MEMBRANE HYBRID SYSTEM IN HIGH QUALITY WATER REUSE

University of Technology, Sydney

SUKANYAH DEVAISY

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University of Technology, Sydney

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CERTIFICATE OF ORIGINAL 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 fully acknowledged within the text.

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

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JOUNRALS AND CONFERENCE PAPERS PRODUCED FROM THIS STUDY

Sukanyah Shanmuganathan, Tien Vinh Nguyen, Sanghyun Jeong, Jaya Kandasamy, Saravanamuthu Vigneswaran Submerged membrane – (GAC) adsorption hybrid system in reverse osmosis concentrate treatment. Separation and Purification Technology, 146 (2015) 8–14

Sukanyah Shanmuganathan, Mohammed A.H. Johir, Tien Vinh Nguyen, Jaya Kandasamy, Saravanamuthu Vigneswaran, Experimental evaluation of micro filtration-granular activated carbon (MF-GAC)/nano filter hybrid system in high quality water reuse. Journal of Membrane Science, 476 (2015) 1-9

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ABSTRACT

Although membrane filtration treatment for water reclamation is becoming more widespread, the challenges such as membrane fouling, high cost, management of concentrate, and incomplete removal of organic micro pollutants still prevail. This study presents technical alterations to minimize such issues via the development of pre-treatments techniques where fluidized bed contactors and membrane hybrid systems were used. Granular activated carbon (GAC) and an ion exchange resin (Purolite A502PS) were used as adsorbents for the above mentioned pre-treatments respectively. Biologically treated sewage effluent (BTSE) collected from a water reclamation plant, Sydney was used as a feed water for these experiments. The operational conditions such as fluidization velocity and adsorbent dosage of fluidized bed columns strongly influenced the removal of dissolved organics (DOC). GAC was found to be more effective in removing organics compared to Purolite A502PS. This could be due to the competition provided by other inorganic anions present in BTSE for Purolite exchange sites. Plug flow model was successfully used to predict the impact of the amount of adsorbent and of the flow rate on the removal of organic matter.

A similar trend was observed when another pre-treatment technology of membrane hybrid system was used. Micro filtration (MF) – GAC hybrid system effectively removed hydrophobic organics, hydrophilic organics and organic micro pollutants, whilst, the removal of inorganic ions was minimum. Comparatively, the performance of MF-Purolite hybrid system was less efficient in DOC removal; however the removal of sulfate and nitrate ions was good. In both membrane hybrid systems, the addition of adsorbents directly into the membrane reactor reduced membrane fouling by membrane surface scouring and adsorption. Overall, the performance of membrane-GAC adsorption hybrid system was more effective than membrane-ion exchange hybrid system. Based on this, MF-GAC was suggested to combine with nano filtration (NF) system. Here second membrane filtration of NF was to further polish pre-treated BTSE in terms of dissolved organics, organic micro pollutants and for some divalent ions removal. This treatment system is referred as ‘dual membrane hybrid system’ i.e., the combination of MF-GAC adsorption hybrid system followed by NF. Traditionally RO is used as a polishing step in dual membrane systems in waste water reclamation plants. The use of NF instead of RO is found to be cost effective in terms of energy requirements. This dual membrane hybrid system is suggested to produce high quality water reuse where the removal of monovalent ions is not necessary; however the selection of treatment system depends on the requirements of recycled water for end purposes. For example, the recycled water used for irrigation requires sodium adsorption ratio of 3-9 for wide range of salt tolerant crops. Therefore, a study was conducted to determine whether the BTSE can be treated using nanofiltration (NF) and reverse osmosis (RO) to bring these risk parameters within safety limits, because the NF treated BTSE could bring SAR levels only up to 14. As per the results, it was suggested to blend NF and RO permeate in equal proportions to produce a product quality suitable for irrigation with SAR value below 10. Utilizing NF prior to RO reduced the RO membrane fouling and both NF and RO removed most of the organic micro pollutants from BTSE and this may subsequently protect soil and ground water from potential hazards.

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ABBREVIATIONS

AC	Activated carbon
AER	Anion exchange resin
ANZECC	Australian and New Zealand Environment and Conservation Council
AOC	Assimilable organic carbon
ATP	Adenosine tri phosphate
BAC	Biological activated carbon
BOD	Biological oxygen demand
BTSE	Biologically treated sewage effluent
CEC	Critical Environmental concentrations
CFU	Colony forming unit
CMF	Continuous micro filtration
COD	Chemical oxygen demand
DBPs	Disinfection by products
DOC	Dissolved organic carbon
EC	Electric conductivity
EDCs	Endocrine distrupting compounds
EfOM	Effluent organic matter
EPA	Environmental protection agency
F-EEM	Fluorescence excitation emission matrices
FTIR	Fourier transform infrared spectroscopy
GAC	Granular activated carbon
HA	Humic acid
HRT	Hydraulic retention time
HSDM	Homogenous surface diffusion models
IER	Ion exchange resin
IMS	Integrated membrane systems
LC-OCD	Liquid chromatography organic carbon detection
LMW	Low molecular weight
LPRO	Low pressure reverse osmosis
MBR	Membrane bio reactor
MCC	Membrane correlation coefficient
MF	Micro filtration
MIEX	Magnetic ion exchange
MSFD	Multi-stage flash distiller
MW	Molecular weight
MWCO	Molecular weight cutoff
NF	Nano filtration
NOM	Natural organic matter
NSAIDs	Non-steroidal anti-inflammatory drugs
PAC	Powdered activated carbon
PhAC	Pharmaceutically active compounds

PPCPs	Pharmaceuticals and personal care products
RO	Reverse osmosis
ROC	Reverse osmosis concentrate
SAR	Sodium adsorption rate
SDI	Silt density index
SEM	Scanning electron microscope
SMPs	Soluble microbial products
SWRO	Sea water reverse osmosis
TDS	Total dissolved solids
TMP	Transmembrane pressure
TOC	Total organic carbon
TSS	Total suspended solids
UF	Ultra filtration
VOCs	Volatile organic compounds
WHO	World health organization
WRP	Water reclamation plant
WWTP	Wastewater treatment plant

CHAPTER 1

INTRODUCTION

Municipal wastewater reuse, reclamation and recycling are essential to the development of sound water and environment management policies. Wastewater reuse has become an attractive option for protecting the environment and extending available water resources. In the last few years there has been a significant diversification of water reuse practices, such as green space and crop irrigation, recreational impoundment, various urban uses including toilet flushing, industrial applications and water supply augmentation through groundwater or reservoir recharge (Lazarova et al. 2000; Xu et al. 2002).

1.1. Research background

Reclaimed water is becoming increasingly popular worldwide as a valuable water resource because sustainability has become critical. In terms of quantity recycled water is considered to be a reliable water resource because it provides a constant and reliable supply particularly from treated sewage effluent; however, the potential for fully exploiting recycled water is limited by its quality. The presence of contaminants such as microbial pathogens, dissolved organics, persisting organics such as pharmaceuticals and personal care products (PPCPs), heavy metals, high salinity, various inorganics, etc., limits the wide range of reuse applications. For example, water with a high saline content is not suitable for irrigation because it compromises crop growth; the high level of persisting organics and heavy metals may accumulate in the environment and enter the food chain upon their discharge (Toze 2006). As such, proper treatment techniques are mandatory to remove such contaminants to make the water suitable for high quality water reuse.

Until the 1990s not one Australian city had an advanced sewage treatment strategy beyond secondary treatment. The combined treatment technologies of micro filtration (MF), activated carbon adsorption, reverse osmosis (RO), and biological nutrient removal resulted in rapid growth concerning the availability of high quality reclaimed water in the latter 1990s. Figure 1.1 summarises different economic sectors' water reuse, of which mining and agriculture are the most significant.

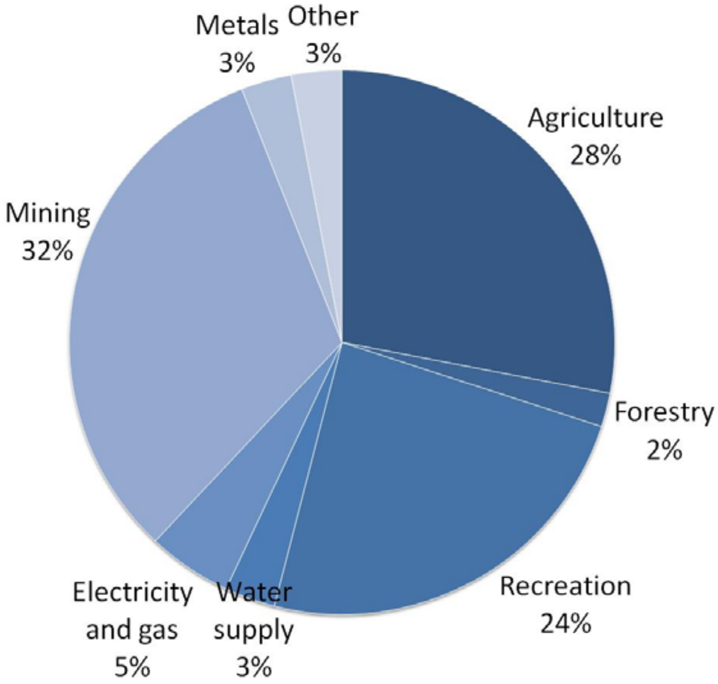


Figure 1.1: Reuse of effluent in Australia according to economic sector (Dilan 2000)

Many Australian businesses use integrated water treatment technologies because they are cost effective. Some examples are as follows (Australian Government, Dept. of Environment (2010).

- Inghams Enterprises has reduced its main water usage by 70% in its poultry processing business, and saved 545 ML a year.
- Amcor's cartonboard mill in Petrie, Queensland, has saved more than 1000 ML/annum and reduced drinking water use by 90%.
- Diageo Australia Limited, a beverage manufacturer, has achieved water savings of 43% at its Huntingwood site in Sydney and achieved an annual saving of 55.5 ML.
- The Rossdale Golf Club in Melbourne, Victoria has achieved an annual reduction of mains water usage of 35 ML, i.e. a reduction of 56% through water treatment and reuse.

Dual membrane treatment process: Several water reclamation plants currently operating all over the world have adapted dual membrane treatment processes where wastewater is passed through continuous micro filtration (CMF) followed by reverse osmosis (RO) (del Pino and Durham, 1999). Hundreds of RO-based reclamation plants are operating in Australia, Asia, Europe, Africa, and the United States, for example the Orange County plant in California (265 MLD) and three plants in Singapore (Bedok, Kranji and Changi, 2010). In Sydney alone two major water reclamation plants are using RO after firstly, micro filtration (Homebush Bay plant) (Chapman, 2006), and secondly, ultrafiltration (St. Marys water recycling plant) of biologically treated sewage effluent (BTSE) (Bleney, 2010). The resulting product from both plants is then used for irrigation and replenishing of Nepean River, respectively.

1.2. Rationale of the research

In water reclamation plants, the BTSE is commonly used as feed water for dual membrane systems. This can have a variable and at times high suspended solids load with a high proportion of colloidal material, organics and bacterial by-products. These constituents can cause membrane fouling and subsequently result in irreversible failure to the downstream RO system if they are not successfully removed during the pre-treatment stage (Durham et al. 2002). In this context, various pre-treatment techniques are used/tested prior to RO to minimize fouling issues.

Although RO produces water of good quality, the high capital and operating costs associated with this process often limits its wide application. In such cases, nanofiltration (NF) membranes are considered to be a good alternative for RO membranes in water reclamation because they have numerous advantages. NF can effectively reject microbial cells, even viruses, natural and persisting organics and its rejection ability approaches that of RO. The low operating pressure required for the NF process and less flux decline substantially reduces energy demands and could result in cost savings (Bellona et al. 2012). Utilizing NF (NF, 90-400) instead of RO (BW30LE-440) resulted in cost savings of \$53,000/year in a 100 m^3/h plant because costs were less for energy consumption, chemicals and concentrate disposal (Yangali-Quintanilla et al. 2010). The only disadvantage of NF is the insignificant amount of monovalent ions rejected. However, this is more relevant where either the presence of monovalent ions is not significant or their removal is not necessary. In order to ensure the long-term uninterrupted operation of NF with fewer cleaning cycles, this NF process has to be integrated with physico-chemical treatment, such as activated carbon adsorption or ion exchange resins. Doing so will help to create an integrated membrane system (IMS).

Depending on the end purpose of recycled water, the water quality of product water may vary. For example, in order to produce water for irrigation with the required levels of monovalent ions such as sodium and chloride ions, the incorporation of RO is vital. In such circumstances, rather than using RO alone, NF can be combined with RO. This provides a good treatment option in terms of quality and cost savings.

RO concentrate (ROC) is the by-product of the RO process that is rich in dissolved organics, persisting organic pollutants, inorganics, etc. The proper management and safe disposal of ROC is another issue in water reclamation practices. Applying cost effective simple pre-treatments such as activated carbon adsorption and ion exchange resins prior to the discharge of ROC can serve as an alternative method for minimizing the entry of toxic constituents into the natural environment.

1.3. Aim and Objectives

In order to maximize water reuse activities, a new membrane hybrid system was developed in this study. The aim was to produce high quality water from wastewater for reuse application that is free of persisting organics (i.e. pharmaceuticals and personal care products) in a cost effective way. The objectives are listed as follows:

i. Development and mathematical modelling of pre-treatments to treat feed water (BTSE) so that organic fouling problems occurring in the RO process are reduced. These pre-treatments were configured in the form of fluidized bed contactors and submerged membrane hybrid systems using granular activated carbon (GAC) and ion exchange resin (Purolite A502PS) as the adsorbents.

ii. Development of dual membrane hybrid system (combining submerged membrane-(GAC) adsorption hybrid system and nanofiltration (NF)) to produce high quality water for reuse where the removal of many monovalent ions is not necessary

iii. Combination of NF and RO membranes to produce water for reuse where removal of monovalent ions is necessary. The use of NF is also intended: (i) to reduce RO fouling; and (ii) to bypass the water going through RO.

iv. Developments of pre-treatment techniques applied to RO concentrate (brine or retentate) to ensure their safe disposal prior to discharge into the environment. The ROC forms 20-35% of water passing through RO.

1.4. Overview of the thesis

In order to meet the above objectives, the experimental work and results are organized into 9 chapters. A summary of each chapter is provided below.

Chapter 1: The introductory part of the research includes a description of the general background of the research problem, rationale, goals and objectives. The specific backgrounds are articulated in Chapters 4 to 8.

Chapter 2: This chapter provides a general review of membrane technology and its limitations (such as fouling, incomplete removal of persisting organics, high cost and energy requirements, and brine disposal). Previous studies on the application of remedial measures such as use of membrane hybrid systems as pre-treatments to RO, and, use of NF instead of RO in dual membrane hybrid systems, are also examined. The specific reviews these remedial measures are articulated in Chapters 4 to 8.

Chapter 3: Experimental materials and methodologies used to achieve the objectives are presented in this chapter. The chapter also provides details regarding how the advanced analytical instruments were used.

Chapter 4: This chapter evaluates the feasibility of using fluidized bed contactors packed with GAC and Purolite A502PS as a pre-treatment to NF/RO in terms of removing DOC, persisting organics and inorganics. The results are also discussed with reference to isotherm, homogenous surface diffusion models (HSDM) and plug flow models.

Chapter 5: The chapter proposes the use of submerged membrane-Purolite A502PS hybrid system as a pre-treatment to NF/RO membranes. The removal of dissolved organics by submerged membrane-Purolite A502PS hybrid system was studied for different doses, filtration fluxes and particles sizes of Purolite A502PS. The experimental results are validated with mathematical models.

Chapter 6: This chapter proposes a dual membrane hybrid system which contains a submerged membrane-GAC hybrid system (MF-GAC) and NF for high quality water reuse and free from persisting organics. Removing DOC and persisting organics via the MF-GAC hybrid system was studied using different conditions (doses and fluxes), and a optimum or ideal condition was chosen to produce influent for NF. This system is suitable for high quality water reuse where the removal of monovalent ions is not necessary.

Chapter 7: The chapter discusses the feasibility of using NF and RO membranes to produce high quality irrigation water that is suitable for sensitive crops. The purpose of combining NF and RO processes was to remove monovalent ions to a certain extent so that the required sodium adsorption ration (SAR) could be obtained for a wide range of crops, varying from very sensitive to salt tolerant crops. This system emerges as a suitable option to produce irrigation water of a suitable quality because it removes persisting organics cost effectively. This safeguards water resources from prolonged toxic outcomes. In fact NF reduces the RO fouling and minimizes the amount of water going through RO.

Chapter 8: This chapter presents two treatment techniques, namely membrane-hybrid system and fluidized bed contactors to remove organics and persisting organics from reverse osmosis concentrates (ROC) prior to its discharge into the environment. Consequently treatment systems can be installed on site to maximize water reuse activities and reduce the volumes of ROC discharged into the environment to prevent aquatic toxic damage.

Chapter 9: The final chapter presents the overall conclusions and recommendations of the study.

CHAPTER 2

LITERATURE REVIEW

This chapter reviews the current status of the membrane technology and physico-chemical treatments used to amend biologically treated sewage effluent (BTSE, also known as secondary effluent). They function to keep water free of organic micro pollutants and especially pharmaceuticals and personal care products (PPCPs). The issues pertaining to current membrane technologies (such as membrane fouling/scaling, incomplete removal of trace organics, high cost and energy, brine disposal, etc.) are discussed here. Reference is also made to the advanced technologies used today to overcome such issues such as application and optimization of feed water pre-treatments, application of membrane-hybrid systems, dual membrane hybrid system, etc., to improve the overall performance of membrane processes.

2.1. Water treatment and Reuse

Although wastewater represents a source of contamination, increasingly it is being considered as a source of reusable water (i.e. an alternative water source). The challenge of wastewater reuse is to eliminate pathogens and organic/inorganic micro pollutants that can damage or seriously compromise the health of living creatures and the environment (Jacob et al. 2010). The reuse and reclamation of BTSE has been increasingly emphasized as a strategy to solve water shortage issues (Shannon et al. 2008). However, the complex matrix of effluent organic matter (EfOM) present in the BTSE becomes problematic and reduces the effectiveness and eventually the end result is poor quality in water reuse.

Conventional municipal wastewater treatment plants treat their wastewater through 3 stages: the primary, secondary, and tertiary treatments. Primary treatment removes coarse and readily settleable particles (sand and grit). Secondary treatment involves biological treatment to remove oxygen-demanding organics. Tertiary treatment removes residual organics, inorganics and microbes. The challenges pertaining to conventional treatment plants are listed as follows (Ang et al. 2014):

i. Limited removal of toxins, pesticides, pharmaceutical residues, arsenic and herbicides from polluted water resources
ii. Vulnerability to micro-organism attack in the distribution systems of water treatment plants as a consequence of biological treatment
iii. Difficulties in eliminating water hardness. The extensive consumption of lime/acids produces large quantities of sludge
iv. Formation of disinfection by-products (DBPs) as a result of chlorination at the disinfection stage.

These major disadvantages of conventional treatment processes have driven researchers to search for alternative treatment technologies. In this context the recent developments in water research have resulted in breakthroughs in water treatment leading to the development of membrane technology. This is the leading widespread technology/process in water treatment today. The excellent separation capability of membrane processes can simply satisfy the required water quality for water reuse applications (Baek and Chang, 2009). The major advantages of membrane technology when compared with conventional filtration are less space and labor requirements, ease of process automation, more effective pathogen removal, etc. As per cost considerations, the membrane plants are 30-50% cheaper than the conventional treatment plants in terms of capital cost. The specific production costs of a simple (micro filtration/ultra filtration) membrane treatment are 5% less than for conventional process at a plant capacity of 30–300 m^3/h. The membrane plants may be cheaper when considering labor costs (Pianta et al. 2000).

2.2. Membrane technology in water reuse

Membrane processes are currently widely accepted and applied as a means of producing various qualities of water from surface water, ground water, brackish water and seawater (Nicolaisen, 2003). Membrane technology is also used in industrial wastewater treatment, and subsequently this has moved into the area of treating secondary and tertiary municipal wastewater and oil field produced water.

A membrane is defined as 'a semi permeable thin layer of material that is capable of separating materials as a function of their physical and chemical properties when a driving force is applied across the membrane' (Mallevialle et al. 1996, pg: 1.1) Membranes can be consist of organic polymers, metals, ceramics, layers of chemicals, liquids, and gases (Johns, 2000). Some materials used in the fabrication of membranes included cellulose, acetate, polypropylene, nylon, polyacronitrile (PA), polycarbonate, polyvinyl alcohol (PVA), and polyvinylidene fluoride (PVDF).

A membrane process usually splits a feed stream into a retentate (or concentrate) and a permeate fraction. Pressure-driven membranes use pressure difference between the feed and permeate side as the driving force to transport the solvent through the membrane. The degree of rejection of contaminants by the membrane is based on its properties such as pore size (Huang et al. 2009), shape, and charge (van der Bruggen et al. 2003). There are three common mechanisms that influence the separation process such as pore size (sieve effect), solution-diffusion mechanism, and electrostatic repulsion (Donnan effect). Membranes used in water treatment can be either porous or nonporous water-permeable polymeric films or ceramic matrices.

2.3. Classification of membranes

Membranes can be classified broadly into four types according to the separation mechanism, namely micro filtration (MF), ultra filtration (UF), nanofiltration (NF) and reverse osmosis (RO).

a. Micro filtration and Ultra filtration

MF can effectively remove suspended particles, organic colloids, turbidity and pathogens (Zularisam et al. 2006) whilst UF has slightly finer pores able to remove viruses, macromolecules, etc. MF and UF function at relatively low transmembrane pressure (TMP) of less than 2 bars (or 2.0 kPa), and as such are typically known as 'low pressure membranes' (LPM), requiring less energy (Huang et al. 2009). Pore sizes of low pressure membranes range from ~10 to 100 nm.

b. Nanofiltration and Reverse Osmosis

The pore size of NF membranes is smaller than that of UF, typically around 1nm, which corresponds to dissolved compounds with a molecular weight of about 300 Da. This makes NF suitable for removing relatively small organics, e.g. organic micro pollutants (active compounds and endocrine disrupting compounds) and colour from surface water or groundwater, and degradation products from the effluent of biologically treated wastewater, dissolved organics and multivalent ions (Mohammad et al. 2013). Since they have the ability to remove multivalent ions, the NF membranes have found useful applications in water softening since the 1990s (Ang et al. 2014).

Apart from size exclusion, NF membranes are capable of rejecting charged compounds/ions by electrostatic forces. Polymeric NF membranes contain ionizable groups, e.g. carboxylic or sulfonic acid groups, which results in a surface charge in the presence of a feed solution. The equilibrium between the charged membrane and the bulk solution is characterized by an electric potential, the Donnan potential, which retains ionic species. This mechanism (also known as 'Donnan exclusion') allows the removal of ions with a size below the pore size of the membrane. NF is an efficient system aiming to produce desirable quality of water for industrial, agricultural and indirect potable reuse applications from BTSE (Jacob et al. 2010). NF systems can provide a better quality of water compared to MF/UF.

RO was the first membrane process to be widely commercialized and it uses the concept of reversal of natural process of osmosis. This is a process by which water from a diluted solution stream passes through a semi-permeable membrane into a more concentrated solution. This RO is used to separate salts and low molecular weight compounds from water.

RO membranes are dense membranes without predefined pores. As a result, permeation is slower and rejection is not an outcome of sieving, but of a solution-diffusion mechanism. The low permeability of reverse osmosis membranes requires high pressure and, consequently, requires a lot of energy. This effect is even more pronounced in the presence of an osmotic pressure due to high concentrations of dissolved components that counteract the effect of the exerted pressure. Thus the membranes such as NF and

RO are known as ‘high pressure membranes’ (HPM) as they require high pressure typically 3-120 bar. However, NF requires low pressure and results in high fluxes compared to RO (Suksaroj et al. 2005).

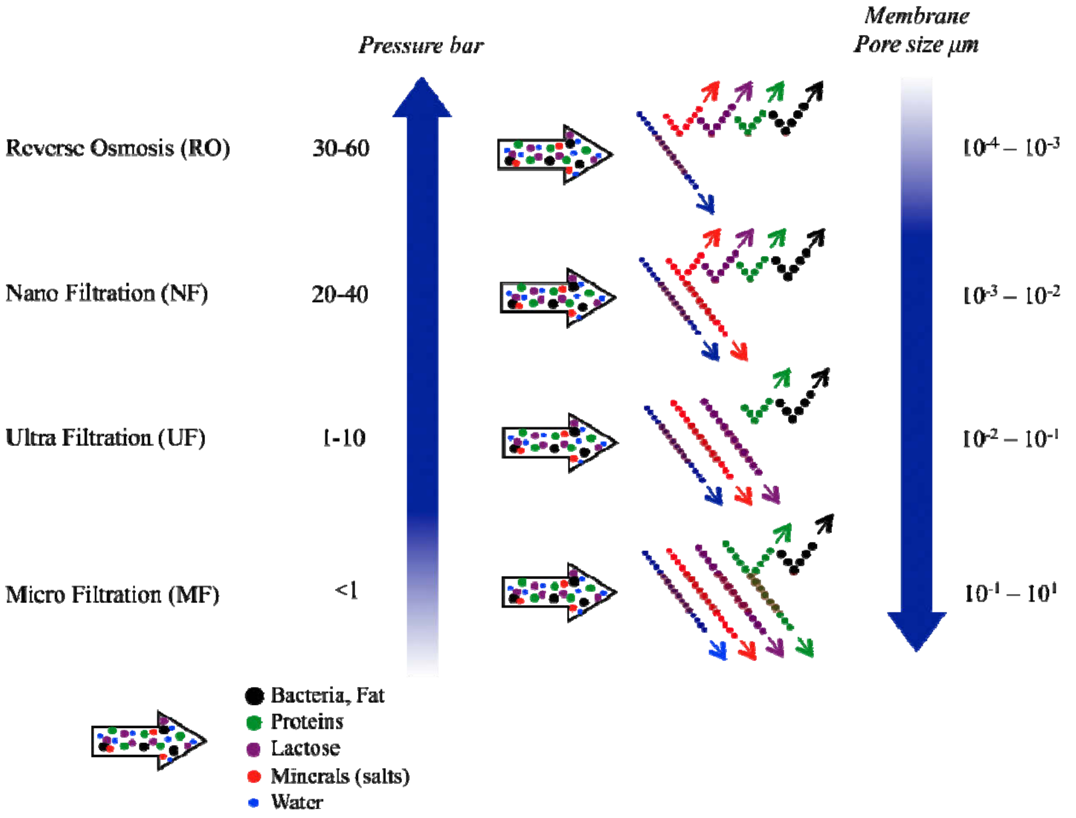


Figure 2.1: Principles of membrane filtration (Wu and Imai, 2012)

A major challenge for membrane technology is the inherent trade-offs between membrane selectivity and permeability and high energy consumption especially for pressure-driven membranes (Qu et al. 2013). An overview of the membranes processes, pore size, applied pressure, and rejection capability is illustrated in Table 2.1 below.

Table 2.1: Overview of pressure-driven membrane processes and their characteristics - adopted from van der Bruggen et al. (2003)

	MF	UF	NF	RO
Permeability (L/m^2.h.bar)	>1,000	10-1,000	1.5-30	0.05-1.5
Pressure (bar)	0.1-2	0.1-5	3-20	5-120
Pore size (nm)	100-10,000	2-100	0.5-2	<0.5
Rejection				
1. Monovalent ions	-	-	-	+
2. Multivalent ions	-	-	+	+
3. Small organic compounds	-	-	-/+	+
4. Macromolecules	-	+	+	+
5. Particles	+	+	+	+
Separation mechanism	Sieving	Sieving	Sieving/ Charge effects	Solution/ Diffusion
Applications	Clarification; pre-treatment; removal of bacteria	Removal of macromolecules, bacteria, viruses	Removal of (multivalent) ions and relatively small organics	Ultrapure water; desalination

Note: '+' denotes significant removal and '-' is insignificant removal

Membranes can be operated as either single or batch processes also in combination with other membranes depending on the quality requirements of the end product. Currently in many cases, one membrane process is followed by another aiming to create the product water of increasingly better quality for various purposes. Thus, one type of membrane may enhance the function of another to meet the goals of the end product ranging from safe disposal of wastewater to production of drinking water (Nicolaisen, 2003).

2.4. The equipment and system design configuration

As per the schematic diagram (Figure 2.2), when a fluid is placed under pressure on one side of a membrane, all material smaller than the pore size can pass through the membrane. This leaves large contaminants concentrated on the feed side of the process. A valve is placed on the concentrate line to maintain the pressure inside the module. The permeate is drawn off at a pressure P_p, nearly atmospheric pressure (P_a) (Johns, 2000). The transmembrane pressure (P_{tm}) is defined as:

$$P_{tm} = \frac{P_{in} - P_{out}}{P_p}$$

Where,

P_{in} = pressure at the inlet of the module

P_{out} = pressure at the outlet

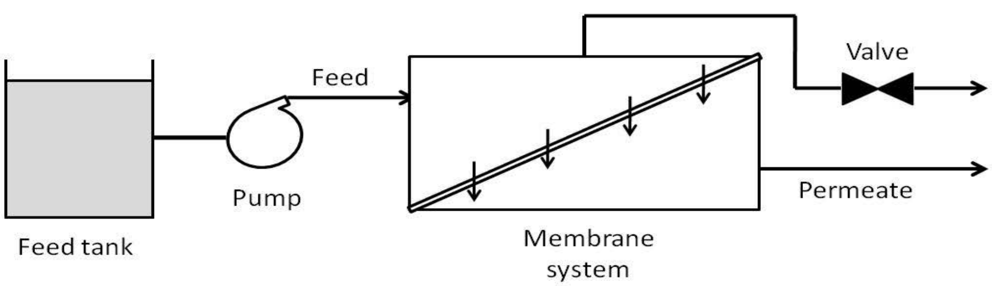


Figure 2.2: Basic schematic of membrane process (Johns, 2000)

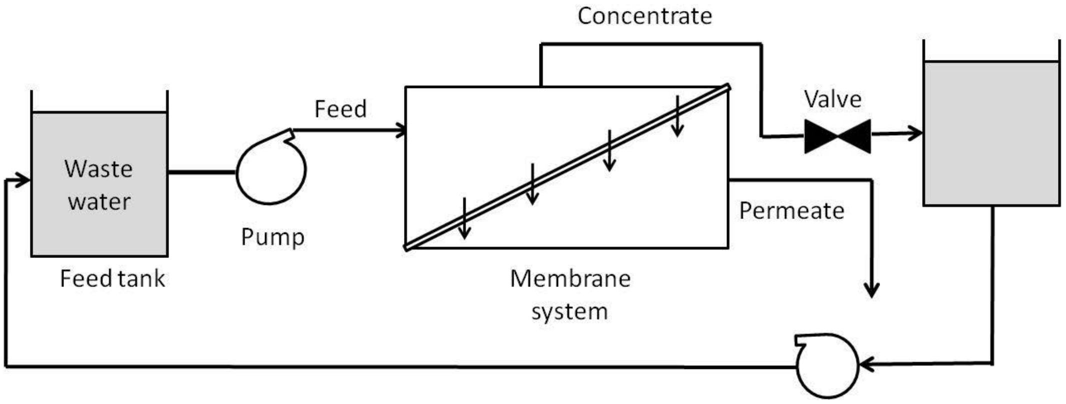
Full scale membrane facilities comprise series/parallel modules and operate accordingly to various modes. The systems range from intermittent single stage to continuous multistage systems. The generally used processing modes are batch and series (Figure 2.3), of which the batch process is generally more efficient and often used despite not being applicable to high solid levels. The series is the most expensive and generally used when a continuous constant composition product stream is required for permeate/concentrate.

The membrane process design and operation must focus on maximum recovery and rejection. Recovery is the percentage of permeate flow compared to the feed flow. The recovery can be increased when the number of membranes increases. If a single membrane element has recovery rate of 15%, the staged membrane system may increase the amount recovered to 90% (Johns, 2000). Rejection can be expressed as a percentage in the following way:

$$\text{Rejection (\%)} = \frac{\text{Feed concentration} - \text{Permeate concentration}}{\text{Feed concentration}}$$

Rejection may be as high as 95-99% for a membrane and is not affected by the staged system.

(a) Batch



(b) Series

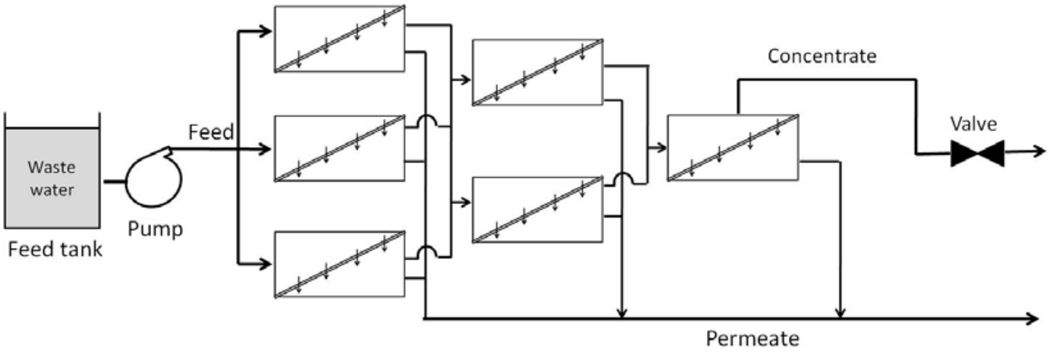


Figure 2.3: Different configurations of membrane (a) Batch (b) Series (Johns, 2000)

2.5. Challenges pertaining to membrane technology

MF and UF membranes have the capacity to remove large suspended particles, bacteria, etc., but do not have the ability to remove dissolved organic carbon and organic micro pollutants (Table 2.1). The only advantage associated with the MF/UF is the low cost. Pressure-driven membranes such as NF and RO have the capacity to remove dissolved organics and organic micro pollutants (especially PPCPs), however, it is still the case that some PPCP residues are detected in RO permeate. The major disadvantages associated with these techniques are the production of brine (concentrate/retenate), high pressure and cost. The challenges pertaining to membrane technology can be thus listed as follows (Naddeo et al. 2012):

a. Membrane fouling
b. Incomplete removal of pharmaceutically active compounds and endocrine disrupting compounds
c. Management and disposal of concentrate/retentate
d. High energy and cost

2.5.1. Membrane fouling

The application of membrane technology has been successfully implemented to produce treated water of recyclable quality (Shon et al. 2004a). However, the performance of this technology is affected by 'membrane fouling' which is often caused by: i) the high levels of effluent organic matter (EfOM) in BTSE (Qu et al. 2013; Park et al. 2006; Miao et al. 2014); ii) biological growth (biofouling); and iii) inorganic precipitates or particles (Kim and Dempsey, 2013).

Membrane fouling occurs due to the accumulation and deposition of the above mentioned substances such as organics/inorganics on the membrane surface and eventually they block membrane pores. This affects the performance of the membrane in terms of permeability and rejection of organics (Speth et al. 1998). The flux decline in the membrane filtration is linked to the formation of the gel layer/surface cake layer material on the membrane surface, formed by colloidal/particulates. This ultimately affects the membrane pore structure (Fan et al. 2001) and in extreme cases it can result in membrane failure (Zularisam et al. 2006).

Membrane fouling is governed by several factors such as natural organic matter (NOM) (including its size, hydrophobicity, charge), the properties of membrane (hydrophobicity, charge, surface roughness), the characteristics of feed solution (pH, ionic strength, hardness ion concentration especially calcium ions) and the hydrodynamics of the membrane system (solution flux, surface shear) (Taniguchi et al. 2003). In previous studies natural organic matter is found to be a major foulant that cause significant loss in membrane permeability (Yamamura et al. 2008; Yuan and Zydney 2000; Lee et al. 2006) and is the major limitation for the wide application of membrane technologies nowadays (Wintgens et al. 2005; Henderson et al. 2011). The challenges pertaining to fouling issues could be due to lack of knowledge on the characteristics of feedwater especially the organic and inorganic composition of EfOM in BTSE.

This BTSE represents a large group of structurally complex and heterogenous compounds derived from raw municipal water and bacterial metabolic activities in biological treatment stages (Zhao et al. 2010). Some of the major components of EfOM are identified such as humics, soluble microbial products, extracellular polymeric substances, lipids, organics and nucleic acids, etc. However, the total amount of EfOM identified only accounts for 15-20% of effluent organic carbon content (Zhao et al. 2010). The chemical composition of wastewater and BTSE water has been poorly studied so far (Nielsen et al. 1992). Moreover, the identified organics are smaller in size and present in colloidal and soluble form, and refractory which makes it difficult for subsequent treatments (Zhao et al. 2010).

2.5.1.1. Organic fouling on membrane surface

Many studies have focused on identifying the potential membrane foulants of EfOM in which the fractions of EfOM can be hydrophilic, hydrophobic and transphilic in character according to their functionality (Miao et al. 2014). Gray et al. (2007) found that the hydrophilic fractions of EfOM constituted the major foulant in MF membrane formed cake/gel layer on the membrane surface and subsequently led to rapid flux decline. The hydrophobic fractions showed a steady decline in flux and the formation of a gel/cake layer was not apparent.

A recent study concluding that membrane fouling was caused by hydrophilic fractions has received consideration attention (Yamamura et al. 2014). Hydrophilic fractions are composed of polysaccharides and proteins and the compounds' structure is rich in aliphatic carbons and hydroxyl groups (Ma et al. 2001). It has been found while comparing the Fourier transform infrared spectroscopy (FTIR) signals of clean and fouled membrane surfaces. The fouled membrane was covered with more polysaccharide substances (Kimura et al. 2004). Chemical analyses (excitation emission matrix (EEM and FTIR) confirmed that the substances such as protein-like, polysaccharide-like and humic-like substances are responsible for membrane fouling in the UF process (Zhou et al. 2014). The humic substances (humic and fulvic acids) are the major fraction of NOM comprising more than 50% of the dissolved organic carbon (DOC) that is mainly responsible for the colour in natural waters (Fan et al. 2001).

Xiao et al. (2013) investigated the membrane fouling using model foulants such as humics, bovine serum albumin (BSA) and sodium alginate as representative compounds of dissolved organic matter (DOMs) The adsorption of dissolved organics such as humic acid, fulvic acid and protein on the membrane surface is influenced by solution pH, ionic strength and calcium ions present in the feed water (Jones and O'Melia, 2000). Adsorption isotherm study (Jones and O'Melia, 2000) revealed the relationship between the adsorption of humics on the membrane as the function of solution pH. A continuous decrease in adsorption of humics and proteins was observed on the membrane with an increase in solution pH due to electrostatic interactions. Increased ionic strength shields some of the repulsive charges between the adsorbing molecules, resulting in increased adsorption.

In addition to organics, the presence of some inorganic ions was also collectively found to be aggravating the organic fouling. Combined membrane fouling (i.e. the organic fouling associated with inorganic ions) has been studied especially in NF membranes and reported that membrane fouling caused by the mixtures of different organic foulants/inorganic ions is more complex than an individual foulant (Lee et al. 2005; Li and Elimelech 2006).

2.5.1.2. Membrane Scaling

In addition to membrane (organic) fouling, another issue associated with membrane technology is ‘scaling’ which is due to the deposition of inorganic salts on the membrane surface. Scaling is frequently encountered in NF/RO desalination plants as they have the capacity to reject such inorganic anions from feed water. Scaling can form through two major mechanisms, such as ‘crystallization’ and ‘particulate fouling’, on the membrane surface. Crystallization occurs when the salt concentrations exceed their solubility limit, and the ions crystallize on the membrane surface (Ang et al. 2014). In the meantime particulate fouling occurs due to convective transportation of colloidal particulate matter from the bulk solution to the membrane surface (Guo et al. 2012).

Mostly, in pressure-driven membranes such as NF and RO systems, the dissolved inorganic salts 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 causes a permeate flux decline during constant operating conditions and it is mainly formed by the precipitation of salts such as $CaCO_3$, $CaSO_4$, silicates and barium sulfates (van de Lisdonk et al. 2000; Morillo et al. 2014) as these pressure-driven membranes retain such salts. The presence of especially the calcium ions in the feed solution was also found to cause irreversible fouling due to the aggregation of small molecules bound by calcium ions that formed larger complexes and often are deposited into the internal structures of the membrane (Zhou et al. 2014).

The higher the concentration of salt in feed water the greater the inorganic scaling which can possibly cause organic fouling to occur (Guo et al. 2012). Scaling mitigations normally in practice are alterations of feed water characteristics, addition of antiscalants or acid, optimization of operation parameters and design, etc. (Ang et al. 2014). Fouling and flux decline are two of the most important factors affecting membrane treatment process costs. As such the lifespan of the membrane is obviously related to the feed water characteristics, hydraulic conditions of operation and frequency of membrane cleaning, and membrane fouling (Gwon et al. 2003).

2.5.2. Incomplete removal of organic micro pollutants

The focus of environmental research has been recently extended beyond classical environmental organic micro pollutants, and now looks at pharmaceuticals and personal care products (PPCPs) which enter the environment mainly through domestic use (Ternes et al. 2004). Pharmaceuticals are mainly prescribed drugs and over-the-counter therapeutic drugs and veterinary drugs. Personal care products refer to products used for personal and cosmetic reasons such as soaps, fragrances, and cosmetics (see the US EPA website).

The organic micro pollutants 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 potential environmental risks in non-target species (Gunnarsson et al. 2008). The principle 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 main 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 (adopted from Pal et al. 2010).

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 and anti-		
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 can 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 in 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).

2.5.3. Concentrate disposal

Recently, the application of RO has grown as an alternative to conventional water treatment techniques due to its highly efficient removal capabilities. With the development of RO desalination, concern for potential environmental problems has grown. The production and discharge of a huge amount of concentrate is the major disadvantage of the RO process (Morillo et al. 2014). The RO concentrate produced in an RO plant as a by-product makes all the rejected contaminants by RO and comprised of concentrated stream 4-7 times larger than RO feed (Wang et al. 2013). The improper discharge of such reverse osmosis concentrate (ROC) may potentially cause human and ecological health problems because this may contain high concentrations of rejected compounds such as refractory substances and PPCPs. The discharge of RO concentrate in large quantities causes a considerable loss of water resources and damages the environment (Ge et al. 2014). As such, providing a ROC treatment prior to discharge is mandatory to ensure any potential health hazards to the environment and living creatures are circumvented (Radjenovic et al. 2011; Pérez-González et al. 2012).

For example an RO-based advanced water reclamation plant was planned for construction in Canberra, Australia in 2007. However, the sustainable management of ROC remains a major environmental and economic hurdle for the plant and has limited the implementation of the membrane process (Umar et al. 2013). In Queensland, Australia, the Bundamba advanced wastewater treatment plant which is part of Australia’s largest water recycling scheme is required to treat its ROC and monitor the nutrients and metal concentration in the effluent prior to its discharge into Brisbane River (Vargas and Buchanan, 2011). The installation of proper systems for the treatment and management of ROC produced from inland water treatment plants is mandatory in order to safeguard the ecology of receiving water bodies.

Concentrate disposal is normally considered to be a major issue in the engineering design of any desalination facility (Ahmed et al. 2001). For a typical brackish water desalination plant, the cost of brine disposal incurs an additional 15% of the total cost of desalination for an inland desalination compared to plants disposing brine into the sea (Glueckstern and Priel, 1997).

2.5.4. High cost and energy

Over the years, costs associated with desalinated water production have decreased as technological advances emerged (Khawaji et al. 2008). Of the four types of membrane processes ranging from MF to RO, the reverse osmosis (RO) system remains costly mainly due to energy consumption and membrane replacements.

Water desalination cost varies with the type of feed water used (Karagiannis and Soldatos, 2008). According to US Congress (1988), the RO unit cost ranged from \$0.32 - \$0.44 for brackish water whilst it was \$1.57 to \$3.55 for seawater, which is ten times more concentrated than brackish water in terms of contaminants being present. The application of MF/UF pre-treatment will reduce RO operating costs due to less fouling potential and longer membrane life (Vedavyasan, 2007). According to Durham (1997), the installation of MF pre-treatment has resulted in a 40% reduction in the size of the RO plant installed.

In order to overcome these issues associated with the membrane technology discussed above, most of the wastewater treatment plants adapt various types of pre-treatments. The pre-treatment can significantly alter the quality of feed water, i.e. by reducing the level of contaminants in raw water to a certain extent. In this way fouling can be reduced, the removal of contaminants can be maximized and cost and energy can be maintained at an affordable level. A wealth of published scientific studies is available and ongoing in this particular area.

As such, the factor which influences the challenges discussed above is the feed water quality. Most of the wastewater treatment plants use BTSE as the first feed water for the membrane process in water reuse applications. Therefore, knowledge and expertise regarding the feed water quality of BTSE (especially organics and trace organics) must be thorough. Some work done in this area is discussed in subsequent sections.

2.6. Characteristics of BTSE

The biological treatment significantly alters the characteristics of sewage effluent and reduces DOC from approximately 56-60mg/L to 4.8-11mg/L (Guo et al. 2011). The majority of this DOC left in the BTSE is refractory organics which are resistant to biological degradation. BTSE contains a complex mixture of organic materials known as Effluent Organic Matter (EfOM) which mainly consists of: 1) refractory organics; 2) trace levels of synthetic organic compounds produced during disinfection processesp; and 3) soluble microbial products (SMPs) derived during the biological treatment process of wastewater (Guo et al. 2011; Shon et al. 2006a).

EfOM in BTSE is mostly found in soluble form (86% of the chemical oxygen demand) (Shon et al. 2006a; Shon et al. 2006b) and these soluble/dissolved organics (DOC) are always difficult to remove (Guo et al. 2011). A (SEC) UV chromatogram of BTSE showed several sub peaks in the range of 500–3000 Da. Stronger absorbance appeared at MW of 650 Da, 1000 Da, 1700 Da, and 2000 Da, demonstrating the presence of humic-like refractory substances. The weaker absorbance appeared at MW < 500 Da and MW > 10,000 Da shows the presence of high MW organics and SMPs, respectively (Guo et al. 2011).

The presence of EfOM not only affects the current discharge standards of BTSE, but also becomes a main constraint to wastewater reuse (Jarusutthirak and Amy, 2006). The summary of organic constituents of BTSE below is largely based on the work done by Shon et al. (2006b).

i. Extracellular polymeric substances and soluble microbial products

This kind of organic matter is produced from bacterial metabolism during biological treatment and generally released during cell lysis, and diffusion through cell membrane/excretion (Barker and Stuckey, 1999). These products constitute the majority of the effluent COD (Shon et al. 2006b).

ii. Proteins

Protein is a complex structure and major constituent of living organisms and can decompose easily. Some forms of protein are soluble and others are not. Proteins contain carbon, hydrogen and nitrogen which is about 16% of protein. Urea and proteins are the main sources of protein in BTSE (Shon et al. 2006b). The organic nitrogen resulting to form nitrogenous DBPs is a potential cause of health problems (Bolto et al. 2004).

iii. Carbohydrates

Carbohydrates include starch, cellulose, sugars, etc. which can be degraded by enzymes of some bacteria and produce alcohols and carbon dioxide (Shon et al. 2006b).

Carbohydrates provide a carbon source for microbes, and these are important for an effective biological treatment. However, such compounds are found to be major foulants in membrane processes (Jarusutthirak et al. 2002).

iv. Fat, oil and grease (fog)

These can be measured as fatty acids and their elimination during the biological treatment stage is 98-100%.

v. Surfactants

Surfactants normally lower the surface tension of a liquid and thus generally permit easier spreading. These are made up of organic compounds consisting of hydrophobic and hydrophilic groups and are known to be significant pollutants.

vi. Endocrine-disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs)

EDCs and PPCPs are found in trace amounts (µg-ng per Litre) in the aquatic environment and also known as trace organics which are considered to be potential threats to ecosystems. An EDC has been defined by the Organization of Economic and Cooperative Development (OECD), as "an exogenous substance or mixture that alters the function(s) of the endocrine systems and consequently causes adverse health effects in an intact organism, or its progeny or (sub) populations" (Lister and Van Der Kraak, 2001, pg: 176). EDCs can be pesticides, persistent organochlorines and organohalogens, heavy metals, phytoestrogens, synthetic and natural hormones, etc. (Daughton and Ternes, 1999). PPCPs are mainly medications used by humans and animals and these include a wide range of chemical contaminants originate from human use and excretion, veterinary applications of a variety of products, such as prescribed or non-prescribed medications, disinfectants, etc. The PPCPs found in an aquatic environment are analgesics, anti-inflammatory drugs, antibiotics, antiepileptic drugs, beta-blockers, blood lipid regulators, etc. (Daughton and Ternes, 1999). Pharmaceuticals are designed to be biologically active and may affect non-target organisms (Ying et al. 2004). The molecular weight of PPCPs ranges from 200 - 500 to 1000 Da.

Of the pharmaceuticals, non-steroidal anti-inflammatory drugs (NSAIDs), anticonvulsants, lipid regulators and antibiotics are considered to be a potential group of environmental contaminants as these are often detected in aquatic environments. These NSAIDs are drugs with analgesic, antipyretic and anti-inflammatory effects, and drugs such as ibuprofen and doclofenac fall into this category. Anticonvulsants such as carbamazepine which is used in the treatment of epileptic seizures are often found in municipal sewage effluent. Lipid regulators such as gemfibrozil are used to lower the lipid levels in blood. Antibiotics are employed to treat infectious diseases and these include penicillins, tetracyclines, sulfonamides, and fluoroquinolones (Virkutyte et al. 2010).

Pharmaceuticals compounds are complex molecules and are developed and used due to their specific biological activity (Kümmerer, 2009). The pharmaceuticals taken by humans or other organisms are not completely metabolized by their body and residues can be excreted via urine and faeces as unchanged parent compounds, and as metobolites. Effluent from municipal WWTPs is the main source of discharging such compounds into the environment.

Toxicity experiments with a mixture of NSAIDs showed that combined toxicity of pharmaceuticals are much higher than the single compound due to synergistic effects (Cleuvers, 2004). Pharmaceuticals usually occur in aquatic environments as mixtures (Virkutyte et al. 2010).

Lee et al. (2011) studied the chronic effect of pharmaceuticals on fresh water crustaceans and on fish, in which both species were exposed to diclofenac for up to 3 months. There is a marked decrease in reproduction observed at 25 mg/L for *Daphnia magna*, whilst it was 50 mg/L for *Moina macrocopa*. A long-term (3 months) exposure of diclofenac at 25mg/L on *Daphnia magna* significantly reduced reproduction. Another study (Nassef et al. 2010) revealed that adult Japanese medaka fish (*Oryzias latipes*) exposed to a mixture of PPCPs (composed of carbamazepine, dicofenac, triclosan) for 9 days affected their feeding behavior and altered the swimming speed.

2.7. Operation and configurations of Membranes

The use of membrane processes in water treatment can be broadly configured and operated as stand-alone membrane processes and integrated membrane processes (Ang et al. 2014).

2.7.1. Stand-alone membrane processes

Stand-alone membrane processes are simple in that they only involved treating/filtering water through membranes such as MF/UF/NF/RO. However, stand-alone membranes may not be feasible for producing adequate quality of drinking water as recommended by WHO. This has led to the concept of integrated/hybrid membrane processes.

2.7.2. Integrated/membrane Hybrid processes

Integrated/hybrid membrane processes refer to an application of pre-treatment (such as adsorption, coagulation, ion exchange, membrane filtration, etc.) prior to the membrane process (Ang et al. 2014). The main idea behind this integrated system is to reduce the organic loading of raw water to minimize the subsequent organic fouling as well as to enhance the removal of contaminants.

2.7.2.1. Pre-treatment: Conventional treatments

The application of conventional treatment techniques coupled with membrane technologies would benefit the uninterrupted smooth operation of membrane processes. Integrating different treatment strategies with membrane filtration in water treatment is a very important trend for improving the performance of membranes. Pre-treatment is commonly used for two major reasons: firstly, to enhance the removal efficiency of micro-pollutants and DBPs precursors; and secondly, to reduce membrane fouling (Huang et al. 2009).

a. Conventional treatment technologies

The advantages and disadvantages of several conventional treatments associated with membrane processes are summarized as follows (Table 2.3).

Table 2.3: Mechanisms, effects, advantages and disadvantages of various conventional treatments used prior to membranes

Conventional treatments	Coagulation	Adsorption	Pre-oxidation	Pre-filtration
Chemicals applied	Coagulants/flocculants at proper chemical dose	Porous/nonporous adsorbents in suspension/fixed contractor	Gaseous/liquid oxidants	Granular media with/without coagulants, membranes
Physical mechanism	Increases the size of aquatic contaminants to filterable level	Binds small contaminants to adsorbents much better than membrane pores	May dissociate organic colloids into smaller sizes	Removes coarse materials that may cause cake/gel layer formation on downstream membranes
Chemical mechanism	Destabilizes contaminants to cause aggregation/adsorption on coagulants precipitates or membrane surface	Provides new interfaces to adsorb/accumulate substances detrimental to membrane performance	Oxidize/decompose NOM, possibly by mineralization if UV used	Selectively removes contaminants or other particles that are sticky to filter media and downstream membranes
Biological mechanism	Partially removes autochthonous NOM and hinders bacterial growth in feed water or on membrane	May adsorb organic contaminants relevant to biofouling	Suppress microbial growth	Partially remove microbes that can cause biofouling
Targeted contaminants	Viruses, humics/fulvics, proteins, polysaccharides with acidic groups, colloids smaller than membrane	Humics/fulvics, small NOM, DBPs, synthetic micro pollutants	Viruses and organic contaminants with ozonation	Particulate and colloidal organics/inorganics, microbiota

	pores			
Advantages on the effect on membrane fouling	Reduces colloidal and NOM fouling Significantly improves MF/UF performance	May increase/decrease membrane fouling and increase the removal of DBPs and its precursors	May reduce biofouling and NOM fouling Reduces the occurrence of biofouling; increases organic removal	May reduce fouling to different extents May reduce biofouling, colloidal fouling/solids loading
Disadvantages	i. Difficult to use proper dose if feed water quality varies significantly ii. May exacerbate fouling iii. Produce solid wastes iv. Ineffective in mitigating the fouling caused by hydrophilic neutral organics	i. Possible exacerbation of membrane fouling ii. Difficult to remove PAC fine particles from treatment facilities	i. Formation of DBPs ii. May damage membranes, incompatible with oxidants iii. May be ineffective in suppressing the growth of some microbiota resistant to oxidation	i. Performance of pre-filters may deteriorate and be difficult to recover ii. May require pre-treatment (coagulation/pre-oxidation) to enhance the efficacy

There was a significant improvement in pre-treatment with the advent of membrane technology which made the membrane process simple and cost effective by reducing fouling effects, extending membrane lifespan and replacements. The level of pre-treatment of feed water depends on the ultimate purpose of the end product water. The pre-treatments used can be carried out as follows.

i. Coagulation and flocculation

The BTSE contains some particles (combination of biological organisms, bacteria, viruses, protozoans, colour-causing particles, organics and inorganics) that are not settled within a reasonable time frame. Coagulation/flocculation process normally accelerates the settling process of such particles with the help of specific flocculants. This process refers to the process of overcoming the interparticle repulsive energy barrier by simply increasing its ionic strength. Coagulation of dissolved and colloidal substances in wastewater is explained by Derjaguin–Landau–Verwey–Overbeek theory (DLVO theory) (Lee et al. 2012).

The coagulation and flocculation process consist of several steps as listed below:

a. Coagulation: adding and mixing of chemical coagulants into raw water
b. Flocculation: slow mixing of flocculants (aluminium sulfate, aluminium chlorohydrate, iron salts, etc.) with water to build up particles of floc
c. Sedimentation: allowing the floc to settle out
d. Filtration: removing all the suspended matter by passing it through filters

Many studies have confirmed that coagulation as a pre-treatment to the membrane system improved the membrane's permeability and reduced fouling potential (Konieczny et al. 2006; Huang et al. 2011; Pikkarainen et al. 2004)

ii. (Activated carbon) adsorption

Much information is available on the topic of removing organics by activated carbon from wastewater for various experimental configurations and conditions (Löwenberg et al. 2014; Martin and Iwuco, 1982; Liyan et al. 2009; Jia et al. 2009; Kim et al. 2009a; Guo et al. 2005). Activated carbons are porous carbonaceous adsorbents, and a large variety of organic solutes can be removed from wastewater via adsorption into its pores. This has a high adsroptive surface area (500-1500 m^2g^{-1}) and pore volume ranges 0.7 and 1.8 cm^3 g^{-1}. Activated carbon is commercially available in the form of powdered activated carbon (PAC) and granular activated carbon (GAC).

Adsorption of organic constituents by activated carbon is the accumulation of substances at a surface of the carbon. The adsorbing phase is known as 'adsorbent' and the material being adsorbed is the 'adsorbate'. The adsorption induced by Van der Waals forces is generally referred to as 'physical adsorption' and is reversible, whilst adsorption involving an exchange of electrons between specific surface and solute molecules known as 'chemical adsorption' where chemical bonds are formed (Cecen and Aktas, 2011).

Adsorption mechanism: The transport mechanism of organics can be explained in four different ways: 1. bulk solution transport, 2. external diffusion, 3. intra particle (internal) diffusion, and 4. adsorption (see Figure 2.4).

1. *Bulk solution transport*: adsorbates (organics) must firstly be transported from the bulk solution to the liquid film surrounding the activated carbon particle.
2. *External diffusion*: transport of adsorbates through the liquid film by molecular diffusion where the driving force is the concentration difference. The rate of this diffusion depends on the hydrodynamic properties of the system.

3. *Intraparticle (internal) diffusion*: this involves the transfer of adsorbate from the surface of the adsorbent to sites within the adsorbent. This depends on hydrodynamic conditions in a system.
4. *Adsorption*: an adsorption bond is formed after the transport of adsorbate to an available site of carbon particle. If it is physical adsorption, the actual physical attachment of adsorbate takes place rapidly onto the adsorbent. However, if adsorption is accompanied by chemical reaction, the reaction rate may be slower.

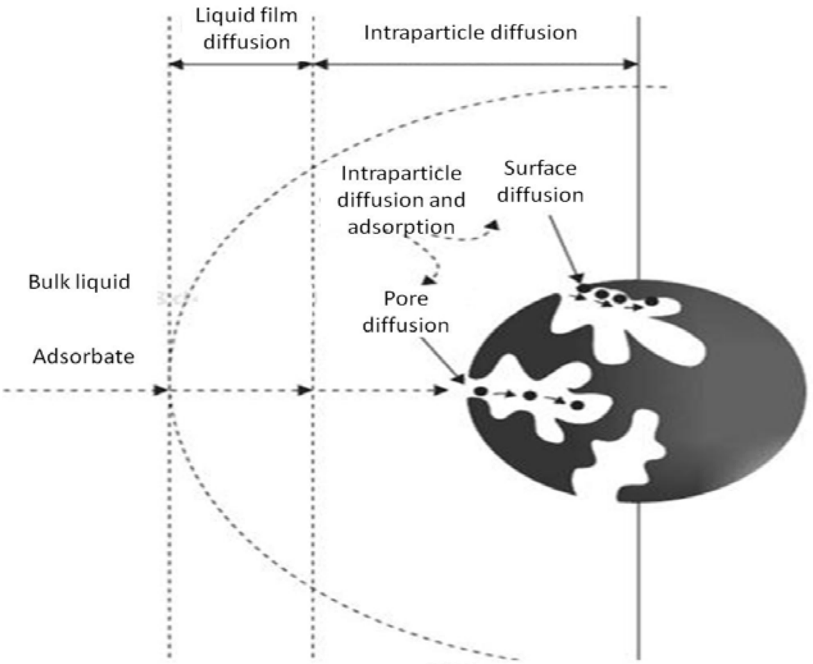


Figure 2.4: External and intraparticle diffusion of adsorbate in activated carbon particle (adapted from Cecen and Aktas, 2011)

In wastewater treatment it is recommended to use the PAC. In suspension form in slurries GAC should be used because GAC filters/column are involved (Cecen and Aktas, 2011). Recent studies have focused on utilizing PAC in submerged membrane hybrid systems to facilitate the removal of organics and improve fouling control (Vigneswaran et al. 2003; Thiruvenkatachari et al. 2004)

iii. Ion exchange resin

With the development of more sophisticated synthetic polymers having tailored functional properties, the ion exchange technology has been significantly advanced (Kammerer et al. 2014). The key features of ion exchange resins (IER) are the selective removal of some targeted pollutants, and reduction of membrane scaling caused by inorganics (Abdulgader et al. 2013).

Many commercially available ion exchange resins are created by the copolymerization of organic polymers, stryrene and divinylbenzene (DVB). Styrene provides the resin's matrix whilst DVB is normally used to cross-link the resin. The cross-linking of the resin provides insolubility and toughness to the resin and the degree of cross-linking determines the internal pore structure which affects the movements of ions into the resin.

Two types of ion exchanges are available – namely cation exchange resins and anion exchange resins. Cation exchange resins are strong acid resins and these are used to exchange unwanted positively charged cations with cation species such as Na^+ or H^+. Anion exchange resins are used to exchange unwanted anions with anion species such as Cl^- or OH^-. These resins can be strong bases or weak bases. The quaternary ammonium resins are normally used in the chloride form when the following reaction takes place, with R- representing the charged DOC (Bolto et al. 2004).

$$\text{Resin} - \text{Nme}_3^+\text{Cl}^- + \text{R}^- <\!\!-\!\!> \text{Resin} - \text{Nme}_3^+\text{R}^- + \text{Cl}^-$$

The mechanism behind the IEX regarding the removal of organics is the exchange of ions, for example exchange of organic electrolytes and chloride ions, rather than physical adsorption (Cornelissen et al. 2008). This is a reversible process which is the main advantage over other DOC adsorption processes. The other advantages of IXR are simplicity of operation, i.e. there is no energy requirement for the exchange phenomenon. Moreover, ion exchange resins can be regenerated with brine solutions (Abdulgader et al. 2013). Figure 2.5 details the mechanism behind the ion exchange and regeneration process for ion exchange resins. The restricted resin exchange capacity and the consumption and disposal of chemicals used for regeneration are the major limitations of employing ion exchange resin in water treatment strategies.

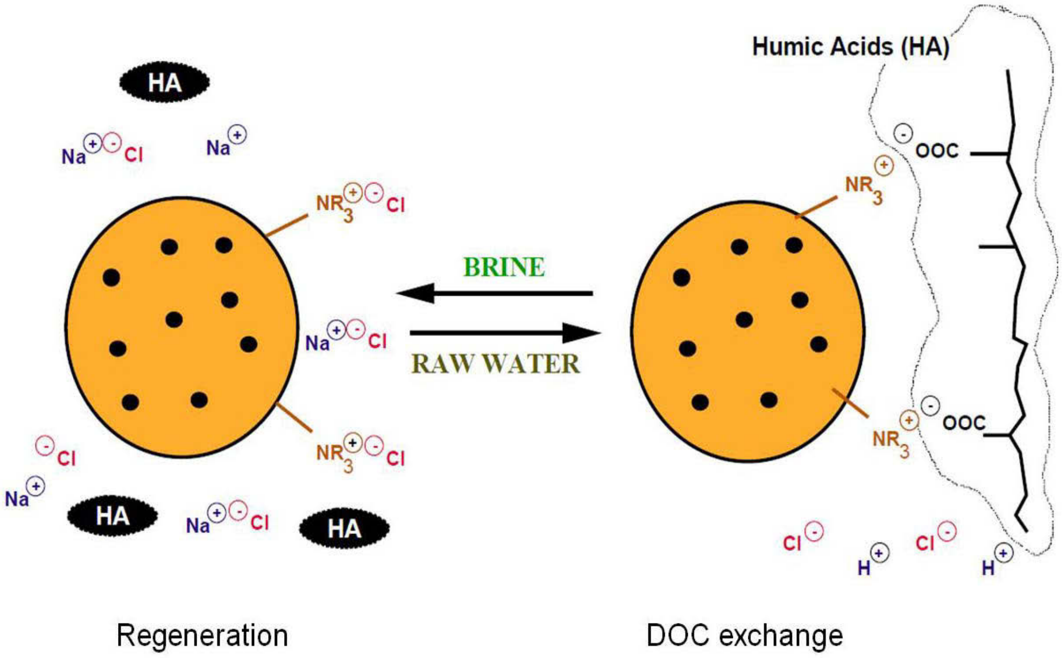


Figure 2.5: Chemistry and mechanism of DOC exchange with ion exchange resin (Slunjski et al. 2000)

iv. Pre-oxidation

The use of oxidizing agents can alter the size and distribution of effluent organic matter, and reduce the subsequent membrane fouling. However, a drawback of pre-oxidation is the formation of oxidation by-products that cannot be removed by the membrane (Huang et al. 2009).

A conventional pre-treatment system produces water to RO with acceptable quality when the system is operated properly and with a consistent quality of wastewater. There are some issues, however, still associated with conventional pre-treatment which results in poorer RO performance (Ang et al. 2014). They are listed below:

i. Fluctuations in performance – the inconsistent quality of feed water (in terms of SDI index, turbidity, etc.) produced by conventional pre-treatments results in deterioration of RO performance

ii. Susceptibility to biofouling attack –food and nutrients become food for bacteria and eventually may cause biofouling on RO

iii. Scaling – the addition of antiscalants can enhance the potential for biofouling in RO and possibly accelerate the biological growth 10-fold.

Conventional pre-treatments are not always effective in producing a consistent feed to the RO system that can prevent RO fouling. Low pressure membrane filtration has proven to be a good alternative to conventional treatments. For this reason various researchers have proposed the integrated/hybrid membrane systems as pre-treatment strategies that can minimize the above mentioned issues to a certain extent.

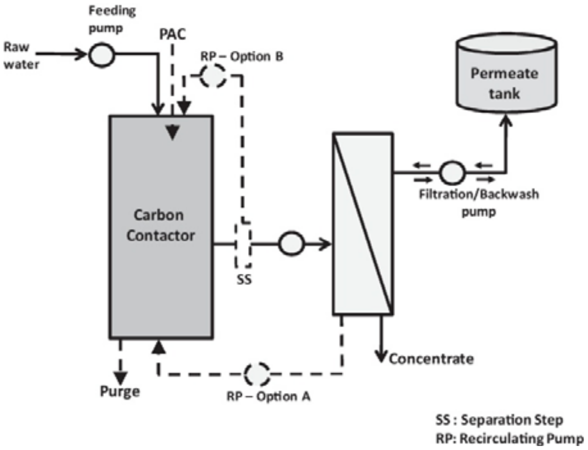
b. Conventional treatment coupled with Membranes

In order to improve treatment performance, the MF/UF membranes can be integrated/coupled with other processes such as coagulation, ozonation or adsorption.

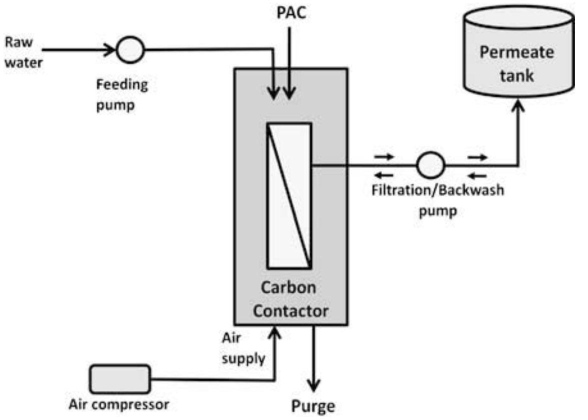
This is known as 'Membrane Hybrid Systems'. Different configurations of membrane hybrid systems are reported in the literature (Stoquart et al. 2012) and presented below:

i. Treatment prior to membrane filtration [pre-treatment]
ii. Treatment with membrane filtrations [integrated]
iii. Treatment after membrane filtration [post-treatment]

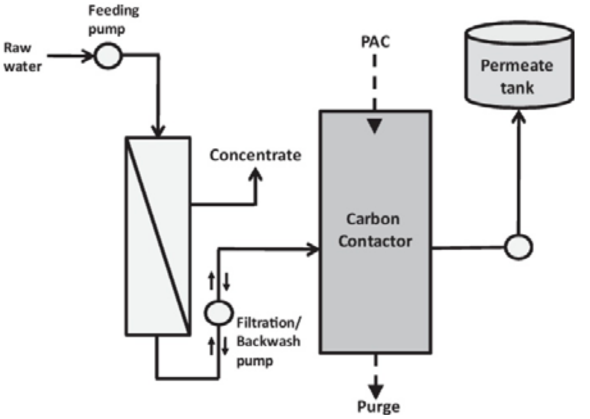
(i) Pre-treatment



(ii) Integrated



(iii) Post-treatment



(iii)

Figure 2.6: Different configurations of membrane-hybrid systems (adapted from Stoquart et al. 2012)

Figure 2.6(i) shows the pre-treatment option where the wastewater is firstly passed through the activated carbon contactor in which the removal of contaminants takes place prior to membrane filtration. The effluent after the carbon contactor is passed through the membrane. This enables the system to optimize removal efficiency by changing the dose of carbon and contact time. The disadvantage of this system is an additional separation step is needed when high carbon concentration is required.

The second configuration presented in Figure 2.6(ii) is the integrated system. The activated carbon is directly added into the membrane reactor which contains raw water to be treated. The adsorption and filtration take place in a single influent tank. The advantages of this system are: (i) simple process at a single stage; (ii) better physical removal of organics; (iii) absolute containment of carbon within the tank; and (iv) aeration and carbon particles minimize membrane fouling via membrane abrasion/scouring effect (Ang et al. 2014; Thiruvenkatachari et al. 2004; Stoquart et al. 2012). Recently, a membrane bioreactor coupled with carbon has been used to treat wastewater (Johir et al., 2013).

The third configuration is post-treatment with activated carbon where raw water is firstly passed through the membrane then followed by the carbon contactor. A possible drawback of this system could be the activated carbon fines may be exported from the carbon contactor with the treated water. In this context, a physical separation barrier is needed to separate the fine carbon particles and it is not common in full scale applications (Stoquart et al. 2012).

i. Pre-treatment to Membrane

Different pre-treatment methods are used to improve the performance of membrane processes. These are explained in more detail below.

Granular media pre-filtration: Deep-bed filtration is used to remove particulates from feed water because they can be detrimental to membrane filtration performance. This is one of the most common and efficient ways of purifying wastewater (Al-Degs et al. 2009). An advantage of packed bed filters from the standpoint of regeneration is that the hydraulic backwashing has proven to be effective in restoring their capacity. Granular media filters are effective in capturing particles of a few μm and smaller than 0.1 μm (Huang et al. 2009). The removal mechanism can be either physical sieving or chemical adsorption.

The packed bed filters can be operated as ‘fixed bed’ or ‘fluidized bed’ contactors. The water flow from top to bottom is known as fixed bed whilst the flow from bottom to top is ‘fluidized bed’ where the bed height of the packed media varies based on flow velocity as well as the density of the packing media. The type of packing media can be determined based on the composition of feed water and requirements of the treated water quality. Commonly sand is used for removing the particulates. GAC or ion exchange resins are packed into the column to remove the contaminants by adsorption or ion exchange.

Adsorption in fixed bed columns: One of the most important criteria in the design of fixed bed adsorption systems is the prediction of column breakthrough which determines the operating lifespan of the bed and regeneration times (Walker and Weatherley, 1997). Factors affecting breakthrough are the height of the packed bed, volumetric flow rate, concentration of contaminant in the feed water, particle size of adsorbent, etc. (Al-Degs et al. 2009; Walker and Weatherley, 1997).

The application of a GAC column in water treatment has been investigated by a number of researchers. According to one comparative study between sand filter and GAC filter by Kim and Kang (2008) the GAC filter performed better in terms of DOC and DBPs removal. A column packed with 58g of GAC removed 55-70% of DOC from synthetic wastewater containing syntan (with initial concentration was 500 mg/L) solution at a low filtration velocity at 0.5 m/h (Thankappan et al. 2014).

When the magnetic ion exchange resin (MIEX) is used as ion exchange in the pre-filtration stage on the fluidized bed, the 80% removal of DOC was observed and this MIEX-fluidized bed pre-filtration helped to restrict any development of TMP in the membrane processes (Zhang et al. 2008).

Kim and Dempsey (2010) studied the effect of four ion exchange resins (IEXs) such as *DAX-8, IRA-958, MIEX and DEAE* on the removal of organics in fixed-bed columns prior to membrane filtration in order to reduce organic fouling on the membranes. The resin *DAX-8* is a non-ionic macroporous, *IRA-958* and *MIEX* are strong base macroporous and *DEAE* is a weak base gel. In terms of removing organic foulants, IEX resins such as DEAE and MIEX were effective and prevented membrane fouling. Resins such as DAX-8 and IRA-958 were the least effective in removing such foulants and caused subsequent membrane fouling.

Unlike fixed beds, the application of moving beds and fluidized beds when removing contaminants is very limited in water treatment (Couper et al. 2010). However, the available few studies suggested the use of ion exchange resins in the column experiments to remove organics and anions. A fluidized bed packed with Purolite®A500PS consistently removed more than 80% of effluent organics from synthetic wastewater (DOC = 10 mg/L) for more than 800 bed volumes (Ahmad et al. 2012).

Zhang et al. (2008) studied the effect of fluidized bed MIEX® reactor prior to membrane filtration. In this study, synthetic wastewater was used as feed water with a DOC 10 mg/L. MIEX fluidized bed reactor was used as pre-treatment to the submerged membrane hybrid system. The removal of DOC by the MIEX® reactor-membrane hybrid system was 75-85% with MIEX pre-treatment (100 ml of volume and 80.3 cm depth during fluidization) whilst submerged membrane alone removed only on average 35%.

ii. Integrated membrane hybrid systems (IMS): Of the three different configurations of the membrane-hybrid system discussed, pre-treatment is the only one with current full scale applications. The post-treatment has not been common in full scale scenarios as it involves an additional step to retain the exported carbon particles. The integrated single stage treatment of the membrane hybrid system has several advantages and is designed to overcome membrane fouling problems through abrasion and membrane scouring. The ability of this system in using relatively high concentrations of carbon can maximize contaminants removal. In addition this system can be operated as membrane bioreactor coupled with carbon within mixed liquor. Yet this configuration has never been applied at full scale (Stoquart et al. 2012). Therefore, in-depth research is needed to adapt this technique in full scale applications.

The membrane-hybrid system is described as the one where the membrane process is coupled with another unit process such as adsorption, ion exchange, coagulation, bioconversion, catalysis, etc. A number of studies examined the membrane hybrid system, i.e. MF/UF coupled with suspended medium (either activated carbon or ion exchange resin) under several experimental conditions (Kim et al. 2009a; Suzuki et al. 1998; Song et al. 2009; Saravia et al. 2006).

The membrane hybrid systems minimize membrane fouling which in turn helps to reduce operation costs through less frequent membrane cleaning and consequently extend membrane life. The efficiency of such treatments in removing contaminants and minimizing membrane fouling strongly depends on the type of agents (coagulants/ adsorbents/ oxidant, etc.) applied, the dosage, and dosing modes (continuous or intermittent), properties of feed water quality (colloidal/dissolved/bulk/synthetic organics/ inorganics), solution chemistry, etc. (Gao et al. 2011). The aeration and particle sizes of the adsorbents collectively play a crucial role in reducing membrane fouling through abrasion and scouring.

Impact of Aeration: Apart from the adsorption of potential foulants in the membrane reactor, another common strategy is the provision of aeration to keep the carbon particles in suspension. This minimizes the fouling effect on the membrane surface

(Stoquart et al. 2012) by optimizing the adsorption of potential foulants from feedwater. The bubbles generated by aeration in the membrane reactor can reduce the accumulation/deposition of solid particles onto the membrane surface by (air) scouring effect (Tian et al. 2010; Bouhabila et al. 2001; Cui et al. 1997). A study done by Pradhan et al. (2012) observed the doubling of air flow rate (from 600 to 1200 L/h/m^2), which helped to reduce TMP development by 32% at a filtration flux of 10 L/m^2.h. Here, the degree of membrane fouling is represented by permeate flux and TMP development. Another study by Tian et al. (2010) reported that continuous air bubbling was more effective than intermittent bubbling to mitigate membrane fouling. However, irreversible membrane fouling caused by the deposition/attachment of soluble organics inside the membrane pores cannot be controlled by aeration alone. As such, the incorporation of adsorbents in the membrane reactor becomes necessary to remove such foulants from the feed water. Thus, it is important to use different types of adsorbents coupled with membrane in the membrane reactor as a suspended medium. Doing so can help to reduce both reversible as well as irreversible membrane fouling through: (i) mechanical scouring; and (ii) adsorption of potential foulants.

Previous studies reported that adding adsorbents as suspended media in the membrane reactor provides mechanical scouring on the membrane surface which helped to reduce the development of transmembrane pressure (TMP) as the result of less membrane fouling (Pradhan et al. 2012; Johir et al. 2013). Johir et al. (2011a) studied the effect of aeration with different filtration fluxes in a membrane bioreactor and found the increase of aeration rate from 1 to 1.5 m^3/(m^2 membrane area h) led the reduction of TMP at flux of 25 L/m^2 h. This could be due to a reduction in the accumulation of foulants on the membrane surface.

Particle sizes of adsorbents: Studies showed that the particle size of the adsorbents did influence the development of TMP and fouling (Johir et al. 2013; Johir et al. 2011). According to Johir et al. (2013) particle size of GAC of 300-600 µm was more effective in reducing membrane fouling than particle sizes of 150-300 or 600-1200 µm. The lowest TMP development of 16 kPa was observed with particle sizes of 300–600 µm and the second lowest TMP development of 21.3 kPa was observed using particle sizes of 150–300 µm. The least development of TMP/fouling with GAC particle size of 300–600 µm could be due to higher mechanical scouring on the membrane surface. It is also necessary to study the effect of aeration on suspended media on fouling reduction and too low aeration may not be effective in retaining the media in suspension. However, the application of suspended medium in the membrane reactor reduces the need for aeration (Johir et al. 2011a). The incorporation of adsorbents into the membrane reactor is able to reduce irreversible membrane fouling through adsorption of dissolved organic foulants before passing through the membrane pores (Kim et al. 2009a; Guo et al. 2005).

a. Membrane-adsorption (GAC) hybrid system

Activated carbon was found to be effective in minimizing organic foulants and therefore provided more stable filtration activity (Matsui et al. 2009). A number of investigators examined the application of activated carbon in membrane-hybrid systems in lowering TMP development and membrane fouling (Li 2014; Kim et al. 2009a; Guo et al. 2005; Stoquart et al. 2012; Johir et al. 2011a; Zhang et al. 2003; Vigneswaran et al. 2007; Matsui et al. 2001). The effect of activated carbon on the membrane hybrid system is two-fold, i.e.: firstly, a certain level of potential organic foulants can be removed onto carbon pores; and secondly, carbon particles are typically abrasive which means they can modify the fouling cake. This probably becomes more porous and so facilitates the filtration flux (Pianta et al. 1998).

Many researchers have focused on the coupling of PAC with MF/UF to improve the removal efficiency of organics. In this context, a study conducted by Vigneswaran et al. (2007) reported that the total organic carbon (TOC) removal of 84% was observed for about 15 days of operation when powdered activated carbon (PAC) dose of 5 g/L was added into a membrane-PAC hybrid system. Another study by Guo et al. (2004) found that adding PAC dose of 5 g/L in the membrane-adsorption hybrid system removed 89.8% of TOC from the BTSE. PAC has been widely applied in the membrane bioreactor to improve the membrane's performance, in which a bench scale membrane hybrid system coupled with PAC indicated no removal of organics with 0 g/L PAC. In the meantime a PAC dose of 40 g/L did remove 85% of dissolved organics (Kim et al. 2007). The addition of PAC removes low molecular weight organics, mainly humics which are smaller than the pores of MF membranes and afterwards the PAC particles can be completely retained by the MF (Suzuki et al. 1998). The PAC/UF hybrid system removed 96% of colour and 89% of humics with PAC dosages 50 - 100 mg l^{-1}, whereas 60% of colour and 40% of HA were only removed by UF membrane without the use of or in the absence of PAC.

Apart from the removal of natural organic matter, the PAC was found to be more effective in removing organic micro pollutants compared to the coagulation–flocculation process (Choi et al. 2008). However, the degree of removal highly depends on the properties of adsorbate (Octonol water partition coefficient (K_{OW}), pK_a, molecular size, aromaticity versus aliphaticity, presence of other functional groups, etc., as well as adsorbent (surface area, pore size and texture, surface chemistry, and mineral matter content). Both PAC and GAC can remove more than 90% of emerging contaminants (Snyder et al. 2007). Another study (Pianta et al. 1998) showed membrane coupled with PAC effectively removes micro pollutants such as trichlorethene, tetrachlorethene and atrazine. Another study (Zhang et al. 2003) observed an inconsistent removal of organics and fouling reduction by the UF-PAC hybrid system. In the meantime more humics were detected on the surface of the UF membrane.

An area that has not been widely investigated is the use of GAC in MF-hybrid systems. Here, Kim et al. (2009a) studied the MF-GAC hybrid system and found that use of GAC with membrane restricted TMP development and reduced the frequency of chemical cleaning by half. In addition, the MF-GAC hybrid system improved the efficiency of removing DOC and COD in the range of 42% and 53%, respectively, whilst the removals were 25–30% and 20–25% with the MF alone.

It was believed that larger particle sizes are better than smaller particle sizes because the scouring effect helps to reduce fouling. Johir et al. (2013) reported that the GAC particle size of 300-600 µm was more effective in reducing TMP development (16 kPa) compared to the particle size 150-300 µm (21.3 kPa). The addition of GAC into MBR reduced TMP development by 50% (Johir et al. 2011a). Studies done by Li et al. (2005) and Fang et al. (2006) reported the addition of carbon reduced TMP development by 44% and 22% respectively.

Removal of organic micro pollutants by GAC: In addition to removing natural organics the demand to remove pharmaceutically active compounds is growing due to their potential health risk to people and aquatic organisms when they are released into wastewater. Advanced oxidation processes such as UV-radiation and ozone treatment can be effective for these compounds, however, these techniques produce some unwanted newly-formed (toxic) by-products (Rossner et al. 2009). Adsorption processes do not add undesirable by-products to drinking water (Bonné et al. 2002; Quinlivan et al. 2005). As such, these advanced oxidation techniques are often followed by activated carbon in order to reduce the excess organics and by-products produced (Bonné et al. 2002).

Activated carbon (both GAC and PAC) is found to be highly efficient in removing organic micro pollutants (Snyder et al. 2007; Verliefde et al. 2007). A dose of 10 mg/L coconut-shell-based activated carbon removed more than 98% of contaminants (Rossner et al. 2009). The performance of zeolites in the removal of such contaminants was less effective. A study done by Snyder et al. (2007) reported more than 90% removal of organic micro pollutants by PAC and GAC from drinking water.

b. Membrane-Ion exchange (PuroliteA502PS) Hybrid System

Activated carbon, alumina, and synthetic sorbents are ineffective in removing hydrophobic ionisable organic solutes. The coagulation process is inefficient in the removal of low molecular weight humics (Edzwald, 1993), whilst polymeric ion exchangers with hydrophobic matrixes show high sorption affinity to these ionic solutes (Li and SenGupta, 2000). Additionally the possible regeneration of ion exchangers is an advantage compared to activated carbon (Abdulgader et al. 2013). Ion exchange resins have been used in water treatment and purification for the last 70 years (Virkutyte et al. 2010).

The application of ion exchange (IEX) resins to remove dissolved organics is well documented (Cornelissen et al. 2008; Li and SenGupta, 2000; Bolto et al. 2002; Boyer and Singer, 2005). Further, Bolto et al. (2004) studied the removal of NOM with approximately 20 resins and found the resins having more water content and more open structures allow easier entry of NOM into IER structures, thereby removing more NOM. In addition, the macroporous structures are more effective than gel form resins as they allow easier access to sizeable organic anions. Another study with magnetic ion exchange resin (MIEX) showed 77% removal of DOC from synthetic wastewater (Nguyen et al. 2011). It had an affinity to most of the small molecular weight organic matter (345–688 Da) (Zhang et al. 2007).

In all these studies, IEX resins were used in batch mode or as ion exchange column. However, very few studies dealt with the integrated application of IEXs with membrane-hybrid systems, i.e. the immersion of membrane module into the adsorption tank, which significantly reduced the size and space of the equipment (Humbert et al. 2012). Integrated anion-exchange-membrane hybrid system was studied by Humbert et al. (2012) with high DOC content water (from 7.5 to 9.7 mg/L) collected from a treatment plant. They used four different sizes ranges of AER (<50; 50–100; 100–200, and, 200–400 µm), in which AER's smaller particle size removed more organics than larger particles with a short contact time of less than 15 mins. When incorporated with the membrane hybrid system, the removal of organics was much greater than that of the membrane alone. However, the smaller range of ion exchange particles (<50 µm) exhibited comparatively severe flux decline (>60%) than larger particle sizes. Increased reversible fouling could be due to the attrition of AER when a centrifugal pump in the external loop is utilized.

Removal of organic micro pollutants by ion-exchangers: The ion-exchange resins were found to be effective in removing charged (synthetic) trace organics. The adsorption of charged trace organics into an oppositely charged polymer was much stronger than the adsorption onto activated carbon and this phenomenon was especially observed with double-charged cation metformin (Bäuerleina et al. 2012).

Landry and Boyer (2013) described the sequence for the removal of diclofenace from different anion exchange resins (dose: 1 mL/L) as follows: Dowex Marathon (78%) > Dowex (60%) > A520E (44%) > IRA958 (9%) from fresh urine. They further reported a strong-base, macroporous, polystyrene resin (Purolite A520E) of dose 8mL/L removed more than 90% of dicofenac from both fresh and ureolyzed urine. However, the available data on the removal of pharmaceuticals by ion-exchange polymer resins (through electrostatic interactions) are still limited (Landry and Boyer, 2013).

Even though several advanced pre-treatment technologies are proposed for the production of effluents with a water quality complying with specific reuse applications, some residues of organic micro pollutants are still detected in the effluent of current wastewater treatment plants (WWTPs). This has led to research into innovative advanced membrane incorporated treatment techniques. According to the results presented in Table 2.4 (Snyder et al. 2003), unit treatment processes such as activated carbon adsorption (AC), biological activated carbon (BAC), ozone/advanced oxidation processes (O_3/AOP), UV, Clorination (Cl_2/ClO_2), coagulation/flocculation, softening/metal oxides, NF, RO and bio/photo degradation/activated sludge have the ability to remove EDCs/PPCPs to a certain extent.

In comparison the performance of the order of unit processes can be RO>NF>BAC>AC in terms of EDCs and PPCPs removal. The AC removed most of the PPCPs (70% to more 90%) except inorganics (<40%) and antibiotics (40-90%). Focusing on membranes, NF rejected most of the contaminants (70% to more than 90%), whilst RO rejected all the contaminants, in fact more than 90%. As such the application of tight membrane processes is more effective than conventional treatment processes in removing trace contaminants.

Table 2.4: Unit treatment processes and operations in the removal of EDCs and PPCPs (E – excellent (>90%); G – Good (70-90%); F – Fair (40-70%); L- Low (20-40%); P-Poor (<20%)) [adapted from: (Snyder et al. 2003)]

Group	*Classification*	*AC*	*BAC*	*O_3/AOPs*	*UV*	*Cl_2/ClO_2*	*Coagulation/ flocculation*	*Softening/ metal oxides*	*NF*	*RO*
EDCs	Pesticides	E	E	L-E	E	P-E	P	G	G	E
	Industrial chemicals	E	E	F-G	E	P	P-L	P-L	E	E
	Steroids	E	E	E	E	E	P	P-L	G	E
	Metals	G	G	P	P	P	F-G	F-G	G	E
	Inorganics	P-L	F	P	P	P	P	G	G	E
	Organometallics	G-E	G-E	L-E	F-G	P-F	P-L	P-L	G-E	E
PhACs	Antibiotics	F-G	E	L-E	F-G	P-G	P-L	P-L	E	E
	Antidepressants	G-E	G-E	L-E	F-G	P-F	P-L	P-L	G-E	E
	Anti-inflammatory	E	G-E	E	E	P-F	P	P-L	G-E	E
	Lipid regulators	E	E	E	F-G	P-F	P	P-L	G-E	E
	X-ray contrast media	G-E	G-E	L-E	F-G	P-F	P-L	P-L	G-E	E
	Psychiatric control	G-E	G-E	L-E	F-G	P-F	P-L	P-L	G-E	E
PCPs	Synthetic musks	G-E	G-E	L-E	E	P-F	P-L	P-L	G-E	E
	Sunscreens	G-E	G-E	L-E	F-G	P-F	P-L	P-L	G-E	E
	Antimicrobials	G-E	G-E	L-E	F-G	P-F	P-L	P-L	G-E	E
	Surfactants/detergents	E	E	F-G	F-G	P	P-L	P-L	E	E

In this context, pressure-driven membranes such as NF and RO membranes are often considered to be potential remediation techniques and can eliminate most organic micro pollutants to a great extent. This is because the MW of these contaminants is between 200–300 g/mol, and the molecular weight cut-off (MWCO) values of NF membranes are also often in this region (Verliefde et al. 2008).

2.7.2.2. Advantage of MF/UF membranes as pre-treatment

Membrane filtration is found to be viable in terms of cost effectiveness and contaminant removal (Ang et al. 2014). This means one membrane can be used as pre-treatment to another (Johns, 2000). In this context, MF/UF membranes are able to produce constant quality effluents irrespective of the performance of prior treatment of activated sludge treatments (Park et al. 2010). It is normally used as pre-treatment to NF/RO where high quality water is required. While comparing the cost of conventional and MF pre-treatment, the total cost of conventional pre-treatment was \$536 whilst micro filtration was \$279 which is approximately 50% less than conventional treatment (Won and Shields, 2001).

In terms of contaminant removal, MF and UF membranes are effective in removing suspended particles, macromolecules, etc., and using such membranes has become widespread as an alternative to conventional water treatment and filtration processes. It can meet stringent regulations particularly in removing pathogens such as *Giardia* and *Cryptosporidium* (Lebeau et al. 1998). The removal of colour, dissolved organics, organic micro pollutants, and inorganic ions by MF/UF membranes is still limited because their pore size (0.1-0.01 μm) is not enough to retain such small molecules (Kim et al. 2009a; Stoquart et al. 2012; Lebeau et al. 1998). As such, the application of membrane pre-treatments such as MF and UF can significantly reduce the fouling potential more than conventional pre-treatment processes (Pearce, 2008).

2.8. High quality water reuse

Water quality is the most important issue in water reuse that determines the acceptability and safety of using recycled water for a given specified purpose. The definition of appropriate water quality is driven by a number of health, safety, socio-psychological and technical-economic criteria (IWA, 2004). In this regard, the need for high quality water, free from toxic, refractory substances becomes important to ensure the safety and well-being of humans and aquatic environment organisms. As such, exploring different innovative advanced membrane treatment technologies is essential.

In this context, Hurlimann and McKay (2007) studied the attitudes of an urban Australian community living at Mawson Lakes in South Australia to using recycled water for non-potable domestic purposes. The results indicate that people prefer to use water with low salt levels for gardening, colourless water for washing clothes, and low price water for toilet flushing. Respondents were willing to pay more for better quality recycled water. As such maintaining the high quality of reuse water is important if it is to be accepted by the general public.

2.8.1. Concept of Dual Membrane system

RO has been used for the last 2-3 decades in water desalination (del Pino and Durham, 1999) and its application in WWTPs is widely accepted because it produces good quality re-usable water for end users. The use of RO in wastewater applications is limited because RO membranes are sensitive to fouling due to suspended/colloidal materials, bacteria/inorganic scales originating in raw water. This leads to irreversible membrane damage, reduced filtration flux, and rising operational costs as a consequence of frequent cleaning/membrane replacements (Durham et al. 2002). The incorporation of effective pre-treatments can improve the RO performance.

The application of pre-treatment technologies such as deep-bed media filters and physico-chemical unit processes has serious limitations with regard to variable quality of the treated water they produce. MF membranes prior to RO have been proven to reduce the power costs of RO plants by up to 60% because the membranes effectively manage fouling of RO. MF pre-treatment reduced turbidity by 60-80% in silt density index (SDI) of the feed water in compared to conventional pre-treatment. The MF always reduces the SDI index significantly below the minimum cut-off value of 3, as recommended by RO manufacturers, whilst the conventional pre-treatment system could reduce the SDI index to between 5-7 (Durham et al. 2001). For this reason MF has proved to be a very reliable and effective pre-treatment strategy because it produces filtrate of a consistent quality irrespective of the feed water (del Pino and Durham, 1999).

Instead of coupling conventional treatments with LPMs such as MF/RO for water reuse, most municipal WWTPs are now adapting MF/UF followed by RO (known as 'dual membrane systems'). This has become the industry standard in many countries including Australia for municipal wastewater reclamation (Durham et al. 2001), especially with reference to water augmentation and groundwater injection (Bellona et al. 2012). Membrane filtration offers some advantages over conventional treatment such as – little/no use of chemicals, good, consistent quality of water produced, reduced sludge production, small plant foot print, etc. This is economically feasible and several conventional treatment techniques can be replaced by a single membrane treatment (Ang et al. 2014).

2.8.2. Worldwide use of Dual membrane systems

Several pilot wastewater treatment plants have tried dual membrane processes such as continuous microfiltration (CMF) followed by RO for municipal wastewater reclamation and reuse. The product water created from the treatment system meets all drinking water standards (del Pino and Durham, 1999). Some earlier water reuse facilities that implement dual membrane processes are discussed below in more detail.

a. *Samsung Chemicals Co, Ltd., Daesan, Republic of Korea:* local polluted rivers treated using conventional pre-treatment systems were not able to reduce SDI to less than 3. Thus, the post-treatment of RO was subject to membrane fouling. However, the RO feed water quality was improved after incorporating the Memcor CMF system and it could treat 30,000 m^3/d of polluted river water. The CMF system reduced the SDI to less than 3 and this system also generated more reliable RO operation.

b. *Vértesi Power Plant Co. Oroszlány, Hungary:* The cooling lake next to this power plant has deteriorated over the past 10 yrs. The total dissolved solids (TDS), total suspended solids (TSS), and algae content increased to 6000 mg/L, 100 mg/L, and 225 million counts/L, respectively. This in turn increased the chemicals used in the deionizer and frequency of regeneration. The installation of CMF/RO prior to the deionizer reduced operation and maintenance costs and ion-exchange operation costs. The TDS level was reduced to 5-10 mg/L in the RO permeate.

c. *The Tias WWTP, Lanzarote, Canary Islands:* Effluent from the Tias WWTP was treated by a commercially sized plant in Lanzarote using the USF Memcor CMF system and RO. The CMF produced 1020 m^3/d of filtrate which was practically free of SS (<1.0 mg/L), turbidity (<1.0 NTU) and completely free of total and fecal coliforms. The SDI was <3.0 and had a water recovery of 85%. The 600m^3/d of micro filtered water was treated by FILMTEC BW30-400 RO membranes (Dow Chemical) which produced 430 m^3/d with a recovery rate of 72%. The RO permeate of 600 m^3/d (TDS content of 20 mg/L) and microfiltered water of 420 m^3/d (TDS content 1100 mg/L) were blended and ultimately used for irrigation.

d. *West Basin Water District at El Sengundo, California:* Two wastewater reuse projects at the West Basin began with the water injection project to control saline water intrusion into the fresh water aquifer. Pre-treatment of the CMF system produced 11,500 m^3/d for RO and made possible the provision of water that negated seawater intrusion. Another reuse project involved the CMF/RO system supplying feed water to the Mobil and Chevron refineries for their high pressure boilers. West Basin operated a CMF/RO facility (12,000 m^3/d) on the Mobil Refinery site. Capital and operating costs for conventional pre-treatment were much higher (\$337/1000 m^3) than the CMF system (\$215/1000 m^3).

CMF systems are able to remove turbidity (100%), BOD (81%), COD (40%), TOC (27%), total and fecal coliforms (100%). The reduction in conductivity and TDS was insignificant. The RO system removes conductivity (95%), TDS (95%), ammonia (91%), nitrates (82%), phosphates (93%), silica (89%), BOD (83%), COD (80%) and TOC (91%) (del Pino and Durham, 1999). However, in the context of organic micro pollutants, the CMF system does not have the capacity to remove such contaminants whilst RO removes more than 90% of them (Snyder et al. 2003).

Organic micro pollutants such as PPCPs, disinfection by-products (DBPs), EDCs that can persist through WWTPs and which are associated with potentially dangerous human health outcomes, are of concern when indirect potable reuse applications are being implemented (Kimura et al. 2003). Removing these compounds in water treatment is gaining attention where a high product water quality is desired. As such, in order to attain proper environmental standards, the use of a dual membrane system, i.e. CMF/RO system, provides a significant solution in wastewater reuse and recovery of water, and recycling valuable components from waste streams. It has good rejection capability and produces high quality product water, and the only disadvantage associated with this RO is the high cost and energy consumption. Researchers are looking for alternative solutions to reduce energy consumption. One area being investigated is the use of NF membranes instead of RO in indirect potable water reuse applications.

2.8.3. NF as an alternative to RO

Some recent studies have suggested using alternative membranes such as low-pressure reverse osmosis (LPRO) and NF membranes instead of pressure-driven RO for IMS applications. This can lower the cost and energy requirements required for RO (Bellona and Drewes, 2007; Bellona et al. 2012).

2.8.3.1. Economic analysis

An economic analysis on different types of membrane revealed that the use of NF membrane (NF270; molecular cut-off ~200 Da) instead of RO membrane could reduce significant annual costs ranging from \$55,123 to \$187,452 (Bellona et al. 2012). Another study assessed the feasibility of using NF (NF90, Dow/Filmtec) membranes and found that NF as a barrier for organic contaminants was just as good as RO (Yangali-Quintanilla et al. 2010). In addition, the NF was found to be cost effective. The total cost of NF was less (\$0.52/m^3) than RO (\$0.59/m^3). This could save \$0.07/m^3 of water treated (i.e. \$53 k/year for a 100 m^3/h plant). According to another study, the use of low pressure and relatively low fouling NF membrane (NF-4040) sustained pressure 3-4 times less than the feed pressure of a conventional RO membrane (Bellona and Drewes, 2007). This in turn resulted in potential savings of \$0.03-0.08/m^3 in treating reclaimed water. The NF membrane required less than 50% of the energy needed by the RO membrane in terms of divalent ion rejection, in addition to providing higher permeability. However, this concept is still new and requires extensive investigation using real water samples (Ang et al. 2014).

2.8.3.2. Contaminant removal

In water reuse applications the tight NF membranes can be used as an alternative to RO. They act as an effective barrier against trace organics such as pharmaceuticals, pesticides, endocrine disruptors and other organic contaminants (Yangali-Quintanilla et al. 2010) and it can successfully attain 96% of overall drinking water standards except for boron, molybdenum and ammonia (Alzahrani et al. 2013).

Three interactions primarily influence the removal/rejection of solutes by the membrane, namely steric hindrance/sieving effect, charge repulsion/Donnan effect and physico-chemical interactions between solute, solvent and membrane (Bellona et al. 2004; Radjenović et al. 2008; Gur-Reznik et al. 2011). The rejection of neutral trace organics by NF and RO membranes is considered to be influenced by size exclusion, whilst the rejection of polar trace organics is mostly governed by Donnan effect with charged membranes (Berg et al. 1997).

A comparative study done on the low pressure RO (LPRO) and NF membranes showed that the LPRO/NF membranes rejected more than 80% of TOC and 60-100% of conductivity (Bellona et al. 2012). The removals of divalent ions (sulfate, calcium, magnesium, etc.) by NF270 membranes were significantly higher than that of monovalent ions (nitrates, chlorides, sodium, etc.). More specifically the removal of monovalent ions by LPRO was significantly higher than NF 270. Nitrate removal by LPRO was 80-100% whilst it was 0-30% when employing NF270.

The removals of PPCPs were also observed. Two micro pollutants (atenolol and TCEP) were detected in the LPRO permeate whilst 10 micro pollutants were detected in NF270 permeate out of 17 detected micro pollutants in feed water. Most of the negatively charged pollutants such as diclofenac, gemfibrozil, ketoprofen, naproxen were not detected in NF270 permeate (Bellona et al. 2012). This phenomenon was further explained by Verliefde et al. (2008) who concluded that positively charged pollutants (atenolol and TCEP) are less efficiently removed by negatively charged NF/RO membranes than negatively charged micro pollutants due to electrostatic repulsion. Another study by Radjenović et al. (2008) on the rejection of pharmaceuticals in groundwater showed that the removals of gemfibrozil, mefenamic acid were significantly less by NF compared to RO. However, the NF membrane's rejection capability was the same as that of RO in terms of the rest of the organic micro pollutants such as hydrochlorothiazide, ketoprofen, diclofenac, sotalol, sulfamethoxazole, metoprolol, carbamazepine, glibenclamide, etc.

2.8.3.3. Issues of NF

Even though NF treatment systems produce high quality water in reuse applications, there are still several limitations such as: firstly, fouling and scaling; and secondly, incomplete removal of organic micro pollutants - pharmaceuticals.

i. Fouling and scaling:

One of the disadvantages associated with the NF membranes is the combined fouling caused by organics (organic fouling) and inorganics (scaling). This issue has been studied especially in NF membranes. The membrane fouling caused by the mixtures of different organic foulants is more complex than individual foulants (Lee et al. 2005; Li and Elimelech, 2006). The particulate contaminants present in BTSE such as refractory organics, trace levels of synthetic organics generated during disinfection processes, soluble microbial products derived from the biological treatment are found to foul the NF/RO membrane (Guo et al. 2011; Shon et al. 2006b).

ii. Incomplete removal of pharmaceuticals:

Even though NF membranes are able to remove organic micro pollutants some residues of PPCPs are still detected in NF permeate (Kimura et al. 2003; Bellona et al. 2004; Nghiem et al. 2004). The removal of charged pharmaceuticals such as diclofenac and salicylic acid was done effectively by NF (92%, 93%) and RO membranes (92%, 95%) whilst non-charged compounds such as 2-Naphtol, Bisphenol-A, Phenacetine, Primidone were less effectively rejected by NF (12%, 45%, 19%, 87%) and RO (43%, 99%, 71%, 84%) (Kimura et al. 2003).

NF plants operate worldwide and they remove organics, pharmaceuticals, pesticides, hardness, etc., from water. However, NF membranes are subject to fouling. According to some case studies, combining conventional treatments with NF can reduce such fouling problems as and improve the removal of pesticides, hardness, and carcinogenic substances such as derivatives of bromine, etc. (Cyna et al. 2002; Listiarini et al. 2010). Pre-treatment prior to NF can thus increase the permeate quality and reduce membrane fouling (Ang et al. 2014).

2.8.4. Membrane hybrid system as pre-treatment to NF

Advanced treatment technologies, such as activated carbon and with RO or NF as post-treatment appear to be viable for the removal of most trace contaminants including EDCs and PPCPs (Snyder et al. 2003). The activated carbon has the ability to remove refractory organics and micro pollutants and eventually reduce membrane fouling. This ensures the long-term performance of NF and low pressure RO membrane. On the other hand, in order to achieve high quality water the NF membrane can be used as a pre-treatment for the RO process. Since the NF membrane is more able to reject divalent ions, hardness can also be eliminated and this may subsequently reduce effect of scaling on the RO membrane (Tang et al. 2011). This can further minimize the need for RO membrane cleaning, membrane replacements and may eventually extend the membrane lifespan.

2.8.4.1. MF-activated carbon followed by NF hybrid system

As discussed above, in order to reduce cost/energy consumption, the NF membranes can be replaced for RO. Elimination of potential organic foulants and trace organics by NF can be maximized by coupling it with activated carbon adsorption. In this regard, Meier and Melin (2005) studied the NF-hybrid system where a combination of PAC and NF (PAC-NF process) was tested for the reclamation of sewage plant effluent on pilot scale. The authors discussed the advantages of this processes as follows:

- The adsorption provides pre-cleaning which reduces subsequent membrane fouling and improves contaminants removal
- PAC acts as a filter and adsorbent and prevents solids and organic pollutants reaching the membrane surface

- Compared to the fixed bed strategy, the PAC dosage can be more easily adjusted depending on the feed quality.

Their earlier research used a PAC-NF hybrid system (Meier et al. 2002) to treat biologically pre-treated landfill leachate. Here the injected PAC into the feed of a nanofiltration unit had a positive effect on permeate quality, permeate flux and fouling layer in the nanofiltration (NF) unit. Compared to RO, the PAC-NF had less operating pressure and energy consumption, however, the concentration of contaminants in the permeate were higher than that of RO permeate but still below the effluent quality standards. Kim et al. (2009b) studied PAC-NF process in terms of removing DOC and micro pollutants with different types of PAC. The removal of DOC with and without PAC was not significant and only approximately 30% removal was observed. The retentions of 17α-Ethinylestradiol and Bisphenol by PAC were 92-94% and 81-86%, respectively. In the final pilot plant effluent, i.e. after PAC-NF process without the addition of PAC the removals of 17α-Ethinylestradiol and Bisphenol were 69% and 49.6%, respectively whilst with PAC the removals were approximately 99% and 95%, respectively. This clearly confirms that adding PAC helped to eliminate organic micro pollutants more than NF alone.

When NF was operated with PAC, a layer of adsorbent particles formed on the membrane surface and this decreased membrane permeability (Meier and Melin, 2005). However, the reduced permeate flux was not observed when the organics were completely removed by PAC. As such, this inadequate removal of adsorbent particles could be overcome by installing an MF process between the PAC treatment and NF process. Thus, NF can replace the CMF/RO dual membrane hybrid system when treating BTSE.

When much hardness is present in feed water the NF must be used as pre-treatment to reduce the Ca and Mg ion concentration. Here the installation of NF would be appropriate for reducing the scaling effect on RO. This is mainly applicable to low quality sea and brackish water which require more intensive pre-treatment prior to RO (Ang et al. 2014).

2.8.5. Membrane hybrid systems as a pre-treatment to RO

Different innovative membrane-based pre-treatments are being designed for RO especially in SWRO and wastewater applications, where the objective is to reduce RO fouling and operating costs. Membranes such as MF and UF are used (Pearce, 2008; Bonnélye et al. 2008) because of their cost effectiveness and ability to reduce potential organic fouling in subsequent RO. Though MF membranes perform well in pre-treatment for SWRO, UF membranes are popular as they have the ability to reject viruses.

Rather than using the membranes alone during pre-treatment prior to RO, the coupling of treatments such as adsorption and coagulation with MF/UF-based pre-treatments was found to remove more contaminants and minimize organic fouling. A study combining coagulation-dual media filtration (sand and anthracite)-MF as a pre-treatment to SWRO reveals the application of combined coagulation-dual media filtration improved the MF flux decline (22%) than without pre-treatment (45%) (Chinu et al. 2010). Even though MF/UF-based conventional treatments remove potential organic foulants, they do not reject all such foulants in the feed water.

Several studies confirmed RO membranes fouling, is certainly due to incomplete feed water pre-treatment. A small concentration (few ppm) of organic macromolecules is enough to cause significant membrane fouling. The pressure increase beyond the level of 10% (weeks to months) is considered to be unacceptable and may cause interruption of continuous operation of RO. Moreover, 10% of flux reduction can be brought about by thin fouling layers formed by small amounts of deposited organic species. The time period taken to reduce 10% of relative flux J/J_0 is considered to indicate when the RO membrane requires cleaning (Sioutopoulos et al. 2010).

Apart from organic fouling, another issue associated with RO is the 'scaling' which results in the deposition of inorganic ions. The rejection capability of such ions by MF/UF membranes is still limited. The subsequent reduction in permeate flow requires high pressure pumps which leads to 85% of energy consumption (Wilf, 2004). In this context NF membranes have the advantage in their ability to remove divalent ion.

2.8.5.1. NF as pre-treatment to RO

The main advantages of NF systems are as follows: (i) lower working pressure than RO and, (ii) greater rejection of divalent cations. NF can successfully be applied to remove scale-forming ions (Morillo et al. 2014) and thus reduce subsequent scaling on RO membranes. A study was conducted by Llenas et al. (2011) on the feasibility of employing NF prior to RO in seawater desalination to prevent scaling in RO. Sulfate ions were rejected 90% by most of the six NF membranes tested. Sulfate rejection is very important for the prevention of RO membrane scaling. In addition to scaling, the removal of organic micro pollutants by MF/UF-based pre-treatment alone is inadequate.

Conversely, NF as a pre-treatment prior to RO can maximize the PPCPs' removal. Therefore, this can be used in treating contaminated wastewater consisting of organic micro pollutants and inorganic ions.

The new approach to membrane and thermal seawater desalination process is to integrate desalination systems of NF-SWRO and NF-MSF (multi-stage flash distiller). NF-SWRO reject-MSF developed by Saline Water Conversion Corporation (SWCC) was tested to assess the performance of NF as pre-treatment for RO. The NF system reduced turbidity and microbes. Furthermore the removals of Ca^{2+}, Mg^{2+}, SO_4^{2-}, HCO_3^-, and total hardness were 89.6%, 94.0%, 97.8%, 76.6% and 93.3%, respectively. The reduction of monovalent ions such as Cl^-, Na^+, K^+ was around 40% and overall seawater TDS was reduced by 57.7%. The adequate quality of water produced by NF resulted in high water recovery (SWRO and MSF at 70% and 80%, respectively). The incorporation of NF also lessened energy consumption by 25-30% and chemical consumption (Hassan et al. 1998). As such, the integration of NF-SWRO led to a marked improvement in seawater desalination processes, and doubled the SWRO recovery ratio. This also led to the production of permeate of high purity (TDS <200 ppm) even with one single stage SWRO (Hassan et al. 2000).

2.9. Development paths and benefits of Membrane-hybrid processes

The development paths from conventional treatment plants to a membrane-hybrid system are illustrated in Figure 2.7. It shows the advances in terms of contaminant removal and system performance. The membrane hybrid system obviously produces enhanced quality of product water. It is environmentally friendly because there is less waste disposal and less chemical usage. Extensive research on this topic is needed to discover the best alternative systems whereby the water industry can manage water scarcity issues (Ang et al. 2014).

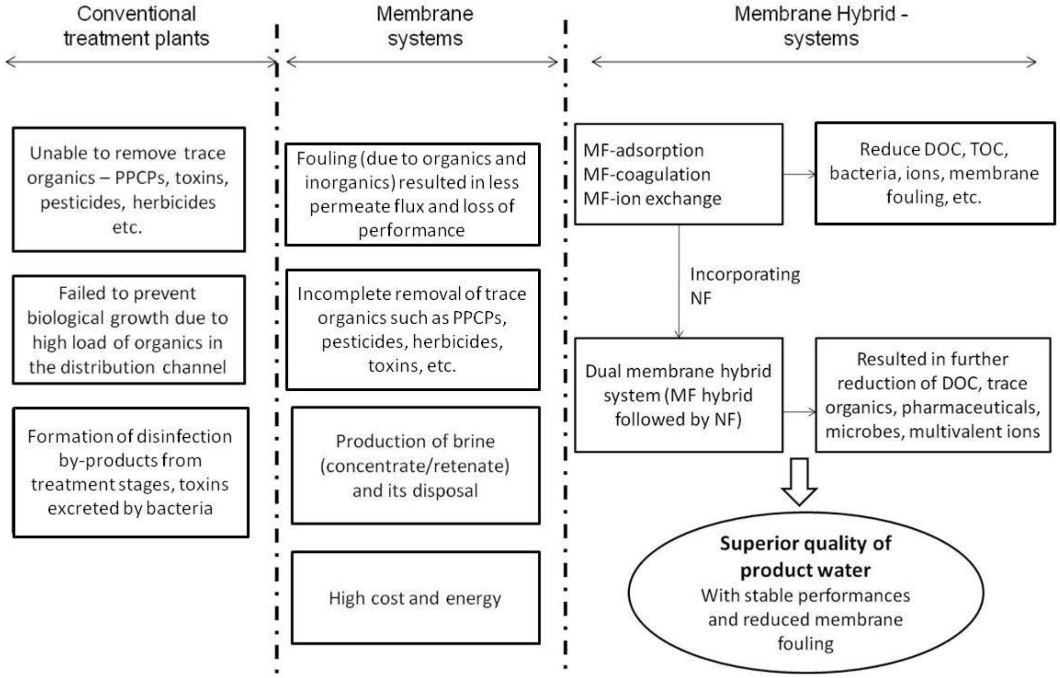


Figure 2.7: Development of membrane hybrid systems (modified from Ang et al. 2014)

2.10. Research Gaps

The past studies investigated membrane hybrid systems for the removal of dissolved organics to minimize organic fouling on membranes. None of the studies focused to the removal of PPCPs by membrane hybrid system.

Further, the management of RO concentrate was reported in terms of advanced oxidation, membrane distillation, etc., which are considered to be costly techniques. In this context, the cost effective membrane hybrid system in treating RO concentrate is rarely studied.

The use of NF and RO membranes for reclaiming BTSE is investigated in the literature and most of the studies focused to SAR value of effluent. The removal of PPCPs from irrigation water is not emphasized in the past studies.

CHAPTER 3

EXPERIMENTAL MATERIALS AND METHODS

This chapter presents a detailed description of the experimental methodologies and materials implemented in this study.

3.1. Materials

3.1.1. Wastewaters

Wastewaters used in this study are as follows:

a. Biologically treated sewage effluent (BTSE) after being filtered through a 0.2 µm pore membrane

b. Reverse osmosis concentrate (ROC), i.e. the rejection of the RO process. This is also known as RO brine, RO retentate, etc.

Wastewaters collected from a water treatment plant (WTP) in Sydney, Australia were transported to the laboratory in several 20 L gallons and were used for the experiments. The room temperature for all water samples was maintained at 20^0 C.

The WTP is designed to treat the combination of biologically treated sewage effluent (BTSE) and treated storm water through a dual membrane system consisting of continuous flow micro filtration (CMF) and reverses osmosis (RO) with a total capacity of 7.5 ML/d for CMF units and a maximum 3 ML/d for RO units. The feed water is firstly passed through CMF to remove all suspended particles larger than 0.2 µm, and a portion of the CMF effluent is then sent to the reclamation tank. The rest of the filtered BTSE is passed through RO filters to reduce salinity and then the RO permeate is directed to the reclamation tank. The schematic of the treatment trains is presented in Figure 3.1. After blending the microfiltered BTSE and RO permeate at an appropriate ratio, the recycled water is sold back to households for non-potable uses such as toilet flushing, washing clothes, washing pets, watering gardens, lawns and parks, filling ornamental ponds, water fountains, fire-fighting, washing cars, windows, brickwork, irrigation of parklands, etc. It is not used for human consumption, showering/swimming (Fact sheet – Sydney Olympic Park, 2006).

The only waste produced by the WTP is the ROC which is 5-7 times more concentrated than feed. It is discharged to the sewer (Chapman, 2006). The BTSE was collected after MF whilst ROC was collected following RO filtration.

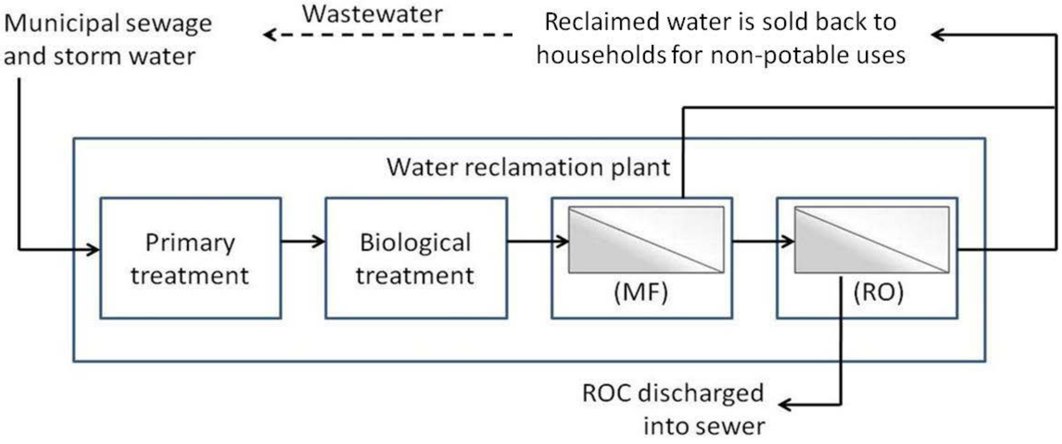


Figure 3.1: Schematic of the WTP, Sydney, Australia

The water quality characteristics of filtered BTSE and ROC are given below in Table 3.1.

Table 3.1: Water quality characteristics of filtered BTSE and ROC

Parameters	Unit	Micro filtered BTSE	ROC
pH		6.8-7.6	5.7-8.0
Conductivity	µS/cm	680 - 1120	2000-3500
DOC	mg/L	4.5-7.5	20-30
F^-	mg/L	0.7-1.1	3.0-7.7
Cl^-	mg/L	132-150	400-900
NO_3^-	mg/L	4.5-6.1	20-40
PO_4^{3-}	mg/L	1.8-2.4	8-15
SO_4^{2-}	mg/L	49-51	150-300
Na^+	mg/L	86-90	300-540
K^+	mg/L	15-21	50-120
Ca^{2+}	mg/L	25-35	75-200
Mg^{2+}	mg/L	10-12	45-100

The detailed organic characterization of both filtered BTSE and ROC of representative samples is given in Table 3.2. Both filtered BTSE and ROC were found to contain less hydrophobics (~15%) and more hydrophilics (~85%) in which humics comprised 50%.

Table 3.2: Detail organic fractions of filtered BTSE and ROC (mg/L)

	DOC	Hydro phobics	Hydro philics	Bio Polymers	Humics	Building blocks	LMW neutrals
BTSE	3.6-7.7	1.0-2.0	2.6-5.7	n.q	1.3-2.9	0.6-1.3	0.6-1.2
ROC	32.8	5.2	27.6	1.0	14.5	6.9	5.2

n.q = non quantified

3.1.2. Membranes

a. Hollow fibre membrane module

The characteristics of hollow fibre membranes (MANN+HUMMEL ULTRA-FLO PTE LTD, Singapore) used in this study are given in Table 3.3.

Table 3.3: Characteristics of Hollow fibre membrane

Item	Characteristics
Material	Hydrophilic modified Polyacrylonitrile (PAN)
Nominal pore size	0.10μm
Outer diameter	2.1mm
Inner diameter	1.1mm
Surface area	0.044m^2 to 0.2m^2
Manufacturer	MANN+HUMMEL ULTRA-FLO PTE LTD, Singapore

b. Flat sheet membrane module

The characteristics of the flat sheet MF membrane module are summarized in Table 3.4. The dimensions of this membrane are: 11.5cm (width), 10.5cm (length), 22.5cm (height).

Table 3.4: Characteristics of flat sheet membrane

Item	Characteristics
Material	polyvinylidene fluoride (PVDF)
Nominal pore size	0.14 μm
Surface area	0.2 m^2
Number of membrane sheets	8 (vertical)
Gap between two adjacent membrane sheets	11 mm
Manufacturer	A3 Membrane Company, Germany

c. Nanofiltration (NF) and reverse osmosis (RO) membranes

Three types of NF membranes (NP 010, NP 030 and NTR 729HF) and an RO membrane were used in the polishing stage of feed water. The characteristics of the NF and RO membranes are presented in Table 3.5.

Table 3.5: Characteristics of NF and RO membranes used

Membrane	Manufacturer	Material	[a]MWCo (Da)	Membrane property	Zeta potential (mV)
NP 010	Macrodyn®Nadir	Polyetersulfone	1000	Hydrophilic	-12[b]
NP 030	Macrodyn®Nadir	polyetersulfone	400	Hydrophilic	-15[b]
NTR 729HF	Nitto Denko	Polyvinylalcoho/ polyamides (Heterocyclic aromatic)	700	Hydrophilic	-100[c]
RO	Woongjin Chemical	Polyamides	100	-	-21[d]

[a] Molecular weight cut off (MWCo)
[b] Kaya et al. (2010)
[c] Shon et al. (2005)
[d] Shon et al. (2009)

3.1.3. Adsorbents

Granular Activated Carbon (GAC) and Purolite A502PS ion exchanger resins served as adsorbent and ion exchangers respectively.

a. Granular Activated Carbon (GAC)

The GAC used in this study was coal-based and the characteristics are described in Table 3.6.

Table 3.6: Characteristics of GAC

Type/structure	Coal-based premium grade (MDW4050CB)
Exchange/adsorption Capacity	Iodine #1000mg/g
Moisture content	2% max
Particle size	425-600µm
Surface area	1000 ± 50 sqm/g
Adsorption average pore diameter	30 Å

b. Ion exchange resin - Purolite A502PS

Purolite A502PS is a macroporous poly (vinylbenzyl-trimethylammonium) exchanger designed for decolorization of sugar syrups (Purolite.com). The characteristics of the Purolite A502PS are given in Table 3.7.

Table 3.7: Characteristics of Ion-exchange resin A502PS ((Purolite Corporation's official website)

Functional group	Type 1 Quaternary Ammonium
Total capacity (min)	0.85 eq/l (18.6 Kgr/ft^3) (Cl$^-$ form)
Moisture retention	66 - 72 % (Cl$^-$ form)
Particle size range	425 - 1200 µm
Reversible swelling Cl$^-$ → OH$^-$ (max.)	25 %
Specific gravity	1.04

3.2. Experimental Methods

3.2.1. Membrane Hybrid System

The term 'hybrid system' refers to coupling of two treatment operations (Thiruvenkatachari et al. 2004) to improve the performance of the ultimate treatment system. One striking peculiarity of this study is that unlike in other studies where adsorption is generally carried out as a pre-treatment, the adsorbents were directly added into the influent tank containing water to be treated. Adsorption and membrane separation take place simultaneously in one single tank. Adding adsorbents can reduce membrane fouling by reducing organic load through adsorption before reaching the membrane surface. The adsorbents also provide a mechanical scouring effect to the membrane surface. In this study adsorption and ion exchange unit operations were combined with the MF membrane process. They are referred to as the membrane-adsorption hybrid system and membrane-ion exchange hybrid system respectively. .

In the hybrid MF membrane system, a MF membrane module was immersed in the influent tank containing the wastewater to be treated. Two master flux pumps were employed to keep the flow rate of influent and effluent equal so that a constant volume of the wastewater in the reactor tank was maintained. A pressure gauge (Novus log box) was used to measure transmembrane pressure (TMP) of the membrane hybrid system. An air diffuser helped to maintain a constant airflow to produce shear stress on the membrane surface as well as to keep the adsorbent and ion exchange resin in suspension in the reactor. The loss of volatile organic compounds (VOCs) due to aeration was neglected because the wastewater used in this study was already biologically treated and hence well stabilized. The schematic diagram of the experimental setup is given in Figure 3.2.

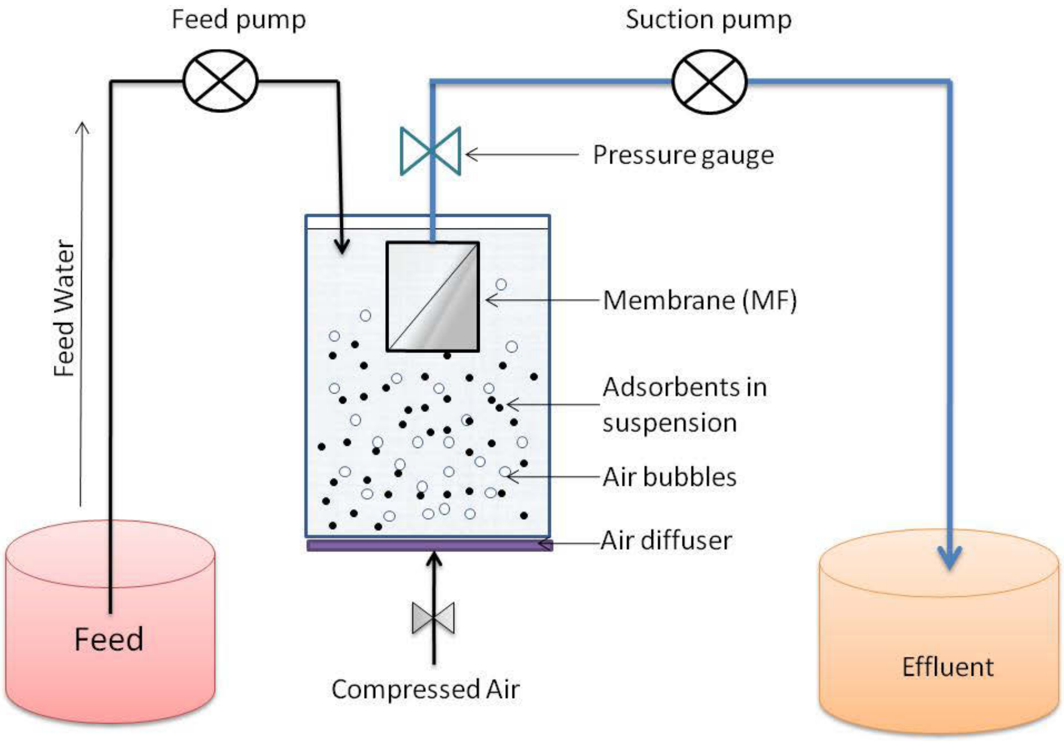


Figure 3.2: Schematic diagram of the membrane-hybrid system

The performance of GAC and an ion exchange resin (Purolite A502PS) in treating wastewater was studied separately in terms of removal of DOC and trace organics. The experimental systems were known as the 'MF-GAC hybrid system' and 'MF-ion exchange hybrid system'. These are explained in more detail below.

3.2.1.1. MF – GAC Hybrid System

The MF-GAC hybrid system was carried out for short and long periods to observe how well it performed. The short-term experiment was done with fixed initial adsorbent dose at high flux for 6 – 8 hours of operation. Long-term experiments were conducted, ranging from a few days to several weeks (i.e. 6-8 weeks) continuously at different experimental conditions with both types of wastewater (filtered BTSE and ROC). The details are given below. The volume of the rector tank was 10 L.

Experiments with filtered BTSE

A long-term experiment was carried out with filtered BTSE with initial GAC dose 2 g/L at different fluxes (2 $L/m^2.h$ to 10 $L/m^2/h$). Different %-GAC replacements were carried out on a daily basis to ensure that the maximum amount of organics was removed. The percentages of daily GAC replacements were calculated based on the volume of the reactor. The effluent was analysed for natural and trace organics.

Experiments with ROC

A short-term experiment was carried out for different initial doses of GAC (5 – 20 g/L) with ROC. The GAC was added only once at the beginning of the experiment to adsorb the dissolved organics before the wastewater reached the membrane surface. The flux was maintained at 36 $L/m^2.h$ over the experimental operation. An air diffuser was utilized to maintain the airflow rate at 3 $m^3/m^2_{\text{membrane area}}.h$. The volume of the reactor was 3 L.

Since the ROC was 5-7 times more concentrated than BTSE, a higher initial concentration of GAC was applied. The doses of GAC were selected based on batch isotherms and suggestions published in previous studies. Additionally a long-term experiment was carried out for ROC with 10 g/L initial GAC dose. A 10% of daily GAC replacement was carried out to ensure that the removal of contaminants remained stable. The filtration flux was maintained at 10 $L/m^2.h$. The volume of the rector was 3L.

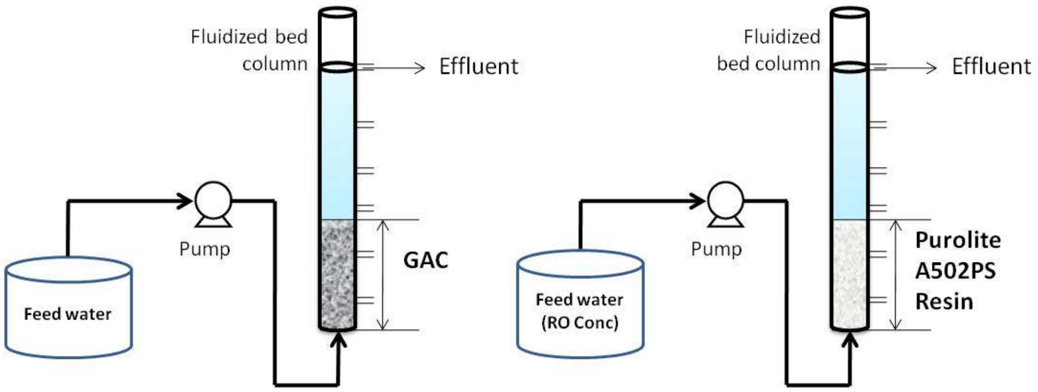
3.2.1.2. MF – Ion exchange Hybrid System

In this system, an ion exchange resin Purolite A502PS was used as an adsorbent. A short-term experiment was conducted with filtered BTSE and ROC. The experimental conditions used are as follows. A short-term experiment (6-8 h) was conducted with filtered BTSE for different sizes and different initial doses of Purolite A502PS. No daily replacement was done for the short-term since the initial concentrations of adsorbents were good enough to remove the organics throughout the experiment. When experiments were conducted with ROC, a comparatively high initial dose of Purolite A502PS (10 – 20 g/L) was used. The filtration flux was set at 36 $L/m^2.h$. An air diffuser was used to maintain the airflow rate at $3m^3/m^2_{\text{membrane area}}.h$. The volume of the reactor was 3L.

Cleaning of membrane unit: At the end of every experiment, in order to remove the foulant layer on the membrane surface, the membrane was cleaned outside the reactor using NaOH for 4 hours and this was followed by NaOCl for overnight. After each cleaning the membrane hydraulic resistance was compared with the clean flux of a virgin membrane.

3.2.2. Fluidized bed Experiments

In addition to the membrane-hybrid system, a comparative study between GAC and Purolite was conducted in a fluidized adsorption bed (Figure 3.3). Vertical columns 1 m in length were used for these experiments. The flow of feed water was maintained at a constant flow rate in the up-flow mode.



(a) (b)

Figure 3.3: Schematic diagram of the experimental setup of fluidized bed columns (a) fluidized bed packed with GAC and (b) Purolite A502PS

During the experiment, expanded fluidized bed heights of packing media were measured using measuring tape. The impact of the fluidized beds with GAC and Purolite A502PS on the removal of DOC from filtered BTSE were studied separately for different doses of GAC (i.e. at different bed heights) and fluidization velocities. The conditions used are listed below.

Experiment with GAC

i. Doses of GAC: 5 g, 10 g, and 15 g
ii. Fluidization velocities: 5.7 and 11.4 m/h

Experiment with Purolite A502PS

i. Doses of Purolite A502PS: 5 g, 15 g, and 30 g
ii. Fluidization velocities: 5.7 and 11.4 m/h
iii. Fresh and regenerated Purolite resins

3.2.3. NF/RO filtration systems

The NF membrane (filtration) unit (Figure 3.4) used was equipped with a rectangular cross-flow membrane cell having a membrane area of 68 cm^2. The membrane charge has been shown to become less negative (reduced zeta potential) when the temperature of the feed water increased (Mo et al. 2008). Therefore, a cooling coil was submerged in the feed water tank to maintain the feed water temperature at constant at 20 ± 2°C. The applied pressure was 4 bar for NF and 40 bar for RO and feed velocity was 0.5 L/min. The cross flow velocity of NF was 13 cm/s whilst RO was 1.8 cm/s. The concentrate (retentate) produced from NF or RO was recirculated back into the feed water.

The NF/RO membranes were soaked in 10% ethanol solution for overnight prior to use. Before each NF experiment, the NF unit was thoroughly cleaned by circulating 0.1 M NaOH solution through it. This was followed by adding 0.1 M HNO_3 solution for 2 hours and then by milli-Q water for 1 hour to remove trace organics and impurities from the unit as well as in the external tubes.

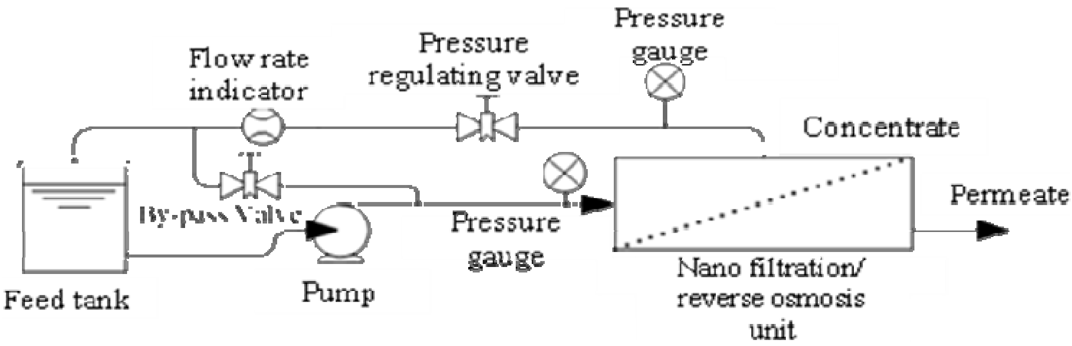


Figure 3.4: Nanofiltration/Reverse osmosis unit

3.3. Experimental configurations used

In order to achieve high quality water, the membrane-hybrid systems, NF and RO were coupled together to remove the contaminants of interest. Two methods proposed in this study are listed as follows:

i. Integrated MF-GAC/NF hybrid system: MF-GAC hybrid system coupled with NF to obtain reusable water free of natural organics as well as PPCPs.

ii. NF coupled with RO to obtain good quality water that is free of natural organics, PPCPs and monovalent ions.

As these two systems consist of two membrane processes, they are termed 'dual membrane – hybrid system'.

3.3.1. MF-GAC/NF hybrid system

The schematic diagram of the integrated MF-GAC/NF hybrid system is presented in Figure 3.5. The MF-GAC hybrid system removes the majority of DOC and trace organics. The treated effluent produced by the MF-GAC hybrid system was used as a feed for NF. As presented in Figure 3.5, the treatment train MF-GAC followed by NF is believed to reduce NF fouling and provide high quality water with a superior ability to remove DOC and trace organics.

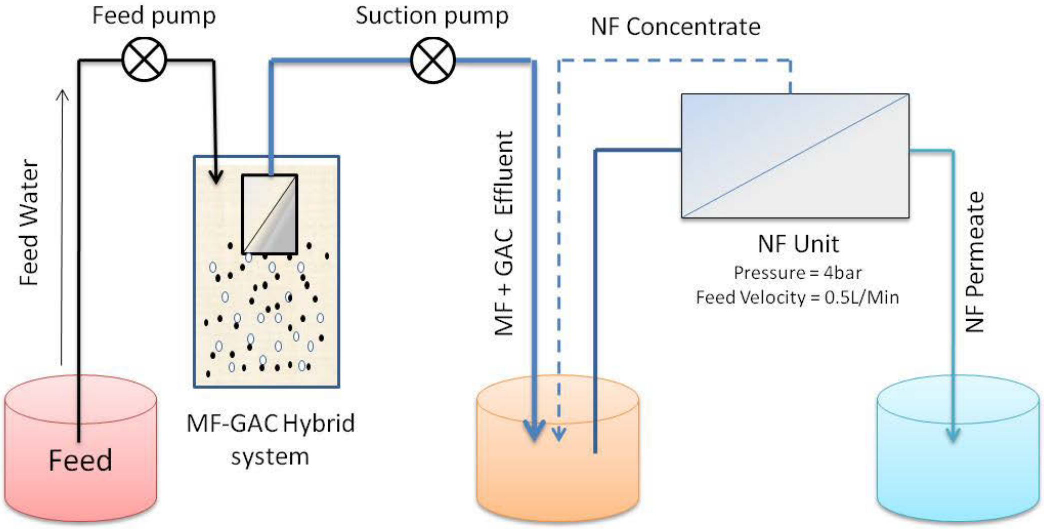


Figure 3.5: Dual membrane-hybrid system (coupled form of membrane-hybrid system and NF)

3.3.2. Combination of NF/RO processes

As shown in Figure 3.6, the filtered BTSE was treated by NF and RO separately and the permeate quality characteristics were examined. Based on the required product water quality and performance of NF and RO processes, both systems were coupled together to produce the optimum water quality characteristics. Further, different blending proportions of NF and RO permeate were also proposed depending on the requirements of product water quality, performance of NF and RO, economy, etc.

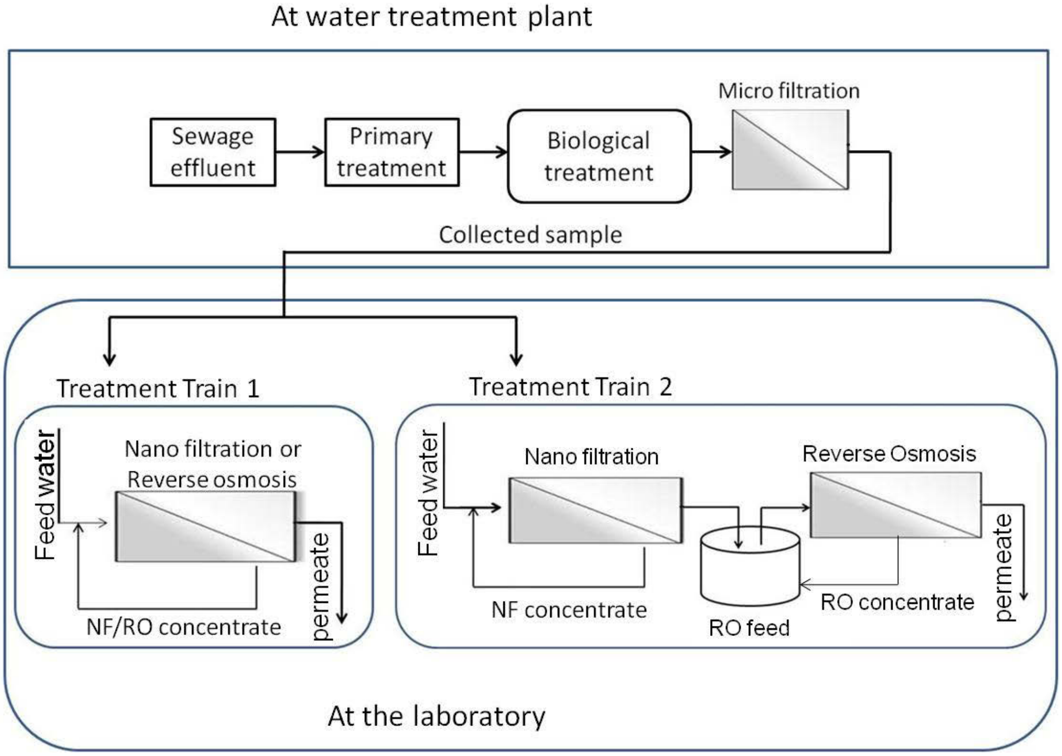


Figure 3.6: Coupling of NF/RO membranes in water reuse applications

3.4. Experimental Analyses

3.4.1. Analysis of DOC

The dissolved organics were measured in terms of total DOC, organic fractions, etc. All the samples were filtered through a 0.45 µm pore membrane prior to analysis, the objective being to remove suspended particles. Total DOC was measured by Multi N/C2000 TOC analyser (Analytik Jena AG) equipped with auto sampler. TOC analyser measures the oxidized form of gaseous CO_2 using a detector non-dispersive infra red (NDIR) cell. The organic fractions were measured by liquid chromatography-organic carbon detection (LC-OCD) and fluorescence excitation emission matrix spectroscopy (F-EEM). The analytical procedure is explained below.

i. Liquid-Chromatography-Organic carbon detection

LC-OCD is a method that separates the pool of NOM into major fractions based on size of molecules and then quantifies these compounds (Huber et al. 2011). The LC-OCD system consists of a size exclusion chromatography column, which separates hydrophilic organic molecules according to their molecular weight size. The separated compounds were then detected using two different detectors: a UV detector (absorption at 254 nm) and a DOC detector (after inorganic carbon purging). The different fractions/classes of the organic matter can be identified quantitatively and qualitatively depending on the size of the molecules. The column has a separation range of 0.1-10 kDa (Huber et al. 2011). In this regard, Model 8 developed by DOC Labor, Dr Huber (Germany) served to characterise the organic compounds in detail. A Toyopearl TSK HW50S column (TOSOH Bioscience GmbH, Stuttgart, Germany) was used in this regard with phosphate buffer mobile phase of pH 6.4 (2.6 g/L KH2PO4 and 1.5mol/L Na2HPO4) at a flow rate of 1.1 mL/min. Injection volumes and retention time were set at 1,000μL and 120 min, respectively. The chromatographic column was a weak cation exchange column based on polymethacrylate.

The organic matter can be broadly categorized into two major types - hydrophobics and hydrophilics. The hydrophilics can be further divided into bio-polymers, humics, building blocks, LMW neutrals and LMW acids. The micro-filtered wastewater consists mainly (~50%) of humics. The derivatives of humics are called building blocks which are also found in significantly large amounts. As the wastewater was collected just after micro filtration, the bio-polymers were low as they would have been captured by micro filtration. The LMWs as well were quite low as they had already been consumed by bacteria at the biological treatment stage.

ii. Fluorescence Excitation Emission Matrix

Fluorescence Excitation – Emission matrices (FEEMs) were obtained using a Varian Eclipse Fluorescence Spectrophotometer. The 3D-EEM technique is a rapid, selective and sensitive one that generates information regarding the fluorescence characteristics of organic compounds by simultaneously changing the excitation and emission wavelength. The fluorescence in different spectral regions is associated with various types of functional groups. The fluorescence signals are basically attributed to protein-like fluorophores, fulvic-like fluorophores and humic-like fluorophores; and they characterize dissolved organic matter in water using fluorescence spectroscopy (Jeong et al. 2013a). EEMs were recorded using scanning emission wavelengths from 250 to 500 nm repeatedly at excitation wavelengths scanned from 220 to 400 nm by 5 nm increments. The excitation and emission bandwidths were both set at 5 nm. The fluorometer was set at a speed of 3000 nm/min, a PMT voltage of 700V and a response time of 2 s. The common five fluorescence peaks observed are shown in Table 3.8.

Table 3.8: Major fluorescent components of seawater organic matter (Jeong et al. 2012)

Ex_{max} (nm)	Em_{max} (nm)	Chemical functionality
270–280	300–310	Tyrosine-like, protein-like
270–280	320–350	Tryptophan-like, protein-like
250–260	380–480	UV humic-like
290–320	380–420	Visible marine humic-like
330–350	420–480	Visible humic-like

3.4.2. Analysis of trace organics (pharmaceuticals and personal care products)

Pharmaceuticals and personal care products were extracted using solid phase extraction (SPE) and examined employing Liquid Chromatograph with tandem mass spectroscopy. 5 mL analytes were extracted using 500 mg hydrophilic/lipophilic balance (HLB) cartridges (Waters, Milford, MA, USA). These analytes were separated using an Agilent (Palo Alto, CA, USA) 1200 series high performance liquid chromatography (HPLC) system equipped with a 150 x 4.6 mm, 5 µm particle size, Luna C18 (2) column (Phenomenex, Torrance, CA, USA). Mass spectrometry was done using an API 4000 triple quadrupole mass spectrometer (Applied Biosystems, 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 described elsewhere (Monsalvo et al. 2014).

3.4.3. Inorganic ions Analysis

The analysis of inorganic anions was done using a Metrohm ion chromatograph (Model 790 Personal IC) equipped with an auto sampler and conductivity cell detector. Separation was achieved using an A SUPP column 3 (4-150 mm). Solutions of Na_2CO_3 (3.2 mmol/L) and $NaHCO_3$ (1.0 mmol/L) were used as mobile phase with a flow rate of 0.7 mL/min.

3.4.4. NF/RO Membrane Autopsy

3.4.4.1. Foulants extraction

When the NF/RO operation was completed, the used fouled membranes were washed with milli-Q water and dried in a beaker by keeping them at 4°C. Once it had dried, a section of the central part of the membrane was cut (21.6 cm^2) and ultra sonicated for

10-20 min to extract the membrane depositions into 40 mL milli-Q water. The dissolved solution was then filtered using a filter with 0.1 µm opening and assessed for organics and inorganics.

3.4.4.2. Field emission - scanning electron microscope

The organic foulants on the membrane surface were observed using Zeiss Supra 55VP field emission scanning electron microscope (FE-SEM). A piece of cut fouled membrane was dried in a desiccator overnight and analyzed on SEM.

3.4.4.3. Contact angle

The contact angle of the membrane surface was utilized to determine if any changes had occurred in the hydrophobicity of the membrane after fouling. A sessile drop method was carried out using a goniometer (Theta Lite) with 1.8–2.0 mL of MQ water droplet on the dried membrane surface. Measurements were repeated 5 times and the average reading was reported in this study.

CHAPTER 4

FLUIDIZED BEDS AS A PRE-TREATMENT FOR REVERSE OSMOSIS IN REMOVAL OF ORGANICS

SUMMARY

Applying pre-treatments to remove dissolved organic matter from biologically treated sewage effluent (BTSE which is used as the feed for reverse osmosis) can help to reduce organic fouling of the Reverse Osmosis (RO) membrane. In this study the performance of granular activated carbon (GAC), a commonly used adsorbent, and Purolite A502PS, an anion exchange resin, was evaluated for its ability to remove effluent organic matter (EfOM) from BTSE collected from a water reclamation plant located in Sydney, Australia. The performance of GAC and Purolite A502PS was evaluated and compared through adsorption equilibrium, kinetics and fluidized bed experiments. The maximum adsorption capacity ($Q_{\max}$) of GAC calculated from the Langmuir model with BTSE was 13.4 mg/g GAC. The operational conditions of fluidized bed columns packed with GAC and Purolite A502PS strongly affected the removal of EfOM. GAC fluidized bed with a bed height of 10 cm and fluidization velocity of 5.7 m/h removed more than 80% of dissolved organic carbon (DOC) during a 7 h experiment. The average DOC removal was 60% when the bed height was reduced to 7 cm. When comparing GAC to Purolite A502PS, more quantities of Purolite A502PS were required to remove the same amount of DOC. The poorer performance of Purolite A502PS can be explained by the competition provided by other inorganic anions present in BTSE. A plug flow model was used to predict the impact of the amount of adsorbent and flow rate on the removal of organic matter.

4.1. INTRODUCTION

In many water reclamation plants, biological treated sewage effluent (BTSE) is used as the feed for RO. The EfOM present in BTSE often has a low concentration but it can lead to organic and bio fouling of the RO membrane (Jarusutthirak et al. 2002; Shon et al. 2004; Herzberg et al. 2010). Membrane fouling is a significant problem in RO applications because it leads to more energy consumption, frequent chemical cleaning and shorter membrane life. This ultimately increases plant treatment costs. Pre-treatment of the feed water is considered to be the most promising solution for controlling the fouling due to its simple and easy implementation. A recent study with seawater (Jeong et al. 2013) shows that a submerged membrane coagulation–adsorption hybrid system (SMCAHS) can be used for pre-treatment of seawater RO. This pre-treatment removed only 48% of DOC from seawater (DOC of 2.4 mg/L) but it helped to reduce the deposition of low molecular weight organic matter (185 Da and 90 Da) on the RO membrane. In turn this reduced initial biomass accumulation (from 4.10E08 cells/cm^2 with raw seawater to 2.75E08 cells/cm^2 with seawater pre-treated by SMCAHS).

Several studies have confirmed that GAC adsorption is effective in removing total organic carbon (TOC) from wastewater (Gur-Reznik et al. 2008; Kim et al. 2002). BTSE contains a significant portion of hydrophilic organic compounds and these compounds are highly ionized, so they can be removed by ion exchange (Fettig, 1999). A number of studies show that TOC reduction is significant when natural surface water is treated with conventional ion-exchange technology. Magnetic ion exchange (MIEX) resin can effectively remove 70% of hydrophilic compounds and 55% of hydrophobic components within a very short contact time of 20 min (Zhang et al. 2006). A fluidized bed packed with Purolite A500PS was able to remove more than 80% DOC consistently in 8 h (more than 800 bed volumes) using 10 mg DOC/L of synthetic wastewater (Ahmad et al. 2012). However, the performance of ion exchange resins can be interfered with by the presence of ions in the feed water (Johir et al. 2011b; Wang et al. 2012).

Thus, in this chapter, the performance of GAC and Purolite A502PS was firstly evaluated through isotherm and kinetic experiments. The fluidized bed columns with different bed heights and flow rates were then carried out in up-flow mode to determine the effects of operational conditions on the efficiency in removing organics. Liquid chromatography–organic carbon detection (LC–OCD) determined the removal of different organic fractions by GAC and Purolite A502PS fluidized bed columns. The regeneration and reuse of exhausted Purolite A502PS that had treated BTSE was also evaluated. In this study, Langmuir, Freundlich, Homogeneous surface diffusion models (HSDM) and plug flow model were applied to determine the equilibrium and kinetics behavior of both GAC and Purolite A502PS.

4.2. MATERIALS AND METHODS

4.2.1. Materials

a. Wastewater: BTSE collected from a water treatment plant, Sydney was used as feed water for the experiments. The DOC, sulfate and nitrate contents of the feed are 4.5-7.5 mg/L, 49-51 mg/L and 4.5-6.1 mg/L, respectively. The remaining physico-chemical parameters of the feed water are described in Chapter 3.

b. Adsorbents: GAC and Purolite A502PS were chosen as adsorbents to study the performance of removal of DOC from feed water. The details of the materials used are given in Chapter 3.

4.2.2. Adsorption equilibrium

Adsorption equilibrium studies were conducted with GAC and Purolite A502PS separately to establish the optimum dose of these substances. Different doses of GAC (0.1 – 1.6 g/L) and Purolite A502PS (0.1 – 5 g/L) were poured into 200 ml conical flasks containing BTSE. The conical flasks were then placed on a Ratek Platform Mixer at 110rpm and shaken continuously for 24 hours. After that, the samples were filtered through a 0.45 µm filter and the DOC was measured in a Multi N/C 2000 analyser.

4.2.3. Adsorption Kinetics

Kinetics experiments were conducted to establish the DOC adsorption rate of GAC and Purolite A502PS. Fixed amounts of GAC (1 g/L) and Purolite A502PS (1 g/L) were separately added into flasks containing 200 mL of either BTSE or ROC and these were placed on the Ratek Platform Mixer at 110 rpm. Samples were collected at different times – ranging from 5 mins to 420 mins - and were filtered through a 0.45 µm filter before DOC measurement.

4.2.4. Mathematical modelling

The Langmuir, Freundlich, and Sips models were used for an equilibrium study of GAC and Purolite A502PS with BTSE. The Langmuir equation assumes that there is no interaction between the sorbate molecules and that the sorption is localized in a monolayer. It also assumes that once a sorbate molecule occupies a site, no further sorption can take place at that site. Theoretically, therefore, a saturation value is reached, beyond which no further sorption occurs (Ochoa-Herrera and Sierra-Alvarez 2008). The Langmuir isotherm is defined by Eq. 4.1:

$$q_e = \frac{q_m.b.Ce}{1+b.Ce} \qquad \text{Eq. 1}$$

Where: q_e is the amount of organic adsorbed per gram of the adsorbent at equilibrium (mg/g); q_m is the saturated maximum monolayer adsorption capacity (mg/g); *b* is Langmuir adsorption constants related to the binding energy of adsorption (L/mg); and C_e is the equilibrium concentration (mg/L).

Adsorption of natural organic matter by anion exchange resins is expected to be a heterogeneous process (Cornelissen et al. 2008; Humbert et al. 2008). Therefore the Freundlich model can be used for adsorption when employing Purolite A502PS. The Freundlich isotherm is an empirical equation developed based on the assumption that the adsorbent has a heterogeneous surface composed of different classes of adsorption sites. Here the relationship between the amount of DOC adsorbed on the Purolite A502PS and the DOC left in the BTSE can be modelled by Eq. 4.2:

$$\mathrm{q_e = K_F.C_e^{\frac{1}{n}}} \qquad \text{Eq. 4.2}$$

Where K_F is a Freundlich constant indicative of the adsorption capacity of the resin, n is an experimental constant indicative of the adsorption intensity of the resin, and C_e is the equilibrium concentration of DOC in the BTSE.

The Sips model is a different empirical model representing equilibrium adsorption data. This isotherm model has features that are common to both the Langmuir and Freundlich isotherm models. As a combination of the Langmuir and Freundlich isotherm models, the Sips model contains three parameters, q_m, b and n which can be evaluated by fitting the experimental data. For single solute equilibrium data, the Sips adsorption isotherm model can be written as follows:

$$q_e = \frac{q_m (bC_e)^{\frac{1}{n}}}{1 + (bC_e)^{\frac{1}{n}}} \qquad \text{Eq. 4.3}$$

The Homogeneous Surface Diffusion Model (HSDM) used to calculate the mass balance of dissolved organic matter inside a spherical porous particle was applied to an analysis of both the GAC and Purolite A502PS adsorption kinetics. The HSDM consists of a three-step process (Najm, 1996): (i) the adsorbate diffuses through a stagnant liquid film layer surrounding the adsorbent particle; (ii) the adsorbate adsorbs from the liquid phase onto the outer surface of the adsorbent particle; and (iii) the adsorbate diffuses along the inner surface of the adsorbent particles until it reaches its adsorption site. The equations of HSDM are as follows:

$$\frac{\partial q_t}{\partial t} = D_s \left(\frac{\partial^2 q_t}{\partial r^2} + \frac{2}{r} \frac{\partial q_t}{\partial r} \right) \qquad \text{Eq. 4.4}$$

The above equation can be numerically solved using the following initial and boundary conditions, t = 0; qt = 0

r = 0; $$\frac{\partial q}{\partial r} = 0$$ Eq. 4.5

r = r_p; $$D_s \rho_p \frac{\partial q_t}{\partial r} = K_f (C - C_s)$$ Eq. 4.6

Where q_t is the rate of change of surface concentration with time (t) at any radial distance (r) from the centre of the GAC and Purolite A502PS particle during the adsorption/ion exchange process (mg/g); D_s is the surface diffusion coefficient which represents the rate of diffusion of the DOC along the surface of the GAC and Purolite A502PS (m^2/s); K_f is the external mass transfer coefficient (m/s); ρ_p is the apparent density of the GAC and Purolite A502PS (kg/m^3); C is the bulk phase concentration, mg/L; and C_s is the concentration on the external surface of adsorbent particles (mg/L).

In order to solve the HSDM equation the orthogonal collocation method (OCM) and the variable coefficient ordinary differential equation solver (VODE) were specifically used (Villadsen and Stewart, 1967). Moreover, to extract the optimized parameters (D_s and k_f), the Nelder–Mead simplex method was employed (Ahmad et al. 2012).

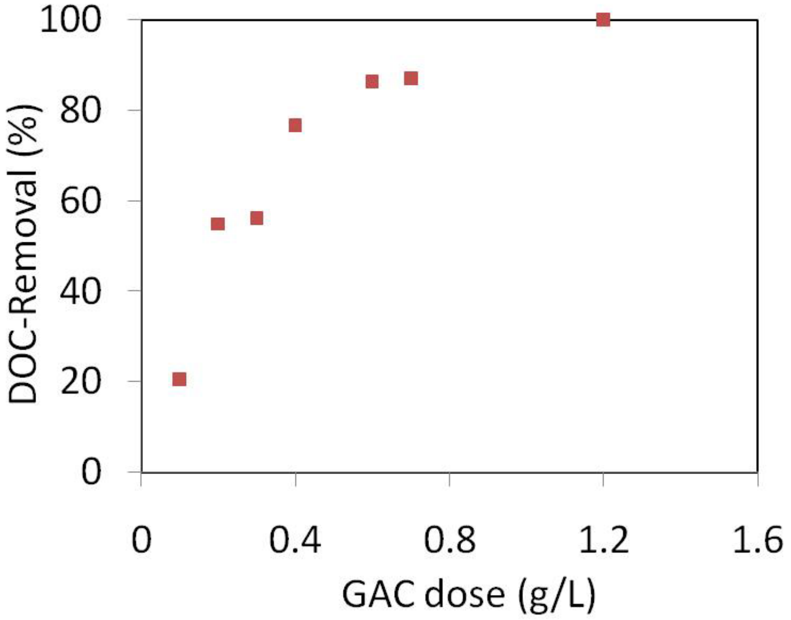
4.3. RESULTS AND DISCUSSION

4.3.1. Batch studies

4.3.1.1. Isotherm

Adsorption equilibrium experiments were conducted to predict the adsorption and exchange capacity of GAC and Purolite A502PS resin with BTSE. Figure 4.1 illustrates the removal efficiency of DOC as a function of GAC and Purolite A502PS dosage. As expected, an increase in adsorbent or resin dose improved the removal efficiency of DOC as there is a larger surface area and more ion-exchange sites to adsorb or exchange organic electrolytes. GAC was able to remove DOC better than Purolite A502PS. It was observed that 98% of DOC was removed with a GAC dose of 1.2 g/L, whereas only 70.2% of DOC was removed using Purolite A502PS dosage of 5g/L.

(a) GAC



(b) Purolite A502PS

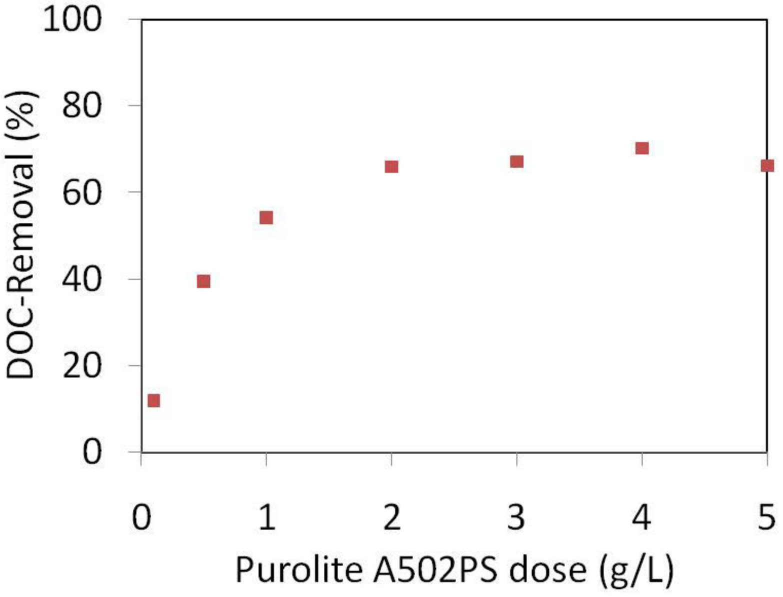


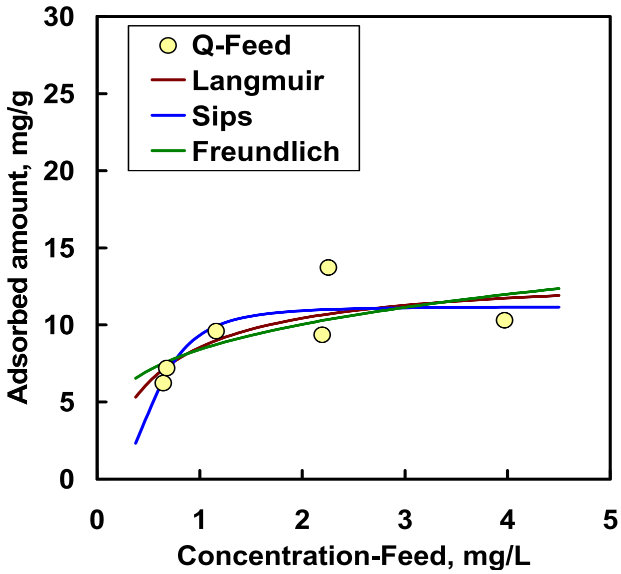
Figure 4.1: (a) Effect of GAC and (b) Purolite A502PS on the removal of DOC from BTSE (initial concentration of DOC 5 – 5.2 mg/L)

The GAC equilibrium results fitted well to the Langmuir, Sips and Freundlich isotherm equations. With reference to Purolite A502PS the equilibrium result fitted only to theFreundlich isotherm equation. The adsorption curves predicted by these models are presented in Figure 4.2. The isotherm parameters are shown in Table 4.1. The adsorption curves predicted by all of these models with GAC and Freundlich model with Purolite A502PS fitted reasonably well with the observed values.

The adsorption curves predicted by all of these models with Purolite A502PS fitted well with observed values, and the correlation coefficient (r^2) for all the isotherm models ranged from 0.808 to 0.948. It is evident that the Langmuir and Sips models yielded nearly similar values for DOC adsorption capacity (q_m) of GAC with BTSE. The maximum adsorption capacity calculated by Langmuir was 13.421 mg/g GAC.

K_F reflects the adsorption/exchange capacity of materials and for a given value of K, a higher value of n indicates a stronger solute affinity (Cornelissen et al. 2008). The results from the Freundlich isotherm (Table 4.1) indicate that the adsorption capacity of GAC with BTSE was much higher than the exchange capacity of Purolite A502PS resin with BTSE. This can be partly explained by GAC's high surface area which was nearly 50 times larger than that of Purolite A502PS. Furthermore the BTSE consists of a high concentration of inorganic anions having a high affinity with ion exchange resin. Matulionytė et al. (2007) used Purolite A500, an earlier version of Purolite A502PS, to remove various components from fixing rinse water They found that Purolite A500 could well adsorb $S_2O_3^{-2}$ (4.34 meq), CH3COO$^-$ (0.69 meq), and SO_4^{2-} (0.48 meq). Similar to Purolite A500, the strong competition among other anions at a high concentration in BTSE reduced the amount of DOC removed by Purolite A502PS.

(a) GAC



(b) Purolite A502PS

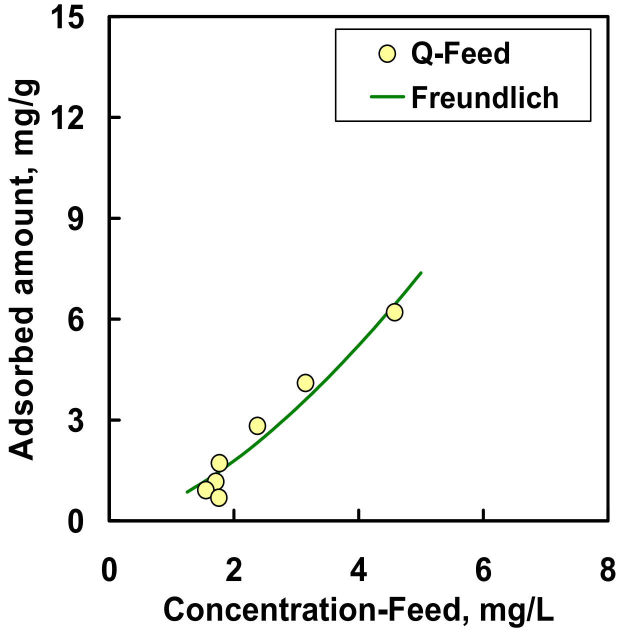


Figure 4.2: Modelling of adsorption and ion-exchange equilibrium for (a) GAC and (b) Purolite A502PS with BTSE

The 1/n value of the adsorption equilibrium of GAC with BTSE was 0.256, which was much lower than 1, indicating that the isotherm shapes were concave curvilinear (favorable) (Cornelissen et al. 2008). In contrast, the 1/n of the adsorption equilibrium of Purolite A502PS with BTSE was 1.55 which confirms that the isotherm is of type III and therefore unfavorable.

Table 4.1: Isotherm model parameters for GAC and Purolite A502PS

Parameters		GAC	Purolite A502PS
Langmuir	q_m	13.421	122.76
	b	1.748	9.679E-3
	r^2	0.594	0.808
Freundlich	K_F	8.404	0.607
	N	3.9	0.644
	r^2	0.490	0.946
Sips	q_m	11.185	102.16
	B	5.054	5.794E-3
	n	0.331	0.621
	r^2	0.679	0.948

DOC removal by Purolite A502PS in the presence of nitrate and sulfate ions: The performance of Purolite resin in removing DOC in the presence of nitrate and sulfate ions is shown in Figure 4.3. The removal of sulfate ions was observed to be higher than DOC and nitrate. The removal of DOC and nitrate was almost similar but the removal of DOC was slightly higher than nitrate.

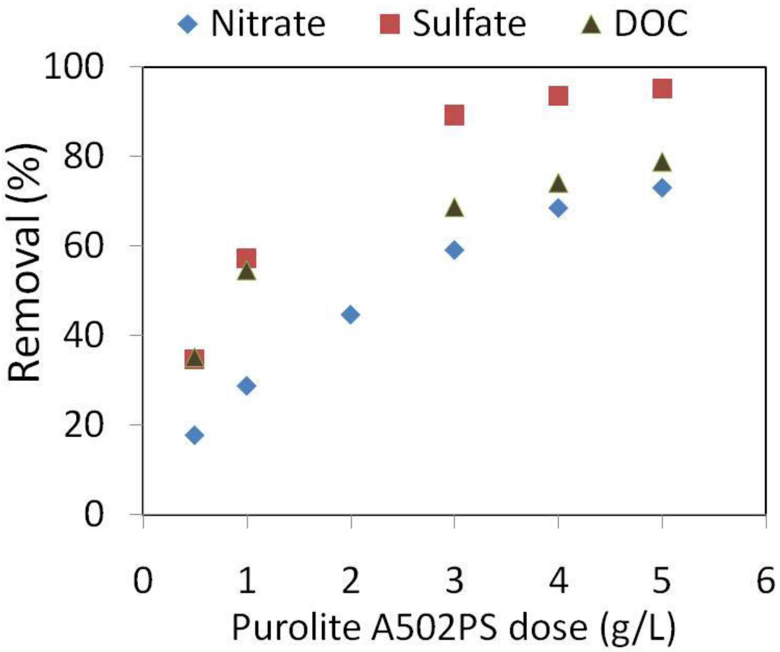
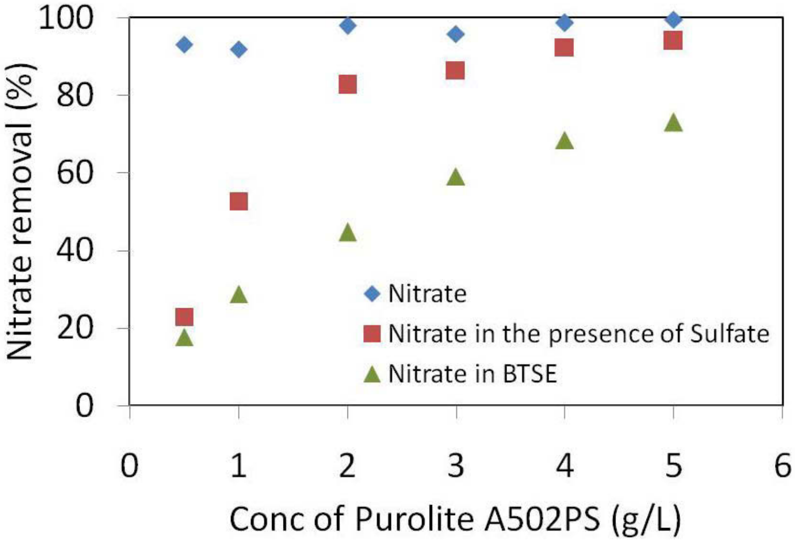


Figure 4.3: The performance of Purolite A502PS in the removal of nitrate, sulfate and DOC (initial concentrations of nitrate, sulfate and DOC in the feed water were 6 mg/L, 45 mg/L, 8 mg/L, respectively).

In this context, the removal of nitrates by Purolite in the presence of sulfates and their subsequent removal in the presence of nitrates were investigated in batch studies. The initial concentrations of sulfate and nitrate ions in the feed water were 45 mg/L and 6 mg/L, respectively. According to Figure 4.4a the removal of nitrate by Purolite is high - between 90-100%; however, the amount removed fell to 20-90% in the presence of sulfate ions. This clearly shows that sulfates have higher affinity to resin and they are quickly exchanged with ion exchange sites in the Purolite and reduce the number of exchange sites available to nitrates. Furthermore, when experiments were done with real wastewater, the presence of organics and other anions is obvious and subsequently created more competition. This further reduced the removal of nitrate to 20-70%. As such, it can be concluded that the presence of anions (nitrates and organics) restricts the performance of resin in the removal of target anions. Figure 4.4b illustrates the removal of sulfates in the presence of nitrates and organics.

(a) **Nitrate removal**



(b) **Sulfate removal**

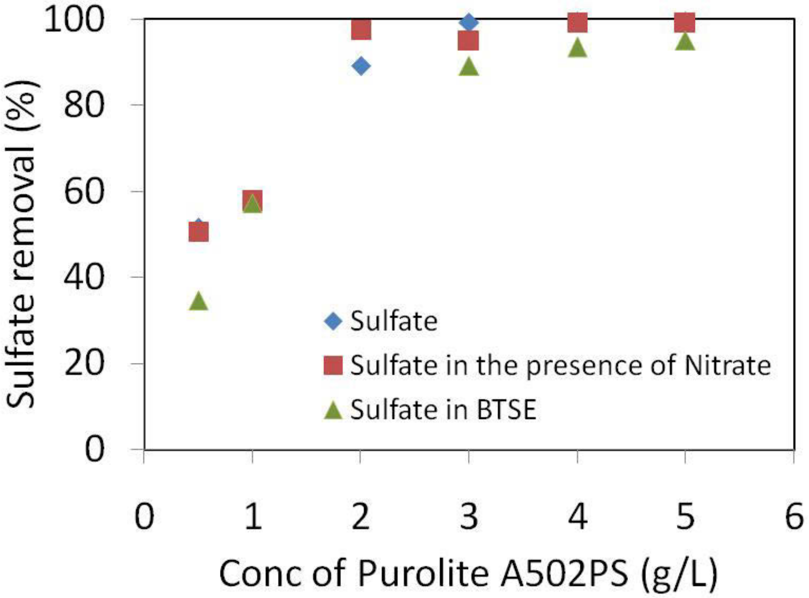


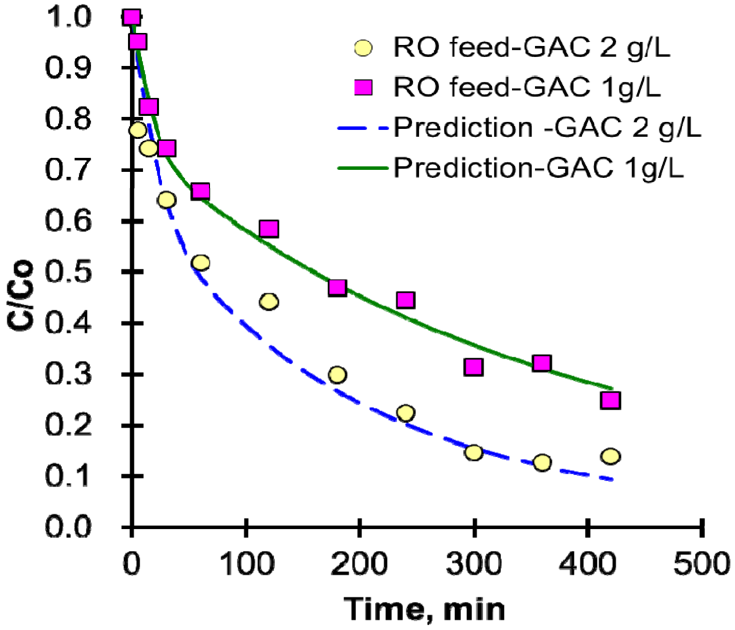
Figure 4.4: (a) The removal of nitrate in the presence of sulfate (nitrate concentration was 6.6 mg/L) (b) the removal of sulfates in the presence of nitrate (sulfate concentration was 22 -29 mg/L)

Unlike nitrate, the anion sulfate is not influenced by other anions such as nitrates and organics. No significant difference was observed between the removal of sulfates with and without nitrate being present. The affinity towards sulfate ions was not influenced by other anions. The affinity towards the removal of sulfates and nitrates may have reduced the adsorption capacity of DOC and this could explain why Purolite A502PS performed more badly than GAC.

4.3.1.2. Kinetics

The kinetics results of GAC and Purolite A502PS were fitted with the HSDM model and results are presented in Figure 4.5. The model parameters are presented in Table 4.2. The experimental results reveal that DOC in BTSE was quickly adsorbed by GAC and Purolite A502PS within the first 300 minutes and thereafter remained constant. In both cases, until they became stable, the available sites on the GAC surface for adsorption and available exchange sites in the Purolite A502PS were abundant.

(a) GAC



(b) Purolite A502PS

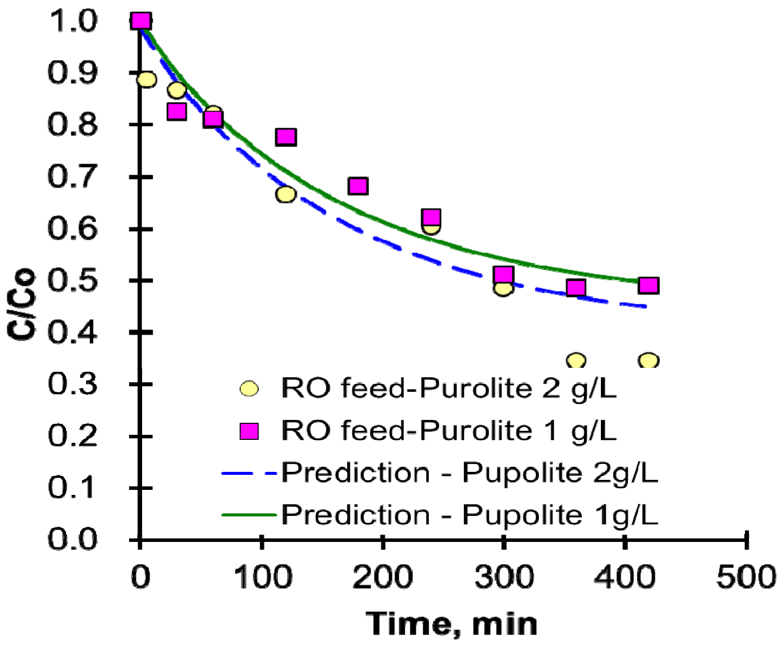


Figure 4.5: Prediction of adsorption kinetics of (a) GAC and (b) Purolite A502PS with BTSE using the HSDM model (initial DOC of BTSE was 4.5–5.8 mg/L).

The results show that the simulation curve fitted well with the experimental values. The external mass transfer coefficient K_f of DOC in BTSE with GAC was higher than that of Purolite A502PS. K_f depends on agitation speed and the higher density of Purolite A502PS compared to GAC could explain lower K_f of Purolite A502PS in contrast to GAC.

The results show that the surface diffusion D_s is a function of the equilibrium concentration C_e. Furthermore the relationship of solid diffusion D_s and equilibrium concentration C_e for GAC and Purolite A502PS can be expressed as equations 4.7 and 4.8, respectively:

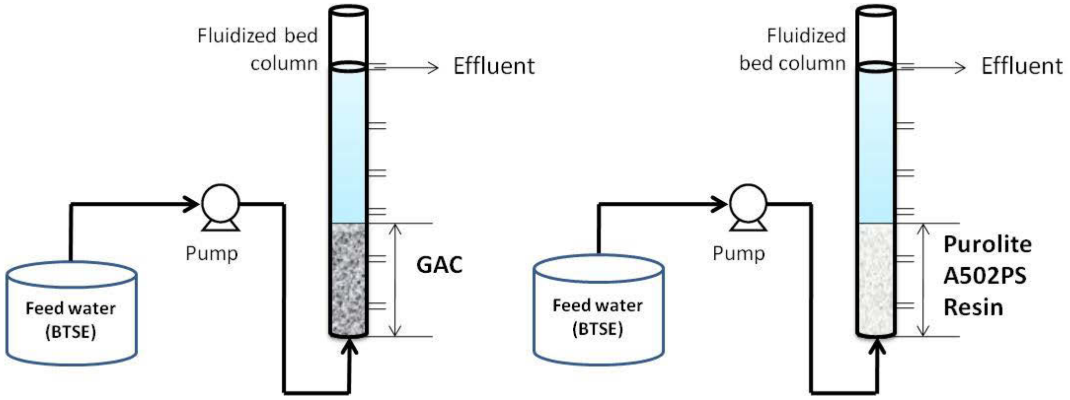
$$D_s = 1.739\text{E-}14e^{4.401\text{E-}0.2Ce} \qquad \text{Eq. 4.7}$$

$$D_s = 1.498\text{E-}13e^{8.115\text{E-}0.2Ce} \qquad \text{Eq. 4.8}$$

Table 4.2: The mass transfer coefficients of GAC and Purolite A502PS with BTSE

	GAC		Purolite A502PS	
	1 g/L	2 g/L	1 g/L	2 g/L
Initial Conc (mg/L)	4.5	5.8	7.7	3.6
K_f (m/s)	12.92E-06	8.50E-06	1.59E-06	3.01E-06
D_s (m^2/s)	2.12E-14	2.25E-14	2.80E-13	2.01E-13

4.3.2. Fluidized beds



(a) (b)

Figure 4.6: Schematic diagram of the experimental setup of fluidized bed columns (a) fluidized bed packed with GAC and (b) Purolite A502PS

In addition to the batch experiments, long-term experiments were carried out. The columns were packed with GAC and Purolite separately and operated at two different fluidization velocities (i.e. 5.7 m/h and 11.4 m/h).

4.3.2.1. GAC-packed fluidized contactor

4.3.2.1.1. Effect of GAC doses

DOC removal: Firstly, the effect of GAC doses on DOC removal efficiency was studied. Figure 4.7 shows the DOC removal efficiency of the GAC fluidized bed contactor for different doses of GAC. In this study, 5 g, 10 g and 15 g of GAC were packed into three separate columns corresponding to 3 cm, 7 cm and 10 cm bed height and the fluidization velocity was maintained at 5.7 m/h.

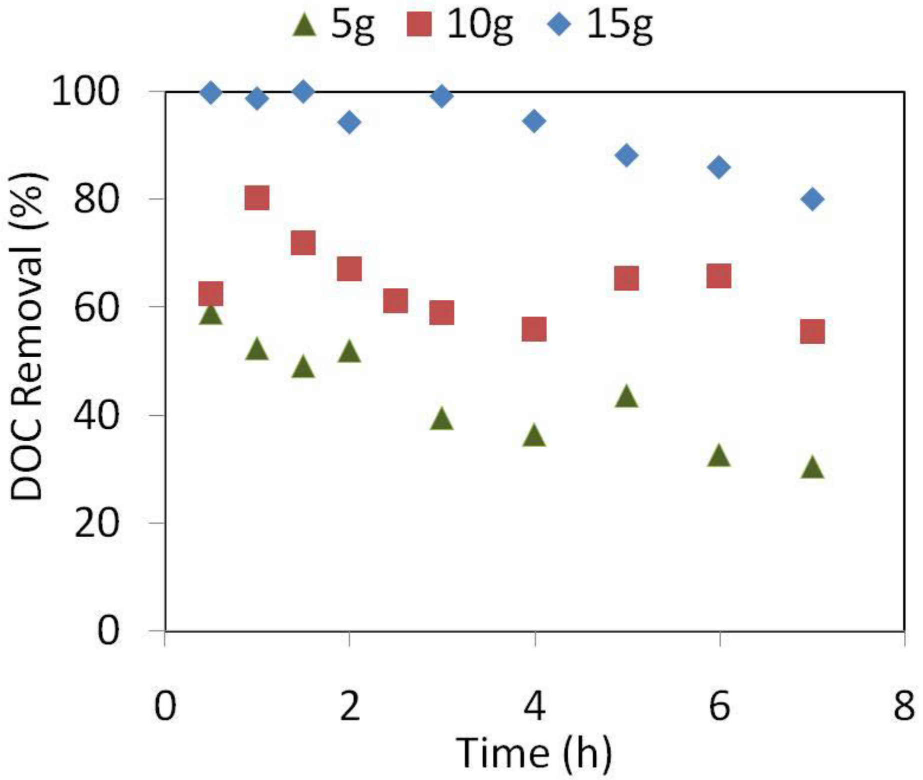


Figure 4.7: Effect of doses on the removal of dissolved organics (DOC was 4.7 mg/L)

Modelling: To quantify and predict the removal behavior of DOC in the column, the experiment employed the "Plug flow model". The mass balance used in this work was coupled with the adsorption isotherm equation and HSDM. To create the model the following assumptions were made: 1) the system followed a plug flow scenario without axial dispersion; and 2) the adsorbents in the bed were uniformly distributed. The equations of this model are as follows:

$$\frac{\partial C}{\partial t} = -\frac{v}{\varepsilon_r}\frac{\partial C}{\partial z} - \frac{(1-\varepsilon_r)}{\varepsilon_r}\cdot \rho_p \cdot \frac{\partial q}{\partial t} \qquad \text{Eq. 4.9}$$

$$\varepsilon_r = 1 - (1 - \varepsilon_{mf}) \cdot \left(\frac{L_{mf}}{L_f} \right) \qquad \text{Eq. 4.10}$$

Where L_{mf} is a height of the initial fixed bed, L_f is the height of the fluidized bed, ε_r is a voidage of the fluidized bed, and ε_{mf} is a voidage of the fixed bed. $\partial q_t / \partial t$ was determined by equations 4.4 - 4.6. Here D_s is determined from batch kinetics and k_f is determined using the Nelder–Mead simplex method (Ahmad et al. 2012).

The bed height before and after fluidization, detention time of wastewater in the column and model parameters are presented in Table 4.3. The model prediction for removing organic matter from the BTSE using the Plug flow model is presented in Figure 4.8. Here the up-flow fluidization velocity and detention time were calculated using equations 4.11 and 4.12, respectively.

$$v = \frac{Q}{\pi r^2} \qquad \text{Eq. 4.11}$$

$$t = \frac{L_f}{v} \times 60 \qquad \text{Eq. 4.12}$$

Where *v* is the up-flow fluidization velocity (m/h), t is the detention time (min), Q is the flow rate (m^3/h), and r is the radius of fluidized column (m).

Table 4.3: Bed height after and before the fluidization, detention time, K_f, D_s of GAC fluidized contactor at different doses

GAC dose (g)	Bed height before fluidization (cm)	Bed height after fluidization (cm)	Detention time (min)	ε_{mf}	K_f (m/s)	D_s (m^2/s)
5	3	4	0.4	0.45	6.42E-6	2.14E-14
10	7	8.5	0.9	0.45	6.96E-6	2.14E-14
15	10	12.5	1.3	0.45	7.75E-6	2.14E-14

As expected, more than 80% of DOC was removed with a larger amount of GAC (15g) over the first 7 hours of the experiment. The smaller doses of GAC (10g and 5g) reduced DOC removal efficiency to 60% and 30% after 7 hours, respectively. The rapid decline in DOC removal efficiency using a small amount of GAC can be explained by the small surface area and a very short detention time.

The larger dose of GAC obviously increases the bed height compared to a smaller dose. Thus a higher bed height can provide more time to contact solutes with adsorbents whilst a lower bed height means there is less time for solutes to achieve contact with GAC. As such the higher dose corresponds to high bed height and results in a decrease in the DOC concentration in the effluent at the same time. This outcome is confirmed by the work of Ahmad and Hameed (2010) who reported the high adsorption capacity of solute at the highest bed height due to an increase in the adsorbent's surface area. This provided more binding sites for the adsorption of solutes.

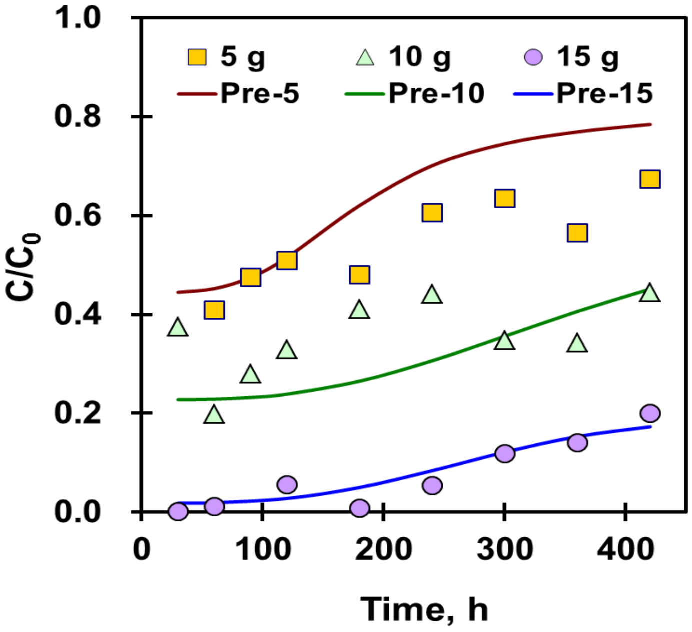


Figure 4.8: Fluidized bed model simulation with different doses of GAC

Organic characterization: The LC-OCD outcome shows that BTSE water contains mostly hydrophilic compounds (74.7%). This result agrees with the analysis by Jarusutthirak et al. (2002) who found more hydrophilic compounds in secondary effluents. These compounds can be further classified as biopolymers (1.6%), humics (42.2%), building blocks (16.2%), and low molecular weight (LMW) (14.7%). Here, biopolymers include polysaccharides and proteins; building blocks include hydrolysates of humic substances; and LMW neutrals and amphiphilics (slightly hydrophobic compounds) include sugars, alcohols, aldehydes, ketones and amino acids (Jeong et al. 2013). The removal efficiency of different organic fractions is presented in Table 4.4.

As expected, the rising amount of GAC in the column increased the adsorption efficiency of all organic fractions and the removal of hydrophilics was found to be more effective than hydrophobic substances. Having 15 g of GAC in the column made it possible to adsorb hydrophilic (82.1%) and hydrophobic compounds (77.5%). Gur-

Reznik et al. (2008) also reported a very similar rejection rate for hydrophobic and hydrophilic fractions when removing organic matter from tertiary wastewater effluent via the GAC column. The medium molecular weight (MW) compounds such as humics (~1000 Da) and building blocks (300-500 Da) were adsorbed effectively (more than 85%) by the 15g GAC column. Biopolymer - a high molecular weight part (about 20,000 Da) - was barely removed by the GAC column. However, this part only accounted for a very small amount in the BTSE.

Table 4.4: The effect of GAC doses on the removal (%) of organic fractions

GAC amount (g)	Hydrophobic (%)	Hydrophilic (%)	Hydrophilic (%)			
			Bio polymers	Humics	Building blocks	LMWs
5	43.9	35.5	17.8	41.3	26.4	30.7
10	50.7	61.3	32.2	68.1	66.8	39.2
15	77.5	82.1	50.0	85.3	85.7	72.3

4.3.2.1.2. Effect of fluidization velocities

Fluidization velocity and detention time are other factors affecting the removal of DOC. As such the effect of fluidization velocities on the adsorption of DOC by GAC was investigated with two different fluidization velocities, 5.7 m/h and 11.4 m/h while maintaining the same dose of GAC (10 g). Results show that the lower velocity is more efficient in removing DOC whilst the higher velocity resulted in poorer removal efficiency (Figure 4.9). The reason is that at the lower velocity the residence/detention time is higher (0.9 min) whilst at the higher velocity the detention time is less (0.6 min). This concurs with other studies (Ahmad and Hameed, 2010 ; Ko et al. 2000). At a high flow rate the adsorption capacity was poorer due to: firstly, the solute having less residence time in the fluidized contactor; and secondly, diffusion of the solute into the pores of the adsorbent. Consequently the solute left the fluidized contactor before equilibrium occurred.

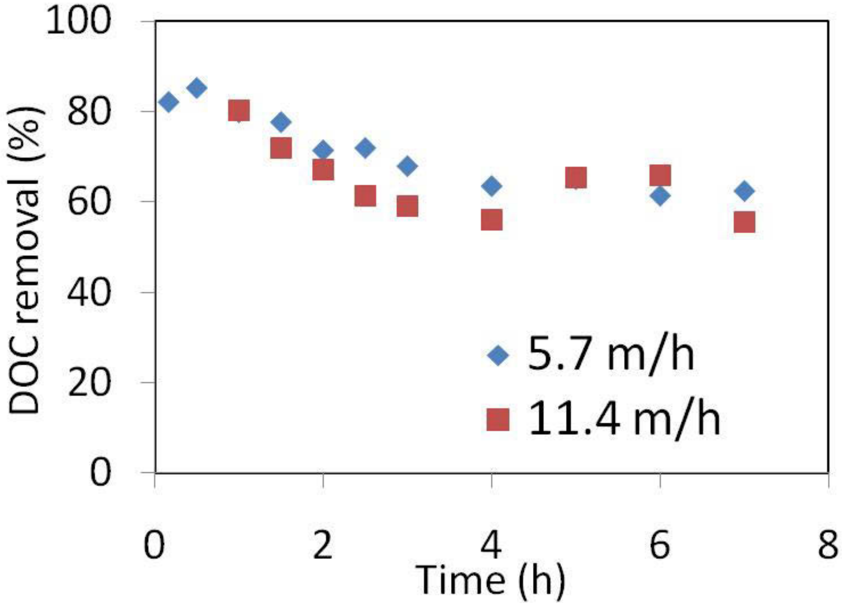


Figure 4.9: The effect of fluidization velocities on the removal of dissolved organics by GAC (DOC was 4.7 – 7.5 mg/L)

The prediction for removing organic material from the BTSE with the GAC contactor using the Plug model is shown in Figure 4.10. The values of the D_s and K_f coefficients of GAC with BTSE are presented in Table 4.5. The increase in fluidization velocity in turn increased the external mass-transfer coefficients K_f. This can be explained by the adsorbent's faster movement in the column and this led to more shear at the particle surface and reduced the boundary layer film.

Table 4.5: Mass transfer coefficients in BTSE at different fluidization velocities – GAC

Fluidization velocity (m/h)	Bed height before fluidization (cm)	Bed height after fluidization (cm)	Detention time (min)	ε_{mf}	K_f (m/s)	D_s (m^2/s)
5.7	7	8.5	0.9	0.45	9.04E-5	2.14E-14
11.4	7	11.5	0.6	0.45	19.88E-5	2.42E-14

Since higher concentrations (7.5 mg/L) of BTSE were used for the flow rate of 11.4 m/h the D_s value for flow rate of 11.4 m/h was consequently higher than that for a flow rate of 5.7 m/h.

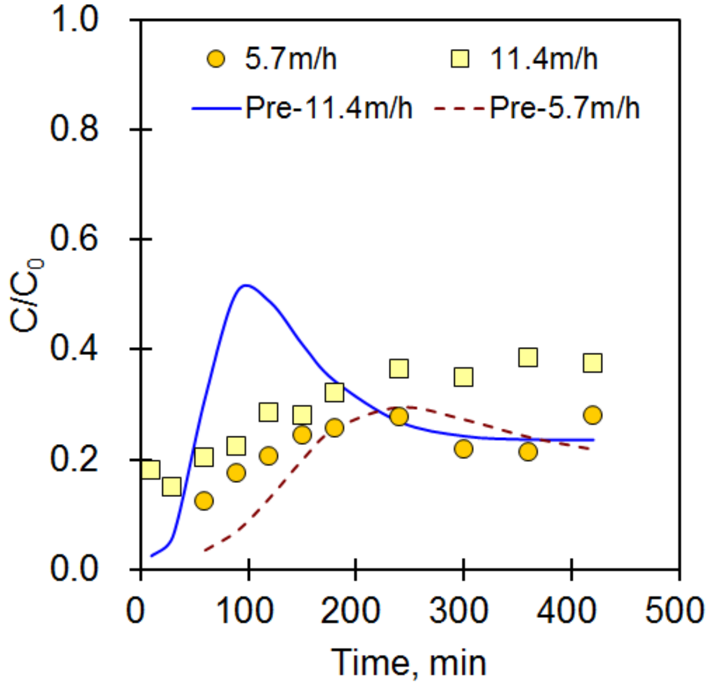


Figure 4.10: Fluidized bed model simulation with different fluidization velocities

4.3.2.1.3. Long-term fluidized bed experiments

In order to establish the breakthrough of GAC fluidized bed contactor, a long-term experiment was done with GAC dose of 30 g at two different fluidization velocities, 5.7 and 11.4 m/h. Figure 4.11 illustrates the removal pattern of DOC by GAC for about 325 hours, which is equivalent to approximately 15 days of continuous operation. Both fluxes initially achieved 100% of DOC removal but then the removal efficiency gradually declined to 20% after 325 hours and 175 hours, respectively, at 5.7 and 11.4 m/h (Figure 4.11).

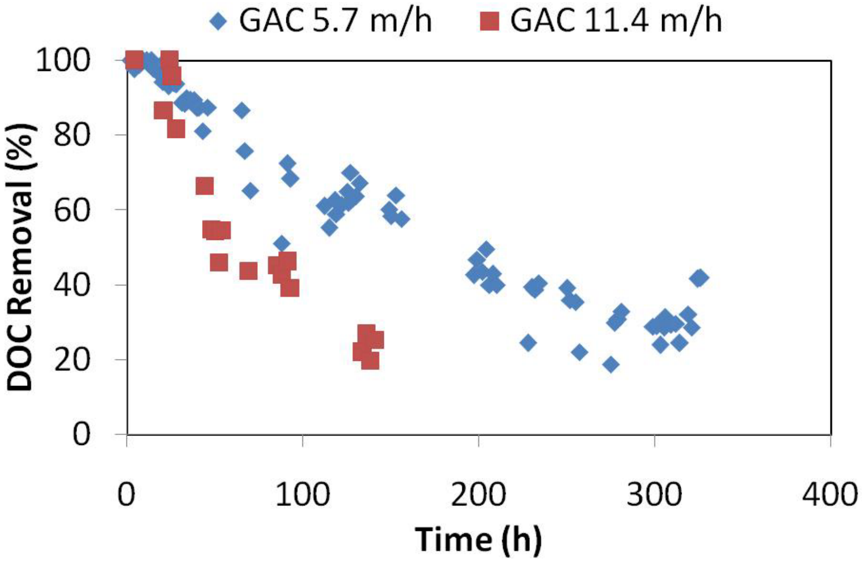


Figure 4.11: Long-term study of GAC-packed fluidized bed contactor in terms of DOC removal of DOC (a) DOC removal efficiency (b) Breakthrough curves for DOC (Initial DOC of BTSE: 6.0-4.0mg/L for flux of 5.7 and 11.4 m/h; GAC amount = 30 g)

It is obvious that high flux passes more solutes with water through the column and exhausts the GAC more rapidly. The doubled fluidization velocity filter double the amount of water and exhausted the GAC in half the contact time. The time taken to reach its breakthrough rapidly decreased with high flux compared to low flux. This outcome could be due to the residence time and amount of solutes passed through the column. It is a result agreeing with Ahmad and Hameed (2010); Ko et al. (2000) and Taty-Costodes et al. (2005).

4.3.2.2. Purolite A502PS packed fluidized contactor

4.3.2.2.1. Effect of Purolite A502PS dose

a. DOC removal

The effect of Purolite A502PS dose on the removal of organics in the fluidized bed was also studied. Figure 4.12 clearly shows that a larger dose of Purolite A502PS resulted in more DOC being removed. The column packed with 30 g of Purolite A502PS could remove around 60-80% DOC over 7 hours. This level of efficiency was slightly poorer than previous results as reported by Ahmad et al. (2012), who found that about 80% of DOC was removed from synthetic wastewater using 28g of Purolite A500PS fluidized bed column over 8 hours. Their experiment was carried out with a detention time of 3 mins and wastewater with 10mg DOC/L. The smaller amount of Purolite A502PS in the fluidized bed column led to much less DOC being removed (less than 27% and 5% with 15g and 5g Purolite A502PS, respectively).

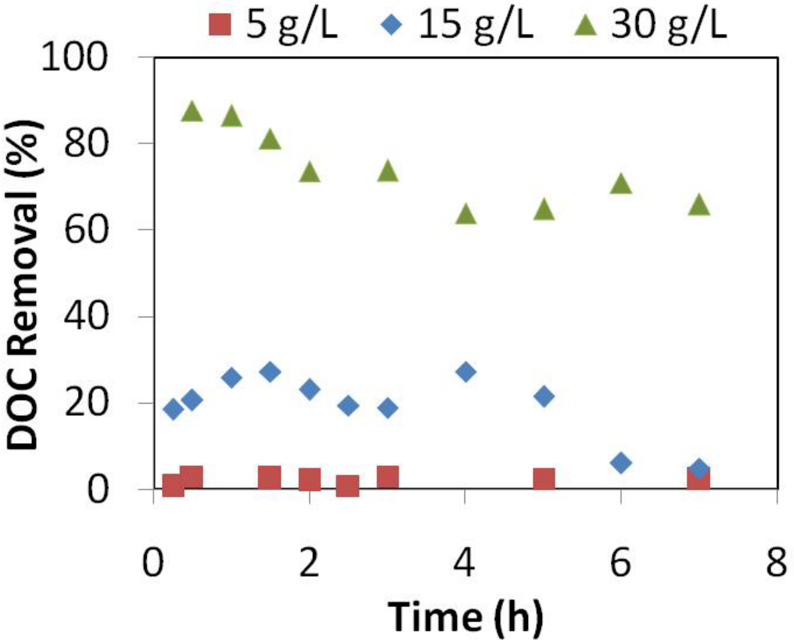


Figure 4.12: Effect of doses of Purolite A502PS on the removal of dissolved organics (initial DOC was 4.2-4.7 mg/L)

Modelling: The Plug flow model was able to predict the DOC removal of Purolite A502PS fluidized column with BTSE. The prediction curve and model parameters are presented in Figure 4.13 and Table 4.6 respectively.

Table 4.6: Bed height after and before the fluidization, detention time, K_f, D_s of Purolite fluidized contactor at different doses

Purolite A502PS dose (g)	Bed height (cm)		Detention time (min)	K_f (m/s)	D_s (m^2/s)
	before fluidization	after fluidization			
5	2.5	3	0.3	9.202E-8	2.110E-13
15	7.5	10.5	1.1	4.836E-7	2.110E-13
30	15	22	2.3	2.145E-5	2.194E-13

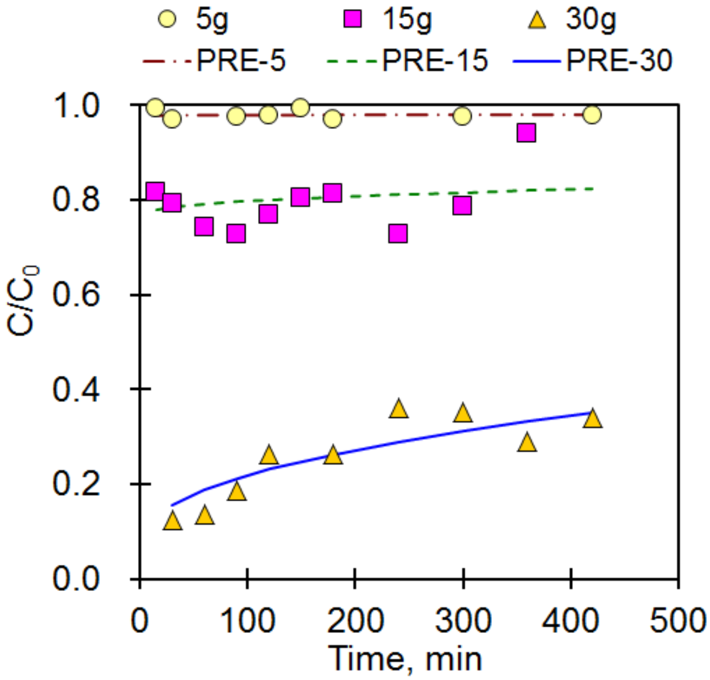


Figure 4.13: Fluidized bed model simulation with different doses of Purolite A502PS

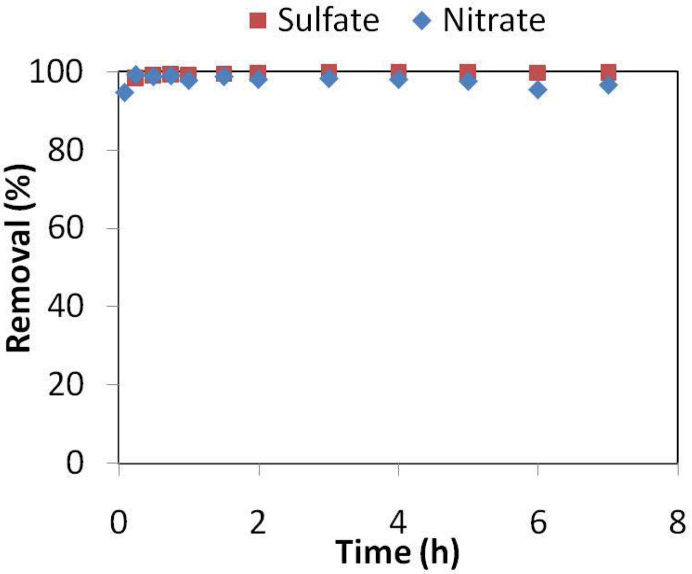
Similar to the previous observation of GAC, a higher K_f value was obtained when a larger dose of Purolite A502PS was employed. Purolite A502PS is heavier than GAC. As such, its movement in the fluidized column was less than GAC for the same fluidized velocity. This led to a bigger boundary layer film and as such the K_f of the Purolite A502PS fluidized bed was smaller than the GAC. The slight difference in initial concentration of BTSE led to a small difference in the D_s.

b. Removal of inorganic anions

Purolite A502PS also has a very high affinity to sulfate and nitrate. In the fluidized bed study with synthetic water containing only sulfate or nitrat,e more than 95% of these components were observed during the 7 hour experiment (Figure 4.14a). It should be noted that the respective removal efficiencies of sulfate and nitrate were more than 94%

and 88% when water contained only sulfate and nitrate ions. Here, the experimental conditions were similar to that of BTSE water (NO_3^-: 5mg/L, SO_4^{2-}: 50mg/L, Purolite amount: 30g, flow rate: 5.7 m/h). The presence of EfOM in BTSE did not affect the ability to remove sulfate. However, the removal of nitrate declined remarkably when sulfates were present (Figure 4.14). It shows that Purolite A502PS has excellent exchange capacity with sulfate and there is a strong competition between nitrate and DOC in exchanging with Purolite A502PS.

(a) In the absence of EfOM BTSE



(b) In the presence of EfOM BTSE

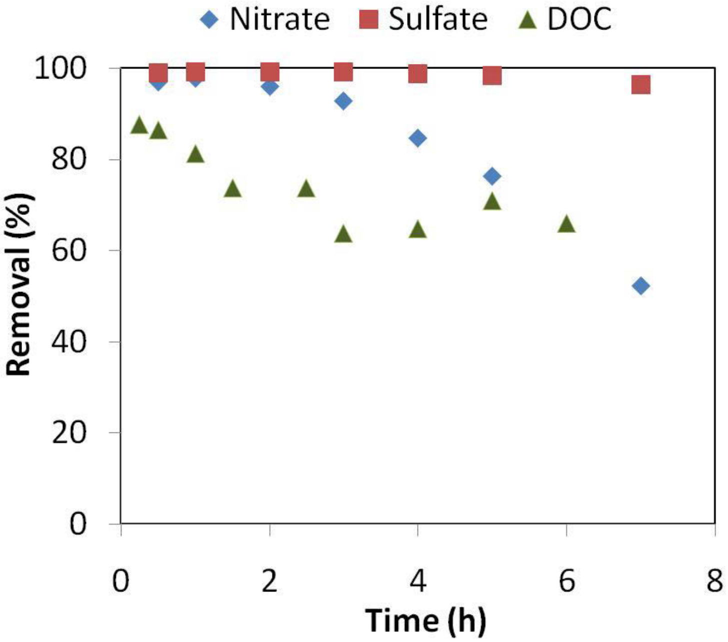


Figure 4.14: Efficiency of Purolite A502PS in removing nitrate and sulfate (a) in the absence of EfOM BTSE and (b) in the presence of EfOM BTSE (NO_3^-: 5 mg/L, SO_4^{2}: 50 mg/L, Purolite amount: 30 g, flow rate: 5.7 m/h)

Better efficiency in removing DOC (more than 80% consistently over 8 hours) was observed with Purolite A500 (a previous version of Purolite A502PS) and synthetic wastewater (Ahmad et al. 2012). The reduction in Purolite A502PS's ability to remove DOC efficiently with BTSE can be explained by the competition of other anions such as sulfate and nitrate; these were present in higher concentrations in BTSE (43 mg/L sulfate and 5 mg/L nitrate, respectively).

4.3.2.2.2. Effect of fluidization velocities

As expected, the comparatively higher DOC removal efficiency was observed with low flux over 7 hours in the experiment. Two different fluidization velocities of 5.7 and 11.4 m/h (corresponding to detention times of 2.3 and 1.8 min) resulted in average removal efficiencies of 75% and 60%, respectively (Figure 4.15).

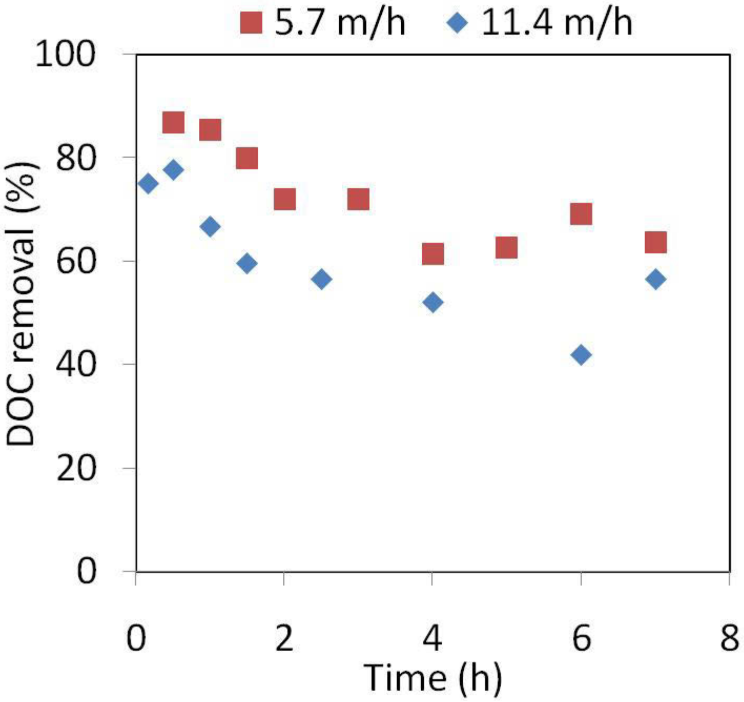


Figure 4.15: DOC removal efficiency of Purolite A502PS fluidized bed with different velocities, i.e. 5.7 m/h and 11.4 m/h (initial DOC = 4.4 mg/L, Purolite A502PS amount = 30 g)

The values of the model parameters (D_s and K_f) and prediction using the Plug flow model are presented in Table 4.7 and Figure 4.16. As noted previously, the external mass-transfer coefficients K_f increased when fluidization velocity accelerated. In terms of fluidized velocity, both K_f and D_s when using the Purolite A502PS column were less than that of the GAC column.

Table 4.7: Bed height after and before the fluidization, detention time, K_f, D_s of Purolite A502PS columns at different fluidization velocities (initial concentration C_0: 4.4 mg/L)

Fluidization velocity (m/h)	Bed height (cm)		Detention time (min)	K_f (m/s)	D_s (m^2/s)
	before fluidization	after fluidization			
5.7	15	22	2.3	1.687E-5	2.141 E-13
11.4	15	34	1.5	2.406E-5	2.141 E-13

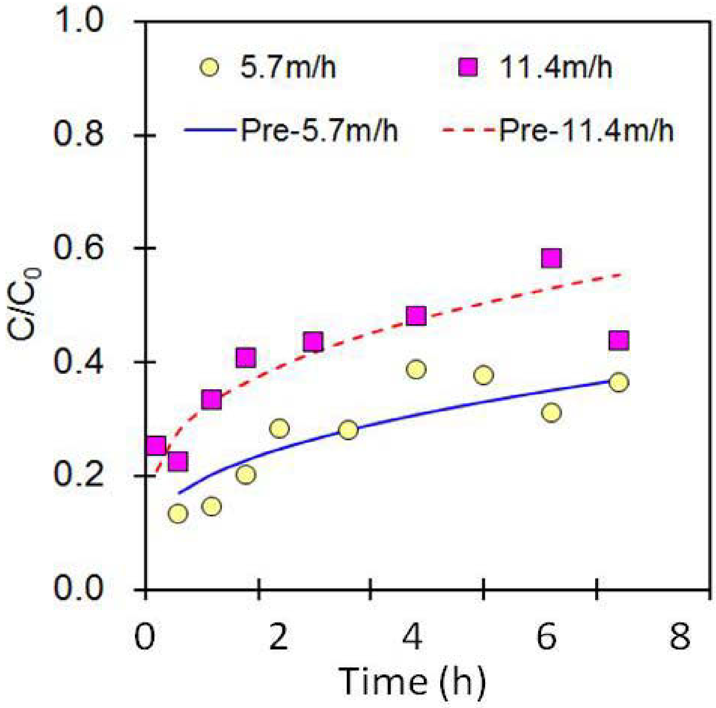


Figure 4.16: Model simulation with different velocities of Purolite A502PS fluidized bed.

Organic fractions: The LC-OCD data explains the removal of organic fractions further. The velocity 5.7 m/h removed DOC more efficiently than 11.4 m/h because the contact time was double with lower fluidization velocity. The removal of humics and building blocks varied from 63.3-73%, more than that of biopolymers (50.7-57.1%). However the removal of LMWs was less than 38% since LMW neutrals are uncharged compounds (Table 4.8). Compared to GAC, Purolite A502PS is not observed to be effective in removing organics.

Table 4.8: The effect of Purolite flow rates on the removal of organic fractions

Purolite A502PS velocity (m/h)	Hydrophobic (%)	Hydrophilic (%)	Hydrophilic (%)			
			Bio polymers	Humics	Building blocks	LMWs
5.7	59.6	61.6	57.1	67.3	73.0	38.2
11.4	53.9	55.8	50.7	64.1	63.3	30.6

4.3.2.2.3. Long-term fluidized bed experiment with Purolite A502PS

The result of a long-term fluidized bed experiment packed with Purolite A502PS with the same experimental conditions (amount 30 g at fluidization velocity 5.7 m/h and 11.4 m/h) over time is shown in Figure 4.18. Unlike GAC, the Purolite resin exhibited a DOC removal efficiency of 75-80% initially but over time this percentage declined. The low velocity (5.7 m/h) reduced efficiency in removing DOC from 80% to 40% in 325 hours while the high velocity (11.4 m/h) fell from 75% to 20% in 150 hours (Figure 4.17).

Figure 4.17 also shows the high flux of 11.4 m/h resulted in a faster breakthrough. At the 100th hour, the Purolite reached its breakthrough at high flux. The reason is that at high flux more solutes pass through the contactor than low flux and this makes the Purolite resin become saturated more quickly.

In comparing the performance of Purolite with GAC in terms of removing DOC, the decline in Purolite A502PS's ability to do so was gentler whilst GAC was comparatively more steep. It means Purolite A502PS began with an initial removal efficiency of approximately 70%, but this dropped to 40% over 300 hours. Even though GAC removed 100% at the beginning, it dropped to 20% over the same number of hours. This clearly confirms Purolite can maintain its performance for a longer period of time compared to GAC, which reaches its breakthrough faster only under similar operational conditions.

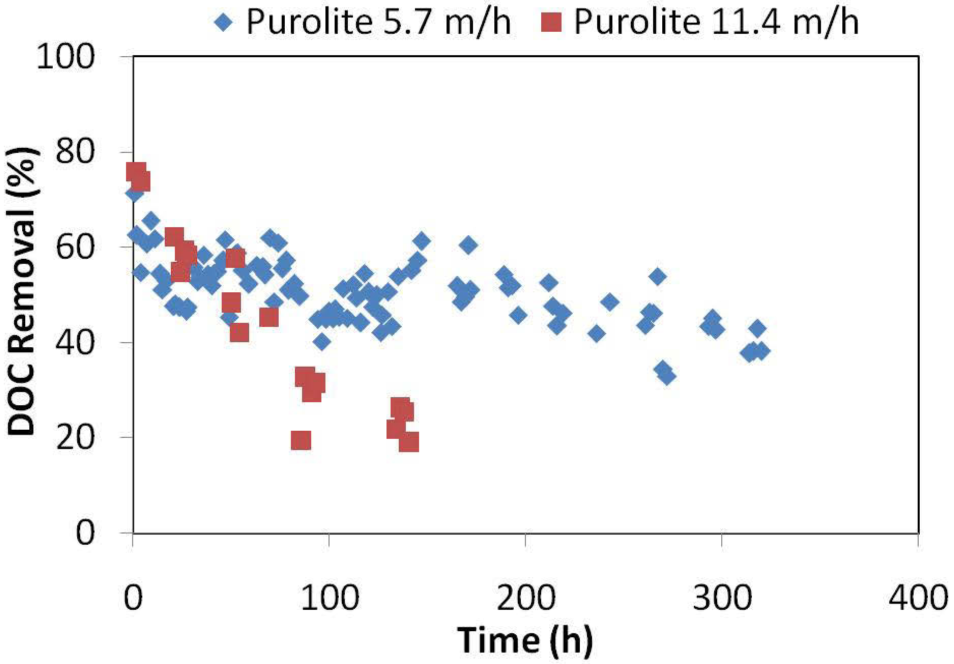


Figure 4.17: Long-term study of Purolite A502PS packed fluidized bed contactor in terms of removing DOC (Initial DOC of BTSE: 6.0-4.0 mg/L for flux of 5.7 and 11.4 m/h; Purolite amount = 30 g)

4.3.2.2.4. Performance of Fresh vs. Regenerated Purolite A502PS

The performance of fresh and regenerated Purolite A502PS was examined to check the feasibility of reusing Purolite A502PS after its saturation with DOC present in the BTSE. After the experiment 1N NaCl was passed through the exhausted Purolite A502PS column for 5 hours and then it was rinsed with deionized water several times to remove any excess NaCl. After that BTSE was passed through the regenerated column at the same velocity. The operational conditions of both fresh and regenerated Purolite A502PS were similar. Figure 4.18 illustrates the trend regarding efficiency in removing DOC using fresh and regenerated material over a 7-hour period. It is observed that the regenerated material still maintained good ion-exchange capacity and achieved a DOC removal efficiency of approximately 60% while the fresh material achieved on average 70%. It suggests that exhausted Purolite A502PS can be recovered and re-used in a cost effective way.

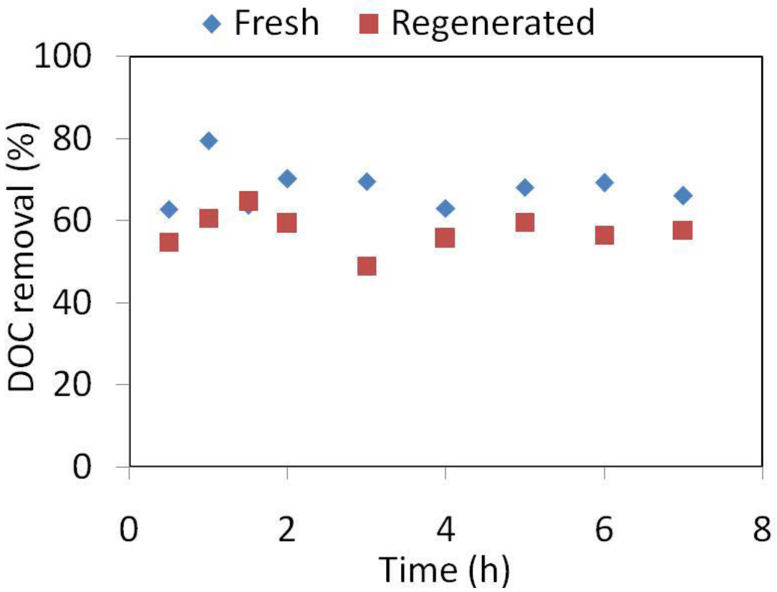


Figure 4.18: DOC removal efficiency of fresh vs regenerated Purolite A502PS (initial DOC of BTSE is 6.0 mg/L; fluidization velocity = 3.8 m/h; amount of Purolite A502PS: 30 g)

4.4. CONCLUSIONS

Fluidized bed contactors packed with GAC and Purolite A502PS constitute an effective pre-treatment strategy for removing dissolved organic matter prior to RO. DOC removal efficiency strongly depends on operational conditions in which the bed height is more important than fluidization velocity. The performance of GAC and Purolite A502PS columns in removing DOC can be modelled using the Plug flow model. Results show that GAC performs better than Purolite A502PS in removing DOC from BTSE. The poorer ability of Purolite A502PS may be due to its smaller surface area and the presence of other inorganic anions in BTSE. Furthermore, regenerated Purolite A502PS can be reused as it still maintains a good ion-exchange capacity. In order to prevent scaling and other problems raised by inorganic dissolved ions, the Purolite fluidization bed is suitable because it can remove anions from feed water better than GAC. A series of fluidized columns can provide better results in that these beds can effectively remove both organic matter and inorganic anions over a longer period of time.

CHAPTER 5

SUBMERGED MEMBRANE – ION EXCHANGE HYBRID SYSTEM AS A PRE-TREATMENT TO REVERSE OSMOSIS

SUMMARY

The performance of ion exchanger Purolite A502PS in treating biologically treated sewage effluent (BTSE) was evaluated in a submerged membrane ion exchange hybrid system. The experimental results showed that adding a small amount (0.5 g/L) of Purolite A502PS increased the removal of organics in the submerged membrane reactor from less than 10% to more than 40%. The homogeneous surface diffusion model (HSDM) could predict the adsorption kinetics of Purolite A502PS. A higher dose of Purolite A502PS in the MF-Purolite A502PS system led to better removal of organics and reduced membrane resistance. After one hour of operation at a flux of 36 $L/m^2.h$, the amount of organic matter retained on the membrane surface decreased from 2.11E−9 kg/m^2 s to 8.25E−10 kg/m^2 s when 1 g/L of Purolite A502PS was added into the submerged membrane reactor. Although the increase of membrane flux from 36 L/m^2 h to 60 $L/m^2.h$ did not have much effect on organic removal, more organics were adsorbed onto the membrane surface at higher flux. This led to a higher transmembrane pressure (TMP) of 12 kPa in the MF-Purolite A502PS hybrid system after eight hours operation at a flux 60 $L/m^2.h$. The increase in TMP was approximately four times higher than that at a flux of 36 $L/m^2.h$.

5.1. INTRODUCTION

Although BTSE has a low dissolved organic carbon (DOC) concentration it plays a major role in organic fouling of membranes. Thus, pre-treatment of BTSE is considered to be the most promising solution to control fouling due to its simple and easy implementation. Using porous membranes - like microfiltration (MF) or ultrafiltration (UF) as a pre-treatment for dense membrane filtration - is a common practice. In recent years many researchers have tried to incorporate supporting media into MF or UF in order to improve the treatment efficiency through scouring some of the foulant off the membrane surface, and capturing some of the fouling causing substances prior to their contact with the membrane surface.

Activated carbon can effectively remove large and small molecular weight hydrophobic organic compounds whilst hydrophilic organics are removed by ion exchange resins. The removal of organics from BTSE using various types of ion exchange resins has been documented in some studies. Zhang et al. (2006) reported that the Magnetic Ion Exchange (MIEX) resin can effectively remove hydrophilic compounds (70%) and hydrophobic components (55%) with a very short contact time of 20 min. Ahmad et al. (2012) used an ion exchange resin, namely Purolite A500PS, for removing DOC from biologically treated sewage effluent. Their results showed that a fluidized bed packed with Purolite A500PS could maintain a consistent DOC removal efficiency of more than 80% with more than 800 bed volumes from synthetic wastewater containing 10 mg DOC/L. However, up to now, most studies on removing organic matter using ion exchange resin were done in either batch or column mode. The addition of ion exchange resins such as Purolite A502PS which are fabricated for organic removal in a low pressure submerged membrane systems should be studied with real BTSE which is usually considered to be a feed for reverse osmosis (RO).

In this chapter, MF-Purolite A502PS hybrid system as a pre-treatment to RO was studied. The performance of Purolite A502PS was firstly evaluated by isotherm and kinetics experiments. Following this, Purolite A502PS was incorporated into a submerged MF reactor to assess the performance of a membrane ion exchange hybrid system (MF-Purolite A502PS) in treating feed in terms of: (i) organic removal; and (ii) membrane fouling through transmembrane pressure (TMP). In this study, Freundlich and homogeneous surface diffusion models were used to examine the adsorption behaviour of Purolite A502PS.

5.2. MATERIALS AND METHODS

5.2.1. Materials

a. Wastewater:

The BTSE water collected from a water reclamation plant (WRP) in Sydney, Australia was used for the experiments. The process stages of WRP and the characteristics are presented in Chapter 3. The DOC of the BTSE varied from 3.6 to 7.7 mg/L during the experimental period.

b. Purolite A502PS as Ion exchange resin:

A macroporous poly (vinylbenzyl-trimethylammonium) exchanger, Purolite A502PS, supplied by Purolite Corporation served to remove organics. The properties of the resin are presented in Chapter 3. Three different sizes of Purolite A502PS were used to study the adsorption kinetics. Purolite A502PS was ground by mortar and separated by sieve into the following sizes: 150 – 300 μm, 300 – 425 μm, and, 425 – 600 μm.

c. Hollow fibre membrane module:

A hollow fibre membrane having a surface area of 0.1 m^2 was used in these experiments. This was supplied by Mann + Hummel Ultra-Flo Pty. Ltd., Singapore. The details of the membrane is given in Chapter 3.

5.2.2. Methods

5.2.2.1. Adsorption/ion exchange equilibrium

Different doses (0.1–5 g/L) of Purolite A502PS resin were added in flasks containing 200 mL of BTSE. The flasks' contents were then mixed using a Ratek Platform Mixer at 110 rpm for 24 h continuously. Preliminary experiments lasting 72 h indicated that the equilibrium was achieved well before 24 h. When the experiments were completed, samples were filtered through a 0.45 µm filter and the DOC was examined.

5.2.2.2. Adsorption kinetics

The kinetics experiment investigated the adsorption rate of Purolite A502PS by adding 0.2 g or 0.4 g of resin into 200 mL of BTSE. The solutions with 1 g/L and 2 g/L of Purolite A502P resin were mixed at 110 rpm and the samples were collected at different times, ranging from 5 - 480 min and then checked for DOC.

5.2.2.3. MF – Ion exchange hybrid system

The schematic diagram of the MF ion exchange hybrid system is shown in Figure 5.1. The hollow fibre membrane module was immersed in a 3 L reactor tank which was continuously fed with BTSE. Different amounts of Purolite A502PS (0.5–1 g/L) were directly added into the reactor only at the beginning of the experiment. Purolite A502PS was not added during the experimental phase. The ranges of doses used were found to be representative based on preliminary experiments. A pressure gauge was used to measure the TMP of the MF-Purolite A502PS. The flow rate and air diffuser rate of the MF-Purolite A502PS were kept at 36–60 L/m^2.h and 1.5 m^3/m^2.membrane area.h, respectively.

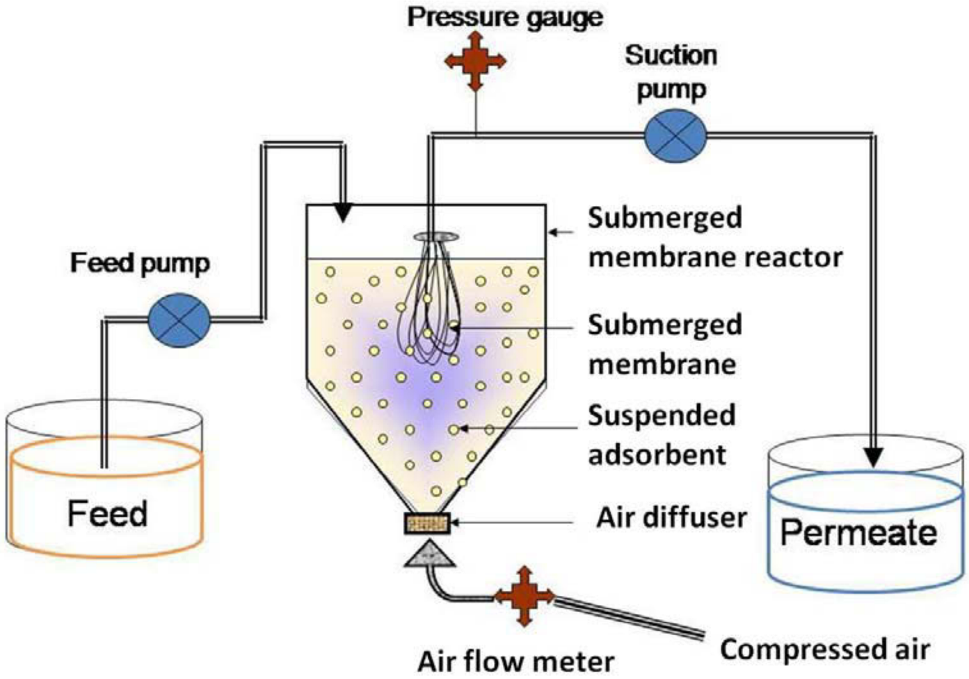


Figure 5.1: Schematic diagram of the submerged membrane ion exchange hybrid system

5.2.2.4. Analyses

DOC in all samples was measured using a Multi N/C 2000 analyzer (Analytik Jena AG) after filtration through a 0.45 μm filter.

5.3. RESULTS AND DISCUSSION

5.3.1. Adsorption equilibrium

Adsorption equilibrium experiments were conducted to predict the adsorption capacity of Purolite A502PS resin with BTSE. Cornelissen et al. (2008) and Humbert et al. (2008) reported that adsorption of natural organic matter by anion exchange resins is expected to be heterogeneous. Thus it can be explained by Freundlich adsorption. The Freundlich isotherm is an empirical equation developed based on the assumption that the adsorbent has a heterogeneous surface composed of different classes of adsorption sites. Here the relationship between the amount of DOC adsorbed (Q_e, mg/g) on the Purolite A502PS and the equilibrium concentration of DOC in the BTSE (C_e, mg/L) can be represented by Eq. 5.1:

$$Q_e = K_F . C_e^{\frac{1}{n}} \qquad \text{Eq. 5.1}$$

where K_F is a Freundlich constant indicative of the adsorption capacity of the resin (mg/g) and n is an experimental constant representing the adsorption intensity of the resin.

The Sips model is an empirical model representing equilibrium adsorption data. This model has features of both the Langmuir and Freundlich isotherm models and the Sips adsorption isotherm model can be written as follows:

$$Q_e = \frac{Q_m (bC_e)^{\frac{1}{n}}}{1 + (bC_e)^{\frac{1}{n}}} \qquad \text{Eq. 5.2}$$

where Q_m is a saturated maximum monolayer adsorption capacity (mg/g) and b is a Sips constant related to the binding energy of adsorption (L/mg).

The equilibrium results were fitted with Freundlich and Sips isotherm equations. Figure 5.2 shows the equilibrium data of DOC on Purolite A502PS. The adsorption curves predicted by these models fitted well with the observed values (r values was more than 0.946). Through the isotherm experiment, the values of K_F and n of the Freundlich isotherm for Purolite A502PS resin with BTSE were 0.61 mg/g and 0.644, respectively. K_F reflects the resin capacity and for a given value of K_F, a higher value of n indicates a stronger solute affinity. The exponent $1/n$ of the adsorption equilibrium of Purolite A502PS with BTSE was 1.55 which indicates that the isotherm is of type III and therefore unfavorable. The maximum adsorption capacity (Q_m) of Purolite A502PS resin for organic compounds in BTSE calculated through the Sips isotherm model was 102.2 mg DOC/g Purolite A502PS.

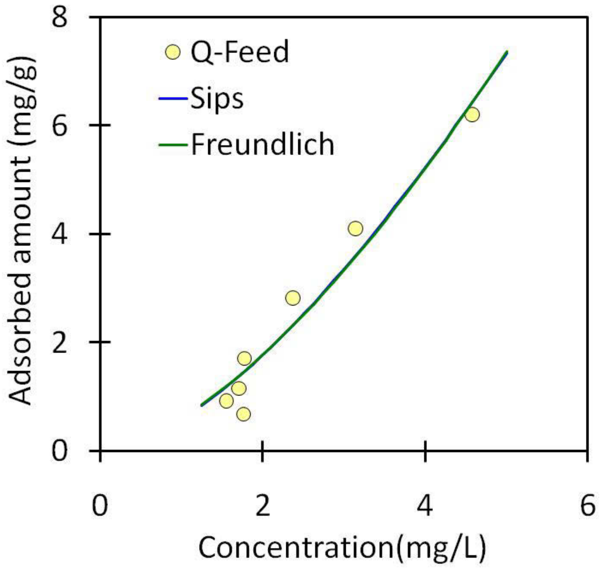


Figure 5.2: Equilibrium adsorption of DOC using Purolite A502PS (amount of Purolite A502PS: 0.1–5 g/L, initial DOC of BTSE: 5.2 mg/L).

5.3.2. Adsorption kinetics

In adsorption kinetics, the DOC slowly decreased and no further removal occurred after 6 h of mixing (Figure 5.3). The homogeneous surface diffusion model (HSDM) used to calculate the mass balance of dissolved organic matter inside a spherical porous particle was applied to study the Purolite A502PS adsorption kinetics. The HSDM consists of a three-step process (Najm, 1996): (i) the adsorbate diffuses through a stagnant liquid film layer surrounding the adsorbent particle; (ii) the adsorbate adsorbs from the liquid phase onto the outer surface of the adsorbent particle; and (iii) the adsorbate diffuses along the inner surface of the adsorbent particles until it reaches its adsorption site.

The equations of HSDM are as follows:

$$\frac{\partial q_t}{\partial t} = D_s\left(\frac{\partial^2 q_t}{\partial r^2} + \frac{2}{r}\frac{\partial q_t}{\partial r}\right) \qquad \text{Eq. 5.3}$$

Eq. 5.3 is based on constant diffusivity assumption. The above equation can be numerically solved using the following initial and boundary conditions: $t = 0$; $q_t = 0$

r = 0; $$\frac{\partial q}{\partial r} = 0 \qquad \text{Eq. 5.4}$$

r = r$_p$; $$D_s \rho_p \frac{\partial q_t}{\partial r} = k_f\left(C - C_s\right) \qquad \text{Eq. 5.5}$$

where q_t is the rate of change of surface concentration with time (t) at any radial distance (r) from the centre of the Purolite A502PS particle during the adsorption/ion exchange process, mg/g; D_s is the surface diffusion coefficient which represents the rate of diffusion of the DOC along the surface of the Purolite, m^2/s; k_f is the external mass transfer coefficient, m/s; ρ_p is the apparent density of the Purolite, kg/m^3; C is the bulk phase concentration, mg/L; and C_s is the concentration on the external surface of adsorbent particles, mg/L.

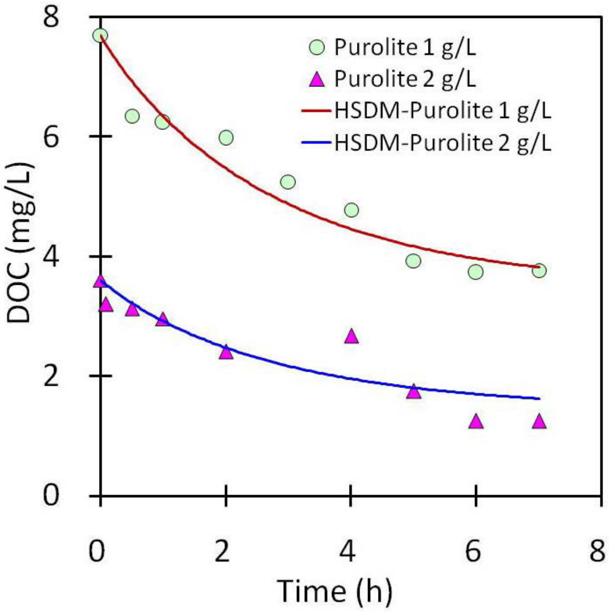


Figure 5.3: Adsorption kinetics of Purolite A502PS resin with BTSE (amount of Purolite A502PS = 1 g/L and 2 g/L, initial DOC of BTSE = 3.6–7.7 mg/L)

The simulation of adsorption kinetics of the Purolite A502PS resin with BTSE is presented in Figure 5.3. The results show that the simulation curve fitted well with the experimental values. In order to obtain the two unknown key parameters, D_s and k_f, the orthogonal collocation method, i.e. the variable coefficient ordinary differential equation solver (VODE) and the Nelder–Mead simplex algorithm, is employed. A detailed explanation of the procedure is described elsewhere (Ahmad et al. 2012). The summary of values of k_f and D_s of the HSDM is shown in Table 5.1.

Table 5.1: The mass transfer coefficients of Purolite A502PS with BTSE

	Purolite A502PS 1 g/L	Purolite A502PS 2 g/L
C_e (mg/L)	7.7	3.6
k_f (m/s)	1.59E−6	3.00E−6
D_s (m^2/s)	2.80E−13	2.00E−13

The value of the surface diffusion coefficient (D_s) was 2.00E−13 m^2/s. As shown in Table 5.1 the determined values of D_s are directly related to the equilibrium concentration. The higher the value of C_e, the greater was the D_s.

5.3.3. Membrane ion exchange hybrid system

The effect of adding Purolite A502PS to a submerged membrane reactor was studied by evaluating the removal of organics and the amount retained on the membrane ($M(t)$), and TMP. Here, the Freundlich isotherm and HSDM served to calculate the mass balance of dissolved organic matter inside the Purolite as presented in Table 5.2.

Table 5.2: System parameters of membrane hybrid system

		Unit	BTSE at flux of 36 L/m^2.h	BTSE at flux of 60 L/m^2.h
Reactor	Inlet concentration*	mg/L	4.62 mg/L at 0 g Purolite/L	5.31–6.05 mg/L at 0.5 g Purolite/L
			5.1 mg/L at 0.5 g Purolite/L	5.32 mg/L at 1 g Purolite/L
			4.92 at 1 g Purolite/L	5.54 mg/L at 1.5 g Purolite/L
	Volume	m^3	3.0×10^{-3}	3.0×10^{-3}
	Flow rate (Q)	m^3/s	1.0×10^{-6}	1.67×10^{-6}
Membrane	Packing density	m^2/m^3	510	510
	Flux (J)	m/s	1.0×10^{-5}	1.67×10^{-5}
Purolite	Radius	m	1.25×10^{-4}	1.25×10^{-4}
	Particle density	kg/m^3	992	992
	Loading amount	kg	0.0 at 0 g Purolite/L	0.0015 at 0.5 g Purolite/L
			0.0015 at 0.5 g Purolite/L	0.003 at 1 g Purolite/L
			0.003 at 1 g Purolite/L	0.0045 at 1.5 g Purolite/L

Note: The DOC concentrations were slightly different (4.6–5.7 mg/L) as they were collected from the water reclamation plant on different days.

In this study, a simple mathematical model using the concept of a continuous flow stirred tank reactor (CSTR) was developed. Membrane packing density (A_M/V_M) and membrane correlation coefficient (MCC) were incorporated into the adsorption model. The mass balance of the bulk solution in the MF-Purolite A502PS system was calculated using the following Eq. 5.6:

$$\frac{dC_b}{dt} = \frac{\mathrm{Q}}{\mathrm{V}} \cdot (\mathrm{C_o} - \mathrm{C_b}) - \frac{\mathrm{M}}{\mathrm{V}} \cdot \frac{dq}{dt} - \frac{\mathrm{A_M}}{\mathrm{V_M}} \cdot MCC \cdot C_b \qquad \text{Eq. 5.6}$$

where C_o is the organic concentration in the feeding tank (mg/L); C_b is the organic concentration in the bulk phase (mg/L); Q is the flow rate (m^3/s); V is the volume of the bulk solution in the reactor (m^3); M is the weight of Purolite A502PS used (g); A_M is the surface area of the membrane (m^2); V_M is the volume of membrane (m^3); and MCC is the membrane correlation coefficient. The membrane correlation coefficient (MCC) in Eq. 5.6 is an empirical coefficient that incorporates both adsorption of organics on the membrane surface and retention of Purolite (associated with organics adsorbed on it). Although the amount of organic matter adsorbed onto the membrane was small and this amount was less than that adsorbed onto the Purolite, the organic adsorption on the membrane was not neglected. Thus the permeate DOC concentration $C_{\mathrm{eff}}(t)$ is not the same as C_b. The second term on the right-hand side of Eq. 5.5 [$(M/V)(dq/dt)$] represents the adsorption of the organics onto Purolite A502PS in suspension. This term implies that all pellets function the same way in adsorption whether they are suspended in liquid phase or deposited on the membrane surface. The third term [$(A_M/V_M)\mathrm{MCC}\cdot C_b$] describes the adsorption onto the Purolite A502PS layer deposited on the membrane surface.

To reasonably simulate the MF-Purolite A502PS performance, the D_s values, which are determined from the batch kinetics, were used. D_s was a function of concentration. From the batch experiment results, the relationship between D_s and C_e was established as $D_s = 2.550\mathrm{E}{-13} \times e^{2.567\mathrm{E}{-2}\mathrm{Ce}}$. k_f, the only remaining value in MF-Purolite A502PS, was determined by matching the experiment data with the model equations. The membrane filtration flux can be expressed by Darcy's law as:

$$J = \frac{\Delta P}{\mu \cdot (R_m + R_d(t))} \qquad R_d(t) = r_c \cdot M(t)$$

$$J = \frac{\Delta P}{\mu \cdot (R_m + r_c \cdot M(t))} \qquad \text{Eq. 5. 7}$$

where J is permeate flux ($m^3/m^2/s$), ΔP is the TMP (kPa), R_m is membrane resistance (m^{-1}), $R_d(t)$ is the average resistance of deposition layer on membrane surface (m^{-1}), r_c is the specific cake layer resistance (m/kg), and $M(t)$ is the amount of organics deposited onto the membrane surface as a function of time (kg/m^2 s or mg/m^2 s).

The amount of organic matter $M(t)$ retained on the membrane (kg/m^2 s or mg/m^2 s) as a function of time was calculated from the equation below:

$$M(t) = Q \cdot \frac{C_{Tank}(t) - C_{eff}(t)}{A_M} \qquad \text{Eq. 5.8}$$

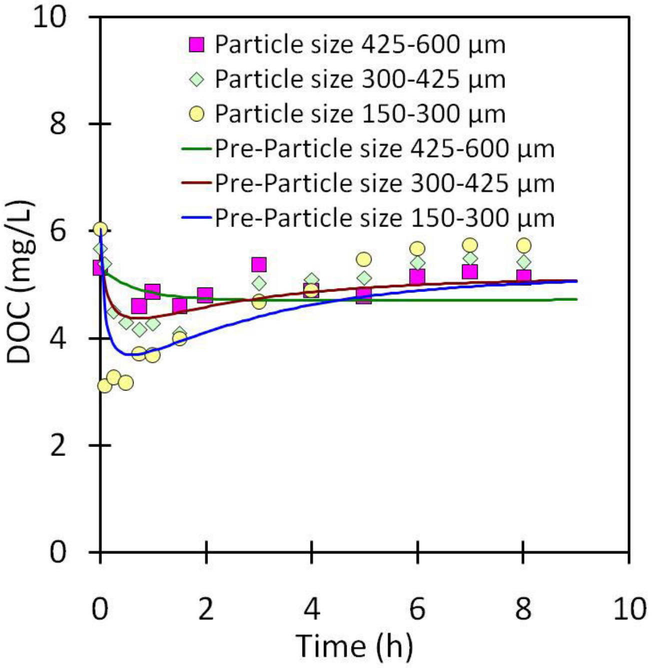
where Q is the flow rate which is the flux (J) multiplied by membrane area (A_M), $C_b(t)$ is the organic (DOC) concentration in the membrane tank at time (t), which can be calculated from the adsorption equation, and $C_{\mathrm{eff}}(t)$ is the organic concentration in the membrane permeate. The value of $C_{\mathrm{eff}}(t)$ was taken from the experiment data and found to be constant during the experiment.

In the calculation, it was assumed that no changes occurred in the concentration of organic matter in the reactor without applying Purolite A502PS and membrane filtration. When these were applied the organic compounds were removed by Purolite (a significant amount) and adsorbed onto the membrane surface (a small amount). The organic compounds adsorbed onto the membrane surface stay on it and not in the bulk concentration in the reactor.

5.3.3.1. Effect of Purolite A502PS sizes on the MF-Purolite A502PS

The first set of experiments was carried out using BTSE. Only a small amount of Purolite A502PS (0.5 g/L reactor) in different particle sizes was added to the submerged membrane reactor. This was done to test the impact of particle size on the membrane hybrid system's performance. The effects of particle size on DOC removal efficiency and TMP development of the MF-Purolite A502PS are presented in Figure 5.4a and Figure 5.4b, respectively. Values of D_s and k_f for different particle sizes of Purolite A502PS are summarized in Table 5.3.

(a) DOC removal



(b) TMP development

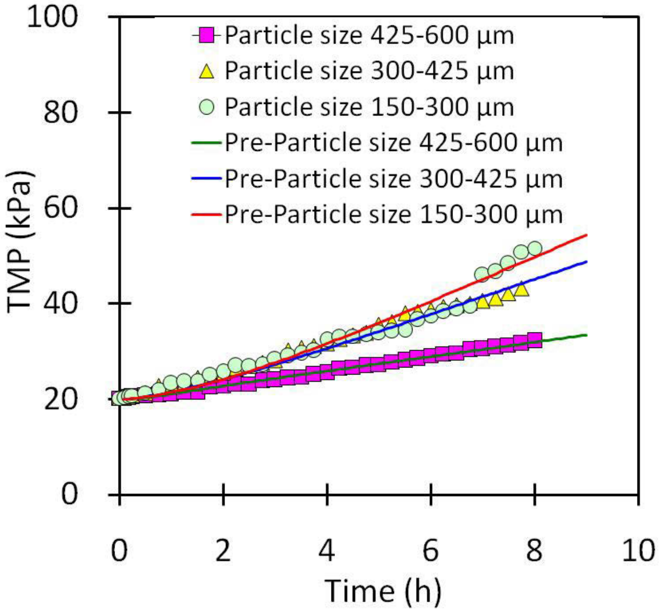


Figure 5.4: Effect of Purolite A502PS size on (a) DOC removal and (b) TMP development of MF-Purolite A502PS (permeate flux: 60 L/m^2.h, DOC of BTSE: 5.31–6.05 mg/L, dose of Purolite A502PS: 0.5 g/L). (Pre = Predicted)

Table 5.3: Effect of Purolite A502PS size on surface diffusion coefficient and external mass transfer coefficient (Flux: 60 L/m^2.h, Purolite A502 dose: 0.5 g/L)

	Purolite A502PS size (μm)		
	425–600	300–425	150–300
Concentration (mg/L)	5.31	5.7	6.05
k_f (m/s)	3.196E−5	1.086E−4	7.952E−4
D_s (m^2/s)	2.922E−13	2.952E−13	2.978E−13

As shown in Figure 5.4a, initially there was a difference in the amount of DOC removed. In the first hour of operation, DOC removal efficiency was about 40%, 25% and 15% with particle sizes of 150–300 μm, 300–425 μm and 425–600 μm, respectively. However, after 3 h there was no remarkable difference with the varying sizes of Purolite A502PS. The smaller particle size of Purolite A502PS removed more DOC initially as it possessed more surface area. The results in the study by Ahmad et al. (2012) showed that the surface area of Purolite A500PS increased 1.2 times (from 20.7 m^2/g to 24.9 m^2/g) when its particle size declined from 425–600 μm to 150–300 μm. In addition, after grinding, more active sites of Purolite A502PS would have been created.

Matulionytė et al. (2007) used Purolite A500 to remove various components from fixed rinse water (containing 0.042–0.048 mol $S_2O_3^{2-}$/dm^3, 0.005–0.006 mol SO_4^{2-}/dm^3, 0.0016–0.0026 mol SO_3^{2-}/dm^3, 0.018–0.028 mol CH_3COO^-/dm^3, and 0.004–0.005 mol AgBr/dm^3). They found that Purolite A500 could well adsorb $S_2O_3^{2-}$ (4.34 meq), CH_3COO^- (0.69 meq), and SO_4^{2-} (0.48 meq). In this study the removal of DOC by

Purolite A502PS with BTSE was less effective than Purolite A500PS when it was employed to remove DOC from synthetic wastewater (Ahmad et al. 2012). This was due to the competition by other anions that were in higher concentrations in real BTSE than in synthetic wastewater.

The experimental results show that the TMP development was 31.5 kPa, 23 kPa, and 12 kPa, respectively, for Purolite A502PS particle sizes of 150–300 μm, 300–425 μm, 425–600 μm (Figure 5.4b). An increase in TMP was observed to be higher with a smaller particle size of Purolite A502PS. This may be due to the plugging of small Purolite A502PS particles on the membrane's surface leading to a reduction in flux.

Similar to the observations made by Ahmad et al. (2012) and, Choy et al. (2004) an increase in particle size reduces the external mass-transfer coefficient k_f (Table 5.3). This can be explained by the faster movement of smaller particles in an agitated solution. This led to more shear at the particle surface which reduced the boundary layer film. There was not much difference in surface diffusion D_s among different particle sizes. The D_s was found to depend on the equilibrium concentration C_e and their relationship can be expressed as, $D_s = 2.55\text{E}{-}13\text{e}^{2.567\text{E}-02\text{Ce}}$.

Even though a smaller particle size results in a more efficient removal of DOC, it also leads to rapid development of TMP in the membrane hybrid system. Considering the above factors and the energy requirements to keep the Purolite in suspension, Purolite A502PS of 425–600 μm was selected for subsequent experiments.

5.3.3.2. Effect of Purolite A502PS doses on the MF-Purolite A502PS

Two different doses of Purolite A502PS (0.5 and 1 g/L) were added to the reactor. The permeate flux of the MF-Purolite A502PS was retained at 36 L/m^2.h. During the experiment the DOC of the BTSE varied from 4.6 to 5.1 mg/L.

i. Effect of Purolite A502PS dose on removal of organics

Without adding Purolite A502PS, the membrane alone could only remove less than 10% of DOC from the BTSE. Adding a small amount (0.5–1 g/L) of Purolite A502PS to the BTSE led to a nearly 40% removal of DOC and this percentage was constant during the 8 h experiment. Figure 5.5 shows the model's prediction for the removal of organics from the BTSE using different doses of Purolite A502PS. The values of the D_s and k_f coefficient of Purolite®A502PS with BTSE are presented in Table 5.4.

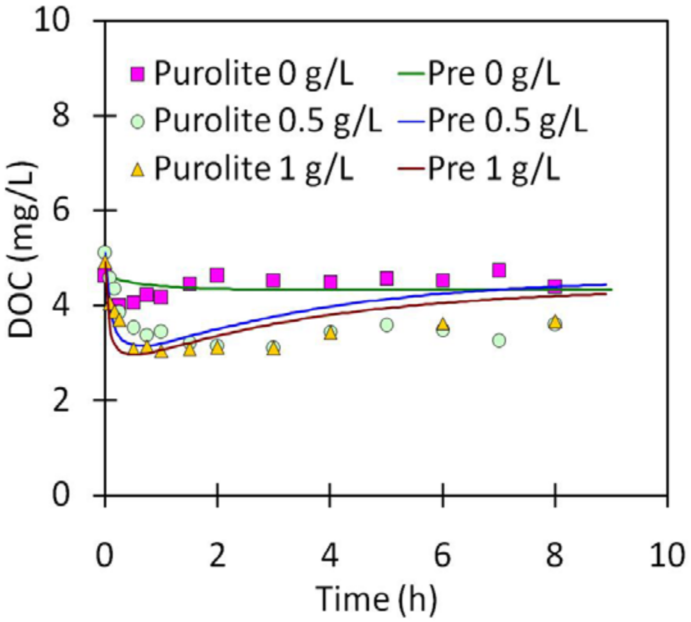


Figure 5.5: Effect of Purolite A502PS dose on removing DOC (permeate flux: 36 L/m^2.h, DOC of BTSE: 4.62–5.1 mg/L, dose of Purolite A502PS: 0.5–1 g/L)

The value of the surface diffusion coefficient D_s for BTSE was not affected by Purolite A502PS dose. Results also show that in the MF-Purolite A502PS, the D_s value was slightly higher than the D_s values determined from the kinetics experiments. This is because D_s is a function of concentration.

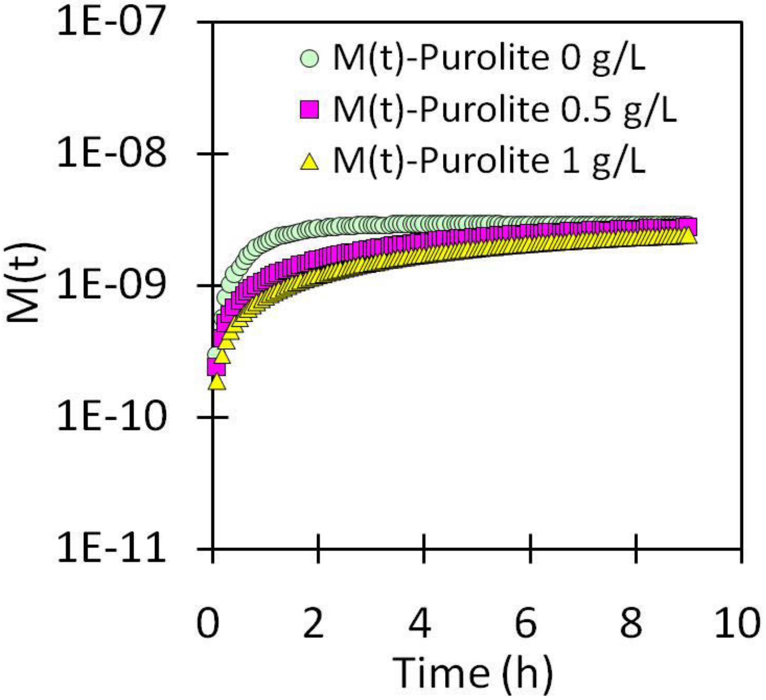
Table 5.4: Effect of Purolite A502PS dose on surface diffusion coefficient, external mass transfer coefficient and membrane cake resistance with BTSE (Flux: 36 L/m^2.h, clean membrane resistance (R_m): 1.8E12 m^{-1})

Purolite A502PS dose (g/L)	Model coefficients			
	C_e (mg/L)	k_f (m/s)	D_s (m^2/s)	r_c (m^{-1})
0	4.62	6.92E−4	2.91E−13	1.20E16
0.5	5.10	4.40E−4	2.89E−13	1.24E16
1	4.92	1.11E−4	2.87E−13	8.00E15

ii. Effect of Purolite A502PS doses on the adsorption of organic matter on the membrane

The cumulative amount of organics retained on the membrane [$M(t)$] is presented in Figure 5.6a. $M(t)$ is the difference between the organic concentration in the reactor and membrane effluent. The membrane effluent concentration and influent concentration were measured experimentally. The amount of organics present in the reactor at different times was determined from the difference between the influent organic concentration and the amount of organics adsorbed by Purolite A502PS at a particular time (Eq. 5.8). The amount of organics adsorbed could be calculated from adsorption isotherm and kinetics.

(a) Mass transfer rate



(b) TMP

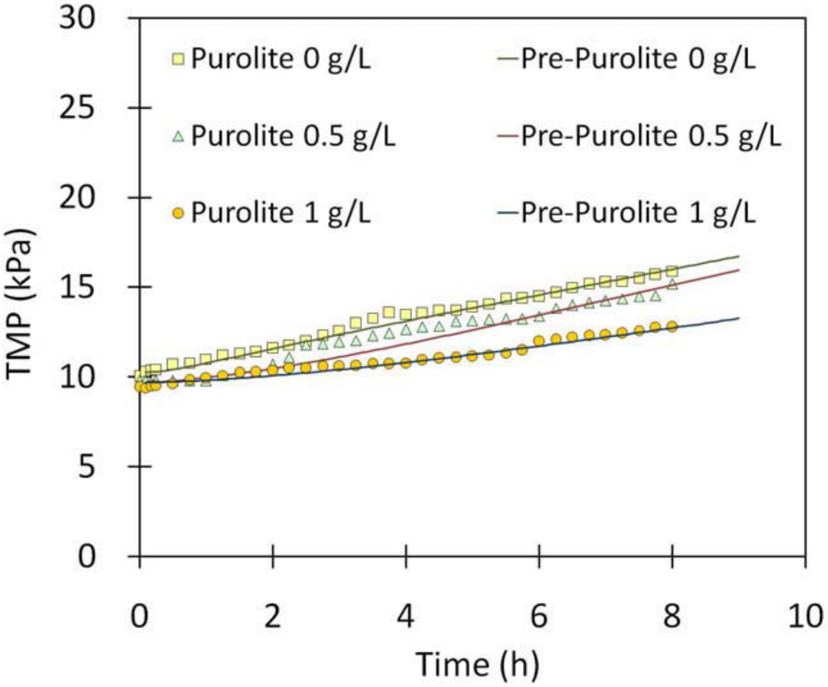


Figure 5.6: Effect of Purolite A502PS dose on (a) amount of organics retained on the membrane [*M*(*t*)] and (b) TMP of MF-Purolite A502PS (permeate flux: 36 L/m^2.h, DOC of BTSE: 4.6–5.1 mg/L, dose of Purolite A502PS: 0.5–1 g/L)

iii. Effect of Purolite A502PS dose on membrane cake resistance (r_c)

Figure 5.6b and Table 5.4 illustrate the effect of the Purolite A502PS dose on the TMP and resistance of cake (or deposit) on the membrane. As presented in Figure 5.6b, the TMP developed in the MF-Purolite A502PS for BTSE at the end of 8 h was about 6 kPa without any addition of Purolite A502PS. However, when 0.5 g/L and 1.0 g/L Purolite A502PS were added, the TMP development fell to about 5 kPa and 3 kPa, respectively. This could be due to the pre-adsorption of organics prior to their contact with the membrane. Furthermore Purolite A502PS in the suspension could act as a mechanical scouring material for the membrane. Figure 5.6b shows that the model and experimental data of TMP matched well.

The model calculation confirms that membrane cake resistance decreased when the Purolite A502PS dose was increased (Table 5.4). A higher dose led to better adsorption of organic matter, meaning that less organic matter was available for adsorption on the membrane surface. As a result less cake resistance was observed.

5.3.3.3. Effect of filtration flux on the MF-Purolite A502PS

Two different fluxes – 36 L/m^2.h and 60 L/m^2.h – were applied. During the experiment the DOC of BTSE and Purolite A502PS dose varied from 4.62 – 5.7 mg/L and 0.5 – 1 g/L, respectively.

i. Effect of filtration flux on removal of organic removal

Figure 5.7 depicts the removal of organic by MF-Purolite A502PS at a flux of 60 L/m^2.h. The values of the D_s and k_f coefficient of Purolite A502PS with BTSE are presented in Table 5.5.

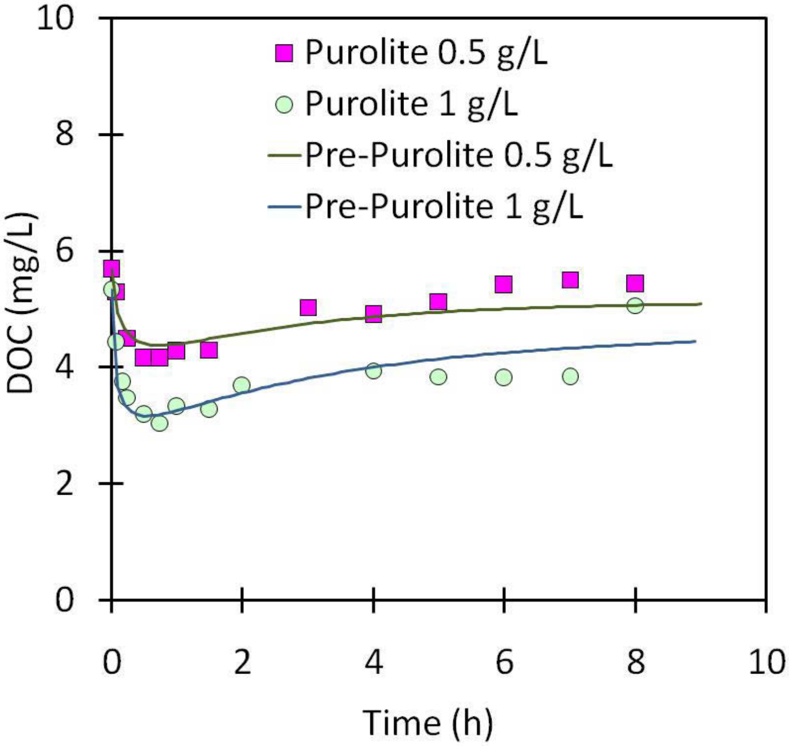


Figure 5.7: DOC removal at flux of 60 L/m^2.h (DOC of BTSE: 4.62–5.7 mg/L, dose of Purolite A502PS with BTSE: 0.5 and 1 g/L).

Table 5.5: Surface diffusion coefficient, external mass transfer coefficient and membrane cake resistance with BTSE at flux 60 L/m^2.h (clean membrane resistance (R_m): 2.1E12 m^{-1})

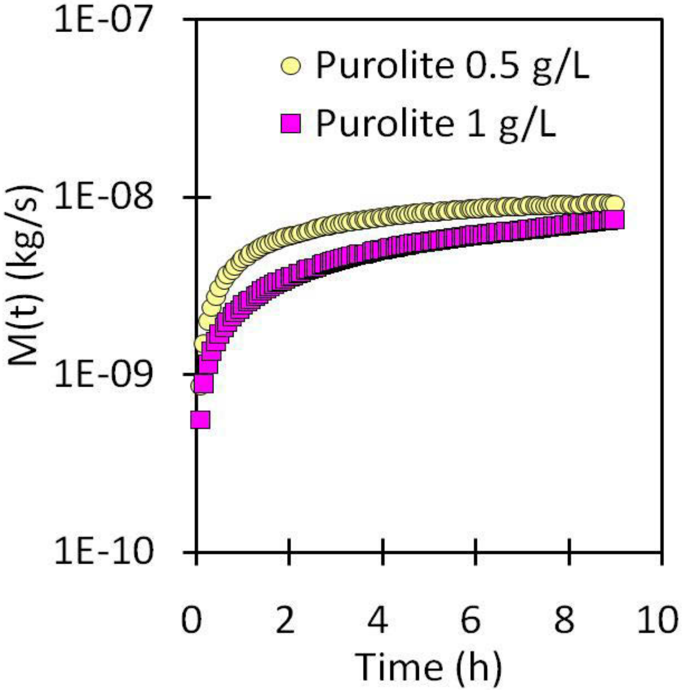
Purolite A502PS dose (g/L)	Model coefficients			
	C_e (mg/L)	k_f (m/s)	D_s (m^2/s)	r_c (m^{-1})
0.5	5.70	1.09E−4	2.95E−13	5.00E16
1	5.32	4.34E−4	2.92E−13	6.30E15

At a low Purolite A502PS dose (0.5 g/L), the higher flux led to MF-Purolite A502PS removing less organic material. However, there was not much difference in organic removal with fluxes of 36 L/m^2.h and 60 L/m^2.h (with Purolite A502PS dose of 1 g/L) (Figures 5.5 and 5.7). This agrees with the kinetics study where there was not much difference in the amount of organic matter removed between 30 min and 60 min when using a Purolite A502PS dose of 1 g/L. The retention time of wastewater in the MF-Purolite A502PS for fluxes of 36 L/m^2.h and 60 L/m^2.h were 50 min and 30 min, respectively. The minor influence of flux on organic removal can also been seen through the small difference between the surface diffusion coefficient and external mass transfer coefficient values (Table 5.5).

ii. Effect of Purolite A502PS dose on the adsorption of organic matter on the membrane

The amount of organics retained on the membrane [$M(t)$] at a flux of 60 L/m^2.h is presented in Figure 5.8a. While the two different fluxes at a Purolite dose of 1 g/L did not result in much difference in organic removal, the amount of organics adsorbed onto the membrane surface was smaller at the flux of 36 L/m^2.h (Figures 5.6 and 5.8). This can be explained in terms of the concentration differences ($C_{\mathrm{tank}} - C_{\mathrm{eff}}$) when the two different fluxes were utilized. The experiment was carried out at the same flow rate (Q) and membrane so according to Eq. 5.7, the $M(t)$ value depended on the concentration difference.

(a) Mass transfer rate



(b) TMP

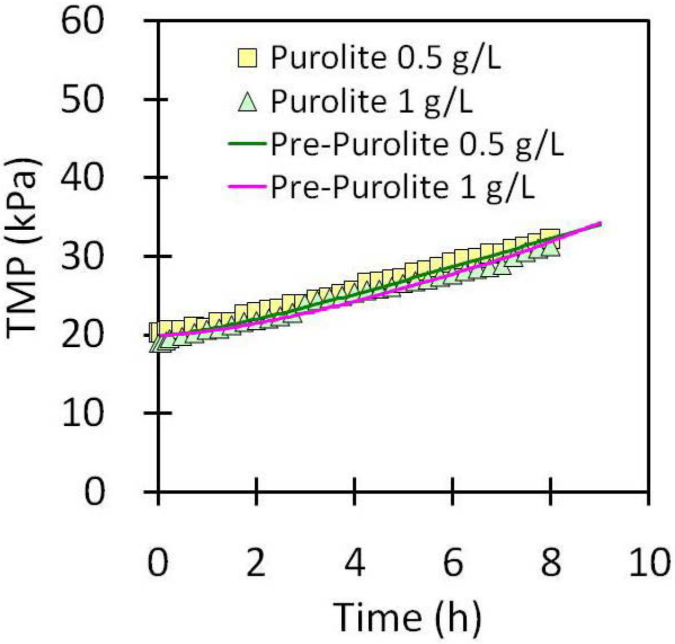


Figure 5.8: (a) Amount of organics retained on the membrane [$M(t)$] and (b) TMP of MF-Purolite A502PS at flux of 60 L/m^2.h (DOC of BTSE: 4.62–5.7 mg/L, dose of Purolite A502PS with BTSE: 0.5 and 1 g/L).

iii. Effect of flux on membrane cake resistance (r_c)

The effect of a flux of 60 L/m^2.h on the TMP and cake resistance of MF-Purolite A502PS is presented in Figure 5.8b and Table 5.5. The results show that a higher flux led to greater TMP development in MF-Purolite A502PS. For both doses of Purolite A502PS, i.e. 0.5 and 1 g/L, the TMP increased about 12 kPa after 8 h operation at a flux of 60 L/m^2.h. This increase was higher than that at 36 L/m^2.h (3–5 kPa at Purolite A502PS doses of 0.5–1 g/L) (see Figures 5.6b and 5.8b). This can be explained by the larger amount of organic compounds adsorbed onto the membrane surface at a higher flux. At a high flux of 60 L/m^2.h, there was not much difference in cake resistance at both Purolite A502PS doses of 0.5 g/L and 1 g/L. Thus the TMP development in both cases was nearly the same.

5.4. CONCLUSIONS

Purolite A502PS can be used to remove organics from the BTSE. The removal of DOC by Purolite A502PS with BTSE was about 40% efficient. Adding Purolite A502PS into a low pressure submerged membrane reactor can help not only to improve the removal of organics but also reduce the direct loading of DOC onto the membrane surface and the TMP development. As a result the fouling of RO (used as post-treatment) can be reduced. A larger dose of Purolite A502PS enabled the MF-Purolite A502PS to perform better. Its performance can successfully be predicted by the homogeneous surface diffusion model together with the simplified membrane model proposed in this study.

CHAPTER 6

MICROFILTRATION – GRANULAR ACTIVATED CARBON (MF-GAC)/NANO FILTER HYBRID SYSTEM IN HIGH QUALITY WATER REUSE

SUMMARY

In order to achieve high quality water reuse, a dual membrane hybrid system (combining micro filtration-granular activated carbon (MF-GAC)) adsorption hybrid system followed by nanofiltration (NF)) was used. This system's performance was evaluated in terms of dissolved organics, organic micro pollutants especially pharmaceuticals and personal care products (PPCPs), and removal of inorganic matter. Biologically treated sewage effluent (BTSE) collected from a water reclamation plant in Sydney, Australia was used as the water source. The efficiency in removing dissolved organic carbon (DOC) from MF-GAC strongly depends on the dose of GAC and filtration flux. The MF-GAC system effectively removed hydrophobic organics (45-80%) and hydrophilic organics (50-80%). The removal of various PPCPs ranged from 33 to 92%, and as expected, the amount of inorganic matter removed by the MF-GAC system was very small. Hence, the NF system, as a second membrane system, was employed to polish the effluent from the MF-GAC hybrid system. The NF system rejected most of DOC (>95%), sulfates (99%) and a substantial amount of calcium (70%), and magnesium (60%) from MF-GAC effluent. Additionally, more than 90% of PPCPs were removed by the NF system. Overall the dual membrane hybrid system proved to be very effective in removing organics, PPCPs and inorganic matter. The MF-GAC followed by NF results in high quality water reuse and this system can serve as an effective treatment option for water reuse schemes.

6.1. INTRODUCTION

The application of membrane technology for treating wastewater is considered to be a promising technology for producing better quality water for water supply and water reuse. Microfiltration or ultrafiltration (UF) is a cost effective option but the removal of DOC is limited because the MF/UF's pore size is not small enough to retain dissolved organics. The nanofilter or reverse osmosis (NF/RO) are highly efficient in removing dissolved organics/ions. However, while NF/RO produces high quality water, numerous challenges still prevail such as fouling and scaling issues, large energy requirements, generation of concentrate as by product and incomplete removal of a few trace organics.

The main objective of this chapter is to provide an alternative cost effective 'Dual membrane – hybrid system' (combination of submerged membrane adsorption (GAC) hybrid systems and NF) which can function as a second stage membrane process to provide high quality water free of trace organics. This system can be used instead of RO where the removals of monovalent ions are not necessary. As such biologically treated sewage effluent (BTSE) was used as feed water for a submerged MF-GAC hybrid system. The NF system served as a post-treatment system to remove most of the remaining hydrophilic, hydrophobic, and organic micro pollutants (especially pharmaceuticals and personal care products), and some inorganic contaminants. It is believed that applying the MF-GAC hybrid system prior to NF will effectively reduce potential foulants and PPCPs, ensuring that NF will function better in the long-term with less fouling.

6.2. MATERIALS and METHODS

6.2.1. Materials

a. Feed water

Micro-filtered BTSE collected from a water reclamation plant (WRP) in Sydney, Australia was used as feed water for the MF-GAC/NF hybrid system. This WRP consisted of biological treatment, MF followed by RO. In the WRP, the BTSE was passed though MF in order to remove particulate matter and pathogens. RO is used to reduce inorganic salts (conductivity) and PPCPs.

The physico-chemical characteristics of BTSE water are summarized in Table 6.1. This BTSE has a DOC of 3.6-7.7 mg/L. In this DOC, 42% is hydrophobic and 58% is hydrophilic organics. The hydrophilic organics can be further sub-divided into bio-polymers (3±1%), humics (52±3%), building blocks (25±2%), low molecular weight (LMW) neutrals (18±1%) and LMW acids (2±0.7%).

Table 6.1: Physico-chemical characteristics of BTSE (measured at different collection times during the experimental period).

Parameters	Unit	BTSE
pH		6.8-7.6
Conductivity	µS/cm	520 - 1120
DOC	mg/L	3.6 – 7.7
F^-	mg/L	0.7-1.1
Cl^-	mg/L	150-300
NO_3^-	mg/L	4.5-6.1
PO_4^{3-}	mg/L	1.8-2.4
SO_4^{2-}	mg/L	49-51
Na^+	mg/L	81-120
K^+	mg/L	15-21
Ca^{2+}	mg/L	21-40
Mg^{2+}	mg/L	10-15

b. GAC as adsorbent

Coal-based premium grade GAC (MDW4050CB) was supplied by James Cumming & Sons Pty Ltd (Auburn, New South Wales) and used as an adsorbent. The particle size of GAC used ranged between 300-600 µm. This size was chosen because it leads to the lowest transmembrane pressure (TMP) development (Johir et al. 2013).

c. Membrane

Flat sheet MF membrane and NF membrane were used in the experiments. Flat sheet MF membrane made up of polyvinylidene fluoride (PVDF) (A3 Membrane Company, Germany) with a surface area of 0.2 m^2, pore size 0.14 µm was used. NF (NTR 729HF) flat sheet membrane which consisted of Polyvinylalcohol/polyamides and molecular weight (MW) cut off of 700 Da was employed in this study for the polishing stage. The effective membrane area was 68 cm^2. Details regarding the characteristics of membranes are presented in Chapter 3.

6.2.2. METHODOLOGY

6.2.2.1. Optimization of GAC replacement

Optimizing the daily replacement of GAC was determined using a 60 day semi-batch test. GAC replenishment was done to optimize the amount of daily GAC replacement in the MF-GAC hybrid system so that as much organic material as possible was removed with minimum membrane fouling. This replenishment also helped in investigating whether any biological activity had occurred. Experiments were conducted with 0, 2, 5 and 10% replacement of GAC. The ideal GAC replacement amount was chosen based on the efficiency of removing organic matter. The above percentages for replacement rate were selected based on preliminary results.

Here six beakers were used for three different experimental conditions with two replicates. An initial dose of 2 g/L of GAC was chosen; meaning 0.4 g of GAC was added into each beaker containing 200 mL of BTSE. All the beakers were shaken on a Ratek Platform Mixer at 110 rpm under controlled temperature of 24±2^{o}C. From the second day onwards different percentages (0%, 2%, and 10%) of fresh GAC replacements were achieved daily. At the same time all the beakers in the batch experiments had their 50% BTSE replaced daily, in order to provide a continuous supply of organic matter to the reactor for adsorption and possible bio-sorption by GAC. Bioactivity on the GAC and BTSE was measured based on the plate cell count (colony forming unit; CFU/mL), assimilable organic carbon (AOC) and adenosine triphosphate (ATP) of the beaker content following ultra sonication. This would have extracted the bio-film (if any) on the GAC. During each daily replacement, the samples were collected and regularly analyzed for DOC.

6.2.2.2. MF–GAC Hybrid System followed by NF system

a. MF-GAC Hybrid System

The schematic diagram of the membrane hybrid system is shown in Figure 6.1. A flat sheet MF membrane module was immersed in the reactor tank (10 L). The reactor tank was continuously fed with BTSE and an air flow rate of 1.5 $m^3/m^2{}_{\text{membrane area}}$.h was applied: firstly, to produce shear stress on the membrane surface; and secondly, to keep the GAC particles in suspension in the reactor (Johir et al. 2011). The initial GAC dose of 2 g/L of the reactor's volume was added into the reactor at the start of the experiment, i.e. 20 g of GAC was added for the total reactor volume of 10 L. Two different filtration fluxes of 2.5 and 10 L/m^2.h were applied for different daily GAC replacements of 5% and 10%. Bioactivity within the membrane reactor was measured based on the cell count, AOC and ATP of samples of the content (which contains both GAC and wastewater) after ultra-sonication. The functionality of the submerged membrane adsorption hybrid system is discussed in Chapter 3.

b. Dual membrane system

The effluent collected from the MF-GAC hybrid system was used as feed for the NF system. Before each NF experiment, the NF unit was thoroughly cleaned by circulating 0.1 M NaOH solution through it. This was followed by adding 0.1 M HNO_3 solution for 2 hours and then by milli-Q water for 1 hour to remove any trace organics and impurities from the unit. The NF membrane was soaked in 10% ethanol overnight prior to the experiment. The NF feed flow was set at 0.5 L/min at pressure of 400 kPa (4 bar). The NF concentrate was recirculated with the feed and the sample was collected from permeate to examine DOC, inorganic anions (Ca^{+2}, Mg^{+2}), PPCPs, etc. The experimental setup is shown in Figure 6.1. The NF feed water's temperature was maintained using a temperature controller at 20±2°C.

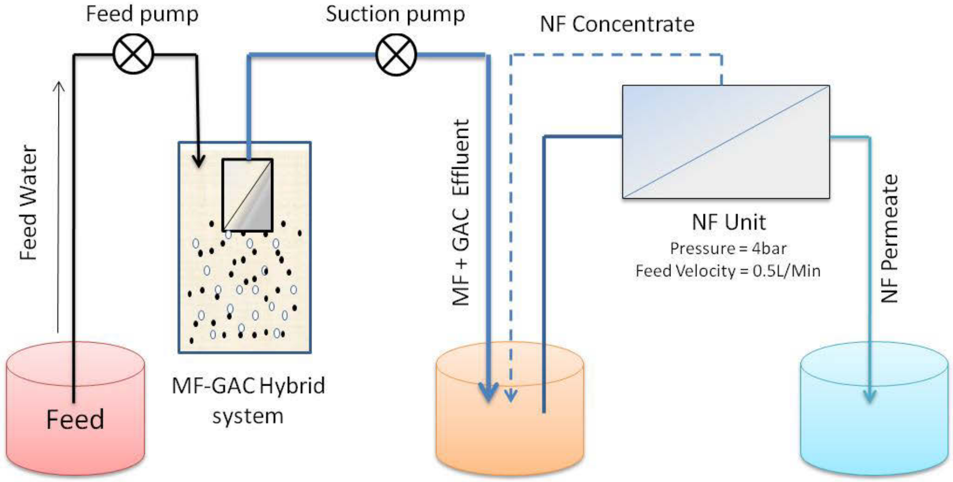


Figure 6.1: Experimental schematic diagram of dual membrane system

6.2.2.3. Analytical methods

Dissolved organics (DOC) was measured after filtering through a 0.45 µm filter using Multi N/C 2000 Analyzer (Analytik Jena AG). Liquid Chromatography-Organic Carbon Detection (LC-OCD) Model 8 developed by Huber et al. (2011) was equipped with a TSK HW 50-(S) column that measured the hydrophilic and hydrophobic fractions of organic materials and provided qualitative information on organics' molecular size distribution. Organic micro pollutants such as pharmaceuticals and personal care products (PPCPs) were extracted using solid phase extraction (SPE) and examined by Liquid Chromatograph with tandem mass spectroscopy. The details are provided in Chapter 3.

6.3. RESULTS AND DISCUSSION

6.3.1. Optimization of GAC Replenishment

The DOC removal efficiency for different amounts of GAC daily replacement is presented in Figure 6.2. It emerged that daily 5% and 10% GAC replacements ($R._{GAC\text{-}5\%}$ and $R._{GAC\text{-}10\%}$) maintained a steady removal of DOC at 40-70% and 60-80% from the beginning to the end of the experiment – a period of 60 days. It should be noted that 50% of BTSE was replaced every day. However, small daily replacements of GAC of 0% and 2% resulted in a decrease in the removal of DOC over time. Removing DOC at a low GAC replacement rate of 2% ($R._{GAC\text{-}2\%}$) fell from around 50% to 20% during a run period of 60 days.

Biological activity on the carbon was measured in terms of ATP and cell count (colony forming unit; CFU/mL) and AOC. No significant biological growth was observed during the study period which may have been too short for biodegradation of BTSE, which mainly consisted of humics and building blocks (i.e. slowly bio-degradable organic components). These are difficult to biodegrade compared to LMW organics. BTSE had only a small amount of LMW organics. In a recent study on seawater pre-treatment, activated carbon was used and after 14 days of operation a significant increase in biological activity was observed (Jeong et al. 2013c). This may be because the LMW compounds are dominant in seawater (Naidu et al. 2013). In this study, however, bio-available organics in BTSE were too low to maintain microbial activity in the GAC reactor during the short period of experimentation.

In the membrane reactor some biological activity was detected, although bioactivity in the reactor (which contained carbon and wastewater) did not increase since AOC was insufficient within the experimental period to maintain continuous bacterial growth. Bio-available organics in BTSE was very low since the BTSE used had already been biologically treated in the WRP. The AOC concentration was very low and in the order of 5 µg/L–C glucose equivalent per L in the membrane reactor (which contained BTSE and GAC). Cell count and ATP concentration in the reactor were 2.5E+03 CFU/mL and 1.47 nM, respectively, on day 1. After 60 days the cell count and ATP concentration in the reactor rose to 1.8E+04 CFU/mL and 11.7 nmol, respectively. Unfortunately, this was not high enough for biological activity to occur. Furthermore, organic fraction measured by LC-OCD showed that BTSE contained mainly humics and building blocks which are difficult to be utilized by microbes compared to LMWs. However, a longer operation period may lead to their biodegradation.

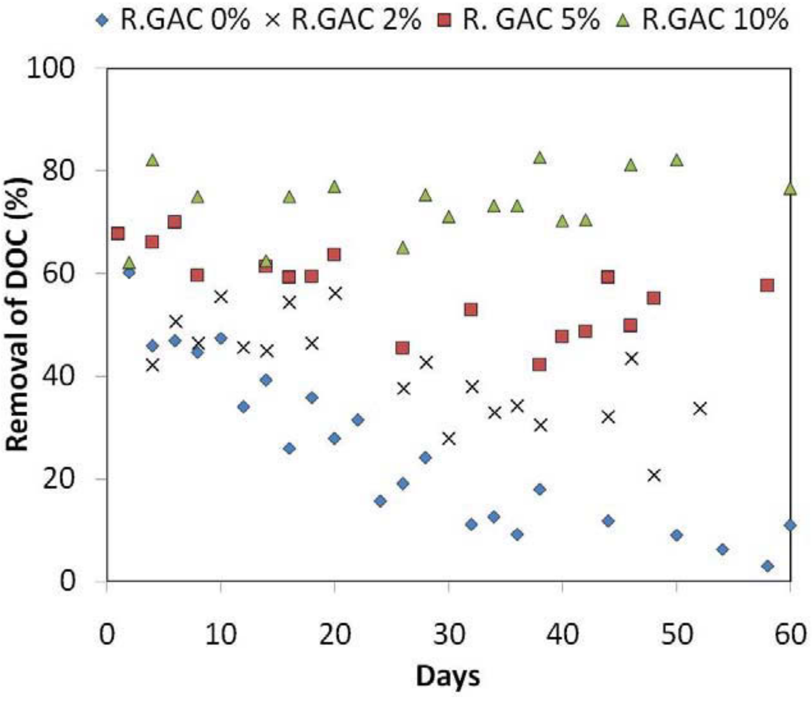


Figure 6.2: Removal of DOC from BTSE with different rates of GAC replenishment (DOC of BTSE = 4-7 mg/L; Initial GAC dose 2 g/L; different replacement of daily GAC % [R.$_{GAC\ 0\%}$; R.$_{GAC\ 2\%}$; R.$_{GAC\ 10\%}$]; Fresh BTSE replacement = 50%, i.e. 100 ml)

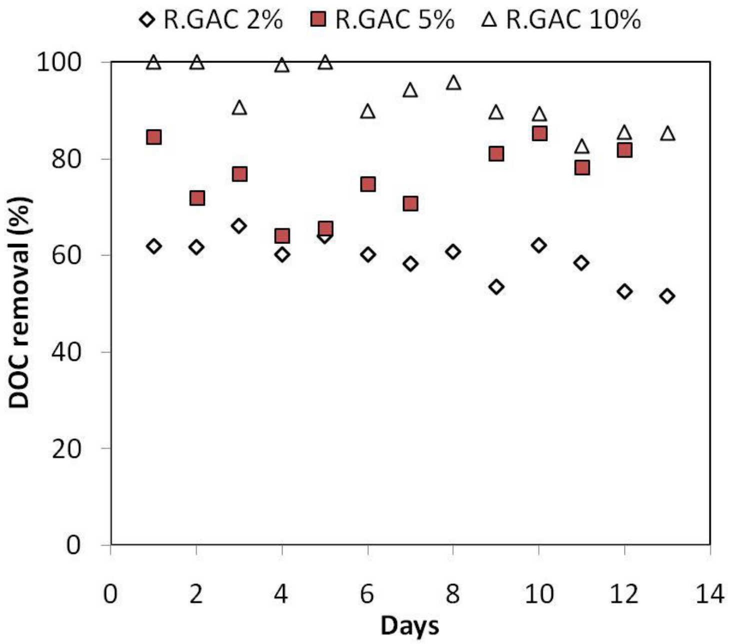
6.3.2. MF-GAC Hybrid System

6.3.2.1. Removal of dissolved organics

Based on the results obtained from the above semi-batch test, continuous (long-term) MF-GAC hybrid system experiments were conducted. The effect of flux (2.5 and 10.0 L/m^2.h) on the DOC removal efficiency for different daily GAC replacements (2% - 30%) is presented in Figure 6.3. GAC replacement of 2% was not studied at high flux (10 L/m^2.h) as the batch test showed it could not obtain a consistent rate of DOC removal. On the other hand, a very high GAC replacement (30%) may result in more organics being removed through adsorption due to the availability of higher surface area; however, it is not economical. It was discovered that the filtration flux of 2.5 L/m^2.h resulted in better removal of DOC (85-100%) than a flux of 10 L/m^2.h (30-50%) with a 10% daily replacement of fresh GAC (Figure 6.3). This implies a four-fold increase of filtration flux reduced the removal efficiency by approximately 50%. Referring to the lower GAC replacement rate (R.$_{\text{GAC 5\%}}$), 10-40% of DOC removal was observed at 10 L/m^2.h, whilst it was 60-90% at 2.5 L/m^2.h (Figure 6.3). It was also observed that the DOC removal was highly influenced by filtration flux (or hydraulic retention time, HRT) as the retention time and hydraulic loading play important roles. Low flux increases the retention time of water with adsorbents as well as reducing organic loading to the hybrid system. The HRT with a filtration flux at 2.5 and 10.5 L/m^2.h were 20 and 5 h, respectively. In terms of organic adsorption by GAC in the reactor, it was calculated that 38.8 mg of DOC was adsorbed by R.GAC$_{5\%}$ whereas 52.3 mg of DOC was adsorbed by R.GAC$_{10\%}$ per day at 2.5 L/m^2.h.

In the MF-GAC hybrid system, the effects of daily replacements of GAC in removing DOC are illustrated in Figure 6.3. As expected, more DOC removal was achieved with a higher replacement of GAC. In fact, a 10% daily replacement of GAC achieved a maximum removal of up to 100% whereas 2% GAC replacement meant that only between 40-60% DOC was removed over 14 days (Figure 6.3a). It should be noted that water quality of BTSE varies from time to time. At a filtration flux of 10 L/m^2.h, a 5% GAC daily replacement resulted in 20-40% removal of DOC and a 10% daily replacement of GAC yielded an average DOC removal of 40% (Figure 6.3b). In order to remove a larger amount of DOC at high flux, the GAC replacement was increased up to 30% and in this scenario, 40-60% DOC removal was observed (Figure 6.3).

(a) Filtration flux: 2.5 L/m^2.h



(b) Filtration flux: 2.5 L/m^2.h

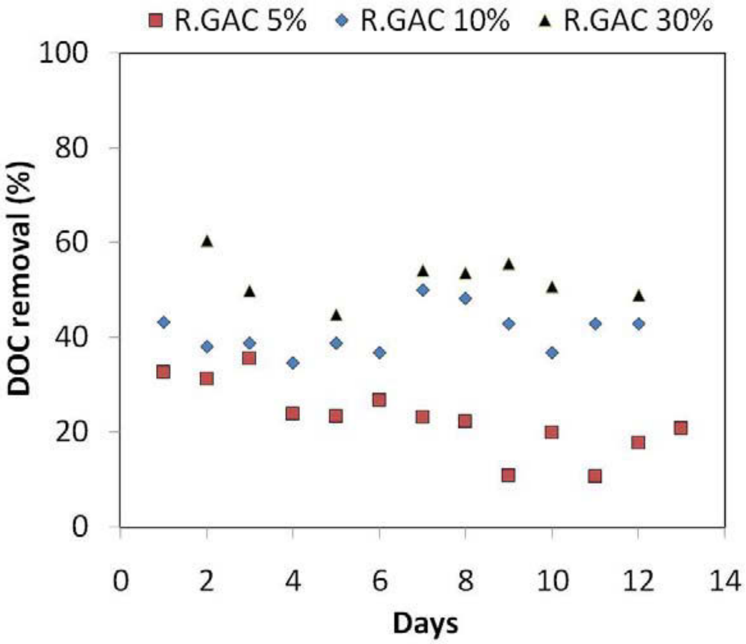


Figure 6.3: The MF-GAC hybrid system's efficiency in removing DOC (GAC dose = 2 g/L; (a) Flux = 2.5 L/m^2.h) (b) Flux = 10 L/m^2.h)

To compare the removal of DOC an intermediate filtration flux of 5 L/m^2.h was selected and an experiment was conducted for 5% and 10% GAC daily replacement. The MF-GAC hybrid system with 5% and 10% GAC replacement at 5 L/m^2.h removed 20-40% and 50-60% DOC, respectively (Figure 6.4). It is observed that removing DOC strongly depends on the flux rather than GAC replacement.

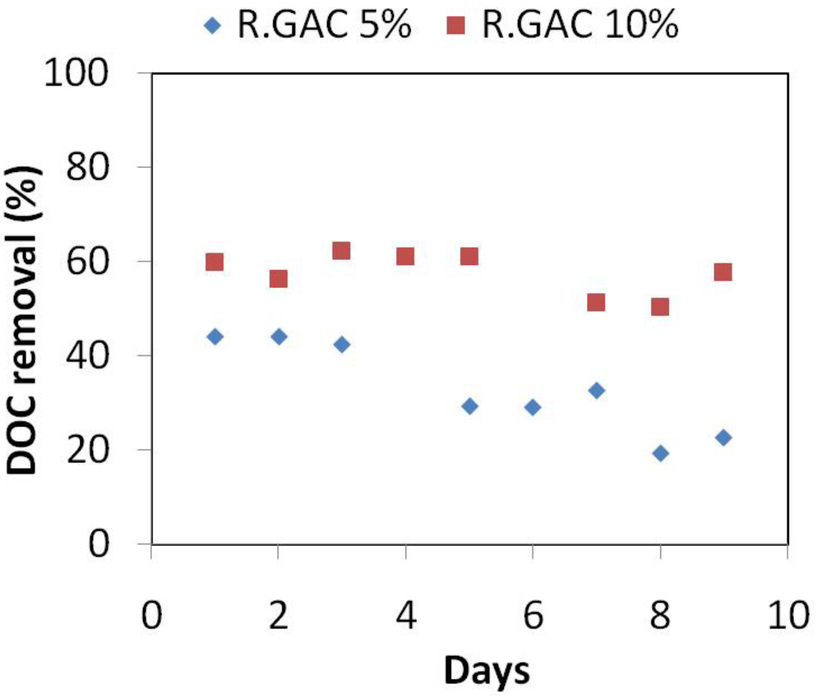


Figure 6.4: The MF-GAC hybrid system’s efficiency in removing DOC with filtration flux 5L/m2.h at two different GAC replacements (R.GAC 5% and R.GAC 10%)

In this study, 20 g of GAC was added when the experiment began (i.e. 2 g/L of the volume of the reactor). Then, daily replacements of the GAC at percentages of 2%, 5% and 10% of the initially added amount were implemented. The total dose of GAC used is the equivalent of only 20 - 40 mg GAC/L of water treated at a flux of 10 L/m^2.h. Therefore the amount of GAC leaving the system as waste was relatively small.

Additionally, the GAC is likely to function as biological activated carbon (BAC) if it is operated for a long period, and this in turn will further reduce the GAC requirement.

The TMP was virtually constant (3 – 5 kPa) throughout the experiment for all GAC replacement rates. This demonstrates that the removal of organic foulants by GAC was effective, and these organics did not reach the membrane surface which helped to reduce the fouling. Less than 5% removal of DOC was observed with the membrane filtration system without the incorporation of GAC.

6.3.2.2. Liquid Chromatography and Organic Carbon Detection

The LC-OCD size exclusion column separates the natural organic materials according to their size: the larger molecules eluted first and after 28 mins of elution, large MW bio-polymers were detected. No significant amount of bio-polymers was found in the feed water as they may have been captured by the MF in the water reclamation plant. In this study, BTSE after MF application was used as feed. MF was used in the WRP to remove the small suspended particles or colloids which were not previously removed in BTSE. Humics and building blocks were detected afterwards at 42 and 48 min of elution. The LMW acids were detected at 48-51 mins followed by LMW neutrals which contain neutral and amphiphilic organics and these eluted after 60 mins till the end of the chromatogram (Huber et al. 2011).

In order to identify the removal of organic fractions by GAC, samples were analysed by LC-OCD. The results indicated that the removal of different classes of organic fractions depends on the amount of daily GAC replacement and filtration flux. GAC is able to remove humics, building blocks and LMWs since these components are easily adsorbed into GAC pores (Ciputra et al. 2010; Velten et al. 2011). A filtration flux of 2.5 L/m^2.h even at low replacement of GAC of $R._{GAC\ 2\%}$ could remove organics by more than 50%. It also removed 59.4% hydrophobic and 50.2% hydrophilic organics. The application of GAC in this study served mainly to remove humics and building blocks which are the major components in the hydrophilic portion of BTSE (Table 6.2). Compared to $R._{GAC\ 2\%}$, slightly higher removal was observed with $R._{GAC\ 5\%}$ where 57.6% of humics and 63.8% of building blocks were removed. Of the three replacement rates studied, the $R._{GAC\ 10\%}$ resulted in superior removal of organics; specifically, 80% of organic compounds were removed (76.9% and 80.3% of hydrophobic and hydrophilic organics, respectively). Increasing the GAC daily replacement from 2% to 10% significantly increased the removal of both hydrophobics and hydrophilics (Table 6.2).

Table 6.2: Concentration of organic fractions in the effluent (mg/L) at different daily replacement rates of GAC (at a flux 2.5 L/m^2.h) (the removal % of organic fractions are given in parentheses)

%-GAC	DOC	Hydrophobic	Hydrophilic	Humics	Building blocks	LMW neutrals + acids
Flux: 2.5 L/m^2.h; GAC replacements 2%, 5%, and 10%						
Influent (mg/L)	3.6-7.7	1.0-2.0	2.6-5.7	1.3-2.9	0.6-1.3	0.6-1.2
Effluent R.$_{GAC\ 2\%}$	3.6-7.7 (52.6±3.0)	0.39 – 0.83 (59.4±1.5)	1.3-2.8 (50.2±2.0)	0.73-1.56 (45.8±2)	0.62-0.86 (36.0±2)	0.17-0.37 (70.0±0.7)
Effluent R.$_{GAC\ 5\%}$	1.4 – 3.0 (61.7±2.0)	0.34 – 0.73 (64.1±3.0)	1.04 – 2.22 (60.8±3.0)	0.57 – 1.22 (57.6±3)	0.23 – 0.48 (63.8±3)	0.23 – 0.50 (53.8±0.5)
Effluent R.$_{GAC\ 10\%}$	0.7 – 0.5 (79.4±4.0)	0.22 – 0.47 (76.9±2.0)	0.52 – 1.12 (80.3±2.0)	0.30 – 0.65 (77.4±3)	0.12 – 0.26 (80.5±3)	0.07 – 0.15 (86.9±0.8)
Flux: 10 L/m^2.h; GAC replacement 5%						
Influent (mg/L)	4.9-3.8	1.6-2.1	2.2-2.8	1.1-1.4	0.4-0.5	0.6-0.8
R.$_{GAC\ 5\%}$	1.8-2.3 (52.6±5.0)	0.9-1.1 (45.4±5.0)	0.9-1.2 (57.9±2.0)	0.6-0.8 (42.6±4)	0.1 (74.5±3)	0.2 (71.8±8)

The removal of organic fractions at a flux of 2.5 L/m^2.h (Table 6.2) was compared to a higher filtration flux of 10 L/m^2.h. Here, the 5% GAC daily replacement removed only 45% and 58% of hydrophobic and hydrophilic organics, respectively. Regarding the hydrophilic organics, significant amounts of humics and building blocks were removed. The results for organics removal indicates that at both filtration fluxes and different GAC daily replacement, 2.5 L/m^2.h resulted in a better removal rate than 10 L/m^2.h. The latter requires a higher GAC daily replacement to achieve the same efficiency (Table 6.3). The amount of LMW organics was small compared to the humics and building blocks. Unlike LMW organics, humics and building blocks cannot be easily biodegraded and utilized by microbes because these compounds are stable and highly complex in nature. Thus the GAC reactor acts as a type of physical adsorption during the period of 13 ± 2 days of operation.

Table 6.3: Removal (%) of organic fractions by MF-GAC hybrid system with filtration flux 10 L/m^2.h at different daily replacement rates of GAC (R.GAC 5%, R.GAC 30% and R.GAC 50%)

%-GAC	DOC					
		Hydrophobic	Hydrophilic			
				Humics	Building blocks	LMW neutrals
5%	52.6±5.0	45.4±5.0	57.9±2.0	42.6±4	74.5±3	74.0±8
30%	71.6±3.0	70.8±2.0	72.3±2.5	65.2±3	82.2±9	81.5±9
50%	77.6±4.0	77.1±1.3	78.0±2.0	75.7±5	78.5±12	82.0±10

In addition to operational conditions, the physical characteristics of GAC also influence the removal of organics. The adsorption of organic fractions primarily takes place in mesopores (2 – 50 nm width) and large micropores (1 – 2 nm width) (Velten et al. 2011; Cheng et al. 2005). The GAC used in this study had an average pore size of 30 Å (3 nm) and provides binding sites for organic fractions. The GAC removed both hydrophilic and hydrophobic fractions of organics. The removal of hydrophilic compounds by GAC was due to hydrophobicity-independent mechanisms such as anion exchange, surface complexation and hydrogen bonding which play significant roles in the sorption of organic/traces organics onto GAC (Johir et al. 2013; Nguyen et al. 2012). On the other hand, the removal of hydrophobic molecules by GAC is governed by the hydrophobic interaction between hydrophobic molecules and hydrophobic carbon surfaces (Moreno-Castilla, 2004). In this study, 45-77% of hydrophobics and 50-80% of hydrophilics were removed by MF-GAC from BTSE using different operational conditions.

6.3.2.3. Removal of organic micro pollutants

The concentrations of 30-35 commonly occurring micro pollutants were measured in the BTSE and most were not detected (<5 ng/L). Those PPCPs that were detected (i.e. above 5 ng/L) include naproxen (31-34 ng/L), gemfibrozil (21-101 ng/L), triclosan (8-11 ng/L), diclofenac (17-19 ng/L), atenolol (15-34 ng/L), sulfamethoxazole (65-242 ng/L), caffeine (158-450 ng/L), trimethorprim (24-119 ng/L), and carbamazepine (238-1110 ng/L). Of the detected PPCPs, carbamazepine had the highest concentration (up to 1.1μg/L). Carbamazepine [Log Kow (octanol–water partitioning) = 2.45] is the most frequently detected pharmaceutical residue in water bodies and it is in fact a drug (5H-dibenzo [b,f]azepine-5-carboxamide) used to control certain types of seizures (Mohapatra et al. 2014). According to present European union legislation on the classification and labelling of chemicals (92/32/EEC), Carbamazepine has been classified as "…R52/53 harmful to aquatic organisms and may cause long term adverse effects in the aquatic environment" (Tsiaka et al. 2013).

Adsorption of PPCPs onto an adsorbent normally occurs through hydrophobic interactions which increase with larger log D value of the adsorbates where D is the ratio of concentrations of a compound in a mixture of two immiscible phases (octanol and water) at equilibrium. Log D values were calculated based on the following equations – Eq. 1 and Eq. 2 (de Ridder et al. 2009):

Acids (negatively charged): $\mathrm{logD} = \mathrm{logKow} - \log(1+10\ (\mathrm{pH}-\mathrm{pKa}))$ Eq (1)

Bases (positively charged): $\mathrm{logD} = \mathrm{logKow} - \log(1+10\ (\mathrm{pKa}-\mathrm{pH}))$ Eq (2)

As per Nguyen et al. (2012), GAC can remove a large amount of hydrophobic compounds ($\log D > 3.2$). In this study, a defined pattern was observed between the concentration of PPCPs in the effluent and the corresponding Log D values of PPCPs. Four PPCPs, specifically carbamazepine, caffeine, sulfamethoxazole, and naproxen were detected at concentrations of more than 5 ng/L in effluent collected at two different fluxes of 2.5 and 10 L/m^2.h. Their Log D values were low (i.e. negative). Comparatively speaking, most of the PPCPs with higher Log D values had significant removal rates and they were detected at concentrations of less than 5 ng/L in the treated effluent. This phenomenon is shown in Figure 6.4.

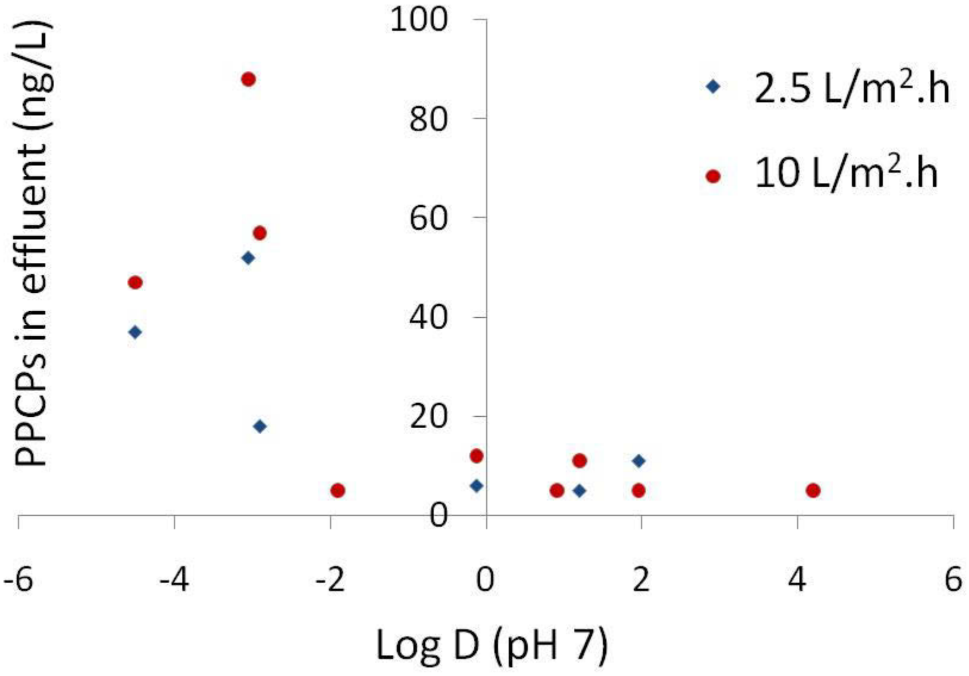


Figure 6.5: Concentration of PPCPs in the treated effluent and their corresponding Log D values (at pH 7)

The influence of filtration fluxes and GAC % - daily replacement on the removal of PPCPs by the MF-GAC hybrid system was also assessed. The MF-GAC hybrid system can remove PPCPs from BTSE to the extent that atenolol, trimethoprim and triclosan were completely eradicated and not detected in the effluent (< 5ng/L); significant amounts of diclofenac and gemfibrozil were also removed and detected at a maximum concentration of 11ng/L in the effluent. Generally the remaining PPCPs were reduced significantly and found to be at a concentration less than 60 ng/L, except carbamazepine which was partially removed and left at a concentration of 88 ng/L in the effluent. The filtration flux of 2.5 L/m^2.h was observed to be more effective than 10 L/m^2.h (Table 6.3) and this phenomenon can be explained by the residence time of feed water within the MF-GAC reactor. A low filtration flux of 2.5 L/m^2.h corresponds to residence time of 20 hours whereas at filtration flux of 10 L/m^2.h, it is only 5 hours. This fact has been further confirmed by Luo et al. (2014) who reported the contact time of GAC is a key factor that plays an important role in the removal of PPCPs.

Several researchers have reported the removal of PPCPs by GAC in which more than 98% of diclofenac and more than 23% of carbamazepine were removed (Grover et al. 2011). GAC successfully removed 95% of triclosan (Hernández-Leal et al. 2011) and GAC in a full-scale GAC adsorption beds (with an empty bed contact time of 15 min) removed 100% of diclofenac, 90% of trimethoprim, 75% of carbamazepine, and 45% of caffeine (Yang et al. 2011). The amount removed depends on the operational conditions, initial concentrations of PPCPs, etc. For example, different studies have reported variations in how much carbamazepine was removed (de Ridder et al. 2009).

Table 6.4: Removal of PPCPs at different filtration fluxes (Daily replacement rates of GAC 5% for around 14 days; Feed water – BTSE). It should be noted here that during the calculation of %-removal, the values <5 ng/L were taken as value 5 ng/L.

Concentration of PPCPs (ng/L) (Class)	Log Kow (pH 7)	pKa	Log D	BTSE	Effluent (ng/L) (2.5 L/m^2/h)	Removal (%)	BTSE	Effluent (ng/L) (10 L/m^2/h)	Removal (%)
Atenolol (β-blocker)	0.16	9.6	-1.9	34	<5	>85.3	15	<5	>66.7
Caffeine (Stimulant)	-0.07	10.4	-2.9	450	18	96	158	57	63.9
Carbamazepine (Anti analgesics)	2.45	<2	-3.05	1110	52	95.3	238	88	63
Diclofenac (Analgesics)	4.51	4.1-4.2	1.2	17	<5	70.6	19	11	42.1
Gemfibrozil (Lipid regulator)	4.77	4.7	1.96	101	11	89.1	21	<5	>76.2
Naproxen (Analgesics)	3.18	4.2	-0.12	82	6	92.7	31	12	61.3
Sulfamethoxazole (Therapeutic)	0.89	<2.1	-4.5	242	37	84.7	65	47	27.7
Tricloson (Anti infective)	4.76	7.9	4.2	8	<5	37.5	11	<5	>54.5
Trimethoprim (Anti infective)	0.91	7.1	0.91	119	<5	95.8	24	<5	>79.2

As shown in Table 6.4 below, both R$_{\text{.GAC 5\%}}$ and R.$_{\text{GAC 10\%}}$ are able to remove PPCPs from BTSE. However, the influence of R.$_{\text{GAC 10\%}}$ on the removal of PPCPs was only marginally better than R.$_{\text{GAC 5\%}}$. Here too, the removal of PPCPs by GAC can be explained based on Log D values. The detection of PPCPs such as caffeine, carbamazepine in the treated effluent at R.GAC 10% may be due to their low Log D values (-2.9 to -4.5). The removal of gemfibrozil, atenolol, and trimethoprim proved to be very similar for both conditions. A higher rate of GAC replacement made it possible to remove more PPCPs.

Table 6.5: Influent and effluent PPCPs, removal efficiency (%) of PPCPs for different doses of GAC by Membrane-GAC hybrid system

Concentration of PPCPs (ng/L)	Log Kow (pH 7)	Log D	pKa	BTSE	Effluent (ng/L) ($R._{GAC\ 5\%}$)	Removal (%) ($R._{GAC\ 5\%}$)	Effluent (ng/L) ($R._{GAC-10\%}$)	Removal (%) ($R._{GAC\ 10\%}$)
Atenolol	0.16	-1.9	9.6	15	<5	>66.7	<5	>66.7
Caffeine	-0.07	-4.5	10.4	158	57	63.9	20	87.3
Carbamazepine	2.45	-2.9	<2	238	88	63	26	89.1
Diclofenac	4.51	0.91	4.1-4.2	19	11	42.1	<5	>73.7
Gemfibrozil	4.77	-3.05	4.7	21	<5	>76.1	<5	>76.2
Naproxen	3.18	-0.12	4.2	31	12	61.3	<5	>83.9
Sulfamethoxazole	0.89	1.96	<2.1	65	47	27.7	19	70.8
Triclosan	4.76	4.2	7.9	11	<5	>54.5	<5	>54.6
Trimethoprim	0.91	1.2	7.1	24	<5	>79.2	<5	>79.2

To study the effect of a double membrane system, a MF-GAC hybrid system experiment was also carried out at a lower filtration flux (5 L/m^2.h) for 2 days. The effluent collected from the MF-GAC hybrid system underwent a further polishing stage through NF (referred to as dual membrane hybrid system in this paper). The results are discussed below in more detail.

6.4. Dual membrane hybrid system (MF-GAC followed by NF)

In order to reduce NF fouling and to remove the trace organics left in the effluent of the MF-GAC hybrid system, a dual membrane hybrid system was tested. It involved a combination of the MF-GAC and NF filtration systems where the feed water was firstly passed through the MF-GAC hybrid system [at R.$_{GAC\ 5\%}$ and R.$_{GAC\ 10\%}$; Flux = 5 L/m^2.h; initial GAC dose = 2 g/L], and then through the NF unit [Permeate flux = 48.5 L/m^2.h; Pressure = 400 kPa]. The final permeate collected from the dual membrane filtration system was analyzed for DOC, PPCPs, inorganic ions, etc.

6.4.1. Removal of dissolved (bulk) organics

The removal of dissolved organics by the dual membrane hybrid system is summarized in Table 6.5. The MF-GAC hybrid system removed 37% and 53% of organics with R.$_{GAC\ 5\%}$ and R.$_{GAC\ 10\%,}$ respectively and following this, more than 95% rejection was achieved by NF.

Table 6.6: Removal of DOC by dual membrane system (filtration flux and initial GAC dose of MF+GAC hybrid system is 10 L/m^2.h, and 2 g/L; NF at pressure: 400 kPa)

	Dual Membrane 1			Dual Membrane 2		
	[MF+GAC(R.$_{\text{GAC 5\%}}$)] → NF			[MF+GAC(R.$_{\text{GAC 10\%}}$)] → NF		
	BTSE (mg/L)	After MF+GAC (%-removal)	After MF+GAC →NF (%-removal)	BTSE (mg/L)	After MF+GAC (%-removal)	After MF+GAC→ NF (%-removal)
DOC (mg/L)	7.2±0.2	4.5±0.2	0.3±0.1	5.8±0.5	2.4±0.2	0.2±0.1
Removal (%)	Blank	37±5%	>95±1%	Blank	53±5%	>95±1%

The rejection percentage of organic fractions by NF was measured by LC-OCD. Compared to all organic fractions, rejection of hydrophilic compounds was good where 98% rejection of humics and building blocks was observed. Bio-polymers were completely removed by NF as the MW cut-off of NF membrane (700 Da) was small enough to retain bio-polymers with a molecular weight of more than 20,000 Da. However, a slightly lower rejection (84%) was observed for LMW neutrals. These results clearly indicate that the LMW neutrals percolate through the NF membrane to a greater extent than charged organics. In fact, LMW neutrals generally enjoy greater permeability through the NF than charged compounds with similar MW (Nilson and DiGiano, 1996). Electrostatic interactions play a predominant role as the transport of negatively charged molecules is hindered through negatively charged pores of the membrane, whereas neutral compounds do not undergo such repulsion (Meylan et al. 2007).

The analysis of the DOC fractions in the permeate showed that only 16% of LMW neutrals passed through the NF. The removal of bio-polymers achieved a 100% success rate while the humics and building blocks fractions were virtually the same at 98.6% and 98.2%, respectively.

The DOC of BTSE was 5.8–7.2 mg/L which was reduced to 2.4-4.5 mg/L by MF-GAC pre-treatment and to 0.3 mg/L (i.e. ~95%) by NF. The removal of DOC by NF alone (without MF-GAC pre-treatment) was also more than 95%. Organic deposits on the NF membrane surface were calculated to be 16 mg/m^2 for hydrophobics and 19 mg/m^2 for hydrophilics. Employing MF-GAC pre-treatment therefore reduced the potential NF foulants (both hydrophobic and hydrophilic fractions in BTSE) by approximately 45-80%, at different operational conditions and eventually reduced the organic load to the NF membrane. Pre-treatment in effect reduces the frequency of NF membrane cleaning cycles.

6.4.2. Removal of trace organics - PPCPs

In this experiment, 33 commonly available PPCPs in municipal wastewater were investigated. Of these, 16 PPCPs were in the undetectable range (below 5 ng/L), namely: simvastatin, hydroxyacid-simvasatin, polyparaben, phenylphenol, 4n-nonylphenol, paracetamol, dilantin, enalpril, risperidone, atrazine, linuron, omeprazole, clozapine, triameterene, hydroxyzine, and, diazepam. The remaining 17 PPCPs were detected above 5 ng/L and they comprised 53% of the total: ketoprofen, naproxen, ibuprofen, gemfibrozil, triclosan, diclofenac, triclocarbon, atenolol, sulfamethoxazole, caffeine, trimethoprim, carbamazepine, fluoxetine, amitriptyline, primidone, verapamil, and simazine. Of these 17 PPCPs, the concentration of 8 PPCPs was higher than 0.1 μg/L (>100 ng/L) where carbamazepine was detected at the highest concentration level

(541 and 307 ng/L) in BTSE. The different values are due to the fact the BTSE was collected on two different days.

The dual membrane hybrid system is able to remove most of the PPCPs by more than 65% except simazine, triclocarbon, fluoxetine, verpamil, and amitriptyline. PPCPs were present in feed water at a concentration of less than 0.018 μg/L. Higher removal (>80%) was observed with naproxen, trimethoprim, diclofenac, gemfibrozil, carbamazepine, primidone, sulfamethoxazole, atenolol, and ibuprofen where their concentrations were significant in the feed. The PPCPs remaining in the effluent due to the MF-GAC hybrid system were then removed by NF. All the PPCPs in the final effluent remained below the level of detection except caffeine (0.03μg/L), carbamazepine (0.02 μg/L), and atenolol (0.008 μg/L).

The NF membrane's efficiency in removing PPCPs largely depends on the MW of the PPCPs and molecules' hydrophobicity. Negatively charged PPCPs such as diclofenac, naproxen, sulfamethoxazole, and ibuprofen were more effectively removed than positively charged/neutral compounds because electrostatic forces between PPCPs and membrane dominate (Chon et al. 2012). Sudhakaran et al. (2013) reported that NF removed triclosan (90%); caffeine, carbamazepine, DEET, gemfibrozil, ibuprofen, diclofenac, etc. (80-85%); naproxen (50%); and TCEP (40%). The NF membranes' removal efficiency is very close to that of the RO membranes. The average removal efficiency by tight NF was 82% for neutral contaminants and 97% for ionic contaminants (Luo et al. 2014).

6.4.3. Removal of inorganic ions

The removal of inorganic ions (especially for calcium, magnesium, sulfate and nitrate) by the MF-GAC hybrid system and NF was studied using selected representative samples. As expected, the MF-GAC hybrid system did not remove the inorganic ions unless they were attached to organics. Only 68% and 58% rejection of calcium and magnesium ions were observed by NF, respectively. In the case of inorganic anions, 99% of sulfate ions were rejected by NF whilst no rejection of nitrate ions was observed. The results are presented in Table 6.7. Van der Bruggen et al. (2003) observed a similar removal pattern of such ions by NF.

Table 6.7: Effluent concentrations (mg/L) of inorganic ions in the effluents of MF-GAC and NF systems. The percentage removal is shown within parentheses.

	Dual Membrane 1 (R.GAC 5%)			Dual Membrane 2 (R.GAC 10%)		
	Feed (mg/L)	Removal after MF+GAC (%)	Removal after NF (%)	Feed (mg/L)	Removal after MF+GAC (%)	Removal after NF mg/L (%)
Calcium	34	33.7 (<1)	11 (67.6)	31.3	31 (<1)	8.0 (74.4)
Magnesiu	13	12.9 (<1)	5.5 (57.6)	21.5	21.5 (0)	7.0 (67.4)
Sulfate	55	54.7 (<1)	0.5 (99)	45	44.2 (<2)	0.45 (99)
Nitrate	6.5	6.4 (<1)	6.2 (<1)	6.2	6.0 (<1)	6.1 (0)

6.5. CONCLUSIONS

The dual membrane hybrid system (MF-GAC hybrid/NF system) proved to be an effective treatment strategy for removing dissolved organics, organic micro pollutants such as pharmaceuticals, and most of the divalent inorganic ions. The membrane-GAC hybrid system's efficiency in removing organics is highly dependent on operating conditions, i.e. filtration flux and daily replacement rates of GAC:

The MF-GAC hybrid system was very effective at low filtration flux of 2.5 L/m^2.h and removed organics by more than 80% and 60% at $R._{GAC\ 10\%}$ (0.2 g GAC/Litre$_{\text{volume of the reactor}}$/d) and $R._{GAC\ 5\%}$ (0.1g GAC/Litre$_{\text{volume of the reactor}}$/d), respectively. Increasing the filtration flux to 10 L/m^2.h resulted in poorer removal efficiency of 40-60% despite a higher GAC replacement rate of 30% ($R._{GAC\ 30\%}$). Low filtration flux and high GAC replacement rates are not sustainable, and consequently a filtration flux of 5 L/m^2.h and 10% of GAC replacement is suitable.

The MF-GAC hybrid system was effective in removing major organic foulants. Hydrophobics and hydrophilics (especially humics) were removed and this subsequently reduced membrane fouling. No TMP increase and no flux decline were observed with NF when the MF-GAC hybrid system was used as pre-treatment. The removal of organics by NF was excellent (95%). The removal of organic fractions by NF was influenced by the size and charge of the molecules. The rejection of LMW neutrals was found to be less (84%) compared to humics/building blocks (98%).

The MF-GAC followed by the NF hybrid system was effective and completely rejected most of the trace organics. Carbamazepine which had the highest concentration level in the feed water was also significantly reduced by the combined MF-GAC/NF hybrid system. Referring to the removal of inorganic ions a significant rejection of calcium, magnesium, sulfate was observed with NF (60% to 99%). The MF-GAC hybrid system alone did not remove cations/anions.

Finally, it is evident that the MF-GAC hybrid system can remove most organic foulants from feedwater and reduce organic loading to NF. This allowed the NF system to operate for a long time and produce high quality reusable water virtually free of organic micro pollutants such as pharmaceuticals.

CHAPTER 7

USE OF NANOFILTRATION AND REVERSE OSMOSIS IN RECLAIMING WASTE WATER FOR IRRIGATION

SUMMARY

Micro filtered, biologically treated sewage effluent (BTSE) generally has high sodium adsorption ratio (SAR) and sodium (Na) and chloride (Cl) concentrations. Therefore it cannot be directly used for irrigating sensitive crops. A study was conducted on a micro filtered BTSE from a Sydney water reclamation plant to determine whether the BTSE can be treated using nanofiltration (NF) and reverse osmosis (RO) to bring these risk parameters within safe limits. The study showed that using NF and RO alone could not produce the required ratio of SAR. Furthermore, NF alone did not remove the necessary levels of Na and Cl ions while RO did. However, blending equal proportions of NF permeate and RO permeate obtained from a two stages hybrid treatment system consisting of NF followed by RO resulted in a product quality suitable for irrigation in terms of the above mentioned risk factors. Utilizing NF prior to RO reduced the RO membrane fouling as well as leading to cost effective solutions. Both NF and RO removed most of the pharmaceutical and personal care products from the feed water and this may subsequently protect soil and ground water from potential hazards.

7.1. INTRODUCTION

Reclaimed wastewater for irrigation serves as an economical water resource in many countries (Bixio and Wintgens, 2006). It also has several benefits in improving soil health and reducing the need to use fertilizers. However, excessive salts, pathogens, trace organics, sodium (Na) and chloride (Cl) can cause dangerous environmental risks. The water quality criteria for irrigation are mainly characterized in terms of salinity and Na hazards, pH, and concentrations of some specific ions such as Cl^-, borate (BO_3^{3-}), and nitrate (NO_3^-).

Salinity is a hazard that results from high salt content in the water which directly affects plant growth, crop performance and soil properties (Bunani et al. 2014) and it can be expressed by electrical conductivity (EC). High EC may cause physiological drought in plants. Sodium hazard is measured by sodium adsorption ratio (SAR) which provides the relative concentration of Na to calcium (Ca) and magnesium (Mg) ions. An excessive level of Na in relation to Ca and Mg affects the permeability characteristics of soil profile by changing the soil structure (ANZECC, 2000). In addition to these, some specific ions such as Cl^-, BO_3^{3-} and NO_3^- at excessive levels can severely damage plant growth.

According to Ayers and Westcot (1985) an excess concentration of Cl^- in soil solution causes this element to accumulate in plant leaves and cause leaf burn/dead leaves. This eventually results in necrosis (dead tissue). While boron (B) is an essential element for plant growth the high concentration of this element causes older leaves to turn yellow and this ultimately causes chlorosis. Nitrogen (N) is also an important element but its over-supply may over-stimulate plant growth, leading to delayed maturity of produce and ultimately its poor quality. As such, nutrient balanced irrigation water is essential in order to have a positive impact on plant growth. According to the water quality standards reported by ANZECC (2000), the allowable safe limits of SAR, Cl, Na and B are 2-8, < 175 mg/L, < 115 mg/L, and < 0.5 mg/L for very sensitive crops. The desirable range of pH for irrigation water is 6.5 to 7.6. The pH beyond this range (due to bicarbonates and carbonates) causes Ca^{2+} and Mg^{2+} ions to form insoluble precipitates and consequently Na^{+} ions become dominant.

However, these standards may vary depending on the sensitivity of crops, SAR and EC of the water, and soil type. Besides these inorganic constituents, organic micro pollutants in irrigation water are increasingly accumulating in crop tissues and this has important implications for people's health upon consumption (Liu and Wong, 2013). Organic micro pollutants are contaminants that have the properties of toxic biological hazards even at low concentrations. Carter et al. (2014) reported the accumulation of some pharmaceuticals in the tissues of radish (*Raphanus sativus*) and ryegrass (*Lolium perenne*). Another study reported the presence of pharmaceutical residues in plant tissues (especially for alfalfa and apple) which were irrigated by reclaimed water containing pharmaceuticals (Calderón-Preciadoa et al. 2011). The long-term use of irrigation water containing organic micro pollutants may eventually lead to potential groundwater contamination. The occurrence of organic micro pollutants in groundwater has been documented in some studies over the last decade (Díaz-Cruz and Damià, 2008; Drewes et al. 2003; Fang et al. 2012). However, the critical toxic values for most of the organic micro pollutants have not been reported in the literature.

Membrane technologies play a key role in reclaiming micro filtered biologically treated sewage effluent (BTSE) and have received much attention during the past few decades owing to the need to overcome water shortage problems (Oron et al. 2006). Studies have mainly investigated combining membrane filtration (MF) and ultrafiltration (UF) with RO membranes to remove suspended particles as well as to reduce salinity levels (Ning and Troyer, 2007; Prihasto et al. 2009). Bunani et al. (2014) used RO technology to treat biologically treated sewage effluent (BTSE) for irrigation and suggested blending 20-30% of BTSE and 80-70% of RO permeate to make product water suitable for irrigation. However, it is not economical to blend high volumes of RO. Mrayed et al. (2011) reported a combination of NF and RO treatment processes to treat BTSE and recommended a blending of NF concentrate and RO permeate for irrigation. The reason for this particular blending was to enrich the product water with divalent nutrients as well as to reduce monovalent nutrients in the product water because NF has the ability to reject divalent ions. Conversely, RO can reject both monovalent and divalent ions (Rautenbach et al. 1997). They suggested blending NF concentrate and RO permeate at the ratio of 32:68 which resulted in a SAR of 8.2. However, this resulted in a high concentration of Na ions (588 mg/L) which is not suitable for Na sensitive crops.

None of the above studies have investigated the removal of organic micro pollutants along with inorganics from BTSE water for irrigation use. The objective of this study was to evaluate combining NF and RO (a two stages hybrid system) to raise the quality of micro filtered BTSE water in terms of SAR value and Na and Cl concentrations so that it was suitable for irrigation. The possibility of using NF followed by passing part of the NF permeate through RO and combining the NF and RO permeates at suitable ratio to achieve good irrigation water quality was tested. The product water's quality was also evaluated for organic micro pollutants to prevent them from poisoning groundwater and soil over the long-term. Furthermore, the layout/configurations of NF and RO membranes were investigated in terms of reducing potential RO membrane fouling.

In this context a study was conducted on a micro filtered BTSE from a Sydney water treatment plant to determine whether the BTSE can be treated using nanofiltration (NF) and reverse osmosis (RO) to bring these risk parameters within safe limits. The study showed that using NF and RO alone could not produce the required ratio of SAR. Furthermore, NF alone did not remove the necessary levels of Na and Cl ions while RO did. However, blending equal proportions of NF permeate and RO permeate obtained from a two-stages hybrid treatment system consisting of NF followed by RO resulted in a product quality suitable for irrigation in terms of the above mentioned risk factors. Utilizing NF prior to RO reduced the RO membrane fouling as well. Both NF and RO removed most of the pharmaceutical and personal care products from the feed water and this may subsequently protect soil and ground water from potential hazards.

7.2. MATERIALS AND METHODS

7.2.1. Materials

a. Feed water

The micro filtered BTSE collected from a water reclamation plant located in Sydney, Australia was used as feed water. Its characteristics and water quality criteria for irrigation use are presented in Table 7.1. The use of this feed water itself is unsuitable for sensitive crops as the SAR value was 39, and levels of Na^+ and Cl^- were 81-120 mg/L and 150-300 mg/L, respectively. Therefore the feed water needs to be further treated.

Table 7.1: Physico-chemical characteristics of feed water

Parameter	Unit	Micro filtered BTSE	Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC, 2000)
Dissolved organic carbon (DOC)	mg/L	3.6-7.7	
pH	-	6.8-7.6	6.5-8.0
conductivity	dS/cm	0.52-1.12	<0.65; 0.65-2.9; 2.9-5.4; >8.1 for very sensitive; sensitive to moderately tolerant; tolerant to very tolerant; too saline.
SAR		39	2-8; 8-18; 18-146; 46-102 for very sensitive; sensitive; moderately tolerant and tolerant crops.
F^-	mg/L	0.7-1.1	1.0 and 2.0: long-term trigger value and short-term trigger value
Cl^-	mg/L	150-300	<175; 175-350; 350-700; >700 for very sensitive; sensitive; moderately tolerant and tolerant crops
NO_3^-	mg N/L	1.0-1.3	5; 25-125 for long-term trigger value and short-term trigger value
PO_4^{3-}	mg P/L	0.74-0.99	0.05; 0.8-10 for long-term trigger value and short-term trigger value
SO_4^{2-}	mg S/L	49-51	
Na^+	mg/L	81-120	<115; 115-230; 230-460; >460 for sensitive; moderately sensitive; moderately tolerant and tolerant crops.
K^+	mg/L	15-21	
Ca^{2+}	mg/L	21-40	
Mg^{2+}	mg/L	10-15	
BO_3^{3-}	mg B/L	0.04-0.06	<0.5; 0.5-2.0; 2.0-6.0; 6.0-15.0 for sensitive; moderately sensitive; moderately tolerant and tolerant crops.

b. Membranes

Three types of NF membranes and an RO membrane were used in this study to compare their effectiveness in removing contaminants of concern. The characteristics of the membranes are presented in Table 7.2.

Table 7.2: Characteristics of NF and RO membranes

Membrane	Manufacturer	Material	[a]MWCO (Da)	Membrane property	Zeta potential (mV) at pH 7
NP 010	Macrodyn®Nadir	Polyetersulfone	1000	Hydrophilic	-12[b]
NP 030	Macrodyn®Nadir	polyetersulfone	400	Hydrophilic	-15[b]
NTR 729HF	Nitto Denko	Polyvinylalcoholic polyamides (Heterocyclic aromatic)	700	Hydrophilic	-100[c]
RO	Woongjin Chemical	Polyamides	100	-	-21[d]

[a] Molecular weight cut off (MWCO); [b](Kaya et al. 2010); [c](Shon et al. 2005); [d] (Shon et al. 2009)

7.2.2. Methodology

A known quantity (20 L) of micro filtered BTSE was filtered through NF or RO membrane (Figure 7.1). The NF and RO filtration units are equipped with a rectangular cross-flow cell having a membrane area of 68 cm^2. The membrane charge has been shown to become less negative (reduced zeta potential) when the temperature of the feed water increased (Shon et al. 2009). Therefore, a cooling coil was submerged in the feed water tank to maintain the feed water temperature at a constant 20 ± 2^{o}C. A pressure of 4 bar was used for all NF membranes. The clean water fluxes (L/m^2.h) were 55, 12, and 62 for NP 010, NP 030, and NTR 729HF, respectively. Thus the permeabilities (L/m^2.bar.h) were 13.75, 3 and 15.5. The pressure used for RO was 40 bar. The clean water flux (L/m^2.h) was 23.5 L/m^2.h; the permeability was 0.59 L/m^2.bar.h. The concentrate (retentate) produced from NF or RO was recirculated back into the feed water. The performance of each membrane was tested using the same operating conditions of the membrane unit. Of the three types of NF membranes the best one was selected for combining with a RO post-treatment. The schematic diagram of the NF/RO unit is presented in Chapter 3.

The direct application of RO leads to RO membrane fouling resulting in reduced RO operation time. In order to solve this problem the micro filtered BTSE was passed through NF and the NF permeate served as the feed for RO. This is explained in the schematic diagram in Figure 7.1 (i.e. Treatment Train 2). It is assumed here that NF will remove most of the foulants and thus prevent them from reaching the RO membrane. This assumption was tested by doing a membrane autopsy for both RO membranes – one RO membrane which used NF permeate as feed and the other one using BTSE directly as feed so that the extent of fouling in the two systems can be compared. Another advantage of using NF before RO is that NF may remove most of the organic micro pollutants and this aspect was also tested in this study. Even if NF reduces fouling of the RO membrane, it cannot satisfactorily remove the toxic monovalent ions, Na^+ and Cl^-. Therefore RO is required to remove these ions. However, RO is more expensive than NF and therefore a blend of RO permeate and NF permeate at a suitable ratio is tested to understand whether irrigation water of a satisfactory quality can be produced. This is a cheaper option than using RO alone.

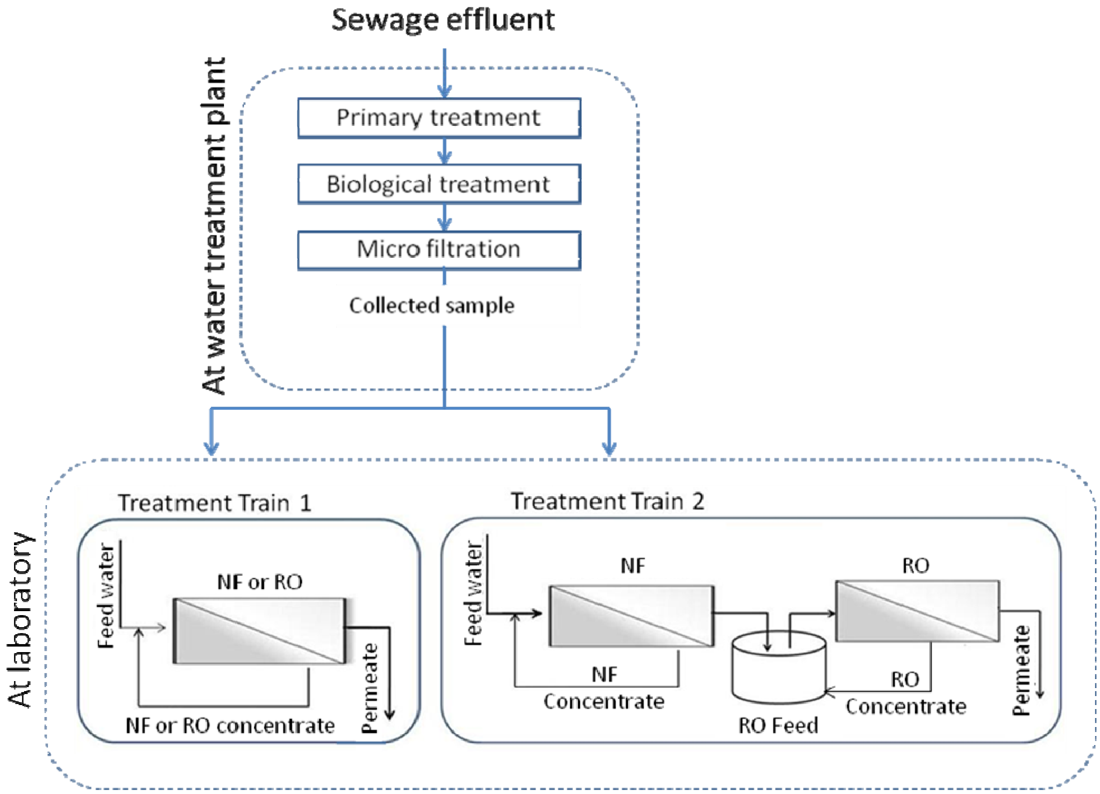


Figure 7.1: Schematic diagram of the treatment trains of sewage effluent at water treatment plant and in the laboratory.

At the end of the RO operation, a section of the central part of the RO membrane was cut (21.6 cm^2) and ultra sonicated for 10-20 min to extract the membrane deposits into 40 mL milli-Q water. The dissolved solution was filtered using a filter with 0.1 μm opening and analyzed for organic fractions. The details of the analysis have been documented elsewhere (Jeong et al. 2013b). Moreover, membrane fouling was observed using contact angle analysis and scanned electro microscopy (SEM) images. Details concerning the analyses are given in Chapter 3.

7.2.3. Chemical analysis

Samples of feed water and permeates were collected at different times after the experiments had started depending on the membranes' operational time. Dissolved organic carbon (DOC) was examined using a Multi N/C 2000 TOC Analyser after filtering samples through a filter with a 0.45 µm opening. Organic fractions were measured on Liquid Chromatography-Organic Carbon Detection (LC-OCD) Model 8 developed by Huber et al. (2011). A TSK HW 50-(S) where the column measured the hydrophilic and hydrophobic fractions of organic matter. The analysis of inorganic anions was carried out using a Metrohm ion chromatograph (Model 790 Personal IC) equipped with an auto sampler and conductivity cell detector. Separation was achieved using an A SUPP column 3 (4-150 mm). Solutions of Na_2CO_3 (3.2 mmol/L) and $NaHCO_3$ (1.0 mmol/L) were employed as the mobile phase with a flow rate of 0.7 mL/min. The details can be found elsewhere (Jeong and Vigneswaran, 2013).

Pharmaceuticals and personal care products were extracted using solid phase extraction (SPE) and analyzed by Liquid Chromatograph with tandem mass spectroscopy. Details of the analysis are discussed in Chapter 3.

7.3. RESULTS AND DISCUSSION

7.3.1. Characterization of feed water

The suitability of feed water for irrigation was assessed mainly in terms of SAR value, and Na and Cl concentrations. In addition, organic micro pollutants were measured to determine whether any potential health hazards to underlying aquifers and soil environments can be caused by irrigation. As the BTSE feed is micro filtered, it can be assumed that bacterial cells/pathogens were removed to a safe level. Moreover, the presence of heavy metals/radioactive substances was not considered because the existence of these contaminants in reclaimed water is negligible (Chen et al. 2013).

7.3.2. Rejection of inorganic solutes and dissolved organics by NF

The rejection of inorganic solutes by NF is mainly governed by two mechanisms, namely electrostatic screening and Donnan effect (Teixeira et al. 2005). As shown in Table 7.3 the removal of inorganic solutes by NF varied according to the type of NF membrane. The NTR 729HF was more effective than NP 010 and NP 030 in removing inorganic anions because of its significantly higher negative zeta potential (-100 mV) compared to the other two membranes (-12 and -15 mV). Of the anions, this membrane was the most efficient in removing sulfate (SO_4^{2-}) ions, achieving 99% of rejection followed by $Cl^-$and NO_3^- rejections which were 11% and <5%, respectively. This agrees with the results obtained by Paugam et al. (2004) who reported that the rejection of inorganic solutes by polyamide NF membranes (same as NTR 729HF) was in the order $SO_4^{2-} > Cl^- > NO_3^-$. Paugam et al. (2004) explained this order as being due to SO_4^{2-} having higher charge and hydration energy compared to the other two anions. An increase in anion charge leads to greater electrostatic interaction and Donnan effect

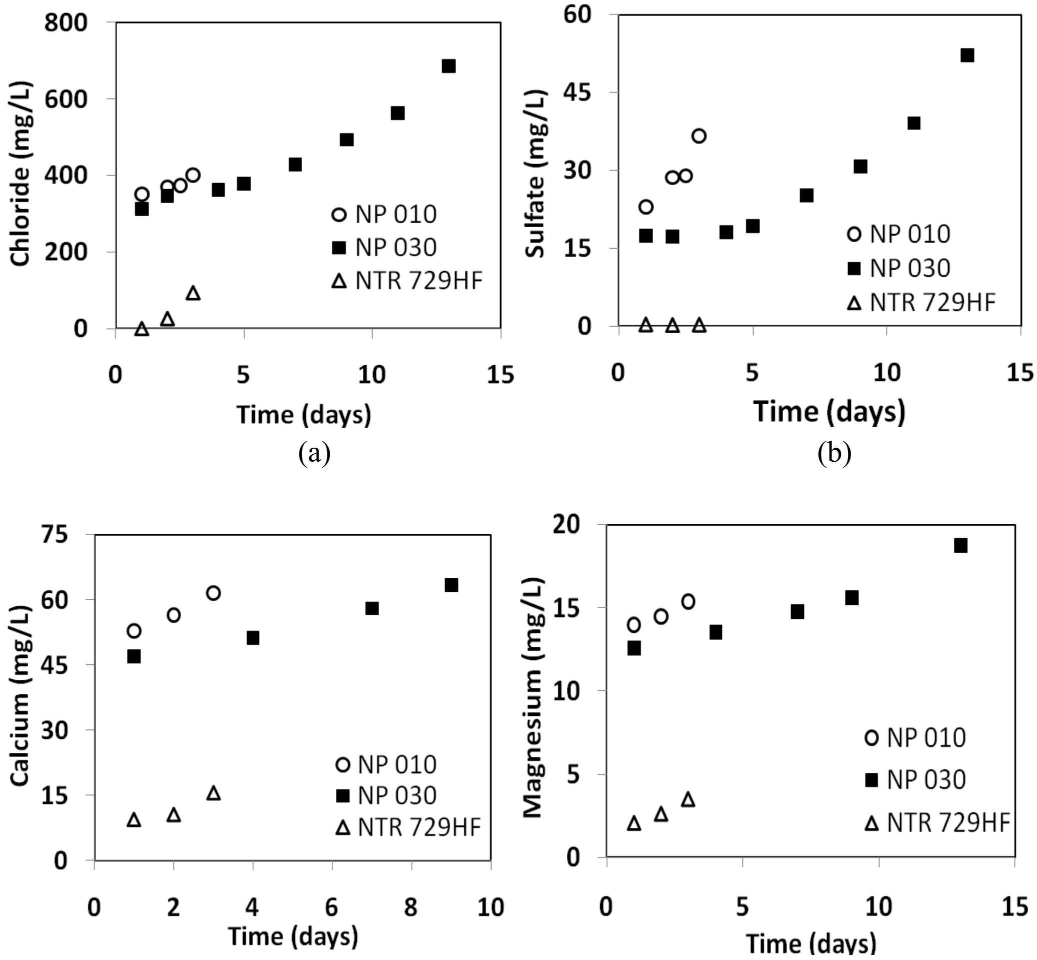
(Paugam et al. 2004; Rautenbach et al. 1997) and the more hydrated the ion is the more difficult is its transfer across the membrane (Paugam et al. 2004). RO was used as a post-treatment because NF is not expected to remove most of the monovalent ions.

The retention of organics by NF during the first 10 h of operation was efficient and only 0-0.8 mg/L of the influent DOC of concentration of 7.5 mg/L was found in NF permeate which corresponds to a 93-97% rejection rate. NTR 729HF and NP 030 removed a larger percentage of DOC than NP 010 probably because of their lower MWCO, which produced higher physical sieving of the organic molecules (Bellona et al. 2004). RO with the lowest MWCO removed the largest amount of DOC.

Table 7.3: Rejection (%) of inorganic solutes and organics by NF/RO membranes

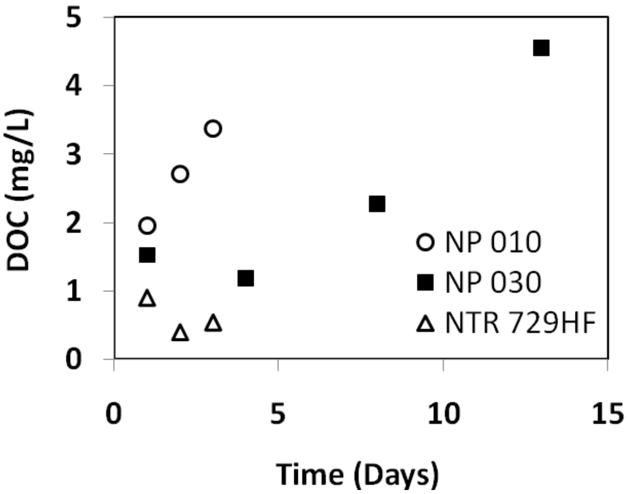
Inorganic solutes	NP 010	NP 030	NTR 729HF	RO
Ca^{2+}	12±4	20±5	62±7	99±1
Mg^{2+}	16±5	22±2	62±11	98±1
NO_3^-	Nil	18±5	<5	88
SO_4^{2-}	41±6	43±12	99±1	>99
Na^+	Nil	Nil	19	96±1
Cl^-	4±1	5±1	11±1	92±1
DOC	76±3	84±2	95±2	>99

The NF permeate concentrations of inorganic solutes and organics increased over time during the operation (Figure 7.2). As the concentrate was recirculated back with the feed water, the concentration of solutes in the feed water increased over time. This in turn raised the solute concentration in the permeate. Past studies have reported a similar phenomenon where the increased salt concentration in the feed water decreased the retention rate of solutes (Labbez et al. 2002; Mazzoni et al. 2007). The reason for this increased concentration in permeate would be due to the membranes' adsorption sites reaching saturation at high salt concentrations with less adsorption sites available for further adsorption. Another reason may be due to membrane pore swelling at high salt concentration. According to Escoda et al. (2010), an increase in salt concentration produces larger pores of the membrane (pore swelling) as a result of the higher repulsive forces between counter ions inside the pores which increased membrane charge density.



(a) (b)

(c) (d)



(e)

Figure 7.2: Effluent level contaminants of interest after NP 010, NP 030 and NTR 729HF (a) chloride ions (mg/L); (b) sulfate (mg/L); (c) calcium (mg/L); (d) magnesium (mg/L); and (e) DOC (mg/L)

Luo and Wan (2013) reported that a high concentration of charged organic electrolytes present in the feed water can also result in a smaller retention of monovalent co-ions by NF. The continuous increase of organics in the feed water observed in this study could be another reason for less inorganic solutes being retained.

The more negatively charged NTR 729HF membrane surface is better able to retain positively charged ions compared to NP 010 and NP 030. In fact the NTR 729HF had higher percentages of rejection of Na, Ca, and Mg than the other NFs (Table 7.3). The rejection percentage was higher for the divalent cations Ca and Mg than the monovalent Na due to higher electrostatic attraction of the ions to the membrane. The membrane rejection capacity exhibited by the NTR 729HF to both monovalent and divalent ions lasted longer than NP 010 and NP 030 (Figure 7.2). Thus NTR 729HF was used in the subsequent experiments. However, when comparing the performance of NF membranes with RO in terms of removing inorganics, the RO membrane demonstrated an excellent ability to remove both divalent and monovalent ions.

7.3.3. Rejection of pharmaceuticals and personal care products

The rejection of organic micro pollutants by NF and RO membranes is shown in Table 7.4 where the RO is found to be highly efficient followed by NTR 729HF. The rejections of micro pollutants by NP 010 and NP 030 were also significant but considerably less compared to RO and NTR 729HF. When comparing NP 010 and NP 030, the latter had higher rejection for 9 micro pollutants and equal rejection for two micro pollutants.

Several mechanisms have been proposed to explain the rejection of organic micro pollutants, unlike inorganic ions which involve mainly the interaction of charges on membranes and inorganic anions. Rejection of organic micro pollutants is based on their charge interaction (charge and pKa values) and membrane, MWCO, and hydrophobicity interactions (Bellona et al. 2004). Hydrophobicity of organic micro pollutants is measured by log K_{ow} value where K_{ow} is defined as the ratio of the concentrations of a solute in octonol to that in water (Demare et al. 2007). Organic micro pollutants rejections presented in Table 7.4 are explained using these mechanisms below.

Table 7.4: The removal (%) of organic micro pollutants by NF and RO membranes from BTSE

Organic micro pollutants	MW	pKa (pH 7)	Log Kow[a] (Octonol-water) (pH 7)	Charge	Organic micro pollutants in Feed water (ng/L)	Removal % (effluent level ng/L)			
						NP010	NP030	NTR 729HF	RO
Atenolol (Beta-blocker)	266	9.6[b]	0.16	Positive	77.6 – 220	<5 (76)	58 (33)	75.5 (20)	98 (<5)
Sulfamethoxazole (Antibiotic)	253	2.1[c]; <2[c]	0.89	Negative	109 – 174	27 (80)	50 (55)	98 (<5)	97 (<5)
Caffeine (Therapeutics)	194	10.4[d]	-0.07	Neutral	88 – 675	Nil (646)	Nil (631)	35 (57)	97 (39)
Trimethoprim (Anti-biotic)	290	6.6 – 7.2[e]	0.91	Neutral	146 – 229	8 (146)	8 (146)	79 (31)	98 (<5)
Carbamazepine (Anti-seizure)	236	<2[c]	2.45	Neutral	362 – 434	<5 (345)	<5 (352)	87 (50)	98 (<5)
Fluoxetine (Anti-depressive agent)	309	10.1[e]	4.05	Positive	<5 – 20	13 (11)	68 (<5)	ND[f]	ND[f]
Amtriptyline (Analgesics)	277	9.4[a]	4.92	Positive	11 – 37	52 (7)	74 (<5)	64 (<5)	89 (<5)
Primidone (Anticonvulsant)	218	-	0.91	Neutral	11 – 26	23 (17)	39 (14)	85 (<5)	62 (<5)
Verapamil (Therapeutics)	455	8.92[a]	3.79	Positive	9 – 28	13 (8)	57 (<5)	66 (<5)	86 (<5)

Diclofenac (Anti-inflammatory)	296	4.1 – 4.2[e]	4.51	Negative	57 – 131	16 (71)	29 (60)	93 (<5)	97 (<5)
Naproxen (Analgesic)	230	4.2[e]	3.18	Negative	68.8 – 211	32 (47)	54 (32)	95 (<5)	98 (<5)
Gemfibrozil (Therapeutics)	250	4.7[c]	4.77	Negative	31 – 430	16 (122)	20 (117)	72 (9)	99 (<5)

[a] MW and Log P values were obtained from the U.S. National Medicine Library. Online http://chem.sis.nlm.nih.gov/chemidplus/; [b] (Hapeshi et al. 2010); [c] (Westerhoff et al. 2005); [d] (Yang et al. 2011); [e] (Serrano et al. 2011); [f] Organic micro pollutants were not detected in feed water

The higher organic micro pollutant rejection of RO is probably due to the lower MWCO of the RO membrane (100 Da) compared to the molecular weights of organic micro pollutants (194-446 Da) (Table 7.1) causing steric hindrance (Sahar et al. 2011). The rejection of organic micro pollutants by steric hindrance cannot be applied to the NF membranes because such organic micro pollutants are small organics and all organic micro pollutants except Verapamil (454 Da) investigated in this study were below 400 Da. These are less than the MWCO values of the membranes (400-1000 Da).

Comparing the performances of NF membranes, the NTR 729HR was observed to be better in rejecting most of the organic micro pollutants despite its higher MWCO (700 Da) compared to the NP 030 (400 Da). Seven of them were significantly rejected by NTR 729HF and detected in permeates below 10 ng/L in which four were negatively charged. The surface of NTR 729HF is more negatively charged (zeta potential -100 mV at pH 7) than the NP 010 and NP 030 (-12 to -15 mV at pH 7), thus the electrostatic repulsion forces between the membrane surface and organic micro pollutants may have played a role in the rejection of the negatively charged organic micro pollutants. However, the higher rejection of the positively charged organic micro pollutants such as Veerapamil and Amtriptyline (pKa 8.92 - 9.4) by NTR 729HF may be explained based on their Log K_{ow} values (3.79-4.92) in which the rejections were mainly due to hydrophobic interactions. Hydrophobicity is another factor that influences the rejection by NF where generally compounds having high Log K_{ow} values are highly rejected by the hydrophilic NF membranes (Chon et al. 2012; Kiso et al. 2001).

The chemical constitutions of the membranes also influence the rejection capacity of organic micro pollutants. For example, Causserand et al. (2005) reported that the retention coefficient of dichloroaniline ranged from 60% to 95% with polyamide membranes whilst it was 10% to 25% with a cellulose acetate membrane. This is further confirmed by Kiso et al. (2000) who noted that the removal of pesticides was significantly higher with NTR 729HF that consisted more of polyamide membranes than polyetersulfone membranes. Polyamide constituent of NTR 729HF could be another reason for the larger rejections of pharmaceuticals observed with NTR 729HF than NP 010 and NP 030 in addition to the higher negative zeta potential of the membrane.

While many studies have examined the removal of micro-pollutants by NF/RO membranes, the mechanisms are still not fully understood due to their complexity (Chon et al. 2012). The presence of interfering compounds like natural organics in the water matrix also hinder the rejection capacities of some pharmaceuticals. Therefore an in-depth investigation of the membrane and solute properties is needed so that predicting the rejection capacities is better understood.

7.3.4. Product water quality evaluation for irrigation

The NF membranes were effective in removing organic micro pollutants and divalent cations (Ca, Mg). However, when evaluating the product water quality for irrigation, NF permeate alone could not reduce the SAR value below 14 (i.e. the safe levels) (Table 7.5). Furthermore, the Cl and Na levels in the NF permeate were 202 mg/L and 110 mg/L, respectively, which are above the maximum allowable levels for crops sensitive to these elements. The RO process eliminated all the inorganic ions below critical levels; however, it also removed the beneficial ions. As such, it was suggested that blending the NF and RO permeate with feed water would be appropriate.

The blending proportions were calculated as follows:

C_a x proportion of 'a' used + C_b x proportion of 'b' used = resulting blend in mg/L

Where, C_a is the concentration of ion in feed/permeate 1 and C_b is the concentration of ion in feed/permeate 2.

In this context, blending 10% of feed water with 90% of RO permeate gave an SAR value of 6; Cl concentration of 40 mg/L and Na concentration of 15.5 mg/L (Table 7.6). In this case the soil infiltration problem can be rectified and the toxicity caused by Cl^- and Na^+ ions is also minimized. However, utilizing 90% of RO permeate is not an economical solution. The blending of NF and RO permeate did emerge as a sustainable solution. Blending 50% of NF permeate and 50% of RO permeate resulted in a SAR value of 8; Cl^- 109 mg/L and Na^+ 57 mg/L (Table 7.7). Furthermore, blending feed water instead of NF permeate with RO permeate may still result in high concentrations of organic micro pollutants. Boron and NO_3^- in the micro filtered BTSE were well within the limits (Table 7.1).

Table 7.5: Different blending ratios of raw feed and NF permeate, and their suitability for irrigation water

Parameters	Raw feed proportion	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
	NF permeate proportion	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0.0
SAR		14	17	19	22	24	27	29	32	34	37	39
Ca		13	14	15	16	18	19	20	21	23	24	25
Mg		9	9	10	11	11	12	13	13	14	15	16
K		12	12	13	13	14	14	14	15	15	16	16
Na		111	111	112	112	113	114	114	115	116	116	117
Cl		202	208	214	221	227	233	239	245	252	258	264
S		0.8	2.5	4.2	6.0	7.7	9.4	11.1	12.8	14.6	16.3	18.0
NO_3^- N		12	12	12	12	11	11	11	11	10	10	10
B		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Table 7.6: Different blending ratios of raw feed and RO permeate, and their suitability for irrigation water

Parameters	Raw feed proportion	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
	RO permeate proportion	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0.0
SAR		3	6	10	31	17	21	24	28	32	35	39
Ca		0.3	2.7	5.2	9.3	10.2	12.6	15.1	17.6	20.1	22.5	25.0
Mg		0.1	1.7	3.2	5.5	6.3	7.8	9.3	10.9	12.4	14.0	15.5
K		0.7	2.2	3.8	9.7	6.8	8.4	9.9	11.4	12.9	14.5	16.0
Na		4	16	27	65	49	61	72	83	94	106	117
Cl		16	40.8	65.6	191.2	115.2	140	164.8	189.6	214.4	239.2	264
S		0.2	2.0	3.8	6.8	7.3	9.1	10.9	12.7	14.4	16.2	18.0
NO_3^- N		2	2	3	14	5	6	7	7	8	9	10
B		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Table 7.7: Different blending ratios of NF permeate and RO permeate required to obtain product water suitable for irrigation.

Parameters	NF permeate proportion	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
	RO permeate proportion	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0.0
SAR		3	4	5	6	7	8	10	11	12	13	14
Ca		0.3	2	3	4	5	7	8	9	10	12	13
Mg		0.1	1	2	3	4	5	5	6	7	8	9
K		0.7	2	3	4	5	6	7	9	10	11	12
Na		4	15	26	36	47	57	68	79	89	100	111
Cl		16	35	53	72	90	109	128	146	165	183	202
S		0.2	0.3	0.3	0.4	0.4	0.5	0.6	0.6	0.7	0.7	0.8
NO_3^- N		2	3	4	5	6	7	8	9	10	11	12
B		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

7.3.5. Performance of the nanofiltration-reverse osmosis hybrid system

In order to minimize RO fouling issues, the micro filtered BTSE was passed through NF and the NF permeate served as the feed for RO. This is explained in the schematic diagram in Figure 7.1, Treatment Train 2. The reduction of membrane fouling on the RO membrane using NF pre-treatment is explained by the membrane autopsy studies, which are described in detail below.

7. 4. Membrane Autopsy

Membrane autopsy was first performed on the NF membrane after filtering 20 L of BTSE. During the operation lasting 66 h, NF flux of NTR 729HF membrane with BTSE decreased marginally from 44 to 42 L/m^2.h (i.e. after filtering 20 L of BTSE at 4 bar though NF). In order to identify the potential foulants, a membrane autopsy was done using foulant extraction, contact angle measurement and SEM images. Figure 7.3 presents the results obtained from foulant extraction studies where significant levels of hydrophobics, hydrophilics, humics, and LMWs were detected on the membrane surface. This was further investigated by contact angle and SEM images.

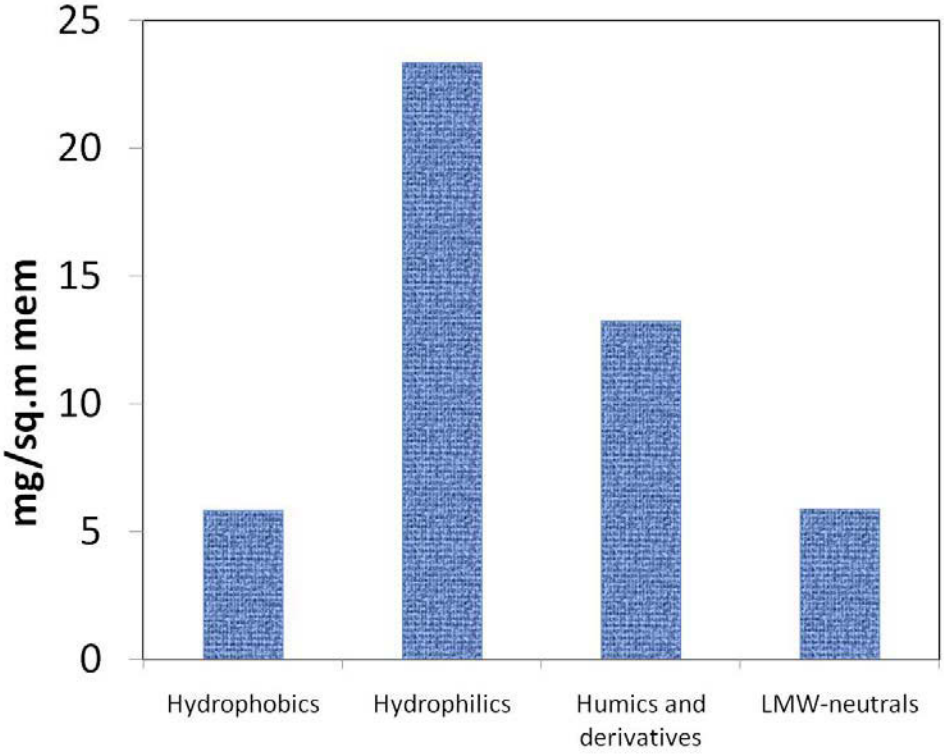
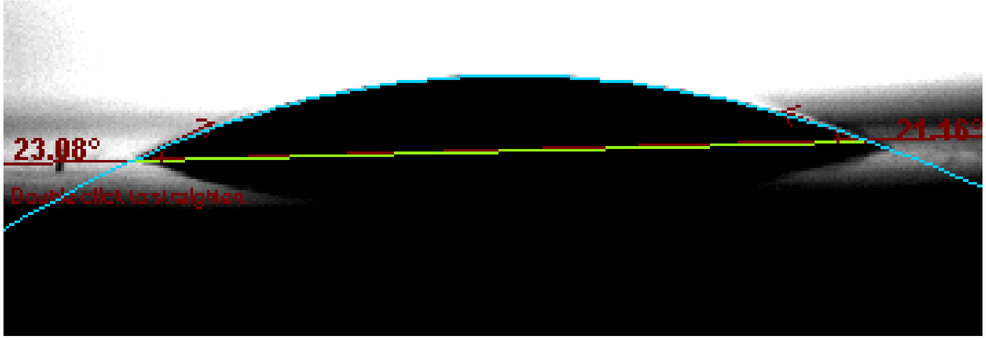


Figure 7.3: Membrane autopsy of NF membrane after filtering 20 L of BTSE

The average contact angle of the virgin NF membrane was 22.13^0 (21.16 - 23.08) and it was increased to 52.1^0 (50.52 – 53.69) in the fouled membrane (Figure 7.4 a-b). This clearly explains why the hydrophilic membrane surface becomes less hydrophilic with the adsorption of hydrophobics from feed water. The NF membrane in this context can effectively remove hydrophobic organics and thereby reduce subsequent RO membrane fouling.

(a) Virgin membrane



(b) Fouled membrane

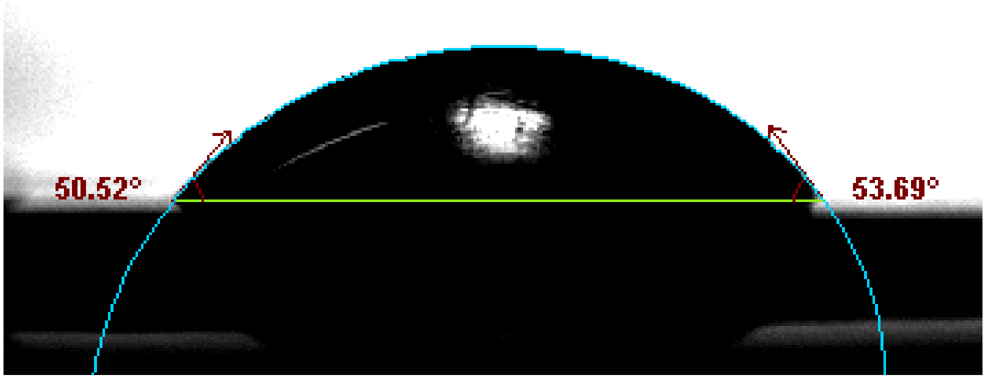
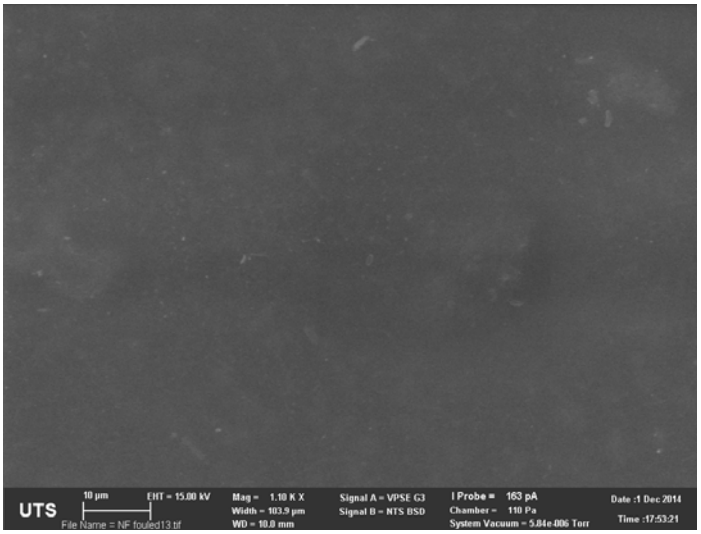


Figure 7.4: Contact angle (a) virgin (b) fouled membrane

The SEM images taken for the virgin and fouled membranes are presented in Figure 7.5. The surface of the fouled membrane was observed as having a deposit layer (Figure 7.5b) compared to the virgin membrane (Figure 7.5a). The membrane deposits_could be the organic/inorganic foulants responsible for NF flux decline during its operation time.

(a) Virgin membrane



(b) Fouled membrane

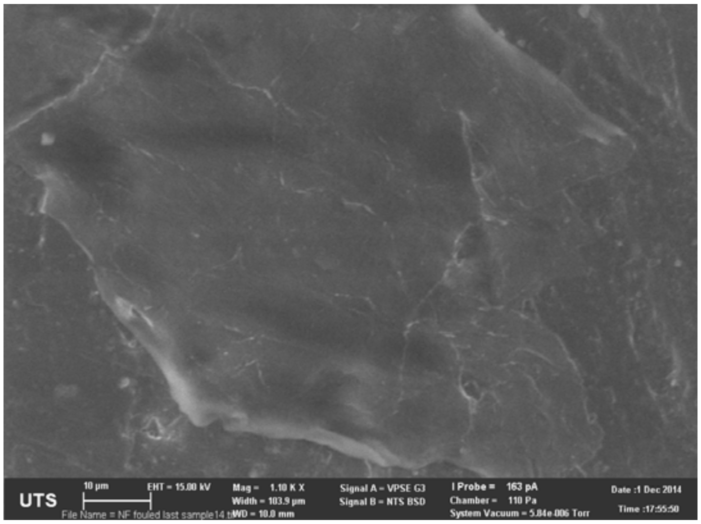


Figure **7.**5: SEM images of virgin and fouled NF membranes after filtering 20 L of BTSE

Secondly, in order to assess the significance of NF pre-treatment to RO, membrane autopsy was conducted on RO membranes with and without NF pre-treatment. The results clearly showed that the organic deposits on the RO membrane exposed directly to BTSE was larger than the RO membrane exposed to NF filtered BTSE (Figure 7.6). NF as a pre-treatment to RO reduced the potential organic foulants on the RO membrane including hydrophilics, humics and LMWs (Figure 7.6). Furthermore Table 7.3 shows that a significant amount of calcium, magnesium and sulfate can be removed by NF (in particular NTR 729HF) and this action reduces scaling on the RO membrane. Thus blending 50% of NF and 50% of RO as per Treatment Train 2 would be advantageous in terms of less interrupted RO operation.

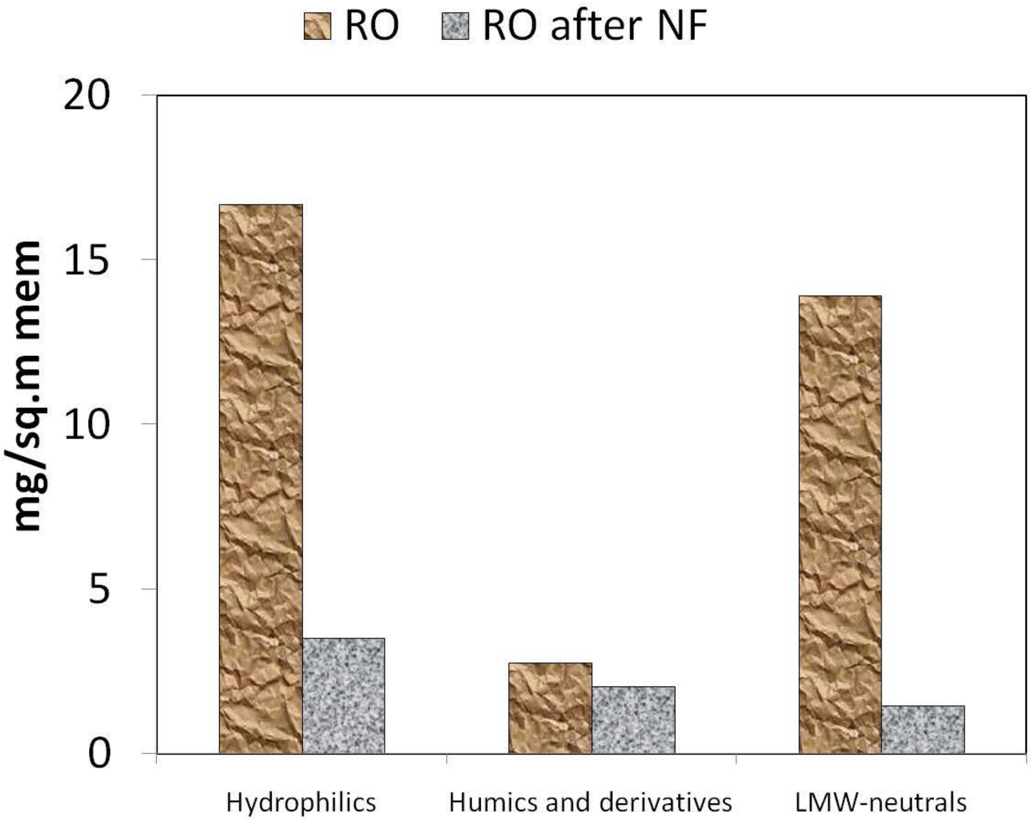


Figure 7.6: Organic foulants on the membrane surface of RO with and without NF pre-treatment.

7.5. CONCLUSIONS

This study showed that utilizing treated BTSE for irrigation is a viable option for maximizing water reuse in arid and semi-arid regions. Raw micro filtered BTSE is not suitable for irrigation because the SAR value, Na^+ and Cl^- concentrations were higher than the maximum allowable limits for sensitive crops. The blend of either 'raw water – RO permeate' or 'NF permeate - RO permeate after NF pre-treatment' (a two-stages system) at the ratios of 10:90 or 50:50, respectively, made the water suitable for irrigation. However, the second option, i.e. blending NF permeate and RO permeate after NF pre-treatment is a cost-effective option as the RO is more expensive than NF. Only 50% of NF permeate needs to be passed through RO based on experimental results. Moreover, in order to ensure the RO membrane operates more smoothly with less fouling, the NF process is used as a pre-treatment to achieve partial removal of potential organic foulants. NF removed all the humics, building blocks and most LMW organics. Both RO and NF successfully removed very large amounts of organic micro pollutants. This study demonstrated that NF permeate can be blended with that of RO after NF pre-treatment at suitable ratios to produce good quality irrigation water. However, the blending proportion of permeates can vary depending on the type of membranes used, soil type, salt tolerance of crops, salts in the soil solution, and wastewater (feed) characteristics.

CHAPTER 8

TREATMENT OF REVERSE OSMOSIS CONCENTRATES

SUMMARY

Wastewater reclamation plants using reverse osmosis as the final polishing treatment produce reverse osmosis concentrate (ROC), which consists of high salinity, nutrients and (recalcitrant) organics. The ROC collected from the water reclamation plant in Sydney was treated with a micro filtration (MF) - GAC hybrid system that removed natural and synthetic organics prior to its discharge into the environment. The performance of MF-GAC hybrid system was studied in terms of trans-membrane pressure (TMP) development, and organics removal. Different fractions of organics were measured using liquid chromatography-organic carbon detection (LC-OCD), Fluorescence Excitation - Emission matrix (F-EEM), and Liquid chromatography with tandem mass spectroscopy (LC-MS). Adding GAC into the membrane reactor reduced the TMP by reducing membrane fouling both through mechanical scouring and pre-adsorption of organics. F-EEM confirms the removal of humics-like and fulvic-like compounds by GAC from ROC. Organic micro pollutants especially pharmaceuticals and personal care products (PPCPs) were also removed by the MF-GAC hybrid system. Long term MF-GAC operated for 10 days was found to be effective in dissolved organics and organic micro pollutants removal. The daily GAC replacement of 10% (i.e., 0.28 g of GAC/L treated water per day) maintained DOC and micro pollutants removals more than 50% and more than 60% from ROC. Further, competitive effect of organic micro pollutants with dissolved organics for GAC binding sites also was minimized at this GAC dose.

8.1. INTRODUCTION

RO is used widely in wastewater reclamation plants as the final treatment stage (Chon et al. 2012; Dialynas et al. 2008; Dolar et al. 2012; Liu et al. 2012; Umar et al. 2015). Hundreds of RO based reclamation plants are in operation in Australia, Asia, Europe, Africa, and America which includes Orange County plant in California, USA (265 MLD) and three plants in Singapore (Bedok, Kranji and Changi) (Global water intelligence, 2010). In Sydney alone two major water reclamation plants are using RO after micro filtration (Homebush bay plant) (Chapman 2006) and ultrafiltration (St. Marys water recycling plant) of biologically treated wastewater. The resulting product from both plants is then used for irrigation and replenishing of Napean River, respectively. Though these RO plants lead to high quality reusable water, they also produce large volumes of RO concentrate (ROC) that are rich in dissolved organics, organic micro pollutants such as pharmaceuticals, persistent organic pollutants (PPCPs), pesticides, inorganics, etc. The direct disposal of ROC into water bodies can pose a severe eco-toxicological risk, threaten aquatic organisms and cause serious environmental problems. Consequently, proper management and safe disposal of ROC are mandatory requirements (Sun et al. 2014).

Advanced oxidation processes have been applied to remove organics from ROC; however, the costs associated with these technologies limit their wider application. In this context, GAC adsorption is recommended as a simple, cost effective option for removing organics from water (Graf et al. 2014). Coupling of membrane-(powdered) activated carbon hybrid system was studied by Guo et al. 2004; Kim et al. 2009 and Vigneswaran et al. 2007, and they reported this process to be efficient in terms of organics removal. Guo et al. (2004) confirmed that 90% of total organic carbon (TOC) was removed with 5 g/L dose of Powder Activated Carbon (PAC). Vigneswaran et al. (2007) noted the efficiency in removing TOC was 84% with 5 g/L initial dose and followed by 2.5% of daily replacement at filtration flux of 12 L/m^2.h. Guo et al. (2004) revealed that the PAC dose of 1 g/L was effective in MF-GAC in terms of removing organics.

An area that has not been widely investigated is the use of activated carbon in granular form in membrane-hybrid systems. Kim et al. (2009) studied MF-GAC hybrid systems and reported that employing GAC with membrane filtration reduced the trans-membrane pressure (TMP) development and frequency of chemical cleaning by half. Absorbents with larger particles are better than smaller ones, because they produce better membrane scouring outcomes that means less fouling. This is in agreement with Pradhan et al. (2012) who found that the addition of GAC provides mechanical scouring and helps to reduce air scouring. As such, GAC is preferred instead of PAC because it ensures that TMP development of a membrane-hybrid system remains small over the long-term while at the same time providing better organics removal. In this study, the performance of MF-GAC in treating ROC was assessed in terms of TMP development and removal of organics. A detailed analysis of organics and pharmaceuticals and personal care products (PPCPs) was also done.

8.2. Materials and Methods

8.2.1. Materials

a. Reverse Osmosis Concentrate (ROC):

The ROC samples collected from a full scale MF/RO water reclamation plant located in Sydney, Australia were used as feed water. The plant treats a combination of storm water and biologically treated sewage effluent. This plant produces around 300 kL of ROC/day and is discharged directly into a sewer system (Chapman 2006). The detailed characteristics of ROC used in this study are summarised in Table 8.1.

Table 8.1: Physico-chemical characteristics of 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
	Sulfate	220 – 250
Cations(mg/l)	Na	330 –360
	K	55 – 63
	Ca	80 – 93
	Mg	65 – 72

b. Membrane:

Two types of hollow fibre membrane made of hydrophilic modified polyacrylonitrile (PAN) (MANN+HUMMEL ULTRA-FLO PTE LTD, Singapore) were selected for use in the short and long term MF-GAC hybrid system. Short term experiment was conducted with a membrane having an effective membrane surface area of 0.2 m^2 and long term experiment was carried out with membrane having surface area of 0.044 $m^{2.}$ The membrane nominal pore size was 0.1 μm. The inner and outer diameters of the hollow fibres were 1.1 and 2.1 mm, respectively.

c. Adsorbents:

Coal-based premium grade GAC (MDW4050CB) was supplied by James Cumming & Sons Pty Ltd. and used as an adsorbent. The detailed characteristics of GAC are given in Chapter 3.

8.2.2. Methods

a. Batch adsorption studies

A batch adsorption equilibrium experiment was conducted to determine the optimum dose of GAC to treat ROC at equilibrium conditions. Different doses of GAC (0 – 1.6 g/L) were placed in contact with 200 mL of ROC in different beakers and equilibrated for 24 h at 25^0C with continuous shaking by a shaker (Ratel Platform Mixer) at 110 rpm. Upon completion of the experiments, samples were filtered through a 0.45 μm filter for DOC analysis.

An adsorption kinetics experiment was conducted to estimate the adsorption rate of organics from ROC. A fixed dose of GAC (2 g/L) was added to the known quantity (200 mL) of ROC and it underwent continuous shaking at 110 rpm. Samples were then collected at different times (5 – 420 mins) and they were filtered through a 0.45 μm filter prior to DOC analysis.

b. MF-GAC hybrid system

The schematic diagram of MF-GAC hybrid system is depicted in Figure 8.1. A hollow fibre membrane module was immersed in a 3 L influent tank containing the ROC to be treated. The membrane reactor tank was continuously fed with ROC at a constant rate. Both inflow and outflow were maintained at constant rates by peristaltic pump. Air flow was provided at a rate of 1.5 m^3/m^2 membrane area.h to produce scouring on the membrane surface as well as to keep the GAC particles in suspension in the reactor.

Short and long term experiments were conducted with MF-GAC hybrid system. Short term experiment was carried out with GAC doses of 5 g/L and 20 g/L volume of the reactor at filtration flux of 36 L/m^2.h. The residence time of water in the membrane reactor was calculated to be 25 min for short term experiment.

Based on the performance of short term experiment, a long term experiment was conducted with different operational conditions. Long term experiment was conducted with an initial GAC dose of 10 g/L. Following this, 10% of GAC in the reactor was replaced with new GAC on a daily basis to maintain good removals of DOC. The residence time was calculated to be 6.7 h (~ 410 mins). The functionality and operation of the system was same as short term experiment.

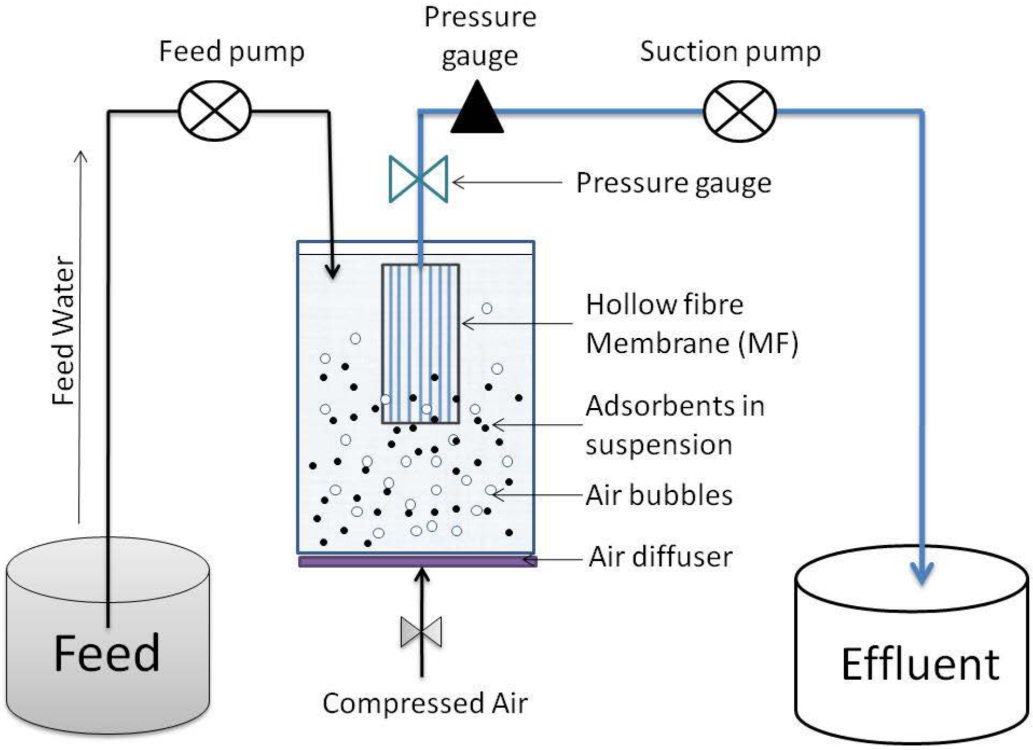


Figure 8.1: Schematic diagram of the submerged membrane – PuroliteA502PS/GAC hybrid system

Sampling of long term experiment is as follows: one litre effluent samples were collected daily for the measurement of effluent DOC. Samples collected on day 1 and day 7 were also used for the measurement of EOCs concentrations. One sample was collected from the bulk feed water and the influent concentrations of EOCs were measured. It was believed that the EOCs concentrations in the influent to be constant throughout the experiment as the feed water was biologically treated and micro filtered. The bacteriological activity in the feed water was considered insignificant. Thus, the single influent data was used to calculate removal efficiencies for day 1 and 7.

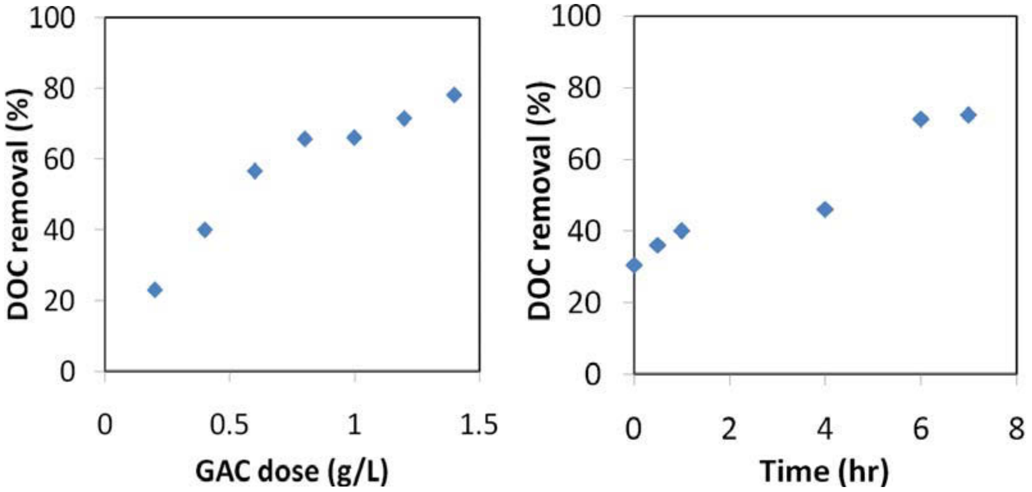
c. Analytical methods

The DOC was measured after filtering through a 0.45 µm filter using a Multi N/C 2000 analyser (Analytik Jena AG). Fluorescence Excitation – Emission matrices (FEEMs) were obtained using a Varian Eclipse Fluorescence Spectrophotometer. The 3D-EEM technique is a rapid, selective and sensitive one that generates information regarding the fluorescence characteristics of organic compounds by simultaneously changing the excitation and emission wavelength. The fluorescence in different spectral regions is associated with various types of functional groups. The fluorescence signals are basically attributed to protein-like fluorophores, fulvic-like fluorophores and humic-like fluorophores, and characterised dissolved organic matter in water using fluorescence spectroscopy (Jeong et al. 2013). F-EEMs were recorded using scanning emission wavelengths from 250 to 500 nm repeatedly at excitation wavelengths scanned from 220 to 400 nm by 5 nm increments. The excitation and emission bandwidths were both set at 5 nm. The fluorometer was set at a speed of 3000 nm/min, a PMT voltage of 700 V and a response time of 2 s. Liquid Chromatography-Organic Carbon Detection (LC-OCD) Model 8 developed by Huber et al. (2011) was equipped with a TSK HW 50-(S) column that measured the hydrophilic and hydrophobic fractions of organic materials and provided qualitative information on organics' molecular size distribution. Organic micro pollutants were extracted using solid phase extraction (SPE) and analysed by Liquid Chromatograph with tandem mass spectroscopy. The details of the analyses are discussed in chapter 3.

8.3. RESULTS AND DISCUSSION

8.3.1. Batch adsorption equilibrium and Kinetics

The results of ROC adsorption equilibrium studies conducted with GAC at different doses and contact times are given in Figure 8.2. As per batch equilibrium, the dose 1.5 g/L achieved up to 80% of DOC removal (Figure 8.2a). The kinetics results presented in Figure 8.2b show as much as 80% was removed using a 2 g/L dose. Batch kinetic experiments with a GAC dose of 2 g/L indicated that DOC removal increased with time up to 6-8 hours.



(a) (b)

Figure 8.2: Batch adsorption results (a) batch equilibrium study (b) batch kinetic (GAC dose = 2 g/L)

8.3.2. Characterization of ROC in terms of DOC and organic micro pollutants

The ROC used in this study contained high concentration of DOC ranged in-between 25-30 mg/L and most of the organic micro pollutants were detected in concentrations of more than 5-10 ng/L (Table 8.2). However, most of the detected micro pollutants in ROC were below the (predicted) critical environmental concentrations (CEC) which is based on literature data on human potencies together with a predicted bio concentration factor in fish for each drug based on lipophilicity (Fick et al. 2010). The concentration of the verapamil (a PPCP) which is a cardiovascular agent was up to 126 ng/L which is well above its CEC (24 ng/L). The concentration of amtriptyline which is a neurotransmitter was upto 69 ng/L and this concentration also exceeded its CEC (48 ng/L). Similarly, simvastatin which is a lipid regulator had a concentration <5 ng/L, however its CEC was reported to be 6.1 ng/L.

Thus, the concentration of a few PPCPs in ROC exceeded its CEC, whilst most of the remaining PPCPs were detected less than their respective CECs in ROC. However, these PPCPs might still cause toxic effects depending on the specific discharge situation if not sufficiently diluted as these concentrations are close to their respective CECs.

The rest of the PPCPs such as carbamazepine (max up to 2240 ng/L), caffeine (max up to 2600 ng/L), trimethoprim (max up to 1100 ng/L), atenolol (max up to 670 ng/L), naproxen (max up to 676 ng/L) were detected at high concentrations, yet these values are still below their respective CECs. However, some studies reported toxic effects even below their CECs. In this regard, Rademaker and de Lange (2009) revealed the lowest measured effect concentration of chronic exposure to carbamazepine was 1000 ng/L at which level kidney damage in carp was detected, and female water fleas reached maturity earlier and produced more offspring as a result of a stress reaction.

The PPCPs such as ketoprofen (377 ng/L), gemfibrozil (574 ng/L), dicofenac (592 ng/L), triclosan (211 ng/L), and triclocarbon (162 ng/L) had their maximum concentrations below their respective CECs. The CECs values reported by Fick et al (2010) that were used to assess the toxicity potentials of the PPCPs in ROC were derived from single compound - single organism toxicity studies. However, the combined and continuous exposure of micro pollutants i.e., PPCPs can cause chronic toxic effects on aquatic test organisms at concentrations below the CEC of individual micro pollutants (Cleuvers 2003; Flaherty and Dodson 2005; Rademaker and de Lange 2009). For example, Cleuvers (2004) reported that the EC_{50} of diclofenac on algal and Daphnia test organisms were 71.9 mg/L and 68.0 mg/L, respectively and these EC50 values were reduced to 18.0 and 17.0 mg/L when these species were exposed to combined micro pollutants i.e., PPCPs (diclofenac, ibuprofen, naproxen, acetylsalicylic acid). Therefore, even though most of the micro pollutants detected in ROC are below their CECs in the current study, the combination of such compounds are likely to cause toxic effects on aquatic organism when they are exposed to this water, especially for a prolonged period of time.

Table 8.2: Concentrations of organic micro pollutants detected in ROC (<5 ng/L and <10 ng/L are detection limits of the micro pollutants) and relevant properties of the micro pollutants

Organic micro pollutants	Class	MW[a]	Conc (ng/L)	Log Kow[a] (pH 7)	Log D (pH 7)	Charge	pKa
Amtriptyline	Anti depressant	277	45-69	4.92	3.01	Positive	9.4[a]
Atenolol	Beta-blocker	266	466-670	0.16	-1.94	Positive	9.6[e]
Caffeine	Stimulant	194	1410-2600	-0.07	-2.97	Neutral	10.4[d]
Carbamazepine	Anti analgesics	236	2200-2240	2.45	-3.05	Neutral	<1 <2[b]
Clozapine	Antipsychotic	327	<5 - 14	3.23	2.93	Neutral	7.5[a]
DEET	Insect repellent	191	<5 - 68	2.18	-3.32	Neutral	<2[c]
Diclofenac	Analgesics	294	337-592	4.51	1.21	Negative	4.1 – 4.2[b]
Fluoxetine	Anti depressant	309	47-62	4.05	1.45	Positive	10.1[b]
Gemfibrozil	Lipid regulator	250	344-574	4.77	1.97	Negative	4.7[c]
Ketoprofen	Analgesics	254	350-377	3.12	0.07	Negative	4.45[a]
Naproxen	Analgesics	230	443-676	3.18	-1.68	Negative	4.2[b]; 4.15[a]
Paracetamol	Analgesics	151	100-114	0.46	-1.45	Neutral	9.38[a]
Primidone	Therapeutic	218	26-187	0.91	0.55	Neutral	N.A
Simazine	Herbicide	202	64-80	2.18	-3.7	Neutral	1.62[a]
Sulfamethoxazole	Therapeutic	253	144-512	0.89	-4.51	Negative	2.1[c]; <2[c]
Triclocarban	Agricultural	316	44-162	4.9	-0.3	Neutral	12.7[f]
Triclosan	Anti infective	290	63-211	4.21	5.19	Neutral	7.9 [b]
Trimethoprim	Antiinfective	290	974-1100	0.38	0.94	Positive/Neutral	6.6 – 7.2[b]; 7.12[a]
Verapamil	Therapeutic	455	83-126	2.37	2.97	Positive	8.92[a]

[a]U.S. National library of medicine (http://chem.sis.nlm.nih.gov/chemidplus/rn/52-53-9); [b]Serrano et al. (2011); [c]Westerhoff et al. (2005); [d]Yang et al. (2011); [e]Hapeshi et al. (2010); [f]Loftsson et al. (2005); MW: molecular weight

The Log D values were calculated based on the equations given in Ridder et al. (2009). The equations are discussed in chapter 6.

8.3.3. MF-GAC hybrid system

8.3.3.1. Short term experiment

a. Selection of GAC dosage

Two different doses of GAC (5 g/L and 20 g/L) of membrane reactor volume were selected for the MF-GAC hybrid system so that the MF-GAC hybrid system's ability to treat ROC could be evaluated. These doses of GAC were chosen based on previous studies and batch adsorption equilibrium and kinetics results. Vigneswaran et al. (2007) commented that increasing the PAC dose from 2 g/L to 10 g/L in a MF-GAC in turn increased DOC removal from 83.4 % to 87.5% in synthetic wastewater (DOC concentrations were between 3.8 and 4.2 mg/L). Furthermore this reduced TMP development from 19.5 to 12.8 kPa. Dialynas et al. (2008) concluded that a GAC dose of 5 g/L removed the most dissolved organic matter (91.3%) from ROC of membrane bioreactor effluent.

Batch studies indicated approximately 1.5 g/L of GAC was required to reach 80% removal efficiency over a 24 h period. In this study the MF-GAC hybrid system was operated only for a short time, i.e. 6 hours where 7-8 litres of ROC were treated. This volume of water required a total of 10.5 – 12 g of GAC based on a batch adsorption study where the most suitable dose was 1.5 g/L. This explained why 5 – 20 g/L of GAC was used in the membrane adsorption hybrid system.

In order to choose proper dose of GAC for long term MF-GAC hybrid system, a preliminary experiment was made with 2 g/L initial dose of GAC. The operation continued only for 24 h and thereafter membrane fouling restricted its operation.

Considering minimum carbon usage and effluent DOC level, the dose of 10 g/L (of membrane reactor volume) was selected for this long term experiment. The daily replacement of GAC is equivalent to a GAC dose of 28 g/m^3 (0.28 g of GAC/L treated water per day). This is comparable to the value of Wang et al. (2013) who calculated the PAC dose to be 0.42 – 0.48 g/L to achieve 70% of DOC removal (approx 12-13 mg/L DOC in the effluent) from ROC by single stage PAC-UF treatment system. The daily GAC replacement dose (0.28 g/L) used in this study was quite low compared to the results obtained by Wang et al. (2013) and this achieved DOC removals 50 – 80% DOC (i.e., effluent DOC level was 5 – 10 mg/L). The higher initial dose of GAC was intentionally used to improve the contaminant removals (both dissolved organics and pharmaceuticals) as well as to reduce TMP development. The flux was maintained at 10 L/m^2.h which correspond to a retention time of 410 min. This particular flux and retention time was chosen based on batch kinetics where maximum removal was observed in between 400-450 min. The parameters used to study the performance of MF-GAC hybrid systems is given in Table 8.3.

Table 8.3: System parameters of membrane hybrid system

		Unit	Values
			DOC GAC
Reactor	Inlet concentration	mg/L	22.9 mg/L - 0 g/L 22.9 mg/L – 5 g/L 21.6 mg/L – 20 g/L
	Volume	m^3	3.0E-3
	Flow rate (Q)	m^3/s	1.0E-6
Membrane	Packing density	m^2/m^3	510
	Flux (J)	m/s	1.0E-5
Adsorbent	Radius	m	4.50E-4

b. Transmembrane pressure (TMP) development

The TMP development of MF-GAC hybrid system is presented in Figure 8.3. The results show that the TMP of submerged MF membrane systems (without adsorbent addition) increased noticeably from 10.2 to 27.4 kPa over 6 hr. The addition of 5 g/L of GAC at the beginning of the experiment helped to reduce TMP development by 10 kPa. It should be noted that GAC was added only at the start of the experiment and no further addition was made. The small development of TMP observed with 5 g/L of GAC in MF-GAC could be due to the pre-adsorption of organics onto GAC prior to their contact with the membrane surface. Also, extra mechanical scouring was provided by GAC to the membrane surface due to the circulation of GAC in the reactor. The additional scouring provided by GAC particles on the membrane surface could help prevent a build-up of the cake layer on the membrane surface. This phenomenon agrees with previous studies. Vigneswaran et al. (2007) observed that a increase in PAC dose from 2 g/L to 10 g/L reduced TMP development from 19.5 kPa to 12.8 kPa at a filtration flux 48 L/m^2.h. Pradhan et al. (2012) observed an 85% reduction in TMP development when GAC was added to the membrane hybrid system.

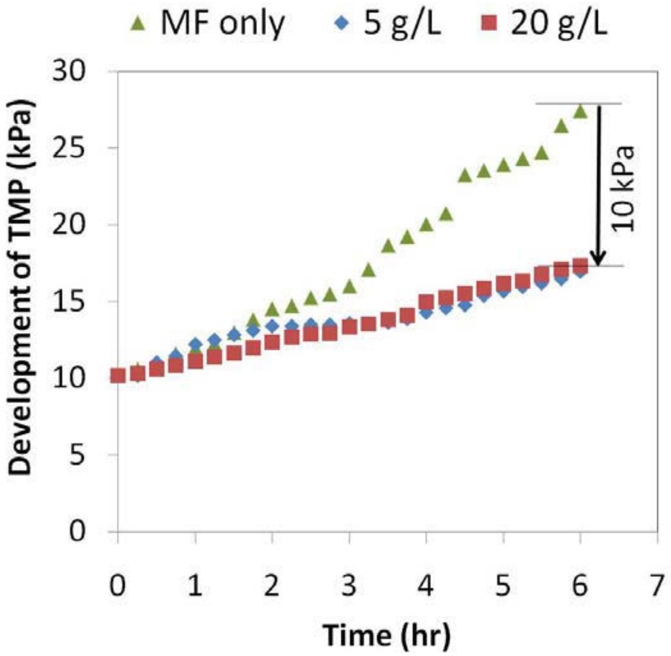


Figure 8.3: The effect of GAC on the development of TMP in MF-GAC hybrid system [DOC of ROC = 21.6-22.9 mg/L; filtration flux 36 L/m^2.h; reactor volume 3 L).

No significant difference was observed in the reduction of the TMP when the GAC dose was increased from 5 to 20 g/L. This is because the pre-adsorption achieved by 5 g/L GAC dose may have been enough to reduce organic deposition/fouling on the membrane surface. This observation on TMP at different GAC doses was made based on the short-term membrane adsorption experimental results. A long-term membrane experiment confirmed that TMP reduction is better at high doses of GAC (Johir et al. 2011a).

It emerged that GAC particles did not have any adverse effect on the membrane surface because: firstly, the clean water flux was the same as that of a virgin membrane; and secondly, the filtered turbidity was reasonably low (less than 0.2 NTU). This finding can also be validated from those in other studies (Johir et al. 2013; Siembida et al. 2010). For example Siembida et al. (2010) used granular polypropylene particle**s** (with a diameter of 2.5 – 3.0 mm) in a submerged membrane bioreactor for more than 600 days. They confirmed via scanning electron microscopy (SEM) images that no damage was done to the membrane's functionality. A long-term submerged membrane adsorption bioreactor experiment conducted with seawater for more than 120 days also revealed no damage had occurred to the membrane surface (Jeong et al. 2014).

c. Detailed organics removal

MF filtration alone did not remove much DOC as shown in Figure 8.4. It was observed to be less than 10%. This is due to the fact that the hollow fibre MF membrane has a larger pore size of 0.1 μm. An observed marginal removal of 10% could be due to the adsorption of organics onto the membrane surface. With the addition of GAC dose of 5 g/L, the removal of DOC rose 20-60%. The DOC removal significantly increased to 65-90% when a dose of 20 g/L of GAC was added.

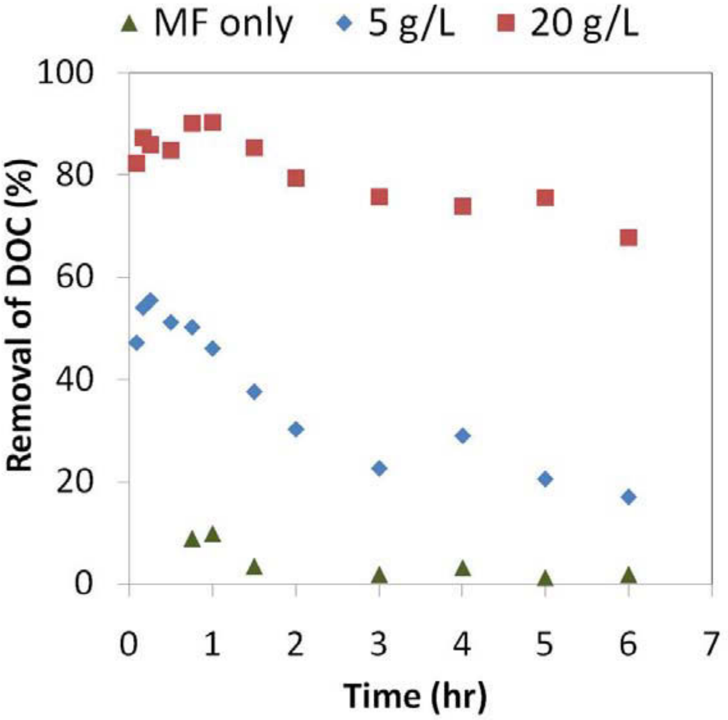


Figure 8.4: Removal of organics by MF-GAC hybrid system (DOC of ROC 32 mg/L; filtration flux 36 L/m^2.h; GAC dose 5 – 20 g/L).

The detailed organics removal can be explained by LC-OCD. The organic fractions before and after treatment with different doses of GAC are presented in Table 8.4. Based on the LC-OCD results, the ROC contains 5.2 mg/L of hydrophobic-DOC and 27.6 mg/L of hydrophilic-DOC which comprised 15.9% and 84.1% of total DOC. The latter is composed of 44.3% of humics, 21.2% of building blocks, 15.8% of LMW neutrals and 3.0% of biopolymers. LMW acids were non-detectable. As this water was microfiltered before RO, and most of the high molecular weight compounds would have been removed, Biopolymers were detected at 1 mg/L. The majority of organics of ROC were hydrophilic compounds (84.1%) and were humics and building blocks with MW in the range of 350-500 $gmol^{-1}$.

Table 8.4 makes it clear that MF-GAC effectively removed most of the organic fractions present in ROC, however, the degree of removal was highly dependent on GAC dosages. The removal of organics nearly doubled when the GAC dose increased from 5 g/L to 20 g/L. The superior removal of organic fractions was due to more micro-pore spaces on GAC being available for adsorption. Among the Hydrophilic-DOC, the adsorption of building blocks was high, followed by humics and LMWs. According to Velten et al. (2011), the ability of organic fractions to be adsorbed decreases with larger molecule sizes as follows: biopolymers < humics < building blocks < LMW organics. Further, they noticed that effective adsorption is highly dependent on the dominance of particular fraction of organics. The reason for the high removal of building blocks (69.1%) in this present study could be explained as follows. Since the feed water is biologically treated, LMWs which are biodegradable would have been removed. The feed water contains humics and its derivatives (building blocks) in high concentrations compared to other fractions. As such, the removals of building blocks and humics are observed to be large following GAC treatment. Johir et al. (2013) also observed the removal of more humics when GAC was added to the membrane bioreactor.

Table 8.4: Removal of organic fractions by MF-GAC at different doses of GAC – 5 g/L and 20 g/L. The effluent level organics are in mg/L and Removal efficiencies (%) are given within parenthesis.

	DOC	Hydrophobics	Hydrophilics				
				Bio polymer	Humics	Building blocks	LMW neutrals
Influent (ROC) (mg/L)	32.8	5.2	27.6	1.0	14.5	6.9	5.2
Effluent GAC5 g/L	18 (45.1)	3 (41.9)	15 (45.7)	0.3 (69.2)	9.1 (37.0)	2.1 (69.1)	3.4 (34.6)
Effluent GAC 20 g/L	4.5 (86.4)	0.8 (84.1)	3.6 (86.9)	0.1 (91.3)	1.9 (87.2)	0.7 (89.6)	0.9 (81.7)

Both hydrophobic-DOC and hydrophilic-DOC compounds are the major foulants causing membrane fouling and are responsible for an increase in TMP. The GAC dose of 5 g/L reduced the hydrophobic-DOC and hydrophilic-DOC to 3 mg/L and 15 mg/L, respectively. This corresponds to approximately 42% and 46% reduction which may be good enough to restrict TMP development in the short-term (Figure 8.3). In long-term experiments, one will need a larger dose of GAC to control the TMP development. It is a well-established adsorption process for the removal of dissolved organic matter (DOM) from water, due to its strong affinity for removing hydrophobic organic compounds even at a low concentration of GAC 5 g/L. Therefore, GAC adsorption can be considered as for a method for reducing membrane fouling.

d. Fluorescence Excitation - Emission matrix (FEEM)

Three characteristic peaks were observed in EEMs including: humic-like substances (ex/em=250–285/380–480 nm); fulvic-like substances (ex/em= 300–370/400–500 nm); and protein-like substances (ex/em = 270-280/300–350 nm). This analysis is semi-quantitative since the average value of fluorescence intensities in the range of ex/em of each peak is employed in comparison to the relative abundance of organics. The FEEM obtained for the untreated ROC and effluent samples with 5 g/L GAC dose and 20 g/L GAC dose are presented in Figure 8.5.

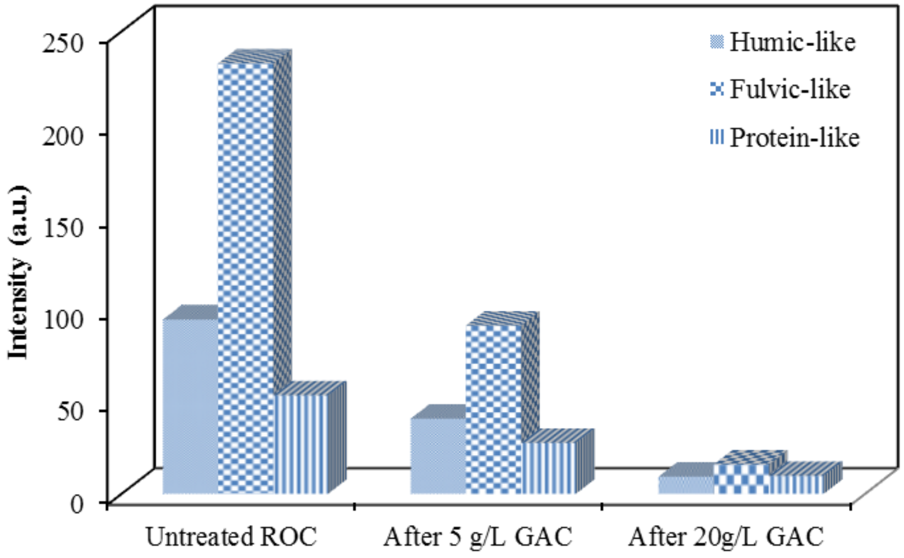


Figure 8.5: FEEM intensity of untreated ROC and after GAC treatment of 5g/L and 20 g/L

Humic substances and building blocks, which are organic compounds that can be detected by LC-OCD with UV detector, are dominant DOC compounds in ROC. Relative to this, biopolymers were low in ROC. Similarly, the significant reduction of humic-like and fulvic-like substances was observed through the FEEM analysis. Fluorescence intensity of protein-like substances was weak in ROC.

Fluorescence intensity of protein-like substances (53.1 a.u.) was less than humic-like (94.3 a.u.) and fulvic-like (232.7 a.u.) substances in ROC. GAC reduced protein-like organics to 27.5 a.u. and 9.7 a.u. with 5 g/L and 20 g/L, respectively. This also revealed that GAC reduced the problem of biofouling during the membrane process. The presence of this peak represents the biofouling potential since the protein-like substances detected in FEEM contain an indole functional group. It is an essential amino acid as demonstrated by its effect on the growth of micro-organisms (Jeong et al. 2012).

As observed in LC-OCD analysis, FEEM results also revealed that humic-like and fulvic-like substances were dominant organic compounds in ROC. This indicated that the hydrophobic fractions (humic and fulvic) in biologically treated effluent were rich and natural waters were mainly composed of hydrophobic fractions. Notably, fulvic-like peaks were much stronger than humic-like peaks indicating that fulvic-like substances presented a larger portion of humic-like substances of ROC. . Fulvic-like substances consist of high molecular weight aromatic humic substances (Sierra et al. 2005). ROC contained the highest amount of aromatic fulvic-like materials, which can damage membranes because they are severe organic foulants. However, GAC was effective in reducing fulvic-like substances from 232.7 a.u. to 90.9 a.u. and 15.8 a.u. with 5 g/L and 20 g/L, respectively.

e. The removal of organic micro pollutants

Many researchers have discussed the occurrence of organic micro pollutants especially PPCPs in the effluents of wastewater treatment plants (WWTPs) (Lin et al. 2014). The elimination of these PPCPs through the use of conventional treatment processes is not effective (Westerhoff et al. 2005). GAC has been found to be effective in the removal of PPCPs (Snyder et al. 2007). The results of this study relating to the removal of organic micro pollutants by GAC are presented in Table 8.5. In this study, the removal efficiency of PPCPs by GAC dose of 20 g/L was found to be more significant (81 – 100%) than that with a GAC dose of 5 g/L (65 – 100%). The removals of PPCPs by GAC can be explained based on hydrophobicity and charge of the molecules of organic micro pollutants and these can be expressed via Log Kow (octonol-water partition coefficient) and pKa (acid dissociation constant) values. The organic micro pollutants having higher Log Kow values are known to have a more hydrophobic nature and these are significantly adsorbed by GAC. In addition, the micro pollutants having higher pKa values (>7) are highly adsorbed by GAC since they are positively charged. As the degree of the removal of micro pollutants i.e., PPCPs is influenced by the combination of solute Log Kow and pKa values, the Log Kow values were corrected and the corrected value is expressed as Log D values. Here D is the distribution coefficient of the PPCPs in n-octonol to water at equilibrium. The Log D values were calculated based on the equations given by de Ridder et al (de Ridder et al. 2009). The equations are discussed in chapter 6.

Organic micro pollutants having higher Log D values are more thoroughly adsorbed by GAC than micro pollutants having lower Log D values. However, no defined relationship was observed between the removals of micro pollutants vs Log D values in this study. This could be due to the high dose of GAC containing abundant available binding sites which may have adsorbed all the micro pollutants due to van der Waals forces.

Table 8.5: Influent, effluent levels of PPCPs and subsequent removal efficiency by MF-GAC hybrid system [The doses of GAC were 5 g/L and 20 g/L; Flux = 36 L/m^2.h].

	Log D (pH 7)	Log Kow[a] (pH 7)	pKa	ROC*	GAC* 5 g	GAC* 20 g	Removal (%) GAC 5 g	Removal (%) GAC 20 g
Amtriptyline	3.0	4.9	9.4[a]	44.5	<5	<5	>89	>89
Atenolol	-1.9	0.2	9.6[b]	466	114	34	76	93
Caffeine	-3.0	-0.1	10.4[c]	1410	97	36	93	97
Carbamazepine	-3.1	2.5	2[d]	2240	386	39.7	83	98
DEET	-3.3	2.2	2[d]	67.8	12.8	6.14	81	91
Diclofenac	1.2	4.5	4.2[e]	337	117	12.4	65	96
Fluoxetine	1.5	4.1	10.1[e]	46.7	6.25	<5	87	>89
Gemfibrozil	2.0	4.8	4.7[d]	344	79.5	8.52	77	98
Ketoprofen	0.1	3.1	4.45[a]	377	34.6	<5	91	>99
Naproxen	-1.7	3.2	4.2[a]	443	46.3	4.99	90	99
Primidone	N/A	0.9	N/A	26	4.75	<5	82	>81
Simazine	-3.7	2.2	1.62[a]	80.1	13.6	<5	83	>94
Sulfamethoxazole	-4.5	0.9	2.1[d]	144	10.7	6.76	93	95
Triclocarbon	-0.3	4.9	12.7[f]	162	18.9	15	88	91
Triclosan	4.2	4.8	7.9[e]	211	47.2	19.3	78	91
Trimethoprim	0.4	0.9	7.12[e]	974	149	13.3	85	99
Verapamil	2.4	3.8	8.92[a]	82.9	5.68	<5	93	>94

* The micro pollutants concentrations are in ng/L; [a]U.S. National library of medicine (http://chem.sis.nlm.nih.gov/chemidplus/rn/52-53-9); [b]Hapeshi et al(Hapeshi et al. 2010); [c]Yang et al (Yang et al. 2011); [d] Westerhoff et al (Westerhoff et al. 2005); [e] Serrano et al (Serrano et al. 2011); [f] Loftsson (Loftsson et al. 2005)

8.3.3.2. Long term MF-GAC hybrid system

a. DOC and TMP development

The ten days long MF-GAC treatment was observed to be effective in removing DOC from ROC. The initial dose of 10 g/L GAC was applied into the reactor to reduce the direct organic load onto the membrane by adsorption of the DOC onto GAC so that the TMP development can be reduced. Thus, the removal of DOC was maintained at 50-80% whilst the TMP was observed to increase from 10 kPa to 60 kPa over the 10 days (Figure 8.6). The experiment was discontinued afterwards due to the high organic fouling. The amount of ROC treated per day by 10% of GAC was 10.5 L. This corresponds to a GAC dose of 0.285 g per litre of ROC treated. Because of the build-up of TMP, the removal of organic micro pollutants was studied only up to 10 d. Thus, the system is capable of maintaining more than 50% DOC removal from 105 L of RO concentrate using a total of 40 g of GAC for 10 days.

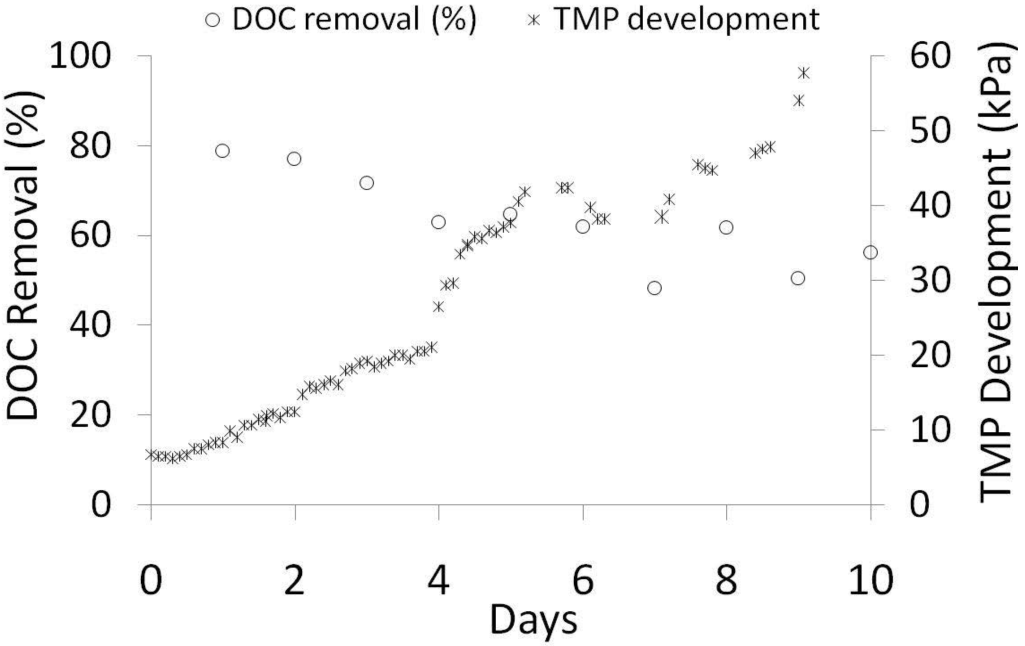


Figure 8.6: DOC removal efficiency and TMP development of the long-term submerged MF-GAC hybrid system used in treating ROC [Flux = 10 L/m^2/h; Initial GAC dose = 10 g/L; 10% GAC daily replacement].

b. Removal of Pharmaceuticals and personal care products

The 10 days long MF-GAC removed overall 60% to more than 99% of organic micro pollutants from ROC in which the removals were noticed to be higher at day 7 than day 1 (Table 8.6). Conversely a decreasing trend of DOC removal was observed in which the removals at day 1 (78%) was higher than that at day 7 (50-60%). The marked increase in micro pollutants removal with time despite a small decrease in DOC removal shows that the adsorption of micro pollutants was not significantly affected by the presence of DOC in ROC. The reason for this phenomenon can be explained as follows: The MWs of micro pollutants are much smaller than the MWs of natural organics as such the access to the fine pores of GAC by micro pollutants is faster than the bulky natural organics. Furthermore, the 10% daily GAC replacement provides new binding sites in which more incoming micro pollutants can be adsorbed quickly onto

GAC than natural organics and this resulted to increased removal of organic micro pollutants. Thus, the 10% GAC daily replacement helped to minimize pore blockage and competitive effect of natural organics for GAC binding sites and maintained the removal of micro pollutants well throughout the experiment.

Table 8.6: The removal of organic micro pollutants by MF-GAC hybrid system from ROC

Organic micro pollutants	Submerged MF-GAC hybrid system				
	Influent (ng/L)	Effluent (ng/L)		Removal (%)	
		Day 1	Day 7	Day 1	Day 7
Amtriptyline	45	<5	<5	>89	>89
Atenolol	466	<5	<5	>99	>99
Caffeine	1410	31	<5	98	>99
Carbamazepine	2240	86	<5	96	>99
Clozapine	68	<5	<5	>93	>93
DEET	68	27	<5	60	>93
Diclofenac	337	<5	<5	>99	>99
Fluoxetine	47	<5	<5	>89	>89
Gemfibrozil	344	9	<5	97	>99
Ketoprofen	377	<5	<5	>99	>99
Naproxen	443	10	<5	98	>99
Paracetamol	114	<5	<5	>96	>96
primidone	26	<5	<5	>81	>81
Simazine	80	<5	<5	>94	>94
Sulfamethoxazole	144	35	<5	76	>97
Triclocarban	162	<10	<10	>94	>94
Triclosan	211	<5	<5	>98	>98
Trimethoprim	974	9	<5	99	>99
Verapamil	83	<5	<5	>94	>94

The micro pollutants removal data obtained for day 1 only was considered to explain the removal mechanisms as the concentrations of all the micro pollutants removed at day 7 were less than the detection limit of 5 – 10 ng/L. As the degree of the removal of micro pollutants is influenced by the combination of solute Log Kow and pKa values, the Log Kow values were corrected and the corrected value is expressed as Log D values as stated by (de Ridder et al. 2009).

The plot of removal (%) of micro pollutants vs the calculated Log D values is illustrated in Figure 8.7 where micro pollutants having higher the Log D values are noticed to be highly removed by GAC (de Ridder et al. 2009). In addition, positively charged were efficiently removed by GAC than negative solutes on pre-loaded carbon for example, negatively charged pollutants such as sulfamethoxazole and DEET showed less removals (upto 66 – 70%) compared to the rest whilst all the positively charged pollutants have achieved removals up to 98 – 100%. This is also can be due to charge interactions in which a GAC particle loaded with organics may carry negative charges which has the tendency to attract positively charged pollutants and may repel negatively charged compounds. This fact can be supported by the 99% removal of positively charged trimethoprim (Log Kow 0.91; pKa 7.1) could be explained based on attractive forces towards GAC rather than based on Log D values. This is in agreement with (de Ridder et al. 2009) who stated positively charged solutes were removed 20-40% more than that of negatively charged compounds due to charge interactions.

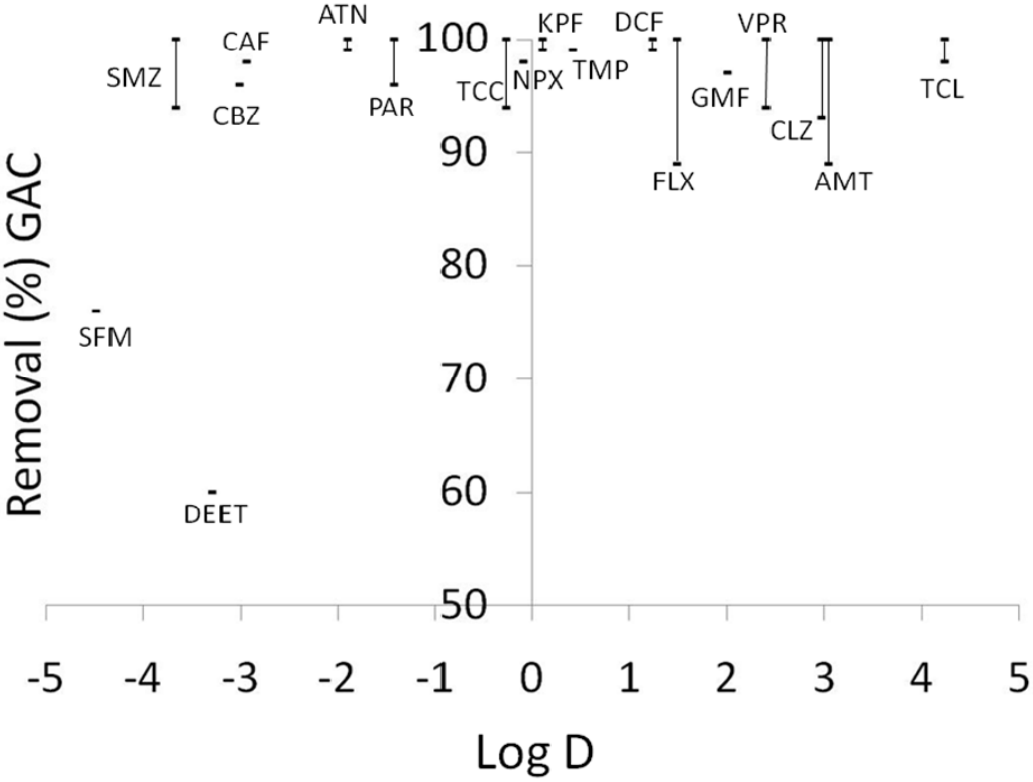


Figure 8.7: Removal of organic micro pollutants by MF/GAC hybrid system from ROC as the function of calculated Log D [CAF – Caffeine; ATN – Atenolol; TMP – Trimethoprim; PAR – Paracetamol; SMZ – Simazine; SFM – Sulfamethoxazole; CBZ – Carbamazepine; KPF – Ketoprofen; NPX – Naproxen; CLZ – Clozapine; VPR – Verapamil; FLX – Fluoxetine; DCF – Diclofenac; GMF – Gemfibrozil; TCL – Triclosan; TCC – Triclorocarbon; AMT – Amtriptyline; DEET - Diethyltoluamide]

c. Long term operation of MF-GAC

MF-GAC hybrid system was found to be more efficient in removing DOC and organic micro pollutants efficiently within over the experimental duration at 10 g/L initial dose of GAC and followed by 10 % daily GAC replacement. With time the removal of micro pollutants was observed to be increasing whilst the removal of DOC was decreased. At day 1, MF-GAC removed 63% of total number of organic micro pollutants below the detection limit of 5 – 10 ng/L in the treated effluent. In the long-run (day 7 sample), excellent removals of micro pollutants using MF-GAC were observed where all the pollutant concentrations in the treated water were less than the detection limit of 5 – 10 ng/L. According to past studies, the presence of organics in the feed water reduces the removal of micro pollutants by competing for GAC binding sites and pore blocking, however, on contrary, the removal of micro pollutants was noticed to be increasing with time in this study. The higher removals of micro pollutants observed at later stage by MF-GAC hybrid system than at beginning of the experiment can be explained based on charge interactions, less competitive effects etc as follows.

As the ROC contained plenty of negatively charged organics (20 – 30 mg/L), the GAC particles suspended in the reactor may get easily preloaded with DOC. The preloaded GAC carries negative charges which can easily attract positively charged micro pollutants (de Ridder et al. 2009). Besides this factor, the introduction of new GAC brings more unoccupied binding sites which may preferentially adsorb more incoming micro pollutants than DOC as micro pollutants are smaller molecules than DOC thus the access to the fine pores of GAC by micro pollutants is faster than the DOC.

This MF/GAC system is also considered as cost effective in micro pollutants removals compared to nanofiltration or reverse osmosis processes. Based on a cost analysis study performed by (Pianta et al. 2000), MF or ultrafiltration (UF) combined with PAC system was found to be cheaper than the integration of NF systems which is not competitive as long as the removal of inorganic ions are not required. The treatment cost (including capital and O&M cost) of UF/PAC was ~ 35 c Euro/m^3) whilst the treatment cost of UF/NF system was ~ 55 c Euro/m^3 for a plant size of 30 m^3/h. as per Pianta et al. (2000) there is no significant cost difference between MF and UF. In our study, the MF/GAC hybrid system was conducted with a filtration flux of 10 L/m^2.h with the applied pressure of 27-85 kPa. As per our preliminary NF studies (NF membrane: NTR 729HF) the estimated applied pressure was 100 kPa to achieve similar flux 10 L/m^2.h with ROC. In addition, the removal of micro pollutants by the NF also was observed to be declining with time due to membrane saturation. Further, the management of NF/RO concentrate is another issue of NF/RO processes that needs further treatments with added costs. These limitations of NF/RO membranes favour the application of MF/GAC hybrid system in terms of the removal of micro pollutants from ROC prior to discharge into environment.

8.4. CONCLUSIONS

The ROC contains significant levels of organics and organic micro pollutants and the concentration of micro pollutants in ROC is high enough to cause aquatic toxic effects upon the direct discharge of ROC to sewer if not sufficiently diluted.

A short term MF-GAC hybrid system experiment of 6 hours of duration showed that the addition of GAC reduced TMP development by 10 kPa which is due to the mechanical scouring effect provided by GAC as well as by the pre-adsorption of organics before reaching the membrane surface. The addition of GAC 5 g/L removed DOC by 20-60% throughout the experiment. Hydrophobic and hydrophilic portions removals were 42% and 46%, respectively. The increase in GAC dose to 20 g/L resulted in up to 85% of DOC. FEEM results revealed that show the removal of humic-like substances and fulvic-like substances were at significant levels. The MF-GAC hybrid system removed the micro pollutants in an effective manner. In fact, 65-100% removal was observed with a GAC dose of 5 g/L (of membrane reactor volume), which increased to 81 – 100% with a GAC dose of 20 g/L. The dose of 5 g/L of membrane reactor volume corresponds to a GAC usage of 2 g/L of treated water based on 6 hours of experimental run. Moreover, the removal of micro pollutants was not affected when natural organics were present, as there were abundant GAC binding sites for incoming micro pollutants and DOC. Organic micro pollutants are smaller molecules and hydrophobic in nature and can find easy access to GAC binding sites.

Long term MF-GAC operated for 10 days was observed to be effective in terms of removals of dissolved organics and organic micro pollutants. The daily GAC replacement of 10% of total GAC i.e., 0.28 g of GAC/L treated water per day maintained DOC and micro pollutants removals more than 50% and more than 60% from ROC over 10 days. Further, competitive effect of organic micro pollutants with dissolved organics for GAC binding sites also was minimized at this higher dose. Thus, MF-GAC is a cost effective system in removing DOC and micro pollutants from ROC compared to NF/RO membrane processes in terms of cost and energy, removal efficiencies, concentrate management etc. This system can be installed at WWTP to treat the ROC either prior to discharge into environment or using feed to RO.

Finally, MF-GAC is an effective system for treating ROC to remove dissolved natural and persisting organics prior to discharge into the environment in a safe manner. Alternatively the effluent can be recirculated and mixed with other feed to a RO process to maximise water reuse.

CHAPTER 9

CONCLUSIONS AND FUTURE RECOMMENDATIONS

9.1. CONCLUSIONS

This chapter summarizes the results of research articulated in Chapters 4 to 8.

9.1.1. Pre-treatment to reduce membrane fouling

Two different types of pre-treatment techniques were studied in order to remove potential foulants from BTSE to minimize their subsequent membrane fouling effects on RO. In this context, pre-treatment experiments were conducted using two different experimental configurations: firstly, fluidized bed contactors; and secondly, membrane hybrid systems.

Fluidized bed contactors: Fluidized bed contactors packed with GAC and Purolite A502PS were effective in removing potential foulants - dissolved organics prior to RO. The efficiency in removing organics depended strongly on operational conditions of fluidized bed contactors in which the bed height was more important than fluidization velocity. Based on short-term experiments lasting 6 h, the GAC packed contactor with a dose of 5 g (bed height 3 cm) was able to remove DOC content of 30 – 60% from feed water, this content comprising hydrophobics (44%), humics (41%), building blocks (26%) and LMWs (31%). When the dose was increased to 15 g (bed height was 10 cm) the amount of DOC removed rose to 80 – 100%, including hydrophobics (77%), humics (85%), building blocks (86%), and LMWs (72%). The Purolite A502PS packed fluidized columns showed less than 10% DOC removal at a dose of 5 g (bed height of 2.5 cm) but this increased to 60-90% when a dose of 30 g (bed height of 15 cm) was employed. These experiments were carried out at a filtration velocity of 5.7 m/h.

GAC packed contactors were more efficient than Purolite A502PS packed contactors when removing organics. The Plug flow model predicted the performance of GAC and Purolite A502PS in removing DOC from BTSE. Long-term experiments showed that the GAC contactor initially removed 100% of DOC but this amount gradually declined to 20% in 325 hours at a dose of 30 g. In similar operational conditions, the Purolite contactor initially removed 755 of DOC 75%, declining to 40%. When the fluidization velocity was increased to 11.4 m/h, the removals rapidly decreased to 40% over 150 h. The observed poor performance of Purolite A502PS may be due to the presence of sulfates (~45 mg/L) and nitrate (~6 mg/L) ions in BTSE which have a higher affinity to Purolite A502PS resin due to their exchange sites. Further, regenerated Purolite A502PS can be reused because it retains a good ion-exchange capacity. In order to prevent scaling and other issues raised by inorganic dissolved ions, the Purolite fluidization bed it is suitable because it is superior to GAC when it removing inorganic anions from feed water. A series of fluidized columns can provide better results in that they effectively remove both organic matter and inorganic anions over a longer period of time.

Membrane-ion exchange hybrid system: As the second configuration, membrane – ion exchange hybrid as a pre-treatment to RO was investigated. The removal of DOC by the membrane – ion exchange hybrid system was evaluated against the particle sizes of Purolite, and doses. The higher particle size of Purolite (425-600 µm) was effective in reducing TMP development compared to particle sizes of 150-300 µm and 300-425 µm. Adding Purolite (0.5-1 g/L) increased the amount of DOC removed by up to 40% and this was constant during the 8 h operational time. Adding Purolite A502PS into a submerged low pressure membrane reactor can help not only to improve the removal of organics but also reduce the direct loading of DOC onto the membrane surface and thus reduce TMP development. As a result the fouling of RO can be reduced. A larger dose of Purolite A502PS encouraged the membrane hybrid system to function better. Its performance was successfully predicted by the homogeneous surface diffusion model together with the simplified membrane model proposed in this study.

9.1.2. Cost effective dual membrane hybrid system instead of RO

The dual membrane hybrid system combining the MF-GAC hybrid andNF systems proved to better a cost effective treatment strategy than RO for removing organics, pharmaceuticals, and most of the divalent inorganic ions. The best operational conditions were chosen in terms of removing organics and costs. The MF-GAC hybrid system was very effective at a low filtration flux of 2.5 L/m^2.h and removed organics by more than 80% and 60% at daily GAC replacement of 10% (R.$_{GAC\ 10\%}$) (0.2 g GAC/Litre$_{volume\ of\ the\ reactor}$/d) and GAC replacement of 5% (R.$_{GAC\ 5\%}$) (0.1 gGAC/Litre$_{volume\ of\ the\ reactor}$/d), respectively. Increasing the filtration flux to 10 L/m^2.h resulted in poorer efficiency when removing DOC (40-60%) despite a higher GAC replacement rate of 30% (R.$_{GAC\ 30\%}$). The MF-GAC experiments were carried out continuously for approximately 14 days. Low filtration flux and high GAC replacement rates were not sustainable. Consequently a filtration flux of 5 L/m^2.h and 10% of GAC replacement is considered to be suitable.

The MF-GAC hybrid system proved to be effective in removing major organic foulants. Hydrophobics and hydrophilics (especially humics) were removed and this reduced the subsequent membrane fouling. No TMP increase and no flux decline were observed with NF when the MF-GAC hybrid system was used as pre-treatment. The removal of organics by NF was excellent (95%) and the removal of organic fractions by NF was influenced by the size and charge of the molecules. The rejection of LMW neutrals was found to be less (84%) compared to humics/building blocks (98%). The MF-GAC followed by the NF hybrid system was effective and completely rejected most of the organic micro pollutants. Carbamazepine which had the highest concentration level in the feed water was also significantly reduced by the combined MF-GAC/NF hybrid system. With respect to the removal of inorganic ions, a significant rejection of calcium, magnesium, and sulfate was observed with NF (60% to 99%).

However, the MF-GAC hybrid system alone cannot remove cations/anions. The MF-GAC hybrid system can remove most of the organic foulants from feedwater and subsequently reduced organic loading to NF. This allowed the NF system to operate for a long time with less flux decline and produced high quality reusable water virtually free of organic micro pollutants. Therefore the dual membrane hybrid system consisting of MF/GAC and NF can serve as a standalone treatment system that produces water of recyclable quality and is free of micro pollutants where the removal of monovalent ions is not necessary.

9.1.3. Combination of NF-RO membrane for high quality water reuse

The untreated BTSE is not always suitable for direct water reuse. For example the raw micro filtered BTSE is not suitable for irrigation because the SAR value (39), Na^+ (81-120 mg/L) and Cl^- concentrations (150-300 mg/L) were higher than the maximum allowable limits for very sensitive crops. Moreover, this recycled water is could become a potential source of toxic organic micro pollutants in agricultural lands and eventually may damage the environment by entering the food chain and groundwater aquifers. For this reason the removal of such micro pollutants was emphasized in this study. This study demonstrated that utilizing treated BTSE for irrigation is a viable option for maximizing water reuse in arid and semi-arid regions.

In this context, treating feed water through NF and RO membranes was examined to obtain product water with suitable quality criteria that made irrigation and the removal of micro pollutants possible. The NF membrane removed some divalent ions (Ca and Mg) and reduced the SAR value to 14. RO membrane removed all the contaminants. The NF process is more cost effective than that RO. Thus, a blend of either "raw water – RO permeate" or "NF permeate - RO permeate after NF pre-treatment" (a two-stage system) at the ratio of 10:90 or 50:50, respectively, made the water suitable for irrigation. However, the second option, i.e. blending NF permeate and RO permeate after NF pre-treatment is a cost effective option as the RO is more expensive than NF and only 50% of NF permeate was treated by RO. Moreover, in order to ensure the RO membrane operates more smoothly with less fouling, the NF process is used as a pre-treatment to achieve partial removal of potential organic foulants. NF removed all the humics, building blocks and most LMW organics. Both RO and NF achieved very high removals of micro pollutants. This study demonstrated that NF permeate can be blended with that of RO after NF pre-treatment in suitable ratios to produce good quality irrigation water. However, the blending proportions of permeates can vary depending on the type of membranes being used, soil type, salt tolerance of crops, salts in the soil solution, and wastewater (feed) characteristics.

9.1.4. Treatment of reverse osmosis concentrates (ROC)

ROC is a by-product of the RO process and contains elevated levels of natural organics, organic micro pollutants and inorganic contaminants 5-7 times higher than feed water. The management and disposal of ROC is one of the major constraints of RO technology. Short- and long-term MF-GAC hybrid system experiments were conducted to treat ROC prior to its discharge in order to safeguard the environment.

The addition of GAC to the short-term MF-GAC hybrid system reduced TMP development by 10 kPa. This is due to the mechanical scouring effect provided by GAC as well as by the pre-adsorption of organics before reaching the membrane surface. Adding GAC (5 g/L) removed DOC by 20-60% throughout the experiment's 6 h duration whereas hydrophobic and hydrophilic portions removals were 42% and 46%, respectively. Elevating the GAC dose to 20 g/L resulted in up to 85% of DOC being removed. FEEM results showed the removal of humic-like substances and fulvic-like substances to be at significant levels. Removing organic micro pollutants by the MF-GAC hybrid system proved to be very effective. In fact, 65-100% removal was observed with a GAC dose of 5 g/L of membrane reactor volume, which increased to 81 – 100% when the dose was increased to 20 g/L. The dose of 5 g/L of membrane reactor volume corresponds to a GAC usage of 2 g/L of treated water. Moreover, the removal of PPCPs was not affected when natural organics were present, as there were abundant GAC binding sites for incoming organic micro pollutants and DOC. Organic micro pollutants are smaller molecules and hydrophobic in nature and can find easy access to GAC binding sites. Therefore, MF-GAC is an effective method for treating ROC, particularly in removing dissolved natural and persisting organics prior to their discharge into the environment in a safe manner. The alternative is to recirculate and mix the effluent with the feed as per the RO process to maximize water reuse.

Finally, a long-term MF-GAC hybrid system that operated for 10 days showed consistent results in terms of contaminants' removal. The daily GAC replacement of 10% of total GAC, i.e. 0.28 g of GAC/L. treated water per day was sufficient to maintain consistent levels of DOC and organic micro pollutants being removed. Furthermore, the effect of organic micro pollutants competing with DOC for GAC binding sites was minimized at this dosage of 0.28 g of GAC/L.

9.2. FUTURE RECOMMENDATIONS

This study explains the significance of membrane hybrid systems with hollow fibre and flat sheet membranes as a pre-treatment to RO. Future work with different types of membrane, for example, different pore size, surface charge, and hydrophillicity would be more interesting in terms of organic characterization and micro pollutant removal.

This study is limited to some selected micro pollutants i.e., pharmaceutical compounds commonly available in BTSE. Further, the identification and removal of more micro pollutants such as herbicides, pesticides, and personal care products should be studied in the future. Analysis of more representative samples is important for micro pollutants along with isotherm and kinetics experiment with different adsorbents.

The NF and RO are essential for wastewater fed irrigation to bring water with desirable range of SAR. More long term NF membrane experiments must be done along with membrane cleaning to minimize membrane saturation ion effects in NF membrane. This should be validated with in-depth advanced membrane autopsy studies to ensure uninterrupted long term operation of NF/RO filtration systems.

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