A Sponge-based Moving Bed Bioreactor for Micropollutant Removal from Municipal Wastewater

by

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A thesis submitted in partial fulfilment
of the requirements for the degree of
Master of Engineering

University of Technology, Sydney
Faculty of Engineering and Information Technology

March, 2014

CERTIFICATE OF ORIGINAL AUTHORSHIP

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

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

Name: Yunlong Luo

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Acknowledgements

This thesis would not have been possible without the help and support of the outstanding individuals I met in the course of my research study. Now it is my turn to acknowledge them all.

First, and foremost, I would like to express the deepest gratitude to my supervisors Dr. Wenshan Guo and Prof. Huu Hao Ngo. I was amazingly fortunate to have the opportunity to be one of their research students. I enjoyed the great benefits of their invaluable suggestions, excellent guidance and endless inspiration. They deserve much of the credit for this thesis as well as my other outcomes.

I would like to extend my particular gratitude to A/Prof. Long Nghiem and Dr. Faisal Hai from the University of Wollongong for their valued feedback about my experiments and academic writing. Dr. Jinguo Kang is indebted for his help in the GC-MS analysis of micropollutants. Kaushalya Wijekoon is thanked for her assistance with the freeze drying of sludge samples.

I wish to thank Faculty of Engineering and Information Technology for providing a fantastic atmosphere for doing research. I am particularly thankful to Mohammed Johir who was being kind, generous and helpful throughout my experiments. Lijuan Deng is acknowledged for her assistance in some of my experimental analysis. My appreciation also goes to my other dear colleagues, Zhuo, Anwar, Zuthi, Atefeh, Hang, Bandita and Thanh, for their generous help in various aspects of this research.

Last but not least, I would also like to give my heartfelt thanks to my parents for their faith their encouragement in all of my pursuits. My sincere appreciation is also due to my friends who were always there to give unconditional support. I greatly value the friendship with them.

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List of Abbreviations

AOP	Advanced oxidation process
BAC	Biological activated carbon
CAFO	Concentrated animal feeding operation
COD	Chemical oxygen demand
CAS	Conventional activate sludge
DBP	Di-butyl phthalate
DEET	N,N-diethyl-meta-toluamide
DEHP	Di(2-ethylhexyl) phthalate
DMP	Di-methyl phthalate
DO	Dissolved oxygen
DOM	Dissolved organic matter
EDC	Endocrine disrupting compound
EPS	Extracellular polymeric substance
GAC	Granule activated carbon
GC-MS	Gas chromatography-mass spectrometry
HRT	Hydraulic retention time
MBBR	Moving bed bioreactor
MBR	Membrane bioreactor
MB-SMBR	Moving bed-submerged membrane bioreactor
MF	Microfiltration
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
NF	Nanofiltration
NLR	Nitrogen loading rate
NOM	Natural organic matter
NSAID	Nonsteroidal anti-inflammatory drug
OLR	Organic loading rate
PAC	Powdered activated carbon
PCP	Personal care product
PNEC	Predicted no effect concentration
PPCP	Pharmaceutical and personal care product

PU	Polyurethane
PVA	Polyvinyl alcohol
PVDF	Polyvinylidene fluoride
RO	Reverse osmosis
SAnMBR	Submerged anaerobic membrane bioreactor
SBBGR	Sequencing batch biofilter granular reactor
SBF	Sponge biofilter
SBR	Sponge batch reactor
SMBR	Submerged membrane bioreactor
SMP	Soluble microbial products
SND	Simultaneous nitrification–denitrification
SPE	Solid phase extraction
SRT	Sludge retention time
TCEP	Tris(2-chloroethyl) phosphate
TCPP	Tris(1-chloro-2-propyl) phosphate
TMP	Transmembrane pressure
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorus
UF	Ultrafiltration
WWTP	Wastewater treatment plant

List of Symbols

$C_{s, a}$	Concentration of micropollutant on the attached biosolids (μg/g)
$C_{s, s}$	Concentration of micropollutant on the suspended biosolids (μg/g)
$C_{w, eff}$	Average effluent concentrations of micropollutants (ng/L)
$C_{w, inf}$	Average influent concentrations of micropollutants (ng/L)
J	Permeation flux ($L/m^2 \cdot h$)
K_d/D	Solid-water distribution coefficient
K_H	Henry's law constant
K_{OW}	Octanol–water partition coefficient
L_{sol}	Load of micropollutant removed via sorption over 30 days (ng)
MLSS	Mixed liquor suspended biosolids concentration (g/L)
pK_a	Acid dissociation constant
ΔP_T	Transmembrane pressure (kPa)
Q	Flow rate of the MBBR (L/day)
R_c	Cake resistance formed by cake layer deposited over membrane surface (m^{-1})
R_f	Fouling resistance caused by pore plugging and/or solute adsorption onto the membrane pore and surface (m^{-1})
R_m	Intrinsic membrane resistance caused by membrane itself and permanent resistance (m^{-1})
ΔSS	Increased amount of attached biosolids over the study period (g)
T	Duration of the study period (day)
μ	Viscosity of the permeate (m^2/s)

Abstract

Over the past few decades, the frequent detection of micropollutants in the aquatic environment has raised particular health and environmental concerns. Wastewater treatment plants (WWTPs) serve as significant barriers to reduce the release of micropollutants. However, due to the diverse characteristics and low concentrations of micropollutants, WWTPs can only achieve variable and often inadequate removals, ranging from 12.5% to 100% for some frequently reported compounds.

This study investigated a sponge-based MBBR for its effectiveness in the elimination of various micropollutants, including pharmaceuticals and personal care products, steroid hormones, industrial chemicals and pesticides. A moving bed-submerged membrane bioreactor (MB-SMBR) was also evaluated in terms of micropollutant removal and membrane fouling.

During the batch experiments, non-acclimatized (virgin) sponge showed significant and rapid sorption of hydrophobic compounds. Acclimatized sponge could achieve much higher elimination of some acidic pharmaceutical compounds, such as acetaminophen, diclofenac, gemfibrozil, ibuprofen, ketoprofen, naproxen and salicylic acid. Carbamazepine, fenoprop and metronidazole were poorly removed during all the batch experiments.

The sponge-based MBBR was effective in removing organics and nutrients (except PO_4-P). Most of the selected micropollutants (16 out of 22) showed removals of higher than 70%. The poorly or moderately removed compounds included carbamazepine (25.9%), fenoprop (31.0%), diclofenac (45.7%), metronidazole (54.8%), ketoprofen (58.2%), and gemifibrozil (62.4%). The low biodegradability and/or polar property were two causes for the insufficient elimination. Overall, the effectiveness of the MBBR for micropollutant removal was comparable with those of other biological treatment processes, including activated sludge and membrane bioreactors (MBRs). Biodegradation was the major removal mechanisms for most compounds during the MBBR treatment. Sorption was only significant for the

refractory compounds, while the readily biodegradable compounds did not considerably accumulate on the biosolids.

With the incorporation of the SMBR, the whole system (MB-SMBR) could significantly reduce the effluent turbidity. However, the SMBR did not achieve much supplementary removal of organic, nutrients and micropollutants. The membrane fouling in the SMBR occurred to a minor extent during the first 84 days of operation, after which an abrupt TMP increase was observed. High EPS levels (16.24 mg/L) in the SMBR was a potential cause for the severe fouling. The overgrowth of filamentous bacteria could also been deemed a factor that accelerated the membrane fouling rate. The total membrane resistance was mainly attributed to the deposited cake layer (76.5%), followed by the pore blocking (12.0%), clean membrane resistance (10.5%) and irreversible fouling (1.0%).

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Chapter 1

Introduction

1.1 Background

Since the Industrial Revolution, our society has produced substantial and miscellaneous chemicals in pursuit of a thriving quality of life. These chemicals are extensively and increasingly used for medical care purpose (pharmaceuticals), hygienic or cosmetic reasons (personal care products, PCPs), plant/crop protection (pesticides), and enhancement of the physical properties and performance of products (industrial chemicals). Due to their massive use, it is inevitable that these chemicals end up in the aquatic environment and cause health and environmental problems. In addition to the anthropogenic compounds, the introduction of naturally produced substances (e.g., estrogenic hormones) in aquatic systems is also an emerging environmental concern.

The above mentioned contaminants are commonly detected in waters at trace concentrations, ranging from ng/L to μg/L, and thus are termed 'micropollutants'. Sources of micropollutants in the environment are diverse because most of them originate from mass-produced materials and commodities. Table 1.1 summarizes the source categories of the major micropollutants frequently detected in the aquatic environment. Figure 1.1 illustrates the possible routes for the introduction of micropollutants into the environment.

The treated effluent discharged from municipal wastewater treatment plants (WWTPs) is a common pathway for micropollutants reaching the aquatic environment. Hence, wastewater treatment can be a vital barrier against the release of micropollutants. However, due to the low concentrations and diverse physicochemical properties, micropollutants often experience inadequate removal during wastewater treatment. As a result, many micropollutants can pass through the WWTPs by virtue of their persistency and/or their continuous introduction. In addition to municipal wastewater, hospital effluents, industrial wastewater, stormwater runoff, rural runoff and manure can also contribute to the accumulation of micropollutants in the aquatic environment.

Table 1.1 Sources of micropollutants in the aquatic environment

Category	Important subclasses	Major sources	
		Distinct	Nonexclusive
Pharmaceuticals	NSAIDs[a], lipid regulator, anticonvulsants, antibiotics, β-blockers and stimulants	• Domestic wastewater (from excretion) • Hospital effluents • Run-off from CAFOs[b] and aquaculture	
Personal care products	Fragrances, disinfectants, UV filters, and insect repellents	• Domestic wastewater (from bathing, shaving, spraying, swimming and etc.)	
Steroid hormones	Estrogens	• Domestic wastewater (from excretion) • Run-off from CAFOs and aquaculture	Sources that are not exclusive to individual categories include: • Industrial wastewater (from product manufacturing discharges) • Landfill leachate (from improper disposal of used, defective or expired items)
Surfactants	Non-ionic surfactants	• Domestic wastewater (from bathing, laundry, dishwashing and etc.) • Industrial wastewater (from industrial cleaning discharges)	
Industrial chemicals	Plasticizers, fire retardants	• Domestic wastewater (by leaching out of the material)	
Pesticides	Organochlorine insecticides, organophosphorus insecticides, herbicides and fungicides	• Domestic wastewater (from improper cleaning, run-off from gardens, lawns and roadways and etc.) • Agricultural runoff	

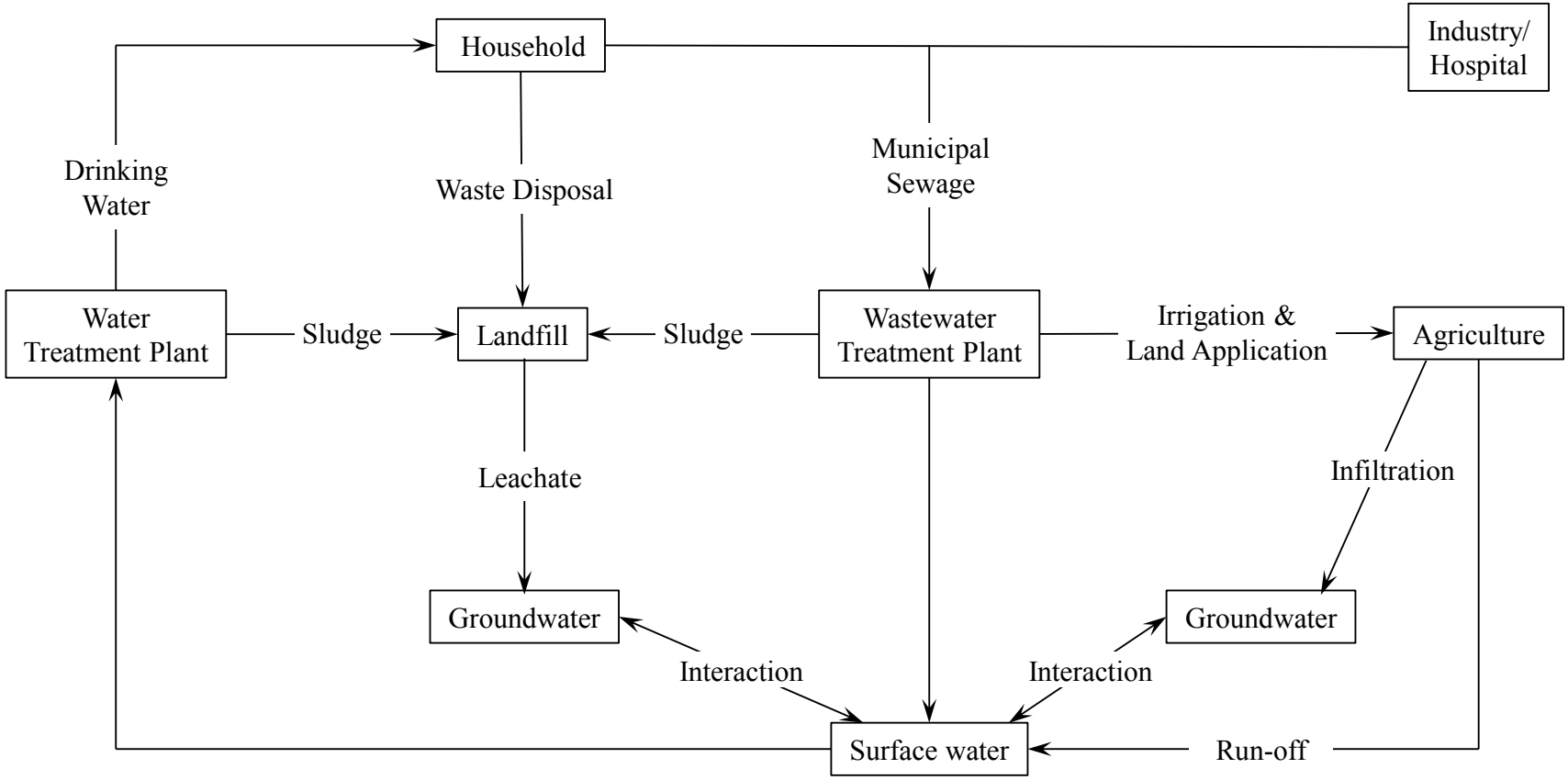

Figure 1.1 Pathways for the introduction of micropollutants into the aquatic environment

After release, micropollutants can pose a risk of harm to wildlife and humans. The common adverse effects of exposure to micropollutants include short-term and long-term toxicity, endocrine disrupting effects and antibiotic resistance of microorganism (Fent et al., 2006; Pruden et al., 2006). To date, discharge guidelines and standards do not exist for most problematic micropollutants. Some countries or regions have adopted regulations for only a small number of micropollutants. For example, environmental quality standards for a minority of micropollutants (e.g. nonylphenol, bisphenol A, DEHP and diuron) have been stipulated in Directive 2008/105/EC (European Parliament and The Council, 2008). Nonylphenol and nonylphenol ethoxylates have also been recognized as toxic substances by the Canadian government (Canadian Environmental Protection Act, 1999). Other micropollutants, such as pharmaceutical and personal care products (PPCPs) and steroid hormones, have not been included in the list of regulated substances yet.

1.2 Statement on current issues regarding micropollutants removal

The activated sludge process is one of the most commonly used wastewater treatment technology. However, in general, it can only achieve incomplete and inconsistent removal of micropollutants. To yield a further reduction of micropollutants, optimization and/or upgrade of the conventional activated sludge processes seems necessary. Advanced treatments (e.g., activated carbon adsorption, membrane filtration, ozonation and advanced oxidation processes) are able to offer more efficient removal of micropollutants. Nevertheless, the applications of these technologies are commonly associated with high operating costs and intractable problems, such as membrane fouling and the formation of by-products and concentrated residues.

As promising alternatives to suspended-growth activated sludge processes, attached-growth processes are effective for wastewater treatment. They offer some advantages over activated sludge processes. One major advantage is that attached-growth processes facilitate the growth of slow-growing microorganisms, which are important for the removal of some micropollutants (Falås et al., 2012; Guo et al., 2012). Moreover, if controlled properly, attached-growth processes can have

different redox conditions within the biofilm. The coexistence of oxic and anoxic conditions can not only facilitate nutrient removal, but also enhance the elimination of a wider spectrum of micropollutants. For instance, oxic condition improves the removal of naproxen, ethinylestradiol, roxithromycin and erythromycin, while anoxic condition aids the degradation of carbamazepine, clofibric acid, diclofenac and iodinated X-ray contrast media (Drewes et al., 2001; Suárez et al., 2010; Zwiener and Frimmel, 2003).

The moving bed bioreactor (MBBR) is a simple yet effective technology developed on the basis of attached-growth principle. Despite its excellent performance in eliminating traditional contaminants (biodegradable organic matter and nutrients), the effectiveness of MBBR in removing micropollutants is still unclear. Accoding to the results from some bench- or pilot-scale studies, MBBR appears to be a promising solution to micropollutant-related problems (refer to Chapter 2). Although a few studies have demonstrated that polyurethane sponge can be used as an ideal attached-growth medium in MBBR (Chu et al., 2011; Guo et al., 2010), so far, no scientific efforts have been directed towards the micropollutant removal in a sponge-based MBBR process. Therefore, the information provided in this thesis is of great significance to fill this gap.

1.3 Objectives of the research

The research aims to evaluate the removal efficiency of various micropollutants in a sponge-based MBBR. In addition, a hybrid system combining the MBBR with a submerged membrane bioreactor (MB-SMBR) was also investigated in terms of micropollutants removal and membrane fouling behaviour. Overall, the objectives of this study are listed as follows:

- To review the occurrence of micropollutants in the aquatic environment as well as their fate and removal during wastewater treatment;
- To assess the short-term micropollutants removal through batch experiments using non-acclimatized and acclimatized sponge, as well as to determine the optimum filling ratio;

- To investigate the long-term micropollutants removal in a sponge-based MBBR under optimum filling ratio of acclimatized sponge;
- To elucidate the fate of the micropollutants during the treatment in MBBR
- To evaluate the performance of the MB-SMBR in terms of micropollutants removal and membrane fouling.

1.4 Outline of the thesis

This thesis is comprised of six chapters as shown in Figure 1.2. Chapter 1 introduces the background and objectives of this study. Chapter 2 systematically presents the recent occurrence of micropollutants from different sources as well as the fate and removal of micropollutants during wastewater treatment processes. Chapter 3 describes the materials, experimental set-ups, operational conditions and analytical methods for the batch experiments, the bench-scale MBBR system and the MB-SMBR system. The results obtained during the study together with detailed discussion are presented in Chapters 4, 5 and 6. The discussion provides the explanation of the underlying mechanisms and the comparison of the micropollutants removal in the MBBR with other treatment systems such as activated sludge and membrane bioreactor. The final chapter draws the conclusion for all the findings from this study and also gives some recommendations for the future research.

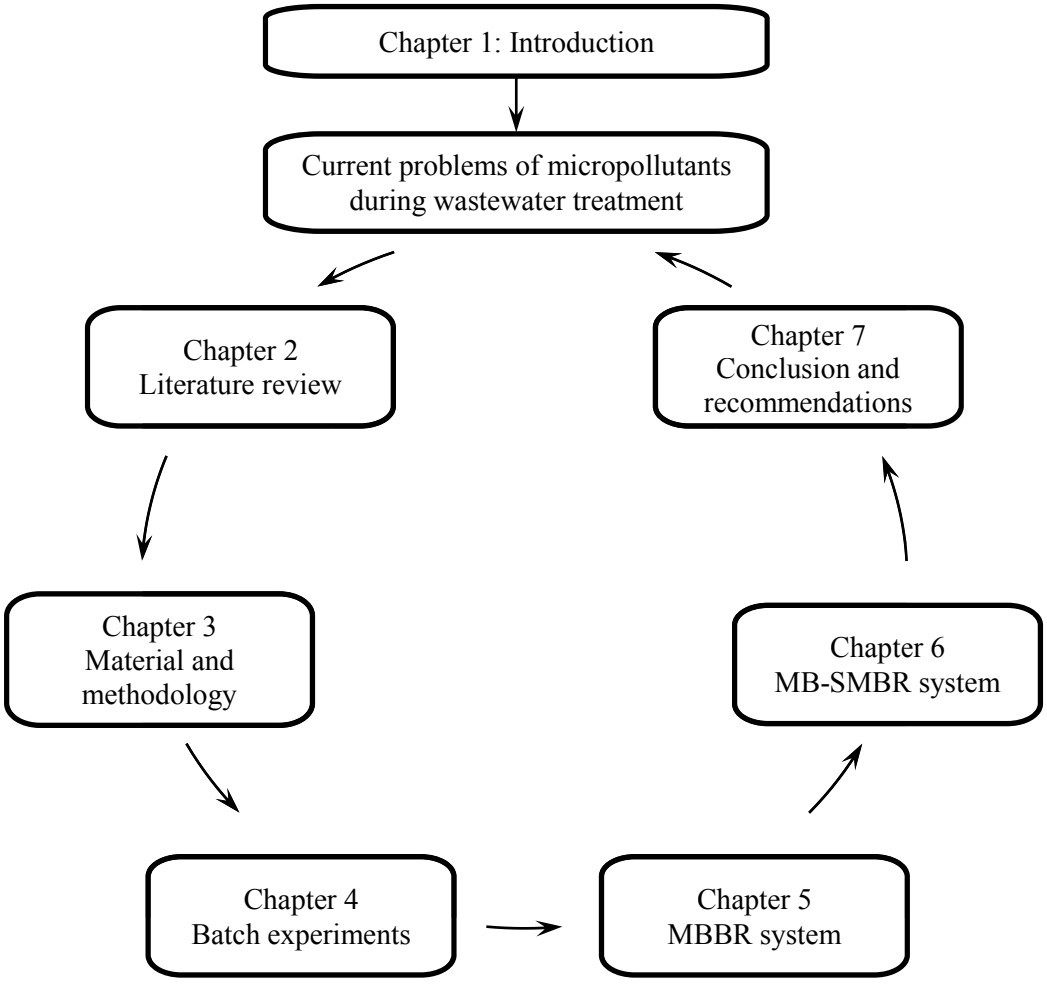

Figure 1.2 The structure of the thesis

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Chapter 2

Literature Review

2.1 Introduction

Micropollutants have been frequently detected in wastewater as well as important drinking water sources. It is essential to examine the abundance of different micropollutants and identify the compounds with high occurrence and eco-toxicological relevance. Section 2.2 summarizes the occurrence of micropollutants in different aquatic systems, including wastewater, surface water, groundwater and drinking water. WWTPs are primary barriers against the spread of micropollutants in the aquatic environment. Understanding the fate and removal of micropollutants in the WWTPs is of great significance. Hence, Section 2.3 elucidates the behaviour of micropollutants during conventional wastewater treatment. In addition, an overview of micropollutant removal in different treatment technologies, including coagulation-flocculation, activated carbon adsorption, ozonation and advanced oxidation processes, membrane filtration and membrane bioreactor, is presented in Section 2.4. The MBBR technology, as an emerging wastewater treatment alternative and also the key component of this research, is described in the final section of this literature review.

2.2 Occurrence of micropollutants in the aquatic environment

The recent occurrence data (2008 to date) of the micropollutants in the aquatic environment has been reviewed in terms of their aqueous concentrations in different types of waters, including wastewater, surface water, groundwater and drinking water. Of all aqueous media, WWTP influent and effluent are comprehensively reviewed. The collected data consist of the studies performed in a number of countries/regions, including Austria, China, EU-wide, France, Germany, Greece, Italy, Korea, Spain, Sweden, Switzerland, Western Balkan Region, UK and US. In general, the micropollutants investigated can be divided into six categories namely pharmaceuticals, personal care products, steroid hormones, surfactants, industrial chemicals and pesticides.

2.2.1 Occurrence of micropollutants in WWTPs

Occurrence data of micropollutants in WWTP influent and effluent from recent studies (2008 – present) are summarized in Figure 2.1. The reported concentrations

of micropollutants in WWTP influent and effluent reveal significant spatial and temporal variations, which are essentially due to a number of factors, including the rate of production, specific sales and practices, metabolism (excretion rate, Table 2.1), water consumption per person and per day, the size of WWTPs, environmental persistence, as well as elimination efficacy of wastewater treatment processes (Jelic et al., 2012; Petrovic et al., 2009).

Table 2.1 Human excretion rates of some common pharmaceutical compounds in the aquatic environment. (adapted from Alder, Hirsch et al., 1999; Huschek et al., 2004; Jjemba, 2006; Ternes, 1998; and the range was selected according to Jjemba, 2006)

Excretion rate	Pharmaceutical
Low (≤5%)	Aspirin (acetylsalicylic acid), carbamazepine, gemfibrozil, ibuprofen
Moderately low (6–39%)	Diclofenac, metroprolol, primidone, sulfamethoxazole
Relatively high (40–69%)	Bezafibrate, norfloxacin, trimethoprim,
High (≥ 70%)	Amoxicillin, ciprofloxacin, tetracycline

Figure 2.1 depicts the average occurrence levels reported for the selected compounds compounds in WWTP influents and effluents. As shown in Figure 2.1, most micropollutants occurred in WWTP influent in the concentration range between 0.1 and 10 μg/L, while some pharmaceutical compounds (acetaminophen, caffeine, ibuprofen, naproxen and salicylic acid), one biocide (triclosan), one surfactant (nonylphenol) and one industrial chemical (DEHP) exhibit relatively high occurrence concentrations. Generally, the compounds with the highest concentrations (mean values > 10 μg/L) in WWTP influent were ibuprofen, atenolol, caffeine and nonylphenol. For instance, ibuprofen was the most abundant compound detected in the influent of four WWTPs in Spain, with the concentration levels ranging from 3.73 to 603 μg/L (Santos et al., 2009). The particularly high levels could be explained by the high consumption and easy accessibility (over the counter drugs) of the compound. Caffeine was detected at the highest concentrations approaching

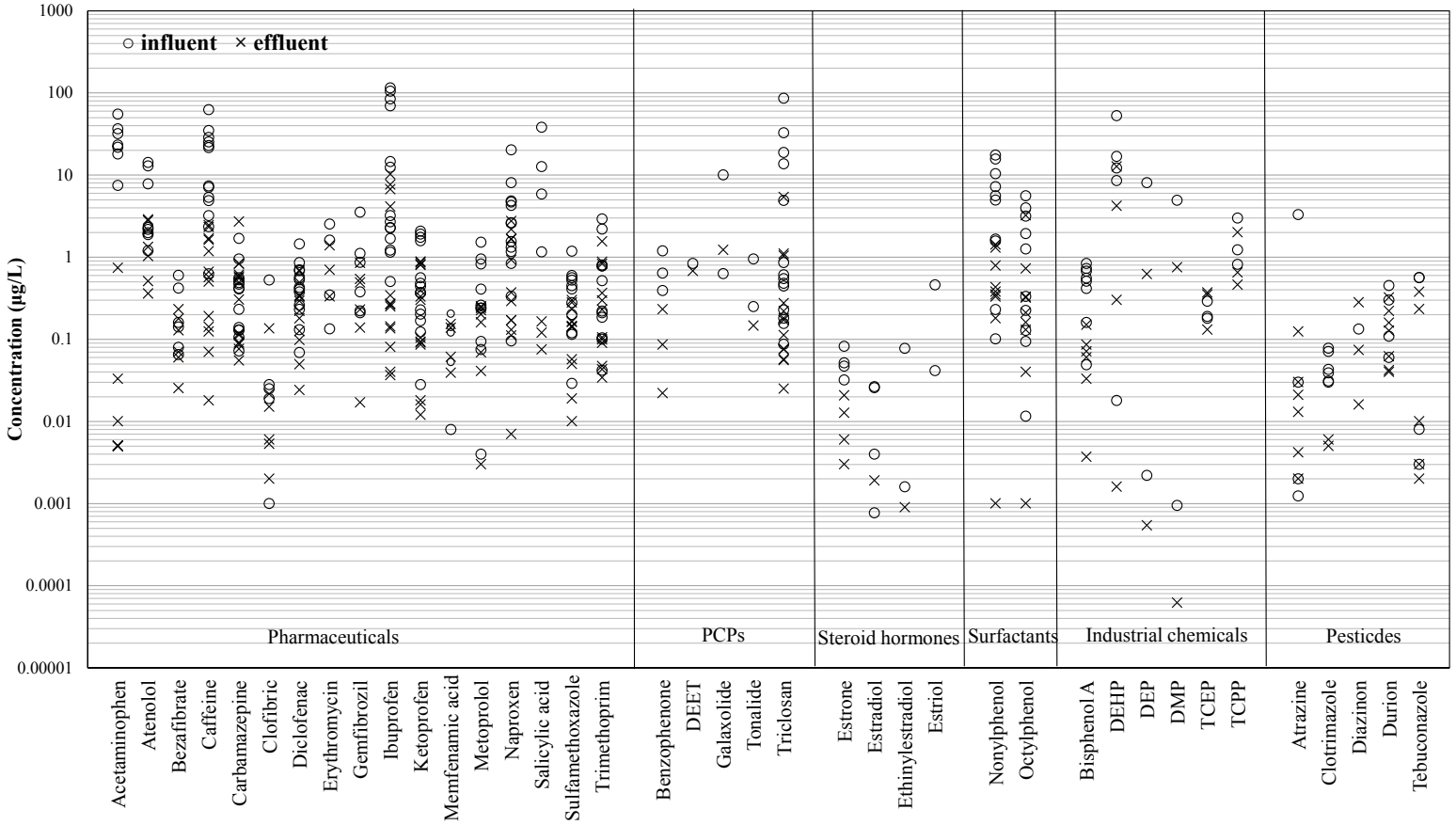


Figure 2.1 Average concentrations (on logarithmic Y axis) reported for the selected micropollutants in WWPT influents and effluents. Data from Alder et al. (2010); Behera et al. (2011); Campo et al. (2013); Céspedes et al. (2008); K. Choi et al. (2008); Clara et al (2010); Gao et al. (2014); Gracia-Lor et al. (2012); Janex-Habibi et al. (2009); Kahle et al. (2008); Kasprzyk-Hordern et al. (2009); Köck-Schulmeyer et al. (2013); Kumar et al. (2010); Loos et al. (2013); Martin et al. (2010); Nie et al. (2012); Pothitou and Voutsa (2008); Reemtsma et al. (2008); Santos et al. (2009); Singer et al. (2010); Stamatis and Konstantinou (2013); Stamatis et al. (2010); Stasinakis et al. (2008); Rosal et al. (2010); Terzić et al. (2008); Yu and Chu (2009); Zhou et al. (2010); and Zorita et al. (2009).

50 μg/L on average in the raw sewage of three WWTPs in China (Zhou et al., 2010). The abundant presence of caffeine is likely associated with the high consumption of coffee, tea and soft drinks as well as the disposal of these items. Steroid hormones and pesticides generally show lower detectedconcentrations (mostly less than 1 μg/L) as compared with compounds from other groups. The concentrations of most micropollutants in effluent ranged from 0.001 to 1 μg/L, which were one to two orders of magnitude lower than those in influent. Some abundant compounds in influent were discharged at relatively high concentrations. For instance, atenolol, caffeine, DEHP, ibuprofen, naproxen, nonylphenol and triclosan were detected in the concentrations higher than 1 μg/L in treated effluent. In contrast, steroid hormones were found in wastewater at much lower levels (< 100 ng/L). However, their occurrence even at low levels is a concern because of their high estrogenic effect.

2.2.2 Occurrence of micropollutants in surface water

According to Table 2.2 showing common micropollutants in surface water from different countries, nonsteroidal anti-inflammatory drugs (NSAIDs), carbamazepine, sulfamethoxazole and triclosan were the most frequently reported compounds in surface water. The high concentrations of micropollutants were found in Costa Rica, which mainly resulted from the discharge of hospital effluents and other highly contaminated waters (Spongberg et al., 2011). Notably, ibuprofen, ketoprofen, gemfibrozil and caffeine were detected at alarmingly high levels, with maximum concentrations of 36.8, 9.8, 17.0 and 1121.4 μg/L, respectively. Caffeine was also detected at relatively high concentrations in the US (224.8 ng/L) and Taiwan (1813 ng/L). Unlike Costa Rica, the reported caffeine concentrations in the US and Taiwan were far below the predicted no effect concentrations (PNECs). In general, the pollution of emerging contaminants in the natural water bodies of the densely populated regions are more severe because of the massive use of these chemicals by the large population. For example, the concentrations of nonylphenol, bisphenol A and triclosan in a surface water in Guangzhou (one of the largest cities in China) were at rather high levels. Nonylphenol was also found at relatively high concentrations in a Greek river, with a maximum of 2704 ng/L. The oberved maximum nonylphenol concentrations in China and Greece were well above the reported PNEC for nonylphenol. In addition to above mentioned factors, population

Table 2.2 Occurrence of some common micropollutants in surface waters in different countries

Compound	Concentration (ng/L)										
	Canada[a,1]	China[2]	Costa Rica[a,3]	France[4]	Germany[5,6]	Greece[7]	Korea[8]	Spain[b,9]	UK[10]	US[11]	PNEC[b]
Ibuprofen	0.98 (79)	ND–1417	5 (36788)	ND–8	–	1–67	<15–414	–	0.3–100	ND–77	5000
Naproxen	1 (87)	ND–328	–	ND–6.4	–	3–322	–	–	0.3–149	–	37000
Ketoprofen	–	–	7 (9808)	ND–22.0	–	0.4–39.5	–	–	0.5–14	–	16×10^6
Diclofenac	–	–	14 (266)	ND–35.0	–	0.8–1043	–	–	0.5–261	–	10000
Mefenamic acid	–	–	–	–	–	–	<30–326	–	0.3–169	–	–
Carbamazepine	3 (749)	–	1 (82)	ND–31.6	102–1194	–	<4–595	–	0.5–684	ND–9.6	25000
Gemfibrozil	–	–	41 (17036)	–	–	–	–	–	–	–	100000
Atenolol	–	–	–	ND–34.0	–	–	<100–690	–	1–560	–	10×10^6
Sulfamethoxazole	0.2 (284)	–	11 (56)	ND–5.1	–	–	–	–	0.5–4	ND–38	20000
Trimethoprim	–	–	–	–	–	–	–	–	7–122	ND–9.1	1000
Triclosan	0.4 (25)	35–1023	11 (263)	–	124–220	3–39	ND[c]	–	5–95	ND–9.8	–
Galaxolide	–	–	–	–	35–1814	–	–	–	–	–	–
Tonalide	–	–	–	–	5–273	–	–	–	–	–	–
Estrone	–	ND–65	–	–	–	–	3.6–69.1	–	–	–	18
Estradiol	–	ND–2	–	–	–	–	1.1–10.1	–	–	–	–
Ethinylestradiol	–	ND–1	–	–	–	–	ND–1.9	–	–	–	0.02
Estriol	–	ND–1	–	–	–	–	–	–	–	–	149
Caffeine	–	–	24 (1121446)	–	–	–	–	–	–	ND–225	10×10^5
Nonylphenol	–	36–33231	–	–	–	558–2704	115–336	–	–	–	330
Bisphenol A	2.1 (87)	6–881	–	–	192–215	55–162	7.5–334	–	6–68	–	1000
TCEP	–	–	–	–	<3–184	–	–	–	–	–	–
TCPP	–	–	–	–	<4–379	–	–	–	–	–	–
Atrazine	–	–	–	–	–	–	–	11 (39)	–	–	2000
Diazinon	–	–	–	–	–	–	–	10(216)	–	–	–
Diuron	–	–	–	–	–	–	–	72(408)	–	–	1800

[a] Median concentration with maximum concentration in the brackets;
[b] Data were derived from Fromme et al., 2002, Köck et al., 2010, Lin et al., 2008, and Loos et al., 2007;
1. Kleywegt et al., 2011; 2. Peng et al., 2008; 3. Spongberg et al., 2011; 4. Vulliet et al., 2011; 5. Regnery and Püttmann, 2010; 6. Reinstorf et al., 2008; 7. Stasinakis et al., 2012; 8. Kim et al., 2009c; 9. Köck et al., 2010; 10. Kasprzyk–Hordern et al., 2009; 11. Wang et al., 2011.

aging has also been linked to the high occurrence levels of pharmaceuticals (Al-Rifai et al., 2007).

2.2.3 Occurrence of micropollutants in groundwater

For selected countries (Table 2.3), most of the compounds were detected at less than100 ng/L in groundwater. NASIDs, carbamazepine, sulfamethoxazole, caffeine and triclosan were of particular research interest. These compounds were also the most commonly detected ones in surface water and wastewater, evidencing a correlation of the presence of micropollutants in different aquatic systems. By comparing the occurrence concentrations of micropollutants with PNEC, most of the compounds were at levels without potential environmental significance. However, it is notable that these PNEC values were determined based on individual compounds rather than mixtures of contaminants such as encountered in the aquatic environments. Considerably high concentrations (2 or 3 orders of magnitude higher than PNEC) of steroid hormones were found in groundwater at a US land application site (Karnjanapiboonwong et al., 2011). The problem probably resulted from the application of wastewater effluent to a portion of the soil. Although the authors did not point out the adverse effects of the high level steroid hormones, their occurrence would be of potential concern if the groundwater was utilized for direct or indirect potable water reuse.

2.2.4 Occurrence of micropollutants in drinking water

A limited amount of publications are available with regard to the occurrence of micropollutants in drinking water (Vulliet et al., 2011). Some recent studies showed that most micropollutants in finished waters from drinking water treatment were below limit of quantitation or limit of detection (Benotti et al., 2008; Huerta-Fontela et al., 2011; Kleywegt et al., 2011; Wang et al., 2011). Therefore, only the data of the most abundant compounds are presented in Figure 2.2. To date, there has been a lack of guidelines for risk assessment for the presence of most micropollutants in drinking water. PNEC values were plotted to superficially describe the potential of negative effects (Figure 2.2). As can be seen in Figure 2.2, the maximum occurrence concentrations of most micropollutants were reported to be below 100 ng/L, with the exception of carbamazepine and caffeine. Notably, carbamazepine was observed at a

concentration exceeding 600 ng/L (a concentration more than 10 times higher than those of most other compounds) in the study conducted by Kleywegt et al. (2011). The high levels of carbamazepine could be explained by its high persistency. Even so, the occurrence level of carbamazepine was far below the PNEC (25,000 ng/L). It is also noteworthy that nonylphenol showed a maximum concentration (100 ng/L) most close to PNEC (330 ng/L, less than 1 order of magnitude). Other compounds were all at safe levels, since the PNEC values were 2 to 5 orders of magnitude higher than the their maximum concentrations. Overall, based on the studies reviewed here, these countries were all able to rule out the adverse impacts of selected micropollutants on drinking water. Nevertheless, since other compounds as well as transformation by-products, which can also pose adverse effects, were not monitored in these studies, the safety of the produced drinking water still needs to be under scrutiny.

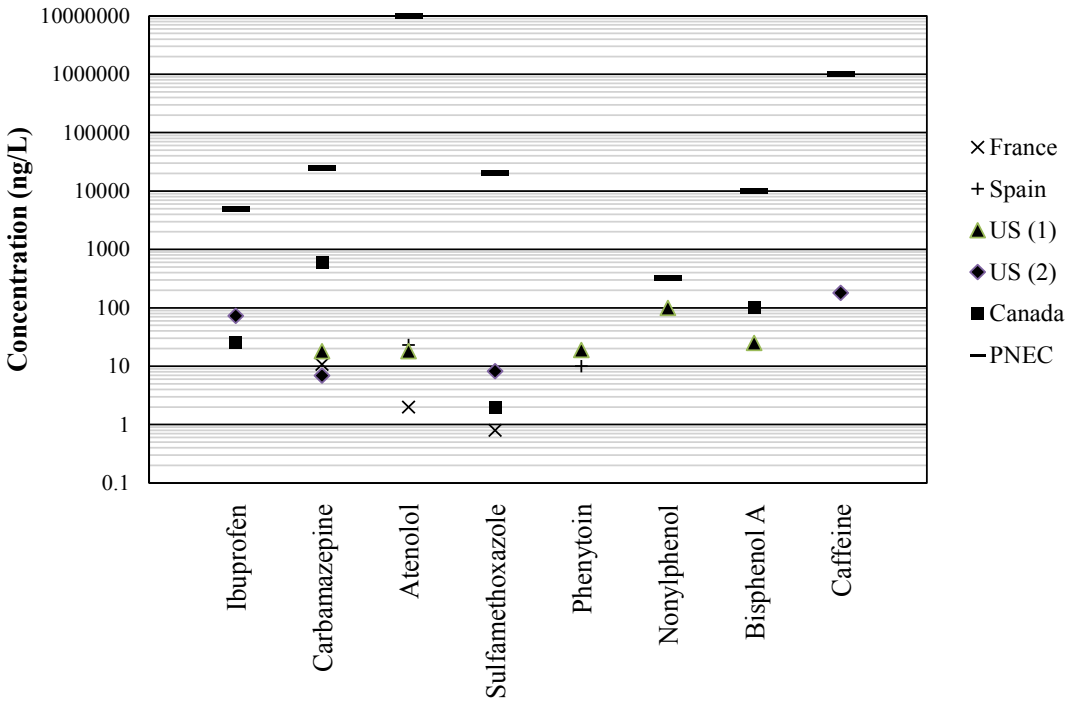


Figure 2.2 Maximum occurrence concentrations of some abundant micropollutants in drinking water (Benotti et al., 2008; Huerta-Fontela et al., 2011; Kleywegt et al. 2011; Vulliet et al., 2011; Wang et al., 2011)

Table 2.3 Occurrence of some common micropollutants in groundwater in different countries

Compound	Concentrations (ng/L)					
	Europe[a,1]	France[b,2]	Germany[c,3,4,5]	Spain[a,d,6,7]	US[a,c,8,9,10]	PNEC[e]
Ibuprofen	3 (395)	0	–	185 (185)	0, 3110	5000
Naproxen	–	1.2	–	204 (145–263)	–	37000
Ketoprofen	26 (2886)	2.8	–	–	–	16×10^6
Diclofenac	0 (24)	9.7	3050	256 (35–477)	–	10000
Carbamazepine	12 (390)	10.4	<50, 2325	–	40 (420)	25000
Gemfibrozil	–	–	–	165.3 (12–574)	–	100000
Bezafibrate	–	0	112	–	–	–
Atenolol	–	5.5		60.8 (18–106)	–	10×10^6
Sulfamethoxazole	2 (38)	3.0	–	47.57 (2–117)	1110, 160 (170)	20000
Trimethoprim	–	1.4	–	–	–	1000
Caffeine	13 (189)	–	–	63.56 (4–505)	130, 170 (290)	10×10^5
Triclosan	0 (9)	–	–	39.8 (2–118)	53	–
Nonylphenol	83 (3850)	–	–	–	–	330
Bisphenol A	79 (2299)	–	–	–	2550	1000
Estrone	0 (4)	0.7	–	–	79	18
Estradiol	–	0.4	–	–	147	–
Ethinylestradiol	–	1.2	–	–	230	0.02
Estriol	–	–	–	–	1661	149
TCEP	–	–	4–51	–	–	–
TCPP	–	–	14–355	–	–	–
Atrazine	–	–	–	36 (756)	–	2000
Diazinon	–	–	–	5.3 (30.8)	–	–
Diuron	–	–	–	8.8 (178)	–	1800

[a] Average concentration with maximum concentration in the brackets;
[b] Average concentration;
[c] Maximum concentration;
[d] Average concentration with minimum and maximum concentrations in the brackets;
[e] Data were derived from Fromme et al., 2002, Köck, 2010, Lin et al., 2008, and Loos et al., 2007;
1. Loos et al., 2010; 2. Vulliet and Cren–Olivé, 2011; 3. Maeng et al., 2010; 4. Müller et al., 2012; 5. Stepien et al., 2013; 6. Postigo et al., 2010; 7. Teijon et al., 2010; 8. Barnes et al., 2008; 9. Fram and Belitz, 2011; 10. Karnjanapiboonwong et al., 2011.

2.3 Fate and removal of micropollutants in WWTPs

Municipal WWTPs are designed to control a wide range of substances, such as particulates, carbonaceous substances, nutrients and pathogens. While these substances can be efficiently and consistently eliminated, the removal of micropollutants is often insufficient. Hence, the evaluation of the fate and removal of micropollutants during wastewater treatment is imperative for the optimization of treatment processes, in order to prevent the release of these potentially harmful micropollutants.

2.3.1 Fate of micropollutants in WWTPs

Wastewater treatment plants generally employ a primary, a secondary and an optional tertiary treatment process. Tertiary treatment processes are commonly used to produce higher quality of discharged water for certain purposes (e.g. water reuse), and are always associated with high treatment cost. Thus, the requirement for tertiary treatment processes is generally based on public and environmental health objectives. Primary treatment processes aim to remove suspended solids that enter WWTPs and are ineffective in removal of most micropollutants (Carballa et al., 2005). Micropollutants are removed mainly by sorption on primary sludge, as distribution of a compound into organic (lipophilic) layer is a predominant way of sorption (Ternes et al., 2004). Fragrances (galaxolide and tonalide) were found to be well removed (40%) during primary treatment (aerated grit chamber followed by circular sedimentation tank) due to their high partition coefficients between the solid and liquid phase (Carballa et al., 2004). Primary treatment (sedimentation tank) was also able to remove some EDCs moderately with removal efficiency ranging from 13% (nonylphenol monoethoxylate) to 43% (Bisphenol A) (Stasinakis et al., 2013). However, primary treatment using aerated grit chamber could cause significant increase of phenolic compounds, such as bisphenol A and nonylphenol, because the compounds originally attached to the grits could be peeled off due to air agitation in grit chamber (Nie et al., 2012). For pharmaceuticals and hormones, removal efficiency in primary treatment ranged up to only 28% (diclofenac and estriol), which suggested that adsorption of investigated compounds to sludge particles was

rather limited (Behera et al., 2011). No considerable reduction was also reported for ibuprofen, naproxen, sulfamethoxazol and estrone (Carballa et al., 2004).
In secondary treatment, micropollutants are subjected to a range of processes, including dispersion, dilution, partition, biodegradation and abiotic transformation. The total removal during secondary treatment generally refers to the losses of a parent compound contributed by different mechanisms of chemical and physical transformation, biodegradation and sorption to solids (Jelic et al., 2011). Biodegradation and sorption rather than volatilization are the major removal mechanisms (Verlicchi et al., 2012).

During secondary treatment, micropollutants are biologically degraded to various degrees, resulting in mineralization or incomplete degradation (production of by-products). Biodegradation of micropollutants can occur via different mechanisms: 1) single substrate growth of a small subset of specialist oligotrophic organisms, which is less common in WWTPs and more likely to occur in receiving water or sediment (Daughton and Ternes, 1999); 2) co-metabolism, in which micropollutants are decomposed by enzymes generated for other primary substation degradation (e.g. ammonia monooxygenase (AMO)) and are not used as carbon and energy source for microbial growth; and 3) mixed substrate growth, in which micropollutants are used as carbon and energy source and become mineralized (Vader et al., 2000). For pharmaceuticals, even if the compounds fall into the same therapeutical group, their biodegradability can show great variability. For example, Salgado et al., (2012) reported that, among NSAIDs, diclofenac exhibited low (< 25%) biodegradation, whereas ibuprofen and ketoprofen were biodegraded to a much higher extent (> 75%). Antibiotics are generally not readily biodegradable (Verlicchi et al., 2012). Regarding polycyclic musk, Clara et al. (2011) indicated that biological degradation serves as a minor removal pathway. 15% and 30% of galaxolide and tonalide were found to be eliminated via biological transformation (Salgado et al., 2012). In contrast, Suárez et al. (2010) reported much higher biodegradation of tonalide and galaxolide (> 75%). As for steroid hormones, significant biodegradation (> 75%) was observed for estrone and estradiol (Suárez et al., 2010). Bisphenol A and triclosan were also found to be susceptible to biodegradation (up to 85% and 81% respectively), while nonylphenol was biologically transformed to a lesser degree (up

to 56%) in two WWTPs using activated sludge (Samaras et al., 2013). In the case of pesticide, Stasinakis et al. (2009) found that almost 60% of diuron was biodegraded during an activated sludge process.

Sorption of micropollutants (Figure 2.3) mainly occurs by (1) absorption, in which hydrophobic interactions occur between the aliphatic and aromatic groups of a compound and the lipophilic cell membrane of microorganisms as well as the fat fractions of sludge, and (2) adsorption, involving the electrostatic interactions of the positively charged groups with the negatively charged surfaces of the microorganisms and sludge (e.g. amino groups) (Ternes et al., 2004). Verlicchi et al. (2012) found that sorption onto solids is insignificant (< 5% in most cases) for most pharmaceuticals. In a study, mefenamic acid showed about 30% sorption (Jelic et al., 2011). In contrast, it was the major removal mechanism for some compounds, such as diclofenac, galaxolide, and tonalide (Clara et al., 2011; Salgado et al., 2012). Nonylphenol (35% to 51%) and triclosan (11% to 41%) were detected to be moderately removed via sorption to solids, while some acidic compounds (e.g., ibuprofen) could not be sorbed because of the charge repulsion between solids and compounds (Samaras et al., 2013). In general, the compounds that tend to be sorbed onto solids are expected to be better eliminated by activated sludge treatment than other low-cost secondary treatments (trickling filter beds, anaerobic lagoon and constructed wet lands) (Camacho-Muñoz et al., 2012). This can be due to the promoted biodegradation under forced aeration during the conventional treatments, together with the enhanced sorption by large amounts of sludge generated in conventional treatment systems.

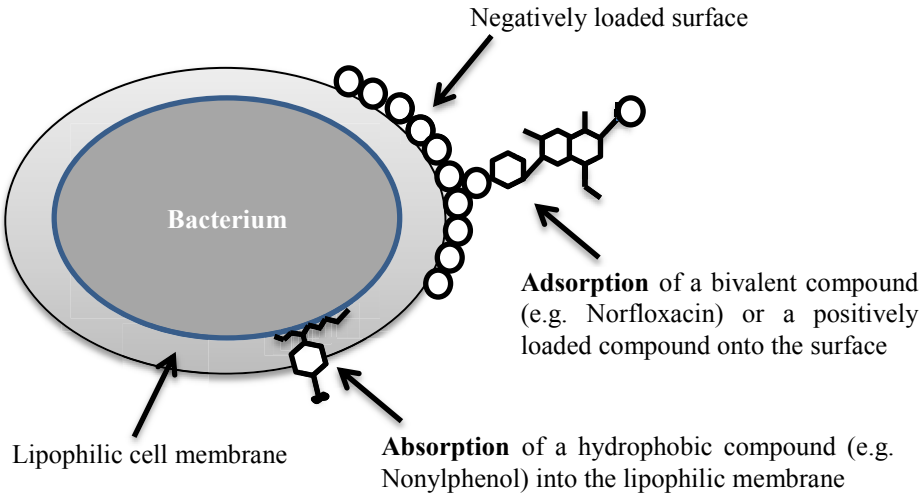


Figure 2.3 Sorption of micropollutants during biological treatment processes

2.3.2 Overall removal of micropollutants in conventional WWTPs

Figure 2.4 shows the removals of the selected micropollutants during conventional wastewater treatment. Ibuprofen, naproxen and ketoprofen exhibited moderate to high removal with average removal efficiency of 91.4%, 75.5% and 51.7%, respectively. In particular, the eliminations of ibuprofen were relatively consistent and commonly higher than 70%. As opposed to other NSAIDs, diclofenac experienced fairly inefficient (average 35.8%) and variable removals. The selected antibiotics showed low (erythromycin, 30.2%) to moderate elimination (sulfamethoxazole, 64.6%). Lipid regulators and β-blockers were also not efficiently eliminated (37.6%–73.3%) in WWTPs. Anticonvulsant carbamazepine seemed to be the most persistent pharmaceutical and was averagely reduced by only 32.7%. Among all the reviewed studies, the highsethighest removal of carbamazepine was observed by K. Choi et al. (2008), reaching 62.3%. As mentioned above, caffeine was the most abundant compounds present in municipal wastewater. WWTPs proved to be effective in eliminating caffeine with an average removal efficiency of 88.7%. In the case of PCPs, relatively high reductions were exhibited, ranging between 74.2% (DEET) and 87.5% (galaxolide). As for steroid hormones, relatively stable and high removal efficiency was observed, which ranged from 71.9- to 100%. Two surfactants, nonylphenol and octylphenol, showed removals of 77.5% and 84.2%, respectively. Contradictory results have been reported for the elimination of nonylphenol, ranging from 21.7% (Stasinakis et al., 2008) to 99.0% (Janex-Habibi et al., 2009). The concentrations of bisphenol A were commonly considerably lowered (82%) during wastewater treatment. Other selected industrial chemicals also showed removal efficiencies exceeding 80%. Due to the fact that pesticides have been typically considered of agricultural rather than of urban origin, few studies have been performed at real plant scale and most of reported plants coincide in showing insufficient removal of pesticides (Köck-Schulmeyer et al., 2013). The selected pesticides, such as atrazine, fluconazole and tebuconazole, were particularly resistant in WWTPs. It is difficult to draw a firm conclusion on the persistency of each compound, as many compounds showed significantly varied removals in different WWTP. However, a simple classification of these compounds is presented in Table 2.4.

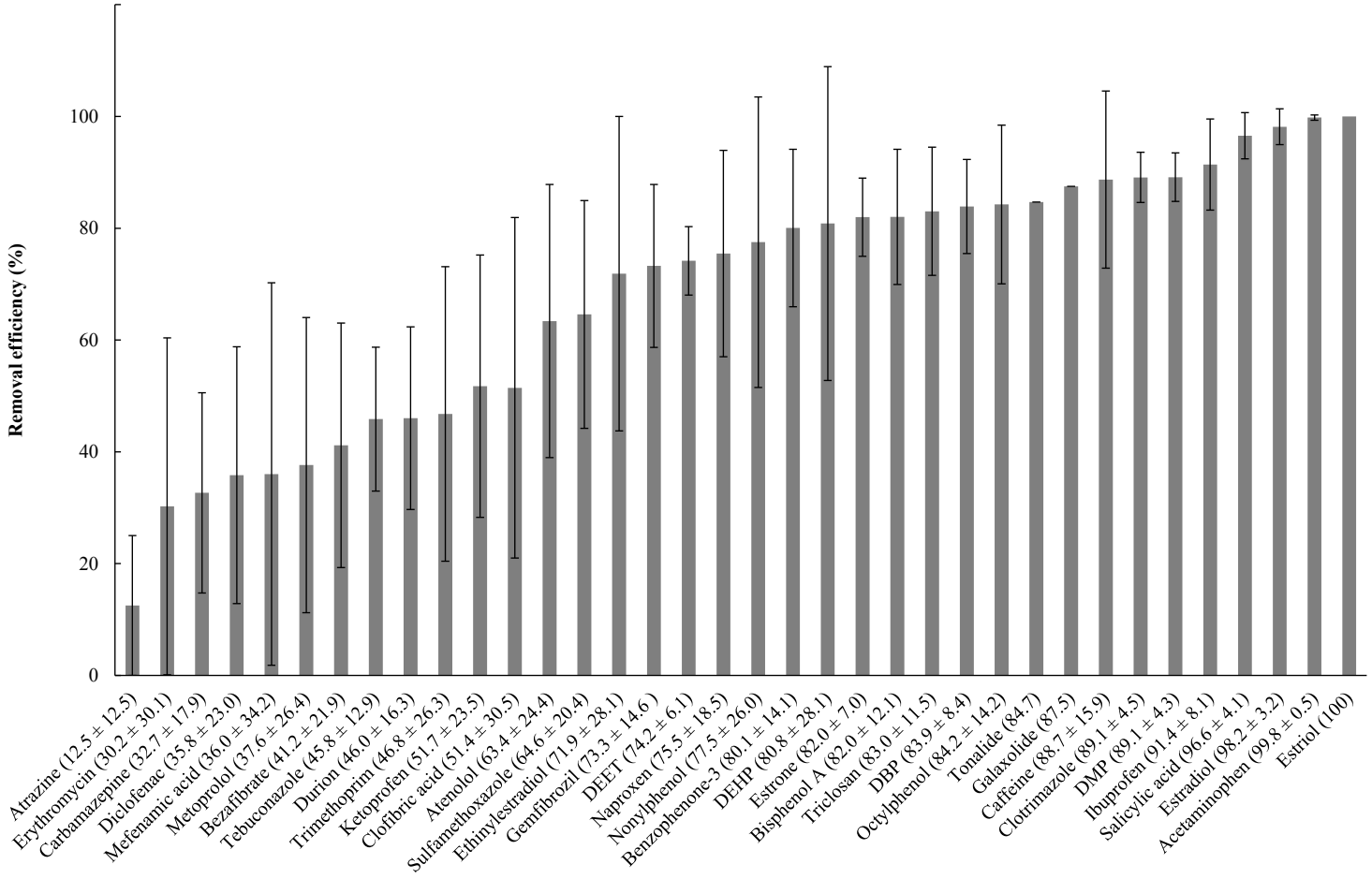


Figure 2.4 Removals of the selected micropollutants in WWTPs (data from Figure 2.1; negative removals not included). X-axis displays the selected compounds and their mean removal efficeincies and standard deveations (in the brackets). Error bars represent the standard deviations of the data.

Table 2.4 Simple classification of micropollutants based on removal efficiency

Degree of removal	Compounds
Poorly removed (<40%)	Atrazine, carbamazepine, diazinon, diclofenac, erythromycin, metoprolol, mefenamic acid, TCEP, TCPP
Moderately removed (40–70%)	Atenolol, bezafibrate, clofibric acid, durion, ketoprofen, nonylphenol, sulfamethoxzole, tebuconazole, trimethoprim,
Highly removed (>70%)	Acetaminophen, benzophenone–3, bisphenol A, caffeine, clotrimazole, DBP, DEET, DEHP, DMP, estradiol, estriol, estrone, ethinylestradiol, galaxolide, gemfibrozil, ibuprofen, naproxen, nonylphenol, octylphenol, salicylic acid, tonalide, triclosan

2.3.3 Factors governing the fate of micropollutants in WWTPs

The fate of micropollutants in WWTPs is under the control or influence of 'internal factors' and 'external factors'. Internal factors are micropollutant-related, including the characteristics of micropollutants (e.g. hydrophobicity, biodegradability, and volatility). In general, polar and non-volatile compounds are more likely to escape wastewater treatment processes. External factors are WWTP-specific, which are linked to the treatment conditions of wastewater treatment processes, the mixture of micropollutants that can act as competitors and nature of wastewater (pH and temperature).

2.3.3.1 Micropollutant-related factors

Sorption of a micropollutant to solids largely depends on the hydrophobicity of the compound. K_{OW} is frequently used to predict absorption of micropollutants on solids. Rogers (1996) provided a general rule of thumb for applying KOW to the estimation of sorption: $\log K_{OW} < 2.5$ indicates low sorption potential, $2.5 < \log K_{OW} < 4$ indicates medium sorption potential, and $\log K_{OW} > 4$ indicates high sorption potential.

Acidity determined by the functional group of a compound can play an important role in chemisorption or/and electrostatic adsorption of micropollutants. Schäfer et al. (2011) indicated that, at the pH above the acid dissociation constant (pK_a), the phenolic hydroxyl group of hormones dissociates and the compounds becomes become negatively charged, facilitating the charge repulsion with the negatively charged membrane. Charge repulsion can also be expected to occur between negatively charged compounds and biomass in the activated sludge reactors, thereby impeding the removal of micropollutants.

In activated sludge processes, the solid-water distribution coefficient (K_d) is defined as the partition of a compound between the sludge and the water phase. Taking into consideration both K_{OW} and pK_a, K_d has been proposed as a relative accurate indicator of sorption behaviourbehavior (Joss et al., 2005; Ternes et al., 2004). For compounds having a K_d of below 300 L/kg ($\log K_d < 2.48$), the sorption onto secondary sludge can be considered to be insignificant. Additionally, Tadkaew et al. (2011) reported that the studied micropollutants with $\log K_d > 3.2$ (e.g. estrone and nonylphenol) were easily removed (> 85%).

As biodegradability of micropollutants depends on their bioavailability, the first phase of the biodegradation process is the uptake of micropollutants by cell, leading to by chance affinity of the compound with the bacterial enzymes (Siegrist et al., 2005). Compound structure also plays an important role in determining resistance of a micropollutant to biodegradation. The biodegradability of a compound intrinsically relies on the complexity of the compound (e.g. monocyclic or polycyclic) and its functional groups (e.g. halogen groups). In general, the easily degraded substances include 1) linear compounds with short side chains, 2) unsaturated aliphatic compounds, and 3) compounds possessing electron donating functional groups. On the other hand, the persistent micropollutants contain 1) compounds with long, highly branched side chains, 2) saturated or polycyclic compounds, and 3) compounds possessing sulfate, halogen or electron withdrawing functional groups (Jones et al., 2005; Tadkaew et al., 2011). Nevertheless, for some pharmaceutical compounds, there is no obvious relationship among chemical structure, functional groups and the removal. For example, two structurally similar compounds such as

ibuprofen and ketoprofen could show different removals, with ibuprofen being eliminated more efficiently (Camacho-Muñoz et al., 2012).

Henry's law constant (k_H) is commonly used to characterize the volatility of a compound. The k_H ranging from 10 – 2 to 10 – 3 mol/(m3·Pa) commonly indicates high tendency of volatilization (Stenstrom et al., 1989). According to Suárez et al. (2008), volatilization of micropollutants is totally negligible for pharmaceuticals and estrogens, nearly negligible for fragrance compounds tonalide and galaxolide and very significant for celestolide. Volatilization was found to account for up to 16% removal of celestolide (Suárez et al., 2010). Furthermore, in activated sludge processes, the volatilization behavior can be intensified due to the additional air supply.

2.3.3.2 WWTP-specific factors

Sludge retention time (SRT) controls the size and diversity of a microbial community. Enhanced elimination of micropollutants can be achieved if the treatment processes have extended SRTs, which facilitate the buildup of slowly growing bacteria, such as nitrifying bacteria. In nitrifying conditions, co-metabolism using ammonium monooxygenase enzyme is a possible degradation pathway for micropollutants. Nitrifying biomass have been found to have positive effects on the removal of a range of micropollutants such as ibuprofen, naproxen, trimethoprim, erythromycin, galaxolide, tonalide, ethinylestradiol, bisphenol A and nonylphenol (Fernandez-Fontaina et al., 2012; Suárez et al., 2010). Clara et al. (2005) suggested that the SRTs allowing nitrogen removal (nitrification and denitrification) above 10 days can enhance the elimination of some biodegradable compounds (e.g. ibuprofen, bezafibrate, natural estrogens and bisphenol A). In a study, the activated sludge treatment with an elevated SRT of 18 days could achieve considerably higher removal of beta blockers and psycho-activate drugs in comparison with the same treatment with shorter SRT of 0.5 days day (Wick et al., 2009). Suárez et al. (2010) identified 10% higher of removal efficiency for fluoxetine, citalopram and ethinylestradiol when prolonged SRT was applied. Enhanced biodegradation was found for 4-n-nonylphenol and triclosan at SRT of 20 days (compared with 3 days and 10 days) (Stasinakis et al., 2010). However, high SRT does not necessarily mean better removal performance. Joss et al. (2005) suggested that variation of the sludge

age between 10 and 60-–80 days showed no noticeable effects on removal efficiency of the investigated pharmaceuticals. High SRT (20 days) also seemed not to appreciably affect the biodegradation of bisphenol A (Stasinakis et al., 2010). Santos et al. (2009) indicated that application of low SRTs (1.5-–5.1 days) had minor effects on the removal of some pharmaceutical compounds (e.g., ibuprofen, diclofenac, naproxen, and carbamazepine).

Hydraulic retention time (HRT) is the amount of time that allows for biodegradation and sorption. The micropollutants having slow/intermediate kinetics such as fluoxetine or some antibiotics will experience less effective biodegradation at shorter HRTs or increasing loading rates (Fernandez-Fontaina et al., 2012)., Huang et al. (2008) indicated that HRT in the range from 5 to 14 h achieved minor removal of DEHP, while higher HRT increased DEHP accumulation in the system and DEHP retention in the waste sludge.

Redox conditions may cause the observed differences by having an effect on certain wastewater or sludge characteristics as wells as on the biodiversity of the microbial flora present (Göbel et al., 2007). Qiang et al. (2013) indicated unfavourablethat unfavorable redox conditions (anaerobic conditions) could result in inefficient biodegradation of some micropollutants. In another study, naproxen, ethinylestradiol, roxithromycin and erythromycin were found only considerably eliminated under aerobic condtioncondition and anoxic removal was much less effective (Suárez et al., 2010). Zwiener and Frimmel (2003) compared short-term biodegradation of clofibric acid, ibuprofen, and diclofenac in oxic and anoxic (denitrification conditions, absence of oxygen while presence of nitrate) biofilm reactor. In the oxic biofilm reactor, clofibric acid and diclofenac were not eliminated, with only 1-–4% loss of their initial concentration being observed. Ibuprofen was reduced by 64–70%. By contrast, the anoxic biofilm reactor achieved much lower removal of ibuprofen (17-–21%) and higher removal of diclofenac (34%-–38%) and clofibric acid (26-–30%). Goel et al. (2003) reported that removal of the nonylphenol ethoxylate surfactant was higher in the oxic reactors (50 to 70%) compared to the anoxic reactors (30 to 50%). Similarly, DEHP were removed by 15%, 19% and 62% in anaerobic, anoxic and aerobic reactors (Huang et al., 2008). Anoxic redox conditions were not necessarily

less favourablefavorable environments for micropollutant removal. For instance, anoxic conditions could lead to improved elimination of iodinated X-ray contrast media, while aerobic environments witnessed minor removal (Drewes et al., 2001). Some persistent substances, diclofenac, sulfamethoxazole, trimethoprim and carbamazepine showed minor removals (< 25%) by the biological treatment with neither either nitrifying (oxic) or denitrifying bacteria (anoxic) (Suárez et al., 2010).

Wastewater characteristics, such as pH and temperature, may have effects on micropollutant removal. The acidity or alkalinity of an aqueous environment can vary the elimination of micropollutants from wastewater by influencing both the physiology of microorganisms (pH optima of microbial enzyme activities) and the solubility of micropollutants present in wastewater (Cirja et al., 2008). Kimura et al. (2010) found that modest pH variation had significant effects on the removal of acidic pharmaceuticals (clofibric acid, ibuprofen, ketoprofen, naproxen and mefenamic acid) by the biosolids, which was presumably ascribed to activation of enzymes involved or enhancement of affinity between the biosolids and pharmaceuticals due to protonation of acidic pharmaceuticals. Seasonal variation of temperature may have impact on micropollutant removal in WWTPs. Temperature variation can affect biodegradation and partition (sorption and volatilization) of micropollutants. To eliminate the seasonal effect, alteration of operation parameters can be taken into consideration. For example, a possible strategy to improve EDCs EDC removal in the cold temperature is to increase the mixed liquor suspended solids solid (MLSS) concentration by raising the SRT (Nie et al., 2012). Generally, enhanced micropollutant removal can be achieved at warmer temperature due to promoted microbial activities (Nie et al., 2012; Qiang et al., 2013). Nevertheless, Hai et al. (2011) found that operation at high temperature levels (45 ° ◦C) could lead to lower micropollutant removal. Some other studies showed that micropollutant elimination was independent of temperature fluctuation (Suárez et al., 2010).

2.4 Overview of treatment alternatives for micropollutant removal

No specific treatment is now available to assure the complete removal of various micropollutants due to their diverse properties. Reliable processes that are able to eliminate both bulk substances as well as micropollutants are yet to be developed. MBBR technique is efficient in organic and nutrient removal, but the understanding of its effectiveness in micropollutant removal is rather limited. The first part of this section focus on the previous studies investigating the performance of MBBR in micropollutant elimination. An overview of the other treatment options is present subsequently to reveal the performance of these technologies for micropollutant removal and to identify the need for improvement.

2.4.1 Coagulation–flocculation

Coagulation–flocculation is used for removing particulate matter, colloids as well as some dissolved substances. Table 2.5 presents some recent literature data regarding the removal of the most studied micropollutants from wastewater by coagulation–flocculation processes. In general, coagulation-–flocculation processes yield ineffective elimination of most micropollutants. Matamoros and Salvadó (2013) evaluated the micropollutant removal in a coagulation/flocculation–lamellar clarifier for treating secondary effluent. The removals ranged from imperceptible elimination to 50%, among which the relatively high removals (20–50%) were observed for the compounds with K_{OW} > 4 at pH = 7–8 (e.g. galaxolide, tonalide, and octylphenol). Suárez et al. (2009) reported significant reduction (around 80%) of musks (e.g. galaxolide and tonalide) during coagulation-–flocculation treatment of hospital wastewater. The other compounds that showed identifiable elimination were diclofenac (max. 46%), naproxen (max. 42%) and ibuprofen (max. 23%). Since landfill leachate has been considered as an important source of some EDCs, Asakura and Matsuto (2009) pointed out that treatment of landfill leachate by coagulation and sedimentation was not able to remove biphenol A but achieved much higher removals for DEHP and nonylphenol (70% and 90% respectively).

As a whole, most micropollutants, as shown above, have been reported to be poorly removed during coagulation-–flocculation processes. Exceptions were some musks, a

few pharmaceuticals (e.g. diclofenac) and nonylphenol due to their high KOW (4–6). Besides, neither coagulant dose nor operation temperature influenced the removal of pesticides significantly (Thuy et al., 2008). Despite the minor differences among different types of coagulants at different doses, Suárez et al. (2009) reported that the addition of 25 mg/L $FeCl_3$ achieved optimal results in most cases. Huerta-Fontela et al. (2011) demonstrated that aluminum sulfate was effective in eliminating some hydrophobic pharmaceutical compounds. Composition of wastewater can exert either positive or negative effects on micropollutant removal during coagulation–flocculation treatment. For example, high fat content in water source was reported to improve the removal of hydrophobic compounds (Suárez et al., 2009). Dissolved humic acid was also able to enhance the elimination of pharmaceutical compounds, such as diclofenac, as diclofenac, ibuprofen and bezafibrate (Vieno et al., 2006). On the contrary, the presence of dissolved organic matters (DOM), especially low-molecular-weight fractions, can possibly inhibit the micropollutant removal due to the preferential removal of DOM through coagulation. Negatively charged DOM could react with positively charged aluminum hydrolysis species, leading to a less amount of coagulant available for elimination of the compounds (K.-J. Choi et al., 2008). In addition, the performance of coagulation-–flocculation processes can be also governed by several operating conditions including mixing conditions, pH, alkalinity, temperature as well as the presence of divalent cations and concentrations of destabilizing anions (e.g. bicarbonate, chloride, and sulfate) (Alexander et al., 2012).

Table 2.5 Removals of some common micropollutants during coagulation–flocculation

Coagulant	Dosage with pH value presented in the parentheses	Compound	Removal (%)	References
$FeCl_3/Al_2(SO_4)_3$	25, 50 ppm (7)	Ibuprofen	12.0 ± 4.8	Suárez et al., 2009)
		Diclofenac	21.6 ± 19.4	
		Naproxen	31.8 ± 10.2	
		Carbamazepine	6.3 ± 15.9	
		Sulfamethoxazole	6.0 ± 9.5	
		Tonalide	83.4 ± 14.3	
		Galaxolide	79.2 ± 9.9	
$FeCl_3$	100, 200 mg/L (4, 7, 9)	Bisphenol A	20	Asakura and Matsuto, 2009
		DEHP	70	
		Nonylphenol	90	
$Al_2(SO_4)_3$	200 mg/L (7)	Aldrin	46	Thuy et al., 2008
	100 mg/L (7)	Bentazon	15	
Not mentioned	Not mentioned	Ibuprofen	4	Matamoros and Salvadó, 2013
		Ketoprofen	4	
		Carbamazepine	2	
		Tonalide	24	
		Galaxolide	16	
		Celestolide	50	
		Triclosan	24	
		DMP	19	
		Octylphenol	50	

2.4.2 Activated carbon adsorption

Adsorption by activated carbons (ACs) is commonly employed for controlling taste and odor in drinking water. This technique has also great potential for treatment of secondary effluent and has proved to be more effective in removing micropollutants in comparison with coagulation-–flocculation process (K.-J. Choi et al., 2008). Both powdered activated carbon (PAC) and granular activated carbon (GAC) have been widely used in adsorption processes (Table 2.6), which can be affected by the properties of both adsorbate (K_{OW}, pK_a, molecular size, aromaticity versus aliphaticity, and presence of specific functional groups) and adsorbent (surface area, pore size and texture, surface chemistry, and mineral matter content) (Kovalova et al., 2013). In addition, the adsorption of micropollutants is also influenced by the properties of wastewater, such as pH, ionic strength, presence of other substances (e.g., NOM).

Table 2.6 Removals of some common micropollutants during adsorption process.

Adsorbent	Dosage	Compound	Removal (%)	References
PAC	8, 23, 43 mg/L	Diclofenac	96, 98, 99	Kovalova et al., 2013
		Carbamazepine	98, 99, 100	
		Propranolol	>91, >94, >94	
		Sulfamethoxazole	2, 33, 62	
GAC	Full scale	Diclofenac	>98	Grover et al., 2011
		Carbamazepine	23	
		Propranolol	17	
		Estrone	64	
		17β–estradiol	>43	
		17α–ethinylestradiol	>43	
	29 g/70.6 mL bed volume	Galaxolide	79	Hernández–Leal et al., 2011
		Tonalide	67	
		Bisphenol A	66	
		Nonylphenol	84	
		Triclosan	95	
	Full scale, empty bed contact time :15 min	Diclofenac	~100	Yang et al., 2011
		Trimethoprim	90	
		Carbamazepine	75	
		Caffeine	45	
		Primidone	30	
		DEET	15	

2.4.2.1 PAC

PAC has been considered as an effective adsorbent for treating persistent/non-biodegradable organic compounds. An advantage of employing PAC is that it can provide fresh carbon continuously or can be used seasonally or occasionally when risk of trace organics is present at a high level (Snyder et al., 2007). Kovalova et al. (2013) investigated the elimination of micropollutants from a MBR-treated hospital effluent using PAC treatment at a retention time of two days. With PAC doses of 8, 23 and 43 mg/L and retention time of 2 days, the PAC reactor achieved efficient elimination for most of the micropollutants (pharmaceuticals, metabolites and industrial chemicals). The reduction of total load of selected pharmaceuticals and metabolites was around 86%.Batch tests performed by Hernández-Leal et al. (2011) also demonstrated marked removal (> 94%) of various micropollutants (personal care products, bisphenol A and nonylphenol) during PAC treatment with initial compound concentrations of 100–1600 μg/L at a dose of 1.25 g/L and a contact time of 5 min.

PAC addition in activated sludge tank or post treatment configurations is a major application of PAC in the full-scale municipal WWTPs. A study was carried out to assess the efficiency of micropollutant removal by addition of PAC in different flow schemes in municipal wastewater treatment (Boehler et al., 2012). It was found that counter-current use of PAC by recycling waste PAC from post-treatment tank to biological treatment tank could enhance micropollutant removal by 10 to 50% in comparison with the application without recycling. PAC addition in WWTPs was shown to be able to reduce micropollutant levels by more than 80%. The PAC dosage for adequate treatment of secondary effluent with dissolved organic carbon (DOC) of 5–10 mg/L was 10–20 mg/L, while a higher amount (30–40 g/m3 influent) was required to achieve similar results if direct PAC addition was employed in biology tank.

The performance of PAC in eliminating micropollutants depends upon PAC dose and contact time, the molecular structure and behavior of the targeted compound, as well as the water/wastewater composition (Boehler et al., 2012; Snyder et al., 2007). Either higher dose or longer contact time can probably result in greater removal of

micropollutants. Westerhoff et al. (2005) revealed that micropollutant removal was improved with higher PAC dosages (20 mg/L) and independent of the initial compound concentrations. Water/wastewater composition also affects the adsorption of micropollutants. The sorption efficiency of PAC could be reduced as the DOC content increases (Boehler et al., 2012). Despite the influence of other contaminants in wastewater, the efficacy of applying PAC to wastewater for micropollutant removal is comparable with that of ozonation. Thus, PAC addition appears an attractive method for upgrading municipal WWTPs for improved micropollutant removal (Bolong et al., 2009).

2.4.2.2 GAC

Rossner et al. (2009) suggested that GAC dosage typically applied to taste and odourodor control in drinking water (< 10 mg/L) was sufficient to provide a 2-log removal for most of various compounds in lake water. Hernández-Leal et al. (2011) evaluated the effectiveness of GAC in treating two wastewaters: (1) spiked (0.1–10 μg/L) aerobic effluent in a GAC column operated at low flow and (2) aerobic effluent with real concentrations (40 ngL/L to 7.9 μg/L) of micropollutants in a GAC column. In the first case, removals for all the compounds were high (> 67%), particularly for ethyl-, propyl- and butylparaben, triclosan and caffeine (> 90%). In the second case, most compounds were also effectively eliminated. Specifically, the removal efficiency ranged from 50% (tonalide and nonylphenol) to more than 90% (galaxolide).

A full-scale granular activated carbon plant treating a WWTP effluent was assessed in terms of the removal efficiency of steroidal estrogens and pharmaceuticals (Grover et al., 2011). Considerable removals of steroidal estrogens from sewage effluent were observed during the GAC tertiary treatment. By comparison, the reduction of pharmaceutical concentrations was more variable. For example, higher removals (84–99%) were observed for mebeverine, indomethacine, and diclofenac, while some compounds (e.g. carbamazepine and propranolol) displayed much less removals (17–23%). In spite of the efficient treatment of sewage effluent, GAC-based removal technology should be carefully operated, as the efficiency will decrease over time due to the saturation of adsorption site.

Similar to PAC, the contact time is a major factor that affects the degree of adsorption. Short contact time is likely to lead to significantly lowered adsorption efficiency. As the elimination of the trace contaminants depends largely upon particle–contaminant interactions, the competition for adsorption sites and/or pore blocking (by particle solids) can reduce the removal efficiency of activated carbon (Bolong et al., 2009). Thus, GAC tends to perform poorly if wastewaters are highly contaminated. Snyder et al. (2007) suggested that a steam-treated GAC could be employed to overcome the drawbacks of GAC due to its greater absorption capacity. Regular regeneration of GAC also seemed of vital importance to maintain minimal breakthrough of micropollutants. Furthermore, pore shape/size and volumes of activated carbons, carbon type, surface charge of compounds and operation time were noted to have influence on the removal performances (K.-J. Choi et al., 2008; Rossner et al., 2009): 1) Broader micropore size distribution of the GAC led to more efficient adsorption of micropollutants with different shapes and sizes; 2) Pore volume was more important to adsorption capacity than specific area and larger pore volume was commonly associated with greater removal efficiency; 3) Negatively charged micropollutants were likely to be poorly adsorbed by the negatively charged carbon and well adsorbed by the positively charged carbon; and 4) Adsorption capacity reduced with operation time.

From the aforementioned studies, GAC and PAC appear to be attractive methods for micropollutant removal. In general, efficient removal is potentially achievable when the compounds have non-polar characteristics ($K_{OW} > 2$) as well as matching pore size/shape requirements (Rossner et al., 2009; Verlicchi et al., 2010b). However, activated carbon efficacy might be significantly lowered by the presence of natural organic matter (NOM) which competes for binding sides, thereby resulting in blocked pores. Besides, PAC dose, GAC regeneration as well as contact time play important roles in efficient removal of micropollutants.

2.4.3 Ozonation and advanced oxidation processes (AOPs)

Due to the refractory nature of some micropollutants, conventional physico-chemical and biological treatments are not able to provide adequate elimination of these compounds. To overcome the problem, ozonation and AOPs can be considered.

Performance of these processes in micropollutant removal is reported in Table 2.7. Ozonation and AOPs are efficient redox technologies which demonstrate some superiority over conventional treatments, such as high degradation rates and non-selectivity. Moreover, these processes have disinfecting effects, which are essential for reuse applications that involve direct human contact, e.g., household reuse applications (Hernández-Leal et al., 2011). Ozone can degrade contaminants directly and indirectly (mainly via formation of stronger and less selective oxidizing agent, •OH). Some micropollutants are susceptible to both ozone and AOPs (e.g., naproxen and carbamazepine), whereas some are only subject to •OH (e.g. atrazine and meprobamate) and some are resistant to both (e.g. TCEP and TCPP) (Gerrity et al., 2011). The generation of •OH can be promoted by electroanalysis (with the presence of H_2O_2, Fenton and ultraviolet).

Table 2.7 Removals of some common micropollutants during ozonation and AOPs.

Treatment	Compound	Removal (%)
O_3 (5 mg/L): 15 min	Carbamazepine	>90
(Sui et al., 2010)	Diclofenac	>90
	Metoprolol	80–90
	Bezafibrate	0–50
	Trimethoprim	>90
	DEET	50–80
O_3 (15 mg/L)	Tonalide	79
(Hernández–Leal et al., 2011)	Galaxolide	>87
	Nonylphenol	>79
O_3 (5 mg/L)+H_2O_2 (3.5 mg/L)	Ibuprofen	83
(Gerrity et al., 2011)	Diclofenac	>99
	Carbamazepine	>99
	Sulfamethoxazole	98
	Triclosan	>99
	Bisphenol A	>78
	Estradiol	>83
	Estrone	>98
	Atrazine	69
UV_{254}: 10 min	Ibuprofen	34
(De la Cruz et al., 2012)	Diclofenac	100
	Carbamazepine	23
	Sulfamethoxazole	51
	Atrazine	69
UV_{254} + H_2O_2 (50 mg/L):	Ibuprofen	100 (10 min), 100 (30 min)
10min, 30 min	Diclofenac	100 (10 min), 100 (30 min)
(De la Cruz et al., 2012)	Carbamazepine	75 (10 min), 100 (30 min)
	Sulfamethoxazole	98 (10 min), 100 (30 min)
	Atrazine	100 (10 min), 100 (30 min)

Ozonation is a promising technique to considerably decrease the micropollutant load of full-scale WWTPs (Hollender et al., 2009). Hernández-Leal et al. (2011) examined the efficiency of ozonation for the removal of a wide range of micropollutants (UV-filter, fragrance, biocide and surfactant) from biologically treated grey water. In general, the compounds were significantly removed (> 79%) from the biologically treated effluent at an applied ozone dose of 15 mg/L. In another study, lower ozone dose of 5 mg/L also showed high removal efficiency for most of the targeted micropollutants (Sui et al., 2010). The concentrations of carbamazepine, diclofenac, indomethacin, sulpiride and trimethoprim were considerably reduced by more than 95%. The reductions of DEET and metoprolol were modest. By contrast, bezafibrate was very resistant to ozonation and was removed by only 14%.

A study conducted by Gerrity et al. (2011) focused on the application of O_3/H_2O_2 for removing a suite of micropollutants (PPCPs and steroid hormones) during water reclamation. The process showed considerable removal efficiency (> 90%) for almost all of the target contaminants, except TCEP (13%), TCPP (26%), atrazine (69%), meprobamate (80%), and ibuprofen (83%). They indicated that micropollutants which exhibited the highest levels of oxidation were characterized by high ozone and •OH rate constants associated with their electron-rich moieties (e.g., phenols, anilines, olefins and activated aromatic). Although the formation of •OH was enhanced under alkaline conditions, Zhang et al. (2012) reported lower pH was beneficial for EDCs removal by ozone when treating synthetic secondary effluent. This is because ozone was less reactive to the inorganic and organic matters (non-target compounds) in the synthetic secondary effluent as compared to •OH (generated at high pH) and a greater amount of O_3 could thereby be preserved for the reactions with target compounds. Furthermore, in spite of the fact that suspended sludge particles could lead to higher O_3 consumption, which might reduce the efficiency of ozonation for micropollutant removal, this effect was not significant and had only a minor impact on ozonation as well as oxidation by •OH at low O_3 dosages (Hernández-Leal et al., 2011; Huber et al., 2003).

Kim et al. (2009b) examined the effectiveness of UV (wave length: 254 mm)-based processes (UV and UV/H_2O_2) for the elimination of 41 pharmaceutical compounds.

UV alone could significantly remove (> 90%) only a few compounds (e.g. ketoprofen, diclofenac and antipyrine) while ineffective removals (24–34%) were observed for macrolides. By contrast, with the addition of H_2O_2 (7.8 mg/L), the process considerably improved its efficacy and removal efficiency increased up to 90% for 39 out of 41 compounds. Treatment of 32 selected micropollutants (pharmaceuticals, corrosion inhibitors and biocides/pesticides) in an effluent coming from a municipal activated sludge WWTP was also investigated using UV (wavelength: 254 nm), UV/H_2O_2, Fenton ($Fe^{2+,\ 3+}/H_2O_2$) and photo-Fenton ($Fe^{2+,\ 3+}/H_2O_2$/UV and $Fe^{2+,\ 3+}/H_2O_2$/simulated sunlight) (De la Cruz et al., 2012). The process with only UV irradiation yielded a global degradation of 46% for the micropollutants after 10 min. Four compounds (diclofenac, ketoprofen, memfenamic mefenamic acid and diuron) were completed removed during the process. In contrast, the concentrations of gabapentin, trimethoprim, metformin, primidone, azithromycin and clarithromycin were unaltered or only slightly reduced (< 10%). Comparing with UV treatment alone, UV and H_2O_2 (50 mg/L) exhibited elevated transformation (a total degradation of 81%) of the micropollutants. After 30 min of UV/H2O2, the transformation increased further up to 97%. Fenton process (5 mg/L $Fe^{2+,\ 3+}$/50 mg/L H_2O_2) achieved 31% degradation. It was able to completely eliminate only one of the micropollutants, norfloxacin, after 30 min, and the concentrations of ten compounds were reduced by less than 15%. When UV was applied to the Fenton process (under the same conditions mentioned above), significantly increased global degradation (97%) was observed. For the photo-Fenton process, either increased H_2O_2 dosage or extended reaction time was found to have positive impact on the global degradation. Fenton/UV254 (100% degradation after 90 min) displayed much higher degradation efficiency compared with Fenton/sunlight (47% degradation after 90 min). In addition, the presence of dissolved organic matter in the wastewater seemed to enhance the micropollutant removal during all the processes. In another study, Klamerth et al. (2010) reported much higher efficiency of photo-Fenton with solar light for treatment of 52 micropollutants (PPCPs and pesticides) in a WWTP effluent. The process was able to reduce 48 compounds to below their limit of detection.

Since oxidation processes do not commonly result in complete mineralization of micropollutants, the major concern of applying these processes is the formation of oxidation by-products (or transformation products) from micropollutants. Research data indicated that the by-products generally have low concentration levels as well as insignificant estrogenic and antimicrobial activity compared to the parent compounds (Hollender et al., 2009; Reungoat et al., 2010). To further reduce parent compounds and oxidation by-products, biological post-filtration (sand filtration or activated carbon filtration) can be considered.

2.4.4 Membrane processes

Table 2.8 presents some recent research data concerning the effectiveness of membrane technology in eliminating micropollutants. The retention of micropollutants in membrane processes can generally achieved by size exclusion, adsorption onto membrane, and charge repulsion. These removal mechanisms are largely dependent on a number of factors, such as membrane process type, membrane characteristics, operating conditions, specific micropollutant characteristics and membrane fouling (Schäfer et al., 2011).

Although microfiltration (MF) and ultrafiltration (UF) are proven processes to efficiently eliminate turbidity, micropollutants are generally poorly removed during UF and MF, as the membrane pore sizes are much larger than the molecular sizes of micropollutants. However, micropollutants can be removed via adsorption on to membrane polymers, as well as interaction with NOM in wastewater. Jermann et al. (2009) examined the fate of ibuprofen and estradiol during an UF process and the effects of fouling by NOM. Without NOM, UF with hydrophilic membrane showed insignificant removal for ibuprofen and low (8%) removal for estradiol, while hydrophobic membrane retained much larger amount of estradiol (up to 80%) and ibuprofen (up to 25%). The higher retention of estradiol was due to the higher Carbon-–Water Partitioning Coefficient (K_{oc}) value of the compound. As for the effect of NOM, NOM substances of high molecular weight such as alginate and Aldrich humic acid showed a greater effect than the lower molecular weight Nordic aquatic humic acid on enhancing micropollutant removal. Due to the low removal efficiency, MF or UF alone is not feasible for micropollutant removal. Hence, the

combination of MF or UF with other processes (e.g. NF or RO) is essential for enhanced elimination of different micropollutants. Garcia et al. (2013) combined MF with RO to remove micropollutants for municipal wastewater reuse. MF was found to be able to reduce the concentrations of some compounds, such as DEHP, by more than 50%. With the incorporation of RO, the removal efficiency was significantly improved, ranging from 65% to 90% for most micropollutants (except ibuprofen and nonylphenol). Similarly, a tertiary MF/RO treatment process exhibited very efficient retention (> 95%) of most of the studied PPCPs, except mefenamic acid and caffeine (Sui et al., 2010).

In comparison with MF and UF, nanofiltration (NF) and reverse osmosis (RO) have much 'tighter' structures. NF and RO are widely used in water reuse industry due to their high contaminant removal efficiency. However, NF and RO membranes are still somewhat permeable to some relatively small compounds (Steinle-Darling et al., 2010). Röhricht et al. (2009) investigated two different types of submerged NF flat sheet modules for the removal of pharmaceuticals from WWTP effluent. Naproxen and diclofenac (60%) were retained to a greater extent compared with carbamazepine (slight removal). At pH 7 and 8, naproxen and diclofenac (with pK_a values of 4.2 and 4.15, respectively) were deprotonated, while carbamazepine (pK_a = 13.9) was not. Hence, naproxen and diclofenac could be rejected by the negatively charged membrane surface, whereas carbamazepine could not be removed. This was in accordance with the viewpoint indicated by Schäfer et al. (2003) and Nghiem et al. (2005): the speciation of pharmaceuticals may result in a significant change in rejection as a function of pH, with much greater retention occurring for ionized, negatively charged pharmaceuticals. For uncharged pharmaceuticals, intrinsic physicochemical properties of the pharmaceutical molecules play a role in their retention. Apart from electrostatic repulsion, adsorption can serve as the overriding removal mechanism in some cases. This was demonstrated in a study evaluating the removal of a variety of EDC/PPCPs using UF or NF (Yoon et al., 2006). For more polar compounds, the NF membrane (44–93% removals except naproxen of no rejection) was more efficient than the UF membrane with most reported removals of less than 40% (exception: triclosan, 87%; oxybenzone, 77%; progesterone, 56%).

Table 2.8 Removals of some micropollutants during membrane processes

Membrane	Water type	Membrane conditions	Compound	Removal (%)	References
UF	Synthetic water	PES[a] flat–sheet, 100 kDa; TMP = 0.5 ± 0.01 bar	Ibuprofen	7	Jermann et al., 2009
		RC4[b] flat–sheet; TMP = 0.5 ± 0.01 bar		Minor	
		PES flat–sheet, 100 kDa; TMP = 0.5 ± 0.01 bar	Estradiol	Up to 80	
		RC4 flat–sheet; TMP = 0.5 ± 0.01 bar		Up to 25	
NF	WWTP effluent	Flat–sheet, area 3.5 m^2; TMP = 0.3 or 0.7 bar	Diclofenac	60	Röhricht et al., 2009; Yangali–Quintanilla et al., 2011
		Flat–sheet, area 3.5 m^2; TMP = 0.3 or 0.7 bar	Naproxen	60	
		Flat–sheet, area 3.5 m^2; TMP = 0.3 or 0.7 bar	Carbamazepine	Minor	
		Filmtec NF90; TMP = 345 kPa		91	
		Filmtec NF200; TMP = 483 kPa	Acetaminophen	23	
		Filmtec NF200; TMP = 483 kPa	Ethynilestradiol	90	
		Filmtec NF90; TMP = 345 kPa	Atrazine	97	
RO	WWTP effluent	–	Ibuprofen	99	Sahar et al., 2011; Yangali–Quintanilla et al., 2011
	Secondary effluent	Filmtec TW30; TMP = 9.5–10.2 bar	Ibuprofen	>99	
		Filmtec TW30; TMP = 9.5–10.2 bar	Sulfonamides	>93	
		Filmtec TW30; TMP = 9.5–10.2 bar	Diclofenac	95	
		Filmtec TW30; TMP = 9.5–10.2 bar	Macrolides	>99	
		Filmtec TW30; TMP = 9.5–10.2 bar	Bisphenol A	>99	

[a] PES: polyethersulfone;
[b] RC: regenerated cellulose.

(triclosan, 87%; oxybenzone, 77%; progesterone, 56%). By contrast, for the less polar compounds, many permeate EDC/PPCP concentrations (14 out of the 25 compounds) were below detection, suggesting high removal efficiency by both NF and UF membranes. Better performance was also observed for NF.

RO generally shows great potential to partially or significantly remove micropollutants. Sahar et al. (2011) applied RO after CAS-UF and MBR processes and assessed its efficiency in eliminating micropollutants. The two processes, CAS-UF/RO and MBR/RO, exhitbited relatively similar and high elimination efficiencies: > 99% for macrolides, pharmaceuticals, cholesterol and bisphenol A, 95% for diclofenac, 97% for sulfamethoxazole, and > 93% for both sulfamethazine and trimethoprim. Despite the highly effective RO treatment, 28–223 ng/L residuals of ibuprofen, diclofenac, salicylic acid, cholesterol, and bisphenol A were detected in the permeates from both units. This elucidated that RO was not an absolute barrier for micropollutants and complementary treatment processes should be considered to aid the RO to achieve complete elimination of micropollutants. Yangali-Quintanilla et al. (2011) compared the various micropollutants (pharmaceuticals, pesticides, endocrine disruptors and others) removal by NF and RO. The elimination efficiency of NF membranes was very close to that achieved by RO membranes. The average retention efficiency by tight NF was 82% for neutral contaminants and 97% for ionic contaminants, while RO was able to achieve 85% removal of neutral contaminants and 99% removal of ionic contaminants.

2.4.5 Membrane bioreactor

The membrane bioreactor (MBR) process combines activated sludge biological treatment and membrane filtration (MF and UF). MBRs possess the following advantages over conventional wastewater treatment in the following aspects (Ngo et al., 2012) such as high effluent quality, excellent microbial separation ability, absolute control of SRTs and HRTs, high biomass content and less sludge bulking problem, low-rate sludge production, small footprint and limited space requirement, and possibilities for a flexible and phased extension of existing WWTPs.

Table 2.9 Removals of some micropollutants during MBR processes.

Water type	Membrane & experimental conditions	Compounds	Removal (%)	References
Raw wastewater	Full–scale HF [a] (Koch Puron); MA[b] 235 m^2; Pore size 0.1–0.2 μm; SRT: 10–15 d; HRT: 1 d; MLSS: 7.5–8.5 g/L	Ibuprofen	~100	Trinh et al., 2012
		Diclofenac	43	
		Carbamazepine	24	
		Sulfamethoxazole	60	
		Trimethoprim	30	
		Estrone,	~100	
		Estriol	~100	
		BisphenolA	~100	
Synthetic wastewater	Lab–scale Polyvinylidene fluoride HF; MA 0.2 m^2; Pore size 0.4 μm; HRT: 1 d or 3 d; MLSS: 2.3–4.6 g/L	Ibuprofen	~100	Bo et al., 2009
		Diclofenac	Minor	
		Carbamazepine	Minor	
Synthetic wastewater	Lab–scale Polyethylene hollow fibre; MA 0.2 m^2; Pore size 0.4 μm; HRT: 8, 6 and 4 h; SRT: 350 d; MLSS: 5.2–13.7 g/L	BisphenolA	>93.7	Chen et al., 2008

Hospital effluent	Pilot–scale Submerged PES UF flat sheet; Area 7 m^2; Pore size 38 nm; SRT: 30–50 d; MLSS: 2 g/L	Carbamazepine	–6	Kovalova et al., 2012
		Trimethoprim	96	
		Sulfamethoxazole	7	
		Atenolol	99	
Synthetic wastewater	Lab–scale submerged HF UF module; MA 0.047 m^2; Pore size 0.04 μm; SRT:70 d; HRT: 24 h; MLSS: 8.6–10 g/L	Ibuprofen	96.7 ± 0.7	Tadkaew et al., 2011
		Diclofenac	17.3 ± 4.2	
		Carbamazepine	13.4 ± 4.3	
		Sulfamethoxazole	91.9 ± 0.6	
		17β–estradiol	>99.4	
		17α–ethynylestradiol	93.5 ± 1.2	
		Bisphenol A	90.4 ± 3.1	
		Nonylphenol	99.3 ± 0.2	
		Atrazine	4.4 ± 3.7	
Hospital effluent	Full–scale 5 Kubota EK 400 flat sheet; Q 130 m/d	Ibuprofen	>80	Beier et al., 2011
		Carbamazepine	<20	
		Diclofenac	<20	

[a] hollow fiber;

[b] MA: membrane area.

MBRs are able to effectively remove a wide spectrum of micropollutants including compounds that are resistant to activate sludge processes (Radjenovic et al., 2009). This is because 1) They are able to retain sludge to which many compounds are adhered; 2) The membrane surface can also intercept the compounds; and 3) The longer SRT in MBRs may promote microbial degradation of the compounds (Spring et al., 2007). Table 2.9 summarizes some recent studies involving MBR processes. The removal of micropollutants in MBR can be affected by a number of factors, such as sludge age and concentration, existence of anoxic and anaerobic compartments, composition of the wastewater, operating temperatures, pH and conductivity (Kovalova et al., 2012).

Trinh et al. (2012) investigated the micropollutant removal efficiency of a full-scale MBR. High elimination (> 90%) was observed for most of the micropollutants. Nevertheless, some compounds were incompletely removed (24-–68%), including amitriptyline, carbamazepine, diazepam, diclofenac, fluoxetine, gemfibrozil, omeprazole, sulfamethoxazole and trimethoprim. Hence, these compounds were considered as potential indicators for evaluating the micropollutant removal using MBR processes. Generally, hospitals are the major source of many pharmaceuticals released into the environment (Verlicchi et al., 2010a). A pilot-scale MBR was employed for on-site treatment of hospital effluent (Kovalova et al., 2012). The overall reduction of all pharmaceuticals and metabolites was only 22%, as a large fraction (80%) of the feed was persistent iodinated contrast media. However, if the iodinated contrast media were not taken into account, the reduction would be up to 90%. Full-scale MBR studies for hospital wastewater treatment were also investigated by Beier et al. (2011), which suggested that separation of rainwater collection and water streams with low pharmaceutical concentrations, and maintenance of sludge age > 100 days should be considered in the design of MBR for hospital wastewater treatment.

Biological treatment combined with membrane filtration (MF or UF) are also employed for treating wastewater. Sahar et al. (2011) compared the removals of several macrolide, sulphonamide and trimethoprim antibiotics from raw sewage using a fullscale CAS system coupled with a subsequent UF filtration (CAS–UF) and

a pilot scale MBR. Antibiotics removal in the MBR system was generally higher than that in the CAS–UF system. The elimination of trimethoprim, sulfamethoxazole and erythromycin was 99%, 70%, 61% in the MBR system, and 45%, 52% and 71% in the CAS–UF system, respectively. It was assumed that antibiotics removal in both systems was due either to sorption to biomass (rather than biological transformation) or to enmeshment in the membrane biofilm (as the pore size of UF is significantly larger than the antibiotic molecules).

Recently, membranes in conjunction with anaerobic reactors have been gaining popularity due to their intrinsic advantages over aerobic systems, such as low sludge production, net energy generation and a fully enclosed environment (Hu and Stuckey, 2006). The applications of anaerobic MBRs for micropollutant removal have been investigated in some recent studies (Abargues et al., 2012; Xu et al., 2008). A pilot-scale submerged anaerobic MBR (SAnMBR), a conventional activated sludge (CAS) unit and a pilot-scale aerobic MBR were evaluated for removing some alkylphenols and hormones (Abargues et al., 2012). The observed concentrations of alkylphenols in the SAnMBR effluent were consistently at significantly higher levels than those in the permeates from other units, indicating the ineffective removal of alkylphenols by SAnMBR.

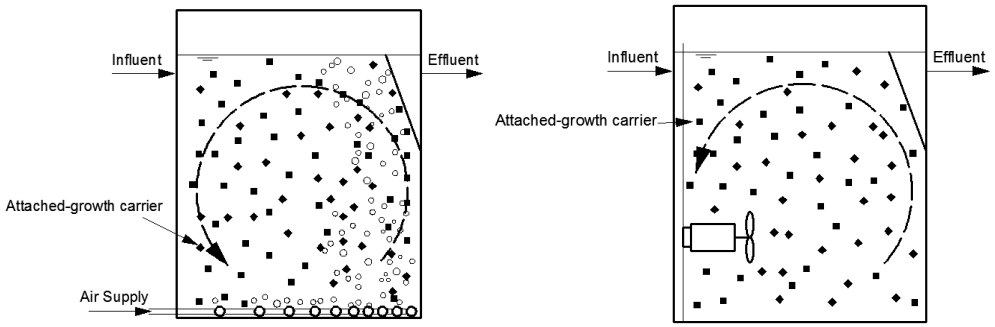
During MBR processes, several operational parameters (e.g. SRT, HRT and temperature) can influence the reduction of micropollutants. In general, MBRs have high SRTs, thus diverse microorganisms, including some slow growing bacterial, can reside in the reactors. When biomass is rich in nitrifying bacteria, higher biodegradation efficiency for certain micropollutants can be achieved (Roh et al., 2009). De Gusseme et al. (2009) reported a high elimination (99%) of 17α-ethinylestradiol (at initial concentration of 83 ng/L1) when a nitrifier enrichment culture was applied in a MBR. The degradation of micropollutants by nitrifying bacteria has also been evaluated in other types of systems (e.g., activated sludge and fixed bed reactor) (Batt et al., 2006; Forrez et al., 2009; Zhou and Oleszkiewicz, 2010). A general conclusion drawn from these studies is that nitrifying conditions have positive effects on micropollutant removal. Temperature variability has been linked to decrease in bulk water quality parameters and unreliability of system, as

microbial growth and activity as well as solubility and other physicochemical properties of organics are significantly affected by temperature (Hai et al., 2011). Effects of temperature variation were explored in a lab scale. MBR treating wastewater containing selected micropollutants (Hai et al., 2011). Both hydrophobic compounds (logD > 3.2) and less hydrophobic compounds (logD < 3.2) showed reduced elimination at 45 °C, which was ascribed to disrupted metabolic activity typically linked to such elevated temperature. The removal of hydrophobic compounds was unaffected in the temperature range of 10–35 °C, while a relatively more obvious variation was found in the removals of less hydrophobic compounds.

2.5 Moving bed bioreactor (MBBR)

2.5.1 Description of the MBBR

Over the recent years, the moving bed bioreactor has emerged as an effective treatment option for a range of wastewaters in terms of organic matter removal, ammonia nitrification and total nitrogen removal. MBBR is a completely mixed and continuously operated attached-growth reactor where the biomass is grown on inert carriers that circulate in suspension in the reactor (Shore et al., 2012). The biomass attached to the carriers is enclosed in a biofilm (self-produced extracellular polymeric matrix) which improves structural integrity, bacterial protection and intercellular communication, formation and maintenance of the microcolony, and capturing and consumption of nutrients (Huang et al., 2014). The circulation of carriers (Figure 2.5) in the reactor is caused by aeration in an aerobic reactor or by mechanical stirring when anoxic or anaerobic treatment is used (Jahren et al., 2002).



(I) Aerobic MBBR treatment (II) Anaerobic MBBR treatment

Figure 2.5 Diagrams of aerobic and anaerobic or anoxic systems for MBBR technology

The MBBR technology has demonstrated high full-scale applicability for a broad range of wastewaters. It has been used for the aerobic and anoxic treatment of municipal wastewater, landfill leachate, aquaculture water, pulp and paper industry waste, poultry processing wastewater, cheese factory wastes, refinery and slaughter house waste, phenolic wastewater, pharmaceutical wastewater and dairy wastewater (Boley et al., 2000; Hu et al., 2013; Kermani et al., 2008; Kulikowska et al., 2009; Rusten et al., 2006). Currently, there are more than 400 full-scale wastewater treatment plants employing MBBRs in 22 different countries throughout the world (Rusten et al., 2006). The major strength of the moving bed techniques is that they incorporate the advantages of different biological treatment technologies (e.g. activated sludge and biofilm systems). Demonstrated superiorities of employing MBBRs include 1) reduced space requirement as compared with traditional activated sludge systems, 2) ease in facility modification and upgradation, 3) lower headloss as compared to submerged filter configurations, 4) elimination of backwashing costs, 5) high volumetric efficacies and improved process stability, 6) higher resistance to extreme loading conditions (e.g., fluctuations in pH, nutrient concentration, toxic substances), and 7) increased solid retention favouring slow growing organisms, such as nitrifiers. (Guo et al., 2010; Shore et al., 2012).

2.5.2 Attached-growth carriers for MBBRs

Moving bed attached-growth carriers have great variation in material composition, shape, specific surface area and treatment capabilities (Levstek et al., 2009). Plastic carriers (Figure 2.6) are the original and most used moving bed carriers. These polyethylene carriers are small cylinder-shaped carriers with a cruciform support in the inside and grooved structure on the outside (Jahren et al., 2002). The carrier filling ratio commonly ranges between 40–70%. The carriers have a theoretical attached-growth area of approximately 465 m^2m^{-3} at the standard filling ratio of 67% (Ødegaard et al., 2006). The effective attached-growth area is estimated to be approximately 350m^2m^{-3} (Jahren et al., 2002).

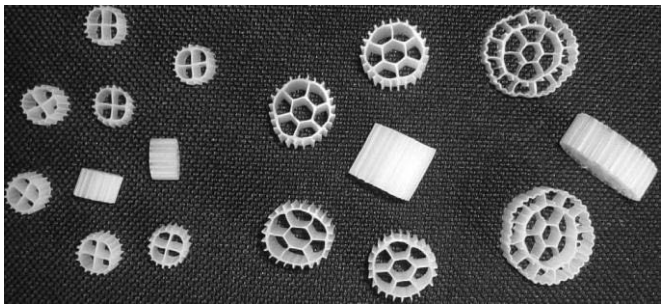


Figure 2.6 Kaldnes type K1, K2 and K3 (from left to right) biofilm carriers (Rusten et al., 2006)

Due to their high efficiency and practicality, Kaldnes-like carriers have been deemed the most suitable carriers for MBBR treatment (Ødegaard et al., 2006). However, these plastic-based carriers are not easily manageable after the end of their life cycle. The disposal of these carriers is often associated with high cost and technical difficulty. With the development of polymer science, affordable and feasible polymers from natural sources have been discovered and/or synthesised to produce sustainable and biodegradable plastic (bioplastic) (Accinelli et al., 2012). In this context, a fair amount of research has been directed toward employing biodegradable carriers in the MBBR systems. For instance, Accinelli et al. (2012) proposed a MBBR using bioplastic–based carriers (Figure 2.7). The carrier was composed of a cylinder and four rods. Cylinders were the screw neck (internal diameter and height of 2 cm) obtained from water bottles made of biopolymer. Four bioplastic hollow rods were inserted crosswise to the wall of the cylinder. Chu and Wang (2011) applied 20% filling ratio of biodegradable polycaprolactone (PCL) carrier for the treatment of wastewater with a low C/N ratio. They found PCL carrier not only served as support for attached growth but also provided carbon sources for the biological denitrification process.

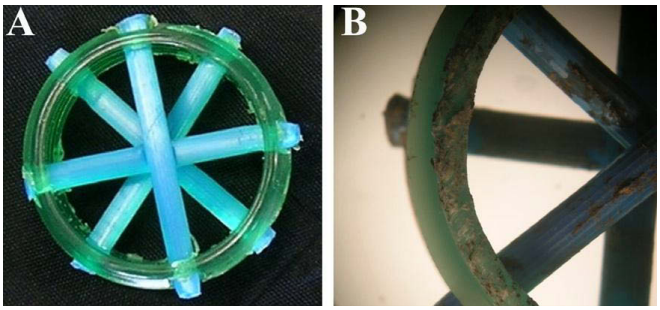


Figure 2.7 Bioplastic-based moving bed biofilm carrier (virgin carrier, A) and (carrier with biofilm, B) (Accinelli et al., 2012).

Polyvinyl alcohol (PVA, Figure 2.8) gel has also been used for manufacturing moving bed attached-growth carriers (Rouse et al., 2007). The PVA carriers (in the form of 4-mm beads) have a specific gravity of 1.025. These carriers are generally hydrophilic and possess high porosity with low solid contents (10%) and intertwining micro-tunnels (10–20 μm in diameter) within the beads. The beads are typically used at much lower filling ratios of 5 to 15% as compared with 50 to 70% for other carriers.

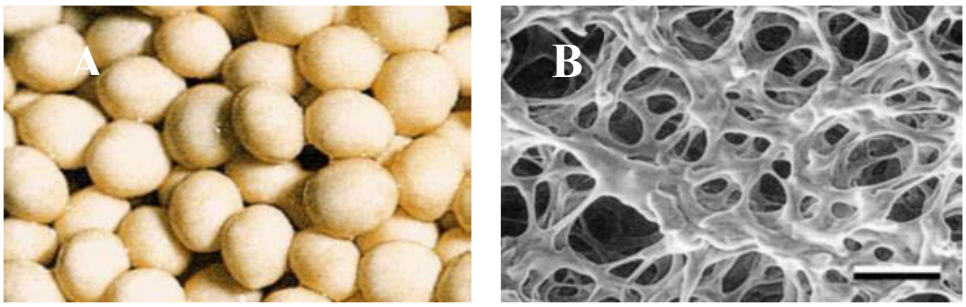


Figure 2.8 PVA gel beads (A) and Environmental scanning electron micrograph of the structure on the surface of an unused PVA gel bead (Rouse et al., 2005)

The use of polyurethane foam (sponge, Figure 2.9) for microbial immobilization has been reported by some wastewater researchers (Guo et al., 2010). The sponge is a highly porous material with cell counts ranging between 45 and 90 cells per 25 mm. The carriers are commonly prepared by cutting polyurethane foam into small cubes (with side lengths ranging from 1 mm to 3 mm). The typical filling ratios reported in previous studies were 10% and 20% (Guo et al., 2010; Chu and Wang, 2011). In addition to providing attached-growth support, polyurethane foam has demonstrated to be able to reduce cake layers formed on the surface of the membrane when membrane-coupled MBBRs were applied (Guo et al., 2010).

Figure 2.9 Polyurethane sponge cubes with attached-growth biomass

2.5.3 MBBR applications in wastewater treatment

The applications of MBBR can be arranged in many flow schemes (e.g., organic removal, nitrification, pre- and post-denitrification, see Figure 2.10). The selection of suitable flow schemes should be based on site-specific treatment targets, wastewater characteristics, WWTP layout, hydraulic profile and the feasibility of retrofitting existing treatment systems.

In most applications, MBBRs were able to achieve efficient removal of organic matter. In general, the biodegradable and soluble fraction of organic matter can be rapidly removed in the reactors, while the particulate organic matter is normally partially eliminated by adsorbing to the irregularities of the sludge (Ødegaard et al., 2006). Di Trapani et al. (2010) suggested that the addition of moving bed carriers is a good solution to enhance organic removal at high loading rates. Due to the compactness of MBBRs, the residence time in the reactors for effective organic matter removal is generally low (15–90 min, according to the organic loading rate and the strength of the influent) (Ødegaard et al., 2006).

In addition to high BOD removal efficiency, MBBRs have well-proven nitrification ability (Guo et al., 2010), as these reactors fulfil the necessary requirements (e.g., high sludge age) for developing adapted and specialized biomass for ammonia oxidation (Bassin and Dezotti, 2011). Denitrification can be achieved by systems with a pre- or post- denitrification process. The denitrification process is commonly affected by the nitrate concentration biodegradable COD and DO concentration (Ødegaard et al., 2006). Efficient denitrification only takes place under special conditions (sufficient carbon source and anoxic environments). Therefore, a reduced denitrification rate may be observed when the influent is deficient in organic substances or rich in oxygen.

To demonstrate the effectiveness of MBBRs for organic matter and nutrient removal, the major findings from some recent studies were collected and presented in Table 2.10. The reviewed studies mainly focused on municipal wastewater applications, but it should be noted that the employment of MBBRs for industrial wastewater treatment is also commonly encountered.

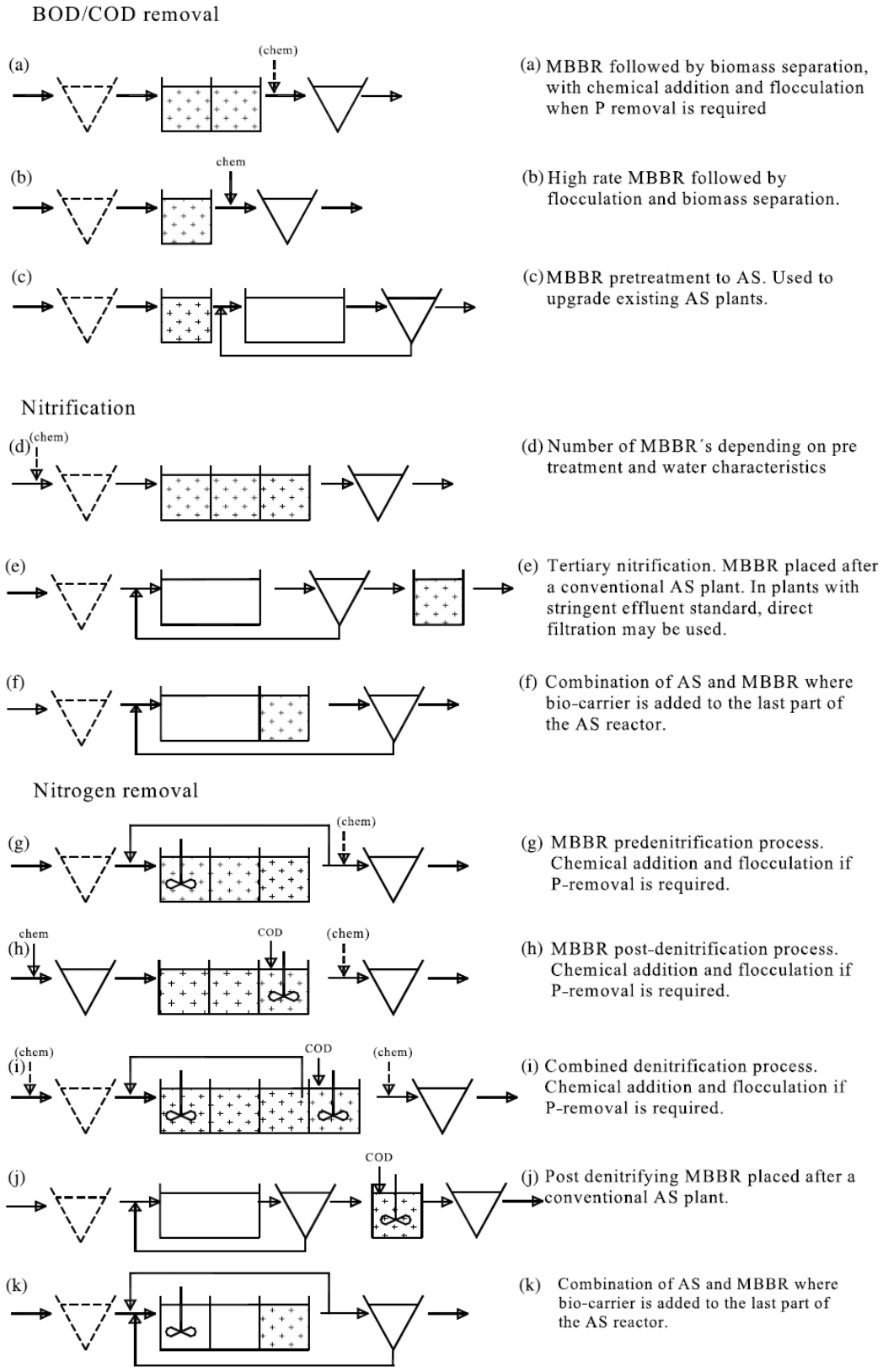


Figure 2.10 Typical process flow schemes for different MBBR applications

Table 2.10 Recent publications on MBBR applications

References	Details of the treatment system	Major findings
Chu and Wang, 2011	Description: comparison of MBBRs using polyurethane (PU) foam and biodegradable polymer (PCL). Watewater: synthetic wastewater. Carrier: PU and PCL. Filling ration: PU (16.7%); PCL (20%) Volume: 6 L HRT: 40, 24, 16, 14 h.	The reactor with PU yielded higher reduction of TOC and ammonia as compared with the one with PCL. (90% and 65% for PU; 72% and 56% for PCL). Variations in the COD/TN ratio of the influent did not affect the elimination efficiency of TOC and ammonia in both reactors. Regarding TN removal, the reactor with PCL showed much higher SND ability (59% removal of TN), as the biodegradable polymer could act as an effect electron donor for denitrification. By contrast, the reactor with PU achieved minor TN removal (1–20%).
Di Trapani et al., 2010	Description: comparison between pre-anoxic AS and pre- anoxic MBBR. Wastewater: municipal wastewater. Carrier: AnoxKaldnes^{TM} K1. Filling ratio: 30%. Volume: 6 L (anoxic), 12 L (aerobic). HRT: 12, 6 h for aerobic reactor	When low COD loading (14 g TCOD/day) was used, two systems obtained similar removals (~83%) of COD, indicating that the attached-growth sludge did not make an extra contribution to the COD elimination process. On the other hand, high COD-loaded (30 g TCOD/d) wastewater was only efficiently treated in the hybrid MBBR, suggesting that this system could be used in highly loaded WWTPs. As for ammonia removal, the hybrid MBBR showed slightly better performance and was able to sustain high ammonia loading rate.
Gong et al., 2012	Description: a lab-scale plug-flow A/O reactor. Wastewater: rural domestic wastewater. Carrier: polypropylene ring. Filling ratio: 20%. Volume: 64L with V_{anoxic}:V_{oxic}:$V_{settler}$ = 3:4:1 HRT: anoxic 7.2 h; oxic 9.6 h; settler 2.4 h	The hybrid A/O biofilm reactor operated under long SRT showed high applicability for wastewater treatment in rural areas. In spite of the low carbon-to-nitrogen ratio (2.5–4) in the influent wastewater, simultaneous nitrification–denitrification (SND) was in the range between 37.7–42.2 % in the MBBR.The TN removal remained higher than 69% in the hybrid system and seemed to be independent of the internal recycle ratios.

Guo et al., 2010	Description: sponge biofilter (SBF) and sponge batch reactor (SBR). Wastewater: synthetic wastewater. Carrier: polyurethane foam. Filling ratio: 10, 20%. Volume: 2 L (SBF), 4 L (SBR). HRT: 1.33 h (SBF), 8 L (SBR)	In the experiments with SBF, increased sponge thickness led to decreased organic and nutrient removal and 1 cm sponge exhibited the highest TN and TP removals (39.9% and 61.0% for S45R and 51.7% and 89.1% for S90R, respectively) as compared with 2 and 3 cm sponges, suggesting the sponge thickness could affect the efficacy of attached-growth biomass for pollutant removal. The filling ratio played an important role in phosphorus removal but had minor effects on the reduction of TOC and TN. With sponge volume increased from 10% to 20%, the S90R sponge obtained an enhanced TP removal of 99% and 100% within short retention times (6 h and 3 h, respectively), whereas S45R sponge was less effective (68.7% and 69.2% of TP removal within 8 h).
Kermani et al., 2008	Description: a laboratory scale MBBR with anaerobic, anoxic (two) and aerobic units in four separate reactors. Wastewater: municipal wastewater. Carrier: FLOCOR-RMP® media. Filling ratios: 50, 50, 50, 70 %. Volumes: 3.33, 3.33, 3.33, 10 L. HRTs: 4, 4, 4, 12 h.	The denitrification process in the second anoxic unit removed most of the biodegradable organic substances. The aerobic phosphate uptake rate displayed a good correlation to the anaerobic phosphate release rate. High nitrification (99.72%) was achieved in the aerobic reactor. As a whole, the lab-scale MBBR system demonstrated very high removal efficiency of organics and nutrients removal, with average dissolved COD, nitrogen and phosphorus removals of 96.9, 84.6 and 95.8%, respectively.
Kulikowska et al., 2009	Description: a two-stage MBBR process Wastewater: landfill leachate. Carrier: polyethylene carriers. Filling ratio: 30%. Volume: 10 dm^3 each.	Complete nitrification (>99%) was obtained in the two-stage reactors at ammonium load of 0.14 g $N\text{-}NH_4/m^3 \cdot d$. Nitrate was the principal product of nitrification. The increase of ammonium load to 0.27 g $N\text{-}NH_4/m^3 \cdot d$ and 0.36 g $N\text{-}NH_4/m^3 \cdot d$, lead to lower nitrification efficiency (86.3% and 58.6%, respectively).

Despite the advantages mentioned above, one principal drawback of MBBR application is the decrease of sludge settleablility when the WWTP is highly loaded with organic matter. This may cause severe operational problems when clarifiers are employed as solid separation systems. This limitation can be solved by adding coagulants (metal salts or cationic polymers) or applying membrane filtration or floatation as the solid separation process (Ødegaard et al., 2006). To date, various MBBR-based MBRs have been developed and investigated for their performance in treating a wide array of wastewaters, such as municipal wastewater, seafood processing wastewater, tannery wastewater (Table 2.11). AS-based MBR applications are often subjected to severe fouling due to high biomass concentrations, while MBBR-MBRs are effective alternative strategies to significantly reduce biofouling, and, at the same time, are capable of handling high loads of soluble and particulate pollutants (Leiknes and Ødegaard, 2007).

2.5.4 Micropollutant removal during MBBR processes

In spite of the extensive investigations on the MBBR treatment of traditional contaminants (COD and nutrients), little attempt has been made to evaluate the micropollutant removal in MBBRs. Nevertheless, the results from some bench-scale studies demonstrated that MBBR technology is a promising treatment method for eliminating micropollutants from wastewater. Falås et al. (2012) compared the micropollutant removal in batch experiments with activated sludge and suspended biofilm carriers (K1, AnoxKaldnes). Although biofilm carriers and activated sludge exhibited similar removal rate constants for ibuprofen (around 2–5 L/g biomass·d) and naproxen (around 0.5–1 L/g biomass·d), significantly higher removal rate constansts (per unit biomass) of diclofenac, ketoprofen, gemfibrozil, clofibric acid and mefenamic were found in the reactors with carriers (0.06–0.38, 0.9–3.6, 0.6–2.1, 0.05–0.17 and 0.08–0.48 L/g biomass·d, respectively) as compared with activated sludge (0–0.02, 0.01–0.32, 0.01–0.27, 0–0.04 and 0–0.06 L/g biomass·d, respectively). Their subsequent study (Falås et al., 2013) confirmed that a reactor with biofilm carriers (Bio-film Chip M, AnoxKaldnes) achieved rapid removals of diclofenac (1.3–1.7 L/g biomass·d) and trimethoprim (1.0–3.3 L/g biomass·d), while the elimination of both compounds in the suspended-growth treatment system was found to be insignificant (≤0.1 L/g biomass·d).

Table 2.11 Recent publications on MBBR-MBR applications

References	Details of the of study	Major findings
Yang et al., 2013	Description: a comparative study between a conventional membrane bio-reactor (CMBR) and a moving bed membrane bioreactor (MBMBR). Wastewater: synthetic wastewater. Carrier: nonwovens carrier. Filling ratio: 30%. Volume: 30 L. HRT: 12 h.	MBMBR and CMBR achieved comparable organic matter removal, with average COD removals being 95.6% and 96.2%, respectively. As for TN removal, MBMBR seemed less affected by the variation of COD/TN ratio. Even operated at low COD/TN ratio (8.9), MBMBR achieved good NH_4-N and TN removals of above 80% and 70%, respectively. The investigations on membrane fouling showed that MBMBR experienced more severe fouling as compared with CMBR. Such finding can be explained by the sludge bulking occurring at the final stage of the study.
Artiga et al., 2005	Description: an innovative membrane hybrid bioreactor composed by an aerobic MBBR and an ultrafiltration membrane module. Wastewater: fish-canning and tannery wastewaters. Carrier: polyethylene rough product Filling ratio: 20%. Volume: 5.5 L. HRT: 1.3, 2.6 h.	System was able to simultaneously achieve high COD and ammonia removal rates at high nitrogen loading rate (NLR = 1.8 kg $N\text{-}NH_4/m^3 \cdot d$) and organic loading rate (OLR = 6.5 kg $COD/m^3 \cdot d$) during the treatment of fish-canning wastewater. Specifically, the COD removal and nitrification efficiencies were 99% and 50–60%, respectively. On the other hand, treatment with tannery was also subjected to high OLR (4.5 kg $COD/m^3 \cdot d$) and NLR (1.2 kg $N\text{-}NH_4/m^3 \cdot d$). Similar COD elimination (95%) and much higher ammonia removal (97%) were observed.
Guo et al., 2010	Description: a sponge-submerged membrane bioreactor (SSMBR). Wastewater: synthetic wastewater. Carrier: polyurethane foam. Filling ratio: 10%. Volume: 8L.	The organic removals remained high (96%) and were independent of variations in filtration flux (10–20 L/m^2 h) and pH (5–8). Ammonium removal increased with the increase of pH value. At filtration rates of 10 L/m^2 h (HRT of 4.1 h) and 15 L/m^2 h (HRT of 2.74 h), complete nitrification was achieved at the pH range of 6.0–7.5. The longer HRT improved TP removal. Under the pH of 5.5–7, more than 91% of TP was eliminated. When pH was increased above 7, the TP removal reduced noticeably (<90%).

In another study with MBBR, Accinelli et al. (2012) suggested that the addition of moving bed carriers could enhance the removal of bisphenol A, oseltamivir and atrazine by 34%, 49% and 66%, respectively. Li et al. (2011) focused their study on simultaneous PAC adsorption within a MBR. During the treatment, PAC could not only act as an adsorbent but also provided support for biomass growth. With a high PAC dosage of 1.0 g/L, enhanced elimination of sulfamethoxazole and carbamazepine was observed in the PAC-amended MBR system (82% and 92% respectively) in comparison with the MBR system alone (both 64%).

2.6 Conclusion

Considerable research effort has been directed toward the assessment of occurrence of micropollutants in the aquatic environment. In particular cases, the occurrence levels of some micropollutants in surface waters were much higher than their PNECs, which revealed an environmental concern. WWTP effluent has been considered as the primary source of many micropollutants in aquatic systems. Given their diverse properties and low concentrations, micropollutant removal in current WWTPs is incomplete, ranging from 12.5% to 100% according to the literature data. Biological treatment is commonly unable to remove polar persistent micropollutants. However, its efficacy can be improved under favorable conditions (e.g., extended SRT and HRT, warm temperature, and fine tuning redox conditions). Although advanced treatment technologies have been demonstrated to be promising alternatives for micropollutant removal, there are concerns, such as high operation costs and formation of by-products and concentrated residues.

Although MBBR processes have not been applied broadly and specifically to micropollutant removal, the results from some recent bench-scale studies showed that they are promising methods for reducing discharges of micropollutants. By addition of moving carriers, an increased microbial community can be maintained in the system, which facilitates the growth of slow-growing microorganisms for micropollutant removal (Serrano et al., 2011). As a consequence, micropollutant removal by MBBR is a strategy showing excellent possibilities and is likely to be the subject of considerable future research.

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Chapter 3

Experimental Investigation

3.1 Introduction

This chapter describes the materials, experimental setups and analytical methods used for the batch experiments, the MBBR system and the MBBR-SMBR system. The batch experiments with non-acclimatized and acclimatized sponge were conducted initially to evaluate short-term removal rates of the selected micropollutants. Subsequently, the continuous bench-scale MBBR was set up for a long-term assessment of micropollutant removal. Finally, the MBBR-MBR system was investigated in terms of its micropollutant removal efficiency and membrane fouling.

3.2 Materials

3.2.1 Synthetic wastewater

A synthetic wastewater (simulating medium strength municipal wastewater primary effluent) spiked with micropollutants was used in this study. A concentrated stock solution was prepared according to Table 3.1. The stock solution was stored in a refrigerator at 4 °C. The synthetic wastewater was produced by diluting the stock solution with tap water and was fed continuously and evenly to the treatment system to avoid any fluctuation in the feed concentration and provide a sufficient source of biodegradable organic pollutants such as glucose, ammonium sulphate and potassium dihydrogen orthophosphate. The synthetic wastewater contains chemical oxygen demand (COD) of 320–360 mg/L, total organic carbon (TOC) of 100–120 mg/L, NH_4-N of 13–16 mg/L, NO_2-N of 0–0.02 mg/L, NO_3-N of 0.4–1.1 mg/L and PO_4-P of 3.0–3.5 mg/L. $NaHCO_3$ or H_2SO_4 was used to adjust the pH in the MBBR and SMBR to a constant value of 7.

3.2.2 Selected micropollutants

A set of 22 frequently detected and diversely structured compounds were selected (Table 3.2, Nguyen et al., 2012) to represent five important groups of micropollutants, namely pharmaceuticals and personal care products (PPCPs), pesticides, hormones and industrial chemicals. A concentrated stock solution containing 100 mg/L of each micropollutant was prepared in pure methanol and kept

in a freezer. The stock solution was added to attain an initial concentration of 5 µg/L for each compound during both batch and continuous experiments (MBBR).

Table 3.1 Composition and concentration of the stock solution

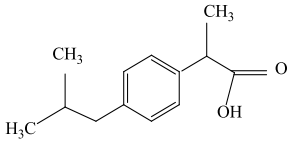
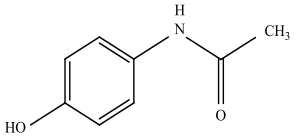
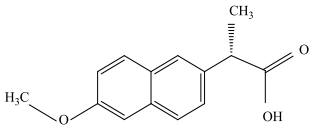
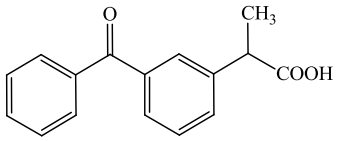
Compound	Chemical formula	Molecular weight (g/mol)	Concentration (mg/L)
Organics and nutrients			
Glucose	$C_6H_{12}O_6$	180.0	280
Ammonium sulfate	$(NH_4)_2SO_4$	132.1	142
Potassium phosphate	KH_2PO_4	136.1	26
Trace nutrients			
Calcium chloride	$CaCl_2 \cdot 2H_2O$	147.0	0.368
Magnesium sulfate	$MgSO_4 \cdot 7H_2O$	246.5	5.07
Manganese chloride	$MnCl_2 \cdot 4H_2O$	197.9	0.275
Zinc sulfate	$ZnSO_4 \cdot 7H_2O$	287.5	0.44
Ferric chloride anhydrous	$FeCl_3$	162.2	1.45
Cupric sulfate	$CuSO_4 \cdot 5H_2O$	249.7	0.391
Cobalt chloride	$CoCl_2 \cdot 6H_2O$	237.9	0.42
Sodium molybdate dihydrate	$Na_2MoO_4 \cdot 2H_2O$	242.0	1.26
Yeast extract			30

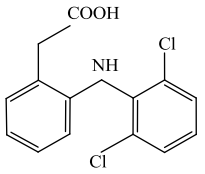
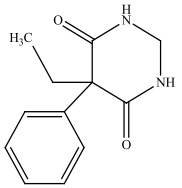
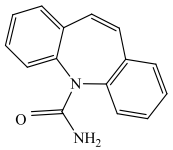
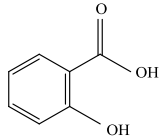
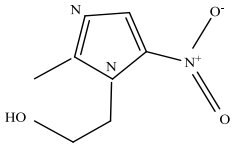
3.2.3 Sponge (polyurethane foam)

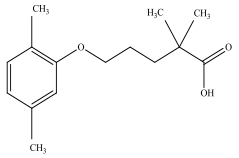
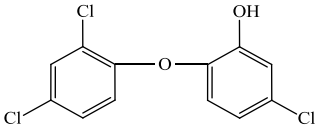
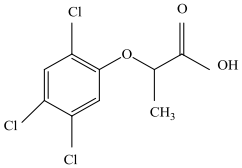
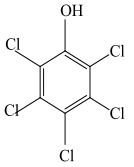
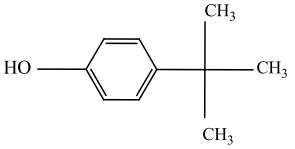
The biofilm carriers were made of reticulated sponge S28/80R (Joyce Foam Products), composed of skeletal strands and containing a homogenous structure of evenly sized air cells. The sponge has a density of 28–30 kg/m^3 with 80 cells per 25 mm. The sponge was cut into small sponge cubes (2 cm × 2 cm × 2 cm, Figure 3.1). Before the experiments, the sponge was acclimatized using activated sludge fed with synthetic wastewater without the addition of micropollutants.

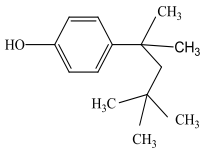
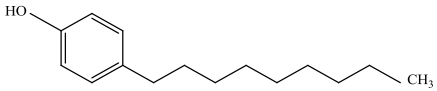
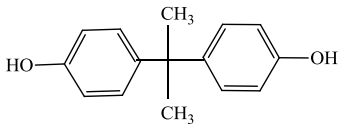
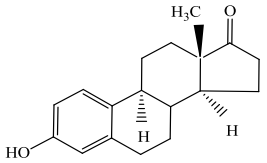
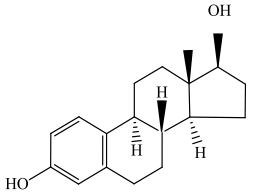
Figure 3.1 The attached-growth carriers (sponge cubes) used in this study

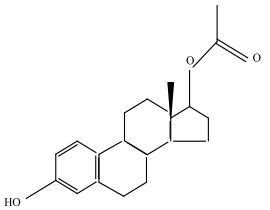
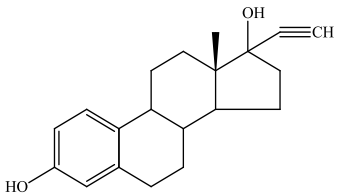
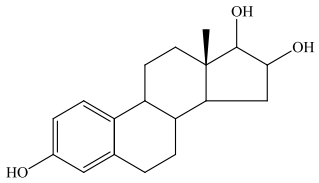
Table 3.2 Physicochemical properties of the selected trace organics

Category	Compound	CAS number	Molecular weight (g/mol)	Log K_{OW}[a]	Log D (pH 7)[a]	Dissociation constant[a] (pKa)	Water solubility (mg/L)[b]	Vapor pressure[a] (mm Hg), at 25°C	Chemical structure
Pharmaceuticals	Ibuprofen ($C_{13}H_{18}O_{2)}$	15687-27-1	206.28	3.50 ± 0.23	0.94	4.41 ± 0.10	21	1.39E-4	
	Acetaminophen ($C_8H_9NO_{2)}$	103-90-2	151.16	0.48 ± 0.21	0.47	9.86 ± 0.13 1.72 ± 0.50	14000	1.43E-6	
	Naproxen ($C_{14}H_{14}O_{3)}$	22204-53-1	230.26	2.88 ± 0.24	0.73	4.84 ± 0.30	16	3.01E-7	
	Ketoprofen ($C_{16}H_{14}O_{3)}$	22071-15-4	254.28	2.91 ± 0.33	0.19	4.23 ± 0.10	16	3.32E-8	

Diclofenac ($C_{14}H_{11}Cl_2NO_{2)}$	15307-86-5	296.15	4.55 ± 0.57	1.77	4.18 ± 0.10 -2.26 ± 0.50	2.4	1.59E-7	
Primidone ($C_{12}H_{14}N_2O_{2)}$	125-33-7	218.25	0.83 ± 0.50	0.83	12.26 ± 0.40 -1.07 ± 0.40	500	6.08E-11	
Carbamazepine ($C_{15}H_{12}N_2O$)	298-46-4	236.27	1.89 ± 0.59	1.89	13.94 ± 0.20 -0.49 ± 0.20	18	5.78E-7	
Salicylic acid ($C_7H_6O_{3)}$	69-72-7	138.12	2.01 ± 0.25	-1.13	3.01 ± 0.10	2240	4.45E-5	
Metronidazole ($C_6H_9N_3O_{3)}$	443-48-1	171.15	-0.14 ± 0.30	-0.14	14.44 ± 0.10 2.58 ± 0.34	9500	2.67E-7	

	Gemifibrozil ($C_{15}H_{22}O_3$)	25812-30-0	250.33	4.30 ± 0.32	2.07	4.75	19	6.13E-7	
	Triclosan ($C_{12}H_7Cl_3O_2$)	3380-34-5	289.54	5.34 ± 0.79	5.28	7.80 ± 0.35	10	3.36E-5	
Pesticides	Fenoprop ($C_9H_7Cl_3O_3$)	93-72-1	269.51	3.45 ± 0.37	- 0.13	2.93	71	2.13E-6	
	Pentachloro-phenol (C_6HCl_5O)	87-86-5	266.34	5.12 ± 0.36	2.58	4.68 ± 0.33	14	3.49E-4	
Surfactants and industrial chemicals	4-tert-butylphenol ($C_{10}H_{14}O$)	98-54-4	150.22	3.39 ± 0.21	3.40	10.13 ± 0.13	580	0.0361	

	4-tert-octylphenol ($C_{14}H_{22}O$)	140-66-9	206.32	5.18 ± 0.20	5.18	10.15 ± 0.15	5	1.98E-3	
	4-n-nonylphenol ($C_{15}H_{24}O$)	104-40-5	220.35	6.14 ± 0.19	6.14	10.15	6.35	8.53E-5	
	Bisphenol A ($C_{15}H_{16}O_{2)}$	80-05-7	228.29	3.64 ± 0.23	3.64	10.29 ± 0.10	120	5.34E-7	
Steroid hormones	Estrone ($C_{18}H_{22}O_{2)}$	53-16-7	270.37	3.62 ± 0.37	3.62	10.25 ± 0.40	677	1.54E-8	
	17-β-estradiol ($C_{18}H_{24}O_2$)	50-28-2	272.38	4.15 ± 0.26	4.15	10.27	3.9	9.82E-9	

17-β-estradiol – acetate ($C_{20}H_{26}O_3$)	1743-60-8	314.42	5.11 ± 0.28	5.11	10.26 ± 0.60	na	9.88E-9	
17-α ethinylestradiol ($C_{20}H_{24}O_2$)	57-63-6	269.40	4.10 ± 0.31	4.11	10.24 ± 0.60	11.3	3.74E-9	
Estriol (E3) ($C_{18}H_{24}O_3$)	50-27-1	288.38	2.53 ± 0.28	2.53	10.25 ± 0.70	441	1.34E-9	

[a] Source: SciFinder database https://scifinder.cas.org/scifinder/view/scifinder/scifinderExplore.jsf

[b] Source: http://chem.sis.nlm.nih.gov/chemidplus/

na: data not available

3.3 Experimental setup and operation protocol

3.3.1 Batch experiments

Batch experiments were conducted using 15 L fully-aerated tanks (working volume = 10 L; aeration rate = 1.5 L/min; dissolved oxygen (DO) = 5–6 mg/L) filled with different volumetric ratios of acclimatized or non-acclimatized (virgin carrier without attached biosolids) sponge. Four filling ratios (0%, 10%, 20% and 30%) were initially examined. With the fixed aeration rate, unsatisfactory and non-uniform carrier circulation was observed at 30% filling ratio; therefore this ratio was excluded in subsequent investigations. Samples for micropollutant (300 mL), TOC (30 mL) and nutrient (30 mL) analyses were collected from the tanks at 0, 2, 6, 12 and 24 h during the 24-hour batch test. When the wastewater sample was withdrawn from the tank, a corresponding quantity of sponge cubes were taken out simultaneously to maintain the initial filling ratios (10% or 20%).

Table 3.3 Operational conditions of the batch experiments

Tank	Filling ratio (%)	Carrier	Sampling time (h)	Volume of wastewater (L)
1	0	-	0, 2, 6, 12, 24	10
2	10	Acclimatized sponge	0, 2, 6, 12, 24	10
3	10	Non-acclimatized sponge	0, 2, 6, 12, 24	10
4	20	Acclimatized sponge	0, 2, 6, 12, 24	10
5	20	Non-acclimatized sponge	0, 2, 6, 12, 24	10

3.3.2 MBBR system

A bench-scale MBBR system with a working volume of 40 L was used in the study (Figure 3.2). The reactor was filled with 20 % (determined from the batch experiments) of acclimatized sponge cubes. Due to the refractory nature of some micropollutants, a prolonged hydraulic retention time (HRT), comparable to that in previous MBR studies (Nguyen et al., 2013; Wijekoon et al. 2013), was deemed necessary for efficient removal of the micropollutants. Thus, the HRT in this study was longer than the typical HRTs (less than 15 h) applied in WWTPs.

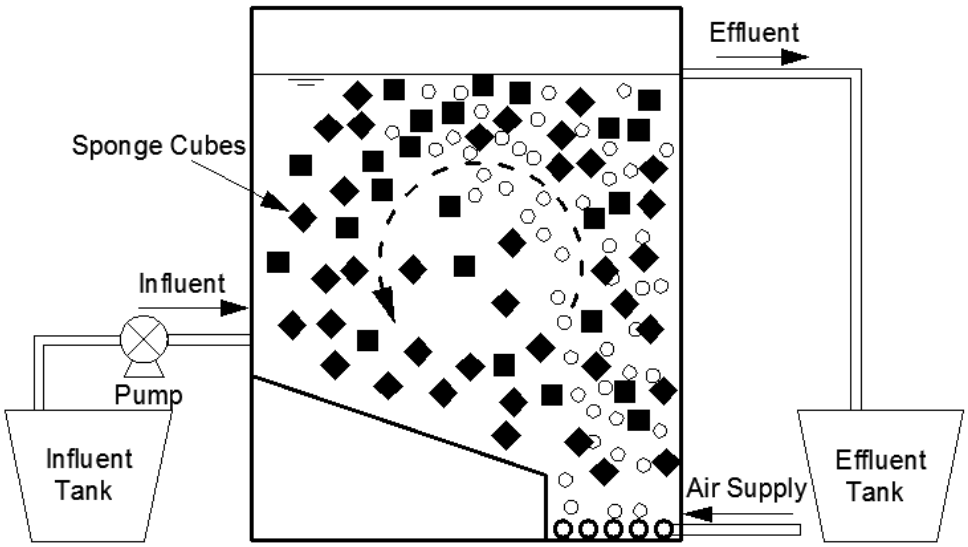


Figure 3.2 On-site photo and schematic diagram of the MBBR

Accordingly, the reactor had a flow rate of 27.8 mL/min and a COD loading of 0.32–0.36 kg/ (m^3·d). To avoid excessive detachment of the biosolids within the sponge cubes, the aeration of the MBBR was adjusted to around 4 L/min to achieve gentle circulation of the sponge cubes. The DO concentration of the MBBR was in the range between 5.5–6.5 mg/L. Before the experiment with addition of micropollutants, the MBBR system was acclimatized to the synthetic wastewater (without addition of micropollutants) for 20 days until TOC, TN, and PO_4-P removal became stable. After the acclimatization stage, micropollutant-bearing wastewater was continuously introduced to the MBBR and the investigation of micropollutant removal was carried out over a period of 150 days.

Every five days, 300 mL of influent and effluent aqueous samples were collected in duplicate for micropollutant analysis. Effluent samples were centrifuged at 3000 rpm for 30 min to improve filterability. The influent and centrifuged effluent samples were filtered with 1μm glass microfiber filter paper (47 mm DIA, Filtech) and acidified to pH 2 with 4 M HCl for subsequent solid phase extraction (SPE).

To assess the extent of sorption of micropollutants on biosoilds (in suspension and on the sponge cubes), mixed liquor and sponge samples were withdrawn on Day 70 and Day 100. The sludge within the sponge cubes was collected by squeezing the cubes. Subsequently, the micropollutants were extracted from sludge using a solvent extraction method previously described by Wijekoon et al. (2013, Figure 3.3). The sludge sample was initially centrifuged. The obtained pellet was freeze-dried for 4 h in an Alpha 1-2 LDplus Freeze Dryer (Christ GmbH, Germany). The dried sludge was ground to powder and 0.5 g of the dried sludge powder was transferred to a glass test tube. 5 mL of methanol was added to the test tube, followed by thorough mixing in a vortex mixer (VM1, Ratek, Australia) for 3 min and ultrasonic extraction for 10 min at 40 °C. The sample was then centrifuged at 3270 × g for 10 min (Alleegra X-12R, Beckman Coulter, USA) and the supernatant was stored in a glass beaker for subsequent analysis. Dichloromethane (5 mL) and methanol (5 mL) were added to the remained sludge. The above mentioned process of mixing, ultrasonic extraction and centrifugation was repeated. The supernatants from both steps were then mixed in a beaker. Milli-Q water was added into the beaker to fill up a solution volume of

50 mL. The residual methanol and dichloromethane were purged using nitrogen gas. Finally, Milli-Q water was filled in to obtain an aqueous sample of 500 mL.

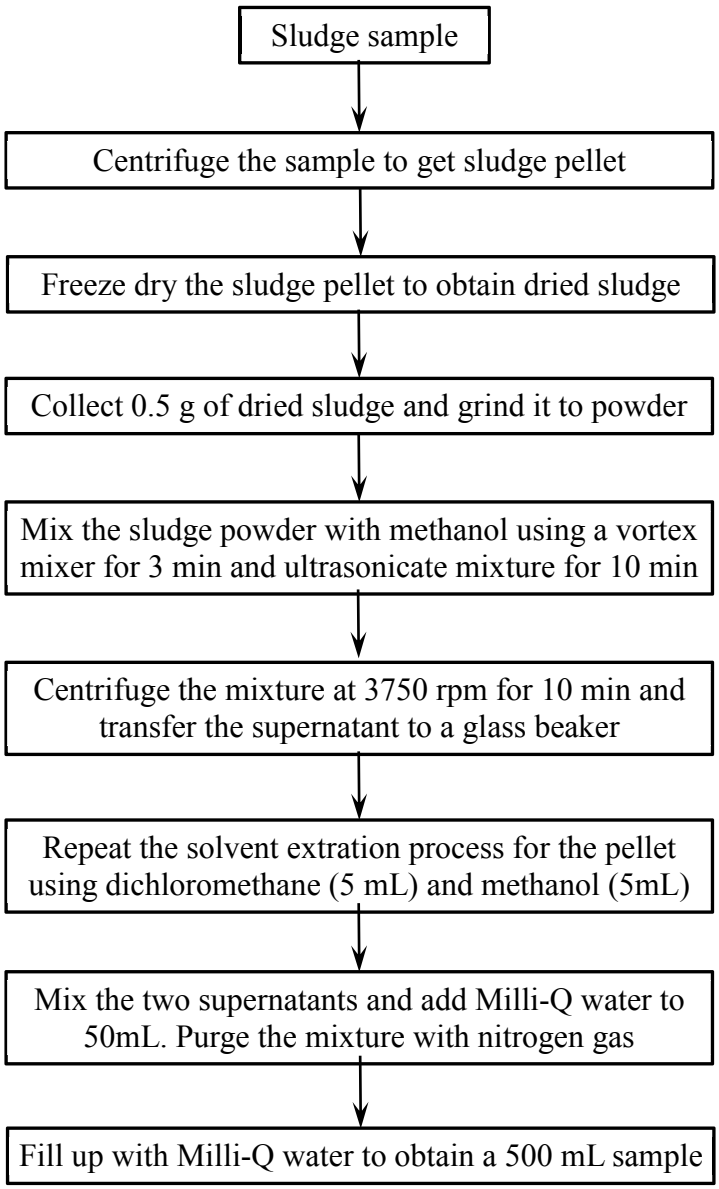


Figure 3.3 Schematic diagram of solvent extraction process of sludge samples

3.3.3 MBBR-SMBR system

The MBBR-SMBR system (Figure 3.4) consisted of the MBBR described above and an SMBR (working volume: 10 L). The membrane used for the SMBR was a polyvinylidene fluoride (PVDF) hollow fiber module with a pore size of 0.2 μm and surface area of 0.2 m^2. A buffer tank was used between the MBBR and the SMBR. The sludge retained in the buffer tank was withdrawn every day to avoid undesired microbial activity or micropollutant desorption. The SMBR permeate flow was controlled by a suction pump in order to obtain a constant flux of 8.83 L/m2·h.

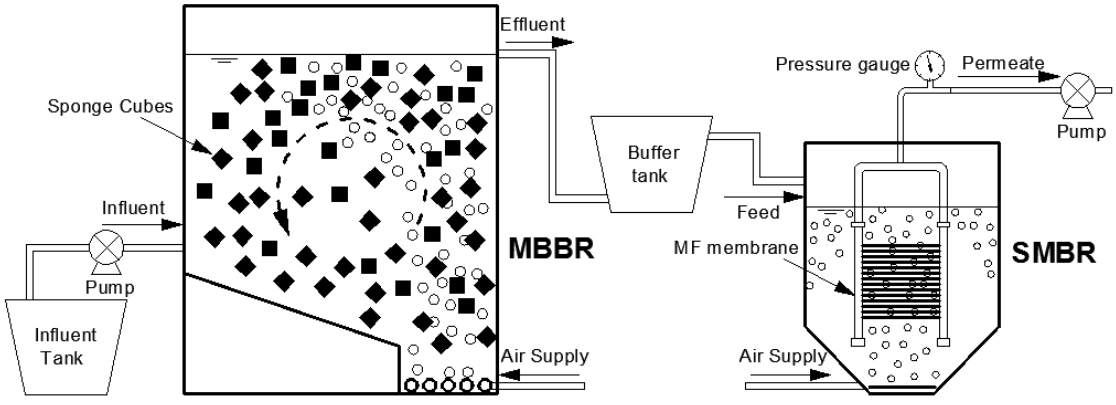


Figure 3.4 On-site photo and schematic diagram of the MBBR-SMBR system

A pressure gauge was used to measure the transmembrane pressure (TMP). A soaker hose air diffuser was mounted at the bottom of the SMBR unit to provide aeration (6L/min). The DO concentrations were in the range of 6.4–7.6 mg/L. The SMBR was operated in a continuous mode and no backwash or cleaning was carried out during the operation. Samples for the analyses of soluble microbial products (SMP) and extracellular polymeric substance (EPS), sludge hydrophobicity, zeta potential and particle distribution were collected at TMPs of 3, 10, 15, 20, 23, 26, 29, 32 and 35 kPa.

3.4 Analytical methods

3.4.1 Organic matter, nutrients, pH and DO

TOC of the influent and effluent was measured using a TOC analyzer (Analytikjena Multi N/C 2000, Figure 3.5). The analysis of COD was carried out according to Standard Methods (APHA, 1998). NH_4-N, NO_2-N, NO_3-N and PO_4-P were measured by spectrophotometric method using Spectroquant Cell Test (NOVA 60, Merck, Figure 3.5). The pH and DO of the reactor were measured everyday using pH meter (Hach Company, model no. HQ40d) and DO meter (Horiba Ltd. Japan, model no. OM -51E), respectively (Figure 3.5).

3.4.2 MLSS and MLVSS

The measurement of biosolids (monitored as mixed liquor suspended solids, MLSS) and biomass (monitored as mixed liquor volatile suspended solids, MLVSS) concentrations was conducted based on the method described in Standard Methods (APHA, 1998). A well-mixed sample was first filtered with 1μm glass microfiber filter paper (47 mm DIA, Filtech). The retained residue on the filter was dried in an oven at 105 ºC for 2 h. The increment in weight of the filter paper indicates the total SS in the sample. Subsequently, the filter paper was ignited in a furnace at 550 ºC for 20 min. The weight reduced during ignition represents the volatile SS in the sample. The attached-growth biosolids was obtained by hand squeezing the sponge cubes and rinsing the squeezed cubes with Mill-Q water.

Figure 3.5 The analytical instruments used in this study, including Analytikjena Multi N/C 2000 (A), Hach HQ 40d Portable Meter (B), Photometer NOVA 60 A Spectroquant (C), and Horiba OM-51 Portable Dissolved Oxygen Meter

3.4.3 Micropollutants

Oasis® HLB 6 cc cartridges (containing polymeric reversed-phase sorbent) were used for the SPE process (Figure 3.6). After SPE, the cartridges were kept in a freezer and sent to the University of Wollongong for gas chromatography-mass spectrometry (GC-MS) analysis within one month.

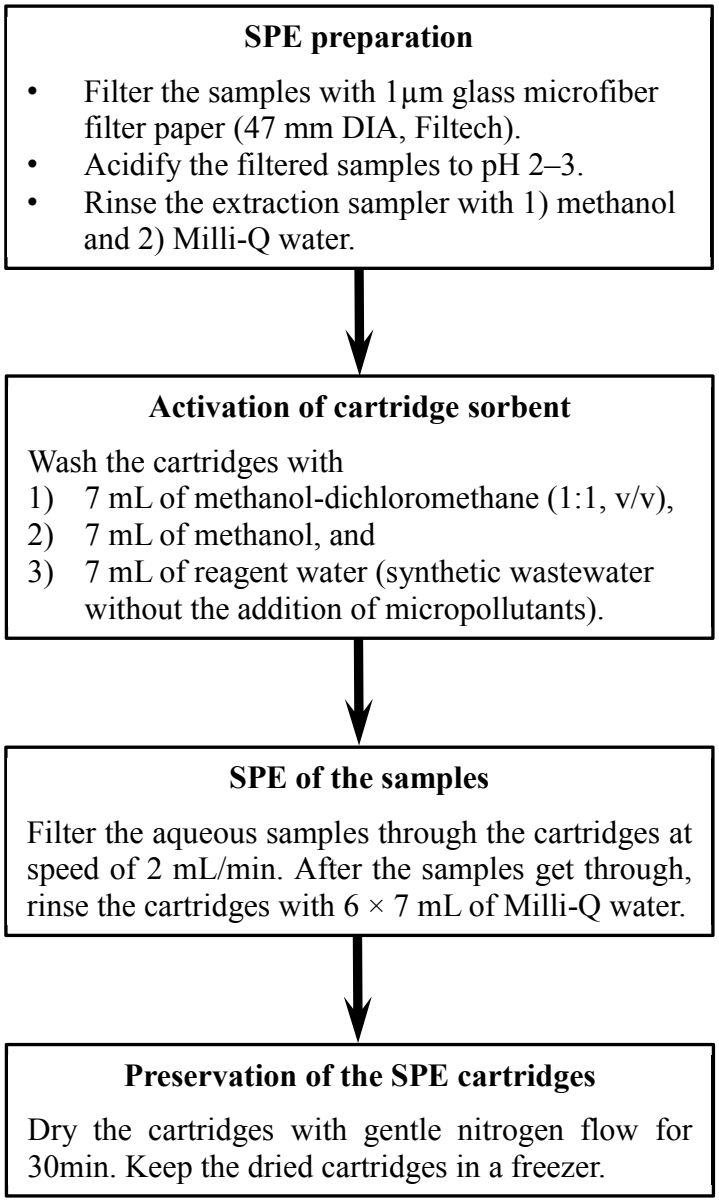


Figure 3.6 Schematic diagram of SPE process for GC-MS analysis of micropollutants

3.4.4 Fouling resistance

Fouling resistance of the SMBR was determined after the MBBR-SMBR experiment by applying the resistance-in-series model described by Choo and Lee (2006):

$$J = \Delta P/\mu R_T \quad (1)$$

$$R_T = R_M + R_C + R_P \quad (2)$$

Where J is the permeation flux; ΔP is the transmembrane pressure; μ is the dynamic viscosity of the permeate; R_T is total resistance; R_M is the intrinsic membrane resistance; R_C is the cake layer resistance; and R_P is the pore blocking resistance. To analyze each membrane resistance, a membrane cleaning process was carried out as follows:

1. To determine cake layer resistance: gently shake the membrane in a tank filled with distilled water until the cake layer on the membrane surface was completely removed. The decrease in membrane resistance before and after the physical cleaning represented the cake layer resistance.

2. To obtain pore blocking resistance: firstly clean the membrane with 0.5% citric acid for 6 hours to remove inorganic scaling deposit; then apply 6 hours' sodium hydroxide (0.4%) wash to eliminate organic substance; lastly immerse the membrane in 0.8 % sodium hypochlorite for 6 hours to destroy microorganisms. The pore blocking was determined by calculating the difference between the membrane resistances before and after the chemical cleaning.

The samples for SMP and EPS analysis were prepared as follows (Figure 3.7). A 30 mL of mixed liquor sample was drawn from the SMBR and immediately centrifuged at 3,000 rpm for 30 min. The supernatant and sludge pellet were collected separately. The supernatant was centrifuged again at 3000 rpm for 30 min, followed by a filtration process through 0.45 μm of Whatman 934-AH glass fiber filter (to ensure the particles and bound EPS were removed). The filtered sample was kept in the refrigerator for subsequent SMP analysis. The previously obtained sludge pellet was re-suspended in 30 mL of phosphorus buffer solution. Cation exchange resin was added to the solution and a centrifuge process was then performed at 900 rpm for 2h to extract EPS from the pellet. The centrifuged EPS sample was filtered using 1.2

μm Whatman 934-AH glass fiber filter (in order to separate particles) and then stored in the refrigerator. The SMP and EPS samples were analysed for proteins (SMP_P and EPS_P) and polysaccharides (SMP_C and EPS_C) concentrations using Anthrone-sulfuric acid and modified Lowry method (Sigma, Australia) method, respectively.

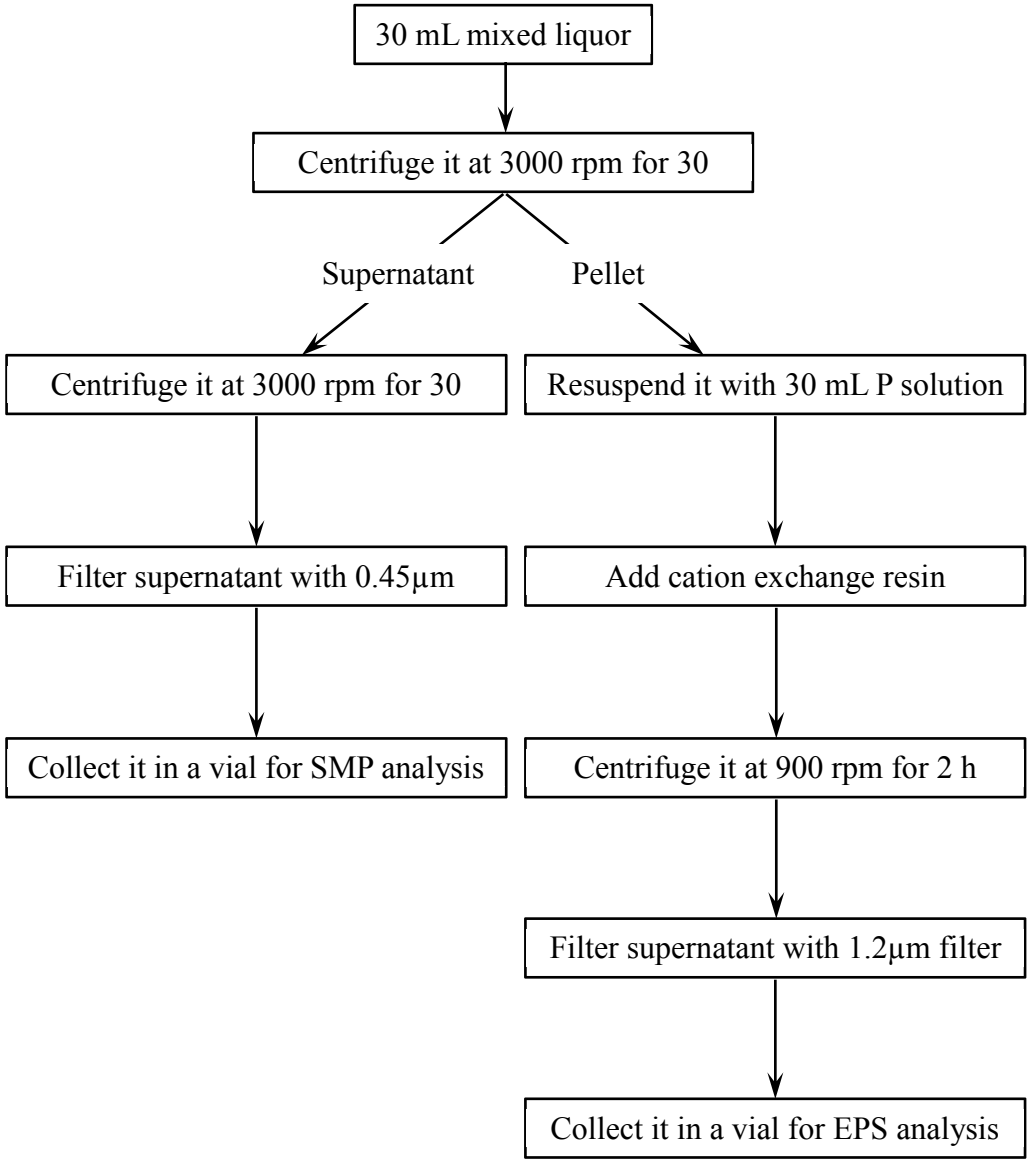


Figure 3.7 Schematic diagram of processes for SMP and EPS extraction

Several physical properties of mixed liquor in the SMBR were analyzed, including relative hydrophobicity (RH), zeta potential, and particle size distribution. RH is determined by analyzing the distribution of sludge between mixed liquor and hydrocarbon. 50 mL mixed liquor and 50 mL n-hexane were added in a separatory funnel (Figure 3.8) and shaken by hand vigorously for 30 min. The mixture was then

allowed to settle for 30 minutes to achieve complete separation of the two solvents. The concentration of suspended solids ($MLSS_e$) in the aqueous phase was measured. RH was calculated by RH (%) = (1-$MLSS_e$/$MLSS_i$) × 100%, where $MLSS_i$ is the initial concentration of suspended solids in the mixed liquor. The surface charge of sludge flocs (represented by Zeta potential) was measured by Zetasizer Nano ZS (Malvern Instruments, UK). Olympus System Microscope Model BX41 (Olympus, Japan, Figure 3.8) was used to obtain the images of sludge flocs for the subsequent examination of microorganisms and analysis of particle size distribution (using Image-Pro Plus software).

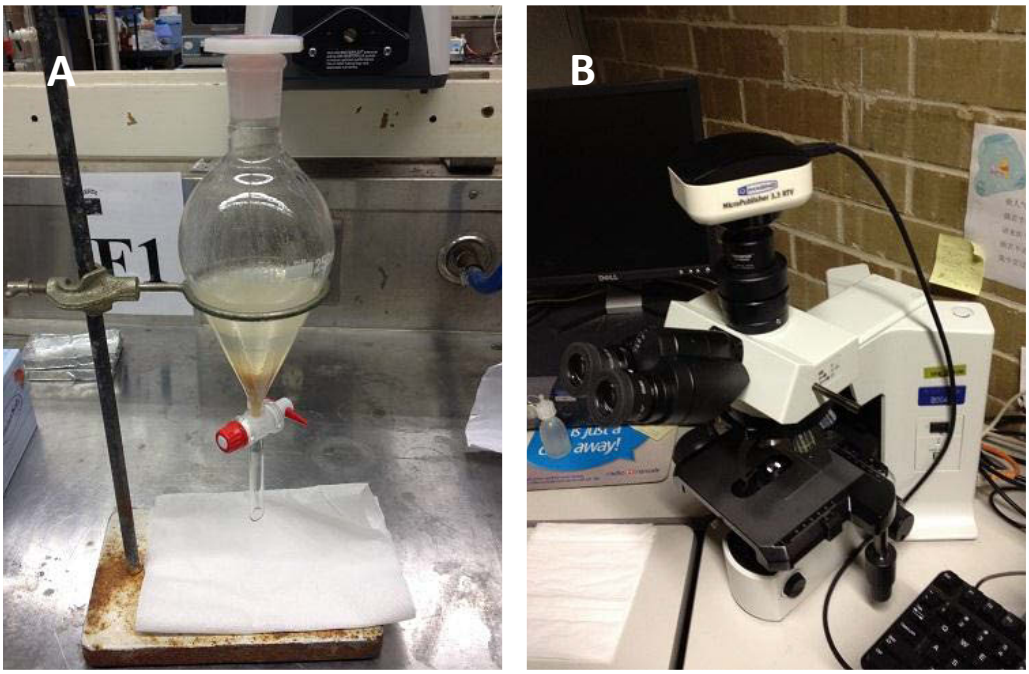


Figure 3.8 Relative hydrophobicity test (A) and microscopic analysis (B)

University of Technology, Sydney

Faculty of Engineering and Information Technology

Chapter 4

Short-term Micropollutant Removal in Batch Experiments

4.1 Introduction

Batch experiments are commonly conducted to evaluate the short-term contaminant removal efficiency and determine the optimal operational conditions for a specific treatment processes. Numerous studies have involved batch experiments to assess the fate and removal of micropollutants during suspended and attached growth biological treatment processes (Falås et al., 2012; Joss et al., 2006; Ternes et al., 1999; Yu et al., 2006). Ternes et al. (1999) performed aerobic batch experiments to explore the persistence of natural estrogens and contraceptives during activated sludge process. 17β-estradiol was rapidly transformed in the batch experiments at both spiking concentrations of 1 μg/mL and 1 ng/mL. It was found that after a period of 1–3 hours, more than 95% of the unconjugated 17β-estradiol was eliminated, while the estrone level rose to 95% relative to the initial 17β-estradiol level, suggesting that most 17β-estradiol was immediately oxidized to estrone. Regarding the batch experiments spiked with estrone, the behaviour of this compound at a concentration of 1 μg/mL was similar to that of 17β-estradiol. The estrone level decreased steadily to around 50% after 24 h without detection of any transformation products. The authors suggested that sorption contributed insignificantly to the removal of estrone and 17β-estradiol. In another study, Joss et al. (2006) carried out batch experiments using activated sewage sludge to characterize the biological transformation of various micropollutants, including pharmaceuticals, musk fragrances and estrogens. Based on their degradation constants k_{biol}, these compounds was grouped into three classes: 1) compounds with $k_{biol} < 0.1$ L/(g_{ss}·d) were not considerably eliminated (<20%); 2) compounds with $k_{biol} > 10$ L/(g_{ss}·d) were removed by more than 90%; 3) the rest experienced moderate degradation.

While the microplutant removal kinetics in activated sludge has been extensively investigated, no attempt, however, has been made to explore micropollutant elimination in sponge based MBBR batch experiments. This chapter reports the results of short-term micropollutant removal in the batch MBBR experiments using different filling ratios of non-acclimatized and acclimatized sponge as attached-growth carriers. The underlying removal mechanisms of non-acclimatized and acclimatized sponge is discussed. In addition, the removal of organic matter and nutrients during the batch experiments is also presented.

4.2 Organic and nutrients removal

Table 4.1 displays the variations in TOC, COD, NH_4-N, NO_2-N, NO_3-N, and PO_4-P levels during the batch experiments. The blank experiments exhibited insignificant removal of organic and nutrients. The removals of the TOC, COD, NH_4-N and PO_4-P were 2.5%, 3.1%, 3.8% and 2.8%, respectively. The experiments with non-acclimatized sponge also showed limited elimination. The removal efficiency was all below 15%. By contrast, acclimatized sponge could achieve organic and nutrient removal to some extents. High removal rates were observed for TOC and COD during experiments with 10 and 20% of acclimatized sponge and all the concentrations were significantly reduced within the first two hours. NH_4-N was moderately eliminated by acclimatized sponge, with the removal efficiencies being 54.1 % and 64.3 % for 10 and 20% of acclimatized sponge, respectively. High concentrations of NO_3 in the tanks suggested the limited denitrification ability of the sponge biomass. This can possibly be due to the high DO concentration (5–6 mg/L) during the experiments. The low PO_4 removal could be due to the high aeration level.

4.3 Removal of selected micropollutants

Table 4.2 shows the variations of compound concentrations in the tanks with no sponge (blank experiment), non-acclimatized sponge (10% or 20%) and acclimatized sponge (10% or 20%) during the 24-h operation time. Micropollutant removal can be achieved via four pathways, namely sorption onto biomass or carrier, biological degradation, air stripping and photolysis. As no or negligible micropollutant removals were observed during the blank experiment, air stripping and photolysis can be deemed as insignificant removal mechanisms for the micropollutants during the batch experiments.

With the non-acclimatized sponge (control experiments), biodegradation of micropollutants was not expected to occur due to the absence of biomass on the sponge. Hence, sorption was the major removal pathway for these compounds. Unlike other plastic attached-growth carriers, which showed no sorption capacity for micropollutants (Falås et al., 2012), the results from experiments with

Table 4.1 Variations of organic and nutrients levels (mg/L) during the batch experiments (aeration rate: 1.5 L/min; DO= 5–6 mg/L).

Substances	Sampling time (h)					Removal at 24h (%)
	0	2	6	12	24	
0% sponge						
TOC	102.7	101.9	102.1	101.8	100.1	2.5
COD	323	318	316	315	313	3.1
NH_4	13.1	13.0	13.3	12.9	12.6	3.8
NO_2	0.01	0.03	0.03	0.02	0.02	-
NO_3	0.9	1.1	0.9	1.3	1.2	-
PO_4	3.23	3.09	3.18	3.15	3.14	2.8
10% non-acclimatized sponge						
TOC	99.89	99.26	101.4	95.25	86.17	10.7
COD	328	326	321	299	291	11.3
NH_4	15.3	15.5	15.5	15.2	14.5	5.2
NO_2	0.03	0.03	0.15	0.18	0.05	-
NO_3	1.8	2.1	1.7	1.2	1.3	-
PO_4	2.97	3.11	2.88	2.79	2.66	10.4
20% non-acclimatized sponge						
TOC	100.6	100.0	99.51	94.54	86.19	14.3
COD	342	341	340	309	301	11.9
NH_4	14.2	14.2	14.4	14.1	14.0	1.4
NO_2	0.02	0.02	0.04	0.15	0.06	-
NO_3	1.1	1.1	1.8	0.2	1.5	-
PO_4	3.15	2.89	3.51	2.78	3.06	2.9
10% acclimatized sponge						
TOC	103.7	15.38	9.20	8.13	7.78	92.5
COD	318	67	48	28	18	94.3
NH_4	14.6	13.3	12.6	11.1	6.7	54.1
NO_2	0.03	0.3	0.38	0.2	0.05	-
NO_3	1.6	10.3	13.3	16.2	25.5	-
PO_4	3.24	1.69	2.78	3.25	2.55	21.3
20% acclimatized sponge						
TOC	104	11.26	9.38	7.98	7.58	92.7
COD	326	54	43	27	20	93.9
NH_4	16.8	14.4	13.2	12.1	6.0	64.3
NO_2	0.02	0.36	0.13	0.13	0.21	-
NO_3	0.9	13.9	9.5	15	24.5	-
PO_4	3.32	2.03	3.73	3.77	3.14	5.4

Table 4.2 Variations of micropollutant concentrations (ng/L) during the batch experiments (aeration rate: 1.5 L/min).

Compound[a]/ Condition[b]	0 h	2 h	6 h	12 h	24 h	% removal after 24h	Compound/ condition	0 h	2 h	6 h	12 h	24 h	% removal after 24h
ACM							GFB						
B	1666	1626	1598	1572	1629	2.2	B	3797	3612	3811	3537	3512	7.5
N(10)	1394	1329	1354	1263	1214	12.9	N(10)	2871	2751	2869	3117	2540	11.5
N(20)	1373	1306	1334	1220	1237	9.9	N(20)	3105	2583	2669	2760	2460	22.5
A(10)	1420	1106	751	794	785	44.7	A(10)	3797	2903	2714	2517	1398	63.2
A(20)	1951	1577	602	491	463	76.3	A(20)	3849	3443	1963	1389	634	83.5
BP							IBP						
B	3298	3172	2899	3071	3089	6.3	B	2940	2759	2885	2974	2943	1.0
N(10)	2549	1394	983	1003	889	65.1	N(10)	3051	2760	2897	2991	2814	7.8
N(20)	2621	954	977	1029	943	64.0	N(20)	3057	2714	2660	2997	2920	4.5
A(10)	3571	2386	1966	1543	1397	60.9	A(10)	3669	2917	2263	1414	697	81.0
A(20)	3591	1643	1583	1097	851	76.3	A(20)	3574	3354	719	623	480	86.6
BPA							KTP						
B	3665	3591	3124	3472	3212	12.4	B	4759	4677	4816	4670	4623	2.9
N(10)	3477	580	543	563	589	83.1	N(10)	4251	4226	3971	4137	4060	4.5
N(20)	3398	537	594	586	591	82.6	N(20)	4112	3954	3949	3811	3889	5.4
A(10)	4500	649	546	526	564	87.5	A(10)	5146	4194	4569	4412	2694	47.6
A(20)	4394	249	373	306	277	93.7	A(20)	4869	5189	3825	2783	1014	79.2
CBZ							MTZ						
B	3181	3355	3090	2967	3037	4.5	B	1132	1207	1082	1053	1164	-2.8
N(10)	3340	2849	2711	2489	2383	28.7	N(10)	1100	1063	1054	1077	1037	5.7
N(20)	2988	2509	2371	2377	2202	26.3	N(20)	1121	960	1049	934	1006	10.3

	A(10)	4463	3534	3574	3489	3699	17.1
	A(20)	4951	3766	3711	3809	2997	39.5
DCF							
	B	2745	2658	2798	2553	2599	5.3
	N(10)	2474	2209	2174	2097	1966	20.5
	N(20)	2984	1866	1729	2003	1916	35.8
	A(10)	2220	1823	1817	1171	920	58.6
	A(20)	2360	1291	1408	1011	563	76.1
E1							
	B	2123	1842	1958	2154	2031	4.3
	N(10)	1920	171	143	143	131	93.2
	N(20)	2212	83	77	74	102	95.4
	A(10)	2326	566	466	433	446	80.8
	A(20)	2246	69	286	183	160	92.9
E2							
	B	5340	5142	4833	4959	5461	-2.3
	N(10)	4446	460	377	366	346	92.2
	N(20)	4631	246	217	209	227	95.1
	A(10)	5177	154	80	120	133	97.4
	A(20)	4957	246	138	134	103	97.9
E2AC							
	B	2114	2209	1934	2195	1953	7.6
	N(10)	2260	51	94	37	14	99.4
	N(20)	1998	51	23	0	9	99.5
	A(10)	1551	1460	1426	1414	1238	20.2
	A(20)	1591	1571	1435	1520	1334	16.2
NP							
	B	1203	1106	934	1122	1006	16.4
	N(10)	1200	149	117	74	20	98.3
	N(20)	1001	117	74	83	48	95.2
	A(10)	1297	71	126	102	76	94.1
	A(20)	1089	94	192	111	123	88.7
NPX							
	B	3609	3748	3776	3641	3745	-3.8
	N(10)	3094	2717	2580	2789	2937	5.1
	N(20)	2867	2746	2631	2623	2594	9.5
	A(10)	3254	2714	2531	2102	1276	60.8
	A(20)	3303	3283	1802	740	57	98.3
OP							
	B	1857	1885	1954	2002	1843	0.8
	N(10)	1803	54	80	40	20	98.9
	N(20)	1808	80	31	34	37	98.0
	A(10)	1789	86	60	48	53	97.0
	A(20)	1943	66	61	34	43	97.8
PECP							
	B	2365	2413	2394	2086	2265	4.2
	N(10)	2417	2394	1993	1683	1580	34.6
	N(20)	2612	1097	940	943	671	74.3

	A(10)	1951	71	66	33	46	97.6		A(10)	2760	849	549	376	244	91.2
	A(20)	2194	69	111	0	34	98.5		A(20)	2697	1363	239	134	97	96.4
E3								PRM							
	B	2671	2744	2644	2643	2609	2.3		B	3194	3258	2965	3206	3010	5.8
	N(10)	2689	1994	1686	1777	1760	34.5		N(10)	3094	2069	1674	1834	1849	40.2
	N(20)	2534	1649	1380	1283	1219	51.9		N(20)	3111	1614	1366	1380	1262	59.4
	A(10)	2951	800	223	159	76	97.4		A(10)	3897	1600	1020	731	625	84.0
	A(20)	2794	1674	40	0	89	96.8		A(20)	2549	1640	928	460	229	91.0
EE2								SA							
	B	3256	3226	3386	3202	3180	2.3		B	4392	4496	4302	4272	3938	10.3
	N(10)	2786	89	80	77	66	97.6		N(10)	3706	3309	3397	3466	3340	9.9
	N(20)	2822	46	43	34	31	98.9		N(20)	3983	3129	3077	3020	3425	14.0
	A(10)	3180	186	109	60	61	98.1		A(10)	4034	1780	380	316	305	92.4
	A(20)	3163	14	97	97	123	96.1		A(20)	4046	1406	501	274	214	94.7
FNP								TCS							
	B	2462	2227	2260	2376	2419	1.7		B	2491	2559	2481	2447	2237	10.2
	N(10)	2217	2183	1900	2034	2097	5.4		N(10)	2406	46	74	23	29	98.8
	N(20)	2139	2057	2151	2160	1998	6.6		N(20)	2105	60	29	11	10	99.5
	A(10)	2571	2160	2151	2081	2198	14.5		A(10)	2574	57	49	48	50	98.1
	A(20)	2417	2394	1993	1683	1580	34.6		A(20)	2546	69	84	40	63	97.5

a ACM: acetaminophen; BP: 4-tert-butylphenol; BPA: bisphenol A; CBZ: carbamazepine; DCF: diclofenac; E1: estrone; E2: 17-β-estradiol; E2AC: β-estradiol 17-acetate; EE2: 17-α ethinylestradiol; E3: estriol; FNP: fenoprop; GFB: gemfibrozil; IBP: ibuprofen; KTP: ketoprofen; MET: metronidazole; NP: 4-n-nonylphenol; NPX: naproxen; OP: 4-tert-octylphenol; PECP: pentachlorophenol; PRM: primidone; SA: salicylic acid; TCS: triclosan;

b B: blank experiments (0 % fill ratio); N(10), N(20): non-accmilmatised sponge with filling ratio (10% or 20%) in the parentheses; A(10), A(20): acclimatised sponge with filling ratio (10% or 20%) in the parentheses.

non-acclimatized sponge revealed that sponge was able to adsorb, to varying extents, most of the studied micropollutants. This could be due to the presence of polar and non-polar functional groups in the structure of sponge material (Baldez et al., 2008). It was noted that the sorption of micropollutants onto sponge occurred promptly. The equilibrium was commonly reached within 2 hours. In the case of acclimatized sponge, the presence of attached biosolids (0.25 gMLSS/g sponge) resulted in biodegradation of micropollutants as well as sorption of these compounds onto biosolids. According to Falås et al. (2012), sorption onto biosolids is a rapid process and can reach equilibrium within 30 min for many micropollutants.

As shown in Table 4.2, bisphenol A, etrone, 17-β-estradiol, β-estradiol 17-acetate, 17-α ethinylestradiol, 4-n-nonylphenol, 4-tert-octylphenol and triclosan were considerably eliminated (>80%) during the first two hours in the experiments with either non-acclimatized sponge or acclimatized sponge, which indicates sorption played a significant role in the removal of these compounds. This could be explained by the high hydrophobicity (Log D > 3.2) of these compounds. However, a previous long-term investigation showed that nonylphenol (35% to 51%) and triclosan (11% to 41%) were only moderately sorbed during biological treatment.

Acetaminophen, diclofenac, gemfibrozil, ibuprofen, ketoprofen, naproxen and salicylic acid were hardly removed (mostly < 20%) with non-acclimatized sponge. The low sorption tendency of these chemicals was ascribable to the charge repulsion between the negatively charged compounds (with low acid dissociation constant, pK_a) and negatively charged sponge surface. By contrast, these micropollutants showed markedly improved reduction when acclimatized sponge was used. The large removal disparity between the use of non-acclimatized and acclimatized sponge might be attributed to two aspects, sorption onto biosolids on the sponge and biodegradation. The contribution of sorption onto biosolids could be estimated with the help of solid-water distribution coefficient (log D, as shown in supplementary data Table S1). Joss et al. (2005) reported that for compounds having a log D < 2.5, the sorption onto secondary sludge can be considered insignificant. As all the above mentioned compounds have log D values less than 2.5, their sorption onto biosolids could be deemed negligible. Hence, the removal of these compounds mainly resulted

from biodegradation, while sorption (onto sponge and biosolids) was of fairly limited importance. The rapid biodegradablility of ketoprofen, gemfibrozil, ibuprofen and naproxen has also been demonstrated in a previous study (Falås et al., 2012).

Despite its fairly low solid-water distribution coefficient, primidone exhibited moderate sorption onto non-acclimatized sponge (40.2% and 59.4 at 10% and 20% filling ratios, respectively). The acclimatized sponge could achieve even higher elimination (>80%) of primidone. Unlike other studied estrogenic hormones, estriol has a much lower log D value (2.53), which explains the less efficiency of estriol sorption onto non-acclimatized sponge (34.5% and 51.9% at 10% and 20% ratios, respectively). With the use of acclimatized sponge, the removal of estriol was significantly increased to above 95%. Pentachlorophenol was sorbed by 34.6% and 74.3% onto non-acclimatized sponge (10% and 20% filling ratios), respectively. Biodegradation seemed to contribute considerably to the elimination of pentachlorophenol. The tanks filled with 10% and 20% of acclimatized sponge were able to reduce the concentrations of penta-chlorophenol by 91.2 and 96.4%, respectively.

Carbamazepine, fenprop, and metronidazole were poorly eliminated (mostly < 30%) in the experiments with non-acclimatized and acclimatized sponge. The results suggest that these compounds were resistant to biodegradation and sorption during the experiments. The low sorption tendency of carbamazepine, fenprop and metronidazole could be implied by their low log D of 1.89, -0.13 and -0.14. The complicated compound structures of these substances might prevent them from being biologically transformed.

4.4 Effects of sponge filling ratios on micropollutant removal

Filling ratio had insignificant effects on micropollutant removal by non-acclimatized sponge, indicating that the amount of non-acclimiatized sponge was not a limiting factor (i.e. sponge was in excessive amounts) for sorption of these micropollutants. However, apparent sorption difference between two filling ratios was observed for a few micropollutants, including diclofenac (20.5% and 35.8%), estriol (34.5% and

51.9%), penta-chlorophenol (34.6% and 74.3%) and primidone (40.2% and 59.4%), with the 20% non-acclimatized sponge showing higher sorption capacity.

By contrast, the filling ratio seemed to have more significant effects on the experiments with acclimatized sponge. The elimination of many compounds was enhanced by increasing the filling ratio of acclimatized sponge. For instance, acetaminophen, carbamazepine, diclofenac, fenoprop, gemifibrozil, ketoprofen, and naproxen showed higher removals (76.3%, 39.5%, 76.1%, 34.6%, 83.5%, 79.2% and 98.3% respectively) at the filling ratio of 20% as compared with those (44.7%, 17.1%, 58.6%, 14.5%, 63.2%, 47.6% and 60.8% respectively) at the filling ratio of 10%. The elevated removals at the higher filling ratio (20%) were probably because of the increased amounts of microorganisms in the tank.

4.5 Conclusion

Batch experiments were carried out to evaluate the micropollutant removal in the tanks with acclimatized and non-acclimatized sponge. Prompt and significant sorption of bisphenol A, etrone, 17-β-estradiol, 17-α ethinylestradiol, 4-n-nonylphenol, 4-tert-octylphenol and triclosan occurred during the batch experiments with non-acclimatized sponge. Nearly complete removal of these compounds was found during the first 2 hours of experiments. The sorption behaviour of micropollutants could be reasonably estimated using the solid-water distribution coefficient. Acclimatized sponge involved biological processes and could therefore enhance the removal of some less hydrophobic and readily biodegradable micropollutants, such as acetaminophen, diclofenac, gemfibrozil, ibuprofen, ketoprofen, naproxen and salicylic acid. Due to the low solid-water distribution coefficients and complex chemical structures, carbamazepine, fenoprop and metronidazole exhibited very low removals during all the experiments, regardless the treatment conditions. Changing the filling ratio of non-acclimatized sponge did not significantly affect the removal of micropollutants. Increasing the filling ratio of acclimatized sponge could lead to elevated elimination of acetaminophen, carbamazepine, diclofenac, fenoprop, gemifibrozil, ketoprofen, and naproxen due to the presence of higher amounts of microorganisms.

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Chapter 5

Removal of Micropollutants by a Moving Bed Bioreator (MBBR) System

5.1 Introduction

The MBBR technology is a simple, effective and robust biological treatment process. It has demonstrated to be an excellent solution for organic matter removal and nitrogen reduction. The capability of MBBR to remove micropollutants has not been extensively investigated so far. Nevertheless, a few studies have shown that MBBR is a promising treatment method for eliminating micropollutants, especially the persistent compounds. A recent study was conducted to evaluate the performance of a pilot-scale MBBR filled with 50% polyethylene carriers in removing persistent micropollutants (iodinated contrast media), iohexol and diatrizoate, from municipal wastewater (Hapeshi et al., 2013). The MBBR unit consisted of four compartments, including denitrification (23.4 L), oxidation (24.0 L) and two nitrification bioreactors (9 L). The reductions of COD, BOD, total-N and total-P in the MBBR were fairly effective, with removal efficiency being >94%, >95%, >82% and >71%, respectively. The applied concentrations of iohexol and diatrizoate were 0.1 mg/L, 1mg/L, 10 mg/L and 20 mg/L. The results showed that at lower initial concentrations, higher removal efficiency of iodinated contrast media was observed. The author suggested that under real conditions, where the levels of iodinated contrast media were in the range between ng/L to μg/L, the removal efficiency would reach at least 79% for iohexol and 73% for diatrizoate. This indicates that MBBR is able to attain good removal of the micropollutants that are resistant to conventional treatment processes.

Previous MBBR studies on micropollutant removal have primarily focused on the MBBR using polyethylene carrier elements. However, to date, little attention has been paid to the application of MBBRs using sponge as attached-growth carriers. In this chapter, long-term (150 days) effectiveness of a sponge-based MBBR for removing five groups of micropollutants is presented and discussed based on compound's biodegradability and hydrophobicity. During the MBBR treatment, the micropollutants were subjected to biodegradation and sorption to different extents. To provide insight into their fate in the MBBR system, a mass balance for each compound was determined taking into consideration biodegradation, sorption to suspended biosolids and sorption to attached biosolids.

5.2 Organic and nutrient removal

During the study, a synthetic wastewater was used to provide continuous and stable sources of organic matter and nutrients. The synthetic wastewater generally contains COD of 320–360 mg/L, TOC of 100–120 mg/L, NH_4-N of 13–16 mg/L, NO_2-N of 0–0.02 mg/L, NO_3-N of 0.4–1.1 mg/L and PO_4-P of 3.0–3.5 mg/L. Figures 5.1, 5.2, 5.3 5.4 and 5.5 illustrate the influent and effluent concentrations of TOC, COD, NH_4-N, TN and PO_4-P as well as the corresponding removal efficiencies. The length of the study was 170 days, including 20 days of acclimatization period and 150 days of investigation period (with micropollutants addition).

Excellent and stable removals were achieved for TOC (92.6–95.8%) and COD (93.0–96.1%) and the effluent TOC and COD concentrations were 5.9 ± 0.6 mg/L and 18.6 ± 2.6 mg/L. NH_4-N removal was in the range between 73.6 and 95.6 % throughout the study. Despite the high DO concentration (5.5–6.5 mg/L) in the reactor, a distinctive DO gradient occurred toward the core of the sponge, leading to an anoxic/anaerobic condition inside the sponge and thereby facilitating partial denitrification (Guo et al., 2010). As a result, the MBBR system was able to achieve a TN removal of 45.2 ± 9.3 %. Although the PO_4-P removal was relatively high (around 89%) during 20-day acclimatisation period, the MBBR only achieved around 35% removal for the study period. The high PO_4-P removal during the acclimatization period could be due to the use of phosphate for biomass growth as well as the phosphorus uptake by phosphate accumulating organisms under the aerobic condition (Guo et al., 2010). On the other hand, biomass growth on the sponge slowed down after acclimatization, which could contribute to the lower but stable PO_4-P removal. Overall, the effluent NH_4-N, NO_2-N, NO_3-N and PO_4-P concentrations were 3.0 ± 0.8, 0.03 ± 0.02, 5.9 ± 1.7 and 1.4 ± 0.7 mg/L, respectively. It is noteworthy that the addition of micropollutants did not affect the biomass growth as well as organic matter and nutrient removal efficiency. Previous investigation also revealed that the production and settling properties of biosolids as well as COD removal did not vary significantly in the presence of micropollutants (Dionisi et al., 2007). Nevertheless, in that study, the ammonia removal efficiency was apparently reduced from 82% (without micropollutants) to 29–37%.

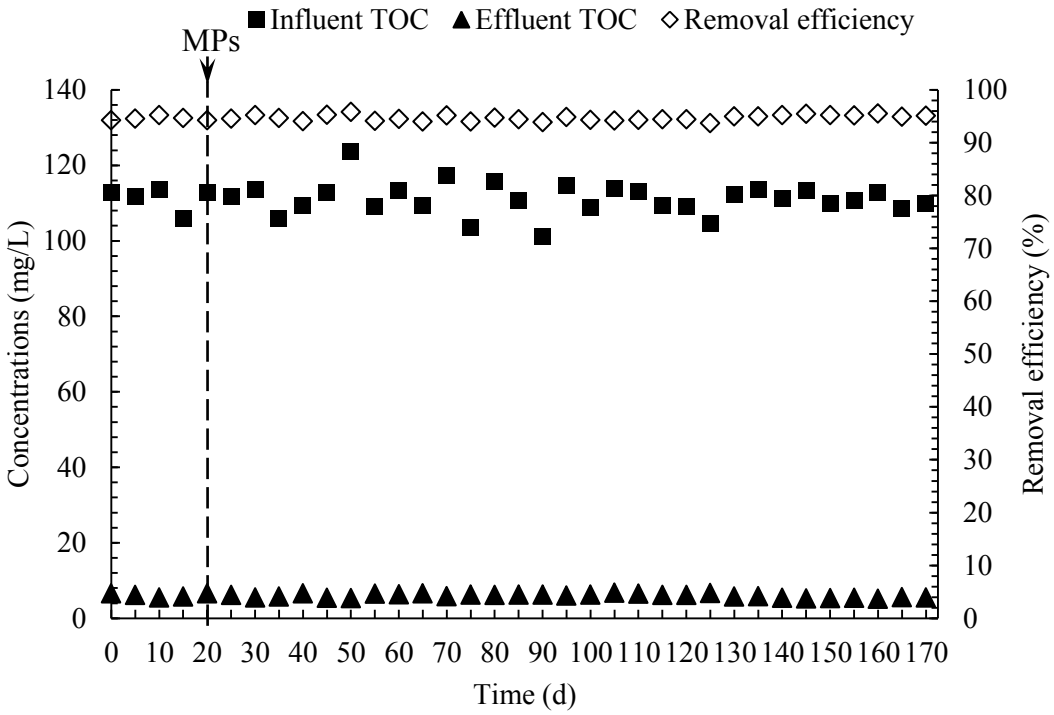


Figure 5.1 TOC removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 24 h; day 20 is the start of micropollutants addition; MPs: micropollutants).

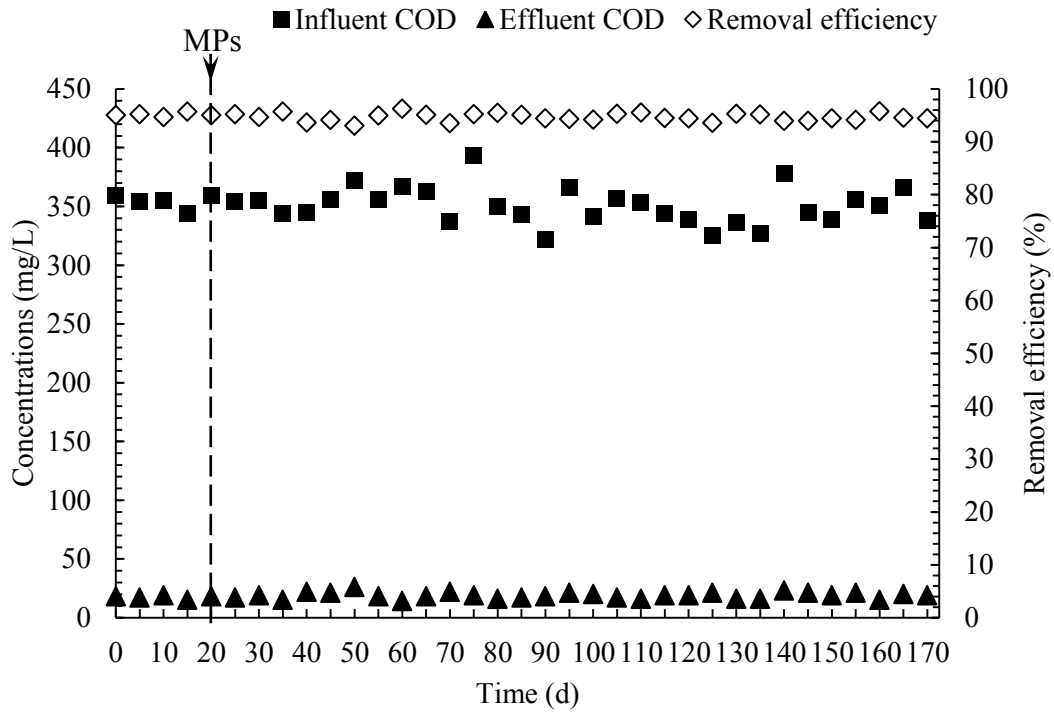


Figure 5.2 COD removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 24 h; day 20 is the start of micropollutants addition; MPs: micropollutants).

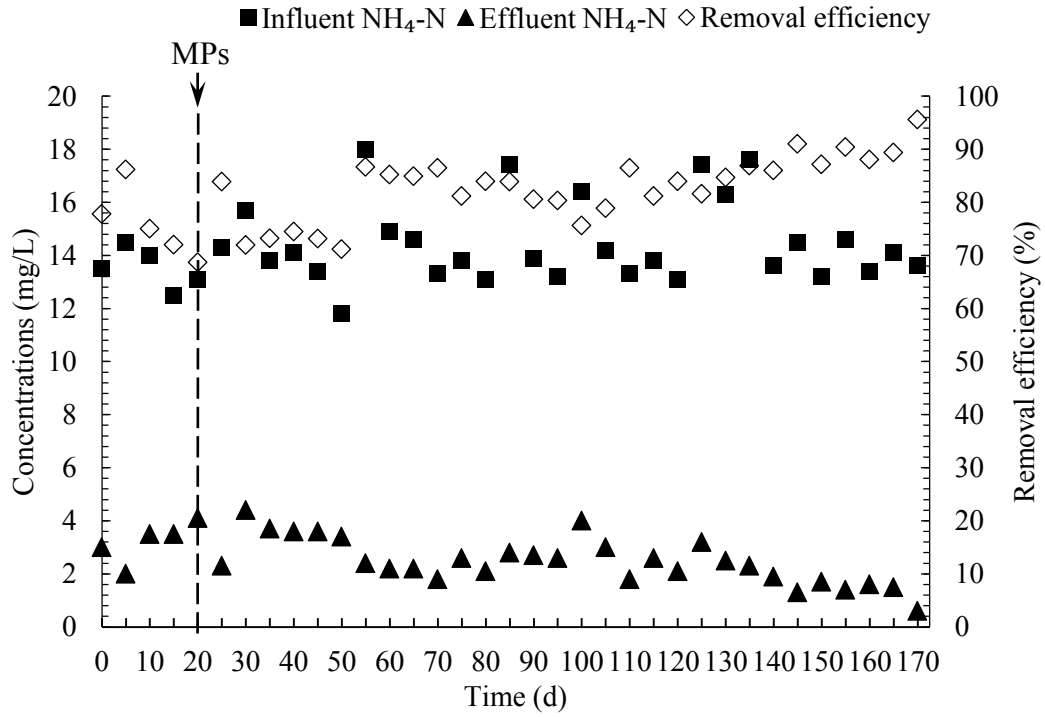


Figure 5.3 NH_4-N removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 24 h; day 20 is the start of micropollutants addition; MPs: micropollutants).

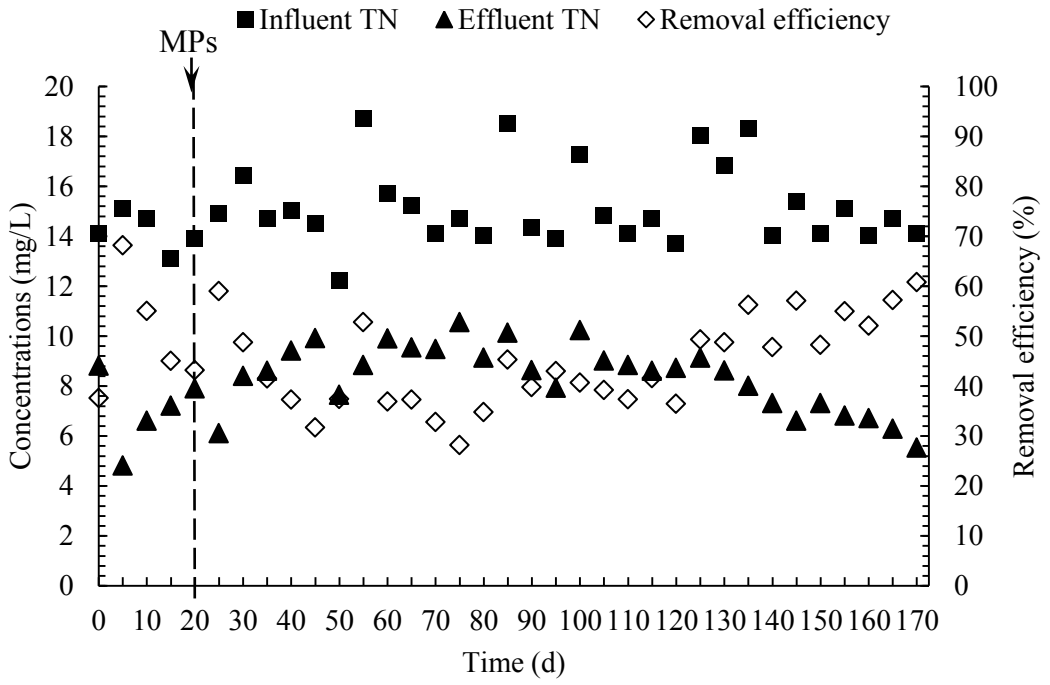


Figure 5.4 TN removal in the MBBR (aeration rate: 4 L/min; DO = 5.5–6.5 mg/L; HRT: 24h; day 20 is the start of micropollutants addition; MPs: micropollutants).

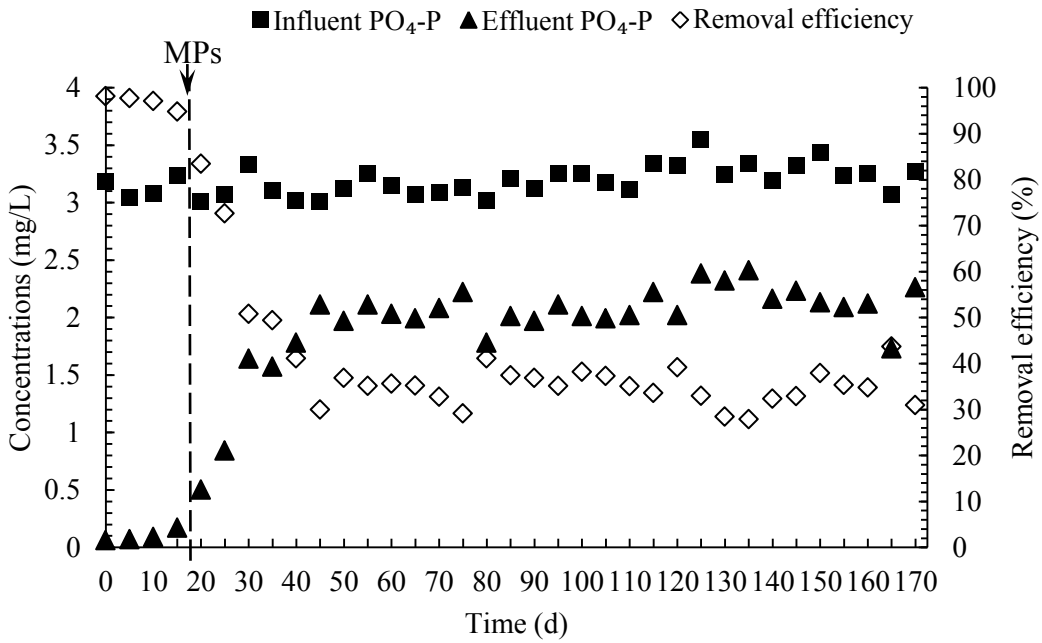


Figure 5.5 PO_4-P removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 24 h; day 20 is the start of micropollutants addition; MPs: micropollutants).

The initial amounts of attached biosolids (total solids) and biomass (volatile solids) on the sponge was 0.25 g MLSS/g sponge and 0.23 g MLVSS/g sponge, respectively. The amount was decreased to 0.19 g MLSS/g sponge and 0.18 g MLVSS/g sponge within the first 20 days of operation owing to the loss of biosolids from the surface of the sponge cubes caused by aeration. Afterwards, with the stabilization of the MBBR system, a gradual increase in the attached biosolids and biomass concentrations was observed and on day 150, the biosolids and biomass concentrations on the sponge were around 0.48 g MLSS/g sponge and 0.44 g MLVSS/g sponge, respectively. During the study, the ratio of MLVSS to MLSS remained at a high level (0.79–0.95), indicating no or minor accumulation of inert compounds in the biosolids. The microscopic examination of the sponge revealed that the sponge obtained at the late stage of the study contained higher amounts of biosolids. During the experiments, some biosolids sloughed off due to the aeration as well as the friction and collision among sponge cubes, but such loss was fairly low. The MLSS and MLVSS in the mixed liquor were stable at 0.13 ± 0.05 and 0.12 ± 0.06 g/L, respectively. Hence, the attached biosolids on sponge can be considered as the principal contributor to the removal of pollutants.

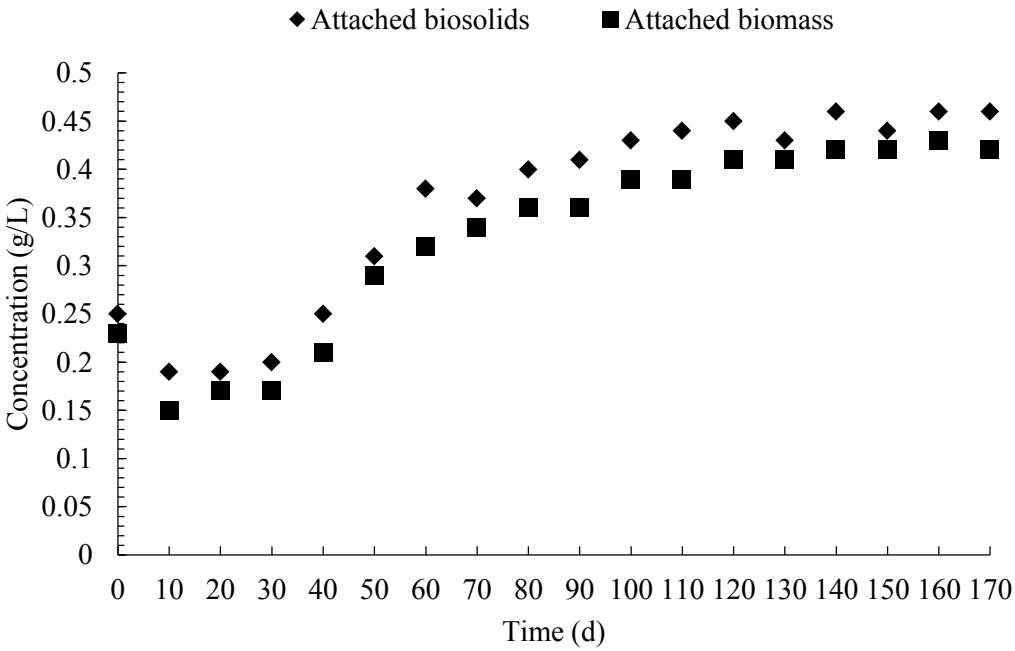
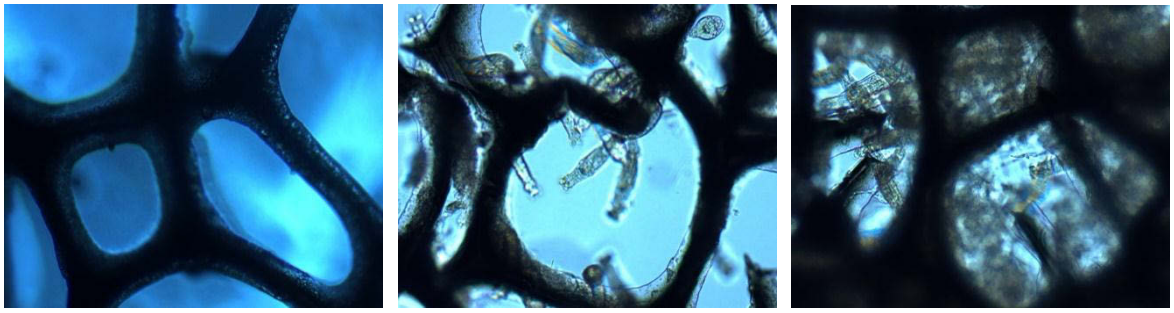


Figure 5.6 Variation of attached biosolids and biomass concentrations in the MBBR.



(A) (B) (C)

Figure 5.7 Microscopic view of biomass growth within the sponge (A) virgin sponge; (B) sponge at the early stage; (C) sponge at the late stage.

5.3 Removal of selected micropollutants

The removal efficiencies of the micropollutants in the MBBR are presented in Figure 5.8. Apparent variation in removals was observed for different compounds. This could be ascribed to numerous micropollutant-related factors, such as hydrophobicity, bioavailability, compound structure, and volatility. Overall, 16 out of 22 compounds were significantly removed (> 70%) during the MBBR treatment.

Pharmaceuticals are complex synthetic substances with highly variable physico-chemical properties. In this study, the selected pharmaceuticals generally displayed low hydrophobicity (log D < 2.5). Therefore, biodegradation (rather than sorption) was the major removal pathway of these compounds. Four of the studied PPCPs were efficiently eliminated (>80%): these were ibuprofen (93.7%), salicylic acid (91.1%), primidone (83.5%) and naproxen (81.1%). The high removal efficiency could be ascribed to the inclusion of strong electron donating (readily biodegradable) functional groups (e.g., –OH) in these compounds. Ketoprofen, acetaminophen, metronidazole, and gemifibrozil were moderately removed (58.2%, 71.4%, 54.8% and 62.4%, respectively) in the MBBR. It should be noted that the MBBR seemed to less effective for the removal of acetaminophen as compared with other biological treatment processes (activated sludge and MBR) (Luo et al., 2004). Diclofenac and carbamazepine, as opposed to other pharmacueticals, were resistant to MBBR treatment. The average removal of diclofenac in the MBBR was 45.7%. Zhang comprehensively surveyed the literature and found that diclofenac experienced fairly variable removals (0–80%) in different WWTPs and the removals were mainly in the range of 21–40%. Diclofenac is generally poorly biodegraded because of its refractory property induced by the inclusion of chlorine group in its molecule. In addition, its solid-water coefficient is too low (log D = 1.77) for considerable sorption (log D>3.2) onto the biosolids. Carbamazepine showed an even lower removal of 25.9%. Zhang et al. (2008) confirmed that carbamazepine is persistent to biological transformation at low concentrations. The authors found that the removal efficiencies of carbamazepine in the WWTPs are mostly less than 10%. Joss et al., (2006) also stressed the recalcitrance of carbamazepine and classified carbamazepine as a ‘no removal’ compound.

In the case of estrogenic hormones, the removal was consistently high (>85%), which could be attributed to the high hydrophobicity (log D > 3.2) of these compounds (except estriol) as previously suggested by Tadkaew et al. (2011). According to Andersen et al. (2003), estrogenic hormones could be efficiently biodegraded under nitrifying conditions. Hence, they could be successfully eliminated in the MBBR with high nitrification efficiency. As the synthetic hormone 17α-ethinylestradiol was more resistant to biodegradation, it exhibited slight lower removal (85.2%) as compared with 17β-estradiol, β-estradiol 17-acetate and estriol (96.2%, 96.8% and 92.5%, repsectively). The removal of estrone was also marginally lower (89.6%). According to Ternes et al. (1999), 17β-estradiol could be transformed to estrone during areobic biological treatment processes, thereby increasing the effluent estrone concentration to some extent.

Regarding industrial chemicals, the observed removals were generally high (>70%), especially for 4-tert-octylphenol (91.6%) and 4-n-nonylphenol (95.7%), as these compounds are commonly characterized by high hydrophobicity (log D>3.2). The less removals of bisphenol A (77.8%) and 4-tert-butylphenol (74.9%) could be due to the lower log D of these compounds (3.64 and 3.39, respectively) in comparison with 4-tert-octylphenol (5.18) and 4-n-nonylphenol (6.14).

Pesticides are commonly less biodegradable compounds and some of them are even harmful to microorganisms due to certain toxic effects. As pesticides have been commonly considered of agricultural origin instead of urban origin, a limited amount of investigation has been performed at full scale and most documented WWTPs tended to show inadequate elimination of pesticides (Köck-Schulmeyer et al., 2013). In this study, two pesticides displayed different removals. Fenoprop exhibited inefficient elimination (31.0%), whereas pentachlorophenol experienced much higher removal (78.9%). The poor removal of fenoprop could be attributed to its low hydrophobicity (log D = –0.13) and recalcitrance (Hai et al., 2011).

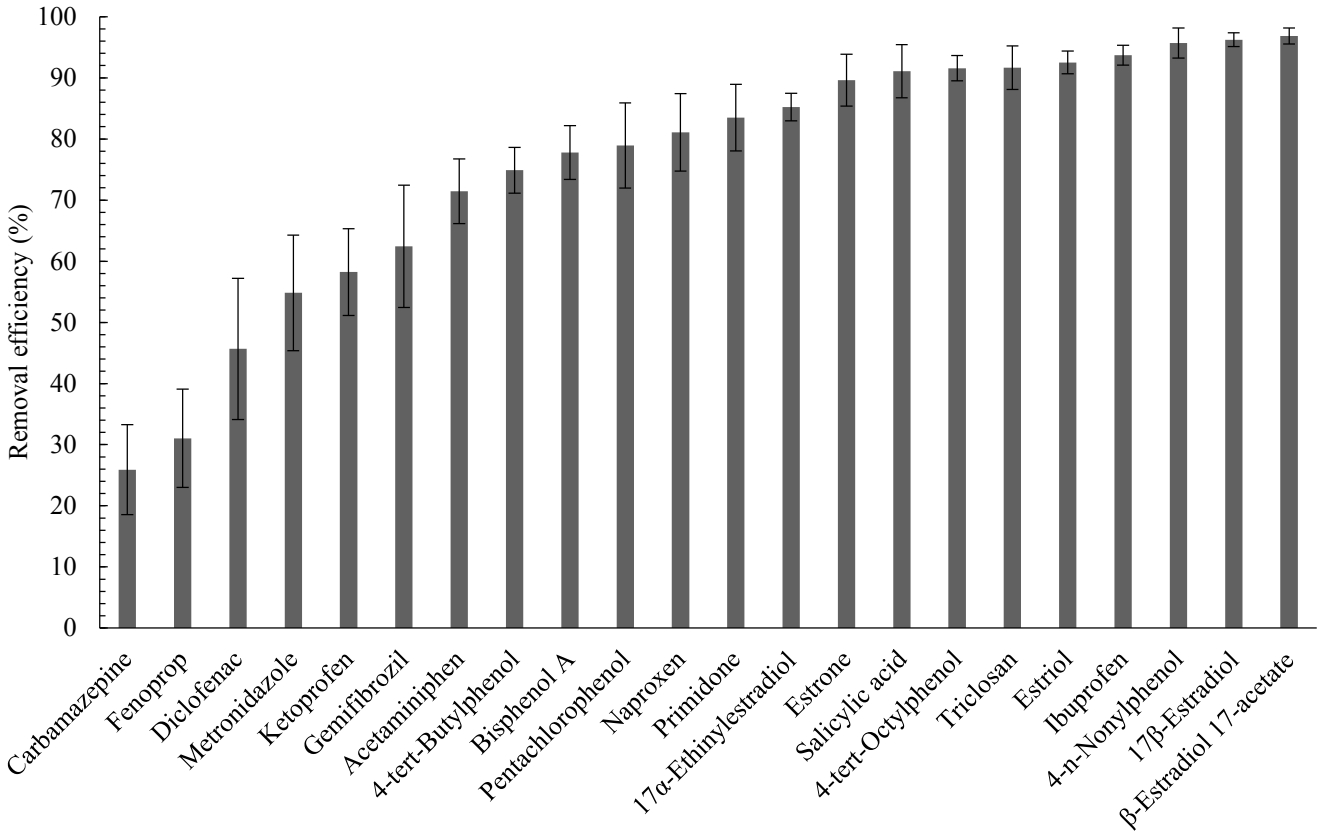


Figure 5.8 Removal efficiency of micropollutants during the MBBR treatment. (An error bar represents the standard deviation of 25 measurements over 150 days; aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 24 h)

5.4 Fate of micropollutants in the MBBR and application of mass balance

During the MBBR treatment, the micropollutants might be subjected to biodegradation, sorption, air stripping and photolysis. Air stripping depends on the volatility and hydrophobicity of micropollutants (Cirja et al., 2008). Henry's constant (k_H) is used to determine volatility. The k_H ranging from 10^{-3} to 10^{-2} commonly indicates marked tendency of volatilization (Stenstrom et al., 1989). As can be seen from supplementary data Table 3.2, the k_H of most selected micropollutants are within the range of 10^{-4} to 10^{-11}, indicating a minor role of volatilization in the removal of these compounds. Two exceptions are 4-tert-butylphenol (3.61×10^{-2}) and 4-tert-octylphenol (1.98×10^{-3}). However, given the high hydrophobicity of these two compounds, removal by air stripping can also be considered to be insignificant for them. Photolysis occurs when the treatment system is exposed to direct lights. Although Zhang et al. (2008) suggested photolysis may contribute the elimination of some micropollutants in surface waters and real-life wastewater treatment processes, most previous lab-scale studies did not take into consideration of photolysis due to its insignificant effects. Therefore, in this study, it was assumed that the micropollutant removal only resulted from sorption and biological degradation.

Figure 5.9 illustrates the concentrations of micropollutants sorbed to sludge. As shown in the figure, the compounds with lower removal efficiency generally accumulated to biosolids (in suspension and on the sponge cubes) to a greater extent, indicating compound persistence is a factor that affects micropollutant sorption. For instance, carbamazepine, ketoprofen and pentachlorophenol were found at particularly high concentrations on suspended biosolids (7.87, 6.05 and 5.55 μg/g, respectively). There are two possible reasons for this. Firstly, the compounds with high persistence (low removal) were present at high concentrations in the aqueous phase, which may have resulted in high amounts of sorbed compounds at their sorption equilibriums. Secondly, after sorption to biosolids, the recalcitrant compounds were resistant to further biodegradation and therefore remained attached to the solids.

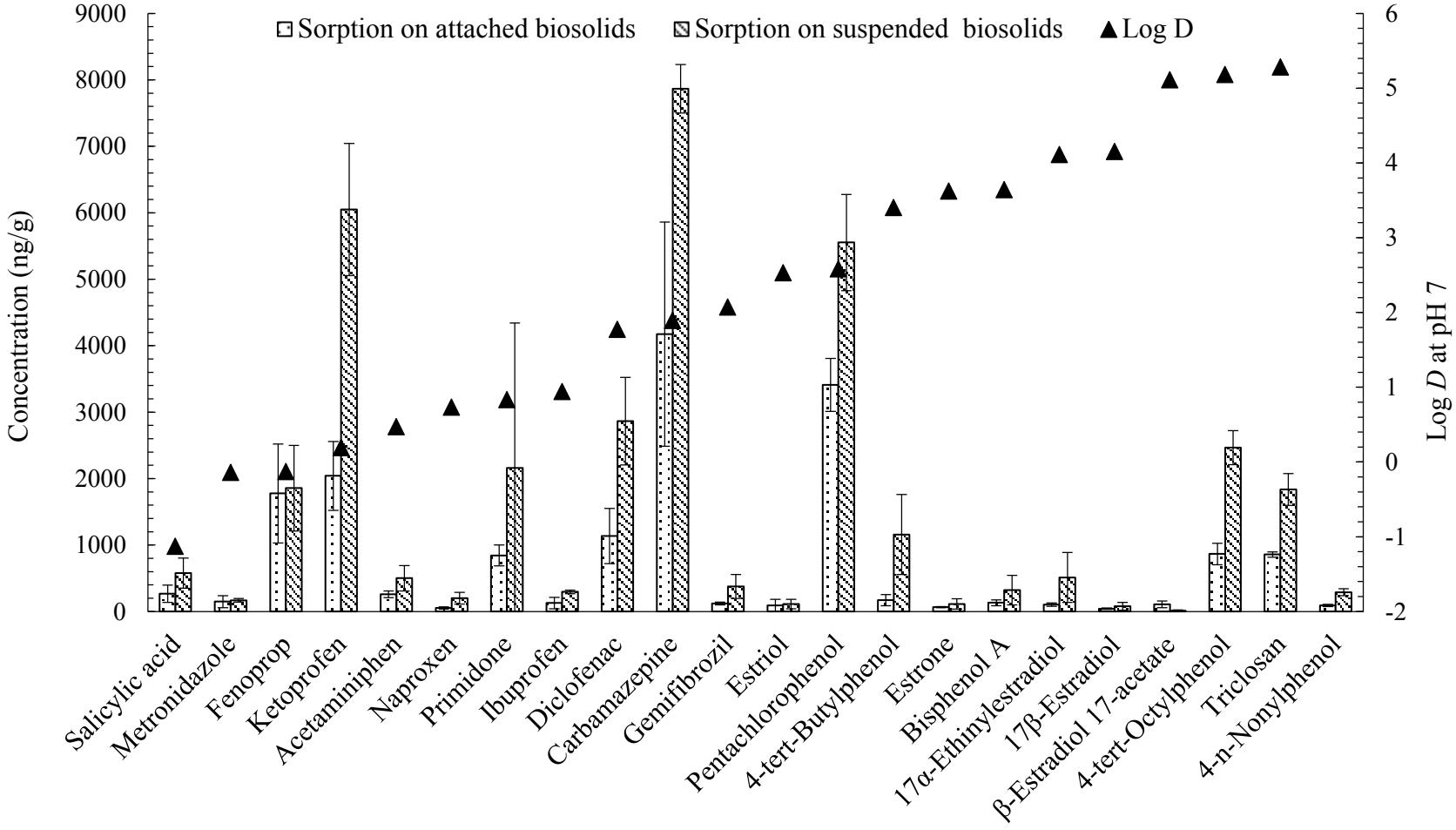


Figure 5.9 Average concentrations of micropollutants on the suspended and attached biosolids (An error bar represents the standard deviation of the sample measurements on Day 70 and 100; aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 24h).

Hydrophobicity is another influential factor for micropollutant sorption. However, in this study, no evident correlation was found between compound hydrophobicity and its concentration on biosolids. Except for triclosan and 4-tert-octylphenol, most hydrophobic compounds were found at insignificant amounts on biosolids, possibly because of their higher biodegradability (Section 3.2). Additionally, Figure 5.9 showed that suspended biosolids had higher accumulation of micropollutants than attached biosolids. Thus, the attached biosolids appears to possess better biodegradation capacity, possibly due to more diverse microbial community and the existence of different sludge characteristics on and inside the sponge carrier. Further studies are, however, required to substantiate this hypothesis.

To gain a better understanding of micropollutant removal in the MBBR system, a mass balance calculation was carried out over a period of 30 days (from day 70 to day 100), taking into consideration the sorption and biodegradation of micropollutants.

Micropollutant sorption was quantified based on the production of new biosolids, which was presumably responsible for the adsorptive removal of the compounds (Joss et al., 2005). In the MBBR, the production of new biosolids can be divided into two parts: one is the suspended biosolids which was continuously washed out and the other one is attached biosolids that was retained in the MBBR. Therefore, the load of compound removed via sorption can be calculated as follows:

$$L_{sol} = Q \cdot T \cdot MLSS \cdot C_{s,\,s} + \Delta SS \cdot C_{s,\,a} \quad (5.1)$$

where L_{sol} is the load of micropollutant removed via sorption over the 30 days (ng), Q is the flow rate of the MBBR (L/day), T is the duration of the study period (day), MLSS is mixed liquor suspended biosolids concentration (g/L), $C_{s,\,s}$ is the concentration of micropollutant on the suspended biosolids (µg/g), ΔSS is the increased amount of attached biosolids over the study period (g), and $C_{s,\,a}$ is the concentration of micropollutant on the attached biosolids (µg/g).

The load of micropollutant removed via biological degradation was determined by calculating the difference of the reduction of micropollutant load (L_{inf} - L_{eff}, ng) and the load of sorbed micropollutant (Eq 5.2).

$$L_{biol} = L_{inf} - L_{eff} - L_{sol} = Q \cdot T \cdot (C_{w,\,inf} - C_{w,\,eff}) - Q \cdot T \cdot MLSS \cdot C_{s,\,s} - \Delta SS \cdot C_{s,\,a} \quad (5.2)$$

where $C_{w,\,inf}$ and $C_{w,\,eff}$ are the average influent and effluent concentrations of micropollutants over the study period.

The average biosolids concentration in suspension during the 30-day period was 0.15 g/L. The initial and final attached biosolids concentrations were 0.37 and 0.43 gMLSS/g sponge, respectively. The total mass of sponge in the MBBR was 232 g, which was estimated by multiplying the total volume (8 L) of sponge by the density (29 g/L). Hence, the production of attached biosolids was 13.9 g. The calculated percentages of micropollutant loads which were released from MBBR, sorbed to sludge and biodegraded were presented in Figure 5.10. As shown in the figure, biodegradation served as the major removal pathway for most micropollutants. Even for some highly hydrophobic compounds, such as 4-tert-octylphenol, 4-n-nonylphenol, triclosan, 17-β-estradiol 17–acetate, sorption accounted for minor removals (<0.1 % to 5.5 %). The results are generally in good agreement with those obtained from an MBR, except that 50% the overall loading of triclosan accumulated onto the suspended biosolids of the MBR (Wijekoon et al., 2013). However, sorption was still significant for some persistent compounds (e.g., carbamazepine, diclofenac and fenoprop). In particular, despite the low hydrophobicity (log D=1.89), carbamazepine experienced similar degrees of biodegradations (16.5%) and sorption (15.1%) from day 70 to day 100. It is noteworthy that the sorption by acclimatised sponge played a significant role in the batch experiments (Table 4.2), while the continuous MBBR experiment showed a limited contribution from sorption (Figure 5.10). This could be explained by the facts that 1) sorption is a more rapid process than biodegradation, thus sorption might act as an important removal mechanism within the short-term batch experiments; and 2) in the long-term experiment, the acclimatized sponge remained fully occupied by biomass over time, and the reduced sorption site for micropollutants resulted in the limited sorption efficiency.

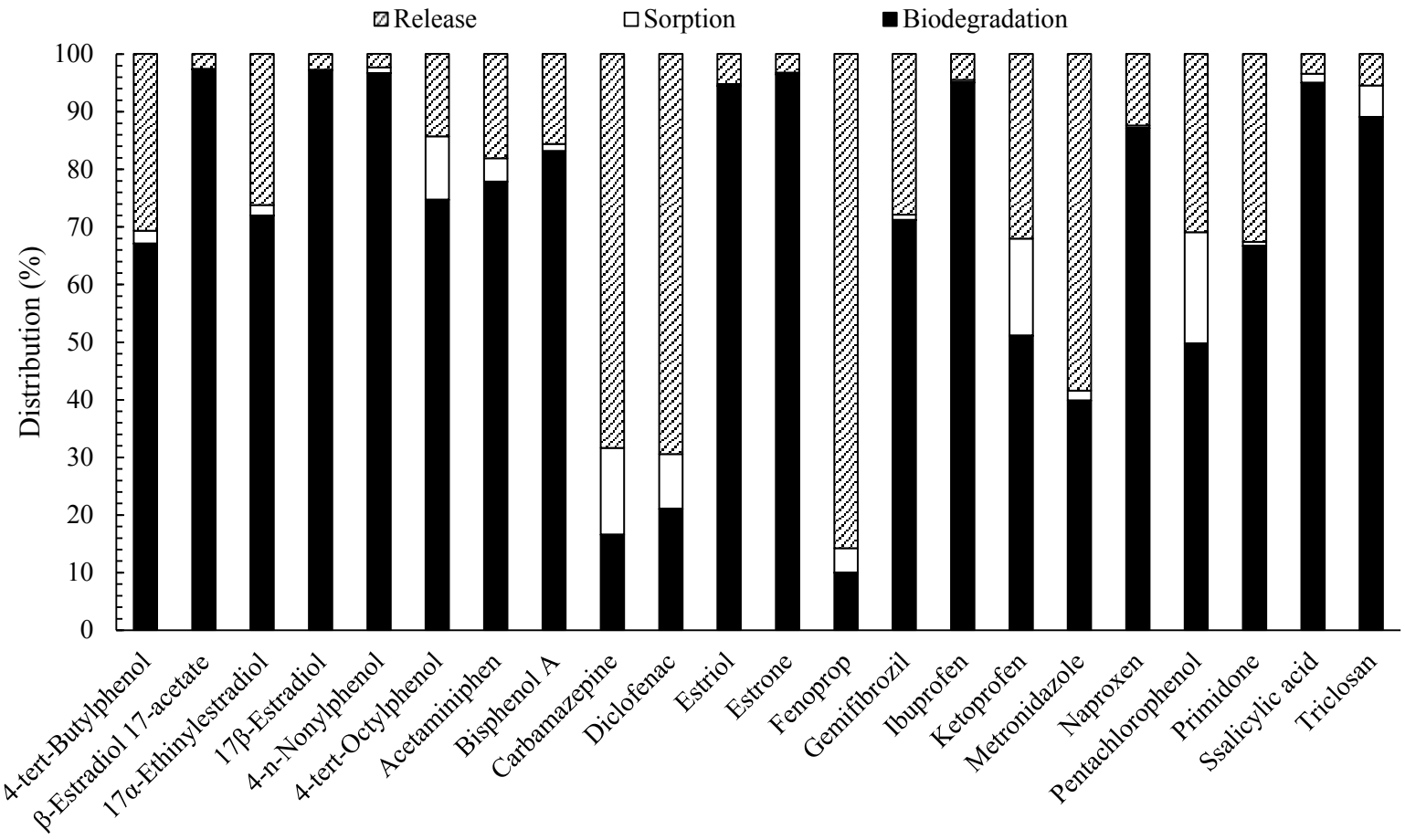


Figure 5.10 Fate of the studied micropollutants in the MBBR system (aeration rate: 4L/min; HRT: 24 h).

5.5 Comparison between the MBBR and other techniques for micropollutant removal

Since WWTPs are not able to provide a complete barrier for micropollutant removal, establishing optimal removal strategies for micropollutants remains a challenge to environmental engineers in order to minimize their adverse effects on the environment. Table 5.1 compares the micropollutants removal in the studied MBBR, suspended-growth activated sludge processes and MBRs. Generally, the effectiveness of MBBR for micropollutant removal was comparable with those of activated sludge processes and MBRs. Moreover, the MBBR seemed to be very effective in eliminating ibuprofen, metronidazole, naproxen, primidone, triclosan, estrone, 17-α ethinylestradiol, 4-n-nonylphenol, 4-tert-octylphenol and fenoprop. It is also noteworthy that the removal of diclofenac in the MBBR (46%) was significantly higher than that reported for a MBR (20%) (Nguyen et al., 2012). Falås et al. (2012) demonstrated that the presence of biofilm carriers played an important role in the biodegradation of diclofenac. They found that biofilm carriers from full-scale nitrifying wastewater treatment plants had apparently higher removal rates per unit biomass for diclofenac in comparison with the activated sludge. Nevertheless, MBR systems had the ability for more efficient removal of ketoprofen, acetaminophen, gemifibrozil and 4-tert-butylphenol (Nguyen et al., 2013; Wijekoon et al., 2013). Although Servos et al. (2005) stated that activated sludge processes tended to have higher removal of estrogenic potentials (58–>99% with an average of 81%) than some attached-growth processes (0–75% with an average of 28%), such as trickling filters and rotating biological contactors, the MBBR in this study was able to achieve similar or higher elimination of the estrogenic hormones (85.2–96.8%) compared with the activated sludge processes.

In addition to biological treatment, phsycio-chemical techniques serve as important barriers against the release of micropollutants. A general comparison of different treatment technologies was provided in Table 5.2. The provided information is based on the recent literature and may be helpful to select suitable techniques for micropollutants treatment. However, the table only gives the qualitative assessment of these techniques. Comprehensive quantitative assessment is needed in future

research to better compare different techniques from both economic and technical points of view.

Table 5.1 Comparison of micropollutant removal efficiency (%) in the MBBR and in other biological treatment technologies.

Compounds[a]		This study (MBBR, %)	Activated sludge[b] (%)	MBR[c] (%)
Pharmaceuticals	ACM	71.4 ±10.6	98.7-100	40–100
	CBZ	25.9 ± 14.7	<0-63.2	0–35
	DCF	45.7 ± 23.1	<0–81.4	0–87
	GFB	62.4 ± 20.0	<0–92.3	90–98
	IBU[d]	93.7 ± 3.3	72–100	50-99
	KTP	58.2 ± 14.2	10.8–100	52–92
	MET	54.8 ± 18.9	0–64.0	36–40
	NPX	81.1 ± 12.6	43.3–98.6	10–84
	PRM	83.5 ± 10.9	30-50	10–91
	SA	91.1 ± 8.7	89.6–100	93–98
	TCS	91.7 ± 7.1	71.3–99.2	70–99
Steroid hormones	**E1**	89.6 ± 8.5	74.8–90.6	96–99
	E2	96.2 ± 2.2	92.6–100	97–99
	E2AC	96.8 ± 2.6	-	98–99
	EE2	85.2 ± 4.5	43.8–100	60–98
	E3	92.5 ± 3.7	100	83–97
Industrial chemicals	BP	74.9 ± 7.4	-	93–98
	BPA	77.8 ± 8.8	62.5–99.6	52–98
	NP	95.7 ± 4.9	21.7–99	87–97
	OP	91.6 ± 4.2	<0–96.7	97-98
Pesticides	**FNP**	31.0 ± 16.1	-	10–21
	PECP	78.9 ± 13.9	-	61–99

[a] ACM: acetaminophen; BP: 4-tert-butylphenol; BPA: bisphenol A; CBZ: carbamazepine; DCF: diclofenac; E1: estrone; E2: 17-β-estradiol; E2AC: β-estradiol 17-acetate; EE2: 17-α ethinylestradiol; E3: estriol; FNP: fenoprop; GFB: gemfibrozil; IBP: ibuprofen; KTP: ketoprofen; MET: metronidazole; NP: 4-n-nonylphenol; NPX: naproxen; PECP: pentachlorophenol; PRM: primidone; OP: 4-tert-octylphenol; SA: salicylic acid; TCS: triclosan.

[b] Data from Kasprzyk-Hordern et al., 2009; Lin et al., 2009; Luo et al., 2014; Wick et al., 2009.

[c] Data from Nguyen et al., 2013.

[d] Listed in bold type are the compounds whose percentage removals are close to or above the maximum removals reported in activate sludge or/and MBR.

Table 5.2 Assessment of different treatment processes for micropollutants removal.

Technique	Common removal efficiency[a]				Major factors		Disadvantage/problems	Residues
	P	PCP	SH	IC	Process–specific	MP–related		
Coagulation	L–M	M–H	L	L–H	• Dosage • pH • Wastewater composition	• Hydrophobicity • Molecular size	• Ineffective MP removal • Large amount of sludge • Introduction of coagulant salts in the aqueous phase	Sludge
AC	M–H	M–H	H	M–H	• Adsorbent properties • Dosage • Contact time • pH	• Hydrophobicity • Molecular size • Structure • Functional group	• Relatively high financial costs • Lower efficiency in the presence of NOMs • Need for regeneration • Disposal of used carbon	Used material
Ozonation and AOPs	M–H	M–H	H	M–H	• Dosage • pH • Interfering ions (e.g., Br^-) • Wastewater composition	• Compound structure	• High energy consumption • Formation of byproducts • Interference of radical scavengers	Residual oxidants
NF	M–H	H	M–H	M–H	• Membrane properties • pH • Transmemrane pressure	• Hydrophobicity • Molecular size	• High energy demand • Membrane fouling • Disposal of concentrate • Desorption of sorbed chemicals	Concentrate

					• Feed quality		from membrane	
RO	M–H	H	H	H	• Membrane properties • pH • Transmemrane pressure • Feed quality	• Hydrophobicity • Molecular size	• High energy consumption • Disposal of concentrate • Corrosive nature of the finished water	Concentrate
Activated sludge	L–H	M–H	M–H	L–H	• SRT • HRT • Organic loading • Redox conditions	• Hydrophobicity • Biodegradability	• Inconsistent removal of polar and resistant compounds • Increase of environmental risk due to the disposal of sludge containing micropollutants	Wasted sludge
MBR	L–H	M–H	H	M–H	• SRT • HRT • Organic load • Redox conditions	• Hydrophobicity • Biodegradability	• Moderately high energy consumption • Inconsistent removal of polar and resistant compounds • Membrane fouling • Less sorption of micropollutants on the aged MBR sludge	Wasted sludge
Attached growth	L–H	M–H	M–H	M–H	• HRT • Organic loading • Redox conditions	• Hydrophobicity • Biodegradability	• Long start–up time • Difficulty in control of biofilm thickness	Wasted sludge

[a] P: pharmaceutical; SH: steroid hormone; IC: industrial chemical; L: low; M: medium; H: high

5.6 Conclusion

The investigated MBBR demonstrated excellent performance in removing organics, nutrients as well as micropollutants during the 170-day investigation. TOC and COD removal was fairly high and stable throughout the study. Due to the high DO concentrations (5.5–6.5), the MBBR did not yield significant reduction of TN and PO_4-P concentrations. Varying removals of the selected micropollutants were detected in the MBBR due to their diverse physicochemical properties (e.g. biodegradability and hydrophobicity). The least removed compounds were carbamazepine (25.9%), fenoprop (31.0%) and diclofenac (45.7%). These compounds are generally characterized by non-biodegradable and polar properties. Biodegradation was shown to be the principal removal mechanism for most compounds. The micropollutants that were susceptible to biodegradation did not significantly accumulate to the biosolids (regardless their hydrophobicity) and sorption was only considerable for compounds with high persistency (e.g., carbamazepine). This is probably because 1) the persistent compounds were present at high levels in the aqueous phase, which might lead to more significant compound adsorption at equilibrium; 2) the attached compounds were resistant to further biological transformation and could therefore remain sorbed on the biosolids.

Overall, the removal efficiency by the MBBR is comparable with other processes (activated sludge and MBR). The MBBR appeared to be an effective process for removing ibuprofen, metronidazole, naproxen, primidone, triclosan, estrone, 17-α ethinylestradiol, 4-n-nonylphenol, 4-tert-octylphenol and fenoprop. Furthermore, it is possible that, after future optimization of experimental conditions, more efficient micropollutant removal could be achieved.

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Chapter 6

Removal of Micropollutants by a Moving Bed-Submerged Membrane Bioreactor （MB-SMBR）System

6.1 Introduction

The development of membrane bioreactors (MBRs) for municipal and industrial wastewater treatment has been focused on modifying the configurations of the combined membrane process (e.g., microfiltration and ultrafiltration) and the suspended-growth activated sludge process. Practically, the principal driver for the applications of the MBR technique is its capability of rejecting virtually all the particles and producing an effluent extremely low in undesired substances. Moreover, the elimination of secondary clarification can reduce the footprint significantly. However, membrane fouling is the biggest existing challenge for the proliferation of MBR application. An alternative to the conventional activated sludge MBR is to integrate a biofilm reactor with a membrane filtration process. The combined biofilm-MBR system can not only produce good quality effluent at high bioreactor loading rates but also mitigate the membrane fouling caused by high biomass concentration (Leiknes and Ødegaard, 2007; Melin et al., 2005). Leiknes and Ødegaard (2007) investigated the potential of a MBBR-MBR system for wastewater treatment at different loading rates. Results demonstrated that consistently high removal of COD (85–90%), filtered COD (70%–75%) and suspended solids (100%) was observed in the MBBR-MBR, regardless of loading rates. The authors suggested that the MBBR-MBR system was able to handle volumetric loading rates of 2–8 kg/COD/m^3d and HRTs up to 4 h. Regarding the alleviation of membrane fouling, the MBBR-MBR system also showed positive results, especially at low loading rates.

To date, little is known about the effectiveness of the MBBR-based membrane processes for micropollutant removal. This chapter focuses on the performance of a moving bed-submerged membrane bioreactor (MB-SMBR) hybrid system in removing micropollutants over 89 days of operation. The roles of the MBBR and SMBR in contaminant removal are discussed and compared. In addition, the fouling of SMBR is evaluated based on sludge characteristics, such as extracellular polymeric substances (EPS), soluble microbial products (SMP), zeta potential, and relative hydrophobicity (RH). The quantitative contributions of different types of membrane resistances (cake layer resistance, pore blocking resistance and irreversible resistance are also addressed.

6.2 Organic and nutrient removal

The MB-SMBR was started after 80-day operation of the MBBR. The hybrid system was operated in a continuous mode (without any backwash or relaxation) and the length of the study was 89 days. The influent and effluent concentrations of TOC, COD, NH_4-N, TN and PO_4-P as well as the removal efficiencies are presented in Figures 6.1, 6.2, 6.3, 6.4 and 6.5. In general, the removal of organic and nutrients was principally achieved in the MBBR, while the SMBR offered very limited further elimination due to the low MLSS and MLVSS.

Steady performance in the removals of TOC (93.9–96.0%) and COD (93.8–96.4%) was observed in the MB-SMBR system and the effluent TOC concentration was 5.5 ± 0.6 mg/L. The COD removal is slightly higher than that in a similar study conducted by Leiknes and Ødegaard (2007), in which the COD level was reduced by 85–90%. However, the COD loading rate was much higher in Leiknes and Ødegaard's study (1.1–3.9 kg/ m^3·d) as compared with this study (0.32–0.36 kg/ m^3·d). The MB-SMBR system yielded a NH_4-N removal of 79.5 to 95.6% and the effluent NH_4-N level was 2.0 ± 0.5 mg/L. The TN removal exhibited apparent variation throughout the study and was in the range of 28.2–61.6% during the MB-SMBR treatment. PO_4-P removal of the MB-SMBR system was relatively constant (34.9 ± 3.9 %) throughout the study, with effluent PO_4-P concentration of 2.1 ± 0.2 mg/L.

By comparison between the TOC and COD concentrations in MBBR effluent and MB-MBBR effluent, it is noted that the SMBR was able to achieve slight further TOC reduction (8.5 ± 0.6%) after the MBBR treatment. Marginal elimination of NH_4-N (7.3 ± 3.7%) was also found in the SMBR. With regard to TN and PO_4-P, the SMBR showed none or only minor reduction. Despite the minor role of SMBR in removing organics and nutrients, this process was able to reduce considerably turbidity in the SMBR feed (31.6 ± 8.3 NTU) and to produce effluent with low turbidity (0.21 ± 0.06 NTU).

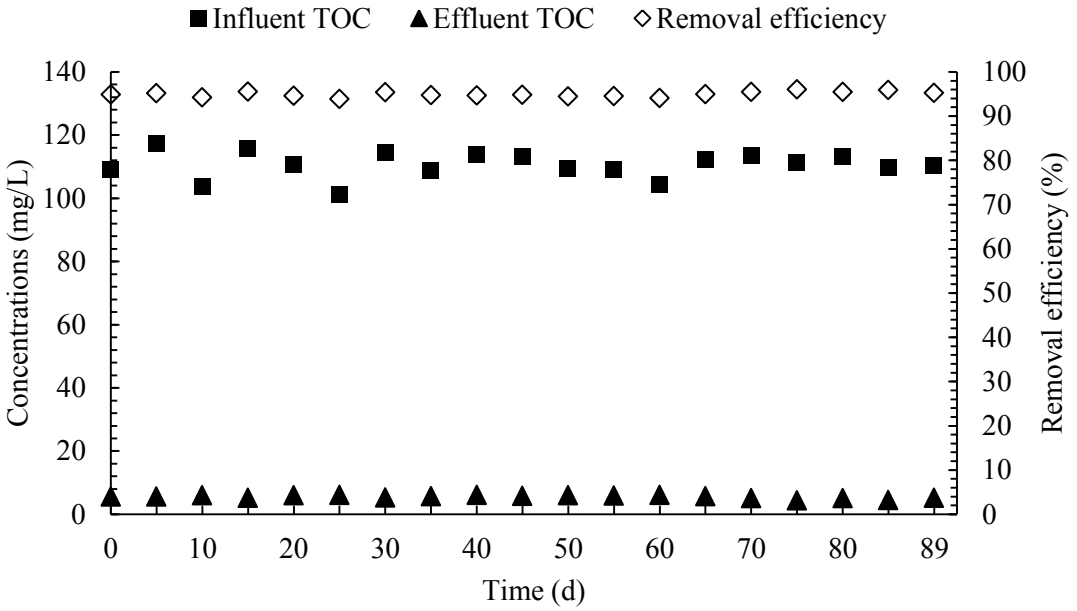

Figure 6.1 TOC removal in the MB-SMBR system (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h; SMBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

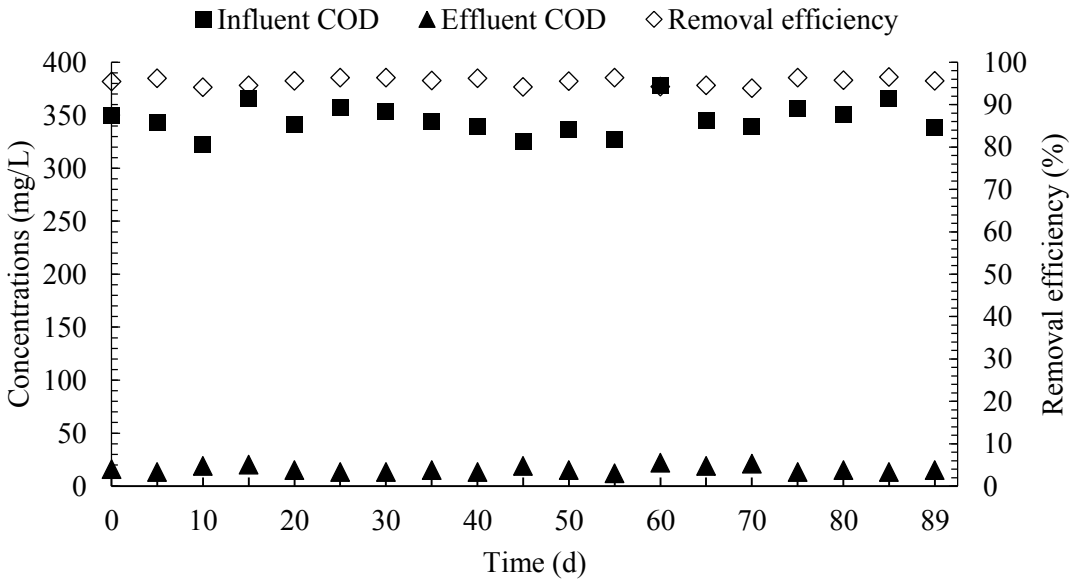

Figure 6.2 COD removal in the MB-SMBR system (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h; SMBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

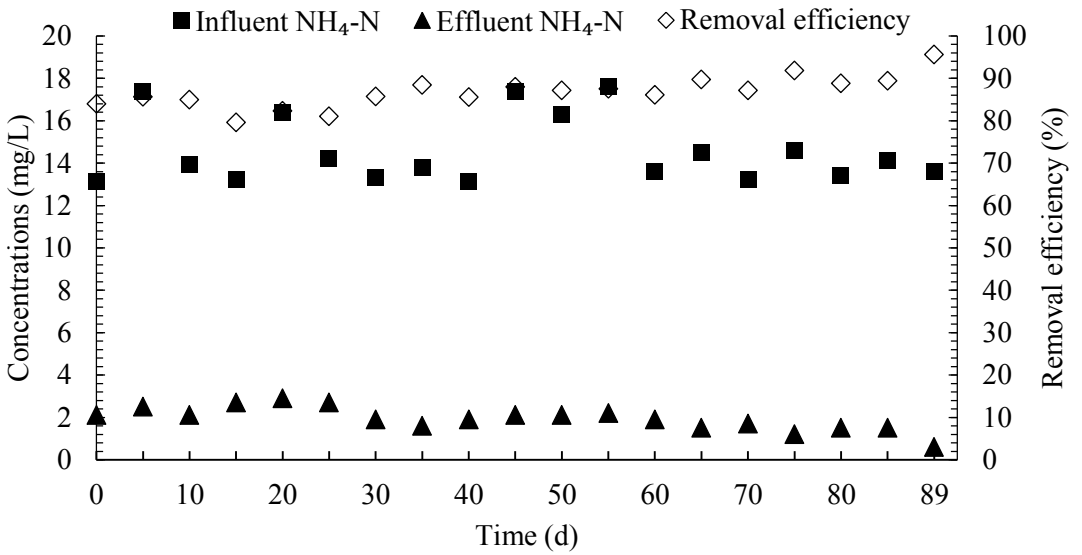

Figure 6.3 NH_4-N removal in the MB-SMBR system (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h; SMBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

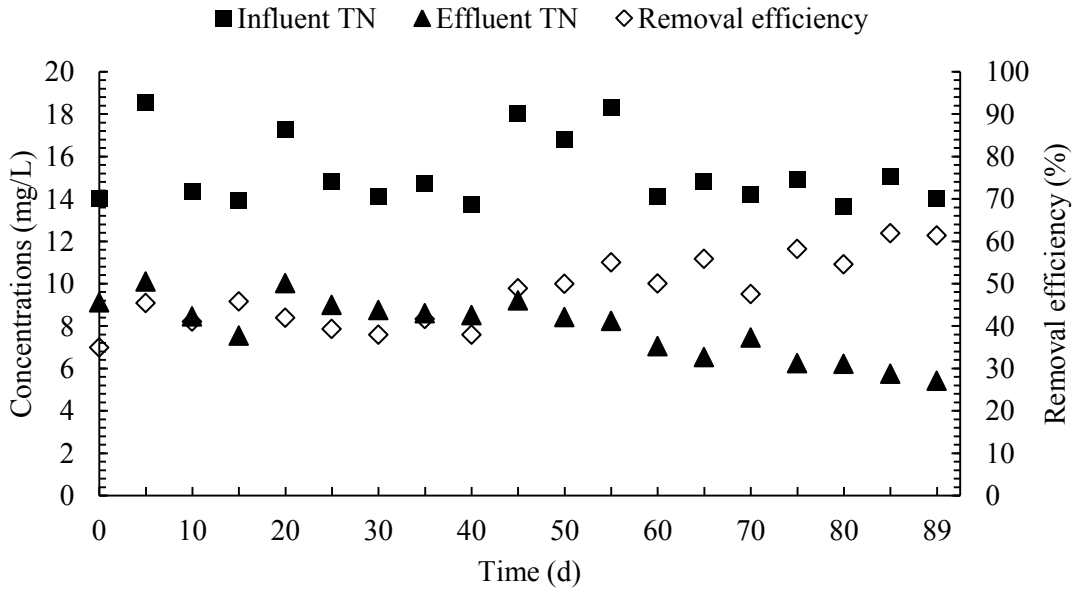

Figure 6.4 TN removal in the MB-SMBR system (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h; SMBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

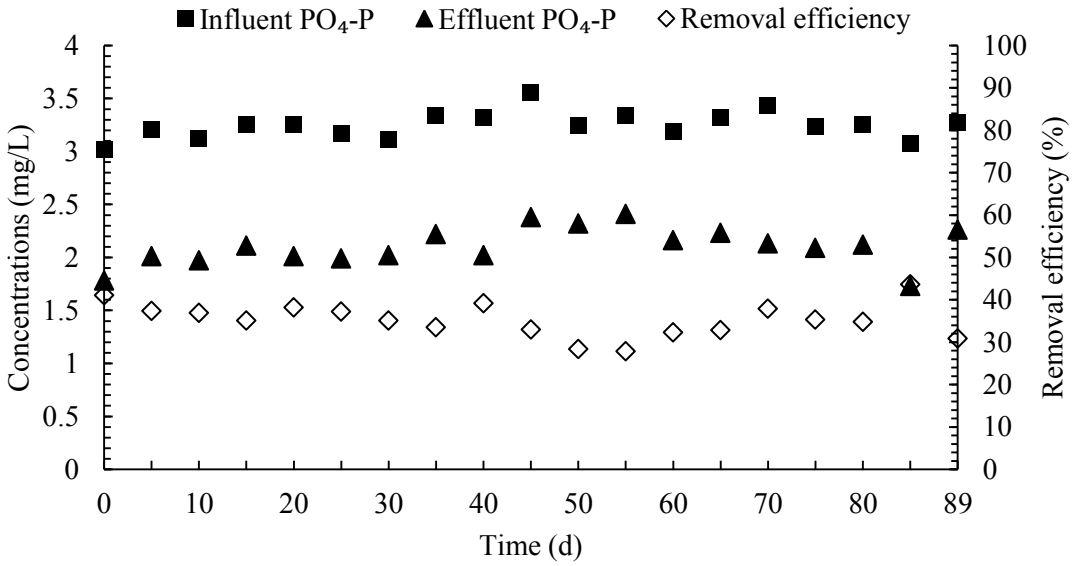

Figure 6.5 PO_4-P removal in the MB-SMBR system (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h; SMBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

Figure 6.6 illustrates the variation of MLSS and MLVSS in the SMBR. The initial MLSS and MLVSS concentrations were 0.06 and 0.05 g/L, respectively. Both MLSS and MLVSS increased steadily during the operation and reached 0.91 and 0.89 g/L, respectively, at the end of the study. The continuous increment could be due to the introduction of suspended solids from the MBBR effluent and the biomass growth within the SMBR. The increase, however, was fairly slow because of the limited supply of organic matter, nutrients and biosolids from the MBBR effluent (SMBR feed). The microscopic examination of the SMBR mixed liquor revealed that nematodes (Figure 6.7) were presented in large numbers. The observed nematodes had cylindrical bodies and moved in an S-shape in the sludge. According to Salvadó et al. (2004), the presence of nematodes indicated the low organic loading level in the reactor. Furthermore, nematodes could facilitate good floc formation and might therefore alleviate the membrane fouling caused by sludge bulking.

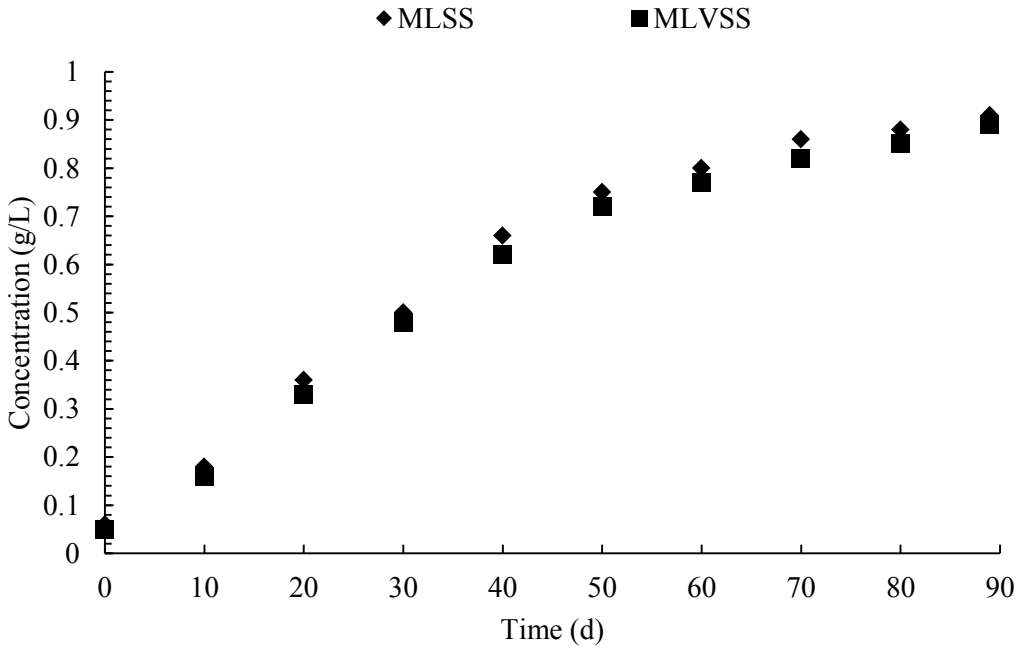

Figure 6.6 Variations of MLSS and MLVSS concentrations in the SMBR.

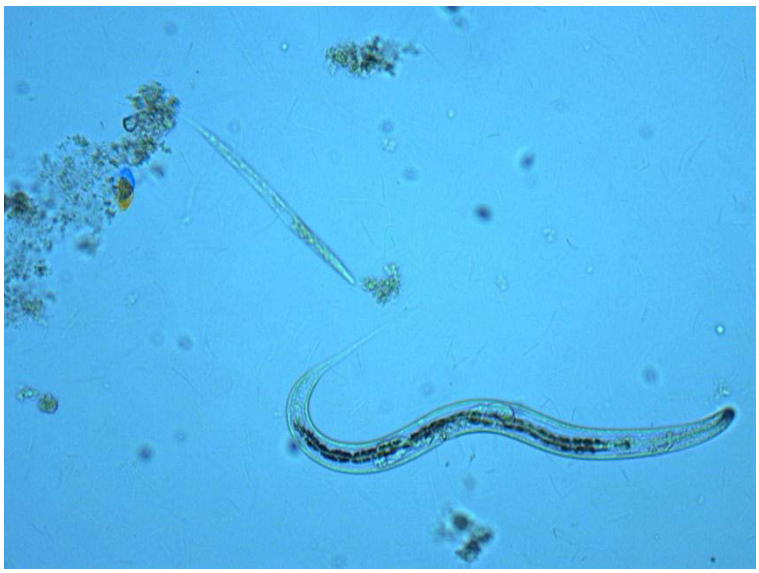

Figure 6.7 Nematodes (×20) in the SMBR.

6.3 Removal of selected micropollutants

Figure 6.8 compares the removals of selected micropollutants in the MBBR and the MB-SMBR. It is obvious that the elimination of micropollutants mainly occurred in the MBBR, whereas the SMBR obtained limited complementary removal. The elimination of the micropollutants in the SMBR might result from biodegradation, sorption by the biomass in the reactor and rejection by the membrane. Due to the low biomass concentration (<1 g/L) and relatively low HRT (6h) in the SMBR, the biological removal of these compounds was not expected to be high. The mechanisms for micropollutant retention by the membrane include size exclusion, charge repulsion, adsorption, sorption diffusion, solute-solute interactions and fouling layer interactions (Schäfer et al., 2011). During the MF process, micropollutants are commonly not retained as their molecular sizes are much smaller than the membrane pore sizes. However, retention can occur to some extent via adsorption onto membrane polymers and interaction with particles in wastewater. For instance, an MF polymer surface can significantly adsorb more than 95% of estrone (Chang et al., 2003). The highest supplementary removals of micropollutants by the SMBR (relative to the influent concentrations) were detected for octylphenol (20.9%), metronidazole (14.9%), gemfibrozil (13.4%), pentachlorophenol (13.2%), butylphenol (11.4%) and diclofenac (10.9%). For relatively hydrophobic compounds (e.g., octylphenol, pentachlorophenol and butylphenol), the removal could be explained by the sorption onto biomass and membrane surface polymers (Luo et al., 2004). Regarding gemfibrozil, pentachlorophenol and diclofenac, biodegradation could be a possible cause of their elimination. In addition, during the SMBR operation, these compounds were negatively charged (due to low pK_a), thus charge repulsion could occur between the compounds and the negatively charged membrane surface (Nghiem et al., 2005).

The overall effectiveness of MB-SMBR for micropollutant reduction is comparable with those reported for activated sludge and MBR (Luo et al., 2014; Nguyen et al., 2013). 16 out of 22 compounds exhibited removals higher than 70% in the MB-SMBR, with some persistent compounds (e.g. metronidazole and diclofenac) demonstrating good removals.

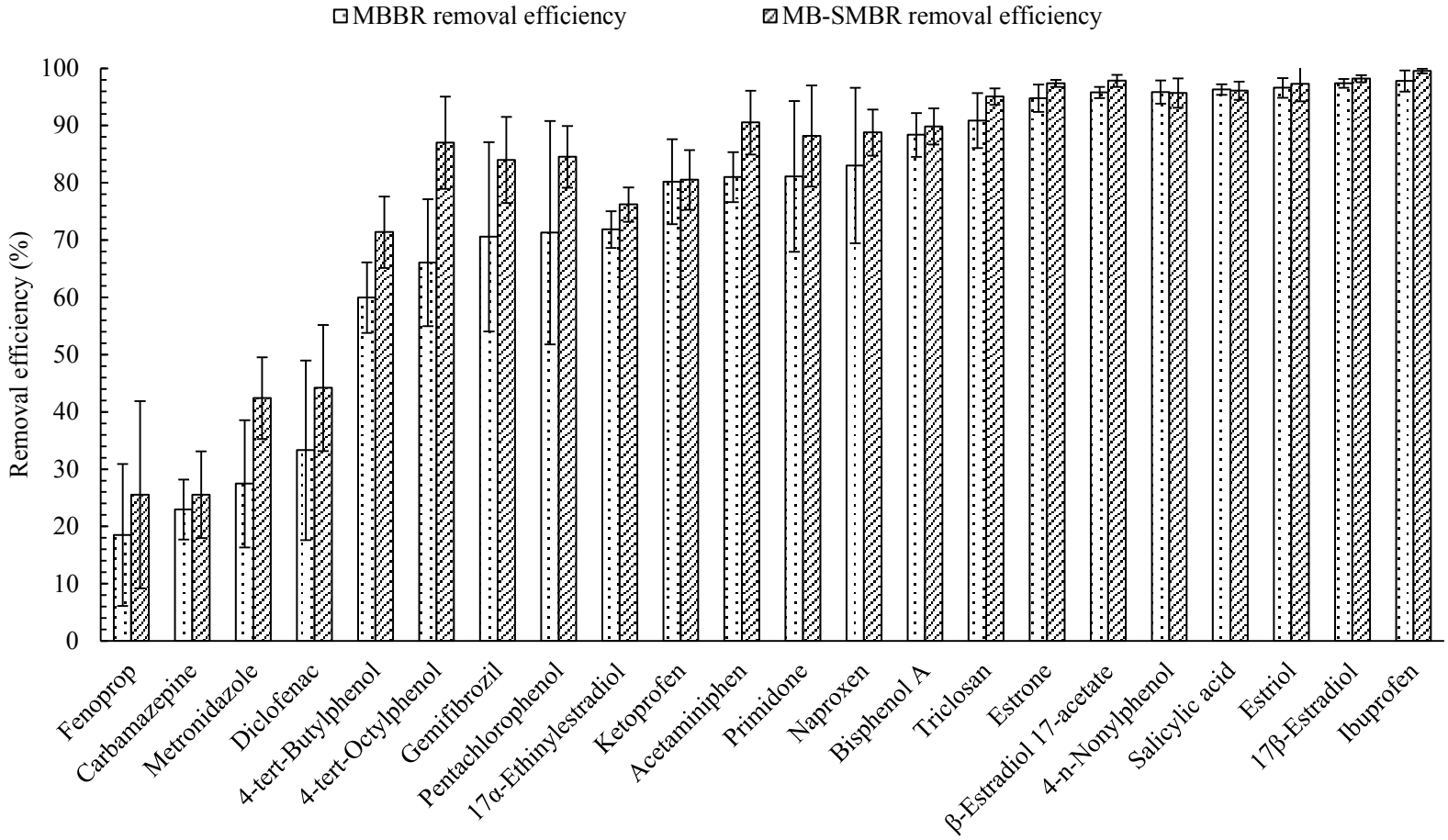

Figure 6.8 Micropollutant removal in the MBBR and MB-SMBR. An error bar represents the standard deviation of 8 measurements over 89 days (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h; SMBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

6.4 Membrane fouling analysis

Membrane fouling can be indicated by an increase in trans-membrane pressure (TMP) when a particular flux is maintained (Guo et al., 2012). Figure 6.9 shows the variation of TMP during the 89 days of MB-SMBR operation. The TMP in the MF remained less than 20 kPa for 84 days. After then, an abrupt increase in TMP was observed and the TMP exceeded 35 kPa within 5 days, suggesting that chemical cleaning was needed at this stage of operation. The TMP jump during MBR operation has not yet been fully understood by researchers, but could be attributed to 1) the variations in the local fluxes (owing to fouling), thereby causing local fluxes to exceed critical fluxes; and 2) the release of excessive EPS from the inner cells (Meng et al., 2009).

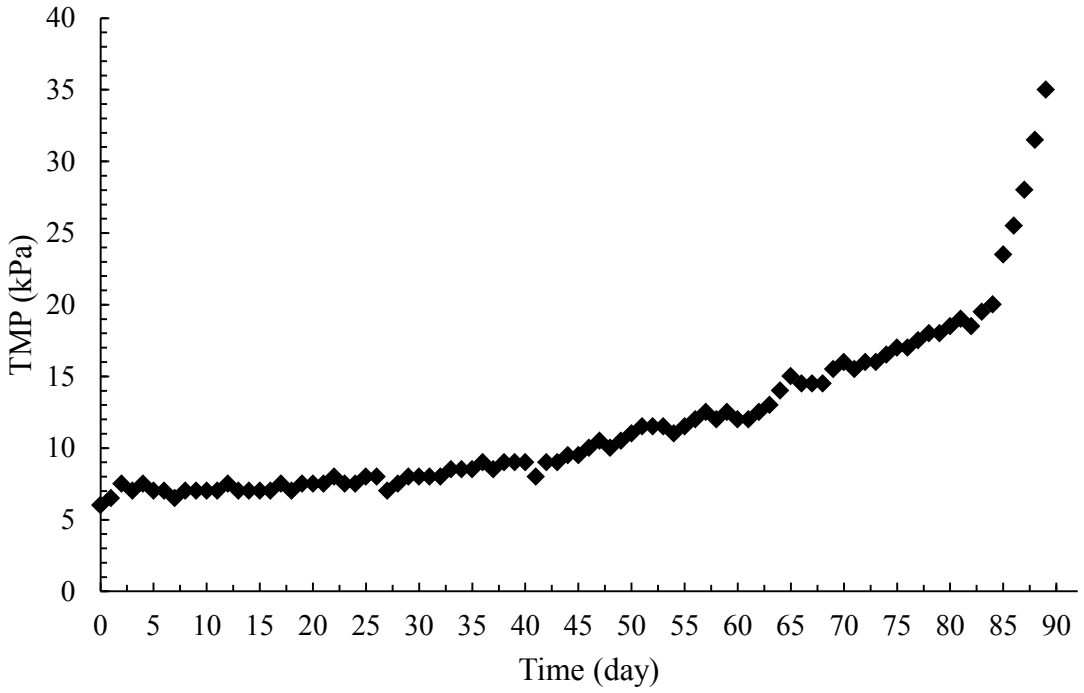

Figure 6.9 TMP profile over the 89 days of MB-SMBR operation.

During MBR operation, the fouling behaviour is directly dependent on sludge characteristics and hydrodynamic conditions (Meng et al., 2009). To gain a better understanding of the membrane fouling in the MB-SMBR, several potential influential factors, including bound EPS, SMP, Zeta potential and relatively hydrophobicity of the SMBR sludge, were analyzed.

The sludge characteristics, such as RH, zeta potential and particle size, have a potential impact on membrane fouling resistance. In general, higher RH, lower zeta potential and smaller particles may cause more severe membrane fouling (Lim et al., 2003; Meng et al., 2006). In this study, the Zeta potential was in the range of -12.1 and -19.0 mV, which was lower than the range (-20–-30 mV) commonly reported for activated sludge (Liu and Fang, 2003). The RH varied from 75.0% to 83.3%, indicating a high hydrophobicity of the sludge flocs. According to Meng et al. (2006), both the Zeta potential and RH of the SMBR implied a low membrane fouling potential. The particle size distribution analysis indicated that the size of most sludge flocs ranged between 5 and 25 μm. The relatively small particle might result in a more compact cake layer formation and thus a low permeability (Le-Clech et al., 2006). The microscopic investigation showed that the sludge in the SMBR became 'fluffy' over time and filamentous microorganisms were detected in large numbers at the final stage of the study (Figure 6.10). The overgrowth of filamentous microorganisms could be considered as another cause of the severe membrane fouling at the end of the study. The excessive presence of these bacteria also led to increased EPS levels, decreased zeta potential, more irregular floc shape and higher hydrophobicity (Le-Clech et al., 2006).

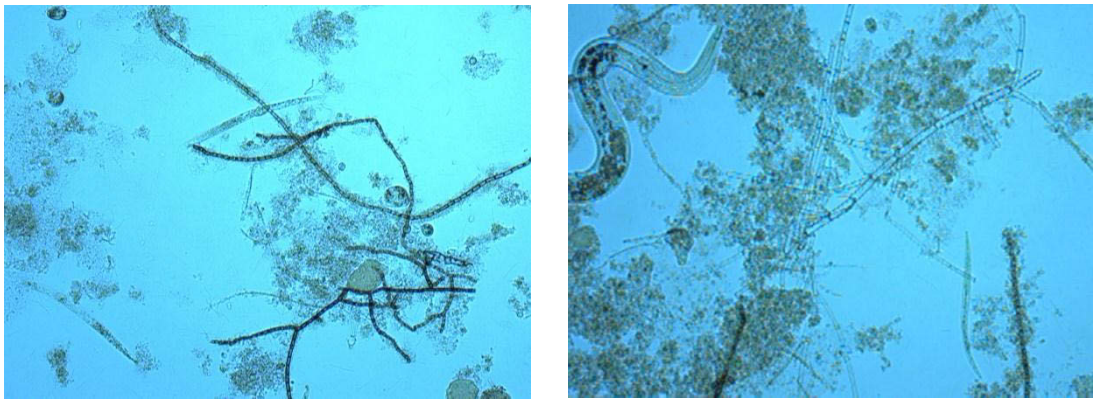

Figure 6.10 Overgrowth of filamentous bacteria observed at the final stage of the study.

Table 6.1 presents the EPS and SMP concentrations in the SMBR at different TMPs. EPS in either bound or soluble form are deemed the primary cause of membrane fouling in MBRs (Meng et al., 2009). It is noted from Table 6.1 that the EPS concentration continued increasing throughout the study and reached 16.24 mg/L at

the end. The continuous rise in EPS might result from the introduction of EPS (4.94–6.42 mg/L) through MBBR effluent as well as the biomass growth in the SMBR. As noted in Table 6.1, the ratio of proteins to polysaccharides in bound EPS increased during the treatment, which had the potential to increase hydrophobicity and zeta potential of the sludge floc, and thus impacted on the agglomeration of the sludge (Deng et al., 2014).The increase of the protein was attributable to the decreasing food to microorganism (F/M) ratios as a result of MLSS accumulation (Lee et al., 2003). EPS are not the sole factor that affects membrane fouling. SMP have also been recognized as an important membrane foulant (Rosenberger et al., 2005). In this study, despite the presence of SMP residual (4.97–6.48 mg/L) in the SMBR feed, SMP concentration remained at a low level and did not vary significantly during the operation.

Table 6.1 EPS and SMP concentrations at different TMPs (SMBR conditions: aeration rate = 6 L/min; DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

	7 kPa	10 kPa	15 kPa	18 kPa	21 kPa	24 kPa	27 kPa	30 kPa	35 kPa
EPS	4.25	6.35	6.99	6.53	7.21	8.39	11.3	15.42	16.24
Polysaccharides	2.01	3.77	3.68	4.85	4.36	5.57	3.27	6.96	5.69
Proteins	2.24	2.58	3.31	1.68	2.85	2.82	8.03	8.46	9.55
SMP	4.89	6.13	5.59	4.32	4.02	4.49	6.24	6.18	6.32
Polysaccharides	2.81	2.31	2.05	2.67	2.51	2.39	1.73	1.73	1.81
Proteins	2.08	3.78	3.54	1.65	1.51	2.2	4.51	4.45	4.51

Shirazi et al. (2010) reviewed the application of a resistance-in-series model for assessing membrane fouling using Darcy's Law. The model is as follows:

$$J = \Delta P_T/(\mu \cdot R_t) \quad (6.1)$$

$$R_t = R_m + R_C + R_f \quad (6.2)$$

Where, J is permeation flux; ΔP_T is transmembrane pressure; μ is viscosity of the permeate; R_t is total resistance of membrane filtration; R_m is intrinsic membrane resistance caused by membrane itself and permanent resistance; R_c is cake resistance formed by cake layer deposited over membrane surface; R_f is fouling resistance

caused by pore plugging and/or solute adsorption onto the membrane pore and surface.

After the experiment, the fouled membrane (Figure 6.11) was subjected to physical and chemical cleaning (see Chapter 3 for details), in order to determine different membrane fouling resistances using the equations given above. Table 6.2 displays the calculated membrane fouling resistances. As shown in the Table, the cake layer resistance contributed the most to the total resistance (76.5%), while irreversible fouling resistance, pore blocking resistance and membrane resistance were much less significant (1.0, 12.0 and 10.5%, respectively). The results were in good agreement with the results of an MBR study which reported that membrane resistance, cake layer resistance and fouling resistance due to irreversible adsorption and pore blocking accounted for 12%, 69% and 19% of the total resistance (Lee et al., 2003). Deng et al. (2014) also found that cake layer formation was one of the main factors contributing to the membrane fouling of a sponge-submerged membrane bioreactor and a conventional membrane bioreactor when treating synthetic domestic wastewater, whereas pore blocking was of much less significance.

Figure 6.11 The fouled membrane after the MB-SMBR operation (SMBR conditions: aeration rate = 6 L/min; DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

Table 6.2 Membrane resistances for different types of fouling.

Parameter	Resistance (10^{12}/m)	Percentage (%)
Clean membrane	1.33	10.5
Cake layer	9.63	76.5
Pore blocking	1.51	12.0
Irreversible fouling	0.12	1.0
Total resistance	12.59	100

6.5 Conclusion

The MB-SMBR showed stable and effective removals of TOC (93.9–96.0%), COD (93.8–96.4%) and NH_4-N (79.5–95.6%). TN showed marked variation in removal (28.2–61.6%). PO_4-P was poorly eliminated and the removal efficiency was 34.9 ± 3.9 %. The removal of organic matter and nutrients was primarily yielded in the MBBR, whereas the SMBR only achieved slight further elimination of TOC (8.5 ± 0.6%) and NH_4-N (7.3 ± 3.7%). The overall performance of the MB-SMBR in micropollutants removal was comparable with those reported for other systems (e.g., activated sludge and MBR). The SMBR unit displayed fairly limited micropollutants removal due to relatively large membrane pore size. The highest supplementary reductions in the SMBR (relative to the influent concentrations) were obtained for octylphenol (20.9%), metronidazole (14.9%), gemfibrozil (13.4%), pentachlorophenol (13.2%), butylphenol (11.4%) and diclofenac (10.9%). The development of TMP remained very slow for 84 days. A rapid increase in TMP was observed afterwards. The accelerated fouling rate at the end of the study might be due to the high EPS level caused by the accumulation of biomass as well as the overgrowth of filamentous bacteria. The overall membrane fouling was mainly contributed by the cake layer formed on the membrane surface (76.5 %), whereas pore blocking and irreversible fouling did not occur significantly.

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Chapter 7

Conclusions and Recommendations

7.1 Conclusions

The literature review revealed that current WWTPs are not able to provide an absolute barrier for micropollutant removal. Establishing optimal removal strategies for micropollutants remains a challenge to environmental engineers in order to minimize their adverse impact on the environment and human health. The MBBR technology has been considered as an effective solution for removing organic and nutrients from wastewater. However, its effectiveness for micropollutant removal is still unknown. Therefore, this study investigated the effectiveness of a sponge-based MBBR for micropollutant removal. Furthermore, a hybrid system combining the MBBR with a submerged membrane bioreactor (MB-SMBR) was also evaluated with respect to micropollutant removal and membrane fouling.

Batch MBBR experiments were conducted to assess short-term micropollutant removal. Bisphenol A, etrone, 17-β-estradiol, 17-α ethinylestradiol, 4-n-nonylphenol, 4-tert-octylphenol and triclosan were significantly adsorbed by non-acclimatized sponge. The sorption efficiency of micropollutants was dependant on the hydrophobicity of the compounds. The experiments with acclimatized sponge showed considerably higher removals of some less hydrophobic and readily biodegradable micropollutants, such as acetaminophen, diclofenac, gemfibrozil, ibuprofen, ketoprofen, naproxen and salicylic acid. Carbamazepine, fenoprop and metronidazole were poorly eliminated under all the experimental conditions due to their non-degradable characteristics and low hydrophobicity. The removals of acetaminophen, carbamazepine, diclofenac, fenoprop, gemifibrozil, ketoprofen, and naproxen were elevated when the filling ratio of acclimatized sponge was increased.

The sponge-based MBBR showed effective removals of organic matter and ammonia during the 170-day operation. The reductions of TOC and COD were consistently high (>90%). Ammonia was also significantly eliminated (73.6–95.6%). By contrast, TN and PO_4-P exhibited limited removals because of the high DO concentrations in the reactor. The MBBR system achieved varying removals of the selected micropollutants due to their diverse physicochemical properties (biodegradability and hydrophobicity). 16 out of 22 compounds were eliminated by more than 70%. As

a whole, the effectiveness of MBBR was comparable with those of activated sludge processes and MBRs. The MBBR appeared to be effective in removing ibuprofen, metronidazole, naproxen, primidone, triclosan, estrone, 17-α ethinylestradiol, 4-n-nonylphenol, 4-tert-octylphenol and fenoprop. However, carbamazepine, fenoprop and diclofenac exhibited poor removals (25.9%, 31.0% and 45.7%, respectively) because of their low biodegradability and hydrophobicity. Biodegradation served as a major removal pathway for most compounds. Sorption onto biosolids was a notable removal mechanism of some persistent micropollutants. Particularly, carbamazepine, ketoprofen and penta-chlorophenol were found at high concentrations on both suspended- and attached-growth biosolids. This was because 1) the recalcitrant micropollutants were abundant in the aqueous phase, which resulted in high compound levels on biosolids, and 2) the adsorbed compounds were poorly biodegradable and could thus remain adsorbed on the biosolids.

To produce an effluent with low turbidity, an SMBR was installed after the MBBR system. The MB-SMBR yielded good removals of TOC (93.9–96.0%), COD (93.8–96.4%) and NH_4-N (79.5–95.6%). In contrast, TN removal was variable (28.2–61.6%) and PO_4-P could only be eliminated by around 35%. The combination of MBBR and SMBR demonstrated appreciable micropollutant removal efficiency. The results showed that most of the micropollutant removal was observed in the MBBR, while the SMBR demonstrated a limited supplementary effect. The greatest complementary eliminations by the SMBR (relative to the influent concentrations) were detected for octylphenol (20.9%), metronidazole (14.9%), gemfibrozil (13.4%), pentachlorophenol (13.2%), butylphenol (11.4%) and diclofenac (10.9%). The TMP of the SMBR increased slowly during the first 84 days. Severe membrane fouling occurred after then, which could be ascribed to the high EPS level. In addition, the abundant filamentous bacteria observed at the late stage of the study could be another significant contributor to the membrane fouling. The total membrane fouling was principally caused by the cake layer deposited on the membrane surface, while pore blocking and irreversible fouling appeared to be much less relevant.

7.2 Recommendations for future research

In the course of this study, various aspects were found worthy of further research:

1) Since the sponge carrier is the key element in the MBBR, future research is needed to assess the effects of the size of sponge cubes, filling ratio and circulating velocity on micropollutant removal. It is also worthwhile to compare the MBBR efficiency using different attached-growth media, such as polymer carriers.

2) Carbamazepine, fenoprop and diclofenac were found highly resistant to the MBBR treatment. In order to improve the removal efficiency of these compounds, further studies on the upgrade of the current treatment system (e.g., supplementary biosorption, PAC addition and post-ozonation) would be interesting.

3) As suggested in the literature review, wastewater characteristics significantly affect the micropollutants removal. As only synthetic wastewater was used for this study, further investigations using various wastewaters (e.g., municipal wastewater, industrial wastewater and hospital effluents) are necessary to elucidate the effectiveness of the MBBR in removing micropollutants.

4) Previous studies have reported that there was a considerable influence of nitrifying conditions on micropollutant removal. The research on evaluating the correlation between the nitrification capacity of the MBBR and the removal efficiency of micropollutants should be considered.

5) In this study, the attached-growth biomass appeared to possess better biodegradation capacity as compared with the suspended-growth biomass. It was possibly due to a more diverse microbial community and the existence of different sludge characteristics on and inside the sponge cubes. Further studies are required to substantiate this hypothesis.

6) In-depth studies on membrane fouling of MB-SMBR are essential to identify the major fouling contributors and to establish effective fouling control strategies for the sustainable operation of MB-SMBR systems.

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Publications Related to This Research

Accepted

Luo Y, Guo W, Ngo HH, Nghiem LD, Hai FI, Zhang J, etc. A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. Sci Total Environ 2014; 473–474: 619–41.

Luo Y, Guo W, Ngo HH, Nghiem LD, Hai FI, Kang J, etc. Removal and fate of micropollutants in a sponge-based moving bed bioreactor. Bioresour Technol 2014; 159: 313–9.

In preparation

Luo Y, Guo W, Ngo HH, Nghiem LD, Hai FI, Kang J, etc. Removal of Micropollutants by a Moving Bed-Submerged Membrane Bioreactor (MB-SMBR) System.