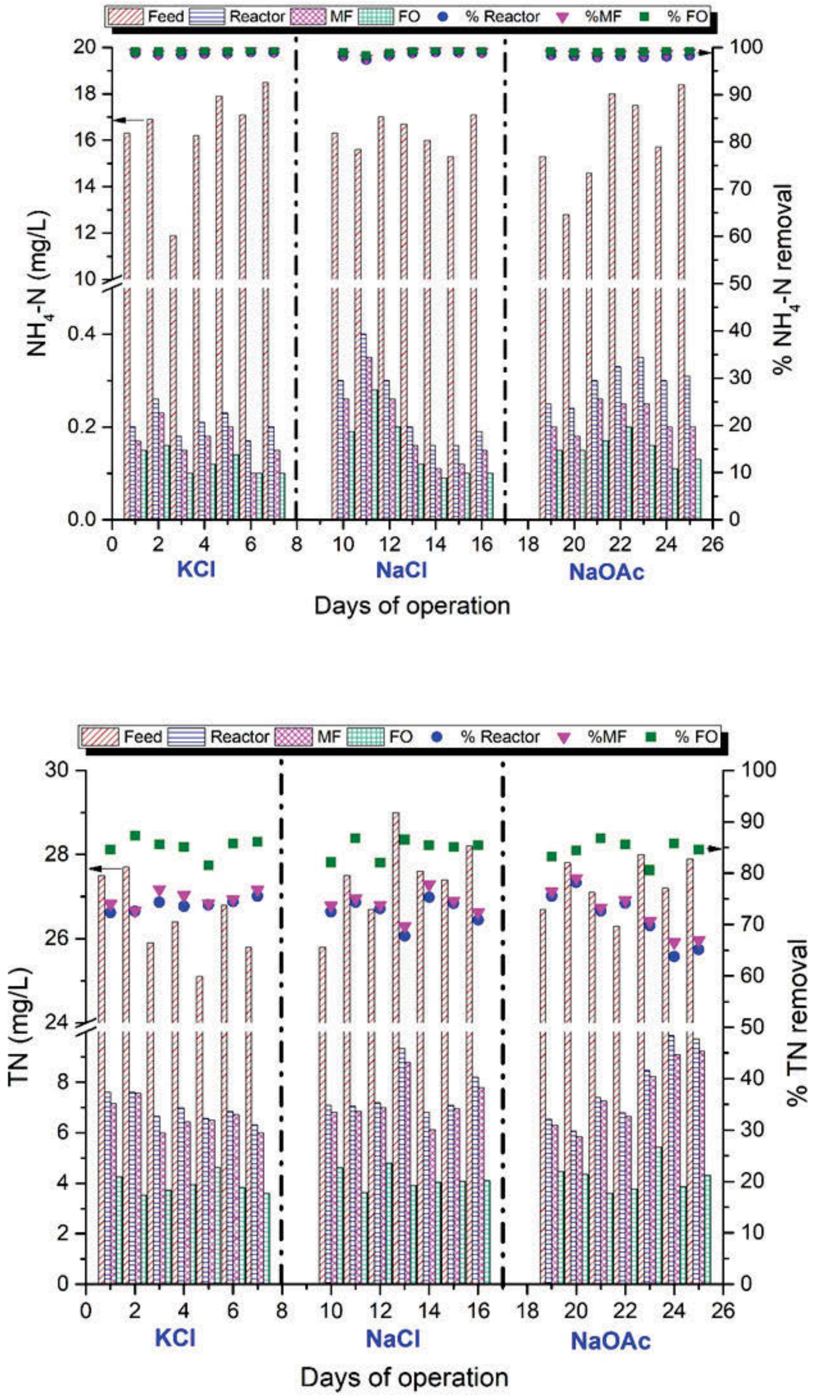


Figure 6.8 Variations of (a) NH$_4$-N and (b) TN removal in OMBR-MF hybrid system using different DS. Experimental conditions are as described in Fig. 6.3.

6.4.5 Fouling behaviour in OMBR-MF hybrid system

6.4.5.1 SMP and EPS measurement

It is well known that the SMP and EPS play important roles in membrane fouling. SMP and EPS are both heterogeneous and generally comprise a range of organics mainly polysaccharides, proteins, humic acid, glycolipids and deoxyribonucleic acid (DNA) (Wang et al., 2014a). The different fractions of organics in OMBR mixed liquor supernatant were analysed by LC-OCD (integration values for chromatograph are shown in Table 6.4. The biopolymer ratio was around 1 %, 6 % and 23 %, respectively in supernatant of KCl, NaCl and NaOAc, respectively. The humic substance ratio at MW 1000 g/mol was 2, 2 and 8 % in the supernatant of KCl, NaCl and NaOAc, respectively. Zhang et al. (2012b) also reported in their OMBR study higher humic concentration as compared to the conventional MBR. Further, this difference may stem from the high retention by FO membranes of the humic substances. The biopolymer percentage trend indicates there is an increasing amount of biofilm growth on the FO membranes and SMP formation in the order NaOAc > NaCl > KCl as a DS.

Proteins and polysaccharides content in the mixed liquor EPS were extracted as per the details mentioned in chapter 3. Total amount of protein and polysaccharide to volatile suspended solid ratio in the mixed liquor were 16.1, 15.4 and 14.2 mg/g VSS for KCl, NaCl and NaOAc DS, respectively**.** Further, protein like substances contributed more to the EPS than polysaccharide in all three DS examined. Proteins in EPS have been reported to have a strong positive influence on the hydrophobicity of microbial flocs and hence affect membrane fouling positively. Zhang et al. (2012a) also suggested that one of the main contributing factors to the biofouling was bound proteins content in EPS and its impact on sludge hydrophobicity.

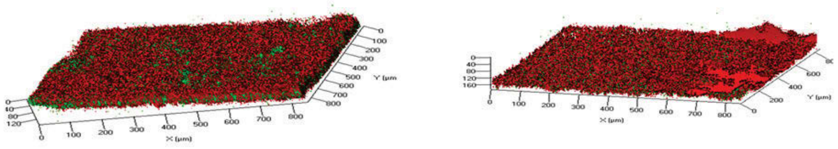
Table 6.4 Different fractions of soluble microbial products in the initial reactor mixed liquor and different DS mixed liquors at the end of the experiment

			Approximate molecular weights (g/mol):				
			>> 20,000	*~1000*	*~300-500*	*< 350*	*< 350*
		DOC	**Biopolymers**	**Humic substances**	**Building blocks**	**LMW neutrals**	**LMW acids**
Initial Reactor	mgC/L	9.25	0.22	0.05	0.19	0.26	< 0.01
	% DOC	100%	2%	1%	2%	3%	--
KCl DS	mgC/L	18.58	0.12	0.34	1.30	2.24	0.20
	% DOC	100%	1%	2%	7%	12%	1.00%
NaCl DS	mgC/L	17.66	1.00	0.40	0.56	2.86	0.56
	% DOC	100%	6 %	2 %	3 %	16 %	3 %
NaOAc DS	mgC/L	10.10	2.28	0.78	1.76	3.46	1.80
	% DOC	100%	23%	8%	17%	34%	18%

6.4.5.2 Organic foulant on FO membrane

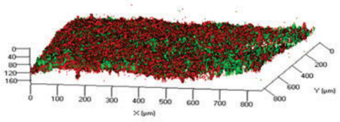
In order to describe foulant morphology on the FO membrane surface CLSM analysis was performed for all three DS tested. The CLSM images have shown that the average biofilm thickness at the end of each test run (7 days) was 84 µm, 94 µm and 113 µm for KCl, NaCl and NaOAc, respectively (Figure 6.9). However, attachment of a thick biofouling layer (113 µm) on the membrane surface was observed at the end of the filtration run with NaOAc which may add to the hydraulic resistance. In fact, the reverse organic salt flux (the acetate ion) acted as a carbon/food source for microbial growth resulting in a thick biofilm formation on the membrane surface, as described by Ansari et al. (2015).

To get a better understanding of the foulants characteristics on the FO membrane surface, fouled membrane coupons were prepared after experiments and sonicated to extract and recover the foulants for LC-OCD analysis. The biopolymer and humic substances are considered as major fouling contributors. The foulant layer comprised of biopolymers (5, 6 and 12 % with KCl, NaCl and NaOAc DS respectively) followed by humic substances (Figure 6.10). This can be correlated with increasing fouling layer thickness for NaOAc > NaCl > KCl.



0.75 M KCl- 84 µm

0.75 M NaCl- 94 µm



0.75 M NaOAC- 113 µm

Figure 6.9 CLSM image of biofilm on FO membrane surface captured after 7 days employing (a) KCl (b) NaCl (c) NaOAC DS.

The particle volume distributions of sludge granules in the OMBR-MF system with different DS were measured, with results shown in Figure 6.11. The sludge granules size distribution (in volume) was found to increase in the order KCl > NaCl > NaOAc, with average volume sizes of 144.94, 130.86 and 122.39 µm with three DS respectively.

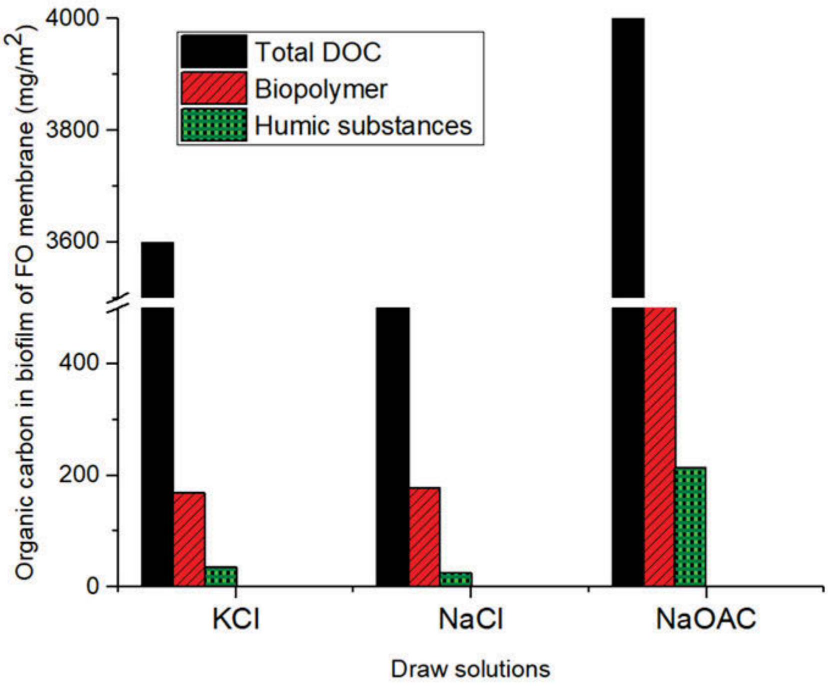


Figure 6.10 Different fractions of foulants on FO membranes when using KCl, NaCl and NaOAc DS.

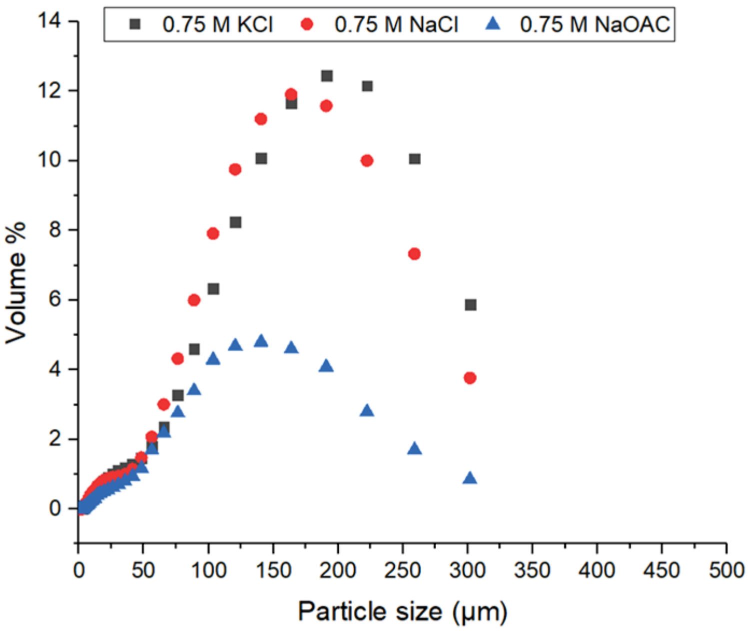


Figure 6.11 Particle size distribution of sludge granules in baffled OMBR-MF hybrid system employing different DS.

The larger floc size favoured a reduction of membrane fouling, which agreed with the variations of fouling layer thickness with three DS. Al-Halbouni et al. (2008) reported the positive effect of larger flocs who argue that large microbial flocs have a lower impact on membrane fouling. This is due to large flocs restricts other foulants once porous cake layer is established on the membrane (Le-Clech et al., 2006). In a recent OMBR study, an increase in particle size was observed for organic DS as acetate salts (NaOAc and MgOAc) (Siddique et al., 2017). In this study, however, floc size was found to decrease with NaOAc in addition to substrate COD reduction from 350 mg/L to 200 mg/L when NaOAc DS was used. The SRSF from NaOAc DS was 0.26 g/L that could supplement essential substrate requirement, however the organic load of system could not have delivered sufficient food for bacterial growth because of the low water flux (7.06 to 2.61 LMH) provided by the organic solute NaOAc (Eyvaz et al., 2016). Hence, the food to the microorganism (F/M) ratio might have been reduced or may have fluctuated as compared to the other two inorganic DS. This could be the possible reason for the low EPS quantity into the mixed liquor as evidenced by slightly less EPS content with NaOAc DS, subsequently resulting in the smaller floc size for NaOAc as compared to the other two DS.

However, thick biofouling layer (113 µm) with NaOAc should not be confused with smaller NaOAc average particle size (122.39 µm) among three DS. The possible explanation could be low reverse salt flux (RSF) from NaOAc DS in the first instance had to pass through active layer of FO membrane. Organic DS as a food source was easily available to the microbes attached to the membrane surface. Microbes were easily proliferated due to this favourable conditions as compared to inorganic DS thereby accelerated biofilm growth. When acetate ions reached to the reactor mixed liquor available food would be insufficiently led to lower F/M ratio consequently smaller floc size was observed.

6.5 Conclusions

This study investigated OMPs removal, flux performance and fouling behaviour employing three different DS in a novel hybrid baffled OMBR-MF system. With inorganic DS caffeine showed higher removal (94-100 %) as compared to atenolol (89-96 %) and atrazine (16-40 %) respectively. Atrazine as a refractory compound exhibited significant anoxic removal with alterations in redox conditions in anoxic zone and due to probably different microbial community proliferation. The organic DS NaOAc showed maximum biofilm thickness due to readily available acetate from RSF supporting microorganisms growth on the membrane surface as compared to the other two inorganic DS.

CHAPTER 7

UNIVERSITY OF TECHNOLOGY SYDNEY

Faculty of Engineering & Information Technology

EVALUATING THE EFFECT OF DIFFERENT DRAW SOLUTES IN A BAFFLED OSMOTIC MEMBRANE BIOREACTOR-MICROFILTRATION TREATING REAL WASTEWATER

7 Evaluating the effect of different draw solutes in a baffled osmotic membrane bioreactor-microfiltration treating real wastewater

7.1 Introduction

Currently, wastewater is increasingly considered as a source of water, nutrients and energy rather than a waste (Wang et al., 2016d). Wastewater recycling and reuse in domestic, manufacturing and agriculture applications is therefore gaining increasing attention around the world (Pathak et al., 2017). In recent years, osmotic membrane bioreactors have gained more popularity for sewage treatment applications (Wang et al., 2016d). OMBR has many advantages such as excellent permeate water for reuse, low biofouling than conventional membrane processes and better energy efficiency. However, the salinity build-up in the reactor due to the reverse salt flux from the draw solution and the osmotic concentration of the feed solution can reduce the driving force for water transport (Pathak et al., 2017, Nguyen et al., 2016a).

Nutrient removal in domestic wastewater treatment is one of the main goals of biological wastewater treatment since excess of nutrients in the final treated water may cause accelerated eutrophication (Randall et al., 1998). For removal of nitrogen, anoxic and aerobic zones are applied where the mixed liquor is circulated between the anoxic tank and the aerobic MBR tank. Kimura et al. (2007a) proposed a baffled membrane bioreactor that can eliminate the energy needed for the mixed liquor circulation. In our previous work, Pathak et al. (2017) have successfully demonstrated the performance of a novel baffled osmotic membrane bioreactor in which baffles are inserted in the reaction tank and feed water is drawn through the FO membrane. By utilizing this method, both nitrification and denitrification can be promoted in a single reaction tank. As a result, sludge recirculation pump and anoxic tank mixer can be omitted.

However, in membrane applications fouling is considered as main concern for a wide application of OMBRs, shortening the membrane life, decreasing water production, and increasing operating costs (Bell et al., 2016). FO membrane biofouling is a dynamic, and relatively slow process manifested as an attachment of self-organized bacterial cells to the membrane surface by gel-like, self-produced extracellular polymeric substances (EPS) (Inaba et al., 2017). EPS originate from biomass are the main component which contribute to biofouling and cause of membrane permeability decline with time (Wang et al., 2016d).

In order to operate conventional MBRs, hydraulic backwashing or relaxation can be applied. However, in OMBRs with FO membrane modules chemical cleaning or osmotic backwashing is feasible alternatives (Achilli et al., 2009). One of the major issue limiting membrane fouling control is the inadequate understanding of the basic mechanisms governing adhesion and deposition of foulants inside the pores as well on membrane surface. To assess and mitigate membrane biofouling, it is important to explore FO fouling mechanisms during OMBR applications and to develop competent control strategies (Inaba et al., 2017). Different tactics are proposed to study the biofilm architecture in the literature. The majority of techniques requires displacing the membrane from the reactor for sampling and those techniques are destructive. Hence, non-destructive direct observation of biofilm formation and development is vital (Fortunato and Leiknes, 2017, Inaba et al., 2017). Optical techniques for studying biofilms are gaining more attention because they are non-destructive and capable of non-contact and in situ measurements as compared to conventional destructive methods (Fortunato et al., 2016).

This paper proposes for the first time to evaluate the biofilm growth on FO membrane in the novel baffled OMBR-MF hybrid system treating real wastewater. On-line monitoring of biofouling growth and changes in morphology on a flat sheet CTA-FO membrane was performed non-destructively with optical coherence tomography (OCT), allowing an *in-situ* and real-time examination of the biofilm structure over 21 days.

Thus, the present study systematically investigate the complex fouling phenomenon of FO membranes in a baffled OMBR employing an OCT technique. Furthermore, the majority of FO fouling tests were performed with simulated wastewater and a few studies have been reported employing real sewage in OMBR membrane fouling examinations. In order to overcome this major shortcoming, real wastewater was used in order to assess its influence on membrane fouling. Moreover, other sludge characteristics like soluble microbial products (SMP), bound extracellular polymeric substances (bEPS) and floc size were measured employing three different draw solutes in an OMBR-MF hybrid system.

7.2 Experimental

7.2.1 Feed solutions characteristics

Real wastewater (RWW) was sampled from the flow equalisation tank at the wastewater treatment plant (WWTP) of King Abdullah University of Science and Technology (KAUST, Thuwal, Saudi Arabia). The WWTP is a conventional AS-MBR (activated sludge- membrane bioreactor) designed to treat an average daily flow of 9,500 m^3/d (Jumat et al., 2017). The characteristics of real sewage used in this study were: pH 7.45 ± 0.2, TSS 65 ± 24, TDS 645 ± 32, FOG 9.8 ± 2.1, COD 180 ± 29.5, TN 14.7 ± 3.4, NH_4-N 12.6 ± 0.5, PO_4-P 3.1 ± 0.3.

7.2.2 Draw solutions

The DS employed in this study were prepared by dissolving respective salts of three different chemicals sodium chloride (NaCl), ammonium sulphate (SOA) and potassium dihydrogen phosphate (KH_2PO_4) in deionized (DI) water. The chemicals used in this study were reagent grade purchased from Sigma-Aldrich, Saudi Arabia. Thermodynamic properties of DS were determined at temperature of 20 ºC using OLI Stream. The osmotic pressure of 1 M NaCl, ammonium sulphate ($(NH_4)_2SO_4$) and KH_2PO_4 were 46.8, 46.1 and 36.5 atm respectively. The corresponding diffusivities were 1.32×10^{-9} m^2/s, 1.14×10^{-9} m^2/s and 1.02× 10-9 m^2/s for NaCl, ammonium sulphate ($(NH_4)_2SO_4$) and KH_2PO_4 respectively.

7.2.3 Baffled OMBR-MF experimental set-up with OCT camera and operating procedure

The schematic of the lab-scale baffled OMBR-MF system used in this study is shown in Figure 7.1**.** This baffled OMBR-MF system consisted of a feed tank, a plate-and-frame FO membrane cell submerged in a plexiglass bioreactor and a hollow fibre MF membrane module, a concentrated DS reservoir and a diluted DS reservoir. The effective volume of the bioreactor tank was 10.5 L (*i.e.* 24.5 (L) x 15.5 (W) x 40.0 (H) cm). On the three inside walls of the tank, plexiglass partition of 25 cm (height) was running from top to 5 cm above the bottom of the tank thus making hollow baffle box inside the tank with the size of 18.5 cm length, 12.5 cm width and 25 cm height. The details of baffled tank can be seen elsewhere (Pathak et al., 2017). The seed sludge was collected from the AS-MBR (activated sludge-membrane bioreactor) wastewater treatment plant (WWTP) in the

KAUST (Thuwal, Saudi Arabia). Bioreactor was acclimatized for two weeks prior to adding into the baffled OMBR-MF system. Also, real wastewater (RWW) was employed to perform acclimatization and when evaluating different draw solute performances. Real wastewater was collected in clean containers (20 L) which were rinsed in the wastewater sample prior to sampling. Wastewater was transported from KAUST AS-MBR plant to KAUST laboratory using dedicated cart. Wastewater collection was performed twice a week and it was stored at 4 °C in cold storage. This acclimatization time for 15 days at infinite SRT (except sample collection) prior to begin with experiments might have helped to achieve steady performance during test runs. During acclimatization steady state reached when more than 90 % TOC removal efficiency was obtained.

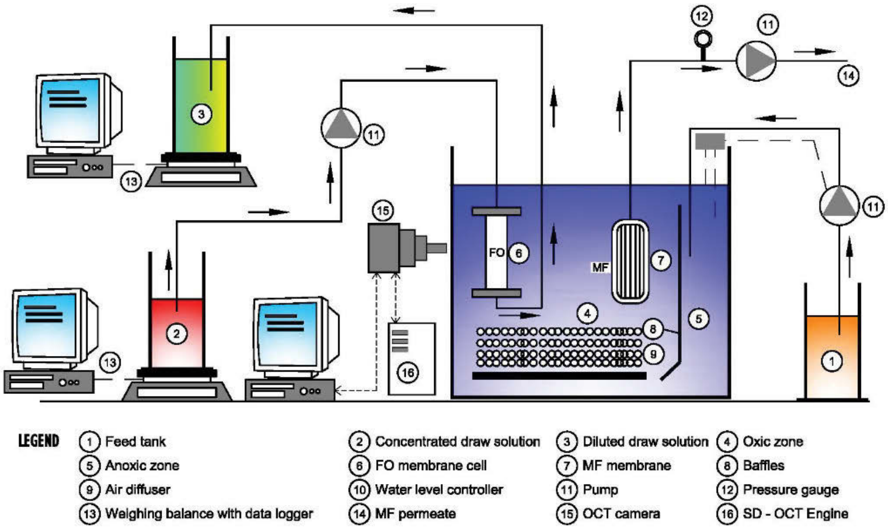


Figure 7.1 Schematic of lab scale baffled OMBR-MF hybrid system with OCT camera.

By employing the level controller, the oxic cycle time was set 0.5 h (level controller leg 0.5 cm above the baffle tip) and anoxic cycle time 1.5 h (level controller leg 1.5 cm below the baffle tip) can be adjusted accordingly. The hydraulic retention time (HRT) and solid retention time (SRT) of the OMBR-MF system was 34 h and 70 d respectively. The air diffuser was installed inside the oxic zone and 3 LPM airflow rate was maintained. The concept and operating details of the baffled reactor are discussed elsewhere (Kimura et al., 2007a, Pathak et al., 2017). The continuous-flow experiments were conducted as per the operational protocol (Table 7.1)in active layer facing feed side (AL-FS) mode using the CTA-FO membrane.

Table 7.1 Operational protocol of the hybrid OMBR-MF system using different DS

Time (d)	Procedure
	Continuously operating the hybrid OMBR-MF system
1 – 7	1 M NaCl DS
9 – 16	1 M SOA DS
18 – 25	1 M KH_2PO_4 DS
7-9 and 16-18	Ceasing FO extraction; operating MF for 48 h to extract OMBR mixed liquor and bring down TDS (salinity) to initial value
0, 9, 18	FO membrane was replaced and draw solution was changed

7.2.4 *In-situ* biofilm monitoring

In order to measure *in-situ* biofouling growth on the FO membrane optical coherence tomography (OCT) technique was used for the OMBR-MF hybrid system. Thus FO membrane fouling characterization was facilitated without disturbing FO module from the reaction tank (Fortunato et al., 2016). Biofouling monitoring was performed twice a day for each DS for 7 days of operation. While performing OCT analysis, air scouring was stopped for about 15 minutes to allow the sludge to settle down prior to image analysis. The fouling monitoring was performed with an OCT (Thorlabs GANYMEDE SD-OCT, Thorlabs, GmbH, Dachau, Germany) equipped with a 5 × telecentric scan lens (Thorlabs LSM 03BB). The OCT scan lens was mounted on a 3-axis motorized stage slide (Velmex) (Fortunato et al., 2016). The OCT scans had a resolution of (3500 x 1024 pixel) corresponding to 7.00 mm x 2.05 mm (width x depth). The images were cropped and filtered (Li et al., 2017a). The fouling layer thickness was calculated using a customized MATLAB code (Fortunato et al., 2017).

7.3 Results and discussion

7.3.1 Process performance of OMBR-MF hybrid system

Figure 7.2 illustrates the FO and MF water fluxes as a function of time for each DS as well as the TDS concentration inside the bioreactor. Among the three different DS, NaCl produced the highest initial flux followed by SOA and KH_2PO_4, respectively, at a constant molar concentration. A notable decrease in water flux was observed by the higher salinity (means -low osmotic pressure difference) of the reactor mixed liquor in the presence of inorganic ions (Na, NH_4-N, PO_4-P) (Zou and He, 2016). The significant flux decline of NaCl and SOA than the KH_2PO_4 DS, which can be attributed to the higher initial flux and reverse solute flux specifically for NaCl DS, both contributing to decreased driving force and hence permeate flux declined. Thus, SRSF (defined as the ratio of reverse salt flux to water flux in FO process) of NaCl led to higher salt accumulation in the mixed liquor than the other two draw solutes (Figure 7.3). These results correlated well with previous findings (Wang et al., 2017a, Kim et al., 2016, Wang et al., 2014a). In addition, salinity build up in the reactor mixed liquor could increase viscosity and decrease oxygen solubility then aggravates membrane fouling and flux decline (Lay et al., 2010). Xiao et al. (2011) noted that in OMBR operation steady state is reached when the solutes entering into the bioreactor is balanced by the solutes discharge via waste sludge. Holloway et al. (2015b) reported that salt accumulation in OMBRs was modelled by different modelling studies. It was deduced that the steady state salt concentration in the osmotic membrane bioreactor would reach a constant value depending on the solids retention time (SRT).

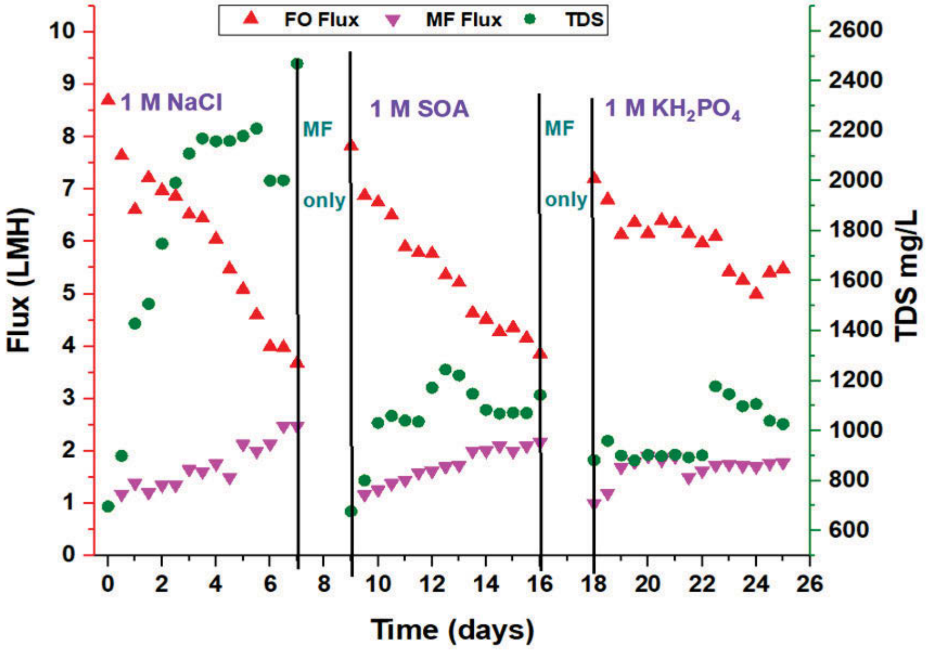


Figure 7.2 Variation of FO and MF water flux and reactor salinity using different draw solutions (Feed: synthetic wastewater; draw solution: 1 M NaCl, 1 M SOA and 1 M KH_2PO_4; temperature: 22 ± 5°C; membrane orientation: active layer facing the feed solution; 7 days operating time for each draw solution; SRT 70 d).

However, an alternative strategy for minimizing salt concentrations in the bioreactor without changing the SRT would be to operate MF/UF membrane parallel to the FO membrane in the bioreactor. Wang et al. (2014b) and Holloway et al. (2015b) kept 10 d and 30 d single SRT in their MF/UF-OMBR study respectively. In our study by incorporation of MF membrane even at higher SRT of 70 d salinity build up was mitigated. This salinity level (2.5 g/L) does not affect biomass activity and sludge characteristics as reported by other studies (Nguyen et al., 2015). This situation in combination with other constant operating parameters (HRT, SRT, F/M ratio) might have facilitated to operate baffled OMBR-MF in reasonably equilibrium conditions within short time operations of 7 d employing different DS.

Other OMBR reports suggest that when salinity increases > 2 g/L it has adverse impact on biomass specifically ammonia-oxidizing bacteria (AOB) responsible for nitrification were inhibited (Nguyen et al., 2015). In this study except NaCl DS (2.5 g/L) very less salinity build up for SOA (1.3 g/L) and KH_2PO_4 (1.2 g/L) DS was observed. Due to N and P nutrient content in SOA and KH_2PO_4 DS it is believed that it has favourable impact on the biomass evidenced by increase in floc size (section 7.3.6).

Wang et al. (2014a) also reported that flux quickly reduced from the initial value of about 9 LMH to the steady value of approximately 3.5 LMH during the first week operation of OMBR at 1 M NaCl DS. In another OMBR study, (Wang et al., 2014b) incorporated MF membrane to alleviate salinity build up and they achieved 2.5 times higher water flux as compared to OMBR study performed without MF membrane by Wang et al. (2014a). This indicates that it is feasible to maintain stable FO flux in the OMBR by adding a MF membrane under similar operating conditions (Zou and He, 2016). Incorporation of a MF module in this study helped reduce the salinity build up and maintain a constant hydraulic retention time (HRT), where the flux decline for NaCl is attributed to the accumulation of salt, increasing from 0.7 to 2.5 g/L within the bioreactor. In another study employing 1 M SOA as DS, a rapid flux decline from 6.9 to 2.5 LMH was observed in four days using a similar HTI CTA FO membrane without incorporation of a MF/UF membrane

(Wang et al., 2017a). In another recent OMBR study using fertilizer DS the water flux dropped sharply from 5.8 to 2.8 LMH within three days without combining MF/UF membrane (Zou and He, 2016). In contrast to the reports in previous studies, higher water flux was achieved in the present study from 7.8 to 5.5 LMH in the first three days working with 1 M SOA as DS. This was achieved by integrating a MF module that reduced salt accumulation in the osmotic reactor. Salinity build up was much lower for SOA (TDS 1.3 g/L) compared to NaCl (TDS 2.5 g/L) KH_2PO_4 fertilizer DS showed a lower initial flux (7 LMH) compared to the other two DS, and less salinity build up, thus a much lower flux decline was observed. In case of KH_2PO_4 DS TDS increased up to 1.2 g/L. This TDS rise was two times higher than initial TDS value in the beginning of KH_2PO_4 DS run (day 18-25). Lower TDS rise with KH_2PO_4 DS can be related to the very low specific reverse salt flux (SRSF) 0.45 g/L of KH_2PO_4 DS (Figure 7.3). Also, initial lower flux with KH_2PO_4 DS required MF membrane to operate at relatively higher MF flux to maintain constant HRT as compared to other two DS test runs. MF membrane had withdrawn more permeate in order to operate OMBR-MF hybrid system at constant HRT and reduced salt concentration in bioreactor when KH_2PO_4 was employed as a DS.

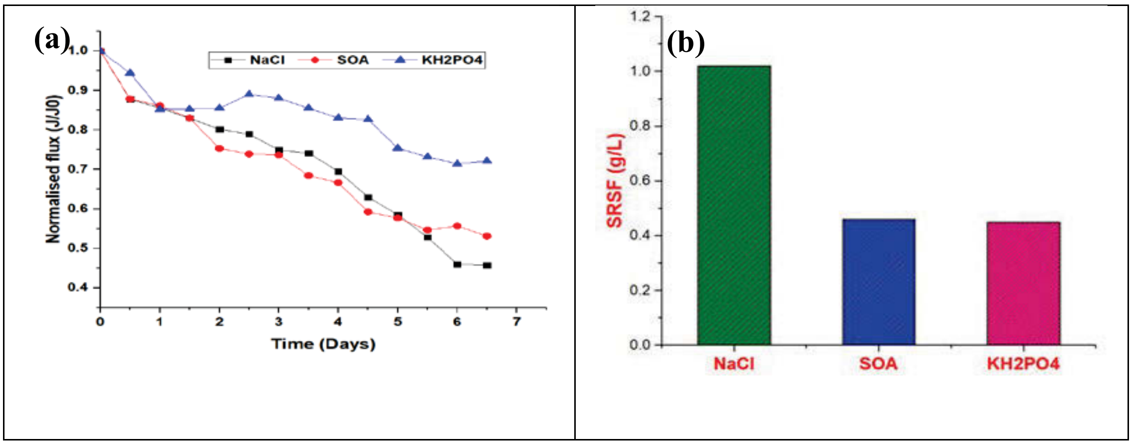


Figure 7.3 Normalized FO flux and SRSF in OMBR-MF hybrid system (Testing conditions are shown in Figure 7.2).

It should be noted that after each run with different DS, MF membrane solely was operated for 48 h (Figure 7.1). This allowed OMBR-MF hybrid system to resume with almost initial value of TDS concentration when different DS was employed. The rapid flux decline observed with SOA, similar to that of NaCl, is therefore attributed to the biofilm formation on the FO membrane in the presence of nutrients. In order to investigate the effect of biofouling on the FO membrane, *in-situ* observation in real time was performed and is deliberated in following section.

7.3.2 *In situ* biofouling examination using OCT

The adhesion and growth of bacterial community on the membrane surface is a dynamic process. Most of the imaging techniques employed for the biomass characterization are destructive enabling the imagining of the fouling at the end of the operation. The OCT allows acquiring information about the morphology online non-invasively. In this study, the biomass morphology formed on CTA–FO membrane was acquired *in-situ* through on-line OCT scanning during the entire period of operation over 21 d. The OCT scan at time 0, where no biomass was adhered on the membrane surface; the depth-resolved study allowed a cross-section imaging of the clean membrane (Figure 7.4). The thick porous layer of around 100 µm, with an embedded woven mesh, corresponds to the support layer, while the upper thin bright layer corresponds to the skin layer for the salt separation. Over time, accumulation of the fouling layer on the membrane surface led to a decrease of the signal intensity corresponding to the membrane.

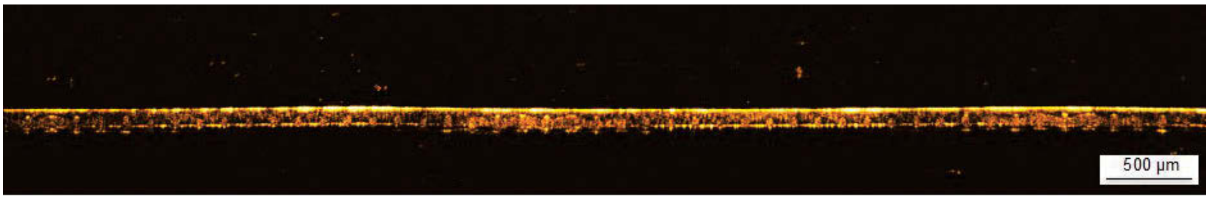


Figure 7.4 OCT scan of CTA-FO membrane at the beginning of the experiment (Time 0).

Figure 7.5 presents a set of 2D scans of the biomass development (bright orange) with time. The amount of biomass increased over time for all three different DS. As first insight, the in-situ observation enabled to observe and to depict the difference in biomass morphologies deposited on the membrane surface among the different DS. In the first 2 weeks of operation, where NaCl and SOA were used as DS, the presence of an irregular and loose structure corresponding to sludge flocs was observed above a thick, dense and compact fouling layer. In the last week, where KH_2PO_4 was used as DS, the amount of flocs deposited decreased due to the improvement of the sludge characteristics. This can be ascribed to the better acclimation of biomass with time as well as to the decrease in salinity with KH_2PO_4 as DS. The result was confirmed by the amount of EPS content in the reactor that corresponds to the higher amount in flocs size. When KH_2PO_4 was used, a more stabilised water flux was observed compared to the other two DS. It has been noted that some microbes and EPS dislodged from membrane surface under steady water flux (Yuan et al., 2015). This could be a possible reason for thin biofouling layer observed for KH_2PO_4. A more detailed discussion regarding floc size and its implications is presented in section 7.3.6. Beside the possibility of visualize the biomass deposited in the system under continuous operation, the image analysis performed on the OCT scans allowed the assessment and quantification of the fouling deposition over time for each DS. The MATLAB code employed for the thickness calculation enabled the selection of the fouling layer, without considering the flocs deposited above the layer. As shown in

Figure 7.5 using MAT LAB coding it is possible to calculate the thickness of the fouling layer over the time for each DS. Moreover, the in-situ observation is capable of providing an insight into the fouling mechanism and the impact of the biomass on the membrane performances (Fortunato et al., 2017).

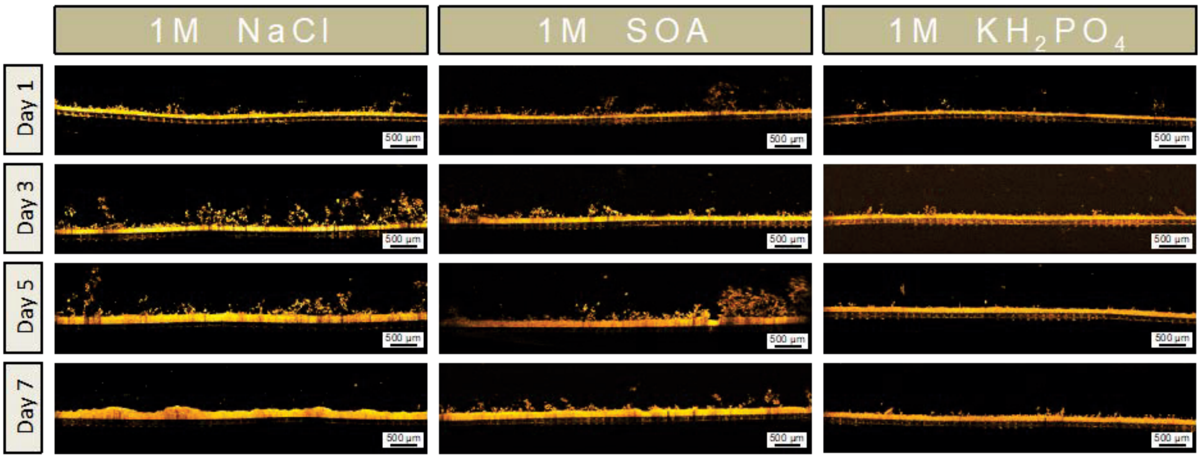


Figure 7.5 Evolution of the biofilm morphology over the time in OMBR-MF hybrid system during 21 days operation for three different draw solutes.

Respect to the high pressure driven systems the FO is usually defined as low fouling process for the lack of hydraulic pressure and the lower flux conditions. However, in the case of the OMBR treating wastewater the scenario is more complex. The flux decrease over the time is due to the increase of the hydraulic resistance and/or the concentration polarization effect. In this study, the thickness of the biomass deposited on the membrane in an OMBR treating real wastewater was correlated to the permeate flux. As shown in Figure 7.6, the decrease in flux corresponds to the increase of biomass thickness over the time. By comparing the different DS, SOA and NaCl showed a similar trend in fouling thickness, which is in good agreement with the similar flux trend measured for the two DS (Figure 7.7). In the case of KH_2PO_4 that showed less flux decrease over the time and the highest flux at the end of the observation period, the lower amount of fouling was observed on the membrane surface compared with the other DS. After 7 days of operation, a fouling layer of 163 µm, 147 µm and 100 µm, and permeate flux of 3.7 LMH, 3.9 LMH and 5.5 LMH, were observed respectively for NaCl, SOA and KH_2PO_4.

Hence, the amount of biomass deposited on the membrane can be inversely correlated with the permeate flux. Operating the OMBR for 7 days with a different DS, the flux decrease measured is mainly affected by the thickness of the fouling layer formed on FO membrane. This implies that over time, generation of a cake-layer is the dominant fouling mechanism. In fact, the increment in biomass thickness also led to an increase of water diffusion resistance from the feed to the draw side (Zhao et al., 2016). In OMBR-MF operation with all three DS, the online non-destructive analysis performed in real time information on the biofouling was linked to the variation in flux trend. This further explains the successful monitoring of the dynamic evolution of the biofilm.

In this study OCT technique was employed for the first time to assess real time fouling analysis. So, system was operated for relatively shorter time. Therefore this study is valuable as a preliminary test employing OCT technique since it revealed some interesting findings. Thus, having performed successful monitoring of the dynamic evolution of the biofilm in this study the future scope of the work should be to operate OMBR in longer run employing OCT technique to assess biofouling.

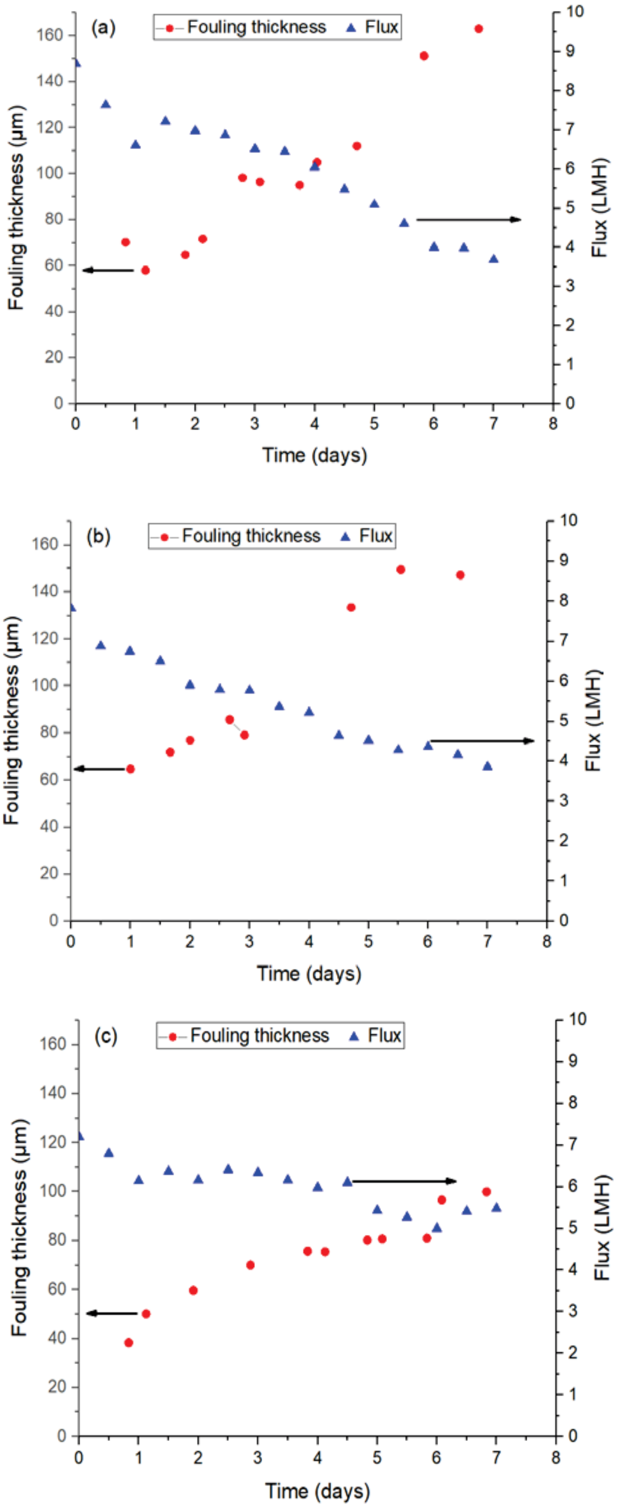


Figure 7.6 Variation of fouling thickness calculated through the OCT scans and flux with time for (a) NaCl, (b) SOA and (c) KH_2PO_4 DS.

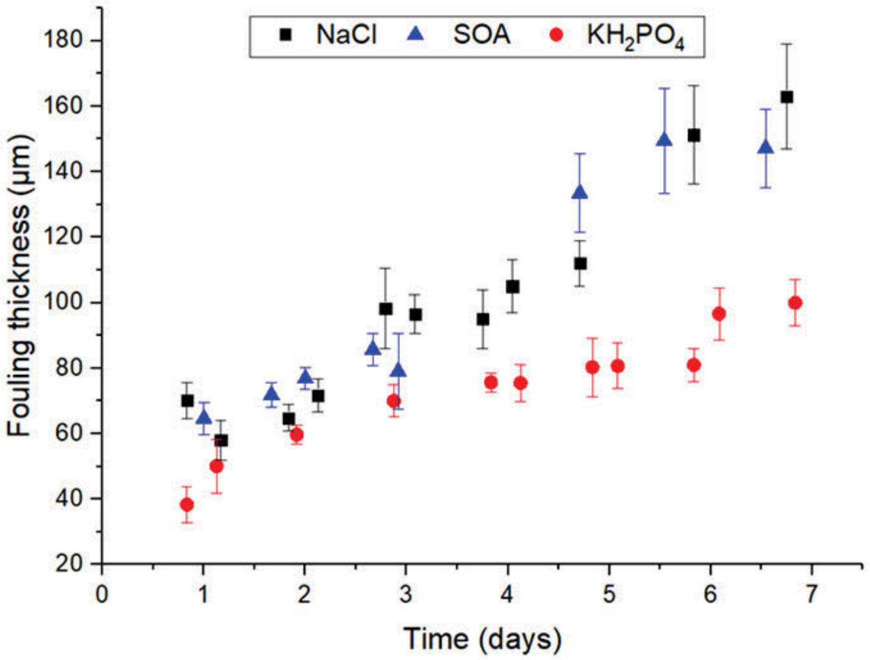


Figure 7.7 Variation of fouling thickness with time for different draw solutes.

In this study OCT technique was employed for the first time to assess real time fouling analysis. So, system was operated for relatively shorter time. Therefore this study is valuable as a preliminary test employing OCT technique since it revealed some interesting findings. Thus, having performed successful monitoring of the dynamic evolution of the biofilm in this study the future scope of the work should be to operate OMBR in longer run employing OCT technique to assess biofouling.

It is to be noted that new FO membrane was substituted when changing over draw solution in this OMBR-MF study. However, in long-term operation, biofouling layer on FO membrane could largely affect system performance. Researchers suggested different cleaning techniques for FO fouling mitigation in long-term OMBR-MF operation. Physical cleaning of the FO membrane can be performed with deionised water and then by gentle scrubbing with sponge ball (Wang et al., 2017a) . When desired flux recovery cannot be obtained with physical cleaning then Holloway et al. (2015a) have proposed chemically enhanced osmotic backwashing. Backwashing is performed circulating a very low strength acid or base solutions inside the draw channel. The main advantages of chemically enhanced osmotic backwashing include simplicity, less amount of cleaning solution as compared to external cleaning and direct exposure of cleaning agents at the membrane foulant interface. Moreover, in long-term OMBR-MF hybrid study to examine FO fouling employing OCT technique we shall focus in detail on fouling issues, cost-effective cleaning strategy and flux recovery.

7.3.3 Organic matter and phosphorous removal

Regardless of the DS, the high retention characteristics of the FO membrane, longer HRT and SRT in OMBR-MF hybrid system and integration of MF to control salinity build-up all conditions showed an impressive removal in terms of TOC **(**Figure 7.8**).** The average concentration of TOC in the NaCl, SOA and KH_2PO_4 DS was 1.3 ± 0.3, 1.2 ± 0.4 and 1.2 ± 0.3 mg/L, respectively. Overall, 96.6±0.5, 97±0.9 and 96.6±0.6 % TOC was removed from the influent to the FO permeate with three DS respectively. In OMBR study an excellent TOC removal efficiency (96 %) was reported in the bioreactor (Luo et al., 2015b, Wang et al., 2014a). Qiu and Ting (2013) demonstrated more than 90% TOC removal in reactor mixed liquor during moderate salinity conditions. In this OMBR-MF hybrid study, similar high TOC removal performance by OMBR process was achieved.

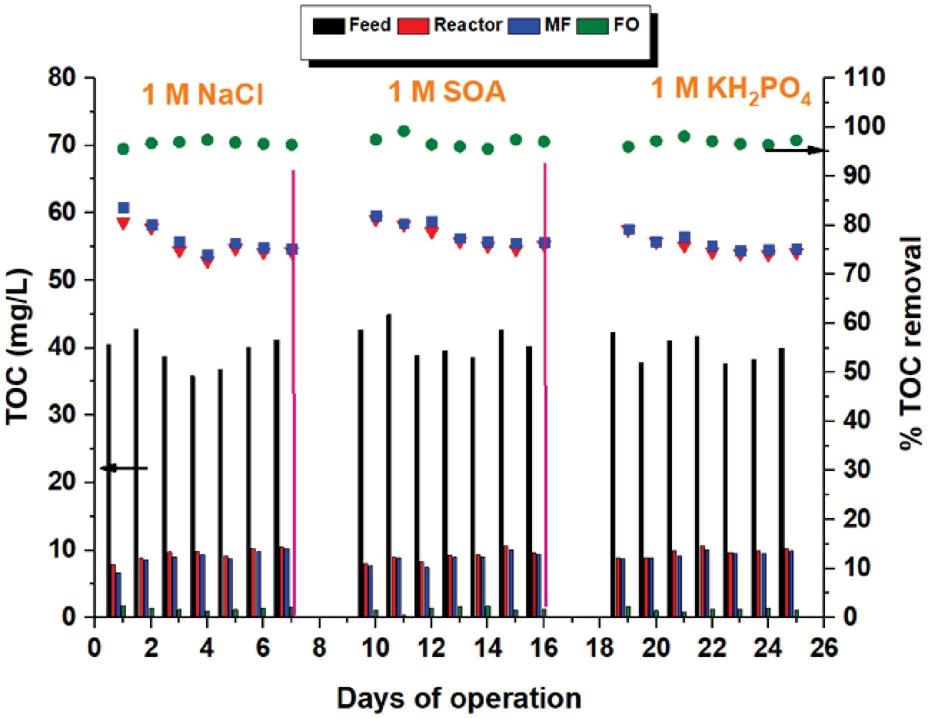


Figure 7.8 Variation of TOC concentration in the influent, bioreactor, MF and FO effluents and TOC removal in OMBR-MF hybrid system employing different draw solutes. Experimental conditions are as described in Fig. 7.2.

The OMBR performance in terms of phosphate (PO_4-P) removal was evaluated for NaCl and SOA DS (Figure 7.9). Due to the phosphate ion presence in KH_2PO_4 DS PO_4-P accumulation took place in the bioreactor from RSF and hence the removal was not possible. It was anticipated that high rejection of FO membrane would allow substantial enrichment of phosphate within the bioreactor. An accumulation was reported in other OMBR studies and related to the effective FO membrane rejection based on a negatively charged and larger hydrated diameter of the ortho-phosphate ion (Luo et al., 2015d, Luo et al., 2016a). With an average influent phosphate concentration of 2.9±0.3 mg/L, the concentration in the mixed liquor was found to be < 1 mg/L with NaCl and SOA as DS (Figure 7.9). However, the salinity build-up in the case of inorganic DS generates a detrimental condition for phosphorous accumulating organisms (PAOs). It is generally hypothesized that salt accumulation within the cells not only adversely affects the sensitivity of PAOs but also reduces the phosphate accumulating ability of microbes increasing the osmotic stress within the cells (Lay et al., 2010, Luo et al., 2016a). A reasonable phosphate removal (67.4 %) with NaCl and SOA under strict anoxic conditions was the result of higher biomass activity. In the baffled OMBR-MF hybrid system, mixed liquor suspension is cyclically exposed to aerobic and anoxic conditions, and enhanced biological phosphorus removal might have occurred to some extent. Further, oxic-anoxic cycle variation must have created a pseudo-anaerobic condition in the baffled reactor with extended anoxic cycle time. During aerobic condition, phosphorous uptake by microbial consortia could have happened. Thus, phosphorus removal could be achieved in similar way which was observed by (Kimura and Watanabe, 2005a). In our study, possible phosphorous release in anoxic zone could also be linked to the existence of attached biomass on to the outer baffle wall as well to the inside wall of the reactor in anoxic chamber. During extended anoxic cycle (1.5 h), the diffusion limitation in the anoxic chamber might have created anaerobic condition into the biofilm that was adhered to the baffle wall. This situation had possibly stimulated phosphorous release. Thus, during aerobic cycle phosphorus uptake followed by regular sludge discharge possibly managed phosphorus removal through biomass. Aftab et al. (2015a) also reported a lower accumulation of phosphate due to increased microbial activity resulting in higher phosphate consumption. The FO process achieved more than 98 % removal of phosphate for each DS because of the high rejection of the FO membrane.

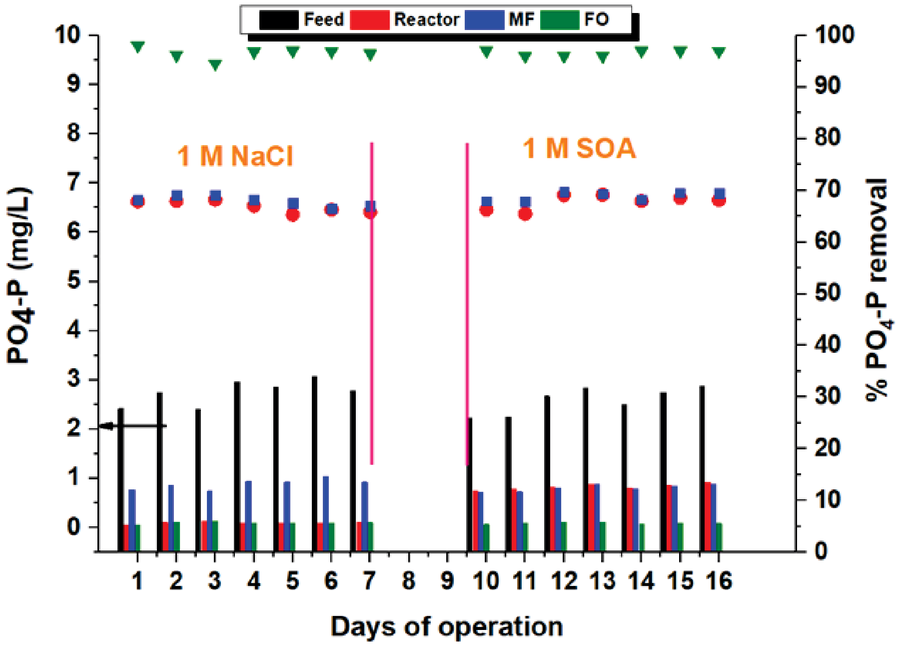


Figure 7.9 Variation of Phosphate concentration in the influent, bioreactor, MF and FO effluents and Phosphate removal in OMBR-MF hybrid system employing different draw solutes. Experimental conditions are as described in Fig. 7.2.

7.3.4 Total nitrogen removal

Nitrification of ammonia in domestic wastewater is first required before it can be further denitrified into molecular nitrogen. However, nitrification remains a limiting step in simultaneous nitrification-denitrification (SND) process due to high DO and longer SRT requirement (Kimura and Watanabe, 2005a). Almost complete nitrification was achieved in this study can be attributed to sufficient oxygen availability and maintaining longer SRT of 70 d and hence limitation in nitrification was not observed. Figure 7.10 and Figure 7.11 show the removal of NH_4-N and TN for NaCl and KH_2PO_4 at the same molar concentration. For SOA, NH_4-N and TN accumulation was noticed during OMBR-MF operation (data not shown), which can be ascribed to the reverse salt transfer from draw solution to the mixed liquor. The TN level in the reactor increased considerably to 50 mg/L. The trend of NH4-N build-up was also observed for inorganic draw solutes in previous studies with high saline stress in the bio-tank (Aftab et al., 2015a, Luo et al., 2015b, Qiu and Ting, 2013). Nitrification is a very sensitive process, as the nitrifying microbes involved in the process are slow growing and highly susceptible to conditions such as DO concentration and salt concentration (Lay et al., 2010). Compared to other OMBR studies, incorporating a MF membrane in the bioreactor mitigated excessive salinity build-up, and good nitrification was achieved with the high SRT and sufficient aeration as provided in the present study. Permeate quality showed more than 98% of NH_4-N removal was achieved for both NaCl and KH_2PO_4 DS. In contrast to previous results for inorganic DS (Holloway et al., 2015b, Siddique et al., 2017, Aftab et al., 2015a, Zou and He, 2016), a high removal of NH_4-N within the bioreactor was observed **(**Figure 7.10**)** throughout the operation with both the NaCl and KH_2PO_4 DS.

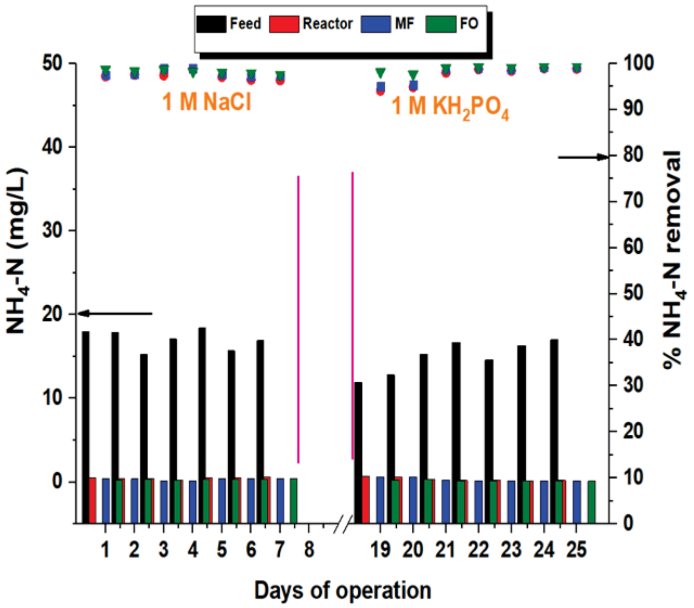


Figure 7.10 Variation of NH_4-N concentration in the influent, bioreactor, MF and FO effluents and NH_4-N removal in OMBR-MF hybrid system employing different draw solutes. Experimental conditions are as described in Fig. 7.2.

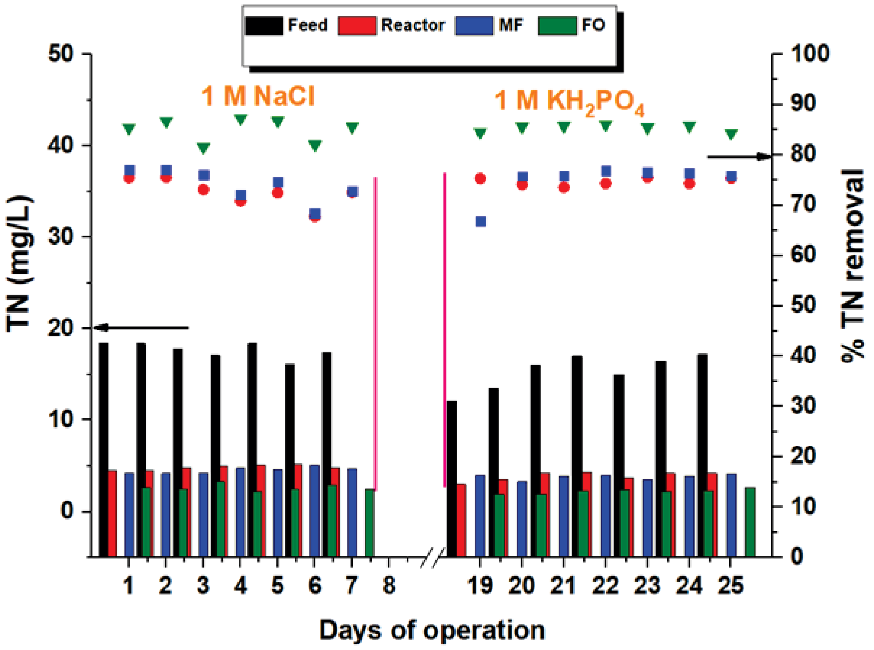


Figure 7.11 Variation of TN concentration in the influent, bioreactor, MF and FO effluents and TN removal in OMBR-MF hybrid system employing different draw solutes. Experimental conditions are as described in Fig. 7.2.

TN removal efficiencies in the reactor were 72.5±1.7 % for NaCl and 74.6±0.7 % for KH_2PO_4 at a low aeration rate of 2-3 L/min. With both DS more than 85 % total nitrogen removal in FO permeate was observed. Remarkable denitrification achieved in the baffled OMBR-MF hybrid system was possibly related to the NOx ions exclusion by FO membrane which prolonged NOx retention in the bioreactor, thus facilitating their removal during the anoxic cycle under very low DO (<0.5 mg/L). A high initial C/N ratio in the reactor (around 11) also gave favourable conditions for an efficient simultaneous nitrification-denitrification (SND) process that might have occurred when the nitrification and denitrification rates were possibly in a stable equilibrium (Chiu et al., 2007). Dey (2010) also reported that sufficient electron donor is necessary for sustaining denitrification, where a C/N ratio above 10 is needed to have a significant effect on overall nitrogen. Holloway et al. (2014) in their UF-MBR study reported that high nitrate concentrations were detected in the bioreactor. They deduced that elevated nitrate might have been either due to a carbon limitation or an insufficient hydraulic retention time (HRT) in the anoxic zone.

In the present work, the influent was fed to the anoxic zone of the reactor to supply COD to achieve a good C/N ratio for better denitrification to occur. In contrast, TN accumulation was found in the reactor with SOA, which is most likely due to the RSF of SOA from the DS to reactor mixed liquor. The nitrogen build-up occurred gradually in the reactor, increasing the ammonium-loading rates due to RSF from the DS side at constant COD loading. Subsequently, a lower C/N ratio in the reactor represents less carbon source available for biomass. Hence, the lower C/N ratio caused TN accumulation in the reactor.

Lay et al. (2010) noted that especially some microorganisms, like denitrifying bacteria, are apparently more sensitive under osmotic stress. In the current study, combining MF membranes with FO in the osmotic reactor helped alleviate salinity build up in the hybrid OMBR-MF system thereby providing favourable conditions for growth of denitrifying bacteria to achieve SND. In other studies carried out by Zajzon (2012) in laboratory-scale MBR system with higher SRT showed SND to become more significant, supporting the microenvironment theory outlined in section 7.3.6.

Finally, impact of different DS was investigated in a baffled OMBR-MF hybrid system. We could see that the fertilizer DS did not affect the bioreactor performance seriously. Nevertheless, one week operation time was a little short with individual DS yet was sufficient to achieve carbonaceous and total nitrogen removal. It might be due to MF membrane incorporation which controlled salinity build up and the bacterial community structures were not significantly changed with different DS. Therefore, future studies will focus on long term operation of hybrid OMBR-MF system to investigate the impact of fertilizer DS on the process performance via the analyses of bacterial community structures in order to understand how these DS influence the oxic-anoxic process (which is one of the most important parts in this hybrid system).

7.3.5 Biomass characteristics

Biomass characteristics play an important role in MBR operations, which governs the efficiency of the biological treatment as well as affects the membrane filtration processes (Lay et al., 2010, Siddique et al., 2017).

7.3.5.1 Organic foulants behaviour

It is well known that the SMP and EPS play important roles in membrane fouling. Understanding the characteristics of SMP and EPS in the hybrid OMBR-MF system is therefore helpful, to give a better insight into the membrane fouling mechanisms of FO processes (Qiu and Ting, 2014a). Both SMP and EPS are heterogeneous and generally comprise a range of biological origin substances like proteins, humic acid, triglycerides, carbohydrates and nucleic acid (Wang et al., 2016a). Proteins and carbohydrates are the dominant components found naturally in extracted SMP and EPS, and their respective concentrations were used to represent SMP. bEPS has been normalised as the sum of protein and carbohydrate concentrations to the sludge concentration in the reactor. The concentrations of initial SMP and bEPS in the reactor and at the end of experiments for each of the DS were measured in the OMBR-MF system (Figure 7.12). Salt accumulation within the bioreactor increases the osmotic stress on microbial activity, which translates to a noticeable increase in the SMP concentration, particularly with NaCl. These observations are consistent with previously reported results, where salt accumulation in the mixed liquor resulted in an increased SMP concentration in the OMBR (Luo et al., 2015d). The SMP are in direct contact with membrane surface thus protein and polysaccharide fraction of SMP has pronounced impact on flux profile as compared to EPS component (Johir et al., 2013). Initially, the reactor had 30.4 mg/L SMP increasing to 61.6 mg/L over a week when NaCl was employed. Increased SMPs production, mainly as a carbohydrate fraction, facilitates the formation of a gel layer on the membrane surface that is not readily removed by physical cleaning (Di Bella et al., 2013). The increase in SMP is mainly due to plasmolysis and release of intracellular constituents as well as accumulation of intermediate and unmetabolised fractions and microbial produced polymers (Johir et al., 2013).

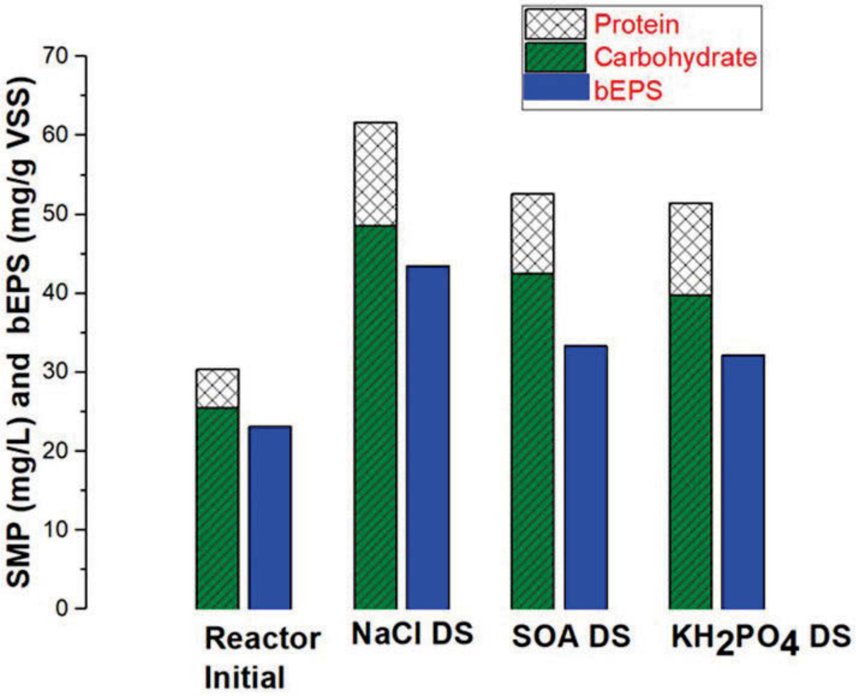


Figure 7.12 Soluble microbial products (SMP) and extracellular polymeric substance (EPS) with different DS in the OMBR-MF system.

After each test run with SOA and KH_2PO_4 DS, the final SMP was observed to be lower than with NaCl; 52.6 mg/L and 51.4 mg/L, respectively. This is possibly because of less saline stress in comparison to NaCl DS. The decreases in SMP employing SOA and KH_2PO_4 can also be attributed to the different characteristic of the DS, both fertilizer DS having nutrient components as well as less RSF compared to NaCl DS. This provides a more favourable environment to the biomass resulting in less SMP released as the system becomes more stabilised.

At the same time, increase in the EPS concentration was also found with all three DS compared to the initial reactor EPS. However, the experiment with NaCl showed more EPS mass in comparison to the other two DS. After 7 days of operation with NaCl, bound EPS values increased due to increase in salt concentration, probably as a protective response by mixed bacterial population in sludge with high salinity (2.5 g/L). Reid et al. (2006) evaluated short term effect of salinity build up in pilot-scale experimental campaign. They reported immediate flux decline using NaCl and when chloride (Cl^-) concentration was raised to 4.5 g/L respectively. Also, both SMP and EPS significantly increased to 24.9 g/L and 86.7 g/kg MLSS respectively. In this study, at the end of experiments with SOA and KH_2PO_4 DS, measured EPS concentration was higher than initial reactor EPS content. However, measured EPS was less in the runs carried out under low salinity conditions (1.3 g/L for SOA and 1.2 g/L KH_2PO_4) than that with NaCl DS.

7.3.6 Floc size

The variation in mean floc size (d_{50}), evaluated in terms of volume of particles. The measured floc size for reactor mixed liquor was 22 μm. The floc size for all three DS was found to increase. In other OMBR studies, floc size was found to decrease with salinity build up in the reactor, for example, the mean floc size decreased slightly from 45 µm to 42 µm with an increase in salinity by NaCl from 0 to 2.5 g/L (Qiu and Ting, 2014b). This could be due to a decrease in the amount of filamentous bacteria in activated sludge flocs with increased salinity. These filamentous organisms are the backbone of sludge flocs, contributing to the development of larger flocs (Johir et al., 2013). Zhang et al. (2014) also reported that release of EPS from flocs, because of cell lysis, and the production of more SMP in the supernatant with the increased salinity, may also deteriorate the settling and flocculating properties of mixed liquor. On the contrary, Moussa et al. (2006) observed larger floc size and better sludge settling properties with increased salinity. In addition, average particle size improved from 100 µm to 200 µm at increased salinity conditions as compared to the fresh water environment. However, in this OMBR-MF study, increase of floc size was observed for NaCl DS. The slow and gradual increase of salinity over time may have provided time for the biomass to acclimatise with the changing environment thus not adversely affecting the floc size.

It was reported that higher EPSs content corresponded to higher floc size and stability (Lin et al., 2014). EPS increased with NaCl DS from 23.1 to 43.5 mg/g VSS**,** which is assumed to have affected the EPS content of sludge flocs and thus allowed floc size to increase from 22 to 64 µm when NaCl DS was employed In this study the maximum salt load was 2.4 g/L with NaCl DS, increased gradually over one week and therefore did not adversely affect the floc size.

Many reports on conventional MBR studies show that membrane filtration realised with the small floc/particles in the activated sludge may have higher fouling potential than the larger sludge floc/particles (Sun et al., 2011). In an OMBR study Wang et al. (2014a) reported decrease in floc size from 137 µm to 116 µm with decreasing EPS in the reactor mixed liquor. This was due to increase in salinity up to 25 g/L. However till 15 d operation they found increased in EPS with increasing salinity (20 g/L). This does not adversely affect floc size which was reported to 137 µm very much similar to initial floc size 136 µm in the reactor. In our study the higher EPS contents in the reactor mixed liquor for all three DS compared to initial reactor mixed liquor EPS content should therefore result in greater floc size. Furthermore, higher SRT in the OMBR-MF reactor might have resulted in an increase in EPS in sludge samples that has been shown to enhance floc formation (Zajzon, 2012).

The floc size can also explain the SND phenomena observed in the baffled hybrid OMBR-MF system. SND occurs on account of DO concentration gradients within microbial flocs due to diffusional limitations. The nitrifiers will survive in the outer regions of the flocs where there is a higher DO concentration, while the denitrifiers will preferentially be active in the inner zones of the floc with very low DO concentrations (Münch et al., 1996). Results obtained in this study support the microenvironment theory and the mechanism of SND.

MLSS and MLVSS concentrations as a function of time was measured and it clearly revealed that MLSS and MLVSS concentration was not affected much with all three DS (data not shown). The MLVSS/MLSS ratio decreased from 0.84 to 0.77 when NaCl DS was used. Luo et al. (2015a) also reported that, due to increased osmotic stress on the feed side, a reduction in MLVSS/MLSS ratio was observed which decreased the concentration of active biomass in the sludge. In the current work, due to very low salinity build up in the reactor (due to MF membrane) no more decrease of biomass was observed for each inorganic draw solute. The average MLVSS/MLSS ratio above 0.80 suggests an abundance of living microorganism, except slightly less (0.77) with NaCl DS.

7.4 Conclusions

This study investigated the flux performance and fouling behaviour of three different draw solutes in a hybrid OMBR-MF system. Biofouling behaviour was monitored using the OCT technique treating real sewage. The maximum biofilm thickness was observed with NaCl (163 μm) due to its higher specific RSF, resulting in elevated salinity (2.5 g/L). The lower fouling layer thickness measured for SOA and KH_2PO_4 DS is attributed to the lower salinity (1.2 g/L SOA and 1.2 g/L KH_2PO_4) and lower EPS concentrations. Incorporating a MF membrane helped control the salinity which also improved sludge characteristics such as EPS and enhanced flocculation characteristics.

CHAPTER 8

UNIVERSITY OF TECHNOLOGY SYDNEY

Faculty of Engineering & Information Technology

CONCLUSIONS AND RECOMMENDATIONS

8 Conclusions and recommendations

8.1 Conclusions

This thesis aimed to develop the novel baffled osmotic membrane bioreactor-microfiltration (OMBR-MF) hybrid system and investigated its feasibility for municipal wastewater treatment specifically focusing on total nitrogen and organic micropollutants and wastewater reuse. This was achieved by designing and fabricating novel baffled reactor, performing laboratory scale experiments, evaluating baffled OMBR-MF hybris system performance for range of draw solutions and also by performing fouling characterization using non-destructive optical coherence chromatography (OCT) technique. Moreover, baffled OMBR-MF hybrid system performance was evaluated employing both simulated and real wastewater.

8.1.1 Optimization of oxic-anoxic cycle time for simultaneous nitrification-denitrification using baffled OMBR-MF hybrid system

Prior to investigating long term performance of OMBR-MF hybrid system it is required to understand the impact of oxic-anoxic cycle time on the simultaneous nitrification-denitrification performance and thereby to achieve total nitrogen removal. Therefore, in Chapter 4, an optimum oxic-anoxic cycle time for SND process was investigated. From preliminary laboratory experiments in baffled OMBR-MF system employing simulated reverse osmosis brine draw solution, four different oxic-anoxic cycle time were tested for one week each. Very good TN removal efficiency was achieved. The 0.5-1.5 h oxic-anoxic time (Run 3) has achieved best 92 % TOC, 76 % TN and 63 % phosphate removal. Based on results obtained from this study, long-term OMBR-MF operation for TN removal, organic micropollutant removal and fouling characterization study were operated and further evaluated.

8.1.2 Long-term performance of a novel OMBR-MF system under continuous operation for simultaneous nutrient removal and mitigation of brine discharge

After investigating the optimum oxic-anoxic cycle time the potential of OMBR-MF hybrid system was assessed in Chapter 5 to treat municipal wastewater employing simulated SWRO brine DS. Thus baffled OMBR-MF system could treat organic matters, nutrient as well as help mitigate concentrated RO brine discharge issue into the sea. Moreover, obtained permeate from MF filter can be utilised for vertical farming after suitable post treatment. Reasonably high stable water flux (8 LMH) and low salinity build up (1.4 g/L) were observed due to MF membrane. High organic matter (97.84 %) and nutrient removal efficiency (PO_4-P 87.36 % and TN 94.28 %) was obtained. These results are very promising for the wastewater treatment applications and simultaneous brine mitigation. In Chapter 4 and Chapter 5 study, an OMBR-MF hybrid system performance was examined employing TFC-PA FO membrane.

8.1.3 Application of baffled OMBR-MF system for organic micropolluatnt removal

After investigating long-term performance of baffled OMBR-MF hybrid system in nutrient removal, the potential of baffled OMBR-MF hybrid system was further evaluated for most emerging organic micro pollutant (OMPs) compound. Three different OMPs were tested employing three different inorganic (NaCl, KCl) as well as organic (sodium acetate) draw solution respectively. The effect of unique oxic-anoxic conditions on OMPs removal was evaluated. With inorganic DS caffeine (94–100%) revealed highest removal followed by atenolol (89–96%) and atrazine (16–40%) respectively. All three OMPs exhibited higher removal with organic DS as compared to inorganic DS. Significant anoxic removal was observed for very persistent atrazine under very different redox conditions with extended anoxic cycle time. This can be linked with possible development of different microbial consortia responsible for diverse enzymes secretion. Overall, the OMBR-MF process showed effective removal of total organic carbon (98%) and nutrients (phosphate 97% and total nitrogen 85%), respectively. Thus, novel baffled OMBBR-MF hybrid system can effectively treat organic micropollutns.

8.1.4 Fouling characterization in baffled OMBR-MF hybrid system using optical coherence tomography (OCT) with real wastewater

The most significant factor that contributes to the decline in performance and limitation of widespread use of the OMBR is the fouling of the membranes. Different approaches are proposed to study the biofilm architecture in the literature, however, most of them are destructive and involve the removal of the membrane from the system and sampling of the fouled surface. A detailed knowledge with regards to fouling characteristics and development would be clearly advanced if a reliable and repeatable, non-invasive study tool would be available. Hence, the real-time monitoring or assessment is highly essential. For this purpose, lastly we examined the biofouling development on FO membrane in the novel baffled OMBR-MF hybrid system treating real wastewater. On-line monitoring of biofouling growth and changes in morphology on a flat sheet cellulose tri-acetate (CTA)-FO membrane was conducted non-destructively using optical coherence tomography (OCT), allowing an in-situ and real-time investigation of the biofilm structure over 21 days. The measured biofouling layer thickness was in the order sodium chloride (NaCl) > ammonium sulfate (SOA) > potassium dihydrogen phosphate (KH_2PO_4). The sludge characteristics and biofouling layer thickness suggest that less EPS and higher floc size were the governing factors for less fouling. OCT technique has successfully accomplished monitoring of the dynamic evolution of the biofilm.

8.2 Recommendations

In this study, the OMBR-MF hybrid process is proposed for municipal wastewater treatment specifically targeting total nitrogen and organic micropollutant removal.

This novel concept of the baffled OMBR-MF was successfully demonstrated by i) evaluating long term OMBR-MF performance employing SWRO bine DS. Very high nitrogen removal was achieved and the produced diluted brine could reduce seawater discharge issues, ii) evaluating the baffled OMBR-MF hybrid system performance for successfully treating OMPs, and iii) demonstrating the performance of OCT technique for the first time in fouling characterization of forward osmosis membrane in OMBR treatment.

Nevertheless, there are still some challenges and scope for future work exists for this novel baffled OMBR-MF hybrid process and therefore the following recommendations are suggested:

1. In our baffled OMBR-MF study organic draw solute (DS) has shown better performance. Despite excellent nutrient and OMPs removal achieved, due to their ability to provide carbon source it also had more fouling propensity to FO membrane. It is required to explore other divalent organic DS and to compare their performance in baffled OMBR-MF system.
2. There is also scope to assess draw solutes incorporating surfactants in baffled OMBR-MF system. The performance can be evaluated in terms of water flux and salinity, nutrient removal and OMP removal as compared to simple FO process as already studied in our FO research group.

3. Due to longer HRT in OMBR soluble COD and organic micropollutant can be effectively removed. Since microbial consortia plays a vital role in biodegradation of organics, it would be interesting to address microbial community dynamics in oxic and anoxic zone in the baffled bioreactor to elucidate its impact on nutrient and OMPs removal.
4. Osmotic membrane bioreactor for wastewater treatment is very promising and attractive process. It has shown very promising results for organic, nutrient removal and recovery and trace organics removal. However, most of all experiments are performed in lab-scale. Therefore, more studies both in pilot and in full-scale plants are necessary to gain knowledge leading to achieve a better OMBR performance. Moreover, to come up with commercial membrane (in order to achieve long term stable performance) and to design membrane modules are one of the biggest challenges for reaching this technology to mature stage. In order to commercialise OMBR, full scale benchmarking and efficient process controls intensification are major challenges. Submerged OMBR modules would demand different module design than commercial MBR. This is due to draw solution usage in OMBR which necessitates unique DS channel design for better mass transfer and membrane support.
5. Nanotechnology may also offer unique opportunities to combat biofouling, often called the ‘Achilles’ heel’ of membrane processes. So, new membranes with less fouling potential need to be explored, such as fabricated from nanomaterials or carbon nanotubes (CNT). Further, it is essential to characterise fouling on FO membrane in long run without disturbing continuous operation and to devise robust automatic antifouling and cleaning strategy.

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