MEMBRANE HYBRID SYSTEMS IN

WASTEWATER TREATMENT

by

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CERTIFICATE OF AUTHORSHIP

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as part of the collaborative master degree and fully acknowledged within the text.

I also certify that I have written the thesis. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Signature of Candidature

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Abstract

The production of fresh water and the disposal of wastewater are the major challenges for the last few decades. Reverse osmosis (RO) membrane plants are extensively used for industrial water purification. The large quantities of concentrate generated by RO plant have a disposal issue especially when the plant is located inland. Due to high disposal costs, there is need to reuse. RO reject concentrate is being increasingly processed to recover additional potable water. To achieve higher recoveries alternate processes are used.

Reverse osmosis concentrate (ROC) produced from water reclamation plant can threaten the environment, if it is not appropriately treated before discharge. Membrane bioreactor (MBR) is an attractive technology. Membrane bioreactor is an efficient, cost-effective and reliable treatment system to produce high-quality water from wastewater. This study examined the use of MBR with and without activated carbon such as granular activated carbon (GAC) or powdered activated carbon (PAC) for further treating wastewater and removal of organic micro-pollutants.

Fouling is an important and inevitable phenomenon in MBR. Lower membrane fouling implies more production of water, less cleaning of the membrane, long-term operation and longer membrane life, therefore, reducing operational and capital costs. Fouling can not fully reversed in MBR by physical cleaning alone. However, the combination of physical cleaning and chemical cleaning could almost fully restore the activity of the membrane. Thus, in this study, chemical cleaning in MBR was studied and the performance was compared with that of membrane adsorption hybrid system (MAHS). Synthetic wastewater was used in this study.

The composition of this wastewater was similar to reverse osmosis concentrate (ROC) from a wastewater reclamation plant. The influence of filtration flux and chemical cleaning was studied. The cleaning chemicals such as sodium hypochlorite (NaOCl) and nitric oxide (NO) was experimentally evaluated. Low concentration nitric oxide (NO) reduced the growth of biofilms in an MBR system. NO treatment could delay the formation of new biofilm on the membrane. NO also had the superiority over

the traditionally used sodium hypochlorite (NaOCl) for backwashing as the later may have an adverse effect on the activated sludge and environment. NO treatment resulted in the reduction of the relative abundances of bacterial communities while might be encouraged in other bacterial communities.

- ***Submerged membrane adsorption hybrid system with granular activated carbon (GAC)***

In this study, the effect of GAC on fouling reduction was studied in submerged MBR. The addition of GAC into the MBR system deferred TMP development. This is because of the mechanical scouring effect by GAC as well as by the pre-adsorption of organics before reaching the membrane surface. Also, it was observed that the addition of GAC in MBR system can effective for removing DOC by 94% throughout the experiment period for 120 days. These results further showed that the addition of GAC helped to reduce organic fouling.

- ***Membrane adsorption Bioreactor hybrid system***

The operation of MBR resulted in the sudden rise of trans-membrane pressure (TMP). The sudden development of TMP was minimized by introducing activated carbon such as granular activated carbon (GAC) and powdered activated carbon (PAC) in MBR as a suspended medium. The incorporation of GAC and PAC prevented sudden TMP increase and also helped to remove an additional amount of dissolved organic matter.

- ***Submerged membrane adsorption hybrid system with powered activated carbon (PAC)***

A detailed study was made with the real reverse osmosis concentrate (ROC) from a wastewater reclamation plant. Biologically activated carbon uptakes the soluble organics, therefore MBR-PAC hybrid system showed the superior removal of organic matter in this study. After the addition of PAC into the reactor, total organic carbon (TOC) removal increased sharply and went up to 91 %. The recovery of TOC removal was due to the adsorption of organic on PAC initially and then by bioadsorption. The addition of PAC was mostly responsible for the improved filtration performance in the MBR system by modifying the sludge characteristics and the cake layer on the membrane surface. Thus, the addition of PAC in the MBR led to a superior organic removal by a combination of bio flocculation and adsorption phenomena.

- *Biofilter*

Many wastewater treatment plants use MBR as their biological treatment step. MBR cannot remove persisting organic pollutants. Thus, in this study, the performance of granular activated carbon (GAC) biofilter and membrane adsorption hybrid system (MAHS) was evaluated for its ability to reduce effluent organic matter from MBR effluent collected from a decentralized MBR plant treating domestic wastewater. The up-flow biofilter column was packed with GAC to a height of 10 cm and 40 cm. The column was operated at a low velocity of 1.79 and 3.58 m/h and resulted in a high removal of dissolved organic carbon (DOC).

The MBR effluent consisted of eleven pharmaceuticals and personal care products (PPCPs). After a post-treatment of MF membrane-GAC adsorption hybrid system (MAHS), most of the micro pollutants were removed except for three compounds with very low concentrations. However, bisphenol A was found at the concentration of 316 ng/L at the end of the experiment.

Chapter 1

University of Technology Sydney

1 Introduction

1.1 Background

1.1.1 Water scarcity

Water is essential for life, but the amount of fresh water in the earth is finite. The world's water resources face huge threats due to urbanization and population growth. If the current patterns of water consumption continue unabated, two-thirds of the world's population will suffer from water shortage. Furthermore, billions of people already live in water-scarce regions, and almost 3.5 billion people will experience water scarcity by 2025 according to the World Economic Forum's 2017 Global Risks' report. **Figure 1.1** shows the current map of water scarcity region provided by the World Resource Institute. There is no new water source on the planet. The availability of water is recycled through a process of circulation of the atmosphere. This means that the amount of available fresh water is limited despite an increasing population. Therefore, research on an alternative water source is inevitable.
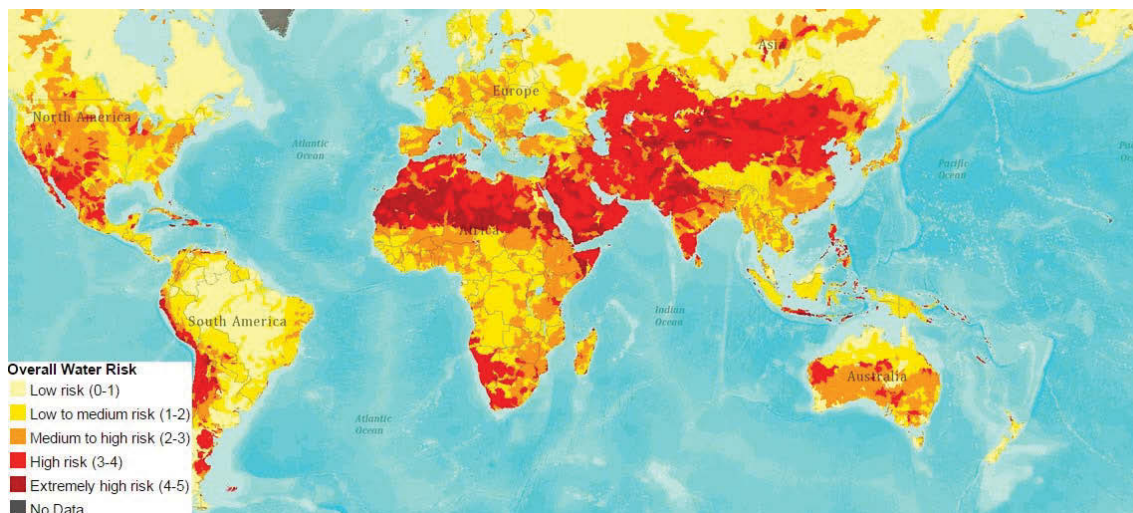
Figure 1.1 Map showing water scarcity (The World Resource Institute 2013)

1.1.2 Wastewater reuse

To solve water shortage issues, alternative water resources need to be explored. Natural water ecosystems should be protected. Further new approaches of managing water resources are also required while fulfilling the increasing demand for fresh water for the growing population. During the past three decades, wastewater reuse has become an attractive option due to protection for aquatic ecosystem and extending reliable water resources. There has been a meaningful diversification of water reuse practices.

Reclaimed water is gaining popularity globally as a reliable water resource because of its sustainability. Concerning the quantity, recycled water is regarded as reliable water resource since it provides a constant and reliable supply of treated sewage effluent. However, the potential for entirely exploiting recycled water is limited by its quality. The contaminants such as microbial pathogens, dissolved organics, persisting organics such as pharmaceuticals and personal care product (PPCPs), heavy metals, high salinity, and various inorganic matters limit the reuse of wastewater. Thus, adequate treatment techniques are required to remove these contaminants to make the water suitable for high-quality water reuse.

1.1.3   Membrane bioreactor (MBR)

One of the most promising technologies in wastewater treatment is the membrane bioreactor (MBR). MBR is a combination process of an activated sludge and membrane separation. A small footprint, absolute solid-liquid separation, remarkable removal of organics and production of high quality of water are the significant merits of the MBR process.

The performance of MBR depends on different operating conditions such as filtration flux, hydraulic retention time (HRT), solid retention time (SRT), organic loading rate (OLR), etc. A number of researchers have investigated the effect of SRT on MBR performance. For example (Grelier et al., 2006) reported that the increase of SRT improved membrane performance. Lower SRT causes a higher concentration of floc bound exo-polymeric substances (EPS) than higher SRT of 40 days (Al-Halbouni et al., 2008). Further, Laera et al (2009) recommended and SRT of more than 40 days for reliable operation of MBR in treating municipal wastewater (Laera et al., 2009). Along with SRT, the parameters such as HRT, filtration flux, mixed liquor suspended solids (MLSS) and organic loading rate (ORL) also play an essential role in the performance of MBR.

The MBR process usually removes organic matter and a portion of nutrients from water. Therefore, it is crucial to remove nutrients through physicochemical processes such as ion exchange, reverse osmosis, electrodialysis and catalytic reduction (Nur et al., 2012). Of various methods, the adsorption process is a suitable option for the removal of nitrate and phosphate due to their economic

and straightforward operation (Nur et al., 2012). Thus, a strategy employing MBR especially to remove organic and a post-treatment to remove nutrients and micro pollutants should be explored.

1.1.4 Membrane fouling

The application of MBR technology is limited by membrane fouling. Fouling is referred as the deposition of soluble and particulate matter onto membrane surface and inside the membrane pores due to physicochemical and biological interactions between the membrane and the activated sludge. This impedes the efficiency of membrane filtration and reduces the permeate quality. Thus, a frequent membrane cleaning and membrane replacement are required leading to higher system operation costs (Jefferson et al., 2004). Membrane fouling can be divided into reversible, irreversible and irrecoverable fouling.

Membrane fouling could be reduced by utilizing a medium in suspension in the MBR such as activated carbon, which could help to adsorb organic matter prior to reaching of organic matter to the membrane. The medium can also provide extra shear stress on the membrane surface, and this will prevent the deposition of sludge particles on the membrane surface. Several studies have been conducted on the addition of medium in suspension to reduce membrane fouling (Li et al., 2005). In addition, fouling can be controlled by careful selection of chemical cleaning agent such as nitric oxide (NO).

1.1.5 Chemical cleaning with NO

Chemical cleaning in one of the commonly used methods to reduce organic and biofouling. The use of nitric oxide (NO) to mitigate MBR fouling has been researched. NO is an intracellular signalling molecule, which has been shown to be related to biofilm dispersal (Barraud et al., 2006). NO induces the transition from the biofilm mode of growth to the free swimming planktonic state as shown in **Figure 1.2** (Schlag et al., 2007). This particular chemical was found to have a universal effect on the dispersal of sessile bacteria, including both Gram-positive and Gram-negative bacteria (Charville et al., 2008). Thus NO would have a significant potential in controlling microbial attachment and membrane biofouling. One disadvantage of NO is its low solubility in water and its oxidizability, such that direct addition of NO into water or an aqueous solution would hamper its anti-fouling efficiency. A number

of NO donors, including the enzymatic and non-enzymatic NO donor, have been proven to be efficient in the dispersal of biofilms. The addition of a NO donor increases the biofilm removal efficiency and dispersal of multi-species biofilms from the water. The mechanism of the reaction between NO and the biofilm occurs at pico molar and nan molar levels (Barraud et al., 2009). NO-based method for biofouling control is currently being optimized and restricted to in vitro studies; therefore, the potential of NO in membrane biofouling mitigation has plenty of room for discovery and potential.
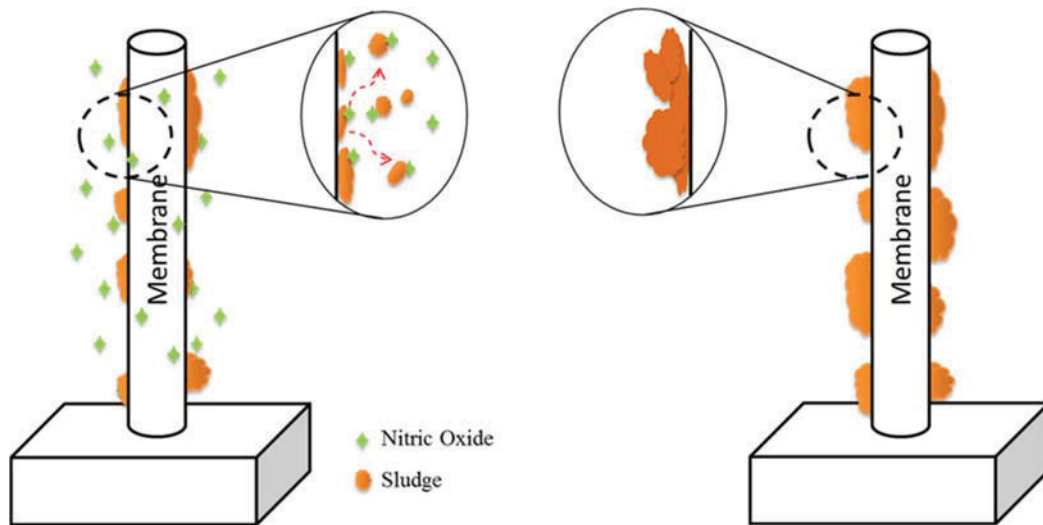
Figure 1.2 The mechanism of Nitric Oxide (NO) backwashing

1.1.6   Activated carbon adsorption

The use of adsorbents such as activated carbon in conjunction with MBR can reduce the fouling and also provide superior quality of effluent. Past studies showed that use of granular activated carbon (GAC) helped to reduce membrane fouling by around 50% and also removed a higher amount of organic matter (Johir et al., 2011a). Also granular support medium in a submerged membrane reactor reduced the membrane fouling by around 85% (Pradhan et al., 2012). The addition of powdered activated carbon (PAC) removed slowly biodegradable organics (Akram and Stuckey, 2008). Also, PAC has proved to be a cost-effective approach, not only for flux enhancement but also for improved chemical oxygen demand (COD) removal (Park et al., 1999). Thus, employing an activated carbon as adsorbent is an effective way to mitigate the fouling in MBR.

1.1.7 Post-treatment to MBR effluent

The MBR effluent contains some effluent organic matter including PPCPs and slowly degradable organics. They can be removed by biofilters, membrane hybrid systems employing activated carbon. They also can be removed by processes such as membrane distillation (MD). MD is an effective way of removing non volatile organics and inorganic salts.

1.2 Objectives of this study

1) Reduction of fouling in MBR: study on the influence of sodium hypochlorite (NaOCl) and nitric oxide (NO) as a chemical cleaning agent to reduce biofouling in a membrane bioreactor. Effectiveness of granular and powdered activated carbon (GAC and PAC) as suspended medium in MBR was also studied to mitigate the membrane fouling. Both synthetic and real ROC was used as feed.

2) The use of advanced technologies such as MD as post-treatment to obtain the superior quality of effluent.

3) MBR treating domestic wastewater dose not remove persisting organic pollutants. Thus, this study investigated on the efficiency of GAC biofilter and membrane GAC hybrid system as post treatment to treat MBR effluent to remove persisting organic pollutants.

1.3 Structure and major contents of this thesis

This thesis has been divided into 5 chapters as follows:

- **Chapter 1**: Introduction: It presents a general background on the treatment proceses and objectives of this study. The specific background is presented under in each Chapter.

- **Chapter 2**: A detailed literature review on the status of objectives proposed in this study and their limitations. This chapter presents the basics of the MBR system, factors influencing MBR process, review of membrane fouling including biofouling and mitigation strategies of

membrane fouling. Membrane hybrid system as post-treatment is also examined. More detailed and specific review is also incorporated in Chapter 4.

- **Chapter 3**: The general experimental investigation and methodologies used in this study are presented and explained.

- **Chapter 4**: This chapter presents the MBR performance and membrane fouling reduction strategies. The strategies used are chemical cleaning and the use of the membrane adsorption bioreactor hybrid system. The performance of sodium hypochlorite and nitric oxide was studied in their capability in reducing biofouling in a membrane bioreactor. The results of MBR performance with and without the addition of GAC and PAC as suspended medium are presented to show the merits of using GAC and PAC in reducing the membrane fouling. The MBR and MBR-GAC hybrid systems were conducted with synthetic ROC representing ROC from wastewater reclamation plant. The performance of MBR-PAC hybrid system was evaluated with real ROC obtained from a wastewater reclamation plant in Sydney. The experimental results of membrane distillation (MD) in treating the MBR effluent are also presented. The MBR treating domestic sewage dose not remove persisting organic pollutants. The use of biofilter and hybrid membrane systems in removing persisting organic pollutant from MBR effluent was also investigated.

- **Chapter 5**: This chapter summarises the conclusions and finding of this study. In addition to this, it also gives recommendations for future study.

Chapter 2

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2 Literature review

Introduction

Wastewater is increasingly regarded as a source of reusable water even though it contains contaminants due to a shortage of fresh water. However, the primary challenge of reusable water is removing pollutant that can harm the environment and human health.

This chapter presents a critical review of the MBR and biofilter processes used in wastewater treatment. Also, different membrane technologies and their applications, advantages and disadvantages are also presented here. The factors affecting the performance of MBR processes including membrane fouling and the fouling reduction approaches are also discussed. The post-treatment methods to obtain high quality water such as membrane distillation are discussed.

2.1 Membrane technologies for water treatment

Membrane technology plays an essential role in water and wastewater treatment and reuse. The use of membrane technology is widely accepted in the production of clean water from various water sources such as surface runoff, aquifers, brackish water, seawater, stormwater, rainwater, wastewater etc. Membranes also play a major part in industrial processes, mainly municipal and industrial wastewater treatment (Nicolaisen, 2003).

Several technologies are currently used to treat the water and among these treatment processes, membrane-based water purification processes are found to be the most reliable. The membrane treatment processes used in water purification are microfiltration (MF) (Alzahrani and Mohammad, 2014), ultrafiltration (UF) (Wolf et al., 2005), nanofiltration (NF), membrane distillation (MD) (Tijing et al., 2014), reverse osmosis (RO) (Greenlee et al., 2009), and forward osmosis (FO) (Chanukya et al., 2013).

Membrane separation process is only able to separate substances (organic and inorganic molecules) based on pore size or molecular weight cut-off (**Table 2.1**). MF can efficiently remove suspended particles, organic colloids, turbidity, and pathogens, while UF can also do the same. It can also remove viruses and macromolecules. NF and RO, on the other hand, involve diffusion, sorption,

and partitioning. The pore size of NF membrane is smaller than that of UF, thus making NF membranes suitable for removing comparatively small organic compounds, such as micro pollutants, dye, and degradation products from the effluent of biologically treated wastewater. Aside from a wider variety of organic substances, NF membrane can also reject charged compounds and multivalent inorganic ions depending on the surface charge of NF membrane. Therefore, NF can produce higher quality water compared to MF and UF membrane processes. Natural osmosis is a process by which water from a solution of lower concentration goes through a semi-permeable membrane to move to a solution of higher concentration. Since RO utilizes the concept of reversal of natural osmosis process, this process uses very high applied pressure. RO is mainly used to separate salts and low molecular weight compounds from water. Aside from desalination, RO can also be applied to wastewater treatment (Dialynas et al., 2008) as a final treatment to remove inorganics, salts and micro pollutants.

Table 2.1 Membrane type

2.2 Membrane bioreactor

Membrane bioreactor (MBR) is a combined process of biological treatment and membrane separation. MBR process is the most widely researched and studied technologies in wastewater treatment. Compared with other advanced wastewater treatment technologies, such as sequencing batch reactors and aerated biological filters, MBR is more cost-effective and energy-efficient (Hoinkis et al.,

2012). The advantages of the MBR process are as follows: (1) excellent performance at higher mixed liquor suspended solids (MLSS) concentrations, (2) small footprint, (3) able to produce effluent of high quality and provide disinfection, (4) ability to remove organic contaminants effectively, (5) independent control of solids and hydraulic retention times (SRT and HRT, respectively), and (6) low production of sludge. (Chang et al., 2006). However, MBR process also has disadvantages such as (1) complexity of the removal mechanisms, (2) additional membrane cleaning and maintenance costs, and (3) higher capital equipment and operational costs.

In conventional MBR process, MF or UF membranes are used as separation process. The module configuration of MF and UF membranes can be either flat sheet or hollow fiber. There are two primary configurations of the MBR process namely (i) side-stream (or external) and (ii) immersed (or internal) (**Figure 2.1**). In the side-stream MBR configuration, the membrane module is installed outside of the reactor. The biomass is either pumped directly through the membrane modules in series and back to the bioreactor or pumped to the modules and circulates the biomass through the modules in series. In the case of submerged MBR, the feed water is directly in contact with the biomass. Since the membrane is directly immersed in the bioreactor, this configuration is usually preferred over side-stream configuration, especially for domestic wastewater treatment. The submerged MBR configuration avoids recirculation. Thus it leads to less operational costs. Both MBR configurations need continuous removal of excess sludge to maintain MLSS concentration. The use of aeration in submerged MBR processes reduces membrane fouling.
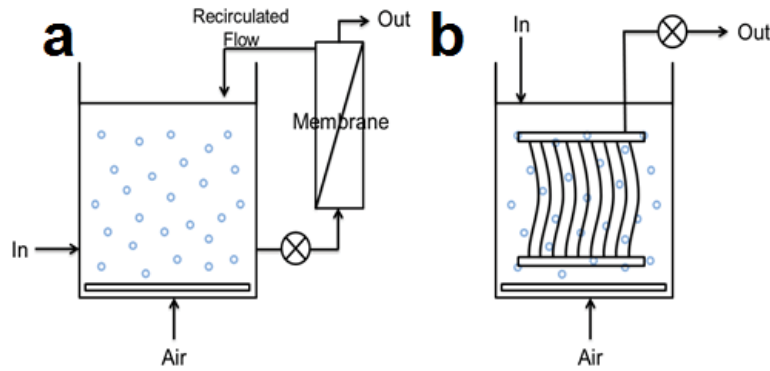
Figure 2.1 Configurations of the conventional MBR process: (a) side-stream, or external, and (b) submerged (Marrot et al., 2004).

2.2.1 MBR in wastewater treatment

Conventional wastewater treatment processes for municipal wastewater processes usually consist of three stages: (1) sedimentation to remove solids matters present in the feed water, (2) aerobic degradation of the organic matter, and (3) final sedimentation to remove the biomass (**Figure 2.2**). However, in MBR, the biomass is filtered through a membrane while it is undergoing aerobic degradation. The use of membrane module in MBR replaces the clarifier in the conventional sludge treatment process. The resultant water from MBR is expected to have higher water quality than that obtained from the conventional water treatment. Thus, there is less need for further extensive disinfection and post-treatment processes.
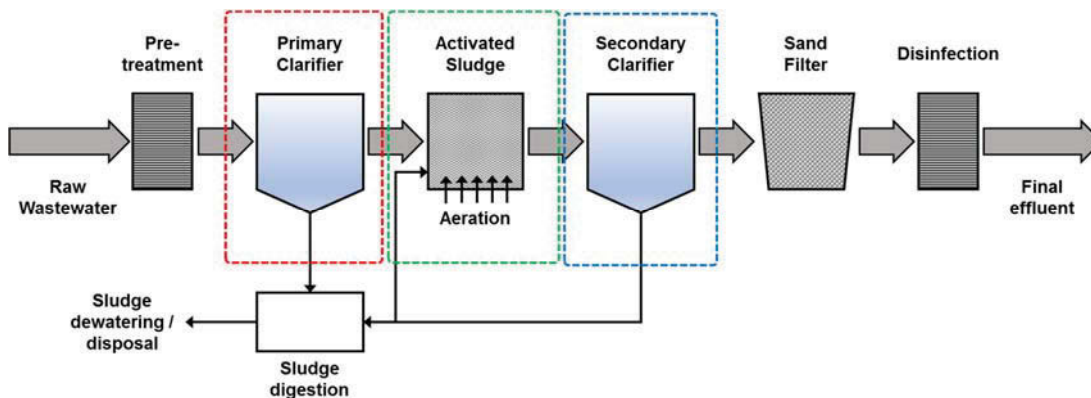
Figure 2.2 Typical conventional wastewater treatment process diagram (Judd, 2008)

2.2.2 Wastewater reclamation

Reverse osmosis (RO) is used in wastewater reclamation plants as the final treatment. RO-based reclamation plants are used for wastewater reuse all over the world. In Sydney, Australia, there are a number of water reclamation plants, which use RO after MF or UF of biologically treated wastewater: some experiments include wastewater treatment plant and water recycle plant. Wastewater reclamation plants use reverse osmosis (RO) as the final polishing treatment.

Even though RO process produces high-quality reusable water, it also produces a significant volume of RO concentrate (ROC) (10-20 % of feed water volume). ROC is rich in dissolved organics such as pharmaceuticals and personal care products (PPCPs), pesticides and inorganic substances. The direct disposal of ROC into water bodies can pose a severe eco-toxicological risk, threaten aquatic organisms and cause serious environmental problems. Thus, sustainable management and safe disposal of ROC are required to minimise the adverse effect on the environment resulting from the direct disposal of ROC into the natural water body.

2.2.3 Fouling in the MBR process

The most significant drawbacks of the MBR process is membrane fouling. Fouling is the phenomenon of the blocking of the membrane pores. Membrane fouling reduces the production of water through the membrane (Lee et al., 2001). Membrane clogging, on the other hand, is the deposition of the sludge or floc particles on the membrane surface. Membrane clogging can be controlled by changing operating conditions and by adopting effective membrane cleaning procedure. Membrane fouling is usually classified as inorganic, organic, or biofouling.

2.2.3.1 Organic fouling

Organic fouling is caused by the deposition or attachment of organic substances on the membrane surface or into the membrane pores. The organics that are responsible for membrane fouling are biopolymers (proteins, carbohydrates, sugar etc.), humic, fulvic and low molecular weight acid and neutrals. Most of the organic fouling may have three layers: (1) top layer which is porous and loosely bound, similar to sludge flocs, (2) middle layer which contains soluble microbial products (SMPs), bacteria aggregates and high concentration of polysaccharides, and (3) the irremovable bottom layer

predominated by soluble microbial products (SMPs) and extracellular polymeric substances (EPS) (Meng et al., 2017). Many studies have shown that both SMPs and EPS cause the most severe organic fouling in MBR.

2.2.3.1.1   Effect of EPS on membrane fouling

Among the different organic foulants, EPS has the significant ability to block membrane pores and adhere to the membrane surface. EPS is a colloidal material that contains construction materials for microbial aggregates and a wide range of organics such as carbohydrates, proteins, nucleic acids, lipids, humics, etc (Barker and Stuckey, 1999). High initial carbohydrate concentration usually results in fouling. High EPS concentration increases the viscosity (Meng et al., 2007), and the highly hydrated gel matrix of these biopolymers are responsiblde for the reduction of permeate flux in MBR (Cho et al., 2005). Loosely bound EPS was found to cause fouling more severely than tightly bound EPS (Ramesh et al., 2006). In fact, dissolved organic matter rejection in sludge supernatant showed much higher EPS concentration than the effluent (Drews et al., 2006). Furthermore, the concentration of bound EPS, especially carbohydrates, in the sludge influences foaming in MBR (Lesjean et al., 2005). This problem is further compounded when bound EPS interacts with filamentous bacteria. This result is significant occurrence of fouling and scum growth increase. Bound EPS cannot be regarded as the only cause of membrane fouling although it has significant influence on sludge characteristics and membrane fouling. Thus, bound EPS concentrations are closely related to sludge characteristics such as sludge volume index, flocculation ability, hydrophobicity, surface charge and sludge viscosity. Both bound EPS and sludge characteristics should be considered together to mitigate membrane fouling.

2.2.3.1.2   SMP

SMPs are the soluble organic matter produced by the bacterial populations in the bioreactor. SMP includes a wide range of organics similar to EPS and are of moderate molecular weights. They are biodegradable and are related to the formation of effluent chemical oxygen demand (COD) and biochemical oxygen demand (BOD) in the biological wastewater treatment process (Laspidou and Rittmann, 2002). SMPs can either be substrate-utilisation-associated products, which are the by-products of metabolism and biomass growth, or biomass-associated products, which are formed from

biomass decay. SMP can quickly accumulate in MBR and penetrate through the membrane pores. Furthermore, the concentration and composition of SMP in the MBR can even increase fouling propensity, as filterability also becomes poorer (Geng and Hall, 2007).

2.2.3.2 Inorganic fouling

Inorganic fouling is a result of chemical precipitation which occurs from the reactions between the components in the feed and sludge. Chemical precipitation occurs when saturation point has been exceeded due to concentration polarization. Inorganic fouling will then result in scaling and formation of an inorganic cake which is very difficult to remove. Mainly, carbonates of metals such as Mg, Fe, and Ca produce membrane scaling due to their insolubility in water (Meng et al., 2017).

Scaling mainly occurres in NF/RO desalination plants as they can remove such inorganic anions from feed water. Mostly, the dissolved inorganic salts in NF/RO system are usually concentrated 4-10 times, and possibly precipitate on the surface of the membrane as a result of exceeding their solubility (van de Lisdonk et al., 2000). Scaling which leads to a permeate flux decline during regular operational conditions can be built through two principal mechanisms, namely crystallization and particulate fouling on the membrane surface. Crystallization takes place when the salt concentrations exceed their solubility limit, and the ions crystallize on the membrane surface.

2.2.3.3 Biofouling

Biofouling is the deposition, growth, and metabolism of bacterial cells forming a biological cake. Biofouling involves not only attachment of microbial cells, but also the adsorption of organic matter produced by microorganisms (Malaeb et al., 2013). SMPs and EPS produced from the microbial community are the main cause for the formation of biological fouling and cake layer on the membrane surface. While shear stress created by aeration can remove cells, not all of them can be removed, and most of them hold onto the membrane surface tightly (Chen et al., 2015).

Bacteria are probably ubiquitous in natural ecosystems. Some bacteria can bring about severe pollution in many industrial and clinical settings. Biofilms which are formed by bacteria are a group of microorganisms which stick to each other and often these cells adhere to the surface. Biofilm, in

particular, can block membrane pores or worsen fouling in water treatment, as well as biofilm grown microorganism can contribute to the increased metabolism of micropollutants.

2.2.4 The effect of operating parameters on fouling in MBR

Management of fouling can be achieved by adjustment of operational conditions, as well as control of feedwater characteristics. Presence of foulants can be controlled by varying temperature, sludge retention time (SRT), organic loading rate (OLR), mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MLVSS), hydraulic retention time (HRT), and pH. Optimization of process design and operation parameters are often related to a compromise between efficient treatment and low overall cost and energy expenditure.

2.2.4.1 Effect of flux

Flux (volumetric flow rate per unit membrane area) of the water through the membranes should be maintained at an optimal value which suppresses fouling and clogging (Le Clech et al., 2003). The membrane fouling rate was found to be exponentially related to flux. The trans-membrane pressure (TMP) development also increases with the increase in flux (Germain et al., 2005).

Johir et al. (2012) studied the effect of flux on membrane resistance with equal cumulative filtered volume at different flux values. It was found that higher flux resulted in higher membrane resistance compared with lower flux. Furthermore, it was observed that membrane resistance started out lower and stayed stable during the initial stage of MBR operation, noting a sudden increase in membrane resistance at high flux (Johir et al., 2012c). This phenomenon can be explained by the fact that at higher flux, the cake layer structure was also changed, thus affecting the membrane resistance. This phenomenon has also been observed also in another study (Navaratna and Jegatheesan, 2011).

2.2.4.2 Effect of pH and temperature

The pH can impact on the cleaning efficiency since the number of deprotonated functional groups including carboxyl is a function of pH (Li and Elimelech, 2004). Most carboxylic groups can be deprotonated at pH 11. During the chemical cleaning with NaOCl, caustic conditions allow the organic matters to have negatively charged, which will improve the repulsion forces between molecules of

foulants and therefore encourage the enhancement of cleaning efficiency. In acid cleaning, pH value is usually kept around 2-3 to remove inorganic fouling (Judd, 2010, Itokawa et al., 2008).

Temperature also influences membrane cleaning. For instance, the permeability of the UF membrane was 15% higher as cleaning temperature is 50-60°C compared with 40-50°C in an MBR system used for wastewater treatment (Xing et al., 2003). Flux recovery rate increased when the temperature was increased from 30 to 50 °C because the kinetics of the chemical oxidation increases according to the increase in temperature (Bartlett et al., 1995). The stainless steel membrane and the ceramic membrane were used with on optimum NaOH concentration of 0.2 wt% and 0.4wt% as a chemical cleaning agent. These results show the increase of mass transfer and reaction rate with the increase in temperature.

2.2.4.3 Effect of organic loading rate (OLR) and food to microorganism (F/M) ratio

Organic loading rate (OLR) also plays a vital role in the treatment of wastewater by MBR. Increase in OLR effectively decreases filterability of the MBR (Trussell et al., 2006). Past study showed that steady-state membrane fouling rates increased food to microorganism (F/M) ratio and decreased COD removal efficiency from 90% to 74% when OLR was increased from 1 to 2.5 kg COD/m^{3}d (Khoshfetrat et al., 2011). The F/M ratio (**Equation 2.1**) is one of the critical design and operation parameters of activated sludge system to determine the suitable number of microorganisms, as well as to measure the amount of food (or biological oxygen demand (BOD)) present for the microorganisms in the MBR system.

$$\frac{F}{M} = \frac{BOD^5\left(\frac{g}{m^3}\right) \times Q\left(\frac{m^3}{d}: \text{Influence flow rate}\right)}{MLVSS\left(\frac{g}{m^3}\right) \times V(m^3: \text{Reactor volume})}$$ --Equation 2.1

F/M ratio can decide how much BOD per day is available for the microorganisms in the aeration tank. Furthermore, decomposition of organic matter and the type of activated sludge are highly dependent on the F/M ratio. In general, higher F/M ratios lead to formation of larger granules, while lower F/M ratios cause the slower formation of smaller granules (Li et al., 2011).

2.2.4.4 Effect of HRT and SRT

MBRs can be controlled easier as their HRT and SRT can be controlled easily and appropriately. Biokinetics depend on these two parameters, i.e. the speed at which microorganisms break the components in the MBR down. Longer SRTs are typically preferred for slow-growing microorganisms, and less amount of sludge is produced since complete retention of the solids occurs (Judd, 2008). Shorter SRTs are found to increase sludge production, thereby decreasing membrane permeability (Trussell et al., 2006).

2.2.4.5 Effect of MLSS

MLSS is defined as the concentration of suspended solids in an aeration basin during the activated sludge process of wastewater treatment. The MLSS is the index of the biomass production and calculated by **Equation 2.2**. It is usually measured in mg/L or g/L and is the measure of microorganisms and non-biodegradable suspended matter. One can confirm, through MLSS, if the active biomass available in the aeration tank is sufficient for the consumption of the microorganisms. MLSS concentration increases as SRT increases and oxygen transfer decreases exponentially with the increase in MLSS concentration (Germain et al., 2007). Biological treatment requires dissolved oxygen for the microorganisms to allow aerobic degradation of pollutants. Additional oxygen in the tank efficiently reduces fouling. Thus, a low oxygen transfer demands higher aeration rate and higher energy expenditure. Higher sludge concentrations lead to increased energy expenditure and risk in membrane fouling.

MLSS = (withdrawal of biomass + increment of biomass in the bioreactor) / (inflow of substrate into the bioreactor) --Equation 2.2

2.2.5 Organic micro-pollutants

The attention of environmental research has been consistently extended beyond traditional environmental organic micropollutants, and deals with pharmaceuticals and personal care products (PPCPs) which enter the environment mainly through domestic use (Ternes et al. 2004). Pharmaceuticals are mainly prescribed as drugs. Personal care products refer to products used for personal and cosmetic reasons (see the US EPA website).

The organic micropollutants are also known as trace organics because of their presence in the environment ranging from nanogram to microgram (ng - μg). The occurrence of such pollutants has the environmental possibility of risks in non-target species (Gunnarsson et al. 2008). The principal sources of such PPCPs are from the discharge of wastewater treatment plants (WWTP), hospital effluents, chemical manufacturing plants, livestock and agriculture, etc. (Pal et al. 2010). WWTPs are the primary source that continuously releases PPCPs into water bodies such as small streams. No monitoring actions/precautions for micro-pollutants are defined in most of the WWTPs (Bolong et al. 2009), and WWTPs are not specifically designed to remove PPCPs. These contaminants can escape from the treatment system and may end up in aquatic environments (Luo et al. 2014). Their peak concentrations can be more than 1 μg/L (Cleuvers, 2003). Concern for the need to remove such PPCPs has risen (Cleuvers, 2003; Kümmerer, 2009) and many studies have now been published on the topic (Pal et al. 2010; Cleuvers, 2003; Li, 2014). Published data on the occurrence of various pharmaceuticals in Australia is summarized below (adapted from Pal et al. 2010) (**Table 2.2**).

Table 2.2 Occurrence of pharmaceuticals in Australia (Pal et al. 2010)

Compounds	Effluent, WWTP (ng/L)	Freshwater, rivers, canals (ng/L)
Anti-biotics		
Trimethoprim	58-321	4-150
Ciprofloxacin	42-720	23-1300
Sulfamethoxazole	3.8-1400	1.7-2000
Analgesics inflammatory		
Naproxen	128-548	11-181
Ibuprofen	65-1758	28-360
Ketoprofen	-	<0.4 – 79.6
Diclofenac	8.8-127	1.1-6.8
Antiepileptic		
carbamazepine	152-226	25-34.7
Beta-blockers		
Propranolol	50	-
Atenolol	-	-
Blood lipid regulators		
Gemfibrozil	3.9-17	1.8-9.1

Conventional wastewater treatment plants are mainly designed to eliminate large suspended particles, pathogens and dissolved organics to some extent. However, the removal of pharmaceuticals by such treatment plants is not satisfactory (Heberer, 2002; Kimura et al. 2009). In primary treatment, these PPCPs are mainly removed by sorption onto sludge (Ternes et al. 2004), in which 28% removal of PPCPs and hormones was formed to be achieved when wastewater passes through a sedimentation tank (Behera et al. 2011). Insignificant removal of naproxen and sulfamethoxazole was observed in the primary stage (Carballa et al. 2004). The secondary treatment associated with biological treatment can remove PPCPs through biodegradation/biotransformation and sorption (Carballa et al. 2004). However,

in some circumstances, the effluent level of diclofenac, carbamazepine, erythromycin, and sulfamethoxazole can exceed their influent concentration. This happens due to the subsequent transformation of PPCPs back into parent compounds during biological treatment (Kasprzyk-Hordern et al. 2009).

Since the WWTPs are the main source that discharge PPCPS into the environment (da Silva et al. 2011), the application or incorporation of advanced wastewater treatment techniques becomes important to eliminate such compounds before their discharge. In line with producing high quality recycled water, membranes are increasingly being used (Snyder et al. 2007; Urtiaga et al. 2013), in which pressure-driven RO membranes are proving to be effective in rejecting PPCPs (Bellona and Drewes, 2007; Radjenovic et al. 2011). This is despite the fact some PPCPs compounds were detected at trace levels in RO permeates (Snyder et al. 2007).

2.3 The control strategies of fouling in MBR

The main obstacle of MBR system is membrane fouling. To reduce membrane fouling, three approaches may be applied: (i) physicochemical, (ii) hydrodynamic, and (iii) microbiological. For better efficiency of fouling control, a combination of any of these approaches may be performed.

2.3.1 Physicochemical fouling mitigation

Fouling which cannot be removed easily would require physical or chemical fouling mitigation process. Physicochemical approach to solving fouling problem includes process design, chemical additives, membrane surface modification, and implementation of hybrid systems. Membrane cleaning is required especially at higher flux operations to maintain membrane permeability.

2.3.1.1 Physical cleaning

Physical cleaning of the membranes is commonly categorized into in-situ and ex-situ, depending on the location of the membrane modules while cleaning takes place, i.e., whether inside or outside the bioreactor. In-situ methods include ultra-sonication, particle or suspended carrier scouring,

backwashing, and aeration. Ex-situ cleaning method just requires the removal of the membrane module from the bioreactor before cleaning.

In general, the physical cleaning process is widely used to eliminate reversible membrane fouling in MBR; however, it is less efficient to control irreversible fouling in MBR, when compared with chemical cleaning. The advantages of physical cleaning methods are (i) it does not produce by-products during cleaning, and (ii) does not change or alter chemical properties of the activated sludge. Physical cleaning methods used to mitigate membrane fouling are backwashing, aeration, and membrane relaxation.

Backwashing is mostly preferred as a method when the crucial parameters during MBR operation are flux, duration, temperature, and frequency (Hwang et al., 2009, Raffin et al., 2012). Backwashing of the membrane is done by reversing the flow of water or air through the membrane. At higher pressure, backwashing can remove the fouling layer from the membrane surface. It was also found that backwashing efficiency can be improved by controlling TMP. TMP profoundly influences the cleaning efficiency and system productivity of backwashing (Villarroel et al., 2013). Backwashing is usually performed when the filtration flux drops below a rate of specified flux or when the TMP reaches a maximum specified level. Commonly, the backwashing flux is almost 0.8 to 3.3 times higher than the working flux for hollow fiber membranes. Also, short duration of backwashing with higher flux and higher backwashing pressure is more efficient, compared to the longer duration of backwashing (Zsirai et al., 2012). Aside from just water, air can also be applied while backwashing (Bessiere et al., 2009, Remize et al., 2006). However, backwashing with air may cause partial drying of some membranes, which will then lead to fragility and lower membrane integrity.

Also, membrane fouling can also be mitigated by using aeration or air scouring. Air scouring can also be performed, wherein highly pressurized air easily dislodges the fouling layer. This method induces shear stress on the membrane surface to remove fouling layer (attached biomass or organic and inorganic substances) from the membrane surface and reduce membrane fouling. This physical cleaning method is a preferred membrane cleaning method since several studies have shown that this membrane cleaning method improved the sustainable membrane permeability (or the flux per unit TMP) of the

membrane (Le-Clech et al., 2003b, Liu et al., 2003). Furthermore, aeration was shown to have a positive effect on membrane filtration, and higher aeration rates led to more prolonged membrane operation (Johir et al., 2012c). Sustainable membrane permeability increases almost linearly with the increase of aeration rate for most membranes. Another study has noted that the improvement of aeration intensity can expedite natural cleaning, due to the positive effect of aeration on increased cross-flow velocity and induced shear stress (Wu et al., 2008). Furthermore, bubble size, shape, and geometry of diffuser can influence membrane cleaning efficiency and induce good shear stress on the membrane (Çulfaz et al., 2011). In their study, significant cap-shaped bubbles were found to be better in membrane cleaning, when compared with more significant bubble aeration in MBR. This can be explained by the hydrodynamic conditions affecting membrane cleaning, wherein not only size and shape affect membrane cleaning efficiency, but also, bubble flow velocity, channel gap, membrane module, sludge concentration, and reactor geometry influence (Nagaoka et al., 2006, Prieske et al., 2010, Yamanoi and Kageyama, 2010).

In-situ relaxation of membranes enables diffusive back transport of membrane fouling away from the membrane surface driven by a concentration gradient and is often related to air scouring to enhance the diffusion. Relaxation is often combined with backwashing to increase cleaning efficiency (Martinez-Sosa et al., 2011, Diez et al., 2012).

2.3.1.2 Chemical cleaning

If the fouling is irreversible or too substantial to be removed by physical means, then chemical cleaning is performed. Among the strategies used for fouling control, chemical cleaning is the most effective method for the permeability recovery of severely fouled membranes. This method utilizes aggressive chemicals, such as acids (e.g., citric or volatile fatty acids), bases (e.g., caustic soda), or oxidants (mostly hypochlorite) to dissolve most irreversible inorganic foulants, as well as SMPs and EPS. However, this method weakens the integrity of the membrane, such that excessive cleaning using chemicals makes the membrane more susceptible to deterioration (Le-Clech et al., 2005). The choice of suitable cleaning chemical is significant to clean the membrane efficiently, and at the same time,

maintain the integrity of the membrane. The typical membrane cleaning mechanisms of chemical reagents and their characteristics are presented in **Table 2.3** (Meng et al., 2017).

Table 2.3 Characteristics of chemical cleaning reagents

Type	Reagent	Mechanisms	Advantages	Disadvantages
Acid	HCl	Solubilization, neutralization Chelation	Effective, low cost	pH shock, membrane damage
	HNO_3			
	H_3PO_4		Maintain pH	Contribute to TP at the effluent
	Citric Oxalic		effective at removing metal cations compared with mineral acids	Higher cost compared with Oxalic mineral acid
Base	NaOH	Hydrolysis, solubilization and saponification	pH regulation	Extreme alkaline
Oxidant	NaOCl	Oxidation, disinfection	Effective	Membrane damage, produce toxic by-products
	H_2O_2		Do not produce toxic by-products	Membrane damage
Other chemicals	EDTA	Chelation/ligand exchange reaction	Effective	Non-biodegradable
	SDS	Hydrophilic/hydrophobic interactions		Foam formation
Emerging cleaning chemical	FNA	Solubilization and disinfection	More efficient than NaOH	Extreme low pH, contribute to NO 2-N in the effluent
	Rhamnolipid	Hydrophilic/hydrophobic interactions	Biodegradability, low toxicity and cost-effectiveness	

Acids aim to reduce inorganic fouling, which is typically caused by chemical precipitation of inorganic matter and biologically-induced mineralization between biopolymer and salts (Meng et al., 2009, Malaeb et al., 2013). The primary mechanisms by which acids remove the chemically- and biologically-induced precipitates on the membrane surface are neutralization and double-displacement. Among the most common acids used are hydrochloric acid (HCl), nitric acid (HNO_3), oxalic and citric acid, phosphoric acid (H_3PO_4), and sulfuric acids.

Alkaline cleaning reduces the organic fouling deposited on membrane surfaces, with the same mechanism as those of acids. Sodium hydroxide (NaOH) is the most commonly used primary cleaning agent and is more effective in removing protein-related fouling compared with carbohydrates (Kimura et al., 2013) because NaOH readily desorbs proteins. NaOH is also used to clean membranes treating protein-rich industrial wastewater. In highly alkaline environments, large organic particles, such as colloids and microbes, can be disintegrated into fine particles and soluble organic matter (Yu et al., 2013).

Oxidants are also used as membrane cleaning agents due to their ability to remove organic and biological fouling through oxidation and disinfection. The widely used oxidants are sodium hypochlorite (NaOCl) and hydrogen peroxide (H_2O_2). H_2O_2 does not produce toxic by-product compared with NaOCl. Ozone can be employed as well to clean submerged membranes. It is found that intermittent ozone backwashing method is highly efficient than the air for flux recovery (Kim et al., 2007).The primary mechanism of oxidants is to disinfect the membranes and to oxidize the functional groups of organic foulants to ketone, aldehyde, or acetyl groups. These functional groups have higher hydrophilicity. Thus adhesion of the foulants onto the membranes is reduced. Oxidants can also disintegrate the colloids and microbe flocs into fine particles and soluble organic matters, leading to further degradation. NaOCl is a highly-stable and active chemical, and is easy to use together with other chemicals. Although it is beneficial in the removal of foulants, NaOCl also affects the membrane integrity negatively, as it can induce chain scission of polyethersulfone polymer, leading to the formation of phenyl sulfonate, thus disintegrating the membrane (Arkhangelsky et al., 2007). Aside from the detrimental effects of oxidants on membrane integrity, the use of oxidants in membrane

cleaning may lead to the formation of organic halogens and trihalomethanes, which are non-environmentally-friendly substances (Han et al., 2010, Krause et al., 2010, Grélot et al., 2008).

2.3.1.3   Use of additives

Another popular physicochemical fouling mitigation schemes are the use of additives in the feed. Suitable additives can control the presence and growth of foulants. Some examples include activated carbon, zeolite, diatomite, bentonite, vermiculite, aluminium sulphate, polyacrylamide, poly aluminium chloride, poly ferric sulphate, and chitosan.

2.3.2   Hydrodynamic fouling mitigation

One of the hydrodynamic approaches to mitigate biofouling is to operate below critical flux. Aeration is also a hydrodynamic approach that can be implemented. In a submerged MBR, aeration creates shear stress. Aside from supplying dissolved oxygen for microbes, aeration provides the sludge flocs with a suspended state which then alleviates membrane fouling (Braak et al., 2011). A high aeration rate can reduce sludge attachment to the membranes, but it also has a significant effect on the biomass characteristics. Too strong aeration will cause breakage of sludge flocs and the production of SMP will increase, which would become the significant membrane foulant (Fan and Zhou, 2007). Regular aeration is an efficient method to control fouling on the membrane surface, which reduces high energy expenditure (Braak et al., 2011). Thus, aeration must be optimized to decrease energy usage and cost. A study has shown that intermittent aeration can potentially improve removal of nutrient in MBR (Ćurko et al., 2010) as the microorganisms which are responsible for N and P removal can be enriched as a result of the switch of high and low dissolved oxygen (DO) concentrations (Chang et al., 2011). However, intermittent aeration can induce sludge de-flocculation (Monsalvo et al., 2015). The dynamics between de-flocculation and re-flocculation by the cyclic high and low aeration rates can cause reduction in SMP and rise in EPS, eventually contributing to changes in the fouling mechanisms of mixed liquor. The relationship between intermittent and continuous aeration has yet to be fully explored.

2.3.3   Microbiological fouling mitigation

Biological cleaning is widely used for cleaning MBR systems. The bioactive agents includes enzymes or signal molecules to improve the removal of membrane fouling. Various biological cleaning

methods have been reported the enzymatic cleaning, energy uncoupling, quorum quenching, nitric oxide-induced biofilm detachment, cell wall hydrolases addition, and bacteriophage addition (Xiong and Liu, 2010). Among the ways to mitigate biofouling by microbiological means is a determination of the following: cell physiology, microorganism population dynamic, quorum sensing mechanism, and biofouling mechanism. Various biological strategies have been considered as promising methods to control fouling in general and biofouling in particular. Biological strategies showed higher efficiency, lower toxicity, more sustainability, and less bacterial resistance, compared to other mitigation methods (Xiong and Liu, 2010, Yeon et al., 2009).

The use of an enzymatic agents is one of the most prevalent biological cleaning methods; however, enzymatic agents are mainly specific for the biopolymers. The interaction between the enzyme and the biopolymer induces rupturing the fouling layer on the membrane surfaces, thereby inhibiting the damages by the physical and chemical destruction of the membrane materials. Enzymes have a particular spectrum of activity for fouling degradation according to the natural biochemical structures, selection of suitable cleaning agents. Recent research reveals that enzymatic cleaning method might be a tempting alternative to remove the irreversible fouling during ultrafiltration of wastewater treatment plant effluent (Grélot et al., 2008). Also, enzymes may not induce membrane ageing or deterioration and do not result in the formation of by-products. However, at present, the enzymatic agents are costlier than NaOCl. Thus, optimization of operating conditions is essential for enzymatic cleaning.

Energy uncoupling uses predatory microorganisms. Uncoupling proteins can be capable of dissipating the proton gradient thus hinder adenosine triphosphate (ATP) synthesis. Studies reported that uncoupling of energy metabolism affected the stability of biofilm and subsequently resulted in the dispersed growth of microorganisms (Xu and Liu, 2011).

Quorum quenching method which mainly focused on the inhibition of bacterial biofilm development (Lade et al., 2014) is also another biological strategy for fouling in membranes. Bacteria used in quorum sensing produce and secrete specific signalling molecules which might determine the behaviour of biofilm communication. Quorum quenching method can be accomplished by three ways

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(Grandclément et al., 2016): (i) inhibition of N-acyl homoserine lactones synthesis, which commonly exists in MBR, (ii) enzymatic degradation of N-acyl homoserine lactones signal molecules and (iii) blocking of transport or acceptance of N-acyl homoserine lactones signals. Quorum quenching strategy is efficient to remove the biofilm fouling comprised of living microorganisms, on the other hand, less efficient to clogging by inorganic compound, dead cells and organic-inorganic complexes.

2.4   Biofilter

Apart from MBR, biofiltration is another most promising development in biological processes for the treatment of municipal and industrial wastewater. Biofilters are the filters in which microorganisms are attached to a porous medium. Biofilters are mostly used to break down pollutants and undesired substances present in wastewater. The microorganisms are either cultivated into a biofilm on the medium surface or suspended in the water wherein it is surrounded by the medium particles (Srivastava and Majumder, 2008). The filter bed medium is made up of relatively inert substances, which have high surface areas to ensure high adsorption capacity of the unwanted substances. The high surface area of the medium is essential to make sure complete surface attachment occurs. This also allows nutrients to be supplied for the microorganisms. Essential characteristics of the support medium include porosity, the degree of compaction, water retention ability, and suitability to host populations of microorganisms. Efficiency in the operation of biofiltration is highly reliant on the following operational parameters: medium pH, temperature, medium moisture, microbial inoculation, nutrient content, oxygen content, and wastewater toxicity (Srivastava and Majumder, 2008). Should biofiltration performance be insufficient, chemical modification of the filter media or genetic modification of the microorganisms may be performed to improve biofiltration efficiency.

2.4.1   Basic principle

The biodegradable pollutants are removed using the biofilter through a biological degradation mechanism, and not physically, like most filtration systems (Chaudhary et al., 2003). The micro organics that used in biofoulant are aerobic bacteria, anaerobic bacteria, facultative bacteria, fungi, algae, and protozoa. The desired microorganism strains are grown on the surface of the filter media to

form a film-like layer, known as a biofilm. It is highly essential that as biofiltration process is implemented, the biofilm layer remains intact and the microorganisms are healthily attached to the filter medium surface. Therefore, a constant supply of nutrients, which include organic and inorganic substances, is necessary for consistent and efficient operation; otherwise, starvation of microorganisms results to impediment in metabolism or even death, disrupting microbial activities, thereby disrupting the biofiltration process.

Three biological processes that take place in a biofiltration system are: (1) attachment of microorganisms onto the medium surface, (2) growth of microorganism, and (3) death, decay, and detachment of microorganisms. While the microorganisms grow on the medium surface, it can carry out biodegradation of the contaminants, wherein biotransformation occurs. Through microbial activity, the contaminants are transformed into biomass, metabolic by-products, carbon dioxide, and water. The way microorganisms attach on the medium surface is highly dependent on: diffusion, convection, sedimentation due to gravity, the active mobility of the microorganism, initial adhesion, firm attachment, and colonization (van Loosdrecht et al., 1990).

2.4.2 Biofilter media

The biofilter contains a porous medium whose surface is directly exposed to water and microorganisms. Most biofilter media are adsorbent in nature, such that the contaminants may form complexes with other substances in the water which will then be absorbed by the medium. Thus, the choice of the suitable medium is highly crucial in biofiltration performances. The following substances are commonly used as media for biofilters (Chaudhary et al., 2003): anthracite, sand, granite, blast-furnace slag, glass beads, plastic, zeolite, and activated carbon.

The excellent adsorption capacity of activated carbon makes it an excellent choice for a medium for biofiltration (Hwang et al., 1994). Activated carbon is an amorphous solid widely used as an adsorbent in full-scale applications due to its large surface area and porosity, as well as low cost (Gonzales et al., 2016). Biological systems which utilize activated carbon can efficiently treat organic and inorganic pollutants in water and wastewater (Duan et al., 2006). In biofiltration, activated carbon not only supports the microorganisms, but also acts as a buffer for fluctuation. Activated carbon

biofilters show enhanced performances in contaminant removal and shorter acclimation periods of the microorganisms in the system, compared to other conventional biological systems.

2.4.3   Empty Bed Contact Time (EBCT)

The contact time of the water in the achieved carbon bed is termed, as empty bed contact time (EBCT). This is a crucial design parameter of a biofilter. The dimensionless contact time (EBCT) together with the specific surface area of the medium, substrate diffusivity and the rate of biodegradation decides in explaining the removal efficiency of biofilter (Zhang and Huck, 1996). Usually, the removal of an organic substance increases with an increase of contact time up to an optimum value. Both the filter depth and hydraulic loading rate can be changed to vary the EBCT. For a given EBCT, organic removal is independent of hydraulic loading. (Servais et al., 1994).

2.5   Post-treatment to MBR effluent

MBR cannot remove all the pollutants especially the inorganic ions, trace organics and persistent organic pollutant. Thus, in this study, membrane distillation (MD) was used as post-treatment.

2.5.1   Membrane distillation (MD) principle

Membrane distillation (MD) is a promising thermal separation technology, and it is used in a number of applications including wastewater reuse, treatment of mine water, radioactive waste, brackish water, seawater and reverse osmosis (RO) brine treatment (Tijing et al., 2015). MD systematically reduces brine volume, potentially achieving near zero liquid discharge (Gryta, 2016). Among the different membrane techniques such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, etc., membrane distillation (MD) is considered as one of the promising techniques in seawater or brackish water desalination applications. The advantages of MD include high rejection of non-volatile components, lower operating pressure than reverse osmosis (RO), lower operating temperature and smaller foot-print than conventional distillation processes (Lawson and Lloyd, 1997). In MD process, the membrane, which is hydrophobic, is placed in between a hot feed water and a cold permeate, only allowing vapour molecules to pass through the membrane and condenses at the permeate

side (Gryta, 2002). The primary driving force for such separation is the vapour pressure gradient resulting from a temperature difference between hot feed water (heated MBR effluent in our case) and cold permeate (pure water) separated by a porous and hydrophobic membrane barrier. The hydraulic pressure in MD is much lower compared to the pressure-driven separation processes such as RO. The benefit is that there is no hydraulic pressure restriction and the possibility of obtaining high solute rejection. Thus, it can lead to many applications such as treating highly saline feed solutions (Ji et al., 2010, Gryta, 2002, Chen et al., 2014, Edwie and Chung, 2013, Jiang et al., 2016, Julian et al., 2016, Meng et al., 2015, Creusen et al., 2013). Further, the MD process is able to concentrate feed water to a supersaturated state, forming salt crystals (Naidu et al., 2014). As such, besides producing fresh water, the recovery of salts can also be achieved using MD coupled with crystallization process. Although heat loss in a conventional cross flow MD set-up is inevitable, high thermal consumption can be addressed using alternative energy sources such as solar energy, waste heat etc. (Shim et al., 2015, Duong et al., 2016). The bulk feed solution temperature tends be reduce as the feed solution is channelled out to the membrane module.

2.5.2 Membrane distillation configuration

There are four basic MD configurations depending on the way the permeate side is processed (**Figure 2.3**): (1) direct contact membrane distillation (DCMD); (2) vacuum membrane distillation (VMD); (3) air gap membrane distillation (AGMD); and (4) sweep gas membrane distillation (SGMD). Each configuration has its own merits and demerits, however, among the four types; DCMD is the most studied MD configuration, which attracts more than half of all studies on MD due to its simplicity in design and operation. However, DCMD presents the lowest energy efficiency among all configurations. AGMD is considered to have the highest energy efficiency and is more poplular in commercial applications. The air gap width is usually in the range of $1 \sim 10$ mm, which is higher than the membrane thickness which is usually less than 300 µm. In VMD process, the downstream side of the membrane is operated under vacuum conditions or low pressure (Chiam and Sarbatly, 2013). The applications of VMD have been further explanded into three primary processes: the single component transport process, the binary component transport process and the multicomponent transport process (Dong et al., 2014).

SGMD is similar to AGMD, but, the gas is sweeping, and the vapour is condensed in an external condenser in SGMD. It has lower conduction heat loss than DCMD.

(a) DCMD

(b) VMD

(c) AGMD

(d) SGMD
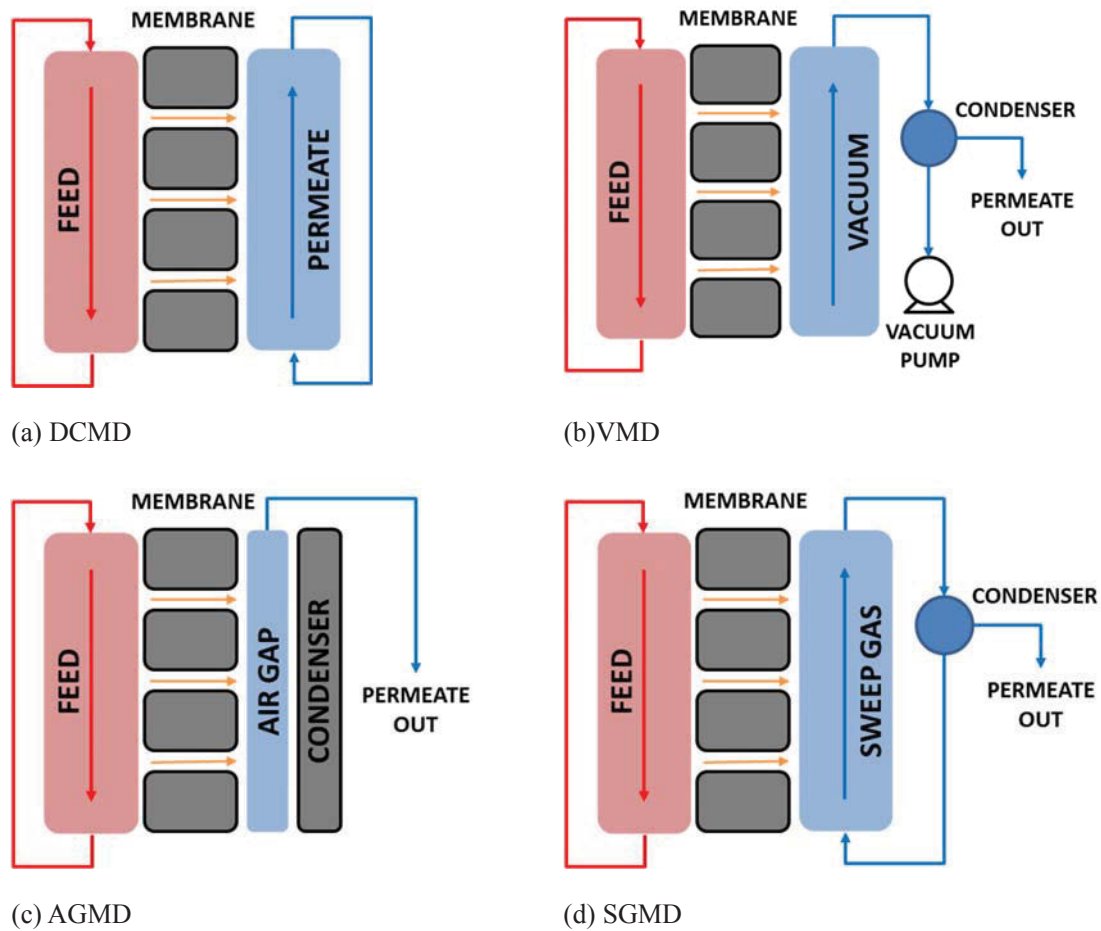
Figure 2.3 Different configuration of membrane distillation process.

Nowadays, combined MD processes are investigated such as vacuum DCMD. It uses vacuum pressure of VMD configuration as well as the advantage of DCMD configuration. It leads to superior performance than sole DCMD and sole VMD configurations because of the two drive forces achieved in DCMD and VMD processes. Besides, hybrid systems with MD process have been investigated such as membrane distillation-crystallisation (MDC), membrane distillation -Forward osmosis (MD-FO) etc. MD process can remedy shortcoming of other membrane processes.

Chapter 3

University of Technology Sydney

3   Experimental materials and methods

3.1 Background

The first set of experiment was conducted with synthetic reverse osmosis concentration (ROC) water to study the performance of MBR in treating ROC. The second set of experiment was conducted with the real ROC collected from a wastewater reclamation plant, Sydney, Australia. Another set of experiment was also conducted with MBR effluent collected from decentralized plant located in Sydney, Australia.

The water characteristics, experimental and analytical procedures are described in this chapter.

3.2 Experimental Materials

3.2.1 Activated sludge

At the beginning, the MBR was initially seeded with 5 L of mixed liquor obtained from activated sludge plant of a domestic sewage treatment plant in Sydney, Australia. After initial seeding, the MBR was continuously fed with a synthetic ROC, ROC, and MBR effluent. The sludge was acclimatized for 4-50 days to achieve stable removal of organic carbon. The diffused aeration system was used for mixing the sludge and supplying the air for biofouling oxidation.

3.2.2 Wastewaters

The wastewaters used in this study are as follows

i) Synthetic ROC representing high strength wastewater for detailed MBR study

ii) Real ROC collected from a water reclamation plant in Sydney

iii) MBR effluent from a decentralized sewage treatment plant (representing low strength wastewater)

The detailed characteristics of wastewaters used in this study are as follows:

3.2.2.1 Reverse osmosis concentrates (ROCs)

Synthetic ROC: The reactor was continuously fed with synthetic ROC. The characteristics of synthetic ROC as follows:

Table 3.1 Characteristics of synthetic ROC.

Parameters	Unit	Value
$CaCl_2 2H_2O$	mg/L	292
NaCl	mg/L	750
KCl	mg/L	90
KNO_3	mg/L	35
NaF	mg/L	7
$MgSO_4 3H_2O$	mg/L	450
KH_2PO_4	mg/L	15
$NaHCO_3$	mg/L	70~80
Glucose	mg/L	200
Yeast	mg/L	300
DOC	ppb-c	49590

Real ROC: The ROC was obtained from a full-scale MF/RO water reclamation plant located in Sydney, Australia. The plant treats wastewater, which is a combination of stormwater and biologically treated sewage effluent. This plant produces around 300 kL ROC per day (Chapman, 2006). The characteristic of real ROC is given in **Table 3.2**.

The treatment process in reclamation plant are as follows: sequencing bioreactor (SBR) as secondary biological treatment : continuous micro-filtration to remove particles larger than 0.2 microns including water parasites, viruses and bacteria and reverse osmosis (RO) process as final clarification process. The plant produces up to 7.5 million litres of water per day and 300KL of ROC.

The chemical properties of ROC reflect the RO feed water source. The quality of ROC can be different from municipal concentrates based on location. For example, contaminated groundwater treatment have a higher concentration of calcium, silica and sulphate as well as metals (Subramani et al., 2012). The salt content such as chloride and sulphate and silica concentration of ROC coming from wastewater treatment plants are lower than those of groundwater treatment plants (Lee et al., 2009).

Total organic carbon (TOC) of ROC from wastewater treatment plants is high and needed to be removed before discharging. The water quality of the ROC used in this study is summarized in **Table 3.2**. The DOC composition of the ROC was characterized by using liquid chromatography-organic carbon detection (LC-OCD). It revealed that DOC is composed of biopolymers, humic substances, building blocks and low molecule weight (LMW) neutrals (**Table 3.3**).

Table 3.2 Characteristics of real ROC

Characteristics		Value
Conductivity (μS/cm)		2350
pH		7.5
DOC (mg/L)		32-35
TDS (mg/L)		2250
Anions (mg/L)	Fluoride	3.0-4.0
	Chloride	400-650
	Nitrite	1.3-1.5
	Bromide	1.0-1.5
	Nitrate	23-26
	Phosphate	8-9
	Sulphate	220-250
Cations (mg/L)	Na	330-360
	K	55-63
	Ca	80-93
	Mg	65-72

Different organic fraction present in the synthetic ROC and real ROC is given in **Table 3.3**.

Table 3.3 Detailed organic fraction of synthetic ROC and real ROC used in this study

	DOC	Hydrophobic. (ppb-c)	Hydrophilic. (ppb-c)	BIO-polymers	Humics Substances.	Building Blocks	LMW Neutrals
ROC	49590	-	49590	11380 (22.9%)	19963 (40.3%)	6715 (13.5%)	11533 (23.3%)
Real ROC	29277 (100%)	1960 (6.7%)	27317 (93.3%)	1041 (3.6%)	14641 (50.0%)	4901 (16.7%)	6734 (23.0%)

3.2.2.2 MBR effluent collected from decentralized treatment plant in Sydney

The characteristics of MBR effluent collected from decentralized plant is presented in **Table 3.4**. The detailed schematic diagram of the decentralized treatment plant system is given in **Figure 3.1.** The organic fractionations of MBR effluent given in **Table 3.4.** The fractionation of organic matters show that the majority of organics present in the MBR effluent are hydrophilic (90.1 %) in nature. Also, in the fraction of hydrophilic organic, humic substances was higher in concentration (almost 66.5%) than other hydrophilic organics such as biopolymers, building blocks and low molecular weight acid and neutrals. Hydrophilic organics contains biopolymers (0.7%), humics (66.5%), building blocks (6.2%) and LMW neutrals (16.7%) comprised. LMW acids were non-detectable.

Further, the concentration of micro-pollutant present in the MBR effluent is presented in **Table 3.5**. The compound with the highest value was sulfamethoxazole. The other selected micro-pollutants measured were less than 300 ng/L.
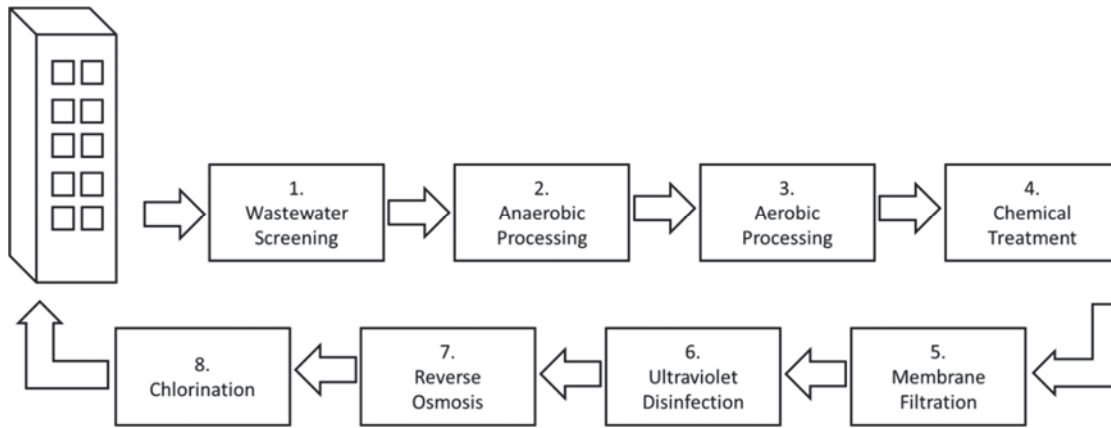
Figure 3.1 Flow diagram of decentralized plant located in Sydney, Australia

Table 3.4 Detail organic fraction of MBR effluent collected from decentralized plant

	DOC (ppb-c)	Hydrophobic.	Hydrophilic.	BIO-polymers	Humics Substances.	Building Blocks	LMW Neutrals
MBR Effluent	8393 (100%)	831 (9.9%)	7563 (90.1%)	60 (0.7%)	5580 (66.5%)	523 (6.2%)	1399 (16.7%)

Table 3.5 The concentration of selected micro pollutant in MBR effluent collected from decentralized plant

Representative compounds	Value (ng/L)
Salicyclic acid	42
Naproxen	81
Diclofenac	220
Ibuprofen	11
Triclocarban	25
PFOA	35
Sulfamethoxazole	270
Trimethoprim	9
Benzotriazole	183
TCEP	51
Carbamazepine	35

3.2.3 Activated carbon

Two different activated carbon adsorbents are used in this study, namely, granular activated carbon and powdered activated carbon.

3.2.3.1 Granular Activated Carbon (GAC)

The activated carbon was used to pack the filter column during biofilter experiments and as suspended media in submerged membrane adsorption hybrid system. The GAC used in this study was coal-based and was purchased from James Cumming and Sons Pty. Ltd, Australia. The physical characteristics of GAC are presented in **Table 3.6**.

Table 3.6 Physical characteristics of GAC used in this study

GAC	
Specification	**Value**
Type/ Structure	Coal-based premium grade
Particle size	0.60 – 2.36 mm
Surface area	1000 ± 50 m^2/g
Bulk density (kg/m³)	$250 - 300$ kg/m^3
Iodine number (mg/(g.min))	1000 mg/g min
Maximum moisture content (%)	2%
Water soluble (maximum)	0.5%
Hardness	80-85

3.2.3.2 Powdered activated carbon (PAC)

Powered activated carbon was also used as an adsorbent in the submerged membrane adsorption hybrid system (MAHS) to compare its performance with that of GAC. The PAC used in this study was also purchased from purchased from James Cumming and Sons Pty. Ltd, Australia. The characteristics are presented in **Table 3.7**.

Table 3.7 Characteristics of PAC

PAC	
Specification	**Value**
Type	Coal based
Mean diameter	19.7 μm
Nominal size	75.0 μm

3.2.4 Membrane material and characteristics

a. Microfiltration (MF) membrane

The hollow fiber membrane used in this study was made of HF Polyvinylidene fluoride (PVDF). It comprised of three different materials, which were Polysulfone, Polyethersulfone and Polyvinylidene Fluoride (PVDF) as a coating layer. The braid-reinforced hollow fiber MF was obtained from Cleanil-S, Kolon, South Korea. The detailed characteristics of the hollow fiber membrane are given in **Table 3.8**. PVDF membrane was selected for its higher water permeation rates, its resistance to high and low pH. It can also tolerate strong oxidizing agents such as sodium hypochlorite during membrane cleaning.

Table 3.8 Hollow membrane characteristics

Characteristics	
Nominal pore size	0.1 μm
Length	17.5 cm
Outer diameter	2.0 mm
Inner diameter	0.8 mm
Number of Fiber	9
Material	Polysulfone, Polyethersulfone, Polyvinylidene Fluoride
Effective surface membrane area	0.01m²

3.2.5 Chemical cleaning agent of membranes

3.2.5.1 Nitric oxide (NO)

Nitric oxide (NO) has been regarded as an essential messenger molecule that may control biofilm dispersal on the membrane surface. Many NO donors such as the enzymatic and non-enzymatic NO have been identified to be efficient in the dispersal of biofilm. For instance, adding NO at a low level of non-toxic concentrations leads the dispersal of a biofilm of Pseudomonas aeruginosa. The addition of NO increased the removal efficiency of biofilm on RO membranes, and various NO donors induced the dispersal of multi-species biofilm at picomolar or nanomolar levels (Barraud et al., 2009). Furthermore, NO was discovered as the universal effect on dispersal of sessile bacteria of Gram-positive and Gram-negative bacteria (Charville et al., 2008). NO can have a high possibility of regulating microbial attachment on the membrane surface even though NO has low solubility in water and is easy to oxidize. Therefore, the addition of NO to aqueous solution directly may make it less efficient in biofouling control (Wang et al., 2005).

NO donor was used in this study to backwash the membrane. The detailed characteristics of NO donor provided by Sigma-Aldrich are given in **Table 3.9**. The empirical formula and molecular weight of NO donor are $C_4H_{13}N_5O_2$ and 163.18, respectively. Experiment was conducted in which donor was immediately diluted.

Table 3.9 The detailed characteristics of NO donor

Assay	≥97%(NMR)
Form	Solid
Storage condition	Desiccated under inert gas
Empirical formula	$C_4H_{13}N_5O_2$
Molecular weight	163.18
solubility	$H_2O : >20mg/mL$
Shipped in	Dry ice
Storage temp	-20°C

3.2.5.2 Sodium hypochlorite (NaOCl)

Sodium hypochlorite can remove filamentous fungi in the conventional activated sludge process (Smith and Purdy, 1936). Sodium hypochlorite prevents the growth of the microorganism and oxidize organic substances. On the other hand, employing high concentrations of sodium hypochlorite can cause a negative influence on activated sludge and effluent. It also removes biofouling on membranes in MBR system.

In this study, sodium hypochlorite solution produced from Chem-supply Pty Ltd was used to backwash the membrane. Its molecular weight is 74.44. Sodium hypochlorite is the most commonly used as a disinfectant. Although other chemicals are also utilized to reduce membrane fouling and microbial populations, sodium hypochlorite still has superior cleaning performance in comparison with other chemicals. Some advantages and disadvantages of sodium hypochlorite are summarized in **Table 3.10** (Fukuzaki, 2006). Also, it is easy to be combined with other cleaning chemicals. Nonetheless, it can also be dangerous or kill the useful microbes recovery for biodegradation.

Table 3.10 Characteristics of sodium hypochlorite as disinfectant

Advantages	Disadvantages
• Broad antimicrobial action • Fast bactericidal action • Reasonable persistence in water • High solubility in water • Low cost	• Damage the membrane and activated sludge • Evolution of toxic chlorine gas when mixed with acid

3.3 Experimental Methods

3.3.1 Submerged MBR system with and without addition of suspended media

The schematic diagram of the MBR used in this study is presented in **Figure 3.2.** It consists of an aerobic tank with a working volume of 10 L. A hollow fiber membrane module was immersed inside the reactor. The effluent was withdrawn by using a peristaltic pump at constant flux. The data on trans-membrane pressure (TMP) development was recorded automatically in the computer using a data logger

every 5-10 min. The schematic diagram of the submerged membrane adsorption hybrid system (MAHS) is given in **Figure 3.3.** Membrane adsorption hybrid system used in this study is membrane bioreactors with the addition of GAC or PAC. The GAC was added only once at the beginning of the experiment and it also adsorb, the dissolved organic. A long-term experiment was conducted with ROC with initial GAC dose of 2g/L of the volume of the reactor (i.e a total of 20 g in 10 L reactor). In the hybrid reactor, adsorption and membrane separation occurred in a single reactor. The GAC in the suspension reduces the membrane fouling by adsorbing potential organic foulants. It was found that the addition of GAC helped to reduce fouling by 50% due to the GAC particles by also providing a scouring effect to the membrane surface (Johir et al., 2011b). The details of membrane characteristics and operation parameters are presented in **Table 3.8** and **Table 3.11.**
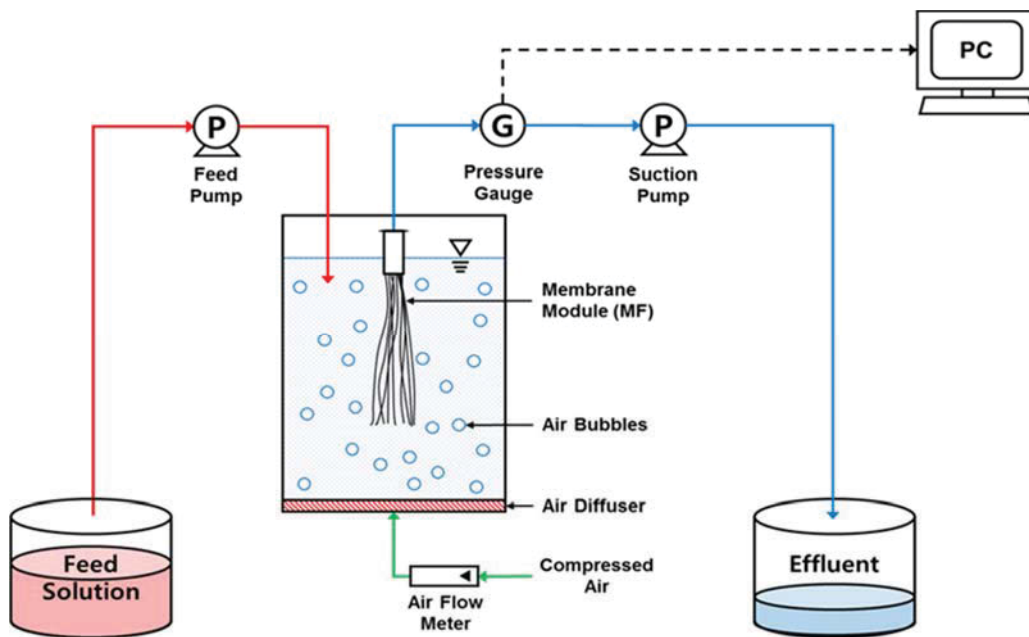
Figure 3.2 Schematic diagram of membrane bioreactor (MBR)
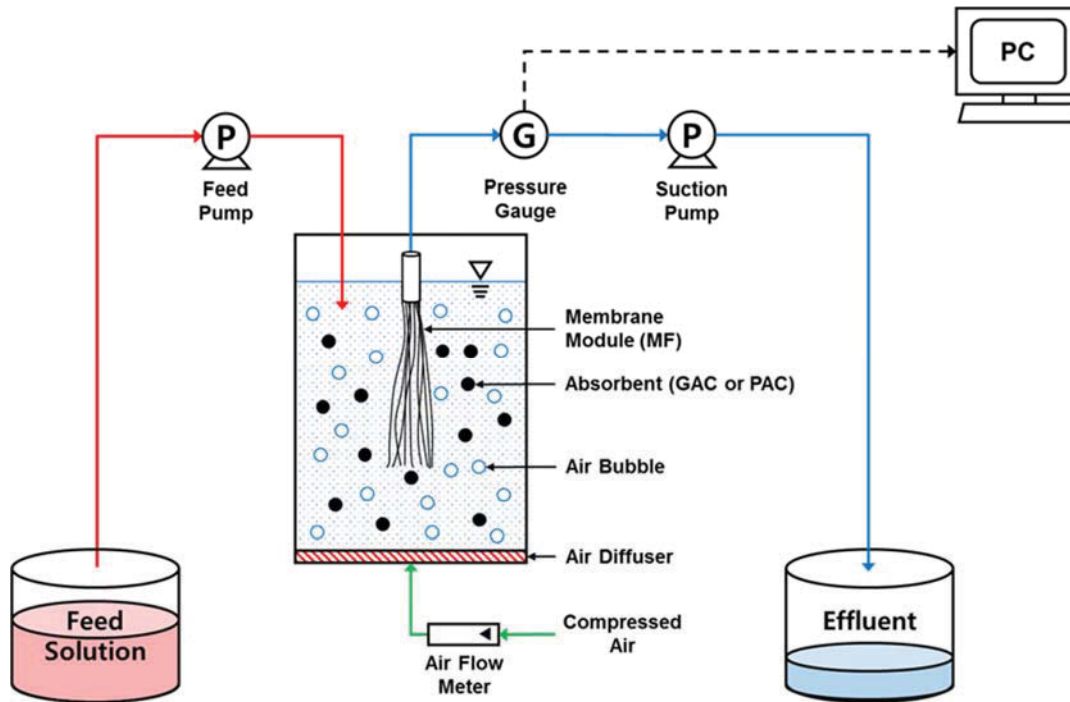
Figure 3.3 MBR with the addition of GAC/PAC

Table 3.11 Operating Conditions of Laboratory Scale SMBR with and without GAC and PAC in suspension

Parameters	Unit	Values
Volume of reactor	L	10
Flux	L/m^2.h	15, 20
HRT	h	1.04
SRT	Days	No discharge of sludge
pH	-	6.5-7.5
MLSS	g/L	5.0-6.0
MLVSS	g/L	4.5-5
Temperature	°C	23±1
GAC dose	g/L (of the volume of reactor)	2

3.3.2 Up-flow adsorption column experiments

Apart from membrane hybrid system, comparative experiments with column adsorption were carried out. The up-flow adsorption column used is shown in **Figure 3.4.** The transparent acrylic column has a diameter of 2 cm with sampling ports along the length and at the top of the column. The flow of feed water was kept constant, and up-flow filtration mode was used. Two different filtration velocities of 1.79 m/h and 3.58 m/h were used. Experiments were operated at a relatively low filtration velocity to obtain stable bacterial growth and activity. The media was packed in the column up to a depth of 10 cm and 40 cm to study the effect of bed height on the removal of organic matter. The GAC medium height was measured. Before packing the GAC, it was washed with deionized water and dried in an oven. Then this GAC was packed with the predetermined amount (or height of GAC). Glass beads were then placed on top of GAC to prevent GAC from floating and going out of with the effluent. Feed water was pumped from feed tank to the bottom of the column and then passed upwards through the bed. The experiments were run continuously for 3 to 8 weeks. Effluent samples were collected at the top sampling port of the column for water quality analysis.

The operational conditions are listed below.

I. Bed height of GAC column: 10 and 40 cm
II. Filtration velocities: 1.79 and 3.58 m/h
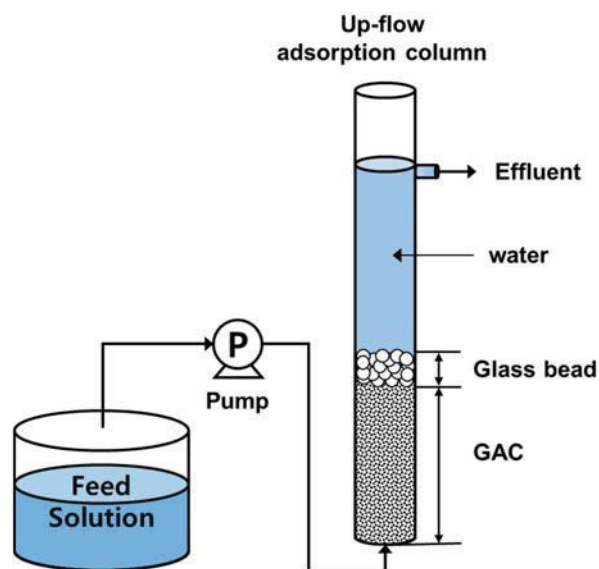
Figure 3.4 Schematic diagram of up-flow adsorption column with GAC

3.3.2.1   Batch adsorption studies of GAC

A batch equilibrium adsorption experiment was performed to decide the ideal dose of GAC to treat the feed. Different doses of GAC were placed in contact with 200 mL of MBR effluent in different beakers and mixed continuously using a shaker (Ratel Platform Mixer) at 120 rpm for 48 h at room temperature 23±1°C. After 48 hours of mixing, samples were filtered through a 0.45 μm filter for TOC analysis.

3.3.3   Direct contact membrane distillation (DCMD) experiment

A post treatment of direct contact membrane distillation (DCMD) was used. A bench-scale DCMD system was used in this study as presented in **Figure 3.5.** The feed and distillate tanks were placed on electronic mass balances to monitor the permeate production and feed reduction with time. The membrane cell used was made of acrylic. The dimension of the membrane cell was 0.2 cm x 5.0 cm x 8.0 cm (depth, width and length). A hydrophobic polytetrafluoroethylene (PTFE) flat sheet membrane with an effective membrane area of 40 cm² was used in this study. The support layer of the membrane is made of polypropylene. The porosity, average pore size and thickness of the membrane were 70-80 %, 0.2 μm in this study (Naidu et al., 2015). The feed solution was maintained at the set temperature of 60 °C in a sealed feed tank. Permeate solution was regulated at a temperature of 20 °C

using a cooling unit. The temperatures were measured at the inlet and outlet of the membrane module using temperature sensors. The hydraulic pressures on the feed inlet and permeate side outlet were measured using pressure gauges. The feed and permeate solutions (2 L each) were channelled into the membrane cell at a feed and permeate flow velocity of 0.06 m/s in a counter-current mode with a gear pump.
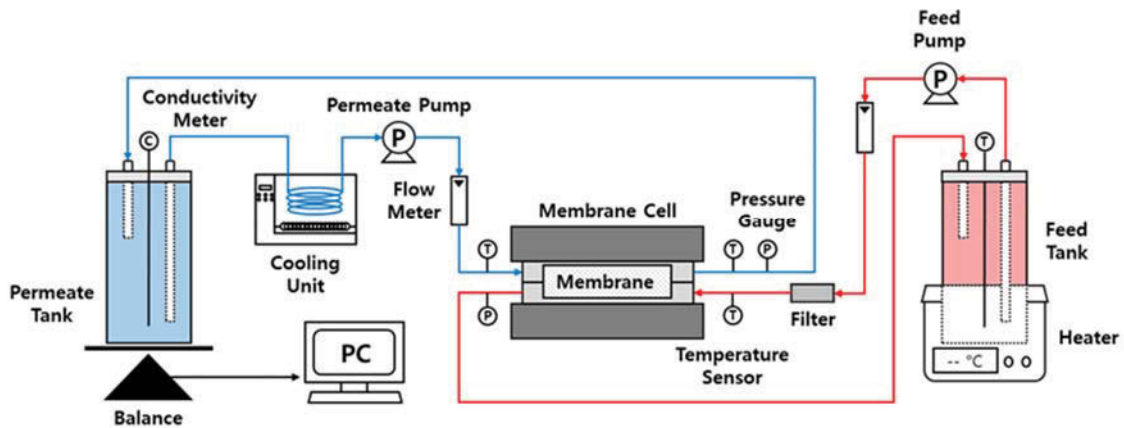
Figure 3.5 Schematic diagram of DCMD

3.3.4 Backwashing of MBR

Backwashing is one of the standard operation strategies in hollow fiber filtration systems to mitigate fouling. Lee at al. (2012b) suggested that the chemical backwashing was efficient in controlling fouling and the activity of the microorganisms. Sodium hypochlorite solution has been commonly used as chemical cleaning agent. It commonly used to as a biocide in industrial applications to control bacteria formation in the water system. Sodium hypochlorite can control filamentous fungi growth in the conventional activated sludge process, and it is also used to remove membrane foulants in MBR system. Thus, sodium hypochlorite can inhibit the growth of microorganisms and oxidize organic matters.

Nevertheless, frequent chemical or mechanical backwashing has adverse affect the membrane with time, porosity change and damage the membrane. Moreover, hollow fiber membrane backwashing is a highly complex process and is related to many variables such as the characteristics of the membrane

(length, pore diameter and material) and operation modes (backwashing duration, flow rate and cleaning agents).

In this study, a fouled membrane was also backwashed by using 0.1 M NOate for 1 hr to reduce and remove biofouling.

3.4 Experimental Analysis

3.4.1 Mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS)

Mixed liquor (content in the membrane reactor) was filtered by using glass fiber filter (pore size of 1.2μm). The filter paper was then dried at 100 °C for 3 h in an oven. It was then put in a desiccator for 24 h before measuring the suspended solids (i.e MLSS). After the measurement of MLSS, the filter paper was put in the furnace oven at 550 °C for 30 min. After that, the filter paper was placed in the desiccator for 24 h and the solid remaining was measured. The amount of The MLSS and MLVSS were measured once a week.

3.4.2 Measurement of DOC

All samples were filtered before DOC measurement using a 28 mm syringe filter with pore size of 1.2 μm to remove suspended particles. DOC was measured by multi N/C 3100 TOC analyser which is a compact and efficient device for determining the total carbon content or the nitrogen content of aqueous samples (Analytik Jena). The principle of operation is shown **Figure 3.6**. The radiation detectors incorporated in the non-dispersive infrared (NDIR) adsorption detector are selective for CO_2. Measurement ranges are dynamically changed according to the CO_2 level in the test gas. The organic fraction was measured using liquid chromatography-organic carbon detection (LC-OCD).

Control and display · Data Printout · Data Export/import · Sample

NDIR detector → NO Detectors (optional) → Flow meter → PC

Syringe pump

Water traps

NO, CO_2, H_2O, O_2

O_2

Halogen trap

Phosphoric Acid pump

TIC condenser

Dryer

Combustion furnace

Condensate pump

Disposal Waste
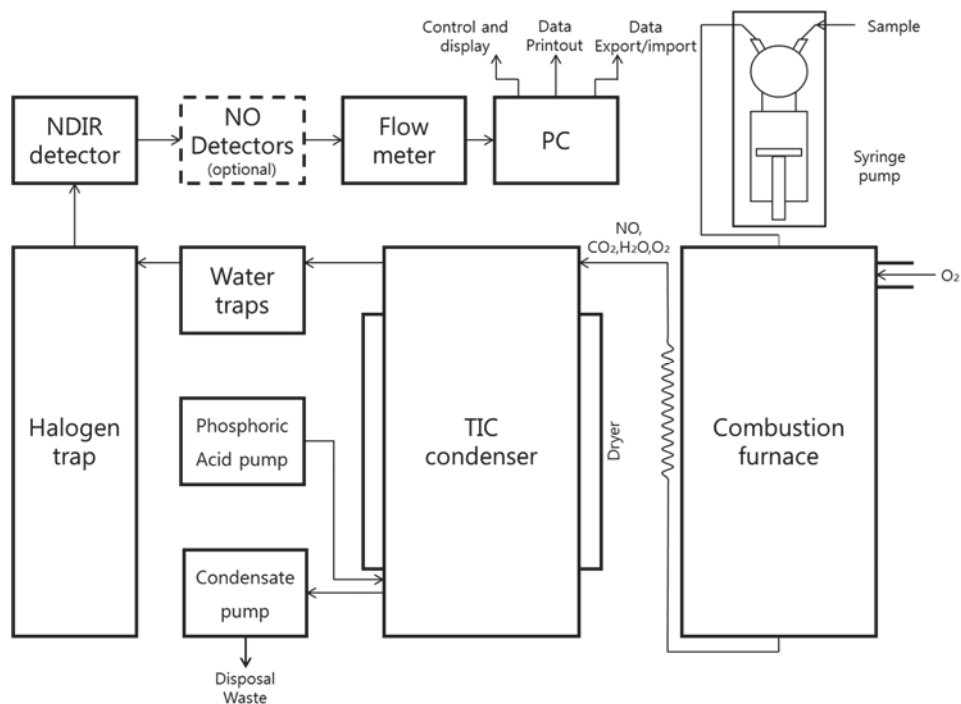
Figure 3.6 The flow of TOC principle for operation

a. LC-OCD

It is used to measure the DOC and the organic fractions. The LC-OCD system shown in **Figure 3.7** separates DOC compounds using a size exclusion chromatography column, which separates hydrophilic organic molecules according to their molecular weight size. A Toyopearl TSK HW50S column (TOSOH Bioscience GmbH, Stuttgart, Germany), with phosphate buffer mobile phase of pH 6.4 (2.6 g /L KH_2PO_4 and 1.5 mol/L Na_2HPO_4) at a flow rate of 1.1 mL/min is used to separate different organic fractions. To obtain a better resolution for wastewater samples, a single column is applied while the dual column is used for analysis of seawater sample (saline). The separated compounds are detected using two different detectors first by fixed wavelength UV-detector (UVD) (absorption at 254 nm) and then an OCD detector for the organic carbon (after inorganic carbon purging). At the inlet of the OCD detector, the solution is acidified at a flow of 0.2mL/min to convert carbonates to carbonic acid. The column is bypassed with a limited flow (flow rate 0.1mL/min, back pressure-driven) to gain a DOC value at the dead volume time of each chromatographic operation. The different fraction of the organics matter can be measured and based on the size of the molecules. The amount of each organic fraction is

calculated by using a software program (ChromCALC, DOC-LABOR, Karlsruhe, Germany) based on the chromatogram obtained from the LC-OCD analysis. OCD and UVD calibration is based on potassium hydrogen phthalate. Injection volume and retention time are set at 1 mL and 120 min, respectively. The chromatographic column is a weak cation exchange column consisting of polymethacrylate.

The organic substance can be divided into two types: hydrophobic and hydrophilic. The hydrophilics can be further categorized into biopolymers, humic substances, building blocks, LMW neutrals and LMW acids. Quantified depending on their molecular size from LC-OCD analysis are (i) biopolymers, (ii) humic substances (or humics), (iii) building blocks and (iv) low molecular weight neutrals (LMW-N). Biopolymer has high molecular weight (20,000–100,000 g/mol) compounds such as polysaccharides, amino sugars, polypeptides, proteins, hydrophilic fraction and not UV-absorbing. Humic substance represents compounds with molecular weights of approximately 1000 g/mol. The building block is defined as humic-hydrolysates and sub-units of humic substance with molecular weights between 300 and 500 g/mol. LMW-N consists of LMW weakly charged hydrophilic compounds such as alcohols, aldehydes, ketones and amino acids.

As the wastewater samples were collected after filtration, the biopolymers were low, as filtration would have screened them. The LMW was also low because bacteria had already consumed them at the biological treatment stage.
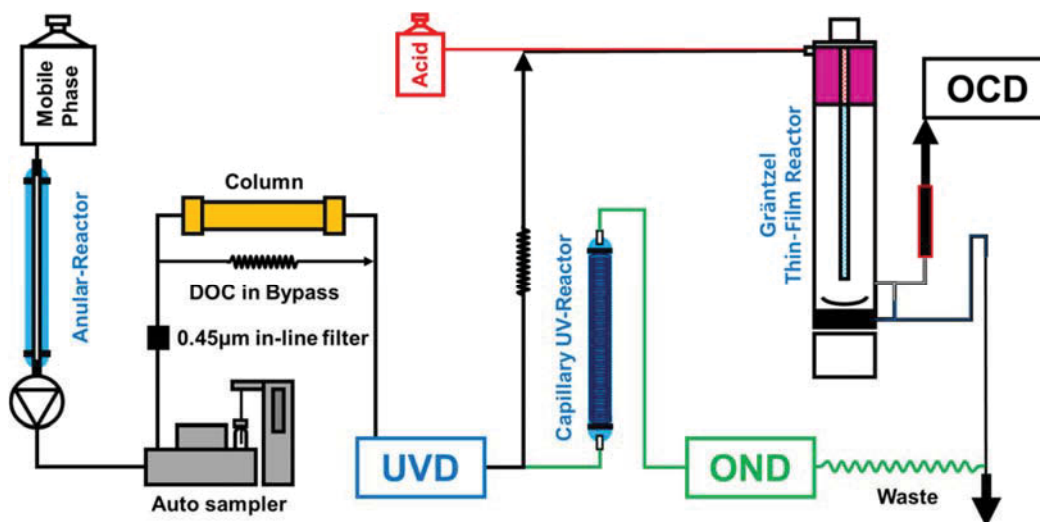
Figure 3.7 Flow scheme of the liquid chromatographic SEC-OCD system

3.4.3 Analysis of trace organics (Pharmaceuticals and personal care products (PPCPs))

Recently, pharmaceuticals and personal care products (PPCPs) have been widely regarded as contaminants of emerging issue because they are continuously growing into aquatic environments, and then their residues finally enter and get accumulated in the food chain through discharge and the reuse of treated sewage and sludge for agricultural applications (Rajapaksha et al., 2015). The adverse effects of PPCPs on health and the environment have been researched widely (Tanoue et al., 2012, Rajapaksha et al., 2015, Jiang et al., 2013). PPCPs are known to be emitted into the aquatic environment over various courses such as wastewater, hospital discharge, manufacture, sewage system and water treatment plant (Leung et al., 2012, Liu and Wong, 2013). PPCPs usually exist in surface water, groundwater, drinking water and sewage with concentrations range from parts-per-trillion (ng/L) to part-per-billion (μg/L) (Dai et al., 2015). Nevertheless, the removal of PPCPs is relatively low in conventional sewage treatment plants (Behera et al., 2011) because PPCPs which are either individual or complexes may exert substantially toxic or harmful effect on activated sludge bacteria, resulting in aggravated removal efficiency (Thomaidi et al., 2015).

Micro pollutants, which include pharmaceuticals and personal care products (PPCPs) and pesticides, can be extracted using solid phase extraction (SPE) and analysed by liquid chromatography

with tandem mass spectroscopy. Five-millimetre analyses were extracted using 500 mg hydrophilic/ lipophilic balance (HLB) cartridges (Waters, Milford, MA, USA). These analyses were separated using an Agilent (Palo Alto, CA, USA) 1200 series high performance liquid chromatography (HPLC) system equipped with a 150×4.6mm, 5 μm particle size, Luna C18 (2) column (Phenomenex, Torrance, CA, USA). Mass spectrometry was conducted using an API 4000 triple quadrupole mass spectrometer (Applied Biosystem, Foster City, CA, USA) equipped with a turbo-V ion source employed in both positive and negative electro-spray modes. All calibration curves had a correlation coefficient of 0.99 or better. Details of the analysis are presented elsewhere (Vanderford and Snyder, 2006).

3.4.4 Nutrients and chemical oxygen demand (COD) analysis

Nutrients such as phosphorus (PO_4-P), nitrate (NO_3-N), ammonia (NH_3-N) and chemical oxygen demand (COD) were measured by using spectrophotometer of cell test method (DR9300, HACH).

3.4.5 pH

The pH was measured regularly by using portable digital pH measurement meter (Model-HQ11D, HACH) in the influent and effluent.

3.4.6 Trans-membrane pressure (TMP)

Pressure transducer installed between the suction pump and the membrane measured TMP. The trans-membrane pressure was continuously monitored online, and data was saved in the data logger connected with a pressure transducer that was then transferred to the personal computer.

3.4.7 Turbidity

Turbidity was measured in terms of NTU (Nephelometric Turbidity Units) using 2100P turbidity meter, HACH, USA. The measurement of turbidity was made weekly.

3.4.8 DNA extraction

The samples taken for analysis included feed water (RO concentrate), activated sludge, biofilm on the membrane before NO treatment and biofilm on the treated membrane after NO treatment (collected at day 45). The samples were stored at -20ºC until DNA was extracted. After thawing, each

sample was centrifuged at 18407 X g for 1 minute to obtain approximately 0.5 g of biomass. DNA was extracted by FastDNA® Spin Kit for Soil (MP Biomedicals, Illkrich, France). The DNA was purified by using of the DNA purification kit from QIAGEN (Qiagen, Valencia, CA) and the purified DNA samples were sent to the Singapore Centre for Environment Life Science Engineering (SCELSE) to Nanyang Technological University for Illumina sequencing for further analysis.

3.4.8.1   Pyrosequencing

The DNA was sequenced using Illumina sequencing (Solexa Ltd, UK). The primers (the forward primer, 5'-GTGYCAGCMGCCGCGGTAA-3' and the reverse primer, 5'-CCGYCAATTYMTTTRAGTTT-3') are used to amplify the hypervariable V4-5 region of the 16S rRNA gene (Claesson et al., 2009). The samples were individually barcoded to enable multiplex sequencing. The sequence results were analysed by QIIME (Caporaso et al., 2010) to determine microbial community structure. All of the sequences from the samples are clustered at 97% sequence similarity with uclust. Each resulting cluster is considered as a genus. A representative sequence from each OUT cluster picked by the software is assigned to taxonomic data using the Ribosomal Database Project (RDP) classifier. For some OTUs, they can be assigned as specific as a bacterial species, but others may be assigned to nothing more specific than the bacterial domain (Kuczynski et al., 2012).

Chapter 4

University of Technology Sydney

4   Result and Discussion

Detailed experiments were conducted with two types of high strength wastewater: reverse osmosis concentrate (ROC) from a wastewater reclamation plant and synthetic wastewater mimicking ROC. The synthetic wastewater was used to keep the composition of water constant throughout the long-term membrane bioreactor experiments.

Membrane bioreactor effluent from a domestic wastewater treatment plant was also used in some experiments to study the appropriateness of hybrid biofilter in polishing this wastewater.

Section 4.1 presents the chemical cleaning investigation of MBR treating synthetic ROC.

Section 4.2 presents the effect of GAC in MBR hybrid system in treating synthetic ROC.

Section 4.3 presents the effect of PAC in suspension in MBR hybrid system in treating real ROC obtained from a wastewater reclamation plant.

Section 4.4 presents the importance of post treatment of biofilter, submerged membrane adsorption system in removing remaining organics and micro pollutants in the effluent of MBR used for treating domestic wastewater.

4.1 Detailed study on synthetic high strength wastewater

4.1.1 Background

Membrane bioreactor (MBR) process is an integrated technology of conventional activated sludge system and advanced membrane separation of clean water from mixed liquor sludge suspension in a single system. It is used widely for producing a high quality effluent from sewage through a combination with membrane filtration and biological treatment (Judd, 2008). Therefore, MBR system allows the independent control of sludge retention time and hydraulic retention time and retains a high concentration of sludge biomass in the reactor. In comparison to conventional activated sludge system with settling tank, MBR process has significant merit such as a smaller footprint, less sludge production and better effluent quality (Engelhardt et al., 1998). However, one of the most critical limitations caused by MBR system is membrane fouling which is a big hurdle for long-term MBR application (Krause et

al., 2010, Yang et al., 2006). Membrane fouling is caused both by membrane pore clogging and sludge cake deposition on the membrane (Lee et al., 2001). This brings about a reduction of permeate flux or an increase of trans-membrane pressure (TMP) when the system is operated in constant flux mode (Meng et al., 2009). Ultimately, it results in a reduction of productivity, increased treatment costs as well as the shorter lifespan of the membrane.

In particular, biofouling remains a significant issue for MBR system. The biofilm on the membrane surface composed of cells bound by a self-produced matrix of extracellular polymeric substances (EPS) contributes to clogging of the membrane pores (Meng et al., 2009). Many strategies have been tried to reduce biofouling in MBR. Modification of membrane surface properties (Tan and Obendorf, 2007), ultrasonic vibrations (Veerasamy et al., 2009, Li et al., 2016), turbulence (Pourbozorg et al., 2016) and chemical cleaning with acid or alkaline (Madaeni et al., 2009) are some of the strategies. Chemical cleaning is the most accepted method for controlling the biofouling from the membrane (Lee et al., 2013). Although physical methods can reduce reversible fouling, the removal of irreversible fouling is complicated, and thus chemical cleaning is necessary for the recovery of membrane flux or membrane permeability (Huyskens et al., 2008).

Among a variety of chemical agents used for backwashing, sodium hypochlorite is the common one in chemical backwashing of MBR process owing to its availability, reasonable cost and capacity to remove biofouling using efficient cleaning (Wang et al., 2010). However, it changes the membrane properties and thus affect the life-span of membranes and also lead to environmental and health risk (Estrela et al., 2002). It may have a negative influence on micro-organisms ability in biodegradation of organic and increase foulants such as EPS or SMP. Some study discovered that the organic degradation performance by microbes is overly damaged (Lim et al., 2005). Thus, the negative impact of sodium hypochlorite for microorganism and removal efficiency should be taken into consideration. Lately, some biological strategies have been considered as prospective methods to control the biofilm development on membranes. Nitric Oxide (NO) is used widely as a signalling molecule in biological systems, which has been found to be related to biofilm dispersal, inducing the conversion from the

sessile biofilm cells to the free swimming planktonic bacteria at low and nontoxic concentrations (Barraud et al., 2006).

The primary objective in this part of experimental study was thus to assess (i) the effect of sodium hypochlorite on microorganisms and (ii) the application of NO as a novel strategy to reduce membrane biofouling by complex microbial communities in MBR process.

4.1.2 Experimental

Details on the experimental methods and material are given in Chapter 3.

Synthetic wastewater: A laboratory scale submerged MBR system was operated to treat synthetic wastewater. The characteristics of synthetic wastewater is presented in **Table 3.1**. We refer this wastewater as synthetic reverse osmosis concentrate (ROC) as the characteristics of this wastewater are similar to ROC in wastewater reclamation plant.

Membrane: A hollow fiber membrane module having a surface area of 0.01 m² was used in this experiment. The characteristic of the hollow fiber membrane is given in **Chapter 3, Table 3.8**.

Backwashing chemical: In this study, two types of backwashing chemicals were used. The detailed characteristics of nitric oxide (NO) and sodium hypochlorite solution (NaOCl) are given in **Table 3.9**, **Chapter 3**.

MBR system: The synthetic wastewater representing wastewater reverse osmosis concentrate (ROC) was pumped up to the MBR where it underwent biodegradation. Feed water was biodegraded by the biomass activated sludge and then subsequently the biomass was separated by the membrane module. The clean effluent was extracted using a suction pump connected to the membrane module as shown in **Figure 3.2.** The permeate flux was kept constant at a predetermined value. The flux was maintained at 15 and 20 L/m²h. The volume of aeration tank membrane bioreactor was 10 L. Experiments were conducted at a temperature of 23±1 °C. The other characteristics of MBR system are discussed in **section 3.3.1** in **Chapter 3**.

Seed activated sludge was obtained from an activated sludge plant (a sewage treatment facility) in Sydney, Australia. The mixed liquor in the MBR was acclimatized for 45 days for allowing the organism to adjust to a change in its environment and to maintain performance across a range of environmental conditions.

Figure 4.1 presents the change of mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) during the acclimatization process. Even though the mixed liquor in the MBR became stable in terms of MLSS and MLVSS after the first 30 days of acclimation, the acclimation was continued over 40 days as a security measure. The pH was 6.5 to 7.5 during this time. The MLSS concentration was maintained constant by withdrawing excess sludge periodically. From the literature it is found that an increase of MLSS concentration from 2.4 to 9.6 g/L led to an increase of cake resistances on the membrane ranging from 9 to $22 \times 10^{11} m^{-1}$ (Fang and Shi, 2005). MLSS and MLVSS concentrations were of similar range during the experiment even the experimental conditions were varied. The concentration of MLSS and MLVSS was between 5 and 6 g/L and between 4.5 and 5.0 g/L, respectively. The parameters such as flux, TMP, pH, and temperature were monitored and recorded automatically using a data logger.
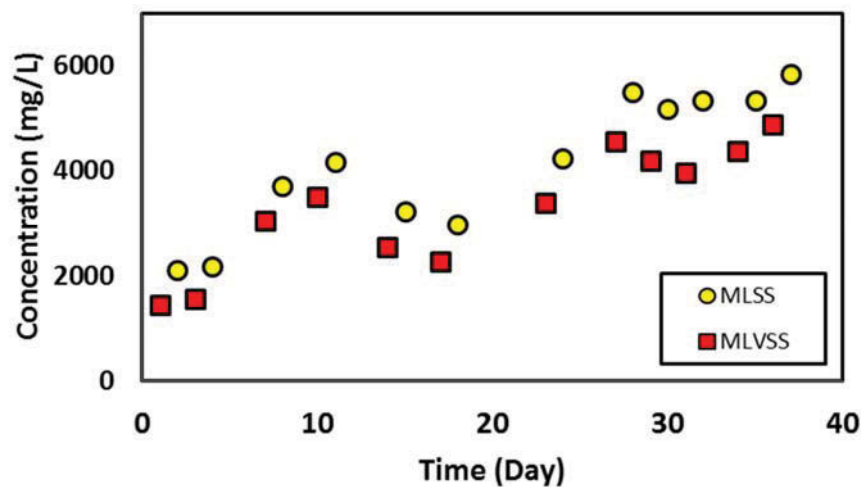
Figure 4.1 MLSS and MLVSS profile with time during acclimation period

Backwashing method: The effect of nitric oxide (NO) and sodium hypochlorite (NaOCl) as chemical cleaning agent on membrane biofilm reduction was tested by using them to backwash the membrane module chemically. NO, and NaOCl were used to remove foulants deposited on the membrane surface or within the membrane pores. To compare the cleaning efficiency between NO and NaOCl, backwashing was conducted at the same time. After the TMP reached a particular level (i.e when the TMP development was 15 kPa), the backwashing was conducted by taking out the membranes outside the MBR and placing them in two separate beakers outside of the MBR tank. The fouled membrane was backwashed using 200 ml of NO solution containing 16.318 mg of NO agent for 1 h. In the other beaker, the fouled membrane was backwashed with sodium hypochlorite solution, which contained 40 ml of sodium hypochlorite and 160 ml of deionized water. After backwashing, the membrane modules were returned to the MBR tank and the operation was continued.

Analytical methods: The samples taken from MBR effluent were analysed according to standard methods for nutrients such as nitrate, phosphate and ammonia. Analysis of NO_3-N, NH_4-N, Phosphate and COD were conducted by using the cell test kit method and spectrophotometer (DR3900, HACH). To minimize the experimental error, all analyses were duplicated, and the average values were recorded.

DNA from the biofouling community growing on the hollow fiber membrane as well as from the activated sludge in the reactor was extracted by FastDNA® Spin Kit for Soil (MP Biomedicals, Illkrich, France). The aqueous DNA samples were kept at -80 °C. DNA samples were sent to the Singapore Center for Environment Life Science Engineering (SCELSE) for Illumina sequencing. The other details are explained in **section 3.4.8** of **Chapter 3**.

4.1.3 Result and Discussion

4.1.3.1 Effect of Flux

Long-term MBR experiments were operated at filtration fluxes of 10, 20 and 23 L/m²h, respectively to study TMP development and membrane fouling phenomena. The variations of TMP at different flux are presented in **Figure 4.2.** The experiment was first conducted at a low flux of 10 L/m²h.

The flux was then increased to 20 L/m²h and operated at a constant flux for another 4 days. A pressure transducer with online data acquisition was used to monitor the trans-membrane pressure development. The data was recorded every 5 min using a data logger attached to the pressure traducer. Synthetic ROC was used as feed water for the experiments. A two-step fouling phenomenon was observed: a slow increase of TMP followed by a rapid increase of TMP. In the case of the flux of 10 L/m²h, a gradual increase of TMP was observed for the first 4 days (TMP increased from 0 to 1.5 kPa) and the TMP was increased quickly (TMP increased up to 4.3 kPa at around day 6). On the other hand, at a higher flux of 20 and 23 L/m²h, rapid TMP rise occurred earlier after day two and one of operations respectively. A higher flux resulted in a higher membrane resistance compared with the lower flux of 10 L/m²h. Higher membrane fouling indicates higher TMP development. When the TMP is lower, it is stayed longer during the initial period compared with high TMP, which occurred at high flux. The TMP jump occurred earlier for high flux compared with 10 L/m²h. At higher flux, this jump may be not only due to change of flux but also due to the change of cake layer structure. Therefore, the deposition of the sludge on the membrane surface at higher flux is faster than at a lower flux. In this study, a higher flux was used deliberately in long-term experiments to study the effect of fouling on the membrane.

The concept of critical flux was introduced by (Field et al., 1995) to illustrate membrane fouling phenomenon. Critical flux is a broadly accepted as a parameter for characterizing membrane fouling in MBR (Le-Clech et al., 2003a). The critical (or sustainable) flux is the maximum flux which showed no or relatively low increase in TMP. The sustainable flux of the MBR system with synthetic wastewater without any absorbents was observed to be at 20 L/m²h, where no sharp and sudden TMP increase was observed.
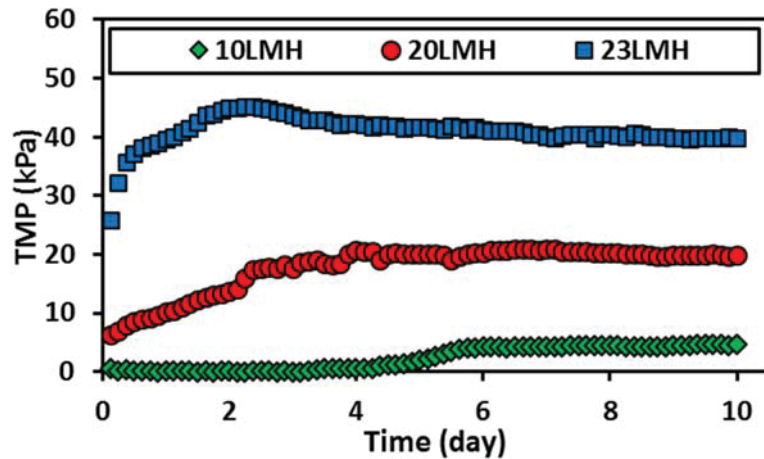
Figure 4.2 Temporal variation of TMP at different fluxes (membrane area: 0.01m², Volume of the reactor: 10L, HRT: 1.04 h, Flux: 10, 20 and 23 L/m²h)

4.1.3.2 Long term experiments with chemical backwashing

4.1.3.2.1 TMP

Figure 4.3 and **Figure 4.4** present the TMP development at two different permeate flux values (15 and 20 L/m²h). The TMP development is related to the fouling on the membrane. In the MBR process, the TMP variation exhibits two distinct stages: a slow increase and then a sharp increase stage (Hwang et al., 2008). The sharp TMP increase, which separates the two TMP development is termed as "TMP jump" (Kaneko and Funatsu, 2013).

The MBR was operated for 58 days at an operating flux of 15 L/m²h, whereas, it was operated for 34 days when the flux was increased at 20 L/m²h (**Figure 4.3** and **Figure 4.4**). When the chemical cleaning was performed, there was a reduction in TMP. The MBR equipped with two identical membranes was operated in parallel at a constant flux of 15 L/m²h till TMP reached 14.2 and 15.4 kPa after 23 days respectively (**Figure 4.3)**. After backwashing on the 23rd day, the TMP dropped to 5 kPa and showed a slow rise with time when the operation resumed. This illustrates that chemical cleaning had a good restoration of permeability of this membrane.

In the MBR experiment with the higher flux of 20 L/m²h, the TMP jump took place within 2-3 days of operation (10.1 and 12.12 kPa). Then it steadily rose up to 20.7 and 21 kPa before chemical backwashing was performed. The rapid TMP increase attributes to the deposition of fine particles at the

beginning of the experiment (Pradhan et al., 2011). Fine particles are easily attached to membrane surface at higher flux forming dense cake layer. Membrane clogging by the biomass onto the hollow fiber membranes to form biofouling has been suggested to be the main reason for the rapid increase in the TMP (Chen et al., 2013).
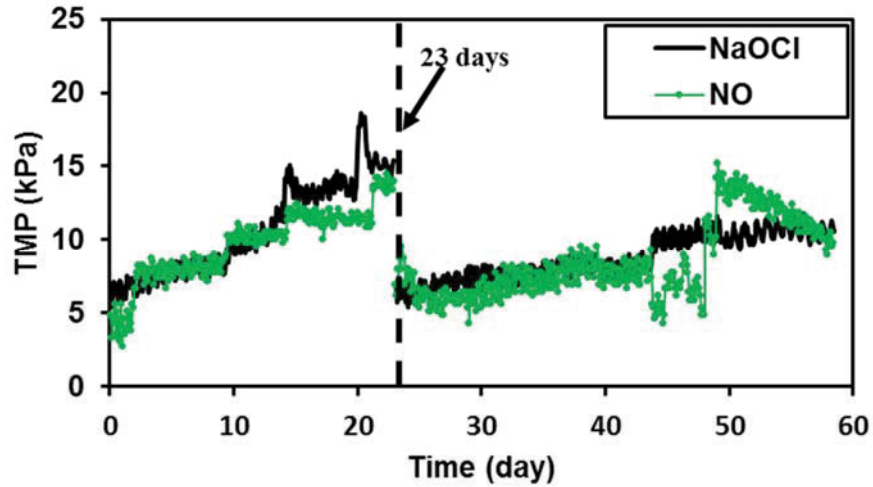
Figure 4.3 TMP development profile in MBR before and after chemical backwashing with NaOCl and NO (Membrane area: 0.01m², Volume of the reactor: 10L, HRT: 1.04 h, Flux: 15 L/m²h)
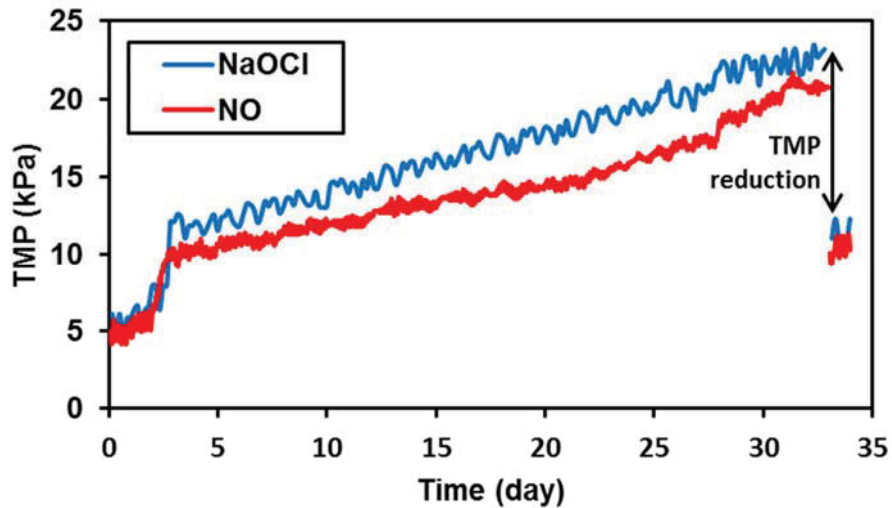
Figure 4.4 TMP development profile in MBR (Membrane area: 0.01m², Volume of the reactor: 10L, HRT: 1.04 h, Flux: 20 L/m²h)

4.1.3.2.2   Removal of TOC

Sodium hypochlorite (NaOCl) prevented filamentous fungi growth in the activated sludge process (Smith and Purdy, 1936). Thus, it can be used to reduce membrane fouling in MBR process. Sodium hypochlorite can hinder the growth of microorganisms and oxidize organic matters (or biodegradable organic). According to the TOC removal results in the MBR operated at 15 L/m²h and 20 L/m²h, it was observed that both sodium hypochlorite and NO did not have any harmful impact on microorganism immediately. As such, there was no difference in TOC removal at least 3 days after backwashing. (**Figure 4.5** and **Figure 4.6**)
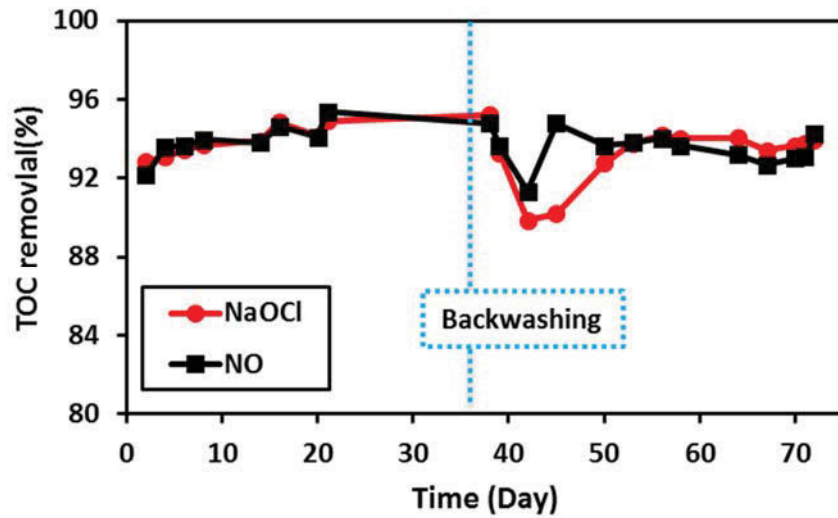
Figure 4.5 TOC removal in MBR before and after chemical backwashing (Membrane area: 0.01m², Volume of the reactor: 10L, HRT: 1.04 h, Flux: 15 L/m²h)
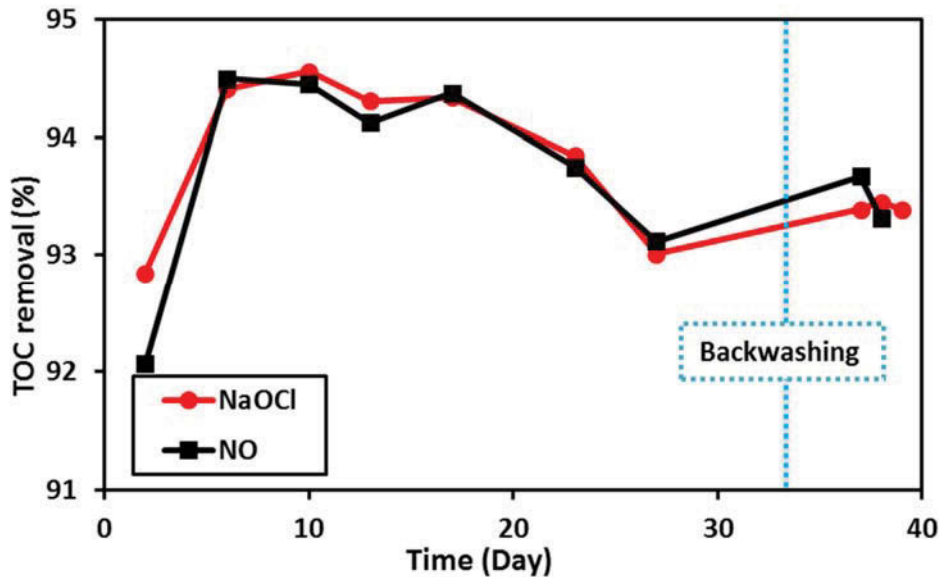
Figure 4.6 TOC removal in MBR before and after backwashing (Membrane area: 0.01m², Volume of the reactor: 10L, HRT: 1.04 h, Flux: 20 L/m²h

4.1.3.2.3 Nutrients and organic matter removal

The removal of organic matters and nutrients such as nitrogen and phosphate are given in **Table 4.1** and **Table 4.2**. The nitrogen could be removed by assimilation into biomass or by nitrification-denitrification. From **Table 4.1** and **Table 4.2**, it was found that the removal of dissolved organic carbon (DOC) was over 85 % in all experiments. As expected, higher DOC removal of around 87.6 % was achieved when the MBR was operated before backwashing at 15 L/m²h. High DOC removal is due to the aerobic heterotrophic microbial biomass present in the reactor (Johir et al., 2012b). The removal of NH_4-N was very high over 99 % except for one case that was 97 % at 15 L/m²h after backwashing with NO donor. It may be due to the impact of NO donor on the removal of NH_4-N. However, it was only a small difference. The ammonia removal was achieved by the microorganism assimilation, biosynthesis and nitrification. As expected, the MBR did not have any effect in removing phosphorus. The total nitrogen concentration in the effluent was also low due to the low level of nitrogen in the influent. **Table 4.1** presents the COD concentration before and after backwashing with the different chemical at 15 L/m²h. The COD removal efficiency was more than 97 % at the flux of 15 L/m²h. There was only a minor change in COD removal after backwash (less than 1%). The COD removal efficiencies were very

high during the entire experiment, and the average effluent COD concentration was from 6.56 to 12.5

mg/L. In the MBR, the removal of NH3-N usually occurred through conversion of ammonia into nitrite

and nitrate by a nitrification process.

Table 4.1 The removal of NH_4-N, NO_3-N, PO_4-P, COD and DOC by MBR (15 L/m²h, cleaning by NaOCl and NO, Membrane area: 0.01m², Volume of the reactor: 10L, HRT: 1.04 h)

	Flux (L/m²h)		NO_3-N (mg/L)	NH_4-N (mg/L)	Phosphate (mg/L)	COD (mg/L)	DOC (ppb-c)
NaOCl	15	Influent	4.86	2.85	17.88	453	49590
		Effluent before backwashing	27.16	0.017	15.56	6.56	6169
		removal (%)	-	99.40	-	98.55	87.56
		Effluent after backwashing	31	0.025	20.6	12.5	6538
		removal (%)	-	99.12	-	97.24	86.82
NO	15	Effluent before backwashing	26.84	0.015	15.12	8.01	6151
		removal (%)	-	99.47	-	98.23	87.60
		Effluent after backwashing	31.16	0.077	20.36	10.3	6485
		removal (%)	-	97.30	-	97.73	86.92

Table 4.2 The removal of of NH_4-N, NO_3-N, PO_4-P and DOC by MBR (20 L/m²h, cleaning by NaOCl and NO, Membrane area: 0.01m², Volume of the reactor: 10L, HRT: 1.04 h)

	Flux (L/m²h)		NO_3-N (mg/L)	NH_4-N (mg/L)	Phosphate (mg/L)	DOC (ppb-c)
NaOCl	20	Influent	3.91	2.92	18.06	49590
		Effluent before backwashing	35.72	0.029	21.52	
		removal (%)	-	99.01	-	
		Effluent after backwashing	31.52	0.012	19.32	
		removal (%)	-	99.59	-	
NO	20	Effluent before backwashing	34.68	0.027	21.72	7168
		removal (%)	-	99.08	-	85.55
		Effluent after backwashing	31.6	0.013	19.4	6968
		removal (%)	-	99.55	-	85.95

4.1.3.2.4 Bacteria DNA of the foulants

Phylogenetic spectrum was used to determine the microbial communities at different levels of taxonomy. The environmental conditions in MBRs are essential for abundances of functionally critical microbial groups (Xia et al., 2016). Therefore, bacterial communities, which were not able to adapt to the conditions, were decreased or removed from the system. For example, one OTU in the family of Acetobacteraceae was showed 6.7% of OTUs in feedwater, but reduced to an undetectable level in activated sludge and biofilm samples (**Figure 4.7**). Similarly, the relative abundance of Planctomyces was reduced from 13.9% in feedwater to 5.4% in activated sludge and 1.5% in biofilm before the treatment.

					k__Bacteria;p__Proteobacteria;c__Betaproteobacteria;o__Burkholderiales;f__Comamonadaceae;g__

k__Bacteria;p__Proteobacteria;c__Betaproteobacteria;o__Burkholderiales;f__Comamonadaceae;g__

k__Bacteria;p__Proteobacteria;c__Alphaproteobacteria;o__Sphingomonadales;f__;g__

k__Bacteria;p__Proteobacteria;c__Alphaproteobacteria;o__Rhodobacterales;f__Rhodobacteracea

k__Bacteria;p__Proteobacteria;c__Alphaproteobacteria;o__Rhizobiales;f__Phyllobacteriacea

k__Bacteria;p__Bacteroidetes;c__Cytophagia;o__Cytophagales;f__Cytophagaceae;g__

k__Bacteria;p__Planctomycetes;c__Planctomycetia;o__Planctomycetales;f__Planctomycetaceae;

k__Bacteria;p__Nitrospirae;c__Nitrospira;o__Nitrospirales;f__Nitrospiraceae;g__Nitrospira

k__Bacteria;p__Chloroflexi;c__Anaerolineae;o__Caldilineales;f__Caldilineaceae;g

A   **B**   **C**   **D**

Taxonomy (genus level)	OTU (%)			
	A	B	C	D
k__Bacteria;p__Proteobacteria;c__Alphaproteobacteria;o__Sphingomonadales;f__;g__	16.7	5.1	11	0.1
k__Bacteria;p__Proteobacteria;c__Alphaproteobacteria;o__Rhizobiales;f__Phyllobacteriaceae;g__	10.1	5.3	2.3	0.4
k__Bacteria;p__Proteobacteria;c__Betaproteobacteria;o__Burkholderiales;f__Comamonadaceae;g__	9.6	3.2	4.3	1.7
k__Bacteria;p__Proteobacteria;c__Alphaproteobacteria;o__Rhodobacterales;f__Rhodobacteraceae;g__Paracoccus	7.2	7.3	7.8	0
k__Bacteria;p__Chloroflexi;c__Anaerolineae;o__Caldilineales;f__Caldilineaceae;g__	5	4.4	7.3	2.3
k__Bacteria;p__Nitrospirae;c__Nitrospira;o__Nitrospirales;f__Nitrospiraceae;g__Nitrospira	2.7	9	6.3	0.2
k__Bacteria;p__Planctomycetes;c__Planctomycetia;o__Planctomycetales;f__Planctomycetaceae;g__Planctomyces	1.1	7.5	4.7	0.2
k__Bacteria;p__Bacteroidetes;c__Cytophagia;o__Cytophagales;f__Cytophagaceae;g__	1.5	5.4	2.8	13.9
k__Bacteria;p__Proteobacteria;c__Alphaproteobacteria;o__Rhodospirillales;f__Acetobacteraceae;g__	0	0	0	6.7

Figure 4.7 The relative bacterial community abundance on genus level (A) Biofilm before NO backwashing; (B) Activated sludge; (C) Biofilm after NO backwashing; and (D) Feedwater.

On phylum level, Proteobacteria accounted for 48% ± 10% of total OTUs in all samples was the most predominant phylum in the MBR (**Table 4.3**). Among Proteobacteria, Alphaproteobacteria was responsible for the highest relative abundance of 32.8% ± 7% of the total OTUs, followed by Betaproteobacteria, 8.3% ± 4.3%, and Gammaproteobacteria, 5.1% ± 1.5%. It is noted that Alphaproteobacteria occupied 43% of OTUs in biofilm before the NO backwashing compared with 29.3% in feedwater, 28.8% in activated sludge and 29.8% in the biofilm after NO treatment. The results suggested that Alphaproteobacteria played a crucial role in the development of biofilm on the membrane surface.

Table 4.3 The relative bacterial community abundances of Proteobacteria in the MBR

Taxonomy	OTU (%)			
	A	B	C	D
k__Bacteria;p__Proteobacteria	62.4	39.5	43.9	46.2
k__Bacteria;p__Proteobacteria;c__Alphaproteobacteria	43.3	28.8	29.8	29.3
k__Bacteria;p__Proteobacteria;c__Betaproteobacteria	10.7	4.2	5.2	13.1
k__Bacteria;p__Proteobacteria;c__Deltaproteobacteria	1.8	2.3	2.4	0.1
k__Bacteria;p__Proteobacteria;c__Gammaproteobacteria	6.6	4	6.2	3.7

There were four dominant OTUs found in biofilm before the treatment. Three of them were derived from Alphaproteobacteria, one dominant OTU (16.7%) from the order Sphingomanadales, the other two (10.1% and 7.2%) from the family Phyllobacteriaceae and the genus Paracoccus. The last dominant OTU (9.6%) was from Betaproteobacteria, the family Comamonadaceae. These dominant OTUs were responsible for low relative abundances in feedwater (0%-1.7%). Therefore, the results suggested that the species of Sphingomonadales, Phyllobacteriaceae, Comamonadaceae and Paracoccus are probably one of the mainly essential species for biofilm formation in the MBR. Although the relative abundances of Cytophagaceae and Nitrospira were high in activated sludge (7.5%/9.0%), they were less abundant in biofilm before the treatment (1.1%/2.7%), respectively. They may not play a key role in biofilm formation in the MBR.

It was also noted from the results that NO treatment was responsible for the reduction of 34%-77.2% in the relative abundances of bacteria belonging to Sphingomonadales, Comamonadaceae and Phyllobacteriaceae, respectively in biofilm after NO treatment compared with biofilm before NO treatment. Especially, species of the family Phyllobacteriaceae was shown the significant reduction in relative abundance from 10.1% to 2.3% after NO treatment. The results suggested that NO treatment reduced the relative abundances of essential species responsible for biofilm formation. However, NO backwashing led to the slight reduction in the relative abundance of species of the order Sphingomonadales from 16.7% to 11%. The relative abundance of these bacteria was still high in the treated biofilm that can lead to the regrowth of biofilm in the system for further operation. On the other hand, bacteria including Caldilineaceae (7.3%), Cytophagaceae (4.7%), Planctomyces (2.8%) and Nitrospira (6.3%) in the treated biofilm sample were significantly more abundant than that in biofilm before NO treatment (5%, 1.1%, 1.5% and 2.7%), respectively. The results indicated that these bacteria were not sensitive to NO-induced dispersal.

In this study, bacteria of Sphingomonadales, Phyllobacteriaceae, Comamonadaceae and Paracoccus, which were shown the high relative abundance (7.2%-16.7%) in biofilm before the treatment, were responsible for biofouling formation. In previous studies, Alphaproteobacteria was pioneer bacterial species responsible for membrane biofouling (Zhang et al., 2006, Barnes et al., 2015)

and the majority of Alphaproteobacteria sequences belonged to the orders Sphingomonadales and Rhizobiales (White et al., 1996, Bereschenko et al., 2010). Bacteria of the Sphingomonadales order and Phyllobacteriaceae of the order Rhizobiales can degrade a wide range of carbon substrates which help them to adapt to the limitation of readily biodegradable organic carbon sources in wastewater treatment plants. Also, these bacteria can produce EPS, the primary biological component of biofilms, which could quickly lead to biofouling formation (Pang and Liu, 2007, Liu et al., 2012b, White et al., 1996). The spreading of the EPS on membrane surfaces led to modify the surfaces that allowed other microorganisms able to attach and proliferate (Bereschenko et al., 2010). This can explain for their dominance in the biofilm. Previous investigations revealed that Betaproteabacteria responsible for the development of the mature biofilms caused to the severe irreversible membrane biofouling (Miura et al., 2007) and the Comamonadaceae was the dominant family in the phylum (Liu et al., 2012b, Ge et al., 2015, Sadaie et al., 2007). The results were consistent with this study that Comamonadaceae, the family of Betaproteabacteria, was accounted for the high relative abundance of 9.6% in the biofilm before NO treatment. Members of the Comamonadaceae can utilise a wide range of organic acids, such as amino acids that may give them a competitive benefit to be abundant in biofilms, EPS of which are mainly composed of proteins and polysaccharides (Chu and Wang, 2013, Ge et al., 2015). A previous study indicated that the increase in the relative abundance of Comamonadaceae resulted of the limitation of oxygen supply in the conventional wastewater treatment plant (Sadaie et al., 2007). That can explain the higher abundance of these bacteria in biofilm before the treatment than activated sludge. The genus Nitrospira, the dominant nitrite oxidizers in wastewater treatment plants and lab-scale reactors (Daims et al., 2001, Ma et al., 2013, Gao et al., 2011), and Paracocus, denitrifying bacteria found in both activated sludge and biofilms (Reyes et al., 2015), played an important role for nitrogen removal (the removal efficiency of 99%) in the MBR that can explain their high abundance in the system. They were not susceptible to NO-mediated dispersal because they may use NO donor for the growth. On the other hand, Planctomyces was more abundant in feedwater than that in activated sludge and biofilm samples. This is in agreement with a previous study Planctomyces accounted for the low relative abundance in MBR-RO biofilms (Pang and Liu, 2007).

Backwashing with NO led to reducing the relative abundance of the essential species responsible for biofouling formation, including Sphingomonadales, Comamonadaceae and Phyllobacteriaceae. These bacteria are sensitive to NO-induced dispersal, resulting in a transition from biofilm mode of growth to the free swimming planktonic state. The decrease of TMP from 22 kPa to 10kPa after NO treatment was the result of biofilm dispersal through the reduction of the relative abundances of these bacteria. The result suggested the potential of NO donor to control biofouling membrane. However, the relative abundances of Caldilineaceae, Cytophagaceae, Planctomyces increased after NO treatment. This suggested that the NO treatment resulted in the decrease in the relative abundances of some bacterial communities, but might be encouraged in others. Further experiments are needed to give a better explanation for the increase in the relative abundance of these bacteria.

4.2 Membrane adsorption hybrid system with high strength wastewater

The aim of this study was to evaluate the influence of removal performance in the membrane hybrid system treating high strength synthetic wastewater (synthetic ROC).

The addition of GAC in an MBR treating high strength wastewater containing recalcitrant components would enhance reactor performance with minimum fouling.

4.2.1 Background

Reverse osmosis (RO) is commonly used in wastewater reclamation plants as the final treatment stage (Chon et al., 2012, Umar et al., 2015, Liu et al., 2012a, Dialynas et al., 2008, Dolar et al., 2012). Consequentially, RO produces significant volume of the reverse osmosis concentrate (ROC) containing abundant dissolved organics, pharmaceuticals, persistent organic pollutants, pesticides, inorganics, etc although these plants produce high-quality reusable water. The improperly managed concentrate can cause serious negative impact on the environment, much more than the case of secondary effluent. The direct disposal of ROC into water bodies can generate a critical eco-toxicological risk, and also threaten aquatic organisms. Therefore, proper management and suitable disposal of ROC is very important (Kazner et al., 2014).

ROC can be treated by forward osmosis, membrane distillation, advanced oxidation processes (Kazner et al., 2014) (Martinetti et al., 2009, Zhou et al., 2011). However, the high cost involved in these technologies restricts broader application. In this respect, granular activated carbon (GAC) was reported to remove humics, building blocks and LMW efficiently (Ciputra et al., 2010). It is found that MF-GAC hybrid system reduced the transmembrane pressure (TMP) development and frequency of chemical cleaning by half (Kim et al., 2009). The addition of GAC also provides mechanical scouring (Pradhan et al., 2012) and reduces fouling.

In this study, the performance of MF-GAC to treat ROC was studied in terms of TMP development and removal of organic matters. The synthetic ROC was used as a feed to maintain the wastewater characteristics content.

4.2.2 Experimental Details

Wastewater: High strength synthetic wastewater mimicking ROC was used as feed water. The detailed characteristic of ROC are presented in **Chapter 3, section 3.2.2**.

Membrane: Hollow fiber membrane was used in this experiment. This was supplied from Cleanil-S, Kolon, South Korea. The details regarding of characteristics of the hollow fiber module are presented in **Chapter 3, section 0.**

GAC as adsorbent: GAC was chosen as an adsorbent to study the enhancement of membrane performance and reduction of membrane fouling. The details of the GAC used are given in **Chapter 3, section 3.2.3.**

MBR-GAC hybrid system: The schematic diagram of the membrane hybrid system used in this study is presented in **Figure 3.3**. The hollow fiber membrane module was submerged in the reactor tank (10 L). The initial GAC dose of 20 g in the reactor at the start of the experiment. The function of the submerged membrane adsorption hybrid system is discussed in **Chapter 3, section 3.3.1.**

Post-treatment of MD: MD experiment was used as post treatment and the details are discussed in **section 3.3.3** in **Chapter 3**.

Analytical methods: Liquid Chromatography-Organic Carbon Detection (LC-OCD) was used to measure the removal of DOC and different fractions of organics. The details are provided in **Chapter 3**.

4.2.3 Result and Discussion

4.2.3.1 Trans-membrane pressure (TMP) development

During the 120 day of operation, TMP development was low and it can be divided into two stages. Steady increase was observed during the initial 23 days. The TMP development was flattened from 23 to 120 day as shown in **Figure 4.8**. There was no chemical backwashing performed during the 120 days of operation. The TMP increased from 10.5 to 15.9 kPa during the first 23 days. After that TMP remained stable between 15 to 16 kPa. The results of the TMP profile indicated that the addition of GAC into reactor prevented the TMP jump. The past also studies showed the addition of GAC reduced membrane fouling by 50% through pre-adsorption of organics by GAC and membrane (Johir et al., 2011a).
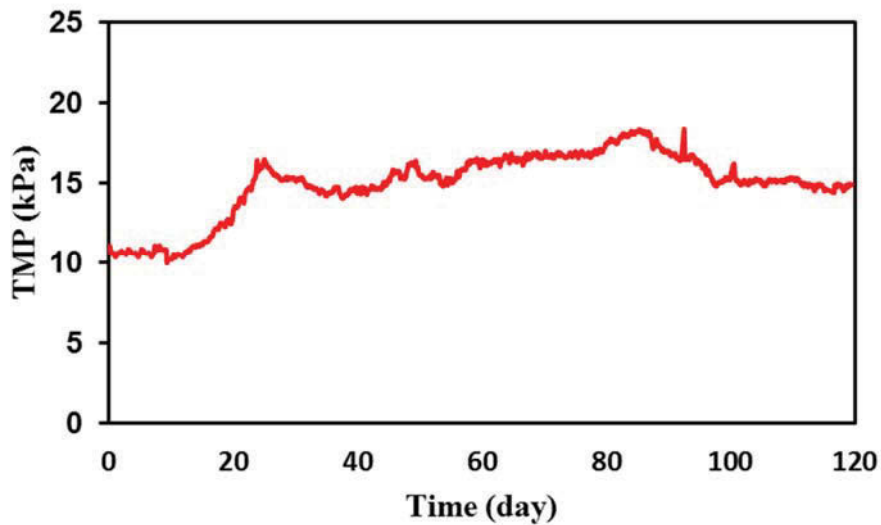
Figure 4.8 TMP profile of the MBR-GAC hybrid system (Membrane area: 0.01m², Volume of the reactor: 10L, HRT: 1.04 h, Flux: 20 L/m²h)

4.2.3.2 Detailed organic removal

The removal of DOC was noticeable with the addition of GAC (dose of 20 g) at the beginning of the experiment. MF filtration alone can not remove DOC because the hollow filber microfilter membrane has a relatively large pore size of 0.1 μm (Shanmuganathan et al., 2015a). The addition of GAC achieved up to 94.8 % of DOC removal as shown in **Figure 4.9**. After 9 day of operation, DOC removal reduced slightly to 89.5% remained constant until the 100th day.

Table 4.4 presents the detailed organic fractions. The feed water is composed of mainly hydrophilic which contains 40.3 % of humics, 13.5 % of building blocks, 23.3 % of LMW neutrals and 22.9 % of biopolymers. LMW acids were non-detectable. Long-term operation results indicated the MBR adsorption hybrid system removed a majority of biopolymers. Biopolymer is one of the main foulant responsible for membrane fouling (Johir et al., 2012a). This indicated that the use of GAC as suspended media has a beneficial effect in reducing hydrophilic organic matter. It was found that GAC can effectively remove hydrophobic as well as hydrophilic organic matter (Nguyen et al., 2012). The adsorption of these organic fraction predominantly occur in mesopore (2-50nm width) and large micropores (1-2 nm width) (Velten et al., 2011), (Cheng et al., 2005). The pore size of GAC used in this study was 0.6-2.36mm that offers favourable environment for the adsorption of these compounds. The superior removal of organic fractions was due to more micro-pore spaces on GAC being available for adsorption (Shanmuganathan et al., 2015b). Among the hydrophilic DOC, the adsorption of biopolymers was high. Velten et al (2011) observed that ability of organic fractions to be adsorbed decreased with larger molecule size as follows: biopolymers < humics < building blocks < LMW organics. They also found that effective adsorption depends highly on the dominance of particular fraction of organics. Johir et al (2013) also found the removal of more humics when GAC was added in the bioreactor.
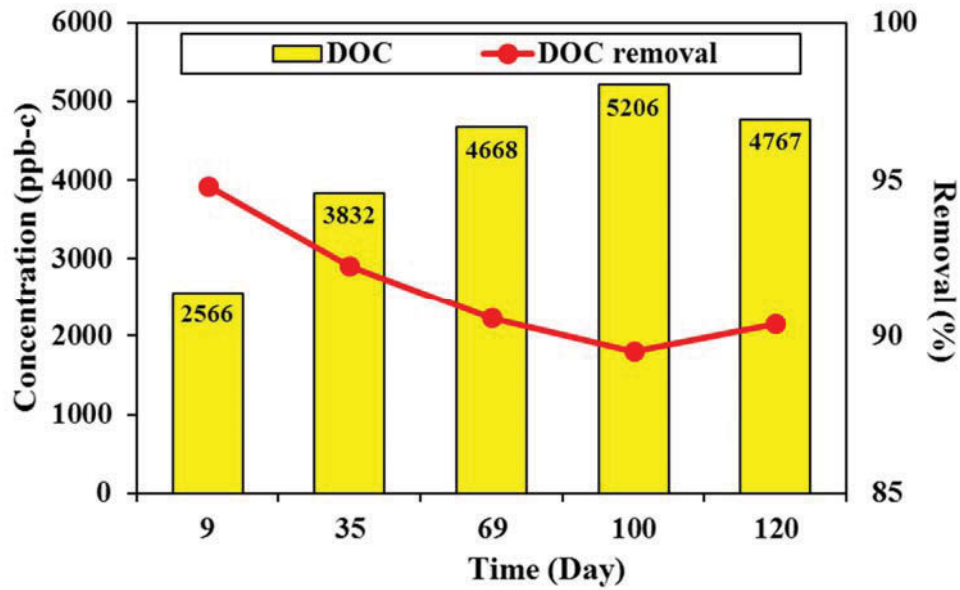
Figure 4.9 DOC removal during the 120 days of operation (Flux: 20L/m²h)

Table 4.4 Detailed organic fraction of influent and effluent

	Hydrophobic. (ppb-c)	Hydrophilic. (ppb-c)	BIO- polymers	Humics Subst.	Building Blocks	LMW Neutrals
Feed water	-	49590	11380	19963	6715	11533
Day 9	217	2349	46	1448	356	498
Day 35	203	3629	55	2424	465	685
Day 69	213	4454	43	3600	123	688
Day 100	489	4717	28	3231	410	1048
Day 120	340	4427	9	3149	370	898

4.2.3.3 Nutrients and organic matter removal

It can be seen from **Figure 4.10**, that long-term experiment resulted in the high removal of COD, ammonia and TOC despite the increase of MLSS from 1.8 to 4.8 g/L as shown in **Figure 4.11**. The removal of NH_4 was high at 93-100%. The removal of NH_3-N usually occurred through conversion

of ammonia into nitrite and nitrate by a nitrification process and through nitrogen loss by denitrification (Johir et al., 2012a).
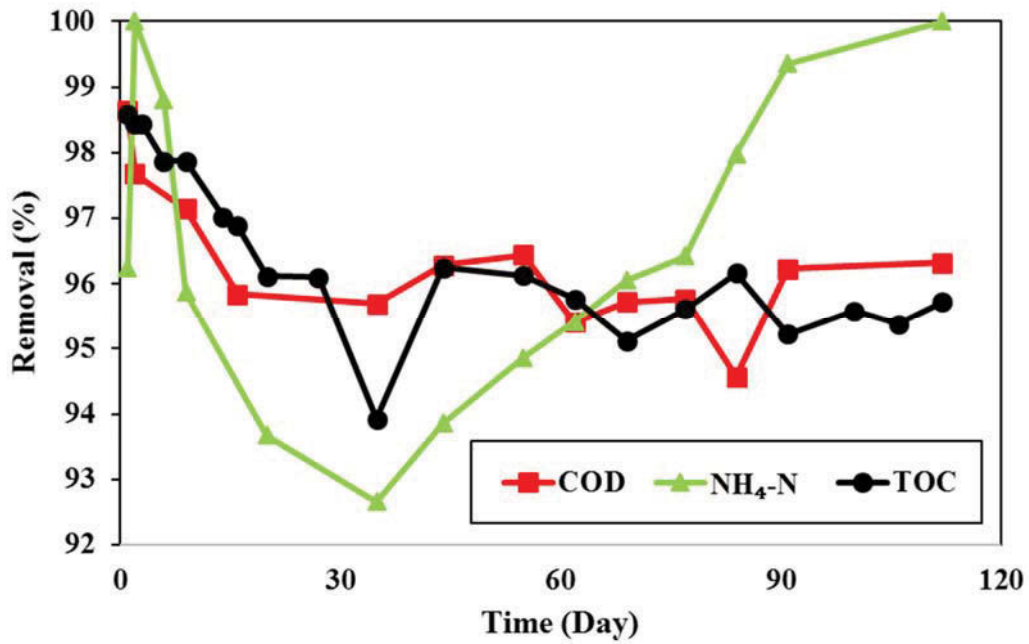
Figure 4.10 Removal of COD and nutrients by MBR-GAC hybrid system (Membrane area: 0.01m², Volume of the reactor: 10L, HRT: 1.04 h, Flux: 20 L/m²h)
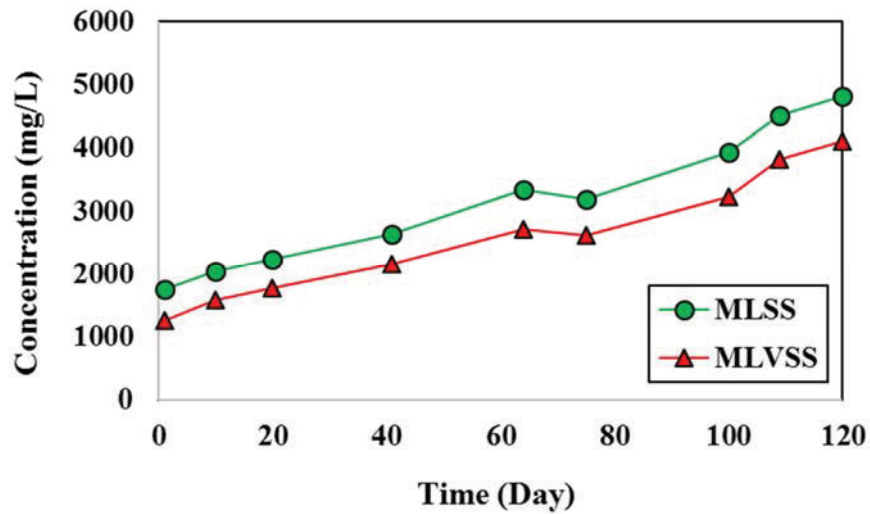
Figure 4.11 Concentration of MLSS and MLVSS with time (Flux: 20 L/m²h)

4.2.3.4 Post Treatment with membrane distillation

The performance of DCMD was evaluated as post treatment to polish the water for high quailty waster reuse. As can be seen in **Figure 4.12**, DCMD could also to be operated a very high flux of 40L/m²h without any flux decline even after a VCF of 2.75. The inorganics was removed more than 99%.
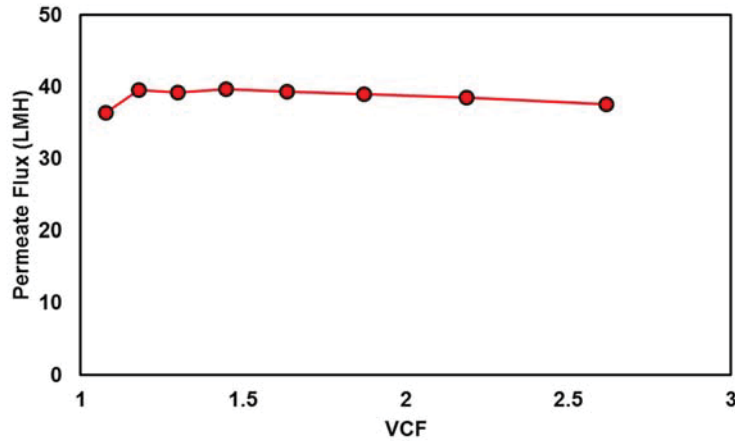
Figure 4.12 MD performance

4.3 MBR-PAC hybrid system in the treatment of real ROC

4.3.1 Background

The addition of powder activated carbon (PAC) in MBR (MBR-PAC hybrid system) has been found to alleviate organic and biological fouling. The addition of PAC into MBR tends to adsorb organic matter prior to their entry to membranes. The addition of PAC can also reduce foulant deposition on the membrane surface and pores and change the cake layer structure (Li et al., 2005). It has also been reported that regular addition of PAC to MBR could accomplish proper fouling mitigation in MBR (Fang et al., 2006).

The main objective in this study was to evaluate the influence of PAC as absorbent on fouling mitigation in hybrid MBR system. Real ROC from a wastewater reclamation plant.

4.3.2   Experimental Details

Wastewater: The ROC samples collected from a full-scale reclamation plant located in Sydney, Australia was used as feed water. The operating conditions of a laboratory scale submerged MBR system used in this study is presented in **Table 3.11.** The characteristics of real ROC is given in **Table 3.2**.

PAC as absorbent: PAC was used as an adsorbent to study the removal of DOC in a submerged MBR. The details of the PAC is given in **Table 3.7** in **Chapter 3**.

MBR-PAC hybrid system: The schematic configuration of MBR-PAC hybrid system is shown in Error! Reference source not found. **(Chapter 3)**. In this experiment, the real ROC was fed to the membrane reactor. Continuous aeration was provided by air diffuser to provide oxygen for biological reaction. The aeration also provided scouring effect on the membrane surface and helped to keep PAC in suspension. A predetermined amount (10 g) of PAC was added at the start of the MBR-PAC system, and then a daily addition of 0.5 g of PAC was made into the reactor for 10 days. The other details of MBR system were discussed in **Chapter 3, section 3.3.1**.

Post-treatment of MD: The effluent of MBR-PAC hybrid system was sent through the DCMD. The DCMD was used to remove the persisting organics and inorganics. DCMD set-up consists of the membrane module, feed and permeate tank, heater unit, stirrer, gear pump, cooling unit, temperature sensor, electronic mass balance and so on. The permeate flux was calculated based on the weight difference with time using an electronic mass balance. The other specific details regarding DCMD set-up is presented in **section 3.3.3** in **Chapter 3**.

4.3.3   Result and discussion

MBR experiment was also conducted with the periodic addition of PAC. PAC was added in the reactor after 14 days of MBR operation in order to complete the MBR results without and with PAC addition.

4.3.3.1 TOC removal efficiency

Figure 4.13 presents the TOC removal profile in MBR-PAC hybrid system. It was found that PAC addition enhanced organics removal. When real ROC was fed into the reactor, the removal of TOC in the MBR without PAC addition was only 21%. When PAC was added in the MBR, TOC removal increased rapidly and reached up to 91 %. The improvement of TOC removal was due to the adsorption of organic on PAC. The addition of PAC was mostly responsible for the improved filtration performance in the MBR system by modifying the sludge characteristics and the cake layer on the membrane surface (Jamal Khan et al., 2012). In long-term operation, PAC gradually integrated into the biofloc to form biologically activated carbon (Aun Ng et al., 2006). Thus, the addition of PAC in the MBR led to a superior organic removal by a combination of bio flocculation and adsorption phenomena.
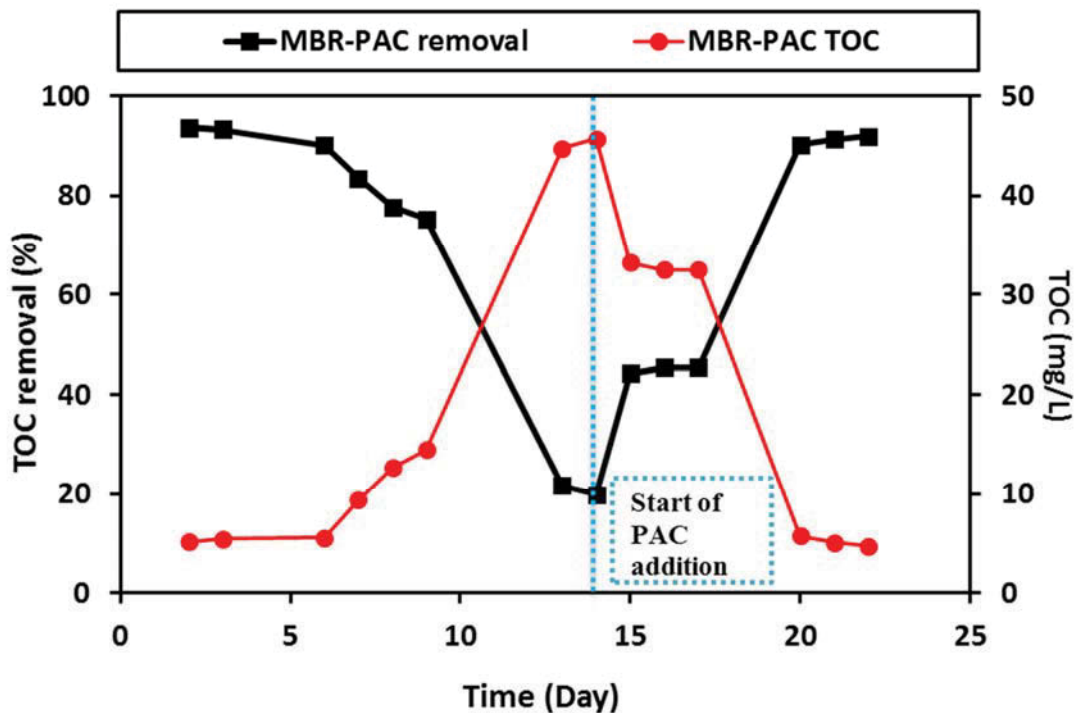
Figure 4.13 Profile of TOC removal before and after PAC addition in MBR (Membrane area: 0.01m², Volume of the reactor: 10L, HRT: 1.04 h, Flux: 20 L/m²h)

4.3.3.2 Effect of PAC in DOC removal

Table 4.5 presents the change in removal efficiency before and after the addition of PAC. DOC was further fractionated into various organic fractions using LC-OCD. In LC-OCD chromatography,

the peaks are divided into (i) biopolymers having 30-40 min of retention time, (ii) humic substance having around 40-53 min of retention time, (iii) building blocks having around 52 min of retention time after humic substance, (iv) low molecular weight acids whose retention time is round 55 min and (v) low molecular weight neutrals having around 60 min retention time or later (Huber et al., 2011). These results show that only 23 % of DOC was removed by MBR alone while MBR-PAC hybrid system could achieve a removal of DOC of 84.7 %. It was noted that all hydrophobic organic matter was removed (100%) by MF-PAC hybrid system. The hydrophilic fraction of feed water was 93.3 %. 83.6 % of hydrophilic fraction was removed by MBR-PAC hybrid system. The results of removal of different hydrophilic compounds are presented in **Table 4.5.** The removal of the biopolymers, humics, building blocks and neutrals were as high as 93.3 %, 79.5 %, 83.5 % and 91.1 %, respectively. Interestingly, this result revealed that the MBR-PAC hybrid system rejected most of the biopolymers. The biopolymer fraction of wastewater represents a significant fraction of protein which is also an indicator of microbial activity (Drewes and Croue, 2002). Fang showed 22% reduction of membrane cake resistance by the addition of PAC (Fang et al., 2006). Li also reported a 44 % reduction of membrane resistance with the addition of PAC (Li et al., 2005).

Table 4.5 Removal of a different fraction of organic matter by MBR and MBR-PAC hybrid system (Membrane area: 0.01m², Volume of the reactor: 10L, HRT: 1.04 h, Flux: 20 L/m²h)

	DOC	Hydrophobic. (ppb-c)	Hydrophilic. (ppb-c)	BIO-polymers	Humics Subst.	Building Blocks	LMW Neutrals
Real ROC	29277	1960	27317	1041	14641	4901	6734
MBR[*1]	22672	737	21935	713	13894	3867	3462
MBR-PAC[*2]	4482	0	4482	70	3007	806	599
Removal efficiency by MBR(%)	23	62	20	31	5	21	49
Removal efficiency by MBR-PAC (%)	84.7	100.0	83.6	93.3	79.5	83.5	91.1

*1 Effluent sample was affected on day

*2 Effluent sample was affected on day

4.3.3.3 Post-treatment of MD

Direct contact membrane distillation was used as post treatment to MBR effluent to study the removal of inorganics. The flux decline in DCMD was only from 23 to 19 L/m²h due to the MBR pretrement of ROC. The lower flux decline in DCMD was observed even after a volume concetnration factor (VCF) of 5. Without the MBR pretretment it reduced to less than 15 L/m²h. The inorganics removal was more than 99 %.
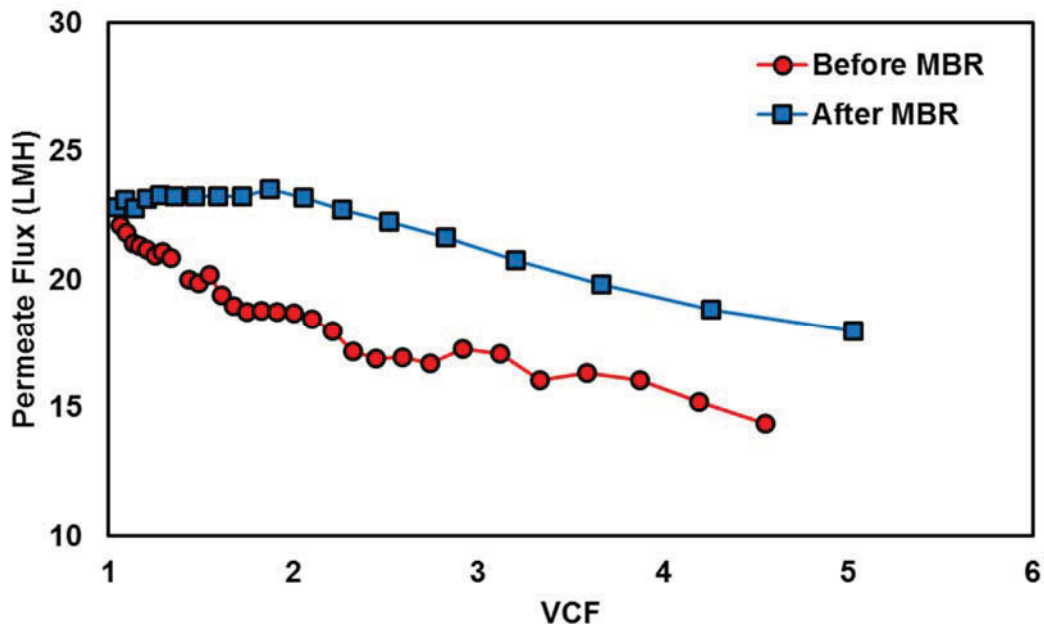
Figure 4.14 Effect of post-treatment on permeate flux of MD (feed temperature: 60°C, permeate temperature: 20°C, permeate flow rate: 0.5 L/min, initial feed volume: 2 L)

4.4 Hybrid system as post treatment to effluent from MBR used in domestic wastewater treatment (Low strength wastewater)

4.4.1 Background

Water shortage is becoming an important issue in particular in countries in the Middle East, North Africa and South-East Asia (Norton-Brandão et al., 2013). Global population growth, rapid urbanization and industrialization have induced massive consumption of water resources and produce polluted water, which affects the waterways. Moreover, demand for water is supposed to increase by

about 44 % by 2050 according to population growth and urbanization for the cost (UN-Water/United Nations University/UNIDO 2014).

Therefore, water treatment technologies for providing safe and sufficient water are promptly required. Wastewater reclamation is not only a suitable way to solve the problem, but also essential to meet the more restrictive standard of discharge. If secondary effluents directly enter the water body, it can cause aggravation of water quality and eutrophication of lakes and rivers. Therefore, improved removal of pollutants from secondary effluent has become a pressing issue. To enhance the quality of reuse water and to reduce potential environmental impact, post-treatment system is highly advised.

Up to date, technological alternatives such as advanced oxidation processes, membrane filtration and activated carbon adsorption are being studied in wastewater treatment plants. GAC and PAC are used as adsorbents in post-treatment systems to remove organic matters by adsorption without the creation of transformation products. The use of biological filters has been suggested as they have several advantages such as small foot-print, energy input, improved effluent quality and minimising the presence of transformation products (Lee et al., 2012). In this context, biofilters provide in-situ bio-regeneration due to the biological transformation of the pollutants previously adsorbed on the filter media, thereby increasing its lifespan (Çeçen and Aktas, 2011). Previous studies found that GAC adsorption is useful in removing total organic carbon (TOC) from wastewater (Gur-Reznik et al., 2008).

Thus, the objective of this section was to study the performance of GAC biofilters and MF membrane-GAC adsorption hybrid system as post-treatment to secondary effluents (in this case MBR effluent) in removing remaining organics and PPCPs.

4.4.2   Experimental Details

Wastewater: In this study, MBR effluent from a decentralized wastewater treatment located in Sydney was used. The average turbidity, pH and dissolved organic carbon (DOC) values of the MBR effluent were 0.0141 NTU, 7.26 and about 8 mg/L respectively. Detailed characteristics of the MBR effluent are presented in **Chapter 3, Table 3.4**.

Biofilter: The parameters that can affect the performance of a biofilter are the characteristics of the filter medium, hydraulic retention time, organic loading rate, etc. The economic and efficient operation of biofilter depends on the characteristics of the filter media. The widely used filter media is GAC along with other filter media such as sand, anthracite, zeolite, purolite etc. Furthermore, previous research showed that GAC could give better removal of organic substance than anthracite or sand (LeChevallier et al., 1992, Paredes et al., 2016). In this study, the biofilter column was packed with GAC purchased from James cumming & Sons P/L, Sydney, Australia. The physical characteristics of GAC is summarized in **Table 3.6**. In this study, of the effect of GAC bed height (10 and 40 cm) along with two different filtration velocities (1.79 m/h and 3.58 m/h) was studied on the removal of organic matter. Long-term GAC biofilter column experiments were conducted. The experiments continued from 21 to 55 days to study the long-term effect of adsoprtoin/biosorption. The experimental set-up is described in **Figure 3.4** in **Chapter 3**. To keep a constant filtration rate in the system, a pump was used, and the effluent was collected at the top port of the column.

MF-membrane-GAC adsorption hybrid system (MAHS): MAHS is another effective system in removing trace organics from MBR effluent. The schematic diagram of MF-GAC hybrid system is shown in **Figure 3.3** in **Chapter 3**. This set-up had 10 L of the influent tank with a hollow fiber membrane module. A hollow fiber membrane composed of Polysulfone, Polyethersulfone, Polyvinylidene Fluoride was used for this study. The properties of the hollow fiber membrane are given in **Table 3.8** in **Chapter 3**. The membrane reactor tank was continually fed with MBR effluent (taken from an MBR plant in Sydney) at a constant rate with a peristaltic pump. The 20 g of GAC was added into the membrane reactor once only at the beginning of the experiment. The flux of MBR was kept at 20 L/m²h by peristaltic pumps. Air flow was supplied, which provided scouring on the membrane surface. This also maintained the GAC particles in suspension in the reactor. The air also provided oxygen for possible biodegradation of organics.

Batch adsorption studies: A batch adsorption equilibrium experiment was conducted to decide on the optimum dose of GAC to treat feed water. Different doses of GAC (0-5 g/L) were placed in 200 mL of feed water (MBR effluent) in different beakers and equilibrated for 48h at 23±1 °C. Continuous shaking

by a shaker (Ratel Platform Mixer) at 120rpm was provided. At the end of the experiments, supernatant samples were collected and filtered through a 0.45µm filter for DOC analysis.

4.4.3 Results and Discussion

4.4.3.1 Batch adsorption-experiments

A batch adsorption equilibrium experiment test was conducted before conducting the biofilter experiments. The predetermined amount of GAC was put into the feed water (MBR effluent) and mixed for 48 hours at 23±1 °C to estimate the adsorption capacity of GAC. **Figure 4.15** presents the TOC removal at different GAC dose. As anticipated, an increased amount of adsorbent dose improved the removal efficiency of TOC owing to a larger surface area available. It was formed that 100 % of TOC was removed when a GAC dose was 1 g/L or more.
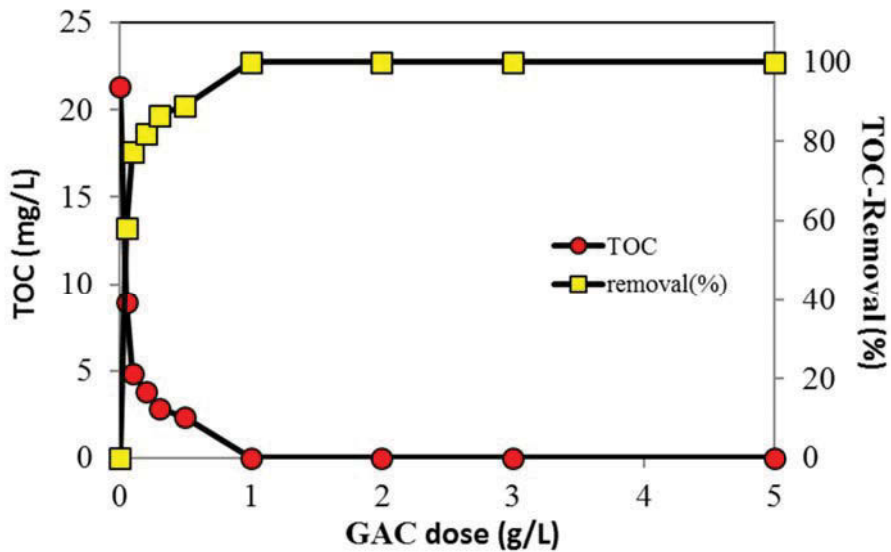
Figure 4.15 The performance of GAC on the removal of TOC (Feed: MBR effluent)
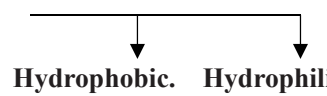
4.4.3.2   Up-flow GAC adsorption column as biofilter

4.4.3.2.1   Effect of GAC height

Organic matter removal: The DOC concentration of the MBR effluent was 8.39 mg/L. From the fractionation of organic matter, it was found that a majority of the organic matter was hydrophilic (90%) in nature with a small amount of hydrophobic fraction (9.9%). This result is in accordance with the previous studies (Jarusutthirak et al., 2002). They also observed high proportion of hydrophilic compounds in secondary effluent. The DOC was fractionated into the following five major components according to molecular weight: (1) Biopolymers whose molecular weight is more than 20000g/mol. Biopolymers represent polysaccharides, proteins and sugars. (2) Humic substances whose molecular weight is less than 1000 g/mol. The humic substance is comprised of humic acids and fulvic acids. (3) Building blocks whose molecular weight is in the range of 300 – 500 g/mol. Building blocks are the breakdown products or hydrolysates of humics. (4) Low molecular weight (LMW) neutrals whose molecular weights are less than 350 g/mol. LMW neutrals are accountable for the mono and oligosaccharides, alcohols, aldehydes and ketones. (5) LMW acids that are organic acids with molecular weights also less than 350 g/mol. In this study, the fractionation of organic matter was done using LC-OCD for the effluent from the GAC column with bed height of 10 and 40 cm as presented in **Table 4.6** and **Table 4.7**. These tables also include the data collected at different times of filter run (after 2, 14 and 21 days from 10 cm column and after 6, 13, 20, 35 and 44 days from 40 cm column). Both biofilters were operated at the same velocity. It can be seen from this results that both biofilters removed the majority of the DOC at the early stage of the experiment, 2 and 6 day, respectively. Both hydrophobic and hydrophilic fractions from tertiary wastewater effluent were removed as observed by Gur-Reznik et al. (2008). As experiment time goes by, the removal efficiency of DOC started decreasing. Notably, the removal of DOC by the biofilter with bed height of 10 cm showed a sharper decline of DOC removal (from 93 % to 24 %) than the biofilter with the bed height of 40 cm. A long-term result shown in **Table 4.7** indicated a majority of hydrophobic were removed by biofilter with the bed height of 40 cm during the whole experimental period (96-84%).
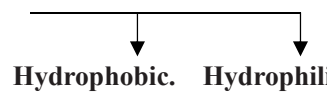
a)   10 cm

Table 4.6 Organic fraction by biofilter with a GAC height 10 cm with the velocity of 1.79m/h

Day	DOC	Hydrophobic. (ppb-c)	Hydrophilic. (ppb-c)	BIO-polymers	Humics Substances.	Building Blocks	LMW Neutrals
MBR effluent	8393	831	7563	60	5580	523	1399
2	611 (93%)	28 (97%)	583 (92%)	29 (52%)	373 (93%)	67 (87%)	114 (92%)
14	5638 (33%)	246 (70%)	5392 (29%)	38 (37%)	3949 (29%)	546 (-)	860 (39%)
21	6372 (24%)	353 (58%)	6019 (20%)	62 (-)	4251 (24%)	679 (-)	1028 (27%)

b) 40 cm

Table 4.7 Organic fraction by biofilter with a GAC height 40 cm with the velocity of 1.79m/h

Day	DOC	Hydrophobic. (ppb-c)	Hydrophilic. (ppb-c)	BIO-polymers	Humics Substances.	Building Blocks	LMW Neutrals
MBR effluent	8393	831	7563	60	5580	523	1399
6	443 (95%)	-	443 (94%)	35 (42%)	262 (95%)	31 (94%)	116 (92%)
13	1695 (80%)	32 (96%)	1664 (78%)	95 (-)	1286 (77%)	92 (82%)	191 (86%)
20	2997 (64%)	20 (98%)	2977 (61%)	95 (-)	2381 (57%)	204 (61%)	297 (79%)
35	4609	132	4477	111	3598	256	513

	(45%)	(84%)	(41%)	(-)	(36%)	(51%)	(63%)
44	4964	95	4869	54	3698	478	639
	(41%)	(89%)	(36%)	(10%)	(34%)	(9%)	(54%)

4.4.3.2.2   Effect of filtration velocity

In this study, two different filtration velocities were applied in the biofilter. **Figure 4.16** presents the DOC removal profile of GAC biofilters operated at 1.79 m/h and 3.58 m/h. The EBCT was 13.41 min and 6.70 min for filtration velocities of 1.79 and 3.58 m/h, respectively. The EBCT can the calculated using the **Equation 4.1**.

EBCT=Bed height (m)/ linear velocity (m/h) -- Equation 4.1

Doubling the velocity means that twice the amount of water passed through the column. Earlier research showed that organic removal performance does not considerably vary within a small range of EBCT (Hozalski et al., 1995). They reported the effect of organic removal in sand biofilters with EBCT ranging between 4 and 20 min for water treatment and found the minimal influence of EBCT on organic removal. However, in this study, higher DOC removal efficiency was observed by biofilter operated at a lower filtration velocity of 1.79 m/h. Initially, the biofilter operated at lower filtration velocity removed 95 % of DOC (**Table 4.7**). The lower filtration velocity is more efficient in removing DOC whereas the higher filtration velocity resulted in poorer removal of DOC which decreased with time (form 75 to 21 %) (**Table 4.8** and **Figure 4.16**). At high filtration velocity, adsorption capacity was inadequate because of lower residence or contact time in the up-flow contactor.
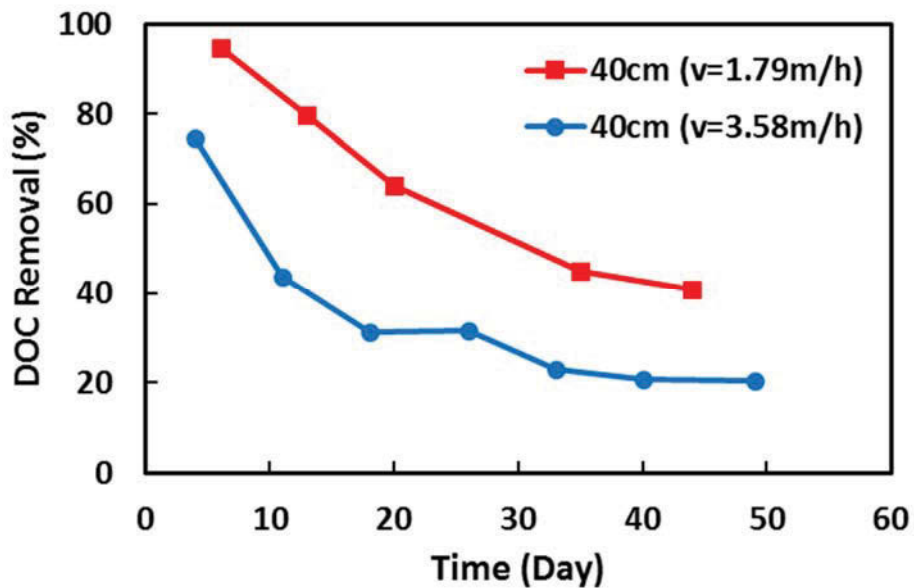
Figure 4.16 Removal of dissolved organic carbon (DOC) by GAC filter (Bed: 40cm, Filtration velocity: 1.79 and 3.58 m/h)

Table 4.8 Fractionation of organic present in the effluent of GAC filter (Bed: 40 cm; filtration velocity: 3.58 m/h)

Day	DOC	Hydrophobic. (ppb-c)	Hydrophilic. (ppb-c)	BIO- polymers	Humics Substances.	Building Blocks	LMW Neutrals
MBR effluent	8393	831	7563	60	5580	523	1399
4	2128 (75%)	-	2128 (72%)	99	1728 (69%)	107 (79%)	193 (86%)
11	4711 (44%)	-	4711 (38%)	89	3953 (29%)	263 (50%)	407 (71%)
18	5766 (31%)	9 (99%)	5757 (24%)	59 (2%)	4762 (15%)	377 (28%)	559 (60%)
26	5746 (32%)	192 (77%)	5554 (27%)	49 (18%)	4182 (25%)	494 (6%)	829 (41%)

33	6450	361	6089	40	4573	573	904
	(23%)	(57%)	(19%)	(33%)	(18%)	(-)	(35%)
40	6639	384	6255	23	4490	717	1025
	(21%)	(54%)	(17%)	(62%)	(20%)	(-)	(27%)
49	6668	384	6285	27	4512	678	1068
	(21%)	(54%)	(17%)	(56%)	(19%)	(-)	(24%)

4.4.3.3   Membrane-adsorption hybrid system

In this study, MBR-adsorbent hybrid system was operated with the addition of GAC as support medium in suspension to remove the remaining organics.

4.4.3.3.1   Trans-membrane pressure (TMP) development

Submerged membrane adsorption hybrid system (SMAHS) experiments were conducted with the addition GAC of 20 g at the beginning of the experiment. The feed was MBR effluent. The reactor had a volume of 10 L. Thus, the GAC dose was 2 g/L of the volume of the reactor. During the first 5 days, a complete TOC removal was observed. This was due to adsorption as a main mechanism of organics by GAC. In addition, there was an increase of TMP (6.2 to 9.13 kPa) over the first 2 days of the operation (**Figure 4.23**). However, there was no or minimum development of TMP after the first 2 days of operation. It was due to the pre-adsorption of organics onto GAC particles before their contact with the membrane surface. GAC particles provided extra scouring to the membrane surface during circulation of GAC in the reactor. The additional scouring by GAC particles could hinder the accumulation of the cake layer on the membrane surface. This was the reason why there was no TMP development till 118 days of operation. The previous study showed a similar pattern that an increases of PAC dose reduced TMP development even when membrane hybrid system was operated at high filtration flux 48 L/m²h (Vigneswaran et al., 2007). Also, membrane hybrid system with the addition of GAC demonstrated the 85% reduction in TMP development as compared to the membrane with no GAC system (Pradhan et al., 2012).

4.4.3.3.2   Removal of trace organics – Pharmaceuticals and personal care products (PPCPs)

The presence of pharmaceuticals and personal care products (PPCPs) in the effluent of wastewater treatment plants have then documented by many researchers (Lin et al., 2014). The reduction of these PPCPs by the use of conventional treatment processes is ineffective (Westerhoff et al., 2005) while GAC has been found to be effective in the removal of PPCPs (Snyder et al., 2007). Biofilter has been demonstrated to be effective for PPCPs removal (Zuehlke et al., 2007, Meffe et al., 2010, Zearley and Summers, 2012). The performance of PPCPs removal by pilot-scale biofilter was evaluated (McKie et al., 2016). In comparison to conventional dual-media filtration, biofiltration systems with and without the addition of coagulant enhanced the PPCP removal from 13 % to 39% and 70%, respectively.

PPCPs are normally found in wastewater effluent, and MBR does not remove them. Activated carbon has been found as an effective treatment process in removing PPCPs from treated effluents. GAC achieved 90-98% PPCP removal with ozone treatment (Ek et al., 2014). GAC filtration can efficiently eliminate the PPCPs with high hydrophobicity (Huerta-Fontela et al., 2011). Lin et al (2014) studied the existence and removal of 39 PPCPs in a water treatment plant installed with ozonation and GAC filtration. 14 of the PPCPs found in the raw water were absolutely removed by the advanced water treatment plant. Paredes et al (2016) evaluated the removal efficiency of secondary effluent by sand and GAC biofilter. Several reactors were used to determine the contributions of adsorption and biotransformation to the removal of several PPCPs.

Selected PPCPs in the MBR effluent and post-treatment of biofilters are presented in **Figure 4.17**. Eleven PPCPs compounds were detected in the primary effluent of MBR in **Table 3.5**. After MBR treatment, a majority of PPCPs were reduced to less than 300 ng/L. The MAHS as post-treatment to MBR removed most of the compounds from MBR effluent except for benzotriazole, diclofenac and salicylic acid. The post-treatment of biofilter also removed all of them except for only two compounds, which were bisphenol A and salicylic acid. Biological treatment achieved notable removal of bisphenol A, but the removal of bisphenol A by GAC filter was limited.
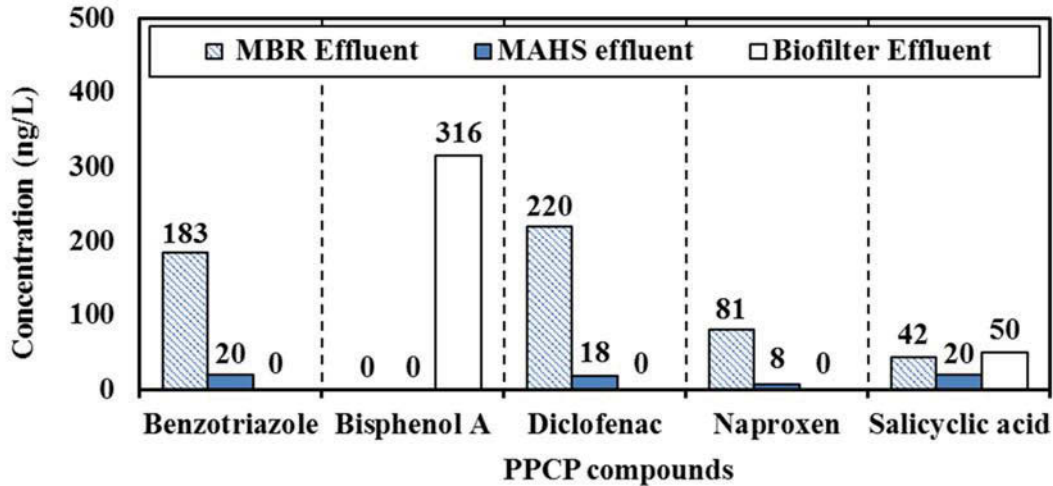
Figure 4.17 The comparison of PPCP compounds of MBR, MAHS effluent and biofilter effluent

4.4.3.3.3 Organic, ammonia and nitrate removal

The COD removal by the post-treatment of biofilter and membrane adsorption hybrid system (MAHS) is presented in **Figure 4.18**. Biofilters showed better COD removal than MAHS at the beginning of experiment during 6 days. Although all biofilters showed the higher removal of COD at the early stage of operation, the removal of COD drastically dropped after 6 days. Biofilter equipped with 10 cm height of GAC showed a COD removal of up to 78.9% at the initial stage, and the COD removal dropped drastically. On the other hand, biofilter operated at a velocity of 1.79 m/h and height of 40 cm declined gently. MAHS resulted in a COD removal from 68 % at an early stage and almost 35 % removal from 30 days to the end of the operation (120 days) (**Figure 4.18**).

The TOC removal of biofilters and MAHS is given in **Figure 4.19.** Biofilter packed with GAC with bed height of 40 cm and filtration velocity of 1.79 m/h showed almost 100% TOC removal for 9 days. The TOC removal with biofilter with a bed height of 10 cm dropped sharply from 72 % to 23 %. The lower removal of TOC could be due to the low EBCT. This time was not sufficient for the microorganism to assimilate the nutrients.

The biofilters and MBR-GAC hybrid system showed high ammonia removal throughout the experiment (**Figure 4.20**). Even though the GAC biofilter column with the height of 40 cm and velocity

of 3.58 m/h alone did not remove the ammonia at the beginning, the removal efficiency increased steadily up to 100 %. Only the MBR-GAC hybrid system led to the removal of nitrate (**Figure 4.21**).
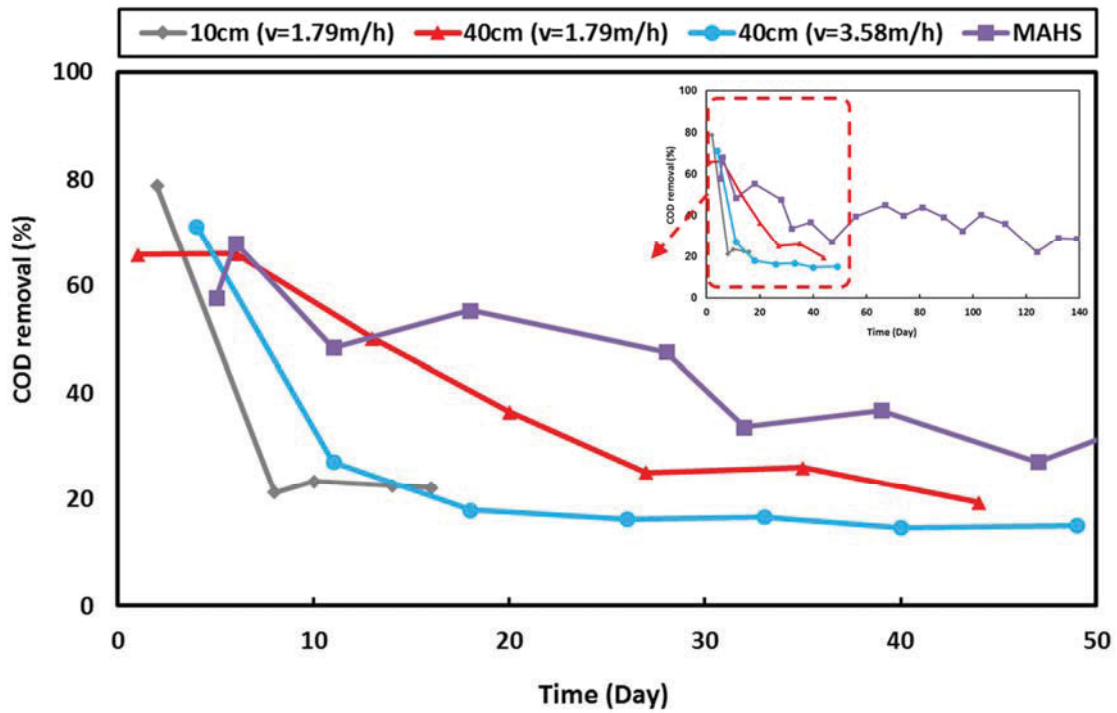
Figure 4.18 Removal of COD with biofilters and MAHS (Bed: 10 and 40 cm, Filtration velocity: 1.79 and 3.58m/h, Membrane area: 0.01m², Volume of the reactor: 10L, HRT: 1.04 h, Flux: 20 L/m²h)
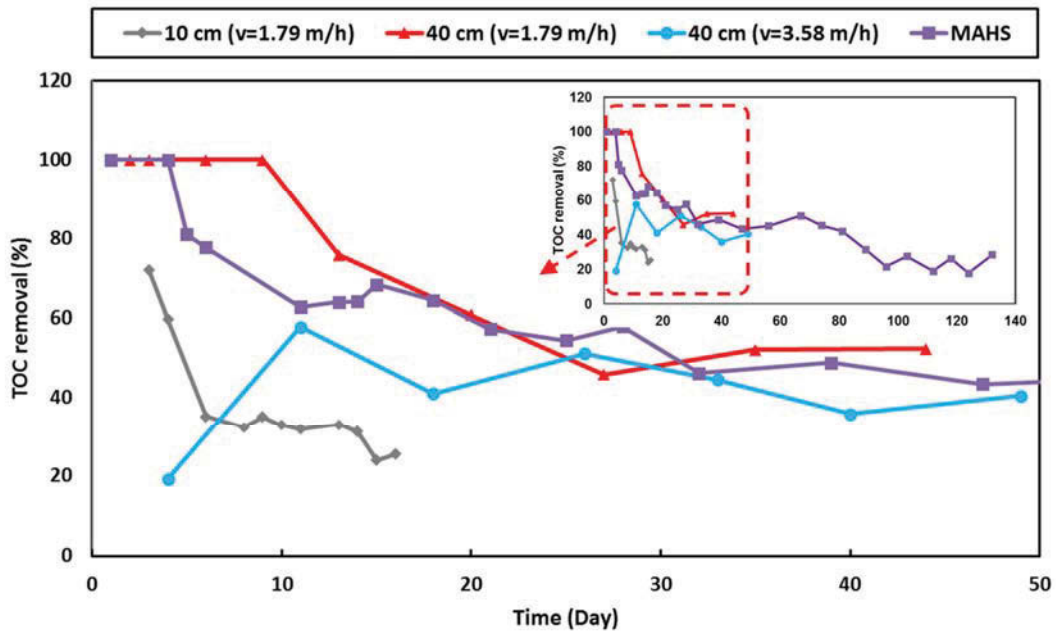
Figure 4.19 Removal of TOC with biofilters and MAHS (Bed: 10 and 40 cm, Filtration velocity: 1.79 and 3.58 m/h, Membrane area: 0.01m², Volume of the reactor: 10L, HRT: 1.04 h, Flux: 20 L/m²h)
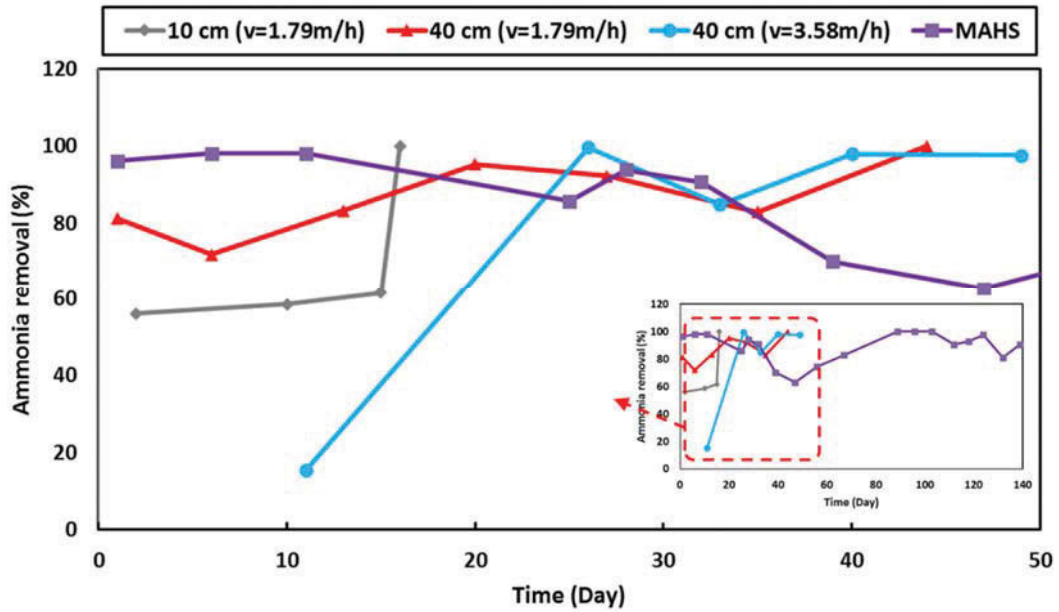
Figure 4.20 Removal of ammonia by biofilters and membrane adsorption hybrid system as post-treatment (MAHS) (Bed: 10 and 40 cm, Filtration velocity: 1.79 and 3.58m/h, Membrane area: 0.01m², Volume of the reactor: 10L, HRT: 1.04 h, Flux: 20 L/m²h)
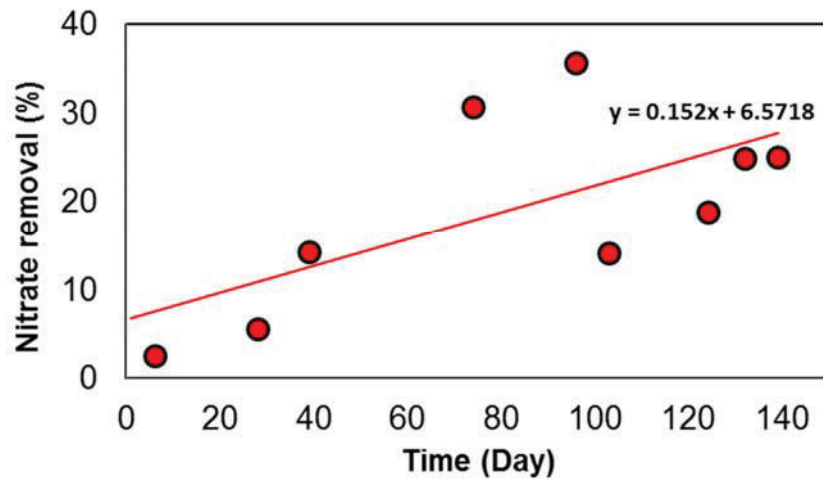
Figure 4.21 Removal of Nitrate by MAHS (Membrane area: 0.01m², Volume of the reactor: 10L, HRT: 1.04 h, Flux: 20 L/m²h)

4.4.3.3.4   MLSS and MLVSS

The MLSS and MLVSS concentration with the MAHS are presented in **Figure 4.22**. The MLSS and MLVSS concentrations were 410-650 and 330-480 mg/L, respectively. Even though the MLSS concentration is usually high in MBR system, MLSS was found to the low in MAHS treating MBR effluent as in the cases of previous studies (Kawasaki et al., 2011); (Janga et al., 2007). Low MLSS led to lower TMP removal (**Figure 4.23**) in this study. Higher MLSS concentration can induce operational problems such as rapid blocking of the membrane. High MLSS concentrations can increase the sludge viscosity and also influence the oxygen transfer efficiency (Germain and Stephenson, 2005).
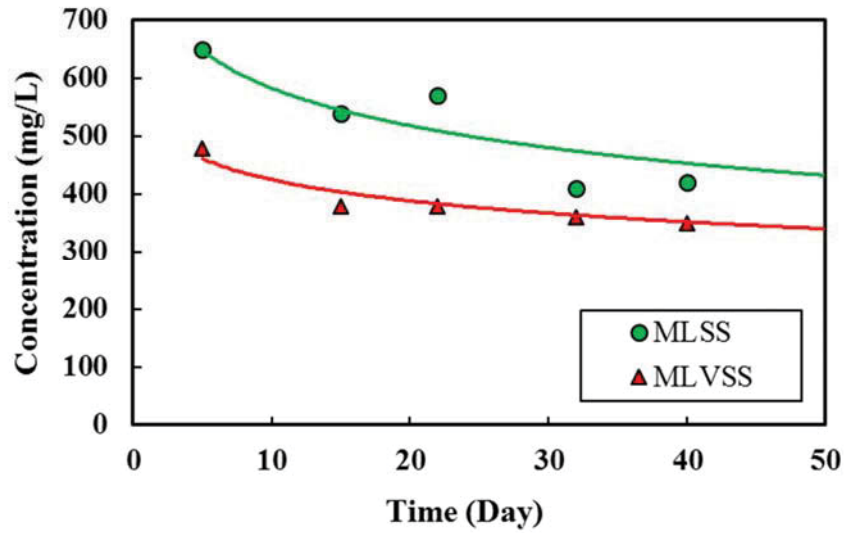
Figure 4.22 MLSS and MLVSS in MAHS (Membrane area: 0.01m², Volume of the reactor: 10L, HRT: 1.04 h, Flux: 20 L/m²h)
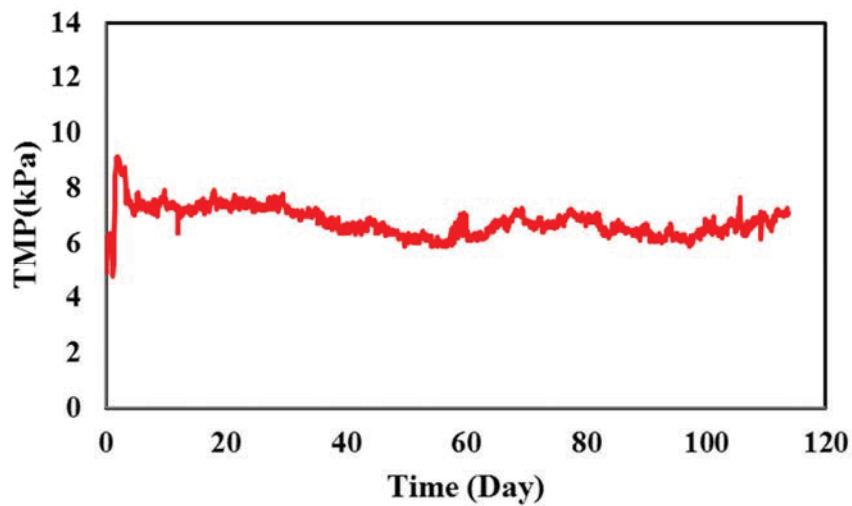
Figure 4.23 The effect of GAC on the development TMP in MAHS (Membrane area: 0.01m², Volume of the reactor: 10L, HRT: 1.04 h, Flux: 20 L/m²h)

4.4.3.3.5   Post-treatment of MD performance

A few experiments were conducted membrane distillation (MD) as post-treatment to MAHS and biofilter. The purpose of this experiment was to remove the remaining non-biodegradable inorganic ions present.

The performance of MD as post-treatment was examined in terms of initial permeate flux and volume concentration factor (VCF) as shown in **Figure 4.24**. The experimental result shows that the initial patterns of permeate flux are similar. The flux decline causes membrane fouling which depends on the composition of the feed water and hydrodynamic condition. In this study, hydrodynamic condition was maintained the same. Therefore, flux decline was mainly due to the feed water quality. The reduction in permeate flux with MAHS effluent was found to be much lower. This phenomenon can be explained in terms of DOC. The inorganic was removed more than 99%.
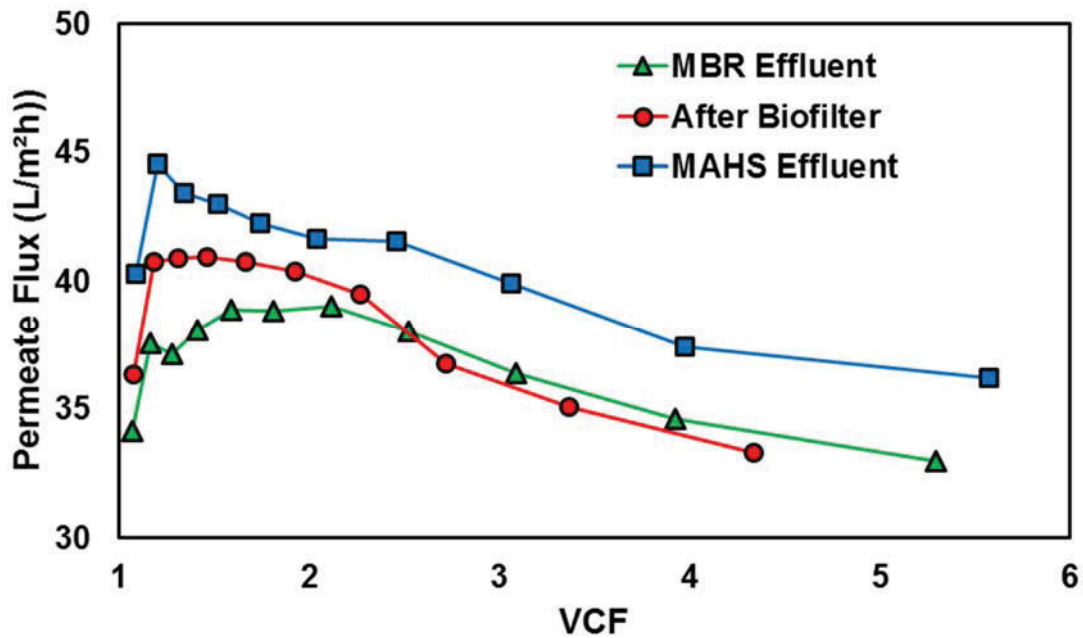
Figure 4.24 Effect of post-treatment of differently treated effluents (feed temperature: 60°C, permeate temperature: 20°C, permeate flow rate: 0.5 L/min, initial feed volume: 2 L), membrane adsorption hybrid system (MAHS)

Chapter 5

5   Conclusions and recommendations

5.1   Summary of the major findings of this study

This chapter summarizes the finding of the research articulated in Chapter 4. Although membrane bioreactor (MBR) is a promising technology, it suffers from the problem of microbial and organic attachment on the membrane surface, which causes membrane biofouling. This deteriorates membrane performance and increases overall operational costs. Thus, sustainable methods to reduce fouling and to remove undesirable materials such as organic matters are essential.

This study aimed to treat the reverse osmosis concentrate from a wastewater reclamation plant. This method was compared with post-treatment (MD) and MBR-adsorption hybrid systems. The effect of chemical backwashing with NO was studied in detail. Backwashing with Nitric oxide (NO) delayed the formation of new biofilm on the membrane. Also, NO does not have any adverse effect on activated sludge and environment. The incorporation of GAC in MBR helped to reduce membrane fouling. Also, the MBR-GAC hybrid system demonstrated the removal of PPCPs. The more specific experimental findings are described below.

MBR operation with synthetic ROC wastewater (high strength wastewater)

Chemical cleaning of membranes with sodium hypochlorite was performed to reduce biofouling. However, the application of sodium hypochlorite has negative impact on the structure of the membrane and activated sludge and therefore, it causes damage to the membranes and biological function of activated sludge (Lee et al., 2013). In this study, it was observed that the low concentration of NO reduced the growth of biofilms in an MBR system. NO treatment could also delayed the formation of new biofilm on the membrane as TMP development was low after backwash. This finding is in line with a previous study, where a 30 % reduction of total microbial biovolume was found when the biofilms were treated with PROLI NONOate (Barnes et al., 2013). The present results and previous research showed that NO could be used to reduce the growth of biofilm in MBR system, deferring the TMP jump and thereby allowing the operation of an MBR for a long period. Also, NO does not have any adverse effect on activated sludge and environment. The removal efficiency of organic matter continued to be good even after chemical backwash.

MBR GAC hybrid system in the treatment of high strength ROC

This study examined the effect of GAC in treating synthetic high strength wastewater. The addition of GAC into the MBR-GAC hybrid system controlled the TMP development to minimum. This is because of the mechanical scouring effect by GAC as well as by the pre-adsorption of organics before reaching the membrane surface. The addition of GAC in MBR was effective in removing DOC by 94% throughout the experimental period for 120 days.

MBR-GAC hybrid system was thus an effective system in reducing fouling and for treating ROC to remove dissolved organics before the discharge of the effluent into the water body safely. The treated effluent can also be recirculated and mixed with the ROC feed to maximize water reuse.

Biofilter and membrane adsorption hybrid system as post treatment in treating MBR effluent.

Membrane bioreactor treating domestic wastewater is nor effective in removing micro pollutants. Thus, post treatments such as biofilter with GAC and MBR-GAC hybrid system were investigated. The biofilter was effective in removing significant amount of organics which were not removed by MBR. Both systems had influence in additional organic removal. The addition of GAC into the MBR-GAC membrane hybrid system also removed significant amount of remaining organics and reduced TMP development. This implies that the addition of GAC extend the operation period of the MBR-GAC hybrid system due to supplementary mechanical scouring effect as well as the pre-adsorption of organics by GAC before reaching the membrane surface.

The MBR-GAC hybrid system removed PPCPs by 80-90%. Eleven compounds were detected in the MBR effluent. After the post treatment of MBR-GAC membrane hybrid system, the concentration of benzotriazole, diclofenac and Salicylic acid formed in MBR effluent furthers decreased to 18 - 20 ng/L. Also, biofilter with GAC showed good removal of PPCP from MBR effluent except for two compounds which are Bisphenol A and Salicylic acid.

Thus, both GAC biofilter and membrane-GAC adsorption hybrid system are efficient in treating secondary effluent to remove remaining dissolved organics and persisting organics from MBR effluent before its discharge into the environment.

5.2 Recommendations for future studies

The following recommendations are made further study:

- Future research is needed to explore highly efficient; low cost suspended media for the use as suspended media in the membrane reactor. The media chosen should not affect membrane life.

- Study on the impact of MBR effluents with the addition of suspended activated carbon needs to be explored further.

- Low-cost adsorbents with high adsorption capacity are needed to be developed for the removal of nutrients.

- The MBR-GAC hybrid system developed in this study for the removal of nutrient needs to be expanded and tested in pilot plant scale as it has the potential for the removal and recovery of nutrients.

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