Evaluating the Performance of A Sponge-based Moving Bed Bioreactor on Micropollutants Removal

by

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CERTIFICATE OF ORIGINAL AUTHORSHIP

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

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

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Date: 23/05/2016

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List of Abbreviations

CAS	Conventional activate sludge
DO	Dissolved oxygen
EPS	Extracellular polymeric substance
GAC	Granule activated carbon
GC-MS	Gas chromatography-mass spectrometry
HRT	Hydraulic retention time
MBBR	Moving bed biofilm reactor
MBR	Membrane bioreactor
MBBR-MBR	Moving bed biofilm reactor-membrane bioreactor
MF	Microfiltration
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
OLR	Organic loading rate
PAC	Powdered activated carbon
PCP	Personal care product
PPCP	Pharmaceutical and personal care product
PU	Polyurethane
PVA	Polyvinyl alcohol
PVDF	Polyvinylidene fluoride
SMP	Soluble microbial products
SND	Simultaneous nitrification–denitrification
SPE	Solid phase extraction
SRT	Sludge retention time
TMP	Transmembrane pressure
TN	Total nitrogen
TOC	Total organic carbon
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_{OW}	Octanol–water partition coefficient
L_s	Load of micropollutant removed via sorption (ng)
L_b	Load of micropollutant removed via biodegradation (ng)
L_{inf}	the influent load of micropollutants over the experimental period (ng)
L_{eff}	the effluent load of micropollutants over the experimental period (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

The ubiquitous occurrence of micropollutants and their metabolites in the aquatic environment has posed threats to living organisms to a great extent. However, effective micropollutants removal normally requires longer hydraulic retention time (HRT) when using biological treatment systems. As an ideal and low-cost material for attached-growth microorganisms, polyurethane sponge has exhibited high potential to eliminate micropollutants. In this study, a sponge-based moving bed biofilm reactor (MBBR) was investigated at four different HRTs (24, 18, 12, 6 h), to better understanding of the effect of HRT on micropollutant removal. The MBBR as pretreatment to a membrane bioreactor (MBBR-MBR hybrid system) was also evaluated. Four groups of frequently detected micropollutants in wastewater (total 22 compounds) were selected, namely pharmaceuticals and personal care products (PPCPs), pesticides, hormones and industrial chemicals.

The MBBR alone showed stable and effective removals of TOC (92.6% - 95.8%), COD (93.0% - 96.1%) and NH_4-H (73.6%-95.6%) at all HRTs while improving PO_4-P removal at HRT of 18 h. The MBBR showed the highest performance efficiency for removing DOC, COD, NH_4-N, PO_4-P and TN at HRT of 18 h, which were 96.1±0.4%, 97.4±0.8%, 91.1±1.6%, 49.9±7.2%, and 72.3±6.9%, respectively. This could be explained by the food to microorganisms (F/M) ratio in the MBBR. In addition, higher NH_4-N removal at HRT of 18 h could be attributed to the increased population of ammonium oxidation bacteria in the MBBR unit. Moreover, the use of phosphate for biomass growth and the phosphorus uptake by phosphate accumulating organisms (PAOs) could contribute to the high removal of PO_4-P at HRT of 18 h. In terms of micropollutants removal, MBBR achieved comparable removal compared to other biological treatment such as activated sludge processes and membrane bioreactor. Although the micropollutants were subjected to biodegradation and sorption, the results indicated compound-specific variation in removal at all HRTs, ranging from 10.7% (carbamazepine) to 98.4% (ibuprofen). Among the selected micropollutants, most of them were biodegradable excluding carbamazepine, fenoprop and metronidazole. In addition, the micropollutants removal could remain constantly high even at lower HRTs with more consistent removal efficiency over the

experimental period (except for carbamazepine, fenoprop, 17α-ethinylestradiol and 4-tert-octylphenol). Particularly, at HRT of 18 h, the removal of diclofenac was significantly improved by more than 30% and the removals of ketoprofen, gemifibrozil, acetaminiphen, bisphenol A, and pentachlorophenol were also better. Overall, HRT of 18 h was the optimum HRT for biological degradation of the micropollutants in the MBBR.

When using an MBBR as pretreatment to an MBR, the MBBR-MBR hybrid system achieved better removal efficiencies for selected micropollutants, such as metronidazole and carbamazepine. Both metronidazole and carbamazepine are nitrogen bearing compounds, where nitrogen is bound to the cyclic structure. The infinite SRT applied in this study could have facilitated the enhanced removal of the nitrogenous compounds. Even MBR can prevent the washout of slow-growing microorganisms like nitrifiers, the impact of MBR removal was minimal at all HRTs. This may probably due to the low MLSS concentration and the large pore size (0.2 μm; two orders of magnitude larger than the molecular sizes of micropollutants) of the MF membrane used in this study. In addition, a longer HRT (e.g. HRT of 24 h or 18 h) can significantly mitigate membrane fouling when compared with a relatively short HRT (e.g. HRT of 6 h). Especially, the TMP value maintained less than 15 kPa for 60 days (HRT of 18 h) and 68 days (HRT of 24 h). The level of EPS were similar at the beginning of all HRTs, then gradually increased to 15.24 mg/L, 16.43 mg/L, 19.88 mg/L and 22.93 mg/L at the end of operation for MBBR unit under HRT of 24 h, 18 h, 12 h, and 6 h, respectively. The SMP concentration varied for different HRTs but showed minor variation under the same HRT. The SMP concentration was lower at HRT of 24 h, while a significantly higher SMP concentration was observed at HRT of 6 h. As a whole, the MBBR-MBR hybrid system showed improvement in both micropollutants elimination and mitigation in membrane fouling.

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Chapter 1

Introduction

1.1 Background

Under the strong impetus of ever-growing industrialisation, the continued rise in chemical consumption is to achieve high material living standards. The extensive use of chemicals is mainly in medicines, pesticides, personal care products and industrial merchandises. The constant input of these problematic substances leads to their accumulation in the ecosystem, posing great threads to public health and environment. In addition, the mentioned substances are mostly polar and persistent, which affect fundamental biochemical processes in the aquatic environment, even at trace concentrations. We commonly refer them as 'micropollutants'. The main pathway of micropollutant contamination is through wastewater discharge from diverse sources (e.g. municipal wastewater).

Due to the nature of micropollutants, many of these potentially harmful compounds are not biodegradable and do not absorb easily, which makes it difficult or impossible to eliminate them. Moreover, the effluents containing micropollutants from conventional wastewater treatment plants (WWTPs) cannot be well-treated with current treatment systems. In order to improve the water quality and reduce the potential negative ecological effects, development of various treatment processes is essential to ensure the adequate removal of micropollutants.

1.2 Impact of micropollutants and reduction strategies

A wide range and a large amount of chemicals used on a daily basis at homes, in workplaces or in the urban environment go into the aquatic environment in many ways. Fig. 1.1 illustrates the possible source and pathways for the introduction of micropollutant into the environment. These micropollutants are pharmaceutical and personal care products (PPCPs), steroid hormones, surfactants, industrial chemicals, and pesticides. They mostly end up in the sewer system and being treated in the wastewater treatment plants (WWTPs). However, micropollutants often experience inadequate removal due to the low concentration, diverse physiochemical properties (hydrophobicity, biodegradability, and volatility etc.) and types of treatment. The micropollutants residue in the treated effluent discharging from WWTPs becomes a common route into the aquatic environment.

Besides municipal wastewater, the accumulation of micropollutants could also from hospital discharges, industrial wastewater, stormwater runoff, agricultural runoff, landfill leachate, and livestock waste (Nakada et al., 2008 ;Hillebrand et al., 2012; Kuroda et al., 2012; Tran et al., 2014). For example, a possible route for agricultural pesticides could be migrate from the soil surface through the soil zone, the unsaturated zone and the saturated zone in the well-established way (Stuart et al., 2012). In addition, landfill leachates may contain a large amount of pharmaceuticals, personal care products, as well as a range of industrial compounds (Barnes et al., 2004; Buszka et al., 2009).

Groundwater not only supplies a large portion of public water supply, but also provides water for industry and irrigation, baseflow support to surface water (Clara et al., 2004; Tran et al., 2013; Tran et al. 2015). The interaction between groundwater and surface could consider being another important pathway for various micropollutants. As some treated discharge from industrial premises and sewage treatment is going to surface water directly, certain untreated micropollutants may then infiltrate to groundwater.

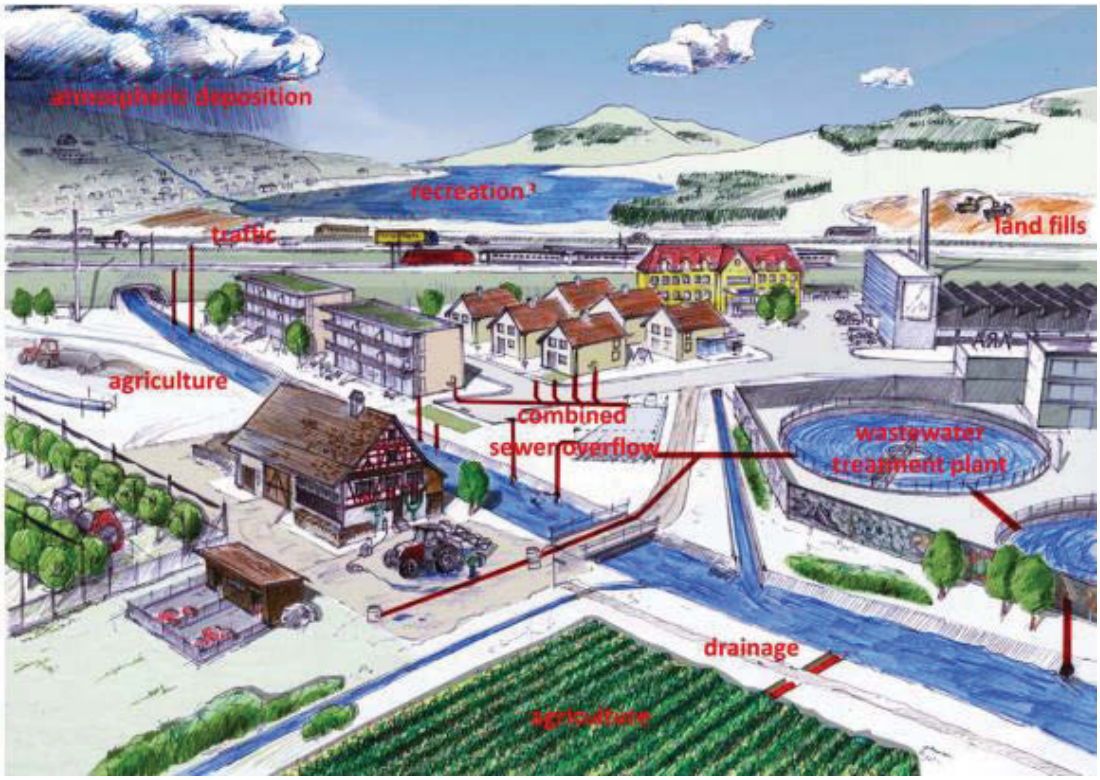


Figure 1.1 Schematic presentation of diffuse and point source entry paths of micropollutants in the environment

To combat the current micropollutant-related issues, it is imperative that non-technological measures (e.g., regulations) and technological methods (e.g., source control and wastewater treatment techniques) are economically and effectively available. Today's wastewater treatment plants (WWTPs) are primarily designed to remove solids, biodegradable substances and nutrients. However, the presence and detection of micropollutants has posed a new challenge for the current wastewater treatment processes to ensure the quality of treated effluent. In this context, attached-growth processes are dramatically emerging and have been considered as an attractive choice for upgrading current WWTPs. Compared to conventional activated sludge (CAS) processes, attached-growth processes perform more efficiently, due to their simplicity of operation with low operational and maintenance cost, feasibility of growing microorganisms with relatively low specific growth rates, tolerance to variation in hydraulic and pollutants loading rates, higher biomass concentration and treatment stability, better oxygen transfer and high nitrification rate and greater

resistance to toxicity (Albertson, 2000; Guo et al., 2012; Loupasaki and Diamadopoulos, 2012).

The moving bed biofilm reactor (MBBR) is a technology based on the concept of attached growth process. The MBBR delivers a flexible, cost-effective, and easy-to-operate means to address current wastewater issues and the expandability to meet future loads and increasingly stringent discharge requirements. Continued research and experience have demonstrated that MBBRs can offer enhanced biological process and improved treatment efficiency, and are especially well suited to biological nutrient removal (Ødegaard, 2006; Kermani et al., 2008; Di Trapani et al., 2008). While the MBBR has become a proven technology for eliminating conventional contaminants, little is known about the micropollutant removal capacity of this treatment technique. Therefore, the paucity of knowledge has led to some recent efforts to evaluate the effectiveness of MBBR technology for micropollutant elimination (Falås et al., 2012; Falås et al., 2013; Lim et al., 2013; Luo et al., 2014a; Hassani et al., 2014; Dvořák et al., 2014). Encouragingly, these studies have shown successful results for micropollutant removal applications. It has been generally agreed that, by adding attached growth carriers, the MBBR system is able to provide favourable conditions, such as a diverse microbial community and the coexistence of different redox conditions, for the decomposition of a wider spectrum of micropollutants.

Despite the advantages of MBBR, the major concern of its applications is the decrease of sludge settleability when treating high strength wastewater, which may lead to severe operational problems when clarifiers are employed as solid separation systems. To counter this, various hybrid systems have been developed, which involve modifications of the basic MBBR system by adding coagulants (metal salts or cationic polymers) or applying membrane filtration or floatation as the solid separation process (Ødegaard et al., 2006). Among all these modifications, combining membrane technology with MBBR is an established concept with growing popularity, which also results in better membrane performance (Yang et al., 2008; Phattaranawik and Leiknes, 2010; Sun et al., 2012; Duan et al., 2013; Ye et al., 2013). Although there are limited number of studies concerning MBBR-membrane

hybrid systems, some of the results highlighted the potential to mitigate membrane fouling due to the decreased suspended solid environment in the process, regardless system configurations and the choices of biocarriers (Leiknes et al., 2006; Ivanovic et al., 2006; Ivanovic and Leiknes, 2008; Dong et al., 2014). However, some researchers indicated that the MBBR-membrane filtration hybrid system could experience severe membrane fouling when large amounts of submicron colloidal particles were present in the reactor (Leiknes et al., 2006; Sun et al., 2012). In addition, the occasional sludge bulking in the hybrid systems could also contribute on a negative level to the membrane performance.

1.3 Objectives of the research

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

- To investigate the long-term micropollutants removal in a sponge-based MBBR under different HRTs (HRT of 24h, 18h, 12h and 6h);
- To elucidate the fate of the micropollutants during the treatment in the MBBR
- To evaluate the performance of the MBBR-MBR 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 reviews the use of attached growth system regarding micropollutants removal. Chapter 3 describes the materials, experimental set-ups, operational conditions and analytical methods for the MBBR and MBBR-MBR hybrid system. Chapter 4 presents the results of operation of the MBBR system under HRT of 24 h, 18 h, 12 h and 6 h, in terms of micropollutants removal. In Chapter 5, the results of micropollutants removal and membrane fouling were obtained from the MBBR-MBR hybrid system and were analysed to gain the

optimal condition for the MBBR-MBR system and membrane fouling reduction. The final chapter draws the conclusion for all the findings from this study and also gives some recommendations for the future research.

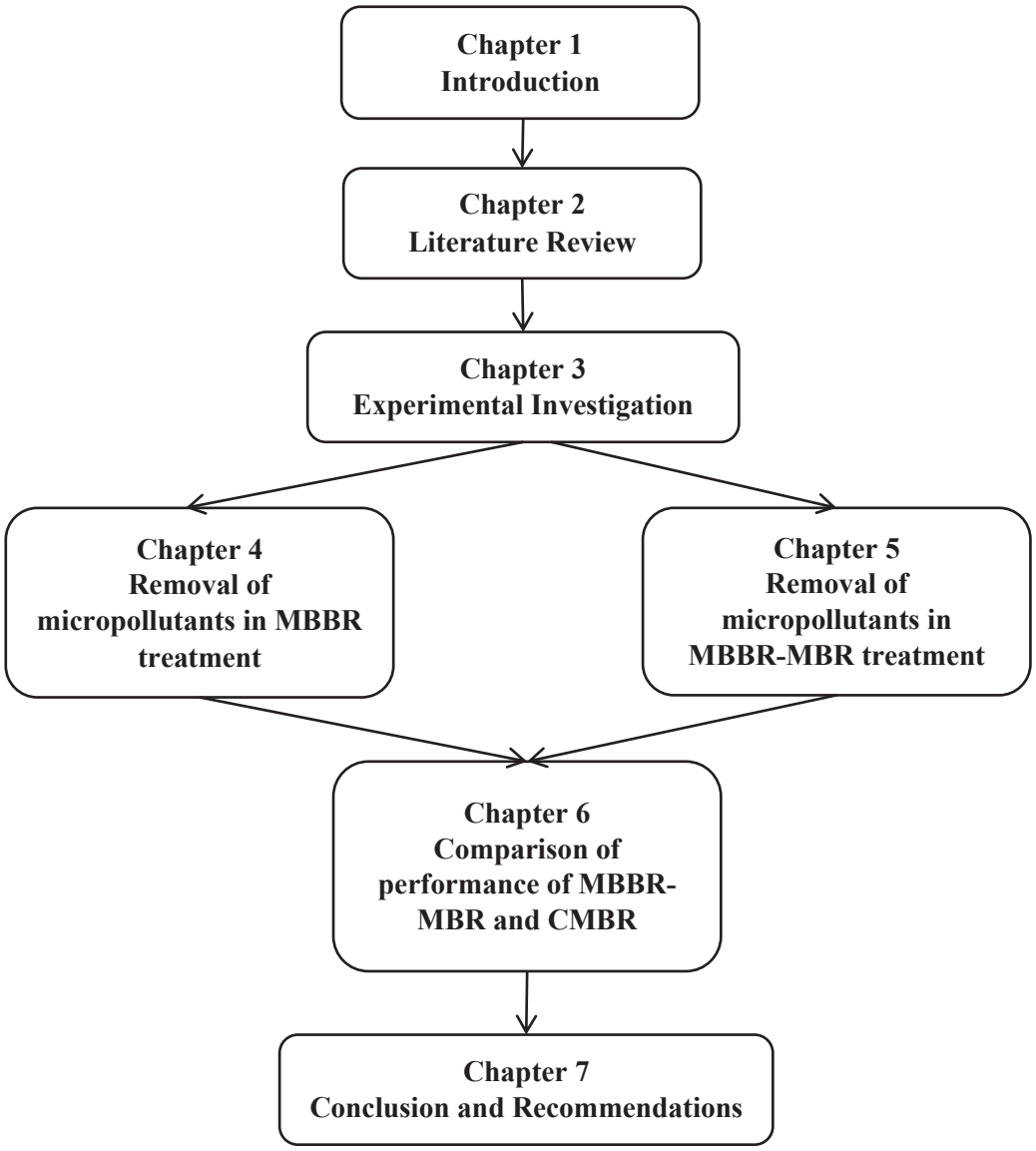
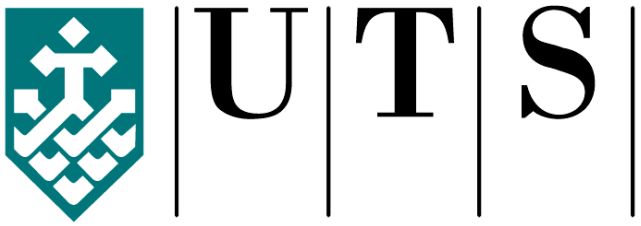


Figure 1.2 The outline of the thesis



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Chapter 2

Literature Review

2.1 Introduction

During the last decades, the concerns over water scarcity and more stringent discharge limits have driven the demand for more advanced and cost-effective technical solutions to wastewater treatment. In this context, attached-growth processes are dramatically emerging and have been considered as an attractive choice for upgrading current wastewater treatment plants (WWTPs). Compared to conventional activated sludge (AS) processes, attached-growth processes perform more efficiently, due to their simplicity of operation with low operational and maintenance cost, feasibility of growing microorganisms with relatively low specific growth rates, tolerance to variation in hydraulic and pollutants loading rates, higher biomass concentration and treatment stability, better oxygen transfer and high nitrification rate and greater resistance to toxicity (Albertson, 2000; Guo et al., 2012; Loupasaki and Diamadopoulos, 2012).

Attached growth processes are biological treatment processes employing media that supports biomass on its surface and within its porous structure. This highly active attached biofilm enables the attached growth systems to provide more efficient treatment. The attached growth systems include trickling filter (TF), submerged fixed-bed biofilm reactor, granular media biofilter, rotating biological contactor (RBC), fluidized bed reactor, and moving bed biofilm reactor (MBBR). To date, several review papers have been published regarding the use of attached growth reactors in wastewater treatment and the factors that affecting the treatment efficiency. Barwal and Chaudhary (2014) summarized the performance of biocarriers in MBBR, and pointed out that the attached biofilm on media degrades dissolved pollutants in the wastewater stream. Each biofilm media adds productivity via the provision of an active surface area sustaining bacteria within protected cells. It is high-density population of bacteria that achieves high-rate biodegradation with the attached growth system, therefore making the effective surface area of media an important design parameter. Ivanovic and Leiknes (2012) reviewed the status of MBR technology with biofilm implementation for wastewater treatment to identify performance and operational characteristics. They reviewed that the utilization of biofilm media in MBR was to reduce the negative impact of suspended solid,

improve the filterability and lower membrane fouling, enhance nutrient removal and reduce the membrane cake layer formation. Guo et al. (2012) reviewed the roles of various attached growth media used in hybrid membrane processes in enhancement of system performance. They concluded that MBR-coupled attached growth processes have outstanding advantages over the conventional biological treatment process, because attached growth media (e.g. BAC, plastic media and porous sponge) is inclined to improving the performance of MBR by migrating membrane fouling and retaining the membrane permeability. Loupasaki and Diamadopoulos (2012) outlined the design and operational characteristics of attached growth processes in terms of packing media, organic loading rates, temperatures, and achieved removal rates. The review mentioned that the media material selection was crucial in determining what microorganisms would be established and dominated the system. McQuarrie and Boltz (2011) summarized and expended on MBBR process design procedures, provided an overview of some commercially available systems and their components. They mainly focused on the impact of some commercially used plastic media on the MBBR performance as a design parameter. Although part of the above reviews included some information concerning biofilm media and its impact on system performance, no attempt has been made to systematically summarize the effects of media material on various attached-growth systems. Due to the specialty of the attached-growth process, the media is of great importance to maintain a large amount of active biomass and a wide variety of microbial populations, as the high specific surface that provided by attached growth media is good for biofilm attachment and development. Furthermore, the media plays a key role in governing biofilm attachment, because the contaminants in wastewater can be removed by biological degradation incorporated into the attached microbial biomass, adsorbed to the media material or to the microbial biofilm (Guo et al., 2009). Additionally, the characteristics of media determine the structure of the biofilms developed in the reactors, as well as the reactor operation mode and the process effectiveness. Therefore, to better understand the roles of media materials in the attached growth systems, this review was to sum up properties of various biofilm supporting media, as well as to offer a comprehensive overview about their influences on the performance of attached growth systems. The future research needs regarding media materials were also included.

2.2 Micropollutants contanmination

With the revolutionized development of technologies and significant advancement of analytical methods, micropollutants have been frequently detected in wastewater recently. Despite the low concentration of micropollutants, they raise considerable ecological issues and are a major concern to the living organism. In addition, most of these micropollutants, such as pharmaceuticals and personal care products (PPCPs) and various industrial chemicals, are not metabolized and have been discharged into sewer system, which pose challenges to the current operation and future upgrade of wastewater treatment plants (WWTPs). Therefore, necessary methods should be taken to protect the aquatic environment from micropollutant contamination.

2.2.1 Adverse effects of micropollutants

The issues of micropollutants have been considered as a detrimental threat to the environment, especially the toxicity on living organisms, due to their biologically active and persistent characteristics. The adverse impacts of micropollutants can be different according to their categories (including PPCPs, steroid hormones, pesticides, and industrial chemicals), doses, and physiochemical properties (Table 2.1).

For PPCPs, pharmaceuticals are basically commercial drugs and medicines that are taken to treat illness, disease, and medical conditions in both humans and animals, while personal care products include a wide variety of compounds, such as perfumes, masks, and make ups etc. These PPCPs are mostly persistent and remain biologically active after disposal. For instance, several antibiotics not only have been reported to significantly inhibit algae and cyanobacteria growth with low concentration, but also potentially favour the development of antibiotics resistant pathogens when they reach certain concentration (Ebert et al., 2011; González-Pleiter et al., 2013; Sandegren, 2014). They also may have unexpected biochemical interactions when mixed with other compounds, and may concentrate in food chain and affect the aquatic organisms. Most of these impacts are chronic sub-lethal, but it also means that constant exposure to very low level of PPCPs can be harmful, especially when the municipal WWTP effluents could cause surface water contamination, raising the

question of drinking water pollution. Therefore, efforts should be made to protect the aquatic environment and human health.

In terms of steroid hormones, they are steroids that act as hormones, including a variety of natural and synthetic compounds. Steroid hormones help control metabolism, inflammation, immune functions, salt and water balance, development of sexual characteristics, and the ability to withstand illness and injury. Natural steroid hormones (estrone, estriol and 17β-estradiol) are mostly found in human and mammalian urine, while synthetic hormones (ethinylestradiol) are widely used as ingredient of contraceptive pills. Because steroids are lipid-soluble, they can diffuse fairly freely from the blood through the cell membrane and into the cytoplasm of target cells, hence exposure to them from the environment widely impacts biological communities. The high endocrine disrupting activity of steroid hormones cannot be ignored.

Regarding pesticides, they are substances meant for attracting, seducing, and then destroying any pest. The primary upsides of pesticides include controlling 1) pests and plant disease vectors, 2) human/livestock disease vectors and nuisance organisms and 3) organisms that harm other human activities and structures. Despite the benefit of pesticides, their impacts on the environment and human health still are of great concerns. The United States Environmental Protection Agency pointed out that pesticide exposure can cause a variety of adverse health effects, ranging from simple irritation of the skin and eyes to more severe effects such as affecting the nervous system, mimicking hormones causing reproductive problems, and also causing cancer. In addition, some persistent pesticides accumulate in the contaminated area as a result of their widely usage in the past.

As for industrial chemicals, their toxicity to the aquatic living organisms is of great concern. Bisphenol A (BPA) is an organic synthetic compound that commonly used in manufacturing consumer plastic goods, such as water bottles, sports equipment, CDs, and DVDs. In addition to being present in many products that people use daily, BPA has the ability to bioaccumulate, especially in water bodies, even after wastewater treatment.

Table 2.1 Summary of adverse effects from micropollutants

Micropollutants	Examples of adverse effects on aquatic organisms	References
PPCPs	• Estrogenic/mutagenic activity and genotoxicity causing by bioaccumulation of diclofenac, ibuprofen and gemfibrozil in fish blood and plasma	Brown et al., 2007
	• Triclosan affects river biofilms and algae community structure at concentration potentially less than 0.5 μg/L	Franz et al., 2008; Ricart et al., 2010
	• Triclosan and its bi-product can bioaccumulate in algae, snails and fish	Stasinakis and Gatidou, 2010
	• Extensive use of antibiotics could increase the development of antibiotic resistant bacteria in the environment	Dreising, 2011
	• Diclofenac residue accumulation led to extraordinarily high mortality of oriental white-backed vultures in India and Pakistan	Fatta-Kassinos et al., 2011
	•	
Steroid hormones	• Even low level of steroid hormones could cause feminization of aquatic and terrestrial special such as frogs, turtles and mice	Stasinakis and Gatidou, 2010
	• 4 ng/L concentration of ethinylestradiol prevented development of secondary sexual characteristics of male fathead minnows	Länge et al., 2001
	• Estrogen use led to prostate cancer development	Hess-Wilson and Knudsen, 2006
Pesticides	• Human sperm DNA damage caused by several organophosphoric pesticides	Salazar-Arredondo, 2008
	• Poisoning events associated with organophosphate insecticides and carbamates are frequently reported	Li et al., 2014
Industrial chemicals	• Interaction with protein and its endocrine disruptor characteristics, Bisphenol A is toxic to aquatic and terrestrial organisms	Rubin, 2011

2.2.2 Occurrence of micropollutants in aquatic environment

A wide range and a large amount of chemicals used on a daily basis at homes, in workplaces or in the urban environment go into the aquatic environment in many ways. Fig. 2.1 illustrates the possible source and pathways for the introduction of micropollutant into the environment. These micropollutants are pharmaceutical and personal care products (PPCPs), steroid hormones, surfactants, industrial chemicals, and pesticides. They mostly end up in the sewer system and being treated in the wastewater treatment plants (WWTPs) (Stuart et al., 2012). However, micropollutants often experience inadequate removal due to the low concentration, diverse physiochemical properties (hydrophobicity, biodegradability, and volatility etc.) and types of treatment. The micropollutants residue in the treated effluent discharging from WWTPs becomes a common route into the aquatic environment.

Besides municipal wastewater, the accumulation of micropollutants could also from hospital discharges, industrial wastewater, stormwater runoff, agricultural runoff, landfill leachate, and livestock waste (Nakada et al., 2008 ;Hillebrand et al., 2012; Kuroda et al., 2012; Tran et al., 2014). For example, a possible route for agricultural pesticides could be migrate from the soil surface through the soil zone, the unsaturated zone and the saturated zone in the well-established way (Stuart et al., 2012). In addition, landfill leachates may contain a large amount of pharmaceuticals, personal care products, as well as a range of industrial compounds (Barnes et al., 2004; Buszka et al., 2009).

Groundwater not only supplies a large portion of public water supply, but also provides water for industry and irrigation, baseflow support to surface water (Clara et al., 2004; Tran et al., 2013; Tran et al. 2015). The interaction between groundwater and surface could consider being another important pathway for various micropollutants. As some treated discharge from industrial premises and sewage treatment is going to surface water directly, certain untreated micropollutants may then infiltrate to groundwater.

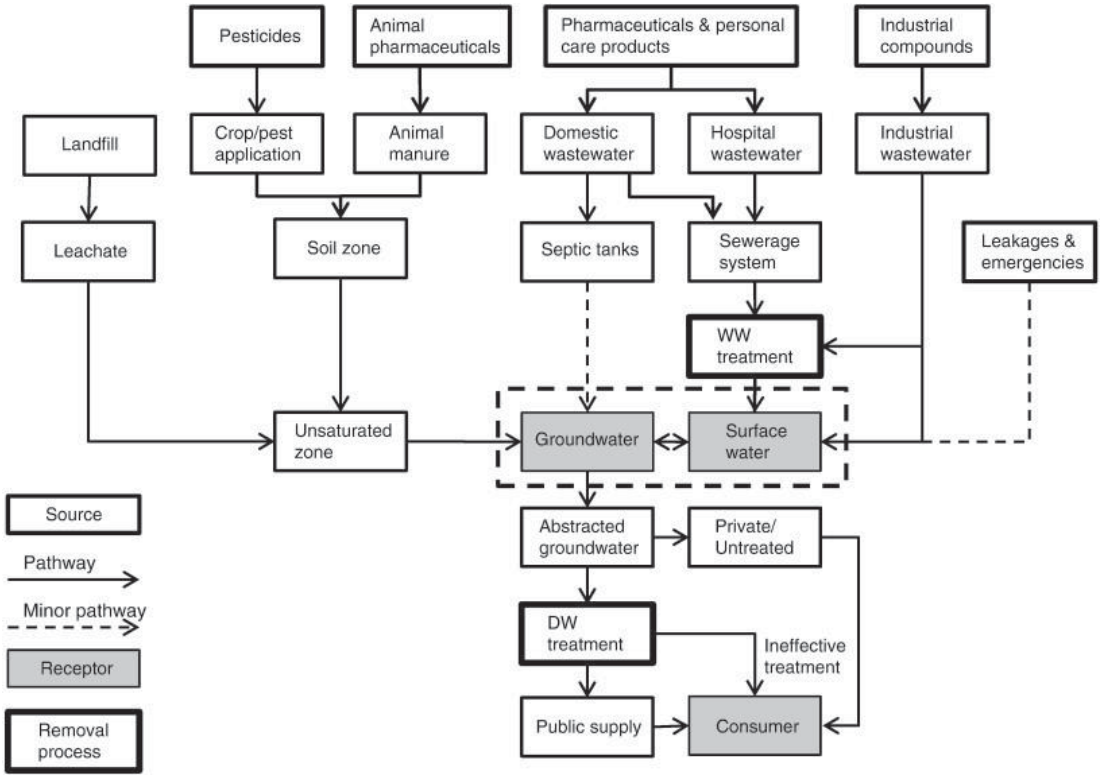

Fig. 2.1 Contamination pathways for micropollutants into the aquatic environment (adapted from "Review of risk from potential emerging contaminants in UK groundwater" by Stuart et al., 2012, *Science of the Total Environment*, 416, 1-21.)

In general, pharmaceuticals are biologically active compounds and they are intended not to be easily biodegradable but are water soluble. A wide range of detected pharmaceutical products in the aquatic environment include: veterinary and human antibiotics (e.g. ciprofloxacin, erythromycin, lincomycin, sulfamethoxazole, and tetracycline); prescription drugs (e.g. codeine, salbutamol, and carbamazepine); non-prescription drugs (e.g. acetaminophen, ibuprofen, and salicylic acid) and iodinated X-ray contrast media (e.g. iopromide and iopamidol) (Barnes et al., 2008; Miller and Meek, 2006; Nikolaou et al., 2007; Pérez and Barceló, 2007; Ternes and Hirsch, 2000; Vulliet and Cren-Olivé, 2011; Watkinson et al., 2009; Stuart et al., 2012). They primarily entered the environment through human excretion, disposal of unused products and agricultural use (Poynton and Vulpe, 2009). Personal care products (such as bacteriocide, antifungal agents, polycyclic musks and UV filters/sunscreen etc.) are commonly transmitted into the environment via wastewater treatment discharges. The possible fates of personal care products and their metabolites are as follows: a) mineralization to CO_2 and water; b) retention of the solids portion

(sludge/biosolids) if the compound entering the plant or the product of biologically mediated transformation is lipophilic; c) release to the receiving water either as the original compound or as a degradation product (Jiang et al., 2013). For instance, triclosan is widely used in household products and its metabolite methyl triclosan are considered to be persistent (Stuart et al., 2012).

Hormone steroids are a group of endocrine disruptors that are synthesized from cholesterol and have in common a cyclopentan-*o*-perhydrophenanthrene ring (Ying et al., 2002). Some types of hormone steroids (estradiol, estrone and estriol etc.) are essential to human for maintaining the health of the reproductive tissues, skin and brain. Some synthetic steroids (ethynylestradiol and mestranol) are used as contraceptives. Hormone steroids have been detected in wastewater treatment plant effluent and surface water, receiving from domestic discharge and animal waste disposal.

As pesticides post threat to the environment, some compounds have been banned or replaced other substitutes (Stuart et al., 2012; Gavrilescu et al., 2015). Current studies have been focused on pesticide metabolites that are often being detected in water sources and wastewater effluents at high concentrations and also biologically active and toxic (Lapworth and Gooddy, 2006; Clausen et al., 2007).

Industrial chemicals have been found to bioaccumulate and have potential endocrine disrupting properties. The ingredients of the production of alkyl phenol ethoxylates (APEs) are octyl- and nonyl-phenol. APEs are used in the manufacture of surfactants and also are used as pesticide adjuvants, therefore these can be found in groundwater as a result of agricultural activity (Stuart et al., 2012).

The concentration levels of selected micropollutants are listed in Table 2.2. PPCPs such as non-steroid anti-inflammatory drugs and antibiotics have frequently been found in raw sewage at concentrations reaching mg/L level (Kolpin et al., 2002; Ashton et al., 2004). Ibuprofen is the most abundant PPCPs found in raw sewage followed by the gemfibrozil, naproxen, salicylic acid and ketoprofen, possibly because of their excessive usage. About 160 different pharmaceuticals and their

metabolites have been identified in domestic wastewater treatment plants, surface water and groundwater in Northern Europe (Kallenborn et al., 2008). Because of high usage possibly triggered by health effect at cold climates and the readily access to medical treatment, high concentrations of antibiotics, analgesic and non-steroidal anti-inflammatory contaminants (e.g. ibuprofen, naproxen, ketoprofen, diclofenac salicylic acid and acetaminophen) have been detected in raw sewage and wastewater treatment plant effluent in Europe and North America (Pal et al., 2010). For example, concentration of near 20, 000 ng/L of ibuprofen has been detected in hospital wastewater (Gómez et al., 2006). The concentration of acetaminophen was 36,950 ng/L in hospital effluents of Taiwan and 16,020 ng/L in that of Spain, while its concentrations were less than 100 ng/L in wastewater treatment plant effluents and rivers (Lin et al., 2008; Gómez et al., 2006; Pedrouzo et al., 2007; Bueno et al., 2007; Kim et al., 2007; Zhang et al., 2007).

The concentrations of estriol, estrone, 17β-estradiol and 17α-ethinylestradiol (EE2) exceed the reported lowest predicted no-effect concentration (PNEC) values in freshwaters of most countries (Pal et al., 2010). Labadie et al. (2007) reported that estrogens (such as estrone) could transport through riverbed sediments and penetrate into the underlying groundwater. The concentration level of these contaminants in Asia and Australia is relatively low (Kallenborn et al., 2008). Excessive concentrations of estrogenic contaminants have also been detected in hospital effluent, wastewater treatment plant effluents and surface waters in USA and Europe. This could mainly be attributed to the animal husbandry and excessive usage of contraceptives. It could also indicate insufficient removal of hormone compounds in wastewater treatment plants.

Surface water recharge using the treated effluent has been the primary cause for the presence of micropollutants in surface water bodies (Luo et al., 2014a; Kasprzyk-Hordern et al., 2008). It is notable that ibuprofen, carbamazepine, triclosan, and pentachlorophenol were detected at alarmingly high levels with concentrations of several μg/L. Micropollutants are subjected to dilution, sorption onto suspended solids and sediments, photolysis and biodegradation after discharge to the surface water. Occurrence level of micropollutants in surface water depends on the

abundance and the persistency of the compound. Ibuprofen is a ready biodegradable compound, but is the most abundant in raw sewage also detected in surface water at high concentration. Triclosan and pentachlorophenol are persistent compounds, present in raw sewage at high levels, and also rich in surface water. In contrast, steroid hormones were detected at low concentrations in surface water either due to low level of raw sewage and efficient removal during treatment.

In comparison to the surface water, ground water contamination is found to be low. Landfill leachate and artificial recharge using treated wastewater have been a significant cause for micropollutants contamination in ground water. Micropollutant polarity is a vital factor for their occurrence in ground water. Polar compounds have less affinity for subsoil and are likely to infiltrate through soil and contaminate the ground water. Most pharmaceutical compounds are polar (e.g. carbamazepine, diclofenac and primidone), and under recharge conditions, can leach through the subsoil and contaminate the groundwater (Heberer 2002b). Additionally, compounds with a high molecular weight and a high log K_{ow} of >5 are easily sorbed to sediments and can be primarily removed by coagulation. Hence, such compounds are unlikely to be present in surface water (Vieno et al., 2007). On the other hand, compounds with low log K_{ow} of <2.5 have low sorption, and are thus likely to be present in surface water (Mompelat et al., 2009).

Table 2.2 Concentration of selected micropollutants in aquatic environment

Micropollutants	Concentration (ng/L)				Reference
	WWTP effluent	**Surface water**	**Ground water**	**Raw sewage**	
PPCPs					
Salicylic acid	<2098	<302	6.5	340-8000	Pal et al., 2010; Heberer 2002a; Yu et al., 2013
Metronidazole	0.055	-	-	-	Gavrilescu et al., 2015
Ketoprofen	20-1620	3.4-329	<80	80-5700	Pal et al., 2010; Yu et al., 2013
Acetaminophen	1.8-220	4.1-777	<5.0-4689	1520-182853	Gavrilescu et al., 2015; Tran et al., 2014
Naproxen	1-5100	1-610	1.2-263	8000	Pal et al., 2010; Yu et al., 2013; Luo et al., 2014
Primidone	110-200	55-635	-	-	Díaz-Cruz & Barceló, 2008
Ibuprofen	20-48240	<5044	<200	1000-56500	Kolpin et al., 2002; Ashton et al., 2004; Heberer 2002b; Santos et al., 2007; Andreozzi et al., 2007; Yu et al., 2013; Joss et al., 2005
Diclofenac	8.8-5450	1.1-568	<380	86-1000	Pal et al., 2010; Ashton et al., 2004; Heberer 2002b; Andreozzi et al., 2007; Yu et al., 2013; Joss et al., 2005; Kasprzyk-Hordern et al., 2008
Carbamazepine	73-2100	<1075	<10.4	1000-2000	Pal et al., 2010; Heberer 2002a; Andreozzi et al., 2007; Joss et al., 2005;

					Kasprzyk-Hordern et al., 2008; Standley et al., 2008
Gemifibrozil	<4000	1.8-790	<340	1090-8500	Pal et al., 2010; Kolpin et al., 2002; Heberer 2002b; Yu et al., 2013;
Triclosan	12-9300	35-2300	2-118	180-4400	Stasinakis & Gatidou, 2011; Kolpin et al., 2002; Yu et al., 2013; Peng et al.,2008; Gómez et al., 2007
Steroid hormones					
Estriol	0.4-30	5-19	149-1661	0.5-10	Pal et al., 2010; Laganà et al., 2004; Cargouet 2004
Estrone	1-196	1-65	0.7-79	1-160	Pal et al., 2010; Yu et al., 2013; Kuch & Ballschmiter, 2001; Laganà et al., 2004; Vanderford et al., 2003; Servos et al., 2006
17α-Ethinylestradiol	1-17	0.1-831	-	1-15	Pal et al., 2010
17β-Estradiol	1-43	5-21.4	-	1-15	Pal et al., 2010; Kuch & Ballschmiter, 2001; Laganà et al., 2004; Servos et al., 2006; Cargouet 2004
Pesticides					
Pentachlorophenol	-	2000	-	-	Kolpin et al., 2004
Industrial chemicals					
Bisphenol A	4.8-800	0.5-140	5-2550	60-600	Kolpin et al., 2002; Yu et al., 2013
4-tert-Octylphenol	<1000	-	-	80-3900	Kolpin et al., 2002;
4-n-Nonylphenol	<4400	0.1-7300	-	220-870	Kolpin et al., 2002; Yu et al., 2013; Shao et al., 2005; Jonkers et al., 2009

2.2.3 Removal of micropollutant in wastewater treatment

Activated sludge treatment technology is most commonly used biological treatment process for conventional wastewater treatment plants (WWTPs). However, activated sludge process is not specifically designed to remove micropollutants. Therefore, the removal of micropollutants in conventional WWTPs is inefficient and often inadequate (Luo et al., 2014a). The micropollutant removal depends on certain operating parameters including redox conditions, nitrification/denitrification capacity, solid retention time, hydraulic retention time, temperature and mixed liquor pH value (Tadkaew et al., 2010; Hai et al., 2011a; Hai et al., 2011b; Clara et al., 2005; Joss et al., 2004; Czajka and Londry, 2006; Miège et al., 2008). In addition, compound specific parameters, such as polarity, molecular structure and biodegradability, also have significant influence on micropollutant removal during biological treatment (Tadkaew et al., 2011; Hai et al., 2011c).

Fig.2.2 shows the main mechanisms for micropollutant removal in conventional wastewater treatment as follows: (a) biological transformation, (b) sorption, (c) volatilization and (d) abiotic degradation. Sorption and volatilization consist of a transfer of the micropollutant from one compartment (water) to another (solid or gas) while degradation leads to the transformation of the micropollutant. Complete mineralization produces water, CO_2 and minerals.

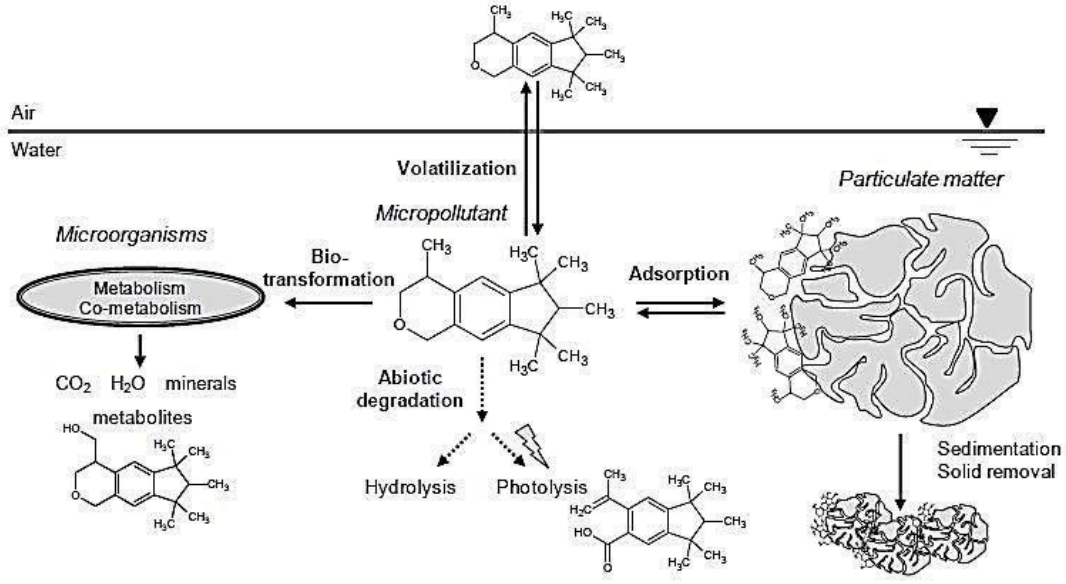

Fig. 2.2 Main removal mechanisms of micropollutants in conventional WWTPs

Biological transformation is the main removal mechanism for many hydrophilic organic micropollutants in conventional wastewater treatment. Micropollutant concentrations in wastewater are usually too low (ng/L to µg/L) to support the growth of microorganisms or to induce the corresponding enzymes and/or cofactors for their biodegradation. Under this situation, there is probably no acclimatization / adaptation occurs at such low concentrations. Thus, biological transformation of micropollutants generally requires the presence of other growth substrates (e.g. carbon and energy sources) (Tran et al., 2013). Biotransformation of trace contaminants can be separated in two main processes: metabolic reactions on mixed substrate or co-metabolic reactions.

In metabolic reactions of mixed substrates, microorganisms use organic micropollutants and other organic compounds as a growth substrate. These substrates are used as energy (catabolism) and/or carbon source (anabolism) for their cell development (Margot 2015). Catabolic reactions lead to transformation of the pollutant to smaller molecules, ultimately until their complete bio-mineralization, i.e., their conversion to water, carbon dioxide and other minerals (Benner et al., 2013). Many bacterial strains are able to utilize and mineralize specific pollutants as the sole energy source, meaning that metabolic pathways exist for these substances. The degradation of these pollutants at very low concentrations requires the presence of other substrates that will sustain the growth of cells. However, high concentrations of easily biodegradable substrates in wastewater can repress the expression of these specific catabolic pathways. This preferential substrate selection may thus reduce micropollutant degradation until all the readily degradable substrates are consumed (Benner et al., 2013).

During co-metabolic reactions, micropollutants are not used as a growth substrate but are biologically transformed, by side reactions catalysed by unspecific enzymes (e.g. mono-oxygenases or di-oxygenases, nacetyltransferases, hydrolases) or cofactors produced during the microbial conversion of the growth substrate (Margot 2015). Therefore, co-metabolism can be defined as “the transformation of a non-growth substrate in the obligate presence of a growth substrate or another transformable compound” (Fischer and Majewsky, 2014). Co-metabolism often leads to the

formation of transformation products (TPs), but these TPs may possibly be used as growth substrates for other microorganisms (Benner et al., 2013; Tran et al., 2013). Although co-metabolic transformations require the presence of a growth substrate, if present at high concentrations the substrate can reduce the transformation of some micropollutants by competitive inhibition, i.e., competition between the growth and the co-metabolic substrate to the non-specific enzyme active site (Plósz et al., 2012; Plósz et al., 2010).

Biological transformation of micropollutants in WWTPs depends on the sludge concentration, their biodegradability in the sludge, and the hydraulic retention time within the reactor. Bioavailability of the pollutant is a prerequisite for bio-transformation. The soluble fraction is considered as being available but the bioavailability of the sorbed fraction is assumed to be much lower (Pomiès et al., 2013). As the sorbed fraction is in equilibrium with the dissolved one, desorption occurs during the degradation of the soluble fraction. Thus, part of the sorbed fraction can also be degraded when no sequestered in the sludge.

Sorption onto sludge or particulate matter can be considered as an important removal mechanism for hydrophobic or positively charged micropollutants, especially when they are poorly biodegradable. Adsorption onto biological sludge can be differentiated into two main processes (Joss et al., 2006): (a) *Hydrophobic interaction*s between pollutants and suspended solids or sludge components, such as extracellular polymeric substances (EPS) or the lipophilic cell membrane of microorganisms. (b) *Electrostatic interactions* between positive charged groups of the pollutant and the mainly negative charged surfaces of microorganisms or effluent organic matter. Other phenomena such as active/passive cells uptake (absorption by microorganisms), cationic exchanges, cationic bridges, surface complexation and hydrogen bridges may also play an essential role in sorption mechanisms (Pomiès et al., 2013). Adsorption is a complex process dependent on the physico-chemical properties of the pollutant (such as charge, hydrophobicity) and the properties of the sludge (such as surface charge, specific surface area, EPS content, oxidation degree of the organic matter, mineral content). Different adsorption capacities are thus observed among different sludge (primary or secondary, flocs or biofilms) (Barret et

al., 2010a; Mailler et al., 2013). Electrostatic interactions are influenced by the pH of the wastewater as slight variation in the pH can lead to either protonation (positively charged or neutral) or deprotonation (neutral or negatively charged) of compounds containing functional moieties with a pKa around 6-9.

Micropollutants not only sorb to particulate matter, but also onto colloidal particles, which are considered as part of the "dissolved" phase (Pomiès et al., 2013). Sorption onto dissolved or colloidal matters increases the solubility of hydrophobic substances, such as persistent organic pollutants, polycyclic aromatic hydrocarbons or heavy metals (Barret et al., 2010a; Barret et al., 2010b; Katsoyiannis and Samara, 2007). This means that the presence of dissolved or colloidal matters or dissolved organic carbon (DOC) in wastewater can significantly affect the partitioning of these pollutants between the "dissolved" and the "particulate" phases, limiting their removal by adsorption onto the sludge and therefore facilitating their discharge into the environment together with the treated effluent. Reversible sorption is usually process composed of two reactions which occur simultaneously: adsorption and desorption. Sorption equilibrium is reached when the rate of both reactions is equal (Joss et al., 2006a). The sorption kinetics of various pollutants onto secondary sludge, including hydrophobic PAHs and hydrophilic substances such as polar pharmaceuticals and pesticides, are reported to be fast, with sorption equilibrium reached in less than 0.5 to 2 h (Barret et al., 2010b; Ternes et al., 2004; Wick et al., 2011). The sorption equilibrium on colloids is reached even faster (<5 min) (Maskaoui et al., 2007). Due to longer hydraulic retention time (HRT) in biological treatments, equilibrium can be assumed for solid-liquid partitioning in WWTPs.

Volatilization of micropollutants can occur during wastewater treatment, occurring as surface volatilization but more significantly by stripping during aeration. The transfer of the pollutant from water to air depends on the volatility of the compound (Henry's law constant) and the operation conditions of the process (aeration, agitation, temperature and atmospheric pressure) (Pomiès et al., 2013). Stripping should not be considered as an option for water treatment if the gas flow is not treated afterwards, otherwise the WWTP could cause atmospheric pollution.

Organic micropollutants can potentially be degraded during wastewater treatment by abiotic reactions, such as photolysis, hydrolysis or reaction with other chemicals. Direct *photolysis* occurs when a photon is absorbed by a compound, leading to bond cleavage to form a new compound. Pollutants can be also degraded by indirect photolysis, due to the production, during sun irradiation of dissolved organic matter, NO_2^-/NO_3^- or HCO_3^-/CO_3^{2-}, of transient excited species (reactive oxygen, radicals) which can react with the pollutants (Wang and Lin, 2014). In conventional treatments, photolysis by natural sunlight is very restricted due to the low surface-to-volume ratio available for sunlight irradiation and the high turbidity of the wastewater, which strongly limits the penetration of light into the water. Phototransformation is not expected to be a significant degradation mechanism in conventional systems. Photolysis can play a significant role in wastewater treatment with open water lagoons for compounds having aromatic rings, heteroatoms, and other functional chromophore groups that can either absorb solar radiation or react with photogenerated transient species (Verlicchi and Zambello, 2014). Hydrolysis is the result of the cleavage of chemical bonds by substitution of an atom or group of atoms in an organic compound by a water molecule (Schwarzenbach et al., 2003). But not all micropollutants can be hydrolyzed. Rates of hydrolysis in water are strongly dependent on the pH and the temperature (Mabey and Mill, 1978). Rates usually increase rapidly with the temperature, and hydrolysis at high pH (base-catalyzed) is often faster than acid-catalyzed or neutral hydrolysis for many compounds (Mitchell et al., 2014). Hydrolysis half-lives ($t_{1/2}$) of micropollutants at neutral pH and 25°C vary from few seconds (e.g., *tert*-butyl chloride) to thousands of years (e.g., trichloromethane) (Schwarzenbach et al., 2003). Pollutants with very fast hydrolysis rates are expected to be completely transformed in sewers before reaching the WWTP. On the other hand, compounds with $t_{1/2} > 7$ days will not be significantly hydrolyzed (< 10%) during wastewater treatment (HRT < 24h). In domestic wastewater (pH 6.5-8 and 10-25°C), hydrolysis rates are relatively slow for most micropollutants ($t_{1/2} > 7$ d) compared to biodegradation or sorption (Schwarzenbach et al., 2003). Thus, hydrolysis can be considered as a negligible removal mechanism in WWTPs.

The removal of micropollutants is also like to the treatment process conditions including solid retention time, hydraulic retention time, redox conditions, temperature and mixed liquor pH value. The higher the SRT, the less the amount of micropollutants to be adsorbed onto the sludge, as high SRT leads to longer sludge age for microorganism to biodegrade micropollutants. But high SRT is not necessary for better removal of micropollutants (Luo et al., 2014a). Longer HRT allows micropollutants that have slow/intermediate kinetics to experience more effective biodegradation or sorption. Redox conditions may affect the wastewater or sludge characteristics and the microbial biodiversity (Göbel et al., 2007), resulting in inefficient biodegradation of some micropollutants. The acidity or alkalinity of wastewater can have influence on the physiology of microorganisms and the solubility of micropollutants in wastewater (Cirja et al., 2008).

2.3 Background of the attached growth systems

2.3.1 Attached growth systems

As a promising and effective technology, the attached-growth process provides not only excellent performance in removing organic matters and nutrients, but also has a potential to eliminate micropollutants in recent years (Li et al., 2011; Falås et al. 2013; Luo et al. 2014a). Unlike suspended growth processes, the attached-growth technology possesses certain advantages due to the fixed biofilm that grows on media. The media can be either fixed or moving freely in attached-growth reactors. With the development of wastewater treatment technology, different configurations of attached-growth systems were invented and have been in use commercially, such as trickling filters, rotating biological contactors (RBCs), fixed media submerged biofilters, fluidized bed reactors, and moving-bed biofilm reactors etc.

The primary and well-known form of attached-growth system is trickling filter (TF), which was introduced in 1890 (Bitton, 2005). The TF was the main alternative to activated sludge for the secondary treatment of settled domestic wastewater for BOD and NH_3 reduction. The BOD removal by TF is between 65% and 90%, while the nitrification rate is from 75% to 95%. TFs can be operated as single-stage or two-stage in either single pass mode or recirculation mode (Guo et al., 2012), based upon

their hydraulic or organic loading rate and the media provided to support bacterial growth. There are several factors are important in the function of TF, particularly the filter media (Lekang and Kleppe, 2000). With respect to supporting media for TFs, the important characteristics to be considered are the specific surface and the percent of void space. The surface area is related directly to the available active biological population, while the void space is significant in conveying both waste and the oxygen required for stabilization. There are several materials can be used to trickling filters as supporting media: crushed limestone, large gravel, rock, ceramic material, treated wood, hard coal and plastic etc.

Rotating biological contactors (RBCs) are widely used in wastewater treatment for secondary treatment since they were market in the 1960s. The RBCs allow obtaining high performance in the removal of dissolved carbon and ammonia at the expense of less energy consumption than to use AS systems. In addition, another advantage of RBCs stems from the fact that the interfacial area generated is very high and practically independent of the speed of rotation (Patwardhan, 2003). The performance of RBCs depends on parameters like rotational speed, organic and hydraulic rates, HRT, and media material etc., while the RBC media further affects biofilm characteristics. Studies indicated that the biofilms on the media of RBCs were structurally heterogeneous, consisting of cell clusters and voids with spatial microbial distribution of nitrifiers and heterotrophs (Rodgers and Zhan, 2003). In full-scale disc RBCs, it is reported that the thickness of biofilm ranged from 0.5 to 4.5 mm (Cortez et al., 2008). The control of biofilm thickness is very important to avoid clogging or material fatigue stresses in wastewater treatment (Griffin and Findlay, 2002). The materials of media that used in RBCs are producing from Styrofoam, polycarbonate sheet, high-density polyethylene and other non-corrosive durable materials (Cortez et al., 2008; Guo et al., 2012).

Fluidized-bed reactor (FBR) was the most volumetric efficient biological reactor available in mid-70s because of the high biomass concentration covered on media surface (Harremoes and Henze, 2002). The level of biomass can be up to 1,000 times higher than the level found in conventional AS systems (Guo et al., 2012). The FBR technology can be used in industrial wastewater treatment, post-nitrification of

drinking water and municipal wastewater. In a FBR process, the biofilm carriers are usually small particles, such as granular activated carbon, sand, anion and cation exchange resins (Rodgers and Zhan, 2003). However, the FBRs are not widely utilized in wastewater treatment due to certain drawbacks, including complicated inlet and outlet design, high energy requirement and the difficulty in control the thickness of attached-growth biofilm.

Submerged fixed-bed biofilm reactor (SFBBR) works on the basis of biofilm attached to submerged monolithic plastic supports with no sludge recirculation, so the issues related to clogging of support media and control problem of biofilm growth can be effectively minimized. In this case, the media properties, such as durability, specific surface area density and void space percentage, are the main concerns for SFBBRs operation. Chapanova et al. (2007) reported that greater surface density permitted a larger biomass per unit volume, while greater void space allowed for a higher oxygen and mass transfer to the biofilm and reduced the clogging risks. Hence, those factors should be taken into consideration in order to improve the treatment efficiency of SFBBRs. If designed properly, the SFBBRs could consistently provide BOD removal $\geq$ 95%, COD removal $\geq$ 80% and TKN (Total Kjeldahl Nitrogen) $\geq$ 90% in municipal wastewater treatment (Schlegel and Koeser, 2007).

Moving-bed biofilm reactor is an effective and affordable attached-growth biological process and has been attracted increasing attention over the last decade in wastewater treatment. The basic concept of MBBR is to provide additional biomass attached on media, without increasing the suspended mixed liquid concentration in the reactor. The MBBR technology has showed success in organic matter and nutrient removal, designed to meet a wide range of effluent quality standards. More recently, MBBR has proven its potential in treating micropollutants in wastewater (Li et al., 2011; Falås et al. 2013; Luo et al. 2014a). The types of media can be used in a MBBR are polyethylene media, activated carbon, reticulated polyurethane, polymer foam pads, and nonwoven media etc.

Table 2.3 presents recent research data concerning the performance of different attached-growth systems. As can be seen from table 2.3, the attached-growth processes are widely used in wastewater treatment, which are not only applied for municipal wastewater, but also expended to treat some specific effluent, such as oilfield produced wastewater and coal gasification wastewater. In addition, the treatment efficiencies are varied even for the same type of attached-growth system, when different media is employed. For instance, Chu and Wang (2011) examined two different media in a MBBR, showing that the TOC removal was 90% for polyurethane foam while 72% for biodegradable polymer.

Table 2.3 Performance of different attached growth systems

					Organic		Nutrient		Reference
Attached-growth system	**Support media**	**Influent**	**HRT**	**SS removal efficiency**	**Load**	**Removal efficiency**	**Load**	**Removal efficiency**	
BAF	Expended clay	Sedimentation effluent	2.44 h	65±5%	3.7-8 kg COD/m3/d	35±5%	0.78±0.12 kg NH_4-N /m^3/d	91±2%	Farabegoli et al., 2009
BAF	Ceramic or Zeolite or Carbonate media	Synthetic wastewater	0.5-2.5 h	93% 90% 90%	< 6 kg COD/m^3/d	88% 85% 87%	< 1.2 kg NH_3-N /m^3/d	73% 85% 83%	Qiu et al., 2010
BAF	Lightweight ceramisite	Synthetic wastewater	2.5-5 h	-	234-780 mg/L COD	92%	58.6 mg/L NH_4-N	> 62%	Liu et al., 2010
BAF	Grain slag	Synthetic wastewater	1-5 h		116-245 mg/L COD	84%	32 mg/L NH_3-N	91.5%	Feng et al., 2012
Biofilm filter	Non-woven	Pond water	3 h	91-96%	-	Up to 90% COD	-	Up to 63.9%	Chang et al., 2010
Moving bed sequencing batch reactor	Polyurethane foam cubes	Low C/N wastewater	-	-	-	70%	-	100%	Lim et al., 2011
MBBR	Polyurethane foam Biodegradable polymer	Synthetic wastewater	-	-	200-401 mg/L COD	90% TOC 72% TOC	49.8±8.5 mg TN/L	42.6% 60.1%	Chu and Wang, 2011

MBBR	Ceramic bioreactor	Oilfield produced water	36-10 h	-	343-365 mg/L COD	73%	41-48 mg/L NH_3-N	79-86%	Dong et al. 2011
MBBR	Polyethylene media	Coal gasification wastewater	48-32 h	-	1712-2340 mg/L COD	81%	182-259 mg/L NH_3-N	93%	Li et al., 2011
Fixed bed sequencing batch reactor	Polypropylene carriers	Synthetic wastewater	4 h, 6 h, 8 h	-	0.5-1.5 kg COD/m^3/d	95-96%	0.56-2.23 kg NH_4-N /m^3/d	70-88% TN 76-90% TP	Rahimi et al., 2011
Sequencing batch biofilter granular reactor	Wheel shaped plastic elements	Primary effluent	300 min	Up to 90%	2.5 kg COD/m^3/d	80-90%	28-47 mg/L NH_4-N	80-100%	Di laconi et al., 2010
Aerobic submerged filter	Lava rock	Grit tank effluent	3.96-8.31 h	-	0.45-3 kg COD/m^3/d 9.4 kg COD/m^3/d	80% 54%	0.06±0.02 kg NH_4-N/m^3/d	20-90%	Morgan-Sagastume and Noyola, 2008
Fluidized bed bioreactor	Lava rock	Municipal wastewater	2.3 h 9 h	86%	4.3±0.5 kg COD/m^3/d 528±88 mg/L COD	87% 63±7.4%	0.51 kg/m^3/d N 0.06 kg/m^3/d P 8.6±2.5 mg/L PO_4-P	84.5±1.3% N 55.0±8.0% P 7.3±13.6% PO_4-P	Andalib et al., 2010

HBR	Polyurethane	Domestic wastewater	2.5 h	-	10.5 $gCOD/m^2/d$	67±7.5%	0.23 $g/m^2/d$	86.6±4% NH_4-N	Tawfik and Klapwijk, 2010
Moving bed MBR	Nonwoven carriers	Synthetic wastewater	12h	-	400 mg/L COD	95.6%	20 mg/L NH_4-N	91.8% NH_4-N	Yang et al., 2009

2.3.2 Media used in attached growth systems

When engineering biofilm to be utilized for wastewater treatment, it is of great importance to pay more attention to media development. The characteristics of the support media have significant impact on the attached biofilm structure in the reactor, the operational mode and the process effectiveness (Guo et al. 2012b). Therefore, the ideal media not only should provide a large surface area to maximize microbial attachment and growth, and sufficient void space for air diffusion as well as allow sloughed microbial biofilm passing through, but also should not be toxic to microorganisms and be stable both chemically and mechanically (Grady and Lim, 1980).

The design of biofilm carrier is important due to requirements for good mass transfer and nutrients to microorganisms. The key parameters of the biofilm carriers are its shape and the percentage of the tank filled with it (Robescu et al., 2009). For the effective growth of biofilm and its performance in a reactor we need to take special care while we design the specific surface area of the carrier and the filling fraction of the carrier in the reactor (Odegaard et al., 2000). The specific surface area of the carrier reflects the amount of surface area available for biofilm development per unit volume of the carrier on a bulk volume basis. The reactor specific surface area equals the specific surface area of the carrier multiplied by the fraction of the total reactor volume that the carrier occupies (bulk volume basis) (Weiss et al., 2005). The attachment of microorganism to the surface and the subsequent growth of the biofilm community depend upon the surface of the biofilm carriers that are rougher, more hydrophobic, and coated with surface-conditioning films (Vayenas, 2011). Sponge has been considered as a reasonable attached growth media because it can act as a mobile carrier for active biomass resulting in improved organic and nutrient removal as well as reduces fouling of the membrane by reducing the cake layers formed on the surface of the membrane and retain microorganisms by incorporating a hybrid growth system (Guo et al., 2009; Ngo et al., 2006).

Table 2.4 summarized the amount of biomass content that attached-growth on various types of support media.

Table 2.4 Biomass content on various attached growth media

Media type		Structural characteristics			The amount of attached growth biomass	Application	References
		Media size	Density	Specific surface area			
Powdered minerals	Bentonite	29.72 µm	2.48 g/cm^3	118.94 m^2/g	570-1180 mg MLVSS/L	Hybrid biological reactor treating synthetic wastewater	Lee et al., 2002
	Clinoptilolite	27.55 µm	2.32 g/cm^3	323.15 m^2/g	4020-4620 mg MLVSS/L		
polyurethane forms		10×10×10 mm	28-30 kg/m^3	-	2.58–3.34 g/L	Hybrid biological reactor treating sewage	Wang et al., 2000
Inner tube of used tyres		2×2×2 mm	1.925±0.21 g/cm^3	-	5400–6700 mg/reactor	Moving biofilm-aerobic-sequencing batch reactor treating synthetic wastewater	Sirianuntapiboon and Yommee, 2006
Polyethylene granule		1-3 mm	0.9 g/cm^3	-	< 2 g protein/L reactor	Hybrid membrane bioreactor treating tannery wastewater	Artiga et al., 2005
Kaldnes K$_3$ biofilm carriers		Diameter = 25 mm	0.95 g/cm^3	500 m^2/m^3	2000 mg/L	Hybrid membrane bioreactor treating municipal wastewater	Liu et al., 2010
Kaldnes K$_3$ biofilm carriers		Diameter = 25 mm	0.95 g/cm^3	500 m^2/m^3	0.03- 0.12 g-VSS/g-COD	Hybrid membrane bioreactor treating industrial wastewater	Artiga et al., 2008
Kaldnes K$_3$ biofilm carriers		Diameter = 25 mm	0.95 g/cm^3	500 m^2/m^3	2.4 – 12.6 g/m^2	Integrated fixed-film activated sludge treating municipal	Regmi et al., 2011

					wastewater	
Polyether foam cubes	-	-	-	< 0.85 g/g	Moving bed biofilm reactor treating synthetic wastewater	Marques et al., 2008
Polyurethane foam		84-117 kg/m^3	620 m^2/m^3	< 2 g-VSS/g	Sequencing batch reactor treating synthetic wastewater	Moe and Irvine, 2000
Polyurethane sponge	-	-	-	19-24.6 g VSS/L sponge volume	Combination of UASB and DHS reactor treating sewage	Tandukar et al., 2006
Sponge strips	2.5×2.5×50 cm	-	-	< 26 g-VSS/L sponge volume	Combination of UASB and DHS reactor treating municipal wastewater	Tandukar et al., 2005
Polyurethane sponge	12×12×12 mm	-	-	22,000-26,000 mg/L	Moving bed biofilm reactor treating caprolactam wastewater	Chae et al., 2004
	15×15×15 mm				Moving bed biofilm reactor treating synthetic wastewater	Chae et al., 2008
Biological powder activated carbon (BGAC)	-	-	-	3 g/L	-	Xing et al., 2008
Polyethylene bio-carrier	Diameter = 7 mm	0.97-0.98 g/cm^3	900 m^2/m^3		Anaerobic-aerobic moving bed biofilm reactor treating landfill leachate	Chen et al., 2008
Full-scale disc		-		Thickness of 0.5 – 4.5 mm	Rotating biological contractors treating municipal wastewater	Cortez et al., 2008
Polyvinyl chloride	Diameter	1004.2	30.7 m^2/kg	400-1700 mg/L	suspended carrier biofilm reactor	Wang et al., 2005

cylindrical particles	= 2.5 mm	kg/m^3			treating synthetic wastewater	
Nonwoven geotextiles baffles		-		1.4 – 3.4 g/baffle	Treating wastewater from a combined sewer system	Korkut et al., 2006
Polyurethane carrier	Diameter = 8-10 mm	0.3-0.5 kg/L	900 m^2/m^3	0.067 ± 0.006 g/sponge	Moving bed biofilm reactor treating synthetic wastewater with low C/N ratio	Chu and Wang, 2011
Polyurethane cubes	2×2×2 mm	-	455±7 m^2/m^3	49±9 g	Moving bed sequencing batch reactor treating low C/N wasterwater	Lim et al., 2011
	3×3×3 mm	-	451±7 m^2/m^3	35±5 g		
	4×4×4 mm	-	438±7 m^2/m^3	33±4 g		
	5×5×5 mm	-	412±6 m^2/m^3	30±3 g		
Kaldnes K1 biofilm carrier	Diameter = 10 mm	0.95 g/cm^3	500 m^2/m^3	3234-6749 mg TS/L	Moving bed biofilm reactor treating municipal wastewater	Xiao and Ganczarczyk, 2005
Hollow cylinder biofilm carrier	Diameter = 10 mm	0.96-0.98 g/cm^3	1200 m^2/m^3	0.7±0.2 g/L (AMBR) 0.8±0.2 g/L (AMBRb)	Attached-growth MBR treating synthetic wastewater	Hu et al., 2012

Plastic media is the most popular support carrier currently used in attached-growth system, the material of plastic media includes polycarbonate (PC), polyethylene (PE), polypropylene (pp), polytetrafluoroethylene (PTFE), polyvinyl chloride (PVC), acrylonitrile butadiene styrene (ABS), nylon (Ny) and tufnol (Tu) etc. The most widely reported plastic media for use at full-scale wastewater treatment facilities are Kaldnes media, while the PE media can be employed for simultaneous nitrification and denitrification (SND) (Guo et al., 2012b). Stephenson et al. (2013) tested 8 different plastic media in order to determine the relation between the media properties and the development of nitrifying biofilms in mixed cultures for wastewater treatment. Their result indicated that nitrifiers are better adapted to adhere to low-energy surfaces, or possibly the inability of low-energy surfaces to support greater biomass associated with the rapid growth of heterotrophic biofilm (Table 2.5). These findings have significant implications for media selection in wastewater treatment.

Table 2.5 Data of 8 different plastic media (adapted from "Media surface properties and the development of nitrifying biofilms in mixed cultures for wastewater treatment" by Stephenson et al., 2013, *Process Safety and Environmental Protection,* 91, 321-324)

Parameter	**Material**							
	PC	**ABS**	**PTFE**	**PP**	**Tu**	**Ny**	**PE**	**PVC**
R_a (nm)	6	34	162	25	62	107	603	75
R_{max} (nm)	0.28	0.75	2.02	1.85	1.96	2.75	6.58	2.10
SA (nm^2)	5639	5891	5839	5719	5735	5799	6322	5737
Surface adhesion force (nN)	11.7	nd	8.0	10.5	12.5	40.0	21.0	23.5
Dry Biomass (g/m^2)								
Week 8	46.8	56.4	44.7	33.1	40.7	56.2	36.5	17.3
Week 10	35.2	51.9	24.7	42.2	42.2	50.5	40.6	22.0
Nitrification rate (g/m^2 d^{-1})								
Week 8	0.24	0.02	1.52	0.19	0.26	0.00	0.04	0.01
Week 10	0.39	0.36	0.32	0.17	0.49	0.07	0.15	0.06

R_a: average roughness; R_{max}: maximum range of the profile; SA: surface area; Nd: no data

According to Chu and Wang (2011), synthetic support media consisting of polyurethane foam are particularly suitable for microbial attachment and growth due to the presence of high specific surface area, huge void volume, and long service life. In addition, Ngo et al. (2008) demonstrated that reticulated polyurethane foam not only is ideal media for active biomass, but also reduce cake layers formed on the membrane surface and retain microorganisms by incorporating in a SSMBR. Apartfrom effective removal for nitrogen and phosphorus, the requirement for removing micropollutants has become the interest of the future research and development. Luo et al. (2014a) investigated the effectiveness of a sponge-based MBBR for removing five groups of micropollutants. They found that the MBBR achieved varying removals for the selected micropollutants due to their diverse physicochemical properties and the acclimatized sponge improved the removal of some less hydrophobic (logD < 2.5) compounds.

Other than the media material mentioned above, biological activated carbon (BAC) and nonwoven (NW) fabric are also used in attached-growth system as carrier material. Generally, BAC can act as an absorbent and show strong affinity for attaching organic substance, while NW offers a large surface-to-volume ratio for biological attachment. However, NW may be a more attractive option due to its low capital cost (Roy et al., 1998; Turbak, 1993).

2.4 Moving bed biofilm reactors (MBBRs)

The MBBR was developed in order to adopt the best features of the AS process and those of the biofilm process without being restrained by their drawbacks (Ødegaard et al., 1994). The idea was basically achieved by allowing the biomass grows on small media that freely move inside a reactor. The reactor can be used for aerobic, anoxic or anaerobic processes (Ødegaard et al., 1994).

A MBBR consist of a tank equipped with an outlet sieve to retain the media, the media itself, and a means of aeration or mixing. Aeration is by coarse bubble, using stainless steel laterals. Within the reactor, the media, effluent and air are completely mixed resulting in very efficient contact between the biofilm and substrates within

the liquid. One of the important features of this process is that biofilm thickness is controlled by the movement of the carriers so the oxygen diffusion through the biofilm is encouraged. Detached biofilm is suspended with the reactor and leaves the reactor with the effluent. Mechanical mixing is required in anoxic and anaerobic reactors, usually provided by slow speed submersible mixers (Ødegaard et al., 2004).

The MBBR is an effective, affordable attached growth biological process and has been attracted increasing attention over the last decade in wastewater treatment and reuse field. The merits of MBBR systems are compact space requirement, low head loss, no filter-bed channeling, no need for periodic backwashing and sludge recycle, and large surface for colonization and high specific biomass activity (Guo et al, 2010; Lee et al, 2006; Ødegaard et al., 2006). Additionally, MBBR may use almost any reactor shape or may choose various operating loading rates in a given reactor volume, due to the fact that the choice of carrier filling fraction is subjected to preference (Ødegaard et al., 2004).

2.4.1 Media material

Inside the Kaldnes MBBR, polyethylene carriers with various shape and size can be used to offer the treating flexibility depending on wastewater characteristics, pre-treatment, discharge standards and available reactor volume (Ødegaard et al., 1994, 1999; Rasmussen, 2011). Other than polyethylene, a wide range of biocarriers, including polyurethane (PU), granular activated carbon, sand and diatomaceous earth, have been utilized in MBBR system (Chu and Wang, 2011). In general, polymer carriers have low density and excellent processability, and expansion can be obtained easily as the water circulates. However, the poor hydrophilicity and biocompatibility of plastic carriers often cause some deficiencies in the rate and amount of biofilm culturing, and the adhesion extent of biofilm (Dong et al., 2011). In addition, biomass buildup and reactor head-loss may occur due to rapid clogging and jamming of the plastic carriers below the upper grid, including the upper retention grid to break (Dupla et al., 2006). In terms of inorganic carriers, such as limestone, zeolite, activated carbon, graystone, slag, and coke, they have good mechanical strength and biocompatibility. However, relatively high density of inorganic carriers can increase the energy requirement for expansion. Ideally, PU is

the perfect growth medium with high porosity for microorganism immobilization, good mechanical strength and low cost (Chea et al., 2008; Chu and Wang et al., 2011; Kim et al., 2009).

Because the properties of media have effects on the ability to form biofilms, the quality of biomass and the efficiency of treatment (Dong et al, 2011), many efforts have been put on the development and application of novel carriers recently. Chen et al. (2007) used tube chip shaped biocarriers, which consist of organic polymer mixed with nano-sized inorganic ingredients material, in a MBBR combined with Fenton-coagulation pretreatment to treat pesticide wastewater. The results supported that the MBBR has excellent advantages such as flexibility, easy operation and strong resistance against loading impact, due to high biomass attached on the surface of the biocarriers and high biofilm activity. Delnavaz et al. (2010) investigated a MBBR filled with light expended clay aggregate (LECA) for a toxic and hard biodegradable aniline removal using artificial neural network (ANN) model. The results showed that up to maximum of 90% removal efficiencies were gained for COD of 2000 mg/L after 3 days. The PU foam (sponge) was applied as an active mobile carrier in aerobic moving bed bioreactor by Guo et al. (2010) for treating a high strength synthetic wastewater. The results showed outstanding ammonium (100% at filtration flux of 10 and 15 L/m^2h) and phosphorus (> 91% at all fluxes range) removal with optimum pH range of 6 – 7. Chu and Wang (2011) presented a comparison between inert PU foam and biodegradable polyer polycaprolactone (PCL) particles as carriers in MBBR system for the removal of organics and nitrogen from wastewater with low C/N ratio. Their results demonstrated that total organic carbon and ammonium removal efficiency were 95% and 65% in the reactor filled with PU carriers, compared with 72% and 56% in the one filled with PCL carriers at an hydraulic detention time of 14 h. The good performance of the reactor with PU media was because the fact that numerous microorganisms were entrapped on the pores of the PU carriers so that enhanced the nitrifiers to inhabit. On the other hand, reactor with PCL media showed good behavior in terms of TN removal as the biodegradable polymer was an effective substrate for denitrification. Dong et al. (2011) utilized both unmodified and sepiolite-modified suspended ceramic carriers to feed two MBBRs with a filling fraction of 50% to treat oilfield produced water. The results

indicated that the suspended ceramic carrier was an excellent MBBR carrier. Particularly, the modification of ceramic biocarrier with sepiolite produced better outcomes in removal efficiencies of chemical oxygen demand, ammonia nitrogen and polycyclic aromatic hydrocarbons. The feasibility of using bioplastic-based carrier for removal of three selected xenobiotic from synthetic wastewater was evaluated in Accinelli et al. (2012) study. Their result suggested that the concept behind the MBBR technology can be extended to biodegradable carriers inoculated with bioremediation microorganisms.

2.4.2 Media geometry and size

In MBBR, the geometry and sizing of specially designed biofilm medium have been considered to optimize performance. Ødegaard et al. (2000) investigated how carrier size and shape influenced the performance of MBBR system. Three different types of carriers (Kaldnes, AWT and ANOX) were used and the MBBR was operated at relatively high organic loads (10 – 120 g COD/m^2d and 5 – 45 s SCOD/m^2d). The results demonstrated that once the effective surface area had been established, the difference of shape and size of the carriers had minor effect on removal efficiency. However, smaller carriers required less bioreactor volume than larger ones, in terms of given organic effective surface area load. Levstek and Plazl (2009) studied the influence of carrier type on nitrification in moving bed biofilm process. Two types of carriers were utilized: a cylindrical high-density polyethylene ring shaped carrier (K1) and a spherical polyvinyl alcohol (PAV) gel bead shaped carrier (PVA-gel). Their results supported the conclusion that the effective surface area was the key factor for MBBR design. Therefore, a 9.7 % of PVE-gel filling performed equally well as a 37% of K1 filling in a bioreactor as far as nitrification is concerned. Chai et al. (2013) investigated treatment performance of winery wastewater in two MBBRs (R9 and R30) with low-density polyethylene carriers differing in size, shape, structure, and specific surface area. The results implied that the performance of the anaerobic MBBR was enhanced by an increase in the specific area of the carrier used. In conclusion, the shape and size of the MBBR carriers can affect the specific surface area on which grows biofilm, resulting in influencing the treatment performance.

2.4.3 Media filling ratio

In most MBBR systems, treatment performance highly depends on the surface area available for biofilm growth, which accordingly related to filling ratios of the carrier elements. Regards to recommended filling fraction (carrier volume versus total bioreactor volume), it varies in different literature. Ødegaard et al. (1994, 2004) recommended that a filling fraction could be 67% (but maximum 70%) for cylindrical plastic carriers to enable smooth carrier suspension movement inside MBBR. Andreottola et al. (2000) occupied the bioreactor tank volume with 70% of elements for treating municipal wastewater. The average efficiency for totCOD removal was 76% and average ammonium removal efficiency was 92%. Canziani et al. (2006) used MBBR for enhancing denitrification in treatment of leachate from Italian landfills ranges from 0.5 to as high as 3 g/L. The K1 plastic carriers were filled with 37.5% of the denitrification tank volume. Both Di Trapani et al. (2008a) and Mannina and Viviani (2009) investigated the organic matter and nutrient removal performance of hybrid MBBR at 35% and 66% filling ratio and a very high efficiency was obtained from the results. In Falletti and Conte (2007) pilot-scale studies, it was reported that 80% of ammonium was nitrified with 43% of tank volume occupied by carriers while about 86% of ammonium was removed with 60% of tank volume occupied by carriers. Guo et al. (2010) applied 20% volume of sponge in a MBBR coupled with submerged membrane bioreactor. The results showed outstanding ammonium and phosphorus removal efficiency, which were 100% at filtration flux of 10 and 15 L/m^2h and >91% at all fluxes range respectively. Levstek and Plazl (2009) used 37% filling fraction for K1 and 9.6% for PVA-gel carriers for evaluation of nitrification potential in MBBR system. Feng et al. (2012) investigated the effects of packing rates (29%, 30%, and 40%) of PU foam on removal of organics and nitrogen in MBBR. Their results indicated that filling ratio of PU foam carriers had little influence on COD removal but affected the ammonium removal efficiency, presumably due to the different relative abundances of nitrifying bacteria. Consequently, filling ratios are subject to specific surface area of a particular carrier element, which may considerably vary due to its physical characteristics.

2.4.4 Other impact factor

The optimal range of temperature for microorganism activity is between 25 to 35°C. The MBBR usually operate around 20 – 25°C. The temperature in a MBBR often relate to feedwater and the ambient temperature, while the temperature of media depend upon the material. The temperature of surface layer of media could be different from that of the core of the media (Loupasaki and Diamadopoulos, 2012). The change of temperature has effects on the system performance, such as nitrification rate. Chu and Chen (2002) conducted experiment on the impact of temperature on nitrification rate and the results indicated that the effect of temperature on nitrification was less significant than modeling prediction. In Zhang et al. (2013) study, the dependence of nitrification kinetics on temperature in MBBR systems treating low ammonia polluted raw water was investigated. The impacts of temperature on NH_4^+-N and NO_2^--N oxidation kinetics could be described by the temperature coefficients of 1.099 and 1.098, respectively, after exclusions of the inhibitory impacts of temperatures below 5.0 °C and the variations in nitrifying community structure. They believed that these temperature coefficients should be considered when designing and operating such MBBRs.

2.4.5 Micropollutant removal in 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.

Luo et al. (2014a) investigated the removal of micropollutants using polyurethane sponge as attached-growth carrier. Batch experiments demonstrated that micropollutants could adsorb to non-acclimatized sponge cubes to varying extents. Acclimatized sponge showed significantly enhanced removal of some less hydrophobic compounds (logD < 2.5), such as ibuprofen, acetaminophen, naproxen, and estriol, as compared with non-acclimatized sponge. The results for bench-scale sponge-based MBBR system elucidated compound-specific variation in removal,

ranging from 25.9% (carbamazepine) to 96.8% (b-Estradiol 17-acetate) on average. In the MBBR system, biodegradation served as a major removal pathway for most compounds. However, sorption to sludge phase was also a notable removal mechanism of some persistent micropollutants. Particularly, carbamazepine, ketoprofen and pentachlorophenol were found at high concentrations (7.87, 6.05 and 5.55 μg/g, respectively) on suspended biosolids. As a whole, the effectiveness of MBBR for micropollutant removal was comparable with those of activated sludge processes and MBRs. Dvorák et al. (2014) used a full-scale MBBR to remove aniline, cyanides and diphenylguanidine from industrial wastewater. Long-term (5-years) MBBR operation has demonstrated that, following initial stabilisation and implementation of additional pretreatment, the system is capable of treating such hardly biodegradable industrial wastewater with high removal efficiency, with mean cyanide removal efficiency ranging from 75% to 99%. Aniline removal efficiency also reached more than 85%, while diphenylguanidine, phenylurea and N,N-diphenylurea removal was almost quantitative. The results given in this study indicate that MBBR technology is promising option for treatment of poorly biodegradable and toxic industrial wastewater, furthermore with very high removal efficiency.

2.5 Attached growth based membrane hybrid system

Membrane technology has been rapidly advanced around the world and membrane bioreactors (MBRs) are being increasingly applied for municipal and industrial wastewater treatment. The membrane separation technique provides a solution to non-settling sludge, therefore, it can be used to replaced secondary clarifier and to obtain high effluent quality and compactness of treatment plants (Moore et al., 2006). Despite the benefits of MBR, the wide implementation of MBR technology still faces some challenges, such as issues related to membrane fouling. The sludge characteristics in MBR are one of the vital factors to membrane fouling. In terms of attached-growth biofilm media, they can not only reduce the suspended solid in the reactor, but also can affect the characteristics of the sludge, thereby mitigating membrane fouling (Hu et al., 2012). Hence, membrane hybrid systems that combine

attached-growth processes with membrane filtration are able to decrease membrane fouling to a great extent (Guo et al., 2012b).

2.5.1 Membrane fouling

Membrane fouling remains the main concern in the application of MBRs, resulting in reduced filtration performance, shortened life of membrane and higher operating cost (Rodríguez-Hernández et al., 2013). Fouling of membranes is caused by complex physical and chemical interactions between the various fouling constituents in the feed and between these constituents and the membrane surface. Mass transport can lead to the attachment, accumulation, or adsorption of materials onto membrane surfaces and/or within membrane pores (Guo et al., 2012a). For a given membrane, fouling is directly related to sludge characteristics (Meng et al., 2009). However, the fouling behavior in MBRs is complicated, considering the complex nature of the activated sludge. The use of support media shows a potential in controlling and minimizing membrane fouling, because the media can be effectively remove organic impurities and turbidity.

Previous work done by Basu and Huck (2005) demonstrated the impact of high density polyethylene media on an integrated biofilter-membrane system treating difficult-to-treat surface water. They found that fouling rate in a biofilter-membrane process with 40% fill fractions of high density polyethylene media was at least two times slower than the same system without support media. Guo et al. (2009) conducted an experiment to examine the feasibility of using nonwoven fabric material as bedding material in a biofilter-submerged membrane absorption hybrid system. Their results showed that the system could eliminate dissolved organic pollutants ranging from 90 to 4200 Daltons and EBCT applied to the system was the main factor governing the membrane fouling during high rate operation. Also, other researchers have used mechanical cleaning of membranes by introducing granular material into the submerged membrane reactor to assist with fouling control (Siembida et al., 2010; Johir et al., 2011). The granular medium resulted in the enhancement of scouring of the membrane surface. These results indicate that introducing support materials has a potentially significant role in controlling fouling. Hu et al. (2012) investigated the effect of media on membrane fouling in 3 reactors

and the results showed that membrane fouling was considerably mitigated by the carriers' biochemical effects on sludge characteristics rather than by the carriers' physical effects. Alresheedi and Basu (2013) examined the impact of high-density polyethylene (HDPE) media on a submerged hollow fiber PVDF ultrafiltration membrane system filtering synthetic water with different organic and inorganic matter content using a factorial design of experiments. The addition of support media into the membrane reactor resulted in a 35–50% reduction in membrane fouling compared to the control system with no media. Deng et al. (2014) also compared membrane fouling in a sponge-submerged bioreactor and a conventional membrane bioreactor based on sludge properties. They found that sponge addition could mitigate membrane fouling significantly by preventing pore blocking and reducing cake layer formation.

2.5.2 Enhanced hybrid membrane system with attached growth media

In hybrid MBRs application, the attached-growth media play a significant role in enhancement of system performance by mitigating membrane fouling and retaining membrane permeability. In addition, the characteristics of the attached-growth media enable a large amount of biomass remain in the bioreactor, attributing to the high interaction between attached-growth biofilm and suspended solid. Among all the media, BAC, plastic media and sponge have been commonly used to improve the performance of SMBR.

Table 2.6 listed some information regarding the performance of enhanced membrane hybrid systems by adding biofilm support media.

Table 2.6 Performance of enhanced membrane hybrid systems

Attached-growth media material	Hybrid system	Raw Water	Treatment Performance	References
BPAC (5 g/L)	SMBR (MF with pore size of 0.1 μm)	Synthetic biologically treated effluent	• The average TOC removal efficiency was up to 86% and the TOC removal efficiency was maintained over 85% even after 55-day operation. • The hybrid system was able to remove effectively the small- and large-molecular weight organic matters from 270 to 36,270 Da. • The TMP development during 55 days was only 49 kPa, as the PAC replacement enhanced both biological activity and adsorption which helped reducing membrane fouling.	Guo et al., 2006
BPAC (1.5 and 3 g/L)	SMBR (MF with pore size of 0.4 μm)	Tannery industrial wastewater	• COD removal stability appeared to increase as PAC concentration increased. • The fouling rate decreased with an increasing PAC concentration and showed complete reversibility both in presence and in absence of PAC. • PAC dosing enhances typical MBR system stability in terms of effluent quality, allowing a better control of the operational criticisms related to the fouling rate, fouling reversibility and membrane life cycle.	Munz et al., 2007
PAC (2 g/L)	MBR (MF with pore size of 0.22 μm)	Micro-polluted lake water	• Adding PAC helped to improve the quality of the treated water, with effective removal of ammonia nitrogen above 80%. • The addition of PAC enhanced the microbial activity in the bioreactor, contributed to the increase of the removal efficiency of organic pollutants • The experiment proved that PAC addition relieves membrane fouling.	Sagbo et al., 2008
PAC (2 g/L)	MBR (submerged 30 μm nylon mesh filter with 0.05 m^2 filtration area)	Distillery effluent	• PAC enhances filtration performance in terms of increasing the critical flux and extending the operation period without mesh cleaning. • For a given OLR, the COD removal is higher with PAC addition.	Satyawali and Balakrishnan, 2009

PAC (1.5 g/L)	SMBR (PVC UF with pore size of 0.01 μm)	Synthetic polluted raw water	• PAC supplementation results in adsorption of low molecular weight components (<6000 Da) but PAC dosage has a major impact on the extent of adsorption. • Due to the pre-treatment of BAC, the membrane fouling of sMBR in the hybrid process was substantially mitigated; and less frequent membrane cleaning was required. • The results confirmed the synergetic effects between the BAC and the subsequent sMBR.	Tian et al., 2009
PAC (750 mg/L)	SMBR (PVDF flat sheet membrane with 0.4 m^2 filtration area)	municipal secondary effluent	• Approximately 63%TOC, 95% NH_4^+-N and 98% turbidity in secondary effluent were removed by the PAC-MBR process. • The addition of PAC significantly increased organic removal and responsible for the largest fraction of organic removal. • Membrane fouling analysis showed the enhanced membrane performance in terms of sustainable operational time and filtration resistances by PAC addition.	Lin et al., 2011
Kaldnes K1	MBBR-MBR (tubular zirconium ceramic with pore size of 50 nm)	old landfill leachate	• Compared to conventional nitrification, the process tested during this experimentation (ammonia oxidation stopped to nitrite) allows up to 25% savings in oxygen demand and up to 40% in COD demand for denitrification. • When DO concentration in the MBR was kept in the range 0.2–0.5 mg L−1, 90% oxidation of ammonia to nitrite was achieved, with stable inhibition of nitrite-oxidizing bacteria even at sludge retention time higher than 45 days.	Canziani et al., 2005
Polyurethane sponge	SMBR (PVDF with pore size of 0.2 μm)	Synthetic wastewater	• Sponge addition could mitigate membrane fouling significantly by preventing pore blocking and reducing cake layer formation. • High NH_4-N removal could be attributed to the enhanced population of ammonium oxidation bacteria on the acclimatised sponge. • As sponge could provide the anoxic condition around the surface of the sponge and the anaerobic condition inside the sponge, the system achieved high removal efficiency of PO_4-P.	Deng et al., 2014

2.5.3 Micropollutant removal in attached-growth based hybrid membrane system

The membrane bioreactor (MBR) has been considered as a reliable and effective alternative to conventional activated sludge (AS) processes in terms of pollutants removal. In addition to excellent removal of traditional contaminants (organic matters and nutrients), MBRs are also able to considerably eliminate a broad range of micropollutants, some of which are impervious to the conventional activate sludge treatment. This is due to the facts that 1) MBRs are able to retain sludge that can adsorb micropollutants (Abegglen et al., 2009); 2) The membrane surface can also reject the release of micropollutants (Kimure et al., 2003; Kimure et al., 2004; Radjenović et al., 2008); and 3) The prolonged SRT in MBRs can enhance the removal efficiencies of some micropollutants (Kimure et al., 2007; Luo et al., 2014b). The superiority of MBRs over conventional activated sludge treatment in terms of micropollutant removal has been well documented in literature. Hai et al. (2011) showed that an exceptionally high removal (68 ± 10 %) of carbamazepine was achieved by MBR under near-anoxic condition. Radjenović et al. (2009) reported that MBR technology could significantly improve the elimination of some pharmaceuticals by 30 – 65%. Chen et al. (2008) found that a submerged MBR was able to achieve much more stable removal of bisphenol A at varied volumetric loadings, as compared to a conventional activated sludge reactor.

In spite of the advantages, the implementation of MBRs has long been limited by a high whole-life cost, due to the substantial energy consumption and constant maintenance. Moreover, the membrane fouling is another remarkable obstacle to the widespread application of MBR technology. Strategies to prevent fouling before its occurrence are of great significance and many efforts have been made to achieve the goal (Fang et al., 2006; Guo et al., 2004; Liao et al., 2004; Yang et al., 2006;) by 1) improving the anti-fouling properties of the membrane, 2) operating the MBR under specific non-or-little-fouling conditions, 3) pretreating the biomass suspension to limit its fouling propensity (Le-Clech et al. 2006).

On the other hand, moving bed biofilm reactor (MBBR) is a compact system with high concentrations of attached-growth biomass but significantly low suspended solids production. By integrating MBBR with a MBR, the considerably low solid

concentrations contribute to reduced fouling potential. Furthermore, readily biodegradable chemical oxygen demand (COD) can be removed in the MBBR and hence biological activity on the membrane surface will be minimized (Pervissian et al., 2011). Accordingly, the fouling tendency of a MBR could be alleviated by using MBBR as a pretreatment. Among all suspended media used in MBBR, the superiority of polyurethane foam (sponge) has been proven in terms of removal of both conventional and unconventional pollutants (Chu and Wang, 2011; Luo et al., 2014b).

Luo et al. (2015) compared a moving bed biofilm reactor-submerged membrane bioreactor (MBBR-MBR) hybrid system and a conventional membrane bioreactor (CMBR) in terms of micropollutant removal efficiency and membrane fouling propensity. The results show that the MBBR-MBR hybrid system could effectively remove most of the selected micropollutants. By contrast, the CMBR system showed lower removal of some micropollutants including ketoprofen, carbamazepine, primidone, bisphenol A and estriol. Mass balance calculations suggest that biological degradation was the primary removal mechanism in the MBBR-MBR system. During operation, the MBBR-MBR system exhibited significantly slower fouling development as compared to the CMBR system, which could be ascribed to the wide disparity between the SMP levels of the two systems. It is evident that adding a MBBR process prior to MBR treatment can not only enhance micropollutant elimination but also mitigate membrane fouling.

2.6 Conclusion

Moving bed biofilm reactor (MBBR) is a compact system with high concentrations of attached growth biomass but significantly low suspended solids production. In MBBR, attached growth media moves freely in the aeration reactor and enables better oxygen transfer with high nitrification rate. Moreover, enhanced process stability can be achieved as most biomass is attached onto the media rather than being washed away. Compared to activated sludge (AS) processes, the operation of MBBR requires less energy consumption and low maintenance cost. Thus, MBBR delivers a flexible, cost-effective, and easy-to-operate mean to address current

wastewater issues and the expandability to meet future loads or more stringent discharge requirements. In addition, the MBBR is able to remove a board spectrum of micropollutants as it is more likely to have different redox conditions within biofilm.

By integrating with membrane bioreactor (MBR), MBBR also offers a promising alternative to activated sludge based technology. It has been reported that high mixed liquid suspended solid (MLSS) concentration caused high suspension viscosity in membrane unit. It might be expected to have a profound influence on membrane performance due to its effect on both the dynamic cake layer thickness and the viscosity. Considering the relatively low suspended solid concentration in MBBR, this unique characteristic contributes to low viscosity of suspended solid and reduced fouling potential in membrane unit. In this context, the combination of MBBR and membrane filtration could sufficiently reduce MLSS content in the whole process, resulting in a different composition and properties of the membrane feed solution.

Although there are limited amount of studies on the performance of MBBR-MBR hybrid system in previous research, the results from the available reports illustrate a potential for improved membrane fouling control and mitigation due to a decreased suspended solid environment in the process, regardless system configurations and the choices of biocarriers. In addition, the performance of MBBR-MBR was comparable and competitive with that of the activated sludge (AS)-MBR in terms of removal of COD and ammonium. However, no effort has been made to examine the effectiveness of micropollutants removal by using a MBBR-MBR system so far. Therefore, micropollutant removal by MBBR-MBR 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 MBBR system, the MBBR-SMBR hybrid system and the SSMBR system. A continuous bench-scale MBBR was set up for a long-term assessment of micropollutant removal at HRT of 24 h, 18 h, 12 h, and 6 h. Additionally, an MBBR-MBR system was investigated in terms of its micropollutant removal efficiency and membrane fouling at HRT of 24 h, 18 h, 12 h, and 6 h. Furthermore, a SSMBR was also studied in order to compare the treatment efficiency to the MBBR-MBR system.

3.2 Materials

3.2.1 Synthetic wastewater

In order to maintain constant feed pollutant concentration, a synthetic wastewater (simulating medium strength municipal wastewater primary effluent) spiked with micropollutants was used in this study. The chemical composition of synthetic wastewater is shown in 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 on a daily basis 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 to a constant value of 7.

3.2.2 Selected micropollutants

A set of 22 micropollutants that have been frequently detected in municipal wastewater were selected for investigation (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 obtain an initial concentration of 5 μg/L for each compound in the feed wastewater.

Table 3.1 Composition and concentration of the stock solution

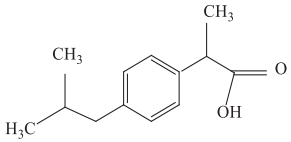
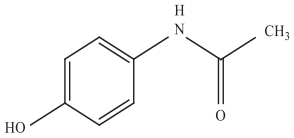
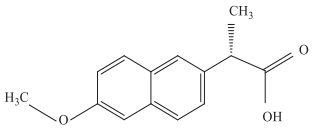
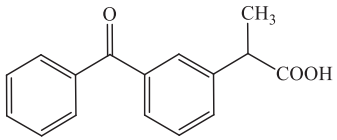
Compound	Chemical formula	Molecular weight (g/mol)	Concentration (mg/L)
Organics and nutrients			
Glucose	$C_6H_{12}O_6$	180.0	280
Ammonium sulfate	$(NH_4)_2SO_4$	132.1	142
Potassium phosphate	KH_2PO_4	136.1	26
Trace nutrients			
Calcium chloride	$CaCl_2 \cdot 2H_2O$	147.0	0.368
Magnesium sulfate	$MgSO_4 \cdot 7H_2O$	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

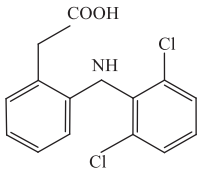
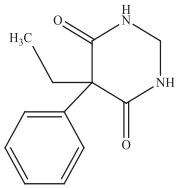
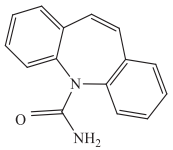
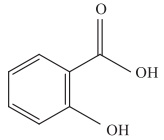
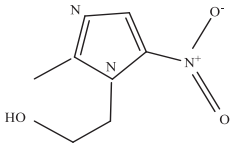
3.2.3 Sponge (polyurethane foam)

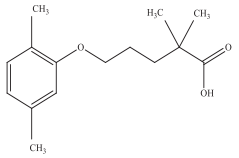
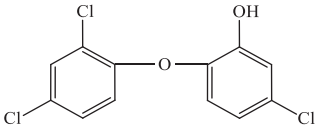
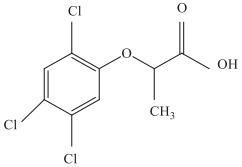
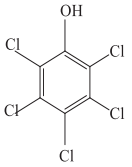
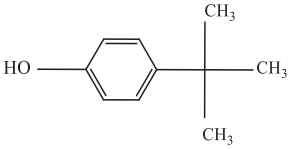
The biofilm carriers were made of reticulated sponge S28/80R (Joyce Foam Products), composed of skeletal strands and containing a homogenous structure of evenly sized air cells. The sponge has a density of 28–30 kg/m^3 with 80 cells per 25 mm. The sponge was cut into small sponge cubes (2 cm × 2 cm ×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

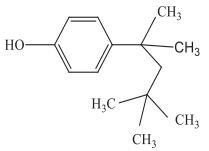
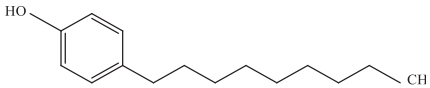
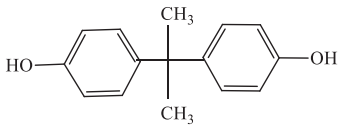
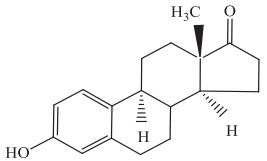
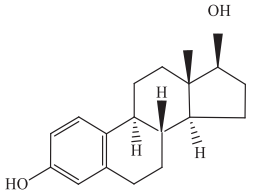
Figure 3.1 The attached-growth carriers (sponge cubes) used in this study

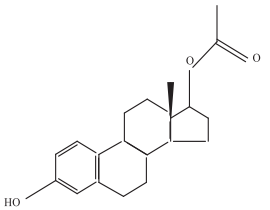
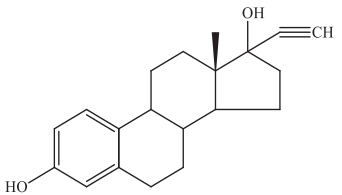
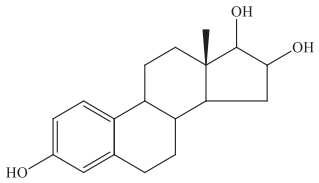
Table 3.2 Physicochemical properties of the selected trace organics

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 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. The HRT were 24 h, 18 h, 12 h, and 6 h, respectively. Accordingly, the reactor had a flow rate of 27.8 mL/min, 37.0 mL/min, 55.6 mL/min, and 111.1 mL/min. To avoid excessive detachment of the biosolids within the sponge cubes, the aeration of the MBBR was adjusted constantly to achieve gentle circulation of the sponge cubes. The DO concentration of the MBBR was controlled 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 100 days for each HRT operation condition.

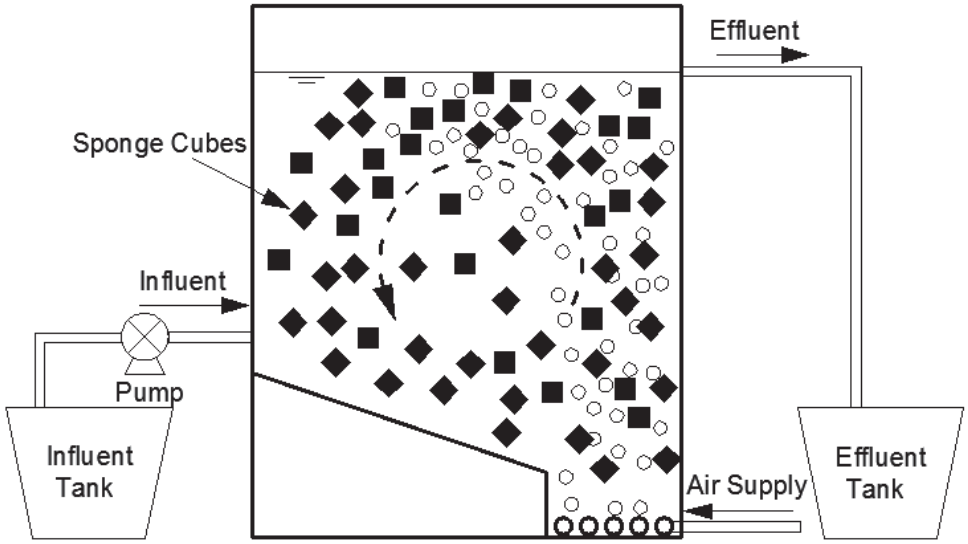


Figure 3.2 On-site photo and schematic diagram of the MBBR

3.3.2 MBBR-MBR system

The MBBR-MBR system (Figure 3.3) consisted of the MBBR and an MBR (working volume: 10 L). The membrane used for the MBR unit was a polyvinylidene fluoride (PVDF) hollow fiber module with a pore size of 0.2 μm and surface area of 0.2 m^2. The MBR unit was fed with MBBR effluent through a buffer tank. The MBR permeate flow was controlled by a suction pump in order to obtain a constant flux of 8.83 $L/m^2 \cdot h$.

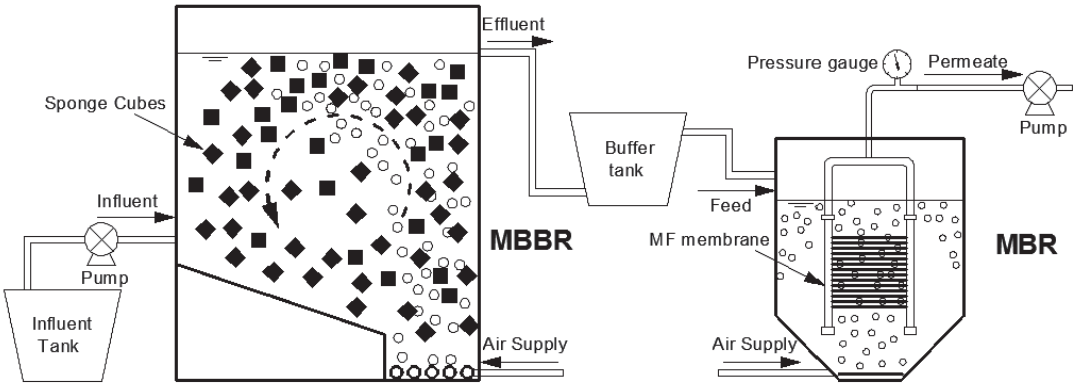


Figure 3.3 On-site photo and schematic diagram of the MBBR-MBR system

A pressure gauge was used to measure the transmembrane pressure (TMP). A soaker hose air diffuser was mounted at the bottom of the MBR unit to provide aeration (6 L/min). The MBR unit was operated in a continuous mode without backwash, relaxation or cleaning and the operation was terminated when the trans-membrane pressure (TMP) exceeded 35 kPa. 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 7, 10, 15, 18, 21, 24, 27, 30 and 35 kPa.

3.3.3 SSMBR system

The SSMBR system (Figure 3.4) was a sponge-submerged membrane bioreactor. The reactor had a working volume of 10 L and was filled with sponge cubes (10% $v_{sponge}/v_{reactor}$). The SSMBR used identical hydrophilic polyvinylidene fluoride (PVDF) hollow fibre microfiltration (MF) membrane modules with a pore size of 0.2 μm and surface area of 0.2 m^2. Polyurethane sponge cubes (S28/80R, Joyce Foam Products; dimension of 1 cm × 1 cm × 1 cm) were used as biofilm carriers. As no sludge withdrawal was performed except for removing sludge from carrier and mixed liquor for measurement, the SRT could be considered infinite. The SSMBR was operated at a constant flow rate of 27.8 mL/min, resulting in a HRT of 6 h. Accordingly, the permeate flux of was 8.34 L/(m^2·h). The SSMBR was operated in a

continuous mode without backwash, relaxation or cleaning and the operation was terminated when the trans-membrane pressure (TMP) exceeded 35 kPa.

Figure 3.4 On-site photo of the SSMBR system

3.3.4 Operation protocol

Every five days, influent and effluent aqueous samples were collected for COD, TOC, NH_4-N, NO_2-N, NO_3-N and PO_4-P analysis. In addition, the attached biomass on sponge cubes and suspended MLSS and MLVSS were also measure in both MBBR and MBR unit, as well as the SSMBR system.

Every ten 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). Figure 3.5 showed the SPE process for GC-MS analysis of 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.

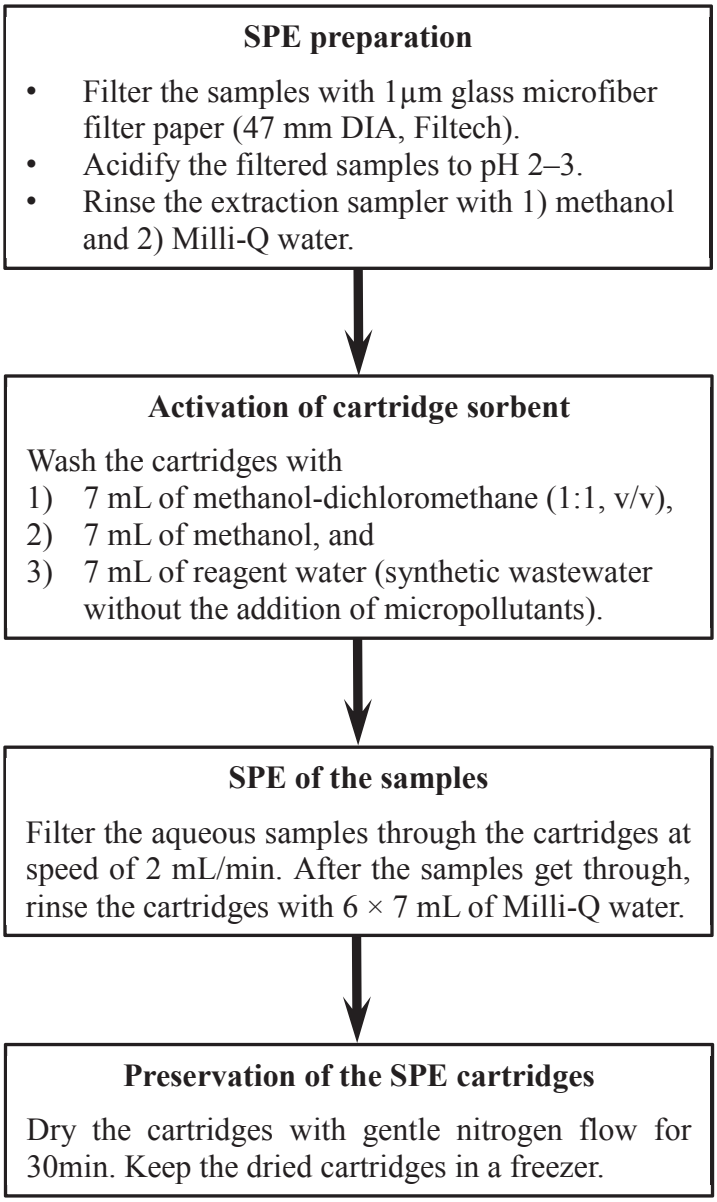


Figure 3.5 Schematic diagram of SPE process for GC-MS analysis of micropollutants

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 1, Day 50 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.

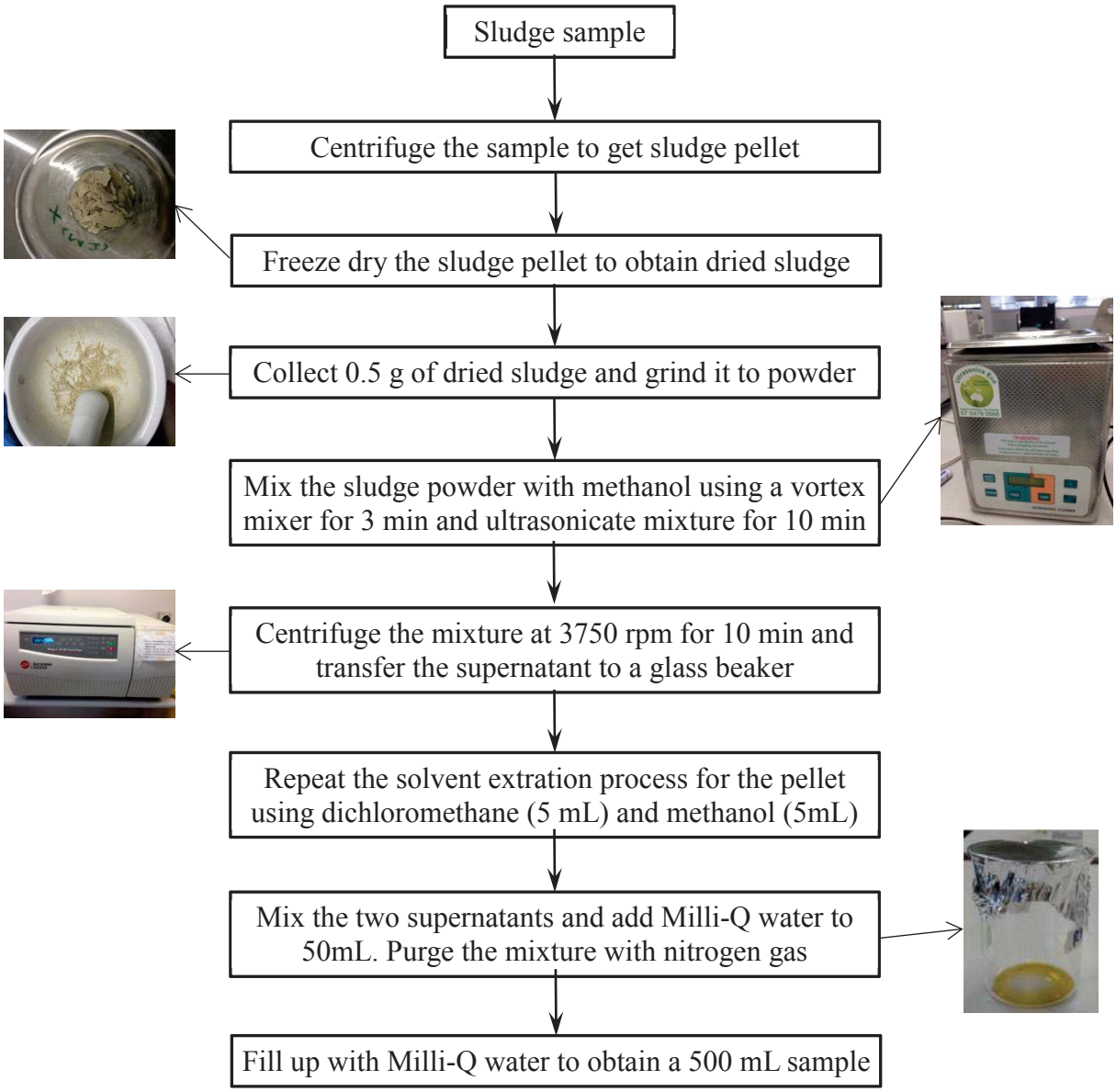


Figure 3.6 Schematic diagram of solvent extraction process of sludge samples

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 3.7).

Figure 3.7 The analytical instruments used in this study

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.

3.4.3 Micropollutants

Micropollutant concentrations in the aqueous samples were determined using an analytical method previously reported by Hai et al. (2011c). This method consists of a solid phase extraction procedure (SPE) followed by gas chromatography and quantitative determination by mass spectrometry with electron ionisation. TrOC concentrations in liquid samples (500 mL each) were extracted using 6 mL 200 mg Oasis HLB cartridges (Waters, Milford, MA, USA). First, the cartridges were preconditioned with 7 mL dichloromethane (DCM) and methanol (MeOH) mixture (1:1 v/v), 7 mL methanol followed by 7 mL reagent water (synthetic feed wastewater excluding TrOCs). The samples were acidified to pH 2-3 (4 M H2SO4) and loaded onto the cartridges at a flow rate of 1-5 mL/min. Then, the cartridges were rinsed with 20 mL Milli-Q water (6× 7mL) and dried in a stream of nitrogen for 30 min.

Figure 3.8 Procedure used for SPE for analysing micropollutants

3.4.4 Fouling resistance

Fouling resistance of the MBR 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.

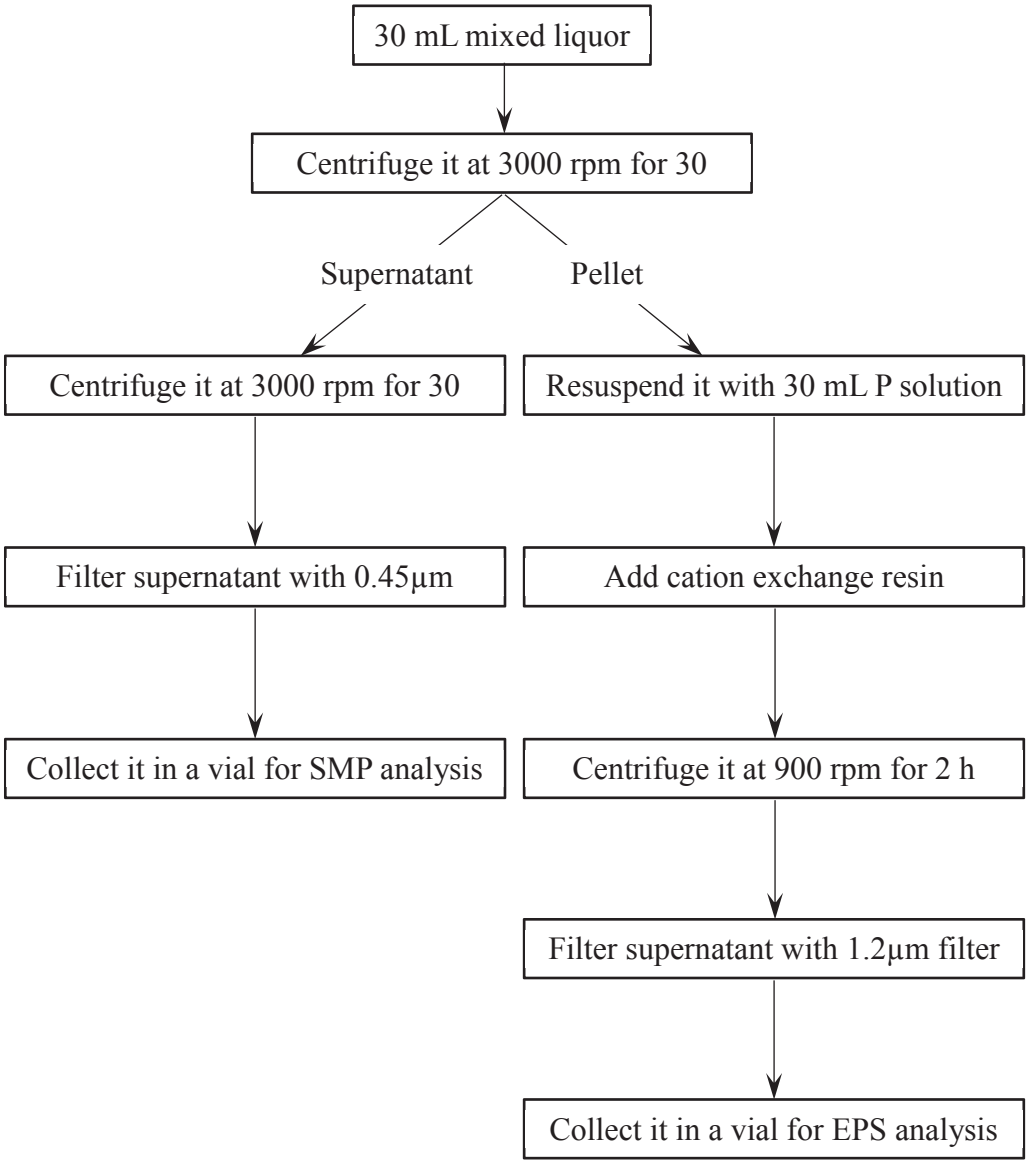


Figure 3.9 Schematic diagram of processes for SMP and EPS extraction

Several physical properties of mixed liquor in the MBR and SSMBR were analysed, 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).

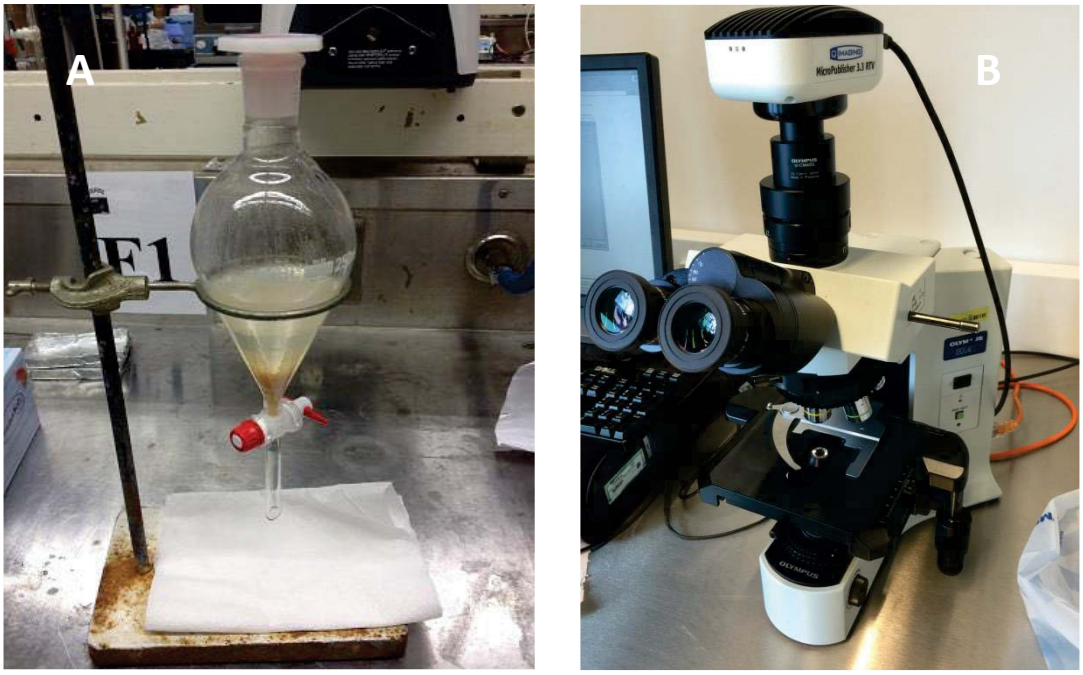


Figure 3.10 Relative hydrophobicity test (A) and microscopic analysis (B)

University of Technology, Sydney

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Chapter 4

Micropollutant Removal in a Moving Bed Biofilm Reactor (MBBR) at Different HRTs

4.1 Introduction

The ubiquitous occurrence of micropollutants and their metabolites in the aquatic environment has posed threats to living organisms to a great extent. However, effective micropollutants removal normally requires longer hydraulic retention time (HRT) when using biological treatment systems. As an ideal and low-cost material for attached-growth microorganisms, polyurethane sponge has exhibited high potential to eliminate micropollutants. In this study, a sponge-based moving bed biofilm reactor (MBBR) was investigated at four different HRTs (24, 18, 12, 6 h), to better understand the effect of HRT on micropollutants removal. Four groups of frequently detected micropollutants in wastewater (total 22 compounds) were selected, namely pharmaceuticals and personal care products (PPCPs), pesticides, hormones and industrial chemicals. The MBBR showed stable and effective removals of TOC (92.6% - 95.8%), COD (93.0% - 96.1%) and NH_4-H (73.6%-95.6%) at all HRTs while improving PO_4-P removal at HRT of 18 h. In terms of micropollutants removal, S-MBBR achieved comparable removal compared to other biological treatment such as activated sludge processes and membrane bioreactor. Although the micropollutants were subjected to biodegradation and sorption, the results indicated compound-specific variation in removal at all HRTs, ranging from 10.7% (carbamazepine) to 98.4% (ibuprofen). Among the selected micropollutants, most of them were biodegradable excluding carbamazepine, fenoprop and metronidazole. In addition, the micropollutants removal could remain constantly high even at lower HRTs with more consistent removal efficiency over the experimental period (except for carbamazepine, fenoprop, 17α-ethinylestradiol and 4-tert-octylphenol). Particularly, at HRT of 18 h, the removal of Diclofenac was significantly improved by more than 30% and the removals of ketoprofen, gemifibrozil, acetaminiphen, bisphenol A, and pentachlorophenol were also better. Overall, HRT of 18 h was the optimum HRT for biological degradation of the micropollutants.

4.2 Organic and nutrient removal

Table 4.1 summarizes the removal efficiencies of DOC, COD, NH_4-N, PO_4-P and total nitrogen (TN) in MBBR at four HRTs (HRT of 24, 18, 12, and 6 h). The MBBR

was able to achieve effective removal of DOC (>94%) and NH_4-N (>82%) at all HRTs. However, unstable TN (45.2-72.3%) reduction and
PO_4-P (26.4-49.9%) elimination were observed throughout the experimental period. It was noteworthy that the MBBR showed the highest performance efficiency for removing DOC, COD, NH_4-N, PO_4-P and TN at HRT of 18 h, which were 96.1±0.4%, 97.4±0.8%, 91.1±1.6%, 49.9±7.2%, and 72.3±6.9%, respectively. This could be explained by the food to microorganisms (F/M) ratio in the MBBR unit, calculated based on COD and MLVSS. The F/M ratio were 0.72, 0.91, 1.83, and 3.06 g COD/ g MVLSS·d at HRT of 24, 18, 12, 6 h, respectively. The amount of food present in the system was sufficient to maintain microorganism growth when the F/M ratio was 0.91 g COD/ g MLVSS·d in the MBBR unit, which is in good agreement with the study of Pozo et al. (2012, 1.05 g COD/ g VSS·d). Villamar et al. (2009) also pointed out that the sludge showed good settler conditions when F/M ratio range between 0.63-1.26 g COD/ g VSS·d. In addition, higher NH_4-N removal at HRT of 18 h could be attributed to the increased population of ammonium oxidation bacteria in the MBBR unit. Moreover, the use of phosphate for biomass growth and the phosphorus uptake by phosphate accumulating organisms (PAOs) could contribute to the high removal of PO_4-P at HRT of 18 h.

Table 4.1 Results for organic matters and nutrients removal by MBBR at HRT of 24 h, 18 h, 12 h, and 6 h

HRT	Removal efficiency (%)				
	TOC	COD	NH_4-N	TN	PO_4-P
24	94.7±0.5	94.7±0.7	81.9±6.4	45.2±9.3	45.4±21.5
18	96.1±0.4	97.5±0.8	91.1±1.6	72.3±6.9	49.9±7.2
12	95.2±0.5	95.2±1.1	85.1±4.5	57.5±4.3	42.8±6.2
6	94.0±0.4	94.1±0.5	82.0±2.1	46.9±3.2	26.4±6.1

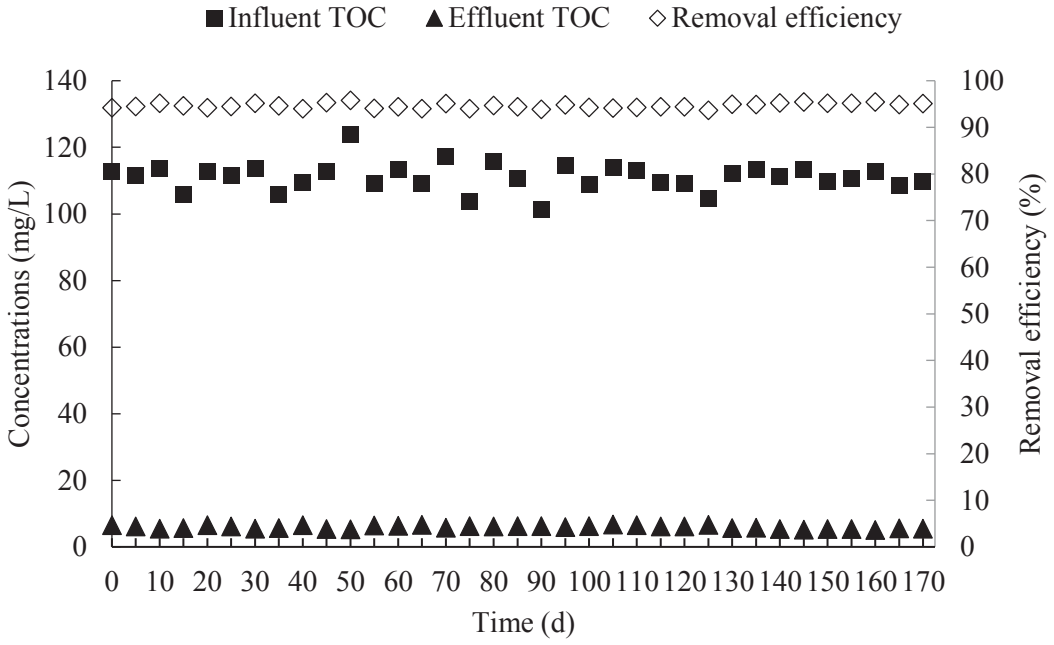

Figure 4.1 TOC removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 24 h).

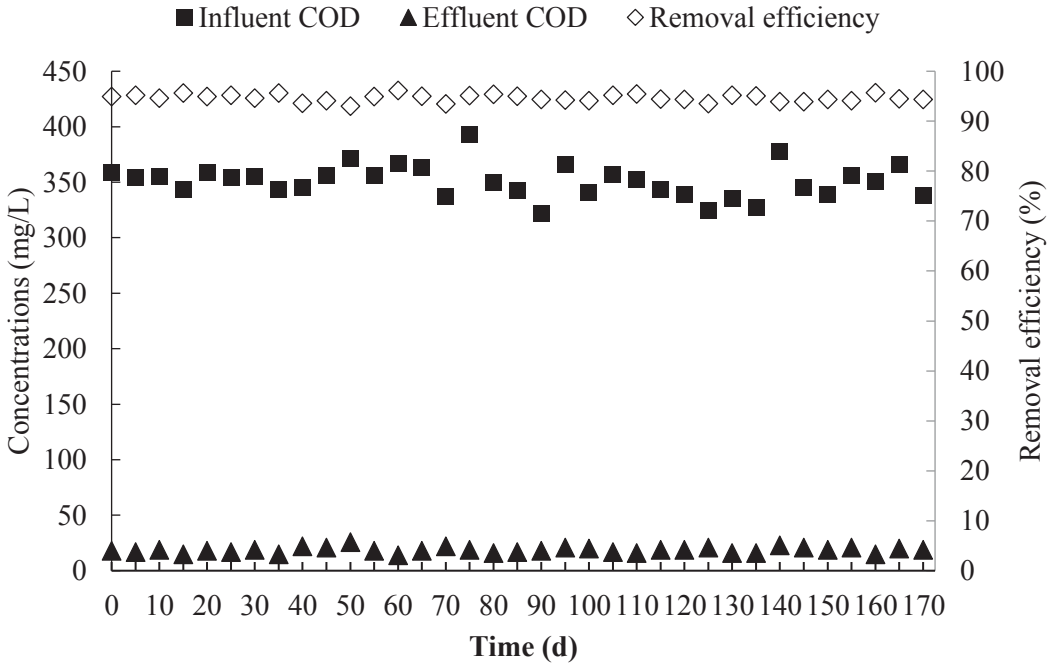

Figure 4.2 COD removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 24 h).

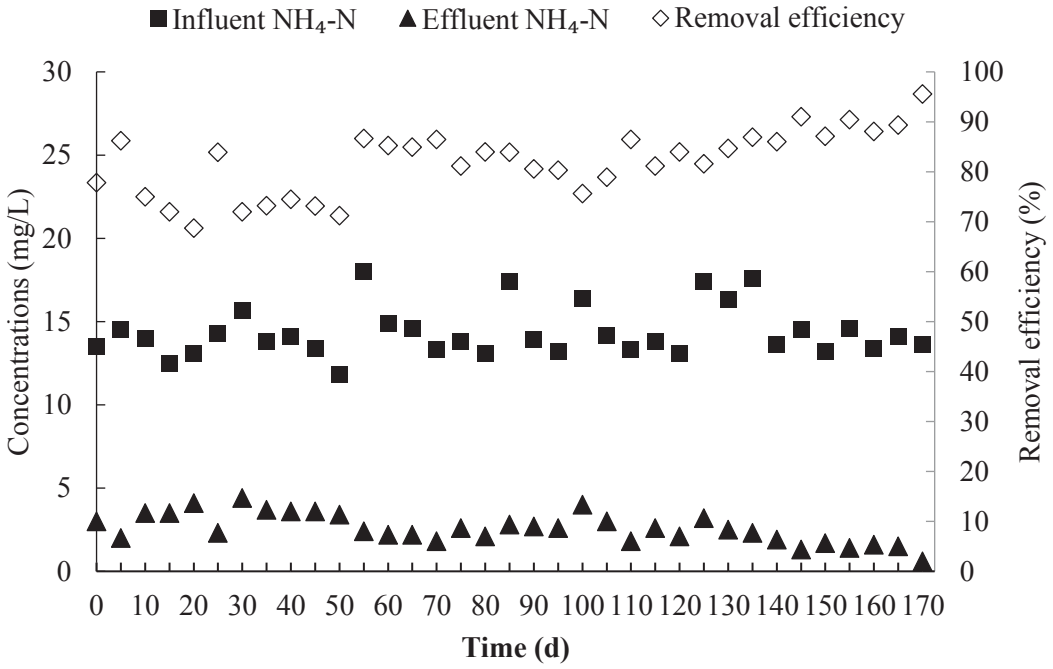

Figure 4.3 NH_4-N removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 24 h).

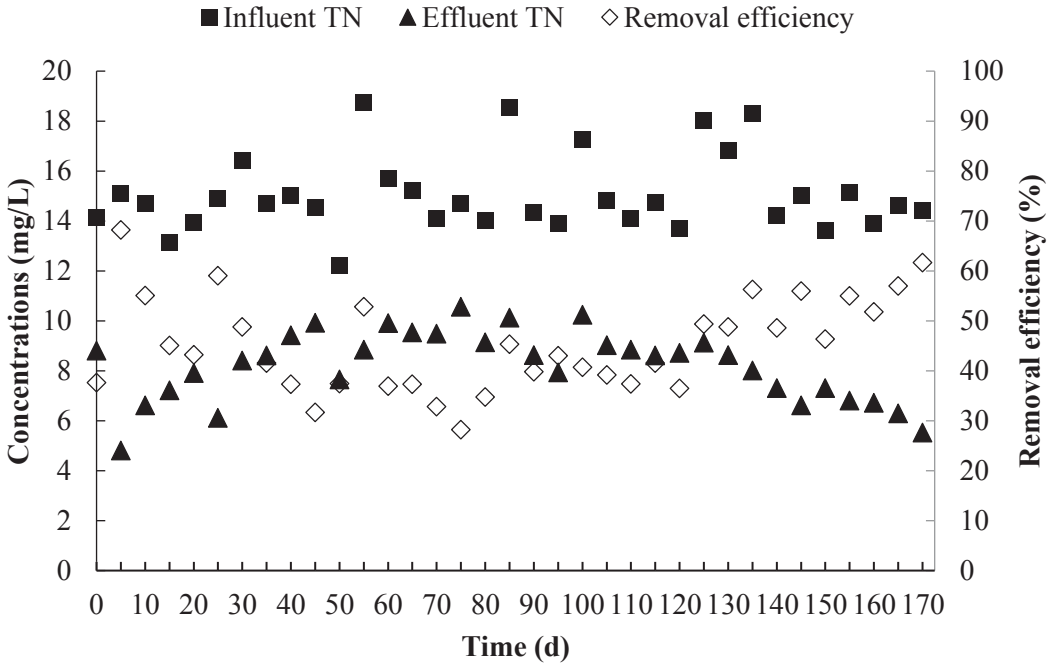

Figure 4.4 TN removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 24 h).

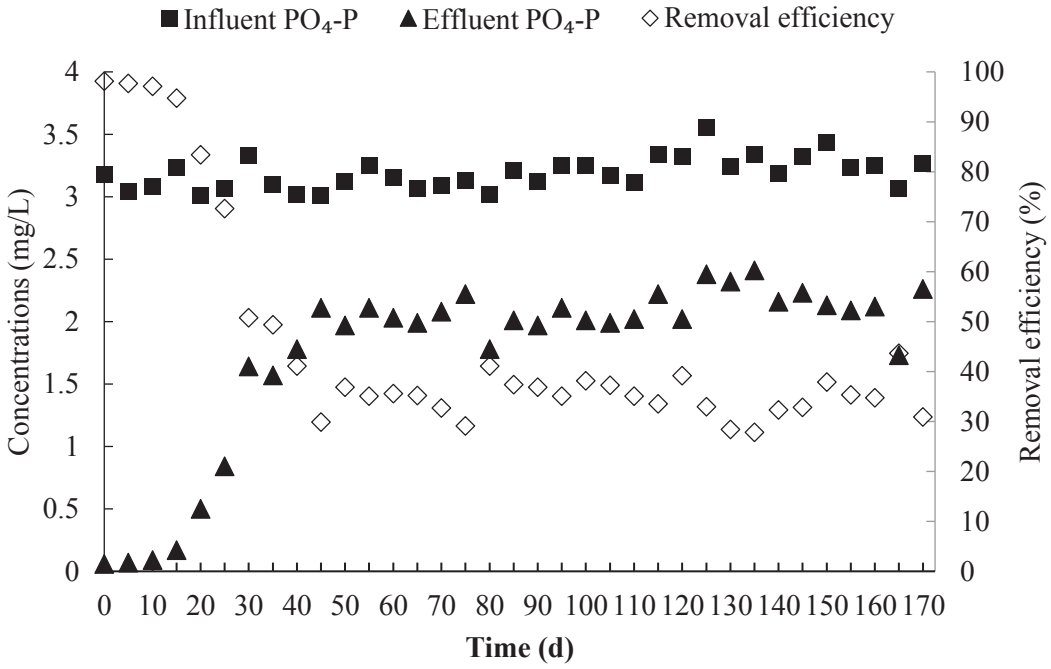

Figure 4.5 PO_4-P removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 24 h).

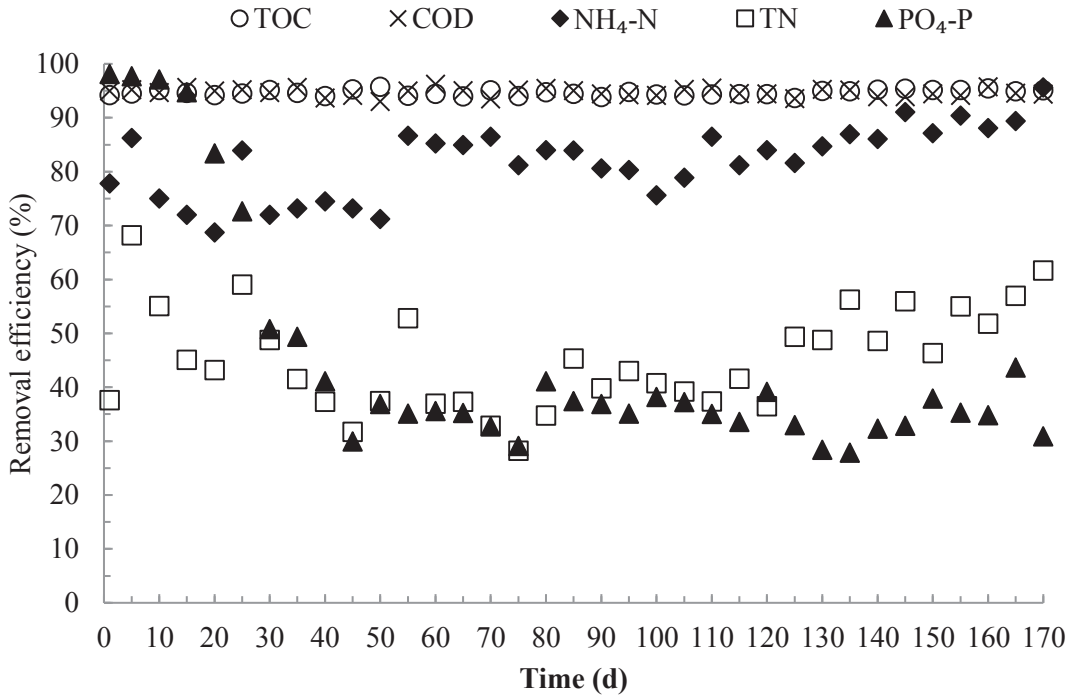

Figure 4.6 Summarized removal efficiencies in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 24 h).

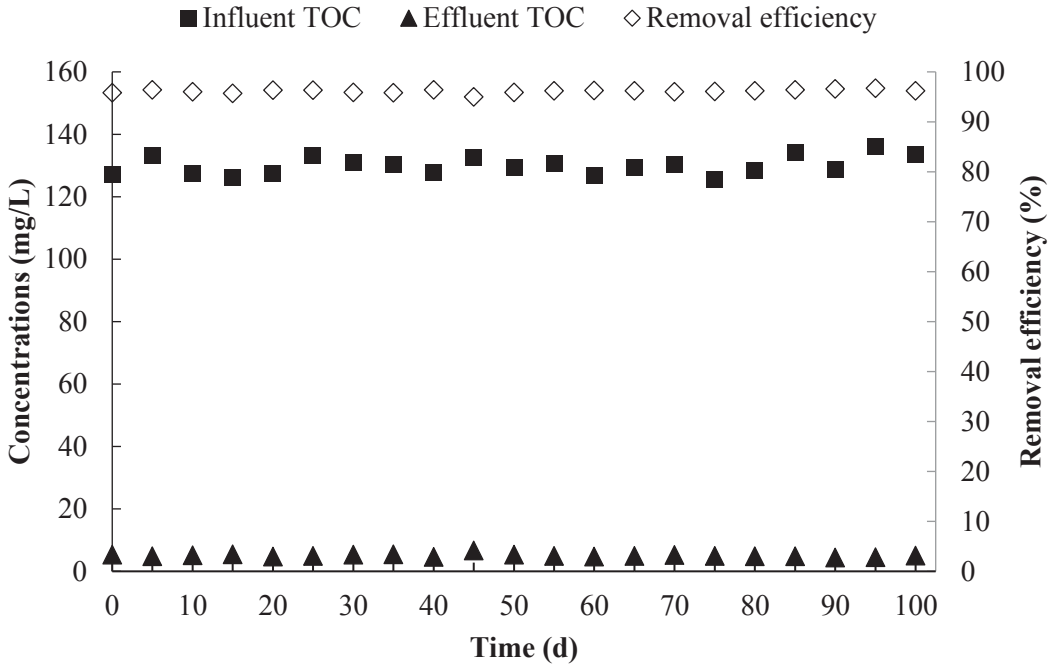

Figure 4.7 TOC removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 18 h).

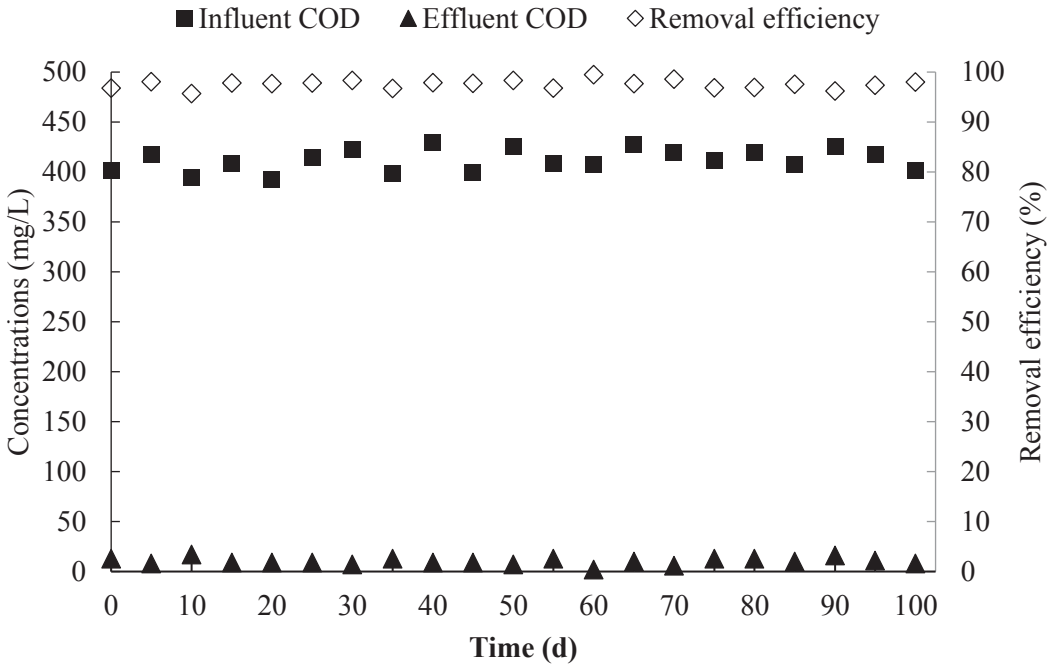

Figure 4.8 COD removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 18 h).

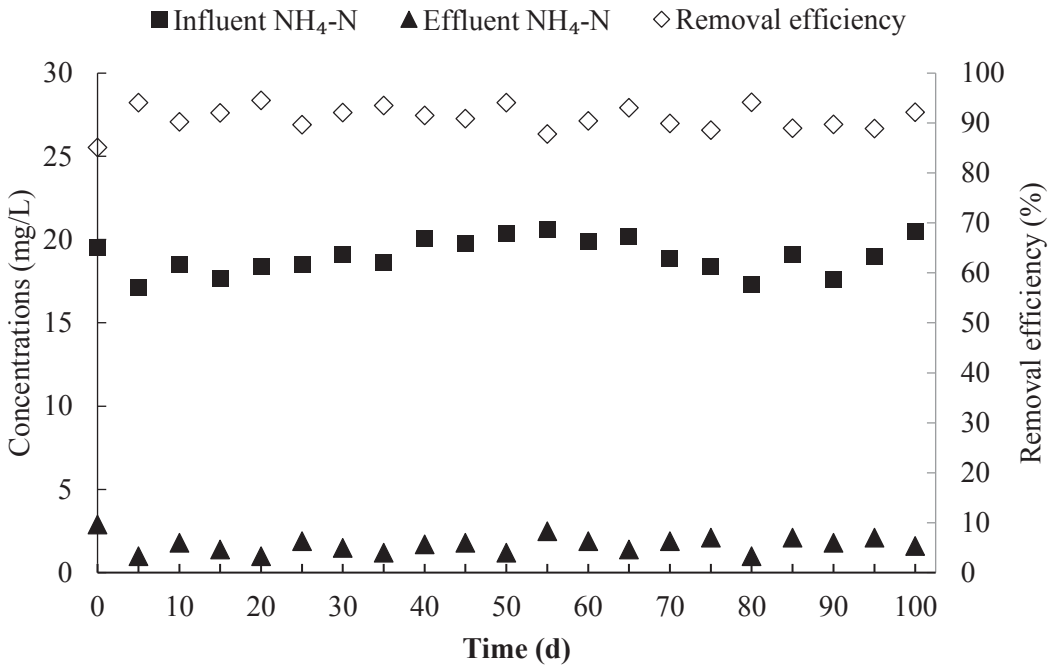

Figure 4.9 NH_4-N removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 18 h).

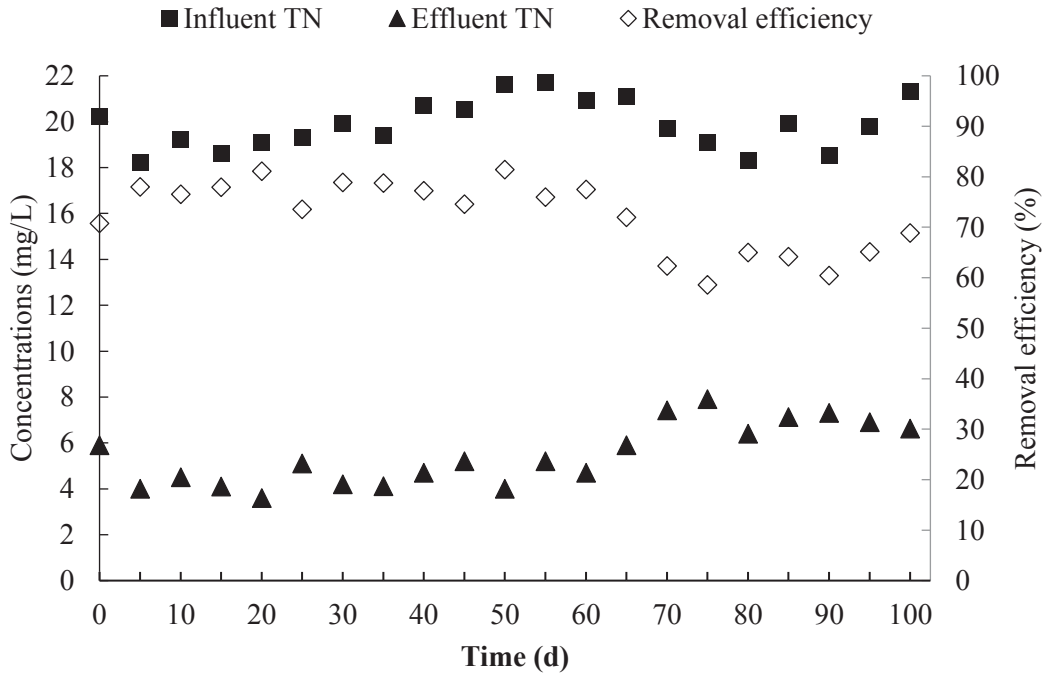

Figure 4.10 TN removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 18 h).

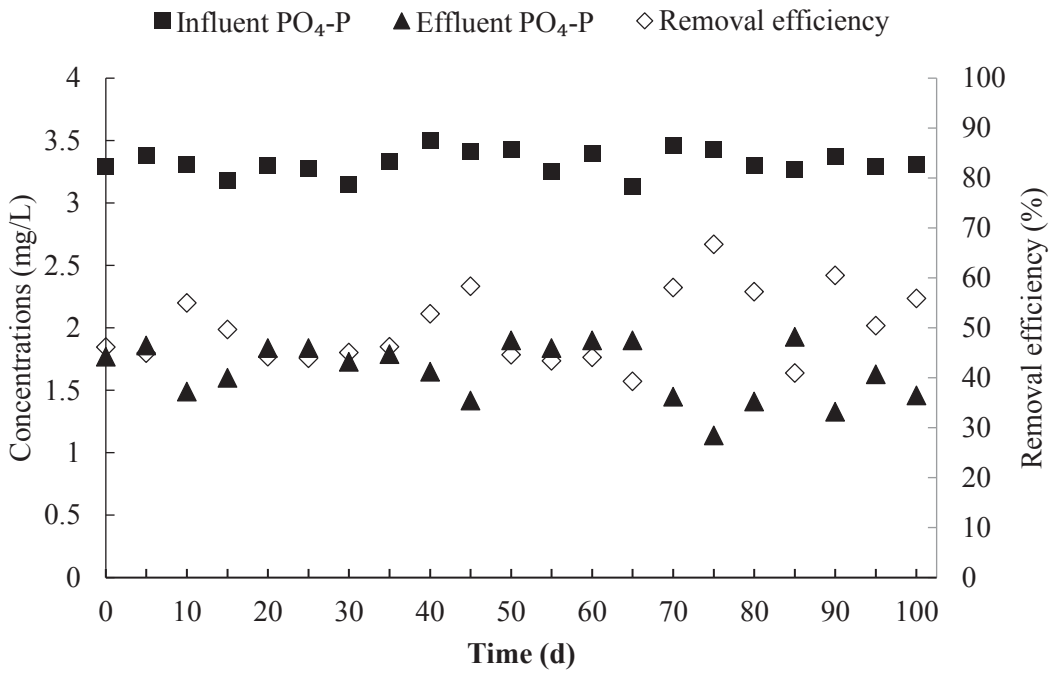

Figure 4.11 PO_4-P removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 18 h).

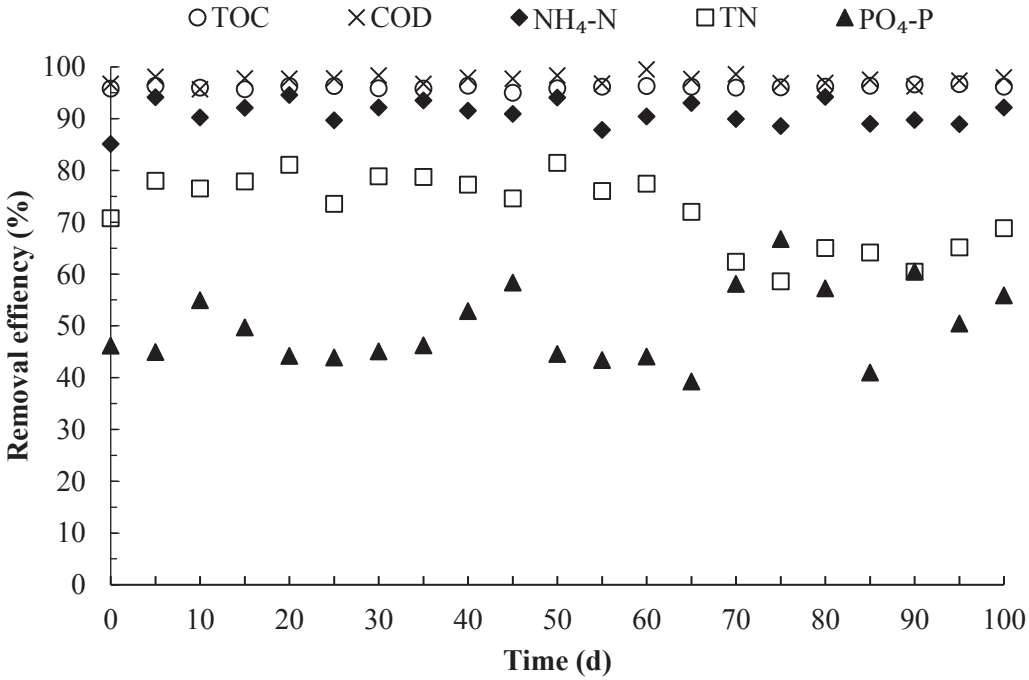

Figure 4.12 Summarized removal efficiencies in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 24 h).

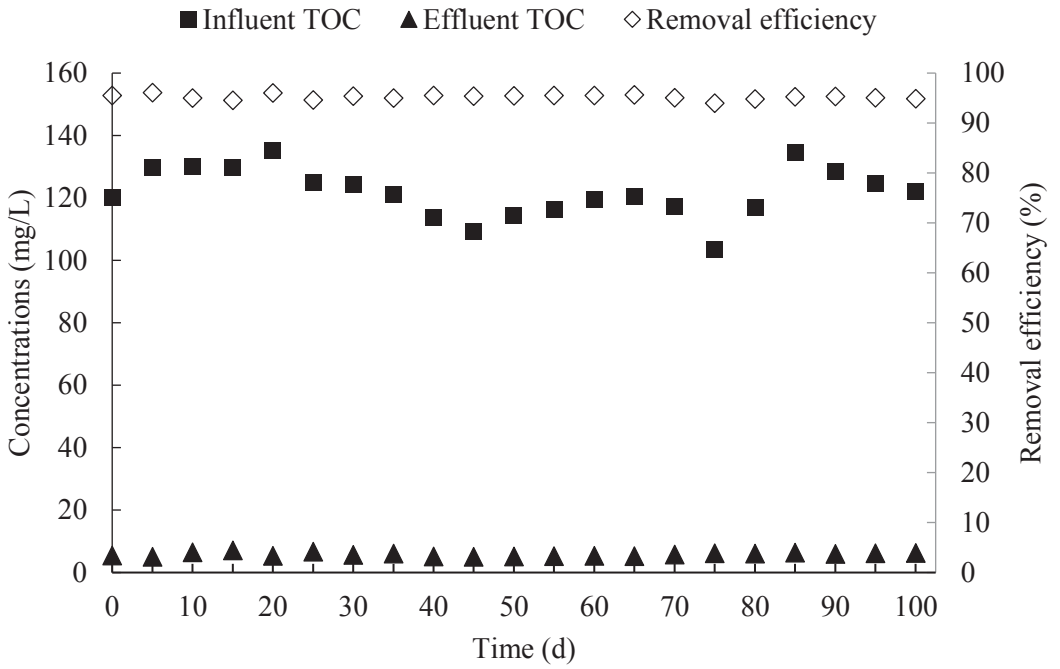

Figure 4.13 TOC removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 12 h).

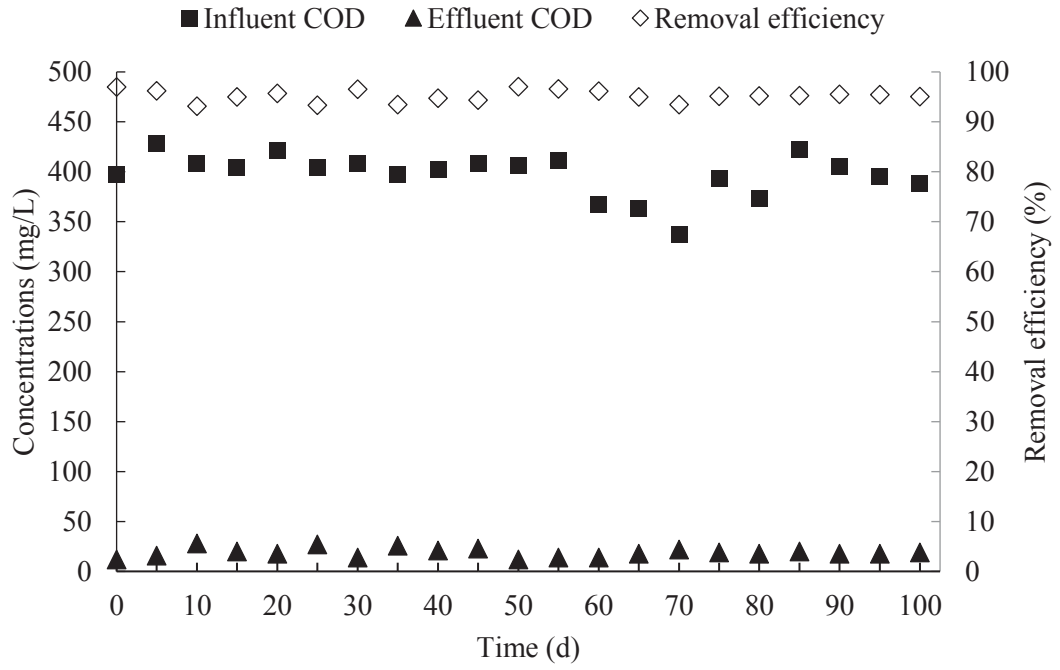

Figure 4.14 COD removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 12 h).

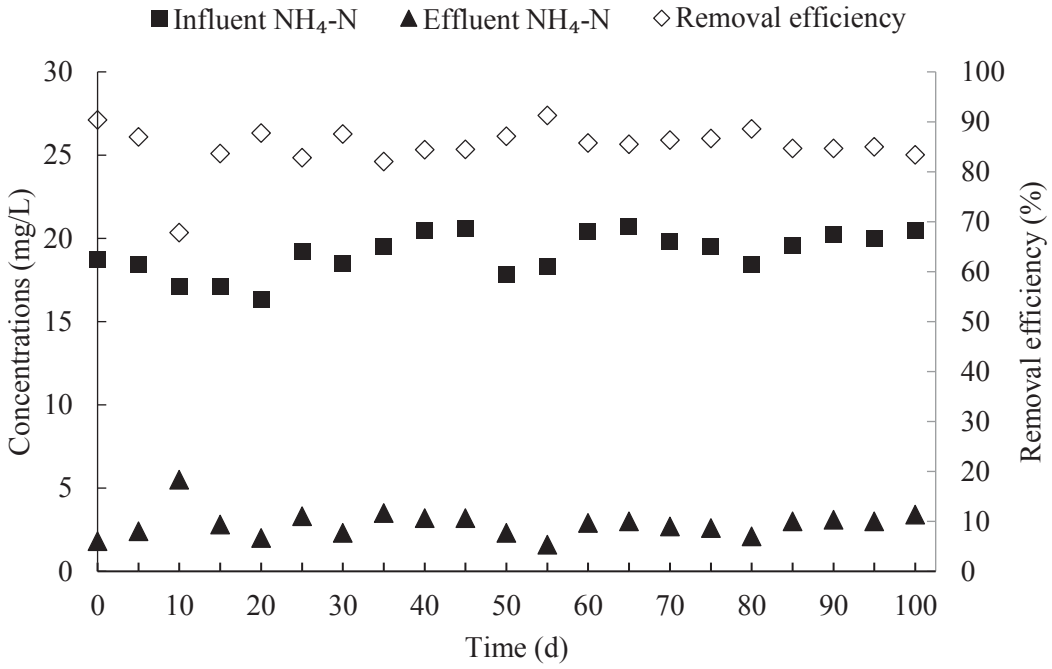

Figure 4.15 NH_4-N removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 12 h).

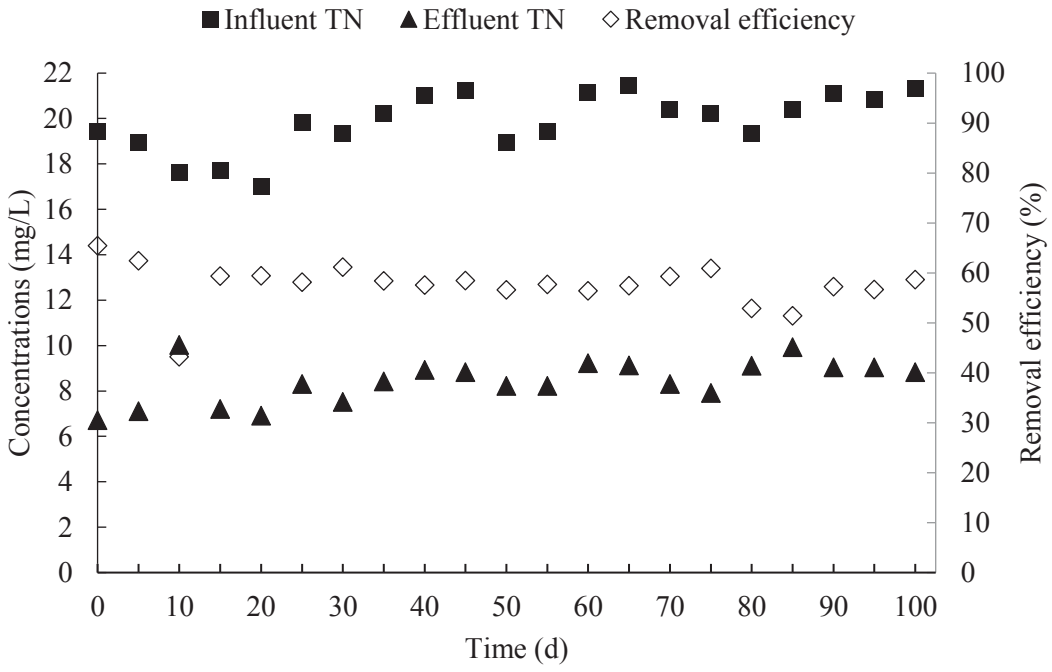

Figure 4.16 TN removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 12 h).

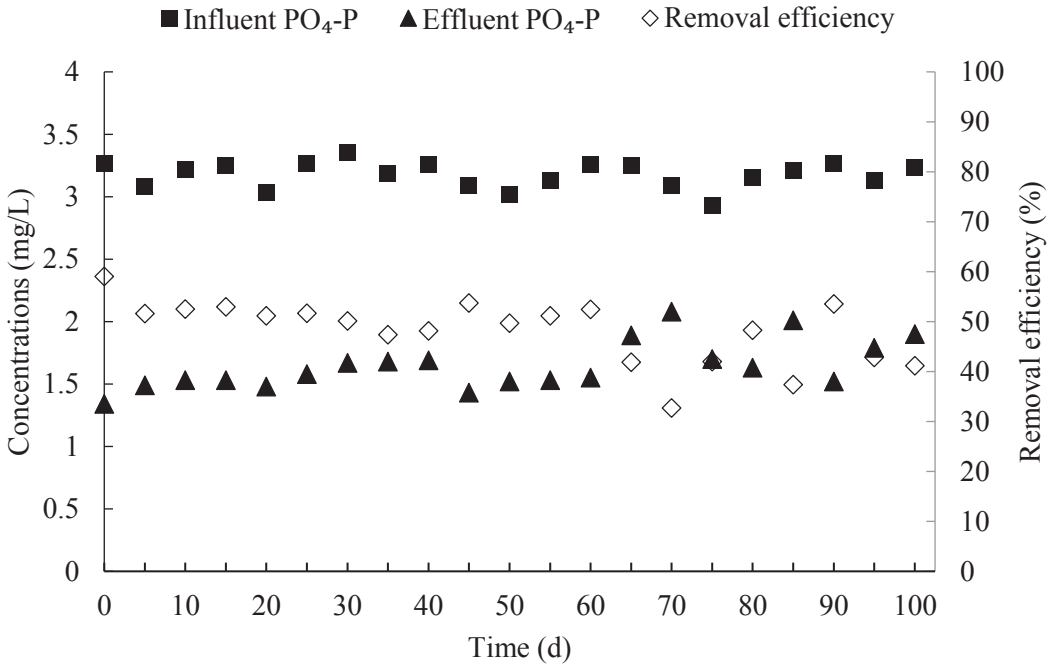

Figure 4.17 PO_4-P removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 12 h).

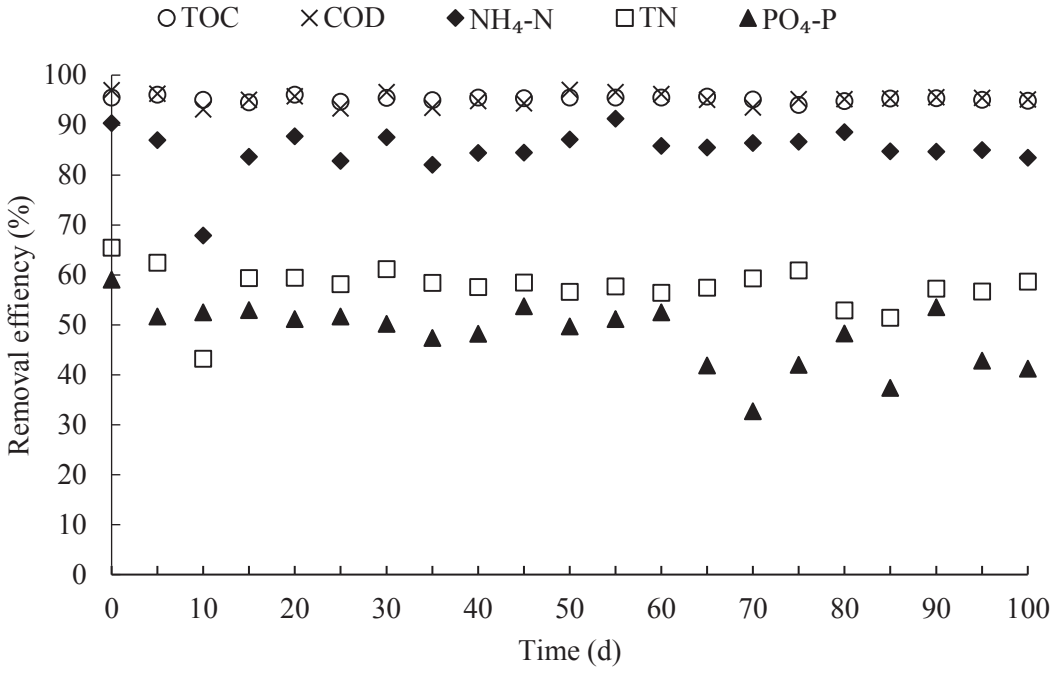

Figure 4.18 Summarized removal efficiencies in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 12 h).

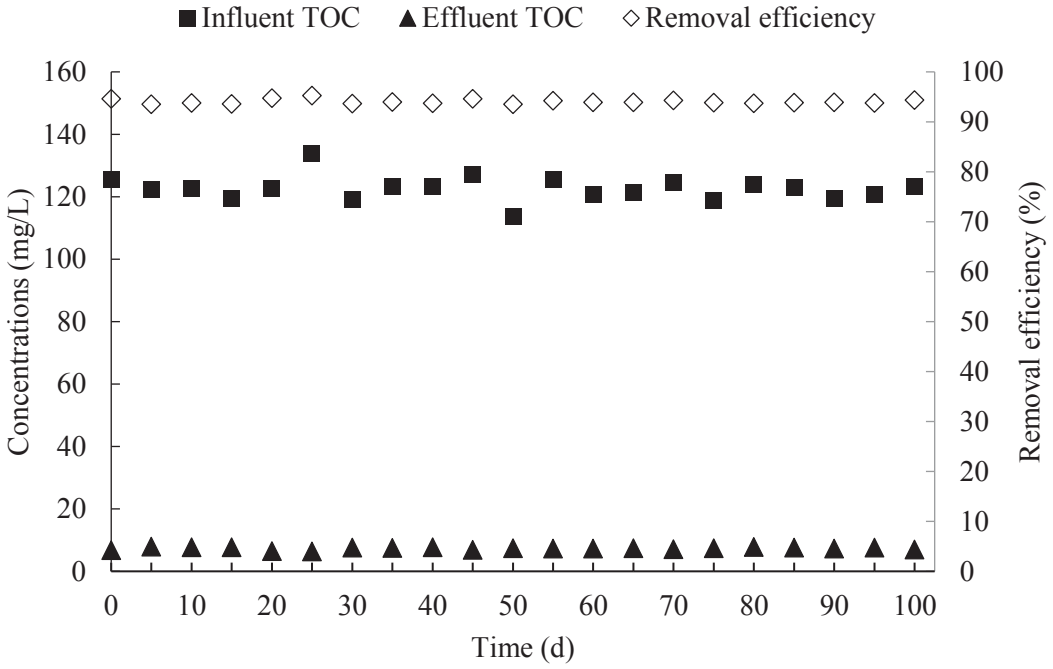

Figure 4.19 TOC removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 6 h).

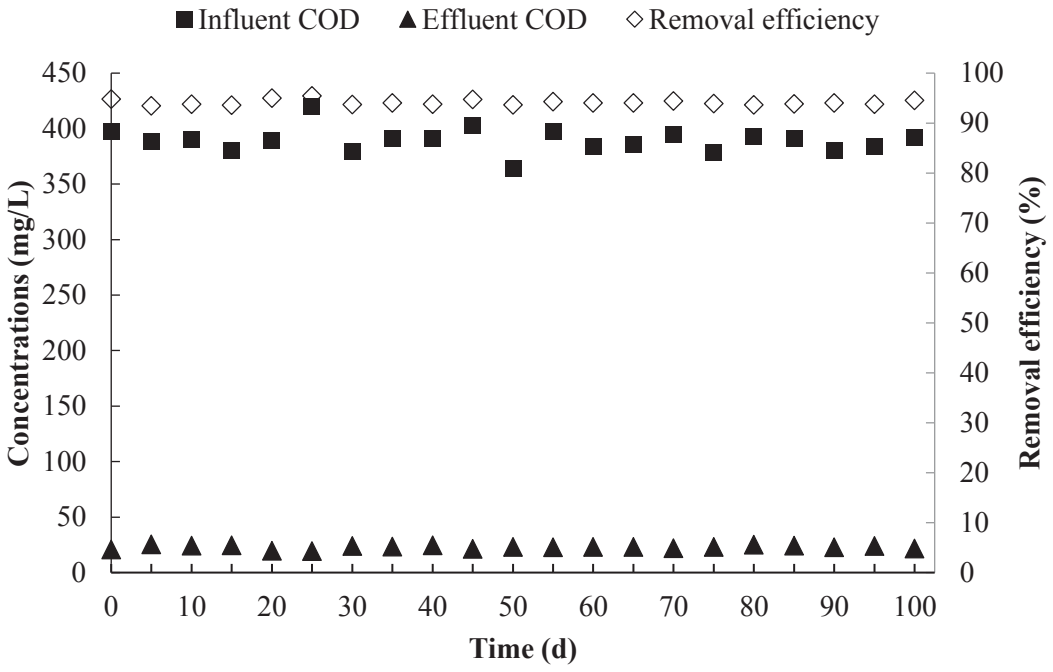

Figure 4.20 COD removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 6 h).

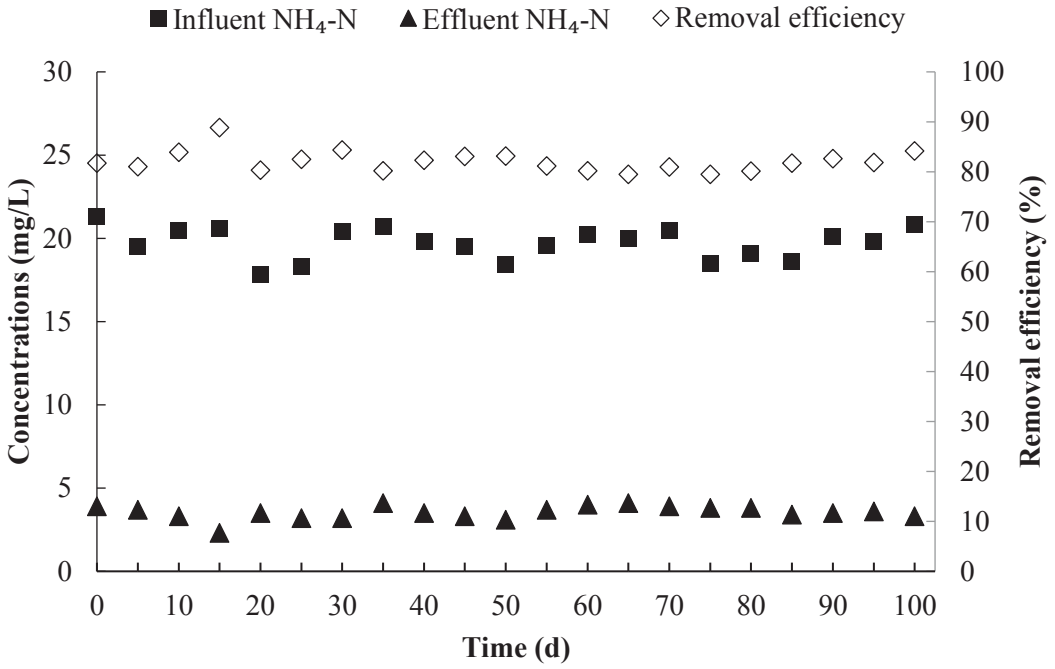

Figure 4.21 NH_4-N removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 6 h).

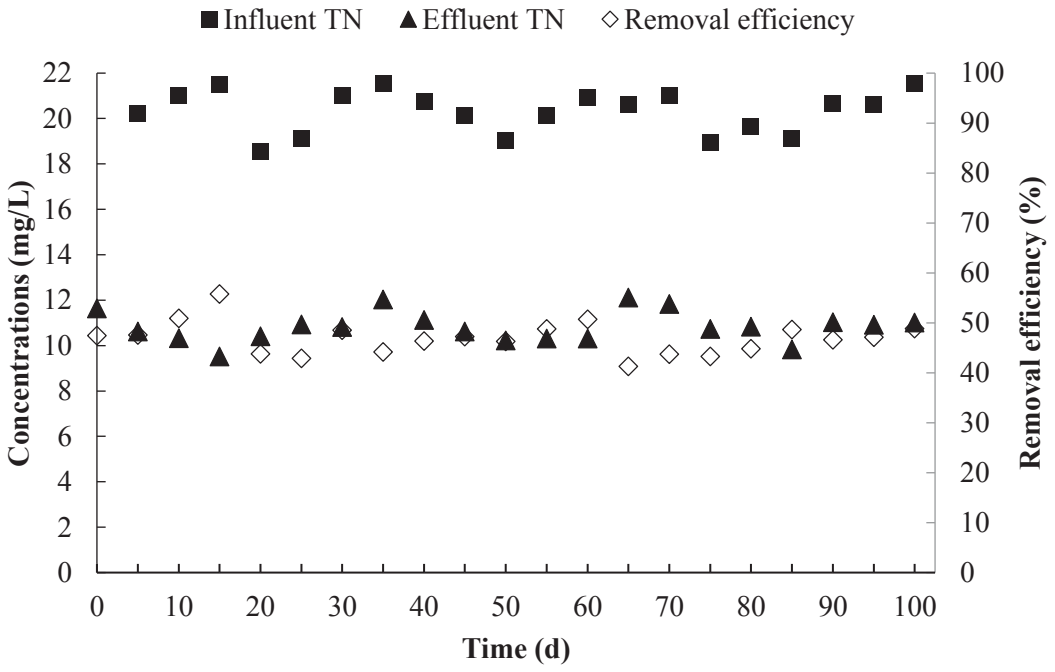

Figure 4.22 TN removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 6 h).

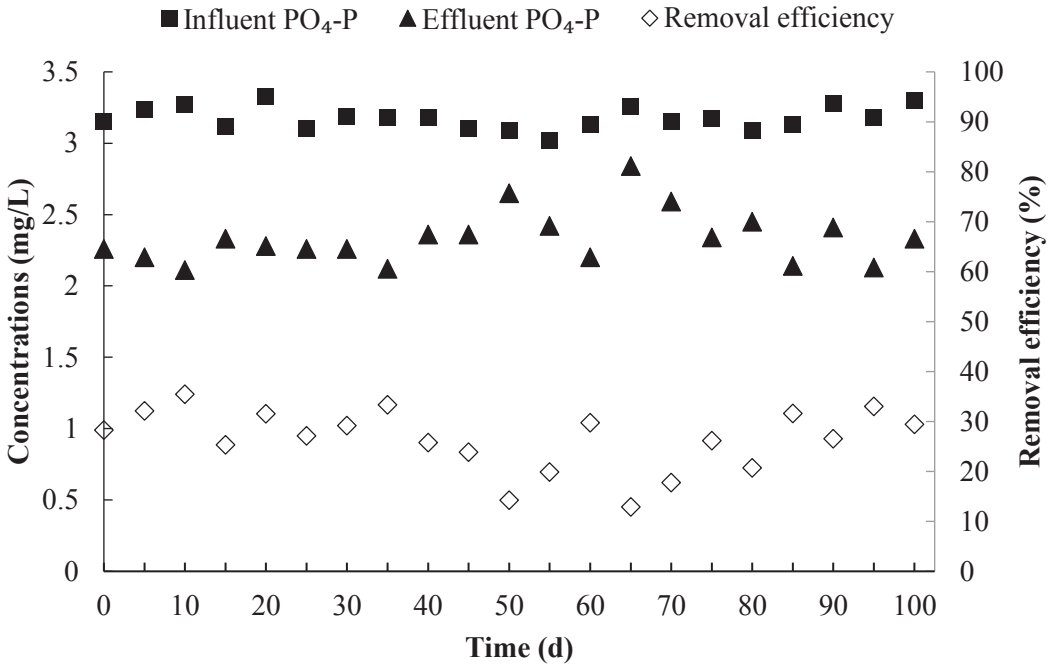

Figure 4.23 PO_4-P removal in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 6 h).

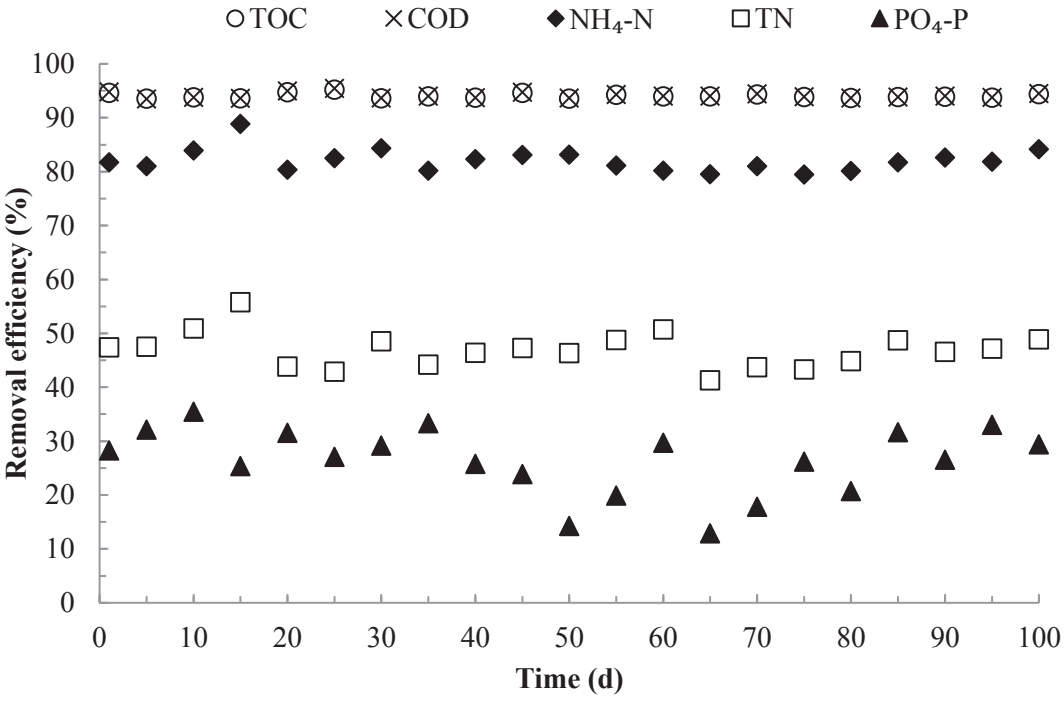

Figure 4.24 Summarized removal efficiencies in the MBBR (aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT: 6 h).

The MLSS and MLVSS concentrations in the MBBR units at HRT of 24 h, 18 h, 12 h, and 6 h were showed in Table 2. In the MBBR unit, the suspended MLSS (0.13±0.05 g/L at HRT of 24 h, 0.09±0.02 g/L at HRT of 18 h, 0.11±0.02 g/L at HRT of 12 h, and 0.13±0.02 g/L at HRT of 6 h) and MLVSS (0.11±0.06 g/L at HRT of 24 h, 0.08±0.01 g/L at HRT of 18 h, 0.10±0.01 g/L at HRT of 12 h, and 0.12±0.01 g/L at HRT of 6 h) concentrations of mixed liquid maintained very low, as the suspended solids were washed away into the subsequent MBR unit and no sludge was recycled back to the MBBR. Furthermore, a large amount of biomass was attached onto the sponge, which were 0.45±0.05 g MLSS/g sponge and 0.41±0.06 g MLVSS/g sponge at HRT of 24 h, 0.51±0.03 g MLSS/g sponge and 0.47±0.03 g MLVSS/g sponge at HRT of 18 h, 0.44±0.04 g MLSS/g sponge and 0.40±0.03 g MLVSS/g sponge at HRT of 12 h, as well as 0.40±0.03 g MLSS/g sponge and 0.37±0.03 g MLVSS/g sponge at HRT of 6 h.

Table 4.2 Results for both suspended and attached biomass in MBBR at HRT of 24 h, 18 h, 12 h, and 6 h

HRT	Suspended		Attached	
	MLSS (g/L)	MLVSS (g/L)	SS(g/g Sponge)	VSS(g/g Sponge)
24	0.123±0.051	0.108±0.052	0.385±0.107	0.348±0.103
18	0.089±0.013	0.083±0.012	0.451±0.039	0.415±0.042
12	0.105±0.009	0.096±0.010	0.435±0.035	0.400±0.032
6	0.127±0.011	0.117±0.011	0.418±0.035	0.382±0.035

4.3 Removals of selected micropollutants

The removal efficiencies of micropollutants in the MBBR at four HRTs are presented in Fig. 4.25. A significant variation in removal among each individual compound was observed over the study period. This could be related to certain factors of various micropollutants, such as hydrophobicity, microbial composition and compound structure. Among the selected micropollutants, most of them were biodegradable excluding Carbamazepine, Fenoprop and Metronidazole. In addition, the micropollutants removal could remain constantly high even at lower HRTs with

more consistent removal efficiency over the experimental period (except for Carbamazepine, Fenoprop, 17α-Ethinylestradiol and 4-tert-Octylphenol). Particularly, at HRT of 18 h, the removal of Diclofenac was significantly improved by more than 30% and the removals of Ketoprofen, Gemifibrozil, Acetaminiphen, Bisphenol A, and Pentachlorophenol were also better. Overall, the highest removal of most micropollutants can be achieved at HRT of 18 h.

As complex synthetic substances, pharmaceuticals are classified into various groups with highly variable physico-chemical properties. As the selected pharmaceuticals (PPCPs) in this study generally displayed low hydrophobicity (log D < 2.5), biodegradation (rather than sorption) was the major removal pathway of these compounds (Luo et al., 2014a). The removal efficiency of these compounds was much more strongly affected by their intrinsic biodegradability when log D value was below 3.2 (Tadkaew et al., 2011). One possible reason is that these micropollutants have diverse molecular structure and functional groups (Wijekoon et al., 2013). Four of the investigated PPCPs were efficiently removal (> 80%), including ibuprofen (97.8±2.1% at HRT of 24 h, 98.4±1.2% at HRT of 18 h, 97.1±1.5% at HRT of 12 h, and 92.6±2.3% at HRT of 6 h), salicylic acid (96.3±0.9% at HRT of 24 h, 98.1±0.5% at HRT of 18 h, 97.3±1.6% at HRT of 12 h, and 90.0±3.9% at HRT of 6 h), primidone (81.1±13.0% at HRT of 24 h, 90.9±1.2% at HRT of 18 h, 87.2±3.5% at HRT of 12 h, and 82.5±5.0% at HRT of 6 h), and triclosan (90.9±4.9% at HRT of 24 h, 90.6±1.0% at HRT of 18 h, 82.6±4.4% at HRT of 12 h, and 80.4±4.2% at HRT of 6 h). This could be ascribed to the inclusion of strong electron donating (readily biodegradable) functional groups (e.g., – OH) in these compounds. Among the studied PPCPs, carbamazepine showed particularly low removals, which were 22.9±5.3% at HRT of 24 h, 26.2±5.7% at HRT of 18 h, 14.2±7.3% at HRT of 12 h, and 10.7±8.1% at HRT of 6 h. This low removal could be attributed to its low hydrophobicity and the occurrence of strong electron donating groups such as amide and chloride in its molecular structure (Wijekoon et al., 2013). It is noted that a significant increase in the removal of metronidazole and diclofenac, which was from 27.4±10.8% and 33.3±11.0% (HRT of 24 h) to 50.8±6.5% and 83.3±7.8% (HRT of 18h), respectively. Ketoprofen, acetaminophen, gemifibrozil, and naproxen were moderately removed (50–80%) in the MBBR at HRT of 24 h, 12 h, and 6 h, but

relatively high (80 - 90%) at HRT of 18 h. The formation of biocoenosis could be influenced by the change of HRT, resulting in the differences in removal efficiencies of micropollutants by the MBBR.

Regarding steroid hormones, high removals (> 90%) of estrone, estriol, β-estradiol 17-acetate, and 17β-estradiol were found at all HRTs, probably due to the high hydrophobicity (log D > 3.2) of these compounds (except estriol), which is in good agreement with Tadkaew et al. (2011).

For industrial chemicals, the observed removals for bisphenol A and 4-n-nonylphenol were generally high (> 70%) at all HRTs, as these compounds are commonly characterized by high hydrophobicity (log D > 3.2). In this study, two pesticides displayed different removals. Fenoprop exhibited inefficient elimination (16.5 – 50.5%), whereas pentachlorophenol experienced much higher removal (71.3 – 92.8%). The poor removal of fenoprop could be attributed to its low hydrophobicity (log D = –0.13) and recalcitrance (Hai et al., 2011).

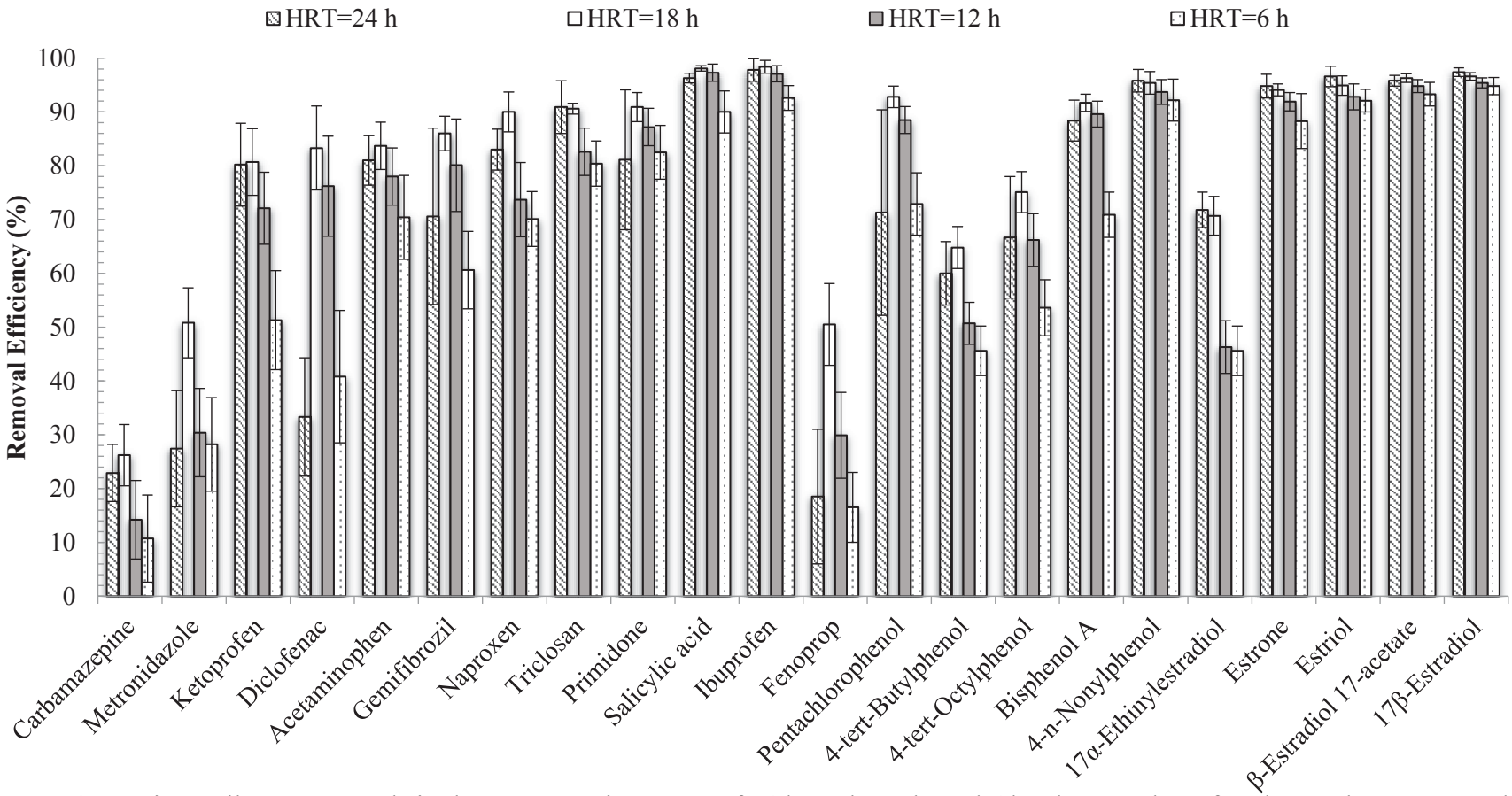

Figure 4.25 Micropollutant removals in the MBBR unit at HRT of 24 h, 18 h, 12 h, and 6 h. The error bar of each sample represents the standard deviation over the experiment period (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h, 18h, 12h and 6 h).

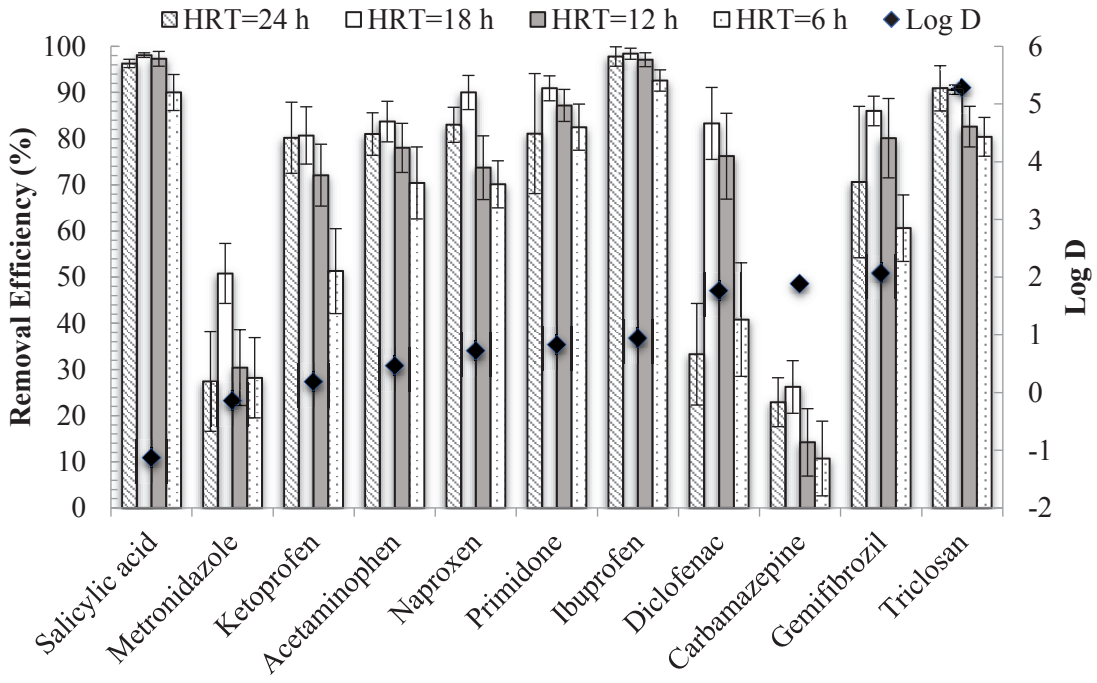

Figure 4.26 Relationship of Log D and pharmaceutical compounds removals in the MBBR. An error bar represents the standard deviation over the experimental period (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L, HRT = 24h, 18h, 12h and 6h)

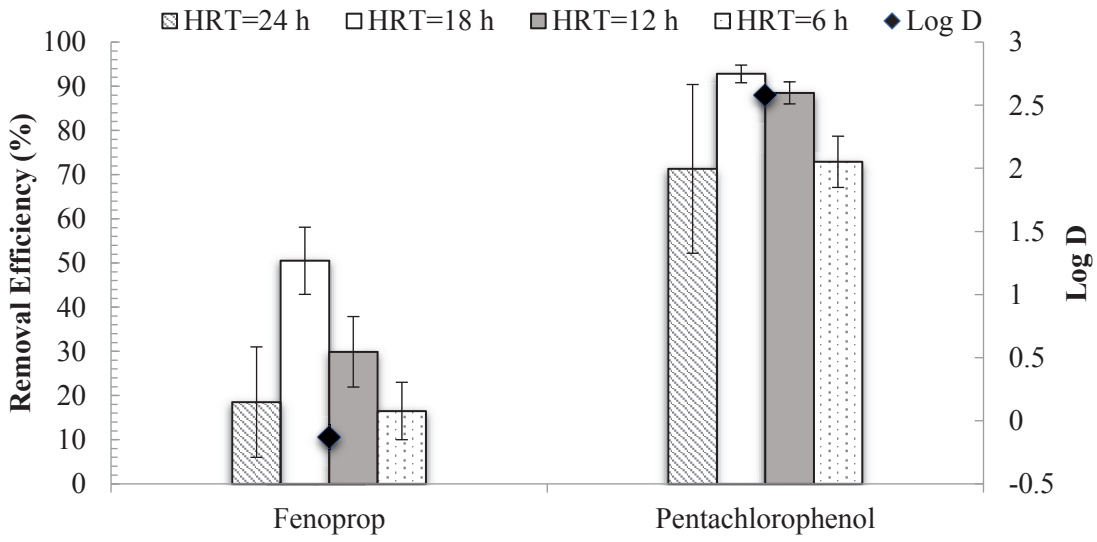

Figure 4.27 Relationship of Log D and pesticides removals in the MBBR. An error bar represents the standard deviation over the experimental period (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h, 18h, 12h and 6h)

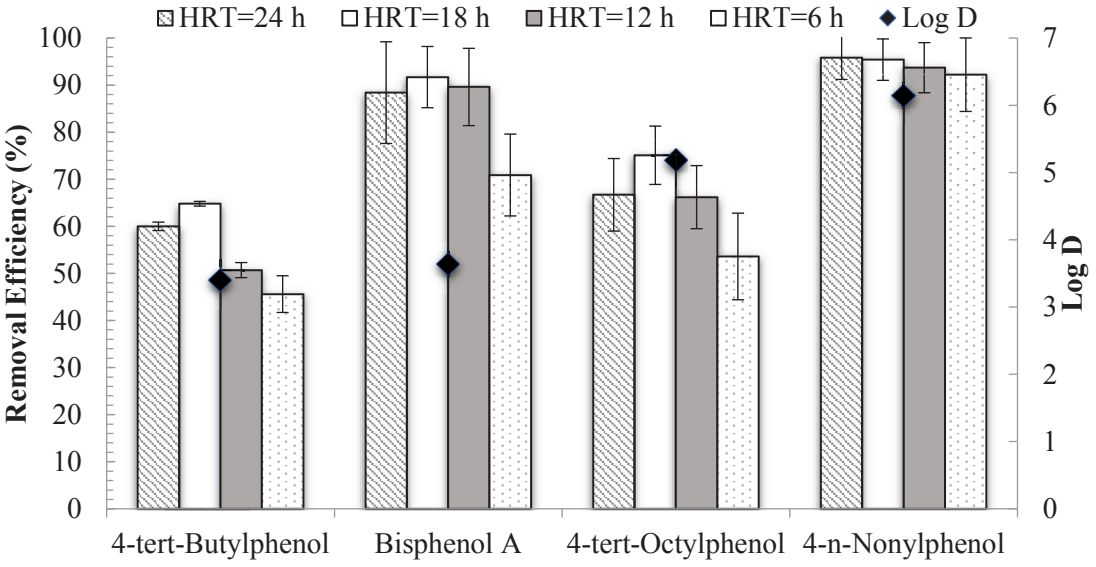

Figure 4.28 Relationship of Log D and industrial chemicals removals in the MBBR. An error bar represents the standard deviation over the experimental period (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h, 18h, 12h and 6h)

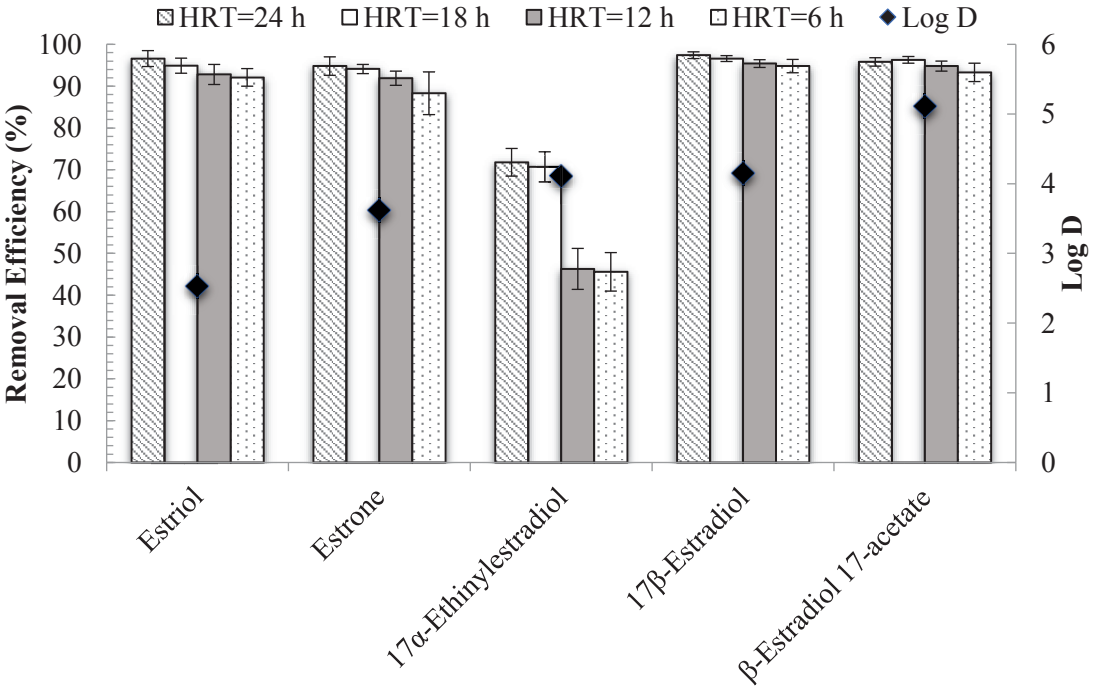

Figure 4.29 Relationship of Log D and estrogenic hormones removals in the MBBR. An error bar represents the standard deviation over the experimental period (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h, 18h, 12h and 6h)

To gain further insight into the fate of micropollutants in the MBBR unit, a mass balance of the investigated compounds was evaluated (Eq. (1)), taking into account the removal pathways of biodegradation and sorption in the MBBR unit.

$$L_{inf} = L_{s,MBBR} + L_{b,MBBR} + L_{eff} \quad (1)$$

where L_{inf} is the influent load of micropollutants over the experimental period (ng), $L_{s,MBBR}$ and $L_{b,MBBR}$ are the amounts of a compound removed via sorption (ng) and biodegradation (ng), respectively, in the MBBR unit; L_{eff} is the amount of a compound released from the system (ng).

The calculation of the sorption and biodegradation in the MBBR was carried out according to Eq. (2) and Eq. (3).

$$L_{s,MBBR} = Q \cdot MLSS_{MBBR} \cdot C_{ss} \cdot t + \Delta SS \cdot C_{sa} \quad (2)$$

$$L_{b,MBBR} = (L_{inf} - L_{eff}) - L_{s,MBBR} \quad (3)$$

where Q is the flow rate of the MBBR (L/day); $MLSS_{MBBR}$ is mixed liquor suspended biosolids concentration in the MBBR (g/L); C_{ss} is the concentration of a compound on the suspended biosolids (ng/g); t is the duration of the experimental period (days); ΔSS is the increased amount of attached biosolids (g); C_{sa} is the concentration of a compound on the attached biosolids (ng/g).

Fig. 4.30-4.33 illustrates the fate of the selected compounds in the MBBR unit at HRT of 24, 18, 12, and 6 h. The results show that biodegradation in the MBBR was the main pathway for the micropollutant removal, which is consistent with outcomes from our previous study involving both MBBR-MBR and CMBR (Luo et al., 2015). Compared to biodegradation, sorption accounted for much less proportion of most micropollutant removals. This probably due to that sorption is a more rapid process than biodegradation. In addition, sorption of micropollutants to biosolids results in longer residence time in the reactor, which may lead to further removal via biodegradation (Tadkaew et al., 2011). Moreover, the acclimatized sponge in the MBBR unit remained fully occupied by biomass over time, and the reduced sorption

site resulted in the limited sorption efficiency in long term experiment (Luo et al., 2014b). As a result, although most micropollutants were effectively removed at HRT of 18 h, the decreased removals of 17α-ethinylestradiol, triclosan and 4-tert-octylphenol were observed. On the other hand, the proportion of sorption varied at different HRTs. It is notable that the percentage of sorption increased after HRT changed to 6 h. One reason could be the excessive nutrient in the MBBR unit leading to over growth and detachment of biofilm. The new biofilm could help adsorbing micropollutant to a certain extent.

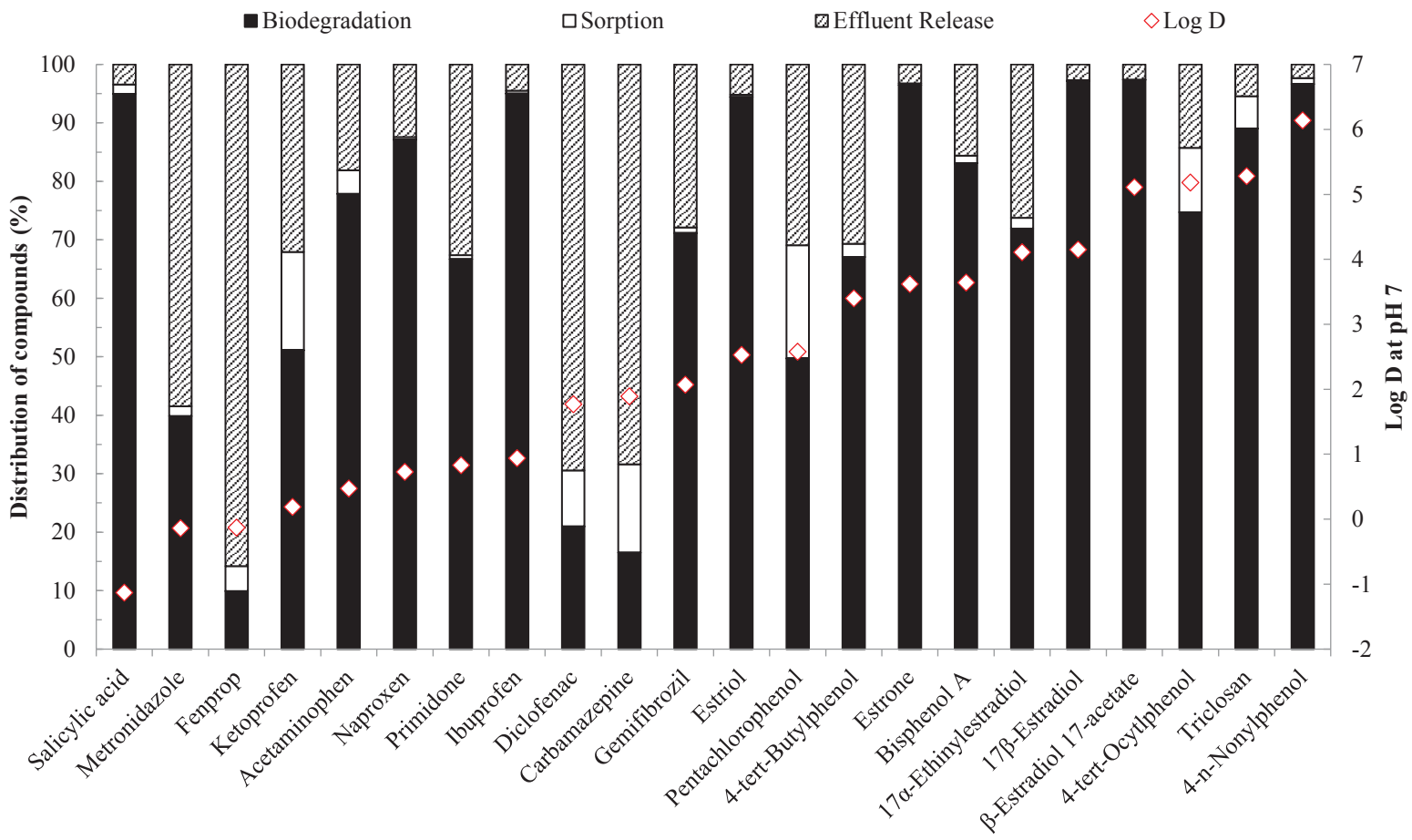

Figure 4.30 Fate of the studied micropollutants in the MBBR system (aeration rate: 4L/min; HRT: 24 h).

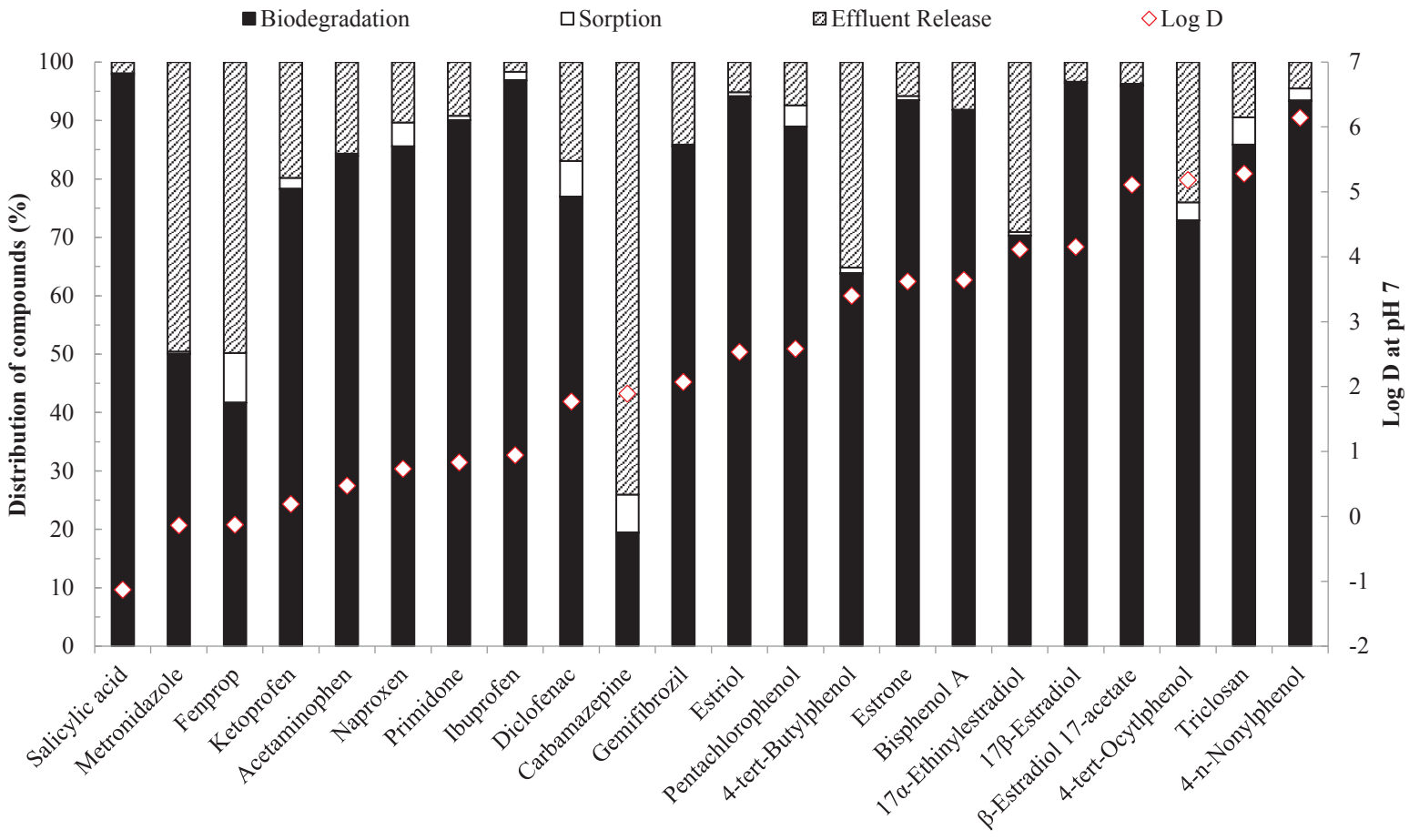

Figure 4.31 Fate of the studied micropollutants in the MBBR system (aeration rate: 4L/min; HRT: 18 h).

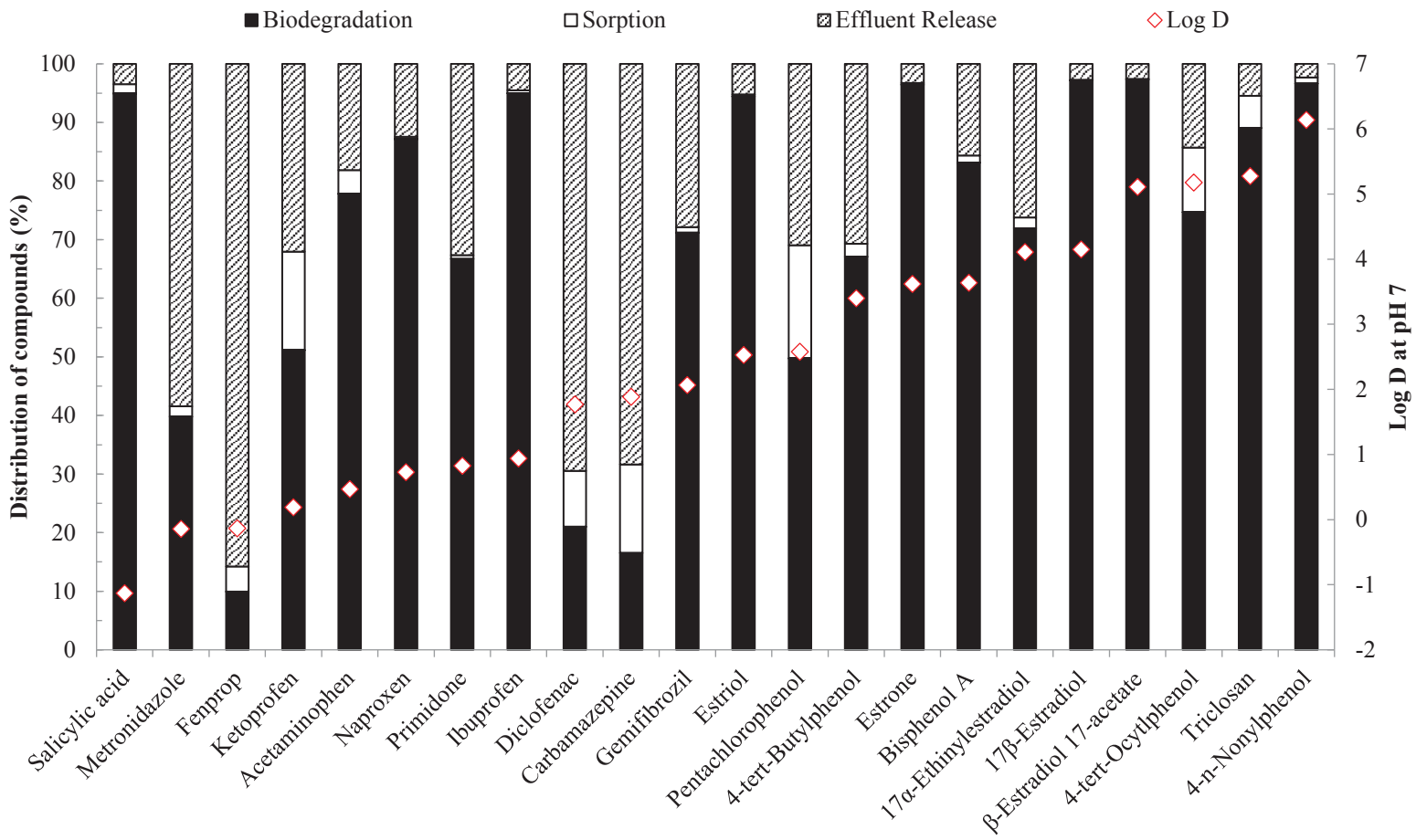

Figure 4.32 Fate of the studied micropollutants in the MBBR system (aeration rate: 4L/min; HRT: 12 h).

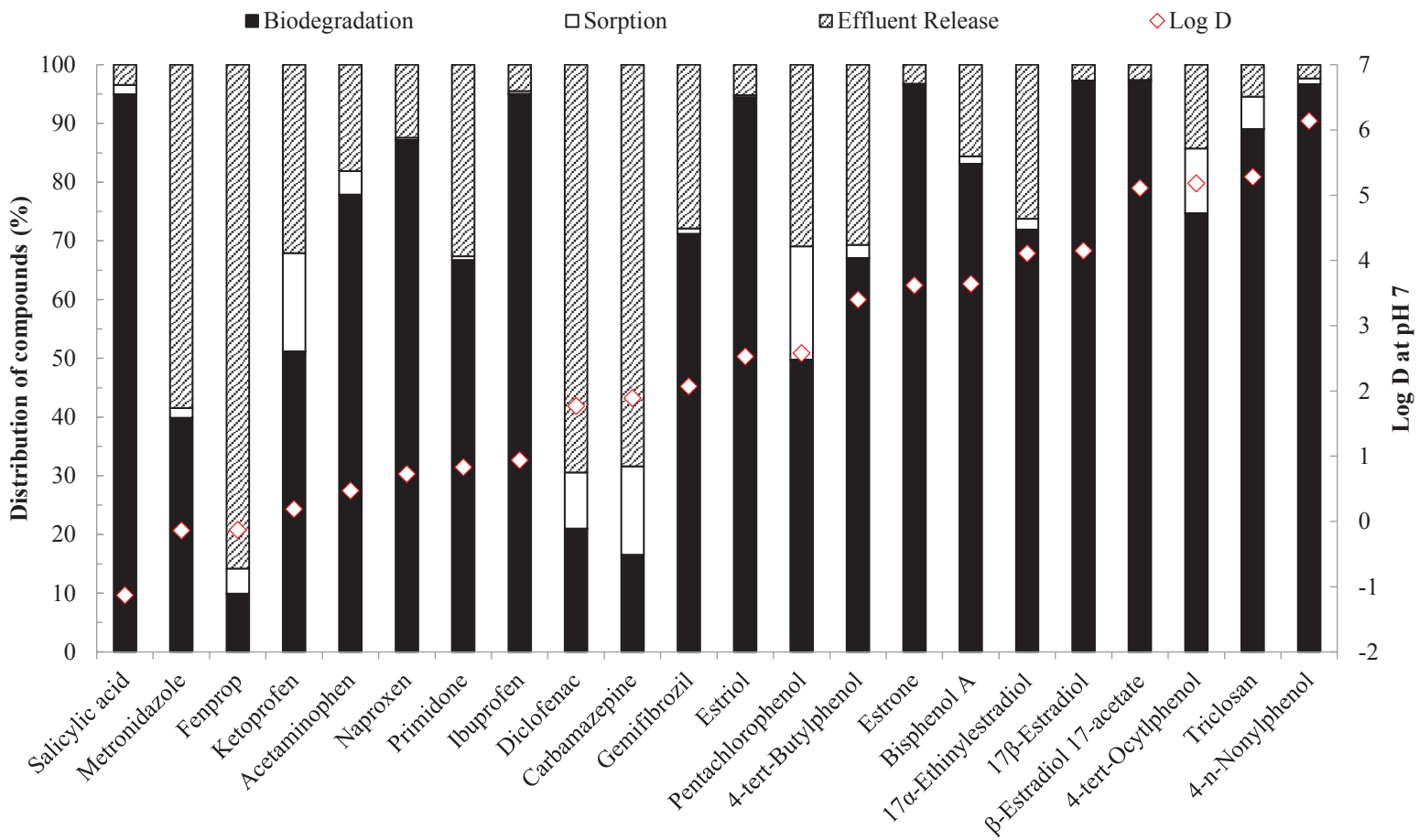

Figure 4.33 Fate of the studied micropollutants in the MBBR system (aeration rate: 4L/min; HRT: 6 h).

4.4 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 4.3 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 most of the investigated micropollutants, except for carbamazepine, fenoprop and metronidazole. The presence of biofilm carriers played an important role in the biodegradation of diclofenac and biofilm carriers from full-scale nitrifying wastewater treatment plants had apparently higher removal rates per unit biomass for diclofenac in comparison to the activated sludge (Falås et al. 2012). Nevertheless, MBR systems had the ability for more efficient removal of 4-tert-butylphenol and 4-tert-butylphenol (Nguyen et al., 2013; Wijekoon et al., 2013; Tadkaew et al. 2011). The MBBR in this study was able to achieve similar or higher elimination of the estrogenic hormones (70.7–96.6%) compared with the activated sludge processes, despite 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.

Table 4.3 Comparison of micropollutant removal efficiency (%) in the MBBR and in other biological treatment technologies

Compounds[a]		This study (MBBR, HRT=18h, %)	Activated sludge[b] (%)	MBR[c] (%)
Pharmaceuticals	ACM	83.7 ±4.4	98.7-100	40–100
	CBZ	26.2 ± 5.7	<0-63.2	0–35
	DCF	83.3 ± 7.8	<0–81.4	0–87
	GFB	86.0 ± 3.2	<0–92.3	90–98
	IBU[d]	98.4 ± 1.2	72–100	50-99
	KTP	80.7 ± 6.2	10.8–100	52–92
	MET	50.8 ± 6.5	0–64.0	36–40
	NPX	80.0 ± 3.7	43.3–98.6	10–84
	PRM	90.9 ± 2.7	30-50	10–91
	SA	98.1 ± 0.5	89.6–100	93–98
	TCS	90.6 ± 1.0	71.3–99.2	70–99
Steroid hormones	E1	94.1 ± 1.1	74.8–90.6	96–99
	E2	96.6 ± 0.7	92.6–100	97–99
	E2AC	96.3 ± 0.8	-	98–99
	EE2	70.7 ± 3.6	43.8–100	60–98
	E3	94.9 ± 1.8	100	83–97
Industrial chemicals	BP	64.8 ± 3.9	-	93–98
	BPA	91.7 ± 1.6	62.5–99.6	52–98
	NP	95.4 ± 2.1	21.7–99	87–97
	OP	75.1 ± 3.8	<0–96.7	97-98
Pesticides	FNP	50.5 ± 7.6	-	10–21
	PECP	92.8 ± 2.0	-	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.

4.5 Conclusion

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 removal of ibuprofen, metronidazole, naproxen, primidone, triclosan, estrone, 17-α ethinylestradiol, 4-n-nonylphenol, 4-tert-octylphenol and fenoprop. In this set of experiment, the optimal HRT was 18h, thus under this condition, further studies could be done to optimise the MBBR system in order to achieve better removal.

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Chapter 5

Removal of Micropollutants by an Moving Bed Biofiln Reactor-Membrane Bioreactor Hybrid System at Different HRTs

5.1 Introduction

The frequent detection of micropollutants in our aquatic environment has gained growing attention in recent years. Even though these micropollutants are at trace concentrations, they may cause long term effects, such as bioaccumulation and carcinogenicity (Soares et al., 2008, Klavarioti et al., 2009). In addition, low biodegradability and highly resistance of micropollutants make their efficient removal a great challenge in conventional wastewater treatment processes (Bu et al., 2013). Generally, carbamazepine, ibuprofen, ketoprofen, naproxen, gemfibrozil, nonylphenol and triclosan were commonly detected in treated effluent at relatively high concentrations (4.60, 55.0, 3.92, 5.09, 5.24, 7.80 and 6.88 μg/L, respectively) (Luo et al., 2014a).

Although some wastewater treatment technologies (e.g. oxidation and advanced oxidation processes, powdered activated carbon addition, nanofiltration and reverse osmosis) have been employed to minimise micropollutants from municipal wastewater, they are normally associated with high operation cost, formation of oxidation by-products, requirement of chemical dosage, as well as permeability to some relatively low molecular weight micropollutants (Gerrity et al., 2011; Boehler et al., 2012; Sahar et al., 2011). MBRs, as a promising biological treatment technology, have been widely used to remove micropollutants (Hai et al., 2011). Radjenovic et al. (2007) and Chen et al. (2008) compared the performance of micropollutant removal in a submerged MBR and a conventional activated sludge (CAS) treatment process (consisting of an aeration tank and a settling tank). Both studies showed that the MBR was more efficient in micropollutant removal than CAS process. Trinh et al. (2012) investigated the removal of 48 trace micropollutants by a full-scale submerged MBR, including steroidal hormones, xenoestrogens, pesticides, caffeine, pharmaceuticals and personal care products. Even though the MBR could remove most examined trace contaminants (>90%) at high filtration flux of 25 $L/m^2 \cdot h$ and hydraulic retention time (HRT) of 1 d, regular physical cleaning (every 360 seconds for a period of 60 seconds) and chemical backwashing (every 3 weeks) were performed to maintain a transmembrane pressure (TMP) less than 20 kPa. Similarly, Tadkaew et al. (2011) conducted experiment to investigate the

removal efficiency in a submerged MBR with respect to 40 micropollutants. The MBR was operated at HRT of 24 h and filtration flux of 4.3 L/m^2·h, along with a relaxation cycle of 14 min suction and 1 min off. Wijekoon et al. (2013) examined the fate of 29 trace organic compounds in a bench scale external MBR with a HRT of 26 h. However, the MBR was operated at very low membrane flux (2.14 L/m^2·h) to eliminate the influence of membrane fouling on micropollutant removal. Moreover, 15 min on and 15 min off relaxation cycle was employed to minimise membrane fouling. Regardless of changes in configurations, general concerns remain during the application of MBR systems. First of all, the membrane fouling is still the major problem while employing membrane related technology. Frequent physical and chemical backwashing or relaxation is essential for alleviating membrane fouling. In addition, it requires long HRT in MBR to remove micropollutants but still has inconsistent removal of some polar and persistent hydrophilic micropollutants, e.g. carbamazepine, diclofenac, and gemfibrozil etc. Therefore, in order to effectively remove micropollutants, optimization of the performance of MBR has been the subject of recent studies and is likely to draw more attention in the future research.

Moving bed biofilm reactor (MBBR) is a fast growing wastewater treatment technique with potential to effectively remove both traditional pollutants and micropollutants (Luo et al., 2014b). Combination of MBBR with MBR in series (MBBR-MBR) is one of recent advances in improving MBR performance, due to the potential of reducing membrane fouling as well as the possibility of prompting microbial degradation of certain organic compounds (Leiknes and Ødegaard, 2007). In comparison to conventional MBR in municipal wastewater treatment, this hybrid system is able to operate at 3-4 times higher flux rate with 10-15 times higher organic loading rate (OLD) and 10-30 times shorter HRT (Guo et al., 2012). Moreover, MBBR-MBR hybrid system could lower fouling and prolong filtration duration compared to conventional MBR (Sombatsompop et al., 2006). With the objective of enhancing micropollutant removal efficiency in MBRs, the impacts of operational parameters including SRT (Weiss and Reemtsma, 2008), pH (Tadkaew et al., 2010) and temperature (Hai et al., 2011) have also been specifically investigated. A general conclusion can be drawn from these studies is that MBRs can achieve

good and stable micropollutant removal under extended SRT (> 15 days), near neutral pH (pH 6-8) and warmer temperature (20 - 35 °C).

Apart from the above-mentioned operational parameters, HRT can also potentially affect the degree of biodegradation and adsorption of micropollutants in MBRs. Generally, mixed liquid suspended solid (MLSS) concentration and sludge viscosity increases with shortened HRT, resulting in the increase in extracellular polymeric substances (EPS) and soluble microbial products (SMP), thereby affecting membrane fouling propensity (Meng et al., 2007; Huang et al., 2011; Shariati et al., 2011). With regard to micropollutants removal in MBR, prolonged HRT enhances the formation of a diverse biocoenosis, including some slow growing bacteria. Higher biodegradation efficiency for certain micropollutants can be achieved when biomass is rich in nitrifying bacteria (Kim et al., 2007; Roh et al., 2009). De Gusseme et al. (2009) reported a high removal (97.7±3.7%) of 17α-ethinylestradiol at HRT of 4 d in a submerged MBR, but lower removal (58.3±2.4%) at HRT of 1 d. Schröder et al., (2012) showed the performance of MBR treatment plant in removing 6 pharmaceutical compounds was better at HRT of 13 h than that of at HRT of 9 h. Nevertheless, Chen et al. (2008) reached a conclusion that the changes in HRT (HRT of 8, 6, and 4 h) had little effect on removal efficiency of Bisphenol A in a lab-scale submerged MBR, probably due to its rapid biodegradation and low potential for bioaccumulation. To date, there has been no comprehensive study regarding the impact of HRT for micropollutant removal. In our previous investigation, a comparison has been performed regarding the micropollutant removal efficiency between an MBBR-MBR hybrid system and a conventional MBR (CMBR) (Luo et al., 2015). The results indicated that MBBR as pretreatment to MBR exhibited better performance than single CMBR, and more importantly MBBR can mitigate membrane fouling of MBR to a great extent. Therefore, in this study, the performance of MBBR-MBR hybrid system was investigated at four different HRTs (24 h, 18 h, 12 h, and 6 h) to determine the optimal HRT in terms of micropollutant removal and membrane fouling control. Moreover, the membrane fouling propensity was examined based on mixed liquor characteristics, such as SMP, EPS, zeta potential, and relative hydrophobicity (RH).

5.2 Organic and nutrient removal

Table 5.1 summarizes the removal efficiencies of DOC, COD, NH_4-N, PO_4-P and total nitrogen (TN) in MBBR-MBR hybrid system at four HRTs (HRT of 24, 18, 12, and 6 h). As shown in Table 5.1, the MBBR-MBR system was able to achieve effective removal of TOC (>94%) and NH_4-N (>82%) at all HRTs. However, unstable TN (46.8-68.7%) reduction and PO_4-P (32.5-51.7%) elimination were observed throughout the experimental period. It was noteworthy that the MBBR-MBR showed the highest performance efficiency for removing DOC, COD, NH_4-N, PO_4-P and TN at HRT of 18 h, which were 96.7±0.2%, 98.1±0.6%, 92.1±1.6%, 51.7±8.3%, and 68.7±7.2%, respectively. This could be explained by the food to microorganisms (F/M) ratio in the MBBR-MBR system, calculated based on COD and MLSS. The F/M ratio were 0.31, 0.43, 0.68, and 1.28 g COD/ g MLSS·d at HRT of 24, 18, 12, 6 h, respectively. The amount of food present in the system was sufficient to maintain microorganism growth when the F/M ratio was 0.43 g COD/ g MLSS·d in the MBBR-MBR system, which is in good agreement with Pozo et al. (2012). Villamar et al. (2009) also pointed out that the sludge showed good settler conditions when F/M ratio range between 0.3-0.6 g BOD_5/ g VSS·d. In addition, higher NH_4-N removal at HRT of 18 h could be attributed to the increased population of ammonium oxidation bacteria in the MBBR-MBR. Moreover, the use of phosphate for biomass growth and the phosphorus uptake by phosphate accumulating organisms (PAOs) could contribute to the high removal of PO_4-P at HRT of 18 h.

Table 5.1 Results for organic matters and nutrients removal by MBBR-MBR at HRT of 24 h, 18 h, 12 h, and 6 h

HRT	Removal efficiency (%)				
	TOC	COD	NH_4-N	TN	PO_4-P
24	95.0±0.6	95.5±0.9	86.5±3.5	47.4±9.2	34.9±3.9
18	96.7±0.2	98.1±0.6	92.1±1.6	68.7±7.2	51.7±8.3
12	96.0±0.4	96.1±0.8	87.5±1.2	58.1±2.8	42.7±4.3
6	94.7±0.1	95.0±0.3	83.1±1.2	46.8±1.0	32.5±3.8

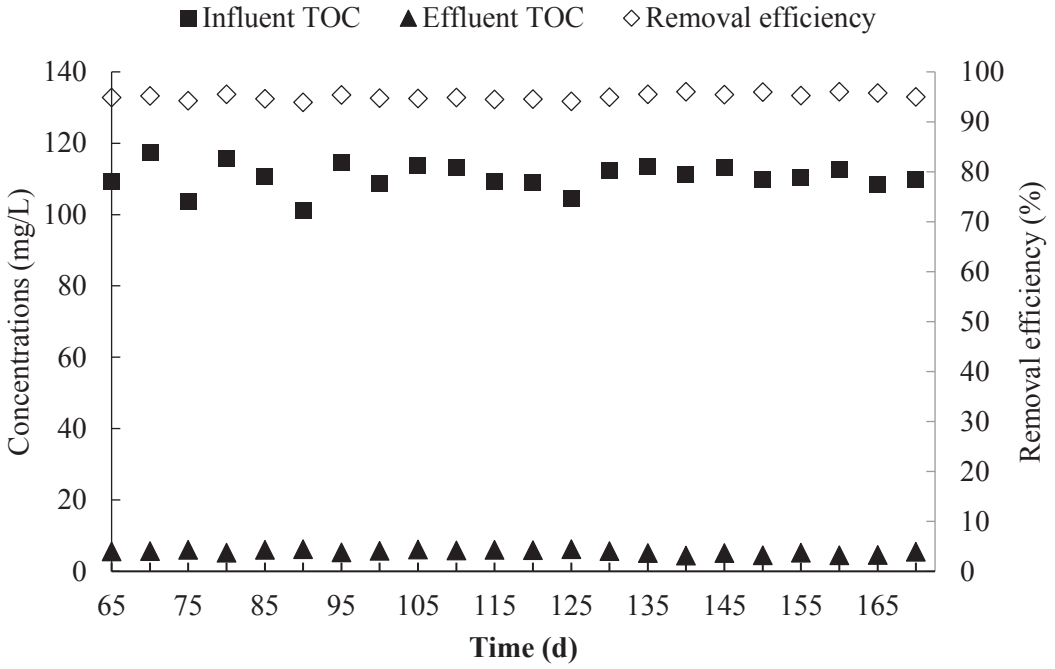

Figure 5.1 TOC removal in the MBBR-MBR
(MBBR conditions: aeration rate = 4 L/min; DO: 5.5–6.5 mg/L; HRT=24 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

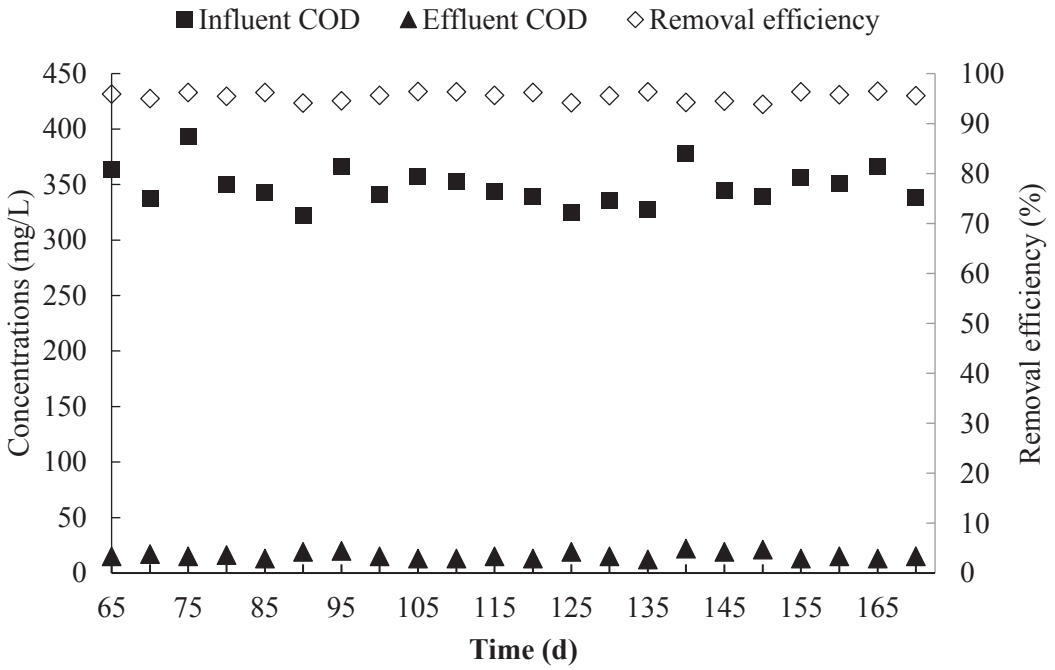

Figure 5.2 COD removal in the MBBR-MBR
(MBBR conditions: aeration Rate = 4 L/min; DO: 5.5–6.5 mg/L; HRT=24 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

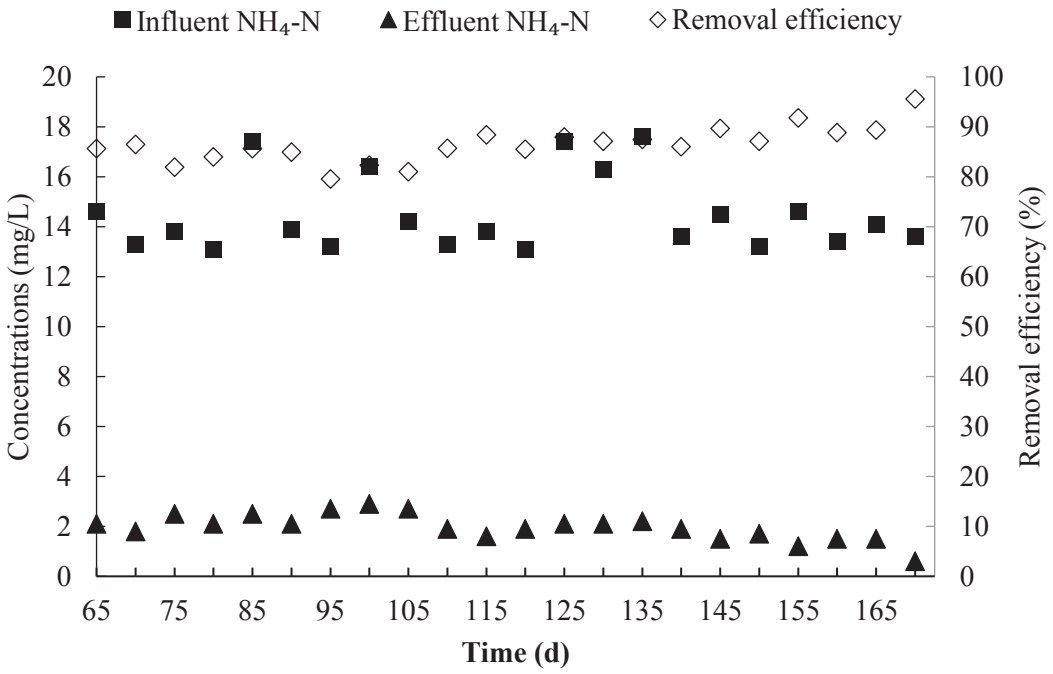

Figure 5.3 NH_4-N removal in the MBBR-MBR
(MBBR conditions: aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT=24 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 $L/m^2 \cdot h$; HRT = 6h; SRT = ∞).

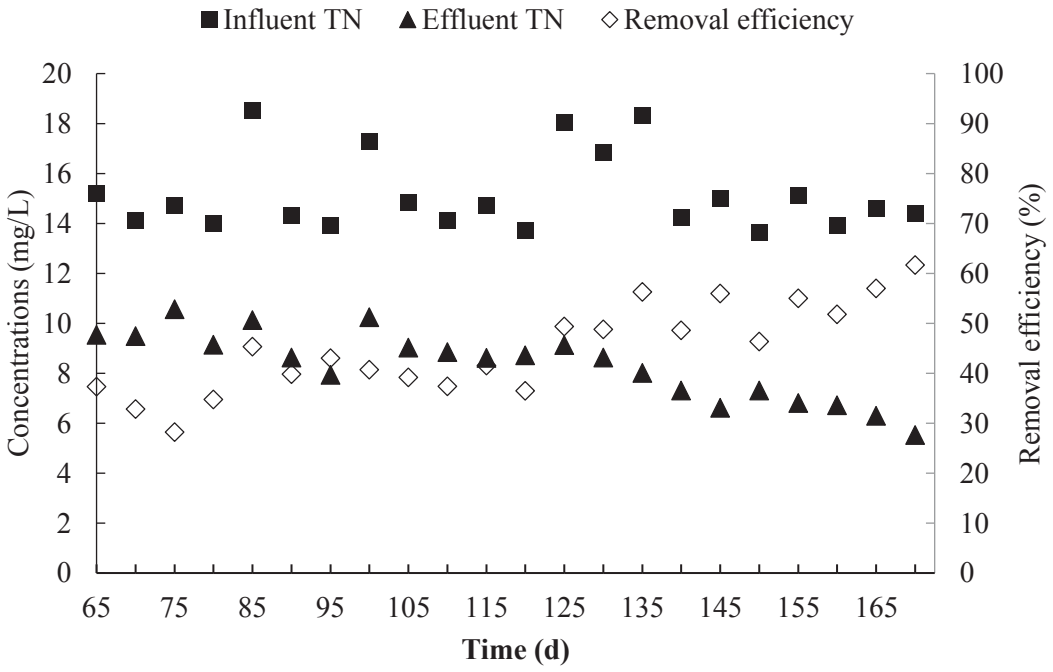

Figure 5.4 TN removal in the MBBR-MBR
(MBBR conditions: aeration rate: 4 L/min; DO: 5.5–6.5 mg/L; HRT=24 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 $L/m^2 \cdot h$; HRT = 6h; SRT = ∞).

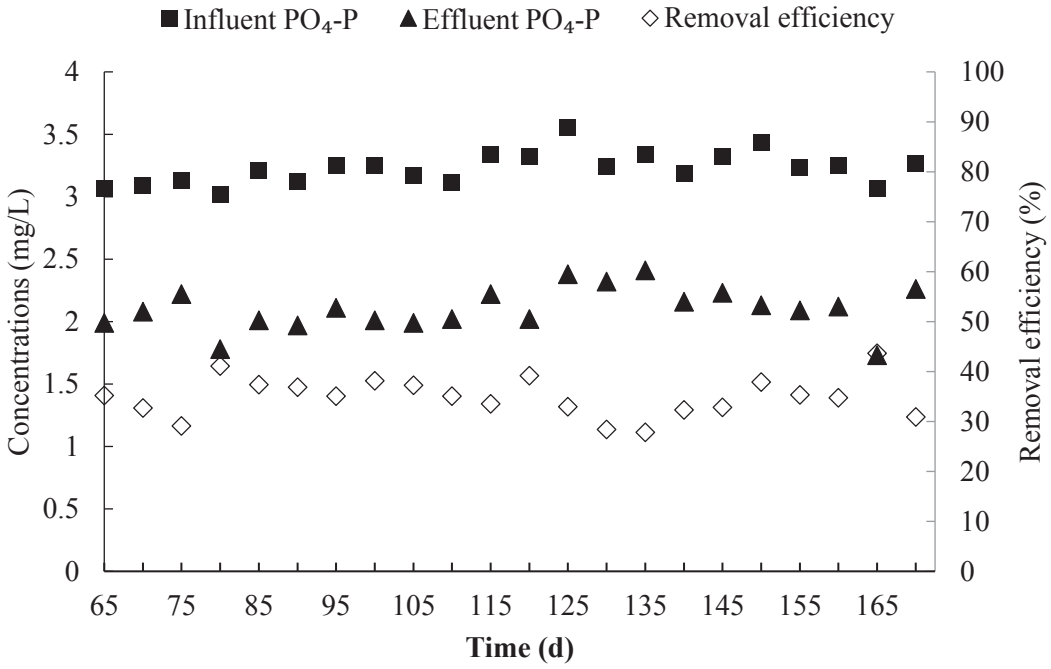

Figure 5.5 PO_4-P removal in the MBBR-MBR
(MBBR conditions: aeration rate = 4 L/min; DO = 5.5–6.5 mg/L; HRT=24 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

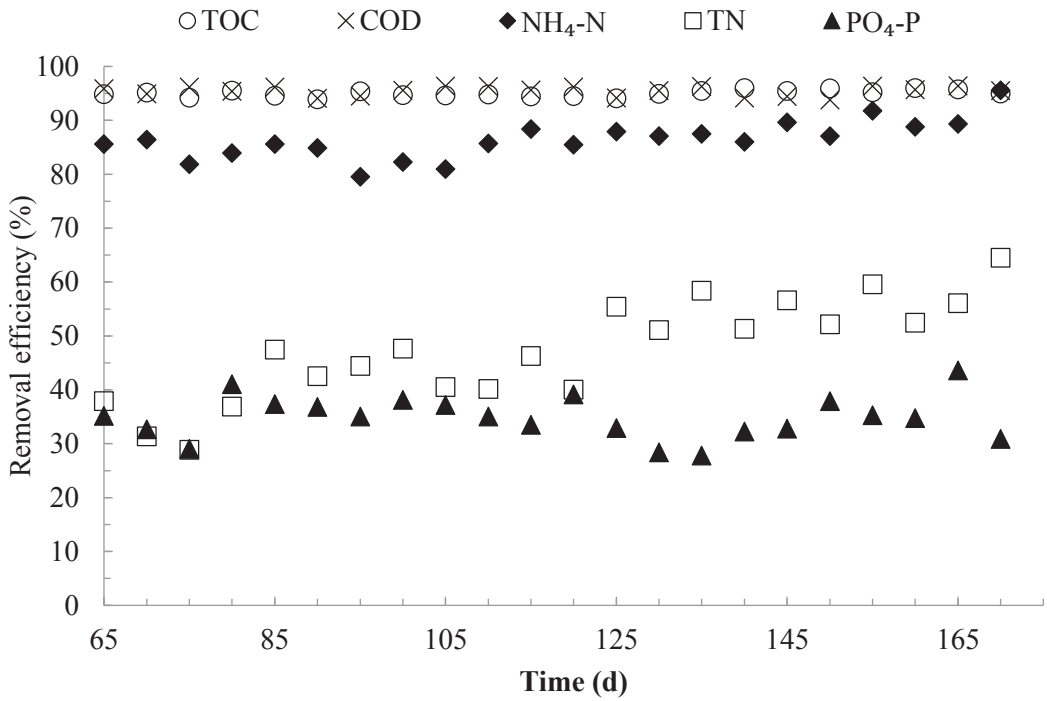

Figure 5.6 Summarized removal efficiencies in the MBBR-MBR
(MBBR conditions: aeration rate = 4 L/min; DO = 5.5–6.5 mg/L; HRT=24 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

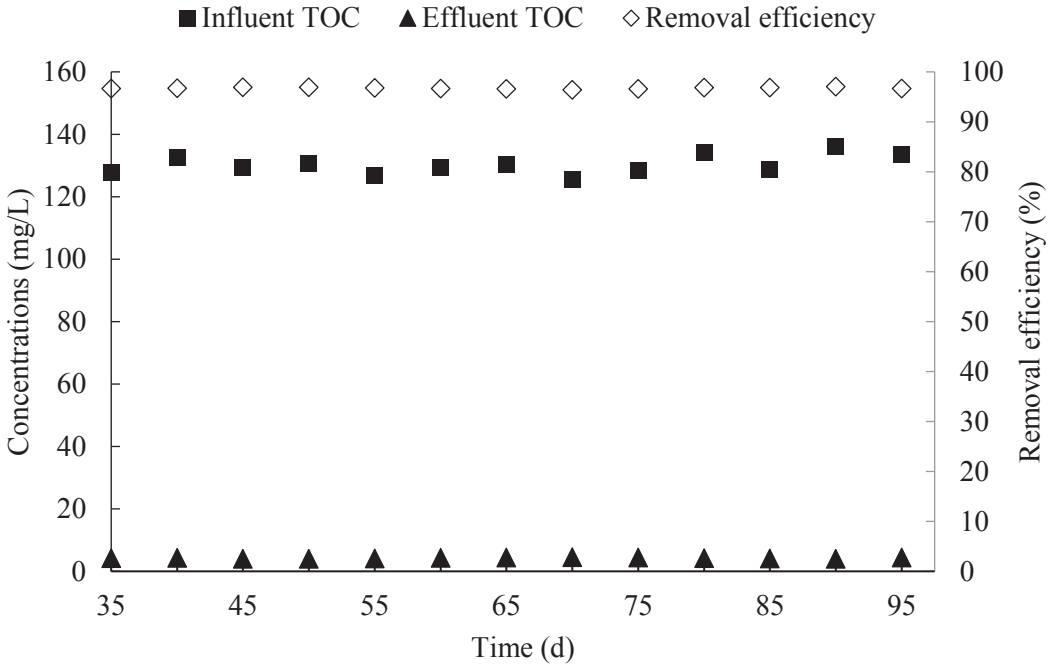

Figure 5.7 TOC removal in the MBBR-MBR
(MBBR conditions: aeration rate = 4 L/min; DO = 5.5–6.5 mg/L; HRT=18 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

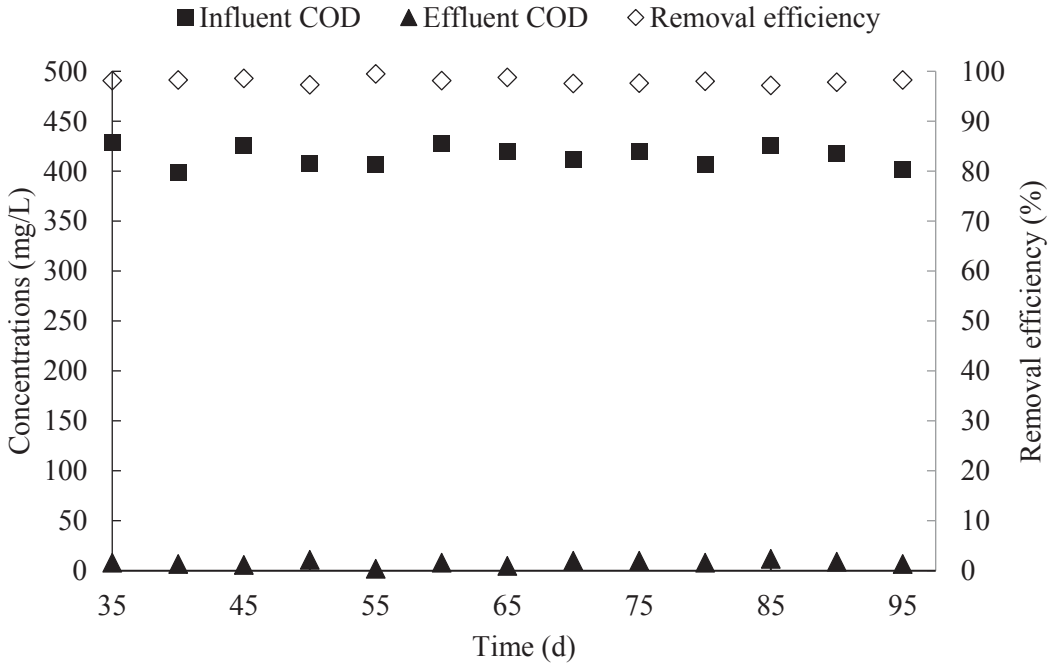

Figure 5.8 COD removal in the MBBR-MBR
(MBBR conditions: aeration rate = 4 L/min; DO = 5.5–6.5 mg/L; HRT=18 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

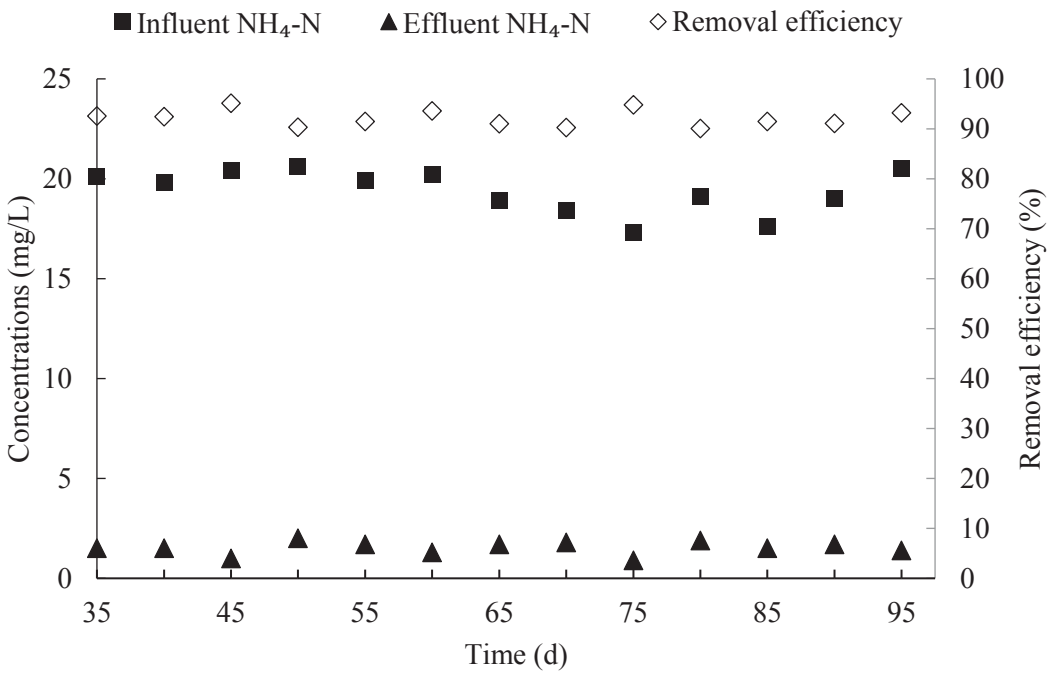

Figure 5.9 NH_4-N removal in the MBBR-MBR
(MBBR conditions: aeration rate = 4 L/min; DO = 5.5–6.5 mg/L; HRT=18 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

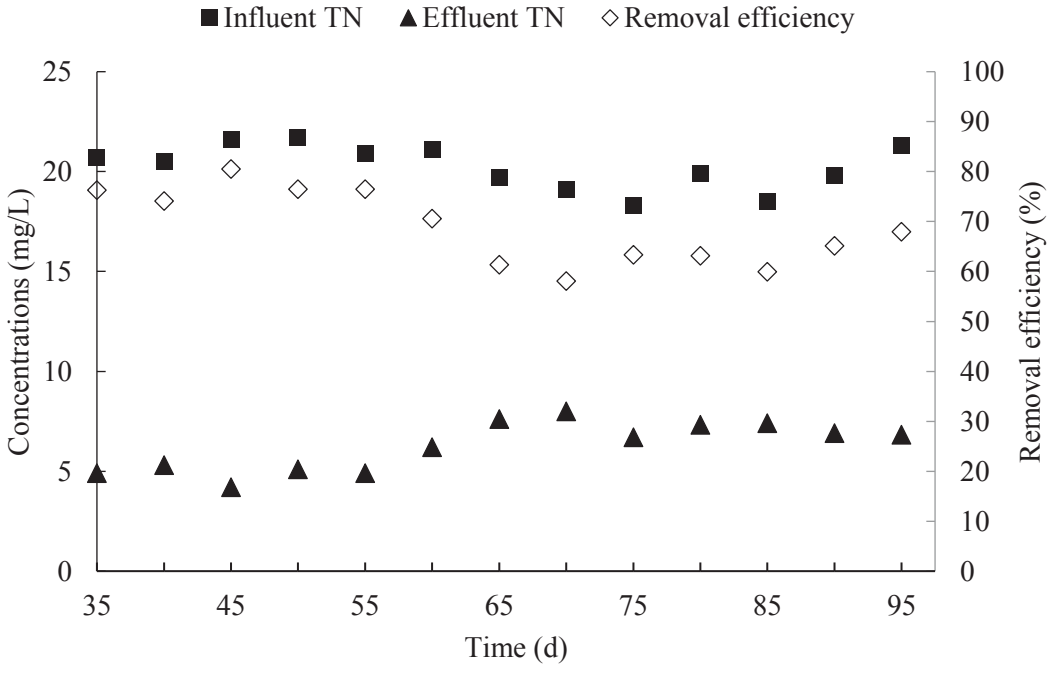

Figure 5.10 TN removal in the MBBR-MBR
(MBBR conditions: aeration rate = 4 L/min; DO: 5.5–6.5 mg/L; HRT=18 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

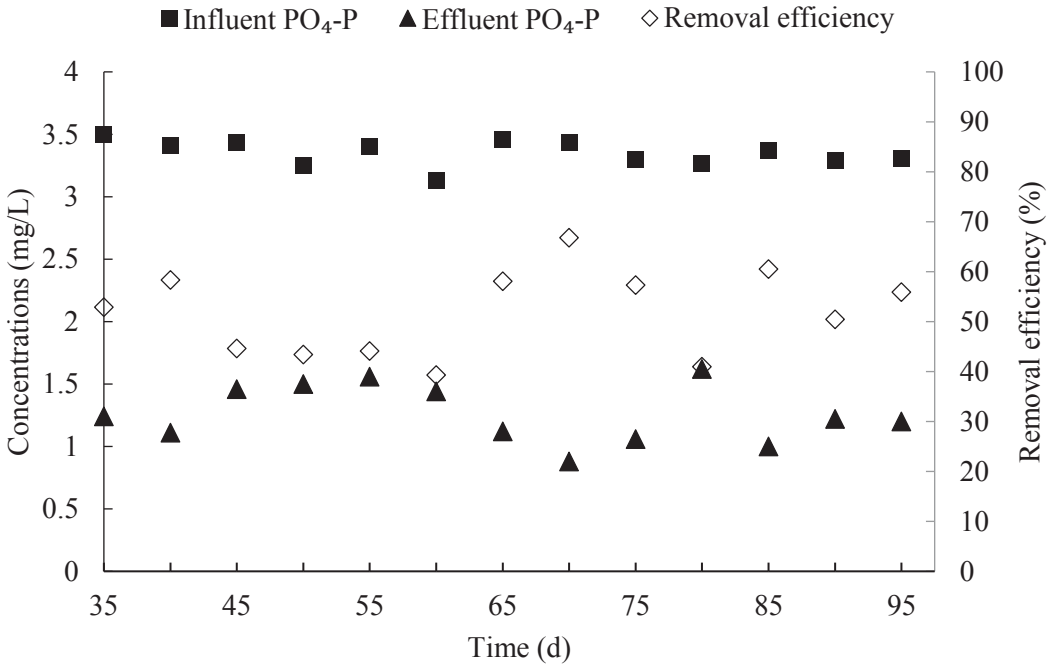

Figure 5.11 PO_4-P removal in the MBBR-MBR
(MBBR conditions: aeration rate = 4 L/min; DO: 5.5–6.5 mg/L; HRT=18 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

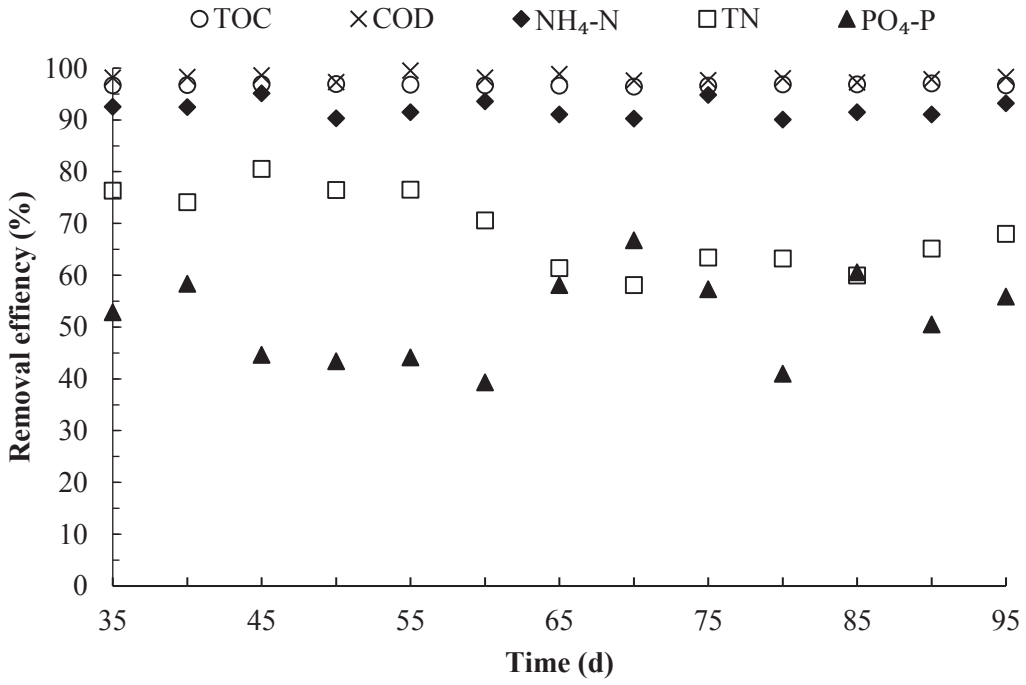

Figure 5.12 Summarized removal efficiencies in the MBBR-MBR
(MBBR conditions: aeration rate = 4 L/min; DO: 5.5–6.5 mg/L; HRT=18 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

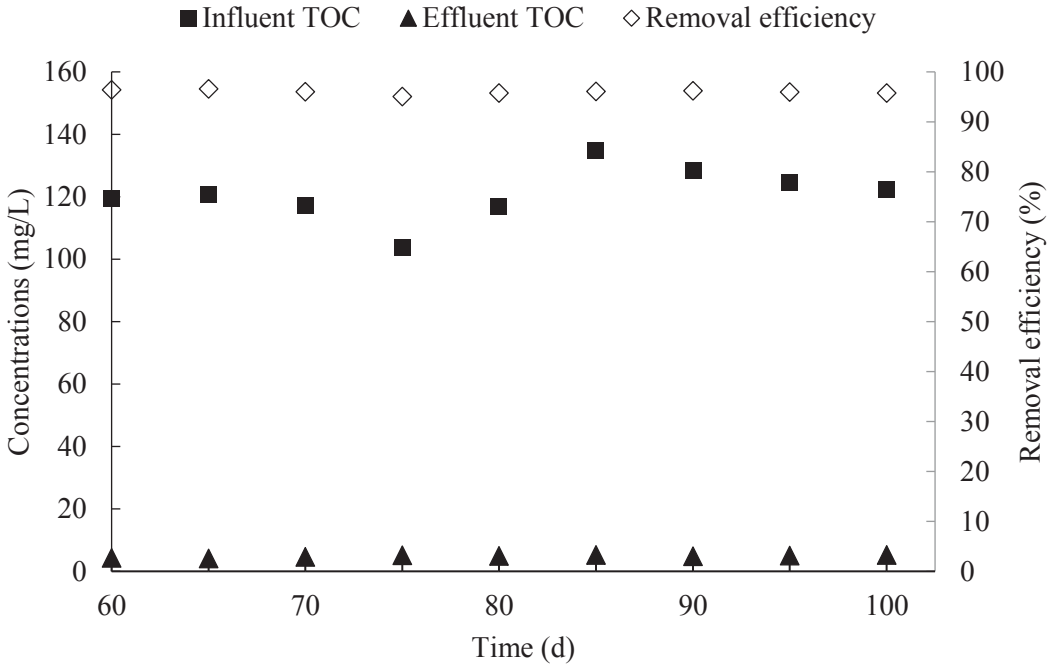

Figure 5.13 TOC removal in the MBBR-MBR
(MBBR conditions: aeration rate = 4 L/min; DO: 5.5–6.5 mg/L; HRT=12 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

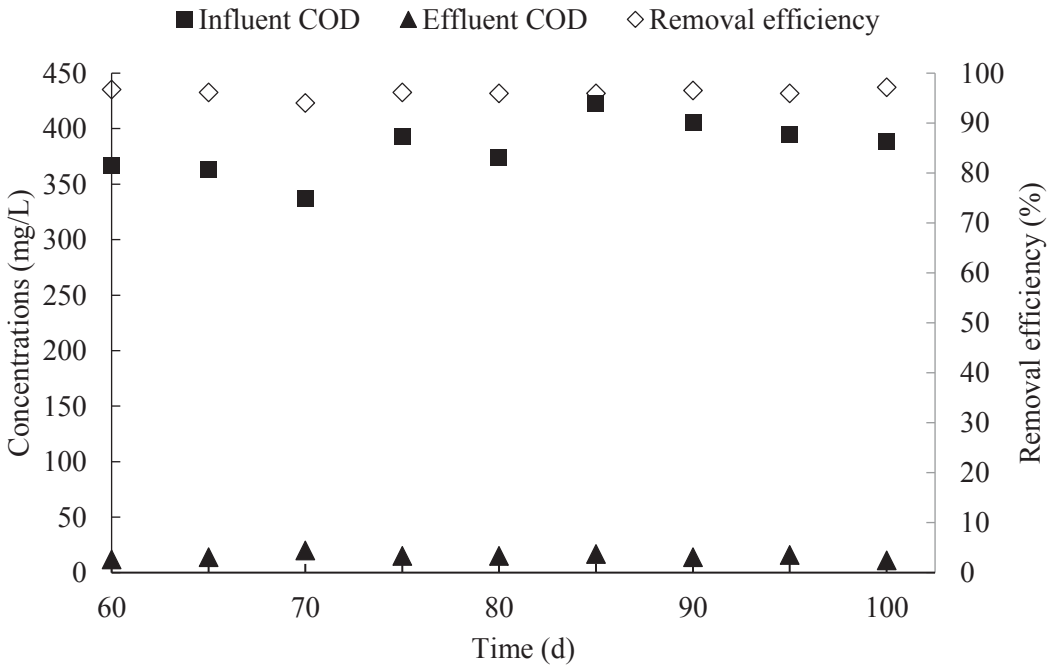

Figure 5.14 COD removal in the MBBR-MBR
(MBBR conditions: aeration rate = 4 L/min; DO: 5.5–6.5 mg/L; HRT=12 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

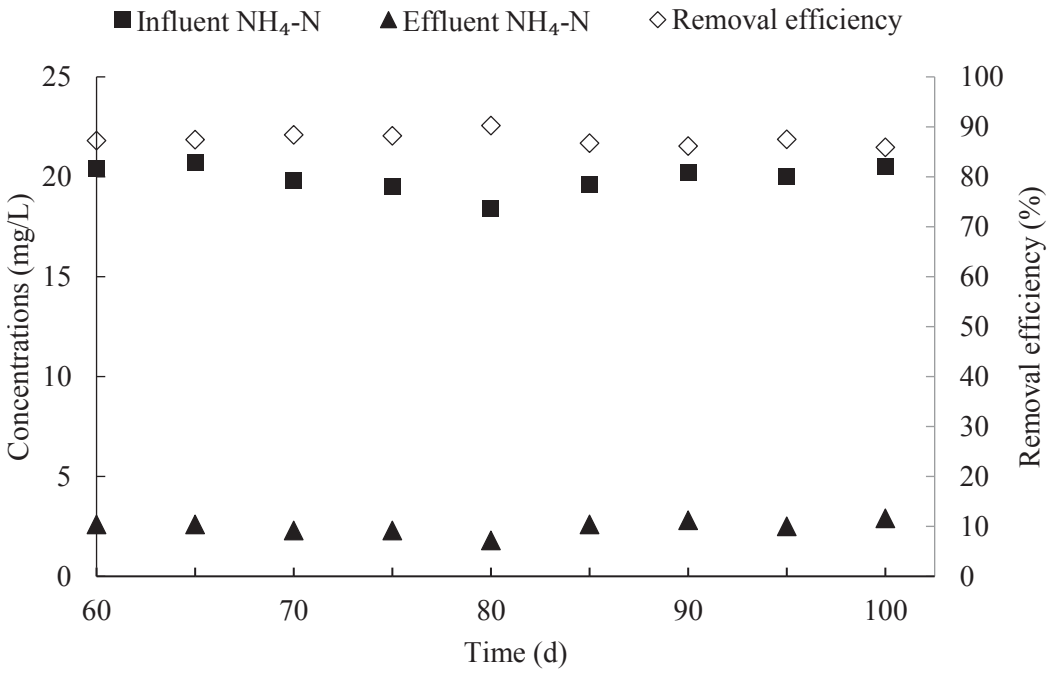

Figure 5.15 NH_4-N removal in the MBBR-MBR
(MBBR conditions: aeration rate = 4 L/min; DO: 5.5–6.5 mg/L; HRT=12 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 $L/m^2 \cdot h$; HRT = 6h; SRT = ∞).

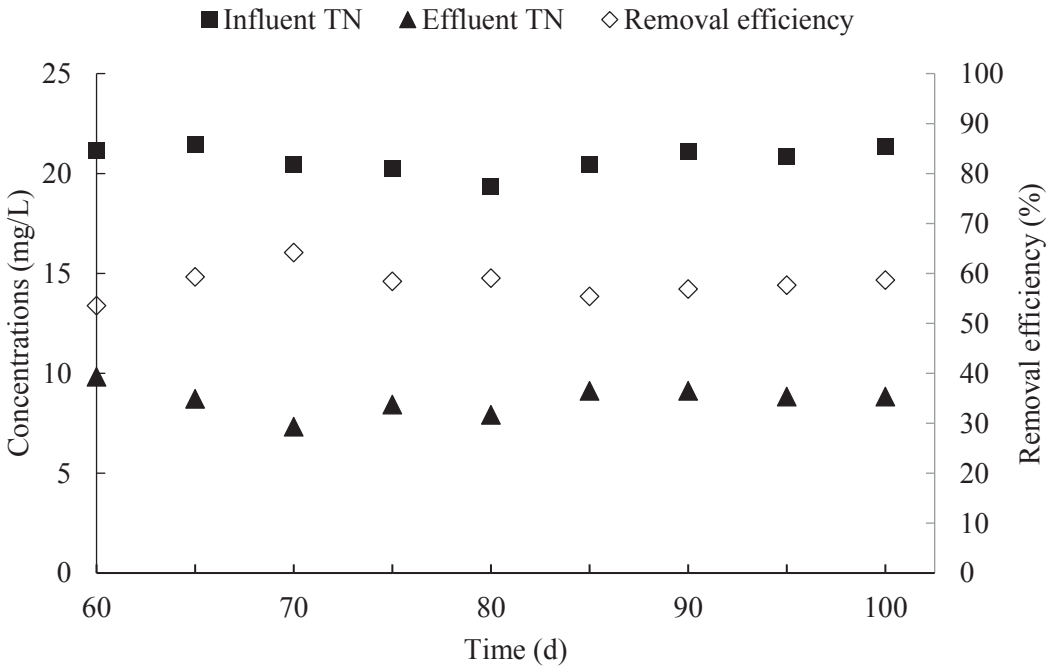

Figure 5.16 TN removal in the MBBR-MBR
(MBBR conditions: aeration rate = 4 L/min; DO: 5.5–6.5 mg/L; HRT=12 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 $L/m^2 \cdot h$; HRT = 6h; SRT = ∞).

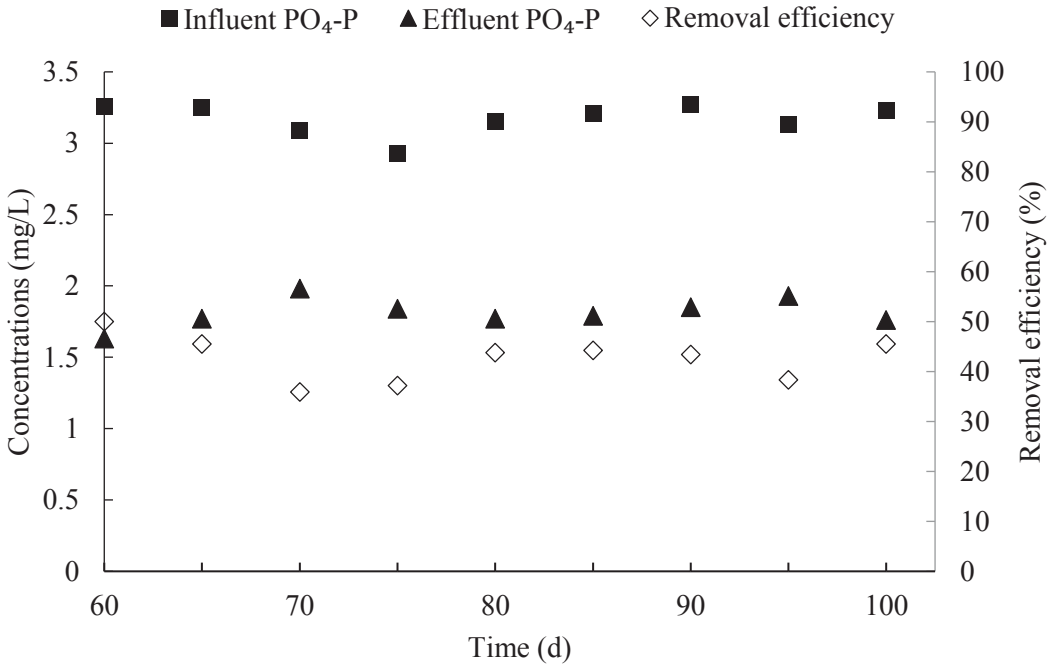

Figure 5.17 PO_4-P removal in the MBBR-MBR
(MBBR conditions: aeration rate = 4 L/min; DO = 5.5–6.5 mg/L; HRT=12 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

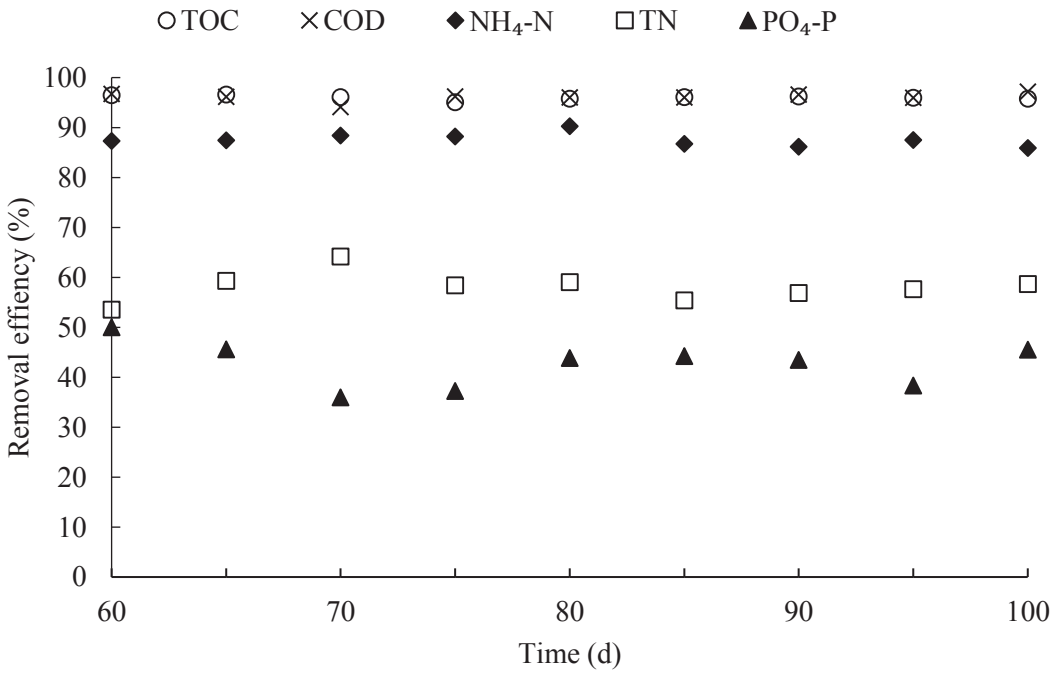

Figure 5.18 Summarized removal efficiencies in the MBBR-MBR
(MBBR conditions: aeration rate = 4 L/min; DO = 5.5–6.5 mg/L; HRT=12 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

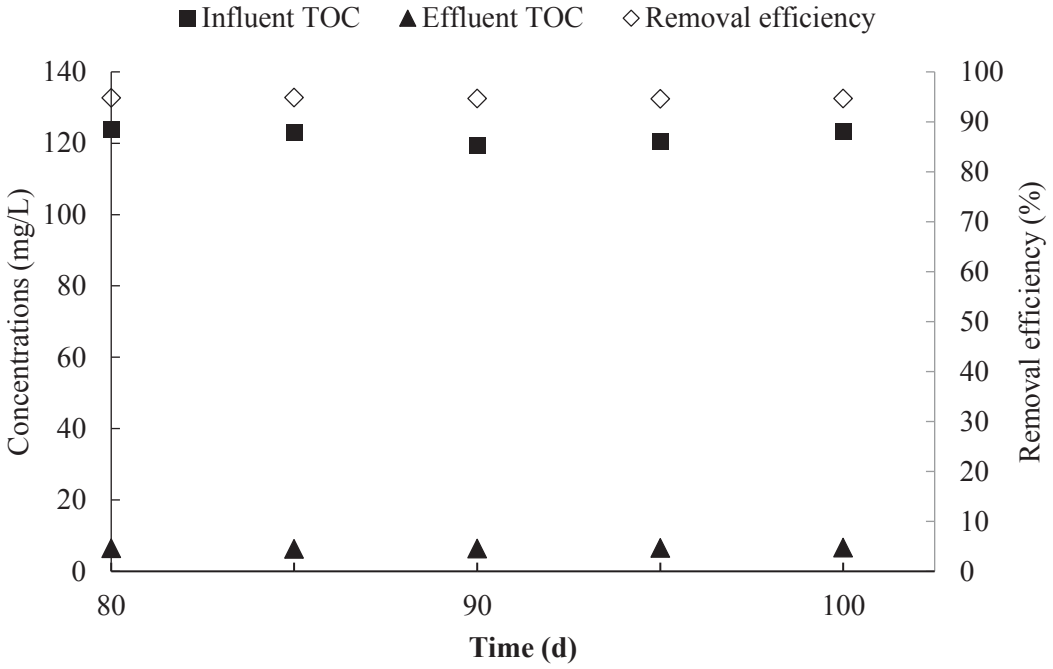

Figure 5.19 TOC removal in the MBBR-MBR
(MBBR conditions: aeration rate = 4 L/min; DO = 5.5–6.5 mg/L; HRT=6 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

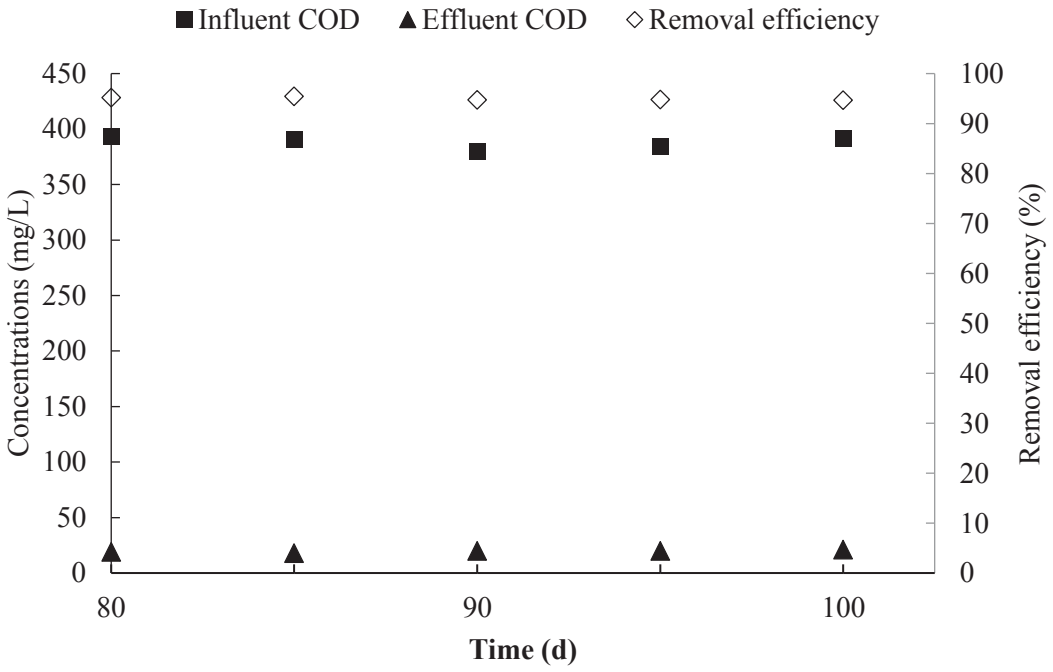

Figure 5.20 COD removal in the MBBR-MBR
(MBBR conditions: aeration rate = 4 L/min; DO = 5.5–6.5 mg/L; HRT=6 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

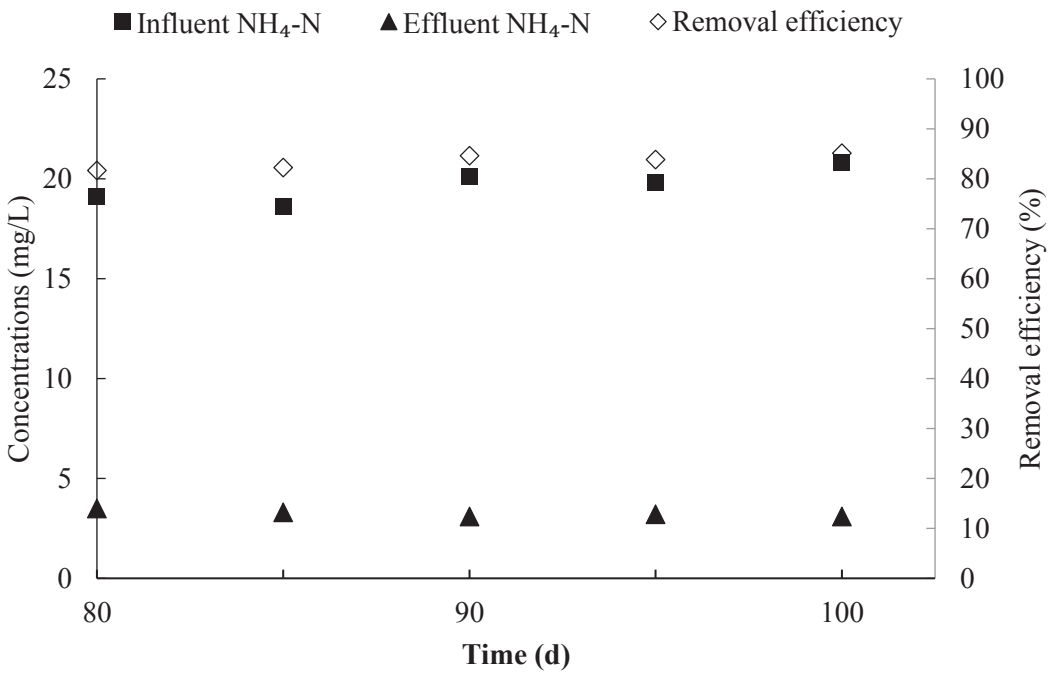

Figure 5.21 NH_4-N removal in the MBBR-MBR
(MBBR conditions: aeration rate = 4 L/min; DO = 5.5–6.5 mg/L; HRT=6 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

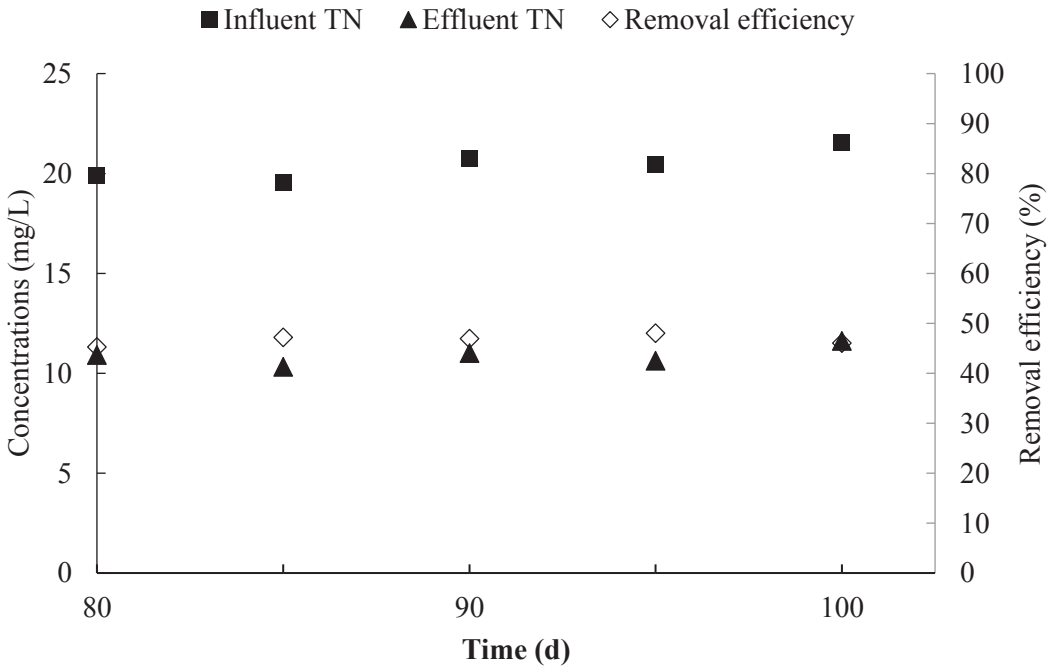

Figure 5.22 TN removal in the MBBR-MBR
(MBBR conditions: aeration rate = 4 L/min; DO = 5.5–6.5 mg/L; HRT=6 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

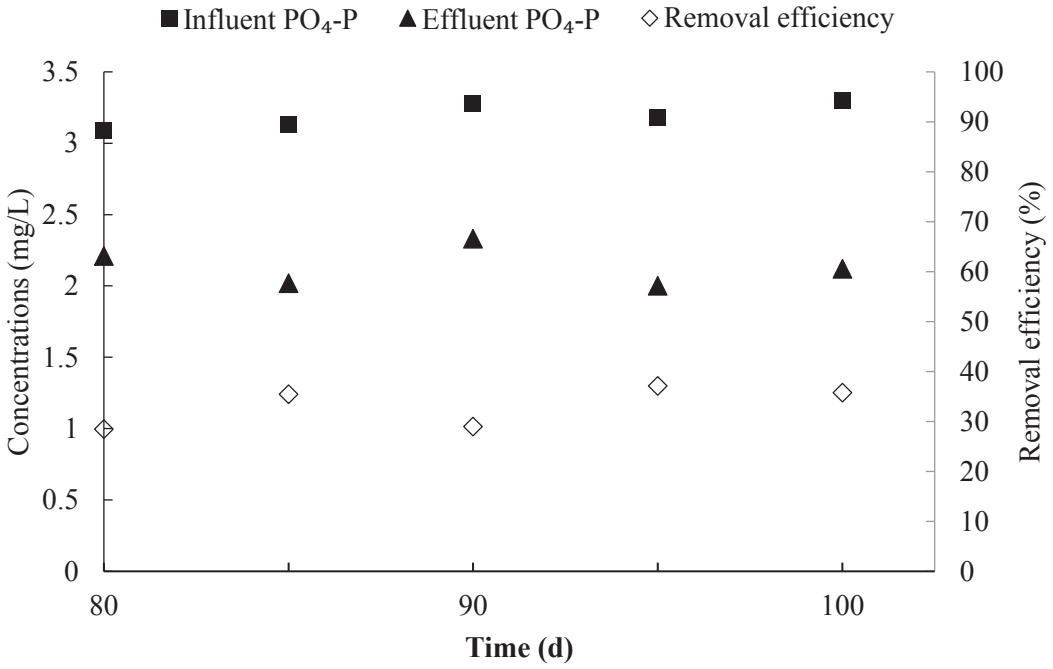

Figure 5.23 PO_4-P removal in the MBBR-MBR
(MBBR conditions: aeration rate = 4 L/min; DO = 5.5–6.5 mg/L; HRT=6 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

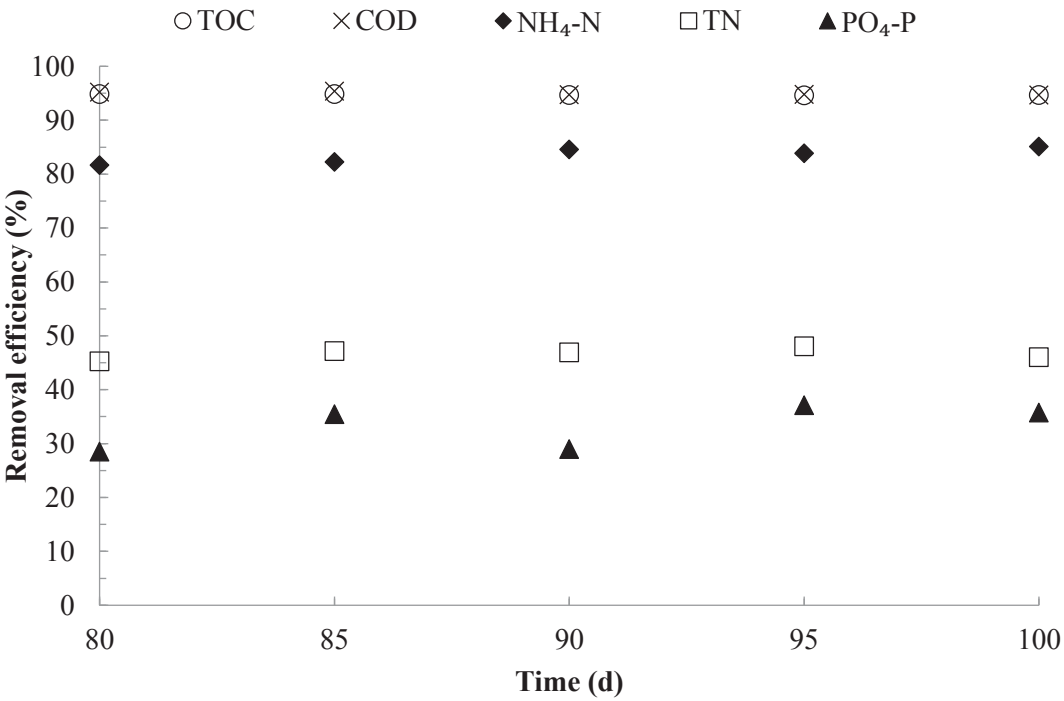

Figure 5.24 Summarized removal efficiencies in the MBBR-MBR
(MBBR conditions: aeration rate = 4 L/min; DO: 5.5–6.5 mg/L; HRT=6 h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

The MLSS and MLVSS concentrations in the MBBR-MBR hybrid system were showed in Table 5.2. In the MBBR unit, the MLSS and MLVSS concentrations were very low, as the suspended solids were washed away into the subsequent MBR unit and no sludge was recycled back to the MBBR. Regarding the MBR unit, the initial MLSS and MLVSS were similar to the values of suspended MLSS and MLVSS concentrations in MBBR tank, and all showed gradual growth during the operation, reaching 0.91 and 0.89 g/L (HRT of 24 h), 1.02 and 0.98 g/L (HRT of 18 h), 1.09 and 1.04 g/L (HRT of 12 h), and 1.05 and 0.96 g/L (HRT of 6 h), respectively.

Table 5.2 Results for both suspended and attached biomass in MBBR unit and MBR unit at HRT of 24 h, 18 h, 12 h, and 6 h

HRT	MBBR		MBR	
	Suspended MLSS (g/L)	Attached biosolids (g/g_{sponge})	Initial MLSS (g/L)	Initial MLVSS (g/L)
	Suspended MLVSS (g/L)	Attached biomass (g/g_{sponge})	Final MLSS (g/L)	Final MLVSS (g/L)
24 h	0.13±0.05	0.45±0.05	0.06	0.05
	0.11±0.06	0.41±0.06	0.91	0.89
18 h	0.09±0.02	0.51±0.03	0.09	0.07
	0.08±0.01	0.47±0.03	1.02	0.98
12 h	0.11±0.02	0.44±0.04	0.11	0.10
	0.10±0.01	0.40±0.03	1.09	1.04
6 h	0.13±0.02	0.40±0.03	0.15	0.11
	0.12±0.01	0.37±0.03	1.05	0.96

5.3 Removals of selected micropollutants

During the MBBR-MBR treatment, the compound-specific removal efficiencies varied significantly, ranging from 11.0 to 99.5%, without an evident correlation (correlation coefficient = 0.35) to their Log Ds. However, most compounds were eliminated to large extents (>70%). One possible reason for the high removal efficiency is that the attached growth pattern could enhance the retention of the biomass, thus promoting the enrichment of slow growing microorganisms and the formation of a diverse biocoenosis. Even MBR can prevent the washout of slow-growing microorganisms like nitrifiers, the impact of MBR removal was minimal. This may probably due to the low MLSS concentration and the large pore size (0.2 μm; two orders of magnitude larger than the molecular sizes of micropollutants) of the MF membrane used in this study. Nevertheless, the MBR unit was able to complement the removal of a few compounds including metronidazole and carbamazepine. Both metronidazole and carbamazepine are nitrogen bearing compounds, where nitrogen is bound to the cyclic structure. The infinite SRT applied in this study could have facilitated the enhanced removal of the nitrogenous compounds mentioned above. Wijekoon et al. (2013) stated that the removal of nitrogen bearing compounds could be selectively enhanced by the nitrifying microbial consortium, but detailed study on the effect of the location of nitrogen molecules in nitrogenous compounds on their degradation by nitrfiers would be required to substantiate this hypothesis. In addition to size exclusion, membrane can intercept the release of micropollutants through charge repulsion, adsorption onto membrane surface, sorption diffusion, solute-solute interactions and fouling layer interactions (Schäfer et al. 2011). For example, Chang et al. (2003) ascribed the complete removal of estrone (feed concentrations: 2.6-154 ng/L) in a MF dead-end process to adsorption on the membrane. However, in this study, estrone (feed concentrations: 43-118 ng/L) experienced a very limited further removal in the MF process. A possible cause was that the adsorption sites of the membrane quickly saturated after the beginning of the operation, and the absence of adsorption sites impeded the retention of estrone. Additionally, biological removal might be helpful in the reduction of the compounds that were less likely to interact with particulate matter and membrane surface, such as gemfibrozil, pentachlorophenol and diclofenac.

In this study, a better removal of certain micropollutants was observed at optimal HRT in MBBR unit (HRT of 18 h) in comparison to several previous studies involving both MBBR (Pozo et al., 2012) and MBR (Wijekoon et al., 2013; Tadkaew et al., 2011). A high removal (92.1±2.5%) of Bisphenol A was obtained at HRT of 18 h in this study, which was 52.8% higher than a low removal of total phenolic compound removal (39.27±8.09%) by a bench scaled MBBR previously reported by Pozo et al. (2012) at HRT of 19.2 h. Pozo et al. (2012) also indicated that HRT exerted an influence on the removal efficiency of a system, which supports the point of view in current study. Relatively higher removal of diclofenac (84.1%) could also be noticed compared to the lower removal (27%) reported by Wijekoon et al. (2013) and (17.3%) by Tadkaew et al. (2011). This could be attributed to the difference in the microbial composition of the sludge and sludge concentrations between the MBBR-MBR system and MBR system. Over time, phenolic and phthalate degrading bacteria were developed along with improved micropollutants biodegradation (Boonnorat et al., 2014).

The impact of hydrophobicity on the behaviour of micropollutants removal in the MBBR-MBR system was also investigated. Noting that most of the hydrophobic compounds presented very low solid phase concentration at all HRTs, despite the high hydrophobicity (Log D>3.2), such as 4-n-nonylphenol. In contrast, some persistent hydrophilic compounds (e.g. carbamazepine) were consistently detected at high concentrations in biosolids.

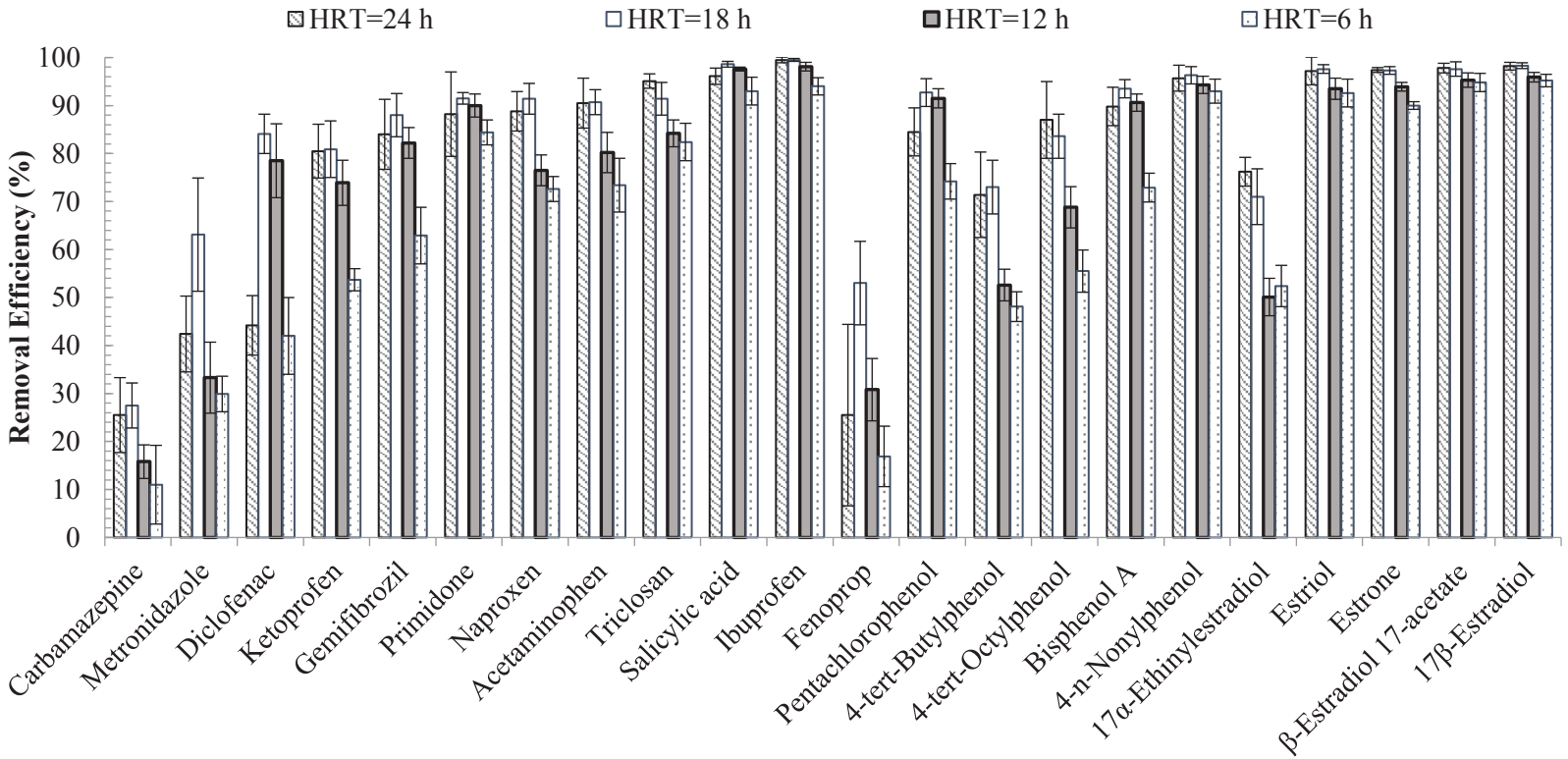

Figure 5.25 Micropollutant removals in the MBBR-MBR while MBBR unit operating at HRT of 24 h, 18 h, 12 h, and 6 h. The error bar of each sample represents the standard deviation over the experiment period
(MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h, 18h, 12h and 6 h;
MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞)

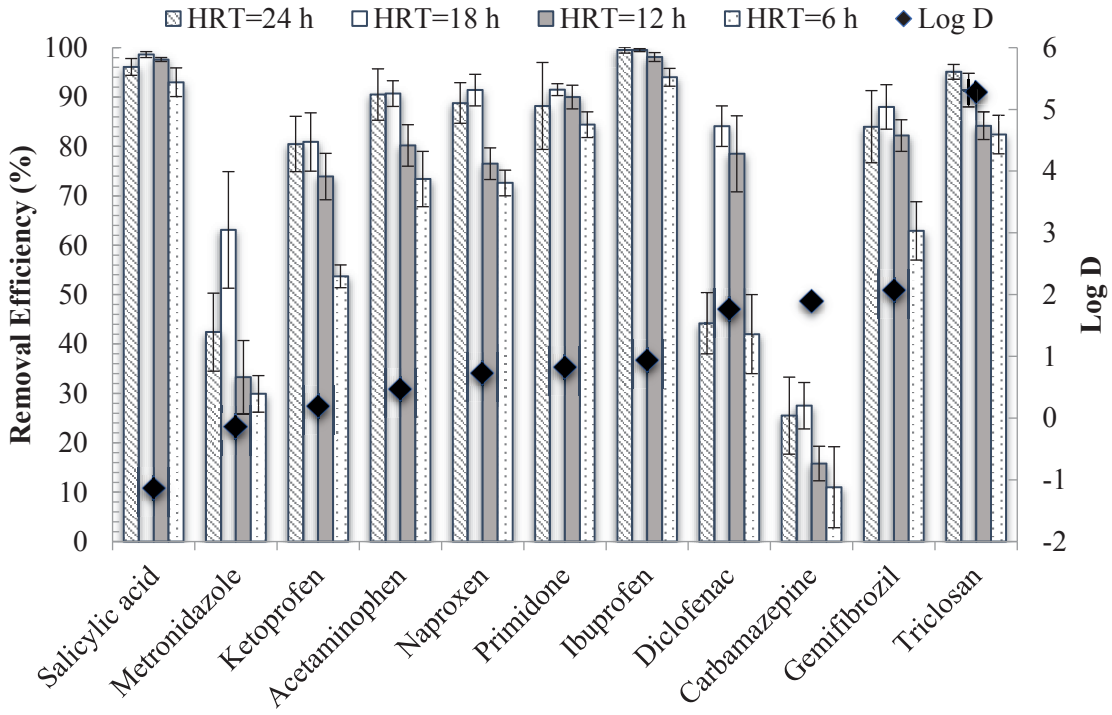

Figure 5.26 Relationship of Log D and pharmaceutical removals in the MBBR-MBR. An error bar represents the standard deviation over the experimental period (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L, HRT = 24h, 18h, 12h and 6h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞)

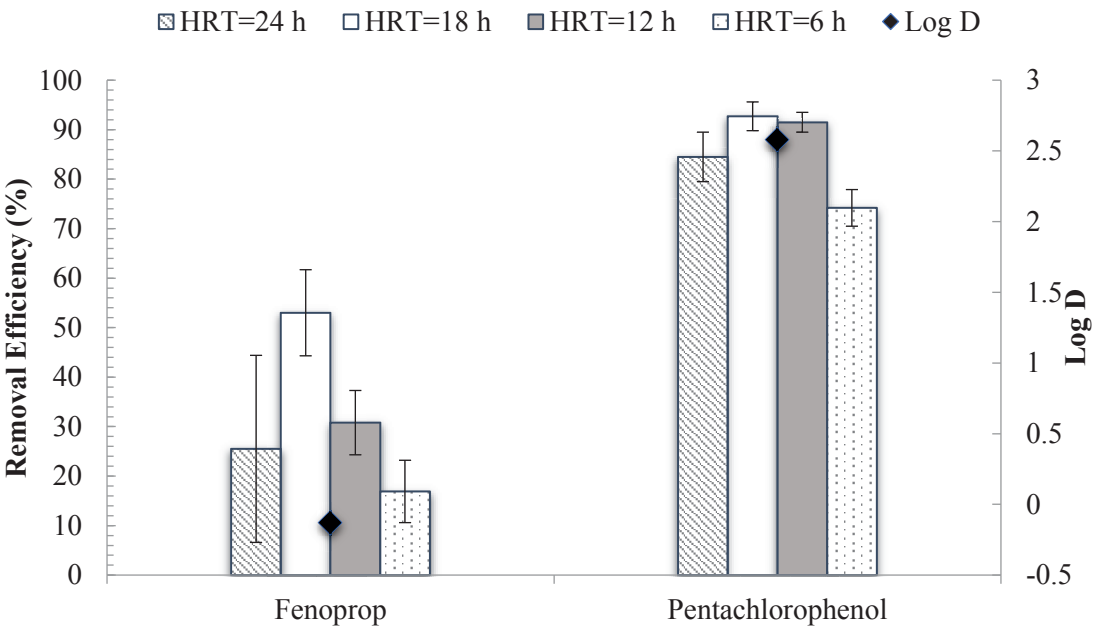

Figure 5.27 Relationship of Log D and pesticides removals in the MBBR-MBR. An error bar represents the standard deviation over the experimental period (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L, HRT = 24h, 18h, 12h and 6h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞)

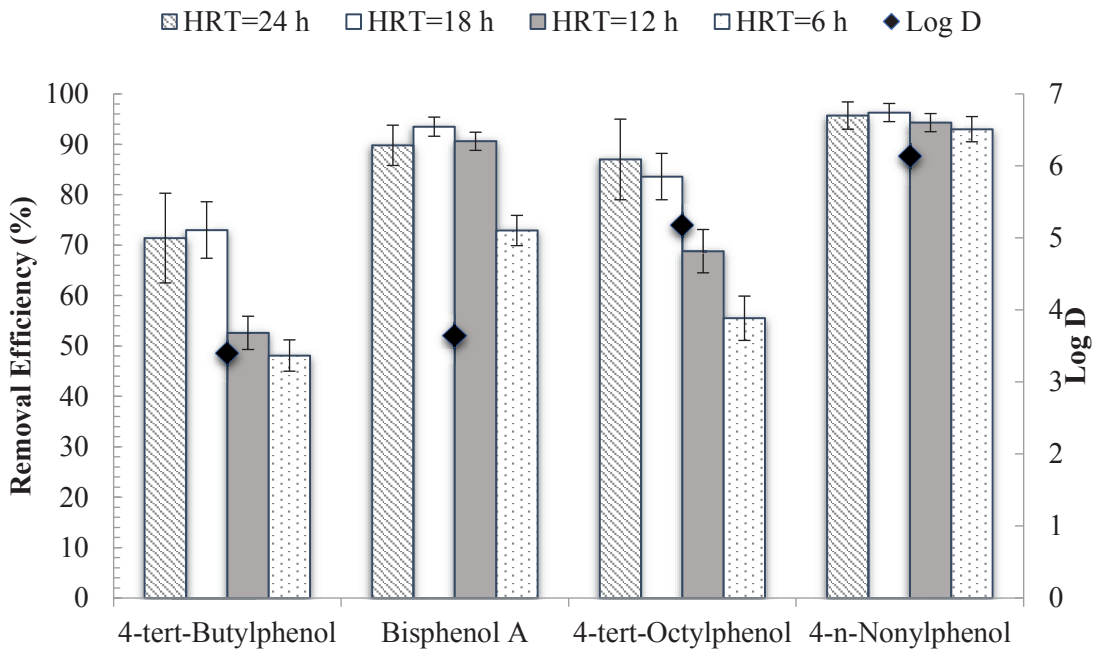

Figure 5.28 Relationship of Log D and industrial chemicals removals in the MBBR-MBR. An error bar represents the standard deviation over the experimental period (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L, HRT = 24h, 18h, 12h and 6h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞)

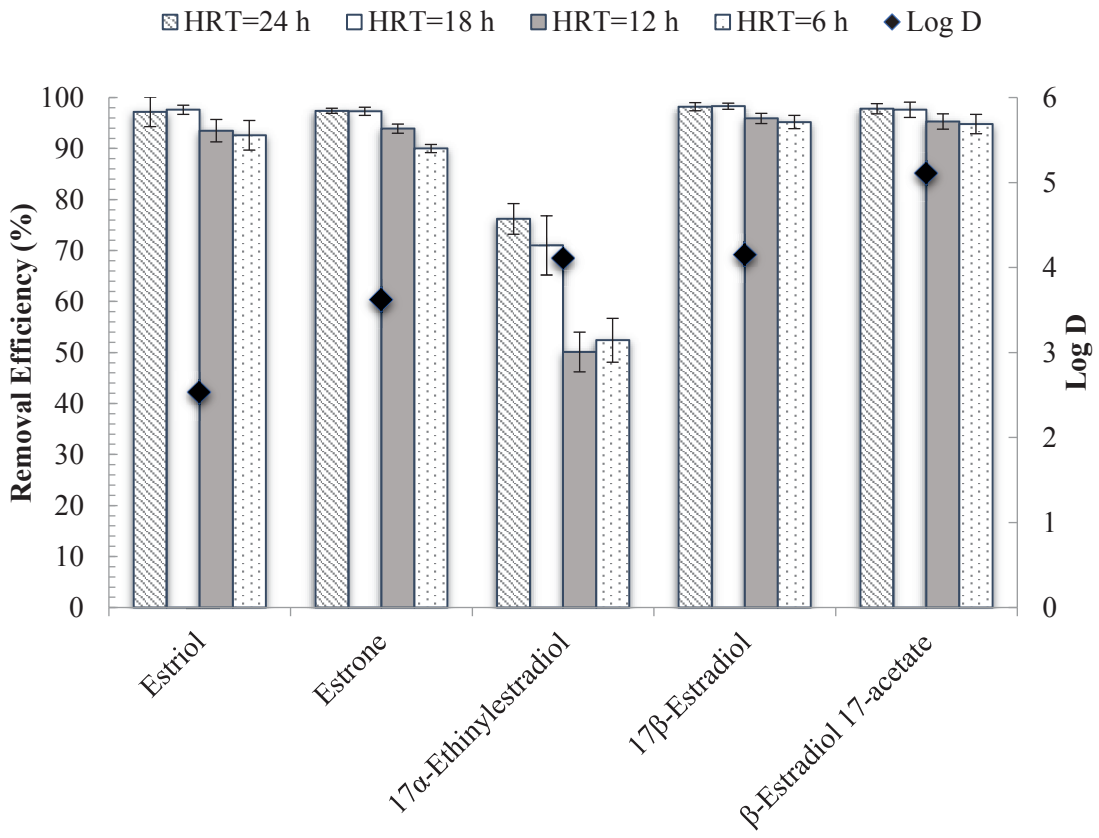

Figure 5.29 Relationship of Log D and estrogenic hormones removals in the MBBR-MBR. An error bar represents the standard deviation over the experimental period (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L, HRT = 24h, 18h, 12h and 6h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞)

To gain further insight into the fate of micropollutants during the MBBR-MBR treatment, a mass balance of the investigated compounds was evaluated (Eq. 1), taking into account the removal pathways of biodegradation and sorption in the MBBR unit, and total removal in the MBR unit.

$$L_{inf} = L_{s,MBBR} + L_{b,MBBR} + L_{MBR} + L_{eff} \quad (6.1)$$

where L_{inf} is the influent load of micropollutants over the experimental period (ng), $L_{s,MBBR}$ and $L_{b,MBBR}$ are the amount of a compound removed via sorption (ng) and biodegradation (ng), respectively, in the MBBR unit; L_{MBR} is the amount of a compound removed in the MBR (ng); L_{eff} is the amount of a compound released from the system (ng).

The calculation of the sorption (Eq. 2) and biodegradation (Eq. 3) in MBBR was carried out according to Luo et al. (2014).

$$L_{s,MBBR} = Q \cdot MLSS_{MBBR} \cdot C_{ss} \cdot T + \Delta SS \cdot C_{sa} \quad (6.2)$$

$$L_{b,MBBR} = \left(L_{inf} - L_{eff,MBBR}\right) - L_{s,MBBR} \quad (6.3)$$

where Q is the flow rate of the MBBR-SMBR system (L/day); $MLSS_{MBBR}$ is mixed liquor suspended biosolids concentration in the MBBR (g/L); C_{ss} is the concentration of a compound on the suspended biosolids (ng/g); T is the duration of the experimental period (days); ΔSS is the increased amount of attached biosolids (g); C_{sa} is the concentration of a compound on the attached biosolids (ng/g); $L_{eff,\ MBBR}$ is the amount of a compound released from the MBBR unit (ng).

Regarding the calculation for the removal in the MBR unit, the following equation was used:

$$L_{MBR} = L_{eff,MBBR} - L_{eff} \quad (6.4)$$

Fig. 5.30-5.33 illustrates the fate of the selected compounds in the MBBR-MBR system at HRT of 24, 18, 12, and 6 h. The results show that biodegradation in the MBBR was the main pathway for the micropollutant removal, which is consistent

with outcomes from our previous study involving both MBBR-MBR and CMBR (Luo et al., 2015). Compared to biodegradation, sorption accounted for much less proportion of most micropollutant removals. This probably due to that sorption is a more rapid process than biodegradation. In addition, sorption of micropollutants to biosolids results in longer residence time in the reactor, which may lead to further removal via biodegradation (Tadkaew et al., 2011). Moreover, the acclimatized sponge in the MBBR unit remained fully occupied by biomass over time, and the reduced sorption site resulted in the limited sorption efficiency in long term experiment (Luo et al., 2014b). As a result, although most micropollutants were effectively removed at HRT of 18 h, the decreased removals of 17α-ethinylestradiol, triclosan and 4-tert-octylphenol were observed. On the other hand, the proportion of sorption varied at different HRTs. It is notable that the percentage of sorption increased after HRT changed to 6 h. One reason could be the excessive nutrient in the MBBR unit leading to over growth and detachment of biofilm. The new biofilm could help adsorbing micropollutant to a certain extent. Even MBR can prevent the washout of slow-growing microorganisms like nitrifiers, the impact of MBR removal was minimal at all HRTs. This may probably due to the low MLSS concentration and the large pore size (0.2 μm; two orders of magnitude larger than the molecular sizes of micropollutants) of the MF membrane used in this study. Nevertheless, the MBR unit was able to complement the removal of a few compounds including metronidazole and carbamazepine. Both metronidazole and carbamazepine are nitrogen bearing compounds, where nitrogen is bound to the cyclic structure. The infinite SRT applied in this study could have facilitated the enhanced removal of the nitrogenous compounds mentioned above. Wijekoon et al. (2013) stated that the removal of nitrogen bearing compounds could be selectively enhanced by the nitrifying microbial consortium, but detailed study on the effect of the location of nitrogen molecules in nitrogenous compounds on their degradation by nitrfiers would be required to substantiate this hypothesis. Additionally, the observed complementary separation effect of the MF membrane could be attributed to the sorption of micropollutants to suspended solid particles and the retention of these solid particles by the MF membrane (Schäfer et al. 2011).

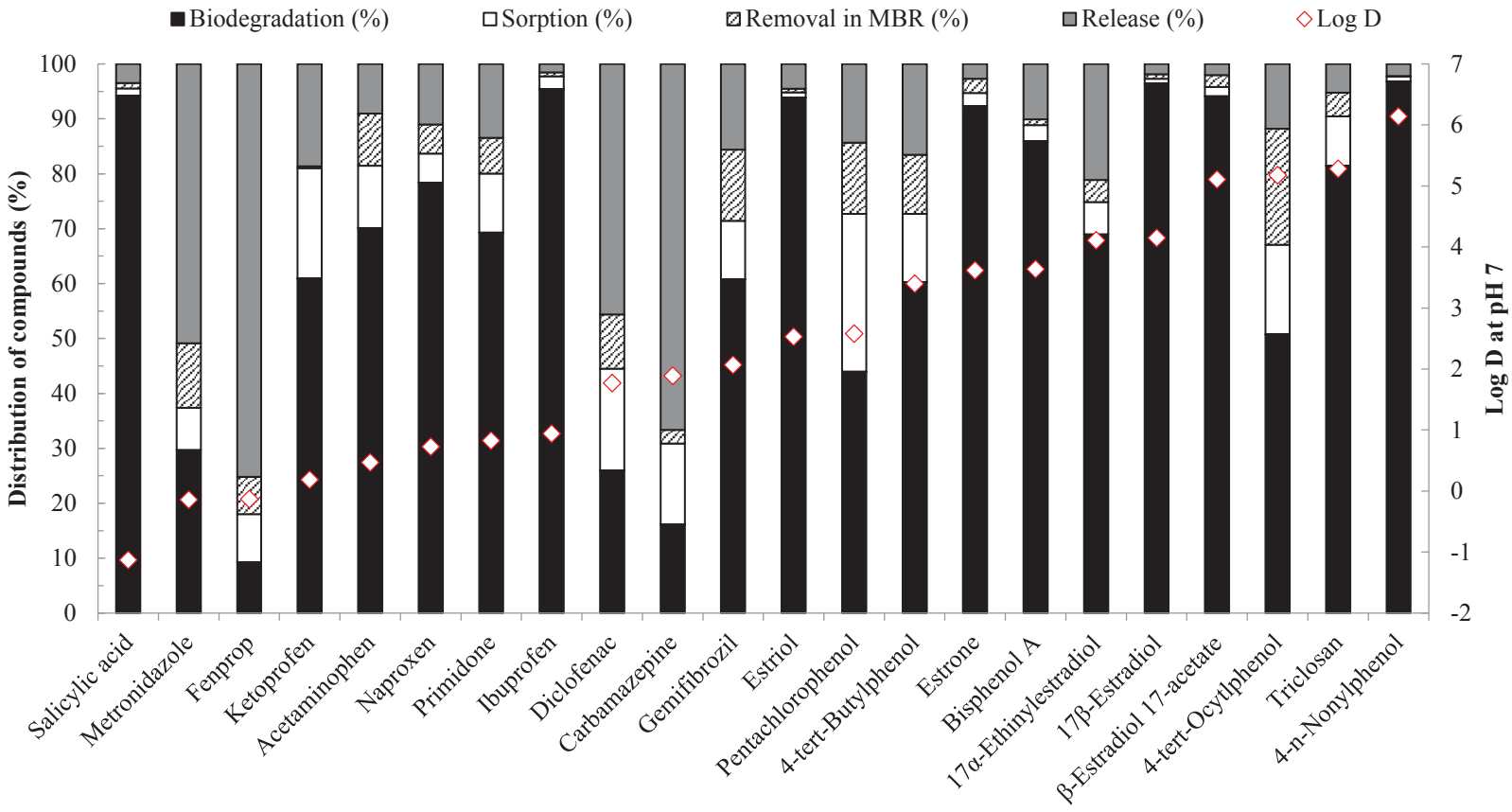

Figure 5.30 Fate of the studied micropollutants in the MBBR-MBR system

(MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L, HRT = 24h;

MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞)

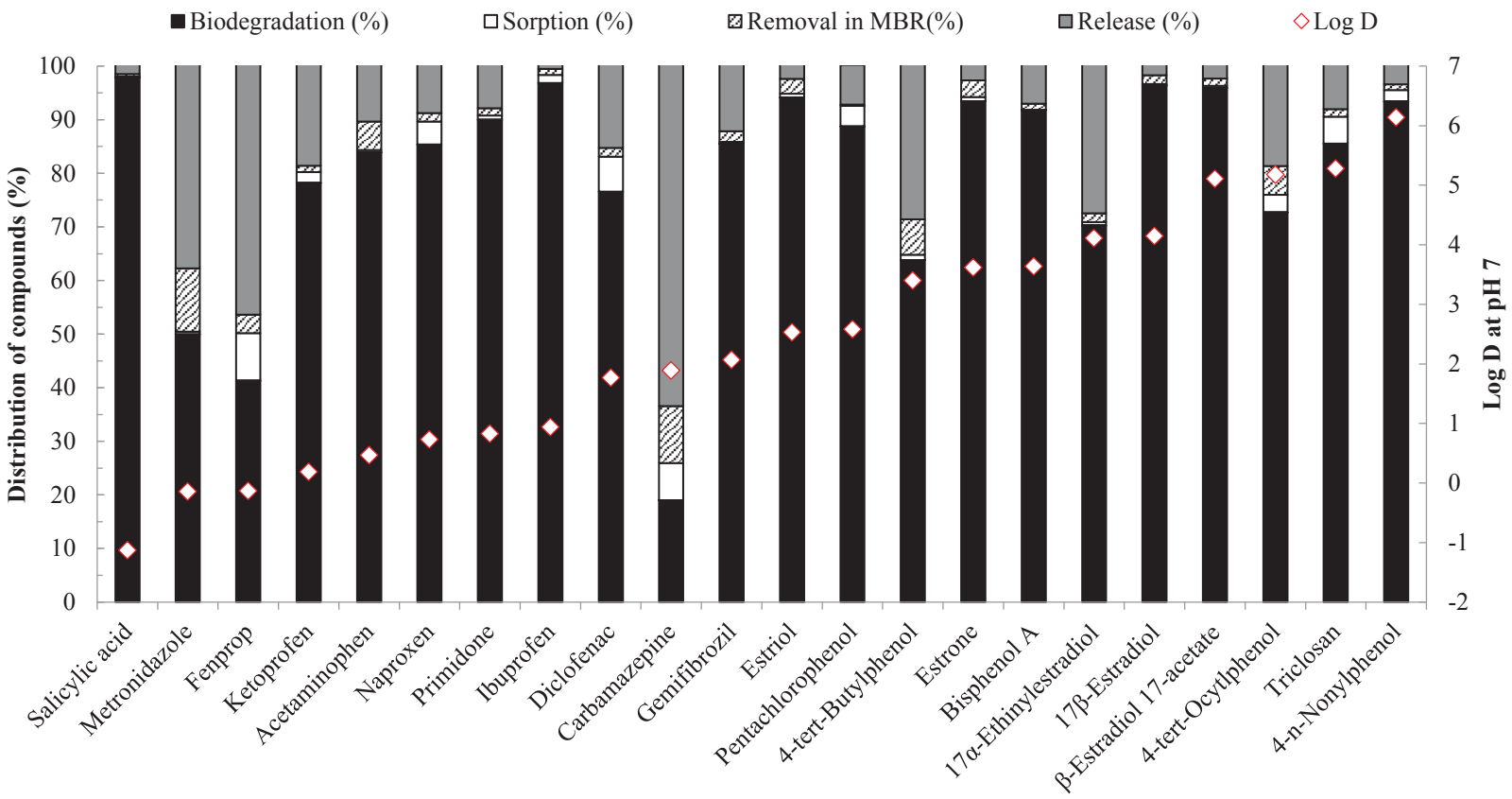

Figure 5.31 Fate of the studied micropollutants in the MBBR-MBR system

(MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L, HRT = 18h;

MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞)

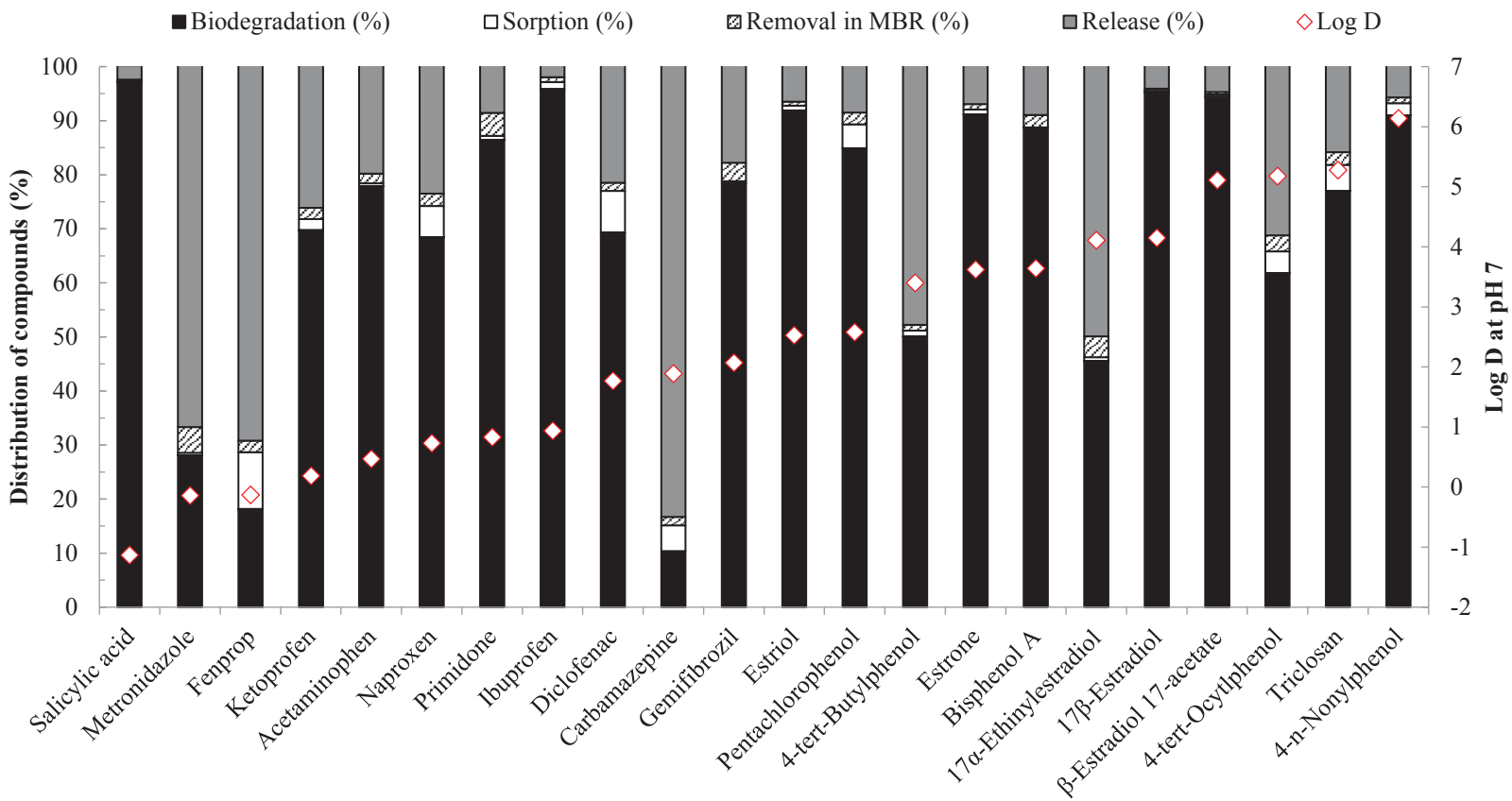

Figure 5.32 Fate of the studied micropollutants in the MBBR-MBR system

(MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L, HRT = 12h;

MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞)

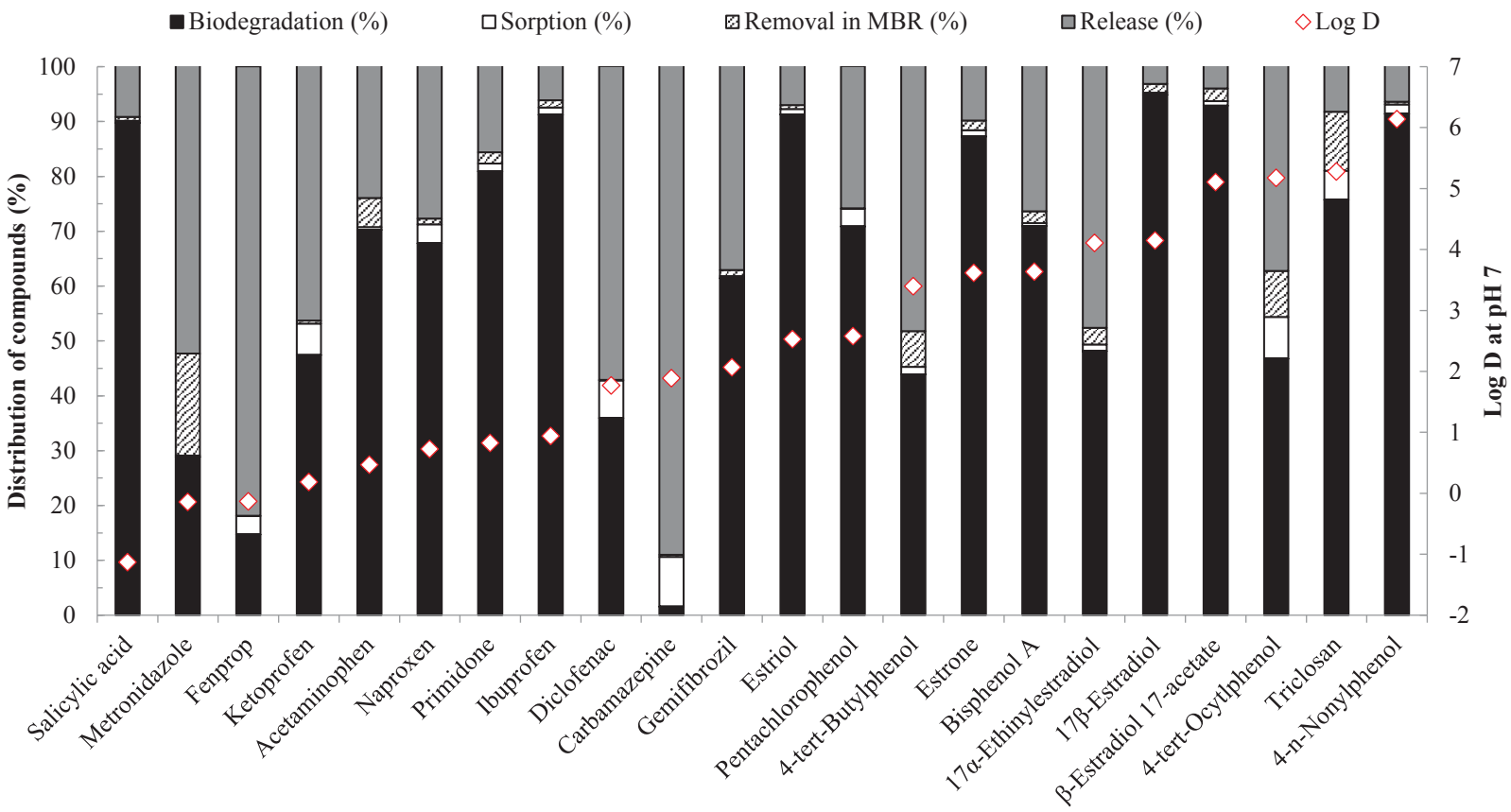

Figure 5.33 Fate of the studied micropollutants in the MBBR-MBR system

(MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L, HRT = 6h;

MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞)

5.4 Membrane fouling analysis

Fig. 5.34 depicts the time course of TMP increase in the MBR unit. The TMP development in the MBR unit was varied when the MBBR unit were operating at four HRTs. The TMP in the MBR unit reached up to 35 kPa, 36.5 kPa, 37.5 kPa and 36.5 kPa in 89 days, 74 days, 42 days and 20 days of operation, respectively, at HRT of 24 h, 18 h, 12 h, and 6 h in MBBR unit. The fouling rate were 0.39 kPa/d (HRT of 24 h), 0.49 kPa/d (HRT of 18 h), 0.89 kPa/d (HRT of 12 h), and 1.83 kPa/d (HRT of 6 h). In our previous study, it is concluded that the use of MBBR as the pre-treatment can lower the fouling propensity and improve the filtration performance of MBR by comparing the TMP profile gained from the MBBR-MBR hybrid system (HRT of 24 h) and a CMBR. According to the result from this experiment, a longer HRT (e.g. HRT of 24 h) can significantly mitigate membrane fouling when compared with a relatively short HRT (e.g. HRT of 6 h). Especially, the TMP value maintained less than 15 kPa for 60 days (HRT of 18 h) and 68 days (HRT of 24 h).

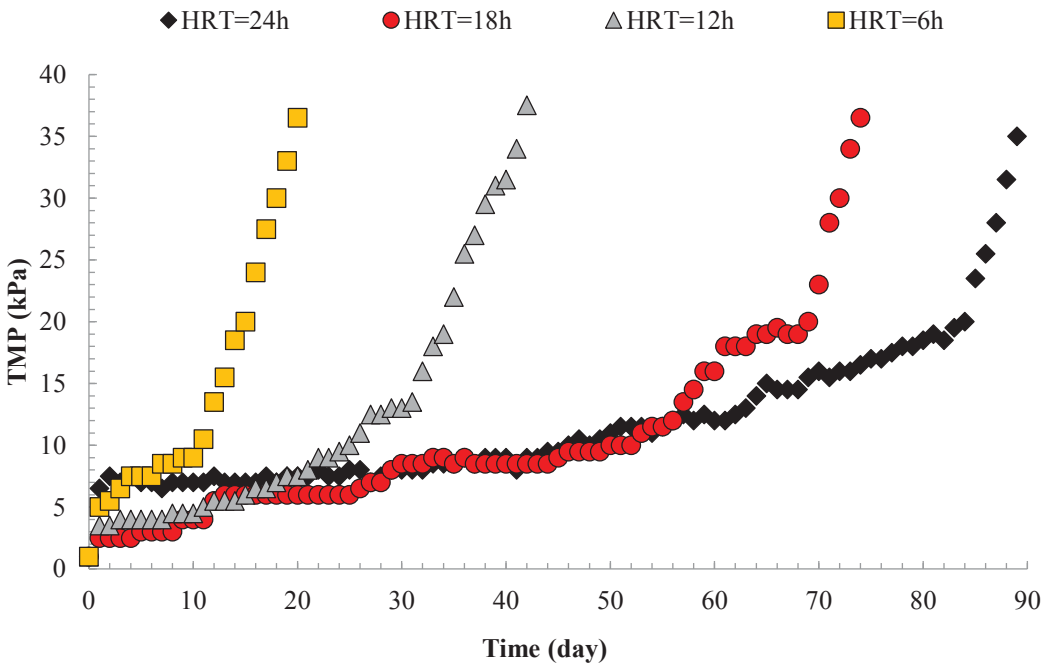

Fig. 5.34 Comparison of TMP profiles in the MBR while MBBR was operating at HRT of 24 h, 18 h, 12 h, and 6 h (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h, 18h, 12h and 6h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞)

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:

$$J = \Delta P_T/(\mu \cdot R_t) \quad (5.5)$$

$$R_t = R_m + R_C + R_f \quad (5.6)$$

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 was subjected to physical and chemical cleaning, in order to determine different membrane fouling resistances using the equations given above. Results of fouling resistance were showed in Table 5.3. The results suggested that cake layer formation was the main factor contributing to membrane fouling at all HRTs. However, pore blocking resistance was higher at short HRT than high HRT. As suspended MLSS concentrations in MBBR were different at each HRT, it could affect the sludge properties in subsequent MBR unit. Higher MLSS concentration may cause formation of sticky cake layer on membrane surface due to higher sludge viscosity (Deng et al., 2014). Besides, small sludge flocs could lead to more severe membrane fouling and induce higher membrane increment rate, while larger sludge flocs could not easily deposit on membrane surface. Hence, severe membrane fouling and higher fouling rate (Fig. 5.34) occurred at HRT of 6 h.

Table 5.3 Membrane resistances for different types of fouling.

Parameter	HRT=24 h		HRT=18 h		HRT=12 h		HRT=6 h	
	Resistance (10^{12}/m)	Percentage (%)	Resistance (10^{12}/m)	Percentage (%)	Resistance (10^{12}/m)	Percentage (%)	Resistance (10^{12}/m)	Percentage (%)
Clean membrane	1.33	10.5	1.33	11.0	1.33	11.0	1.33	11.0
Cake layer	9.63	76.5	8.67	71.8	8.17	70.7	7.83	69.4
Pore blocking	1.51	12.0	1.90	15.7	1.89	16.3	1.92	17.0
Irreversible fouling	0.12	1.0	0.18	1.5	0.16	1.5	0.20	1.7
Total resistance	12.59	100	12.08	100	11.55	100	11.28	100

The severe membrane fouling is often a result of organics accumulation on or in the membrane as bound EPS or SMP, and polysaccharides and proteins are considered as the major fractions of EPS and SMP (Guo et al., 2012, Meng et al., 2009). Fig. 5.35 exhibits the composition of mixed liquor's SMP and bound EPS at different designed TMPs in MBBR-MBR system at HRT of 24 h, 18 h, 12 h, and 6 h. The level of EPS were similar at the beginning of all HRTs, then gradually increased to 15.24 mg/L, 16.43 mg/L, 19.88 mg/L and 22.93 mg/L at the end of operation for HRT of 24 h, 18 h, 12 h, and 6 h, respectively. The SMP concentration varied for different HRTs but showed minor variation under the same HRT. The SMP concentration was lower at HRT of 24 h, while a significantly higher SMP concentration was observed at HRT of 6 h. One reason could be the shortened HRT led to increase in nutrient availability, which may accelerate the death of curtain bacteria releasing SMP.

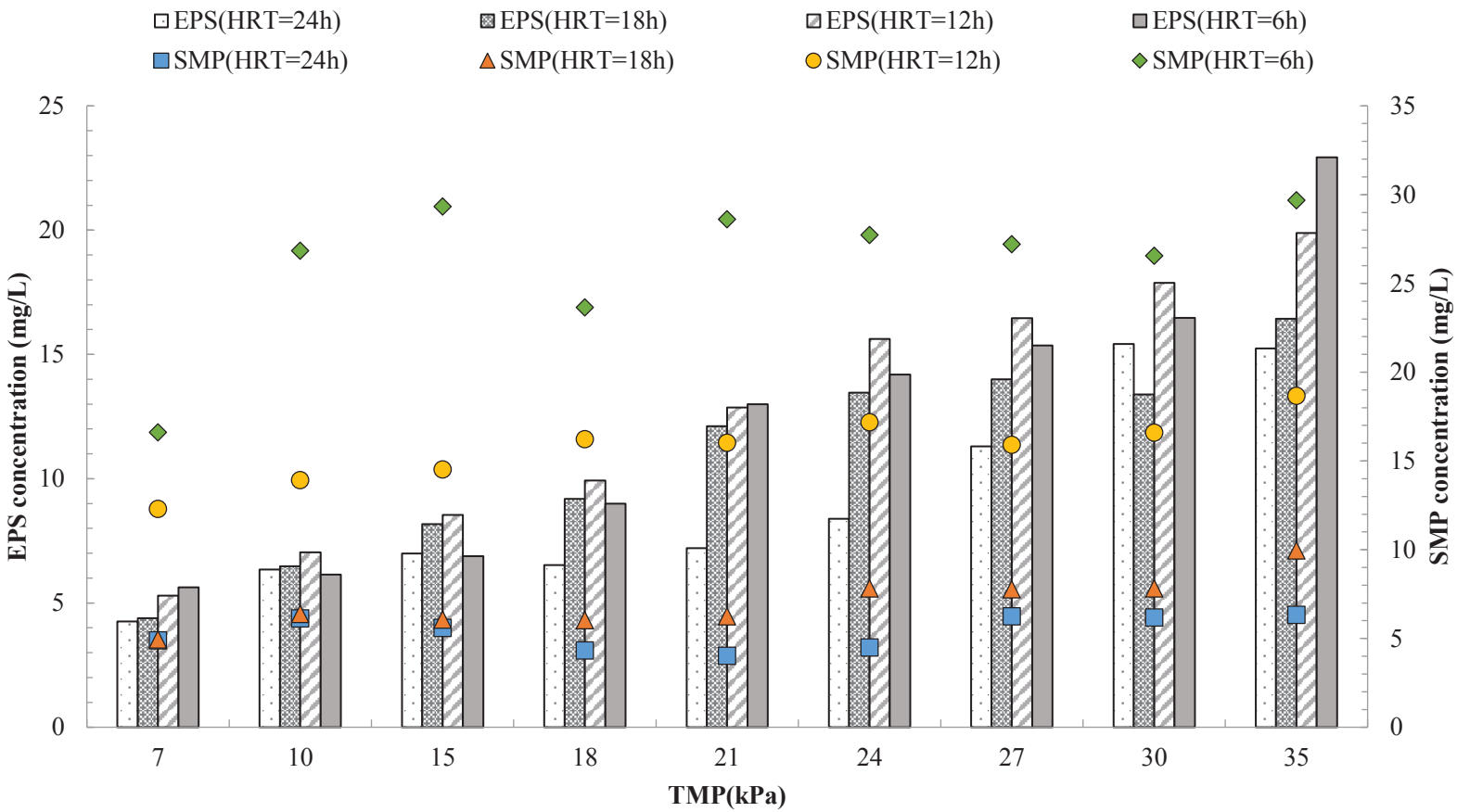

Figure 5.35 Comparison of EPS and SMP values in the MBR while MBBR was operating at HRT of 24 h, 18 h, 12 h, and 6 h (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h, 18h, 12h and 6h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞)

The sludge characteristics (e.g. Zeta potential, hydrophobicity and floc size) were presented at Table 5.4. The zeta potential increased while RH decreased, when the HRT was changed from 24 h to 6 h. According to Ji et al. (2010), increase of zeta potential could neutralise the negative charge on the surface of the floc and form large aggregates, while high RH generally resulted in less interaction between the hydrophobic flocs and the hydrophilic membrane. The floc size of sludge was larger at higher HRT than that of at lower HRT.

Table 5.4 Sludge characteristics in MBR unit at HRT of 24 h, 18 h, 12 h, and 6 h

HRT	Sludge characteristics		
	Zeta potential (mV)	RH (%)	Floc size (μm)
24 h	-12.1 to -19.0	75.0-83.3	15-40
18 h	-11.8 to - 19.6	73.0-80.9	15-40
12 h	-16.1 to -20.2	70.8-78.6	10-30
6 h	-18.1 to -20.9	68.4-75.5	10-25

5.5 Conclusion

The investigated MBBR-MBR demonstrated excellent performance in removing organics, nutrients as well as micropollutants. By using an MBBR as a pretreatment to an MBR, it could not only enhance overall organic and nutrient removal, but also prolong the operative time of the MBBR-MBR due to efficient fouling reduction. Therefore, the use of an MBBR as pretreatment to an MBR could be a promising solution to improve the performance of the MBR system

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Chapter 6

Evaluation of Micropollutant Removal and Fouling Reduction in a Moving Bed Biofilm Reactor-Membrane Bioreactor Hybrid System

6.1 Introduction

In recent years, the frequent detection of micropollutants in the aquatic environment has raised specific concerns due to their detrimental effects on aquatic organisms and human health. It has been reported that micropollutants often exhibit incomplete removal during the activated sludge process. As an alternative to the activated sludge process, the moving bed biofilm reactor (MBBR) technology has demonstrated its suitability for micropollutant removal (Luo et al., 2014).

While MBBR has become an emerging technology for eliminating micropollutants, a major concern for MBBR applications is the decrease of sludge settleability when treating high strength wastewater, which may lead to severe operational problems when clarifiers are employed for the separation of solids. To counter this problem, various hybrid systems have been developed, which involve modifications of the basic MBBR system by adding coagulants (metal salts or cationic polymers) or applying membrane filtration or floatation as the solid separation process (Leiknes et al., 2006). Among all these modifications, combining membrane technology with MBBR is an established concept with growing popularity, which may also result in better membrane performance (Yang et al., 2008; Duan et al., 2013). Several researchers have demonstrated that the MBBR-membrane hybrid systems have the potential to mitigate membrane fouling (Leiknes et al., 2006; Ivanovic and Leiknes, 2008). However, previous studies have also indicated that the MBBR-membrane filtration hybrid system could experience severe membrane fouling when large amounts of submicron colloidal particles were present in the reactor (Sun et al., 2012).

To date, there is a dearth of knowledge regarding the suitability of a MBBR-membrane filtration hybrid system for micropollutant removal. This study aimed to investigate the performance of an MBBR-membrane bioreactor (MBBR-MBR) hybrid system on micropollutant removal and the effectiveness of the MBBR as a pretreatment option for fouling mitigation in MBR. The fouling propensity was investigated based on mixed liquor characteristics, such as soluble microbial products (SMP), extracellular polymeric substances (EPS), zeta potential, and relative hydrophobicity (RH).

6.2 Organic and nutrient removal

The MBBR-MBR system effectively removed DOC (94.7±0.5%) and NH_4-N (84.9±4.5%), are consistent with a previous study by Duan et al. (2013). However, unstable TN reduction (45.2±8.8%) and low PO_4-P elimination (34.9±4.0%) were observed during the experimental period. It was noted that organic carbon and nutrients were principally removed by the MBBR, while the subsequent MBR process offered very limited further elimination. Compared to the MBBR-MBR, the CMBR was less efficient for NH_4-N (56.1±3.9%) and TN (21.9±4.6%) removal, but showed similar DOC removal (94.7±1.6%) and slightly higher PO_4-P elimination (45.1±6.8%) due to the biomass growth.

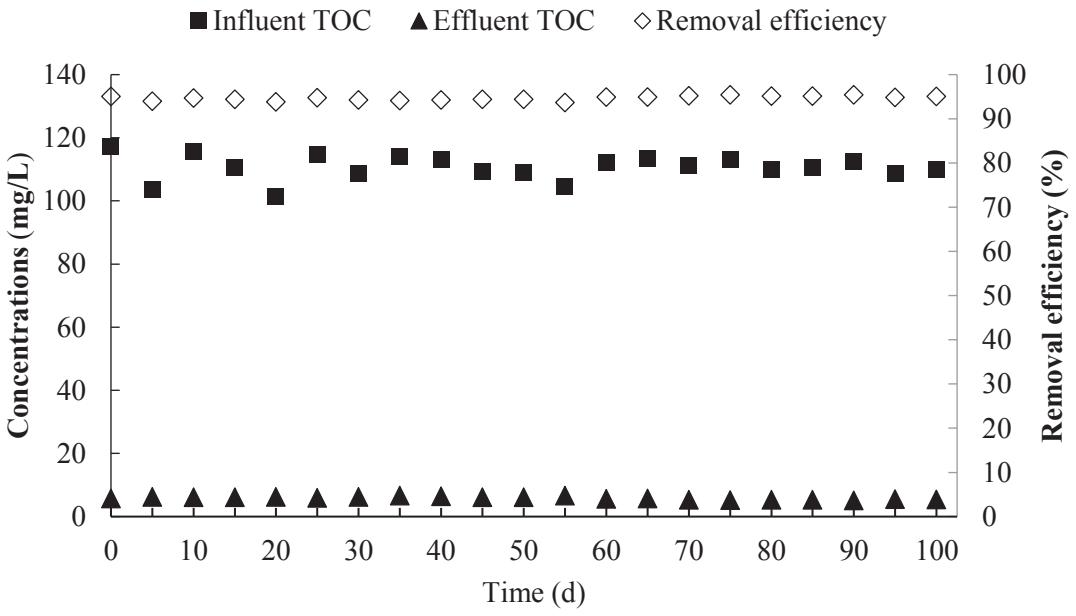

Figure 6.1 TOC removal in the MBBR-MBR system (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

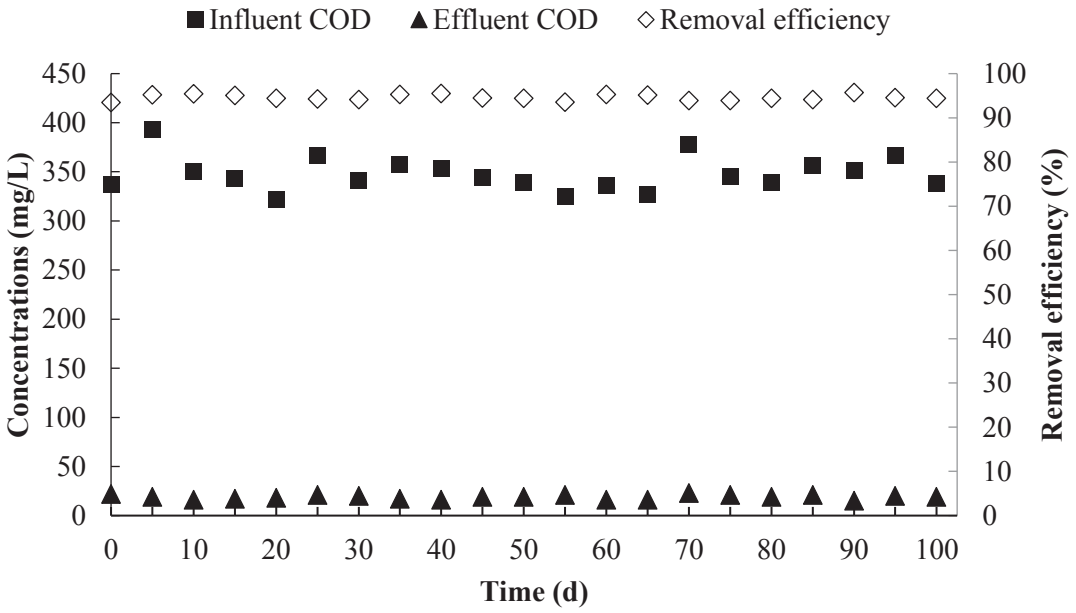

Figure 6.2 COD removal in the MBBR-MBR system (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

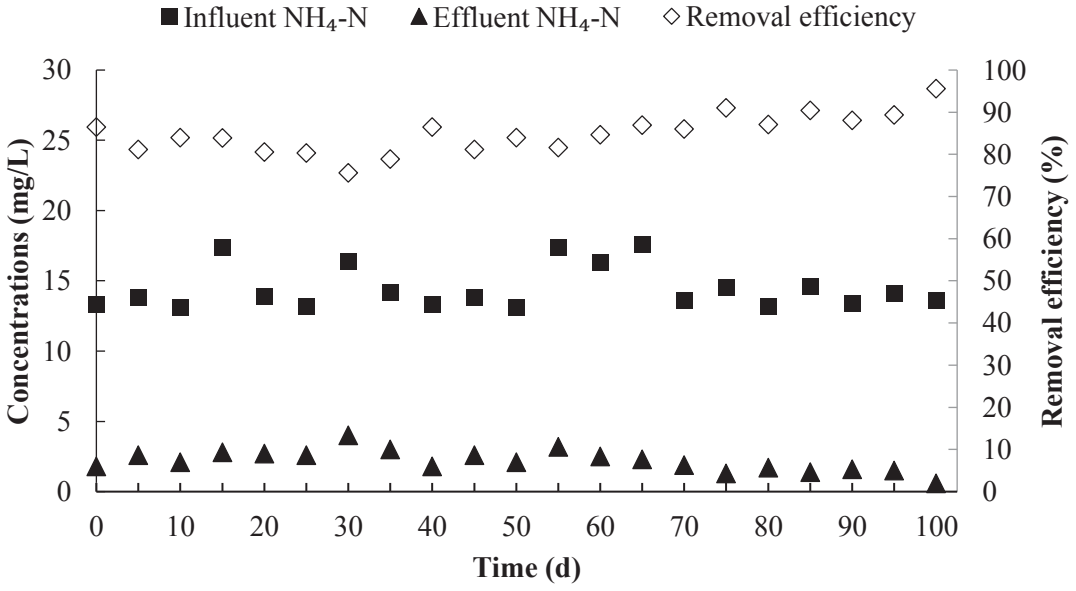

Figure 6.3 NH_4-N removal in the MBBR-MBR system (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

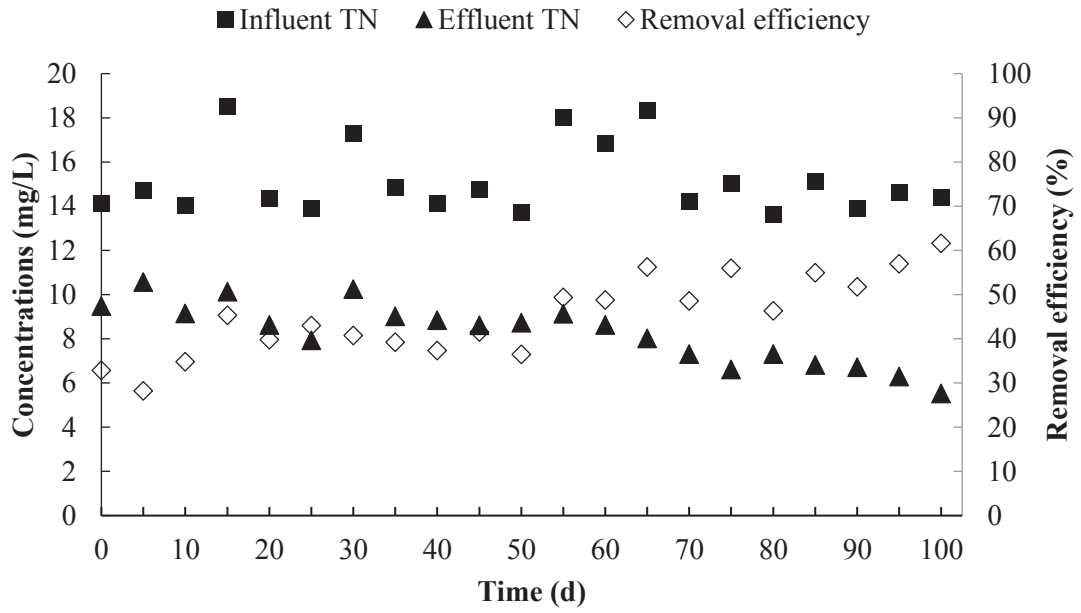

Figure 6.4 TN removal in the MBBR-MBR system (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

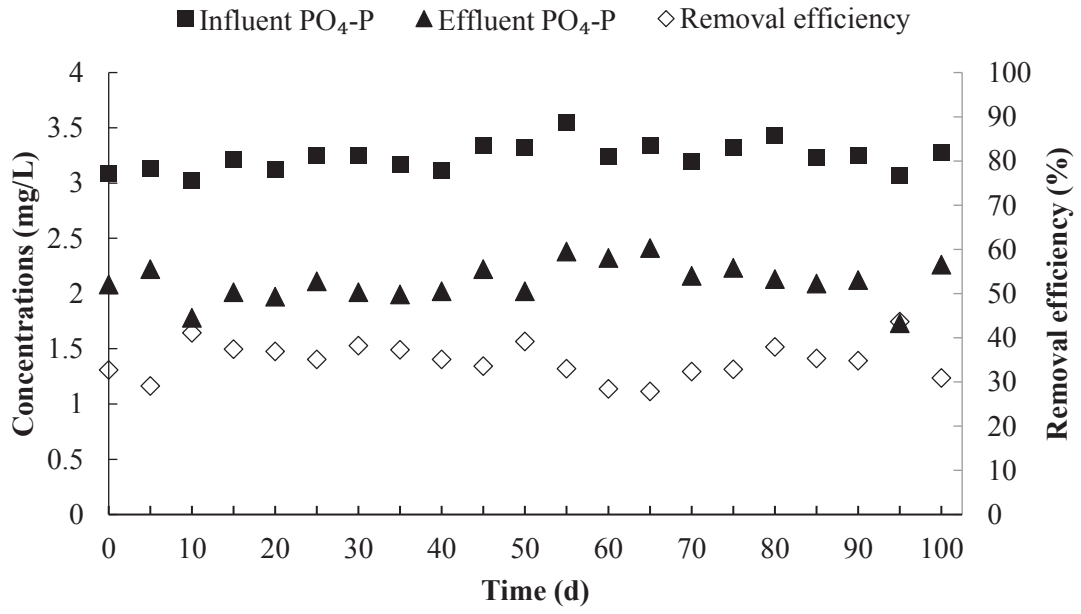

Figure 6.5 PO_4-P removal in the MBBR-MBR system (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h; MBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

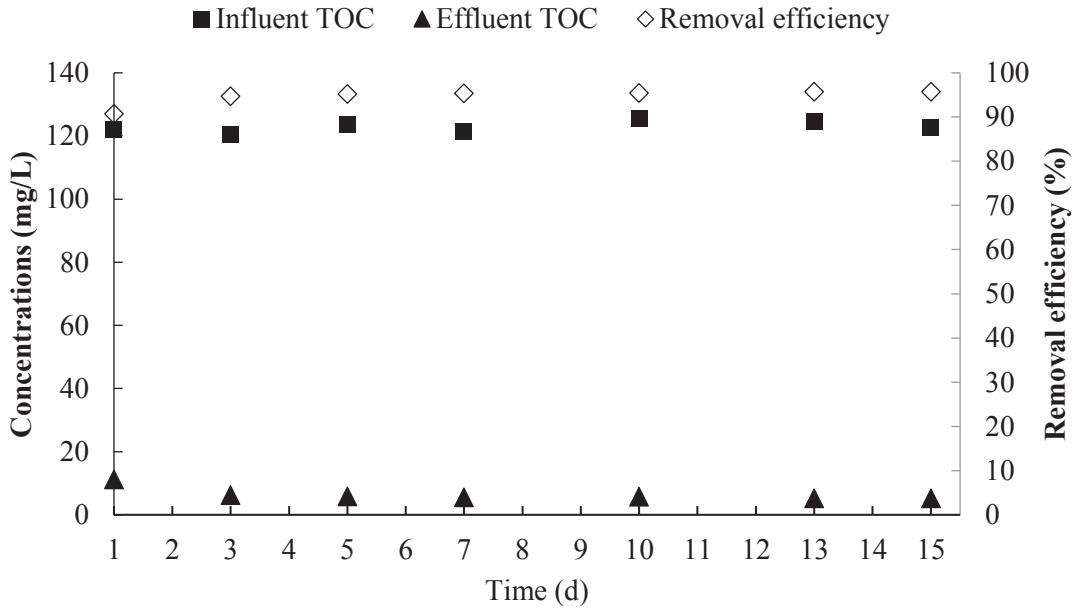

Figure 6.6 TOC removal in the CMBR system (conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

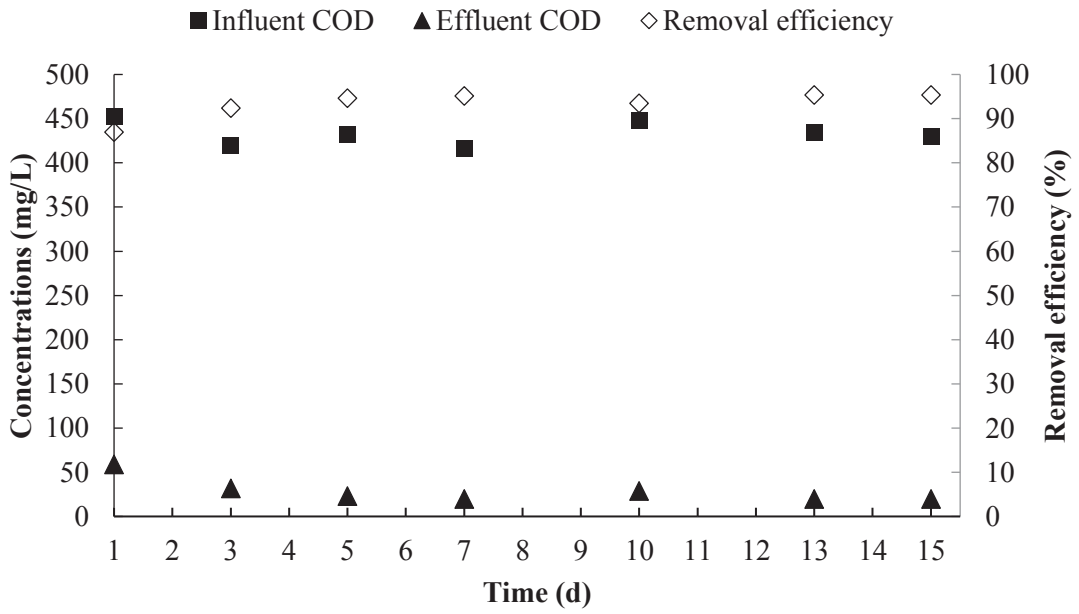

Figure 6.7 COD removal in the CMBR system (conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

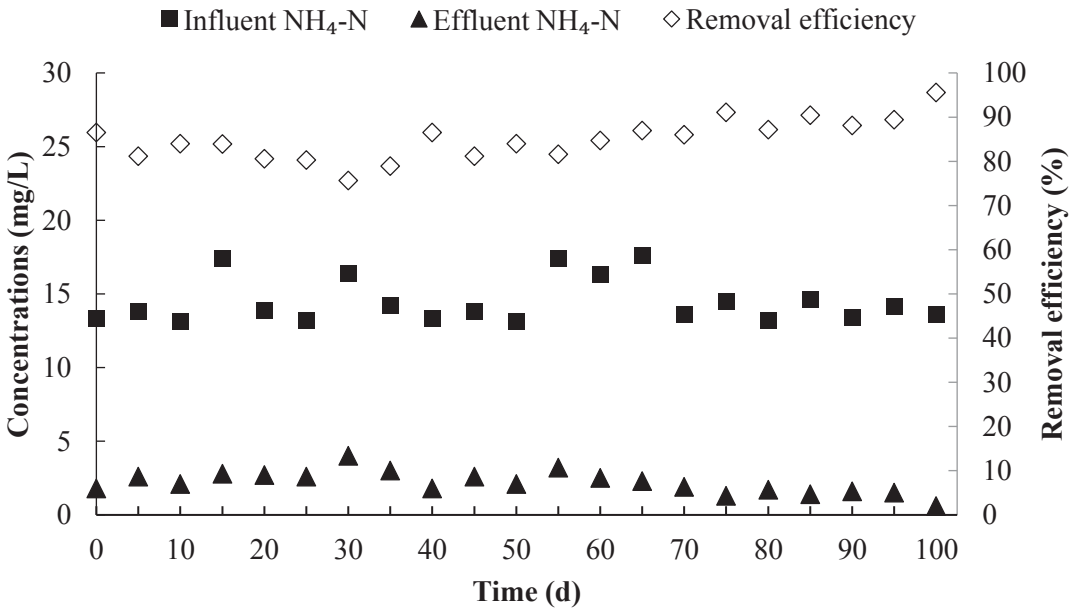

Figure 6.8 NH_4-N removal in the CMBR system (conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

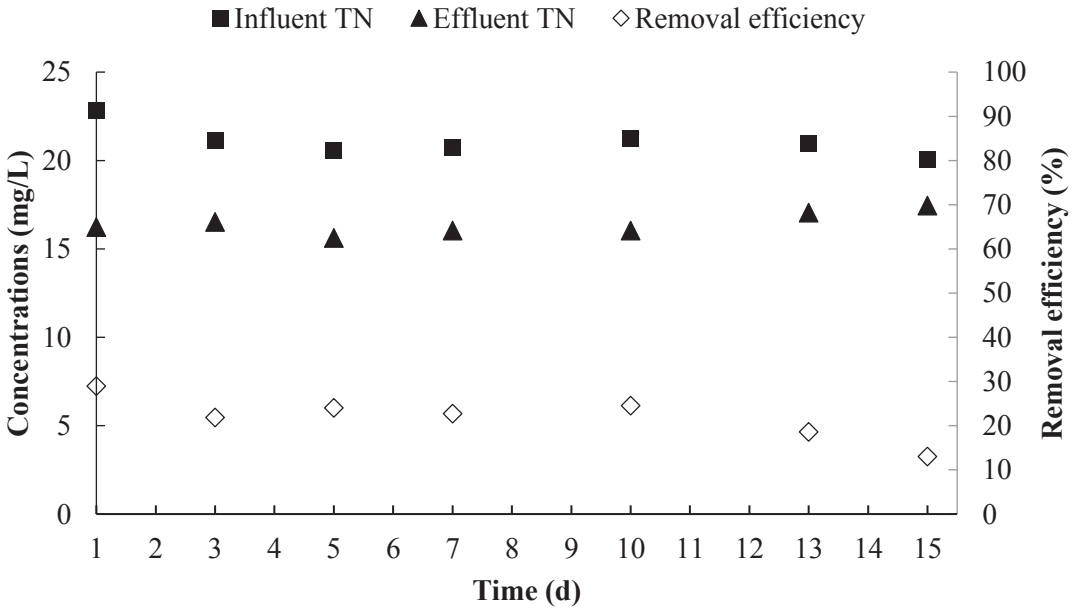

Figure 6.9 TN removal in the CMBR system (conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

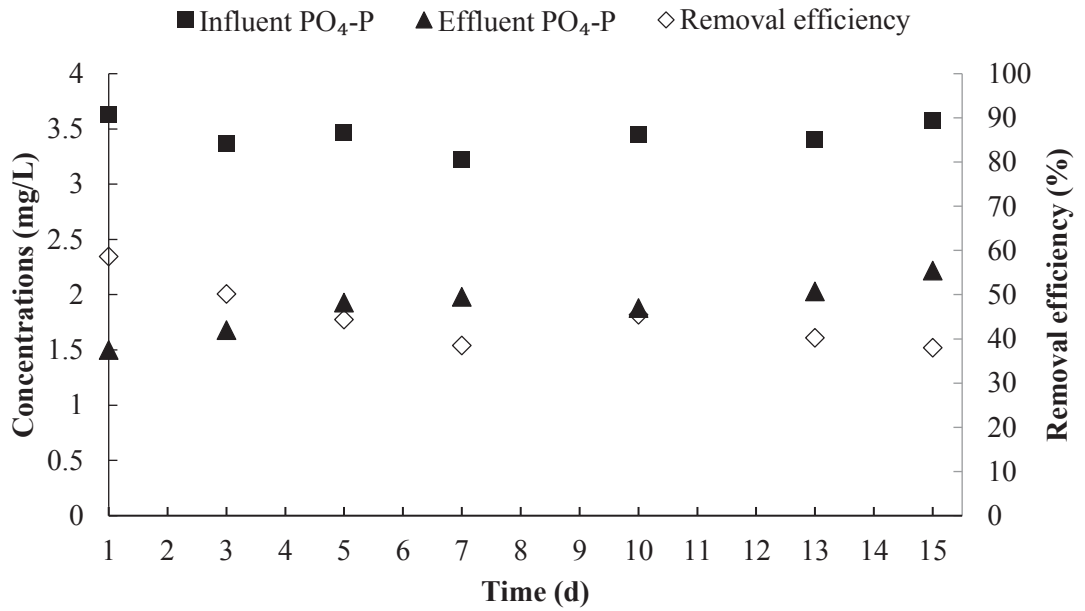

Figure 6.10 PO_4-P removal in the CMBR system (conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞).

The MLSS and MLVSS concentrations in the MBBR tank were very low (0.05–0.13 and 0.04–0.11 g/L, respectively), as the suspended solids were continuously washed away or adsorbed on the sponge cubes and no sludge was recycled back to the MBBR. Regarding the MBR unit, the initial MLSS and MLVSS were 0.06 and 0.05 g/L, respectively, and both showed gradual growth during the operation, reaching 0.91 and 0.89 g/L at the end of the study. As for the CMBR, the MLSS and MLVSS increased from 2.27 and 2.05 g/L to 7.38 and 7.08 g/L, respectively, during operation period.

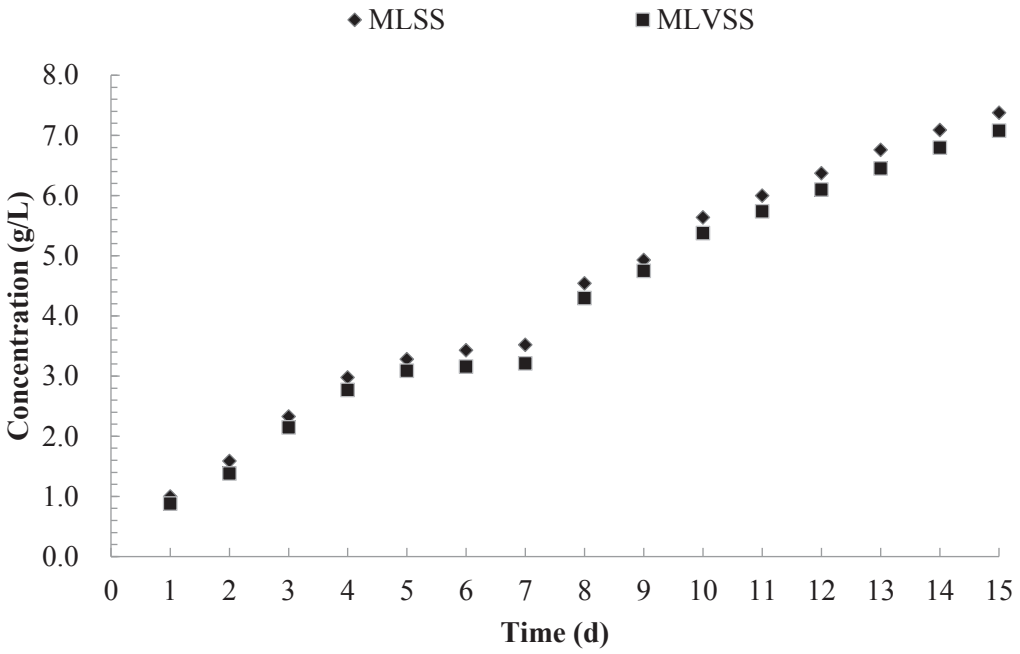

Figure 6.11 Variations of MLSS and MLVSS concentrations in the CMBR.

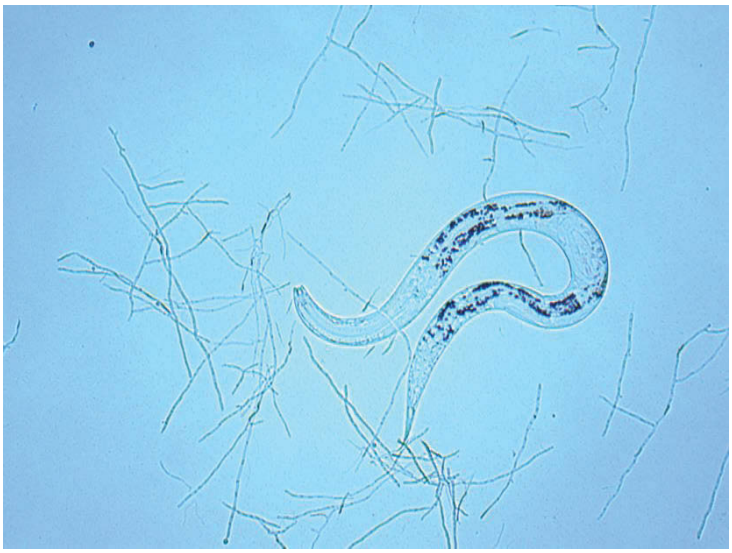

Figure 6.12 Nematodes (×10) in the CMBR.

6.3 Removal of selected micropollutants

During the MBBR-MBR treatment, the compound-specific removal efficiencies (shown in Fig. 6.13) varied significantly, ranging from 25.5 to 99.5%. Although a clear correlation between removal efficiencies and the effective octanol-water partition coefficients (Log D) of the selected micorpollutants could not be obtained, it was found that all hydrophobic compounds (log D>3.2) were effectively removed (>80%). One possible reason is that the attached growth pattern in the MBBR could enhance the retention of the biomass, thus promoting the enrichment of slow growing microorganisms and the formation of a diverse biocoenosis. In general, micropollutant removal by the MBBR-MBR was higher than that by the CMBR. Moreover, the CMBR was less effective for some micropollutants. Particularly, the removals of carbamazepine, ketoprofen, primidone, estriol and bisphenol A were lowered by 16.2, 30.1, 31.9, 34.5, and 39.9 % respectively during the CMBR treatment.

As complex synthetic substances, pharmaceuticals are classified into various groups with highly variable physico-chemical properties. As the selected pharmaceuticals (PPCPs) in this study generally displayed low hydrophobicity (log D < 2.5), biodegradation (rather than sorption) was the major removal pathway of these compounds (Luo et al., 2014a). The removal efficiency of these compounds was much more strongly affected by their intrinsic biodegradability when log D value was below 3.2 (Tadkaew et al., 2011). One possible reason is that these micropollutants have diverse molecular structure and functional groups (Wijekoon et al., 2013). Most of the investigated PPCPs were efficiently removal (> 80%) by the MBBR-MBR, except carbamazepine (25.53±7.83%), metroidazole (42.39±7.86%), and diclofenac (44.19±6.21%). This could be ascribed to the inclusion of strong electron donating (readily biodegradable) functional groups (e.g., – OH) in these compounds. On the other hand, the low removal of carbamazepine could be attributed to its low hydrophobicity and the occurrence of strong electron donating groups such as amide and chloride in its molecular structure (Wijekoon et al., 2013). The formation of biocoenosis could be different in various systems (namely MBBR-MBR and CMBR), resulting in the differences in removal efficiencies of micropollutants.

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 the both systems, two pesticides displayed different removals. Fenoprop exhibited inefficient elimination (25.52±16.68% in the MBBR-MBR hybrid system and 24.4±3.3% in the CMBR), whereas pentachlorophenol experienced much higher removal (84.5±4.99% in the MBBR-MBR hybrid system and 80.9±1.7% in the CMBR). The poor removal of fenoprop could be attributed to its low hydrophobicity (log D = –0.13) and recalcitrance (Hai et al., 2011).

Regarding industrial chemicals, the observed removals were generally high (>70%) in the MBBR-MBR hybrid system, especially for 4-n-nonylphenol (95.68±2.69%), as these compounds are commonly characterized by high hydrophobicity (log D>3.2). The less removals of 4-tert-butylphenol (71.38±8.87%), bisphenol A (89.83±4.03%) and 4-tert-octylphenol (87±8.03%) could be due to the lower log D of these compounds (3.40, 3.64 and 5.18, respectively) in comparison with 4-n-nonylphenol (6.14). In the CMBR, the trend of removals was similar, but the efficiencies were considerably lower than those of in the MBBR-MBR.

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-MBR with high nitrification efficiency. As the synthetic hormone 17α-ethinylestradiol was more resistant to biodegradation, it exhibited slight lower removal (76.2±3.04%) as compared with 17β-estradiol, β-estradiol 17-acetate and estriol (98.17±0.83%, 97.81±1.04% and 97.24±2.91%, respectively).

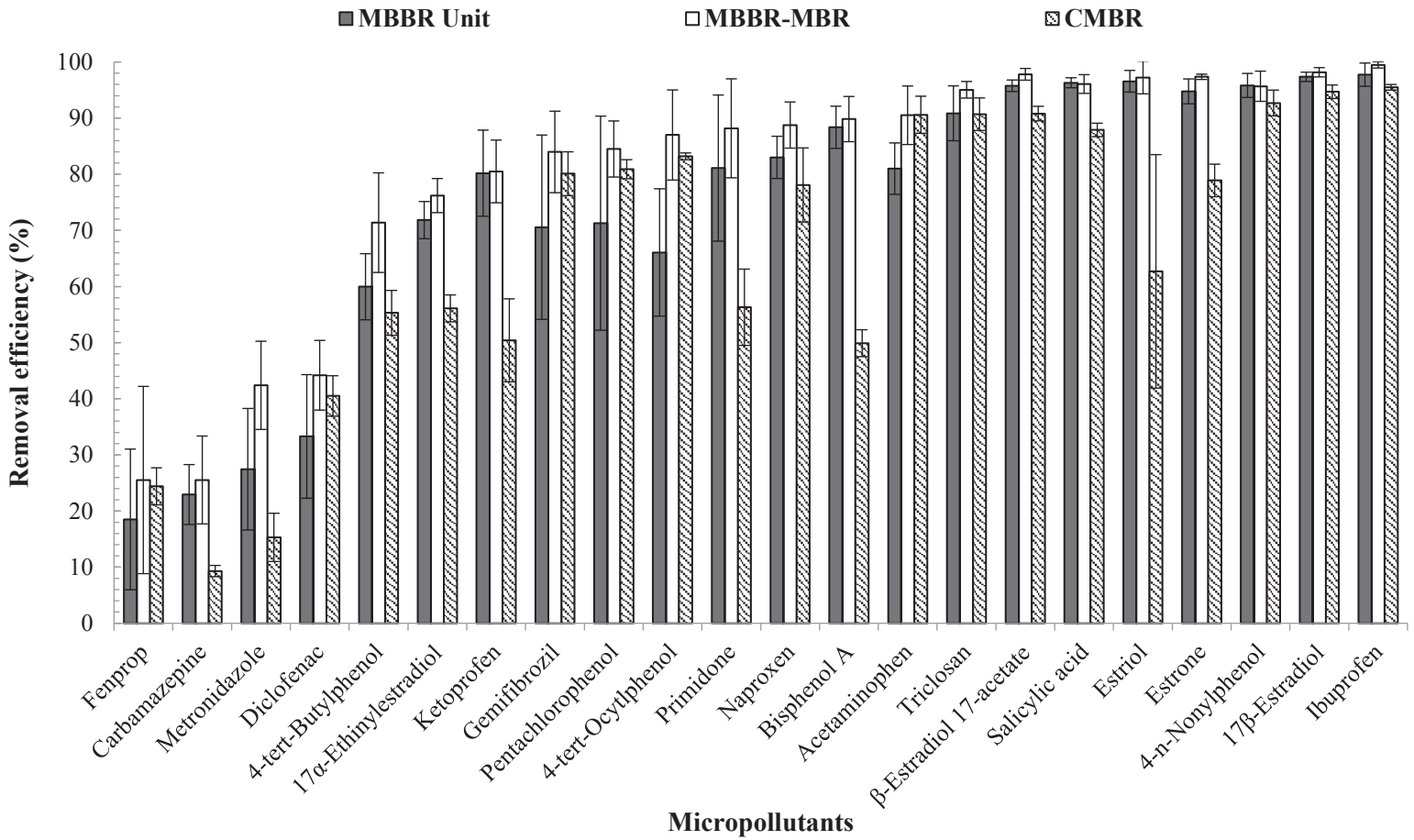

Figure 6.13 Micropollutant removals in the CMBR and MBBR-MBR. An error bar represents the standard deviation over the experimental period (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h; CMBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞)

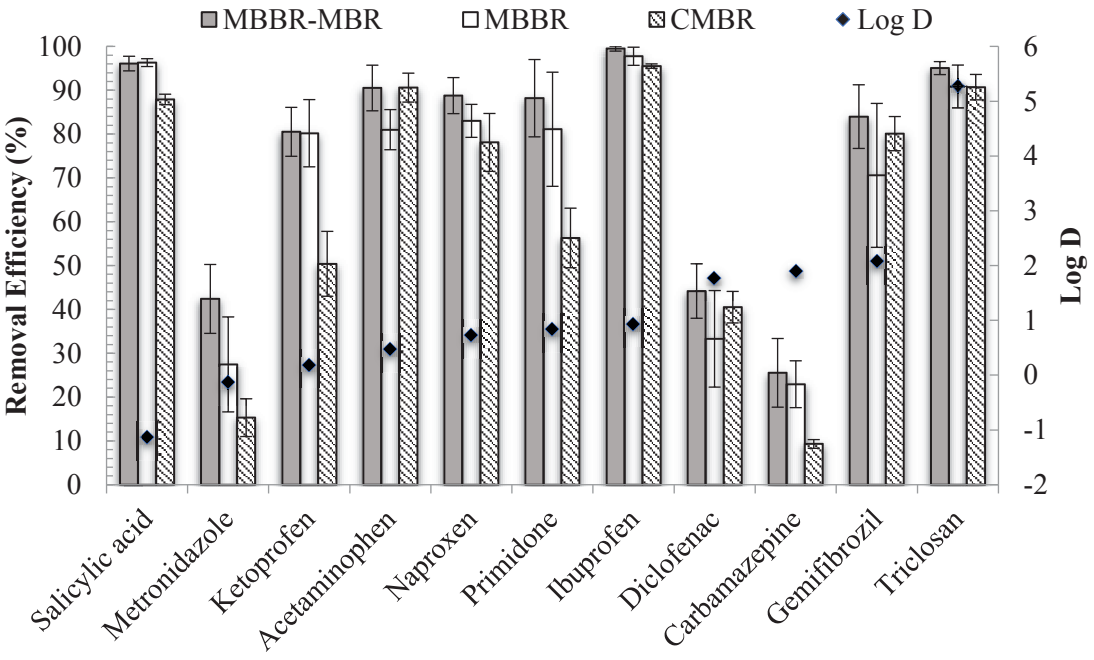

Figure 6.14 Relationship of Log D and pharmaceutical removals in the CMBR and MBBR-MBR. An error bar represents the standard deviation over the experimental period (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h; CMBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞)

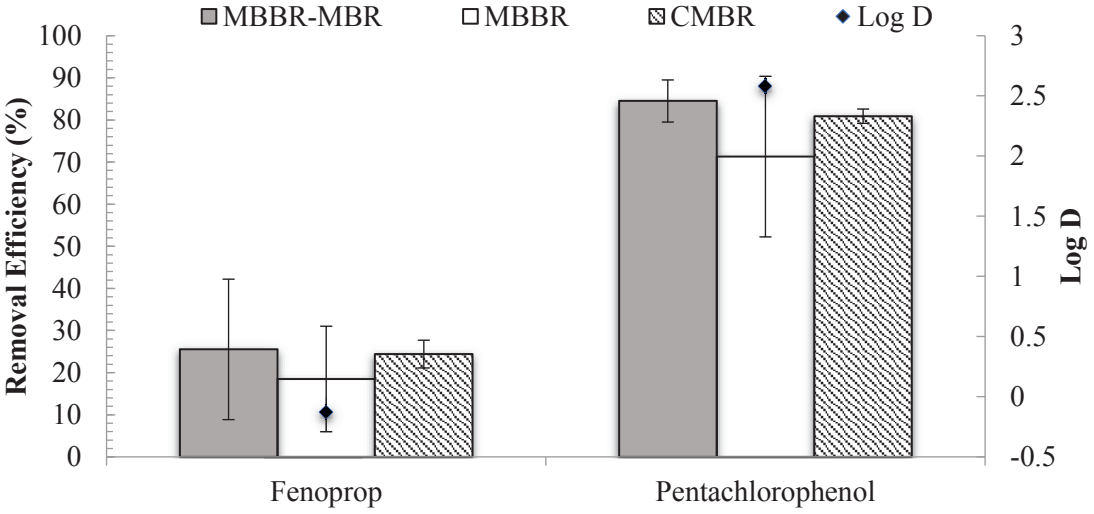

Figure 6.15 Relationship of Log D and pesticides removals in the CMBR and MBBR-MBR. An error bar represents the standard deviation over the experimental period (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h; CMBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞)

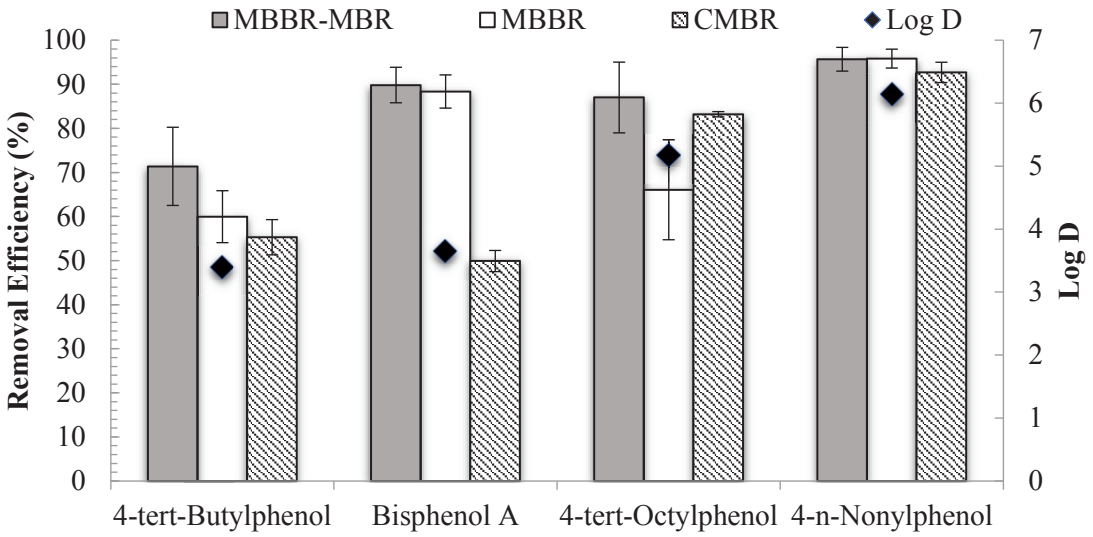

Figure 6.16 Relationship of Log D and industrial chemicals removals in the CMBR and MBBR-MBR. An error bar represents the standard deviation over the experimental period (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h; CMBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞)

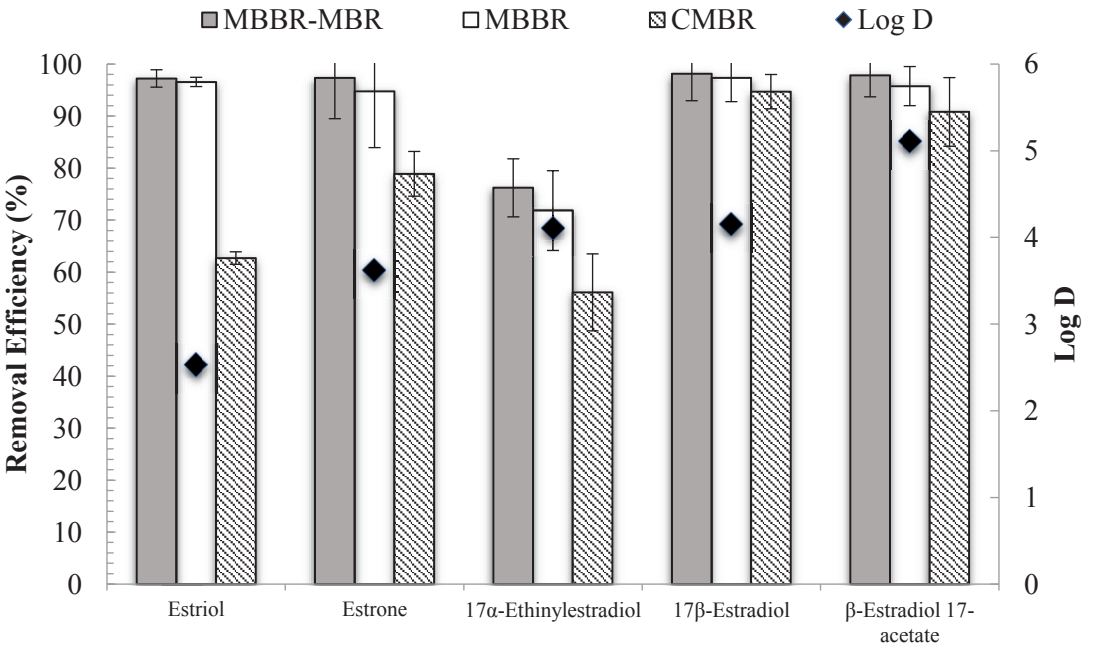

Figure 6.17 Relationship of Log D and estrogenic hormones removals in the CMBR and MBBR-MBR. An error bar represents the standard deviation over the experimental period (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h; CMBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞)

To gain further insight into the fate of micropollutants during the MBBR-MBR treatment, a mass balance of the investigated compounds was evaluated (Eq. 1), taking into account the removal pathways of biodegradation and sorption in the MBBR unit, and total removal in the MBR unit.

$$L_{inf} = L_{s,MBBR} + L_{b,MBBR} + L_{MBR} + L_{eff} \quad (6.1)$$

where L_{inf} is the influent load of micropollutants over the experimental period (ng), $L_{s,MBBR}$ and $L_{b,MBBR}$ are the amount of a compound removed via sorption (ng) and biodegradation (ng), respectively, in the MBBR unit; L_{MBR} is the amount of a compound removed in the MBR (ng); L_{eff} is the amount of a compound released from the system (ng).

The calculation of the sorption (Eq. 2) and biodegradation (Eq. 3) in MBBR was carried out according to Luo et al. (2014).

$$L_{s,MBBR} = Q \cdot MLSS_{MBBR} \cdot C_{ss} \cdot T + \Delta SS \cdot C_{sa} \quad (6.2)$$

$$L_{b,MBBR} = \left(L_{inf} - L_{eff,MBBR}\right) - L_{s,MBBR} \quad (6.3)$$

where Q is the flow rate of the MBBR-SMBR system (L/day); $MLSS_{MBBR}$ is mixed liquor suspended biosolids concentration in the MBBR (g/L); C_{ss} is the concentration of a compound on the suspended biosolids (ng/g); T is the duration of the experimental period (days); ΔSS is the increased amount of attached biosolids (g); C_{sa} is the concentration of a compound on the attached biosolids (ng/g); $L_{eff, MBBR}$ is the amount of a compound released from the MBBR unit (ng).

Regarding the calculation for the removal in the MBR unit, the following equation was used:

$$L_{MBR} = L_{eff,MBBR} - L_{eff} \quad (6.4)$$

Fig. 6.18 illustrates the fate of the selected compounds in the MBBR-MBR system. The results show that biodegradation in the MBBR accounted for the major proportion of the micropollutant removal, which are consistent with findings from previous studies involving both MBR (Wijekoon et al., 2013) and MBBR (Luo et al., 2014). Compared to biodegradation, sorption was a much less significant removal pathway for most micropollutants, except some refractory compounds (fenprop, diclofenac, carbamazepine and pentachlorophenol) and some hydrophobic compounds (4-tert-butylphenol and 4-tert-octylphenol). The impact of MBR removal was minimal in most cases. This was attributable to the low MLSS concentration and the large pore size (0.2 μm; two orders of magnitude larger than the molecular sizes of micropollutants) of the MF membrane used in this study. Nevertheless, the MBR unit was able to complement the removal of a few compounds including 4-tert-octylphenol (21.1%), metronidazole (14.9%), gemfibrozil (13.0%), and pentachlorophenol (13.0%). Generally, the removal in the MBR can be achieved through charge repulsion, adsorption onto membrane surface, sorption diffusion, solute-solute interactions and fouling layer interactions (Schäfer et al. 2011). In addition, biological degradation in the MBR unit might be helpful in the removal of the compounds that were less likely to interact with particulate matter and membrane surface, such as gemfibrozil and diclofenac.

The influence of hydrophobicity on the behaviour of micropollutants removal in the MBBR-MBR system was also evaluated. Although Rattier et al. (2014) indicated that higher affinity for solids may lead to less efficient micropollutant uptake and biodegradation, the biological transformation of the hydrophobic micropollutants (Log D > 3.2) in this study was significant (80.8% on average), compared to 57.5% for the less hydrophobic compounds. The results are also in good agreement with a study conducted by Tadkeaw et al. (2011) who suggested that hydrophobic micropollutants could adsorb onto the sludge phase and thus prolong their retention time in the reactor for subsequent biodegradation. As sorption values reported in Fig. 6.18 only present the residual micropollutant in the sludge phase, it is noteworthy that the most hydrophobic micropollutant, 4-n-nonyl phenol exhibited the highest biodegradability (96.8%) as well as the lowest percentage of sorption in MBBR (0.9%).

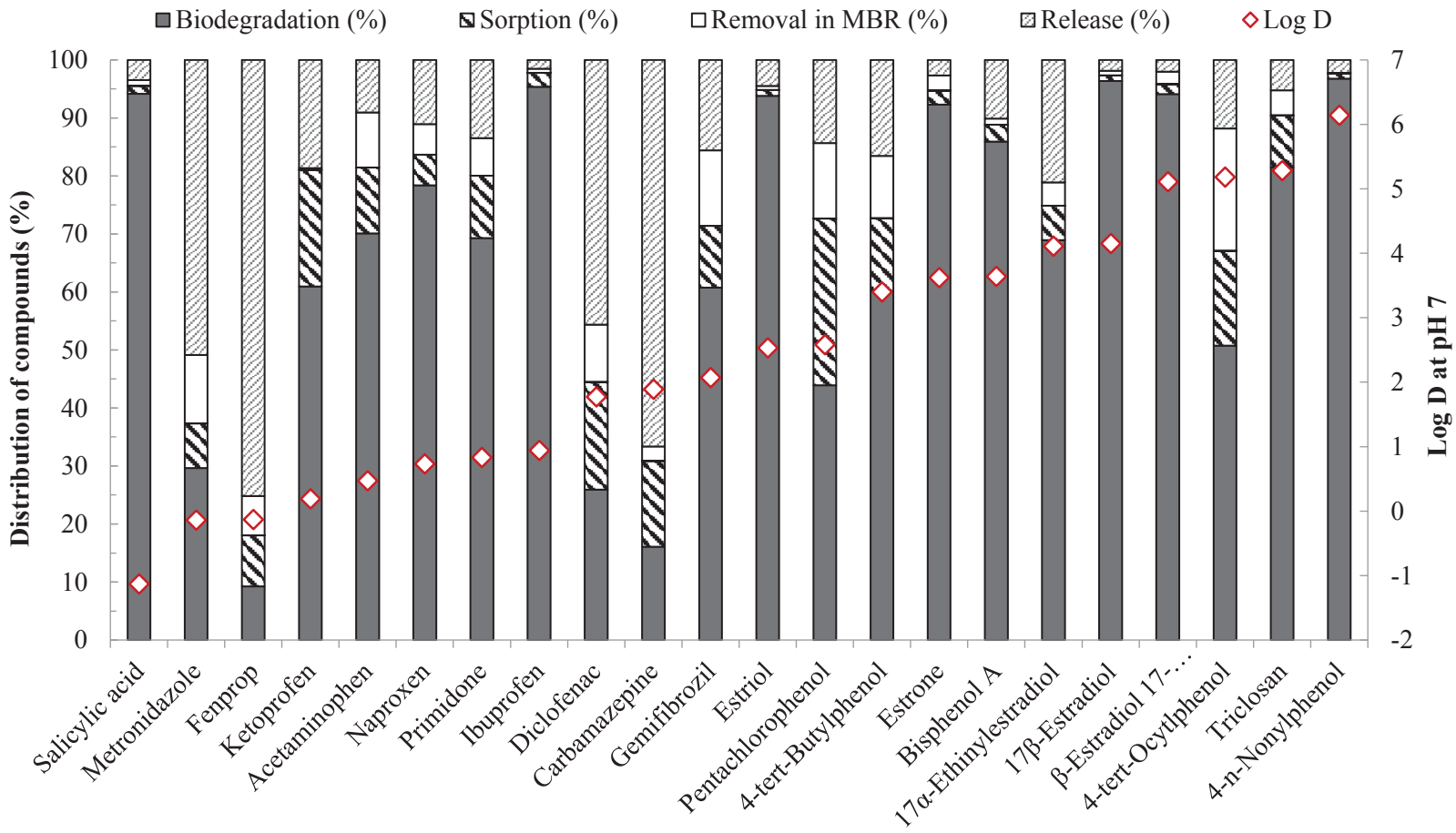

Figure 6.18 Fate of the studied micropollutants in the hybrid MBBR-MBR system
(MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h;
CMBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞)

6.4 Membrane fouling analysis

Fig. 6.19 presents the membrane fouling profile of the MBBR-MBR and the CMBR systems, indicated by TMP. The TMP development in the MBBR-MBR was much less significant (reached up to 35 kPa in 89 days of operation) than that in the CMBR system (reached up to 38.5 kPa within 16 days). Therefore, it is evident that the use of MBBR as the pre-treatment can lower the fouling propensity and improve the filtration performance of MBR.

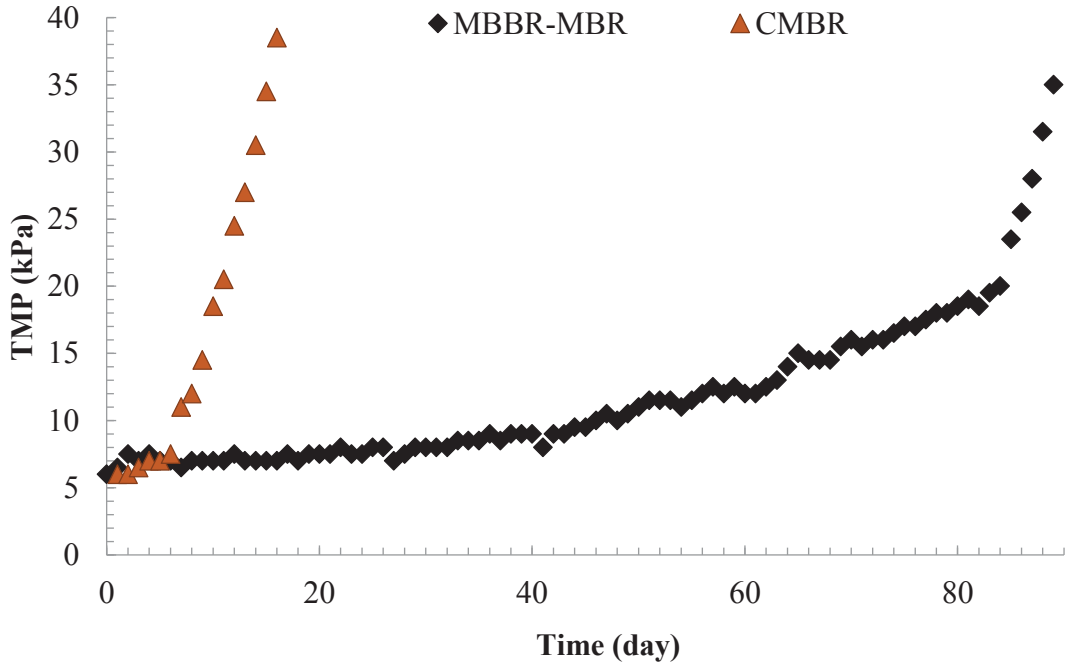

Fig. 6.19 Comparison of TMP profiles between the hybrid MBBR-MBR and the CMBR (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h; CMBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞)

It has been suggested that severe membrane fouling is often a result of organics accumulation on or in the membrane as bound EPS or SMP (Guo et al., 2012; Meng et al., 2009). Fig. 6.16 compares the EPS in activated sludge and SMP in mixed liquor concentrations at different TMPs in both systems. It is clear that EPS concentrations of both systems remained increasing within the time frame, which could be a result of MLSS build-up during the operation. The EPS concentrations peaked at 16.24 mg/L (MBBR-MBR) and 19.53 mg/L (CMBR) at the end when severe membrane fouling occurred. By contrast, the SMP concentrations showed a

wide disparity between the MBBR-MBR and CMBR, with the former ranging from 4.02 to 6.32 mg/L and the latter between 21.78 and 33.04 mg/L. Since the measured concentrations of EPS were similar in the two systems, the SMP levels could be accounted for the considerably different fouling profiles of the two systems. Duan et al. (2013) also reported that the use of moving bed media could alter the composition of EPS and SMP (e.g., different O–H bonds in hydroxyl functional groups, and less polysaccharides and lipids), as well as produce a suspension low in fouling propensity.

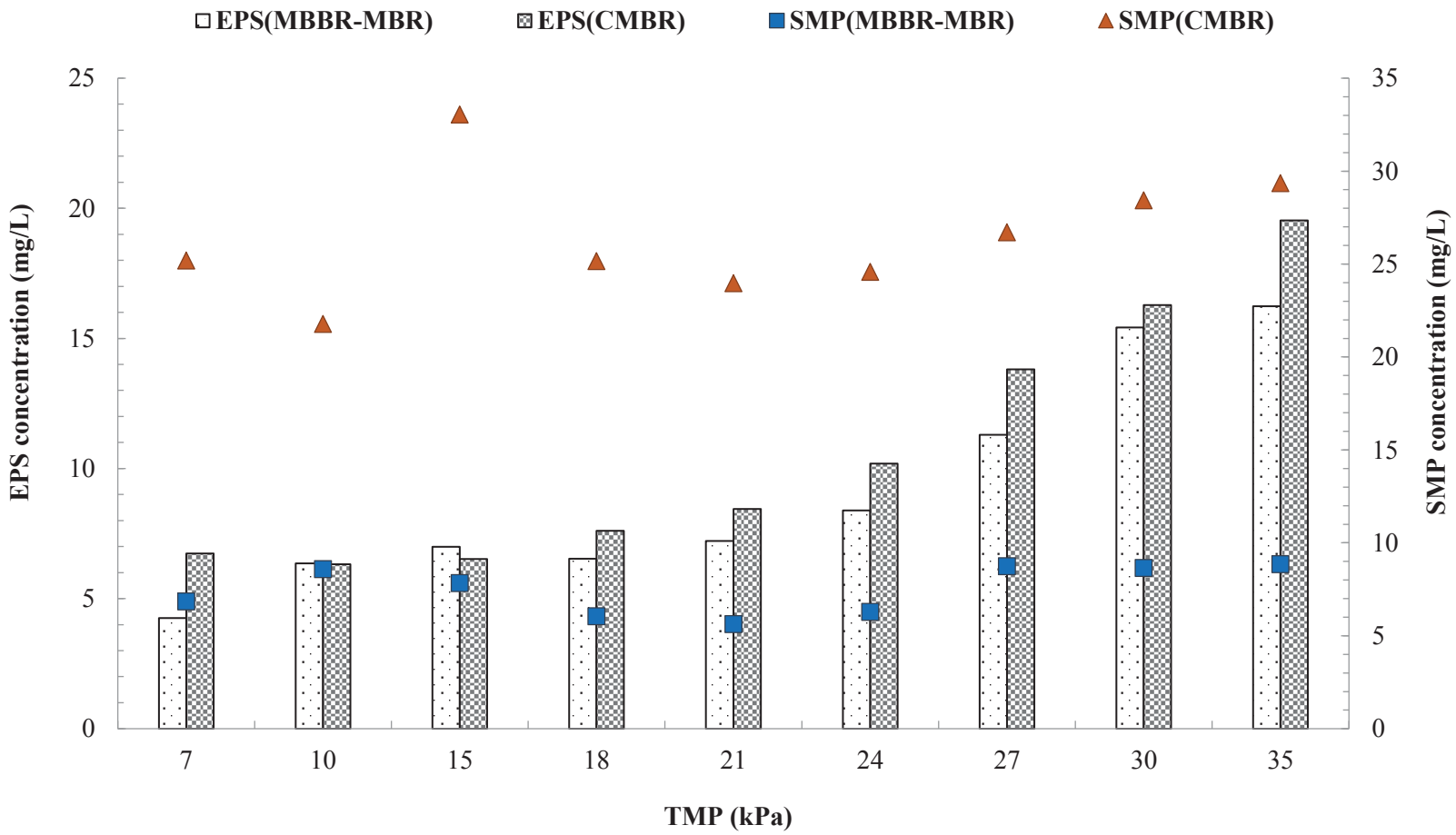

Figure 6.20 Comparison of EPS and SMP values between the hybrid MBBR-MBR and the CMBR (MBBR conditions: aeration rate = 4.5 L/min, DO = 5.5–6.5 mg/L; HRT = 24h; CMBR conditions: aeration rate = 6 L/min, DO = 6.4–7.6 mg/L; filtration rate = 8.83 L/m^2·h; HRT = 6h; SRT = ∞)

The sludge characteristics (e.g., Zeta potential, hydrophobicity and floc size) also play a role in membrane fouling. The sludge flocs in the MBR unit of the hybrid system showed increased zeta potential (-12.1 to -19.0 mV) and higher RH (75.0 to 83.3%) compared to the sludge in CMBR (Zeta potential: -18.0 to -20.8 mV; RH: 66.0 to 75.5%). According to Ji et al. (2010), increase of zeta potential could neutralise the negative charge on the surface of the floc and form large aggregates, while high RH generally resulted in less interaction between the hydrophobic flocs and the hydrophilic membrane. Sludge particle size distribution analysis confirmed that the floc size of sludge in the MBBR-MBR (15 to 40 μm) was larger than that of CMBR sludge (5 to 30 μm), which also supported the alleviated membrane fouling in the MBBR-MBR.

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:

$$J = \Delta P_T/(\mu \cdot R_t) \quad (6.4)$$

$$R_t = R_m + R_C + R_f \quad (6.5)$$

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 was subjected to physical and chemical cleaning, in order to determine different membrane fouling resistances using the equations given above. Table 6.1 displays the calculated membrane fouling resistances. As shown in the Table, the cake layer resistance contributed the most to the total resistance (76.5% in the MBR unit of MBBR-MBR and 68.8% in the CMBR), while irreversible fouling resistance, pore blocking resistance and membrane resistance were much less significant (1.0, 12.0 and 10.5% in the MBR unit of MBBR-MBR and 1.3, 15.3 and 14.6% in the CMBR, respectively). 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.

Table 6.1 Membrane resistances for different types of fouling.

	MBBR-SMBR		SMBR	
Parameter	Resistance (10^{12}/m)	Percentage (%)	Resistance (10^{12}/m)	Percentage (%)
Clean membrane	1.33	10.5	1.57	14.6
Cake layer	9.63	76.5	7.40	68.8
Pore blocking	1.51	12.0	1.64	15.3
Permanent fouling	0.12	1.0	0.14	1.3
Total resistance	12.59	100	10.75	100

Figure 6.21 Comparison of fouled membrane and after physical and chemical cleaning

6.5 Conclusion

The MBBR-MBR hybrid system could effectively remove most of the studied micropollutants, while the CMBR was less effective for some compounds, such as ketoprofen, carbamazepine, primidone, bisphenol A and estriol. In the MBBR-MBR, biodegradation served as the primary pathway for micropollutant removal, while the contribution of other removal mechanisms was less significant. Regarding membrane performance, the hybrid system showed considerably lower fouling tendency than the CMBR. SMP was found to be the key contributor to the high fouling propensity in CMBR. The results proved that MBBR could be a prospective pretreatment to MBR for micropollutant removal and membrane fouling minimisation.

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Chapter 7

Conclusions and Recommendations

7.1 Conclusions

The thesis investigated the effectiveness of a sponge-based MBBR for the removal of micropollutants at four HRTs (HRT of 24 h, 18 h, 12 h and 6 h). In addition, a hybrid system combining the MBBR with a submerged membrane bioreactor (MBBR-MBR) was also evaluated with respect to micropollutant removal and membrane fouling reduction strategy. Furthermore, a comparative study between the MBBR-MBR and a conventional MBR was also performed to examine the effectiveness of the use of an MBBR as pretreatment to an MBR.

The removal efficiency of the MBBR was comparable with other processes such as activated sludge or MBR). The MBBR appeared to be an effective process for removal of ibuprofen, metronidazole, naproxen, primidone, triclosan, estrone, 17-α ethinylestradiol, 4-n-nonylphenol, 4-tert-octylphenol and fenoprop. In this set of experiment, the optimal HRT was 18h, thus under this condition, further studies could be done to optimise the MBBR system in order to achieve better removal.

The investigated MBBR-MBR demonstrated excellent performance in removing organics, nutrients as well as micropollutants. During the MBBR-MBR treatment, the compound-specific removal efficiencies varied significantly, ranging from 11.0 to 99.5%. However, most compounds were eliminated to large extents (>70%). One possible reason for the high removal efficiency is that the attached growth pattern could enhance the retention of the biomass, thus promoting the enrichment of slow growing microorganisms and the formation of a diverse biocoenosis. According to the result from this experiment, a longer HRT (e.g. HRT of 24 h) can significantly mitigate membrane fouling when compared with a relatively short HRT (e.g. HRT of 6 h). By using an MBBR as a pretreatment to an MBR, it could not only enhance overall organic and nutrient removal, but also prolong the operative time of the MBBR-MBR due to efficient fouling reduction. Therefore, the use of an MBBR as pretreatment to an MBR could be a promising solution to improve the performance of the MBR system.

The MBBR-MBR hybrid system could effectively remove most of the studied micropollutants, while the CMBR was less effective for some compounds, such as ketoprofen, carbamazepine, primidone, bisphenol A and estriol. In the MBBR-MBR, biodegradation served as the primary pathway for micropollutant removal, while the contribution of other removal mechanisms was less significant. Regarding membrane performance, the hybrid system showed considerably lower fouling tendency than the CMBR. SMP was found to be the key contributor to the high fouling propensity in CMBR. The results proved that MBBR could be a prospective pretreatment to MBR for micropollutant removal and membrane fouling minimisation.

7.2 Recommendations for future research

For the MBBR unit, various aspects were found worthy of further research:

1) As nitrifying conditions has considerable influence on micropollutant removal in the MBBR unit, the research on evaluating the correlation between the nitrification capacity of the MBBR and the removal efficiency of micropollutants should be considered.

2) Under different HRTs, the removal of micropollutants can be quite different. It is possibly due to the diverse microbial community and the existence of different sludge characteristics on and inside the sponge cubes. Further studies are required to examine the influence of microbial community on micropollutant removal.

3) As attached growth carrier (sponge in this study) plays a key role in the performance of 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.

For the MBR unit, some aspects were found worthy of further research:

4) In this study, MF membrane was used in the submerged MBR unit, but its impact on micropollutants removal was minimal. In further study, other types of membrane can be used to compare the effectiveness of removing micropollutants and membrane fouling behaviours.

5) The optimisation of the operation conditions of the integrated MBBR-MBR to achieve simultaneous micropollutant removal and fouling control needs further investigation.

For other factors, the following issues were found worthy of further research:

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

7) Some compounds (e.g. carbamazepine, metronidazole, fenoprop) were poorly treated under all the examined conditions in this study. It may be interesting to develop removal strategies coupling MBBR with other treatment process(es) for such compounds.

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Publications Related to This Research

Accepted

Luo Y, Jiang Q, Ngo H H, et al. Evaluation of micropollutant removal and fouling reduction in a hybrid moving bed biofilm reactor–membrane bioreactor system. Bioresource technology, 2015, 191: 355-359.

In preparation

Jiang Q, Guo W, Ngo H H, Nghiem LD, Hai FI, Kang J, etc. Removal of Micropollutants in an Moving Bed Biofilm Reactor (MBBR) at Different HRTs.