2015

Removal of trace organic chemicals by membrane bioreactors and hybrid processes

Kaushalya Chandrakanthi Wijekoon
University of Wollgongong

UNIVERSITY OF WOLLONGONG

REMOVAL OF TRACE ORGANIC CHEMICALS BY MEMBRANE BIOREACTORS AND HYBRID PROCESSES

This thesis is presented as part of the requirement for the

Award of the Degree

DOCTOR OF PHILOSOPHY

from

UNIVERSITY OF WOLLONGONG

By

Kaushalya Chandrakanthi Wijekoon

School of Civil Mining and Environmental Engineering

Faculty of Engineering and Informatics Sciences

March 2015

DECLARATION

I, Kaushalya C. Wijekoon hereby declare that this thesis, submitted in fulfilment of the requirements for the award Doctor of Philosophy, in the School of Civil, Mining, and Environmental Engineering Faculty of Engineering and Informatics Science University of Wollongong is wholly my work, unless otherwise referenced or acknowledged. The document has not been submitted for qualification at any other academic institution.

Kaushalya C. Wijekoon

March, 2015

DEDICATION

This thesis is dedicated to my husband Suchinthana Pragathi Dissanayaka who has always stood by me and dealt with all of my hard times with a smile. I also like to dedicate this piece of work to my parents, especially to my father who was not able to share my success.

ABSTRACT

Membrane bioreactors (MBRs) can effectively remove a wide range of trace organic contaminants (TrOCs), yet their fate and recalcitrant contaminant removal during MBR treatment is uncertain. This study focused on revealing the fate and removal of TrOCs during MBR treatment, membrane distillation (MD) and novel membrane distillation bioreactor hybrid treatment (MDBR). It also aimed to elucidate the effect of physicochemical properties (namely, molecular structure, log D, and volatility) on the fate and removal of TrOCs during MBR, MD and MDBR treatment.

The effect of molecular properties on the fate of trace organic contaminants in the aqueous and solid phases during wastewater treatment by MBR was comprehensively examined. A set of 29 TrOCs was selected to represent pharmaceuticals, steroid hormones, phytoestrogens, UV-filters and pesticides that occur ubiquitously in domestic wastewater. Both adsorption and biodegradation/transformation were found to be responsible for the removal of TrOCs by MBR treatment. Molecular structure had an important effect on the biodegradability of a compound while adsorption was the dominant removal mechanism for hydrophobic (log D >3.2) compounds. Compounds with high log D (log D >3.2) but which were readily biodegradable did not accumulate in sludge. By contrast, recalcitrant compounds with a moderate hydrophobicity, such as carbamazepine, accumulated significantly in the solid phase. The results provided a framework to predict the removal and fate of TrOCs by MBR treatment.

This study also investigated the fate of eight N-nitrosamines during MBR treatment. The results suggest that biodegradation is mainly responsible for the

removal of N-nitrosamines during MBR treatment. Other removal mechanisms (e.g. adsorption to sludge, photolysis and volatilization) were insignificant. N-nitrosamine removal efficiencies were found to be from 24 to 94%, depending on their molecular properties. High removal efficiencies of N-nitrosamines such as N-nitrosodimethylamine and N-nitrosodiethylamine could be explained by the presence of strong electron donating functional groups (EDG) in their structure. In contrast, N-nitrosomorpholine possessing the weak EDG morpholine was persistent to biodegradation. The removal efficiency of N-nitrosomorpholine was the lowest amongst all N-nitrosamines investigated.

The feasibility of MD for removing a set of common TrOCs was then examined. The results suggest that the rejection and fate of TrOC during MD are governed by compound volatility and, to a lesser extent, hydrophobicity. All TrOCs with $pK_H > 9$ (which can be classified as non-volatile) were well removed by MD. Among the 29 TrOCs investigated, three compounds (i.e. 4-tert-octylphenol, 4-tert-butylphenol and benzophenone) possess moderate volatility ($pK_H < 9$) and therefore had the lowest rejection efficiencies of 54, 73 and 66%, respectively. In addition, the fate and transport of the TrOCs during the MD process was also investigated. Hydrophilic TrOCs having negligible volatility were concentrated in the feed, while compounds that are hydrophobic or moderately volatile were substantially lost through adsorption or evaporation. When MD treatment was integrated with a thermophilic MBR, near complete removal (>95%) of all 29 TrOCs investigated was achieved despite their diverse physicochemical properties (i.e. hydrophobicity, persistency and volatility). The results suggest that MD could be a promising post-treatment used in conjunction with thermophilic MBR for TrOC removal.

The removal of TrOCs by a novel membrane distillation - thermophilic bioreactor (MDBR) system was then examined. Salinity build-up and the thermophilic conditions to some extent adversely affected the performance of the bioreactor, particularly the removal of total nitrogen and recalcitrant TrOCs. While most TrOCs were effectively removed by the thermophilic bioreactor, compounds containing electron withdrawing functional groups were resistant to biological treatment and their removal efficiency by the thermophilic bioreactor was low (0 to 53%). However, the overall performance of the novel MDBR system with respect to the removal of total organic carbon, total nitrogen, and TrOCs was high and was not significantly affected by the salinity build-up and thermophilic conditions of the bioreactor. All TrOCs investigated were highly removed (>95%) by the MDBR system. Biodegradation, sludge adsorption, and rejection by MD contribute to the removal of TrOCs by MDBR treatment.

ACKNOWLEDGEMENTS

It is a pleasure to express my deep and sincere gratitude to all who supported me to successfully complete this thesis.

I would like to express my sincere thanks to my supervisor Professor Long Duc Nghiem. I am grateful for his continuous support throughout the last three-and-a-half years. Without his insight and guidance I would not have completed this piece of work. He is also thanked for finding a scholarship to support my study.

I am grateful for my co-supervisors Professor William E. Price and Dr Faisal I. Hai for their insightful guidance. Their kind support and constructive comments always encouraged me to successfully complete this piece of work.

Dr Jinguo Kang is greatly appreciated for carrying out trace organic contaminant analysis using GC/MS for Chapter 4, 6 and 7. Dr James MacDonald also is much appreciated for his help in analysing N-nitrosamines using GC/MS/MS for the Chapter 5.

Thanks also extended to our technical staff and the research team. Robert Rowlan and Frank Crabtree are thanked for their support with setting up my systems. They were available to help me whenever I needed. Dr Ling Tie is thanked for helping with the laboratory work. Our research group members are thanked for their technical and mental support during the hard times of this long journey. This long list includes Ming, Nurul, Luong, Hakeem, Kha, Alex Simon, Alex Groeh, Taka, Aileen, Hung, Wenhai, Ashley and Lewa.

The University of Wollongong is thanked for providing me with a postgraduate scholarship.

I would like to express my gratitude to my mother, sisters, brother and parents-in-law for their continuous inspiration. Last but not least I am thankful to my husband for bearing the brunt of frustration and sharing in the joy of success. This thesis would have not been possible but for his understanding, encouragement and patience.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

THESIS RELATED PUBLICATIONS

Peer reviewed Journal Papers

1. Wijekoon, K.C., Fujioka, T., McDonald, J.A., Khan, S.J., Hai, F.I., Price, W.E., Nghiem, L.D. 2013a. Removal of N-nitrosamines by an aerobic membrane bioreactor. *Bioresource Technology*, 141, 41-45.

2. Wijekoon, K.C., Hai, F.I., Kang, J., Price, W.E., Guo, W., Ngo, H.H., Nghiem, L.D. 2013b. The fate of pharmaceuticals, steroid hormones, phytoestrogens, UV-filters and pesticides during MBR treatment. *Bioresource Technology*, 144, 247-254.

3. Wijekoon, K.C., Hai, F.I., Kang., J., Price, W.E., Cath, T.Y., Nghiem, L.D. 2013c. Rejection and fate of trace organic compounds (TrOCs) during membrane distillation. *Journal of Membrane Science*, 453, 636-642.

4. Wijekoon, K.C., Hai, F.I., Kang, J., Price, W.E., Guo, W., Ngo, H.H., Cath, T.Y., Nghiem, L.D. 2014. A novel membrane distillation – thermophilic bioreactor (MDBR) system: Biological stability and trace organic compound removal. *Bioresource Technology*, 159, 334-341.

Conference Presentations

1. Wijekoon, K. C., Fujioka, T., Hai, F.I., McDonald, J.A., Khan, S.J., Price, W.E., and Nghiem, L.D. 2012. Removal of N-nitrosamines by an aerobic membrane bioreactor. Challenges in Environmental Sciences and Engineering Conference, Melbourne, Australia, September 9-13.

2. Wijekoon, K.C., Nghiem, L.D., Hai, F.I., Kang., J., Price, W.E. 2012. Predicting the fate of emerging trace organic contaminants of concern during MBR treatment based on their molecular properties. Euromembrane Conference, London UK, September 23-27.

3. Wijekoon, K.C., Hai, F.I., Kang, J., Price, W.E., Guo, W., Ngo, H.H., Cath, T.Y., Nghiem, L.D. 2013. A novel membrane distillation – thermophilic bioreactor (MDBR) system: Biological stability and trace organic compound removal. International Membrane Science and Technology Conference, Melbourne, Australia, November 25-29.

4. Wijekoon, K.C., McDonald, J.A., Khan, S.J., Hai, F.I., Price, W.E., Nghiem, L.D. 2014. Anaerobic memebrane bioreactors for trace organic removal. Challenges in Environmental Sciences and Engineering Conference, Johor Bahru, Malaysia, October 12-16.

Awards

1. Best student oral presentation award in Challenges in Environmental Sciences and Engineering Conference (CESE). 2012. Melbourne, Australia, September 9-13.

2. Engineering excellence award for the best published paper 2014, presented by the Institute of Engineers Sri Lanaka New South Wales Chapter Australia for the publication Wijekoon, K.C., Hai, F.I., Kang, J., Price, W.E., Guo, W., Ngo, H.H., Cath, T.Y.,Nghiem, L.D. 2014. A novel membrane distillation – thermophilic bioreactor (MDBR) system: Biological stability and trace organic compound removal. *Bioresource Technology*, 159(334-341).

3. Best paper of Bioresource Technology Volume 159 May 2014: Wijekoon, K.C., Hai, F.I., Kang, J., Price, W.E., Guo, W., Ngo, H.H., Cath, T.Y.,Nghiem, L.D. 2014. A novel membrane distillation – thermophilic bioreactor (MDBR) system: Biological stability and trace organic compound removal. *Bioresource Technology*, 159(334-341).

CHAPTER 1

INTRODUCTION

1.1 Trace organic contaminants

Water reclamation is a pragmatic approach to address the scarcity of water supplies in urban areas due to population growth and irregular climate patterns [1]. Through water reclamation, municipal wastewater can be a reliable alternative source for clean water. However, development of advanced treatment processes is necessary to ensure the adequate removal of common contaminants (e.g., organics, nutrients, minerals) and especially trace organic contaminants (TrOCs) that occur in municipal wastewater. A large number of TrOCs have been detected in raw sewage, treated effluent and withdrawn sludge as well as sewage-affected water bodies all over the world. These include steroid hormones, pharmaceuticals, personal care products, surfactants, pesticides, and disinfection by products [2-5]. In recent years, several studies have also highlighted the frequent occurrence of UV filters and phytoestrogens in municipal wastewater as a potential concern [6-8], although little is known about their fate during wastewater treatment. N-nitrosamines also are an emerging class of TrOCs of significant health concern, which have been widely detected at trace levels in several environmental matrices including raw sewage, secondary treated effluent, and even drinking water [9-11]. TrOCs can enter the environment via industrial wastewater, domestic wastewater and livestock wastewater. Chloramination or chlorination of drinking water can also contribute to the elevated N-nitrosamines concentration in municipal wastewater [11, 12].

The presence of TrOCs in the aquatic environment is of significant concern to public health and the ecosystem because of the potential adverse impact on living organisms caused by TrOCs. This can include a range of oestrogenic, mutagenic, endocrine disrupting and genotoxic effects, which have been observed even at low levels of several nanograms per litre (ng/L) [3, 4, 7]. Moreover, most N-nitrosamines have been classified as probable human carcinogens by the US Environmental Protection Agency [13]. As a result, the removal of TrOCs during wastewater treatment has been the subject of many recent publications.

1.2 Membrane bioreactors for trace organic contaminants removal

Membrane bioreactors (MBRs) have recently emerged as an efficient technology for water reclamation, capable of treating wastewater to a high effluent quality suitable for water reuse. [14]. Appreciable removal of certain TrOCs such as natural steroid hormones and phenolic compounds by aerobic MBR treatment has been widely reported in the literature [15-25]. MBR is usually operated with a long solid retention time (SRT) which can improve the removal of some TrOCs via adsorption onto the sludge and subsequent biodegradation. A long SRT can also favour the proliferation of slowly growing bacteria (such as nitrifying bacteria), thus improving the microbial diversity in the reactor and achieving better biodegradation of TrOCs [19, 26-30]. However, given the number of TrOCs and the diversity in their molecular properties, the efficiency of aerobic MBRs as a barrier for some TrOCs and their removal mechanisms is still poorly understood. In addition, previous studies have focussed mostly on the removal of TrOCs in the aqueous phase and little is known about their accumulation in sludge. The current understanding on TrOC removal under oxic conditions of the sludge phase in particular is still limited.

N-nitrosamines appear to be biodegradable under both aerobic and anaerobic conditions. A number of studies have investigated their biodegradability in soils, groundwater, river bed sludge and isolated microbial cultures [31-34]. Notably, only a few studies have reported the removal of N-nitrosamines from either industrial or domestic wastewaters by conventional activated sludge (CAS) treatment [11, 12, 35, 36]. However, very little is known about N-nitrosamines removal efficiency and removal mechanism during MBR treatment.

1.3 Fate and transport of trace organic contaminants during membrane bioreactor treatment

It is noteworthy that the presence of TrOCs in sludge is of concern especially in terms of agricultural applications. Agricultural usage accounts for 50% of the biosolids production in Europe. As a result, the European Union regulates these organic compounds in sludge to secure the safety of agriculture and soil [7]. There is a limited number of studies on removal mechanisms of TrOCs in MBR. Adsorption of TrOCs onto sludge is an important removal mechanism during MBR treatment. MBR, yielding higher biodegradation rate due to the application of a prolonged SRT, could reduce the TrOC load in sludge [29]. Compared to the conventional activated sludge treatment, MBR treatment results in enhanced biodegradation of certain trace organic contaminants [26-28]. Therefore, it is crucial to understand the removal of TrOCs from both aqueous and solid phases in MBR treatment.

Given the diverse range of emerging TrOCs, elucidation of the removal mechanisms and subsequent development of predictive tools for the extent of the removal of specific TrOCs groups is vital to avoid continuous and expensive monitoring of the fate of each individual TrOC.

1.4 Membrane distillation for trace organic contaminant removal

MBRs can effectively remove TrOCs that are hydrophobic and/or readily biodegradable [24, 27, 37, 38]; however, recent studies have highlighted the challenge of removing recalcitrant TrOCs (e.g. carbamazepine and diclofenac) by biological treatment processes, including MBRs [27, 29, 37, 39]. Given the resistant nature of some TrOCs to biodegradation, the use of post-treatment processes to specifically target these resistant TrOCs has also been explored (e.g reverse osmosis, activated carbon adsorption and ultraviolet oxidation) [40-42]. MD is a low temperature distillation process. MD offers complete rejection of all non-volatile solutes because mass transfer occurs in the gas phase [43]. Nevertheless, limited data is available on removal and fate of TrOCs during MD. Also, MD as a post treatment for MBR to enhance TrOC removal is poorly studied.

1.5 Membrane distillation bioreactor for trace organic contaminant removal

High retention MBR represents the integration of a high retention membrane process such as nanofiltration [44], forward osmosis [45-47], or membrane distillation (MD) [48-51] with a bioreactor, and can be an efficient means to achieve high removal of pollutants. Membrane distillation bioreactor (MDBR) is a high retention MBR process where the MD membrane can act as a barrier to the permeation of low molecular weight compounds and recalcitrant compounds. In the MDBR process, the biological reactor can be operated under thermophilic conditions to facilitate the integration of biological treatment with MD.

1.6 Research objectives

The overall goal of this research was to evaluate the removal and fate of TrOCs during high retention MDBR treatment. Specific objectives were to,

1. Evaluate the fate of TrOCs during MBR treatment and examine the effects of hydrophobicity and molecular structure of the compound.
2. Elucidate the removal and fate of TrOCs during MD
3. Investigate the biological stability of MDBR and removal and fate of TrOCs during MDBR treatment.

1.7 Thesis outline

This thesis contains eight chapters (Figure 1.1). Chapter 2 discusses the occurrence and fate of TrOCs in the environment, available knowledge on TrOC removal during MBR process and high retention MDBR treatment. Chapter 3 details the materials and methods used. Chapter 4 to Chapter 7 discusses the findings of four experiments which were carried out to achieve the research objectives. Chapter 4 provides a detailed understanding on the fate of TrOCs during MBR treatment using aqueous phase and solid phase removal of 29 contaminants representing several groups of TrOCs and possessing diverse physicochemical properties. In Chapter 5, removal and fate of N-nitrosamines during aerobic MBR treatment were examined. In Chapter 6 the rejection and fate of a broad range of TrOCs during MD and the potential application of MD as a post treatment for thermophilic MBR to enhance TrOC removal were examined. Chapter 7 provides an insight into the biological stability and the removal of a wide range of TrOCs during MDBR treatment.

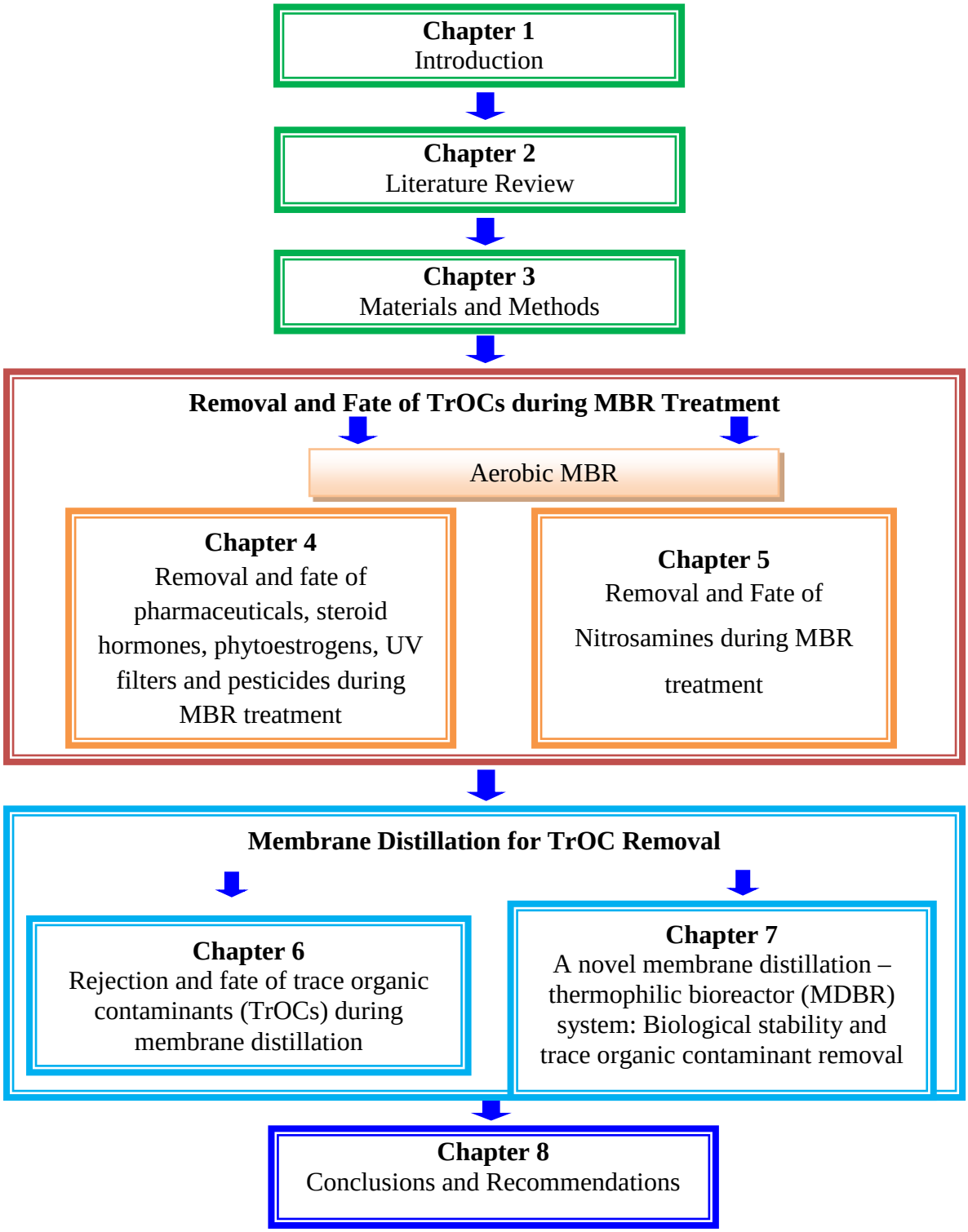


Figure 1.1: Outline of the thesis

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

A large number of trace organic contaminants (TrOCs) have been detected in municipal sewage, treated effluent, digested sludge from wastewater, and sewage-affected water bodies. These include steroid hormones, pharmaceuticals, personal care products, surfactants, pesticides, and disinfection by products. In recent years, several studies have also highlighted the ubiquitous occurrence of UV filters, phytoestrogens and N-nitrosamines in domestic wastewater as being a potential concern. The occurrence of TrOCs in the aquatic environment is of significant concern because of the potential adverse impact on living organisms caused by TrOCs. Given the adverse effects associated with human and environmental exposure to TrOCs, it is important to achieve adequate removal and understand their fate during the treatment process. In particular, knowledge about the removal of N-nitrosamines, UV filters and phytoestrogens during domestic wastewater treatment is still very limited.

Membrane bioreactors (MBRs) have recently emerged as an efficient technology for TrOC removal from municipal wastewater. Nevertheless, given the number of TrOCs and the diversity in their molecular properties, the efficiency of MBR as a barrier for some TrOCs and their removal mechanisms need to be comprehensively investigated. There is limited data and studies on high retention membrane processes such as membrane distillation (MD) as a post treatment for MBR. Integration of membrane distillation with a bioreactor, membrane distillation

bioreactor (MDBR), constitutes the so called High Retention MBR, which can be an efficient means to achieve high removal of low molecular weight and recalcitrant TrOCs.

This chapter provides a comprehensive review of types, health and environmental effects, occurrence and fate of emerging TrOCs within the aquatic environment. This chapter also examines the available knowledge on the removal of TrOCs during MBR treatment and removal mechanisms. Finally, a comprehensive discussion on membrane distillation technology and high retention MDBR is also presented.

2.2 Trace organic contaminants

2.2.1 *Types, health and environmental effects*

TrOCs consist a wide range and expanding collection of anthropogenic as well as naturally occurring compounds. TrOCs can be classified according to their origin, usage, potential health effects and physicochemical properties. According to the usage and origin, TrOCs are categorized into many different groups such as pharmaceutically active compounds (PhACs), steroid hormones, industrial chemicals, pesticides, UV-filters, phytoestrogens and N-nitrosamines. Most TrOCs are of anthropogenic origin. They also contain naturally occurring compounds such as steroid hormones and phytoestrogens. Endocrine disrupting compounds (EDCs), carcinogenic and genotoxic compounds are known to have specific health effects on human and wildlife. EDCs are a diverse collection of compounds including steroid hormones (e.g. estrone, estradiol and 17β-estradiol), UV filters (e.g. benzophenone-3

and benzophenone -4), phytoestrogens (e.g. enterolactone) and industrial chemicals (e.g. Bisphenol A).

2.2.1.1 Pharmaceutically active compounds

Compounds that are pharmaceutically active include prescription and non-prescription medication, beautification products, personal hygiene products and preservatives used by human beings and domesticated animals. There are a wide range of pharmaceutical compounds with a variety of therapeutic groups and physicochemical properties such as non-steroid anti-inflammatory drugs, antibiotics, anticonvulsants, lipid regulators, beta-blockers, antidepressants and vasodilators [3, 19]. Personal care products include microbial disinfectants, preservatives and sunscreen agents, and their metabolites. Examples of common and environmentally concern PhACs are ibuprofen, carbamazepine, ketoprofen, salicylic acid, naproxen, diclofenac, primidone, triclosan and parabens. Eleven PhACs representing different therapeutic groups and physicochemical properties are to be studied in this research.

Pharmaceuticals are produced and used in large volumes worldwide, and a number of new chemicals are introduced to the market every year. Pharmaceuticals are intended to have biological active properties, hence bioaccumulation in human, animal and plant tissues and detrimental effects in human and ecosystems could be expected [3, 4, 7].

Detrimental effects of pharmaceuticals on aquatic and terrestrial species have been reported. Potential toxicity can be due to the combined and synergistic effects of parent compound and metabolites present in the environment [52]. A diverse range of health impacts on aquatic species have been identified, for example,

histopathological changes in kidney and liver of the rainbow trout even at low exposure level (1-5 µg/L) of diclofenac [53], bioaccumulation of diclofenac, ibuprofen and gemfibrozil in fish blood and plasma leading to estrogenic/mutagenic activity and genotoxicity [3, 54]. Adverse effects also have been observed in the higher levels of the food chain. As an example, the extraordinarily high mortality of oriental white-backed vultures in India and Pakistan during 2000-2003 [55] due to renal failure and visceral gout was found to be due to diclofenac residue accumulation [56, 57]. Also, extensive antibiotic usage could increase the development of antibiotic resistant bacteria in the environment [58]. Endocrine disrupting activity of triclosan even at low level of exposure has been identified, for example, in alterations in thyroid hormone receptors in frogs [59, 60]. Triclosan and its transformation bi-product (methyl-triclosan) can bioaccumulate in algae, snails and fish [3]. Being a moderately persistent compound, the triclosan concentration can be magnified in the ecological food chain. Indeed, a triclosan concentration of several nanograms per gram of body weight (ng/g) has been detected in the plasma of dolphins [3].

2.2.1.2 Steroid hormones

Steroid hormones include a variety of both natural and synthetic compounds. Environmentally important natural steroid hormones such as estrone, estriol and 17β-estradiol are largely found in human and mammalian urine. Environmentally significant synthetic hormones include ethinylestradiol and mestranol. Ethinylestradiol is widely used as the active ingredient of the contraceptive pill.

Steroid hormones are also of concern due to their endocrine disrupting activity. Steroid hormones have been demonstrated to have higher endocrine disrupting activity compared to other TrOCs [61]. The estrogenic potency of common steroid hormones is listed in Table 2.1. Steroid hormones, even at low detection levels, can cause feminization of aquatic and terrestrial species such as frogs, turtles and mice [3]. For example, ethinylestradiol at a concentration of 4 ng/L prevented development of secondary sexual characteristics of male fathead minnows [62]. In addition, expression of vitellogenin was induced in rainbow trout by a few nanograms of estradiol [63] and in frog and turtles at 1 µg/g of estriol [64]. Carcinogenic effects in female mice at 5-90 µg/kg.d dose of ethinylestradiol [65] have been observed, whilst prostate cancer development associated with estrogen [66] and a correlation of estriol with breast cancers/endometriosis risk in humans [67] have been identified.

Table 2.1: Physicochemical properties and estrogenic potency of selected steroid hormones

Compound	Molecular Weight (g/mol)	Water solubility (mg/L)	Log K_{ow}	Estrogenic Potency	
				YES	E-screen
Estrone	270.4	30	3.13	0.38,1	0.01
17β-estradiol	272.4	3.6	4.01	1	1
Estriol	288.4	441	2.45	0.001-0.024	0.03
Ethinylestradiol	296.4	116	3.67	1.19-1.5	1.25

Note: Estrogenic potency was determined by yeast estrogen screen (YES) and E-Screen methods [68].

2.2.1.3 Pesticides

According to the US-EPA, pesticides are defined as “any substance or mixture of substances intended for preventing, destroying, repelling or mitigating

any pest". Pesticide contamination in the aquatic environment has been extensively studied due to their wide usage, high persistency and high toxicity. Several classes of chemicals are included in this category, such as insecticides, fungicides and herbicides. Amongst these, based on the environmental and health effects, organochlorine and organophosphoric pesticides are two important classes. Examples include pentachlorophenol, atrazine, aldrin, dieldrin, hexachlorocyclohexane, hexachlorobenzene, lindane, methyl parathion and chlorpyrifos.

The increased and uncontrolled use of pesticides in agriculture has led to significant environmental contamination. Persistent pesticides are abundant in polluted areas due to their wide occurrence and indiscriminate usage in the past. In this study, five persistent pesticides, including clofibric acid, fenoprop, propoxur, pentachlorophenol and atrazine are to be studied. Clofibric acid is an herbicide and it is also a metabolite of lipid lowering pharmaceutical medicine clofibrate. Clofibric acid reduces plant growth by action on the plant hormone system. Fenoprop is also an herbicide which disrupts plant growth and life cycle. Propoxur is a carbamate insecticide, has both acute and chronic residual effects on insects and is widely used in agricultural and livestock pest control. Pentachlorophenol is an organochlorine compound used as a pesticide and a disinfectant while atrazine is an herbicide.

Adverse effects of pesticides are thought to be due to both the parent compound and its metabolites. Metabolites have been shown to have higher toxicity than the parent compound in several studies [69, 70]. Organochlorines are classified as highly to moderate toxic to aquatic species (e.g. aldrin, dieldrin –high toxic and lindane- moderate toxic) [71]. Organophosphoric and organochlorine pesticides have been recognized for their neurotoxic and endocrine disruptive effects on living

organisms, including humans [72]. Interaction of organophosphoric with DNA and resultant chromate exchange in human lymphocytes has been observed [73, 74]. Furthermore, the adverse effects of these pesticides on reproductive systems for example, human sperm DNA damage due to several organophosphoric pesticides, have been demonstrated [70].

2.2.1.4 Industrial chemicals

Compounds investigated in this category are bisphenol A, 4-tert octylphenol and 4-tert butylphenol. Bisphenol A is one of the highest volume chemicals produced worldwide. It is commonly used in manufacturing polycarbamate plastic products such as water bottles, baby bottles, sports equipment, CDs, DVDs, medical and dental devices, household electronics and eyeglass lenses. Bisphenol is also used in epoxy resin coatings on inside of food and beverage cans. Bisphenol is toxic to aquatic and terrestrial organisms probably due to its interaction with protein and it has been identified as an endocrine disruptor [75]. 4-tert-octylphenol and 4-tert-butylphenol are widely used to manufacture alkylphenol ethoxylates, surfactants used in detergents, industrial cleaners, and emulsifiers, and are frequently detected in wastewater and freshwater bodies. In particular the toxic effect of these compounds on reproductive systems of living organisms has been demonstrated [76].

2.2.1.5 Ultraviolet filters

Ultraviolet (UV) filters are widely used as sunscreen agents to absorb and dissipate UV radiation from the sun. Their use has rapidly increased with the increasing awareness of skin cancers, sun burn and photo aging effects of UV radiation [77, 78]. They are used as UV stabilizers in clothes, pharmaceuticals,

personal care products (hair sprays, shampoos, shower gel and beauty cream), agricultural chemicals [77, 79] and food packaging [80, 81]. UV filters are also used as an indirect food additive [79]. Examples of common UV filters are octocrylene, benzophenone, benzophenone-3 (oxybenzone), and benzoic acid [79].

Most UV filters including oxybenzone and benzophenone are classified as endocrine disruptors [79]. UV filters can be absorbed through human skin and ingested from the contaminated food through plastic packaging [81, 82]. The parent compound and the metabolites of most of the UV filters are highly lipophilic [77]. As a result they can accumulate in tissues of wildlife and also in humans [79, 83].

2.2.1.6 Phytoestrogens

Phytoestrogens are natural plant-based compounds which have both inherent estrogenic and androgenic properties. They can be found in a wide variety of plants such as soybeans, cabbages, fruits and nuts [84]. Two of the most common classes of phytoestrogens are isoflavones and lignans [85]. A variety of phytoestrogens and their mammalian metabolic products have been identified in human body fluids. Habitual consumption of phytoestrogens has been shown to be beneficial to human health related to cardiovascular diseases, cancer, osteoporosis and menopausal symptoms [85]. However, recently, there has been an increasing awareness of endocrine disruptive activity of phytoestrogens on humans and animals [86, 87]. Phytoestrogens are structurally or functionally similar to ovarian and placental estrogens and their metabolites [8]. They also possess endogenic activity and genotoxic effects [8]. The significance of phytoestrogens as environmental contaminants has been mostly neglected. In this study, therefore, two common

phytoestrogens, namely formononetin and enterolactone belonging to isoflavone and lignin groups, respectively were selected.

2.2.1.7 N-nitrosamines

N-nitrosamines can be generated as by-products from a range of industries where amines are in contact with nitrite, nitrous acid and nitrogen oxides. Examples include tanneries, circuit board manufacturing, dye manufacturing, metal casting, rubber manufacturing, metal working and food processing [88]. They may also be present in commercial products such as antifreezes, pesticides, detergents, processed meats, beverages, cigarette filters and cosmetics [12]. In addition, N-nitrosamines can be produced as a result of metabolism of amines and nitrate rich food. Furthermore, N-nitrosamines are also generated during chloramination or chlorination of drinking water [11, 12].

N-nitrosamines of concern to environmental authorities include N-nitrosodimethylamine (NDMA), N-nitrosomorpholine (NMOR), N-nitrosomethylethylamine (NMEA), N-nitrosopyrrolidine (NPYR), N-nitrosodiethylamine (NDEA), N-nitrosodipropylamine (NDPA), N-nitrosopiperidine (NPIP), and N-nitrosodi-n-butylamine (NDBA). Most N-nitrosamines have been classified as probable human carcinogens by the US-EPA and many other international agencies [13]. Their carcinogenic effects have been detected even at sub-nanogram per litre (ng/L) levels [35, 89]. Dietary intake of N-nitrosamines incurs a risk of stomach, oesophageal and nasopharyngeal and brain cancers [90, 91]. NDEA in drinking water at low concentrations (0.2 ng/L) could result in an increased lifetime cancer risk of 1 in 10^{6} [90]. As a result, N-nitrosamines have been regulated in both drinking water and

recycling water guidelines in several countries. In California, where high groundwater levels of N-nitrosamines are observed, authorities have set a limit of NDMA in drinking water of 3 ng/L [13]. The Australian Guidelines for Water Recycling sets the maximum value for N-nitrosodimethylamine (NDMA) and N-nitrosomorpholine (NMOR) at 10 and 1 ng/L, respectively [92].

2.2.2 *Occurrence in aquatic environment*

TrOCs are released into the environment in different ways, including domestic wastewater (DWW), industrial wastewater, hospital wastewater, aquaculture wastewater, agricultural runoff, landfill leachate, and livestock wastewater (Figure 2.1). Domestic wastewater is a major source of most of the TrOCs found in the environment [93].

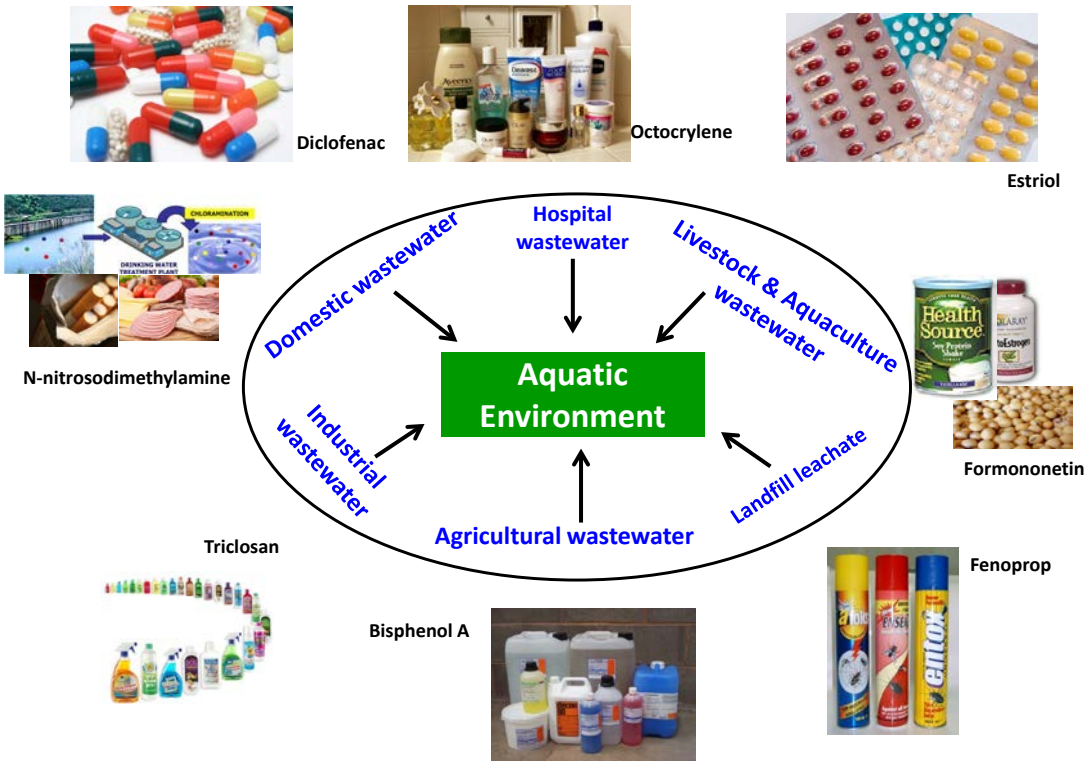


Figure 2.1: Environmental contaminations pathways of TrOCs

A large amount of PhACs and synthetic steroid hormones are used each year worldwide. Annual per capita consumption of PhACs is 15 g and it is three to ten times higher in developed countries [93]. After ingestion in humans a percentage of PhACs and their metabolites are excreted through urine and faeces and enters the environment with domestic wastewater [3]. Phytoestrogens which are present in most edible plants that are commonly consumed by human and livestock are also partly recovered in urine or faeces [84]. UV filters are extensively used as sunscreen agents in cosmetic products and ended up in domestic wastewater. The occurrence of N-nitrosamines in domestic wastewater can be attributed to the consumption of amines and nitrate rich food, cosmetics as well as household detergents. In addition, chloramination or chlorination of drinking water can also contribute to the elevated N-nitrosamines concentration in domestic wastewater [11, 12]. Wastewater treatment plants are not designed for the specific treatment of these contaminants. Wastewater treatment plant effluents are discharged to surface water bodies, applied to ground water recharge and biosolids are used in agriculture with these contaminants. Other than that, uncontrolled disposal of unused or expired drugs into landfill also is a major contamination source.

Moreover, direct and indirect uses of PhACs in aquaculture and farmland application of pesticides are also important environmental sources of TrOCs. Farm runoff is also a key exposure pathway of phytoestrogens [6]. In addition, industrial spillages and wastewater also are significant contamination sources of all types of TrOCs.

A wide range of TrOCs are detected in aquatic environmental matrices, including wastewater treatment plant influent, secondary effluent, surface water,

ground water and drinking water. Their occurrence level is dependent on a range of factors including the annual consumption, excretion rate, climate and efficiency of the treatment process [94]. Orally ingested TrOCs are metabolized in the human body and excreted via urine and faeces. Compounds such as erythromycin, carbamazepine, diclofenac, gemfibrozil, and trimethoprim are discharged as parent compounds in 5, 28, 65, 70, and 80%, respectively, while the rest is metabolized in the liver and discharged to the environment as partially degraded products [3].

Environmental levels of selected TrOCs are summarized in Table 2.2. PhACs are the most abundant TrOCs in DWW [2, 94-96]. PhACs such as non-steroid anti-inflammatory drugs and antibiotics have frequently been found in raw sewage at concentrations reaching mg/L level [96, 97]. Ibuprofen is the most abundant PhAC found in raw sewage followed by the gemfibrozil, naproxen, salicylic acid and ketoprofen, possibly because of their excessive usage. About 160 different pharmaceuticals and their metabolites have been identified in domestic wastewater treatment plants, surface water and ground water in Northern Europe [98]. Because of high usage possibly triggered by health effect at cold climates and the readily access to medical treatment, high concentrations of antibiotics, analgesic and non-steroidal anti-inflammatory contaminants (e.g. trimethoprim, ciprofloxacin, sulfamethoxazole, ibuprofen, naproxen, ketoprofen, diclofenac salicylic acid and acetaminophen) have been reported in raw sewage and wastewater treatment plant effluent in Europe and North America [93]. For example, concentrations of 5000 ng/L, 2000 ng/L and 20, 000 ng/L of trimethoprim, ciprofloxacin and ibuprofen, respectively have been detected in hospital wastewater and high concentration of sulfamethoxazole (794 ng/L) has been detected in raw sewage in USA [93].

Concentration level of these contaminants in Asia and Australia is relatively low [93]. Excessive concentrations of estrogenic contaminants have also been detected in hospital effluent, DWW and surface waters in USA, Europe and Southeast Asia mainly attributed to the animal husbandry and excessive usage of contraceptives. As an example, remarkably high concentration of estriol (>4600 ng/L) reported in hospital effluent in Taiwan [93].

UV filters and phytoestrogens are also detected in raw sewage at relatively high concentrations. Oxybenzone is the most abundant UV filter detected in DWW. Enterolactone and daidzein are two widely occurred phytoestrogens in DWW. The occurrence level of enterolactone and daidzein is of one to two folds higher than that of formononetin (Table 2.2). Formononetin can be converted to daidzein and genistein presumably due to the faecal bacteria [6]. N-nitrosamines concentration in raw sewage is reported to be low (< 100 ng/L), where NDMA being the only exception. Few µg/L concentration of NDMA has been reported in raw sewage presumably through industrial spillage.

Surface water recharge using the treated effluent has been the main cause for the presence of TrOCs in surface water bodies [94, 99]. Notably, ibuprofen, carbamazepine, triclosan, sulfamethoxazole, ciprofloxacin, and pentachlorophenol were detected at alarmingly high levels with concentration at several µg/L. TrOCs are subjected to dilution, sorption onto suspended solids and sediments, photolysis and biodegradation after discharge to the surface water. Occurrence level of TrOCs in surface water depends on the abundance and the persistency of the compound. Ibuprofen is an easily biodegradable compound, but is the most abundant in raw sewage also detected in surface water at high concentration. Triclosan,

carbamazepine, sulfamethoxazole and pentachlorophenol are persistent compounds, present in raw sewage at high levels, and also abundant in surface water. In contrast, steroid hormones, phytoestrogens and N-nitrosamines are detected at low concentrations in surface water either due to low level in raw sewage and efficient removal during treatment. Phytoestrogens as plant derivatives are consistently detected in surface water at low concentration (Table 2.2).

Pollution of NDMA in the surface water and ground water near rocket engine testing facility areas in California USA are very high. For example, 100-400 µg/L of NDMA has been detected in ground water where NDMA is produced as a biodegradation product of rocket engine fuel containing unsymmetrical dimethylhydrazine [9]. Extremely high level of NDMA in both onsite (400,000 ng/L) and offsite (20,000 ng/L) ground water has been reported [9]. High levels of NDMA contamination is attributed to N, N-dimethylhydrazine based rocket fuel used in rocket testing where NDMA is produced as a biodegradation by-product. In addition, N-nitrosodimethylamine (NDMA) frequently detected in water resources in the USA and Canada, which could be mainly attributed to the use of chlorine or chloramine for the disinfection of drinking water or wastewater [9, 12]. In contrast effluent impaired drinking water contamination of NDMA is low in countries like Switzerland and Germany, where wastewater treatment plant effluents are not disinfected using chlorine and no chloramine and hardly any chlorine is used for drinking water disinfection. In addition, Switzerland and Germany enforced stringent water quality standards in terms of free chlorine residual for finished drinking water, where it restricted to <0.1 mg/L and <0.3 mg/L in Switzerland and Germany, respectively.

In comparison to the surface water, ground water contamination is found to be low. Landfill leachate and artificial recharge using treated wastewater have been a significant cause for TrOC contamination in ground water. TrOC polarity is a vital factor for their occurrence in ground water. Polar compounds have less affinity for subsoil and are likely to infiltrate through soil and contaminate the ground water. Polar compounds such as NDMA and NDEA are detected at ground water in similar concentrations as in surface water [12, 90, 100]. NDMA and NDEA (log K_{ow} are -0.640 and 0.34, respectively), are highly soluble in water (solubility at pH 8 & 20 °C 1000 and 147 g/L, respectively), high leaching potential from surface water to ground water [9, 13]. High levels of these compounds have also been detected in surface water and ground water all over the world. Most pharmaceutical compounds are polar (e.g. clofibric acid, carbamazepine, diclofenac and primidone), and under recharge conditions, can leach through the subsoil and contaminate the groundwater [101]. Clofibric acid, which is used as a blood lipid regulatory drug is found in groundwater at significantly high concentration (4000 ng/L) in Berlin Germany from a former sewage irrigation field [95]. High level of clofibric acid also has detected in Berlin drinking water samples [95]. Phytoestrogens which are plant derivatives are present in ground water at substantial levels (100 ng/L). UV filters have hardly been studied in environmental matrices and limited evidence of their presence in the ground water exists to date.

Table 2.2: Concentration of TrOCs in aquatic environment

Compound	Level of contamination (ng/L)				Reference
	Raw sewage	Treatment plant effluent	Surface water	Ground water	
Pharmaceutically active compounds					
Ibuprofen	1000-56500	20-48240	< 5044	< 200	[96, 97, 101-105]
Diclofenac	86-1000	8.8-5450	1.1- 568	< 380	[93, 97, 101, 103-106]
Carbamazepine	1000-2000	73-2100	< 1075	< 10.4	[93, 95, 103, 105-107]
Gemfibrozil	1090-8500	< 4000	1.8-790	< 340	[93, 96, 101, 104]
Trimethoprim	4000	<7900	< 2-710	1.4- 11	[29, 93, 96, 97, 99, 103, 107]
Triclosan	180-4400	12- 9300	35-2300	NA	[3, 96, 104, 108, 109]
Naproxen	8000	1-5100	1-610	NA	[93, 104]
Ketoprofen	80-5700	20-1620	3.4-329	< 80	[93, 104]
Salicylic acid	340-8000	< 2098	< 302	6.5	[93, 95, 104]
Sulfamethoxazole	250-1300	3.8-2800	1.7-2000	1.4-410	[29, 93]
Ciprofloxacin	NA	40-3353	23-1300	NA	[93, 95]
Propranolol	NA	30-50	20	NA	[93]
Atenolol	840-2800*	< 1720	314	NA	[29, 93]
Primidone	NA	110-200	55-635	NA	[110]
Steroid hormones					
Estrone	1-160	< 1-196	1-65	NA	[93, 104, 111-114]
17β-estradiol	1-15	< 1-43	< 21.4-5	NA	[93, 111, 112, 114, 115]
Estriol	< 0.5-10	0.4-30	5-19	NA	[93, 112, 115]
Ethinylestradiol	3.6-14	<0.1-42	1.4-4.3	0.1-0.5	[111, 113, 115]
17α-estradiol	NA	6-13	< 74	NA	[93]
17α-ethinylestradiol	3-450	1-17	0.1-831	NA	[93]
Pesticides					
Atrazine	NA	1.3-430	< 200	NA	[110]
Clofibric acid	57-2000	120-2000	< 248	0-4000	[93, 95, 110]
Pentachlorophenol	NA	NA	2000	NA	[116]
Hexachlorobenzene	7.5 - 319	NA	NA	NA	[117]
Aldrin	10-210	NA	NA	NA	[118]
Lindane	680-1380	NA	NA	NA	[119]
Dieldrin	23-94	NA	NA	NA	[120]
Industrial chemicals and their metabolites					
Bisphenol A	60-600	4.8-800	0.5-140	5-100	[96, 104]

Compound	Level of contamination (ng/L)				Reference
	Raw sewage	Treatment plant effluent	Surface water	Ground water	
4-tert octylphenol	80-3900	< 1000	NA	NA	[96]
Nonylphenol	220-870	< 4400	0.1-7300	NA	[96, 104, 121, 122]
Methylparaben	NA	NA	< 1062	NA	[108, 122]
Propylparaben	NA	< 28	< 2142	NA	
UV-Filters					
Oxybenzone	1000-3100	1000-2800	NA	NA	[8]
Octocrylene	87.5-100	60-120	NA	NA	[8]
Phytoestrogens					
Enterolactone	581-2111	0.1-48	1-74**	NA	[6, 84, 123]
Formononetin	0.1-10	< 0.6	< 35	NA	[6, 84, 124]
Daidzein	341-1688	< 18	2-120	NA	[6, 84]
N-nitrosamines					
NDMA	7-100,000	1.5-400	5-125	4-400000[#]	[9, 11, 12, 100]
NMOR	3-31	2-1390	20-275	< 2	[12, 90, 100]
NDEA	< 68	< 24	8-40	2-26	[12, 90, 100]
NDPA	5*	12	< 5	NA	[12, 90, 100]
NPYR	13-41	NA	2-15	NA	[90]
NPIP	< 40	< 1.8	1-80	NA	[12, 90, 100]
NDBA	< 41	< 19	5-18	2-8	[12, 90, 100]

Note: * denotes the concentration in primary effluent, ** denotes enterolactone concentration in sea water, [#] denotes NDMA concentration in California near rocket engine testing facility.

2.3 Removal and fate of TrOCs during wastewater treatment

A wide range of TrOCs can be effectively removed during wastewater treatment such as activated sludge treatment and membrane bioreactors. The efficacy and the fate of TrOCs is dependent on operating parameters such as oxic/anoxic conditions [22, 125, 126], nitrification/denitrification capacity, solids retention time (SRT) [26, 28, 127], hydraulic retention time (HRT) [26, 127], temperature [23] and mixed liquor pH [21, 128]. Compound specific parameters that have significant influence on removal and fate during biological treatment include polarity, molecular

structure and biodegradability [37, 129, 130]. Biodegradation, adsorption to biosolids, photolysis and volatilization have been the main removal mechanisms of TrOCs during biological wastewater treatment [19, 27, 29, 55, 99, 105]. This section discusses the removal and fate of TrOCs during conventional wastewater treatment processing. A detailed discussion on the fate and removal of TrOCs during MBR treatment is given in Section 2.4.

2.3.1 *Removal of TrOCs*

Recently, increasing attention has been paid to the removal and fate of TrOCs during wastewater treatment. Activated sludge treatment process (ASP) has been the most widely used biological treatment technique for domestic wastewater treatment. However, ASP is not specifically designed to remove TrOCs. As a result, TrOC removal by ASP is generally low and often inadequate [27, 99]. The reported data ranges from negligible to complete removal (Table 2.3). Ibuprofen is highly removed during ASP (>97%) followed by estriol (>90%), lindane (80-90%), oxybenzone (63-95%) and naproxen (58-90%). Diclofenac and carbamazepine are among the lowest removed TrOCs (0-50%).

Biodegradation is a predominant removal mechanism of TrOCs removal during ASP. Easily biodegradable TrOCs are effectively removed (>80%) during ASP [105]. This includes most PhACs (e.g. ibuprofen, naproxen, ketoprofen and gemfibrozil), steroid hormones, phytoestrogens (e.g. enterolactone and formononetin) and UV filters (e.g. oxybenzone and benzophenone) (Table 2.3). PhACs often have a complex structure with polarized ends [2], subsequently making them soluble in water ($\log D > 3$) and largely removed during ASP [19, 99, 105]. It

has been showed that compounds with electron donating functional groups (e.g. hydroxyl and methyl) are prone to aerobic biodegradation while compounds with electron withdrawing groups (e.g. chloride and amide) are recalcitrant [37]. Steroid hormones removal during ASP has been widely investigated and high removal efficiency (>90%) has been observed (Table 2.3) [25, 125, 131]. A case study on phytoestrogen removal by Kang et al. [6] reported more than 97% removal of common phytoestrogens such as enterolactone, daidzein, and genistein.

Persistent TrOCs are negligibly or partially removed during conventional wastewater treatment and include compounds such as diclofenac, clofibric acid, carbamazepine, atrazine, and sulfamethoxazole (Table 2.3). These are also detected at high levels in secondary effluents and in surface waters (Table 2.2). Washout of slow growing/selective microorganisms due to low SRT, low organic retention time due to inadequate retention mechanism and inclusion of electron withdrawing functional groups in the molecular structure may significantly reduce the removal of persistent contaminants during biological wastewater treatment [26, 37]

N-nitrosamines appear to be biodegradable under both aerobic and anaerobic conditions. A number of studies have investigated their biodegradability in soils, groundwater, river bed sludge and isolated microbial cultures [31-34]. Bradley et al. [31] reported more than 54% biodegradation of NDMA in soil from a wastewater reclamation facility under both oxic and anoxic conditions. Drewes et al. [32] conducted a laboratory scale study of the removal of seven N-nitrosamines under conditions relevant to groundwater recharge operations. Half-lives of these seven N-nitrosamines were in the range from 1.3-7 d. However, Drewes et al. [32] also noted some variation in the biodegradation rate of N-nitrosamines and that complete

removal of N-nitrosamines would require the establishment of an adapted microbial community over several weeks or months. Zhou et al. [34] monitored the fate and transport of NDMA in groundwater being recharged with recycled water and reported that up to 80% of the recharged mass of NDMA could be biodegraded. The half-life of NDMA under recharge conditions was 69.4 days [34]. It is noteworthy that only a few studies have reported the removal of N-nitrosamines from either industrial or domestic wastewaters by the ASP [11, 12, 35, 36]. One of the most comprehensive studies to date was by Krauss et al. [12] who examined the fate and removal of N-nitrosamines in 21 full scale conventional wastewater treatment plants in Switzerland. They showed that the removal efficiencies from the aqueous phase by ASP were generally above 40% for NMOR and over 60% for all other N-nitrosamines. The authors also noted the high variation in the removal efficiency of N-nitrosamines amongst the 21 full scale plants investigated [12].

2.3.2 *Adsorption to biosolids*

Adsorption of TrOCs onto sludge (hydrophobic or electrostatic interactions) is also an important removal mechanism during biological wastewater treatment [19, 27, 132]. It is noteworthy that the presence of TrOCs in sludge is of concern especially in terms of their agricultural applications. Agricultural usage accounts for 50% of the biosolids production in Europe. As a result, the European Union regulates these organic compounds in sludge to secure the safety of agriculture and soil [7]. Therefore, it is crucial to understand the removal of TrOCs from both aqueous and solid phases in wastewater treatment (Table 2.3).

Sludge adsorption of a number of TrOCs during ASP has been reported (Table 2.3). This includes, PhACs (e.g. diclofenac, ibuprofen, ketoprofen and triclosan) [29, 104], steroid hormones [104], phenolic compounds (e.g. nonylphenol, 4-tert-octylphenol and pentachlorophenol) [104, 133], organochlorine pesticides (dieldrin and DDT) [117], polybrominated diphenyl ethers [117], bisphenol A [134], UV filters (octocrylene and oxybenzone) [8, 77]. A summary of TrOCs adsorption in ASP is given in Table 2.3. Octocrylene was detected at the highest concentration (9170 ng/g) followed by triclosan (1505 ng/g). Octylphenol (1180 ng/g) and oxybenzone (1020 ng/g). Sludge adsorption of bisphenol, ibuprofen, and diclofenac could be moderate or low. Concentration of estrone, estradiol and 17β-estradiol in activated sludge is in the range of 0 to 49 ng/g, where 17β-estradiol has the highest sludge adsorption [132]. Andersen et al. [132] reported that about 50–75% of total estrogen removal during ASP could be due to sludge adsorption. Removal of alkylphenols (e.g. pentachlorophenol and nonylphenol) by adsorption to sludge is also significant during ASP [133].

TrOCs removal during biological wastewater treatment (WWT) is a combined process of adsorption to biosolids followed by biodegradation [26, 37, 133]. TrOCs removal by sludge phase mainly depends on solids retention time and operating temperature of the process, specific endogenous decay rate of biomass, hydrophobicity and persistency of the compound [26, 135, 136]. The higher the SRT, the lower the amount of TrOCs expected to be adsorbed in the sludge [135, 136]. High SRT results in longer sludge age for microorganism to biodegrade TrOCs attached to bioflocs. Removal of TrOCs by adsorption to sludge is a main removal mechanism for bioreactors with low SRT because (i) a high biomass wastage rate

increases the removal of TrOCs in the solid phase and (ii) at a low SRT, the ASP process has high biomass washout, slow growing microorganisms exist within the reactor and reduce the biodegradation and increase the TrOCs in the solid phase [135, 136]. For example, Kipopoulou et al. 2004 studied lindane adsorption in different sludge matrices during ASP. Primary sludge contained the highest TrOC concentrations compared to secondary sludge [137]. Primary sludge with low SRT exhibits least biodegradation (low biological activity) potential than secondary sludge where adsorption is the main removal mechanism in primary sludge [137]. Other than low SRT, high organic content also is significant for high TrOC adsorption to sludge. Kipopuolu et al. [137] demonstrated a linear relationship between lindane adsorption and the organic content in the primary sludge of ASP. On the other hand, low sludge adsorption could be expected in WWT systems with extended SRT due to the reduced biomass activity (endogenous decay phase). In comparison to ASP, TrOCs removal by sludge phase in membrane bioreactors which operates at high SRT would be low. Detailed discussion of the fate of TrOCs during MBR treatment is given in Section 2.4.2.

TrOCs removal by sludge phase also depends on the hydrophobicity and the persistency of the compound. Hydrophobic compounds (log D >3.2) have high affinity to soils/biosolids. Moderately hydrophobic but persistent compounds can also adsorb to sludge. For example, considerable adsorption of diclofenac, which is a persistent and moderately hydrophobic compound (log $D_{\text{pH 7}} = 1.77$), to subsoil has been reported [95]. By contrast, hydrophilic compounds do not show any substantial adsorption to soils and biosolids. Clofibric acid (log $D_{\text{pH 7}} = -1.06$) is a typical

example. TrOCs adsorption to sludge could be a synergetic effect of hydrophobicity and persistency of the compound.

Operating temperature also is an important parameter determining TrOC adsorption to sludge. High temperature reduces the adsorption of TrOCs to sludge [138]. It is contradicting the fact that smaller floc size provides larger surface area which leads to higher adsorption. In biological treatment, at high temperature, small bioflocs are formed [139, 140]. Large surface area increases the adsorption of TrOCs to the biosolids which will increase the biodegradation resulting in low accumulation in sludge.

Table 2.3 : Summary of removal and adsorption in sludge of selected TrOCs during aerobic wastewater treatment

Compound	Removal efficiency (%)	Reference	Concentration in sludge (ng/g)	Reference
Oxybenzone	63–95	[8]	140–1900	[7, 8, 77]
Octocrylene	70–80	[8]	270–9170	[7, 8]
Bisphenol A	10–96	[26, 27, 104]	53–196	[104]
Ibuprofen	97–100	[29, 105]	100–747	[29, 104]
Naproxen	58–90	[29, 105]	8–53	[104]
Ketoprofen	36.9–76.3	[29, 99]	0–336	[29, 99, 104]
Diclofenac	0–50	[95, 99, 105]	50–381	[29, 99, 104, 105]
Sulfamethoxazole	50–74	[19, 29]	0-25	[29]
Loratidine	0–15	[29]	0-100	[29]
Acetaminophen	99	[29]	0-150	[29]
Erythromycin	0–36	[19, 29]	0-50	[29]
Clofibric acid	49	[19]	0–135	[104]
Triclosan	61	[19]	1430–1581	[104]
Carbamazepine	0–31	[99, 105]	0–67	[29, 99, 104]
Atenolol	0–62	[19]	<70	[29]
Gemfibrozil	0–65	[19, 29]	38–172	[29, 104]
17β-estradiol	20–80	[26, 105, 131]	<49	[132]
17α-ethinylestradiol	<80	[105]	<17	[132]
Estrone	20–98	[26, 105, 131]	<37	[104, 132]
Estriol	40–90	[19, 26, 131]	NA	NA
Lindane	80–90	[137]	1.4%*	[137]
Nonylphenol	60–89	[27, 133]	35–1307	[104]
4-tert octylphenol	27–100	[27]	74–2286	[104]

Note: * lindane concentration in sludge as a percentage of the influent amount.

2.4 Membrane bioreactor for trace organic contaminant removal

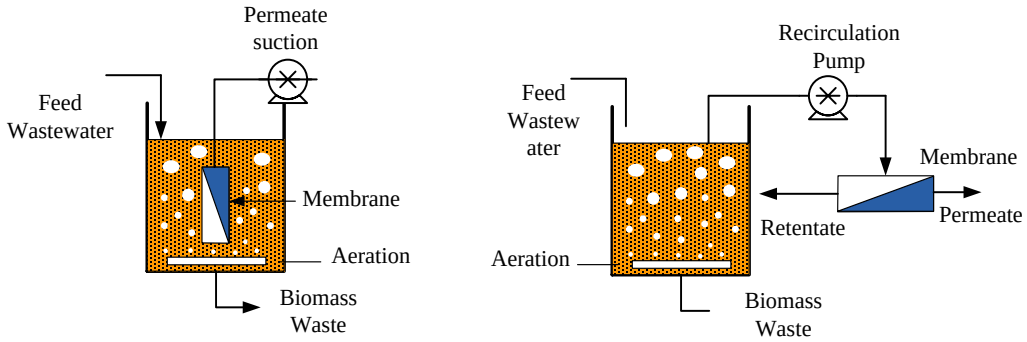
2.4.1 *Membrane bioreactor technology*

Membrane bioreactor can be defined as a combined process of conventional biological wastewater treatment and membrane separation where biomass is separated from treated water by a membrane filtration unit [141]. MBRs are classified into two categories according to the relative position of the membrane with the bioreactor namely, submerged MBR, where the membrane is immersed in the bioreactor and side stream MBR, where bioreactor sludge is pump to the membrane kept outside the bioreactor (Figure 2.2). Micro-porous membranes such as microfiltration or ultrafiltration membranes are commonly used in MBR systems [141].

MBRs have been used for the domestic and industrial wastewater treatment since the 1960s [141]. There also has been a concern on retrofitting MBRs to conventional aerobic wastewater treatment systems [141]. Stringent effluent standards, less land availability, water scarcities and high quality product water are key drivers for wide application of MBR in wastewater treatment [141] There had been more than 500 MBR plants established worldwide by the end of 20^{th} century [142]. In Japan over 250, in United States 24 and Canada nine MBR plants were installed to treat both industrial and domestic wastewater [142]. Also, nearly 300 MBR plants for industrial wastewater treatment and 100 MBR plants for domestic wastewater treatment were used by 2005 [143]. Some examples of full scale MBR plants are given in Table 2.4.

MBR have several inherent advantages compared to conventional WWT. This includes smaller foot print, more flexibility for scaled up or retrofit, high

effluent quality with respect to the removal of suspended solids, pathogens, organics and nutrients [141, 144]. Biomass washout in MBR system is negligible given the high suspended solids retention by micro-porous membranes. In addition, sludge separation is not dependent on the influent characteristics or the flocculation status of the biofloc as the bioflocs are much larger than the membrane pores and totally retained by the membrane [145]. MBRs can work at high organic loading rates with a small foot print given that the biomass is confined within the system providing both the control of a high biomass concentration and decoupling of solids retention time and hydraulic retention time [144, 145].



(a) Aerobic-submerged MBR (b) Aerobic-side stream MBR

Figure 2.2: Membrane bioreactor configurations.

Table 2.4: Examples of full scale aerobic and anaerobic MBR plants

Project	Wastewater	Capacity (m^3/d)	Remarks	Reference
Aerobic MBRs				
Almarai project Saudi Arabia	Dairy industry wastewater	4000	Submerged MBR. Organic loading of 1200 kg/d. Effluent COD and TSS < 100 and 5 mg/L, respectively. Water reuse for general washing and irrigation.	[146]
Palm Jumeirah WWTP - Dubai	Domestic wastewater	18000	Submerged MBR , 18,000 m3/d capacity, 4500 kg/d organic loading, Effluent COD < 30 mg/L, water reuse for gardening and firefighting purposes.	[146]
Al Ansab WWTP- Muscat Oman	Domestic wastewater	76,000	Effluent BOD < 10 mg/L, TSS < 10 mg/L, NH_4-N < 1 mg/L and NO_3-N< 8 mg/L, water reuse for gardening and firefighting.	[146]
Picnic Bay Queensland WWTP	Domestic wastewater	540	Submerged MBR. Target was to protect the great barrier reefs by reducing the pollution load.	[141]
Anaerobic MBRs				
Ken s Foods of Marlborough (USA	Salad dressing and Sauce Manufacturing	530	Operate at 35 ^oC, 99.4% COD removal, World's largest AnMBR	[147, 148]
Shochu distillery (Japan)	Alcohol stillage	20	NA	[148]
Awamori Distilleries (Japan)	Alcohol stillage	15	NA	[147]

2.4.2 *Removal and fate of TrOCs during MBR treatment*

2.4.2.1 Removal of TrOCs

Considerable research effort has been devoted to investigate the TrOCs removal by MBR treatment. MBRs can effectively remove most TrOCs compared to conventional wastewater treatment (Table 2.5). Importantly, TrOCs that are hydrophobic and/or readily biodegradable are effectively removed [24, 27, 37, 38]. The reported data ranged from negligible removal to complete removal. Excellent MBR removal of ketoprofen (>99%) [149], followed by ibuprofen (98%) [28], naproxen (84-89%) [28] and roxythromycin (57-77%) [28, 149] have been reported. Appreciable MBR removal of natural steroid hormones and phenolic compounds also has been reported in the literature [15-25, 149-154]. For example, Wintgens et al. [154] reported effective removal of bisphenol A (73-99%) and nonylphenol (>90%) in their study on MBR treating dumpsite leachate. More than 98% removal of 4-tert octylphenol has been observed by Tadkaew et al. [37]. Clara et al. [26] has reported more than 80% removal of estrone, estradiol, estriol and 17α-ethinylestradiol in full scale MBR plant treating domestic wastewater whereas 17α-ethinylestradiol was more challenging to remove compared to the other three compounds.

Recalcitrant compounds like sulfamethoxazole, carbamazepine, nonylphenol, bisphenol A, atrazine and diclofenac are more likely to be removed in MBR than in conventional treatment plants [18, 151, 155, 156]. For example, 52– 64% removal of sulfamethoxazole and <20% removal of carbamazepine have been reported by Hai et al. [22] and Reif et al. [28] in their lab scale and pilot scale MBRs, respectively.

Kimura et al. [153] reported that compounds with two or more aromatic rings (e.g. ketoprofen, naproxen and mefenemic acid) were not removed by ASP but can be considerably eliminated by MBR. Bouju et al. [157] reported better removal of atrazine in anoxic–aerobic MBR compare to ASP.

Recent studies have highlighted the challenges of removing recalcitrant TrOCs (e.g., carbamazepine, and diclofenac) by biological based treatment processes, including MBRs [27, 29, 37]. For example, MBR removal of TrOCs such as carbamazepine, diclofenac, clofibric acid, atrazine, DEET and dilantin is very low and inconsistent. Kimura et al. [153] found inconsistency in the removal of complex compounds with chloride in their structure (clofibric acid and dicloroprop), with clofibric acid being relatively well removed by MBR while dicloroprop was negligibly removed.

In comparison with the CAS treatment process, very little is known about the efficiency of membrane bioreactor (MBR) for the removal of N–nitrosamines during wastewater treatment. Hatzinger et al. [36] recently demonstrated a novel aerobic laboratory scale propane-fed MBR for the removal of NDMA from artificial groundwater. This appears to be the only study to date which has investigated the removal of N–nitrosamines by MBR treatment. The authors reported over 99.9% removal efficiency of NDMA. Given the unique configuration and operating condition of their propane-fed MBR, the results reported by Hatzinger et al. [36] in case of groundwater may not be representative of a typical MBR used for wastewater treatment. Also, removal of UV filters (e.g. benzophenone and oxybenzone) and phytoestrogens during MBR is indistinct.

2.4.3 *Fate of TrOCs*

Biodegradation or biotransformation by microorganisms and adsorption to sludge are important removal mechanisms during MBR treatment. There is, however, a limited number of studies on removal mechanisms of TrOCs in MBR. Radjenovic´ et al. [29] investigated the fate and distribution of pharmaceuticals in the aqueous and solid phases during the MBR treatment and identified that adsorption to sludge as an important removal mechanism for several pharmaceutical compounds such as mefenamic acid, propanolol and loritidine [29]. They also suggested that MBR enabling higher biodegradation rates could reduce the TrOCs load in sludge. Clara et al. [26, 27] and Reif et al. [28] showed that MBR treatment could enhance the biodegradation of several groups of TrOCs (such as pharmaceuticals, fragrances and endocrine disruptive compounds) compared to conventional activated sludge treatment. Tadkaew et al. [37] further demonstrated that biodegradability of a TrOC can be qualitatively assessed based on the presence of electron donating functional groups (EDGs) or electron withdrawing functional groups (EWGs) in their molecular structure. Fate of TrOCs during MBR treatment and the factors affecting it will be further discussed below.

2.4.3.1 Factors affecting removal and fate of TrOCs during MBR treatment

The molecular structure and hydrophobicity of the TrOCs, operating SRT, mixed liquor pH, temperature and microbial diversity are the key factors affecting removal and fate of TrOCs during MBR treatment [18]. Tadkaew et al. [37] studied the effect of hydrophobicity (measured by log *D*) and functional groups on the removal of TrOCs. They proposed a qualitative predictive framework which

stipulated that: (i) hydrophobic compounds (log D > 3.2) and compounds which are hydrophilic (log D < 3.2) but possess only electron donating groups (EDGs) would achieve high removal during MBR treatment, (ii) the removal efficiency of hydrophilic compounds possessing only electron withdrawing groups (EWGs) would be low, and (iii) hydrophilic compounds having both EWGs and EDGs would achieve varying removal depending on the type of the functional group. In good agreement with that it was found that MBR removal of TrOCs with a chloride moiety, which is a strong electron withdrawing functional group (atrazine, clofibric acid, dichloropop, linuron and diclofenac) is low or negligible [130, 153, 157]. Nevertheless, the negative effect of chroride could be curtailed with the hydrophobicity of TrOCs where hydrophobic compounds with high halogen content and hydrophilic compounds with low halogen content could be well removed during MBR treatment [130]. Tambosi et al. [149] claimed lower removal of naproxen (86%) than ketoprofen (99%) that have similar physicochemical properties would be due to the naphthalene ring in naproxen. Given the diverse range of emerging TrOCs, elucidation of the removal mechanisms and subsequent development of predictive tools for the extent of the removal of specific TrOC groups is vital to avoid continuous and expensive monitoring of the fate of each individual TrOC.

MBR is usually operated with a long solid retention time (SRT). Typical SRT is about 25–80 days compared to the SRT of ASP (8–25 days) [141, 158]. High SRT can affect the fate and removal of TrOCs mainly in three ways namely, (i) provide extended contact time for adsorption onto sludge and subsequent biodegradation (ii) provide sufficient time for microorganisms to acclimatize to the pollutant [18, 26, 159] and (iii) high SRT favours the proliferation of slowly growing bacteria (such as

nitrifying bacteria), thus improving the microbial diversity in the reactor and achieving better biodegradation of TrOCs [19, 26-30]. It is suggested that the SRT of the treatment process has to be chosen based on the persistency of the target pollutant. Cirja et al. [18], has suggested 10–30 days SRT for most of the PhACs like carbamazepine, diclofenac, benzafibrate, naproxen, estrone, estradiol, estriol and 17α–ethinylestradiol. Clara et al. [26] reported increased diclofenac removal from 20 to 60% with increasing SRT from 22 days to 40–80 days, three times higher removal by increasing SRT 2 fold. Extended SRT also could negatively affect the removal of TrOCs due to the low sludge withdrawal and high endogenous decay rate [137].

High MLSS concentration in MBR (typically about 10 g/L compared to 2 g/L in ASP) and total biomass retention would increase TrOC removal by adsorption to sludge and subsequent biodegradation/transformation. Some TrOCs are persistent to biodegradation, but can be removed mainly by adsorption, which is facilitated by a high biomass concentration in MBR [160-162]. The morphology of biomass in a MBR system could also stimulate the effective removal of TrOCs. MBR has smaller flocs than in conventional treatment processes, which enhance the diffusivity, provide larger surface area, and prolong biodegradation. Floc size in MBR and conventional treatment plants are 10–100 µm and 100– 500 µm, respectively [163], Total biomass retention assures the rich microbial diversity of MBR. Free living microorganisms and filamentous microorganisms which are easily washout in conventional treatment processes can be retained by the membrane. This might possibly be a reason for high removal of certain compounds (e.g. carbamazepine, naproxen, and diclofenac) during MBR treatment [18]. Bouju et al. [157] reported the highest removal of atrazine to date (approximately 40%) through a genetically

modified bacterial strain. Also favourable removal of TrOCs by nitrifying bacterial strains has been demonstrated (e.g. for natural and synthetic steroid hormones, halogenated hydrocarbons and phenolic compounds) [15-17, 25].

The operating pH of the MBR can also affect the removal and fate of TrOCs by either changing the microbial properties (both physiological properties and biological activity) and/or changing the solubility of TrOCs. Trace organic contaminants can be positively charged at low pH and neutral or negatively charged around pH 7 (e.g sulfamethoxazole), thus adsorption would only be a significant removal mechanism at low operating pH [149]. This could largely affect the removal of such TrOCs since the sorption is a major removal mechanism in biological removal process. Tadkaew, et al. [21] also revealed that removal of ionisable TrOCs (e.g Sulfamethoxazole, ibuprofen, ketoprofen and diclofenac) are largely dependent on reactor operating pH, whereas non-ionisable compounds (e.g. bisphenol A and carbamazepine) are relatively independent of the reactor operating pH. Incorporating MBR with an anaerobic hydrolytic process, which typically operates at pH about 4–5 would enhance the removal of ionisable TrOCs.

Oxic and anoxic conditions also are imperative for the removal of TrOCs during MBR treatment. Anoxic conditions favour the removal of some contaminants such as carbamazepine [22]. TrOC removal during anaerobic condition is scarcely reported. Some TrOCs are unlikely to biodegrade under anaerobic conditions, (e.g. steroid hormones, alkylphenols (octylphenols and t–nonylphenols) and alkylphenol ethoxylates) [164]. Removal of alkylphenols and 17α–ethinylestradiol under anaerobic conditions is extremely low [126, 164]. In fact, it appears that alkylphenol ethoxylates are transformed into alkylphenols (e.g. 4–nonylphenol and t–

nonylphenol) and estrone is transformed into 17α–ethinylestradiol [126]. Oxic conditions are vital for liquid phase removal (biodegradation) of alkylphenols such as t–nonylphenol [164]. A recent study by Monsalvo et al. [165] showed that only hydrophobic compounds can be effectively removed by AnMBR. Adsorption to sludge seems crucial in determining the fate of TrOCs during anaerobic wastewater treatment. [133, 164]. It is suggested that TrOCs are largely adsorbed onto anaerobic sludge due to their low biodegradability under these conditions. For example, alkylphenols and estrogens significantly accumulate in AnMBR sludge compared to ASP [126, 133, 164]. Abargues et al. [164] also demonstrated that accumulation of phenolic TrOCs (octylphenols and t–nonylphenol) in anaerobic sludge can be enhanced by using high SRT during MBR treatment.

Table 2.5: Selected experimental studies of TrOC removal by membrane bioreactor

Study	Wastewater	T (°C)	TrOCs	Feed TrOCs concentration (µg/L)	SRT (days)	MLSS (g/L)	Removal efficiency (%)	Remarks	Ref.
Nitrification & Denitrification MBR	Dumpsite leachate	NA	Nonylphenol Bisphenol A	NA	NA	22	>90	Ultrafiltration (UF), tubular membrane, reactor size180 m^3	[154]
Aerobic Submerged MBR	Synthetic domestic wastewater	NA	Bisphenol A	0.1, 5 and 20 mg/L	350	NA	>93.7	Hollow fibre (HF) microfiltration (MF) membrane, 10 L reactor size, HRT of 8 h	[151]
Aerobic submerged	Domestic wastewater	NA	Naphthalene sulfonate	3 of each	623	7±1	>97	21 L. HRT of 14 h	[155]
			Napthalene disulfonates				-8 to 93		
			EDTA				14		
			BTSA				78		
			Diclofenac				8		
MBR submerged	Synthetic domestic wastewater	22	Sulfamethoxazole Carbamazepine	750 of each	NA	11	64 < 20	PVDF/HF membrane, HRT of 24 h, 7.8 pH, 9 L reactor	[162]
MBR submerged	Synthetic domestic wastewater	20	15 hydrophobic compounds * 25 hydrophilic compounds**	2 of each	70	8.6-10	> 85 # 40-70 ## < 30 ###	HRT 24 h, pH of 7.5, TOC and TN Removal efficiency >98.5 and > 66 respectively	[40]
MBR submerged	Domestic wastewater	15	Acetaminophen, ketoprofen	50 of each	15 and 30	12	100	HRT of 9 h (at SRT 15day), 13 h (at SRT 30day), UF and HF membrane Naproxen, trimethoprim and sulfamethoxazole, removal values represent the removal at SRT of 15 and 30 days	[149]
			Naproxen				86 - 89		
			Roxithromycin				57 - 64		
			Sulfamethoxazole				55 - 64		
			Ttrimethoprim				86 - 64		

Study	Wastewater	T (°C)	TrOCs	Feed TrOCs concentration (µg/L)	SRT (days)	MLSS (g/L)	Removal efficiency (%)	Remarks	Ref.
Submerged MBR	Synthetic domestic wastewater	18-24	Carbamazepine, diclofenac & erythromycin	10-20 of each	77-72	10 (as VSS)	< 9	Pilot scale study. 220 L reactor, pH 7.5-8.5. HRT 12 h, HF/UF membrane. Short operating time: (2 months acclimatization and 2 month operation); Target compounds cover PhACs and musk fragrances	[28]
			Diazepam				26		
			Ibuprofen				98		
			Naproxen				84		
			Roxithromycin				77		
			Sulfamethoxazole				52		
			Trimethoprim				36		
Submerged MBR, Conventional activated sludge process	Domestic wastewater	NA	Ketoprofen, Naproxen, Ibuprofen, Diclofenac, Clofibric acid, Dicloprop	20-500 ng/L each	NA	10 in MBR and 1.7 in ASP	NA	MF membrane HRT of 9 and 13 h in MBR and ASP, respectively Near total removal of ketoprofen, naproxen and ibuprofen. No considerable removal of diclofenac and dicloprop in both. Better removal of clofibric in MBR.	[153]
Submerged MBR	Synthetic DWW	20	15 hydrophobic compounds *	2 µg/L	70	NA	>85*	HF -UF membrane. 9 L volume, DO of 2±1 mg/L, 24 h HRT.	[37]
			25 hydrophilic compounds**				<20**		
Submerged MBR	Synthetic domestic wastewater	22	Sulfamethoxazole, Bisphenol A, Carbamazepine, Diclofenac, Ibuprofen, Ketoprofen	2-20 µg/L of each	70	NA	*** higher removal of Ionisable compounds at lower pH	HF/UF membrane. 9 L working volume, DO of 2±1 mg/L, 14 min suction 1 min relation operating cycle, 24 h HRT, 4.3 L/m2.h permeate flux, pH 5,6,7,8 and 9	[21]

Study	Wastewater	T (°C)	TrOCs	Feed TrOCs concentration (µg/L)	SRT (days)	MLSS (g/L)	Removal efficiency (%)	Remarks	Ref.
External MBR	Domestic wastewater	20	ibuprofen, naproxen, ofloxacin, acetaminophen,	12–14600 ng/L	NA	1-8 (HF/UF) 7-26 (FS/MF)	>90	Pilot scale (3.6 & 4.7 m^3). HF/UF (HRT 7.2 h) and Flat sheet/MF (HRT 15 h). 29 TrOCs. TrOCs with moderate or low removal in FS/MF MBR is considerably higher than the HF/UF MBR presumably to high HRT of the first MBR.	[29]
			sulfamethoxazole, atenolol, propranolol, bezafibrate,				70-90		
			diclofenac, famotidine,				50-70		
			loratidine, carbamazepine				<30		
Submerged MBR	NA	20-27	Bisphenol A, estrone, estriol, 17β –estradiol, ibuprofen	20-3250 ng/L	20, 40 & 82	-	80-100	Pilot scale (4.2 m^3), with nitrification and denitrification capacity. Removal efficiencies of bisphenol, estrone, estriol, 17β –estradiol, ibuprofen and carbamazepine were stable with SRT. Removal efficiency of diclofenac increased with increasing SRT	[26]
			bezafibrate				60-100		
			17 α –ethinylestradiol				20-100		
			diclofenac				0-60		
			carbamazepine				< 20		
			DEET				0-75		
			Carbamazepine				0-32		
			Bayrepel-acid				88-99		

Note:

BTSA-Bensothiazole-2-sulfonate, EDTA - Ethylenediamine tetraacetic

* hydrophobic compounds (Log *D* >3)- linuron, clozapine, bisphenol A, testosterone, Estrone, amitriptyline, etiocholanolone, 17β-estradiol, simvasatatin, 17α-ethinylestradiol, triclosan, t-octylphenol, triclocarban, Nonylphenol,

** Hydrophilic compounds (Log *D*<3)- enalapril, atenolol,sulfamethoxazole,ketoprofen,caffeine,naproxen,paracetamol,ibuprofen,primidone,Diclofenac, sim-hydroxy acid, meprobamate, trimethoprim, gemfibrozil, triameterene, DEET, hydroxyzine, meprazole,dilantin,trazine,risperidone,carbamezapine,verapamil,androstenedione, estriol

\# Removal efficiency >86% of 11 hydrophilic and 14 hydrophobic compounds

5 hydrophilic compounds (ketoprofen, caffeine &naproxen, sim-hydroxy acid and omeprazole

10 no of hydrophilic compounds

*** Ionisable compounds; Sulfamethoxazole, ibuprofen, ketoprofen show higher removal efficiency below pH 6 and higher removal of diclofenac at pH 5 and negligible removal at pH 7

2.5 Membrane distillation

2.5.1 *Membrane distillation technology*

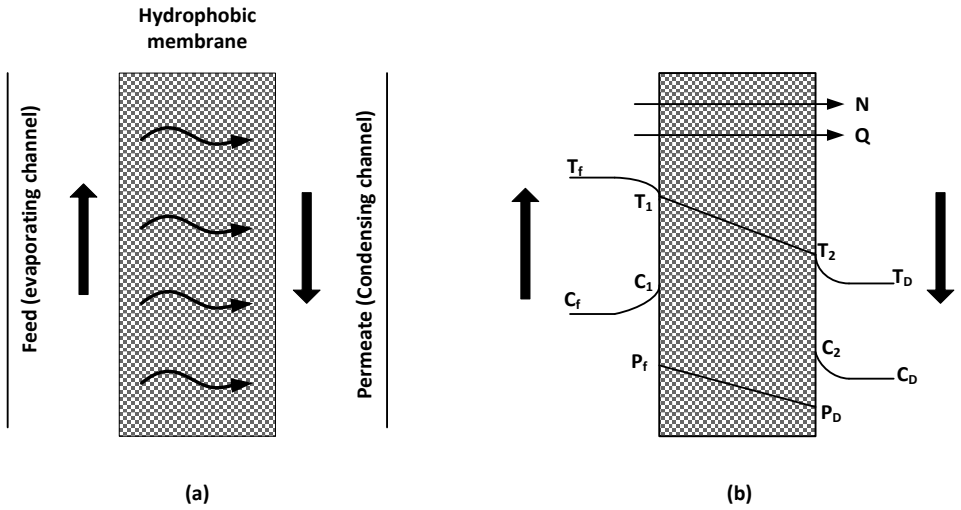


Figure 2.3: Direct contact membrane distillation (a) configuration (b) principle

MD is a low temperature distillation process that involves the transport of water vapour from a feed solution through the pores of a micro-porous and hydrophobic membrane to the distillate (product) side. Because mass transfer occurs in a gaseous phase, MD offers complete rejection of all non-volatile solutes [43]. Direct contact membrane distillation (DCMD) is probably the most widely studied MD system configuration due to its simple operation [43, 166]. The principles of DCMD are illustrated in Figure 2.3. In DCMD, the feed solution is maintained at a higher temperature than the distillate; thus, creating a vapour pressure difference between the feed and distillate. Moderately elevated temperatures (45-80 °C) are required to obtain sufficient driving force and typically, fluxes of 2-20 $L/m^2.h$ can be obtained [43, 49, 166]. The membrane separates the liquid phase of the feed and distillate streams but allows water vapour to transport freely through its dry micro

porous pores. In MD, the membrane material must be hydrophobic to prevent wetting of the pores by liquid feed or distillate under standard operating conditions. The vapour pressure (P°) within the membrane can be determined by the Antoine equation [166]:

$$P^o = \exp\left[A - \frac{B}{C+T}\right] \quad 2.1$$

Where P° is in Pa and T is the temperature (K). Values of A,B,C constants for pure water are 23.1964, 3816.44 K and -46.13 K respectively; for non-ideal binary solutions, the membrane pore vapour pressure can be corrected by considering the solute and solvent molar fractions [43, 166]. In direct contact membrane distillation, the mass transfer and the heat transfer take place simultaneously; the total heat transfer and molar flux are described in Equation 2.2 and 2.3 respectively [166].

$$Q = \left[\frac{1}{h_f} + \frac{1}{h_m + N\Delta H_V / \Delta T_m} + \frac{1}{h_p}\right]^{-1} \times \Delta T_m \quad 2.2$$

$$N = k_f \Delta P^o \quad 2.3$$

Where h_f, h_m and h_p are the heat transfer coefficients of the feed, membrane and permeate respectively, while N, ΔH_v , k_f and T_m are the molar flux molar heat of vapourization, mass transfer coefficient and temperature difference between feed and distillate side of the membrane respectively.

Mass transfer coefficient is a function of temperature, pressure and membrane composition and membrane structure [166]. Meanwhile, $\Delta P°$ is a function of temperature at membrane surface and membrane surface composition but not the bulk solution conditions, thus, heat transfer rate and mass flux are related. However, in the MD process, it is assumed that the pressure on each side of the membrane is

equal to the saturation pressure of water at the membrane surface and the equation 2.4 can be expressed as a function of temperature drop across the membrane as follows [166].

$$N = K \frac{dP^o}{dT} \Delta T_m = K \frac{P^o \Delta H_v}{RT^2} \Delta T_m \quad 2.4$$

2.5.2 *Factors affecting the membrane distillation*

Both the operating conditions and the membrane characteristics have been identified as crucial factors in MD performance. It has been shown that feed temperature, concentration and circulation velocity/stirring rate, permeate inlet temperature, temperature difference are the dominant operating conditions affecting the MD performances [167]. In addition, membrane hydrophobicity/contact angle, thickness, pore size, pore size distribution, tortuosity, surface chemistry and module geometry are the critical membrane characteristics in MD [167, 168]. Exponential increase of membrane distillation flux has been reported with increase of feed temperature; due to exponential increase of vapour pressure of the feed. However, feed temperature range of 40-80 °C and permeate temperature range of 5-30°C are recommended for MD process [43, 166, 167].

High MD flux could be obtained with high feed and permeate velocities as a result of increased heat transfer coefficient at the feed side of the membrane and reduced temperature and concentration polarization outside [167]. Optimising the feed flow velocity has been recommended to maintain turbulence flow conditions and a lower hydrostatic pressure than the liquid entry pressure to avoid membrane

pore wetting. As reviewed by Lawson and Lloyd [166], 0.3 - 0.9 m/s and 0.1 - 0.3 m/s of feed and permeate circulation rates, respectively are widely used.

Membrane wetting is a major limitation in MD process [43, 167]. Due to the surface tension, a pressure drop across the vapour-liquid interface generates up to the liquid entry penetration pressure (Equation 2.5), ΔP_{entry}; once the $\Delta P_{interface}$ exceeds the $\Delta P_{entry,}$ the liquid will penetrate into and through the pores causing the membrane wetting. Once the membrane is wetted, feed liquid can pass through the membrane deteriorating the permeate quality, therefore, wetted membrane is required to dry completely before the next use. Hydrophobic membranes made of polypropylene, polyvinylidine fluoride and polytetrofluroethylene are recommended for MD process. Following properties also recommended for MD membranes to minimise membrane wetting such as low resistant to mass transfer, high liquid entry pressure of water, low thermal conductivity, high thermal stability and chemical resistance.

$$P_{liquid} - P_{vapour} = \Delta P_{interface} < \Delta P_{entry} = \frac{-2B\gamma_L Cos\theta}{r_{max}} \qquad 2.5$$

Where γ_L, θ, r_{max} and B are the liquid surface tension, liquid –membrane contact angle, largest pore size of the membrane and geometric factor determined by the pore size of the membrane respectively.

Membrane thickness is inversely related to MD flux and heat transfer across the membrane. Optimum thickness value has been estimated as 30-60 µm [167, 169]. Pours composite membranes with very low thicknesses (< 5µm) are also reported [167]. The higher the membrane porosity, the higher the flux observed in MD; membrane porosity greater than 70% is recommended for effective MD process.

Positive correlation with MD flux and membrane pore size have been reported [43, 167]. Membranes with pore size from 0.1 to 1 μm have been widely employed for MD and the maximum pore size of 1.0-1.2 μm is recommended to avoid membrane pore wetting [43, 167].

2.5.3 *Membrane distillation for TrOCs removal*

MD can offer complete rejection of all non-volatile solutes such as inorganic salts and pathogenic micro-organisms because mass transfer can occur only in the gas phase. As a result, to date, much of the effort in MD research has focused on desalination applications [43, 170-172]. Unlike pressure driven membrane processes, due to the absence of hydraulic pressure, MD is less susceptible to membrane fouling [170, 173]. Even when membrane fouling does occur, it is expected to be a less compacted layer that can be easily removed [170, 174, 175].

The low operating temperature of MD allows for the utilization of solar thermal or low grade heat as the energy source [43, 48, 166, 176-179]. Given the advantages of high separation efficiency, low fouling propensity, and potentially low energy consumption (when low grade heat is readily available), MD can be used for a range of applications beyond those for brackish and seawater desalination.

Several studies have explored the use of MD for food processing, such as whey protein recovery in dairy processing [175], polyphenolic antioxidants recovery from olive oil wastewater [180], and orange juice concentration [181], separation of fermentation broth [182] as well as treatment of wastewater from the textile [183] and petrochemical industries [48], and municipal water reuse [177, 184]. Despite the growing interest in using MD for the treatment of a range of wastewaters, there is

still a lack of understanding of the rejection mechanisms of trace organic compounds (TrOCs) by MD.

Only a few studies have been conducted to elucidate the rejection of specific organic compounds by MD. The available studies are mostly concerned with industrial chemicals such as benzene [185] and trichloroethylene [186] at an elevated feed concentration. There have been a limited number of studies of the application of MD for wastewater treatment. Examples of these include the investigation by Cath et al. [184] and Cartinella et al. [187] to treat urine and hygiene wastewater by MD for water reuse in long term space missions and the novel membrane distillation membrane bioreactor (MDBR) concept proposed by Phattaranawik et al. [177] and Goh et al. [50].

2.6 Membrane distillation bioreactor

2.6.1 *Membrane distillation bioreactor technology*

Membrane distillation bioreactor (MDBR) is a high retention MBR process that integrates the bioreactor with a MD membrane. There are two main MDBR configurations namely submerged and side stream MDBR (Figure 2.4). The MD membrane can act as a barrier against the permeation of biomass, non-volatile contaminants, low molecular weight compounds and recalcitrant compounds. In the MDBR process, the biological reactor can be operated under thermophilic conditions to facilitate the integration of biological treatment with MD. A thermophilic bioprocess which operates at elevated temperature is advantageous in wastewater treatment because of the high organic biodegradation rate, low sludge yield and enhanced biodegradation [139]. It is also acknowledged that thermophilic wastewater

treatment can work at higher organic loading rates than mesophilic conditions, due to the higher microbial growth rate at elevated temperatures [139, 188]. Lower sludge yield at thermophilic conditions [189, 190] is also an advantage in aerobic wastewater treatment considering the high cost incurred in sludge handling. Thus, MD would effectively couple with thermophilic bioprocesses for wastewater treatment.

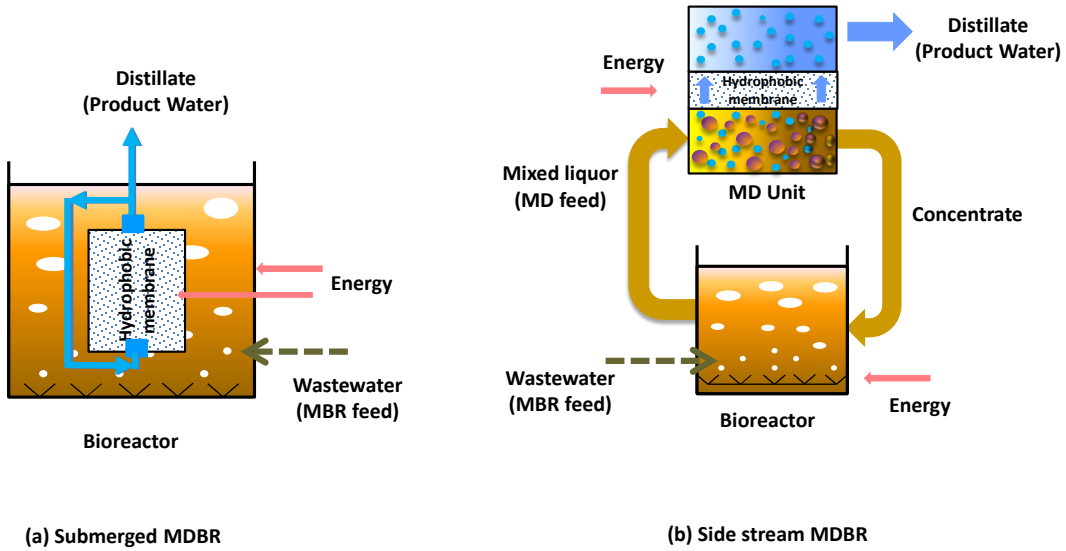


Figure 2.4: MDBR configurations (a) Submerged and (b) Side stream MDBR

2.6.2 *MDBR for wastewater treatment*

The feasibility of MDBR for wastewater treatment has been recognized because of the excellent salt rejection, low operating pressure and moderate operating temperature. MDBR coupling a thermophilic activated sludge process (ASP) with MD has recently been investigated. High quality effluent has been achieved [48, 49, 177] indicating the excellent rejection of non-volatile compounds by MD. Phattaranawik et al. [177], introduced a novel submerged MDBR by combining thermophilic bioreactor and MD for wastewater treatment. Khaing et al.

[48] investigated the feasibility of petrochemical wastewater treatment and reuse using a submerged MD-MBR,where the waste heat of the petrochemical wastewater has been used as the heat source. Excellent quality effluent was achieved regardless of the biological activity of the reactor [48].

Fouling reduction inorder to achieve sustainable flux has been the main focus [50, 51, 191] of MDBR investigations. Phattaranawik et al. [49] has reported rapid flux reduction in their submerged MDBR. They [49] obtained a stable permeate flux of 5 $L/m^2.h$ which is low compared with the typical flux of conventional MBR. Rapid fouling due to cake layer formation is thought to be due to the rapid flux reduction and low stable flux. Gryta [192] suggested feed pre-treatment to avoid fouling propensity. In submerged MDBR, the rapid fouling could be due to the direct interaction of sludge with the MD module. Fouling could also be minimised in side stream MDBR configuration, but all the reported studies have worked only using a submerged MDBR [48, 49, 177].

MDBR for wastewater treatment is yet to be fully understood. Importantly, TrOC removal during MDBR is scarcely reported. Recent studies have highlighted the challenge of removing low molecular weight and recalcitrant TrOCs by biological based treatment processes including MBRs due to the size exclusion mechanism. This demands a high retention MBR process, consequently MDBR could be a promising technology assuring complete retention of TrOCs.

2.7 Summary

The occurrence of TrOCs in the aquatic environment is of significant concern to public health and the environment as a diverse range of potential adverse effects

on living organisms caused by TrOCs has been identified: these may include estrogenic, mutagenic, endocrine disruption and genotoxic effects. As a result, the removal of TrOCs during wastewater treatment has been the subject of many recent publications.

Given the number of TrOCs and the diversity in their molecular properties, the efficiency of MBRs as a barrier for some TrOCs and their removal mechanisms need to be investigated comprehensively. The literature has mainly focused on the fate of TrOCs in the aqueous phase and little is known about the accumulation of TrOCs in sludge.

MD is a low temperature distillation process that involves the transport of water vapour from a feed solution through the pores of a microporous and hydrophobic membrane to the distillate (product) side. Because mass transfer occurs in a gaseous phase, MD offers complete rejection of all non-volatile solutes including non-volatile TrOCs. Unlike pressure driven membrane processes, MD is less susceptible to membrane fouling, due to the absence of hydraulic pressure. Thus MD can successfully use as a post treatment to completely remove TrOCs. Membrane distillation bioreactor (MDBR) is a high retention MBR process where the MD membrane can act as a barrier against the permeation of low molecular weight compounds and recalcitrant compounds. Consequently, MDBR could be a promising technology assuring complete retention of TrOCs.

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

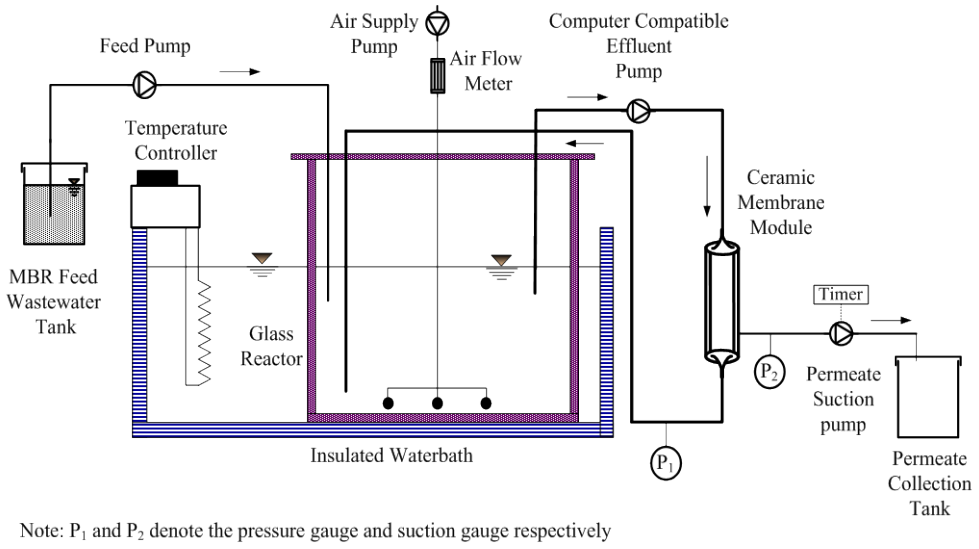
This chapter describes the materials, experimental set-ups, experimental protocol and analytical methods used in this study. Physicochemical properties of the trace organic contaminants (TrOCs) investigated are also discussed. Further details of experimental protocols and physicochemical properties of the TrOCs are also given in subsequent chapters where necessary.

3.2 Experimental Set-ups

3.2.1 *Aerobic membrane bioreactor*

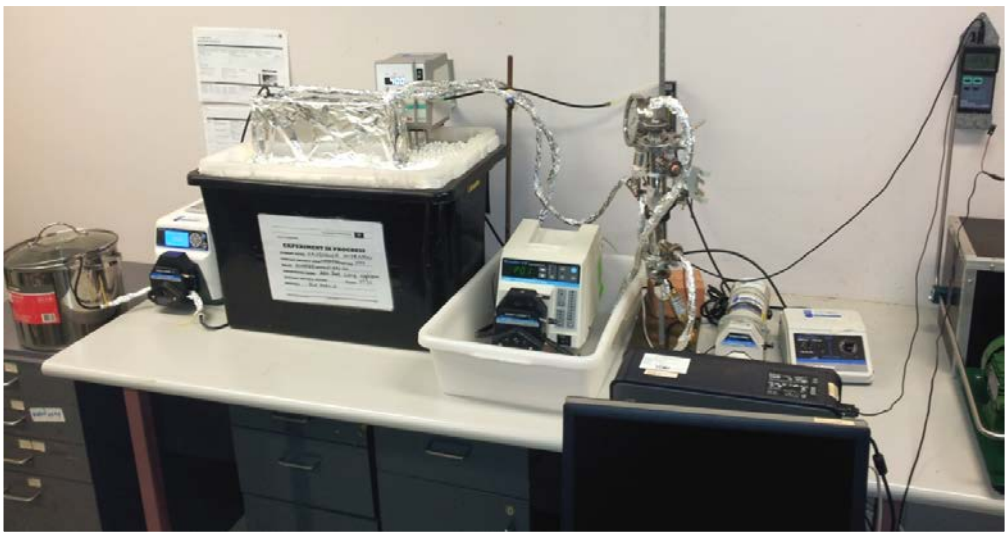
A laboratory scale membrane bioreactor (MBR) was used. A schematic diagram and a picture of the MBR system are shown in Figure 3.1. The MBR system consisted of a 5 L glass reactor, water bath, an influent pump, a recirculation pump, an effluent pump and an external stainless steel membrane vessel that housed a ceramic membrane module. A tubular multi-channel ceramic membrane module (NGK, Japan) made of alumina with a nominal pore size of 1 µm and an effective area of 0.09 m^2 was used in this system. A water bath equipped with an immersion PID controlled heating unit (Julabo, Germany) maintained a constant temperature in the MBR. Peristaltic pumps (Masterflex L/S, USA) were employed for feeding, recirculation, and effluent extraction. The influent pump was continuously operated to provide wastewater to the reactor. The effluent pump was operated employing a 15 min on and 15 min off operating cycle to provide relaxation time to the membrane

module. This represents a longer relaxation time than that used in a typical MBR in order to maintain a stable HRT and avoid excessive membrane fouling. The influent pump flow rate was matched to that of the effluent pump to maintain a constant reactor volume. During the experiment, the MBR was covered with aluminium foil to minimise any loss of TrOCs from photodegradation and evaporation. The bioreactor was aerated with an air pump (Risheng RS 9801, China) connected to a glass diffuser to obtain the desired dissolved oxygen concentration.



Note: P_1 and P_2 denote the pressure gauge and suction gauge respectively

(a)

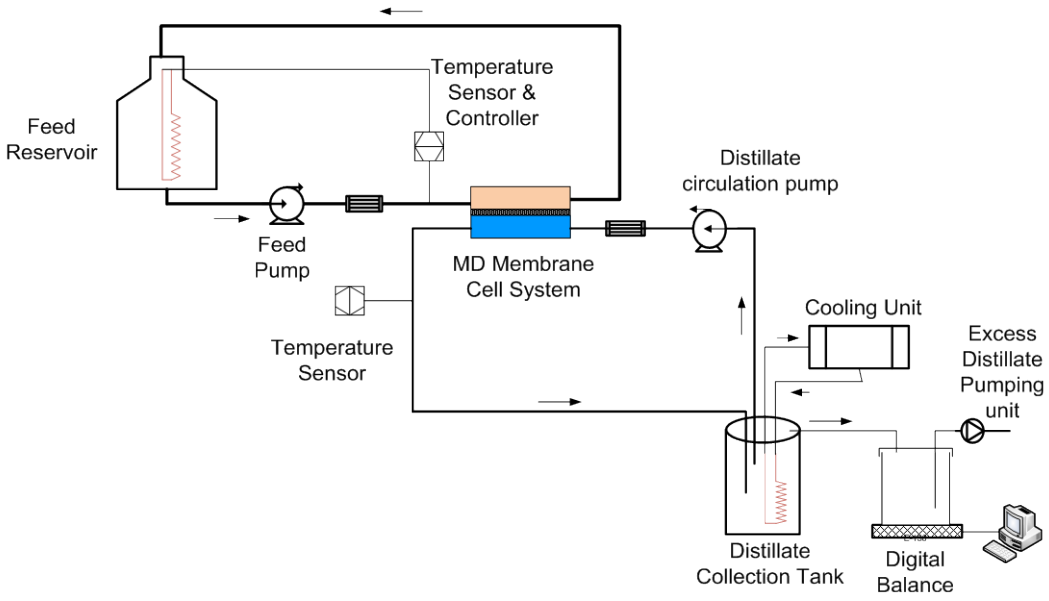


(b)

Figure 3.1: (a) Schematic diagram and (b) a picture of the MBR system

3.2.2 *Direct contact membrane distillation*

The laboratory scale direct contact membrane distillation (DCMD) system used in this study is shown in Figure 3.2. The system comprised a membrane cell, a stainless steel feed tank, a glass distillate tank, two circulation pumps (Micropump Inc., USA), a temperature controller (Coleparmer, USA), and a heating element (Process Technology, USA). The membrane cell was made of acrylic glass, and a flow channel was engraved in each of the two acrylic glass blocks that make up the feed and permeate semi-cells. The length, width, and height of each channel were 145, 95, and 3 mm, respectively. The feed solution was circulated from a stainless steel reservoir to the membrane cell and then returned back to the feed reservoir. A temperature sensor was placed immediately before the feed inlet to the membrane cell. The heating element and the temperature sensor were connected to a temperature control unit that was used to regulate the temperature of the feed solution. Another temperature sensor was installed immediately at the outlet of the distillate semi-cell. The temperature of the distillate was regulated using a chiller (AquaCooler, Australia) equipped with a stainless steel heat exchanging coil immersed directly in the distillate reservoir. Excess water was allowed to overflow from the distillate reservoir into a glass container, placed and continuously weighed on an analytical balance (Mettler Toledo, Switzerland). All pipes used in the DCMD test unit were covered with insulation foam to minimize heat loss. The feed and distillate tanks were covered with aluminium foil to minimise evaporation loss during the experiment. At the end of each experiment, the solution volume was measured again and the total volume loss was found to be less than 6%.

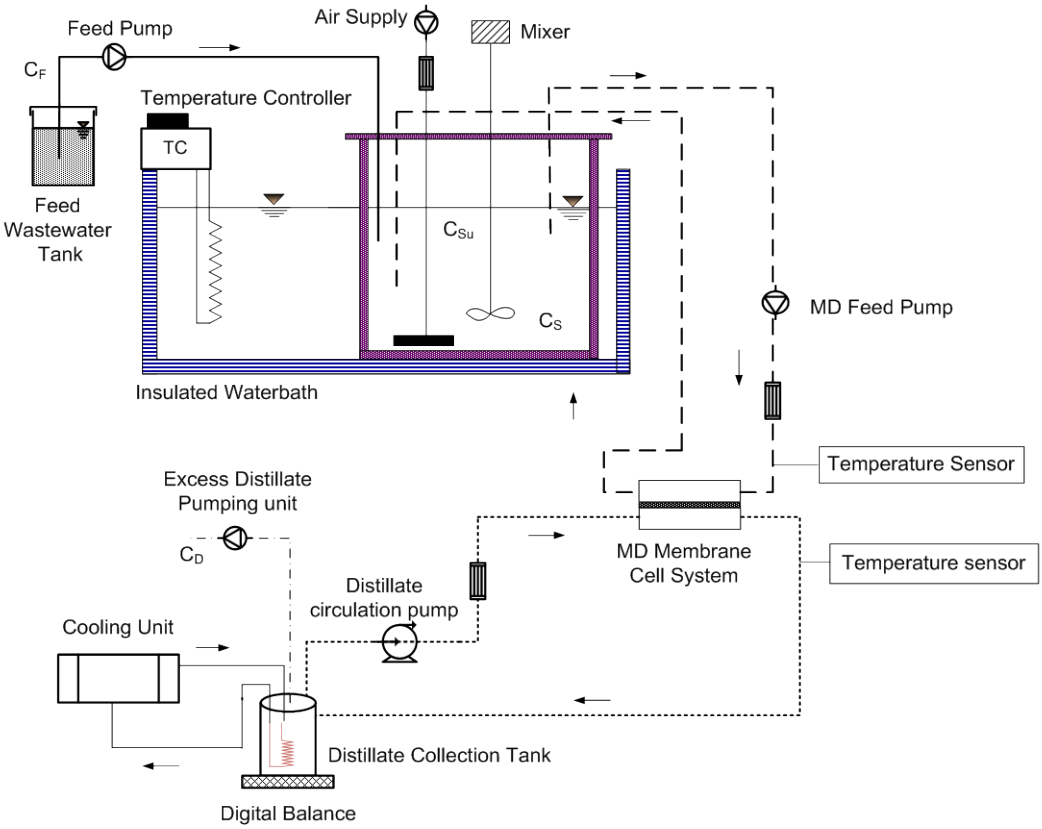


(a)

(b)

Figure 3.2: (a) Schematic diagram and (b) a picture of the DCMD system

3.2.3 *Membrane distillation bioreactor system*



(a)

(b)

Figure 3.3: (a) Schematic diagram and (b) a picture of the novel MDBR experimental system.

A laboratory-scale MDBR system consisting of a glass bioreactor and an external DCMD module was used. A schematic diagram and picture of MDBR system are shown in Figure 3.3. A peristaltic pump (Masterflex L/S, USA) was used to continuously transfer feed wastewater to the bioreactor. The bioreactor had an active volume of 5 L and was submerged in a water bath equipped with an immersion heating unit (Julabo, Germany) to keep the temperature at 40±0.1 ºC. It was also covered with aluminium foil to avoid any exposure to sunlight and heat loss. The bioreactor was aerated using an air pump (Risheng RS 9801, China) connected to a glass diffuser, and an overhead mixer (Heidolph Instruments, Germany) was used to maintain homogeneity within the bioreactor. The mixed liquor of the bioreactor was used as the feed to the external DCMD module.

The DCMD module was made of acrylic glass to minimize heat loss to the surroundings. The flow channels were engraved in each of two acrylic glass blocks that made up the feed and distillate semi-cells. The length, width, and height of each channel were 145, 95, and 3 mm, respectively. The total active membrane surface area for mass transfer was 140 cm2. Feed to the MD system (mixed liquor from the bioreactor) was continuously pumped to the membrane cell and recirculated back to the bioreactor. The temperature of the feed solution entering the MD cell was monitored using a temperature sensor connected to the feed line immediately outside the inlet. The temperature of the distillate leaving the membrane cell was monitored using another temperature sensor located immediately after the outlet of the distillate semi-cell. The temperature of the distillate was kept at 14.0 ± 0.1 °C using a chiller (Neslab RTE7, Thermo Scientific, USA) equipped with a stainless steel heat exchanging coil, which was directly immersed in the distillate reservoir. A glass

container was used as the distillate reservoir and was placed on a digital balance (Mettler Toledo Inc, USA) to calculate the distillate flux. Excess distillate was pumped out from the distillate reservoir intermittently and collected in a stainless steel container for analysis. The MD feed and distillate flow rate were monitored using two rotameters and maintained at 1 L/min (corresponding to a cross flow velocity of 9 cm/s). Milli-Q water (2.25 L) was used as the initial distillate. The MDBR system was covered with insulation foam to minimize heat loss.

3.3 Experimental protocols

3.3.1 *Aerobic membrane bioreactor experiments*

The MBR system was inoculated with sludge obtained from the biological nutrient removal reactor of the Wollongong Wastewater Treatment Plant (Wollongong, Australia). The system was operated at a longer HRT (24 h) than that in a typical MBR to maintain a relatively low membrane flux and to minimise membrane fouling since the focus of the study was on the removal of trace organic contaminants. Excess sludge was withdrawn regularly to maintain the mixed liquor suspended solid (MLSS) concentration in the reactor at 5.0 ± 0.5 g/L. A synthetic wastewater was used to simulate medium strength municipal wastewater and to maintain stable operating conditions. The wastewater characteristics are given in Section 3.6.1. Prior to the addition of the TrOCs to the influent, the MBR system was acclimatised over a period of time under the operating conditions for each experiment as discussed in Section 4.2.2, Section 5.2.1, Section 6.2.2 and Section 3.3.3.

3.3.2 *Direct contact membrane distillation experiments*

One set of MD experiments was conducted using a synthetic feed solution containing approximately 5 µg/L of each TrOC in Milli-Q water. The list of TrOCs and their physicochemical properties are discussed elsewhere (Section 3.7.1). In another set of experiments, effluent obtained from a thermophilic MBR system was used as the feed solution to evaluate the feasibility of combining MD with MBR. Further details of this MBR system are discussed in Section 3.2.1 and MBR experimental conditions are discussed in Section 6.2.2.

In all MD experiments, the feed and distillate temperatures were 40 and 20 °C, respectively, and the cross flow velocity of the feed and distillate circulation flow was 11.7 cm/s. The initial feed volume was 10 L. The experiment was concluded once the water recovery had reached 70% at which stage the feed and distillate samples were collected for TrOC analysis. At the beginning of each MD experiment, 3.35 L of Milli-Q water were used as the initial make-up water. Thus, TrOC concentration in the distillate was corrected for dilution by taking into account the initial volume of make-up water in the distillate.

3.3.3 *Membrane distillation bioreactor experiments*

Prior to the MDBR experiment, the bioreactor sludge was acclimatised at 40 °C by operating the system in an MBR mode using a ceramic microfiltration membrane module (NGK, Japan). Detailed description of the MBR system is given in Section 3.2.1. The bioreactor system was inoculated with activated sludge from the Wollongong Wastewater Treatment Plant (Wollongong, Australia). A synthetic wastewater (Section 3.6.1) was used to simulate medium strength domestic

wastewater and to maintain stable operating conditions. During the acclimatisation period, the bioreactor was operated at a hydraulic retention time (HRT) of 24 h and a solids retention time (SRT) of 88 d. The temperature, dissolved oxygen (DO) concentration and conductivity of the mixed liquor were 40 °C, 2.8±0.5 mg/L, and 425 µS/cm, respectively. The mixed liquor suspended solids (MLSS) concentration was 5.3 g/L, and under these operating conditions the mixed liquor pH remained stable at 7.6. After the bioreactor had been acclimatised for 75 d, the ceramic microfiltration membrane module was removed and the bioreactor was connected to the DCMD system as discussed in Section 3.2.3. TrOCs were then continuously introduced to the influent at a concentration of approximately 5 µg/L of each compound. The MDBR operation commenced at a temperature and DO concentration of 40 °C and 2.8±0.5 mg/L, respectively, and operated for 38 d. The HRT of the MDBR was 9.6 d due to the low distillate flux of the DCMD system.

3.4 Membranes and membrane modules

3.4.1 *Ceramic membrane*

A multi-channel ceramic membrane module (NGK, Japan) made of alumina with nominal pore size of 1 µm was used in the aerobic MBR system. The effective area of the membrane was 0.09 m^2. The membrane module and the membrane characteristics are shown in the Figure 3.4 and Table 3.1, respectively.

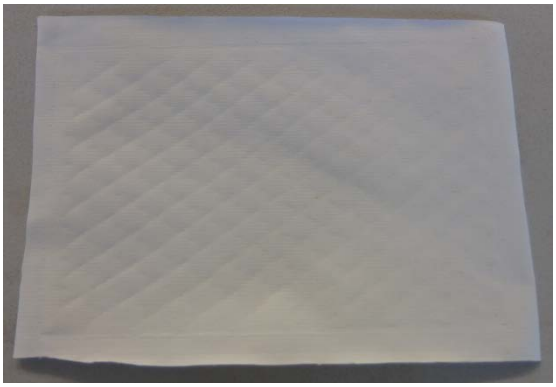
Figure 3.4: Ceramic membrane module

Table 3.1: Characteristics of the ceramic membrane module

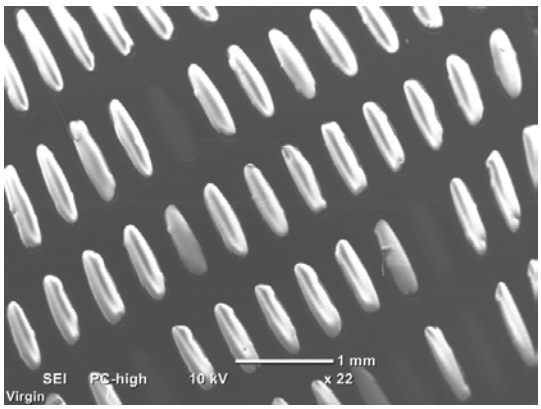
Description	Characteristics
Material	Al_2O_3
Membrane type	Microfiltration
Module configuration	Tubular (multi-channel)
Channel Number	37
Effective surface area	0.09 m^2
Nominal pore size	1 µm
Channel opening diameter	3 mm
Maximum flux	2 m^3/m^2.d (or 83.3 L/m^2.h)
Membrane dimensions Diameter Length	 30 mm 250 mm
Configuration	Inside-out
Maximum operating temperature	300^oC

3.4.2 *Polytetrafloroethylene (PTFE) membrane*

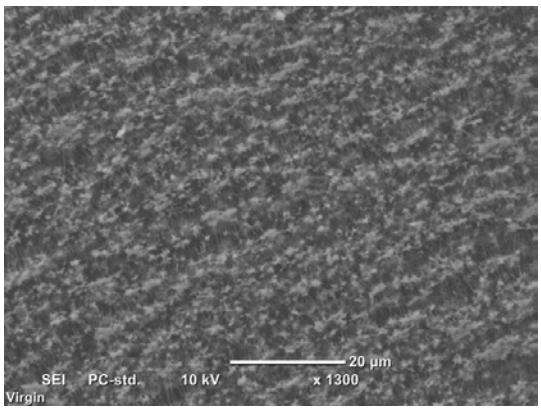
A hydrophobic microporous PTFE membrane (GE, Minnetonka, MN) was used in the membrane distillation experiments. The average pore size, porosity, thickness and active layer thickness of this membrane were 0.22 µm, 70%, 175 µm and 5 µm, respectively [193]. A photo of the virgin membrane and SEM images are shown in Figure 3.5.



(a)



(b)



(c)

Figure 3.5: (a) Picture of the membrane and SEM image of (a) virgin membrane (c) pore of the virgin membrane

3.5 Ceramic membrane cleaning

The ceramic membrane was chemically cleaned once the TMP reached 90 kPa. A standard ceramic membrane cleaning procedure was followed [194]. First, tap water was flushed through the membrane to remove any foulants deposited on the membrane. Membrane module was flushed with a mixture of 2% w/w NaOH and NaOCl solution (400 ppm) at 60 °C for 15 min, and the NaOH and NaOCl mixture was left inside the module for 4 hr. After that membrane was back flushed with 2% w/w NaOH and NaOCl solution (400 ppm) solution for 30 min. Membrane module was then flushed with water (60 °C) until the pH was close to pH 7. The clean water flux was measured with deionised water to confirm the cleaning was completed.

3.6 Synthetic wastewater

3.6.1 *Aerobic membrane bioreactor and membrane distillation bioreactor systems*

A synthetic wastewater was used to simulate medium strength municipal wastewater and to maintain stable operating conditions. The synthetic wastewater was prepared each day by diluting a concentrated stock with Milli-Q water to obtain 100 mg/L glucose, 100 mg/L peptone, 17.5 mg/L KH_2PO_4, 17.5 mg/L $MgSO_4$, 10 mg/L $FeSO_4$, 225 mg/L CH_3COONa and 35 mg/L urea [45]. The concentrated stock solution was prepared every week and kept at 4 °C. TOC, COD, TN, NH_4-N, TP, PO_4-P of feed were 160 mg/L, 550 mg/L, 29 mg/L, 0.5 mg/L, 22 mg/L, and 13 mg/L, respectively.

3.6.2 *Direct contact membrane distillation system*

One set of MD experiments was conducted using a synthetic feed solution containing approximately 5 µg/L of each TrOC in Milli-Q water. In another set of experiments, permeate from the thermophilic ceramic MBR was used as the feed solution, further details are included in Section 6.2.2.

3.7 Target trace organic contaminants

3.7.1 *Pharmaceuticals, steroid hormones phytoestrogens, UV-filters and pesticides*

A set of 29 TrOCs was selected to represent pharmaceuticals, steroid hormones, phytoestrogens, UV-filters (i.e., active ingredients of sunscreens) and pesticides that occur ubiquitously in municipal wastewater [2, 3, 6-8]. Analytical grade samples of these compounds were obtained from Sigma–Aldrich (Saint Louis, MO, USA). A combined stock solution of all TrOCs was prepared in pure methanol and kept at –18 ºC in the dark. Concentration of stock solution was 25 µg/mL. Once the MBR had been acclimatised, these chemicals were continually introduced into the synthetic wastewater to obtain approximately 5 µg/L of each compound which is similar to their occurrence in municipal wastewater [3]. TrOC stock solution of 1 mL was added to 5 L of synthetic feed solution and the mixed feed solution was continuously pumped to the reactor at a flow rate of 3.47 mL/min. Physicochemical properties of these compounds were obtained from the SciFinder Scholar database (https://scifinder.cas.org/scifinder) and detailed in Table 3.2. The vapour pressure, molecular weight (MW), and water solubility of each selected compound were used to calculate the Henry's law constant at 25 °C as: H (atm.m^3/mol) = Vapour pressure (atm) × molecular weight (g/mol) / water solubility (g/m^3)

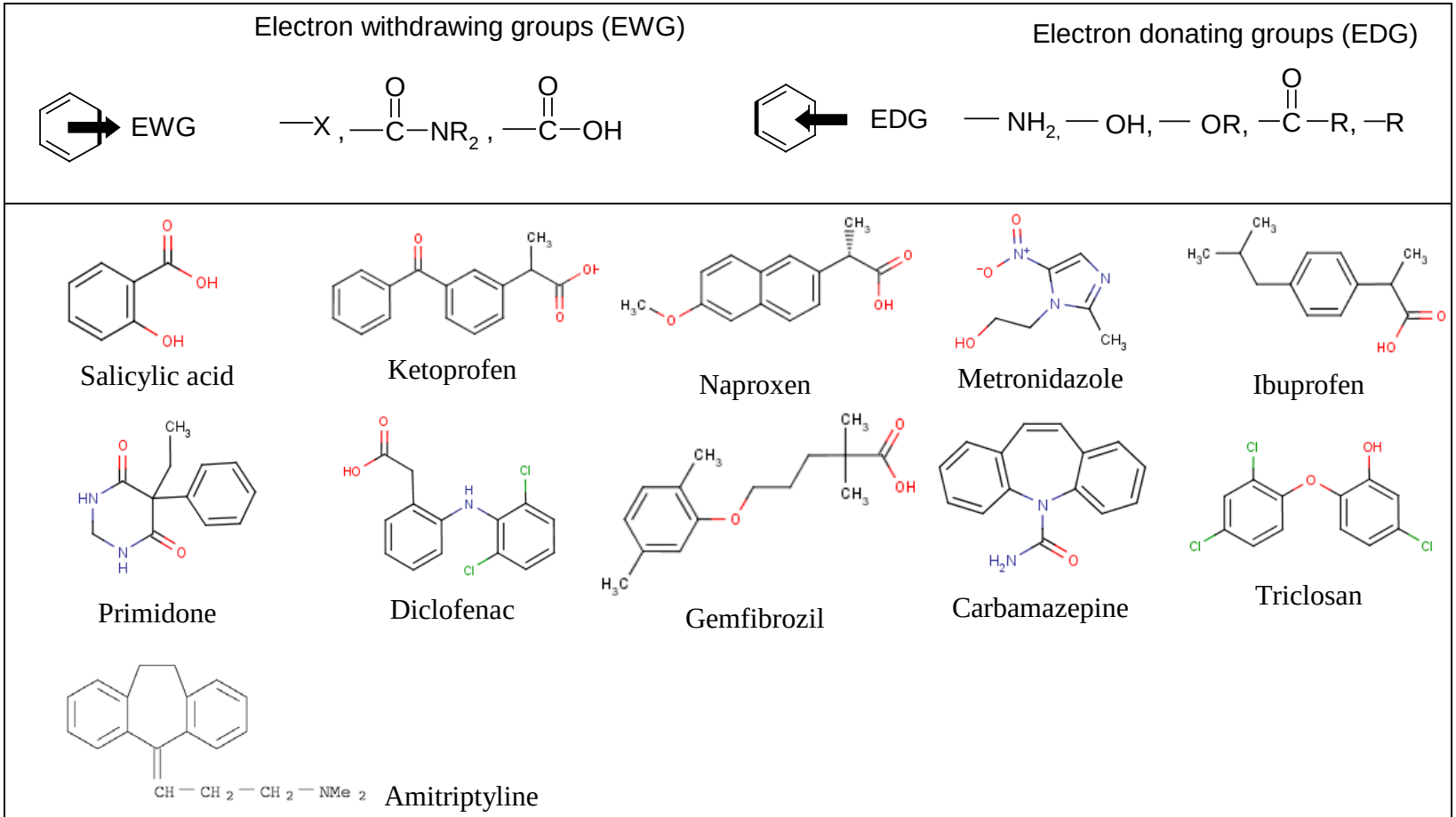
(http://www.epa.gov/superfund/health/conmedia/soil/pdfs/part_5.pdf). The pK_H value presented in Table 3.2 is defined as $pK_H = -\log_{10}H$. Vapour pressure values represent that of pure compound, thus the actual vapour pressure of a compound in the experiment could be slightly varied. Further details of the compounds' physicochemical properties will be described in Section 6.2.3. Molecular structures of the selected compounds are given in Figure 3.6.

Table 3.2: Physicochemical properties of the selected TrOCs

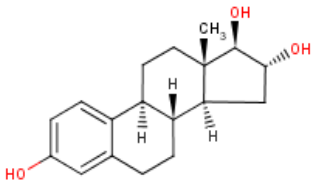
Compound	Compound	Molecular Formula	Molecular Weight (g/mol)	Log *D* at pH 8	Water Solubility at 25 °C & pH 8 (mg/L)	Vapour Pressure at 25 °C (mmHg)	Henry Constant at pH 8 & 25 °C ($atm.m^3/mol$)	pK_H at pH 8 & 25 °C	pka
Pharmaceutical and personal care products	Salicylic acid	$C_7H_6O_3$	138.12	-1.14	1000000	4.45×10^{-5}	8.09×10^{-12}	11.09	3.01
	Ketoprofen	$C_{16}H_{14}O_3$	254.3	-0.55	310,000	3.32×10^{-8}	3.58×10^{-14}	13.45	4.23
	Naproxen	$C_{14}H_{14}O_3$	230.3	-0.18	120,000	3.01×10^{-7}	7.60×10^{-13}	12.12	4.84
	Metronidazole	$C_6H_9N_3O_3$	171.15	-0.14	29,000	2.67×10^{-7}	$2.0\ 7\times 10^{-12}$	11.68	14.44
	Ibuprofen	$C_{13}H_{18}O_2$	206.3	0.14	433,000	1.39×10^{-4}	8.71×10^{-11}	10.06	4.41
	Primidone	$C_{12}H_{14}N_2O_2$	218.25	0.83	1,500	6.08×10^{-11}	1.16×10^{-14}	13.93	12.26
	Diclofenac	$C_{14}H_{11}Cl_2NO_2$	296.15	1.06	12,000	1.59×10^{-7}	5.16×10^{-12}	11.29	4.18
	Gemfibrozil	$C_{15}H_{22}O_3$	250.3	1.18	83,000	6.13×10^{-7}	2.43×10^{-12}	11.61	4.75
	Carbamazepine	$C_{15}H_{12}N_2O$	236.27	1.89	1,100	5.78×10^{-7}	1.63×10^{-10}	9.79	13.97
	Amitriptyline	$C_{20}\ H_{23}\ N$	277.4	3.21	530	1.50×10^{-6}	1.03×10^{-9}	8.99	9.18
	Triclosan	$C_{12}H_7Cl_3O_2$	289.54	4.92	2.9	3.26×10^{-5}	4.28×10^{-6}	5.37	7.80
Steroid Hormones	Estriol	$C_{18}H_{24}O_3$	288.4	2.53	29	1.34×10^{-9}	1.75×10^{-11}	10.76	10.25
	Estrone	$C_{18}H_{22}O2$	270.36	3.62	5.7	1.54×10^{-8}	9.61×10^{-10}	9.02	10.25
	17 α – Ethinylestradiol	$C_{20}H_{24}O_2$	296.48	4.11	3.9	3.74×10^{-9}	3.74×10^{-10}	9.43	10.24
	17 β – Estradiol	$C_{18}H_{24}O_2$	272.38	4.14	3	9.82×10^{-9}	1.17×10^{-9}	8.93	10.27

Compound	Compound	Molecular Formula	Molecular Weight (g/mol)	Log *D* at pH 8	Water Solubility at 25 °C & pH 8 (mg/L)	Vapour Pressure at 25 °C (mmHg)	Henry Constant at pH 8 & 25 °C ($atm.m^3/mol$)	pK_H at pH 8 & 25 °C	pka
	17 β – Estradiol- 17-acetate	$C_{20}H_{26}O_3$	314.42	5.11	1.9	9.88×10^{-9}	2.15×10^{-9}	8.67	-
Pesticides	Clofibric acid	$C_{10}H_{11}ClO_3$	214.64	-1.29	100,000	1.03×10^{-4}	2.91×10^{-10}	9.54	3.18
	Fenoprop	$C_9H_7Cl_3O_3$	269.51	-0.28	220,000	2.13×10^{-6}	3.43×10^{-12}	11.46	2.93
	Pentachlorophenol	$C_{11}H_{15}NO_3$	266.38	2.19	2900	3.49×10^{-4}	4.22×10^{-8}	7.37	4.68
	Atrazine	C_6HCl_5O	215.68	2.64	69	1.27×10^{-5}	5.22×10^{-8}	7.28	2.27
	Propoxur	$C_8H_{14}ClN_5$	209.24	1.54	800	1.53×10^{-3}	5.26×10^{-7}	6.28	12.28
	Ametryn	$C_9\ H_{17}\ N_5\ S$	227.33	2.97	140	1.72×10^{-6}	3.67×10^{-9}	8.43	3.71
Industrial Chemicals	4-tert-butyphenol	$(CH_3)_3CC_6H_4$	150.22	3.39	950	0.0361	7.51×10^{-6}	5.12	10.13
	4-tert-octylphenol	$C_{14}H_{22}O$	206.33	5.18	62	1.98×10^{-3}	8.67×10^{-6}	5.06	10.15
Phytoestrogens	Formononetin	$C_{16}\ H_{12}\ O_4$	268.26	1.81	0.99	8.17×10^{-10}	2.91×10^{-10}	9.54	6.99
	Enterolactone	$C_{18}\ H_{18}\ O_4$	298.33	1.88	160	3.29×10^{-13}	8.07×10^{-16}	15.09	9.93
UV Filters	Benzophenone	$C_{13}\ H_{10}\ O$	182.22	3.21	150	8.23×10^{-4}	1.32×10^{-6}	5.88	-
	Oxybenzone	$C_{14}\ H_{12}\ O_3$	228.24	3.42	390	5.26×10^{-6}	4.05×10^{-9}	8.39	7.56
	Octocrylene	$C_{24}\ H_{27}\ N$	361.48	6.89	0.36	2.56×10^{-9}	3.38×10^{-9}	8.47	-

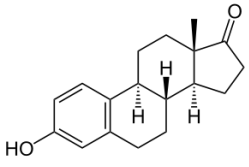
Note: Log D represents the n-octanol/ water partition coefficient which takes into account the compound intrinsic hydrophobicity, pKa and pH of the solution.


Electron withdrawing groups (EWG)
Electron donating groups (EDG)
EWG
—X , —C—NR2 , —C—OH
EDG
— NH2, — OH, — OR, —C—R, —R
Salicylic acid
Ketoprofen
Naproxen
Metronidazole
Ibuprofen
Primidone
Diclofenac
Gemfibrozil
Carbamazepine
Triclosan
CH — CH 2 — CH 2 — NMe 2
Amitriptyline

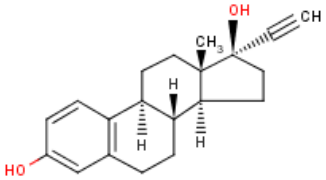
(a)



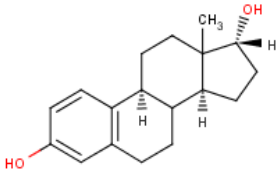
Estriol



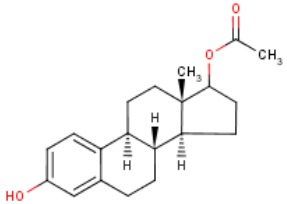
Estrone



17 α – Ethinylestradiol

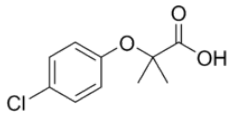


17β – Estradiol

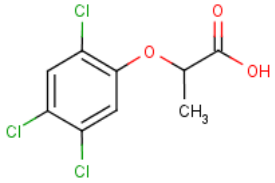


17 β – Estradiol- 17-Acetate

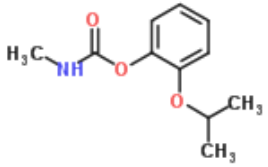
(b)



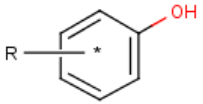
Clofibric acid



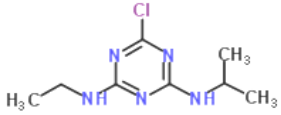
Fenoprop



Propoxur

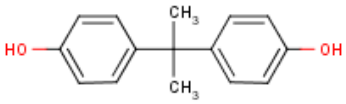


Pentachlorophenol

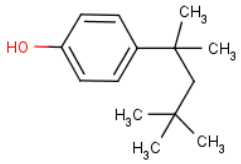


Atrazine

(c)

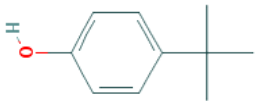


Bisphenol A



4- tert octylphenol

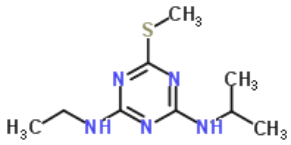
4-



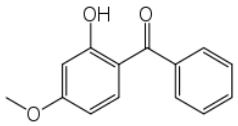
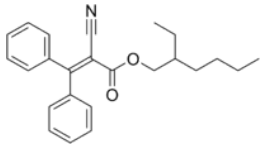
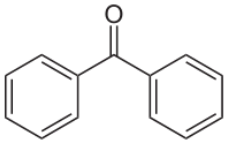
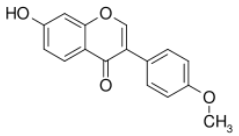
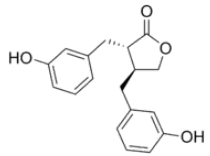
tert butylphenol

(d)

Ametryne



(c)

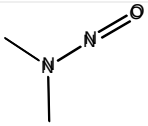
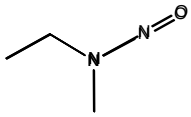
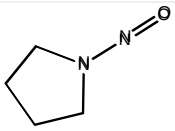
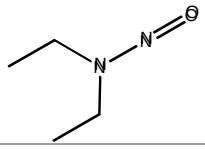
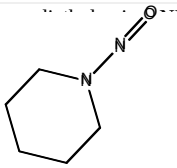
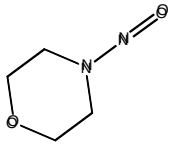
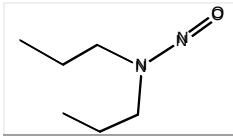
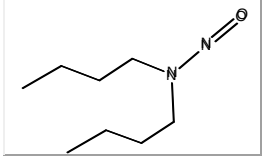
 Oxybenzone	 Octocrylene	 Benzophenone	 Formononetin	 Enterolactone
(e)			(f)	

Note: molecular structures were drawn using ChemBioOffice.

Figure 3.6: Molecular Structures of the selected trace organic contaminants (a) PhACs (b) steroid hormones (c) pesticides (d) industrial chemicals (e) UV filters (f) phytoestrogens

3.7.2 *N-nitrosamines*

Table 3.3: Physicochemical properties of the selected N-nitrosamines

Compound	Structure	Molecular weight (g/mol)	Log *D* at pH 7 & 25 °C	Henry's Law constant at 25 °C (atm m^3/mol)
NDMA		74.05	-0.5	1.2×10^{-6}
NMEA		88.06	0.01	1.44×10^{-6}
NPYR		100.06	-0.09	1.99×10^{-7}
NDEA		102.08	0.52	1.73×10^{-6}
NPIP		114.08	0.44	2.81×10^{-7}
NMOR		116.06	-0.59	2.13×10^{-10}
NDPA		130.11	1.54	3.46×10^{-6}
NDBA		158.14	2.54	9.96×10^{-6}

Note: Properties were adopted from Fujioka et al. [13].

Eight N-nitrosamines (namely NDMA, NMEA, NPYR, NPIP, NDEA, NMOR, NDPA and NDBA) were selected for investigation based on their widespread occurrence in wastewater and probable carcinogenic properties. These compounds have low log *D* values (Table 3.3) and thus they can be classified as being hydrophilic. In addition, because they do not possess ionisable functional groups, these compounds can only exist in the aquatic environment as neutral species. All N-nitrosamines used in this study were of analytical grade and were purchased from Sigma–Aldrich (St Louis, MO, USA). A stock solution of all eight N-nitrosamines was prepared in pure methanol and kept at -18 °C in the dark. Deuterated standards (N-nitrosodimethylamine-d6, N-nitrosomethylethylamine-d3, N-nitrosopyrrolidine-d8, N-nitros-opiperidine-d10, N-nitrosodiethylamine-d10, N-nitrosomorpholine-d8, N-nitrosodipropylamine-d14 and N-nitrosodi-n¬butylamine-d9) were purchased from CDN isotopes (Pointe-Claire, Quebec, Canada) and used as surrogates. The surrogate stock solution was also prepared in methanol and kept at -18 °C in the dark.

3.8 Analytical methods

3.8.1 *Basic water quality analysis*

3.8.1.1 Total organic carbon and total nitrogen analysis

Total organic carbon (TOC) and total nitrogen (TN) concentrations in liquid samples were analysed using a TOC/TN-V_{CSH} analyser with an auto sampler (ASI-V) (Shimadzu, Japan). TOC -VCSH analyser combined with TNM-1 unit measured TOC and TN simultaneously. High purity air was used as the carrier gas. TOC analysis was conducted in non purgeable organic carbon mode (NPOC) to avoid

analytical error caused by the varied inorganic carbon concentrations in samples. Samples were acidified to pH 2 to convert inorganic carbon species to CO_2 and sparged with the carrier gas to drive off the CO_2. Total carbon combustion was at 680 °C. Total carbon in the sample oxidised to CO_2 and detected using a non-dispersive infrared detector (NDIR). TN measurement is a summation of all forms of nitrogen present in liquid phase (organic, nitrite, nitrate and ammonia). For TN measurements, sample combustion was undertaken at 720 °C. TN in the sample decomposes to nitrogen monoxide and is detected by chemiluminescence. Potassium dihydrogen phthalate (KHP) and potassium nitrate (KNO_3) were used as the TOC and TN standard solutions. Standard solutions were checked with an each sample batch and TOC/TN concentrations were corrected according to the standard curves.

3.8.1.2 Nitrate (NO_3^-), nitrite (NO_2^-) and ammonium (NH_4^+) analysis

NO_3^- and NO_2^- concentrations in the liquid samples were analysed by ion chromatography. An ion chromatograph (Shimadzu, Japan) was employed equipped with conductivity detector (CDD-10A VP), degasser (DGU-20A3), liquid chromatograph (LC-20AD), autosampler (SIL-20 AHT) and suppressor (Dionex RFC-10). A high-capacity carbonate based anion-exchange column (IonPac AS23, Dionex) was used. A mixture of 4.5 mM Sodium carbonate and 0.8 mM sodium bicarbonate was used as the eluent. Potassium nitrate (KNO_3) and potassium nitrite (KNO_2) were used as the standard solutions for NO_3^- and NO_2^-, respectively. NH_4^+ concentration was measured according to the phenate method in accordance with standard methods for water and wastewater examinations [195]. Absorbance at 630

nm wave length was measured by a UV-visible spectrophotometer (Shimadzu UV 1700, Japan). NH_4Cl solution was used as the standard solution.

3.8.1.3 Dissolved oxygen, pH, mixed liquor suspended solids and mixed liquor volatile suspended solids

Dissolved oxygen (DO) concentration of the bioreactor mixed liquor was measured using Professional plus YSI equipped with Pro 20 DO probe (YSI incorporation, USA). The pH of the liquid samples was measured using a Orion 4 Star Plus portable pH and conductivity meter (Thermo Scientific, Waltham, MA). Mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) concentration of the mixed liquor were analysed in accordance with the standard methods for water and wastewater examinations [195].

3.8.2 *Solvent extraction method*

To determine the TrOC concentrations in the sludge, a solvent extraction method modified from Trinh et al. [196] was used (Figure 3.7). The sludge sample was first centrifuged and the solid pellet was freeze-dried for 4 h (-53 °C and 0.06 mbar) using an Alpha 1-2 LD plus Freeze Dryer (Christ GmbH, Germany). The dried sludge was ground to powder and 0.5 g was transferred into a glass test tube. Methanol (5 mL) was added to the test tube, thoroughly mixed using a vortex mixer (VM1, Ratek, Australia) for 3 min and ultrasonicated for 10 min at 40 °C. The sample was then centrifuged at 3270 x g for 10 min (Alleegra X-12R, Beckman Coulter, USA) and the supernatant was collected in a glass beaker for further analysis. Dichloromethane (5 mL) and methanol (5 mL) were added to the remaining pellet. The whole process of mixing, ultrasonic extraction and centrifugation was

then repeated. The supernatants from both steps were then mixed together; Milli-Q water added up to a volume 50 mL and residual methanol and dichloromethane purged using nitrogen gas. Finally, Milli-Q water was added to obtain an aqueous sample (500 mL). This sample was then analysed using the analytical method described in Section 3.8.3, and the TrOC concentration per gram of dry sludge was calculated.

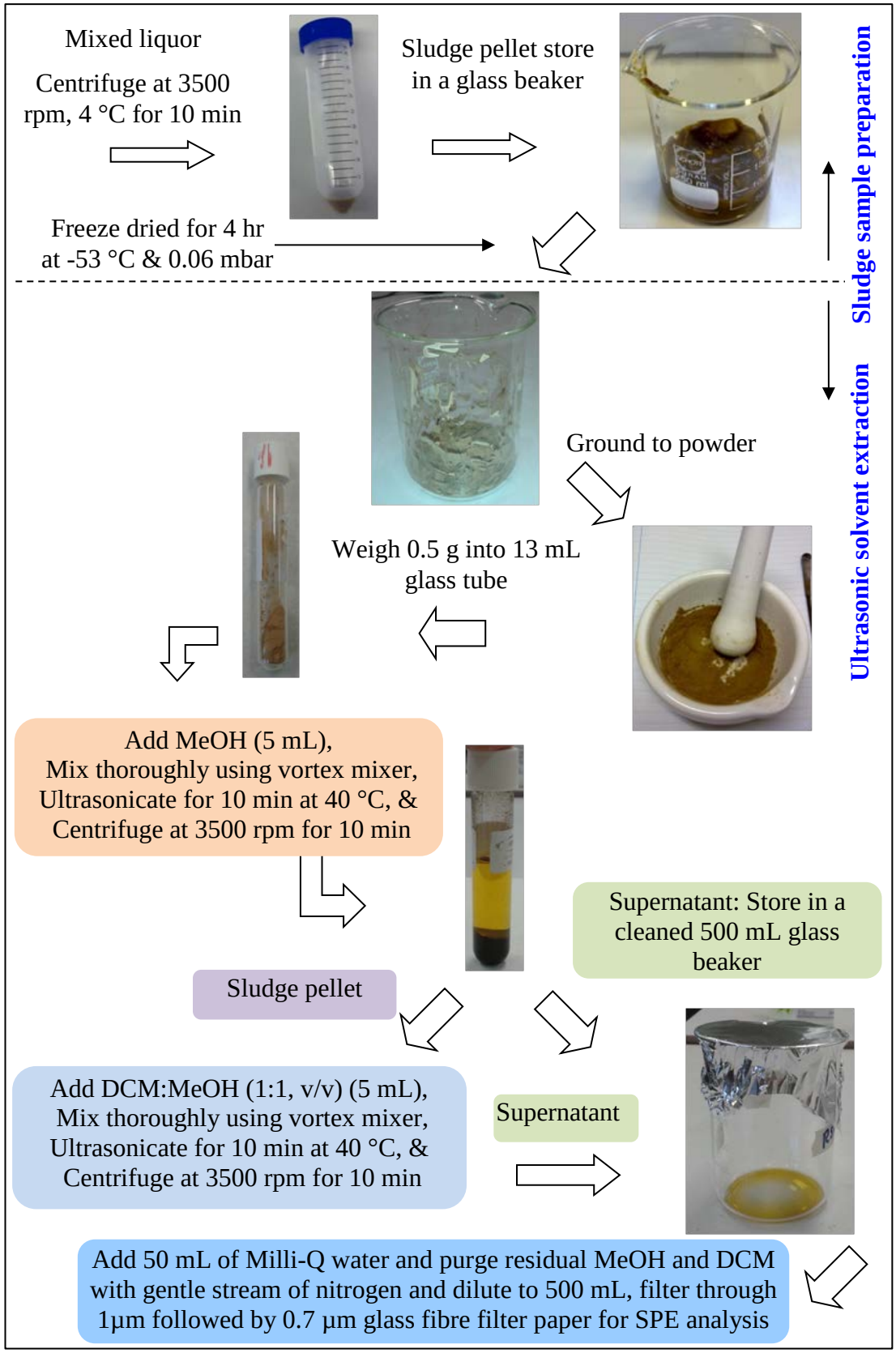


Figure 3.7: Procedure for solvent extraction

3.8.3 *Analysis of pharmaceuticals, steroid hormones phytoestrogens, UV-filters and pesticides*

TrOC concentrations in the aqueous samples were determined using an analytical method previously reported by Hai et al. (2011c). Specific sampling frequencies for the TrOC analysis are given in Chapter 4–7. This method consists of a solid phase extraction procedure (SPE) (Figure 3.8) followed by gas chromatography and quantitative determination by mass spectrometry with electron ionisation. TrOC concentrations in liquid samples (500 mL each) were extracted using 6 mL 200 mg Oasis HLB cartridges (Waters, Milford, MA, USA). First, the cartridges were preconditioned with 7 mL dichloromethane (DCM) and methanol (MeOH) mixture (1:1 v/v), 7 mL methanol followed by 7 mL reagent water (synthetic feed wastewater excluding TrOCs). The samples were acidified to pH 2-3 (4 M H_2SO_4) and loaded onto the cartridges at a flow rate of 1-5 mL/min. Then, the cartridges were rinsed with 20 mL Milli-Q water (6× 7mL) and dried in a stream of nitrogen for 30 min. The extracted TrOCs were eluted from the cartridge using 7 mL of methanol followed by dichloromethane and methanol mixture (1:1 v/v) at a flow rate of 1-5 mL/min. Then the eluents were evaporated using a water bath (40 °C) under a gentle stream of nitrogen. The extracts were dissolved with 200 uL methanol which contained 5 µg bisphenol A-d16 and transferred into 1.5 mL vials, further evaporated under a gentle stream of nitrogen. Finally, the extracts were derivatized by adding 100 µL of N,O-Bis(trimethylsilyl)trifluoroacetamide (1% trimethylchlorosilane) and pyridine (dried with KOH solid), then heated in a heating block (60–70 ºC) for 30 min. The derivatives were cooled to room temperature and analysed using GC–MS using a QP5000 (Shimadzu, Japan) equipped with a AOC20i

auto-sampler and a Phenomenex Zebron ZB-5 (5% diphenyl–95% dimethylpolysiloxane) capillary column (30 m × 0.25 mm ID, df = 0.25 µm). The limit of detection of the selected TrOCs by this analytical method was 20 ng/L or lower [23].

3.8.4 *N-nitrosamines analysis*

N-nitrosamine concentrations were determined using solid phase extraction (SPE), gas chromatography (GC) and analysis by tandem mass spectrometry (MS–MS) with electron ionization (EI) using a method previously reported by McDonald et al. [197].

Prior to the SPE procedure (Figure 3.9) the surrogate stock solution was added to the sample to obtain a concentration of 50 ng/L of each internal standard. The samples were then extracted using the Supelclean™ Coconut Charcoal SPE cartridges (2 g/mL, supplied by Supelco, St. Louis, MO, USA). Extracted compounds were eluted from the cartridges using dichloromethane (4 X 3 mL) and concentrated to 1 mL under a slight stream of high purity nitrogen in a Turbovap LV evaporation system (Caliper Life Sciences, Hopkinton, MA, USA). A volume of 100 µL of toluene was added to the eluted sample to minimize compound evaporative loss. Finally, concentrated samples were transferred to 2 mL GC vials for analysis. Samples were analysed on an Agilent 7890A GC coupled with an Agilent 7000B triple quadrupole tandem mass spectrometer (MS/MS). An injection volume of 1 µL was used. Analytes were separated on an Agilent DB-1701P, (30 m × 0.25 mm, 0.25 µm film thickness) column using a 1.2 mL/min ultrahigh purity helium flow. The

quantitative detection limit of this method was less than 4 ng/L for all N-nitrosamines investigated in this study.

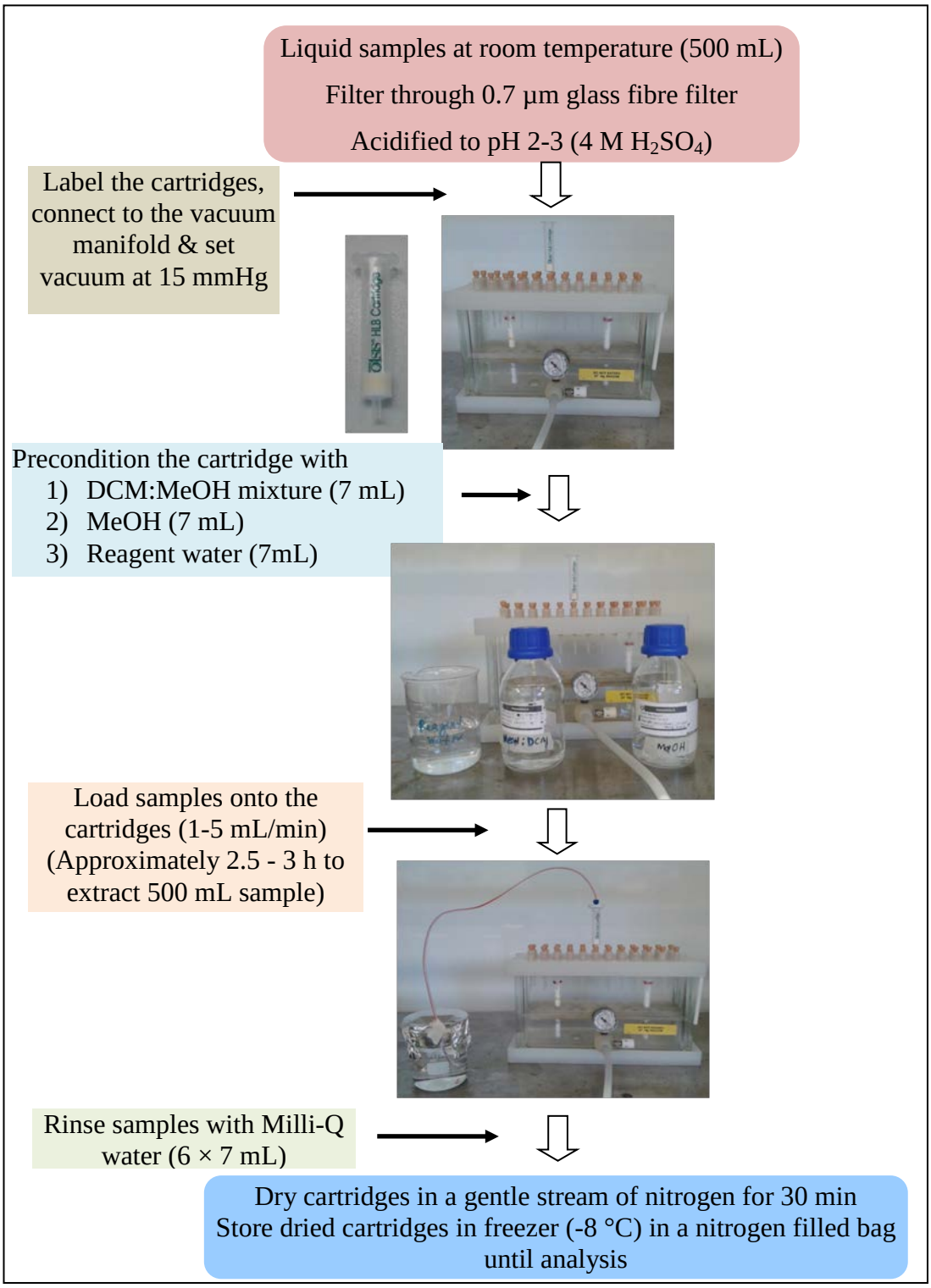


Figure 3.8: Procedure for solid phase extraction for analysing pharmaceuticals, steroid hormones, phytoestrogens, UV-filters and pesticides

Liquid samples (200 mL) at room temperate
(Surrogate was added immediately after sampling)

Label the cartridges (make sure cartridges are packed well), connect to the vacuum manifold and set vacuum at 15 mmHg

Precondition the cartridge with
1) DCM (2 × 3 mL)
2) MeOH (2 × 3 mL)
3) Milli-Q water (4 × 3mL)

Load cartridges onto the vacuum manifold (5 mL/min) (Approximately 1-2 h for 200mL sample)

Rinse sample with Milli-Q water (3 mL)

Dry cartridges in a gentle stream of nitrogen until no condensation is left on cartridges (approximately 1 h) and store cartridges in freezer (- 8 °C) in a sealed bag until analysis

Figure 3.9: Procedure for solid phase extraction for analysing N-nitrosamines

3.9 Summary

This chapter described the experimental procedure used to achieve the objectives (examine the fate and removal of TrOCs during high retention MBR) of the study. Four laboratory scale experimental set-ups such as aerobic MBR, DCMD, MDBR and AnMBR were used. Relevant experimental protocols and analytical methods also discussed. A set of 29 TrOCs with diverse physicochemical properties was used to represent pharmaceuticals, steroid hormones, phytoestrogens, UV-filters (i.e., active ingredients of sunscreens) and pesticides that occur ubiquitously in municipal wastewater. Eight N-nitrosamines were also selected for investigation based on their widespread occurrence in wastewater and probable carcinogenic properties. A synthetic wastewater was used to simulate medium strength municipal wastewater and to maintain a stable operating condition. TrOCs removal and their fate during each process was systematically analysed and discussed in subsequent chapters.

CHAPTER 4

REMOVAL AND FATE OF PHARMACEUTICALS, STEROID HORMONES, PHYTOESTROGENS, UV FILTERS AND PESTICIDES DURING MBR TREATMENT

Corresponding publication: K.C. Wijekoon, F.I. Hai, J. Kang, W.E. Price, W. Guo, H.H. Ngo, L.D. Nghiem, The fate of pharmaceuticals, steroid hormones, phytoestrogens, UV-filters and pesticides during MBR treatment, Bioresource Technology, 144 (2013) 247-254.

4.1 Introduction

A large number of trace organic contaminants (TrOCs) have been detected in raw sewage, treated effluent and withdrawn sludge as well as sewage-affected water bodies all over the world. These include steroid hormones, pharmaceuticals, personal care products, surfactants, pesticides, and disinfection by products [2-5]. In recent years, several studies have also highlighted the ubiquitous occurrence of UV filters and phytoestrogens in municipal wastewater as a potential concern [6-8], although little is known about their fate during wastewater treatment. The occurrence of TrOCs in the aquatic environment is of significant concern to public health and the environment because of the potential adverse impact on living organisms caused by TrOCs, which can include a range of oestrogenic, mutagenic, endocrine disrupting and genotoxic effects [3, 4, 7]. As a result, the removal of TrOCs during wastewater treatment has been the subject of many recent publications.

Appreciable removal of certain TrOCs such as natural steroid hormones and phenolic compounds by membrane bioreactor (MBR) treatment has been widely reported in the literature [15-25]. MBR is usually operated with a long solid retention time (SRT) which can improve the removal of some TrOCs via adsorption onto the sludge and subsequent biodegradation. A long SRT can also favour the proliferation of slowly growing bacteria (such as nitrifying bacteria), thus improving the microbial diversity in the reactor and achieving better biodegradation of TrOCs [19, 26-30]. However, given the number of TrOCs and the diversity in their molecular properties, the efficiency of MBRs as a barrier for some TrOCs and their removal mechanisms is still poorly understood. In addition, studies available in the literature have focussed mostly on the fate of TrOCs in the aqueous phase and little is known about the accumulation of TrOCs in sludge.

Biodegradation and/or adsorption can govern the removal of TrOCs from the aqueous phase during MBR treatment. Molecular structure is an important factor for TrOC biodegradation. A previous study by Tadkaew et al. [37] revealed the effect of physicochemical properties (namely log *D*) and functional groups on the removal of TrOCs. They proposed a qualitative predictive framework which stipulates that: (i) hydrophobic compounds (log $D > 3.2$) and compounds which are hydrophilic (log $D < 3.2$) but possess only electron donating groups (EDGs) would achieve high removal during MBR treatment, (ii) the removal efficiency of hydrophilic compounds possessing only electron withdrawing groups (EWGs) would be low, and (iii) hydrophilic compounds having both EWGs and EDGs would achieve varying removal depending on the type of the functional group. EWGs (e.g. amide and

chloro) impede initial electrophilic attack by oxygenases and electron-donating groups EDGs (e.g hydroxyl and amine) promote electrophilic attack by oxygenases [37]. As a result, TrOCs with EWGs are less biodegradable and TrOCs with EDGs are readily biodegradable.

Given the diverse range of emerging TrOCs, elucidation of the removal mechanisms and subsequent development of predictive tools for the extent of the removal of specific groups is vital to avoid continuous and expensive monitoring of the fate of each individual compound.

Adsorption of TrOCs onto sludge is an important removal mechanism during MBR treatment. It is noteworthy that the presence of TrOCs in sludge is of concern especially in terms of agricultural applications. Agricultural usage accounts for 50% of the biosolids production in Europe. As a result, the European Union regulates these organic compounds in sludge to secure the safety of agriculture and soil [7]. Therefore, it is crucial to understand the removal of TrOCs from both aqueous and solid phases in wastewater treatment.

There are very few reported studies on removal mechanisms of TrOCs by MBR. Radjenovic et al. [29] investigated the fate and distribution of pharmaceuticals in the aqueous and solid phases during the conventional activated sludge and MBR treatment. They have identified adsorption to sludge as a possible removal pathway for several pharmaceutical compounds such as mefenamic acid, propanolol and loritidine. Radjenovic et al. [29] suggested that MBR, yielding higher biodegradation rate due to the application of a prolonged SRT, could reduce the TrOC load in sludge. In addition, Clara et al. [26, 27] and Reif et al. [28]also illustrated that

compared to the conventional activated sludge treatment, MBR treatment results in enhanced biodegradation of several groups of TrOCs (such as pharmaceuticals, fragrances and endocrine disruptive compounds) due to a longer SRT.

This study aimed to provide further insight to the fate of TrOCs during MBR treatment. Aqueous phase and solid phase removal of 29 compounds representing several groups of TrOCs and possessing diverse physicochemical properties were examined. The effects of hydrophobicity and molecular structure on their removal mechanisms were elucidated. Finally, a generalised framework for predicting the removal mechanisms and fate of TrOCs during MBR treatment is proposed.

4.2 Materials and methods

4.2.1 *Membrane bioreactor system*

A laboratory scale aerobic MBR system was used. Detailed description of the set-up is given in Section 3.2.1. During the experiment, the MBR was covered with aluminium foil to minimise any loss of TrOCs from photodegradation and evaporation.

4.2.2 *Experimental protocol*

The MBR system was inoculated with sludge obtained from the biological nutrient removal reactor of the Wollongong Wastewater Treatment Plant (Wollongong, Australia). Glucose and peptone based synthetic wastewater (Section 3.6.1) was used to simulate medium strength municipal wastewater and to maintain a stable operating condition. The hydraulic retention time (HRT), temperature, dissolved oxygen concentration (DO) and mixed liquor pH were 26 h, 26.0 ± 0.2 °C,

2.4 ± 0.3 mg/L and 7.3 ± 0.3, respectively. The system was operated at a longer HRT than that in a typical MBR to maintain a relatively low membrane flux and to minimise membrane fouling since the focus of the study is on the removal of trace organic contaminants. Excess sludge was withdrawn every 3–4 days to maintain the mixed liquor suspended solid (MLSS) concentration in the reactor at 5.0 ± 0.5 g/L, resulting in an SRT of 88 days. Prior to the addition of the trace organic contaminants to the influent, the MBR system was acclimatised for 125 days under the above mentioned conditions.

4.2.3 *Model compounds*

A set of 29 emerging TrOCs (Table 3.2) was selected to represent pharmaceuticals, steroid hormones, phytoestrogens, UV-filters and pesticides that occur ubiquitously in municipal wastewater. A detail description of the selected TrOCs is given in Section 3.7.1.

4.2.4 *Analytical methods*

4.2.4.1 Basic water quality parameters

Basic water quality parameters such as total organic carbon (TOC) and total nitrogen (TN) were analysed using a TOC/TN-V_{CSH} analyser (Shimadzu, Japan). All other basic water quality parameters relevant to the MBR process were analysed according to the standard methods for water and wastewater examination as reported in a previous study.[23]. A detailed description of analysis of basic water quality parameters is given in Section 3.8.1.

4.2.4.2 Trace organic contaminant analysis

TrOC concentrations in the influent, sludge and effluent were determined. Ultrasonic solvent extraction method was used to extract TrOC from sludge, a detailed description is given in Section 3.8.2. Then, TrOC concentrations in liquid samples were determined using a method consisting SPE and gas chromatography followed by quantitative determination by mass spectrometry as previously reported by Hai and co-workers. [23] (Section 3.8.3).

4.3 Results and discussion

4.3.1 *Total organic carbon and total nitrogen removal performances*

As noted earlier, the MBR system was acclimatised for 125 days before the continuous operation using TrOC-laden feed solution. Basic performance parameters including the concentrations of NO_2^-–N, NO_3^-–N, and NH_4^+–N in feed and permeate, TOC and TN removal efficiency, permeate turbidity, DO, pH, mixed liquor volatile suspended solid (MLVSS) and mixed liquor suspended solid (MLSS) in the mixed liquor were continuously monitored to assess the operational stability of the MBR system. NO_2^-–N, NO_3^- –N, and NH_4^+–N concentrations in permeate were found to be stable at less than 0.5 ± 0.2 mg/L, 14 ± 2 mg/L and 4.3 ± 0.6 mg/L, respectively throughout this study. The negligible NO_2^-–N concentration in permeate indicated a good aerobic nitrification capacity of the MBR system and could possibly be attributed to the nitrifying bacteria-rich sludge which was used to inoculate the reactor (Section 0). In the MBR process, the membrane can effectively retain the slow growing nitrifying microorganisms. In addition, the long SRT used in this study was also conducive to maintenance of a nitrifying bacteria-rich sludge within the

bioreactor. With 164 ± 8 mg/L of TOC and 30 ± 2 mg/L of TN in the feed solution, TOC and TN removals were stable at 90 ± 1% and 33 ± 6%, respectively (Figure 4.1). The low TN removal efficiency can be attributed to the absence of an anoxic chamber in our lab scale MBR which is necessary for effective denitrification. In this study, the permeate turbidity was below 0.6 NTU and a MLVSS/MLSS ratio of around 0.8 was consistently observed throughout this study.

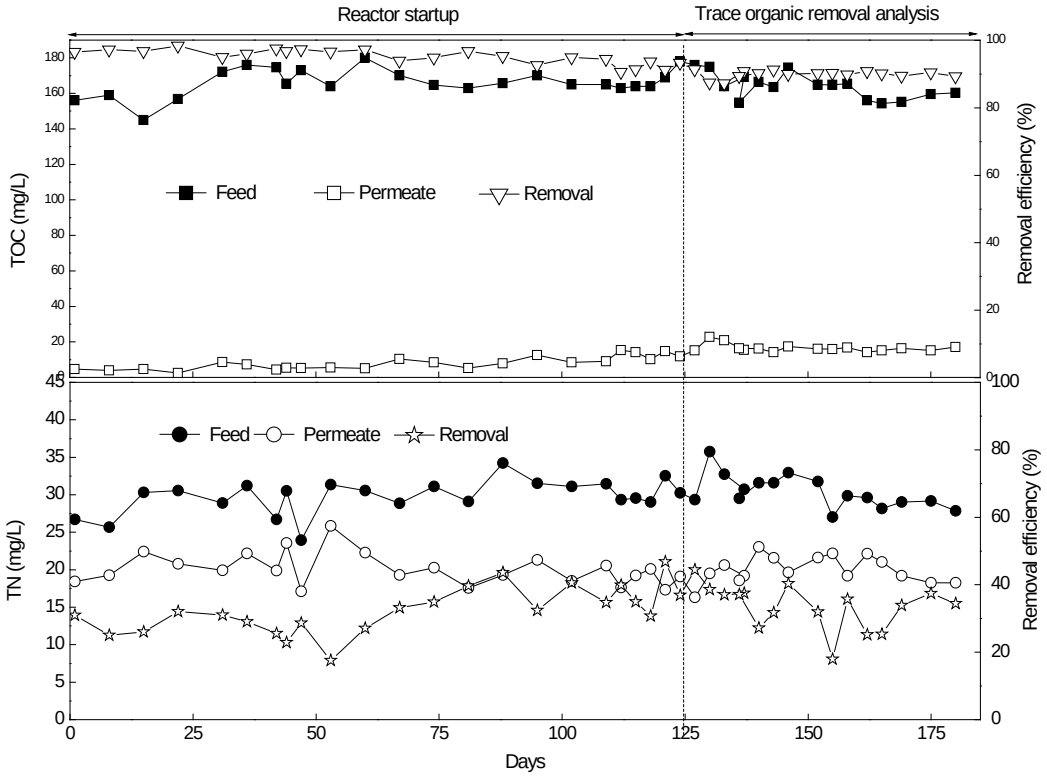


Figure 4.1: Variation of (a) TOC and (b) TN removal performance of MBR : MBR operating temperature, dissolved oxygen, pH, MLSS, HRT and SRT were maintained at 26 ± 0.2 ºC, 2.4 ± 0.3 mg/L,7.5 and 5.0 ± 0.5 mg/L, 26 h and 88 d, respectively.

4.3.2 *Removal of trace organic contaminants from the aqueous phase*

The removal efficiency of each TrOC from the aqueous phase was relatively stable over the study period (Figure 4.2), although a significant variation in removal

between the TrOCs was observed. All eleven hydrophobic TrOCs (i.e., log DpH 8 >3.2) used showed more than 95% removal efficiency, with octocrylene being the only exception (88%). On the other hand, the removal of hydrophilic TrOCs varied from as low as 27% (diclofenac) to almost complete removal (ibuprofen). Since these TrOCs possess diverse molecular structure and functional groups (Figure 3.7), it was not surprising that their removal efficiencies varied significantly. Of the 29 compounds selected in this study, four showed significantly lower removal efficiencies (60% or below). Diclofenac was removed with the lowest level of removal (27%) followed by atrazine (36%), propoxur (58%) and carbamazepine (58%). It is noteworthy that these four compounds are hydrophilic and possess strong EWGs such as amide and chloride in their molecular structure (Figure 3.7). Thus, the low removal efficiency could be attributed to their low hydrophobicity and more importantly the occurrence of strong EWGs in their molecular structure, as previously reported by Tadkaew et al. [37]. Among the UV-filters and phytoestrogens selected, formononetin, enterolactone, benzophenone and oxybenzone were highly removed (>96%) due to the presence of EDGs (hydroxyl and methyl) in their molecular structure (Figure 3.7). By contrast, the removal of octocrylene, with a moderately strong EWG (cyano group), was lower (67–96%) in comparison to the removal of other selected UV-filters and phytoestrogens. Similar removal of octocrylene [8], benzophenone [99] and considerably lower removal of the selected phytoestrogens[84] during conventional activated sludge treatment have been previously reported. However, their removal during MBR treatment has been rarely studied.

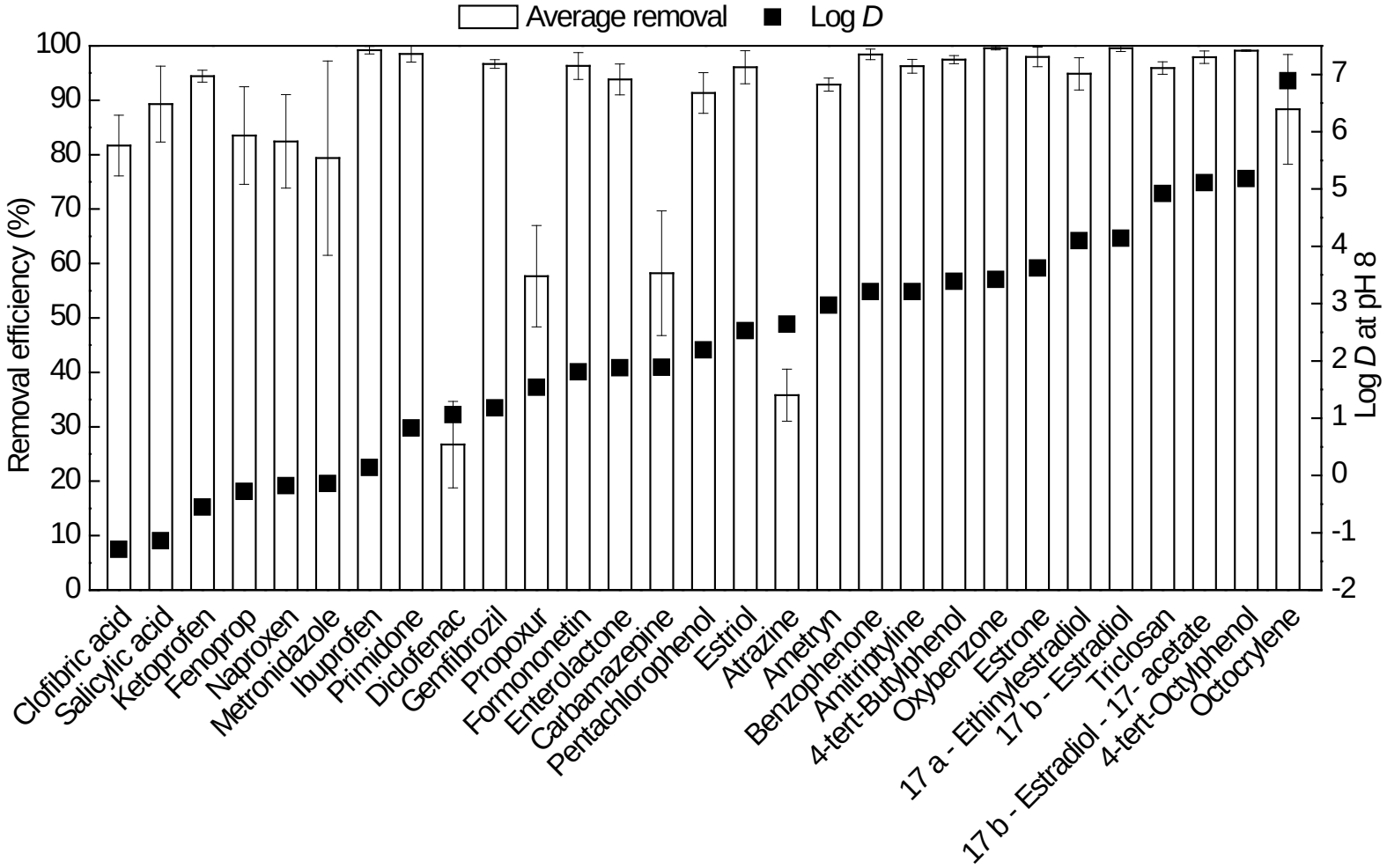


Figure 4.2: Average removal efficiency of trace organic contaminants by MBR; error bars represent the standard deviation calculated from duplicate samples taken once a week for five weeks. Operating conditions of MBR are presented in Section 4.2.2.

In this study, a better removal of nitrogen bearing compounds (where nitrogen is bound to the cyclic structure - atrazine, primidone, metranidazole, carbamazapine, diclofenac and propoxur) was observed (Figure 4.2) in comparison to several previous studies [37, 40]. For instance, a near-complete removal of primidone was observed which was in contrast to the very low removal efficiency (<13%) previously reported by Tadkaew et al. [37]. A higher removal of atrazine (36%) than that reported (<5%) in Tadkaew et al. [37]. and Alturki et al. [40] was also observed. Notably, Bouju et al. [157] reported the highest reported removal of atrazine to date (approximately 40%) through a genetically modified bacterial strain. Relatively high removal of diclofenac and carbamezapine was observed compared to removal (<17%) reported by Alturki et al. [40] and Tadkaew et al. [37] (Figure 4.2). However, amitriptylene, a nitrogen bearing compound where nitrogen is bound to the aliphatic chain, showed similar removal efficiency (95%) to that reported by Tadkaew et al. [37]. Major differences in experimental design between Alturki et al. [40], Tadkaew et al. [37] and the current study are in the membrane type and the seed sludge (Table 4.1). Because of the development of a cake layer over the membrane in MBR, the effect of type of microfiltration/ultrafiltration membranes on TrOC removal is negligible. On the other hand, in the current study, seed sludge was obtained from a biological nutrient removal reactor of a full scale sewage treatment plant, while the seed sludge for the previous studies by Alturki et al. [40] and Tadkaew et al. [37] was from a conventional activated sludge treatment process. Therefore, the significant difference in the removal of atrazine and other nitrogen

bearing compounds between our current and the previous studies could possibly be attributed to the microbial composition of the seed sludge.

Table 4.1: Comparison of operating conditions of previous studies and the current investigation

Parameter	Tadkaew et al. [37]	Current Study
Temperature (°C)	20.0±0.1	26.0 ± 0.2
DO (mg/L)	2±1	2.4 ± 0.3
HRT (h)	24	26
SRT (days)	70	88
Feed	Synthetic wastewater simulating municipal wastewater	Synthetic wastewater simulating municipal wastewater
Membrane module	ZeeWeed (Hollowfiber, ultrafiltration)	Ceramic (Tubular, microfiltration)
Configuration	Submerged	External
Seed Sludge	Activated sludge from conventional organics removal aerobic tank of a full scale plant.	Nitrifiers-rich sludge from biological nutrient removal reactor of a full scale plant.

MBR can prevent the washout of slow-growing microorganisms like nitrifiers [27]. Enhanced removal of TrOCs (such as natural and synthetic steroid hormones, halogenated hydrocarbons and phenolic compounds) by nitrifying bacterial strains has been confirmed in previous studies [15-17, 25]. Furthermore, in the present work the applied SRT (88 d) was sufficiently long, which facilitated the improved removal of the nitrogenous TrOCs mentioned above. Noting further the distinct behaviour of the nitrogenous TrOCs with the nitrogen containing moiety bound to the aliphatic chain or the cyclic structure, it is possible that removal of nitrogen bearing

compounds, where nitrogen is bound to the cyclic structure, is selectively enhanced by the nitrifying microbial consortium. A detailed study on the effect of the location of nitrogen molecules in nitrogenous $TrOC_S$ on their degradation by nitrifiers would be required to substantiate this; however, it is beyond the scope of this study. More importantly, in line with that from the available reports, our results point to the role of nitrifiers in TrOC removal enhancement.

4.3.3 *Fate of trace organic contaminants during membrane bioreactor treatment*

Stable concentrations of most of the TrOC were observed in both the liquid and solid (sludge) phases during MBR treatment (Figure 4.3), demonstrating the stability of the TrOC removal performances of the MBR. Permeate concentrations of almost all hydrophobic compounds were low with octocrylene being the only exception. In contrast, the concentrations of hydrophilic compounds in permeate varied over a wide range.

Among the selected TrOCs, traces of some compounds (carbamazepine, diclofenac, fenoprop, ketoprofen, gemfibrozil, 4-tert butylphenol and octocrylene) were detected in the inoculating sludge even before the TrOCs were introduced to the synthetic feed. This is because the seeded sludge was obtained from a domestic wastewater treatment plant. Various levels of adsorption of the TrOCs onto the sludge were observed once the TrOCs had been introduced to the MBR system. Immediately after introducing the TrOCs, all compounds were detected at higher concentrations compared to their concentration in initial samples (Figure 4.4). Subsequently, no clear relationship was observed with TrOC concentration in sludge with time except for naproxen, diclofenac and amitriptyline. Concentration of

naproxen in sludge gradually reduced over time whereas amitriptyline concentration in sludge increased with time. This could be due to the hydrophilicity of naproxen (log $D_{pH\ 8}$= –0.18) and hydrophobicity of amitriptyline (log $D_{pH\ 8}$= 3.21).

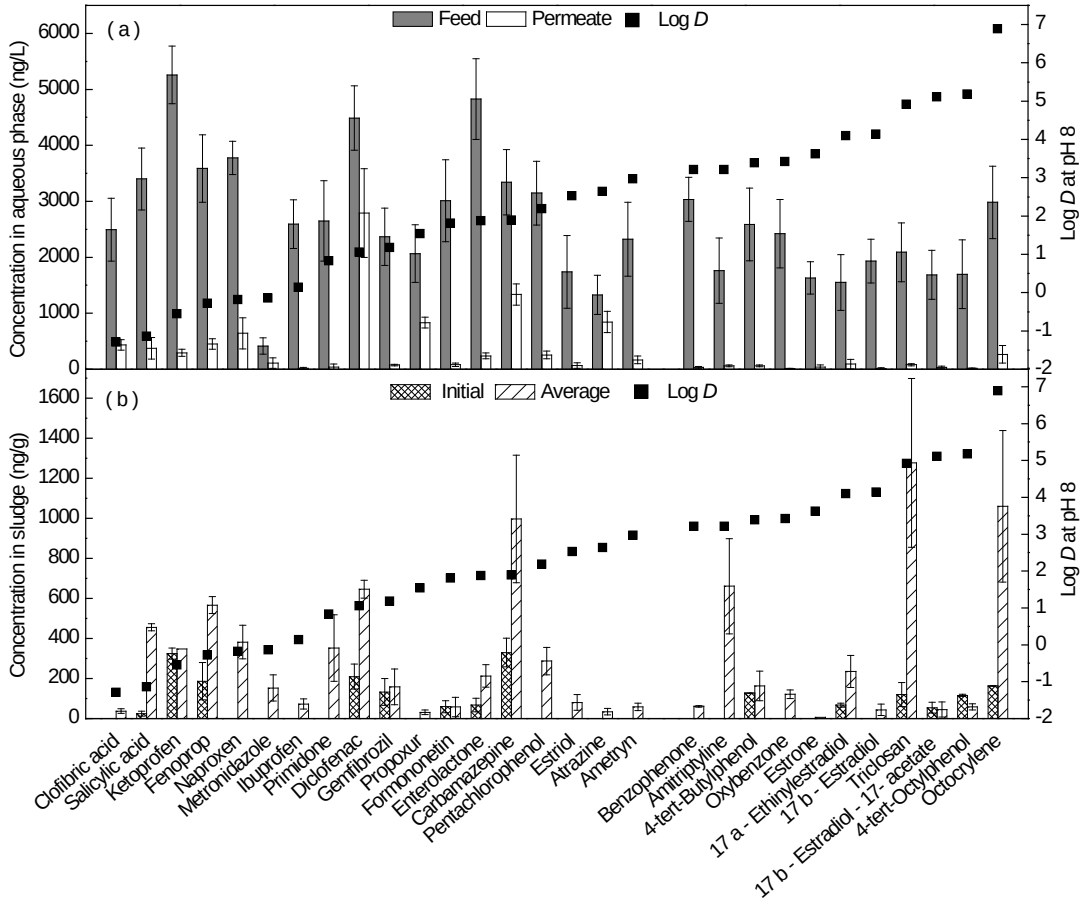


Figure 4.3: Average concentration of trace organic contaminants in (a) feed and permeate streams, and (b) sludge of MBR system. Error bars of the feed and permeate data represent the standard deviation of duplicate samples taken once a week for five weeks. Error bars of sludge data represent the standard deviation of duplicate samples taken once a week for four weeks.

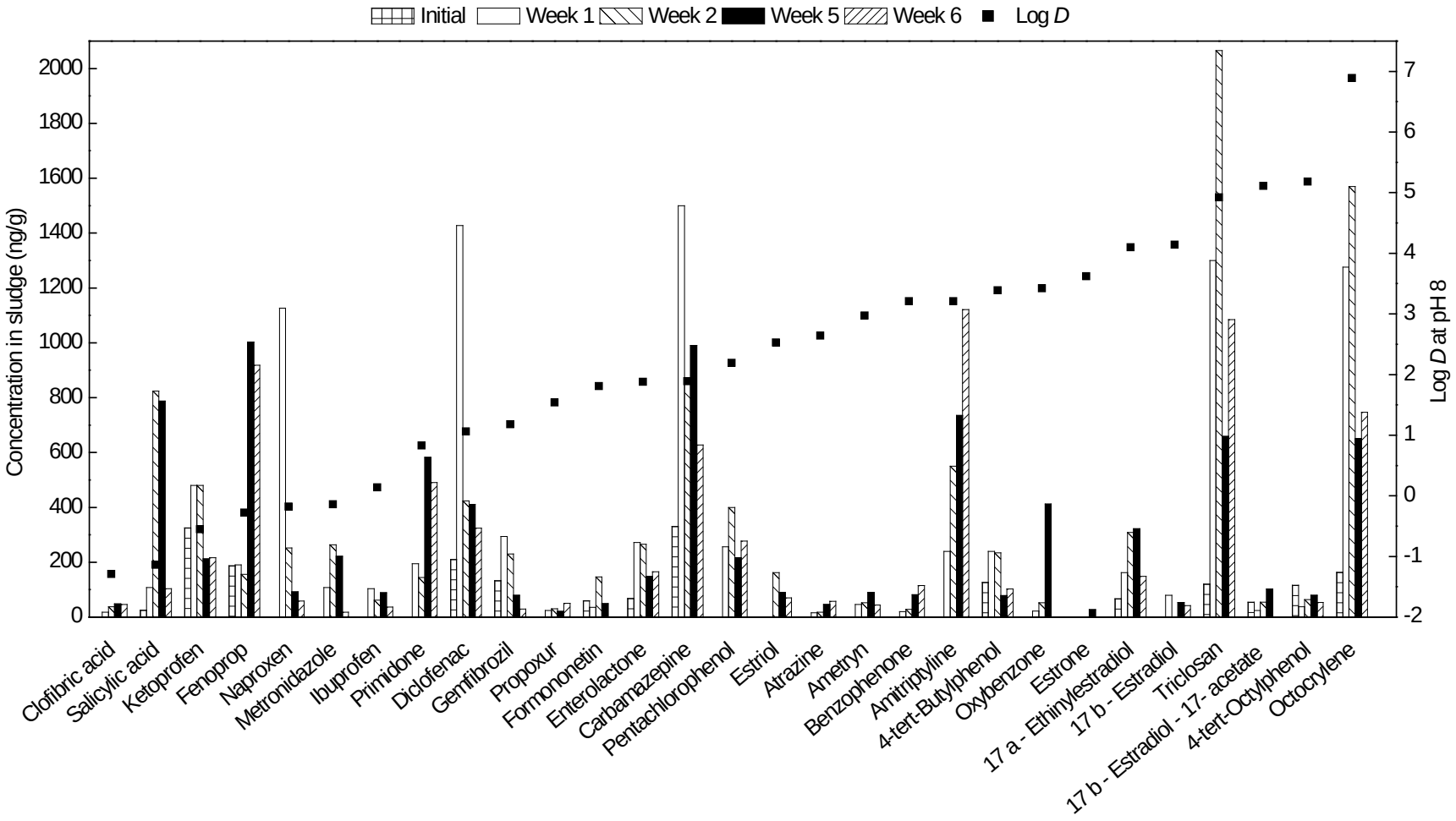


Figure 4.4: Variation of trace organic contaminant concentration in sludge with time in MBR

On the other hand, the variation of diclofenac concentration in sludge could be attributed to the low biodegradability caused by the complex structure regardless of the hydrophilicity (log $D_{pH\ 8}$= 1.06) as discussed below. A significant amount of salicylic acid, fenoprop, naproxen, diclofenac, carbamazepine, amitriptyline, triclosan and octocrylene remained adsorbed to biosolids throughout the experiment. Two factors may be responsible this, namely high hydrophobicity and low biodegradability. Interestingly, despite the high hydrophobicity, most of the hydrophobic compounds exhibited very low solid phase concentration. Among the 11 hydrophobic compounds studied, only triclosan, octocrylene and amitriptyline were detected in sludge at significant concentrations. Triclosan was most abundant in the solid phase (1277 ng/g) followed by octocrylene and amitriptyline. In contrast, despite their low hydrophobicity (log $D_{pH\ 8}$ < 3.2), a few persistent hydrophilic compounds (fenoprop, diclofenac, and carbamazepine) were consistently detected at high concentrations in biosolids. Our results indicated that biodegradability was an important factor governing the residual amount of TrOCs in biosolids. It was also noted that stable amounts of these compounds in sludge over the experimental period could be due to the periodic discharge of sludge from the system.

These results confirm that the removal mechanisms and the fate of TrOCs (Figure 4.5) are governed by their molecular properties. The concentration of the TrOCs in the solid phase increased after they had been introduced into the synthetic wastewater only if they contained EWGs and/or were hydrophobic. In fact, other than triclosan and octocrylene, the solid phase concentrations of all nine compounds with log D at pH 8 of above 3.2 but containing no EWGs in their molecular structure

were negligible. On the other hand, higher concentrations of triclosan and octocrylene in sludge were due to their very high log D (of 4.92 and 6.89 at pH 8, respectively) and the presence of EWG (i.e. chloride and cyano group, respectively). Notably, mass balance calculations revealed that adsorption onto solid phase accounted for 50 and 26% the overall loading of triclosan and octocrylene, respectively, during MBR treatment (Figure 4.5). This signifies that strong EWG (chlorine atoms in triclosan) could cause compounds to accumulate in sludge more than for compounds with moderate EWG in their structure (cyanide group in octocrylene) even if the latter may be more hydrophobic (in this case, octocrylene (log $D_{\text{pH 8}}$ = 6.89) possesses more hydrophobicity than triclosan (log $D_{\text{pH 8}}$ = 4.92). This also demonstrated that adsorption facilitated the occurrence of biodegradation of TrOCs during MBR operation where the long SRT of the MBR system enhanced the biodegradation of hydrophobic compounds due to adsorption to the sludge [19, 27, 29]

During MBR treatment, the concentrations of persistent hydrophilic/or moderately hydrophobic compounds (e.g. propoxur, diclofenac, carbamazepine, and atrazine) in the solid phase were low and adsorption to sludge could only account for a small fraction (5%) of their fate (except for carbamazepine) (Figure 4.5). Despite being a very recalcitrant compound with moderate hydrophobicity (log $D_{\text{pH 8}}$ =1.89) due to the presence of an amide functional group [37], carbamazepine, could significantly accumulate in sludge. Although the overall aqueous phase removal of carbamazepine ranged between 47% to 70% (Figure 4.2), the actual extent of biodegradation/transformation did not exceed 26% (Figure 4.5).

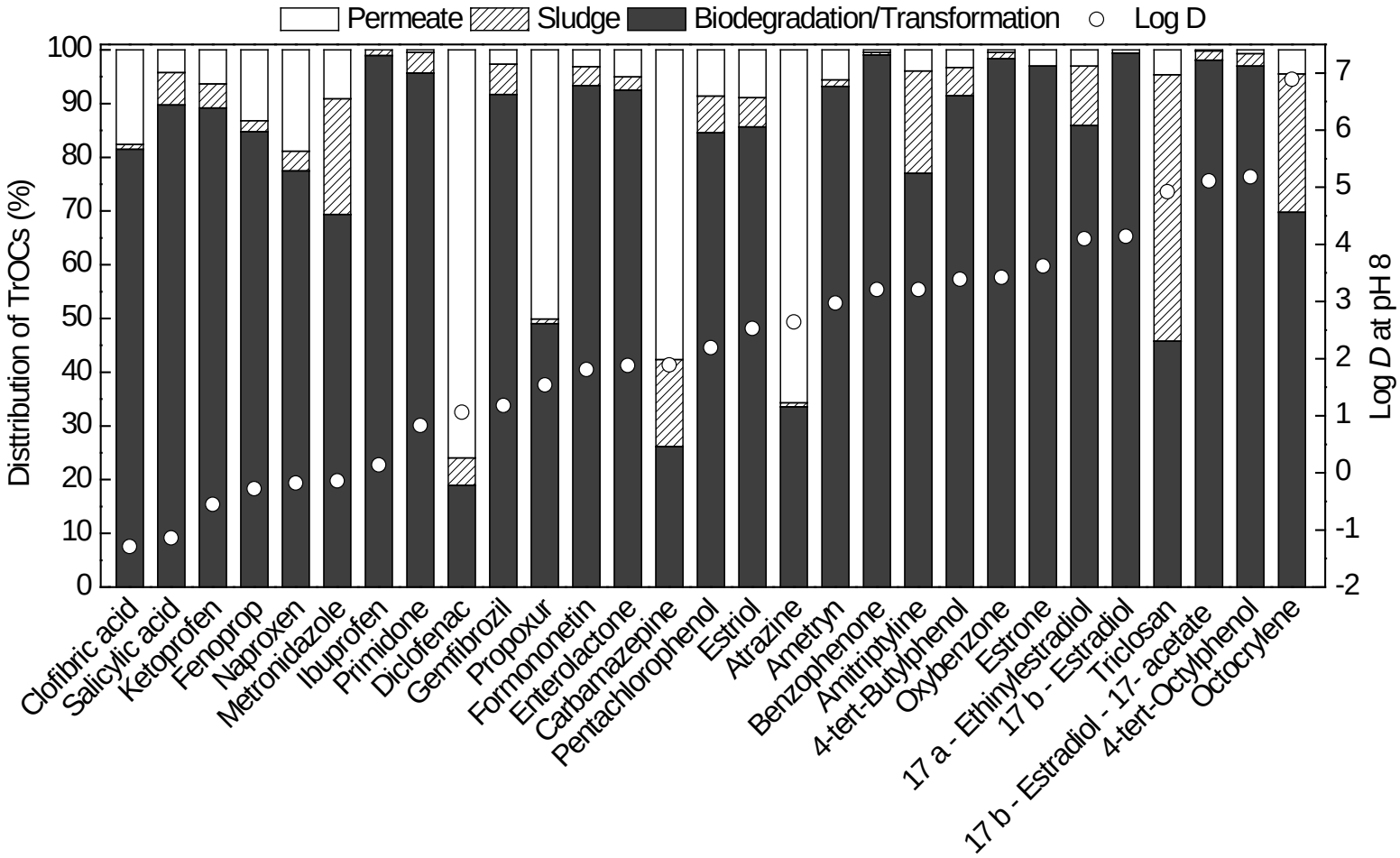


Figure 4.5: Fate of the selected trace organic contaminants during MBR treatment. Operating conditions of MBR are given in Section 4.2.2.

4.3.4 *Removal mechanisms*

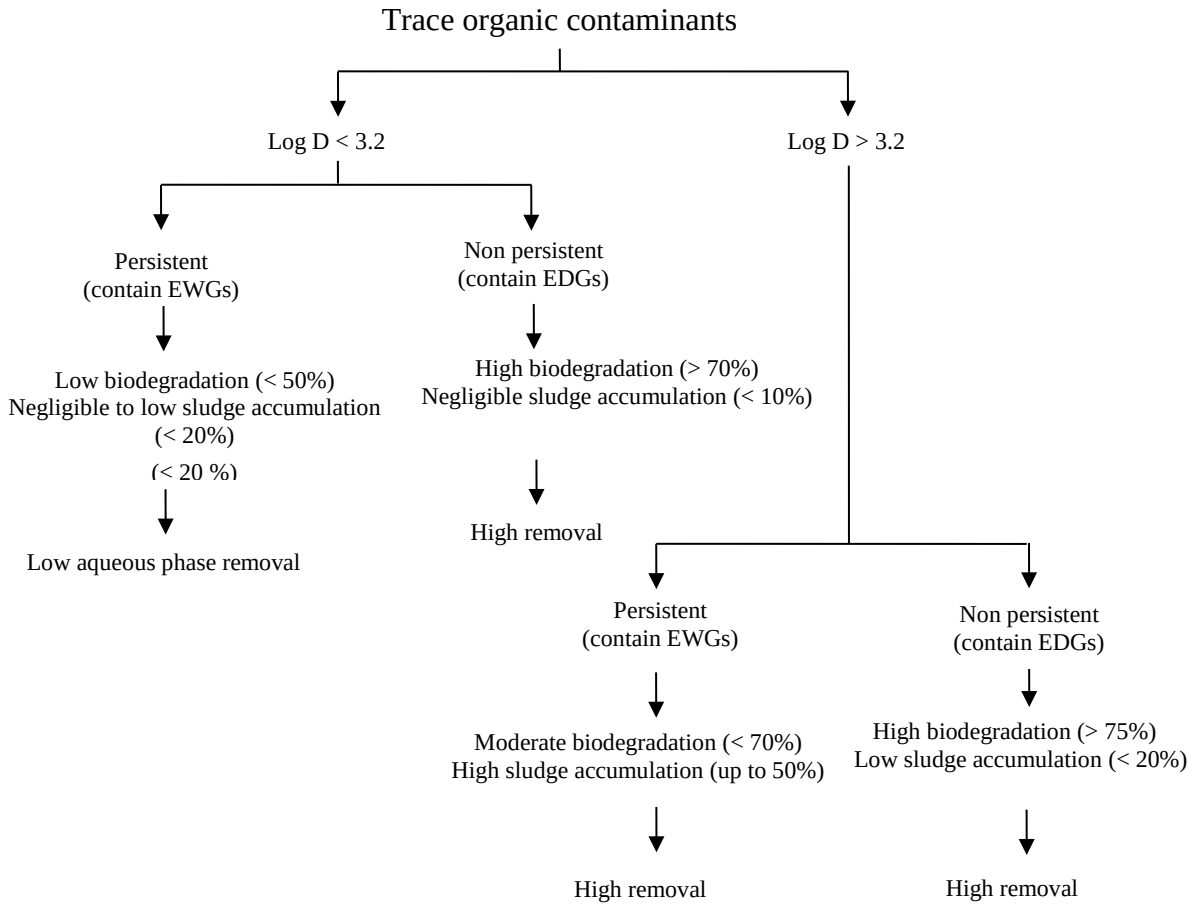


Figure 4.6: TrOC removal mechanisms during MBR treatment. Percentages of biodegradation and accumulation in sludge are with respect to the influent loading. EWGs and EDGs represent the electron withdrawing functional groups and electron donating functional groups, respectively.

Results from this study demonstrate a clear dependence of TrOC molecular structure on their removal mechanism and their fate in aerobic MBR. It appeared that the removal mechanisms and the fate of TrOCs were governed, in addition to hydrophobicity (log D), by the presence of EWGs or EDGs in their structure. Thus, the removal mechanism and the fate of TrOCs could be predicted by assessing the presence of EWGs and/or EDGs in their structure and their log D. Based on the

TrOC concentrations in aqueous and solid phases as well as the extent of their biodegradation/transformation, a generalised framework to predict the removal mechanisms of TrOCs during MBR treatment was proposed in Figure 4.6.

4.4 Conclusion

This study investigated both the solid (sludge) phase and aqueous phase removal of TrOCs and their fate during MBR treatment. The fate of TrOCs during MBR treatment was governed by both biodegradation and adsorption. Biodegradation was the predominant removal mechanism of the hydrophilic TrOCs from the aqueous phase. The removal of hydrophobic TrOCs from the aqueous phase could occur via adsorption. However, readily biodegradable hydrophobic TrOCs did not accumulate significantly in sludge. Additionally, recalcitrant TrOCs which are moderately hydrophobic or even hydrophilic could accumulate significantly in the sludge.

CHAPTER 5

REMOVAL AND FATE OF N-NITROSAMINES DURING MBR TREATMENT

Corresponding publication: K.C. Wijekoon, T. Fujioka, J.A. McDonald, S.J. Khan, F.I. Hai, W.E. Price, L.D. Nghiem, Removal of N-nitrosamines by an aerobic membrane bioreactor, Bioresource Technology, 141 (2013) 41-45.

5.1 Introduction

N-nitrosamines are an emerging class of trace organic contaminants of significant health concern. They have been widely detected at trace levels (of the order of a few nanograms per litre) in several environmental matrices including raw sewage, secondary treated effluent, and even drinking water [9-11]. In particular, elevated concentrations of N-nitrosamines have been reported in some wastewater [9, 11, 12]. N-nitrosamines can originate from both industrial and domestic wastewater discharges. They can be generated as by-products from a range of industrial processes where amines are in contact with nitrite, nitrous acid and nitrogen oxides. Consequently N-nitrosamines frequently occur in wastewater discharges from industries such as tanneries, circuit board manufacturing, dye manufacturing, metal casting, rubber manufacturing, metal working and food processing [88]. They may also be present in commercial products such as antifreezes, pesticides, detergents, processed meats, beverages, cigarette filters and cosmetics [12]. It is estimated that up to several hundred micrograms per litre of N-nitrosamines can be found in either untreated or treated industrial discharges from the above industries [11]. In addition to industrial wastewater discharge, domestic wastewater also contributes to the N-nitrosamines load in wastewater [11]. The occurrence of N-nitrosamines in domestic

wastewater can be attributed to the consumption of amines and nitrate rich food, cosmetics as well as household detergents. Furthermore, chloramination or chlorination of drinking water can also contribute to the elevated N-nitrosamines concentration in domestic wastewater [11, 12].

Most N-nitrosamines have been classified as probable human carcinogens by the US Environmental Protection Agency [13]. Their carcinogenic effects have been detected even at several nanograms per litre (ng/L) [35]. Therefore, some N-nitrosamines have been regulated in both drinking water and recycling water guidelines. For example, the Australian Guidelines for Water Recycling sets the maximum value for N-nitrosodimethylamine (NDMA) and N-nitrosomorpholine (NMOR) at 10 and 1 ng/L, respectively [13]. Other N-nitrosamines of concern to water authorities include N-nitrosomethylethylamine (NMEA), N-nitrosopyrrolidine (NPYR), N-nitrosodiethylamine (NDEA), N-nitrosodipropylamine (NDPA), N-nitrosopiperidine (NPIP), and N-nitrosodi-n-butylamine (NDBA). Considering the probable adverse effects of the environmental occurrence of nitrosamines, their removal from wastewater is of paramount importance for the protection of public health and the environment.

N-nitrosamines appear to be biodegradable under both aerobic and anaerobic conditions. A number of studies have investigated their biodegradability in soils, groundwater, river bed sludge and isolated microbial cultures [31-34]. Bradley et al. [31] reported more than 54% biodegradation of NDMA in soil from a wastewater reclamation facility under both oxic and anoxic conditions. Drewes et al. [32] conducted a laboratory scale study of the removal of seven N-nitrosamines under conditions relevant to groundwater recharge operations. Half-lives of these seven N-nitrosamines were in the range from 1.3 to 7 days. However, Drewes et al. [32] also

noted some variation in the biodegradation rate of N-nitrosamines and that complete removal of N-nitrosamines would require the establishment of an adapted microbial community over several weeks or months. In a more recent study, Zhou et al. [34] monitored the fate and transport of NDMA in groundwater being recharged with recycled water and reported that up to 80% of the recharged mass of NDMA could be biodegraded. The half-life of NDMA under a recharge condition was 69.4 days [34]. Notably, only a few studies have reported the removal of N-nitrosamines from either industrial or domestic wastewaters by the conventional activated sludge (CAS) treatment process [11, 12, 35, 36]. One of the most comprehensive studies to date, by Krauss et al. [12], looked at the fate and removal of N-nitrosamines in 21 full scale conventional wastewater treatment plants in Switzerland. They reported that the removal efficiencies from the aqueous phase by activated sludge treatment were generally above 40% for NMOR and over 60% for all other N-nitrosamines. The authors also noted the high variation in the removal efficiency of N-nitrosamines amongst the 21 full scale plants investigated [12]. In comparison to the CAS treatment process, very little is known about the efficiency of membrane bioreactor (MBR) for the removal of N-nitrosamines during wastewater treatment. An MBR efficiently combines biodegradation and membrane filtration in a single step, compact process, and offers flexibility in operation and expansion as compared to CAS processes [144]. It is also potentially more suitable for water recycling applications and the removal of trace organic compounds [24, 30, 37]. Hatzinger et al. [36] recently reported a novel aerobic laboratory scale propane-fed MBR for the removal of NDMA from artificial groundwater. This appears to be the only study, which has investigated the removal of N-nitrosamines by MBR treatment to date. These authors reported over 99.9% removal of NDMA. Given the unique

configuration and operating condition of their propane-fed MBR, the results by Hatzinger et al. [36] in case of groundwater may not be representative for a typical MBR used for wastewater treatment.

This study aims to increase our understanding of the removal of N-nitrosamines by MBR during wastewater treatment. The fate and removal of eight N-nitrosamines were systematically evaluated by a laboratory scale aerobic MBR by monitoring their concentrations in both the aqueous and sludge phases. Removal mechanisms of the selected N-nitrosamines were also elucidated by relating the removal efficiencies to their molecular structures.

5.2 Materials and methods

5.2.1 *Membrane bioreactor system*

A laboratory scale MBR system was used in this study. Detailed description of the MBR set-up is given in Section 3.2.1. During the entire experiment, the MBR system was covered with aluminium foil to avoid any exposure to sunlight to prevent any possible photolysis of the N-nitrosamines. The system was operated at constant conditions. The hydraulic retention time (HRT), temperature, dissolved oxygen concentration (DO) and mixed liquor pH were 24 h, 30 ± 0.1 °C, 2.68 ± 0.47 mg/L and 7.3 ± 0.2, respectively. The mixed liquor suspended solid (MLSS) concentration in the reactor was maintained at 5.0 ± 0.5 g/L by regular withdrawal of the excess sludge every 4–5 days, resulting in a sludge retention time of approximately 175 days. The relatively low MLSS concentration and high HRT value used here were necessary to avoid membrane fouling and ensure a stable operating condition throughout the experiment.

5.2.2 *Target N-nitrosamine compounds*

Eight N-nitrosamines (namely NDMA, NMEA, NPYR, NPIP, NDEA, NMOR, NDPA and NDBA) were selected for investigation based on their widespread occurrence in wastewater and probable carcinogenic properties. Detailed description of the N-nitrosamines is given in the Section 3.7.2.

5.2.3 *Synthetic wastewater*

Glucose and peptone based synthetic wastewater was used in this study to simulate medium strength domestic wastewater, the composition of which is given in Section 3.6.1. The synthetic wastewater was prepared each day by diluting the concentrated stock with Milli-Q water. A required volume of the N-nitrosamine stock solution was added to prepare a synthetic wastewater with approximately 250 ng/L of each N-nitrosamine.

5.2.4 *Analytical methods*

TOC and TN were analysed using a TOC/TN-V_{CSH} analyser (Shimadzu, Japan) (Section 3.8.1). All other basic parameters of the MBR process were analysed according to the standard methods for water and wastewater examination as reported in a previous study [23] (Section 3.8.1).

5.2.5 *N-nitrosamine analysis*

Nitrosamines concentration in feed, permeate and sludge were analysed. N-nitrosamines were extracted from sludge using a solvent extraction method discussed in Section 3.8.2 and aliquot sample volume was 200 mL. N-nitrosamine concentrations in aqueous aliquot samples were determined using solid phase extraction (SPE), gas chromatography (GC) and analysis by tandem mass

spectrometry (MS–MS) with electron ionization (EI) using a method previously reported. [197] as discussed in Section 3.8.4.

5.3 Results and discussion

5.3.1 *Biological performance of the membrane bioreactor system*

Prior to the main experimental phase of the study, the MBR system was acclimatised for four months under constant operating conditions. Synthetic feed solution simulating domestic wastewater was used to ensure a consistent feed composition. Throughout this acclimatisation period, the effluent quality was stable. N-nitrosamines were introduced to the feed solution and the MBR system continued to operate under the same conditions to maintain operational stability. TOC and TN concentrations of the feed solution were 167.3 ± 8.0 mg/L and 29.8 ± 0.7 mg/L respectively. Key operational parameters including DO and pH were continuously examined to affirm the biological stability of the MBR. As expected, the performance of the MBR system with respect to a range of basic performance parameters, such as TOC removal, TN removal, permeate turbidity, DO and the ratio of MLVSS/MLSS were stable throughout this study. Both TOC and TN removals were stable at 88 ± 0.8% and 48.3 ± 4%, respectively. The low TN removal efficiency observed here can be attributed to the absence of an anoxic chamber in our lab scale MBR which is necessary for an effective denitrification process. Turbidity of the MBR permeate was always below 0.7 NTU with an average of 0.46 ± 0.12 NTU. The MLSS concentration in the reactor was maintained at 5.0 ± 0.5 g/L by withdrawing excess sludge every 4–5 days, resulting in a theoretical sludge retention time of approximately 175 days. The MLVSS/MLSS ratio of the sludge was constant at 0.79 ± 0.02 throughout this study. In addition, MBR system was operated at a

transmembrane pressure below 90 kPa with no abnormal variation in transmembrane pressure being observed throughout the entire study.

5.3.2 *Fate and transport of N-nitrosamines during aerobic MBR treatment*

Fate and transport of the eight N-nitrosamines investigated in this study by MBR treatment are shown in Figure 5.1. Relatively constant concentrations of most N-nitrosamines in the aqueous and solid (sludge) phase can be observed (Figure 5.1). However, some variations were noted in the removal of NPYR and NPIP. Similar temporal variations in the removal rate of NDMA and NMOR by conventional wastewater treatment plants have also been reported in the literature [11, 12]. Given the relatively stable operating conditions of the current study, the small temporal variations described here could possibly be attributed to the sensitivity of N-nitrosamines removal in wastewater treatment.

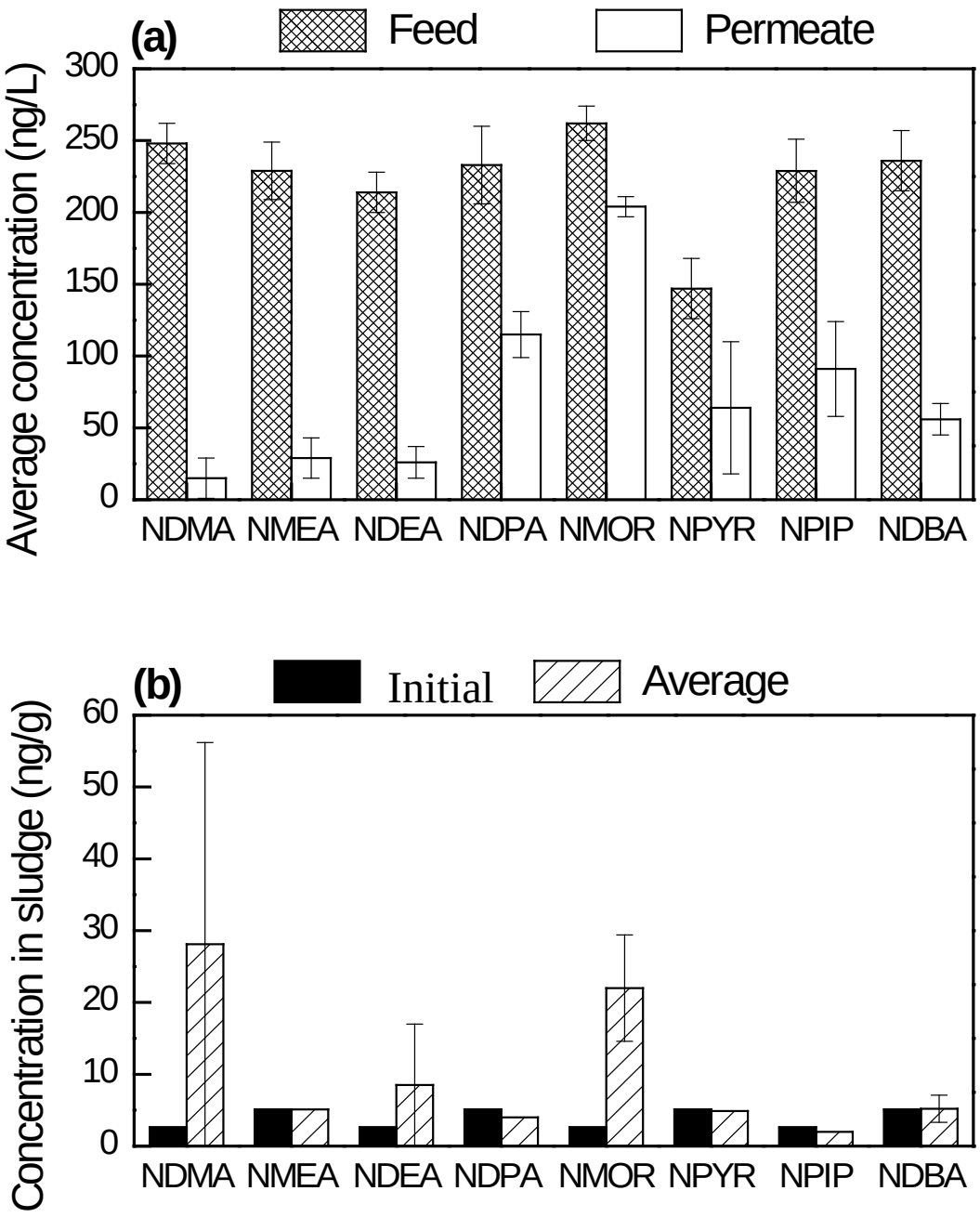


Figure 5.1: (a) Average concentration of the selected N-nitrosamines in feed and permeate streams of MBR system; error bars represent the standard deviation of ten consecutive measurements (b) Average concentration of the selected N-nitrosamines in sludge over the experimental period; error bars represent the standard deviation of four consecutive measurements. MBR operating temperature, dissolved oxygen, pH, MLSS, HRT and SRT were maintained at 30 ±0.1 °C, 2.68 ± 0.47 mg/L, 7.3 ± 0.2 and 5.0 ± 0.5 mg/L, 24 h and 175 days respectively.

Fate and transport of trace organic contaminants during MBR treatment can be governed by biodegradation, adsorption, photolysis and volatilization. UV oxidation or photolysis can be an important removal mechanism of N-nitrosamines [9]. However, in this study, as described in Section 5.2.1, the MBR system was covered with aluminium foil to prevent any accidental photolysis of N-nitrosamines. In addition, all eight N-nitrosamines selected for this investigation have very low Henry's Law constants (Table 3.3). As a result, their volatilization due to aeration is expected to be negligible. N-nitrosamines concentration in solid phase was insignificant due to their hydrophilic nature which is reflected by their low log *D* values (Table 3.3). In addition to its relatively low removal from the aqueous phase, NMOR was detected in the solid phase at approximately 22 ng/g, which was slightly higher than most of the other N-nitrosamines. This can be attributed to the persistence of NMOR to biodegradation, which will be discussed further in the next section. A significant variation in the concentration of NDMA in the sludge phase was also observed. However this is likely to be due to an error during sample preparation and analysis. Overall, it is clear that biodegradation (or transformation) governed the fate of all eight N-nitrosamines selected in this study during MBR treatment (Figure 5.2).

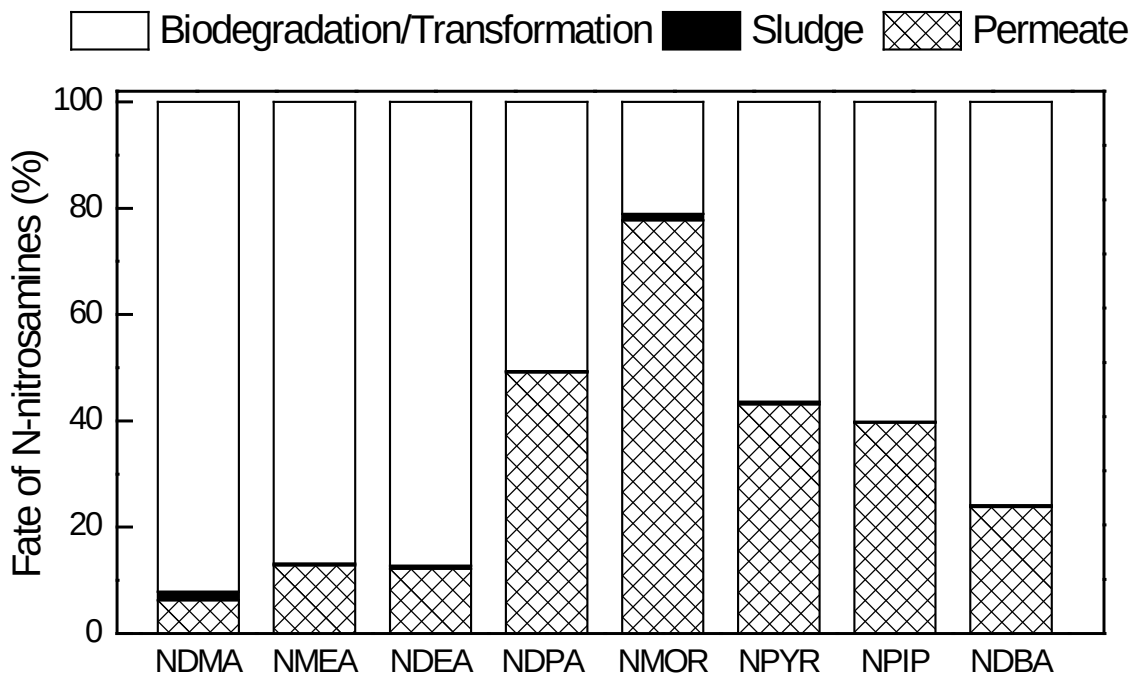


Figure 5.2: Overall fate of the N-nitrosamines during MBR treatment.

5.3.3 *Removal mechanisms of N-nitrosamines during membrane bioreactor treatment*

The removal efficiencies of NDMA (94%), NMEA (87%), NDEA (88%), NDPA (51%), NDBA (76%), NPYR (58%), NPIP (65%), and NMOR (24%) obtained in this study are comparable with their removal efficiencies by the CAS treatment process previously re-ported by Krauss et al. [12] Sedlak et al. [11]. In a comprehensive survey of 21 full scale conventional wastewater treatment facilities, Krauss et al. [12] reported that the removal efficiencies of most N-nitrosamines were generally above 60%. They also singled out NMOR as a persistent compound amongst the seven N-nitrosamines investigated in their study. However, their reported removal efficiency of NMOR (40%) was higher than that obtained in this study (24%).

As discussed in Section 5.3.2, the removal of N-nitrosamines can be attributed mainly to their biodegradability. It appears that biodegradation of N-nitrosamines can be qualitatively predicted based on their molecular structure according to the framework proposed recently by Tadkaew et al. [37]. Indeed, the removal efficiencies of N-nitrosamines reported here (Figure 5.3) are, in general, in the order of acyclic (NDMA, NMEA, NDEA, NDPA, and NDBA) > alicyclic (NPYR and NPIP) > morpholine (NMOR). According to Knackmuss [129], the initial electrophilic attack by oxygenases of aerobic bacteria is often a rate-limiting step and the first of a chain of reactions responsible for the biodegradation of many organic compounds. As a result, the presence of electron withdrawing functional groups (EWGs) generates an electron deficiency and thus renders the compounds less susceptible to oxidative catabolism. Electron donating functional groups (EDGs), on the other hand, render the molecules more prone to electrophilic attack by oxygenases of aerobic bacteria. Thus, biodegradation of trace organic compounds can be predicted based on the occurrence of EWGs or EDGs in their molecular structure [37]. Organic compounds with strong EWGs (such as halogens and nitroso) are more likely to be persistent to biodegradation. In contrast, organic compounds with strong EDGs (such as hydroxyl and alkyl) are readily amenable to biodegradation.

The molecular architecture of N-nitrosamines consists of both EWG (i.e. nitroso) and EDG (i.e. amine or morpholine). Nitroso is a strong EWG while amine is a strong EDG [198]. Thus, all N-nitrosamines except NMOR are quite amendable to MBR treatment despite the presence of the nitroso functional group. In addition, their removal efficiencies can be explained to some extent based on the strength of their electron donating functional groups. The electron donating capacity of amines

is influenced by the alkyl chains by the inductive effect [198]. The inductive effect is weakened as the length of the aliphatic chain increases [198]. Similarly, acyclic alkyl amines have a stronger electron donating capacity than that of alicyclic alkyl amines [198]. As a result, NDMA with two methyl functional groups exhibited the highest removal efficiency amongst all N-nitrosamines investigated here. Furthermore, in general, acyclic N-nitrosamines were better removed by MBR treatment than their aliphatic counterparts. The oxygen atom in the morpholine functional group substantially reduces its electron donating capacity. As a result, NMOR removal is dominated by the strong EWG nitroso. In good agreement to the qualitative framework proposed by Tadkaew et al. [37], NMOR is persistent to biodegradation and this compound exhibited the lowest removal efficiency by MBR treatment amongst all eight N-nitrosamines studied here.

Better removal of acyclic N-nitrosamines in comparison to their alicyclic counterparts is also consistent with their potential biodegradation pathways given in the Biocatalysis/Biodegradation Pathway Database of the University of Minnesota (https://umbbd.ethz.ch/predict/). The aerobic biodegradation of acyclic N-nitrosamines (NMEA, NDEA and NDPA) is likely to be initiated by converting the aliphatic backbone to an alcohol. In fact, demethylation has been identified as a key metabolism pathway of NDMA in mammalian cells [33]. On the other hand, the aerobic biodegradation of NMOR can possibly be initiated by converting the unsubstituted cyclic ether to hydroxyl cyclic ether, which has a much higher energy barrier than the demethylation process. This difference in the potential aerobic biodegradation pathways could possibly explain for the reported lower removal of NMOR compared to the other acyclic N-nitrosamines. In addition to the effect of molecular structure on nitrosamines removal, the microbial population of the

biomass might also influence the removal of N-nitrosamines. Nevertheless, detailed analysis of the microbial population diversity of the biomass is beyond the scope of the current study.

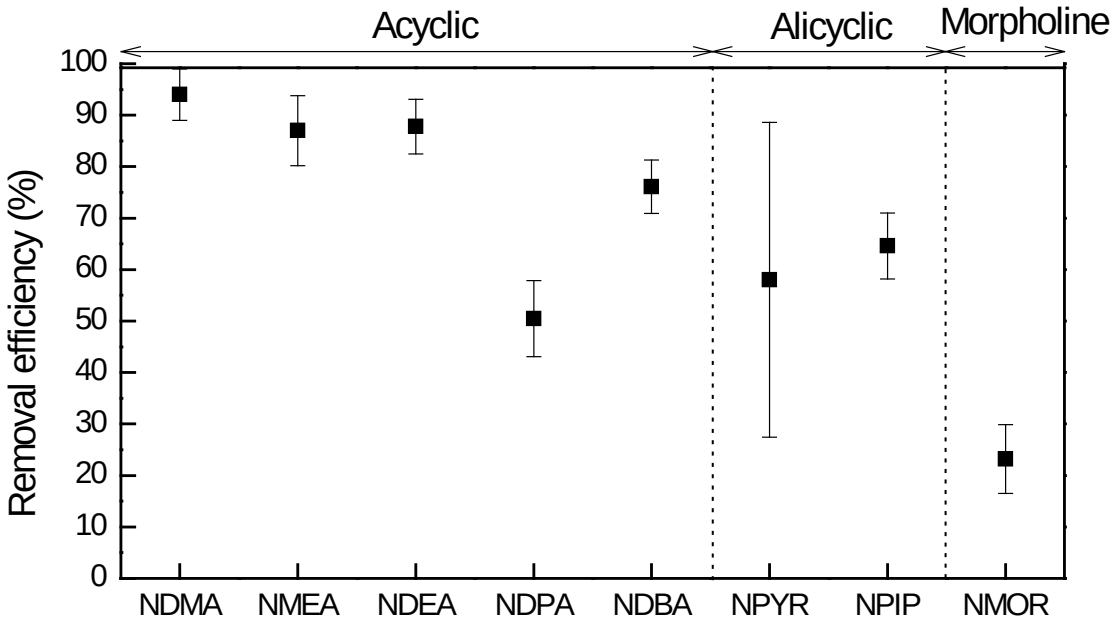


Figure 5.3: Average removal efficiency of selected N-nitrosamines by MBR; error bars represent the standard deviation calculated from ten consecutive removal efficiency measurements. MBR Operating conditions are given in Figure 5.1

5.4 Conclusion

Biodegradation is the predominant removal mechanism for N-nitrosamines. Adsorption to sludge was negligible while photolysis and volatilization were not expected to occur. N-nitrosamine removal efficiencies were dependent on their molecular structure, and ranged from 24% to 94%. The results could be explained by the presence of EWGs and EDGs (and their relative strength) in the N-nitrosamine molecules. N-nitrosamines possessing strong EDGs such as dimethyl-amine and diethyl-amine (e.g. NDMA and NDEA) are readily biodegradable during MBR treatment. By contrast, NMOR which has the weak EDG morpholine was persistent

to biodegradation and its removal efficiency by MBR treatment was correspondingly the lowest.

CHAPTER 6

REJECTION AND FATE OF TRACE ORGANIC CONTAMINANTS (TROC) DURING MEMBRANE DISTILLATION

Corresponding publication: K. C. Wijekoon., F. I. Hai., J. Kang., W. E. Price., T. Y. Cath., L. D. Nghiem. 2013. Rejection and fate of trace organic compounds (TrOCs) during membrane distillation. Journal of Membrane Science, 453 (636-642).

6.1 Introduction

Membrane distillation (MD) is a low temperature distillation process that involves the transport of water in the vapour phase from a feed solution through a microporous and hydrophobic membrane to the distillate (product) side. Direct contact membrane distillation (DCMD) is probably the most widely studied MD system configuration due to its simplicity [43, 166]. In DCMD, the feed solution is maintained at a higher temperature than the distillate, thus creating a vapour pressure difference between the feed and distillate. The membrane separates the liquid phase of the feed and distillate streams but allows water vapour to transport freely through its dry micro porous pores. In MD, the membrane material must be hydrophobic to prevent flooding of the pores by liquid feed or distillate under standard operating conditions. Because mass transfer can occur only in the gas phase, MD can offer complete rejection of all non-volatile solutes such as inorganic salts and pathogenic micro-organisms. As a result, to date, much of the effort in MD research has focused on desalination applications [43, 170-172].

Unlike pressure driven membrane processes, MD is less susceptible to membrane fouling, due to the absence of hydraulic pressure [170, 173]. Even when membrane fouling does occur, it is expected to result in a less compacted layer that can be easily removed [170, 174, 175]. The low operating temperature of MD allows for the utilization of solar thermal or low grade heat as the energy source [43, 48, 166, 176-179]. Given the advantages of the high separation efficiency, low fouling propensity, and potentially low energy consumption (when low grade heat is readily available), MD can be used for a range of applications beyond those for brackish and seawater desalination. Several studies have explored the use of MD for food processing, such as whey protein recovery in dairy processing [175], polyphenolic antioxidants recovery from olive oil wastewater [180], and orange juice concentration [181], separation of fermentation broth [182] as well as treatment of wastewater from the textile [183] and petrochemical industries [48], and municipal water reuse [177, 184].

Despite the growing interest in using MD for treatment of a range of wastewaters, there is still a lack of understanding of the rejection mechanisms of trace organic contaminants (TrOCs) by MD. TrOCs have been frequently detected in raw sewage and biologically treated effluent at concentrations ranging from several ng/L to several µg/L [2, 3, 6-8]. As a result, the removal of these TrOCs from secondary treated effluent by advanced treatment processes such as nanofiltration (NF), reverse osmosis (RO), oxidation and activated carbon adsorption has been extensively investigated in recent years [40, 42, 199-201]. Nevertheless, only a few studies have been conducted to elucidate the rejection of specific organic compounds

by MD. Moreover, the available studies are mostly concerned with industrial chemicals such as benzene [185] and trichloroethylene [186] at an elevated feed concentration.

Given the concerns associated with human and environmental exposure to TrOCs, it is important to elucidate their fate and transport during MD, particularly in water reuse applications. Examples of these include the investigation by Cath et al. [184] and Cartinella et al. [187] to treat urine and hygiene wastewater by MD for water reuse in long term space missions and the novel membrane distillation membrane bioreactor (MDBR) concept proposed by Phattaranawik et al. [177] and Goh et al. [50].

In this Chapter, the rejection of a broad range of TrOCs by MD was investigated. The potential application of MD as a post treatment for thermophilic MBR to enhance TrOC removal was also investigated. The transport and fate of TrOCs during MD treatment are discussed with respect to compound hydrophobicity and volatility (measured by the log *D* and the Henry's law constant, respectively). The results provide further insight with respect to TrOC rejection using MD, which is critical for further development of this technology for wastewater reclamation applications.

6.2 Materials and methods

6.2.1 *Experimental system*

The rejection of TrOCs by MD was evaluated using a hydrophobic microporous polytetrafloroethylene (PTFE) membrane (GE, Minnetonka, MN) and a laboratory-scale DCMD system. A detailed description of the DCMD system is

given in Section 3.2.2. One set of MD experiments was conducted using a synthetic feed solution containing approximately 5 µg/L of each TrOC in Milli-Q water. In another series of experiments, effluent obtained from a thermophilic MBR system was used as the feed solution to evaluate the feasibility of combining MD with MBR. The MBR and MD experiments were conducted separately. Further details of the MBR system are given in Section 3.2.1.

6.2.2 *Experimental protocol*

All MD experiments were carried out as discussed in Section 3.3.2. The experiment was concluded once the water recovery had reached 70%, at which stage the feed and distillate samples were collected for TrOC analysis. The MBR system was operated under thermophilic conditions (40 °C) with an average dissolved oxygen (DO) concentration of 2.9 mg/L, hydraulic retention time of 24 hr, and average mixed liquor pH of 7.7. Excess sludge was withdrawn every week to maintain the mixed liquor suspended solid (MLSS) concentration in the reactor at 5000 mg/L, resulting in a solids retention time (SRT) of 140 days.

Prior to the commencement of this study, the MBR system had been acclimatized at 40 °C and operated for more than two months to produce constant effluent quality (Figure 6.1). TrOCs were introduced to the MBR feed to obtain approximately 5 µg/L of each compound and the MBR system was operated continuously at similar operating conditions. Then, the effluent was collected and used as MD feed. In good agreement with the previous studies [37, 39, 40] no significant difference in the biological performances of the MBR was observed following the introduction of TrOC. Key operational parameters including MLSS,

mixed liquor volatile suspended solid (MLVSS), DO, total organic carbon (TOC), and total nitrogen (TN) removal were periodically monitored to ensure the biological stability of the MBR. The performance of the MBR system was stable throughout this study with respect to these parameters. TOC and TN removal were stable at 91% and 47%, respectively. The turbidity of the MBR permeate was always below 0.9 NTU. The MLVSS/MLSS ratio of the sludge remained constant at approximately 0.76 throughout the experimental period. In addition, the MBR system was operated at a transmembrane pressure (TMP) below 90 kPa to maintain a constant permeate flux, and no abnormal variation in TMP was observed over the entire study (Figure 6.2).

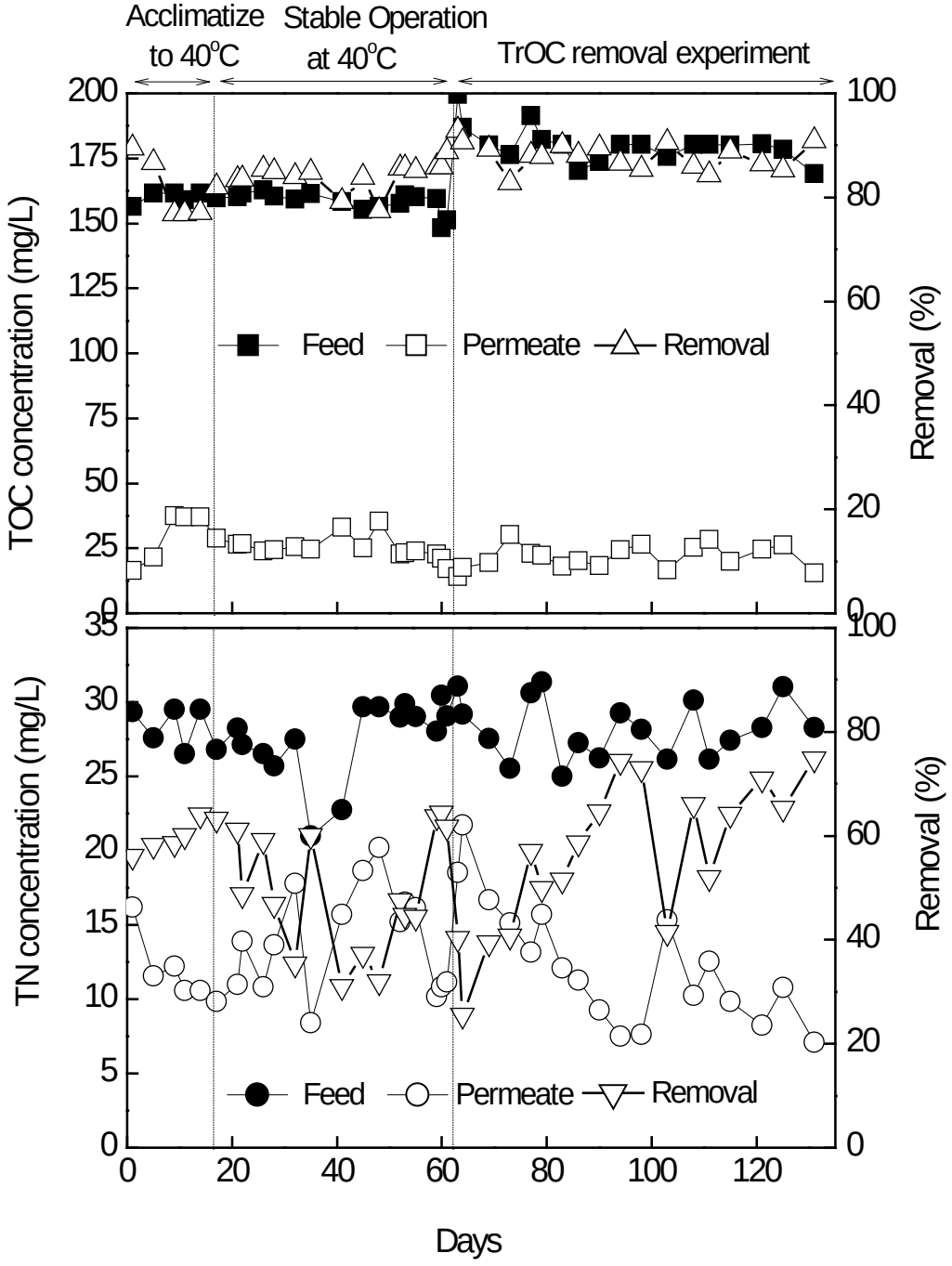


Figure 6.1: Variation of TOC and TN removal of MBR during acclimatization to thermophilic conditions (40 °C) and stable operation. Operated HRT, permeate flux, mixed liquor DO concentration and pH were 24 h, 2.36 L/m^2.h, 2.89 mg/L and 7.68, respectively.

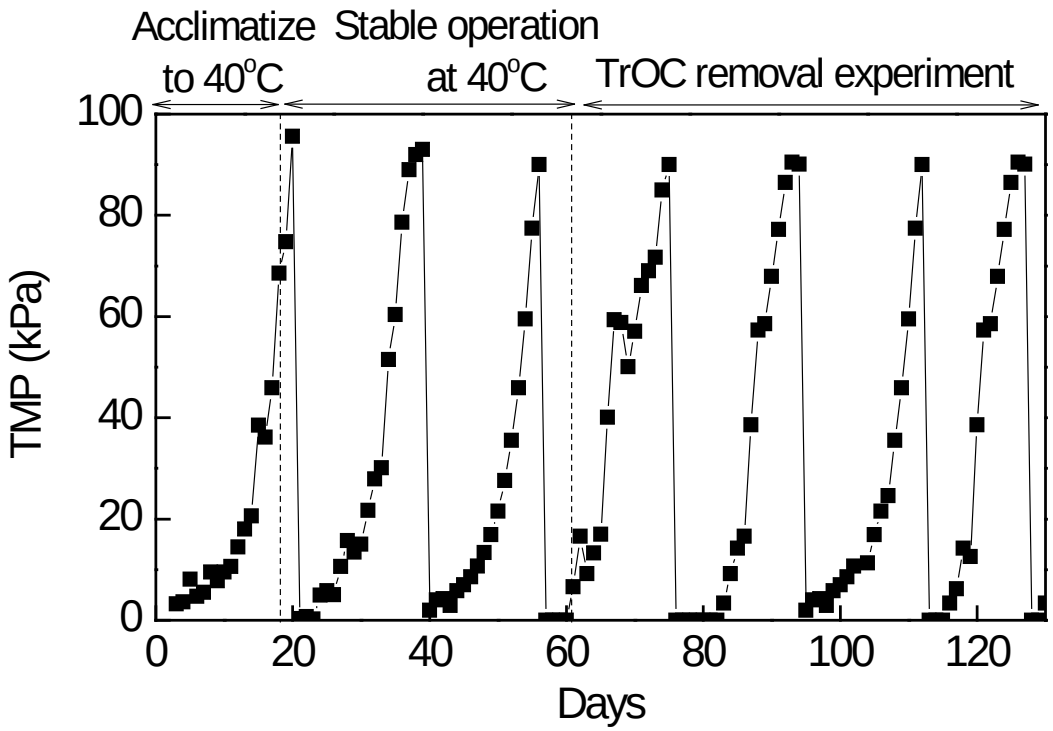


Figure 6.2: TMP profile of the MBR during acclimatization to thermophilic conditions (40 °C) and stable operation. HRT and permeate flux were 24 h and 2.36 L/m^2.h (equivalent to 5 L/d), respectively.

TrOC removal or rejection (R) is defined as:

$$R = 100 \times (1 - \frac{C_P}{C_F}) \quad 6.1$$

where C_p and C_F are the concentration of the specific compound in the permeate and feed, respectively. The term 'rejection' was used for the MD process while the term 'removal' was used for MBR. Taking the combined treatment of MBR and MD into account, the term removal infers that TrOCs can also be biologically degraded. Losses of TrOCs during the MD process were calculated by

considering the mass balance of each compound in the feed, concentrate and distillate as given below.

$$C_F \times V_F = (C_D \times V_D) + (C_C \times V_C) + \text{total loss} \quad 6.2$$

In Equation 6.2, C_F, C_D and C_C are the concentration in the feed, distillate and concentrate, respectively. Similarly, V_F, V_D and V_C are the volume of the feed, distillate and concentrate, respectively.

6.2.3 *Trace organic contaminants*

A set of 29 TrOCs (Table 6.1), was selected to represent pharmaceuticals, steroid hormones, phytoestrogens, UV-filters (i.e., active ingredients of sunscreens), industrial chemicals, and pesticides that occur ubiquitously in municipal wastewater [2, 3, 6-8]. Log *D* values of these compounds were obtained from the SciFinder Scholar database (https://scifinder.cas.org/scifinder) at pH 9 (Table 6.1). Vapour pressure, molecular weight (MW), and water solubility of each selected compound were also obtained from the SciFinder Scholar database (Supplementary Data Table S1) to calculate the Henry's law constant as: H (atm.m^3/mol) = Vapour pressure × MW/water solubility. The pK_H value presented in Table 6.1 is defined as $pK_H = -\log_{10}H$. It is important to note that because the water solubility used to calculate the Henry's law constant was obtained at 25 ºC, the actual pK_H values at 40 ºC (which was used during the MD experiment) could deviate slightly from those values presented in the Table 6.1.

The pH of the synthetic feed solution was 8.5 and 8.6 at the beginning and the end of the MD experiment. The initial pH value of the MBR effluent was 7.8 and it

increased to pH 9.1 at the end of the experiment. Accordingly, the log *D* and pK_H values of the TrOCs investigated in this study were obtained at pH 9 (Table 6.1).

6.2.4 *Analytical methods*

6.2.4.1 Basic water quality parameters

TOC and TN were analysed using a Shimadzu TOC/TN-V_{CSH} analyser (Shimadzu, Kyoto, Japan). Electrical conductivity and pH of the feed and distillate were monitored using an Orion 4 Star Plus portable pH/conductivity meter (Thermo Scientific, Waltham, MA). Analysis of basic water quality parameters is discussed in Section 3.8.1.1.

6.2.4.2 Trace organic contaminant analysis

TrOC concentrations in influent, concentrate and distillate were determined by a previously described method using solid phase extraction followed by gas chromatography separation and quantitative determination using mass spectrometry with electron ionization (Section 3.8.3)

Table 6.1: Physicochemical properties of the selected contaminants

Compound	Chemical Formula	Molecular Weight (g/mol)	Log *D* at pH 9	Water Solubility at 25°C (mg/L)	Vapour Pressure at 25°C (mmHg)	Henry Constant (H) at pH 9 ($atm.m^3/mol$)	pK_H at pH 9
Enterolactone	$C_{18}H_{18}O_4$	298.33	1.89	200	3.29×10^{-13}	6.46×10^{-16}	15.19
Primidone	$C_{12}H_{14}N_2O_2$	218.25	0.83	1,500	6.08×10^{-11}	1.16×10^{-14}	13.93
Ketoprofen	$C_{16}H_{14}O_3$	254.30	-0.84	554,000	3.32×10^{-8}	2.00×10^{-14}	13.70
Formononetin	$C_{16}H_{12}O_4$	268.26	0.88	4800	8.17×10^{-10}	6.01×10^{-14}	13.22
Naproxen	$C_{14}H_{14}O_3$	230.30	-0.73	435,000	3.01×10^{-7}	2.10×10^{-13}	12.68
Gemfibrozil	$C_{15}H_{22}O_3$	250.30	0.67	263,000	6.13×10^{-7}	7.68×10^{-13}	12.11
Metronidazole	$C_6H_9N_3O_3$	171.15	-0.14	29,000	2.67×10^{-7}	2.07×10^{-12}	11.68
Diclofenac	$C_{14}H_{11}Cl_2NO_2$	296.15	0.83	20,000	1.59×10^{-7}	3.10×10^{-12}	11.51
Fenoprop	$C_9H_7Cl_3O_3$	269.51	-0.29	230,000	2.13×10^{-6}	3.28×10^{-12}	11.48
Estriol	$C_{18}H_{24}O_3$	288.40	2.5	32	1.34×10^{-9}	1.59×10^{-11}	10.80
Ibuprofen	$C_{13}H_{18}O_2$	206.30	-0.19	928,000	1.39×10^{-4}	4.06×10^{-11}	10.39
Clofibric acid	$C_{10}H_{11}ClO_3$	214.64	-1.32	100,000	1.03×10^{-4}	2.91×10^{-10}	9.54
17 α – Ethinylestradiol	$C_{20}H_{24}O_2$	296.48	4.08	3.9	3.74×10^{-9}	3.74×10^{-10}	9.43
Oxybenzone	$C_{14}H_{12}O_3$	228.24	2.55	2700	5.26×10^{-6}	5.85×10^{-10}	9.23
Carbamazepine	$C_{15}H_{12}N_2O$	236.27	1.89	220	5.78×10^{-7}	8.17×10^{-10}	9.09

Compound	Chemical Formula	Molecular Weight (g/mol)	Log *D* at pH 9	Water Solubility at 25°C (mg/L)	Vapour Pressure at 25°C (mmHg)	Henry Constant (H) at pH 9 (atm.m^3/mol)	pK_H at pH 9
Estrone	$C_{18}H_{22}O_2$	270.36	3.6	5.9	1.54×10^{-8}	9.29×10^{-10}	9.03
17 β – Estradiol	$C_{18}H_{24}O_2$	272.38	4.12	3	9.82×10^{-9}	1.17×10^{-9}	8.93
17 β – Estrodiol- 17- acetate	$C_{20}H_{26}O_3$	314.42	5.11	1.9	9.88×10^{-9}	2.15×10^{-9}	8.67
Bisphenol A	$C_{15}H_{16}O_2$	228.29	3.62	73	5.34×10^{-7}	2.20×10^{-9}	8.66
Octocrylene	$C_{24}H_{27}N$	361.48	6.89	0.36	2.56×10^{-9}	3.38×10^{-9}	8.47
Ametryn	$C_9H_{17}N_5S$	227.33	2.97	140	1.72×10^{-6}	3.67×10^{-9}	8.43
Amitriptyline	$C_{20}H_{23}N$	277.40	4.01	83	1.50×10^{-6}	6.60×10^{-9}	8.18
Pentachlorophenol	C_6HCl_5O	266.38	1.99	4800	3.49×10^{-4}	2.55×10^{-8}	7.59
Atrazine	$C_8H_{14}ClN_5$	215.68	2.64	69	1.27×10^{-5}	5.22×10^{-8}	7.28
Propoxur	$C_{11}H_{15}NO_3$	209.24	1.54	800	1.53×10^{-3}	5.26×10^{-7}	6.28
Triclosan	$C_{12}H_7Cl_3O_2$	289.54	4.12	19	3.26×10^{-5}	6.54×10^{-7}	6.18
Benzophenone	$C_{13}H_{10}O$	182.22	3.21	150	8.23×10^{-4}	1.32×10^{-6}	5.88
4-tert-butyphenol	$C_{10}H_{14}O$	150.22	3.37	1000	0.0361	7.13×10^{-6}	5.15
4-tert-octylphenol	$C_{14}H_{22}O$	206.33	5.18	62	1.98×10^{-3}	8.67×10^{-6}	5.06

Note: Molecular weight, log D, water solubility and vapour pressure data were obtained from Scifinder Scholar. Henry's constant values were calculated as given in Section 7.2.3.

6.3 Results and discussion

6.3.1 *Basic performance of the membrane distillation process*

Table 6.2: MD and MBR-MD experimental conditions.

Parameter	Phase	MD Experiment with Milli-Q as feed	MD experiment with MBR permeate as feed
pH	MD feed	8.5	7.8
	MD concentrate	8.6	9.1
	Initial distillate	7.3	7.3
	Final distillate	7.7	9.6
Conductivity (µS/cm)	MD feed	18 ± 0.3	322 ± 2.0
	MD concentrate	130 ± 17	1026 ± 46
	Initial distillate	1.1 ± 0.1	1.3 ± 0.2
	Final distillate	6.9 ± 0.4	9.3 ±0.1

Note: The standard deviation was calculated from duplicate experiments.

The MD experiments were analyzed considering the distillate flux, water recovery, pH and conductivity variation (Table 6.2). The distillate flux was continuously monitored to assess the stability (Figure 6.3). There was no notable difference in the performance of the MD process with respect to the water flux and conductivity rejection when either the synthetic solution or MBR effluent was used as the feed. Both experiments achieved satisfactory water recovery at 70%. The average TOC and TN concentrations of the MBR effluent were 15 ± 6 and 17 ± 4 mg/L, respectively. However, this high residual organic content in the MBR effluent

did not exert any negative impact on the MD process. TOC and TN concentrations of the distillate were consistently less than 1 mg/L. When either the synthetic solution or the MBR effluent was used as the feed to the MD process, the water flux was stable at approximately 17.5 L/m^2.h and no flux decline was observed during the entire experimental period (Figure 6.3). The conductivity of the distillate was always less than 10 µS/cm regardless of the salinity level in the feed (Table 6.2).

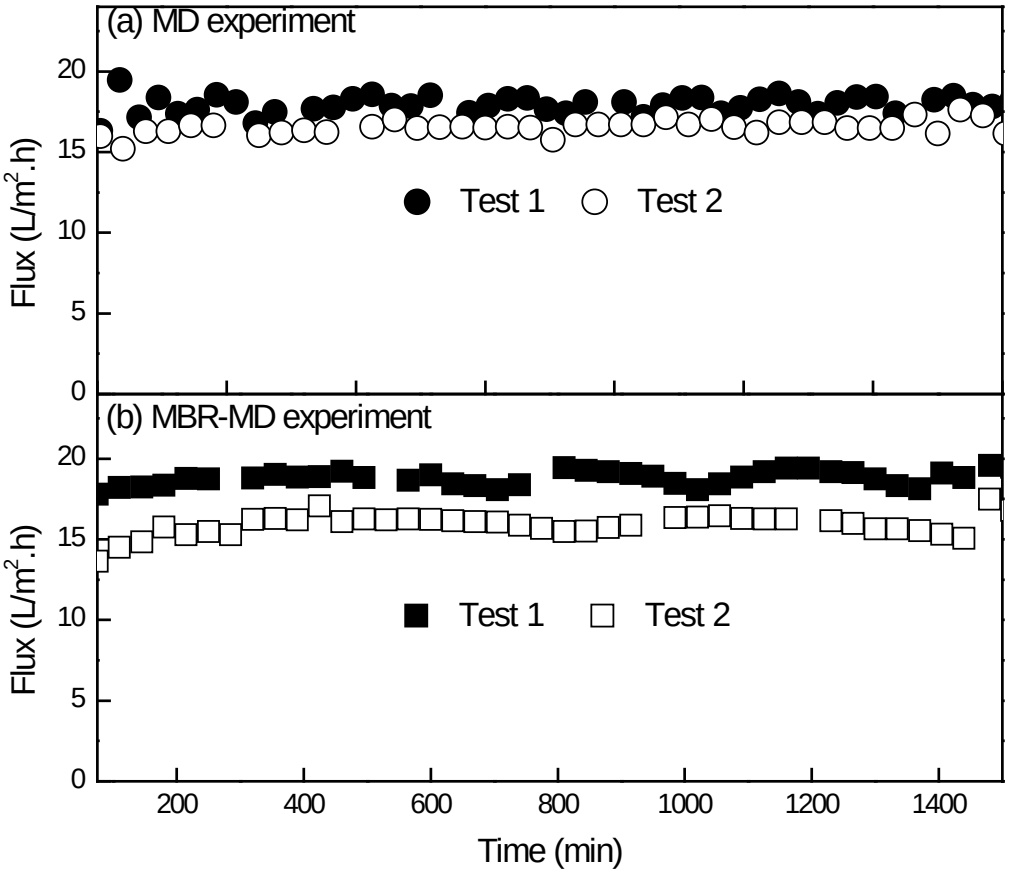


Figure 6.3: Permeate flux variation of MD and MBR–MD experiments: MD was carried out at feed and distillate temperatures of 40 and 20 °C, respectively; and feed and distillate circulation flow rate of 2 L/min (corresponding to 11.7 cm/s).

6.3.2 *Rejection and fate of trace organic contaminants during membrane distillation*

6.3.2.1 Trace organic contaminant rejection

Most of the 29 TrOCs investigated were effectively removed by MD (Figure 6.4). However, it is important to note that only a moderate rejection efficiency was observed for several compounds. In particular, 4-tert-octylphenol showed the lowest rejection (54%). In MD, mass transfer occurs only in the gas (vapour) phase. Thus, the transport of TrOCs from the feed to the distillate solution depends on their volatility. Not surprisingly, all TrOCs with pK_H value higher than 9 (low volatility) were well removed by the MD process. Oxybenzone is the only exception. Compared to other TrOCs, the relatively lower rejection (81%) of oxybenzone in relation to its pK_H value as plotted in Figure 6.4 could be attributed to the strong dependence of its pK_H value on pH. pK_H values at pH 9 have been plotted in Figure 6.4. However, it is noteworthy that the pK_H value of oxybenzone changes from 9.23 to 8.39 when the solution pH decreases from 9 to 8 (Table 6.3). Because in this study the feed solution pH was 8.5 and 8.6 at the beginning and the end of the MD experiment, respectively, the interpolated pK_H (8.6) value of oxybenzone is actually below 9. The three TrOCs with the lowest rejection (i.e., 4-tert-octylphenol, 4-tert-butylphenol and benzophenone) also have the highest volatility (or lowest pK_H) amongst the 29 compounds studied. Low rejection of volatile organic compounds such as benzene [185] and trichloroethylene [186] by MD have been previously reported. However, in this study, there was no obvious correlation between rejection efficiencies and pK_H for TrOCs possessing a pK_H value of less than 9. The data

presented in Figure 6.4 suggest that in addition to volatility, other physicochemical properties such as hydrophobicity (obtained from log *D*) may also influence the transport of TrOCs during MD. In fact, octocrylene, which had the fourth lowest rejection value of 81%, was also the most hydrophobic compound of the 29 TrOCs. In addition, in this study most of the TrOCs with pK_H of less than 9 were also hydrophobic (i.e., log D>3), and their rejection efficiency varied widely from as low as 54% (i.e., 4-tert-octylphenol) to near complete rejection. Significant adsorption of hydrophobic organics to the MD membrane has been previously reported by Zuo and Wang [202]. The results shown in Figure 6.4 suggest that the rejection of TrOCs may be governed by the interplay between their volatility and hydrophobicity.

Table 6.3: pK_H of oxybenzone at different pH values

pH	**Log *D****	**Water Solubility at 25°C (mg/L)***	**Vapour Pressure at 25°C (mmHg)***	**pK_H**
pH 8	3.42	390	5.26×10^{-6}	8.39
pH 9	2.55	2700	5.26×10^{-6}	9.23

Note : * Data from SciFinder Scholar.

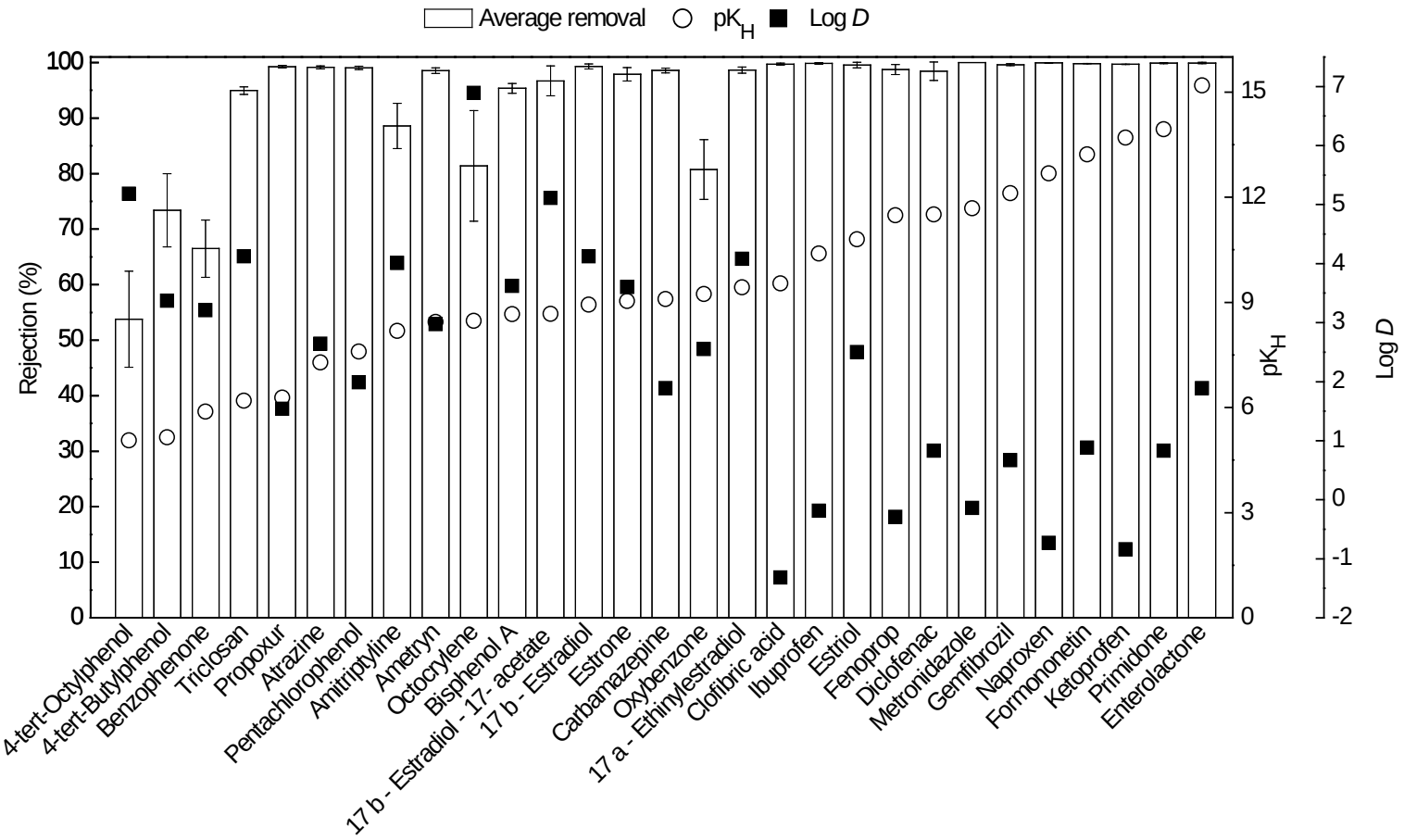


Figure 6.4: Rejection of the 29 TrOCs by DCMD and their log *D* and pK_H values. Log *D* and pK_H represent the values at pH 9. Error bars represent the standard deviation from four replicate measurements. Synthetic solution containing approximately 5 µg/L of each TrOC in Milli-Q water was used as the feed. The MD was carried out at the feed and distillate temperatures of 40 and 20 °C, respectively. The feed and distillate circulation flow rate was 2 L/min (corresponding to 11.7 cm/s)

6.3.2.2 Fate of trace organic contaminants during membrane distillation

The fate of TrOCs during the MD experiments is presented in Figure 6.5. Considering each experiment as a closed system, any loss of TrOCs could be attributed to either evaporation or adsorption to the membrane. The former is governed by the volatility and the latter by the hydrophobicity. Both of these physicochemical properties may be important in determining the fate of TrOCs during MD (Figure 6.5). The results reveal that the hydrophilic TrOCs with low volatility (pK_H>9) can be concentrated in the feed. On the other hand, significant losses through either evaporation or adsorption could be observed for moderately volatile (i.e. pK_H value < 9) and hydrophobic (i.e. log *D* > 3) compounds. As a result, moderately volatile and hydrophobic compounds such as triclosan, propoxur, amitryptyline, octocrylene and 17β–estradiol-17-acetate did not accumulate in the feed. Indeed, concentrations of all three compounds (i.e. 4-tert-octylphenol, 4-tert-butylphenol and benzophenone) with the lowest pK_H in the concentrate at the end of the experiment were lower than the initial values (Table 6.4). In addition, the rejection of these compounds by MD was also the lowest amongst the 29 TrOCs investigated here (Figure 6.5).

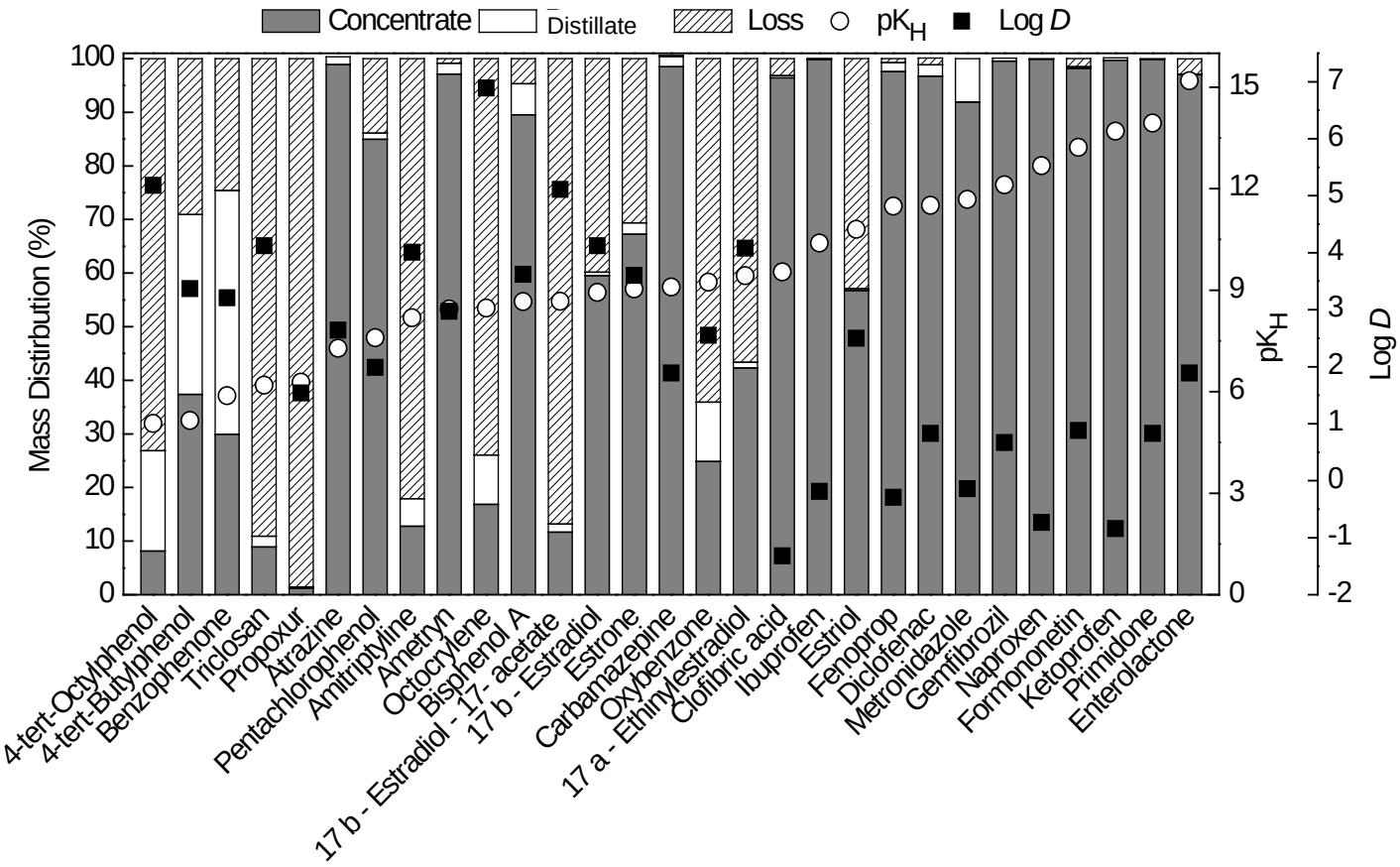


Figure 6.5: The fate of the 29 TrOCs in the DCMD process with their log *D* and pK_H values. Log *D* and pK_H illustrate the values at the pH 9. Synthetic solution containing approximately 5 µg/L of each TrOC in Milli-Q water was used as the feed. The fate of each compound was analyzed by mass balance considering the total input, mass in concentrate and permeate, and loss due to evaporation or adsorption. Calculation of the fate of TrOCs during the MD process was based on the average value from four measurements (duplicate samples from two replicate experiments)

Table 6.4: Aqueous phase concentration of the selected TrOCs when tested in synthetic feed solution (in Milli-Q water)

Compound	pK_H at pH 9	Log *D* at pH 9	Feed (ng/L)		Concentrate (ng/L)		Distillate (ng/L)	
			Mean	Error (±)	Mean	Error (±)	Mean	Error (±)
4-tert-Octylphenol	5.06	5.18	2292	828	585	110	631	109
4-tert-Butylphenol	5.15	3.37	1881	0	350	147	245	58
Benzophenone	5.88	3.21	666	0	274	26	128	44
Triclosan	6.19	4.12	3470	242	1019	232	115	26
Propoxur	6.28	1.54	1653	261	81	92	7	5
Atrazine	7.28	2.64	2462	89	10722	387	57	16
Pentachlorophenol	7.59	1.99	2924	459	8223	253	53	17
Amitriptyline	8.18	4.01	2465	455	1569	105	217	84
Ametryn	8.43	2.97	3133	117	10643	420	100	31
Octocrylene	8.47	6.89	888	229	371	76	95	49
Bisphenol A	8.66	3.62	3077	60	9070	266	283	56
17 β – Estrodiol- 17- acetate	8.67	5.11	3097	202	1192	278	76	62
17 β – Estradiol	8.93	4.12	3557	20	6944	603	38	24
Estrone	9.03	3.6	4163	34	9231	271	140	79
Carbamazapine	9.09	1.89	1806	105	6053	463	57	20
Oxybenzone	9.23	2.55	3531	333	2877	519	638	41
17 α – Ethinylestradiol	9.43	4.08	3276	145	4468	389	55	28
Clofibric acid	9.54	-1.32	3539	115	11594	72	22	14
Ibuprofen	10.39	-0.19	3555	288	13669	50	12	12

Compound	pK_H at pH 9	Log *D* at pH 9	Feed (ng/L)		Concentrate (ng/L)		Distillate (ng/L)	
			Mean	Error (±)	Mean	Error (±)	Mean	Error (±)
Estriol	10.80	2.5	3124	389	6866	1172	16	16
Fenoprop	11.48	-0.29	2330	42	7873	272	63	45
Diclofenac	11.51	0.83	3527	168	11633	414	123	132
Metronidazole	11.68	-0.14	742	156	3448	486	103	146
Gemifibrozil	12.11	0.67	3941	82	13514	191	34	16
Naproxen	12.68	-0.73	3794	199	13581	500	6	3
Formononetin	13.22	0.88	1432	297	5534	285	7	1
Ketoprofen	13.70	-0.84	3268	141	11493	180	24	2
Primidone	13.93	0.83	1698	121	7280	88	5	4
Enterolactone	15.19	1.89	1213	274	3076	933	2	2

Note: Error represents the standard deviation from four measurements (duplicate samples from two replicate experiments). MD was carried out at the feed and distillate temperatures of 40 and 20 °C, respectively. The feed and distillate circulation flow rate was 2 L/min (corresponding to 11.7 cm/s).

6.3.3 *Membrane bioreactor – membrane distillation (MBR-MD) system*

MD can be operated with a feed temperature compatible to that in thermophilic MBR. As discussed in Section 6.1, these two processes can be combined with each other for enhanced TrOC removal. TrOC concentrations in the feed and after each of these treatment steps are shown in Table 6.5. MBR treatment effectively removed most of the 29 TrOCs investigated in this study. The high removal of these compounds during MBR treatment has also been reported elsewhere [24, 37, 39, 199]. However, several compounds including propoxur, atrazine, ametryn, clofibric acid, diclofenac, carbamazepine, naproxen and fenoprop were found to be persistent to MBR treatment, and their residual concentrations in the MBR effluent were relatively high. This is consistent with several previous studies [29, 37, 157]. It is noted that the removal efficiency of these compounds under thermophilic conditions in this study was comparatively lower than that observed in our previous study under mesophilic conditions [39]. The low removal of most of the persistent compounds can be attributed to the disturbed metabolic activity generally associated with the biological treatment at elevated temperatures [23]. Nevertheless, as illustrated in Figure 6.6, all TrOCs including those that were resistant to MBR treatment were effectively removed by the MD process. In this study, complete or near complete (> 95%) removal efficiency of all 29 TrOCs was achieved by the combined MBR-MD treatment.

Table 6.5: Aqueous phase concentration of the selected TrOCs during the MBR-MD experiments with MBR permeate as the MD feed.

Compound	pK_H at pH 9	Log *D* at pH 9	MBR feed (ng/L)		MBR Permeate (MD feed) (ng/L)		MD Concentrate (ng/L)		Distillate (ng/L)	
			Mean	Error (±)	Mean	Error (±)	Mean	Error (±)	Mean	Error (±)
4-tert-Octylphenol	5.06	5.18	4683	9	147	11	278	69	96	65
4-tert-Butylphenol	5.15	3.37	4240	45	112	19	116	30	51	23
Benzophenone	5.88	3.21	1568	166	205	35	78	25	37	41
Triclosan	6.19	4.12	4496	29	114	17	155	17	26	1
Propoxur	6.28	1.54	4445	68	3011	278	164	53	39	14
Atrazine	7.28	2.64	2800	107	3215	98	10034	1142	28	10
Pentachlorophenol	7.59	1.99	4588	150	441	70	1039	254	13	16
Amitriptyline	8.18	4.01	4143	484	149	42	40	3	36	30
Ametryn	8.43	2.97	4032	24	1655	121	4639	410	25	6
Octocrylene	8.47	6.89	1231	235	31	21	50	18	33	14
Bisphenol A	8.66	3.62	4919	854	56	1	756	17	178	13
17 β – Estrodiol- 17- acetate	8.67	5.11	3956	45	12	6	27	27	27	20
17 β – Estradiol	8.93	4.12	4359	22	5	5	0	0	0	0
Estrone	9.03	3.6	4654	26	31	2	40	5	21	17
Carbamazapine	9.09	1.89	3332	142	2093	93	8022	1332	32	12
Oxybenzone	9.23	2.55	5043	8	56	4	31	31	8	5
17 α – Ethinylestradiol	9.43	4.08	4131	339	236	22	125	91	80	11
Clofibric acid	9.54	-1.32	4230	63	2448	156	7245	1092	7	2
Ibuprofen	10.39	-0.19	4915	191	57	16	131	24	5	6

Compound	pK_H at pH 9	Log *D* at pH 9	MBR feed (ng/L)		MBR Permeate (MD		MD Concentrate		Distillate (ng/L)	
			Mean	Error (±)	Mean	Error (±)	Mean	Error (±)	Mean	Error (±)
Estriol	10.8	2.5	3680	387	88	22	22	22	16	17
Fenoprop	11.48	-0.29	3940	202	2071	108	5203	600	25	18
Diclofenac	11.51	0.83	3258	39	3916	49	9993	645	19	5
Metronidazole	11.68	-0.14	851	86	127	2	282	86	5	5
Gemifibrozil	12.11	0.67	4628	17	456	29	1473	183	6	1
Naproxen	12.68	-0.73	4746	196	2292	133	6749	296	2	2
Formononetin	13.22	0.88	1081	727	35	10	61	34	27	4
Ketoprofen	13.7	-0.84	4452	107	273	29	757	41	23	6
Primidone	13.93	0.83	2627	181	14	4	82	41	2	2
Enterolactone	15.19	1.89	5530	29	241	78	23	16	114	49

Note: Error represents the standard deviation from four measurements (duplicate samples from two replicate experiments)

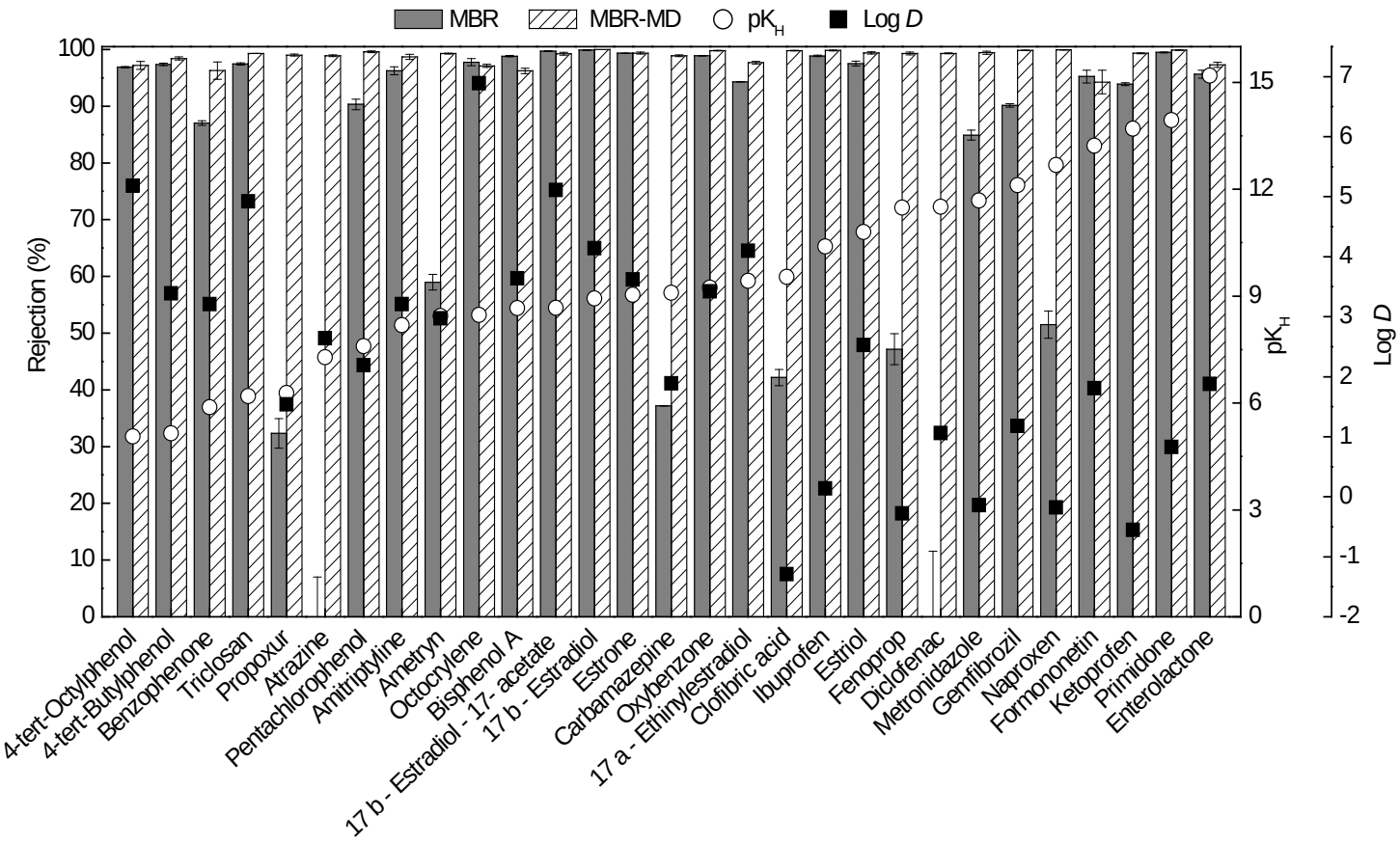


Figure 6.6: Removal of TrOCs by the thermophilic MBR and by the MBR-MD as well as their log *D* and pK_H values. Log *D* and pK_H illustrate the values at the pH 9. MBR permeate was used as the feed for MD. Error bars represent the standard deviation from two replicate experiments.

TrOC removal by MD as a post treatment step following MBR has not been previously reported. On the other hand, the use of other post treatment processes such as NF and RO desalination subsequent to MBR has been demonstrated [40, 199, 203, 204]. Tam et al. [203] reported near complete removal of estrogens and disinfection by-products (trihalomethanes and halo-acetic acids) by a pilot MBR/RO system. Alturki et al. [40] also showed the benefits of coupling MBR treatment and NF/RO desalination for removing 40 TrOCs with a diverse range of physicochemical properties. The current study suggests that an MBR-MD hybrid system could be as effective as an MBR-NF/RO system for removing TrOCs. In addition, high removal of TrOCs by a combination of MBR and MD treatment can be achieved regardless of the diversity of their volatility, molecular structure, and hydrophobicity.

The results shed light on the prospective of integrating MD with MBR for TrOC removal (e.g., MBR coupled MD (multi pass) system and MD bioreactor), and the salinity affected complexities on removal performance would be vital to investigate. However, it was not within the scope of the current study. Overall, the high water flux, excellent distillate quality and the near complete removal of TrOCs reported here suggests that MBR-MD system could be used to ensure safe water reuse.

6.4 Conclusion

In this study the rejection of 29 trace organic contaminants (TrOCs) and their fate in a membrane distillation (MD) system has been investigated. The results suggest that rejection and fate and transport of TrOC during MD would be mainly

governed by the volatility of the compound with additional effects due to its hydrophobicity. All TrOCs with $pK_H > 9$ (which can be classified as non-volatile) were highly removed by MD. However, three compounds (i.e., 4-tert-octylphenol, 4-tert-butylphenol and benzophenone) with $pK_H < 9$ and thus classified as partially volatile showed relatively low rejection efficiencies (i.e., 54, 73 and 66%, respectively). The results also suggest that the rejection of TrOCs with $pK_H < 9$ may be controlled by the interplay between compound hydrophobicity and volatility. In addition, the results show that hydrophilic TrOCs having negligible volatility were concentrated in the feed, while hydrophobic compounds with moderate volatility were substantially lost due to evaporation or adsorption to the membrane. Membrane bioreactor followed by MD treatment resulted in near complete (> 95%) removal of all 29 TrOCs despite their diverse physicochemical properties (i.e., hydrophobicity, persistency and volatility).

CHAPTER 7

A NOVEL MEMBRANE DISTILLATION – THERMOPHILIC BIOREACTOR (MDBR) SYSTEM: BIOLOGICAL STABILITY AND TRACE ORGANIC CONTAMINANT REMOVAL

Corresponding publication: K.C. Wijekoon., F.I. Hai., J. Kang., W. E. Price., W. Guo., H. N. Ngo., T. Y. Cath., L.D. Nghiem. 2014. A novel membrane distillation – thermophilic bioreactor (MDBR) system: Biological stability and trace organic compound removal. Bioresource Technology, 159 (334-341).

7.1 Introduction

Water reclamation is a pragmatic approach to address the scarcity of water supplies in urban areas due to population growth and irregular climate pattern[1]. Through water reclamation, municipal wastewater can be a reliable alternative source for clean water supply. However, development of advanced treatment processes is necessary to ensure adequate removal of common contaminants (e.g., organics, nutrients, and minerals) and especially trace organic contaminants (TrOCs) that occur ubiquitously in municipal wastewater. These TrOCs include steroid hormones, pharmaceuticals, personal care products, surfactants, pesticides, disinfection by-products, and UV filters [4, 5] that have been widely detected in raw sewage and reclaimed effluent from conventional wastewater treatment plants. Their occurrence is of major health and environmental concern because of their potential adverse impact on living organisms [205]. Thus, the removal of TrOCs during water reclamation has been the subject of intensive research in recent years.

Membrane bioreactor (MBR) is an efficient wastewater treatment technology, capable of producing reuse standard effluent[14]. MBRs can effectively remove TrOCs that are hydrophobic and/or readily biodegradable [24, 27, 37, 38]; however, recent studies have highlighted the challenges of removing recalcitrant TrOCs (e.g., carbamazepine and diclofenac) by biological treatment processes, including MBRs [27, 29, 37, 39].

Tadkaew et al.[37] suggested that biodegradability of a TrOC can be qualitatively assessed based on the presence of electron donating functional groups (EDGs) or electron withdrawing functional groups (EWGs) in their molecules. They demonstrated that TrOCs with one or several EDGs can be well removed in an MBR, whereas TrOCs with one or several EWGs (such as chloride and amide) in their structure are usually poorly removed by MBRs. In a subsequent study, Wijekoon et al. [39] have successfully extended this framework to elucidate the fate of TrOCs in the aqueous and sludge phase during MBR treatment (Chapter 4). Given the recalcitrant nature of some TrOCs to biodegradation, the use of post-treatment processes to specifically target these recalcitrant TrOCs has also been explored. Examples of these post-treatment processes subsequent to MBR treatment include reverse osmosis [40], activated carbon adsorption [41], and ultraviolet oxidation [42]. Integration of a high retention membrane process such as nanofiltration[44], forward osmosis [45-47], or membrane distillation (MD) [48-51] with a bioreactor constitutes a so called high retention MBR, which can be an efficient means to achieve high removal of pollutants. The working principles of these integrated processes have been demonstrated in recent studies; however, except for Alturki et al.[45] and

Hancock et al.[206], the removal of TrOCs using these novel high retention MBRs has not been investigated.

MD is a low temperature distillation process that involves the transport of water vapour from a feed solution through the pores of a microporous and hydrophobic membrane to the distillate (product) side. Because mass transfer occurs in a gaseous phase, MD offers complete rejection of all non-volatile solutes [43]. Membrane distillation bioreactor (MDBR) is a high retention MBR process where MD membrane can act as a barrier against the permeation of low molecular weight compounds and recalcitrant compounds. In the MDBR process, the biological reactor can be operated at thermophilic conditions to facilitate the integration of biological treatment with MD. In addition, the thermophilic bioreactor can also result in enhanced biodegradation of organics and low sludge yield [139].

The main aim of this study was to evaluate the performance of a novel hybrid MDBR process. Biological stability of the thermophilic bioreactor and the overall performance in terms of basic water quality parameters, as well as the fate and removal of TrOCs during MDBR treatment were elucidated.

7.2 Materials and methods

7.2.1 *Experimental system*

A laboratory-scale MDBR system consisting of a glass bioreactor and an external direct contact membrane distillation (DCMD) module was used. A detailed description of the system is given in Section 3.2.3.

7.2.2 *Experimental protocol*

Prior to the MDBR experiment, the bioreactor sludge was acclimatized at 40 °C using an aerobic MBR as discussed in Section 3.3.3. After the bioreactor had been acclimatised for 75 d, the ceramic membrane module was removed and the bioreactor was connected to the DCMD system (Section 3.2.3). TrOCs were then continuously introduced to the influent to maintain a feed concentration of approximately 5 µg/L of each compound.

The basic biological performance of the MDBR in terms of total organic carbon (TOC) and total nitrogen (TN) removal, conductivity/pH variation, and MLSS concentration was continuously monitored. The mixed liquor was collected weekly and centrifuged at 3270 × g for 10 min (Alleegra X-12R, Beckman Coulter, USA) to obtain the supernatant and sludge pellets for further analysis. Feed and distillate samples were collected for TrOC analysis on a weekly basis. The concentration of TrOCs in the distillate was calculated by taking into account the volume of Milli-Q water (2.25 L) used as the initial make up water.

TrOC removal by bioreactor (R_1), MD (R_2) and MDBR hybrid system (R_T) are defined as:

$$R_1 = 100 \times (1 - \frac{C_{Su}}{C_F}) \quad 7.1$$

$$R_2 = 100 \times (1 - \frac{C_D}{C_{Su}}) \quad 7.2$$

$$R_T = 100 \times (1 - \frac{C_D}{C_F}) \quad 7.3$$

where C_F, C_{Su}, and C_D are the concentrations of the specific compound in the bioreactor feed, bioreactor supernatant, and distillate, respectively. Biodegradation/transformation of TrOCs during the treatment by the hybrid process was calculated by considering the mass balance of each compound in the feed, supernatant, sludge and distillate as given in Equation 7.4.

$$C_F \times V_F = (C_{Su} \times V_S) + (C_{Sl} \times X_{Sl} \times V_S) + (C_D \times V_D) + \text{biodegradation/transformation} \quad 7.4$$

In Equation 7.4, C_{Sl} is the compound concentration in sludge and X_{Sl} denotes the sludge (MLSS) concentration. Similarly V_F, V_D, and V_S are the volume of the bioreactor feed, distillate, and mixed liquor, respectively.

7.2.3 *Trace organic contaminants*

A set of 25 TrOCs, except for enterolactone, formononetin, Gemfibrozil,4-tert-octylphenol listed in Table 3.2 was selected to represent pharmaceuticals and personal care products, steroid hormones, UV-filters, and pesticides that occur ubiquitously in municipal wastewater. A combined stock solution of all TrOCs was prepared in pure methanol and kept at -18 ºC in the dark.

7.3 Analytical methods

7.3.1 *Basic water quality parameters*

TOC and TN were analysed using a TOC/TN-V_{CSH} analyser (Shimadzu, Japan) (Section 3.8.1). Electrical conductivity and pH of the feed and distillate were monitored using an Orion 4 Star Plus portable pH/ conductivity meter (Thermo Scientific, Waltham, MA).

7.3.2 *Trace organic contaminant analysis*

TrOC concentration in solid phase (sludge) and liquid phase (feed, bioreactor supernatant and distillate) were determined. An ultrasonic solvent extraction method (Section 3.8.2) was used to extract the TrOCs from sludge. TrOC concentrations in aliquot aqueous samples (feed, sludge, supernatant and distillate) were determined using to a method employing solid phase extraction, gas chromatography separation and quantitative determination using mass spectrometry with electron ionization (Section 3.8.3)

7.4 Results and discussion

7.4.1 *Biological performance*

The basic performance of both the thermophilic bioreactor and MDBR system was assessed in terms of the distillate flux and quality (i.e., conductivity, TOC, and TN), mixed liquor characteristics (i.e., DO concentration, conductivity, pH, MLSS, and MLVSS) and organics removal (i.e., TOC and TN). The main performance parameters of the system are summarized in Figure 7.1. Water flux through the MD membrane decreased from 4 to about 2 $L/m^2.h$ within the first three days of operation, and after about 10 days of operation it became stable at approximately 1.2±0.2 L/m^2h (Figure 7.1a). This observed flux profile was consistent with several previous studies [48, 49, 177]. The low water flux observed could be attributed to the low cross flow velocity (i.e., 9 cm/s; see Section 3.2.3) in the MD cell used in a laboratory scale system and can be improved by increasing the circulation flow rate. In addition, the stable water flux after 10 days of operation indicated that membrane wetting did not occur in this study, which was also

evidenced by the low conductivity (<5 µS/cm) of the distillate (Figure 7.1b) during the entire experiment. Changes in hydrophobicity as a result of membrane wetting would lead to lower distillate quality (or an increase in distillate conductivity).

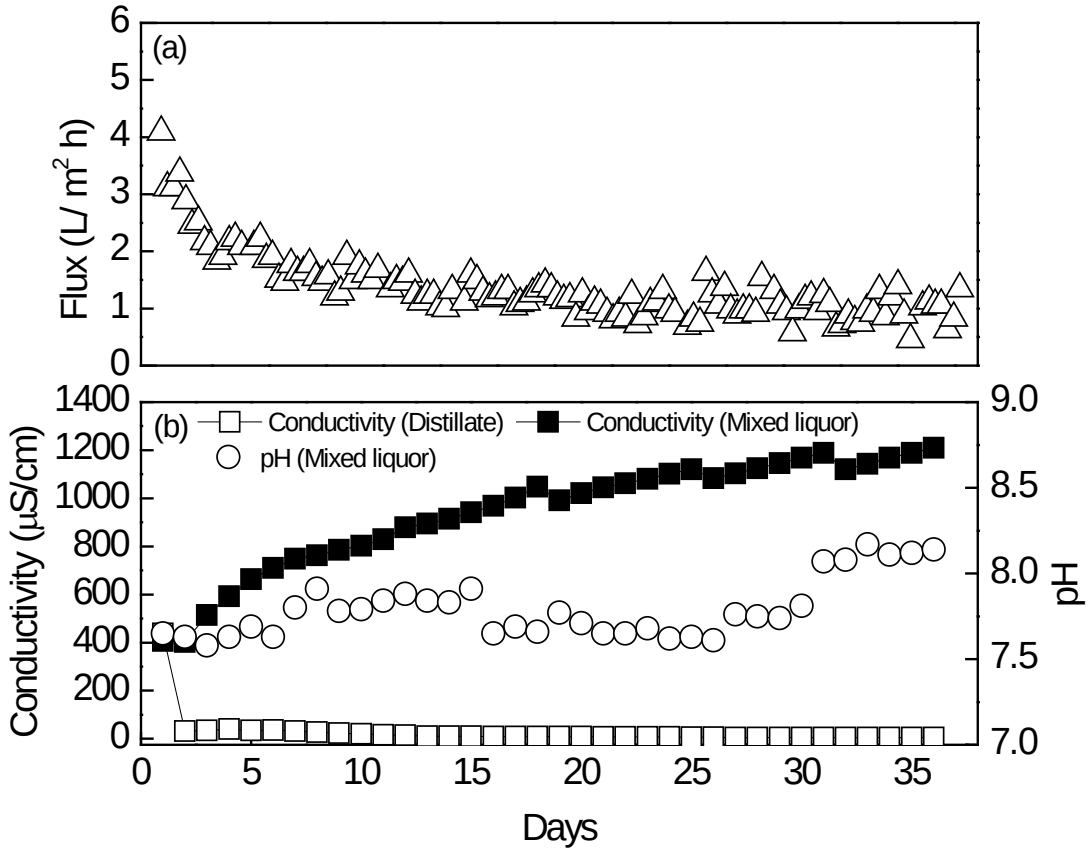


Figure 7.1: (a) Distillate flux profile (b) Conductivity and pH variation of mixed liquor/distillate of MDBR hybrid system during operation. The temperature difference across the MD cell was 24 °C with feed temperature of 38 °C immediately before the cell and distillate temperatures of 14 °C immediately after the cell. The conductivity and pH of feed were 320±17 µS/cm and 7.5±0.1, respectively. The DO concentration and temperature of bioreactor mixed liquor were 2.8±0.5 mg/L and 40 °C, respectively.

The mixed liquor salinity (measured by conductivity) increased continuously as the experiment progressed (Figure 7.1b). It is noteworthy that the occasional slight drop in the mixed liquor salinity was due to the collection of supernatant for

sampling and replenishment with low salinity makeup wastewater. Salinity build-up during MDBR operation was attributed to the complete rejection of salts by MD [48, 49, 207]. Moreover, there was a small increase in pH of the mixed liquor from 7.6 to 8.2, which was possibly due to the stripping of carbon dioxide at thermophilic temperatures [50, 208].

TOC removal by the thermophilic bioreactor was stable at 94%, and the supernatant TOC was always below 14 mg/L (Figure 7.2a). In addition, TOC removal by thermophilic bioreactor before (Figure 7.3a) and after MDBR experiment were almost identical. As most of the heterotrophic bacteria are subspecies of the halophilic and halotolerent microbial community, heterotrophic bacteria are more tolerant to salinity increase. Thus, the impact of salinity increase on TOC removal was insignificant [191]. However, TN removal by the thermophilic bioreactor significantly decreased from relatively stable removal at 51% (prior to MDBR experiment) (Figure 7.3b) to almost zero after only about four days of integration of the bioreactor with the MD unit (Figure 7.2b). The poor removal of TN probably resulted from an increase of mixed liquor salinity which is toxic to nitrifying bacteria [191]. LaPara and Alleman [139] also reported that thermophilic aerobic biological treatment is more susceptible to environmental changes than a mesophilic process. A gradual reduction in MLVSS concentration was noticed after starting MDBR experiment (Figure 7.4 and Figure 7.5), and this can be attributed to salinity build-up as reported by Alturki et al. [45] who explored a bioreactor integrated with a forward osmosis unit. This is also consistent with the reported low sludge yield by thermophilic aerobic biological treatment [139].

Although the thermophilic conditions could exert some negative effects on the performance of the bioreactor due to salinity build up, the overall TOC (> 99%) and TN (> 96%) removals by the hybrid MDBR system were high and independent of the biological stability of the reactor. Distillate TOC and TN concentrations were below 1 mg/L throughout the experiment. These results confirmed that the high performance of MD can offset the negative impact of salinity on the biological treatment and produce a high quality final effluent.

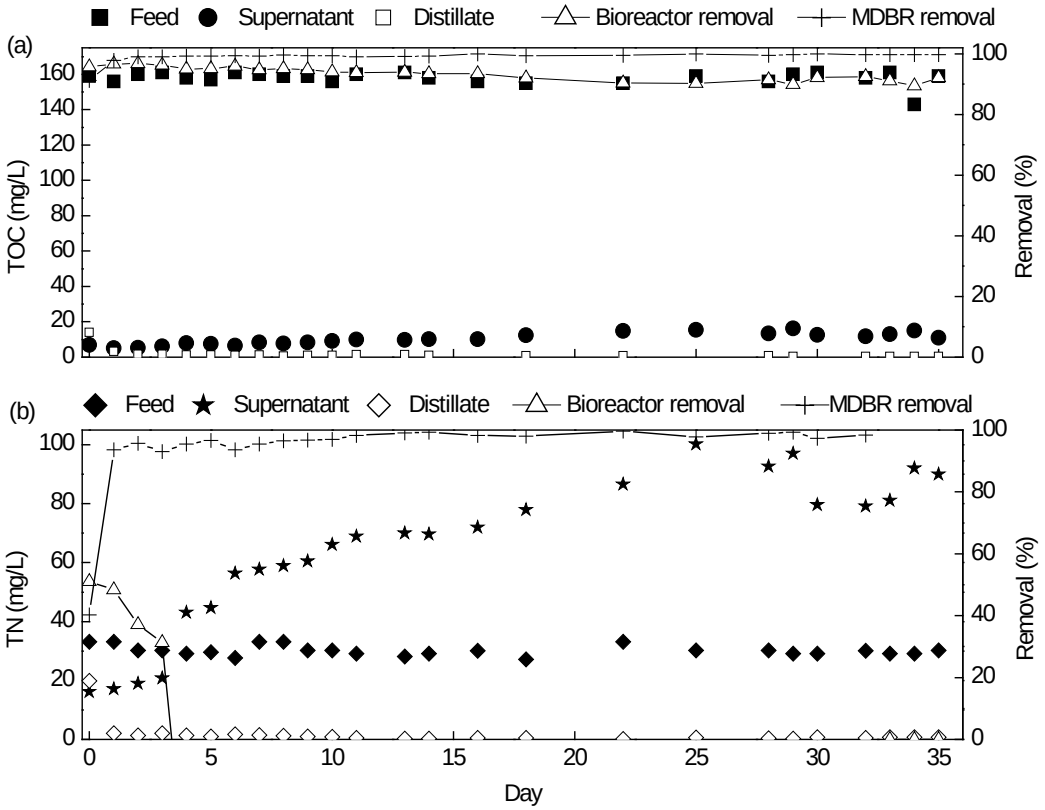


Figure 7.2: The variation of TOC and TN removal of the MDBR hybrid system. The stable flux was 1.2 ±0.2 L/m^{2}h. Operating conditions were as stated in Figure 7.1

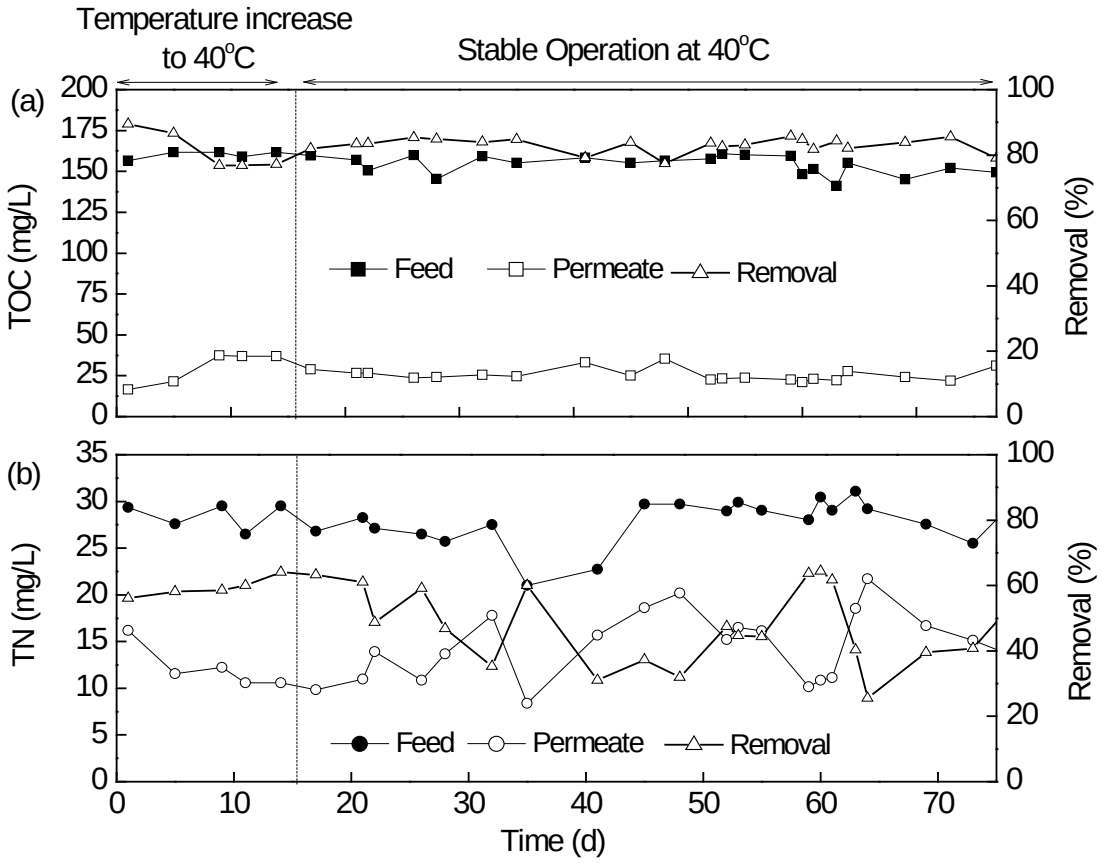


Figure 7.3: TOC and TN removal of thermophilic bioreactor during acclimatisation period (i.e., prior to MDBR experiment). Bioreactor was acclimatised (increase temperature to 40 °C and stable operation) at 40 °C by operating the system in an MBR mode using a ceramic microfiltration membrane module.

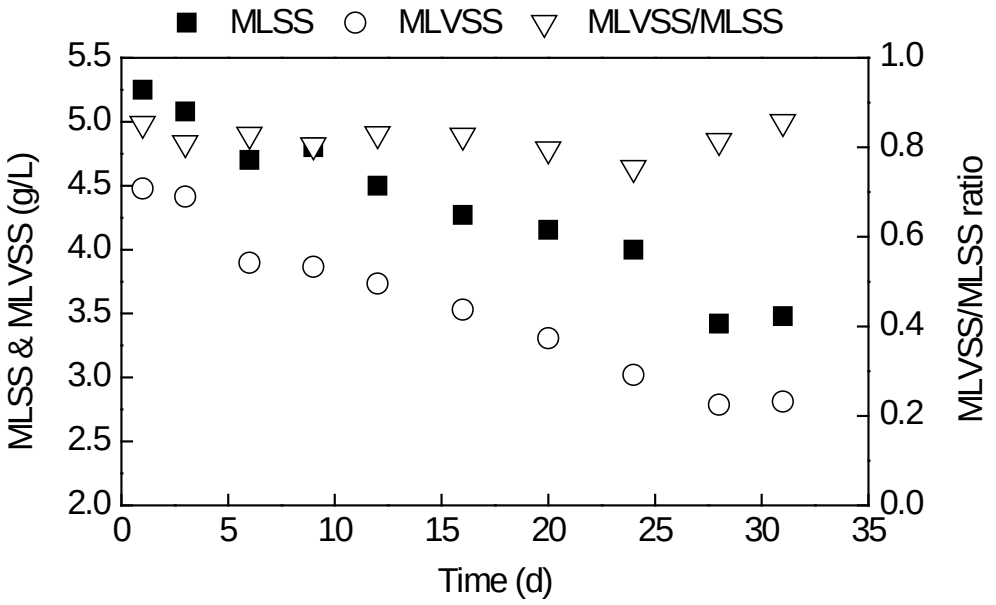


Figure 7.4: Variation of sludge concentration in the thermophilic bio reactor during MDBR experiment

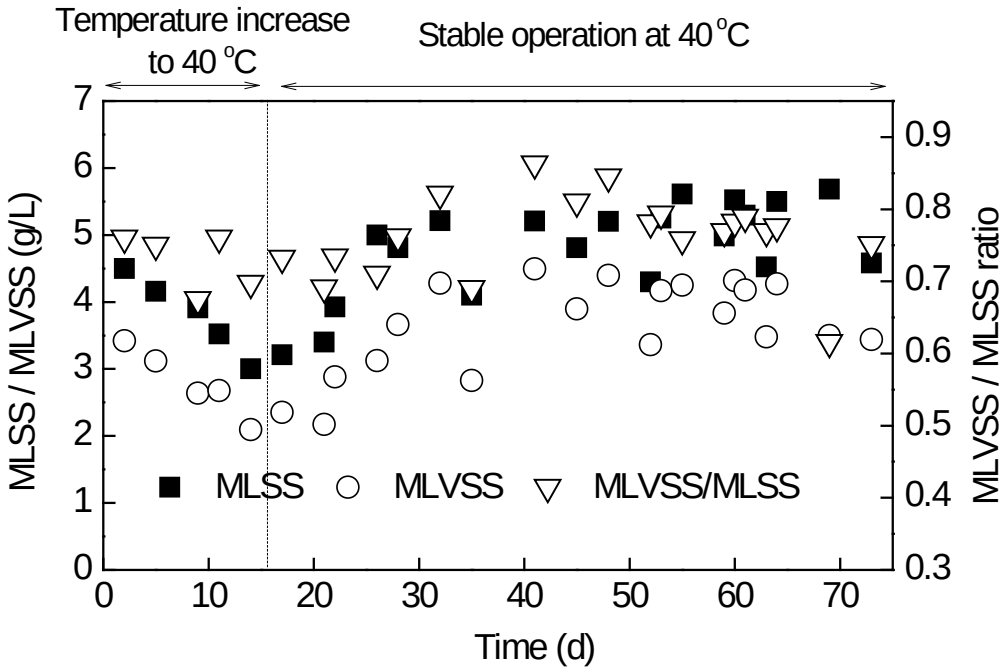


Figure 7.5: Variation of sludge concentration in the thermophilic bioreactor during acclimatisation period (i.e., prior to MDBR experiment).

7.4.2 *Trace organic contaminant removal*

Biodegradation in the thermophilic bioreactor and rejection by the MD membrane are the two removal mechanisms of TrOCs in the MDBR hybrid system. The individual and total removals of the 25 investigated TrOCs are depicted in Figure 7.6. Most TrOCs were moderately or highly removed during thermophilic biological treatment. The results observed showed that salinity build-up did not significantly affect the removal of readily biodegradable TrOCs, and their removal efficiencies were stable over the entire experiment (Figure 7.7). The reason might be that biodegradation of these TrOCs was mainly driven by heterotrophic bacteria, which are tolerant to salinity changes [191]. All TrOCs containing EWGs (i.e., clofibric acid, fenoprop, diclofenac, carbamazepine, atrazine, and triclosan) were poorly removed by the biological process in the thermophilic bioreactor, and their removal efficiencies were in the range of zero to 53%. Moreover, the removal efficiency of carbamazepine, atrazine, and triclosan continually deteriorated with time (Figure 7.8), exhibiting the detrimental effect of salinity build up on the removal of recalcitrant TrOCs by the bioreactor alone. It is notable that despite being a hydrophobic compound, triclosan removal by the bioreactor was remarkably low (53%) compared to the values previously reported in case of conventional MBR treatment [19, 23, 37]. The biological removal efficiency of carbamazepine in this study was also significantly lower than that by a thermophilic MBR operated at similar temperature as reported by Hai et al. [23] and Wijekoon et al. [209]. Low removal of Carbamazepine could be attributed to the low biological activity of nitrifying bacteria caused by the salinity increase. Carbamazepine appears to be

highly removed at anoxic condition compare to aerobic condition [23] and nitrifying bacteria could mainly affect the biodegradation [209].

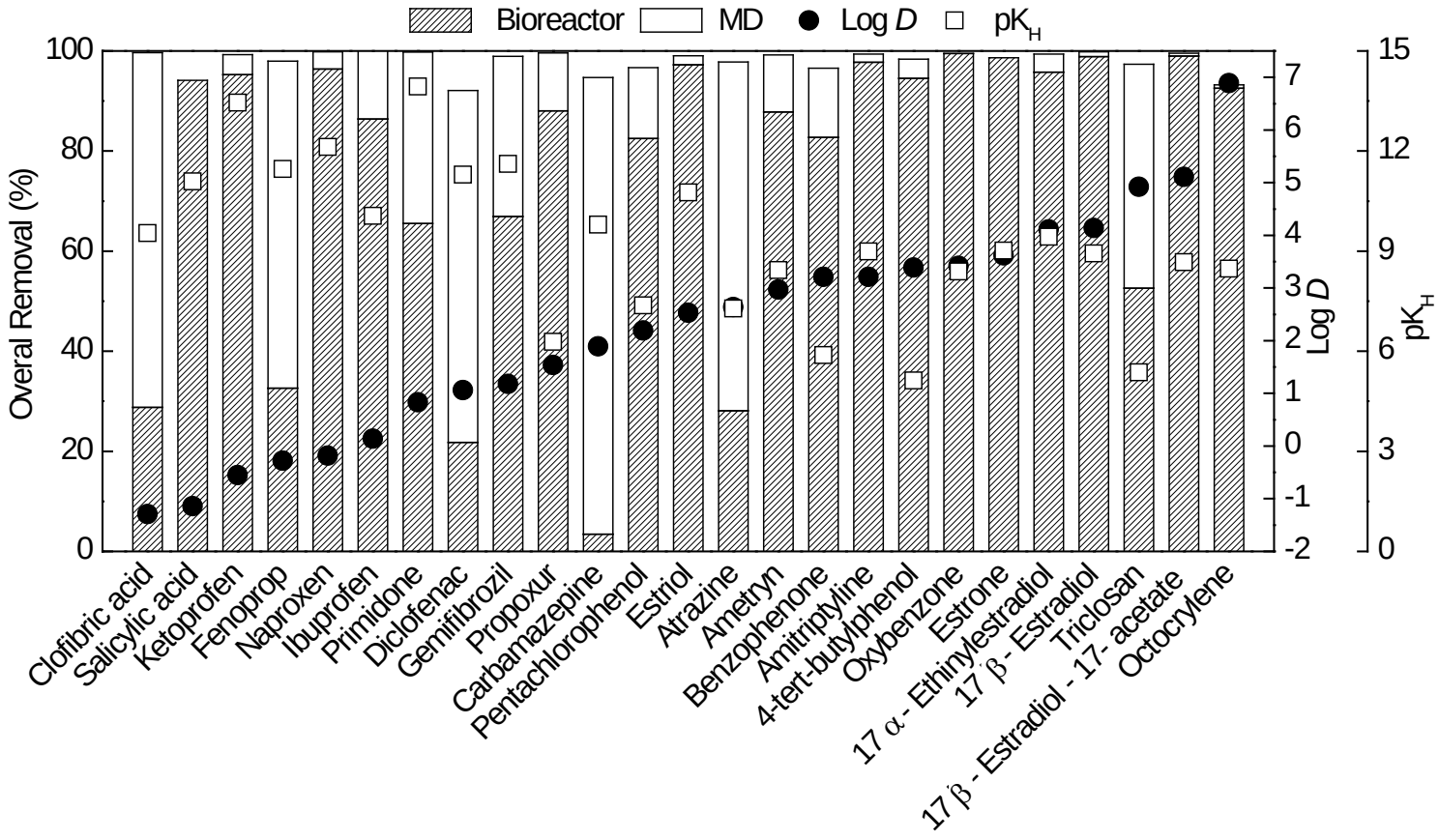


Figure 7.6: TrOC removal by the hybrid MDBR system. Distillate flux was stable at 1.2 ±0.2 L/m^2.h. The DO concentration and temperature of the bioreactor mixed liquor were 2.8±0.5 mg/L and 40 °C, respectively. Removal efficiency represents the average value of duplicate samples taken once a week for five weeks. Operating conditions are as described in Figure 7.1.

The complexity associated with the dynamic salinity level could modify the microbial community of MDBR as nitrifying bacteria are highly susceptible to salinity changes [191]. As carbamazepine is a nitrogenous compound and more likely to be removed by nitrifying bacteria [22, 39], it was substantially affected by salinity increase in the bioreactor. It is noteworthy that this study was conducted over a short period. For long term operation of the MDBR, the impact of salinity build-up may become less critical due to selective microbial growth and natural adaptation of the halophilic bacteria [191].

All TrOCs investigated were well removed (> 95%) by the integrated MDBR system (Figure 7.6) despite the impact of salinity build-up on recalcitrant TrOC removal by the bioreactor. TrOC removal by the MD process was investigated in a previous study [209] (Chapter 6). Although TrOCs with low volatility (pK_H> 9) were well rejected, MD alone was not effective for removal of TrOCs such as 4-tert-butyl phenol and oxybenzone which are moderately volatile (pK_H< 9) [209]. Thus, the results in the current study imply that MD can effectively complement the biological treatment process to achieve high TrOC removal. In addition, the novel MDBR system may offer a high effluent quality independent of the operating conditions of the bioreactor.

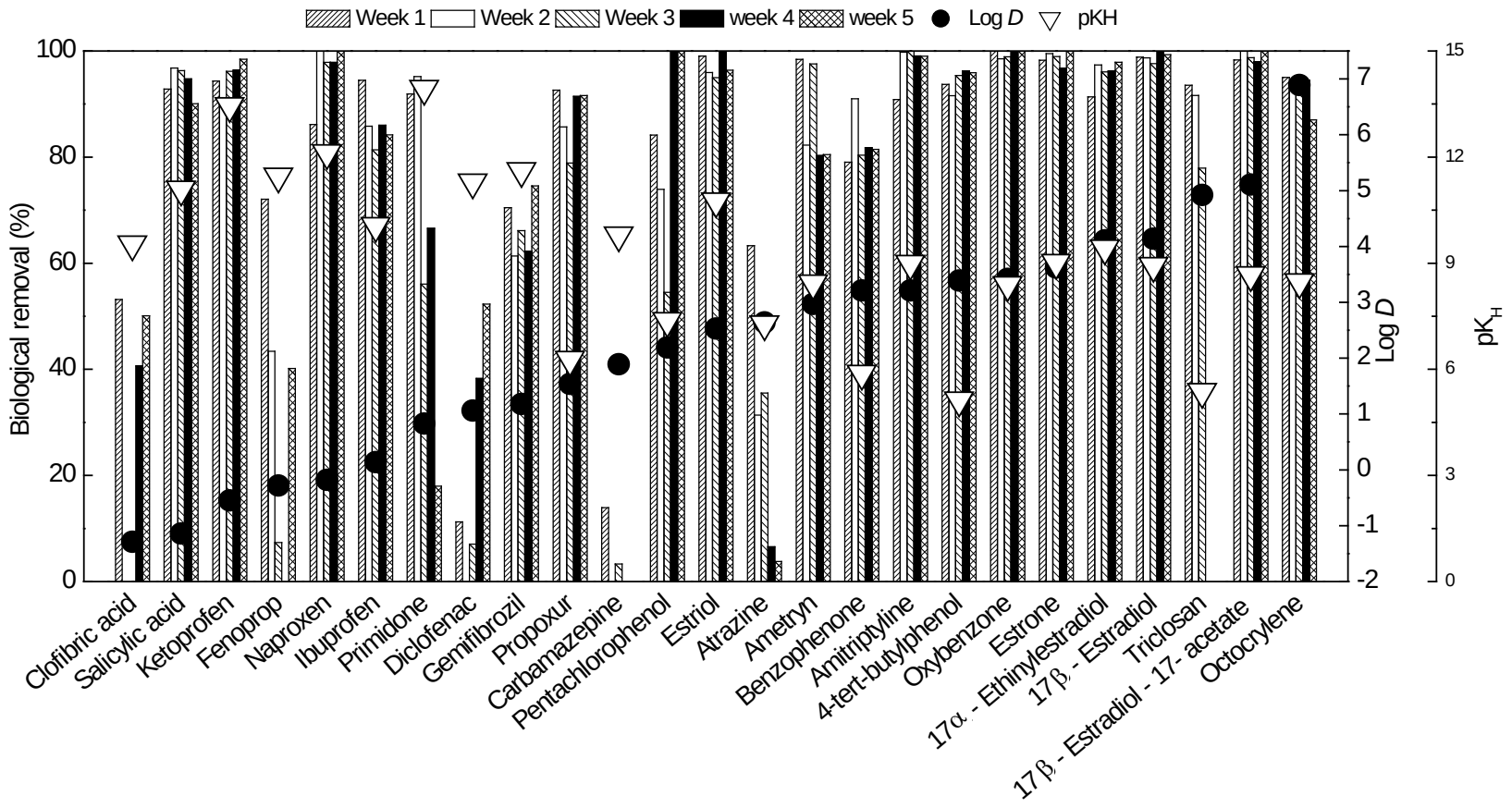


Figure 7.7: Biological removal of TrOCs as a function of time during MDBR treatment.

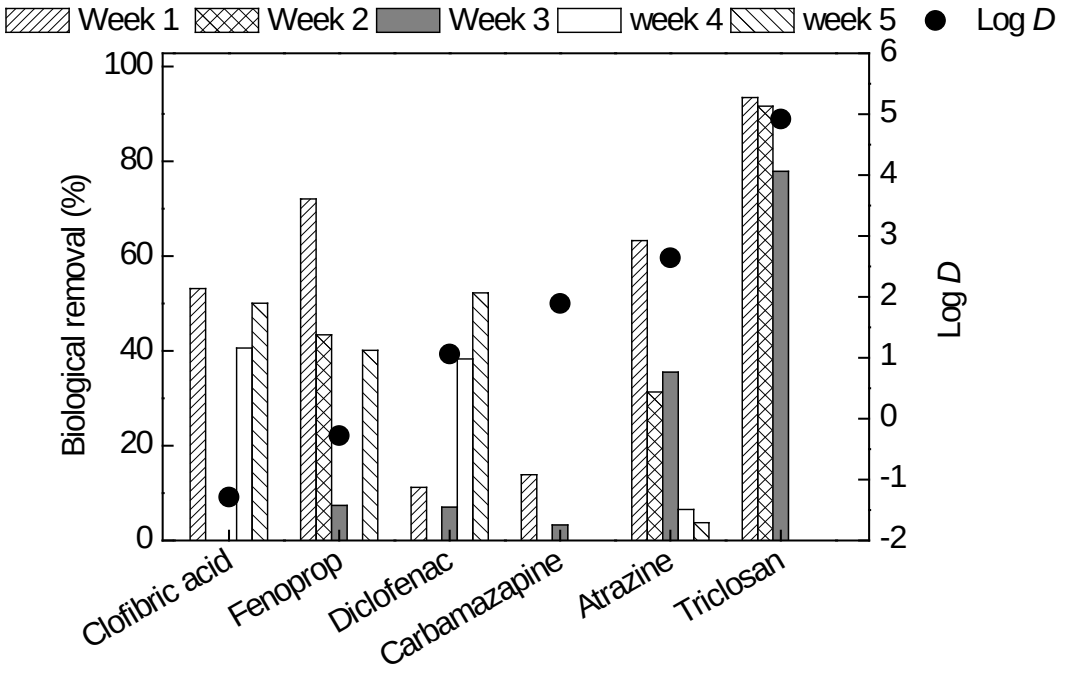


Figure 7.8: Variation in the biological removal of recalcitrant TrOCs with time.

7.4.3 *Fate and transport of trace organic contaminants*

The concentration of TrOCs and their associated Log *D* and pK_H values in the solid and liquid phases of the different streams of the MDBR are summarized in Figure 7.9. The concentration of most TrOCs in the aqueous (i.e., feed to the bioreactor, supernatant, and distillate) and solid phases were stable during the experiment. The accumulation of certain TrOCs in the supernatant (Figure 7.10) may be ascribed to their low biological removal as discussed above. Triclosan was the only TrOC that significantly accumulated in the sludge phase because it is a hydrophobic (log D_{pH8} = 4.92) and recalcitrant compound. Biodegradation/transformation by the thermophilic bioreactor, adsorption to the sludge phase, and rejection by the MD membrane could all contribute to the removal

of TrOCs by the MDBR system. The mass balance of each TrOC was calculated (Equations 7.1-7.4) based on the loading in the feed, supernatant, sludge, and distillate in order to determine the relative contribution between biodegradation/transformation, accumulation in supernatant, adsorption to sludge, and volatilisation during MDBR treatment. Volatilisation during the MD process was calculated by taking into account the compound concentration in the distillate. Finally, the percentage of biodegradation/transformation was determined from the difference of measured concentrations in the feed, the bioreactor supernatant, and the distillate (Figure 7.11).

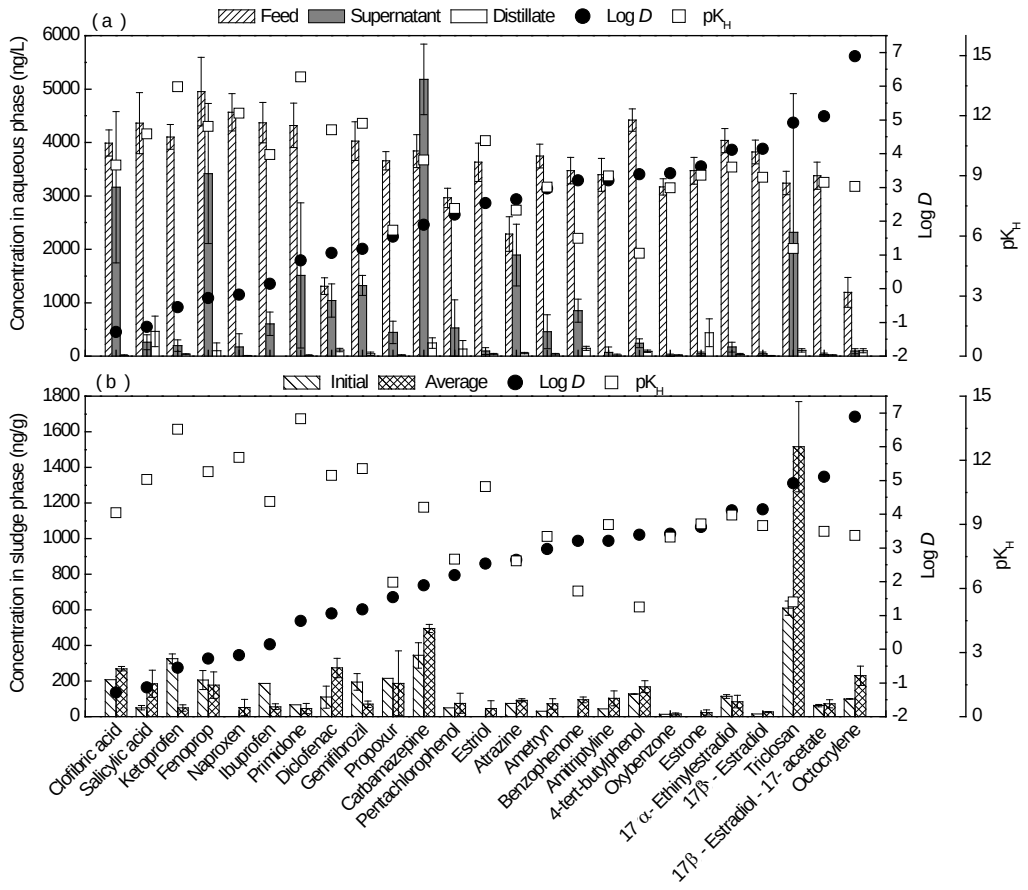


Figure 7.9: Concentrations of the selected TrOC in (a) the aqueous phase and (b) the sludge phase of the MDBR hybrid system. Operating conditions are given in Figure 7.6. Error bars represent the standard deviation of duplicate samples taken once a week for five weeks. Error bars of sludge data represent the standard deviation of duplicate samples taken once a week for four weeks.

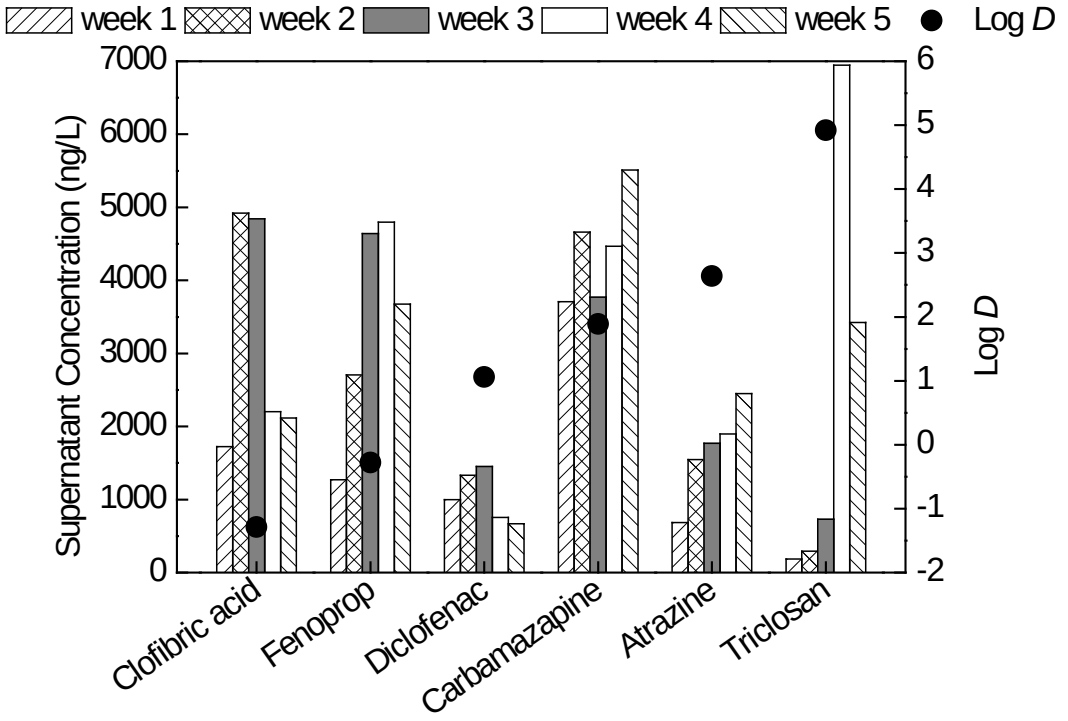


Figure 7.10: Variation in the supernatant concentration of recalcitrant TrOCs with time.

Percentage biodegradation/transformation, adsorption to sludge, and rejection by MD (accumulation in the supernatant) of TrOCs during MDBR treatment are given in Figure 7.11. Volatilization to the distillate was insignificant considering the low volatility (as denoted by low Henry's constant or high pK_H) and negligible distillate concentrations of all TrOCs observed (Figure 7.9). The hydrophobicity (measured by log *D*) and the presence of EDGs and EWGs could also govern the fate and transport of TrOCs. Results revealed that readily biodegradable TrOCs were mainly removed by biodegradation (>70%). As noted earlier, biodegradation of recalcitrant TrOCs (possessing only EWGs) in this study, was considerably low compared to their removal by a conventional MBR process as previously reported

[19, 23, 29, 39, 209]. Biodegradation of triclosan, possessing strong EWG (i.e., chloro) was low (26%) compared to octocrylene (74%), which possesses weak EWGs (i.e., cyano).

TrOC rejection by MD was the main removal mechanism of recalcitrant compounds by the MDBR hybrid system. MD rejection accounted for the greater portion of overall removal of six recalcitrant TrOCs, including triclosan (42%), fenoprop (64%), atrazine (68%), clofibric acid (71%), diclofenac (75%), and carbamazepine (94%). Accumulation in sludge greatly contributed to the aqueous phase removal of hydrophobic recalcitrant compounds (i.e., triclosan and octocrylene). Data from this study reveals that accumulation in sludge was governed more by the strength of the EWG than the hydrophobicity of the compound. For example, sludge adsorption of triclosan, which is less hydrophobic (log $D_{pH\ 8}$ =4.92) but possesses stronger EWGs (i.e., chloro), was higher (33%) compared to that of octocrylene (22%), which is more hydrophobic (log $D_{pH\ 8}$ = 6.89) but possesses weaker EWGs (i.e., cyano).

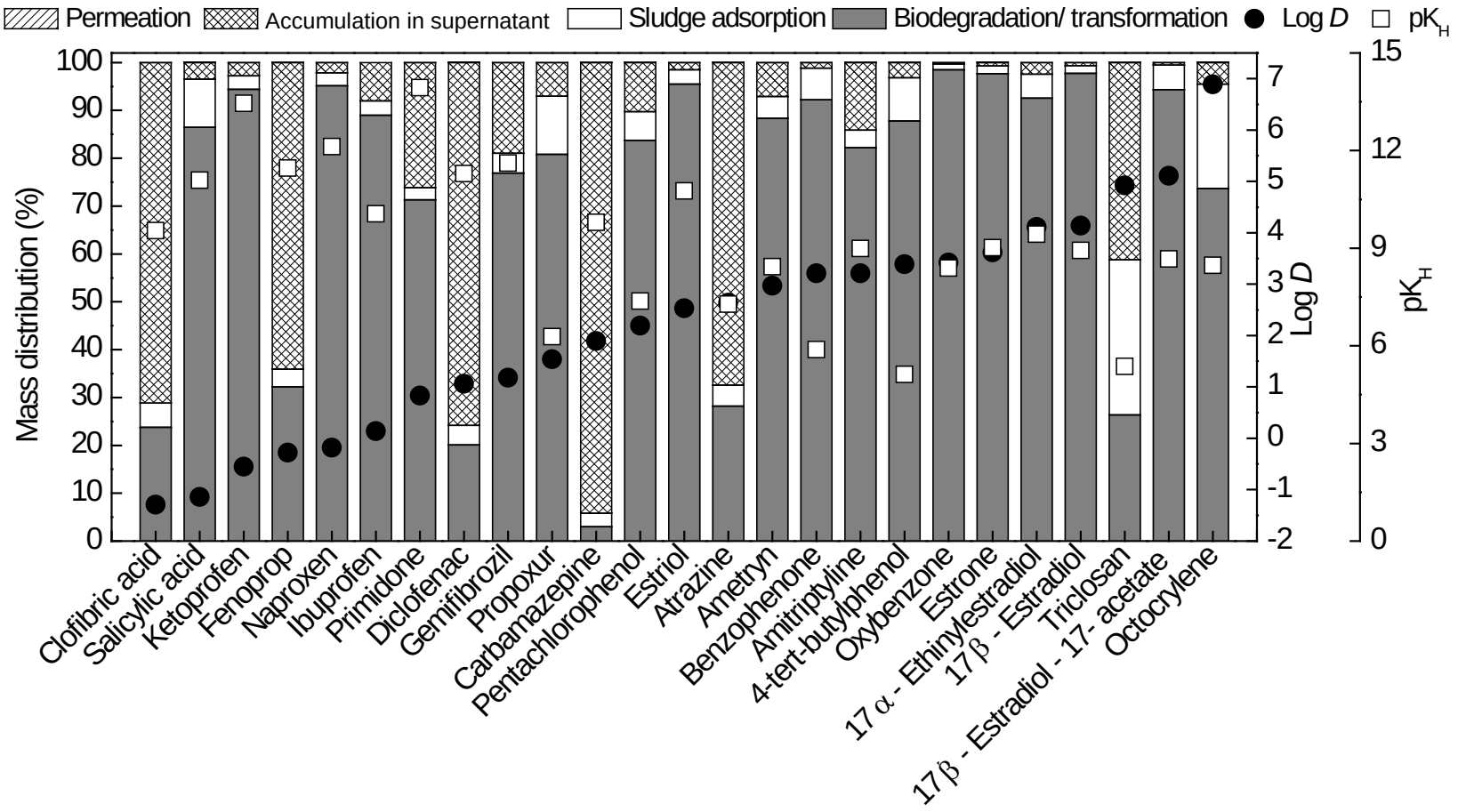


Figure 7.11: Fate of the selected TrOCs during MDBR treatment.

7.5 Conclusion

The removal of 25 TrOCs by a novel hybrid MDBR system was investigated. While most TrOCs were effectively removed by biological processes in the thermophilic bioreactor, compounds containing EWGs in their molecular structure were resistant to biological degradation. Salinity build-up occurred during MDBR operation which negatively affected the performance of the biological processes in the thermophilic bioreactor, lowering the removal of total nitrogen and recalcitrant TrOCs. However, the overall performance of the MDBR system with respect to the removal of all 25 TrOCs, TOC, and TN was high and independent of the performance of the bioreactor.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

This thesis examined the removal and fate of trace organic contaminants (TrOCs) during MBR treatment and proposed a framework to predict the removal and fate of TrOCs by MBR treatment. Membrane distillation as a post treatment to remove TrOCs during membrane bioreactor was also investigated. A novel membrane distillation bioreactor system was evaluated to shed light on the development of MDBR system for TrOC removal.

Chapter 4 examined the removal of TrOCs from both solid (sludge) and aqueous phases as well as their fate during MBR treatment. The fate of TrOCs during MBR treatment was governed by both biodegradation and adsorption. Biodegradation was the predominant removal mechanism of the hydrophilic TrOCs from the aqueous phase. The removal of hydrophobic TrOCs from the aqueous phase could also occur via adsorption. However, readily biodegradable hydrophobic TrOCs did not accumulate significantly in sludge. Additionally, recalcitrant TrOCs which are moderately hydrophobic or even hydrophilic could accumulate significantly in the sludge.

Results from Chapter 5 revealed that biodegradation was the predominant removal mechanism for N-nitrosamines. Adsorption to sludge was negligible while photolysis and volatilization were not expected to occur. N-nitrosamine removal efficiencies were dependent on their molecular structure, and ranged from 24% to 94%. The results could be explained by the presence of EWGs and EDGs (and their

relative strength) in the N-nitrosamine molecules. N-nitrosamines possessing strong EDGs such as dimethyl-amine and diethyl-amine (e.g. NDMA and NDEA) are readily biodegradable during MBR treatment. By contrast, NMOR which has the weak EDG morpholine was persistent to biodegradation and its removal efficiency by MBR treatment was correspondingly the lowest.

The rejection of 29 trace organic compounds (TrOCs) and their fate in a membrane distillation (MD) system were investigated in Chapter 6. Results suggest that rejection and fate and transport of TrOC during MD would be mainly governed by the volatility and partially by the hydrophobicity of the compound. All TrOCs with $pK_H > 9$ (which can be classified as non-volatile) were highly removed by MD. However, three compounds (i.e. 4-tert-octylphenol, 4-tert-butylphenol and benzophenone) with $pK_H < 9$ and thus classified as partially volatile showed relatively low rejection efficiencies (i.e. 54, 73 and 66%, respectively). The results also suggest that the rejection of TrOCs with $pK_H < 9$ may be governed by the interplay between their hydrophobicity and volatility. In addition, the results showed that hydrophilic TrOCs having negligible volatility were concentrated in the feed, while hydrophobic compounds with moderate volatility were substantially lost due to evaporation or adsorption to membrane. Membrane bioreactor followed by MD treatment resulted in near complete (> 95%) removal of all 29 TrOCs despite their diverse physicochemical properties (i.e. hydrophobicity, persistency and volatility).

In Chapter 7, the removal of 25 TrOCs by a novel hybrid MDBR system was examined. While most TrOCs were well removed by biological processes in the thermophilic bioreactor, compounds containing EWG groups in their molecular structure were recalcitrant to biological degradation. Salinity build-up negatively

affected the biological performances of the bioreactor, reducing the removal of total nitrogen and recalcitrant TrOCs. However, impact of salinity increase on TOC removal was insignificant as most of the heterotrophic bacteria are halotolerant. Interestingly, MDBR overall performances with respect to the removal of all 25 TrOCs, TOC, and TN were high and independent of the bioreactor performances. .

8.2 Recommendations to future studies

Fate and removal of TrOCs during anaerobic MBR has been scarcely reported previously. Sludge phase removal of TrOCs during anaerobic MBR could be significant given the high adsorption potential of TrOCs to sludge. Therefore, systematic investigation of the removal of TrOCs during AnMBR treatment is recommended.

Membrane distillation bioreactor is an effective treatment which can produce high quality product water. Basic removal performance and the TrOCs removal of aerobic membrane distillation bioreactor are independent of the bioreactor performance. Yet, AnMBR coupled membrane distillation hybrid process for wastewater treatment has not been reported. Therefore, examining the feasibility of AnMBR coupled membrane distillation hybrid process for TrOCs removal is recommended.

Salinity build-up in MDBR treatment could adversely affect the membrane characteristics and consequently affect the quality of the product water. Salinity build-up may also affect the biological process with the selective growth of microorganisms. Therefore, the removal mechanisms of TrOCs in long term

operation may vary. Long term operation of MDBR should be investigated to comprehensively understand the performance of this novel technology.

REFERENCES

[1] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Marinas, A.M. Mayes, Science and technology for water purification in the coming decades, Nature, 452 (2008) 301-310.
[2] K. Kümmerer, The presence of pharmaceuticals in the environment due to human use - present knowledge and future challenges, Journal of Environmental Management, 90 (2009) 2354-2366.
[3] A.S. Stasinakis, G. Gatidou, Micropollutants and aquatic environment, in: J. Virkutyte, S. Varma R, V. Jegatheesan (Eds.) Treatment of micropollutants in water and wastewatr:Integrate environmental technologies series, Interantional Water Association, London, (2010), pp. 1-51.
[4] J.-L. Zhao, G.-G. Ying, Y.-S. Liu, F. Chen, J.-F. Yang, L. Wang, X.-B. Yang, J.L. Stauber, M.S.J. Warne, Occurrence and a screening-level risk assessment of human pharmaceuticals in the Pearl River system, South China, Environmental Toxicology and Chemistry, 29 (2010) 1377-1384.
[5] N.H. Tran, T. Urase, T.T. Ta, A preliminary study on the occurrence of pharmaceutically active compounds in hospital wastewater and surface water in Hanoi, Vietnam, CLEAN – Soil, Air, Water, 42 (2013) 267–275.
[6] J. Kang, W.E. Price, Occurrence of phytoestrogens in municipal wastewater and surface waters, Journal of Environmental Monitoring, 11 (2009) 1477-1483.
[7] P. Gago-Ferrero, M.S. Díaz-Cruz, D. Barceló, Occurrence of multiclass UV filters in treated sewage sludge from wastewater treatment plants, Chemosphere, 84 (2011) 1158-1165.
[8] Y.S. Liu, G.G. Ying, A. Shareef, R.S. Kookana, Occurrence and removal of benzotriazoles and ultraviolet filters in a municipal wastewater treatment plant, Environmental Pollution, 165 (2012) 225-232.
[9] W.A. Mitch, J.O. Sharp, R.R. Trussell, R.L. Valentine, L. Alvarez-Cohen, D.L. Sedlak, N-Nitrosodimethylamine (NDMA) as a drinking water contaminant: A review, Environemtanl Engineering Science, 20 (2003) 389-404.
[10] Y.-Y. Zhao, J.M. Boyd, M. Woodbeck, R.C. Andrews, F. Qin, S.E. Hrudey, X.-F. Li, Formation of N-Nitrosamines from Eleven Disinfection Treatments of Seven Different Surface Waters, Environmental Science & Technology, 42 (2008) 4857-4862.
[11] D.L. Sedlak, R.A. Deeb, E.L. Hawley, W.A. Mitch, T.D. Durbin, S. Mowbray, S. Carr, Sources and Fate of Nitrosodimethylamine and its Precursors in Municipal Wastewater Treatment Plants, Water Environment Research, 77 (2005) 32-39.
[12] M. Krauss, P. Longrée, F. Dorusch, C. Ort, J. Hollender, Occurrence and removal of N-nitrosamines in wastewater treatment plants, Water Research, 43 (2009) 4381-4391.
[13] T. Fujioka, S.J. Khan, Y. Poussade, J.E. Drewes, L.D. Nghiem, N-nitrosamine removal by reverse osmosis for indirect potable water reuse – A critical review based on observations from laboratory-, pilot- and full-scale studies, Separation and Purification Technology, 98 (2012) 503-515.

[14] T. Melin, B. Jefferson, D. Bixio, C. Thoeye, W. De Wilde, J. De Koning, J. van der Graaf, T. Wintgens, Membrane bioreactor technology for wastewater treatment and reuse, Desalination, 187 (2006) 271-282.
[15] R.E. Rasche, M.R. Hyman, D.J. Arp, Factors limiting aliphatic chlorocarbon degradation by nitrosomonas europaea: Cometabolic inactivation of ammonia monooxygenase and substrate specificity, Applied and Environmental Microbiology, 57 (1991) 2986-2994.
[16] J.S. Vader, C.G. van Ginkel, F.M.G.M. Sperling, J. de Jong, W. de Boer, J.S. de Graaf, M. van der Most, P.G.W. Stokman, Degradation of ethinyl estradiol by nitrifying activated sludge, Chemosphere, 41 (2000) 1239-1243.
[17] J.Y. Kim, K. Ryu, E.J. Kim, W.S. Choe, G.C. Cha, I.-K. Yoo, Degradation of bisphenol A and nonylphenol by nitrifying activated sludge, Process Biochemistry, 42 (2007) 1470-1474.
[18] M. Cirja, P. Ivashechkin, A. Schäffer, P. Corvini, Factors affecting the removal of organic micropollutants from wastewater in conventional treatment plants (CTP) and membrane bioreactors (MBR), Reviews in Environmental Science and Biotechnology, 7 (2008) 61-78.
[19] C. Miège, J.M. Choubert, L. Ribeiro, M. Eusèbe, M. Coquery, Fate of pharmaceuticals and personal care products in wastewater treatment plants - Conception of a database and first results, Environmental Pollution, 157 (2009) 1721-1726.
[20] L.D. Nghiem, N. Tadkaew, M. Sivakumar, Removal of trace organic contaminants by submerged membrane bioreactors, Desalination, 236 (2009) 127-134.
[21] N. Tadkaew, M. Sivakumar, S.J. Khan, J.A. McDonald, L.D. Nghiem, Effect of mixed liquor pH on the removal of trace organic contaminants in a membrane bioreactor, Bioresource Technology, 101 (2010) 1494-1500.
[22] F.I. Hai, X. Li, W.E. Price, L.D. Nghiem, Removal of carbamazepine and sulfamethoxazole by MBR under anoxic and aerobic conditions, Bioresource Technology, 102 (2011) 10386-10390.
[23] F.I. Hai, K. Tessmer, L.N. Nguyen, J. Kang, W.E. Price, L.D. Nghiem, Removal of micropollutants by membrane bioreactor under temperature variation, Journal of Membrane Science, 383 (2011) 144-151.
[24] V. Boonyaroj, C. Chiemchaisri, W. Chiemchaisri, S. Theepharaksapan, K. Yamamoto, Toxic organic micro-pollutants removal mechanisms in long-term operated membrane bioreactor treating municipal solid waste leachate, Bioresource Technology, 113 (2012) 174-180.
[25] H. Hamid, C. Eskicioglu, Fate of estrogenic hormones in wastewater and sludge treatment: A review of properties and analytical detection techniques in sludge matrix, Water Research, 46 (2012) 5813-5833.
[26] M. Clara, N. Kreuzinger, B. Strenn, O. Gans, H. Kroiss, The solids retention time—a suitable design parameter to evaluate the capacity of wastewater treatment plants to remove micropollutants, Water Research, 39 (2005) 97-106.
[27] M. Clara, B. Strenn, O. Gans, E. Martinez, N. Kreuzinger, H. Kroiss, Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants, Water Research, 39 (2005) 4797-4807.

[28] R. Reif, S. Suárez, F. Omil, J.M. Lema, Fate of pharmaceuticals and cosmetic ingredients during the operation of a MBR treating sewage, Desalination, 221 (2008) 511-517.
[29] J. Radjenović, M. Petrović, D. Barceló, Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment, Water Research, 43 (2009) 831-841.
[30] D. Navaratna, J. Elliman, A. Cooper, L. Shu, K. Baskaran, V. Jegatheesan, Impact of herbicide Ametryn on microbial communities in mixed liquor of a membrane bioreactor (MBR), Bioresource Technology, 113 (2012) 181-190.
[31] P.M. Bradley, S.A. Carr, R.B. Baird, F.H. Chapelle, Biodegradation of N-nitrosodimethylamine in Soil from a Water Reclamation Facility, Bioremediation Journal, 9 (2005) 115-120.
[32] J.E. Drewes, C. Hoppe, T. Jennings, Fate and Transport of N-Nitrosamines Under Conditions Simulating Full-Scale Groundwater Recharge Operations, Water Environment Research, 78 (2006) 2466-2473.
[33] D. Fournie, J. Hawari, S.H. Streger, K. McClay, P.B. Hatzinger, Biotransformation of N-Nitrosodimethylamine by Pseudomonas mendocina KR1, Applied Environmental Microbiology, 72 (2006) 6693-6698.
[34] Q. Zhou, S. McCraven, J. Garcia, M. Gasca, T.A. Johnson, W.E. Motzer, Field evidence of biodegradation of N-Nitrosodimethylamine (NDMA) in groundwater with incidental and active recycled water recharge, Water Research, 43 (2009) 793-805.
[35] F. Sacher, C.K. Schmidt, C.C. Lee, U.V. Gunten, Stratergies for minimizing nitrosamine formation during disinfection, AWWA Research Foundation, (2008).
[36] P.B. Hatzinger, C. Condee, K.R. McClay, A. Paul Togna, Aerobic treatment of N-nitrosodimethylamine in a propane-fed membrane bioreactor, Water Research, 45 (2011) 254-262.
[37] N. Tadkaew, F.I. Hai, J.A. McDonald, S.J. Khan, L.D. Nghiem, Removal of trace organics by MBR treatment: The role of molecular properties, Water Research, 45 (2011) 2439-2451.
[38] N.H. Tran, T. Urase, H.H. Ngo, J. Hu, S.L. Ong, Insight into metabolic and cometabolic activities of autotrophic and heterotrophic microorganisms in the biodegradation of emerging trace organic contaminants, Bioresource Technology, 146 (2013) 721-731.
[39] K.C. Wijekoon, F.I. Hai, J. Kang, W.E. Price, W. Guo, H.H. Ngo, L.D. Nghiem, The fate of pharmaceuticals, steroid hormones, phytoestrogens, UV-filters and pesticides during MBR treatment, Bioresource Technology, 144 (2013) 247-254.
[40] A.A. Alturki, N. Tadkaew, J.A. McDonald, S.J. Khan, W.E. Price, L.D. Nghiem, Combining MBR and NF/RO membrane filtration for the removal of trace organics in indirect potable water reuse applications, Journal of Membrane Science, 365 (2010) 206-215.
[41] L.N. Nguyen, F.I. Hai, J. Kang, L.D. Nghiem, W.E. Price, W. Guo, H.H. Ngo, K.-L. Tung, Comparison between sequential and simultaneous application of activated carbon with membrane bioreactor for trace organic contaminant removal, Bioresource Technology, 130 (2013) 412-417.

[42] L.N. Nguyen, F.I. Hai, J. Kang, W.E. Price, L.D. Nghiem, Removal of emerging trace organic contaminants by MBR-based hybrid treatment processes, International Biodeterioration & Biodegradation, 85 (2013) 474-482.
[43] E. Curcio, E. Drioli, Membrane distillation and related operations—A review, Separation & Purification Reviews, 34 (2005) 35-86.
[44] J.-H. Choi, S. Dockko, K. Fukushi, K. Yamamoto, A novel application of a submerged nanofiltration membrane bioreactor (NF MBR) for wastewater treatment, Desalination, 146 (2002) 413-420.
[45] A. Alturki, J. McDonald, S.J. Khan, F.I. Hai, W.E. Price, L.D. Nghiem, Performance of a novel osmotic membrane bioreactor (OMBR) system: Flux stability and removal of trace organics, Bioresource Technology, 113 (2012) 201-206.
[46] A. Achilli, T.Y. Cath, E.A. Marchand, A.E. Childress, The forward osmosis membrane bioreactor: A low fouling alternative to MBR processes, Desalination, 239 (2009) 10-21.
[47] N.T. Hancock, P. Xu, M.J. Roby, J.D. Gomez, T.Y. Cath, Towards direct potable reuse with forward osmosis: Technical assessment of long-term process performance at the pilot scale, Journal of Membrane Science, 445 (2013) 34-46.
[48] T.-H. Khaing, J. Li, Y. Li, N. Wai, F.-s. Wong, Feasibility study on petrochemical wastewater treatment and reuse using a novel submerged membrane distillation bioreactor, Separation and Purification Technology, 74 (2010) 138-143.
[49] J. Phattaranawik, A.G. Fane, A.C.S. Pasquier, W. Bing, F.S. Wong, Experimental Study and Design of a submerged membrane distillation bioreactor: Research article, Chemical Engineering Technology, 32 (2009) 38-44.
[50] S. Goh, J. Zhang, Y. Liu, A.G. Fane, Fouling and wetting in membrane distillation (MD) and MD-bioreactor (MDBR) for wastewater reclamation, Desalination, 323 (2013) 39-47.
[51] S. Goh, Q. Zhang, J. Zhang, D. McDougald, W.B. Krantz, Y. Liu, A.G. Fane, Impact of a biofouling layer on the vapor pressure driving force and performance of a membrane distillation process, Journal of Membrane Science, 438 (2013) 140-152.
[52] B. Quinn, F. Gagné, C. Blaise, Evaluation of the acute, chronic and teratogenic effects of a mixture of eleven pharmaceuticals on the cnidarian, Hydra attenuata, Science of The Total Environment, 407 (2009) 1072-1079.
[53] J. Schwaiger, H. Ferling, U. Mallow, H. Wintermayr, R.D. Negele, Toxic effects of the non-steroidal anti-inflammatory drug diclofenac: Part I: histopathological alterations and bioaccumulation in rainbow trout, Aquatic Toxicology, 68 (2004) 141-150.
[54] J.N. Brown, N. Paxéus, L. Förlin, D.G.J. Larsson, Variations in bioconcentration of human pharmaceuticals from sewage effluents into fish blood plasma, Environmental Toxicology and Pharmacology, 24 (2007) 267-274.
[55] D. Fatta-Kassinos, S. Meric, A. Nikolaou, Pharmaceutical residues in environmental waters and wastewater: Current state of knowledge and future research, Analytical and Bioanalytical Chemistry, 399 (2011) 251-275.
[56] J.L. Oaks, M. Gilbert, M.Z. Virani, R.T. Watson, C.U. Meteyer, B.A. Rideout, H.L. Shivaprasad, S. Ahmed, M.J. Iqbal Chaudhry, M. Arshad, S. Mahmood, A. Ali, A. Ahmed Khan, Diclofenac residues as the cause of vulture population decline in Pakistan, Nature, 427 (2004) 630-633.

[57] G.E. Swan, R. Cuthbert, M. Quevedo, R.E. Green, D.J. Pain, P. Bartels, A.A. Cunningham, N. Duncan, A.A. Meharg, J. Lindsay Oaks, J. Parry-Jones, S. Shultz, M.A. Taggart, G. Verdoorn, K. Wolter, Toxicity of diclofenac to Gyps vultures, Biology Letters, 2 (2006) 279-282.
[58] D. Dreising, EHEC outbreak strain: Professor Karch suspects humans could be a reservoir: It wouldn't be the first time, in, Munich, (2011).
[59] N. Veldhoen, R.C. Skirrow, H. Osachoff, H. Wigmore, D.J. Clapson, M.P. Gunderson, G. Van Aggelen, C.C. Helbing, The bactericidal agent triclosan modulates thyroid hormone-associated gene expression and disrupts postembryonic anuran development, Aquatic Toxicology, 80 (2006) 217-227.
[60] V. Kumar, A. Chakraborty, M.R. Kural, P. Roy, Alteration of testicular steroidogenesis and histopathology of reproductive system in male rats treated with triclosan, Reproductive Toxicology, 27 (2009) 177-185.
[61] T. Christiansen, B. Korsgaard, A. Jespersen, Effects of nonylphenol and 17 beta-oestradiol on vitellogenin synthesis, testicular structure and cytology in male eelpout Zoarces viviparus, Journal of Experimental Biology, 201 (1998) 179-192.
[62] R. Länge, T. Hutchinson, C. Croudace, F. Siegmund, H. Schweinfurth, P. Hampe, G. Panter, J. Sumpter, Effects of the synthetic estrogen 17 alpha-ethinylestradiol on the life-cycle of the fathead minnow (Pimephales promelas), Environmental Toxicology and Chemistry, 6 (2001) 1216-1227.
[63] K.L. Thorpe, T.H. Hutchinson, M.J. Hetheridge, M. Scholze, J.P. Sumpter, C.R. Tyler, Assessing the Biological Potency of Binary Mixtures of Environmental Estrogens using Vitellogenin Induction in Juvenile Rainbow Trout (Oncorhynchus mykiss), Environmental Science & Technology, 35 (2001) 2476-2481.
[64] B.D. Palmer, S.K. Palmer, Vitellogenin induction by xenobiotic estrogens in the red-eared turtle and African clawed frog, Environmental Health Perspectives, 4 (1995) 19–25.
[65] B. Seibert, Data from animal experiments and epidemiology data on turmorignenicity of estradiol velerate and ethynyl estradiol, cited in: Treatment of micropollutants in water and wastewater, IWA, London, (1996) 2-51.
[66] J.K. Hess-Wilson, K.E. Knudsen, Endocrine disrupting compounds and prostate cancer, Cancer Letters, 241 (2006) 1-12.
[67] G.S. Dizerega, D.L. Barbar, G.D. Hodgen, Endometriosis: role of ovarian steroid in initiation, maintenance and suppression, Fertility and sterility, (1980) 649-653.
[68] Z.-h. Liu, Y. Kanjo, S. Mizutani, Removal mechanisms for endocrine disrupting compounds (EDCs) in wastewater treatment -- physical means, biodegradation, and chemical advanced oxidation: A review, Science of The Total Environment, 407 (2009) 731-748.
[69] S.V. Dzyadevych, A.P. Soldatkin, J.-M. Chovelon, Assessment of the toxicity of methyl parathion and its photodegradation products in water samples using conductometric enzyme biosensors, Analytica Chimica Acta, 459 (2002) 33-41.
[70] E. Salazar-Arredondo, M.d.J. Solís-Heredia, E. Rojas-García, I. Hernández-Ochoa, B. Quintanilla-Vega, Sperm chromatin alteration and DNA damage by methyl-parathion, chlorpyrifos and diazinon and their oxon metabolites in human spermatozoa, Reproductive Toxicology, 25 (2008) 455-460.

[71] UNEP, Sub-Saharan Africa regional report :regionally based assessment of persistent toxic substances in, United Nations, Châtelaine, GE, (2002).
[72] C.H. Walker, S.P. Hopkin, R.M. Silby, D.B. Peakall, Principles of ecotoxicology, CRC Press, New York, USA, (2006).
[73] D.S. Rupa, P.P. Reddy, O.S. reddi, cytogeneticity of quinalphos and methyl parathion in human peripheral lymphocytes, Human and experimental toxicology, 9 (1990) 385.
[74] J. Blasiak, V. Kleinwächter, Z. Walter, R. Zaludová, Interaction of organophosphorus insecticide methylparathion with calf thymus DNA and a synthetic DNA duplex, Zeitschrift für Naturforschung C, A Journal of Biosciences, 50(11-12) (1995) 820-823.
[75] B.S. Rubin, Bisphenol A: An endocrine disruptor with widespread exposure and multiple effects, The Journal of Steroid Biochemistry and Molecular Biology, 127 (2011) 27-34.
[76] G.-G. Ying, Fate, behavior and effects of surfactants and their degradation products in the environment, Environment International, 32 (2006) 417-431.
[77] C. Plagellat, T. Kupper, R. Furrer, L.F. de Alencastro, D. Grandjean, J. Tarradellas, Concentrations and specific loads of UV filters in sewage sludge originating from a monitoring network in Switzerland, Chemosphere, 62 (2006) 915-925.
[78] M. Silvia Díaz-Cruz, M. Llorca, D. Barceló, Organic UV filters and their photodegradates, metabolites and disinfection by-products in the aquatic environment, TrAC Trends in Analytical Chemistry, 27 (2008) 873-887.
[79] A. Zenker, H. Schmutz, K. Fent, Simultaneous trace determination of nine organic UV-absorbing compounds (UV filters) in environmental samples, Journal of Chromatography A, 1202 (2008) 64-74.
[80] A.M. Calafat, L.Y. Wong, X. Ye, J.A. Reidy, L.L. Needham, Concentrations of the Sunscreen Agent Benzophenone-3 in Residents of the United States: National Health and Nutrition Examination Survey 2003–2004, Environmental Health Perspectives, 116 (2008) 893-897.
[81] T. Suzuki, S. Kitamura, R. Khota, K. Sugihara, N. Fujimoto, S. Ohta, Estrogenic and antiandrogenic activities of 17 benzophenone derivatives used as UV stabilizers and sunscreens, Toxicology and Applied Pharmacology, 203 (2005) 9-17.
[82] Jiang, Roberts, Collins, Benson, Absorption of sunscreens across human skin: an evaluation of commercial products for children and adults, British Journal of Clinical Pharmacology, 48 (1999) 635-637.
[83] T. Felix, B.J. Hall, J. S. Brodbelt, Determination of benzophenone-3 and metabolites in water and human urine by solid-phase microextraction and quadrupole ion trap GC–MS, Analytica Chimica Acta, 371 (1998) 195-203.
[84] Z.-h. Liu, Y. Kanjo, S. Mizutani, A review of phytoestrogens: Their occurrence and fate in the environment, Water Research, 44 (2010) 567-577.
[85] D.M. Tham, C.D. Gardner, W.L. Haskell, CLINICAL REVIEW 97 Potential Health Benefits of Dietary Phytoestrogens: A Review of the Clinical, Epidemiological, and Mechanistic Evidence, Journal of Clinical Endocrinology and Metabolism, 83 (1997).
[86] J. Barrett, Phytoestrogens. Friends or foes?, Environmental Health Perspectives, 104 (1996) 478–482.

[87] J. Kang, W.E. Price, L.A. Hick, Simultaneous determination of isoflavones and lignans at trace levels in natural waters and wastewater samples using liquid chromatography/electrospray ionization ion trap mass spectrometry, Rapid Communications in Mass Spectrometry, 20 (2006) 2411-2418.
[88] D.L. Sedlak, M. Kavanaugh, Removal and Destruction of NDMA and NDMA Precursors during Wastewater Treatment, WaterReuse Foundation, (2006).
[89] USDHHS, Report on Carcinogens, Eleventh Edition, in, U.S. Department of Health and Human Services, Public Health Service, National Toxicology Program, Washington, DC, (2005).
[90] F. Ma, Y. Wan, G. Yuan, L. Meng, Z. Dong, J. Hu, Occurrence and Source of Nitrosamines and Secondary Amines in Groundwater and its Adjacent Jialu River Basin, China, Environmental Science & Technology, 46 (2012) 3236-3243.
[91] M. Eichholzer, F. Gutzwiller, Dietary Nitrates, Nitrites, and N-Nitroso Compounds and Cancer Risk: A Review of the Epidemiologic Evidence, Nutrition Reviews, 56 (1998) 95-105.
[92] NRMMC, EPHC, AHMC, Australian Guidelines for Water Recycling: Managing Health and Environmental Risks (Phase 2): Augmentation of Drinking Water Supplies, Biotext Pty Ltd, Canberra, (2008).
[93] A. Pal, K.Y.-H. Gin, A.Y.-C. Lin, M. Reinhard, Impacts of emerging organic contaminants on freshwater resources: Review of recent occurrences, sources, fate and effects, Science of The Total Environment, 408 (2010) 6062-6069.
[94] Y. Luo, W. Guo, H.H. Ngo, L.D. Nghiem, F.I. Hai, J. Zhang, S. Liang, X.C. Wang, A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment, Science of The Total Environment, 473–474 (2014) 619-641.
[95] T. Heberer, Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data, Toxicology Letters, 131 (2002) 5-17.
[96] D.W. Kolpin, E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, H.T. Buxton, Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999−2000: A National Reconnaissance, Environmental Science & Technology, 36 (2002) 1202-1211.
[97] D. Ashton, M. Hilton, K.V. Thomas, Investigating the environmental transport of human pharmaceuticals to streams in the United Kingdom, Science of The Total Environment, 333 (2004) 167-184.
[98] R. Kallenborn, J. Fick, R. Lindberg, M. Moe, K.M. Nielsen, M. Tysklind, T. Vasskog, Pharmaceutical Residues in Northern European Environments: Consequences and Perspectives, in: K. Kümmerer (Ed.) Pharmaceuticals in the Environment, Springer Berlin Heidelberg, (2008), pp. 61-74.
[99] B. Kasprzyk-Hordern, R.M. Dinsdale, A.J. Guwy, The removal of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs during wastewater treatment and its impact on the quality of receiving waters, Water Research, 43 (2009) 363-380.
[100] I.M. Schreiber, W.A. Mitch, Occurrence and Fate of Nitrosamines and Nitrosamine Precursors in Wastewater-Impacted Surface Waters Using Boron As a Conservative Tracer, Environmental Science & Technology, 40 (2006) 3203-3210.

[101] T. Heberer, Tracking persistent pharmaceutical residues from municipal sewage to drinking water, Journal of Hydrology, 266 (2002) 175-189.
[102] J.L. Santos, I. Aparicio, E. Alonso, Occurrence and risk assessment of pharmaceutically active compounds in wastewater treatment plants. A case study: Seville city (Spain), Environment International, 33 (2007) 596-601.
[103] R. Andreozzi, M. Raffaele, P. Nicklas, Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment, Chemosphere, 50 (2003) 1319-1330.
[104] Y. Yu, L. Wu, A.C. Chang, Seasonal variation of endocrine disrupting compounds, pharmaceuticals and personal care products in wastewater treatment plants, Science of The Total Environment, 442 (2013) 310-316.
[105] A. Joss, E. Keller, A.C. Alder, A. Göbel, C.S. McArdell, T. Ternes, H. Siegrist, Removal of pharmaceuticals and fragrances in biological wastewater treatment, Water Research, 39 (2005) 3139-3152.
[106] B. Kasprzyk-Hordern, R.M. Dinsdale, A.J. Guwy, The occurrence of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs in surface water in South Wales, UK, Water Research, 42 (2008) 3498-3518.
[107] L.J. Standley, R.A. Rudel, C.H. Swartz, K.R. Attfield, J. Christian, M. Erickson, J.G. Brody, Wastewater-contaminated groundwater as a source of endogenous hormones and pharmaceuticals to surface water ecosystems, Environmental Toxicology and Chemistry, 27 (2008) 2457-2468.
[108] X. Peng, Y. Yu, C. Tang, J. Tan, Q. Huang, Z. Wang, Occurrence of steroid estrogens, endocrine-disrupting phenols, and acid pharmaceutical residues in urban riverine water of the Pearl River Delta, South China Science of The Total Environment, 397 (2008) 158-166.
[109] M.J. Gómez, M.J. Martínez Bueno, S. Lacorte, A.R. Fernández-Alba, A. Agüera, Pilot survey monitoring pharmaceuticals and related compounds in a sewage treatment plant located on the Mediterranean coast, Chemosphere, 66 (2007) 993-1002.
[110] M.S. Díaz-Cruz, D. Barceló, Trace organic chemicals contamination in ground water recharge, Chemosphere, 72 (2008) 333-342.
[111] H.M. Kuch, K. Ballschmiter, Determination of endocrine disrupting phenolic compounds and estrogens in surface and drinking water by HRGC-(NCI)-MS in the picogram per liter range, Environmental Science & Technology, 35 (2001) 3201-3206.
[112] A. Laganà, A. Bacaloni, I. De Leva, A. Faberi, G. Fago, A. Marino, Analytical methodologies for determining the occurrence of endocrine disrupting chemicals in sewage treatment plants and natural waters, Analytica Chimica Acta, 501 (2004) 79-88.
[113] B.J. Vanderford, R.A. Pearson, D.J. Rexing, S.A. Snyder, Analysis of Endocrine Disruptors, Pharmaceuticals, and Personal Care Products in Water Using Liquid Chromatography/Tandem Mass Spectrometry, Analytical Chemistry, 75 (2003) 6265-6274.
[114] M.R. Servos, D.T. Bennie, B.K. Burnison, A. Jurkovic, R. McInnis, T. Neheli, A. Schnell, P. Seto, S.A. Smyth, T.A. Ternes, Distribution of estrogens, 17[beta]-estradiol and estrone, in Canadian municipal wastewater treatment plants, Science of The Total Environment, 336 (2005) 155-170.

[115] M. Cargouët, D. Perdiz, A. Mouatassim-Souali, S. Tamisier-Karolak, Y. Levi, Assessment of river contamination by estrogenic compounds in Paris area (France), Science of The Total Environment, 324 (2004) 55-66.
[116] D.W. Kolpin, M. Skopec, M.T. Meyer, E.T. Furlong, S.D. Zaugg, Urban contribution of pharmaceuticals and other organic wastewater contaminants to streams during differing flow conditions, Science of The Total Environment, 328 (2004) 119-130.
[117] Y. Wang, Q. Zhang, J. Lv, A. Li, H. Liu, G. Li, G. Jiang, Polybrominated diphenyl ethers and organochlorine pesticides in sewage sludge of wastewater treatment plants in China, Chemosphere, 68 (2007) 1683-1691.
[118] B.O. Clarke, N.A. Porter, P.J. Marriott, J.R. Blackbeard, Investigating the levels and trends of organochlorine pesticides and polychlorinated biphenyl in sewage sludge, Environment International, 36 (2010) 323-329.
[119] G. Shukla, A. Kumar, M. Bhanti, P.E. Joseph, A. Taneja, Organochlorine pesticide contamination of ground water in the city of Hyderabad, Environment International, 32 (2006) 244-247.
[120] A. Katsoyiannis, C. Samara, Persistent organic pollutants (POPs) in the sewage treatment plant of Thessaloniki, northern Greece: occurrence and removal, Water Research, 38 (2004) 2685-2698.
[121] B. Shao, J. Hu, M. Yang, W. An, S. Tao, Nonylphenol and Nonylphenol Ethoxylates in River Water, Drinking Water,and Fish Tissues in the Area of Chongqing, China, Archives of Environmental Contamination and Toxicology, 48 (2005) 467-473.
[122] N. Jonkers, H.-P.E. Kohler, A. Dammshäuser, W. Giger, Mass flows of endocrine disruptors in the Glatt River during varying weather conditions, Environmental Pollution, 157 (2009) 714-723.
[123] A. Smeds, S. Willför, S. Pietarinen, P. Peltonen-Sainio, M.T. Reunanen, Occurrence of “mammalian” lignans in plant and water sources, Planta, 226 (2007) 639-646.
[124] A. Bacaloni, C. Cavaliere, A. Faberi, P. Foglia, R. Samperi, A. Lagana, Determination of isoflavones and cumestrol in river water and domestic wastewater sewage treatment Analytica Chimica Acta, 531 (2005).
[125] A. Joss, H. Andersen, T. Ternes, P.R. Richle, H. Siegrist, Removal of Estrogens in Municipal Wastewater Treatment under Aerobic and Anaerobic Conditions: Consequences for Plant Optimization, Environmental Science & Technology, 38 (2004) 3047-3055.
[126] C.P. Czajka, K.L. Londry, Anaerobic biotransformation of estrogens, Science of The Total Environment, 367 (2006) 932-941.
[127] C. Miège, J.M. Choubert, L. Ribeiro, M. Eusèbe, M. Coquery, Removal efficiency of pharmaceuticals and personal care products with varying wastewater treatment processes and operating conditions – conception of a database and first results, Water Science & Technology, 57 (2008) 49-56.
[128] V. Cunningham, Special characteristics of pharmaceuticals related to environmental fate, in: K. Ku¨mmerer (Ed.) Pharmaceuticals in the Environment, Sources Fate Effects and Risks, Springer, Berlin Heidelberg, (2008), pp. 23–34.
[129] H.-J. Knackmuss, Basic knowledge and perspectives of bioelimination of xenobiotic compounds, Journal of Biotechnology, 51 (1996) 287-295.

[130] F.I. Hai, N. Tadkaew, J.A. McDonald, S.J. Khan, L.D. Nghiem, Is halogen content the most important factor in the removal of halogenated trace organics by MBR treatment?, Bioresource Technology, 102 (2011) 6299-6303.
[131] N. Nakada, T. Tanishima, H. Shinohara, K. Kiri, H. Takada, Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment, Water Research, 40 (2006) 3297-3303.
[132] H.R. Andersen, M. Hansen, J. Kjølholt, F. Stuer-Lauridsen, T. Ternes, B. Halling-Sørensen, Assessment of the importance of sorption for steroid estrogens removal during activated sludge treatment, Chemosphere, 61 (2005) 139-146.
[133] D. Dionisi, L. Bertin, L. Bornoroni, S. Capodicasa, M.P. Papini, F. Fava, Removal of organic xenobiotics in activated sludges under aerobic conditions and anaerobic digestion of the adsorbed species, Journal of Chemical Technology & Biotechnology, 81 (2006) 1496-1505.
[134] J. Zhao, Y. Li, C. Zhang, Q. Zeng, Q. Zhou, Sorption and degradation of bisphenol A by aerobic activated sludge, Journal of Hazardous Materials, 155 (2008) 305-311.
[135] D. Dionisi, L. Bornoroni, S. Mainelli, M. Majone, F. Pagnanelli, M.P. Papini, Theoretical and Experimental Analysis of the Role of Sludge Age on the Removal of Adsorbed Micropollutants in Activated Sludge Processes, Industrial & Engineering Chemistry Research, 47 (2008) 6775-6782.
[136] B.N. Jacobsen, N. Nyholm, B.M. Pedersen, O. Poulsen, P. Østfeldt, Removal of organic micropollutants in laboratory activated sludge reactors under various operating conditions: sorption, Water Research, 27 (1993) 1505-1510.
[137] A.M. Kipopoulou, A. Zouboulis, C. Samara, T. Kouimtzis, The fate of lindane in the conventional activated sludge treatment process, Chemosphere, 55 (2004) 81-91.
[138] Q. Zeng, Y. Li, G. Gu, Nitrate-dependent degradation of 17α-ethinylestradiol by acclimated activated sludge under anaerobic conditions, Journal of Chemical Technology & Biotechnology, 84 (2009) 1841-1847.
[139] T.M. LaPara, J.E. Alleman, Thermophilic aerobic biological wastewater treatment, Water Research, 33 (1999) 895-908.
[140] J. van Lier, Limitations of thermophilic anaerobic wastewater treatment and the consequences for process design, Antonie van Leeuwenhoek, 69 (1996) 1-14.
[141] S. Judd, C. Judd, The MBR handbook; Principles and applications of membrane bioreatcors for water and wastewater treatment 2nd ed., IWA, London, (2011).
[142] T. Stephenson, Membrane Bioreactors for Wastewater Treatment, Taylor & Francis Group, (2000).
[143] B. Lesjean, E.H. Huisjes, Survey of the European MBR market: trends and perspectives, Desalination, 231 (2008) 71-81.
[144] C. Visvanathan, R.B. Aim, K. Parameshwaran, Membrane Separation Bioreactors for Wastewater Treatment, Critical reviews in environmental science and technology, 30 (2000) 1-48.
[145] F.I. Hai, K. Yamamoto, C.H. Lee, Membrane Biological Reactors Theory, Modeling, Design, Management and Applications to Wastewater Reuse, The international water association (2013).

[146] M. Bachir, Case Study of MBR Technologies for WW Reuse Applications, in, SAWEA, Dammam, KSA, (2006).
[147] P. McCarthy, Energy Production from Waste Using The Anaerobic Membrane Bioreactor (AnMBR) Process, in, ADI Systems Inc, Fairmont Banff Springs, (2010), pp. presented in Water Technologies Symposium 2010 (WaterTech 2010).
[148] J. McMahon, Anaerobic Membrane Bioreactor System Treats High Strength Wastewater, in: J. Laughlin (Ed.) WaterWorld, Industrial WaterWorld, PennWell Corporation Dripping Springs, (2010).
[149] J.L. Tambosi, R.F. de Sena, M. Favier, W. Gebhardt, H.J. José, H.F. Schröder, R.d.F.P.M. Moreira, Removal of pharmaceutical compounds in membrane bioreactors (MBR) applying submerged membranes, Desalination, 261 (2010) 148-156.
[150] T. Wintgens, M. Gallenkemper, T. Melin, Occurrence and removal of endocrine disrupters in landfill leachate treatment plants, Water Science and Technology, 48 (2003) 127-134.
[151] J. Chen, X. Huang, D. Lee, Bisphenol A removal by a membrane bioreactor, Process Biochemistry, 43 (2008) 451-456.
[152] C.-Y. Chang, J.-S. Chang, S. Vigneswaran, J. Kandasamy, Pharmaceutical wastewater treatment by membrane bioreactor process – a case study in southern Taiwan, Desalination, 234 (2008) 393-401.
[153] K. Kimura, H. Hara, Y. Watanabe, Removal of pharmaceutical compounds by submerged membrane bioreactors (MBRs), Desalination, 178 (2005) 135-140.
[154] T. Wintgens, M. Gallenkemper, T. Melin, Endocrine disrupter removal from wastewater using membrane bioreactor and nanofiltration technology, Desalination, 146 (2002) 387-391.
[155] H. De Wever, S. Weiss, T. Reemtsma, J. Vereecken, J. Müller, T. Knepper, O. Rörden, S. Gonzalez, D. Barcelo, M. Dolores Hernando, Comparison of sulfonated and other micropollutants removal in membrane bioreactor and conventional wastewater treatment, Water Research, 41 (2007) 935-945.
[156] M. Cirja, S. Zühlke, P. Ivashechkin, A. Schäffer, Corvini, Fate of a 14C-Labeled Nonylphenol Isomer in a Laboratory-Scale Membrane Bioreactor, Environmental Science & Technology, 40 (2006) 6131-6136.
[157] H. Bouju, G. Buttiglieri, F. Malpei, Perspectives of persistent organic pollutants (POPS) removal in an MBR pilot plant, Desalination, 224 (2008) 1-6.
[158] G. Tchobanoglous, F.L. Burton, H.D. Stensel, Wastewater engineering treatment and reuse:, 4th edition ed., Tata McGraw hill New Dheli, (2003).
[159] N. Cicek, J. Macomber, J. Davel, M.T. Suidan, J. Audic, P. Genestet, Effect of solids retention time on the performance and biological characteristics of a membrane bioreactor, Water Science and Technology, 43 (2001) 43-50.
[160] L.D. Nghiem, A.I. Schafer, T.D. Waite, Adsorption of estrone on nanofiltration and reverse osmosis membranes in water and wastewater treatment, Water Science and Technology, 46 (2002) 265-272.
[161] L.D. Nghiem, A.I. Schafer, T.D. Waite, Adsorptive interactions between membranes and trace contaminants, Desalination, 147 (2002) 269-274.
[162] X.Q. Li, F.I. Hai, L.D. Nghiem, Simultaneous activated carbon adsorption within a membrane bioreactor for an enhanced micropollutant removal, Bioresource Technology, 102 (2011) 5319-5324.

[163] B. Zhang, K. Yamamoto, S. Ohgaki, N. Kamiko, Floc size distribution and bacterial activities in membrane separation activated sludge processes for small-scale wastewater treatment/reclamation, Water Science and Technology, 35 (1997) 37-44.
[164] M.R. Abargues, A. Robles, A. Bouzas, A. Seco, Micropollutants removal in an anaerobic membrane bioreactor and in an aerobic conventional treatment plant, Water Science & Technology, 65 (2012) 2242-2250.
[165] V.M. Monsalvo, J.A. McDonald, S.J. Khan, P. Le-Clech, Removal of trace organics by anaerobic membrane bioreactors, Water Research, 49 (2014) 103-112.
[166] K.W. Lawson, D.R. Lloyd, Membrane distillation, Journal of Membrane Science, 124 (1997) 1-25.
[167] M.S. El-Bourawi, Z. Ding, R. Ma, M. Khayet, A framework for better understanding membrane distillation separation process, Journal of Membrane Science, 285 (2006) 4-29.
[168] M. Tomaszewska, Membrane distillation- Examples of application in technology and environmental protection, Polish journal of environmental studies, 9 (2000) 27-36.
[169] F. Lagana, G. Barbieri, E. Drioli, Direct contact membrane distilaltion: modelling and concentration experiments, Jounal of membrane science, 166 (2000) 1-11.
[170] A. Alkhudhiri, N. Darwish, N. Hilal, Treatment of saline solutions using air gap membrane distillation: experimental study, Desalination, 323 (2013) 2-7.
[171] C.R. Martinetti, A.E. Childress, T.Y. Cath, High recovery of concentrated RO brines using forward osmosis and membrane distillation, Journal of Membrane Science, 331 (2009) 31-39.
[172] T.Y. Cath, V.D. Adams, A.E. Childress, Experimental study of desalination using direct contact membrane distillation: a new approach to flux enhancement, Journal of Membrane Science, 228 (2004) 5-16.
[173] F. He, J. Gilron, H. Lee, L. Song, K.K. Sirkar, Potential for scaling by sparingly soluble salts in crossflow DCMD, Journal of Membrane Science, 311 (2008) 68-80.
[174] S. Srisurichan, R. Jiraratananon, A.G. Fane, Humic acid fouling in the membrane distillation process, Desalination, 174 (2005) 63-72.
[175] A. Hausmann, P. Sanciolo, T. Vasiljevic, M. Weeks, K. Schroën, S. Gray, M. Duke, Fouling of dairy components on hydrophobic polytetrafluoroethylene (PTFE) membranes for membrane distillation, Journal of Membrane Science, 442 (2013) 149-159.
[176] P.A. Hogan, Sudjito, A.G. Fane, G.L. Morrison, Desalination by solar heated membrane distillation in Proceedings of the Twelfth International Symposium on Desalination and Water Re-use, in, Malta, (1991), pp. 81-90.
[177] J. Phattaranawik, A.G. Fane, A.C.S. Pasquier, W. Bing, A novel membrane bioreactor based on membrane distillation, Desalination, 223 (2008) 386-395.
[178] J.-P. Mericq, S. Laborie, C. Cabassud, Evaluation of systems coupling vacuum membrane distillation and solar energy for seawater desalination, Chemical Engineering Journal, 166 (2011) 596-606.
[179] F. Suárez, S.W. Tyler, A.E. Childress, A theoretical study of a direct contact membrane distillation system coupled to a salt-gradient solar pond for terminal lakes reclamation, Water Research, 44 (2010) 4601-4615.

[180] A. El-Abbassi, H. Kiai, A. Hafidi, M.C. García-Payo, M. Khayet, Treatment of olive mill wastewater by membrane distillation using polytetrafluoroethylene membranes, Separation and Purification Technology, 98 (2012) 55-61.
[181] V.D. Alves, I.M. Coelhoso, Orange juice concentration by osmotic evaporation and membrane distillation: A comparative study, Journal of Food Engineering, 74 (2006) 125-133.
[182] M. Gryta, A. Markowska-Szczupak, J. Bastrzyk, W. Tomczak, The study of membrane distillation used for separation of fermenting glycerol solutions, Journal of Membrane Science, 431 (2013) 1-8.
[183] V. Calabro, E. Drioli, F. Matera, Membrane distillation in the textile wastewater treatment, Desalination, 83 (1991) 209-224.
[184] T.Y. Cath, D. Adams, A.E. Childress, Membrane contactor processes for wastewater reclamation in space: II. Combined direct osmosis, osmotic distillation, and membrane distillation for treatment of metabolic wastewater, Journal of Membrane Science, 257 (2005) 111-119.
[185] F.A. Banat, J. Simandl, Removal of benzene traces from contaminated water by vacuum membrane distillation, Chemical Engineering Science, 51 (1996) 1257-1265.
[186] S. Duan, A. Ito, A. Ohkawa, Removal of trichloroethylene from water by aeration, pervaporation and membrane distillation, Journal of Chemical Engineering of Japan, 34 (2001) 1069-1073.
[187] J.L. Cartinella, T.Y. Cath, M.T. Flynn, G.C. Miller, K.W. Hunter, A.E. Childress, Removal of natural steroid hormones from wastewater using membrane contactor processes, Environmental Science & Technology, 40 (2006) 7381-7386.
[188] P. Becker, D. Köster, M.N. Popov, S. Markossian, G. Antranikian, H. Märkl, The biodegradation of olive oil and the treatment of lipid-rich wool scouring wastewater under aerobic thermophilic conditions, Water Research, 33 (1999) 653-660.
[189] J. Suvilampi, A. Lehtomäki, J. Rintala, Comparative study of laboratory-scale thermophilic and mesophilic activated sludge processes, Water Research, 39 (2005) 741-750.
[190] M. Krzywonos, E. Cibis, T. Miśkiewicz, C.A. Kent, Effect of temperature on the efficiency of the thermo- and mesophilic aerobic batch biodegradation of high-strength distillery wastewater (potato stillage), Bioresource Technology, 99 (2008) 7816-7824.
[191] W.C.L. Lay, Y. Liu, A.G. Fane, Impacts of salinity on the performance of high retention membrane bioreactors for water reclamation: A review, Water Research, 44 (2010) 21-40.
[192] M. Gryta, Water desalination by membrane distillation, in: M.E. Schorr (Ed.) Desalination, Trends and Technologies, INTECH, (2011).
[193] L.D. Nghiem, T. Cath, A scaling mitigation approach during direct contact membrane distillation, Separation and Purification Technology, 80 (2011) 315-322.
[194] Pall Corporation, Membralox users' manual in: Chapter VI: Cleaning and sanitation/sterilisation guidelines Pall Corporation (2007).
[195] L.S. Clescerl, A.E. Greenberg, A.D. Eaton, Standard methods for the examination of water and wastewater 21st ed., American Public health Association, Washington DC, (2005).

[196] T. Trinh, B. van den Akker, H. Coleman, R. Stuetz, P. Le-Clech, S.J. Khan, Fate of pharmaceuticals during wastewater treatment by a membrane bioreactor, GWF-Wasser Abwasser, 152 (2011) 98-102.
[197] J.A. McDonald, N.B. Harden, L.D. Nghiem, S.J. Khan, Analysis of N-nitrosamines in water by isotope dilution gas chromatography–electron ionisation tandem mass spectrometry, Talanta, 99 (2012) 146-154.
[198] F. Carey, R.M. Giuliano, Organic Chemistry, 8th ed ed., McGraw-Hill Science Engineering, New York:, (2010).
[199] L.N. Nguyen, F.I. Hai, J. Kang, W.E. Price, L.D. Nghiem, Removal of trace organic contaminants by a membrane bioreactor–granular activated carbon (MBR–GAC) system, Bioresource Technology, 113 (2012) 169-173.
[200] K. Lekkerkerker-Teunissen, A.H. Knol, L.P. van Altena, C.J. Houtman, J.Q.J.C. Verberk, J.C. van Dijk, Serial ozone/peroxide/low pressure UV treatment for synergistic and effective organic micropollutant conversion, Separation and Purification Technology, 100 (2012) 22-29.
[201] A.R.D. Verliefde, S.G.J. Heijman, E.R. Cornelissen, G.L. Amy, B. Van der Bruggen, J.C. van Dijk, Rejection of trace organic pollutants with high pressure membranes (NF/RO), Environmental Progress, 27 (2008) 180-188.
[202] G. Zuo, R. Wang, Novel membrane surface modification to enhance anti-oil fouling property for membrane distillation application, Journal of Membrane Science, 447 (2013) 26-35.
[203] L.S. Tam, T.W. Tang, G.N. Lau, K.R. Sharma, G.H. Chen, A pilot study for wastewater reclamation and reuse with MBR/RO and MF/RO systems, Desalination, 202 (2007) 106-113.
[204] M. Jacob, C. Guigui, C. Cabassud, H. Darras, G. Lavison, L. Moulin, Performances of RO and NF processes for wastewater reuse: Tertiary treatment after a conventional activated sludge or a membrane bioreactor, Desalination, 250 (2010) 833-839.
[205] R.P. Schwarzenbach, B.I. Escher, K. Fenner, T.B. Hofstetter, C.A. Johnson, U. von Gunten, B. Wehrli, The Challenge of Micropollutants in Aquatic Systems, Science, 313 (2006) 1072-1077.
[206] N.T. Hancock, P. Xu, D.M. Heil, C. Bellona, T.Y. Cath, Comprehensive Bench- and Pilot-Scale Investigation of Trace Organic Compounds Rejection by Forward Osmosis, Environmental Science & Technology, 45 (2011) 8483-8490.
[207] M. Gryta, M. Tomaszewska, K. Karakulski, Wastewater treatment by membrane distillation, Desalination, 198 (2006) 67-73.
[208] K. Suzuki, Y. Tanaka, T. Osada, M. Waki, Removal of phosphate, magnesium and calcium from swine wastewater through crystallization enhanced by aeration, Water Research, 36 (2002) 2991-2998.
[209] K.C. Wijekoon, F.I. Hai, J. Kang., W.E. Price, Cath Tzahi , L.D. Nghiem, Rejection and fate of trace organic compounds (TrOCs) during membrane distillation, Journal of Membrane Science, 453 (2013).