Removal of Organic Micropollutants In Water Using Surface Modified Membrane Systems

By

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STATEMENT OF ORIGINALITY

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ABSTRACT

The health risk of organic micro pollutants in water is yet to be comprehensively established. However, the persistence of these pollutants in the environment as a result of continuous discharge even at trace concentrations is considered to pose major environmental concerns. Advance treatment methods such as membrane-assisted processes (MAPs) are potential technologies capable of removing a wide range of these organic micropollutants (OMPs) detected in water. In this study, investigation of surface-coated ultrafiltration (UF) poly(vinylidene fluoride) (PVDF) hollow fibre membrane for the removal of organic micropollutants (OMPs) in water was performed. Coating of PVDF membranes with poly(1-phenylethene-1,2-diy)/polystyrene and pluronic F68 solutions through physical adsorption was carried out in two modes: “dipping” and “spraying”. Surface characterization of coated membranes showed that the coating layer potentially influenced the surface properties suitable for improved solute-membrane interaction. Characterization of the pore size and distribution through Scanning electron microscopy (SEM) images analysis showed that polystyrene coating in sprayed and dipped coating procedure, exhibited more reduction in pore size (19−31%) and closer pore size distribution than the pluronics F68 dip coating (6%). The average roughness ($R_a$) and maximum peak-to-valley distance ($R_{\text{max}}$) measured using the Atomic Force microscopy (AFM) recorded more roughness and irregularity in surface topography in the polystyrene coated membranes compared to the pluronics F68 coating with the dipped polystyrene coating method attaining more roughness ($R_a$ = 0.393 µm). Contact Angle (CA) measurements showed that the dipped Polystyrene coated membrane achieved the highest increase in hydrophobicity (29%) while the dipped pluronics F68 coating achieved a 10% increase. Correlation between the changes in surface roughness and hydrophobicity was evident in the study. Generally, the polystyrene material impacted the membrane surface the most, and the dipped coating procedure recorded the highest surface modification impacts. The performances of the coated membranes in the rejection of the model organic micropollutants, caffeine (hydrophilic) and carbamazepine (hydrophobic) spiked (as single and mixed components) in various water matrices i.e. deionized water, surface water and synthetic wastewater (at concentration range of 300−1000 µg/L) correlated with the coating materials and methods used. The dip-coated membranes using polystyrene material, achieved better removal of recalcitrant hydrophobic carbamazepine compared to the spray-coated membrane in deionised water, but not in other water matrices. Whereas for both methods of coating, removal of caffeine was relatively insignificant in deionised water but reasonably higher in surface water and synthetic wastewater. From these results, it is inferred that hydrophobic interactions and size exclusion might be the major removal mechanisms involved in rejection by the coated membranes and the colloidal and particulate matter in surface water and fouling in membrane bioreactor system facilitated sorption removal mechanism. The membrane coating enhanced reduction of the pore size, decreasing the membrane permeability and providing more sites for possible solute-membrane interactions. it is demonstrated that physical adsorption of functional polymers is a simple and efficient way to modify the surface properties of polymeric membranes for water filtration application.
ACKNOWLEDGEMENTS

Now unto the King eternal, immortal, invisible, the only wise God, be honour and glory for ever and ever. Amen – KJV Bible

Having somewhere to go is HOME, having someone to love is FAMILY, having both is a BLESSING.

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We make a living by what we GET, but we make a Life by what we GIVE. – Winston Churchill

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I have gone farther than I thought I could because my supervisors thought I could.

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We must find time to stop and thank the people who make a difference in our lives – J F Kennedy

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LIST OF PUBLICATIONS AND CONFERENCE PROCEEDINGS

Publications


Conferences


3. Surface modified UF membrane system for the rejection of caffeine and carbamazepine in water – Abstract accepted for EuroMembrane 2015 conference
CHAPTER 1
INTRODUCTION
CHAPTER 1 Introduction

1.0 INTRODUCTION

1.1 Background

Water is a natural resource that occurs in abundance on our planet, yet drinking water is considered a scarce commodity. A common statistical figure stipulates a minimum of one-fifth of the world's population (about 1.2 billion people) live in areas of physical water scarcity. There is enough freshwater resource available on our planet for six billion people but its distribution is uneven and a significant amount of it is wasted, polluted and unsustainably managed. Environmental pollution caused by anthropogenic activities coupled with increase in population growth, industrialization and urbanization continues to be of great concern as proven evidences show that safe drinking water supply, public health as well as the ecosystem is under tremendous pressure and prospects of sustainable development are threatened (Montgomery and Elimelech 2007; Johnson et al., 2008). Water scarcity on a global scale is one of the pressing issues of concern, with future projections, the problem might be aggravated if sufficient measures are not taken to intervene. Public health is always threatened in circumstances where water supply is deficient both in quantity and quality.

Hazardous chemicals are introduced into the environment from regular agricultural and industrial activities such as; oil and gas exploration and production, manufacturing, pharmaceuticals, food processing, etc., with the potential of causing substantial health problems. These chemicals mostly end up in the water system thereby polluting freshwater resources and contributing to scarcity of drinking water. There is increasing concern that some products that are part of our daily lives are now contributing significantly to pollution of drinking water in most part of the industrialized world. In recent years, some emerging pollutants (Organic micropollutants) are being detected in the environment, which are mostly discharged from the municipality. Organic micropollutants (OMPs) which constitutes a wide range of chemicals used as Pharmaceuticals and Personal care products (PPCPs) and Endocrine disrupting compounds (EDCs) have been detected in drinking water sources and identified as a potential risk to aquatic and human life, thereby becoming a topmost environmental issue of concern (Barnes et al., 2008a; Loos et al., 2010, 2009; Rahman et al., 2009a). Consumption of water containing a mixture of organic micropollutants over a prolonged period of time might pose severe health risk; therefore removal of OMPs in water and wastewater treatment is essentially significant. OMPs are not necessarily being newly introduced into the environment but recent improvements in chemical analytical methods have enhanced the ability to detect their occurrence in the environment even at trace concentrations (Jelić et al., 2012;
Lishman et al., 2006; Wennmalm and Gunnarsson, 2005). Pressing issues associated with OMPs in the environment may include the concern that they are comprised of an extensive and expanding spectrum of compounds; unique challenge in their identification and evaluation from the water (or environmental) matrixes as a result of their form and mechanism of actions; and the fact that there no comprehensive limiting regulations for most of the OMPs, especially PPCPs and EDCs as regards to water and wastewater treatment (Bolog et al., 2009).

The problem to be addressed is how there can be reduction in the input of the OMPs in the environment. (Kümmerer, 2009) suggests that technical approach of improving the conventional treatment systems to advanced treatment applications as a short term to medium term strategy, alongside, the substitution of critical compounds used in production of chemicals with more benign compounds as a long-term strategy, will be an effective tool for managing the risk of OMPs in the environment. The topmost concerns about OMPs in the environment arises from the incompetence of conventional water and wastewater treatment systems in removing most of the pollutants (Kasprzyk-Hordern et al., 2009). OMPs detection in the environment records significant amount detected in discharge from municipal wastewater treatment plant (WWTP) (Behera et al., 2011; Ratola et al., 2012). In order to cope with the problems at hand, conventional treatment processes should be at least ‘upgraded’ with non-conventional or advanced treatment processes such as membrane processes, advanced oxidation processes, Ultraviolent irradiation etc., (Guo et al., 2008; Sahar et al., 2011). Membrane assisted processes (MAP) involving a single and/or integration of membrane processes, namely – microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis(RO) are considered a robust treatment technology in the industry especially in scenarios where water reuse is a reasonable option and effluents are expected to be free of trace organic micropollutants (Deegan et al., 2011). They are showing promising performance levels for the removal of OMPs in wastewater treatment processes compared to alternative processes (AOP, UV etc.,) because of their high adaptability to conventional treatment, wide range of selectivity, less use of chemicals and compact foot print (Deegan et al., 2011; Guo et al., 2008; Nghiem et al., 2006; Sahar et al., 2011). However, some operating parameters still need considerable investigations.

High pressure membrane filtration processes (NF, RO) are reported to be capable of removing a reasonable range of these compounds compared to low pressure membrane filtration processes (MF, UF) because the membrane surface properties of the latter are obviously not suitable in removing most OMPs, which are usually small in molecular weight (and size) and are usually
present at low concentration in water. However, MF and UF have better industrial ‘presence’ at municipal level compared to NF and RO due to the relatively lower capital and operation cost, and suitable for adaptation into conventional treatment processes. Furthermore, some certain OMPs are reported to be removed by tight UF membranes (Acero et al., 2010; Sahar et al., 2011). Improvements in surface properties of UF polymeric membrane through the concept of surface modification can offer a better option for removal of OMPs in water. Simple surface modification techniques using readily available materials can enhance operating and removal performance of low pressure polymeric membranes. Surface modification is applied to membrane for removing micro-pollutants rather than modification of membrane microstructure because, the selectivity of the membrane is mostly influenced by the membrane surface characteristics while the membrane microstructure mostly provides mechanical strength and stability to the membrane during operation. The surface layer which is usually thin, provides the required perm-selectivity while the bulk porous support provides the mechanical strength. In most cases, it is very difficult to get a polymer that possesses high quality of both properties. Hence, modification of polymers to obtain the most desired and improved performance has been of interest in recent years. It is a common practice to focus on surface modification without altering the mechanical properties of high strength polymeric membranes, this is because surface modification provides a better and easier approach compared to process of obtaining new polymer properties by blending different polymers or using other complex methods (Nady et al., 2011).

1.2 Research Motivation and Objectives

UF membrane system has a better industrial 'presence' compared to high pressure membrane systems (NF and RO) at municipality level, and so improvements in its performance in removing emerging contaminants (organic micropollutants) will be a good option in terms of cost and ease of operation and adaptability. The UF membrane system configuration used in this study is relevant and applicable for decentralised and/or potable water purification where water management (treatment) is done by individual households or group of households and low energy is required to drive the system. However, the focus of the study is to examine the suitability of surface modified membrane system in removing some frequently reported organic micropollutants in municipal waste streams.

Therefore, the aim of this research work is to evaluate the potential of surface modified polymeric UF membrane system for the removal of organic micropollutants in water using surface coating method to enhance suitable membrane surface properties.
The following are the corresponding objectives of the research study:

1. Investigate the efficiency of coating method (Physical adsorption) and material (polystyrene and pluronic F68) in achieving suitable surface modification.

2. Establish the effect of surface modification on key properties (such as pore size and distribution, hydrophobicity, surface morphology and roughness) of the membrane that can impact its performance during water filtration.

3. Investigate the potential of surface modification (coating by physical adsorption of functional materials) of polymeric membrane (PVDF) in achieving higher removal of model organic micropollutants.

4. Investigate the rejection and removal mechanism of single and mixed components of model organic micropollutants in different water matrices (i.e. Deionised water, surface water and synthetic wastewater).

1.3 Research approach and contributions

Commercially available PVDF UF membranes were surface coated under laboratory conditions, surface characterised using various material surface characterization equipment and fabricated to suitable modules for filtration experiments on different water matrices dosed with selected model organic micropollutants (MOMP). The following are the major research contributions;

1. Based on literature and recent work done, membrane assisted processes (MAP) is considered a robust treatment technology capable of alleviating the problem at hand. Especially with its option of combination and adaptability into conventional treatment technology. (Chapter 3)

2. Surface coating as a simple surface modification method using suitable coating material is potentially able to affect the surface properties i.e. pore size and distribution, hydrophobicity, surface morphology of Polymeric membranes. (Chapter 5)

3. Surface coating impacted membrane hydraulic properties and filtration operating parameters such as permeability, Flux, transmembrane pressure, but in tolerable proportion compared to tight and high pressure membranes with small pore sizes. (Chapter 6,7)
4. Improvement in performance of PVDF UF membranes in removing neutral hydrophobic and hydrophilic OMP can be achieved using surface coating, mainly as a result of effects of coating material and method, and dependent on water matrix. (*Chapter 6,7*)

5. Removal mechanisms for the removal of selected MOMP is hypothesised to be mainly size exclusion and hydrophobic interaction as well as adsorption to fouling layer in MBR system. (Chapter 6,7 & 8)
CHAPTER 2
ORGANIC MICROPOLLUTANTS IN THE ENVIRONMENT
2.0 ORGANIC MICROPOLLUTANTS IN THE ENVIRONMENT

2.1 Introduction

The health risk of organic micropollutants (OMPs) in water is yet to be comprehensively established. However, the persistence of these pollutants in the environment as a result of continuous discharge even at trace concentrations is considered to pose major environmental concerns. This chapter provides theoretical information and review of the problems of organic micropollutants in water and the environment, showcasing the occurrence, sources and potential health risk involved. Recent studies on the removal of mostly reported OMPs by conventional and membrane assisted processes (MAP) are also discussed with insights into the general performance level of the systems. A more comprehensive and critical review of MAP for the removal of OMPs is presented in Chapter three.

2.2 Organic micropollutants

OMPs are a category of recently detected chemicals or ‘emerging’ contaminants found in freshwater sources, natural water bodies, water treatment effluents and soil sediments at relatively low concentrations (orders of ngL\(^{-1}\) up to several µgL\(^{-1}\)) but are proven to have the potential of severe health risk to humans and aquatic life (Barnes et al., 2008b; Loos et al., 2010, 2009; Rahman et al., 2009b). OMPs represent a wide spectrum of chemicals used in products that are consumed regularly in one form or the other; mostly discharged from the municipality into the environment (especially water systems); and are not efficiently removed by conventional treatment systems (Benotti et al., 2009; Tijani et al., 2013). Though improvement in the sensitivity of monitoring equipment has enhanced their detection in water, there are yet to be stringent limiting regulations specific to most of the OMPs. They constitute chemicals used in Pharmaceuticals and personal care products (PPCPs), Hormones (natural and synthetic), and Endocrine disrupting compounds (EDCs) including pesticides, surfactants, cosmetics, flame retardants, perfumes, waterproofing and spot repelling treatments, insulating foams, etc. They are vast in number and variable in occurrence in water sources as new products are continuously introduced.

PPCPs include a wide range of synthesized chemicals compounds or drugs used internally or externally in the bodies of humans and domestic animals as well as plants. It includes all pharmaceuticals and drugs available over-the-counter and through prescription, designed to cure and prevent the spread of diseases as well as adding value to humans and animals life (Maletz et al., 2013). They include; antibiotics, antiseptics, anti-inflammatory, and
antiepileptic drugs; cosmetics, fragrances, preservatives, toiletries, deodorants, etc. This also include diagnostic agents (e.g., X-ray contrast media), food supplements (bioactive substances such as Huperzine A, etc). Personal care products also include UV protection screens, synthetic musks etc. PPCPs are highly bioactive and most are polar (Daughton, 2001).

EDCs are either naturally occurring or synthetic substances that interfere with the functioning of endocrine systems in animals and humans resulting in unnatural responses. The endocrine system functions primarily to maintain a stable environment within the body as well as control reproduction and growth processes in human and other species.

Table 1.0 shows the range of OMPs detected in water matrixes highlighting the frequently occurring chemicals.

Table 2.1 Some frequently detected organic micropollutants in water matrices (Ojajuni et al., 2015)

<table>
<thead>
<tr>
<th>OMP</th>
<th>Type &amp;/Or Uses</th>
<th>Name of Chemical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pharmaceuticals</td>
<td>Antibiotics</td>
<td>Sulfonamides: Sulfamethoxazole fluoroquinolones: Ofloxacin, ciprofloxacin</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Acetaminophen, Diclofenac, naproxen, Ibuprofen, Ketoprofen, Carbamazepine, paracetamol</td>
</tr>
<tr>
<td></td>
<td>Analgesic/Antiinflammatories</td>
<td>By-products of chemical disinfection</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Trihalomethanes (THMs)’</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Haloacetic acids (HHAs)</td>
</tr>
<tr>
<td>Disinfection and oxidation by-products</td>
<td>Personal care products</td>
<td>Antiseptic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Triclosan</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fragrances</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Musk xylol, Musk Ketone, galaxolide</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Stimulant</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Caffeine</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Antihypersensitive</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Diltiazem, Enalapril, Hydrochlorothiazide</td>
</tr>
<tr>
<td>Pesticides</td>
<td>Herbicides, fumigant</td>
<td>Dioxins, Atrazine, Metam sodium</td>
</tr>
<tr>
<td></td>
<td>Steriodal substances, Hormones, Phenols, phthalates, surfactants</td>
<td>17α-ethinylestradiol, estrone, 17β-estradiol, estriol, Dibutyl phthalate (DPB), alkylphenols, bisphenols</td>
</tr>
</tbody>
</table>

The diversity and use of chemicals that comprises OMPs are increasing significantly every year mainly because most of these products are produced to improve public human health, increased food production, and avoidance of pestiferous arthropods etc. However, their health risk may
out-weight the benefit they provide. They are biologically active even at trace concentrations, consequently, they have potential ability to cause unforeseen adverse effects (such as toxicity, morbidity, mortality etc.,) on non-targeted ecological species when discharged into the environment (Liu et al., 2009; Tamtam et al., 2008). Long-term effects of continuous chemical pollution of freshwater systems with PPCPs are yet unknown, but there are concerns regarding the problem of bioactivity and bioaccumulation of the chemicals in the environment (Tijani et al., 2013). (Roos et al., 2012) suggests ‘prioritisation of effects of pharmaceuticals in the environment should be risk-based’; it was further suggested that exposure of pharmaceuticals to the environment should be assessed not only on sales statistics data, but data on degradation, removal by sewage treatment and bioconcentration should also be considered.

Exposure to EDCs can have severe effect on the exposed species, which may also result in the offspring of those Organisms suffering drastic repercussions. Health impacts noted include endocrine conduit disturbance in aquatic organisms, reproductive behavioural disorder, gene expression disorder resulting in feminization of aquatic species, carcinogenic diseases, cardiovascular diseases, etc., (Campbell et al., 2006; Diamanti-Kandarakis et al., 2009; Ha et al., 2007; Mastin, 2005). Potential health impacts on human may affect; male and female reproduction disorder, breast development and cancer, prostate cancer, neuroendocrinology, thyroid, metabolism and obesity, and cardiovascular endocrinology (Diamanti-Kandarakis et al., 2009).

It is argued that effects of OMPs may lead to problems of similar or even greater magnitude than health risk problems from pathogenic pollution of drinking water (Schwarzenbach et al., 2006). Other concerns are the severe toxicological effects the chemicals may result in as substances in complex mixtures (Halling-Sørensen et al., 1998; Schwarzenbach et al., 2006).

2.2.1 Sources and occurrence of OMPs in the environment

OMP have been detected in the environment with a significant quantity reported to occur in municipal water waste treatment effluent, which makes wastewater treatment plant a potential point source of most OMPs (Figure 3.0). They have been detected in surface water, tap water and other water bodies (Benotti et al., 2009; Halling-Sørensen et al., 1998; Ternes et al., 2002). Concentrations of some OMPs have been found to significantly increase during conventional treatment processes (Watts et al., 2007). Other Sources of OMP may include; runoff from agriculture, concentrated animal feeding operation, urban runoff, landfill leachates (Benotti et al., 2009). In developing countries, indiscriminate and careless disposal of refuse and untreated
industrial effluent into waterways is very common. This also contributes to the high level of OMPs in the environment (Olujimi et al., 2010). Consistent use and disposal of PPCPs into municipal sewage has resulted in consequently making WWTP a potential and significant source of OMP in the environment; furthermore, these contaminants after reaching the treatment plant are not completely removed or degraded in the treatment processes (Figure 2.0). Therefore, the discharge of effluent from WWTP into surface water, groundwater etc., on a regular basis can effectively enhance the persistence of OMPs in the environment, since studies have shown that only low concentrations of major PPCPs are been removed from conventional WWTP (Behera et al., 2011; Ratola et al., 2012). In some cases, effluent concentration of OMPs could exceed the influent concentration mainly due to biological transformation occurring during biodegradation (Kasprzyk-Hordern et al., 2009).

The following general characteristics of OMPs highlights the significance of more robust approach in limiting their presence and persistence in the environment and water systems especially through proper management at the water and wastewater treatment level. They are; (1) resistance to biological degradation processes which is the principle most conventional wastewater treatment processes are based on, (2) presence at trace concentrations which requires sensitive and sophisticated analytical methods, (3) severe health risk they may pose to humans and other ecological species (Klavarioti et al., 2009).
Figure 2.1 Sources and routes of OMP in the Environment
2.2.2 Regulations for OMPs in the environment

The occurrence of OMPs in wastewater from human activity at a personal, domestic and industrial level are a barrier to water reuse and a concern for water quality from water supply sources. There are presently no stringent regulations for most OMPs in drinking water and in discharge to aquatic environment. Control of OMPs at potential sources and monitoring in the environment is very difficult and expensive. This makes traditional regulation methods unusable. The most realistic control will be to set wastewater treatment technology standards with operational monitoring to deliver the necessary or required quality of treated effluents. Therefore, in order to match the pace of change in the shades of pollutants it will be necessary to think more holistically about how water quality are regulated and managed compared the traditional approach which is to regulate the quality of water by standards covering individual microbiological, chemical, physicochemical and other basic quality parameters for drinking water (Fawell, 2015).

Recent proposal aims at ensuring high level protection against risk of aquatic environment and drinking water sources emanating from OMPs out of which 33 substances of priority concern at community level is been listed and adopted by the European water framework directive 2000/60/EC (European Parliament, 2000).

2.2.3 Physicochemical properties of OMPs

Physicochemical characteristics of OMPs are widely varied but most Pharmaceuticals for example are polar, biologically active with relatively high hydrophilicity and persistence in order to get absorbed in the human body as well as to avoid degradation before they have a curing effect (Daughton, 2001). These characteristics coupled with the low concentration at which they occur and their small size or molecular weights make their removal obviously difficult.

*Molecular weight* (MW) is the most used parameter in characterizing the size of molecules, however, studies have shown that MW may not give a direct measurement of the size of the molecules (Kanani et al., 2010; Mehta and Zydney, 2005; Yangali-Quintanilla et al., 2010). This becomes very important as size exclusion mechanism is been considered in solute-membrane interaction. The molecular length and width can be measured as geometric descriptors (Mehta and Zydney, 2005) which gives a good indication of the *molecular size*. Molecular length is the distance between the two farthest atoms, while the molecular width and
depth are measured by projecting the molecule perpendicularly to the plane of the length axis. *Molecular volume* can give transport characteristics of molecules.

*Octonal* – *water partition coefficient* is usually used to indicate the hydrophobicity or hydrophilicity of organic compounds. It is the measure of the equilibrium concentration of a compound between octanol and water i.e. expressed as \( \log K_{ow} = \log \left( \frac{C_o}{C_w} \right) \); where \( C_o \) and \( C_w \) are the concentration of the compound in the octanol phase and the unionised compound in the water phase respectively.

*Solubility* is a key indicator to determine the effect of a compound on its passage through a membrane. The solubility of a compound in water shows its affinity to water; therefore, compounds with high water solubility are generally more likely to remain in the aqueous solution rather than adsorb to the membrane surface.

### 2.3 OMPs removal in water treatment

Consumption of water containing a mixture of organic micropollutants over a prolonged period of time might pose severe health risk; therefore removal of OMPs in water and wastewater treatment is essentially significant. Removal of OMPs is becoming a topmost issue of concern in the water and wastewater treatment industry. Studies show that most state-of-the-art industrial treatment techniques are not designed for the removal of OMPs and therefore, OMPs are not efficiently removed in most treatment facilities (Bernhard et al., 2006; Bolong et al., 2009; Joss et al., 2006; Tijani et al., 2013). Physicochemical treatment technologies such as Coagulation by alum or ferric sulphate, Lime softening, Powder activated carbon etc., were unable to achieve promising result in removing most PPCPs though there were variations in the removal rates for some OMPs. Studies show that the potential of EDC removal by powdered activated carbon (PAC) and granular activated carbon (GAC) may be up to 90% and in comparison to coagulation, sorption by PAC and GAC was more efficient (Bodzek and Dudziak, 2006; Schäfer et al., 2003). Biological treatments such as activated sludge processes and trickling filters are also reported to show low levels of removal mainly because most OMPs are not easily biodegradable, hence the option for their removal is through adsorption to organic-rich solid phase (Johnson and Sumpter, 2001). Increased sludge retention time and hydraulic retention time could also facilitate relatively better removal rates of some OMPs but this will impact on design criteria, operating parameters and waste water treatment plant size (Clara et al., 2005; Servos et al., 2005).
Advanced treatment such as membrane filtration (membrane bioreactor, nanofiltration and reverse osmosis) is considered a promising alternative but there are still problems with the incomplete removal, most systems are yet to be established on industrial scale (Kimura et al., 2003b; Sipma et al., 2010; Vergili, 2013; Yangali-Quintanilla et al., 2009; Yoon et al., 2007).

Improvement on already established advanced treatment processes on industrial scale is desired in this research work especially in regards to membrane filtration processes. Investigations into improving on the application of low pressure membrane systems (MF, UF) through enhancement of desired physicochemical properties of the membrane material and combination with other well established physical or chemical processes could be a good option for OMPs removal. Low pressure membrane processes tend to have a reasonable industrial ‘presence and application’ at the municipality level thus adaptability will be easy. Hybridization of membrane systems with natural systems is considered a sustainable option for removal of OMPs.

2.4 Summary
It is becoming increasingly difficult to ignore the problems associated with the occurrence and the potential health risk of OMPs in the environment because these chemicals are vast in number and variable in occurrence in water sources as new chemical products are continuously introduced. This chapter has discussed the sources of OMP in the environment with highlights on the status of their removal in water and wastewater treatment. The next chapter will discuss a more comprehensive critical review of the application of Membrane Assisted Processes - MAP for the removal of OMP based on laboratory, pilot and full scale studies.
CHAPTER 3
MEMBRANE ASSISTED PROCESSES
3.0 MEMBRANE ASSISTED PROCESSES

3.1 Introduction
Membrane Assisted Processes - MAP refer to water and wastewater treatment processes or combination of processes that involves, in one of its unit processes, the use of membrane filtration in one form or the other. Conventional filtration process (Depth filtration mostly) retains contaminants within the filter media while membrane filtration work on the mechanism of surface retention of contaminants, which makes the characterization of membrane filter pores in terms of size, structure distribution and surface properties, essential and crucial as a performance indicator. Some recent studies in membrane material technology are focused on improving membrane performance by functionalizing surface properties of membranes through surface modification. Aims of surface modification of polymeric membranes in most cases involves management of desired interactions between membrane surface and solution components which contribute significantly to membrane fouling. The other aim is to improve the selectivity and/or formulate novel separation functions (Nady et al., 2011; Peng et al., 2013; Rana et al., 2014; Ulbricht, 2006). This chapter discusses membrane assisted processes with respect to removal of OMPs in waste streams with critical review of recent studies and review. The concept of surface modification as an option for improving performance level for removal of OMPs is also discussed.

3.2 Membrane Filtration Overview
Membrane filtration is considered a robust treatment technology because of its wide range of selectivity or retention of contaminants in water, potential of achieving high quality treated effluent with no addition of chemicals and well-arranged and adaptable process. Two categories of materials are mostly used in membrane filtration for water and wastewater applications. They include ceramic membranes and polymeric membranes. Most of the industrially used membranes are produced to have a thin layer which provides the required retention or perm selectivity which is on top of a thicker open and porous support which provides mechanical stability and strength. Pressure – driven membrane processes are mostly used in water and wastewater treatment; low pressure membrane processes are Microfiltration (MF) and Ultrafiltration (UF), while Nanofiltration (NF) and Reverse osmosis (RO) are high pressure membrane processes. MF and UF membranes are characterised by the molecular weight cut-off (MWCO) which corresponds to the solute molecular weight (MW) the membrane removes with 90% rejection (Mulder, 1996). NF/RO can be either characterised by MWCO or ionic retention of salts such as NaCl or CaCl$_2$. MF and UF can be operated on either positive or negative pressure (vacuum pressure).
3.3.1 gives a more comprehensive description of the different types of pressure driven membrane processes showing their respective pore sizes and operating conditions.

Arrangement of MF and UF as a pre-treatment process to NF and RO is common practise with the advantage of mitigating fouling occurrence in NF/RO and improving the efficiency of the treatment process. This is applicable to water reuse scenarios and desalination processes. MF and UF is easily adaptable and can be combined systematically with most physical and physicochemical conventional processes (adsorption, biological processes, natural systems, etc); as pre/post – treatment process (Fig 3.1).

Figure 3.1 MAP overview showing different combinations and hybridization with other processes for OMP removal.

Integration of membrane processes with biological, physicochemical and natural processes is useful in water and wastewater treatment application. A membrane bioreactor (MBR) for example is a biological process system that combines secondary and tertiary treatment in conventional activated sludge system with a membrane filtration process. MBR systems are growing in popularity for virtually all wastewater treatment applications because they offer many advantages.
over conventional wastewater treatment plants such as consistently high quality effluent with low
turbidity, low bacterial counts, high biodegradation efficiency, while using fewer chemicals than
conventional wastewater treatment plants (Judd and Judd, 2011a; Sipma et al., 2010). The filtrate
quality, in many instances, is suitable for feeding directly into an RO process and ideally
applicable in water reuse scenarios. An additional advantage of an MBR system is its compact
footprint. MBR is also suitable for de-centralised wastewater application which is becoming a
competitive alternative to centralised WWTP in many growing communities.

Integration with coagulation and adsorption processes in form of series unit process or combined
‘in-situ’ unit process is also reported to enhance better performance in achieving energy efficient
treatment processes with high effluent quality. Natural systems such as bank filtration, aquifer
recharge and recovery, wetlands and stabilisation ponds are used as pre-treatment or combined
with membrane processes to establish a multi-barrier integrated system that requires low energy
and carbon footprint (Sudhakaran et al., 2013; van Paassen et al., 1998).

Combination of direct membrane systems with integrated systems in series of treatment processes
is also a feasible option when water reuse is considered. Figure 3.3 gives schematics of the various
integration of MAP to promote multi-barrier system applicable for removal of OMP in water and
wastewater streams.

3.2.1 Fundamental principles and mechanism
The following operating parameters are very significant in membrane system applications. The
flux which is a major operating parameter is typically influenced by some other various factors
and the influence of these factors is a key element to the effectiveness of the membrane process.
These factors may include; membrane resistance, operational driving force per unit membrane
area or Transmembrane pressure- TMP, hydrodynamic conditions at the membrane to liquid
interface and the fouling phenomena of the membrane.

The flux ($J$) is the quantity of material passing through a unit area of membrane per unit time. It
is also referred to as permeate flux, permeate velocity or filtration velocity. This has a strong
impact on the capital costs of the process and hence influences the economic feasibility of the
membrane system. The Transmembrane pressure-TMP is the pressure difference across the
membrane that drives the water flow through the membrane. Hence, TMP is the driver of the
permeate water flux; a relationship can be established between them (Judd and Judd, 2011a).

\[ J = \frac{\text{TMP}}{R \times \mu} \]

\[ \sim 19 \sim \]
And also; Permeability- \( K \) (m/sbar) describes the ratio of Flux – \( J \) (m/hr) to TMP (bar)

Therefore, \[
K = \frac{J}{TMP} = \frac{1}{R\mu}
\]

Where: \( R (/m) \) is the Total resistance of the membrane

\( \mu \) is the viscosity (kg/(ms\(^2\))) which is influenced by temperature change of the water matrix

Because water temperature can significantly influence viscosity (Judd, 2013), as well as membrane flux and permeability, temperature correction factor of flux (TCF) is used. Flux at any temperature is often normalised to the flux at 20°C by the following relationship;

\[
J_{20} = \frac{\mu_T}{\mu_{20}} \cdot J_T = TCF \cdot J_T
\]

**Resistance** (R) is mainly composed of the membrane intrinsic resistance governed by membrane material itself, its pore size, surface porosity and thickness (Judd and Judd, 2011b) and the resistance of fouling layer on the membrane. Sometimes the interfacial region between membrane and solution is also considered to contribute to the total resistance.

**Retention (selectivity)** indicates the extent of separation a membrane can produce with respect to the concentration of pollutants or solutes in the feed stream. It is usually represented as a percentage. While **Recovery** relates to the ratio of the permeate stream flow to the feed stream flow, also expressed in percentage.

**Molecular weight cut-off (MWCO)** is a measure of the retention capabilities of a membrane and refers to the molecular mass (known) of a solute typically surrogate molecules, or proteins where the membranes have a rejection of greater than 90%. The methods and solutes used varies for manufacturers and there is currently no industry standard for the determination of MWCO. The unit for MWCO is Daltons – Da; the more the MWCO (Da), the smaller the pore size of the membranes. The MWCO specification is mostly used to ultrafiltration and nanofiltration membranes characterisation (Cranin, 1987). MWCO for Ultrafiltration ranges from 1,000 – 300,000 Da while Nanofiltration ranges from 200 – 1000 Da depending on operational condition.
3.2.2 Membrane material types and configuration

Two categories of materials are mostly used in membrane filtration for water and wastewater applications. They include Ceramic membranes and polymeric membranes although other new materials such as metals, nanomaterial etc., are been developed. Membrane materials used must be produced in such a way as to allow water to pass through it effectively. Most of the industrially used membranes are produced to have a thin layer which provides the required retention or perm-selectivity which is on top of a thicker open and porous support which provides mechanical stability and strength. This implies that these membranes are anisotropic in structure, i.e., having symmetry only in the plane orthogonal to the surface of the membrane.

3.3 Removal Mechanism of OMPs by MAP

The removal of OMPs is governed by different parameters based on the membrane characteristics, aqueous media/solute characteristics, operating conditions, membrane fouling as well as OMP characteristics, but generally membranes are designed to work as a physical barrier (semi-permeable) that catches or rejects constituents greater than its pore size while allowing water to permeate through it. However, studies have shown that other significant physicochemical phenomenal activities occur during membrane processes. Combinations of certain properties of OMPs, solute parameters as well properties of membranes are reported to orchestrate observed removal mechanisms. Properties of OMPs such as molecular weight and size (MW, length and width), hydrophobicity or hydrophilicity, Charge characteristics and chemical structure (i.e occurrence of electron withdrawing or donating functional group) are reported to have significant effects on their rejection by membrane filtration (Chon et al., 2012; Nghiem and Hawkes, 2007a; Tadkaew et al., 2011). On the other hand, properties of membranes also play a major role in facilitating the rejection of contaminants. They may include membrane’s molecular weight cut-off (MWCO), pore size, surface charge- measured as zeta potential, hydrophobicity or hydrophilicity - measured as contact angle, and surface morphology - measured as roughness (Bellona et al., 2004; Schäfer et al., 2011). While these parameters are being understood there is still need for more investigations on the removal mechanisms in order to achieve a more realistic and predictable performance as presently reported mechanisms show varied results.

3.3.1 Size exclusion

This is the fundamental mechanism of membrane filtration where pollutants are sieved out based on their sizes. OMPs with size larger than the membrane pore size are retained because of the sieving effect (Fig 3.2). This mechanism is well understood especially in MF and UF application for removal of particulate matters and suspended solids which are large in size. As regards to
OMPs which usually are very small in size (molecular weight), inconsistent results have been observed where OMPs with larger size than pore size of membrane are not retained as expected during filtration process (Tadkaew et al., 2011). Furthermore, reports show that size of OMPs should not be exclusively based on molecular weight but molecular length and width (shape) should be considered; and thus attributed the inconsistency in results to this (Chon et al., 2012; Tadkaew et al., 2011). Size exclusion mechanism is mostly observed with uncharged (neutral) OMPs as studies show a correlation between rejection of uncharged OMPs and their molecular weight and/or width (Kimura et al., 2004, 2003b; Ozaki and Li, 2002).

3.3.2 Adsorption

Adsorption of OMPs to polymeric membrane surfaces plays a significant role in the rejection of OMPs. Adsorption is mainly influenced by hydrophobic surface interactions and hydrogen bonding between OMPs and the membranes (Figure 3.2). Association of OMP with retained matter or introduced adsorbent material such as powdered activated carbon (PAC) can also facilitate adsorption. Adsorption could sometimes be confused with deposit formation activities which usually causes fouling. Membrane fouling and presence of humic acid from organic matter retained on surface and pores of membrane could also increase adsorption activities by changing the membrane surface characteristics and pore size, since membrane surface morphology, roughness, active layer thickness and pore size contribute significantly to adsorption effects (Nghiem and Hawkes, 2007a; Schäfer et al., 2011).

Adsorption site on membrane surfaces is relatively low, however larger pore sizes (MF, UF) tend to record higher adsorption than smaller pore sizes (NF/RO) (Tang et al., 2007). Some studies also suggest that apart from adsorption to membrane surface occurring, absorption into the membrane pore structure internally could also occur; this concept appears reasonable but very debatable because of the complexity involved and huge variety of membrane material and structure available. Studies show that adsorption rate decrease with time as a result of saturation after the initial stages of filtration, also adsorption effects measured at the initial stages of filtration show high retention but may be an over estimation of the retention because once membrane becomes saturated, retention decreases significantly (Comerton et al., 2007; Hu et al., 2007; Kimura et al., 2003b). The solution chemistry such as pH as well as solute-solute interaction also affects adsorption. In real waste water where the aqueous solution contains a mixture of OMPs and other pollutants, adsorption phenomena may become complex and theoretically unpredictable.
3.3.3 Hydrophobic interaction

Hydrophobic interaction between OMPs and membrane surface also affects the adsorption phenomena. Hydrophobicity of OMPs which is a function of octanol–water partition coefficient ($\log K_{ow}$) and of the membrane measured as contact angle (Mulder, 1996), promote interaction and adsorption of hydrophobic OMP to hydrophobic membrane surfaces. Generally compounds with relatively high hydrophobicity ($\log K_{ow} > 2.5$) are expected to adsorb onto solid phases rather than being soluble in water. Hydrophobic OMPs are therefore expected to adsorb to the surface of hydrophobic membranes surfaces by hydrophobic interactions. While hydrophobic adsorption contributes to retention, it must be noted that membrane fouling can be excavated by the
hydrophobicity of the membrane affecting membrane operating conditions. Biofouling of membrane surfaces can make the surfaces hydrophilic and thus impact on the rejection of hydrophobic OMPs.

3.3.4 Electrostatic exclusion

Surface charge of membrane could induce electrostatic interaction between charged OMP molecules and the membrane surfaces (Figure 3.2). Electrostatic exclusion could be as result of repulsive force between negatively charged OMPs and negatively charged membrane surfaces. Several studies have shown this phenomenon and compared the retention to uncharged compounds (Kim et al., 2005; Kimura et al., 2003a). Electrostatic repulsion is not expected to change with time of filtration, however studies show that there may be changes due to the effects solution chemistry (Acero et al., 2010; Nghiem et al., 2006).

3.4 Synthesis Of MAP for OMP removal

An overview of the recent work done at laboratory, pilot and industrial scale in the application of MAP for respective OMP is shown on Appendix A. The removal rates and other parameters are described and reviewed. While Pharmaceuticals and personal care products are the most studied class of OMP, there is significant variation in the removal efficiency of compounds studied because the performance of the MAP for OMP removal is seen to depends on peculiar conditions. Membrane filtration (or Membrane assisted processes – MAP) is generally gaining more attention both in research studies and industrial applications for drinking water and waste water treatments especially in water reuse scenarios. Studies are also showing feasible and promising results with integrated system application in achieving suitable improvements compared to conventional treatment technologies.

Several observations as follows can be made from the information on Appendix A:

1. Membrane assisted processes - MAP is a potential and reasonable option for attaining high removal rate of selected OMP in water compared to other advanced treatment processes especially in water reuse scenarios.

2. As a physico-chemical process requiring less use of chemicals, MAP could be adapted to most conventional systems and integrated to other processes.
3. Although fewer chemical is used, the efficiency of the system in removing OMPs is reasonably dependent on the chemistry of influent as well as interaction between the membrane surface and constituents of the influent including the OMPs.

4. Simultaneous interactions causing complexity in predicting the removal efficiency in real waste water matrix containing a cocktail of OMPs is expected in practical application.

5. MAP processes involving loose membranes dominantly remove OMPs through adsorption removal mechanism while tight membranes acts dominantly by size exclusion removal mechanism.

6. Most studies are limited to laboratory conditions and few selected OMPs thus; a genuine representation of industrial application is not expressed. Cost evaluation on the feasibility of practical application is often not considered which in most cases are likely to be unrealistic in municipal water and wastewater treatment especially for NF/RO membranes.
3.5 Assessment of performance of MAP for OMP removal

3.5.1 Direct MAP systems for OMP removal

3.5.1.1 Microfiltration and Ultrafiltration

MF and UF are the loosest amongst the MAP used in water treatment as regards to the pore size of the membrane materials. Pore size for MF ranges between 5µm – 0.1µm and for UF ranges between 0.1µm-0.005µm. MF membranes are obviously not capable of removing most OMP present in water mainly because of the molecular properties of the pollutants; which are in most cases smaller than the pore size of MF membranes. Thus the MF systems cannot act as a barrier for the OMPs unless some form of pre-treatment such as coagulation, adsorption, etc, is done to make the pollutants ‘larger’ and then filtered. On the other hand MF and UF can be used in combination with RO as a pre-treatment to achieve more reasonable removal results as well as reduce fouling of RO membranes.

(Comerton et al., 2007) while studying the removal efficiency of 22 frequently occurring EDCs and PPCP by ultrafiltration at varied temperature reported that the percentage removal was low compared to NF/RO membranes studied alongside; and adsorption as a removal mechanism was more significant with UF membranes. Furthermore, the adsorption strongly correlated with compound’s Log K_ow and membrane pure water permeability, and moderately correlated with compound water solubility while showing that removal efficiency was not affected by variation in temperature. Other studies also reported similar trends in the removal mechanism. Although relatively low percentage removal is recorded, hydrophobic adsorption mostly influenced by the hydrophobicity of the pollutants, was a major removal mechanism that facilitated OMP removal. (Acero et al., 2010; Yoon et al., 2006). As sorption is major mechanism with MF/UF membranes for OMP removal, innovative approach to improve surface morphology, increase sorption site and surface modification can enhance the performance of UF membranes for OMPs removal. Surface modification targeted on reducing pore size and distribution may also be useful.

3.5.1.2 Nanofiltration and Reverse Osmosis

Nanofiltration and Reverse osmosis are high pressure membrane processes with smaller pore sizes below 0.01µm, which requires a corresponding high energy to operate. RO membranes are tighter in pore size than NF membranes and tight NF membranes are reported to be more efficient than loose NF for obvious reasons of smaller pore size. More than half of the studies reported on the application of MAP for OMP removal is centred on the use of NF/RO as a more reliable and
robust application. Studies show that a variety of OMPs can be successfully removed by NF/RO to near complete retention levels. Removal rates above 80% are mostly recorded. However, information on the performance mechanism is still not comprehensive. Removal mechanism based on solute-membrane interaction is dominantly size exclusion (steric hindrance) and electrostatic repulsion, and sometimes hydrophobic adsorption (Comerton et al., 2008; Garcia et al., 2013; Nghiem et al., 2006; Yangali-Quintanilla et al., 2009; Yoon et al., 2006). The ionic strength, hydrophobicity and conditions of the feed solution such as pH, are reported to influence the removal efficiency (Nghiem et al., 2006). Ionic rejection is mainly due to the electrostatic repulsion between the charged compounds and the surface charge of the membrane while uncharged compounds are mostly rejected by size exclusion mechanism (Vergili, 2013; Yangali-Quintanilla et al., 2009). Correlation between rejection and compound hydrophobicity (measured as Octanol-water partition coefficient -Log Kow) as well as membrane pure water permeability is often reported as significant; showing higher removal rate for more hydrophobic OMP especially in situations where hydrophobic adsorption removal mechanism is dominant (Braeken and Van der Bruggen, 2009).

While effect of water solubility on removal is reported to be less significant some other studies strongly suggests that water solubility of a compound should be assessed as the first indicative parameter on its passage in NF membrane filtration as experiments show that uncharged compounds with lower molecular weight (MW), low water solubility and high hydrophobicity (high Log kow values) were removed better than others with relatively higher MW and higher water solubility (Vergili, 2013). Solution chemistry especially pH has effect on the removal mechanism and overall removal because certain characteristics (such as acid dissociation constant pKa) of OMP in the feed solution could change significantly with change in pH. (Nghiem et al., 2006), while using ‘loose’ NF to filter pharmaceuticals (Sulfamethoxazole, carbamazepine, and Ibuprofen), reported poor and variable OMP removal rates and concluded that rejection of OMP was greatly influenced by change in feed solution pH, which affects charges of targeted compounds, and the ionic strength of the OMP. This trend is also reported in other studies (Acero et al., 2010; Jin et al., 2012). Furthermore, contribution of solute-solute interaction should be considered alongside solute-membrane interaction as fundamental parameters for understanding OMP removal mechanism in NF. The presence of humic acid in feed solution for instance can enhance the removal of OMPs as shown by (De Munari et al., 2013), where removal of pesticides endosulfane with MW less than MWCO of NF membranes increased with presence of humic acid in feed solution. In fouled NF membranes size exclusion (steric hindrance) was observed to be a
main removal mechanism and possibility of increased sorption of OMP to fouling material could be experienced (Nghiem and Hawkes, 2007a; Schäfer et al., 2011; Yangali-Quintanilla et al., 2009).

In comparison to OMP removal mechanism in UF membranes which is mostly through sorption to membrane surface, NF membranes predominantly operates by size exclusion removal mechanism thus indicating that pore size plays a major role in OMP removal by NF. Comparing tight NF to RO, (Yangali-Quintanilla et al., 2010) proposed that tight NF is an acceptable barrier for OMP because its removal performance approaches that of RO, and its reduced operation and maintenance (O&M) costs in long-term project implementation. It was also reported that removal rates above 90% is achievable with “loose” NF preceding aquifer recharge and recovery (ARR) in an integrated system. However, the implementation of NF system for municipal water treatment plant is economical unfeasible with present understanding of the technology. The energy cost is outrageous and cost evaluation shows that even if membrane material cost is halved, the total capital and operating cost is high (Braeken and Van der Bruggen, 2009).

Dominant removal mechanism for NF/RO membranes would depend on interaction between the membrane material and interfacial properties, physicochemical characteristics of OMPs and solution chemistry. There is therefore great need for systematic investigations to identify and quantify both relative contributions and effect of these various interactions and develop suitable modelling tools. This is proven to be a difficult task because of the complexity of systems and the possibility of several interactions taking place simultaneously in real waste water matrices.

3.5.2 Integrated MAP System for OMP removal

3.5.2.1 MAP with Biological processes - Membrane Bioreactor MBR

MBR systems are growing in popularity for virtually all wastewater treatment applications because they offer many advantages over conventional wastewater treatment plants such as consistently high quality effluent with low turbidity, low bacterial counts, while using fewer chemicals than conventional wastewater treatment plants. MBR is a biological process system that combines secondary and tertiary treatment in conventional activated sludge system using a membrane filtration process (Fig 3.3). Two major process configurations of MBRs are commonly used, namely; side stream and submerged MBRs. In the side stream MBRs the membrane unit which generates the permeate is separated from the main bioreactor. The sludge retained by the membrane is recirculated back into the reactor tank. The side stream has the advantage of attaining high permeate flux, flexible, and robust, but can become complicated in its operation with high.
energy consumption. Submerged MBRs is an optimised MBR system that reduces energy consumption by directly immersing the membrane unit into the bioreactor. It is simple, easily adaptable to existing conventional treatment, more manageable fouling and lower energy consumption but it’s less capable of coping with variations in influent flow. In MBRs, the filtrate quality, in many instances, is suitable for feeding directly into an RO process. An additional advantage of an MBR system is its compact footprint.

Efficiency of MBR systems in attaining high removal level of OMPs has been studied and some reports show that MBR performed better than Activated sludge systems while others show no significant improvement (Radjenović et al., 2007). Biodegradation and sorption to sludge is reported as the main two removal mechanism for OMPs by MBRs with hydrophobic pollutants having more tendencies to be removed by sludge adsorption. (Tadkaew et al., 2011) while studying the removal of a range of OMPs in a laboratory scale MBR reported that apart from biodegradation and adsorption of hydrophobic OMPs resulting in higher removal, apparent correlation between molecular features and chemical structure (such as, electron withdrawing or donating functional group) and overall removal was observed. Furthermore it was noted that the combined effect of physical parameters (Hydrophobicity, Molecular weight etc.) and aspects of chemical structure (ring composition, side chain associated metabolic pathways, functional groups etc.,) should be taken into account to understand the variableness of OMP removal by MBR. Other removal mechanism for OMP in MBR processes may involve sorption to biomass or to enmeshment in the membrane biofilm (Sahar et al., 2011; Xue et al., 2010).

Major factors influencing the removal efficiency may include; sludge age and concentration, existence of anoxic sludge age and concentration, existence of anoxic and anaerobic compartments, composition of the wastewater, inoculum source and character, technical setup - side stream or submerged MBR (Fig 3.3), operating temperature, mixed liquor pH, and conductivity (Chon et al., 2012; Hai et al., 2011a; He et al., 2013; Tadkaew et al., 2011). Removal efficiency of OMPs by MBR system could also be affected by changes in dissolved oxygen (DO) concentration (Hai et al., 2011b). MBR offers an adaptable alternative for conventional treatment process and if well optimized and improved high removal rates can be achieved more significantly if the concept of surface modification of membranes is applied to enhance the removal mechanism and increase sorption sites and biofilm formation on membrane surface. Although this will result
in increase in fouling but the surface modification could provide a protective layer for the membrane surface during fouling removal.
### CHAPTER 3 Membrane Assisted Processes

#### Figure 3.3 Schematics of various integrated and multi-barrier integrated MAP systems

- **MAP with Biological System - MBR**
  - (A) BIOREACTOR MF/UF — Effluent
  - OR
  - **(B) MF/UF (Submerged) BIOREACTOR**

- **MAP with Adsorption**
  - (C) CONTACTOR (Adsorbent, PAC, GAC, Zeolite etc) — Effluent
  - OR
  - **(D) MF/UF (Pressurised or Submerged) CONTACTOR**

- **MAP with Natural System**
  - (E) — NF/RO

- **Multi-barrier MAP system**
  - (F) MF/UF (Submerged) BIOREACTOR — NF/RO
  - OR
  - **(G) MF/UF (Submerged) BIOREACTOR**
  - **(H) MF/UF (Pressurised or Submerged) CONTACTOR (PAC, GAC, Zeolite etc) — Effluent**
  - OR
  - **(I) MF/UF (Submerged) BIOREACTOR CONTACTOR Adsorbent (PAC, GAC, Zeolite etc)**
  - **(J) MF/UF (Submerged) BIOREACTOR**

Natural Systems:
- Constructed Wetlands
- Riverbank Filtration
- Aquifer recharge and recovery

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~ 31 ~
3.5.2.2 MAP with Adsorption (PAC or GAC)

Adsorption in water and wastewater has been identified as an efficient and economical treatment technology. Activated carbon and zeolite are two major adsorbent used in water treatment. Powdered activated carbon (PAC) and granular activated carbon (GAC) in combination with membrane processes are promising technologies for water treatment for desired high effluent quality (Figure 3.3). The benefits of the combination MAP and PAC are due to the ease of adjustment of technology with PAC possessing high adsorption capacity for trace contaminants and the selectivity of the membrane systems to retain both low and high molecular weight compounds and particles (including PAC particles).

Regarding OMP removal in direct and integrated membrane filtration, dominant removal mechanism may be hydrophobic partitioning for hydrophobic OMPs while hydrophilic OMPs removal mechanism involves hydrogen bond formation between OMPs and activated carbon surface. Influence of charge of OMP on their adsorption is minimal however; presence of natural organic matter (NOM) can alter charge interaction and affect adsorption phenomena as well as reduce adsorption sites by blocking the pores of activated carbon (De Ridder, 2012; Nghiem et al., 2008; Nghiem and Hawkes, 2007b). Addition of PAC to increase the removal rate of OMPs in UF was reported in a study showing UF with GAC post-treatment achieving better OMP removal than UF with PAC pre-treatment and increased dosing of PAC will perform better as regards OMP removal (Acero et al., 2012). In submerged UF membrane system, dosing PAC directly into the system can improve the removal efficiency due to increased contact time compared to side stream or pressurized system (Löwenberg et al., 2014). PAC dosage as high as 1g/L could be added since removal rates are dependent on dosage of PAC. On the other hand, a balance of dosage and membrane fouling mechanism should be assessed.

Zeolite is also a good adsorbent suitable for OMP removal with the advantage of size exclusion and close fit adsorption mechanism as well as good resistance to NOM fouling in contrast to activated carbon (De Ridder, 2012). Hybridization of adsorption with biological systems in membrane processes either in a series process or ‘in situ’ process is also reported to be efficient in attaining high removal rates of OMP is waste streams.

3.5.2.3 MAP with Natural Systems (Bank filtration, ARR, Wetlands)

Natural systems such as bank filtration (BF), aquifer recharge and recovery (ARR), wetlands and stabilization ponds are used as pre-treatment or combined with membrane processes to establish a multi-barrier integrated system (figure 3.3) that requires low energy and carbon footprint.
Natural systems have the advantage of avoiding the use of chemicals and adaptability to other treatment processes providing robust barrier and significant treatment cost reduction. The major setback for the application is the land space requirement as well as the site geological and hydrogeological conditions that must be suitable for the system to be efficient.

ARR acts as pre-treatment for NF to reduce fouling and with loose NF requiring less energy an integrated system will produce higher OMP removal at reduced cost compared to RO system (Bellona et al., 2004; H. Cikurel, 2010). Studies have shown that ARR-NF system can effectively remove recalcitrant OMPs but sufficient assessment and analysis of operational cost of integrated system should be done (Sudhakaran et al., 2013).

3.5.2.4 Enhanced MAP Systems

Polymer-enhanced ultrafiltration (PEUF) and micellar-enhanced ultrafiltration (MEUF) are two classes of enhanced membrane filtration processes that are gaining considerable attention in water and waste water technology. It involves the addition of suitable polymeric compounds that form ‘complexes’ with the pollutants in feed solution hereby making pollutants retainable by the preceding ultrafiltration process. Research show that these concepts can provide the advantage of high selectivity, low operating cost, generation of little to no secondary effluent, and possibility of waste recovery hereby making the method an excellent and potential alternative to currently employed treatment methods (Bade and Lee, 2011; Barakat, 2008; Camarillo et al., 2009; Lee et al., 2005). PEUF involves the use of water-soluble metal-binding polymers in combination with UF is a hybrid system to retain and possibly recover valuable constituents from the waste stream. The complexation process with the use of a macroligand produces pollutant with increased molecular weight with size larger than the pores of the selected UF membrane which can then be retained and the effluent purified (Barakat, 2008, 2008; Jana et al., 2012; Lee et al., 2005). Most reports show that PEUF can attain high removal rates of heavy metals (e.g. Nickel, Mercury, Chromium, etc.) (Barakat and Schmidt, 2010; Jana et al., 2012), and factors such as solution pH, type and concentration of water-soluble polymer used for complexation and the concentration of pollutant play a major role in the efficiency of the system (Barakat, 2008; Lee et al., 2005).

MEUF on the other hand involves the use of suitable surfactants which usually consists of hydrophilic and hydrophobic properties added into the waste stream containing pollutants (e.g metal ion, organic materials, low molecular weight solute) to form large amphiphilic transparent micelles that entrap and solubilize pollutants in the waste stream. The critical micelle
concentration (CMC) is the concentration of surfactants at which micelles start to form spontaneously in the solution and it is one of the most important physical parameters of surfactants to be selected. Micelles containing solubilized contaminants with larger diameter than membrane pore size will then be retained by the ultrafiltration membrane (Bade and Lee, 2011; Camarillo et al., 2009). MEUF has recorded high removal rate of heavy metals, nutrients, organics such as phenols, o-cresol (Barakat, 2008; Camarillo et al., 2009).

While PEUF and MEUF offer a viable alternative for treatment of trace pollutants, little or no work has been reported in the application of PEUF and MEUF for removal of organic micropollutants in water.

### 3.5.3 Combination of Direct and integrated MAP systems for OMP removal

Apart from direct membrane filtration process, coupling of one or more direct membrane process with integrated membrane systems and other physicochemical processes to form series of multi-barrier system is very relevant in producing suitable results both from economical and water quality point of view. These combined systems are reported to have the advantage of higher removal efficiency, reduced cost as well as sustainable application with less toxic waste stream (sludge) after treatment. Combination of MBR system with NF/RO process in series in municipal wastewater treatment is reported to achieve high OMP removal rates and high quality effluent suitable for water reuse. This is obviously as a result of inherent advantages of interplay between biological degradation and biosorption in MBR, and physical separation in NF/RO. (Cartagena et al., 2013) studied hollow fibre and flat sheet comparison for MBR combined with NF and RO in separate systems and showed no significant difference in performance of the two MBR with both combined systems producing high quality effluent (>75% removal). It was further shown from the study that MBR-NF will require 30% less energy compared to MBR-RO to achieve the same result.

Although high removal rates are reported (90-99%), some studies affirms that due to presence of OMPs at low concentration in treated effluents, RO cannot serve as absolute barrier to OMPs, therefore additional treatment systems should be considered alongside. Addition of natural systems in form of aquifer recovery and recharge, bank filtration etc., will be suitable to establish a multiple barrier system for OMP removal (Sahar et al., 2011; Sudhakaran et al., 2013).

The synergy of adsorption and biological process in series or simultaneous operation can produce high quality effluent which in most cases is suitable for groundwater recharge or water reuse. Studies on addition of PAC and GAC to MBRs show very interesting results. Increased removal
efficiency (93-99%) of some recalcitrant pharmaceuticals (carbamazepine and diclofenac) could be achieved compared to MBR systems (Lipp et al., 2012). MBR with GAC (post-treatment) combined system was shown to improve the removal efficiency of both hydrophobic and hydrophilic OMPs compared to ordinary MBR system (Nguyen et al., 2012). The Biomass characteristic in the biological system can also enhanced by the presence of PAC (Serrano et al., 2011).

3.6 Polymeric membranes, surface properties and characterization

Polymers are very capable materials that can be used in many applications ranging from membrane filtration, biomaterials, microelectronic devices, coating etc. In membrane filtration applications, polymers are extensively used in water and wastewater technology mainly because of the suitability of its properties for the application. Performance of polymeric membranes in many applications depends mostly on the combination of their mechanical strength i.e. bulk properties and surface properties. The surface layer which is usually thin, provides the required perm-selectivity while the bulk porous support provides the mechanical strength. In most cases it is very difficult to get a polymer that possesses high quality of both properties. It’s either good surface properties with poor mechanical strength; and a poor surface property with good mechanical strength is possessed. Hence, modification of polymers to obtain the most desired and improved performance has been of interest in recent years. Most studies focused on surface modification without altering the mechanical properties of polymeric membranes, this is because surface modification provides a better and easier approach compared to process of obtaining new polymer properties through polymer blending etc., ((Nady et al., 2011).

Polymers membranes are usually prepared, depending on the membrane shape, using the phase inversion or the dry-wet spinning method. The following are general properties of polymeric membranes targeted for high quality membrane filtration (mostly for MF & UF) applications in water and wastewater; high Porosity, good polymer flexibility, narrow pore distribution or Sharp Molecular weight cut-off, high polymer strength; elongation, high burst and collapse pressure, permanent hydrophilic character, wide range of pH stability, good Chlorine tolerance, low cost etc.

Polymeric membranes commonly used include; Polyvinylidene fluoride (PVDF), Polyether Sulfone, Polyvinyl Chloride, Polypropylene, Polyaclonitrile, Polyethylene.
Polymeric membranes are usually produced to possess the certain properties that enhances high degree of selectivity or rejection of solutes. The materials used for membranes should as much as possible the following properties:

1. High surface porosity
2. Narrow pore size distribution
3. Structural integrity (Mechanical strength)
4. Chemical and thermal tolerance
5. High polymer strength: elongation, high burst & collapse strength
6. Wide range of pH stability
7. Low cost
8. Hydrophilic character

3.6.1 Surface properties and characterization

3.6.1.1 Pore size and distribution

The membrane pores characteristics is an important factor that influences its selectivity and the operation of the membrane system. The pore size of membranes for water treatment applications could range from sub-nanometres to micrometres (figure 3.3, 3.4) with corresponding operating pressure ranging from <1 bar up to 50 bars. Although the nominal pore size provides information on the average size of the membrane pores, information on the pore size distribution is also very useful to characterize the surface property of the membrane. Membranes of similar nominal pore size and different pore size distribution will perform significantly differently in their selectivity as a result of the nature of the size distribution.

Pore geometry can affect the selectivity and permeability of membranes, with slit-shaped pores seen to perform better than cylindrical pores because the slit-shaped pores offers a reduced resistance to flow (Kanani et al., 2010). However, the improved performance can only be achieved with a relatively narrow pore size distribution. The pore geometry of the membranes can essentially be controlled by choosing an appropriate fabrication technique to give the desired result.
<table>
<thead>
<tr>
<th>Types</th>
<th>Pore size MWCO</th>
<th>Operating pressure range</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF</td>
<td>50 nm–5 μm</td>
<td>0.5–5 bars</td>
</tr>
<tr>
<td>UF</td>
<td>5–100 nm</td>
<td>2–9 bars (cross-flow)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2–0.3, &lt; 1 bar (dead-end and submerged)</td>
</tr>
<tr>
<td>NF</td>
<td>1–5 nm</td>
<td>4–20 bars</td>
</tr>
<tr>
<td>RO</td>
<td>&lt; 1 nm</td>
<td>&gt; 15 bars</td>
</tr>
</tbody>
</table>

Figure 3.4 Pore size and corresponding operating pressure range

Figure 3.5 Membrane pore sizes compared to sizes of common materials
3.6.1.2 **Hydrophobicity and hydrophilicity**

Membrane surface affinity for water is described as hydrophilicity and hydrophobicity. This is usually determined by the water contact angle - CA measurements performed by the method where a drop of liquid is placed on the surface of the membrane (flat and smooth) and the contact angle measured geometrically. Surfaces with high affinity for water are hydrophilic and the CA is less than 90°, whereas for low affinity, the surface is hydrophobic and CA is greater than 90° (Mulder, 1996).

3.6.1.3 **Surface morphology**

The surface as well as general morphology of polymeric membranes play a major role in the overall performance of the membrane for separation processes in water purification. Factors in preparation of membrane that affect the morphology and performance of the membrane incudes the polymer-solvent interaction during membrane preparation especial for phase inversion technique. Others includes; evaporation time from polymer-solvent system and type of coagulation bath. The surface morphology can be measured through the roughness, topography.

3.6.2 **Physical properties of PVDF**

PVDF is a semi-crystalline polymer with a glass transition temperature (Tg) of around −39 °C, a melting temperature (Tm) of around 160 °C and a thermal decomposition temperature of above 316 °C. PVDF exhibits low surface energy and critical surface tension (γc) of PVDF, 25 mN/m,18mN/m respectively. This results in high hydrophobicity of PVDF membrane surface. (Liu et al., 2011).

3.7 **Surface modification of Polymeric membranes**

Surface property and structure of membranes play a major role in the performance of the membrane especially in the overall selectivity and fouling phenomena of the membrane. In recent studies, the main focus of surface modification of polymeric membranes involves management of desired interactions between membrane surface and solution components that contribute significantly to membrane fouling. While other studies aim to improve the selectivity and/or formulate novel separation functions (Nady et al., 2011; Peng et al., 2013; Rana et al., 2014; Ulbricht, 2006). Modification of polymeric membranes is considered to be equally important as
the membrane process development itself and surface modification especially, has become a key technology attempting to improve the performance of membrane filters with regards to selectivity, flux and membrane fouling.

A variety of methods and techniques have been employed to modify the surface properties of polymeric membranes, most of which involves the use of complex processes and chemical routes. Frequently reported methods of surface modification available on commercial scale include coating, blending, grafting, chemical, composite and combined methods (Liu et al., 2011; Nady et al., 2011; Xi et al., 2009; Zhao et al., 2011; Zhu et al., 2013). Surface grafting and blending are two common and most effective modifications used, which provides a more stable modification (physical and chemical stability) during the operation and cleaning process of the membrane (Kato et al., 2003); however, on an industrial application they are considered complicated and costly.

3.7.1 Surface modification methods, advantages and disadvantages

3.7.1.1 Coating

Surface coating is the simplest way to improve the surface hydrophilicity of an already prepared polymeric membranes, however there is problem of instability of the coated layer which could be removed along the operation and cleaning process because of the relatively weak physical adsorption interaction between the coating material and the membrane surface (Liu et al., 2011). Coating materials that can achieve stronger bond are potentially able to ameliorate this problem. Furthermore, chemical treatments such as sulfonation or crosslinking can be performed on the membrane surface to anchor the coated layer.

Surface coating of PVDF membranes using self-polymerization of Poly (3, 4-dihydroxy-L-phenylalanine or Poly DOPA) which has a strong adhesive behaviour and subsequent covalent immobilization of Heparin onto the resulting coated membrane was reported to effect significant improvements in the membrane surface hydrophilicity as shown from the water contact angle measurements (Zhu et al., 2009). Xi et al. (2009) also reported similar concept of the facile method of surface coating using poly (DOPA) and poly (dopamine) to improve the hydrophilicity, durability of PE, PVDF and PTFE porous membranes. The use of ethanol as solvent for the solution of coating material allowed DOPA to self-polymerize not only on the membrane surface, but also on the membrane pore walls. Improvement of the surface charge of PES ultrafiltration membranes by coating with sulphonated poly (2,6-dimethyl-1,4-phenylene oxide) was shown to attain reasonable results (Hamza et al., 1997), also the modification of PES ultrafiltration membranes by polyelectrolyte using layer-by-layer deposition technique to reduce the MWCO
was shown to achieve better rejection by converting the membrane with open structure to a membrane with denser active layer (Kochan et al., 2010).

Coating through physical adsorption onto membrane surfaces by dipping is suitable for large scale industrial production. Coating involves the formation or deposition of a functional thin film layer that non-covalently adheres to the surface of the membrane (Zhao et al., 2011). Surface coating is the simplest way to improve the surface properties of an already prepared polymeric membranes. However, there is the problem of instability of the coated layer which could be removed during the operation and cleaning process because of the relatively weak physical adsorption interaction between the coating material and the membrane surface (Liu et al., 2011; Maartens et al., 2002; Zhu et al., 2013). Coating materials that can achieve stronger bonds are potentially able to ameliorate this problem.

While most applied surface modification studies have aimed at improving the fouling resistance and selectivity of polymeric membranes, very little work has been done on investigating the potential of surface modification of low-pressure membranes in the removal of OMPs. Therefore, this research work will focus on evaluating the stability and efficiency of the physical adsorption of the coating on the low-pressure UF PVDF membrane surfaces as well as the filtration performance by measuring the membrane’s ability to achieve enhanced removal of model organic micropollutants (MOMP), which are commonly reported OMP in municipal waste streams; namely caffeine which has high water solubility and recalcitrant carbamazepine with relatively high hydrophobicity, in deionised water. Based on the experimental results and membrane surface characterisations, possible removal mechanism for the MOMP studied are analysed and proposed.

Coating involves the formation or depositing a thin film functional layer (usually hydrophilic) that non-covalently adheres to the surface of the membrane. The coating modification occurs mainly on the top or bottom surface of the membrane, excluding the pores inside the membrane. This is due to the limited diffusion ability of the coating material into the membrane pores (Liu et al., 2011). The binding between the coated layer and the membrane surface can be done through physical adsorption, crosslinking and sulfonation (a substitution chemical reaction where sulfonic groups is added to replace hydrogen atom in the aromatic structure) (Zhao et al., 2011).

3.7.1.2 **Blending**

Blending is achieved when two (or more) polymers are physically mixed together during membrane preparation to obtain a desired functional property. This allows the preparation and
modification of the membrane to be achieved in a single step. However, membranes produced via
this method suffers from relatively low mechanical strength and contains a large quantity of
blended additives that do not contribute to the membrane functions.

Blending is achieved when two (or more) polymers are physically mixed together during
membrane preparation to obtain a desired functional property. Therefore the preparation and
modification of the membrane can be achieved in a single step. The surface as well as the inside-
pore of the membrane can be modified by this method. Polymers to be blended should be
compatible in order to obtain a suitable result, and the formation process needs adequate
optimization since it will differ from the normal process for the basic polymer (Nady et al, 2011).

3.7.1.3 Grafting

Grafting techniques used to initiate grafting may involve covalent bonding of single polymers or
a mixture of polymers (Bhattacharya and Misra, 2004) in a complicated chemical synthesis
procedures including  plasma, photochemical or high-energy radiation (UV photo, electron beam
etc.), enzymatic reactions (Liu et al., 2011; Nady et al., 2011).

Grafting is a method which involves covalent bonding of monomers onto the surface of the
membrane. The grafted layer or material is therefore immobilized through the covalent bonding
interaction. This method provides a more stable modification (physical and chemical stability)
compared to coating during the operation and cleaning process of the membrane (Kato et al.,
2003). The techniques used to initiate grafting may involve grafting of single polymers or a
mixture of polymers (Bhattacharya and Misra, 2004). The grafting techniques include; chemical,
plasma, Photochemical or High-energy radiation (UV photo, electron beam etc), enzymatic (Liu
et al., 2011; Nady et al., 2011). Graft methods in most cases need specialised technique in its
application and could also incur high cost.
3.8 Summary

Membrane systems are showing promising results with the advantage of feasible adaptability to other treatment processes to create integrated systems such as membrane processes combined with biological processes and/or adsorption in a side stream or submerged system. Nevertheless, problems associated with membrane fouling and high energy requirement for high pressure membranes, are still a limitation to industrial application of the technology. Practical application based on present knowledge of MAP for OMP removal might be difficult as real wastewater contains a complex mixture with a complex ‘solute’ behaviour and response.

Surface modification of low-pressure membranes is a potential option to improve the performance of MAP in targeting the OMPs in waste streams. Surface coating through physical adsorption is seen as the simplest method of coating on an industrial scale.
CHAPTER 4
EXPERIMENTAL PROGRAMME
AND OVERVIEW
4.0 EXPERIMENTAL PROGRAMME AND OVERVIEW

4.1 Introduction

While most applied surface modification studies have aimed at improving the fouling resistance and selectivity of polymeric membranes, very little work has been done on investigating the potential of surface modification of low-pressure membranes in the removal of OMPs. Therefore, this research work will focus on evaluating the stability and efficiency of the physical adsorption of the coating on the low-pressure UF PVDF membrane surfaces as well as the filtration performance by measuring the membrane’s ability to achieve enhanced removal of model organic micropollutants (MOMP), which are commonly reported OMP in municipal waste streams; namely caffeine which has high water solubility and recalcitrant carbamazepine with relatively high hydrophobicity, in different water matrices namely; deionised water, surface (lake) water and wastewater (synthetic). Consequently, this work is a Multi-stage laboratory scale experiments involving multidisciplinary analytical and characterization studies. This chapter therefore discusses the experimental work plan and approach to the entire research with the respective discussions and outcomes to follow in proceeding chapters.

4.2 Research approach

As mentioned in section 1.2, ultrafiltration is more industrially used membrane technology at municipal water treatment level. Improvements and optimization of the process through membrane material modification and/or adaptation and hybridization with other conventional treatment technology could provide a sustainable and reliable treatment option especially for the removal of OMPs. Polymeric UF membranes surface modification is gaining considerable attention in material science with regards to formulation of novel separation techniques applicable across various industries including water and wastewater treatment. The major setback in industrial applicability of the concept is the sophistication of the most effective surface modification techniques. They are usually very unrealistic on a large-scale production in terms of cost, footprints, etc.

Commercially available PVDF UF hollow-fibre membranes system are used in this study as base membrane. Surface modification through simple surface coating technique was performed to allow coating material adsorb physically unto the membrane surface to possibly enhance membrane surface properties suitable for improved removal of MOMP. This approach is based on earlier studies establishing the correlation between removal efficiency of membranes with its surface properties such as pore size, distribution, sorption (deposited layer), and morphology as
well as studies on prominent removal mechanisms as discussed in section 3.3. Hence, deposition of thin film /layer of functional material on membrane surface in a simple industrially applicable method is been investigated in this study with useful insight into surface characterization of various membrane materials and coating methods, and membrane filtration experiments for the removal of MOMPs in three different water matrices (Fig 4.0).

4.3 Experimental work overview

The experimental protocol for the study is shown in Fig 4.0. The experimental work plan is comprises of a three aspect experimental procedure namely; membrane modification and fabrication, membrane filtration and Sample analysis.

4.3.1 Membrane modification and fabrication

The membrane modification involved using two coating materials, hydrophobic polymer – Polystyrene and amphiphilic polymer – Pluronics F68. Spray and dip coating methods were also used at different stages of the modification. Surface characterization ( scanning electron microscopy - SEM, Atomic Force microscopy -AFM and contact angle measurements) and image analysis was performed to obtain useful information on the changes in surface properties as a result of the modifications (Chapter 5). Coated membranes were subsequently fabricated into suitable membrane modules ready for filtration test (Appendix B shows picture of the membrane module).
4.3.2 Membrane filtration

The second aspect is the batch mode membrane filtration experiments in a submerged UF system using three water matrices (Appendix B shows the picture of the lab scale membrane filtration setup). The water matrices include; deionised water, surface water (Lake) and synthetic wastewater in MBR system. Information on operating conditions, membrane permeability
properties and samples for MOMP removal efficiency analysis were obtained at this stage (Chapters 6, 7 & 8).

4.3.3 Sample Analysis
The third aspect is the filtration sample preparation and analysis using state-of-the-art equipment and methods (section 6.2.3). Data on quantification of OMPs in filtration experiment were obtained and analysed at this stage (Chapter 6, 7, 8). Other relevant water quality parameters were also analysed.

4.4 Summary
In this chapter, the experimental programme and plan has been described, including an overview of the experimental materials and methods employed at each stage of the study. In subsequent chapters, the detailed experimental materials and methods used at each stage as well as the results would be presented and discussed accordingly.
CHAPTER 5
ULTRAFILTRATION MEMBRANE SURFACE MODIFICATION AND CHARACTERIZATION
CHAPTER 5 Ultrafiltration membrane surface modification and characterization

5.0 ULTRAFILTRATION MEMBRANE SURFACE MODIFICATION AND CHARACTERIZATION

5.1 Introduction
Surface modification of low-pressure ultrafiltration (UF) poly(vinylidene fluoride) (PVDF) hollow fibre membrane through surface coating is investigated in this research work. This chapter provides information on experimental materials and methods employed for the surface coating process as well as evaluating the stability and efficiency of the physical adsorption of the coating on the membrane surfaces. Furthermore, details of the characterization methods and results describing the effects of the coating procedure on the membrane surface properties are provided.

5.2 Experimental Methods

5.2.1 Materials
Surface modifications were conducted on commercially available ultrafiltration PVDF membranes (Hangzhou Microna Membrane Technology Co., Ltd., Hangzhou, China), supplied as hollow-fibre membranes and fabricated to suit laboratory membrane modules, with a nominal pore size of 0.02μm, and inner and outer diameters of 0.9 and 1.5 mm, respectively.

PVDF possesses outstanding properties which makes it suitable for wastewater treatment and a wide range of industrial applications. It has received great attention as a membrane material and also seen as advantageous over other commercialised polymeric materials due to its high mechanical strength, excellent chemical resistance, high hydrophobicity and thermal stability (Boributh et al., 2009; Singh et al., 2005). PVDF as a pure polymer, possesses low level of extractable; which makes it a suitable material in biomedical and bio-separation applications. It also exhibits thermodynamic compatibility with other polymers for polymer modification and fabrication into membrane with varied desired properties (Mijovic et al., 1982; Noland et al., 1971).

Several methods are employed in the preparation and fabrication of PVDF membranes which include phase inversion, use of inorganic particles as a filler or as an additive, sintering, and track etching. However, the main method used for commercial membranes is the phase inversion method mainly because of its simplicity and flexible production scales as well as lower cost of production (Finch, 1986; Mulder, 1996).
Two surface coating polymeric materials are employed in this study namely; Poly(1-phenylethene-1,2-diyl)-polystyrene and Pluronics F68 (Table 5.1). Polystyrene (weight-average molecular weight of 35000 and density of 1.06 g/mL at 25°C)

Figure 5.1 Chemical structure of (A) Polystyrene; (B) Pluronics F68; a central hydrophobic fragment of polypropylene oxide (PPO) and identical hydrophilic chains of polyethylene oxide (PEO) at both sides. For the Pluronic F68, x=75 PEO units and y=30 PPO units

5.2.1.1 **Hydrophobic Polymer - Polystyrene**

Polystyrene is a synthetic aromatic polymer made from styrene monomers. It is a thermoplastic polymer which softens when heated and can be converted into semi-finished products like films and sheets, as well as a wide range of finished items. Polystyrene possesses the following useful properties;

1. It is very chemically inert
2. It is resistant to acids and bases but is easily dissolved by many chlorinated solvents, and many aromatic hydrocarbon solvents
3. It is usually clear or transparent, also has excellent appearance and functionality mainly due to easy-processing
4. It can rigid or foamed, hard and brittle
5. Polystyrene resins are safe and have an excellent cost/performance ratio
6. It is the most widely used plastics and can be substituted for costlier polymers.
7. It is useful for the improvement of surface mechanical, wear resistance and anti-oxidant properties of other polymers such as glassy polymer films (Tsuruta et al., 2013)

5.2.1.2 Amphiphilic Polymer – Pluronics F68

Pluronics F68 is a non-ionic triblock copolymer that belongs to the family of polypropylene oxide (PPO) and polyethylene oxide (PEO) tri-block copolymers famously used in diverse pharmaceutical applications (Devi et al., 2013). Pluronics F68 consists of two hydrophilic chains of ethylene oxide chains (PEO) that sandwiched one hydrophobic propylene oxide chain (PPO) in a triblock structure (Figure 5.1, 5.2), thus resulting in an amphiphilic copolymer. The pharmaceutical application of pluronics F68 for drug delivery purposes involve its use in novel modification of the surface properties of the polymeric drug delivery system to make it compatible with the biological environment. This is essential to avoid spontaneous particle aggregation under certain physico-chemical conditions of pH, ionic strength and temperature, but also to prevent the rapid uptake of intravenously injected particulate drug carriers by the cells of the reticuloendothelial system (Santander-Ortega et al., 2006). They are fundamentally used to increase surface hydrophilicity of hydrophobic substances.

5.2.1.3 Micellization of Pluronics F68

Above a certain concentration in aqueous medium called critical micelle concentration – CMC (Allen et al., 1999), Pluronics molecules aggregate to form micelles through the process of micellization. The driving force for the micellization is the hydrophobic interactions of the PPO blocks which self-assemble into the inner core of the micelles covered by the hydrophilic corona from PEO blocks (Figure 5.2). The micelles formed have spherical morphologies with an hydrodynamic diameter range of 20 – 80 nm (Nagarajan, 1999). Polymeric micelles as a supramolecular structures i.e., self-assembling nano-constructs of amphiphilic copolymers with a core-shell structure have gathered considerable attention and have been used as versatile carriers for delivery of drugs. They have gained immense popularity owing to a host of favourable properties including their capacity to effectively solubilize a variety of poorly soluble pharmaceutical agents, excellent biocompatibility, low toxicity, high stability biological environment (Jhaveri and Torchilin, 2014). In application to removal of pollutants in water, it has a potential of entrapping and solubilizing pollutants in the waste stream (Bade and Lee, 2011;
Ojajuni et al., 2015; Puasa et al., 2011). Pollutants include; heavy metals, nutrients, organics such as phenols, o-cresol etc.

![Figure 5.2 Schematics of micellization of Pluronics F68](image)

Table 5.1 Properties of coating materials; Polystyrene and Pluronics F68 (Bogdanova and Dolzhikova, 2011)

<table>
<thead>
<tr>
<th>Material</th>
<th>Molecular mass g/mol</th>
<th>Density g/mL @ 25°C</th>
<th>CMC, M (molecule, micelle)</th>
<th>Diameter nm (molecule, micelle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>Hydrophobic</td>
<td>35000</td>
<td>--</td>
<td>18</td>
</tr>
<tr>
<td>Pluronic F68</td>
<td>Amphiphilic</td>
<td>8400</td>
<td>1.095 @ 25°C</td>
<td>20 - 80</td>
</tr>
</tbody>
</table>

4.8 x 10^{-5}
5.2.2 Surface Coating with the Polymer-Based Materials

Polystyrene coating solution of 5 g/L concentration was prepared using acetone as the solvent and allowed to shake for over 12 h at 23 °C to ensure complete dissolution and mixing of the polystyrene in the solvent. Two methods of surface coating were employed: spraying and dipping. The spraying procedure is as follows: The surfaces of plain PVDF membranes were sprayed using a hand-pressurized sprayer placed at a distance of 12−15 cm until the whole surface was completely wetted by the solution. Afterward, the solvent was allowed to dry, leaving the coated material physically adsorbed onto the surface of the membrane and forming a thin film on the surface. In the dipping procedure, raw PVDF membranes were immersed in the polystyrene solution and then allowed to dry for 2−3 h as the solvent evaporated, so that the polystyrene again formed a thin-film layer on the membrane surface (Jiang et al., 2011; Lee et al., 2007). This coating procedure terminates once the solvent has evaporated; therefore, the coating is independent of the rate of dipping but dependent on the concentration of the coating solution. This method is similar to that reported by (Lee et al., 2007) who produced multifunctional polymer coatings through the simple dip coating of objects in an aqueous solution of coating material.

Pluronics F68 coating solution of 5g/L concentration was prepared using the direct dissolution method by adding the powder to methanol as the solvent and allowed to shake for over 12 h at 23 °C to ensure complete dissolution and mixing in the solvent (Allen et al., 1999). Since concentration of the coating solution is above CMC, micelles are formed. Micelles formed through self-assembly of block polymers via hydrophobic and hydrophilic effects, electrostatic interactions, hydrogen bonding, potentially creates a supramolecular structure at the surface of the membrane with a possibility of enhancing the surface properties of the membrane as well as act as a biocontainer to capture insoluble MOMP in the aqueous medium (Jhaveri and Torchilin, 2014; Lee et al., 2005).

Only the dipping coating procedure was used for the coating the PVDF with the pluronic F68 solution as the coating material was introduced after the preliminary studies that established the advantage of dip coating compared to spray coating. The same dipping procedure described for the polystyrene coating earlier was also used for the pluronic F68 coating. Plain and coated membranes were then used for surface characterization and fabricated into membrane modules for use in filtration experiments.
The following terms will be used to annotate the different types of coating regime used in the study.

1. Plain membrane – Plain
2. Sprayed coated membrane (polystyrene) – Sprayed poly
3. Dipped coated membrane (polystyrene) – Dipped poly
4. Dipped coated membrane (pluronics F68) – Dipped pluro

5.3 Analytical methods

Membrane Surface Analysis. Scanning electron microscopy (SEM) characterization was performed to examine the membrane pore size, pore distribution, and roughness. A JEOL JSM-7100F field-emission scanning electron microscope (operating at 5 kV) equipped with an energy-dispersive X-ray detector was used. The SEM samples of plain and coated membranes were mounted on aluminium sample holders and then coated with gold before SEM analysis. Selected images from the SEM analysis were further analysed to obtain data on the pore size and pore distribution. For each type of membrane (i.e., plain, coated), an average of 20 SEM images from various locations on the membrane were analysed, and the area of each micrograph analysed was ~150 μm².

Image Analysis was performed using suitable image analysis software, namely, ImageJ, to obtain the data on the pore size and pore distribution (Kochkodan et al., 2014). Data on the thickness of coating layer was also obtained through the analysis. For the analysis of the selected SEM images, it was assumed that the representation was homogeneous for all of the membranes in individual modules.

Water Contact Angle - CA measurements by the sessile drop method using the Kruss DSA25S drop shape analyser were used to characterize the membrane surface hydrophobicity. The static contact angles were obtained immediately after deionized water had been dropped on the membrane surface. At least seven measurements were repeated at different locations on each membrane surface.

Surface morphology and roughness measurements were carried out using the Bruker Dimension Edge Atomic Force microscopy (AFM) system equipment operating in peak force tapping mode. Images from various locations on the membrane were analysed, and the area of each micrograph analysed was ~70 μm².
CHAPTER 5 Ultrafiltration membrane surface modification and characterization

5.4 Results and discussions

5.4.1 Effects of surface coating on membrane surface properties

Polystyrene as a surface coating material acts as a hydrophobic surface with a water contact angle (CA) of approximately 85° (Ducker et al., 1991). Its particles form a relatively rough surface because of their soft interface consisting of loosely bound and dangling polymers (Kajiyama et al., 1997). Furthermore, polystyrene as a hydrophobic material can provide efficient anchorage onto the hydrophobic PVDF membrane surface, as well as forming a functional coating layer (Chiag et al., 2012).

Pluronics F68 on the other hand formed micelles with spherical morphologies on the surface of the membrane (Allen et al., 1999). The coating formed impacted the surface properties of the membrane. In this experimental work, both coating materials exhibited good and stable physical adsorption on to the surface of the PVDF membrane. The effects of the various coating regimes on the pore size and distribution, hydrophobicity and morphology were found to influence the performance of the membrane.

5.4.1.1 Pore size and distribution

The changes in the surface structures of membranes after modification can be monitored through the changes in the pore size and pore size distribution in response to the surface modification (Figures 5.3 and 5.4). As can be observed, the surfaces of the membranes were affected by the coating, with the pores evidently reduced in size and number (Figure 5.3). Also, the coating material, polystyrene, is expected to stay mostly on the surface of the membrane without significant deposition into the walls of the pores because of its molecular size is 18 nm, (Ballard et al., 1973) which is close to (or greater than) the nominal pore size of the plain membrane. The same is also expected for pluronic F68 coating since the hydrodynamic diameter of micelles (20-.80nm) formed is higher than the nominal pore size of the membrane.

The image analyses showed that the plain membranes had a nominal pore size of 0.016 μm, whereas the sprayed poly, dipped poly and dipped pluro membranes had nominal pore sizes of 0.011μm, 0.013μm and 0.015μm, respectively (Table 5.2). The plain membrane showed a wider pore distribution compared to the sprayed poly and dipped poly membranes, which generally had more pores smaller than the average pore size of the plain membrane (Figure 5.5). This might indicate a prospective improvement in the rejection performance of the modified membranes by
the sieving effect because a 19−31% reduction in the nominal pore size was achieved through the modification for polystyrene. The *dipped pluro* showed a 6% reduction in nominal pore size and a relatively wide pore size distribution which had close similarity to the distribution for plain membrane.

Surface coating by dipping is the simplest way to improve the surface properties of already-prepared polymeric membranes. The coating modification occurs mainly in most cases, around the surface of the membrane, excluding the walls of the pores inside the membrane. This is due to the limited diffusion ability of the coating material into the membrane pores (Liu et al., 2011). The membrane structure is also seen from SEM images to be stable and uncompromised after the coating procedure.

### 5.4.1.2 Contact angle measurements

Polystyrene is a hydrophobic coating material, the coated surface is expected to remain hydrophobic. Contact angle (CA) measurements (Figure 5.3G-I) show an increase in hydrophobicity in the *sprayed poly* and *dipped poly* membrane compared to the plain membrane (up to 29% increase), with the latter giving higher contact angle measurements. The CA measurements for the sprayed membrane showed a slightly lower range compared to those for the dipped membrane, indicating a more uniform and homogeneous coating layer with a smoother morphology. The *dipped pluro* coating recorded a slight increase in hydrophobicity (~10% increase) compared to the plain membrane. Therefore, the polystyrene coating had more impact on the hydrophobicity compared to the pluronic F68.
Figure 5.3 (A–D) SEM images of the surfaces of (A) plain membranes and (B,C,D) membranes modified by (B) spraying, (C) dipped poly and (D) dipped pluro, all at 10000× magnification; (E–H) SEM Images of cross-sections of (E) plain membranes and (F,G,H) membranes modified by (F) spraying, (G) dipped poly and (H) dipped pluro; (I–L) Contact angle measurements by the sessile drop method of (I) plain membranes and (J,K,L) membranes modified by (J) spraying, (K) dipped poly and (L) dipped pluro
Figure 5.4 (A–D) AFM images of the surfaces of (A) plain membranes and (B,C,D) membranes modified by (B) sprayed, (C) dipped poly and (D) dipped pluro.

Figure 5.5 (A–D) Pore size distribution plot (A) plain membranes and (B,C,D) membranes modified by (B) spraying, (C) dipped poly and (D) dipped pluro.
5.4.1.3 Surface morphology and roughness

Images observed by SEM (Figure 5.3A–H) showed that a thicker coating layer was achieved with the “dipped” coating compared to the “sprayed” coating. The measured thicknesses of the coating layers were in the ranges of 0.05–2 and 6–10 μm for the sprayed and dipped membranes, respectively. AFM image (Figure 5.4) analysis was used to obtain measurements of the average roughness ($R_a$) and maximum peak-to-valley distance ($R_{\text{max}}$), all measured in micrometres (μm). $R_a$ is the arithmetic average of a set of individual measurements of a surfaces peaks and valleys recorded within the evaluation length (or area). $R_a$ gives a good general description of the height variations in the surface and it is one of the most effective surface roughness measures commonly adopted in general engineering practice. $R_{\text{max}}$ is the maximum peak to lowest valley vertical distance within a single sample length (or area). It is important to emphasize that the ($R_{\text{max}}$) is a relative indicator of surface roughness and that it does not show absolute values of height or depth of channels in the material.

There was increase in the $R_a$ of the coated membranes compared to the plain membrane. The dipped poly coating recorded the highest $R_a$ of 0.393 μm (figure 5.6). Also, the ratio of $R_{\text{max}}$ to the $R_a$ for the dipped coating was higher than that of the sprayed poly and dipped pluro membranes (figure 5.6). This implies that the dipped poly had more irregularities and higher peak heights in its surface topography. Although the membrane surface roughness increased in the coated membranes compared to the plain membranes, more irregularity in the coating thickness and surface of the active layer was observed in the dipped poly coating than the sprayed poly coating and dipped pluro, thereby increasing the number of possible sorption sites on the membrane surface for the dipped poly membranes. Physical adsorption onto the membrane surface by dipping is suitable for the formation or deposition of a functional layer that adheres to the surface of the membrane (Xi et al., 2009; Zhao et al., 2011).

Kochan et al. (2010) reported similar results for the surface modification of poly (ether sulfone) (PES) ultrafiltration membranes by polyelectrolyte using a layer-by-layer deposition technique to reduce the pore size [molecular-weight cut-off (MWCO)] of the membrane, consequently obtaining a better rejection performance by converting a membrane with an open structure into a membrane with a denser active layer. Sorption of pollutants onto the membrane surface through hydrophobic interactions/adsorption is expected to increase because the coating layer and resulting surface roughness provide more sorption sites.
Figure 5.6 Surface roughness measurements of all the membrane types; (A) Average roughness - $R_a$ and Maximum Peak-to-valley distance $R_{max}$, (B) Average Roughness against Contact Angle measurements.
5.5 Matrix of surface modification and surface properties

A matrix of the coating methods and the corresponding effects on the surface properties of the PVDF is shown on Table 5.2. The following chapters reports experimental studies of surface modified UF system applied for the removal of model organic micropollutants in three different water matrices (i.e. Deionised water, Surface water and synthetic wastewater). The different types of membranes used for the filtration experiments in water matrices is also shown (shaded) on Table 5.2. The plain membrane was used in all the filtration experiment as a base study or control. The filtration experiments for MOMPs in deionised water was done using the polystyrene coated membrane (spray poly and dipped poly). Filtration experiments on surface water (Lake water) was done using the dipped polystyrene coating (dipped poly) in comparison with dipped pluronics (dipped pluro), while in the filtration experiment for synthetic wastewater (Membrane bioreactor-MBR system), the dipped polystyrene (dipped poly) coated was used.

Table 5.2 Matrix of coating regimes against effects on surface properties. Also, showing the filtration experiments where the membrane types are used.

<table>
<thead>
<tr>
<th>Pore size &amp; Distribution (SEM)</th>
<th>Plain Membrane (Base)</th>
<th>Polystyrene coated</th>
<th>Pluronics coated (Dipped)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Sprayed</td>
<td>Dipped</td>
</tr>
<tr>
<td></td>
<td>0.016 ± 0.010</td>
<td>0.011 ± 0.012</td>
<td>0.013 ± 0.009</td>
</tr>
<tr>
<td></td>
<td>± 0.010</td>
<td>± 0.012</td>
<td>± 0.009</td>
</tr>
<tr>
<td>Surface Morphology (AFM)</td>
<td>0.0995 µm</td>
<td>0.206 µm</td>
<td>0.393 µm</td>
</tr>
<tr>
<td></td>
<td>1.173 µm</td>
<td>2.606 µm</td>
<td>4.15 µm</td>
</tr>
<tr>
<td>Contact Angle (Hydrophobicity)</td>
<td>71.93 ± 2.3</td>
<td>92.50 ± 1.6</td>
<td>96.80 ± 5.7</td>
</tr>
</tbody>
</table>

Filtration Experiments

- MOMPs in **Deionised** water matrix
- MOMPs in **Surface water matrix**
- MOMPs in **Wastewater matrix (MBR)**
5.6 Summary

Surface modification of polymeric membranes is usually performed to improve surface properties of membranes so as to enhance fouling resistance as well as improve desired and relevant removal mechanism of pollutants. Physical adsorption of hydrophobic polystyrene and amphiphilic pluronic F68 as a facile and suitable way to enhance surface characteristics of the PVDF UF membrane has been demonstrated in this chapter. Both coating materials impacted the membrane surface properties with the polystyrene material showing more impact than the polystyrene. The pluronic F68 solution at 5g/L concentrations (above CMC) formed micelles with average size larger than the plain membrane nominal pore size and was subsequently coated on the membrane surface. There was 19–31% reduction in the nominal pore size with a close range of pore size distribution for the sprayed poly and dipped poly membranes, while the dipped pluro achieved a 6% reduction in nominal pore size and pore size distribution relatively like the plain membrane. An increase in the average roughness - $R_a$ of the coated membranes compared to the plain membrane was also achieved. The dipped poly coating recorded the highest $R_a$ and $R_{max}$ of 0.393μm and 4.15 μm respectively while the $R_a$ for the sprayed poly and dipped pluro were within close range. This implies that the dipped poly membrane had more irregularities and higher peak heights in its surface topography. The dipped Poly membrane achieved the highest increase in hydrophobicity (29%) while the dipped pluro achieved a 10% increase. Correlation between the changes in surface roughness and hydrophobicity was evident in the study. Polystyrene and polymeric micelles of amphiphilic pluronic F68 was evidently deposited on the surface of the plain membrane through the dipped coating procedure to form a functional layer. The modifications on the membrane surfaces can potentially enhance their filterability and selectivity, which will be demonstrated in the preceding chapters.
CHAPTER 6

REMOVAL OF MODEL ORGANIC MICROPOLLUTANTS IN DEIONISED WATER BY SURFACE MODIFIED PVDF-UF SYSTEM
CHAPTER 6 Removal of MOMP in deionised water using surface modified PVDF membranes

6.0 REMOVAL OF MODEL ORGANIC MICROPOLLUTANTS IN DEIONISED WATER BY SURFACE MODIFIED PVDF-UF SYSTEM

6.1 Introduction

This chapter reports investigations done on surface coated ultrafiltration (UF) polyvinylidene fluoride (PVDF) hollow fibre membrane for the removal of organic micropollutants (OMPs) in deionised water. Coating of PVDF membranes with Poly (1-phenylethene-1,2-diyl) - Polystyrene solution through physical adsorption was carried out under two modes, ‘dipped’ and ‘sprayed’ as described in Chapter 5. This Chapter focuses on evaluating the filtration performance by measuring the membrane’s ability to achieve enhanced removal of model organic micropollutants (MOMP), which are commonly reported OMP in municipal waste streams; namely caffeine which has high water solubility and recalcitrant carbamazepine with relatively high hydrophobicity, in deionised water. Based on the experimental results and membrane surface characterisations, possible removal mechanism for the MOMP studied are analysed and proposed.

6.2 Experimental Methods and materials

Surface modifications were conducted on commercially available ultrafiltration PVDF membranes (Hangzhou Microna Membre, China), supplied as hollow fibre membranes and fabricated to suit the laboratory membrane modules, with nominal pore size of 0.02µm, and inner and outer diameter of 0.9mm and 1.5mm, respectively. Details of the coating experiment is discussed in Chapter 5.

MOMPs include; Carbamazepine (Carb, ≥98%purity) and Caffeine (Caf, 99%purity) were purchased from Sigma-Aldrich Ltd and used as received without further purification. The physicochemical properties of Carb and Caf are shown in Table 6.1 (Yangali-Quintanilla et al., 2010).

Table 6.1 Physicochemical Properties of Selected Model Organic Micropollutants (MOMPs)

<table>
<thead>
<tr>
<th>MOMP</th>
<th>water solubility (mg L⁻¹)</th>
<th>log Kow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caffeine (stimulant)</td>
<td>18.7 at 16 °C</td>
<td>−0.13</td>
</tr>
<tr>
<td>Carbamazepine (anticonvulsant)</td>
<td>insoluble</td>
<td>2.67</td>
</tr>
</tbody>
</table>
6.2.1 MOMP Molecular Model Analysis

The molecular weight (MW) is the most frequently used parameter in characterizing the size of molecules; however, studies have shown that MW might not give a direct measurement of the sizes of molecules (Kanani et al., 2010; Mehta and Zydney, 2005; Yangali-Quintanilla et al., 2010). This is very important for membranes because the size-exclusion mechanism is considered in solute–membrane interactions. The molecular length and width can be measured as geometric descriptors (Mehta and Zydney, 2005) that provide a good indication of the molecular size. Molecular length is the distance between the two farthest atoms, whereas molecular width and depth are measured by projecting the molecule perpendicularly onto the plane of the length axis.

Molecular volume can give transport characteristics of molecules. The geometric indicators mentioned were determined using a suitable molecular model analysis package, namely, Avogadro software, and the results were compared with those of earlier studies (Schäfer et al., 2011). Molinspiration Property Calculation Services, a web based cheminformatics tool (www.molinspiration.com), was used to obtain information on the molecular volumes of the MOMP. The molecular sizes and dimensions of the MOMP considered in this work are listed in Table 6.2. From the reported geometries, the two pollutants have almost the same widths, but the carbamazepine molecule has a larger length, depth, and volume.

Table 6.2 Molecular Properties: Size and Dimensions of Investigated MOMP

<table>
<thead>
<tr>
<th>MOMP</th>
<th>Molecular Length (nm)</th>
<th>Molecular Width, Depth (nm)</th>
<th>Molecular Volume (nm$^3$)</th>
<th>Molecular Weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caffeine</td>
<td>0.98</td>
<td>0.70, 0.18</td>
<td>0.17</td>
<td>194.19</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>1.20</td>
<td>0.73, 0.58</td>
<td>0.22</td>
<td>236.27</td>
</tr>
</tbody>
</table>

6.2.2 Ultrafiltration System

The schematics of the laboratory ultrafiltration setup is depicted in Figure 6.1. The filtration unit is a dead-end filtration setup consisting of a 10-L feed tank, a membrane module (length of approximately 220 mm and effective surface area of 34 cm$^2$), a peristaltic pump as a suction pump with a vacuum pressure gauge to measure pressure across membrane (i.e., the transmembrane pressure, TMP), and a 4-L reactor tank with the membrane module submerged in it.
Each experiment was performed with plain and modified membranes previously soaked in deionized water for 24 h to allow saturation of the dry membrane pores and surface before filtration. Stock solutions of caffeine and carbamazepine were prepared in pure methanol and ethyl acetate, respectively. Deionized water was spiked with the pollutants at concentrations of 300 and 500 μg/L and allowed to mix well. The pH in the reactor ranged from 6.7 to 7.1. The same concentration was maintained in the reactor tank and feed tank at the start of each filtration experiment with an average filtration time of 120 min. The operating parameters for filtration were examined, and the retention of pollutants and performance of the coated membranes were observed. Equation 1 shows the removal obtained as a measurement of the efficiency of the membranes

$$R = \frac{C_f - C_p}{C_f} \times 100$$  

(1)

where $R$ is the removal (%) and $C_p$ and $C_f$ are the concentrations of MOMP in the permeate and feed streams, respectively. $C_f$ is the concentration in the feed after OMP dosing at the beginning of the test, and $C_p$ is the average permeate concentration obtained after the system has reached equilibrium, which was usually after 60 min of filtration.
6.2.3 Analytical methods of water samples

Sample preparation for solid-phase extraction (SPE) was done using 6 mL, 500 mg Chromabond Easy SPE cartridges purchased from Hichrom Ltd. The extracted samples were analysed using a Perkin-Elmer Clarus 500 gas chromatograph and Clarus 560D mass spectrometer with Elite Series GC capillary column (30 m × 0.25 mm × 0.25 μm). GC conditions were as follows: For caffeine, 1 μL autosampler injection with oven conditions at 70 °C initial temperature held for 2 min and ramped to 280 °C at 15 °C/min; For carbamazepine, 1 μL autosampler injection with oven conditions at 50 °C initial temperature held for 1 min, ramped to 180 °C at 10 °C/min, held for 7 min, ramped to 220 °C at 10 °C/min, and then held for 3 min. Selected ion recording (SIR) MS scan mode with an electron ionization (EI) source was used because the samples contained single components (Yu and Wu, 2012). Each sample and calibration standards were analysed three times, and the quantification was done using respective calibration standard curves.
6.3 Results and discussions

6.3.1 Operation conditions of coated membrane system

The *dipped poly* produced about 200% increase in TMP during filtration, while the pure water permeability (PWP) decreased by 63% compared to the plain membrane, while the *sprayed poly* showed little increase in TMP and 33% decrease in PWP compared to plain membranes (Table 6.3). This is due to the effects of the coating. Average transmembrane pressure (TMP) across the membrane during filtration of synthetic wastewater is shown to be influenced by the method of coating (Figure 6.2a and 6.2b). Average TMP of 219 mBar with corresponding flux of 24 L/m²hr and PWP of 117 L/m²hrBar is shown to be reasonable compared to operating conditions of UF and NF system of similar studies and typical industrial scale water treatment application (Table 6.3). The flux was observed to be consistent throughout the filtration time depending on the type of membrane used, and no fouling was observed. However, it must be noted that the water matrix (Deionised water) and operating time (120 mins) used in this study is far from ideal situations as other constituents in feed of real surface water and wastewater could impact on the operating conditions causing significant changes in filtration process.
Figure 6.2a  Average transmembrane pressures of (A-B) plain membranes and (C–F) membranes modified by (C,D) spraying and (E,F) dipping for experiments with (A,C,E) carbamazepine and (B,D,F) caffeine
Figure 6.3b Average transmembrane pressures of (A,B) plain membranes and (C–F) membranes modified by (C,D) spraying and (E,F) dipping for experiments with (A,C,E) carbamazepine and (B,D,F) caffeine
Table 6.3  Average TMPs and Computed Fluxes for Plain, Sprayed, and Dipped Membranes during Ultrafiltration Compared to Similar Studies with Wastewater

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>PWP (L/m²·h·bar)</th>
<th>average TMP (mbar)</th>
<th>Computed flux (L/m²·h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>plain</td>
<td>317</td>
<td>76</td>
<td>24</td>
</tr>
<tr>
<td>sprayed</td>
<td>212</td>
<td>90</td>
<td>19</td>
</tr>
<tr>
<td>dipped</td>
<td>124</td>
<td>219</td>
<td>25</td>
</tr>
<tr>
<td>UF</td>
<td>70.5</td>
<td>6000</td>
<td>423</td>
</tr>
<tr>
<td>NF</td>
<td>7.6</td>
<td>30000</td>
<td>228</td>
</tr>
</tbody>
</table>

6.3.2 Removal of MOMP in deionised water filtration experiment

The performance of the coated membranes in the removal of model organic micropollutants (MOMPs) was found to be dependent on the method of surface coating, as well as the physicochemical properties and concentration of the MOMP. It was found that membranes modified by the dip coating method performed better than membranes modified by the spray-coating method, especially for carbamazepine. The percentage removals of caffeine at concentrations 300 and 500μg/L with the plain and modified membranes were less than 20% (Figure 6.3), whereas for carbamazepine, greater than 20% removal was achieved with the sprayed membrane at the higher concentration and greater than 50% removal was achieved with the dipped membrane at both concentrations (Figure 6.3). The high retention achieved by the dipped coating can be attributed to the greater number of sorption sites, smaller pore sizes, and greater surface roughness compared to the corresponding properties of the sprayed coating. UF systems are usually incapable of removing caffeine and carbamazepine at trace concentrations, as studies have shown relatively low percentage removals compared to NF/RO systems (Acero et al., 2010). This is a consequence of the molecular weights (and/or dimensions) of these compounds being smaller than the pore-size range of UF membranes. However, adsorption is reported to be the predominant
removal mechanism in UF compared to size exclusion. (Acero et al., 2012; Comerton et al., 2007; Tang et al., 2007; Yoon et al., 2006).

Figure 6.4 Removal of Caffeine and Carbamazepine in single-component filtration test by plain and modified membranes from MOMP: (a) at concentrations of 300μg/L; (b) at concentrations of 500μg/L (‘Sprayed’ and ‘Dipped’)

~72~
Correlations between the hydrophobic interactions/adsorption of a compound and its octanol/water partition coefficient (log $K_{ow}$), solubility, and membrane pure-water permeability were shown to be evident in a study by (Comerton et al., 2007). Hydrophobic interaction between OMPs and membrane surface also affects the adsorption phenomena. Hydrophobic interactions between OMPs and membrane surfaces also affect their adsorption phenomena. The hydrophobicity of an OMP, which is reflected in its octanol/water partition coefficient (log $K_{ow}$), and the hydrophobicity of the membrane surface, which can be determined by contact angle measurements (Mulder, 1996), both promote the interaction and adsorption of hydrophobic OMPs on hydrophobic membrane surfaces. Generally, compounds with relatively high hydrophilicities (log $K_{ow} > 2.5$) are expected to adsorb onto solid phases rather than being soluble in water. Hydrophobic OMPs are therefore expected to adsorb onto hydrophobic membrane surfaces as a result of hydrophobic interactions. In this study, carbamazepine has a higher log Kow value than caffeine, and coupled with the fact that the dipped membrane has a higher surface hydrophobicity (Table 3), this contributed to the observed higher removal of carbamazepine by dipped membranes. Although hydrophobic adsorption contributes to removal, it must be noted that membrane fouling can be escalated by the hydrophobicity of the membrane affecting membrane operating conditions (Yangali-Quintanilla et al., 2009).

The size-exclusion mechanism is mostly observed with uncharged (neutral) OMPs, as studies have shown correlations between the rejection of uncharged OMPs and their molecular weights, volumes, and/or widths (Kimura et al., 2003a; Ozaki and Li, 2002). A suggested explanation for the trends observed in this study is that caffeine, with smaller molecular dimensions and volume and higher water solubility than carbamazepine (Tables 6.1 and 6.2), is likely to pass through the coated membranes. Although molecular lengths (and/or widths) of both pollutants are smaller than the nominal pore sizes of the coated membranes, a comparison between the molecular lengths of the two pollutants and the pore size distributions of the coated membranes suggests that carbamazepine, with a molecular length of 1.2 nm (0.0012μm), is likely to be retained more than caffeine, as supported by the filtration results demonstrating a higher removal of carbamazepine. Also, the shapes of the pores might have been altered by the surface modifications, which could also affect the removal phenomena. For example, pore geometry can affect the selectivity of UF membranes, with slit-shaped pores being reported to perform better than cylindrical pores (Kanani et al., 2010). However, pore geometry was not studied in this work.
In general, a comparison indicates that the percentage removals of carbamazepine are greater than those of caffeine for all membrane types at both concentrations, except for the plain membrane at 500μg/L concentration, for which the percentage removals are fairly similar. The molecular shapes and volumes (Table 6.2) of the pollutants might have also influenced their removal by size exclusion. Both pollutants are uncharged, implying that charged interactions between the compounds and the charged coated membrane surfaces are minimal. For example, using “loose” NF membranes to filter pharmaceuticals including carbamazepine, (Yangali-Quintanilla et al., 2009); (Nghiem et al., 2006), reported poor and variable OMP removal rates and concluded that changes in solution chemistry parameters such as pH have a significant influence on removal rates by affecting the charges of the targeted compounds and the ionic strengths of the organic micropollutants. It must also be emphasized that the synthetic waste streams used were deionized water containing only a single pollutant at a time. The results might be significantly different in a real wastewater matrix. Other water matrixes will be studied in future work. A recent relevant study in a nanofiltration laboratory test using membranes with a pore size of 0.002 μm to filter selected pollutants including carbamazepine spiked at trace concentrations into water-treatment-plant effluent was able to achieve only 31-39% removal (Vergili, 2013). This was due to the effects of electrostatic interactions based on the solution chemistry, the charges on the pollutants, and the surface charges of the membranes (Vergili, 2013).

A plot of percentage removal against PWP (Figure 6.5) shows the effect of PWP on the removal efficiency. The plain membrane with the highest PWP achieved the lowest overall removals of the MOMPs, whereas the dip-coated membrane with a significantly lower PWP achieved higher removals of hydrophobic carbamazepine at both concentrations. This phenomenon has posed questions for researchers trying to understand the impacts of membrane microstructure (or pore characteristics) on the trade-off between selectivity and permeability for UF membranes. (Kanani et al., 2010; Mehta and Zydney, 2005). Membrane with smaller pores are likely to have lower permeability and better selectivity and vice versa. The major challenge will be how to achieve a balance between these two crucial parameters for membrane performance.
CHAPTER 6 Removal of MOMP in deionised water using surface modified PVDF membranes

6.3.3 Possible removal mechanism by modified membrane surface

The removal of organic micropollutants (OMP) is governed by different parameters based on the membrane characteristics, aqueous media/solute characteristics, operating conditions, membrane fouling and OMP characteristics (Chon et al., 2012; Nghiem and Hawkes, 2007b; Tadkaew et al., 2011; Yangali-Quintanilla et al., 2010), but generally, membranes are designed to work as physical barriers (semipermeable) that reject components greater than the pore size while allowing water to pass through. However, studies have shown that other significant physicochemical phenomena occur during membrane processes, with sorption being considered one of the major phenomena contributing to the removal of pollutants in membrane processes (Comerton et al., 2007; Schäfer et al., 2011).

Removal mechanisms such as size exclusion, charge interactions, and hydrophobic interactions/adsorption and fouling mechanisms of membranes have been altered through various surface modification methods (Liu et al., 2011; Nady et al., 2011; Rana et al., 2014; Xi et al., 2009; Zhao et al., 2011; Zhu et al., 2013). The surfaces of loose UF membranes have also been modified.

Figure 6.5 Percentage removal versus membrane PWP (plain, 317 L/m$^2$·h·bar; sprayed, 212 L/m$^2$·h·bar; and dipped, 124 L/m$^2$·h·bar).
to enhance selectivity by making the pore sizes smaller after modification and/or adding charged coating materials to improve selectivity by charge repulsion (Kochan et al., 2010; Rana et al., 2014). In this study, the coated surfaces have properties suitable for promoting hydrophobic interactions/adsorption of hydrophobic pollutants as well as rejection by size exclusion (Fig. 6.5). Sorption of pollutants to the membrane surface through hydrophobic interaction/adsorption is expected since coating layer and resulting rough morphology provides more sorption sites (Acero et al., 2010; Kimura et al., 2003b; Nghiem et al., 2009; Ojajuni et al., 2015; Schäfer et al., 2011). Although, Polystyrene can be used as a surface charge regulator and is mostly charged in aqueous solutions (Vinogradova et al., 2001); the MOMP studied in this work are both uncharged in deionised water (Acero et al., 2010; Vergili, 2013), so charge interaction between the surface of the coated membrane and the MOMP are not expected to contribute to their removal in the filtration tests.
Figure 6.6 (A) Representation of membrane surface coated by polystyrene showing hydrophobic anchorage. (B) Schematic representation of the possible removal mechanisms of the coated membranes.
6.4 Summary

Filtration experiments’ results show an overall better removal of the MOMPs by the coated membranes compared with plain membranes. The performance of the coated membrane in the rejection of model organic micropollutants, caffeine and carbamazepine spiked in deionised water (at 300μg/L and 500 μg/L), correlated with the coating methods used. *Dipped poly* membrane showed a better removal of recalcitrant hydrophobic carbamazepine compared to the *sprayed poly* membrane; while for both methods of coating, removal of caffeine was relatively insignificant. The percentage removals of caffeine at concentrations 300 and 500μg/L with the plain and modified membranes were less than 20%, whereas for carbamazepine, greater than 20% removal was achieved with the sprayed membrane at the higher concentration and greater than 50% removal was achieved with the dipped membrane at both concentrations. Hydrophobic interactions/adsorption and size exclusion are suggested to contribute to the removal by the coated membranes because carbamazepine, with a larger molecular size and volume and a higher octanol/water partition coefficient (log K_{ow}) exhibited higher removal rates, especially at higher concentrations. Charge interaction is not expected to occur as both MOMPs are uncharged in DI water. Effectively, the coated UF membranes exhibited some NF characteristics in terms of the removal of trace organic micropollutants without any significant corresponding change in operating conditions that the coating might have impacted. The coating layer potentially enhanced reduction of pore size with resulting effect on membrane permeability and providing more sites for possible hydrophobic interaction.

The TMP during the filtration of the MOMPs increased from 76 to 90 and 219 mbar for plain, sprayed, and dipped membranes, respectively. Similarly, a slight change in flux was observed from 24 to 19 and 25 L/m²·h·bar for plain, *sprayed poly*, and *dipped poly* membranes, respectively. The membrane PWP was impacted by surface coating with the *dipped poly membrane* recording more than 50% reduction in PWP compared to the plain membrane. It is therefore suggested that physical adsorption of functional polymers is a simple and efficient way to modify the surface of polymeric membranes for water filtration application.
CHAPTER 7
REMOVAL OF MODEL ORGANIC MICROPOLLUTANTS IN SURFACE WATER MATRIX BY SURFACE MODIFIED PVDF-UF SYSTEM
7.0 REMOVAL OF MODEL ORGANIC MICROPOLLUTANTS IN SURFACE WATER MATRIX BY SURFACE MODIFIED PVDF-UF SYSTEM

7.1 Introduction

In Chapter 6, experimental work to investigate the performance of Polystyrene surface coated ultrafiltration (UF) polyvinylidene fluoride (PVDF) hollow fibre membrane for the removal of organic micropollutants (OMPs) in deionised water matrix was carried out. In this chapter, similar experimental work is reported, but introducing a new coating material and using a mixed component of MOMPs in surface (lake) water matrix. Dip coated PVDF membranes using Poly (1-phenylethene-1,2-diyl) - polystyrene solution and pluronic F68 solution through physical adsorption carried out as described in Chapter 5, were employed in the experimental work. This chapter focuses on evaluating and comparing the MOMPs removal efficiency for the two different dip coated membranes using the two varied coating materials. Based on the experimental results and membrane surface characterizations of the two coated membrane types, possible removal mechanisms for the MOMPs spiked in surface water are analysed and proposed.

7.2 Experimental Methods and Materials

Surface modifications were conducted on commercially available ultrafiltration PVDF membranes (Hangzhou Microna Membrane, China), supplied as hollow fibre membranes and fabricated to suit the laboratory membrane modules, with nominal pore size of 0.02µm, and inner and outer diameter of 0.9mm and 1.5mm, respectively. Details of the coating experiment is discussed in Chapter 5.

The same MOMPs; Carbamazepine (Carb, ≥98%purity) and Caffeine (Caf, 99%purity) described in chapter 6 were used. Information on chemical properties and molecular structure were also discussed in the chapter. Figure 7.1 shows the chemical structure of the MOMPs.
7.2.1 Water Quality Characterization

Basic water quality characterisation was done using the parameters shown in Table 7.1. The parameters were used to monitor the membrane system performance in the filtration experiment. The raw water sample was sourced fresh from a local lake and characterisation experiment was done before every filtration experiment. Turbidity measurements was done using the Cole-palmer turbidity meter; pH and temperature were measured using the Hanna HI 2211 pH and ORP Benchtop Meter, conductivity was measured using the conductivity meter. At least three measurements were carried out for each sample before filtration experiments. Faecal coliform count was carried out using the USEPA membrane filtration method where 1ml, 10ml and 100ml
sample volume passes through a 0.45-micron membrane filter to retain the bacteria present. The filter is placed on an absorbent pad (in a petri dish) saturated with a culture medium - Lauryl sulphate broth. The petri dish containing the filter and pad is incubated, upside down, at 30°C initially for 2 hours and subsequently at 44°C for 16hrs. After incubation, the colonies that have grown are identified and counted using a low-power microscope. Six repeat measurements including blanks were used for each water sample.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity</td>
<td>NTU</td>
<td>25-30</td>
</tr>
<tr>
<td>Conductivity</td>
<td>μS</td>
<td>400-550</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>6.5-8.5</td>
</tr>
<tr>
<td>Faecal Coliform</td>
<td>Counts/100ml</td>
<td>500-700</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>12.1-13.0</td>
</tr>
</tbody>
</table>

7.2.2 Ultrafiltration System

The schematics of the laboratory ultrafiltration setup is depicted in Figure 6.1. The filtration unit is a dead-end filtration setup consisting of a 10-L feed tank, a membrane module (length of approximately 220 mm and effective surface area of 34 cm$^2$), a peristaltic pump as a suction pump with a vacuum pressure gauge to measure pressure across membrane (i.e., the transmembrane pressure, TMP), and a 4-L reactor tank with the membrane module submerged in it.

Each experiment was performed with plain and modified membranes previously soaked in deionized water for 24 h to allow saturation of the dry membrane pores and surface before filtration. Stock solutions of caffeine and carbamazepine were prepared in pure methanol as a mixed component of pollutants.

Lake water was spiked with the pollutants at concentrations of 1000 μg/L and allowed to mix well. The pH in the reactor ranged from 6.5 to 8.5. The same concentration was maintained in the reactor tank and feed tank at the start of each filtration experiment with an average filtration time of 5 hours. The operating parameters for filtration were examined, and the retention of pollutants and
performance of the coated membranes were observed. Equation 1 shows the removal obtained as a measurement of the efficiency of the membranes.

\[ R = \frac{C_f - C_p}{C_f} \times 100 \]  

Where \( R \) is the removal (%) and \( C_p \) and \( C_f \) are the concentrations of MOMP in the permeate and feed streams, respectively. \( C_f \) is the concentration in the feed after OMP dosing at the beginning of the test, and \( C_p \) is the average permeate concentration obtained after the system has reached equilibrium, which was usually after 60 min of filtration.

7.2.3 Analytical methods of water samples
Sample preparation for solid-phase extraction (SPE) was done using 6 mL, 500 mg Chromabond Easy SPE cartridges purchased from Hichrom Ltd. The extracted samples were analyzed using a Perkin-Elmer Clarus 500 gas chromatogaph and Clarus 560D mass spectrometer with Elite Series GC capillary column (30 m × 0.25 mm × 0.25 μm). GC conditions were as follows: 1 μL autosampler injection with oven conditions at 50 °C initial temperature held for 1 min, ramped to 190 °C at 15 °C/min, held for 5 min, ramped to 235 °C at 10 °C/min, held for 1 min and then ramped to 250 at 10°C/min. Selected ion recording (SIR) MS scan mode with an electron ionization (EI) source was used (Yu and Wu, 2012). Each sample were analysed three times, and the quantification was done accordingly. Figure 7.2 show the chromatograph obtained.
7.3 Results and discussions

7.3.1 Operation conditions of coated membrane system

The *dipped poly* and *dipped pluro* produced a 90% and 50% increase in TMP during lake water filtration respectively, while the pure water permeability (PWP) of dipped poly membrane decreased by 63% compared to the plain membrane (as earlier shown in chapter 6), and the dipped pluro membrane showed 33% decrease in PWP compared to plain membranes (Table 7.2). The increase in TMP during lake water filtration is due to the effects of the coating and the characteristics of the feed. Average transmembrane pressure (TMP) across the membrane is observed to be consistent with no significant or sudden change during filtration of the OMP-lake water matrix. The flux was observed to be consistent throughout the filtration time depending on the type of membrane used, Although fouling was observed but there were no significant impacts on the operating condition for the duration of filtration experiment (4hours). PWP comparison between plain, *dipped poly* and *dipped pluro* membrane shows the coating material properties could influence the permeability of the surface modified membrane. Generally, the hydrophobic polystyrene coating impacted more on the permeability of the plain membrane.

Figure 7.2 Chromatograph obtained showing caffeine and carbamazepine peaks
Table 7.2 Average TMPs and Computed Fluxes for Plain, Dipped poly, and Dipped pluro Membranes during Ultrafiltration

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>PWP (L/m²·h·bar)</th>
<th>average TMP (mbar)</th>
<th>Computed flux (L/m²·h)</th>
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<tbody>
<tr>
<td>plain</td>
<td>317</td>
<td>76</td>
<td>24</td>
</tr>
<tr>
<td>dipped poly</td>
<td>124</td>
<td>237</td>
<td>24</td>
</tr>
<tr>
<td>dipped pluro</td>
<td>252</td>
<td>197</td>
<td>21</td>
</tr>
</tbody>
</table>

Figure 7.3 shows a comparison of the changes in the TMP and Flux for the plain and dipped poly membrane for the different water matrices studied. The ratio of the effect of coating of the membrane on the TMP and the Flux was observed to be different in the water matrices with the DI water showing a wider range in the changes. The high TMP value for the plain membrane in lake water filtration compared to the value in the DI water filtration may influenced by the feed solution characteristics (especially the turbidity).

Figure 7.3 TMP and Flux of plain and dipped poly membrane filtration in DI water and lake water matrix
7.3.2 Effluent Water Quality

The UF system performed efficiently in producing quality effluent from the filtration experiment. Turbidity dropped from 28 NTU in raw water effluent to that an average of 1 NTU in the *dipped poly* and *dipped pluro* membranes while the plain membrane recorded an average of 4 NTU (Figure 7.4). The pH did not change significantly, as the pH for raw and effluent water sample was recorded to be within the range of 6.5 -7.2. Conductivity was also consistent within a close range of 450 – 550 μS. Faecal coliform counts for the treated effluent was reduced for all the membrane types with the coated membranes showing lower values of 100 counts/100ml. This value is not acceptable for drinking water. However, it must be noted that drinking water supplies are usually dosed with disinfectants to remove all pathogenic pollutants.
Figure 7.4  Water quality for raw water sample, effluent from filtration and tap water.
Removal of MOMP in Lake water filtration experiment

The performance of the coated membranes in the removal of model organic micropollutants (MOMPs) was found to be dependent on the coating material, as well as influenced by the feed water characteristics and concentration of the MOMP. It was found that dipped pluro membranes performed better than dipped poly membranes for both caffeine and for carbamazepine. The percentage removals of caffeine at concentrations of 1000μg/L with the plain and modified membranes was more than 60% (Figure 7.5), whereas for carbamazepine, lower than 40% removal for plain membranes and greater than 60% removal was achieved with the modified membranes. The high retention achieved by the dipped coating can be attributed to the greater number of sorption sites, smaller pore sizes, and greater surface roughness compared to the corresponding properties of the plain membranes. Generally, the dipped pluro membrane performed better than dipped poly in the removal of the two MOMPs.

As earlier established in the previous chapter, correlations between the hydrophobic interactions/adsorption of a compound and its octanol/water partition coefficient (log Kow), solubility, and membrane pure-water permeability were shown to be evident in recent studies (Comerton et al., 2007). Hydrophobic interactions between OMPs and membrane surfaces also affect their adsorption phenomena. The hydrophobicity of an OMP, which is reflected in its octanol/water partition coefficient (log Kow), and the hydrophobicity of the membrane surface, which can be determined by contact angle measurements (Mulder, 1996), both promote the interaction and adsorption of hydrophobic OMPs on hydrophobic membrane surfaces. Generally, compounds with relatively high hydrophobicities (log Kow > 2.5) are expected to adsorb onto solid phases rather than being soluble in water. Hydrophobic OMPs are therefore expected to adsorb onto hydrophobic membrane surfaces as a result of hydrophobic interactions.

On the other hand, characteristics of the aqueous medium or feed stream can impact on the performance of the filtration system. Solution chemistry especially pH has effect on the removal mechanism and overall removal because certain characteristics (such as acid dissociation constant pKa) of OMP in the feed solution could change significantly with change in pH. Nghiem and Hawkes (2007b), while using ‘loose’ NF to filter pharmaceuticals (Sulfamethoxazole, carbamazepine, and Ibuprofen), reported poor and variable OMP removal rates and concluded that rejection of OMP was greatly influenced by change in feed solution pH, which affects charges.
of targeted compounds, and the ionic strength of the OMP. This trend is also reported in other studies (Braeken and Van der Bruggen, 2009; Kim et al., 2005).

In this experiment, carbamazepine has a higher log $K_{ow}$ value, and coupled with the fact that the dipped poly membrane has a higher surface hydrophobicity (section 5.), this contributed to the observed high removal of carbamazepine by dipped poly membrane compared to the plain. However, dipped pluro membrane which has a relatively lower surface hydrophobicity recorded higher removal rates. This may be attributed to the activities of the Micelles in solubilizing the water insoluble carbamazepine molecules hereby enhancing its removal. Organic compounds can be solubilized into micelle interior and the size of micelles ($\sim$ 80nm) with contaminant is enough to be rejected effectively by dipped pluro membranes (Fillipi et al., 1999; Lee et al., 2005).

Caffeine was better removed by the dipped poly and dipped pluro membranes and it recorded a higher removal rates compared to carbamazepine. This is opposed to the results recorded with DI water matrix (Chapter 6). The presence of dissolved and suspended particulate matter as well as the feed solution characteristics may have enhanced the removal of caffeine. As studies show that the presence of humic acid from organic matter retained on surface and pores of membrane could also increase adsorption activities by changing the membrane surface characteristics and pore size, since membrane surface morphology, roughness, active layer thickness and pore size contribute significantly to adsorption effects (Nghiem and Hawkes, 2009; Schäfer et al., 2011). The presence of humic acid in feed solution for instance enhanced the removal of OMPs as shown by De Munari et al. (2013), where removal of pesticides endosulfane with MW less than MWCO of NF membranes increased with presence of humic acid in feed solution.
Figure 7.5 Removal of Caffeine and Carbamazepine in single-component filtration test by plain and modified membranes from MOMP: (a) at concentrations of 300μg/L; (b) at concentrations of 500μg/L (‘Sprayed’ and ‘Dipped’)

~ 90 ~
7.3.4 Possible removal mechanism by modified membrane surface

Generally, membranes are designed to work as physical barriers (semipermeable) that reject components greater than the pore size while allowing water to pass through. However, other significant physicochemical phenomena occur during membrane processes, with sorption and charge interaction being considered as major phenomena contributing to the removal of pollutants in membrane processes (Comerton et al., 2007; Schäfer et al., 2011). In this study, the coated surfaces have properties suitable for promoting hydrophobic interactions/adsorption of hydrophobic pollutants as well as rejection by size exclusion. Sorption of pollutants to the membrane surface through hydrophobic interaction/adsorption is expected since coating layer and resulting rough morphology provides more sorption sites (Acero et al., 2010; Kimura et al., 2003b; Nghiem et al., 2009; Ojajuni et al., 2015; Schäfer et al., 2011). Adsorption site on membrane surfaces is relatively low; however, larger pore sizes (MF, UF) tend to record higher adsorption than smaller pore sizes (Tang et al., 2007).

A plot of percentage removal against PWP (Figure 7.6) shows the relationship between the PWP and the removal efficiency. The plain membrane with the highest PWP achieved the lowest overall removals of the MOMPs, whereas the dipped-coated membranes with a significantly lower PWP achieved higher removals of both MOMPs. There seems to be a consistent correlation between the PWP and the removal efficiency of the two compounds with the lines showing similar patterns. The dipped Pluro with lower PWP compared to dipped poly membranes recorded higher removal rates for both MOMPs, this is not as expected. This simply suggest that other phenomena may have come to play to enhance the removal efficiency rather than intrinsic permeability properties of the modified membrane. It is appropriate to suggest that the micellization effect on the surface and near surface of the dipped pluro membrane may have enhanced its performance in attaining higher removal rates. In comparison to results shown for removals in previous chapter using DI water matrix and lower concentrations of MOMPs, removal rates for the plain and dipped pluro membranes for both MOMPs in this experiment show a better similarity i.e., high removal rates for dipped poly membrane with lower PWP value and low removal rates for plain membrane with high PWP value for both MOMPs at 1000 μg/L concentration. This suggests that the nature feed water matrix and concentration of MOMP could impact on the performance or selectivity of membranes even with unchanged permeability properties.
Figure 7.6 Percentage removal versus membrane PWP (plain, 317 L/m²·h·bar; dipped poly, 212 L/m²·h·bar; and dipped pluro, 124 L/m²·h·bar).

Micellar enhanced ultrafiltration is reported to be an attractive process to separate the multivalent ions or low molecular weight organics from aqueous phase (Bade and Lee, 2011; Puasa et al., 2011). Metal ions bind to the charged surface of micelles by electrostatic interaction while organic solutes are solubilized into micelle interior. The size of micelles with contaminant is enough to be rejected effectively by ultrafiltration (Lee et al., 2005). This higher removal efficiency can be
explained by building up the surfactant gel layer near the membrane surface (Fillipi et al., 1999; Lee et al., 2005).

7.4 Summary

The performance of the coated membrane in the rejection of mixed component of MOMPs, caffeine and carbamazepine spiked in surface water (at 1000 µg/L), correlated with the coating methods used and was influenced by the colloidal and particulate matter in the water matrix. The average turbidity of effluents for the coated membranes was 1NTU, indicating a good water quality, although the faecal coliform counts were higher than the acceptable limits for drinking water, which could be as a result of contamination within the effluent pipes as no disinfection was used in the experiment. Generally, the removal of the MOMPs was reasonably higher in the surface water matrix compared to the DI water matrix. Dipped pluro membrane showed a better removal of caffeine (82%) and carbamazepine (78%) compared to the dipped poly membrane (caffeine - 76%, carbarmazepine – 74%); and for both materials of coating, a higher percentage removal of caffeine was attained. Hydrophobic interactions/adsorption and size exclusion are suggested to contribute to the removal by the coated membranes as carbamazepine, with a larger molecular size and volume and a higher octanol/water partition coefficient (log $K_{ow}$) attained reasonable removal rates. Whereas, high percentage removal of caffeine in all the membrane types may be attributed to its sorption of caffeine onto the colloidal and particulate matter present in the feed water. Higher percentage removal by the dipped pluro is attributed to the activity of pluronic micelles in solubilising the MOMPs (especially hydrophobic carbamazepine) in its core. Long and continuous operation of the dipped pluro membrane may cause the coating material to wear off into the aqueous media and change the surface properties of the modified membrane. This may be a limitation to the use of pluronics F68 alone as a suitable coating material.
CHAPTER 8

PERFORMANCE EVALUATION OF MBR SYSTEM FOR REMOVAL OF MOMPs
8.0 PERFORMANCE EVALUATION OF MBR SYSTEM FOR REMOVAL OF MOMPS

8.1 Introduction
Membrane Bioreactor - MBR systems are growing in popularity for virtually all wastewater treatment applications because they offer many advantages over conventional wastewater treatment plants such as consistently high quality effluent with low turbidity, low bacterial counts, while using fewer chemicals than conventional wastewater treatment plants. MBR is a biological process system that combines secondary and tertiary treatment in conventional activated sludge system using a membrane filtration process. The filtrate quality, in many instances, is suitable for feeding directly into an Reverse Osmosis process. MBRs were developed to overcome the limitations of activated sludge process which is mainly associated with poor biomass separation. The separation ability of membrane technology to separate biomass flocs and colloidal particles is exploited in MBR systems. An additional advantage of an MBR system is its compact footprint. Two major process configuration is usually used namely; side stream and immersed/submerged MBRs. Immersed MBRs are generally less energy-intensive than submerged MBRs. In this study, a laboratory scale submerged MBR systems with surface modified membranes has been designed to treat synthetic wastewater spiked with MOMPs at varied concentrations. The removal efficiency and mechanism of the system in treating the MOMPs were investigated and reported. Comparison between MBRs based on plain and coated membranes was done. Fouling phenomena is a very important factor in MBR systems and its influence on removal of MOMPs is considered, however, detail study on fouling process and mechanism is not within the scope of this investigation.

8.2 Experimental Methods and materials
Surface modifications were conducted on commercially available ultrafiltration PVDF membranes (Hangzhou Microna Membrane, China), supplied as hollow fibre membranes and fabricated to suit the laboratory membrane modules, with nominal pore size of 0.02µm, and inner and outer diameter of 0.9mm and 1.5mm, respectively. Details of the coating experiment is discussed in Chapter 5.

The same MOMPs; Carbamazepine (Carb, ≥98%purity) and Caffeine (Caf, 99%purity) described in chapter 6 were used. Information on chemical properties and molecular structure were also discussed in the chapter.
8.2.1 MBR System

Two identical (Plain membrane and Dipped Poly membrane) lab-scale MBR for BOD, COD and MOMP removal was built consisting of a membrane module (length of approximately 220 mm and effective surface area of 34 cm$^2$), a peristaltic pump as a suction pump with and a reactor of 2-L working volume with the membrane module submerged in it. The permeate stream was driven by the suction pump while the feed was manually done based on the designed flow rate. Aeration was supplied into the system using an electric air pump within the range of 0.5 – 1 L/min rates to keep the system sufficiently aerated and mixed. The following system operating conditions were used; Solids retention time (SRT) - 24days, hydraulic retention time of – 48h, Influent flow rate – 1L/day, effluent flow rate – 0.9L/day, sludge flow rate – 0.083L/day, Mixed Liquor Suspended Solids (MLSS) concentration – 2.50g/L. the system was operated for a total of 85 days with the first 35 days of stabilization of the MBR.

8.2.2 Synthetic waste water characterization

A simple synthetic waste water with chemical oxygen demand – COD of 265mg/L was spiked with a mixed component of MOMPs- caffeine and carbamazepine was used synthetic wastewater. Stock solutions of MOMPs at 100mg/L was prepared in pure methanol and kept in a freezer. The stock solution was added to the added to the wastewater to obtain initial concentration of 2µg/L with increment to a stable concentration of 300µg/L over a period of 35 days to allow for stabilization.

8.2.3 Analytical methods of water samples

Samples from the influent, supernatant in reactors (Reactor 1 Dipped Poly membrane MBR –and Reactor 2 – Plain membrane MBR), Effluent from the two reactors twice every week with the averages of the quality and operating parameters recorded on a weekly basis. Sampling and measurements were done in at least triplicates.

8.2.3.1 Physical parameters

The turbidity of water samples from the reactors’ supernatants and the effluent was monitored to see the effectiveness of the filtration performance of the MBR. The dissolved oxygen in the reactors was also monitored on a weekly basis.
8.2.3.2 Chemical Oxygen Demand (COD) analytical method

COD was measured using the Hach’s Untied State Environment Protection Agency (USEPA) method. The ready-to-use reagents for COD with a high range of 0-1500 mg/L and low range of 0-150 mg/L testing contain sulphuric acid, mercury sulphate and chromium trioxide to promote the oxidation of organic compounds. The oxygen digestion is carried out in COD Reactor (purchased from Hach) at a temperature of 150°C for two hours incubation. After that, the COD of each sample can be read off using Hach’s DR2800.

8.2.3.3 MOMPs Analytical method

Sample preparation for solid-phase extraction (SPE) was done using 6 mL, 500 mg Chromabond Easy SPE cartridges purchased from Hichrom Ltd. The extracted samples were analyzed using a Perkin-Elmer Clarus 500 gas chromatogaph and Clarus 560D mass spectrometer with Elite Series GC capillary column (30 m × 0.25 mm × 0.25 μm). GC conditions were as follows: For caffeine, 1 μL autosampler injection with oven conditions at 70 °C initial temperature held for 2 min and ramped to 280 °C at 15 °C/min; For carbamazepine, 1 μL autosampler injection with oven conditions at 50 °C initial temperature held for 1 min, ramped to 180 °C at 10 °C/min, held for 7 min, ramped to 220 °C at 10 °C/min, and then held for 3 min. Selected ion recording (SIR) MS scan mode with an electron ionization (EI) source was used because the samples contained single components (Yu and Wu, 2012). Each sample and calibration standards were analysed three times, and the quantification was done using respective calibration standard curves. The detection limits for caffeine and carbamazepine were 10 µg/L and 8µg/L respectively. The sampling and analysis was done only for a duration of 33days after the stabilization period. This is due to a technical problem with the GCMS.

8.3 Results and discussions

8.3.1 Effluent Water Quality

The turbidity, COD and MOMPs concentration measurements were used as parameters to monitor the water quality in the reactors tank and the effluent from the MBR systems. The turbidity readings of the supernatant in the reactors ranged between 25 – 210 NTU with the Reactor 2 membrane showing lower turbidity readings. An average of 125.2 and 70 NTU was observed in Reactor 1 and reactor 2 throughout the period of the study respectively. The effluent turbidity readings ranged between 1 – 7 NTU for the MBRs. Generally, the dipped poly MBR system recorded a better effluent quality with regards to the turbidity with an average of 2.2 NTU. Figure
8.1 shows turbidity of effluent and supernatants of the two reactors throughout the duration of the study. The pH values for in the reactor supernatants and effluent from the MBR were consistently ranged between 6-9.

![Turbidity chart]

Figure 8.1 Turbidity of effluent and supernatants of the two reactors

8.3.2 COD removal comparison

The COD readings in the supernatants of the reactors showed similar patterns (Figure 8.2). Reactor 2 recorded higher values of COD and at some point, it was higher than the influent COD value (266 mg/L). The average percentage removal of COD for the two reactors was <65% with the lowest COD value of 19.44mg/L recorded by reactor 1. Generally, the COD removal by biodegradation was observed to be efficient since the average COD values recorded is within the acceptable limits (125 mg/L) for discharge into surface water (Directive 91/271/ECC, 1999). The Effluent quality for the two MBR system recorded average values below 20mg/L and percentage removal up to 92% (Figure 8.2, 8.3, 8.4). The Dipped Poly MBR performed slightly better in
removing COD with an average effluent COD value of 12.14mg/L. MBR systems are capable of attaining lower COD values depending on the operating conditions and the characteristics or type of the membranes used in the system.

Figure 8.2 COD readings in reactors and synthetic wastewater feed.
Figure 8.3 COD readings of effluent and synthetic wastewater feed

Figure 8.4 COD Percentage removal
8.3.3 MOMP removal comparison for membrane types

8.3.3.1 Caffeine Removal

The concentration of caffeine in the reactors (Figure 8.5) after the system stabilised ranged between 55-125µg/L with the reactor 1 and reactor 2 recording an average of 91µg/L and 99µg/L respectively during the period of sample analysis. The values started to decline slowly 24 days after the stabilization period with the reactor 1 recording the lowest value of caffeine concentration – 58µg/L in the reactor. Percentage removals of caffeine in the reactor (dipped poly) and (plain) reactor 2 were within a close range, there were 70% and 67% respectively (Figure 8.7). The biodegradation of caffeine in the two reactors were similar as shown by the percentage removal results.

The concentration of caffeine in the effluents (Figure 8.6) for the Dipped poly MBR and for the plain MBR ranged between 50-112µg/L with average concentrations of 28µg/L and 81µg/L respectively during the period of sample analysis. The plain MBR recorded slightly lower values I the effluent concentrations compared to the concentration detected in its reactor tank – reactor 2. The Dipped poly membrane performed better than the plain membrane by attaining percentage removal of 91% while the plain membrane recorded 73% removal. It can be suggested that the surface modification of the membrane enhanced its performance in the MBR system since there were significant difference in the percentage removals for the effluents while the percentage removals for the reactors were similar (Figure 6.7).
Figure 8.5 Caffeine concentration in reactors

Figure 8.6 Caffeine effluent concentrations
Figure 8.7 Caffeine Percentage removal
8.3.3.2 Carbamazepine removal

The concentration of carbamazepine in the reactors (Figure 8.8) after the system stabilised ranged between 135-240µg/L with the reactor 1 and reactor 2 recording an average of 175µg/L and 162µg/L respectively during the period of sample analysis. Percentage removals of carbamazepine in the reactor (dipped poly) and reactor 2 (plain) were relatively low and within close range (41% and 46% respectively) (Figure 8.10). The biodegradation of carbamazepine in the two reactors were lower than that of caffeine as shown by the percentage removal results.

The concentration of carbamazepine in the effluents (Figure 8.9) for the Dipped poly MBR and for the plain MBR ranged between 70-180µg/L with average concentrations of 101µg/L and 114µg/L respectively during the period of sample analysis. The dipped poly membrane performed slightly better than the plain membrane by attaining percentage removal of 66% while the plain membrane recorded 62% removal. Both MBR systems recorded closely similar trends in a removal of carbamazepine by biodegradation and membrane filtration especially within the last 10 days of sampling. The performance of the dipped poly compared to the plain membrane was not significant for the removal of carbamazepine in the MBR system. (Figure 8.10).
Figure 8.8 Carbamazepine concentrations in reactors

Figure 8.9 Carbamazepine effluent concentrations
Figure 8.10 Carbamazepine Percentage removal
8.3.4 Computed flux during operation conditions of MBR system

The transmembrane pressure of both MBR systems was kept within 0.1 - 0.3 bar and the flux for each filtration is computed plotted as shown in figure 8.11. After day 13, the flux decline sharply below 10 L/hr/m$^2$ to less than 6 L/hr/m$^2$ after day 24 in both systems. This period coincides with the period were COD reading in the reactors recorded max values. The flux started to stabilise after day 32 with the dipped poly MBR system showing more decline in flux. The decline in flux is associated with the build-up of organic matter and biofilm on the surface of the membranes. The membrane fouling was more in the dipped poly MBR as can be seen from the flux computation. It is expected that the fouling will have effect on the effluent quality and rejection of MOMPs as the fouling layer can potentially increase sorption of pollutants onto the membrane pore and pore walls also creating additional barrier for the MOMPs.
8.3.5 Removal comparison and effects of surface modification on MBR performance

The removal of MOMPs through biodegradation and membrane filtration in the MBR systems were investigated. The effects of the surface modification on the removal efficiency and the MBR performance is also discussed. The percentage removal (Figure 8.7) of caffeine in the two reactors were similar (70% in Reactor 1 (dipped poly) and 67% in Reactor 2 (plain)). The dipped poly MBR attained 91% caffeine removal while the plain membrane attained 73% caffeine removal. Whereas, closely similar percentage removal (Figure 8.10) of carbamazepine in the two reactors were recorded [41% in Reactor 1 (dipped poly) and 46% in Reactor 2 (plain)], and in the MBR systems [66% in Reactor 1 (dipped poly) and 62% in Reactor 2 (plain)] were attained. The performance of the dipped poly MBR compared to the plain membrane was not significant for the removal of carbamazepine but reasonably significant for caffeine. Membrane fouling was more in the dipped poly membrane compared to the plain membrane as seen by the decline in flux from the computed flux plotting (Figure 8.11).

The dipped poly MBR system performed better than the plain MBR. It is suggested that the increased sorption site available on the membrane surface contributed to biofilm and fouling layer
to formation, hereby enhancing removal of MOMPs by sorption mechanism as well as size exclusion. Studies show that major factors influencing the removal efficiency of OMPs in MBRs may include; sludge age and concentration, existence of anoxic sludge age and concentration, existence of anoxic and anaerobic compartments, composition of the wastewater, inoculum source and character, technical setup (side stream or submerged MBR), operating temperature, mixed liquor pH, and conductivity (Chon et al., 2012; Hai et al., 2011a; He et al., 2013; Tadkaew et al., 2011). Removal efficiency of OMPs by MBR system could also be affected by changes in dissolved oxygen (DO) concentration (Hai et al., 2011b).

Biodegradation and sorption to sludge is reported as the main two removal mechanism for OMPs by MBRs with hydrophobic pollutants having more tendencies to be removed by sludge adsorption. In this study, removal of caffeine increased through the membrane filtration than through biodegradation and some quantity may have been adsorbed into the sludge. While carbamazepine removals through filtration and biodegradation recorded close values. Carbamazepine with higher hydrophobicity is expected to be removed more by hydrophobic adsorption on to the surface of the coated membrane, but results show no significant removal through membrane interactions. This implies the predominant removal mechanism for carbamazepine was biodegradation and probably adsorption to sludge. Characterisation of the sludge stream and analysis of the soluble microbial product (SMP) in the sludge will be useful to provide more evidence on the removal of MOMPs by the biomass, as studies reports removal mechanism for OMP in MBR processes may involve sorption to biomass or to enmeshment in the membrane biofilm (Sahar et al., 2011; Xue et al., 2010).

8.4 Summary

The performance of the surface modified MBR system (under similar conditions for 85 days of operation) in the removal of model organic micropollutants, caffeine and carbamazepine spiked in synthetic waste water (at 20-300μg/L) was shown to be more efficient than the plain MBR system. After system stabilization (35 days), COD results show better removal by the MBR systems (up to 92%) through membrane filtration rather than biodegradation as COD values of the supernatant in the reactors were significantly higher than the values in the effluent for the two MBRs. The dipped poly MBR system recorded a better turbidity removal (average of 2.2 NTU). Generally, caffeine was better removed by the MBRs compared to carbamazepine with the biodegradation in reactors also showing reasonable removal rates. Similar percentage removal of caffeine in the supernatants of two reactors [70% in Reactor 1 (dipped poly) and 67% in Reactor 2 (plain)] were recorded, whereas, the dipped poly MBR effluent recorded 91% caffeine removal.
and the plain MBR effluent recorded 73% caffeine removal. Similar percentage removal of carbamazepine in the supernatants of the two reactors [41% in Reactor 1 (dipped poly) and 46% in Reactor 2 (plain)] were attained, whereas in the MBR effluents 66% in Reactor 1 (dipped poly) and 62% in Reactor 2 (plain) were attained. The performance of the dipped poly MBR compared to the plain membrane was not significant for the removal of carbamazepine but reasonable significant for caffeine.

Overall, the dipped poly MBR system performed better than the plain MBR. It is suggested that the increased sorption site available on the dipped poly membrane surface contributed to biofilm and fouling layer to formation, hereby enhancing removal of MOMPs by sorption mechanism as well as size exclusion. The coating layer which potentially enhanced reduction of pore size with resulting effect on membrane surface morphology (roughness) and providing more sites for possible sorption of MOMP. However, the low removal of hydrophobic carbamazepine (with larger molecular size and volume) against expectations based on previous studies and discussion seem to pose further questions about the recalcitrant nature of the pollutant. MBR offers an adaptable alternative for conventional treatment process and if well optimized and improved high removal rates can be achieved more significantly if the concept of surface modification of membranes is optimised to enhance the removal mechanism and increase sorption sites and biofilm formation on membrane surface. Although this will result in fouling problems, however the surface coating could provide a protective layer for the membrane surface during fouling cleaning.
CHAPTER 9
GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH
CHAPTER 9 General conclusions and recommendations for future research

9.0 GENERAL CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

9.1 General Conclusions

This study involved investigations on the potential of surface coated ultrafiltration (UF) polyvinylidene fluoride (PVDF) hollow fibre membrane for the removal of organic micropollutants (OMPs) in water matrices – DI water, surface water and wastewater in a submerged membrane bioreactor. Spray and dip coating of PVDF membranes with Poly (1-phenylethene-1,2-diyl) - Polystyrene solution and dip coating with Pluronic F68 solution through physical adsorption was carried out as surface modification.

Physical adsorption of hydrophobic polystyrene (5g/L solution) and amphiphilic pluronics F68 (5g/L solution) as a suitable way to enhance surface characteristics of the PVDF UF membrane has been demonstrated. The pluronic F68 solution at 5g/L concentrations (above CMC) formed micelles with average size larger than the plain membrane’s nominal pore size and was subsequently coated on the membrane surface. Both coating materials impacted the membrane surface properties with the polystyrene material showing more impact than the plain membrane.

SEM images analysis used for characterization of the pore size and distribution through showed that polystyrene coating in sprayed and dipped coating procedure, exhibited more reduction in pore size (19–31%) and closer pore size distribution than the pluronic F68 coating (6%). The AFM image analysis providing information on average roughness $R_a$ and maximum peak-to-valley distance $R_{\text{max}}$ show that more roughness and irregularity in surface topography was recorded in the polystyrene coated membranes (sprayed poly and dipped poly) compared to the pluronics F68 coating (dipped pluro) with the dipped polystyrene coating attaining more roughness ($R_a$ – 0.393 µm). CA measurements showed that the dipped Polystyrene coated membrane achieved the highest increase in hydrophobicity (29%) while the dipped pluronics F68 coating achieved a 10% increase. Correlation between the changes in surface roughness and hydrophobicity was evident in the study. Generally, the polystyrene material impacted the membrane surface the most, and the dipped coating procedure recorded the highest surface modification impacts. The modifications on the membrane surfaces can potentially enhance their filterability and selectivity.

The performance of the coated membrane (sprayed poly and dipped poly) in the rejection of single component of MOMPs, caffeine and carbamazepine spiked in deionized water (at 300µg/L and
500 μg/L) was investigated and correlation between the removal efficiency and coating method was observed.

The percentage removals of caffeine at concentrations 300 and 500μg/L with the plain and modified membranes were less than 20%, whereas for carbamazepine, greater than 20% removal was achieved with the sprayed membrane at the higher concentration and greater than 50% removal was achieved with the dipped membrane at both concentrations. Hydrophobic interactions/adsorption and size exclusion are suggested to contribute to the removal by the coated membranes. The TMP during the filtration of the MOMPs increased from 76 to 90 and 219 mbar for plain, sprayed, and dipped membranes, respectively. Similarly, a slight change in flux was observed from 24 to 19 and 25 L/m²·h·bar for plain, sprayed poly, and dipped poly membranes, respectively. The membrane PWP was impacted by surface coating with the dipped poly membrane recording more than 50% reduction in PWP compared to the plain membrane.

The performance of the coated membrane (dipped poly and dipped pluro) in the rejection of mixed component of MOMPs, caffeine and carbamazepine spiked in surface water (at 1000 μg/L), correlated with the coating methods used and was influenced by the colloidal and particulate matter in the water matrix. The high concentration of the MOMPs also enhanced there removal. Higher effluent water quality recorded by the coated membrane with turbidity average of 1NTU. The removal of the MOMPs was reasonably higher in the surface water matrix compared to the DI water matrix. Dipped pluro membrane showed a better removal of caffeine (82%) and carbamazepine (78%) compared to the dipped poly membrane (caffeine - 76%, carbarmazepine – 74%); and for both materials of coating, a higher percentage removal of caffeine was attained. Hydrophobic interactions/adsorption and size exclusion are suggested to contribute to the removal by the coated membranes as carbamazepine. High percentage removal of caffeine in all the membrane types may be attributed to its sorption onto the colloidal and particulate matter present in the feed water. Higher percentage removal by the dipped pluro is attributed to the activity of pluronic micelles in solubilising the MOMPs (especially hydrophobic carbamazepine)

The performance of the polystyrene coated (dipped poly) MBR system (under similar conditions for 85days of operation) in the removal of model organic micropollutants, caffeine and carbamazepine spiked in synthetic waste water (at 20-300μg/L) was shown to be more efficient than the plain MBR system. Better removal was recorded in both MBR effluents (up to 92%) through membrane filtration rather than biodegradation as COD values of the supernatant in the reactors were significantly higher than the values in the effluent for the two MBRs. The dipped
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The poly MBR system recorded a better turbidity removal (average of 2.2 NTU). Caffeine was better removed by the MBRs compared to carbamazepine with the biodegradation in reactors also showing reasonable removal rates. Similar percentage removal of caffeine in the supernatants of two reactors [70% in Reactor 1 (dipped poly) and 67% in Reactor 2 (plain)] were recorded, whereas, the dipped poly MBR effluent recorded 91% caffeine removal and the plain MBR effluent recorded 73% caffeine removal. Similar percentage removal of carbamazepine in the supernatants of the two reactors [41% in Reactor 1 (dipped poly) and 46% in Reactor 2 (plain)] were attained, whereas in the MBR effluents 66% in Reactor 1 (dipped poly) and 62% in Reactor 2 (plain) were attained. The performance of the dipped poly MBR compared to the plain membrane was not significant for the removal of carbamazepine but reasonable significant for caffeine.

Removal of caffeine through biodegradation and/or adsorption to biomass was reasonable but not as significant as removal through membrane filtration. Carbamazepine was predominantly removed by biodegradation and/or sludge adsorption but not significantly by membrane filtration in both plain and dipped poly membranes. Characterization of the sludge biomass and the soluble microbial products in the sludge stream is useful to provide information on the adsorption of the MOMPs. This is not considered within the scope of this study.

It is suggested that the increased sorption site available on the membrane surface contributed to biofilm and fouling layer to formation, hereby enhancing removal of MOMPs by sorption mechanism as well as size exclusion. The coating layer which potentially enhanced reduction of pore size with resulting effect on membrane surface morphology (roughness) and providing more sites for possible sorption of MOMP. However, the low removal of hydrophobic carbamazepine (with larger molecular size and volume) against expectations based on previous studies and discussion seem to pose further questions about the recalcitrant nature of the pollutant.

Overall, it is demonstrated that physical adsorption of functional polymers is a simple and efficient way to modify the surface properties of polymeric membranes for water filtration application. Improvement in removal efficiencies of caffeine and carbamazepine in different water matrices by the coated membrane was evident, and dependent on the coating material and coating method. The characteristics of the water matrix is shown to influence the removal of caffeine and carbamazepine.

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9.2 Recommendations for Future Research

Further investigations into the use of better coating material to address the problem of fouling alongside organic micropollutants removal is recommended, as well as the use of other types of membrane material and configuration (such as flat sheet). Coating materials with high hydrophilicity and anti-fouling property that can achieve firm anchorage onto the base membrane surface will be useful in yielding novel barrier structures for pollutants removal while balancing the effect of coating on the water flux as well as limit the fouling effects. Examples include surface active amphiphilic block or comb copolymers - polyethyleneglycol (PEG), natural hydrophilic materials from plants such as; Chitosan, Wax from leave extracts etc. Also, blending of suitable materials with the main membrane polymer material at the production stage may be a good option to improve the water flux and high anti -fouling properties on the pore surface and walls of the produced membrane. For example, pluronics F68 (or any other Pluronics) can be blended with compatible membrane polymer material (polyethersulfone – PES, etc..) to produce blend membranes with high flux recovery and anti-fouling properties. Investigation into the trade-off between the anti-fouling properties, flux recovery capabilities and selectivity or surface functionalization of the coating material for OMP removal will be an interesting for future studies.

A more robust characterisation of the modified based on holistic approach rather than representative approach is recommended. The use of a matrix of two and three-dimensional characterisation method of a large portion of membrane sample will help provide more information. Characterisation methods such as; X-ray Photoelectron Spectroscopy, high resolution Atomic Force Microscopy, Transmission Electron Microscopy in addition to the Scanning Electron Microscopy; can provide relevant information on the surface characteristics and micro structure of the membrane. This will require multi-disciplinary expertise and collaboration.

Continuous operation of dip coated polystyrene and pluronic F68 to investigate the durability of the coating and the effects of dissolved pluronics micelles in the aqueous medium in OMP removal is also recommended. This study was based on synthetic water matrix containing maximum of two organic pollutants at a time. Immediate future study may include testing the system for removal of single components or addition of two or more chemicals from frequently detected class of OMPs of concern (such as hormones, pesticides, etc..). A more realistic study using real municipal wastewater containing a cocktail of pollutants is also recommended. Although investigation into the problems of membrane fouling were not within the scope of this study, future
studies on fouling mitigation within the system through operation optimisation and membrane material functionalization is recommended.
REFERENCES


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## Appendix A  Membrane Systems in organic micropollutant removal at laboratory, pilot and industrial scale.

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<th>% Removal</th>
<th>Summary of Results</th>
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<td>(Comerton et al., 2007)</td>
<td>Ultra Filtration (UF)</td>
<td>Laboratory scale</td>
<td>Two natural waters (source of drinking water and MBR effluent) and Lab-scale water (control)</td>
<td>22 EDCs &amp; PhACs with Mw range 150-290 g/mol</td>
<td>Removal by adsorption was studied and compared between the three Membrane systems @ temperatures 21°C and 4°C</td>
<td>Adsorption strongly correlated with compound log $K_{ow}$ and membrane pure water permeability, and moderately correlated with compound water solubility. Adsorption observed highest by the UF membrane, however, presence of organic matter may compete with OMP for adsorption site; Influence of temperature on adsorption in the range examined was found to be insignificant.</td>
</tr>
<tr>
<td>(Acero et al., 2010)</td>
<td>UF (MWCO: 2000 – 20000Da)</td>
<td>Laboratory</td>
<td>Secondary effluent spiked with compounds</td>
<td>11 contaminants @ 500µg/L: acetaminophen, metoprolol, caffeine, antipyrine, sulfamethoxazole, flumequine, ketorolac, atrazine, isoproturon, 2-hydroxybiphenyl and diclofenac</td>
<td>&lt;50%, except for hydroxybiphenyl</td>
<td>Adsorption is the main mechanism for micropollutants retention by UF filtration membranes. Results show that UF is a feasible options for the treatment of municipal secondary effluent, producing water that can be reused in several applications.</td>
</tr>
<tr>
<td>(Sahar et al., 2011)</td>
<td>UF preceded by CAS</td>
<td>Full scale with UF Pilot setup</td>
<td>Effluents from CAS in WWTP</td>
<td>Antibiotics: Macrolide, Sulphonamide, and Trimethoprim</td>
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<td>UF preceding CAS performed better than CAS. Removal mechanism may involve sorption to biomass or to enmeshment in the membrane biofilm.</td>
</tr>
<tr>
<td>Year</td>
<td>Method</td>
<td>Location</td>
<td>Description</td>
<td>EDCs/PPCPs</td>
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<tr>
<td>(Yoon et al., 2006)</td>
<td>UF (8000Da)</td>
<td>Laboratory scale</td>
<td>Synthetic (model) water and natural surface waters.</td>
<td>52 EDCs/PPCPs with initial conc ranging from 2 to &lt;250mg/L</td>
<td>Up to 80% removal for hydrophobic compounds</td>
<td>UF membrane removed typically hydrophobic OMPs using hydrophobic adsorption as removal mechanism.</td>
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<td>(Kimura et al., 2004)</td>
<td>RO (Polyamide - &lt;200MWCO &amp; Cellulose acetate- 200-300MWCO)</td>
<td>Laboratory</td>
<td>Single solute experiment for all the OMPs.</td>
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<td>57-91% removal for Polyamide membrane; 0-85% removal for Cellulose acetate membrane all depending on MW of OMPs</td>
<td>Nanofiltration/Reverse Osmosis</td>
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<td>NF (Loose)</td>
<td>Laboratory</td>
<td>Synthetic solutions spiked with micropollutant</td>
<td>Sulfamethoxazole, carbamazepine, &amp; Ibuprofen (all at 500µg/L)</td>
<td>50-85% removal</td>
<td>Rejection properties of RO membranes for OMPs should be expressed by the MWCO rather than the salt rejection capability. Dominant rejection mechanism for RO membranes would depend on the membrane material and physico-chemical of OMP.</td>
</tr>
<tr>
<td>(Comerton et al., 2007)</td>
<td>NF/RO</td>
<td>Laboratory</td>
<td>Two natural waters (source of drinking water and MBR effluent) and Lab-scale water (control)</td>
<td>22 EDCs &amp; PhACs with Mw range 150-290 g/mol</td>
<td>Removal by adsorption was studied between the three Membrane systems @ 21 and 4 °C</td>
<td>Adsorption strongly correlated with compound log Kow and NF/RO membrane pure water permeability, and moderately correlated with compound water solubility. Adsorption observed lower in NF and RO membranes compared with UF. Influence of temperature on adsorption in the range examined was found to be insignificant.</td>
</tr>
<tr>
<td>(Comerton et al., 2008)</td>
<td>‘Loose’ and ‘tight’ NF; and RO Polyamide membrane</td>
<td>Bench-scale</td>
<td>Two natural waters (source of drinking water and Lab-scale water (control) spiked with contaminants and MBR effluent containing contaminants.</td>
<td>22 EDCs &amp; PhACs with Mw range 150-290 g/mol and initial concentration ~ 1µg/L for all.</td>
<td>‘Tight’ and ‘loose’ NF –variable removal &gt;90% removal in RO.</td>
<td>Rejection strongly correlates with compound hydrophobicity (LogKow) and water solubility; more hydrophobic, higher rejections; Results suggest MBR-RO Hybrid system could provide efficient rejection of studied OMPs especially for water reuse application. Membrane fouling and compound interactions affects rejection; presence of divalent cations</td>
</tr>
<tr>
<td>Authors and Year</td>
<td>Membrane Type</td>
<td>Scale</td>
<td>Test System</td>
<td>Method</td>
<td>Concentrations</td>
<td>Results</td>
</tr>
<tr>
<td>------------------</td>
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</tr>
<tr>
<td>(Braeken and Van der Bruggen, 2009)</td>
<td>NF (180Da)</td>
<td>Laboratory</td>
<td>Synthetic solutions</td>
<td>EDCs – Estrone, Estradiol and Salicine at initial concentration of 1mg/L, Mw &gt;270</td>
<td>Retention of Salicine &gt;90% while for Estrone and Estradiol retention is &lt;85%.</td>
<td>Compound Hydrophobicity correlates with removal efficiency. Lower than expected removal of estrone and estadiol since Mw&gt;&gt;MWCO of membrane; effect of hydrophobicity on removal decreases with increase Mw compared to MWCO. Economic evaluation shows that NF is not economically feasible for municipal drinking water treatment if investment cost is to recovered in 10 years even if there is 50% reduction in membrane prices.</td>
</tr>
<tr>
<td>(Acero et al., 2010)</td>
<td>NF (150-300 Da)</td>
<td>Laboratory</td>
<td>Secondary effluent spiked with compounds</td>
<td>11 contaminants: acetaminophen, metoprolol, caffeine, antipyrine, sulfamethoxazole, fluomequine, ketorolac, atrazine, isoproturon, 2-hydroxybiphenyl and diclofenac</td>
<td>&gt;70% removal</td>
<td>Removal mechanism is dominantly size exclusion and electrostatic repulsion at High pH. Results show that NF is a feasible options for the treatment of municipal secondary effluent, producing water that can be reused in several applications.</td>
</tr>
<tr>
<td>(Yangali-Quintanilla et al., 2009)</td>
<td>NF NF-90, NF-200 (Clean and Fouled)</td>
<td>Laboratory</td>
<td>Synthetic solutions spiked with micropollutant</td>
<td>17 representative OMP; Mw range 150-290 g/mol; ionic and non-ionic compounds</td>
<td>Rejections of non-ionic compounds - 18 to 90% for NF-200 &amp; 41% to 97% in NF-90 membrane. Rejections of ionic compounds over 84% by NF-200 and over 93% by NF-90</td>
<td>Non-ionic rejection was mainly dominated by size exclusion mechanism. Ionic rejection mainly due to the electrostatic repulsion between the compounds and the surface charge of the membrane. The influence of fouling on rejections was generally low. However, steric hindrance was observed as a main rejection mechanism that becomes more important with fouling.</td>
</tr>
<tr>
<td>(Yoon et al., 2006)</td>
<td>NF (600Da)</td>
<td>Laboratory scale</td>
<td>Synthetic (model) water and natural surface waters.</td>
<td>52 EDCs/PPCPs with initial conc ranging from 2 to &lt;250ng/L</td>
<td>&gt;80% removal for compounds with high logKow (&gt;3.5) and NF membrane removal mechanism was both size exclusion and hydrophobic adsorption. Results also show the significant role pore size plays in retention</td>
<td></td>
</tr>
</tbody>
</table>

(Ca^{2+}) could decrease rejection of OMP from natural waters. 'Loose' NF produced poor and variable OMP Rejection.
<table>
<thead>
<tr>
<th>Study</th>
<th>Membrane Type</th>
<th>Scale</th>
<th>Experimental Details</th>
<th>OMP</th>
<th>Removal Percentage</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Vergili, 2013)</td>
<td>NF (1000Da)</td>
<td>Laboratory</td>
<td>Water treatment plant effluent spiked with pollutants</td>
<td>Carbamazepine, Diclofenac, Ibuprofen at initial conc. range between 0.025-0.1μg/L</td>
<td>31-39% removal for neutral Carbamazepine; 55-61% removal to ionic Diclofenac and Ibuprofen</td>
<td>Low water solubility, high log K&lt;sub&gt;ow&lt;/sub&gt;, negative charge may have resulted in higher rejections of Diclofenac and Ibuprofen. Water solubility of a compound should be assessed as the first indicative parameter on its passage in membrane filtration. M&lt;sub&gt;w&lt;/sub&gt;&lt;MWCO, therefore retention is generally low in the NF.</td>
</tr>
<tr>
<td>(De Munari et al., 2013)</td>
<td>NF (MWCO-165 &amp; 460 Da)</td>
<td>Laboratory</td>
<td>Synthetic solution of OMP spiked in ultrapure water with Humic acid</td>
<td>Pesticide Endosulfane (10-100μg/L)</td>
<td>Removal up to 96% for the NF (165) and 84.4% for NF (460) depending on pH variations and Humic acid concentration</td>
<td>Presence of Humic acid increased the retention of pesticide with M&lt;sub&gt;w&lt;/sub&gt;&lt;MWCO. However, loose NF had increased removal at lower pH (4). Contribution of solute-solute and solute-membrane interactions should be considered as fundamental parameters for understanding micropollutant removal mechanism in NF.</td>
</tr>
<tr>
<td>(Jin et al., 2012)</td>
<td>FO membranes – Cellulose (CTA) and Polymeric (TFC Polyamide) membranes (MWCO~180Da)</td>
<td>Bench – scale</td>
<td>Synthetic spiked solution</td>
<td>Carbamazepine, Diclofenac, Ibuprofen, Naproxen (all @ 250µg/L)</td>
<td>&gt;94% for TFC membranes and &gt;93% for CTA membranes</td>
<td>Rejection related to Membrane interfacial properties, physicochemical characteristics of Pharmaceutical molecules and pH of feed solution. CTA FO membranes; size exclusion and hydrophobic interaction dominate rejection under low pH and electrostatic repulsion and size exclusion in higher pH, while TFC polyamide membranes exhibited superior performance in terms of water permeability, rejection and pH stability.</td>
</tr>
</tbody>
</table>

**Forward Osmosis**
### 9.1 Summary of Results

<table>
<thead>
<tr>
<th>Reference</th>
<th>Membrane processes &amp; Other Processes Involved</th>
<th>Scale</th>
<th>Matrix</th>
<th>Target MP (PPCPs)/ initial Conc.</th>
<th>% Removal</th>
<th>Summary of Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nghiem et al., 2009</td>
<td>MBR (submerged)</td>
<td>Laboratory</td>
<td>Effluent from Activated sludge seeded; Synthetic Wastewater spiked with trace organics.</td>
<td>Bisphenol A (750 µg/L), Sulfamethoxazole (750 µg/L)</td>
<td>90 &amp; 50 respectively under similar conditions; biodegradation and adsorption to the sludge were thought to be responsible for the removal of bisphenol A</td>
<td>Physicochemical properties such as Hydrophobicity ($\log K_{ow}$); of the trace organic contaminants mostly responsible for removal and should be taken into account when assessing their removal efficiency.</td>
</tr>
<tr>
<td>(Radjenović et al., 2007)</td>
<td>MBR</td>
<td>Laboratory</td>
<td>WWTP Effluent</td>
<td>31 pollutants including analgesic and anti-inflammatory drugs, lipid regulators and cholesterol-lowering statin drugs, antibiotics, psychiatric and antiepileptic drugs at 10-100ng/L concentration</td>
<td>&gt;80% removal rates with steady effluent concentration compared to a conventional activated sludge process except for carbamazepine which was not retained efficiently.</td>
<td>MBR was relatively efficient in removing most of the pollutants, however a complete removal was not recorded. It is suggested that membrane treatment process should be optimised by modification of the membrane properties as well as treatment biological process by inoculation of special microorganism or diverse microbial population.</td>
</tr>
</tbody>
</table>
### CHAPTER 9 General conclusions and recommendations for future research

<table>
<thead>
<tr>
<th>Study</th>
<th>Type</th>
<th>Scale</th>
<th>Wastewater Type</th>
<th>Pollutants</th>
<th>Removal</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Xue et al., 2010)</td>
<td>MBR (preceded by anaerobic/anoxic/aerobic process)</td>
<td>Full Scale</td>
<td>Municipal wastewater</td>
<td>19 micro pollutants; 8 EDCs (conc range: &lt;20-&lt;350ng/l) &amp; 11 PPCPs (conc range: &lt;1000-&lt;1600ng/l)</td>
<td>&gt;70% removal of the target EDCs &amp; widely varied removal btw 50%-100% removal for the PPCPs.</td>
<td>Sludge-adsorption and/or biodegradation suggested as removal mechanism deduced through a rough mass balance. Sludge-adsorption (anaerobic tank) particularly significant for the removal of hydrophobic compounds. Study shows that HRT of 5 h in aerobic tanks should be sufficient for the elimination of most targets compounds.</td>
</tr>
<tr>
<td>(Tadkaew et al., 2010)</td>
<td>MBR (submerged)</td>
<td>Laboratory</td>
<td>Synthetic wastewater</td>
<td>Sulfamethoxazole, ibuprofen, ketoprofen, and diclofenac at 2μg/L</td>
<td>Removal rate was variable depending on pH of mixed liquor.</td>
<td></td>
</tr>
<tr>
<td>(Tadkaew et al., 2011)</td>
<td>MBR</td>
<td>Pilot scale (MBR)</td>
<td>Raw wastewater</td>
<td>40 trace organics; 14 very hydrophobic (Log D &gt; 3.2) trace organic compounds; others hydrophilic and moderately hydrophobic (Log D &lt; 3.2) compounds possessing strong electron withdrawing functional groups.</td>
<td>above 85% for Hydrophobic compounds &amp; below 20% for hydrophilic and moderately hydrophobic</td>
<td>Lab scale MBR shows apparent correlation between OMP chemical structures and removal efficiency. Chemical structures such as; electron withdrawing or donating functional group. Sorption removal mechanism was significant for hydrophobic OMPs and combined with functional group feature of OMPs, removal of less hydrophobic (hydrophilic compounds) could be enhanced.</td>
</tr>
<tr>
<td>(Sahar et al., 2011)</td>
<td>MBR (submerged)</td>
<td>Pilot scale</td>
<td>Raw wastewater</td>
<td>Antibiotics: Macrolides, Sulfonamides and trimethoprim</td>
<td>61-99% removal</td>
<td>Sorption to Biomass was significant for antibiotic removal in MBR as detected by extraction experiment of biomass after filtration, thus more attention must be taken to the management of excess sludge after MBR for OMP treatment. Biofilm formed</td>
</tr>
<tr>
<td>(Hai et al., 2011a)</td>
<td>MBR (near anoxic &amp; anaerobic condition)</td>
<td>Laboratory</td>
<td>Synthetic wastewater</td>
<td>Carbamazepine and sulfamethoxazole at initial concentration of 750μg/L</td>
<td>&lt;20% for both compounds under aerobic conditions but increased removal up to 68±10% in near anoxic and anaerobic conditions remarkable for Carbamazepine compared to previous studies</td>
<td>Removal efficiency of OMPs by MBR system could be affected by changes in dissolved oxygen (DO) concentration. Recalcitrant OMP carbamazepine was better removed when DO transited form near anoxic (DO=0.5mg/L) to aerobic (DO&gt;2.0mg/L).</td>
</tr>
<tr>
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</tr>
<tr>
<td>(Hai et al., 2011b)</td>
<td>MBR</td>
<td>Laboratory</td>
<td>synthetic municipal wastewater spiked with selected micropollutants</td>
<td>22 trace organics representative of four major categories of micropollutants; initial conc. 5 μg/L</td>
<td>Most removal rate was consistent with previous studies at ambient temp (20°C) except for significantly hydrophobic phenolic and steroidal compounds(log D &gt; 3.2) which recorded &gt;90% removal at 20°C</td>
<td>Temperature variation affects micropollutant removal by MBR treatment. The removal of most hydrophobic compounds (log D &gt; 3.2) = stable @ temp. range of 10–35 °C. Less hydrophobic compounds (log D &lt; 3.2); comparatively more pronounced variation between removals in the lower temperature regimes (10–35 °C)</td>
</tr>
<tr>
<td>(Cases et al., 2011)</td>
<td>MBR Flat sheet &amp; Hollow fibre membrane</td>
<td>Pilot scale</td>
<td>Effluent from primary treatment of conventional treatment plant.</td>
<td>Selected EDCs detected at primary treatment effluent at concentrations &lt;5μg/L</td>
<td>Removal rate ranged between 68 -98% for all EDCs.</td>
<td>MBR more efficient than conventional CAS treatment. Both MBR membrane types and configuration showed close removal efficiency with only slight differences.</td>
</tr>
<tr>
<td>(Kovalova et al., 2012)</td>
<td>MBR</td>
<td>Pilot scale</td>
<td>Wastewater from hospital collection system</td>
<td>56 Pharmaceuticals, 10 metabolites, 2 corrosin inhibitors all detected in</td>
<td>Removal ranged from no removal to complete removal depending on</td>
<td>The Influent is dynamic system comprising a complex matrix of OMP resulting in pharmaceutical conjugate deconjugating</td>
</tr>
</tbody>
</table>

~ 136 ~
wastewater at concentration range of 0.1μg/L to 2.6mg/L OMP class and in some cases negative removal recorded. (causing negative elimination) and substantial biological transformation during the MBR treatment process. The MBR system was found to be insufficient in eliminating a majority of the OMP (especially antibiotics, antiepileptic, iodinated X-ray contrast media). Hospital disinfectant from influent caused no bacterial inhibition in MBR.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Membrane processes &amp; Other Processes Involved</th>
<th>Scale</th>
<th>Matrix</th>
<th>Target MP (PPCPs)/ initial conc</th>
<th>% Removal</th>
<th>Summary of Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Acero et al., 2012)</td>
<td>MAP with Adsorption</td>
<td>Laboratory</td>
<td>Secondary effluent spiked with compounds</td>
<td>11 contaminants: acetaminophen, metoprolol, caffeine, antipyrene, sulfamethoxazole, flumequine, ketorolac, atrazine, isoproturon, 2-hydroxybiphenyl and diclofenac (all 500μg/L)</td>
<td>Removal rates almost similar to UF system.</td>
<td>UF with GAC post-treatment performed better than UF with PAC pre-treatment. Increased dosing of PAC will perform better as regards OMP removal. Generally low removal of OMP but better removal of other quality parameters.</td>
</tr>
<tr>
<td>(Löwenberg et al., 2014)</td>
<td>2 Hybrid PAC/UF as pressurised system and submerged system</td>
<td>Pilot scale</td>
<td>WWTP Effluent</td>
<td>5 OMPs; sulfamethoxazole, carbamazepine, mecoprop, diclofenac and benzotriazole; 100-200ng/L initial concentration with highest been 30 µg/L</td>
<td>60 – 95% removal</td>
<td>Both systems are capable of achieving reasonable removal rate (PAC dosage of 20mg/L and supporting coagulant- Fe³⁺at 4mg/L), however due to longer contact time up to 30h, submerged PAC/UF showed slightly higher removal rate.</td>
</tr>
<tr>
<td>(Sudhakaran et al., 2013)</td>
<td>MAP with Natural Systems</td>
<td>Pilot scale</td>
<td>WWTP Effluent</td>
<td>24 OMPs removal data obtained from previous experimental work by (Sydner et al, 2007)</td>
<td>Removal of hybrid system estimated by quadrant plots show removal over 85% for hybrid of processes promote a sustainable approach and compensate for the limitations of the individual processes. However, cost analysis associated in operating the hybrids should be assessed.</td>
<td></td>
</tr>
</tbody>
</table>
## COMBINED SYSTEMS

<table>
<thead>
<tr>
<th>Authors (Year)</th>
<th>System Description</th>
<th>Location</th>
<th>Feedstock</th>
<th>Analytes</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Sahar et al., 2011)</td>
<td>MBR-RO (side stream and submerged MBR comparison)</td>
<td>Pilot plant</td>
<td>Real waste water</td>
<td>6 antibiotics, 3 pharmaceuticals (ibuprofen, salicylic acid and diclofenac) and Bisphenol A</td>
<td>Both system showed high removal rate &gt;90% for all the selected OMPs. Although high removal rates recorded, presence of OMPs at low concentration (28-233ng/L) shows that RO cannot serve as absolute barrier to OMPs, therefore additional treatment systems should be considered alongside.</td>
</tr>
<tr>
<td>(Serrano et al., 2011)</td>
<td>MBR-PAC (sequential mode of operation)</td>
<td>Laboratory</td>
<td>Synthetic wastewater spiked with selected OMPs</td>
<td>9 OMPs; Anti-depressant - Fluoxetine, Anti-inflammatories Ibuprofen, Naproxen, Diclofenac, Anti-epileptic- Carbamazepine, Antibiotics- Trimethoprim, Roxithromycin, Erythromycin, Tranquillizer- Diazepam</td>
<td>&lt;20% removal for recalcitrant Carbamazepine and Diazepam but with addition of 1g/L PAC removal efficiency increased to the range of 93-99%. Other OMPs also show improvements in removal with addition in PAC into the system.</td>
</tr>
<tr>
<td>(Chon et al., 2012)</td>
<td>MBR-NF (210Da)</td>
<td>Laboratory</td>
<td>Real wastewater</td>
<td>PPCPs; acetaminophen, atenolol, carbamazepine, clopidogrel, diclofenac, Dilantin, ibuprofen, iopromide, glimepiride, naproxen, and sulfamethoxazole</td>
<td>Up to 95% removal, but carbamazepine and dilantin were recalcitrant to biosorption and/or biodegradaton in MBR showing negative removal.</td>
</tr>
</tbody>
</table>

Process as a pretreatment and GAC, NF, RO, or UV/chlorination as a post-treatment to ARR.

all OMPs including recalcitrant OMPs.
### CHAPTER 9 General conclusions and recommendations for future research

<table>
<thead>
<tr>
<th>Study</th>
<th>Configuration</th>
<th>Location</th>
<th>Medium</th>
<th>OMPs detected in wastewater</th>
<th>Removal efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Dolar et al., 2012)</td>
<td>MBR-RO</td>
<td>Pilot scale</td>
<td>Real wastewater</td>
<td>20 multiple-class pharmaceuticals detected in real wastewater Mean Conc.(0.02 – 2.02μg/L range with some antibiotics over 2.0μg/L)</td>
<td>&gt;99% for all OMPs</td>
</tr>
<tr>
<td>(Alturki et al., 2012)</td>
<td>Osmotic Membrane bioreactor- OMBR (Forward Osmosis system)</td>
<td>Laboratory</td>
<td>Synthetic wastewater with activated sludge (MLSS conc. = 3.4 g/L)</td>
<td>50 OMPs; molecular weights range 138 – 458 g/mol</td>
<td>25 out of 27 trace organic compounds Mn &gt; 266 g/mol = high removal (&gt;85%); 23 other; Mn &lt; 266 removal was scattered</td>
</tr>
<tr>
<td>(He et al., 2013)</td>
<td>MBR anaerobic/anoxic/anoxic/anoxic/anoxic membrane biological reactor (A/A/A/O-MBR)</td>
<td>Full scale</td>
<td>Raw wastewater</td>
<td>Galaxolide(306–316ng L(^{-1})), Estrone (29–129 ng L(^{-1})), 17β-Estradiol (1126–1170 ng L(^{-1})), 17α-ethynylestradiol-EE2 (2193–4437 ng L(^{-1})), diethylstilbestrol (268–421 ng L(^{-1})) Bisphenol A (26–176 ng L(^{-1}))</td>
<td>67-71% removal for Galaxolide, up to 87% removal for the Estrogens compounds</td>
</tr>
<tr>
<td>(Cartagena et al., 2013)</td>
<td>MBR-NF&amp; MBR-RO</td>
<td>Pilot</td>
<td>Real municipal waste water</td>
<td>10 OMPs detected in wastewater including carbamazepine, ibuprofen and caffeine.</td>
<td>&gt;76.9% for all OMPs studied in both systems</td>
</tr>
<tr>
<td>(Lipp et al., 2012)</td>
<td>MBR-PAC (Submerged)</td>
<td>Pilot</td>
<td>Effluent of primary treatment of conventional municipal WWTP containing target OMPs</td>
<td>9 Pharmaceuticals; Bezafibrate, carbamazepine, Clofibric acid, diclofenac, gemfibrocil, ibuprofen, ketoprofen, naproxen, fenofibric acid</td>
<td>60-80% removal</td>
</tr>
</tbody>
</table>

While Removal efficiency of MBR varied (0–95%) depending on the compound due to diverse in the OMP physicochemical properties, the RO addition showed excellent removal rates (>99%) for all compounds. Size exclusion and electrostatic interaction are the main removal mechanisms involved in RO membranes.

OMBR retains the inherent advantages of both MBR and FO. High removal was possibly governed by the interplay between physical separation of the FO membrane and biological degradation.

Removal efficiency of Estrogens in the biological system (A/A/A/O-MBR) related to the Sludge retention time (SRT) and/or hydraulic retention time (HRT) as well as the hydrophobicity of Estrogen. High SRT and HRT in the hybrid MBR system facilitated higher and more stable removal of hydrophobic estrogens.

Hollow fibre and flat sheet comparison for MBR showed no significant difference in performance. High quality effluent obtained in both systems with no major difference in the results. MBR-NF will require 30% less energy compared to MBR-RO.

Results show that with 5-10mg/L dosage of PAC, 50-80% increase in removal efficiency for recalcitrant carbamazepine and diclofenac could be achieved. Second filtration step is required to remove PAC from the MBR (MF) system.
| Nguyen et al., 2012 | MBR-GAC | Laboratory Synthetic wastewater spiked with OMP | 22 compounds representing four major classes of OMP | Little or no removal for carbamazepine, diclofenac and fenoprop; 80-99% removal for all 5 steroid hormones and 4 alkyl phenolic compounds. | MBR effective for removal of hydrophobic (log D > 3.2) and readily biodegradable OMPs but inefficient for hydrophilic and recalcitrant OMPs. MBR-GAC (post-treatment) hybrid system improved the removal efficiency of all OMPs studied. However, an extended period of treatment recorded breakthrough of recalcitrant diclofenac, this implies that strict monitoring is needed for operating MBR-GAC for recalcitrant OMPs. |
Appendix B  Pictures of experimental setups and Fabricated membrane module

C1  Experimental setup

C2  Membrane module

Appendix C  Turbidity readings in MBR system.
<table>
<thead>
<tr>
<th>Turbidity</th>
<th>Reactor 1</th>
<th>Dipped Poly</th>
<th>Reactor 2</th>
<th>Plain</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>126</td>
<td>2</td>
<td>77</td>
<td>3</td>
</tr>
<tr>
<td>16</td>
<td>112</td>
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<td>3</td>
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<td>4</td>
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<tr>
<td>48</td>
<td>89</td>
<td>1</td>
<td>98</td>
<td>4</td>
</tr>
</tbody>
</table>

Average: 125.2, 2.2, 70.0, 3.7
## Appendix D  COD concentrations in MBR system

<table>
<thead>
<tr>
<th>COD</th>
<th>Feed</th>
<th>Dipped poly</th>
<th>Reactor 1</th>
<th>Reactor 2</th>
<th>Effluent 1</th>
<th>Effluent 2</th>
<th>% Rem R1</th>
<th>% Rem R2</th>
<th>% Rem E1</th>
<th>% Rem E2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>265.43</td>
<td>19.44</td>
<td>34.56</td>
<td>7.14</td>
<td>8.45</td>
<td>92.67603511</td>
<td>86.979618</td>
<td>97.3089488</td>
<td>96.81558944</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>263.4</td>
<td>33.21</td>
<td>45.77</td>
<td>9.35</td>
<td>20.95</td>
<td>87.39179954</td>
<td>82.623386</td>
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### Appendix E  Caffeine concentrations in MBR system

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## Appendix F  Carbamazepine concentrations in MBR system

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