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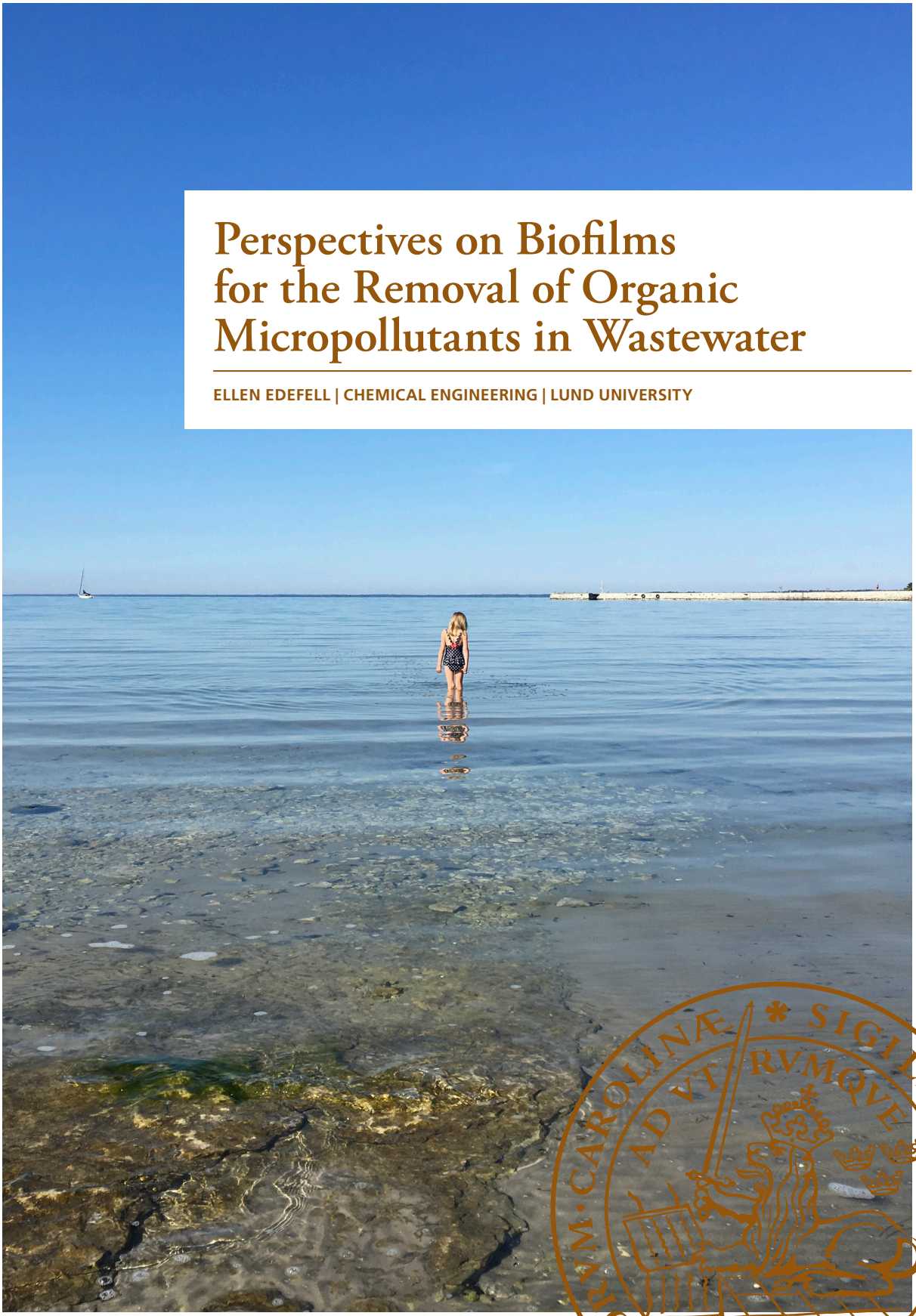

Perspectives on Biofilms for the Removal of Organic Micropollutants in Wastewater

Ellen Edefell

LUND
UNIVERSITY

DOCTORAL DISSERTATION

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Title and subtitle

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Abstract

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The results of the first part showed that additional biological treatment in an innovative process design utilizing a moving bed biofilm reactor (MBBR) increased the degradation rate of several micropollutants. However, further process development is needed to achieve efficient removal of a wide range of micropollutants in full-scale applications at WWTPs.

The results of the second part showed that micropollutants were primarily removed by ozonation when combined with post-treatment in an MBBR. A group of N-oxide transformation products was formed during ozonation and remained stable throughout the MBBR post-treatment. Furthermore, when adding powered activated carbon (PAC) in a nitrifying MBBR, the micropollutants were removed by adsorption onto the PAC, and the biological nitrification was uninhibited by the addition of PAC. Finally, adsorption profiles of micropollutants in a granular activated carbon (GAC) filter were obtained and the biofilm that developed in the filter was able to degrade certain micropollutants such as naproxen, sulfamethoxazole, and diclofenac.

Key words

Biofilm, organic micropollutants, micropollutants, pharmaceuticals, biological degradation, moving bed biofilm reactor, MBBR, ozonation, activated carbon, powdered activated carbon, PAC, granular activated carbon, GAC, wastewater, wastewater treatment

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Bildning är icke vad vi lärt,
utan vad vi har kvar,
nu när vi glömt allt vi lärt
- Ellen Key

Preface

This dissertation is the result of an industrial PhD project carried out in collaboration between Sweden Water Research AB and the Water and Environmental Engineering Group at the Department of Chemical Engineering at Lund University. The research was mainly conducted within two projects: BONUS CLEANWATER and LESS IS MORE. BONUS CLEANWATER received funding from BONUS (Art. 185), funded jointly by the EU and Innovation Fund Denmark, Sweden's Innovation Agency VINNOVA, and the German Ministry for Education and Science (BMBF). LESS IS MORE received funding from the Interreg South Baltic Programme 2014-2020 through the European Regional Development Fund, and from the Swedish Agency for Marine and Water Management. Part of the research was also funded by Svenskt Vatten och Utveckling, Kalmar Vatten AB, and the Swedish Agency for Marine and Water Management (appropriation 1:11 Measures for Sea and Aquatic Environment).

This doctoral dissertation is based on a number of studies on wastewater treatment for the removal of organic micropollutants. The work included pilot-scale studies and lab-scale experiments with various technologies, such as moving bed biofilm reactors (MBBR), ozonation, and powdered and granular activated carbon (PAC and GAC).

Acknowledgments

Some people say that PhD studies can be a lonely journey. My journey has never been lonely, despite endless hours working alone. I have always had the support of the people around me, and for that I am infinitely grateful.

To my supervisors, I have learned so much from you over the years. I want to thank Michael Cimbritz, for always taking the time whenever needed and for believing in me; Per Falås, for the endless devotion, time, and support; and both of you for our late afternoon talks and laughter about work, research, and life in general; Marinette Hagman, for making my industrial PhD project possible; Ola Svahn, for encouraging me to do what I want.

To my colleagues in the Water and Environmental Engineering Group, in good times and bad: thank you for letting me be part of your journeys as well. Gertrud Persson who taught me so much, and who looked out for my health when I didn't; Maja Ekblad who introduced me to life as a PhD student; Mirjam Victorin whose energy and laughter lifted my spirits; and all my colleagues at the Department of Chemical Engineering and Sweden Water Research, for insightful discussions around the coffee tables.

To Sweden Water Research for giving me perspectives as an industrial PhD student and a platform to communicate with the wastewater world outside academia. Kai Bester, for lively discussions and for never saying no to samples. My partners at AnoxKaldnes for their dedication in the large MBBR pilot plant. The staff at Lundåkra wastewater treatment plant (WWTP), Kalmar WWTP, and Sjölunda WWTP, for their help with the pilot plants. All my co-authors, for our discovered insights and for your trust in me.

Last, but not least, my family. Thank you for constantly reminding me to have a reasonable work–life balance. To Rasmus for being the strongest pillar in my life, my biggest supporter, and for always believing in me. Till Minna och Vilma, för att ni gör mig till en bättre människa. Jag växer tillsammans med er. Tack för att ni, i prinsessklänningar, väntade tålmodigt utanför piloten när jag ”skulle bara”. To my dad's words of wisdom, “Doing a PhD is just like doing a normal job but with a twist at the end”. I have now reached the end.

Abstract

The use of biofilms to improve the removal of organic micropollutants in wastewater treatment plants (WWTPs) has been investigated. The work is divided into two parts. In the first part, the use of biofilms for the biological degradation of micropollutants was investigated. In the second part, micropollutant removal was investigated with biofilm processes in combination with ozonation or activated carbon.

The results of the first part showed that additional biological treatment in an innovative process design utilizing a moving bed biofilm reactor (MBBR) increased the degradation rate of several micropollutants. However, further process development is needed to achieve efficient removal of a wide range of micropollutants in full-scale applications at WWTPs.

The results of the second part showed that micropollutants were primarily removed by ozonation when combined with post-treatment in an MBBR. A group of *N*-oxide transformation products was formed during ozonation and remained stable throughout the MBBR post-treatment. Furthermore, when adding powered activated carbon (PAC) in a nitrifying MBBR, the micropollutants were removed by adsorption onto the PAC, and the biological nitrification was uninhibited by the addition of PAC. Finally, adsorption profiles of micropollutants in a granular activated carbon (GAC) filter were obtained and the biofilm that developed in the filter was able to degrade certain micropollutants such as naproxen, sulfamethoxazole, and diclofenac.

Populärvetenskaplig sammanfattning

Öppna på locket till den svarta lådan

Läkemedelsrester i naturen är ett växande problem som kan begränsas av filter med aktivt kol på våra reningsverk. Genom att öppna på locket till ett filter har jag gjort en resa på djupet och en resa i tiden.

En stor del av de läkemedel som vi konsumerar hamnar i avloppet via vår urin och avföring. Dagens avloppsreningsverk har bara möjlighet att minska utsläppen av en del läkemedelsrester. Majoriteten av ämnena släpps ut i mer eller mindre oförändrad koncentration. I våra vattendrag kan läkemedelsresterna störa ekosystemen genom att bland annat påverka beteendet och könsfördelningen hos fiskar.

För att minska utsläppen kan vi använda filter med aktivt kol. Läkemedelsresterna fastnar på det aktiva kolet ungefär på samma sätt som vatten sugs upp i en tvättsvamp. Kolfilter har länge betraktats som svarta lådor, inte bara för att kolet bokstavligt talat är kolsvart, utan för att vi egentligen inte vet vad som händer i filtret. Min forskning har lyckats öppna lite på locket till den svarta lådan.

Vi har sett att kolfilter kan användas som ett arkiv. Vi har kunnat visa att tillfälliga utsläpp av bekämpningsmedlet imidakloprid speglas av förhöjda koncentrationer i kolet. Detta gör det möjlig att konstatera misstänkta utsläpp i efterhand även om vi missar att ta prov vid själva utsläppstillfället.

Vi har också kunnat visa var i kolfiltret läkemedelsresterna fastnar och hur detta förändras över tid. Några ämnen bryts ner biologiskt av mikroorganismer som växer i filtret, bland annat det smärtstillande ämnet diklofenak och antibiotikan sulfametoxazol. Vilka effekter den biologiska nedbrytningen har för filtret återstår att se. Vad vi hittade var några svar men framför allt otroliga möjligheter att lära oss mer framöver.

Min forskning har, förutom att djupdyka i kolfilter, handlat om olika tekniker för att minska utsläppen av läkemedelsrester från avloppsreningsverk. Biologisk rening har varit ett genomgående tema men är inte tillräcklig. Därför har jag undersökt biologisk rening i kombinationer med effektivare tekniker som ozonering och aktivt kol. Med ökad förståelse av de biologiska processernas möjligheter och kapacitet kan vi designa och driva processer för att utnyttja deras fulla potential.

List of publications

This dissertation is based on the publications listed below, which will be referred to throughout this dissertation by their Roman numerals.

Paper I **Edefell, E.,** Falås, P., Torresi, E., Hagman, M., Cimbritz, M., Bester, K., Christensson, M. Promoting the degradation of organic micropollutants in tertiary moving bed biofilm reactors by controlling growth and redox conditions. *Journal of Hazardous Materials*, 414, 125535 (2021).

Paper II **Edefell, E.,** Falås, P., Kharel, S., Hagman, M., Christensson, M., Cimbritz, M., Bester, K. MBBRs as post-treatment to ozonation: Degradation of transformation products and ozone-resistant micropollutants. *Science of the Total Environment*, 754, 142103 (2021).

Paper III Cimbritz, M., **Edefell, E.,** Thörnqvist, E., El-taliawy, H., Ekenberg, M., Burzio, C., Modin, O., Persson, F., Wilen, B.-M., Bester, K., Falås, P. PAC dosing to an MBBR – effects on adsorption of micropollutants, nitrification and microbial community. *Science of the Total Environment,* 677, 571–579 (2019).

Paper IV **Edefell, E.,** Svahn, O., Falås, P., Bengtsson, E., Axelsson, M., Ullman, R., Cimbritz, M. Digging deep into a GAC filter – temporal and spatial profiling of adsorbed organic micropollutants. *Water Research*, 218, 118477 (2022).

Author's contributions to the papers

Paper I	I designed the experiment and setup in dialog with the other authors. I conducted the experimental work, sample preparation and the micropollutant data analysis. I interpreted the results and wrote the manuscript with input from the other authors.
Paper II	I designed the experiment and setup in dialog with the other authors. I conducted the experimental work, sample preparation and the micropollutant data analysis. I interpreted the results and wrote the manuscript with input from the other authors.
Paper III	I planned and performed the lab-scale experiments and assisted in the operation and sampling of the pilot-scale plant. I contributed to the writing of the manuscript.
Paper IV	I designed the experiment together with the other authors. I conducted some of the experiments in the pilot-scale plant and performed the extraction experiments. I interpreted the results and wrote the manuscript with input from the other authors.

Related publications

Edefell, E., Ullman, R., Bengtsson, E. Ultrafilter och granulerat aktivt kol för avskiljning av mikroföroreningar. Report Nr 2019–1, Svenskt Vatten. Stockholm (2019). (In Swedish)

Modin, O., Fuad, N., Abadikhah, M., I'Ons, D., Ossiansson, E., Gustavsson, D.J.I., **Edefell, E.,** Suarez, C., Persson, F., Wilén, B-M. A relationship between phages and organic carbon in wastewater treatment plant effluents. *Water Research X,* 16, 100146 (2022).

Abbreviations and nomenclature

Item	Description	Units
BAC	Biological activated carbon	
BOD	Biological oxygen demand	
BV	Bed volume	
DOC	Dissolved organic carbon	mg/L
EBCT	Empty bed contact time	min
GAC	Granular activated carbon	
HPLC-MS/MS	High-performance liquid chromatography coupled with tandem mass spectroscopy	
HRT	Hydraulic retention time	h
k_{bio}	Biological degradation rate constant normalized to biomass concentration	$L/(g_{SS}d)$
k_{surf}	Biological degradation rate constant normalized to carrier surface area	$L/(m^2d)$
LOQ	Limit of quantification	
MBBR	Moving bed biofilm reactor	
NDMA	*N*-Nitrosodimethylamine	
PAC	Powdered activated carbon	
PFOS	Perfluorooctanesulfonic acid	
SRT	Solids retention time	d
UF	Ultrafiltration	
UPLC-MS/MS	Ultra-performance liquid chromatography coupled with tandem mass spectroscopy	
WWTP	Wastewater treatment plant	

Contents

1 Introduction

Wastewater treatment has developed over the years, from merely collecting it to including the removal of organic material, phosphorus, and nitrogen, as arising environmental challenges have been addressed. Wastewater treatment plants (WWTPs) typically include a combination of mechanical, biological, and chemical treatment steps. Biological treatment is mainly responsible for the removal of the organic and nitrogen-containing fractions, and may be carried out with suspended biomass in activated sludge processes, or with attached biomass growth in biofilm processes, for example, moving bed biofilm reactors (MBBRs).

Biofilms form on practically all surfaces where water is present. The microorganisms in the water adhere to the surface and other organisms by producing extracellular polymeric substances that also offer protection against toxic compounds and dehydration. Biofilms will develop naturally in water and wastewater pipes, potentially causing clogging and corrosion. However, when utilized in engineered processes, biofilms play a key role in the treatment of both drinking water and wastewater.

The presence of organic micropollutants in our aquatic systems poses an environmental challenge. Organic micropollutants include a wide range of organic compounds, for example, pharmaceuticals, hormones, biocides, and perfluorinated compounds. Some of these micropollutants are persistent in aquatic systems, and pose environmental risks such as feminization (Purdom et al., 1994; Routledge et al., 1998) and behavioral changes (Klaminder et al., 2016) in fish, toxicity (Kidd et al., 2007), and long-term and mixture effects (Pomati et al., 2008; Kümmerer, 2009).

It is important to identify the sources of emissions to tackle the problem of increasing concentrations of micropollutants in the environment. WWTPs have been described as major emission points, although the use of micropollutants originate from households and industries. Upstream solutions with source control strategies may reduce the use of specific compounds by substitution with other, possibly less harmful, micropollutants. However, downstream, or end-of-pipe solutions at WWTPs are necessary to reduce the emission of a wide range of micropollutants to the aquatic environment.

End-of-pipe solutions at WWTPs for micropollutant removal are being implemented in some countries, e.g., Switzerland (VSA, 2022a), Germany (KomS, 2021), Sweden (Svenskt Vatten, 2021), France (Penru, 2018), and the USA

(Audenaert et al., 2014). The main motives for implementing micropollutant removal often involve reducing the negative effects on the aquatic environment and protecting drinking water resources, invoking the precautionary principle. The Swedish Environmental Protection Agency has recently been charged by the Swedish Government to provide investment funding to facilitate the implementation of micropollutant removal at WWTPs and to increase our knowledge and experience of the treatment techniques available for Swedish conditions (Swedish Regulation, SFS 2018:495).

Treatment techniques for micropollutant removal that are considered compatible with large-scale implementation at WWTPs are ozonation, dosing of powdered activated carbon (PAC) or granular activated carbon (GAC) filtration. Ozonation is an oxidation process in which micropollutants react with ozone or hydroxyl radicals to form transformation products, while other compounds in the wastewater matrix may form problematic by-products, such as bromate and *N*-nitrosodimethylamine (NDMA). To address the challenges associated with these by-products, and possibly also transformation products, a biological post-treatment step is recommended to mitigate adverse effects in the recipient waters (Zimmermann et al., 2011; Prasse et al., 2015). Proposed or investigated post-treatment steps involve biofilm processes in sand filters, fixed bed biofilm reactors, MBBRs, or GAC filters (Magdeburg et al., 2014; Stalter et al., 2010a; 2010b; Bourgin et al., 2018; Kienle et al., 2022).

With activated carbon, used in dosing of PAC or in GAC filtration, the micropollutants are adsorbed onto the surface of the activated carbon and are thus removed from the treated water. PAC can be dosed continuously into, or after, the biological treatment step, and is then separated as waste sludge. GAC filtration is integrated as a polishing step at WWTPs. GAC can be used for several months or years (Graese et al., 1987) before its adsorption capacity is depleted, when it can be regenerated and used again. During the operation of GAC filters, a biofilm develops on the carbon allowing biological degradation of the organic fraction (Scholz & Martin, 1997) and certain micropollutants (Betsholtz et al., 2021). Due to their biological activity, GAC filters are sometimes referred to as biological activated carbon (BAC) filters.

A possible alternative to ozonation or activated carbon is to develop biological treatment processes to improve the biological degradation of micropollutants. Some micropollutants appear to be more readily degradable by biofilms in MBBRs than by the biomass in activated sludge systems (Falås et al., 2012a; 2013; Nguyen et al., 2021). The number of applications of MBBRs has increased since the technique was invented in the late 1980s for the removal of the organic fraction and nitrogen (Ødegaard et al., 1994) to include applications such as biological phosphorus removal (Rudi et al., 2019) and partial nitritation/anammox (Rosenwinkel & Cornelius, 2005; Lackner et al., 2014). Efforts have been made to develop MBBRs for micropollutant removal (Escolà Casas et al., 2015a; Torresi et al., 2016; Tang

et al., 2017; 2021), but further work is needed before MBBRs can be competitive with processes based on ozonation or activated carbon.

Biological treatment of wastewater is important to ensure that micropollutant removal is designed and operated in a resource-efficient way. Both ozonation and activated carbon are negatively affected by the presence of organic fractions in the water (Huber et al., 2005; Altmann et al., 2014; Guillossou et al., 2020). An improved understanding of how the biological treatment of nutrients, organic fractions, and micropollutants affects the overall removal of micropollutants is needed to integrate and design micropollutant removal efficiently. Biofilm processes are of particular interest since they allow process configurations for pre-, post-, and simultaneous removal of micropollutants and nutrients in combination with ozonation or activated carbon treatment. Synergies yet to be discovered may arise when combining treatment technologies.

1.1 Aims

The main aim of the work described in this dissertation was to evaluate how biofilms can be utilized to improve the removal of organic micropollutants in WWTPs. Particular attention was paid to: i) biofilms in MBBRs after conventional biological treatment, ii) biofilms as post-treatment following ozonation, and iii) biofilms integrated with PAC or GAC treatment. The work was divided into two parts with associated objectives.

Part 1: Biofilms for biological degradation of micropollutants

- To investigate the effects of growth and redox conditions on the degradation rates of micropollutants in MBBRs after conventional biological treatment

Part 2: Biofilms in combination with ozonation or activated carbon

- To investigate the removal of micropollutants and formation of *N*-oxide transformation products during ozonation, as well as the potential for biological degradation of these compounds in a post-treatment MBBR
- To evaluate the effects of dosing PAC into an MBBR on micropollutant removal and nitrification
- To describe the adsorption profiles of micropollutants in a GAC filter and evaluate the possible influence of biological degradation

The studies were performed on a wide variety of organic micropollutants, but particular attention was focused on pharmaceuticals. The research was carried out using long-term pilot-scale studies with complementary lab-scale experiments.

1.2 Outline of dissertation

Wastewater treatment, organic micropollutants and the removal of these are described in Chapter 2. The methods used in the studies for Papers I to IV are briefly described in Chapter 3. To achieve the aim of this dissertation, the conducted studies were divided into two parts were biological degradation of micropollutants serve as the main or supplementary removal mechanism of micropollutants, respectively, according to Figure 1.

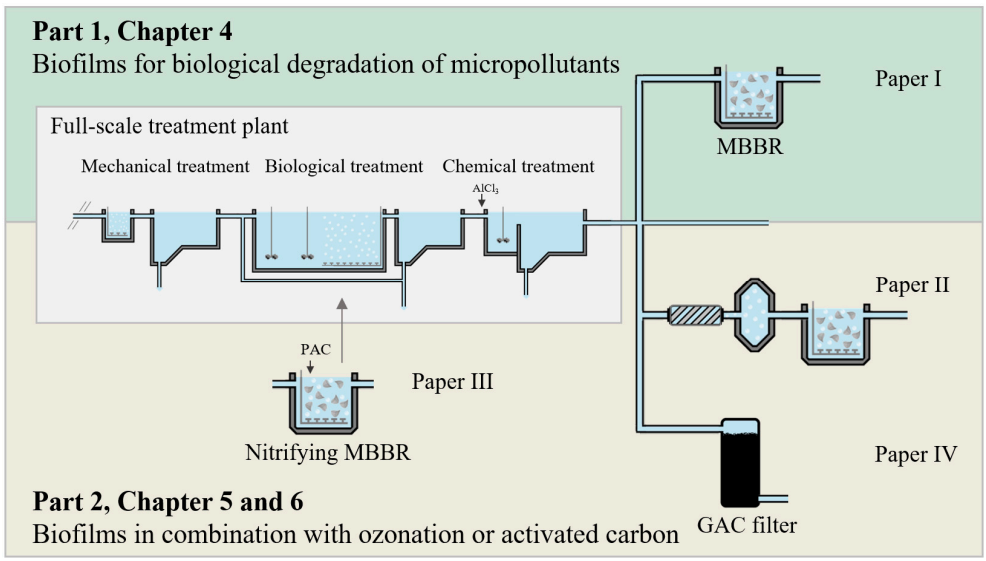


Figure 1. Illustration of the process configurations for micropollutant removal described in this dissertation involving pilot-scale studies on moving bed biofilm reactors (MBBRs), ozonation, dosage of powdered activated carbon (PAC) and filtration with granular activated carbon (GAC).

Part 1 (Chapter 4) describes the removal of micropollutants using additional biological treatment processes implemented after the conventional treatment at Lundåkra WWTP, Sweden, with the main aim of removing micropollutants (Paper I). The effects of growth and redox conditions on the biological degradation rates of micropollutants were investigated for several MBBR process configurations.

In part 2, biological degradation is then described as a supplementary method for the removal of micropollutants in combination with ozonation (Chapter 5) or activated carbon (Chapter 6). The combination of ozonation and post-treatment with an MBBR is described in Paper II, where the removal of micropollutants and the formation of a group of transformation products during pilot-scale ozonation are

described, as well as the potential for further biological degradation in the post-treatment MBBR at Lundåkra WWTP.

The combination of MBBR treatment and dosing of PAC is described in Paper III and discussed in Chapter 6. The effects of PAC dosing on nitrification and simultaneous micropollutant adsorption were investigated in a pilot-scale MBBR at Sjölunda WWTP, Sweden.

Finally, GAC filtration is described in Paper IV and also discussed in Chapter 6. The removal of micropollutants during long-term pilot-scale operation at Kalmar WWTP, Sweden, was evaluated and adsorption profiles of micropollutants in the GAC filter were described. Influence of biological degradation of micropollutants by the biofilm that developed on the GAC is also discussed.

2 Micropollutants in wastewater treatment

The use and fate of organic micropollutants affect the measures that can be taken to reduce emissions to the aquatic environment. WWTPs are currently not designed to remove micropollutants from wastewater, but several techniques are available, such as ozonation, and dosing or filtration with activated carbon.

2.1 Organic micropollutants

Organic micropollutants include a wide range of organic compounds such as pharmaceuticals, hormones, biocides, and perfluorinated compounds, and can be found in the ranges of ng/L to µg/L in wastewater, surface water, ground water, and drinking water (Focazio et al., 2008; Benner et al., 2013; Barbosa et al., 2016). Many micropollutants are designed to affect specific biological reactions, which results in several of them being difficult to degrade, and thus being persistent in aquatic systems, where they may pose environmental risks. Possible effects include chronic and acute toxic effects on aquatic organisms (Flaherty and Dodson, 2005; Yang et al., 2008) and feminization of fish (Jobling et al., 1998).

There are several thousand micropollutants on the market world-wide and the compounds are used in widely varying applications in households, agriculture, and industry. Many of these micropollutants end up in the aquatic environment through wastewater, stormwater, or landfill leachate. In an effort to understand the occurrence and risks associated with micropollutants, the European Commission has implemented a monitoring program within the European Union in which certain micropollutants on a watch list have to be monitored in surface waters (European Commission, 2015). The first watch list was adopted in 2015, and has since been revised twice (European Commission, 2018; 2020). The watch list includes pesticides, industrial chemicals, personal care products, hormones such as estrone, and human pharmaceuticals, such as ciprofloxacin, diclofenac, sulfamethoxazole, trimethoprim, and the macrolide antibiotics erythromycin and clarithromycin. In addition, a national monitoring program has been implemented by the Swedish Agency for Marine and Water Management (*Havs- och Vattenmyndigheten*),

targeting additional micropollutants, metals, and nutrients, so-called river-basin-specific pollutants (*Särskilda förorenande ämnen*, SFÄ). The occurrence of these micropollutants is monitored, and the ecological status of surface waters is evaluated (Swedish Regulation, HVMFS 2019:25). Limits have been specified for the listed micropollutants, e.g., the yearly average of diclofenac, 0.1 µg/L, and the maximal concentrations of ciprofloxacin, 0.1 µg/L, and PFAS11, 0.09 µg/L.

Depending on their use and transportation routes, methods of abatement for micropollutants differ. Compounds found in wastewater from households and certain industries may be reduced by implementing treatment techniques for micropollutant removal at WWTPs, whereas micropollutants entering the aquatic environment through stormwater, landfill leachate, and agriculture may be reduced by source control, substitution of compounds, or, in some cases end-of-pipe treatment. This dissertation addresses reduction at WWTPs only.

2.2 Conventional wastewater treatment

The treatment processes at WWTPs include a combination of mechanical, chemical, and biological steps (Figure 2), depending on the effluent demands determined by the geographical location, plant size, and recipient water. Effluent demands are commonly related to concentrations of organic matter measured as biological oxygen demand (BOD), nitrogen, and phosphorus. Mechanical treatment usually includes screening, grit removal, and primary settling for the removal of particulate matter, and is often referred to as primary treatment. Secondary treatment includes biological treatment and the separation of sludge. The purpose of biological treatment is to remove BOD and in some cases nitrogen and phosphorus. Phosphorus is, however, commonly removed by chemical precipitation, using pre-, co-, or post-precipitation. Excess biomass and chemical sludge are usually removed by settling. Additional separation techniques include sand, disc, and membrane filtration.

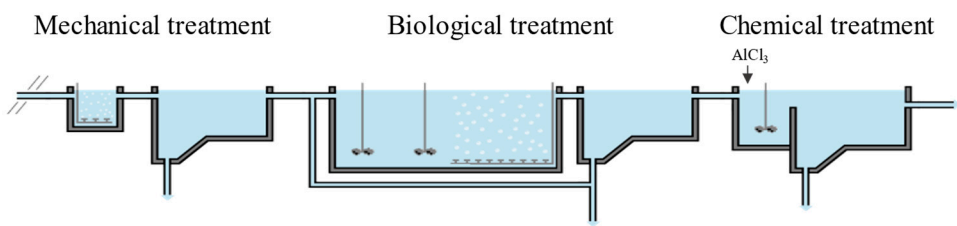


Figure 2. Schematic of a conventional wastewater treatment plant. Mechanical treatment typically includes screening, grit removal, and primary settling. Biological treatment includes activated sludge or biofilm processes, and the separation of sludge. Chemical treatment can be separate or integrated into the mechanical or biological treatment steps. (Sludge handling is not included in the figure.)

2.2.1 Biological wastewater treatment

Biological treatment can be used to remove BOD, nitrogen (through nitrification and denitrification), and phosphorus. In biological treatment, microorganisms degrade organic compounds and nutrients to metabolites such as carbon dioxide, nitrogen gas, and water. The growth and performance of microorganisms can be controlled to a certain extent by adjusting the operating conditions, such as the solids retention time (SRT) and degree of aeration. The hydraulic retention time (HRT), and nutrient and organic loads also affect the performance, but these are usually determined by the design of the process, rather than operational settings.

The biological processes are either based on suspended growth, in which biomass forms flocs in activated sludge processes, or attached growth, in which biomass grows on support material in biofilm systems, such as trickling filters and MBBRs. Activated sludge processes have been used for more than a century and have played an important role in the development of biological treatment technologies and design configurations. Activated sludge processes allow flexible operation and have low maintenance demands but require careful process control. The HRT in activated sludge processes typically ranges from 3-5 h for BOD removal, up to 8-20 h for nitrogen removal (Davis, 2010). The activated sludge process is also sensitive to large variations in wastewater flux and toxic disturbances. Biofilm systems are often more compact than conventional activated sludge processes, and less sensitive to variations in water quality and flux, however, they allow only limited flexibility in operational settings.

MBBRs were introduced in the late 1980s to combine the benefits of the activated sludge and fixed biofilm processes (Ødegaard et al., 1994). Today, MBBRs are used for several purposes worldwide, such as denitrification (Mases et al., 2010; McQuarrie & Boltz, 2011), combined nitrogen and phosphorus removal (Rudi et al., 2019), and the treatment of reject water from anaerobic digesters (Kanders et al., 2019). In MBBRs, the biofilm grows on plastic carriers with examples shown in Figure 3, which are kept in suspension in the reactor by mechanical mixers or aeration. The carriers are designed to provide a large, protected surface area for biofilm growth, while shielding the biofilm from detachment due to collisions between carriers and the shear forces in the water.

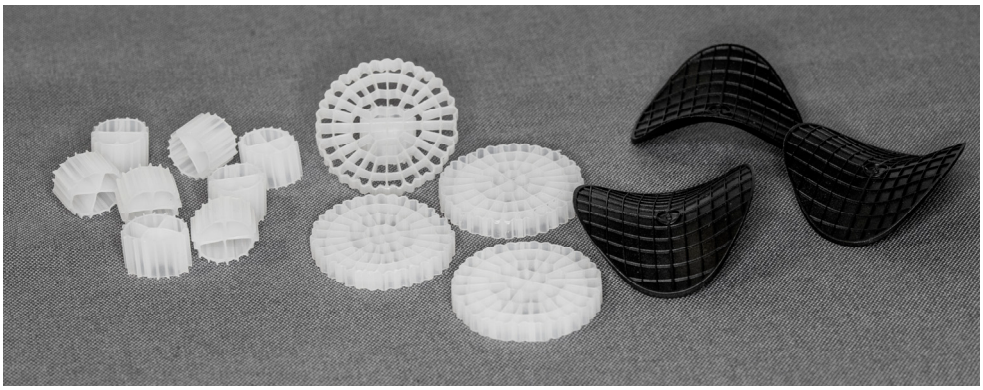


Figure 3. Biofilm carriers, from left to right K1, K5, and Z-400 from AnoxKaldnes, Lund, Sweden.

Nutrients and oxygen are transported in biofilms by diffusion, creating concentration gradients through the depth of the biofilm. Oxygen concentration gradients create stratification of the biofilm into an aerobic outer layer and an anaerobic inner layer. This stratification of the biofilm allows simultaneous nitrification and denitrification, however, removal rates can be limited by the diffusion rate of substrates through the biofilm (Hem et al., 1992). So-called Z carriers were developed to control the depth of the biofilm by the grid height of the carriers, in order to reduce diffusion limitations (Piculell, 2016).

Long biomass retention times in MBBRs enable microbial communities to form with slow-growing bacteria, which may facilitate the degradation of micropollutants (Shreve & Brennan, 2019). However, biofilms are complex structures, and our understanding of the ecology and physiology of biofilm communities and their effects on the performance of the biofilm is not yet complete.

2.3 Removal of organic micropollutants

The removal efficiency of micropollutants in WWTPs depends on the treatment processes used and the kind of micropollutant, as can be seen in Figure 4. Generally, removal is rather low for the majority of micropollutants, mainly attributed to the biological treatment (Joss et al., 2006; Miège et al., 2008; Verlicci et al., 2012; Luo et al., 2014; Park et al., 2017). WWTPs with nitrogen removal tend to have lower effluent concentrations of micropollutants than plants without nitrogen removal (Schaar et al., 2010; Falås et al., 2012b).

	Influent concentration (ng/L)	
	Kalmar WWTP	Lundåkra WWTP
	n=18	*n=3*
Ibuprofen	85,000 ± 32,000	12,000 ± 7,000
Ketoconazole	270 ± 190	-
Naproxen	7,200 ± 2,000	-
PFOS	80 ± 120	-
Estrone	70 ± 10	-
Sulfamethoxazole	410 ± 270	150 ± 80
Gabapentin	-	25,000 ± 31,000
Sertraline	200 ± 130	-
Atenolol	1,500 ± 460	860 ± 470
Valsartan	-	1,100 ± 520
Citalopram	220 ± 100	260 ± 80
Zolpidem	4.6 ± 1.3	-
Trimethoprim	100 ± 32	90 ± 47
Losartan	1,000 ± 330	1,000 ± 450
Erythromycin	440 ± 380	120 ± 110
Clarithromycin	170 ± 130	34 ± 16
Venlafaxine	450 ± 140	1,500
Tramadol	140 ± 40	1,500 ± 800
Metoprolol	1,500 ± 410	2,200 ± 1,200
Iohexol	-	20,000 ± 33,000
Diclofenac	960 ± 250	3,300 ± 4,000
Oxazepam	300 ± 90	360 ± 160
Propranolol	56 ± 17	68 ± 30
Carbamazepine	420 ± 160	19,000
Imidacloprid	20 ± 50	-
Fluconazole	73 ± 29	-

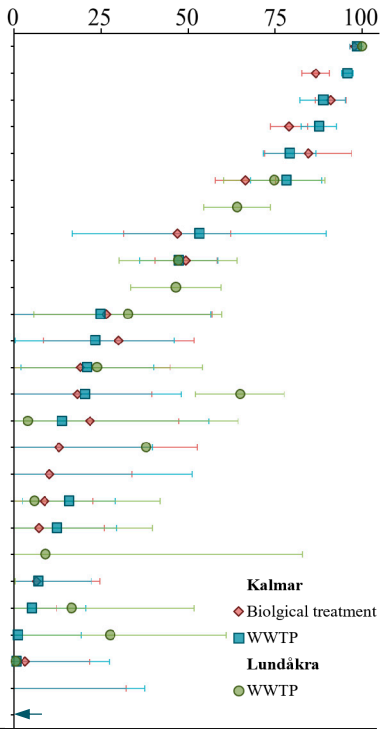


Figure 4. Influent concentrations and removal of micropollutants at Kalmar WWTP and Lundåkra WWTP, Sweden. Compounds not analyzed (-). Error bars represent standard deviations (Kalmar; biological treatment, n=12, WWTP, n=18; Lundåkra WWTP, n=3). The arrow indicates increasing concentrations at Kalmar WWTP.

2.3.1 Biological removal

In conventional wastewater treatment, micropollutants are removed mainly through biological degradation and sorption onto particles and sludge, although the extent of removal is highly compound-specific. The fractions of biodegradation and sorption are commonly expressed as in Equation 1 and Equation 2, respectively:

$$F_{biodegraded} = (1 - \frac{1}{1+k_{bio} \cdot X_s \cdot \theta}) \cdot 100 \qquad \text{(Equation 1)}$$

$$F_{sorbed} = (1 - \frac{1}{1+K_d \cdot SS}) \cdot 100 \qquad \text{(Equation 2)}$$

where $F_{biodegraded}$ denotes the fraction of the micropollutant removed via biodegradation in stirred tank reactors (%), k_{bio} is the degradation rate constant

normalized to biomass concentration ($L/(g_{SS}d)$), X_s is the biomass concentration (g_{SS}/L), θ is the HRT (d), F_{sorbed} is the fraction of the micropollutant removed via sorption (%), K_d is the linear sorption constant (L/g_{SS}), and SS is the concentration of suspended solids (g_{SS}/L).

Micropollutants can sorb to both primary and biological sludge, and sorption constants have been determined for several compounds (see e.g., Ternes et al., 2004; Stevens-Garmon et al., 2011; Lakshminarasimman et al., 2018). In Figure 4, examples of compounds known to be removed by sorption are ciprofloxacin, citalopram, sertraline, and ketoconazole (Hörsing et al., 2011; Svahn & Björklund, 2019), and perfluorooctanesulfonic acid (PFOS) (Zhou et al., 2010).

Biological degradation is essentially dependent on the coincidence of two factors. The chemical structure of the micropollutant must have at least one moiety available for a bioreaction, and the enzyme catalyzing that specific bioreaction must be present. Bioreactions are often oxidation/reduction processes, and the biodegradability is therefore affected by the electron availability of the micropollutants (Nguyen et al., 2021). Electron-donating groups, such as amine, hydroxyl, ether, and alkyl groups, and monocyclic aromatic structures may increase the biodegradability under aerobic conditions (Tadkaew et al., 2011), whereas halogens and complex ring structures tend to reduce the biodegradability (Bertelkamp et al., 2016; Alvarino et al., 2018). Figure 5 shows the chemical structures of the easily degradable micropollutant ibuprofen, diclofenac which has varying degradability, and the recalcitrant compound carbamazepine.

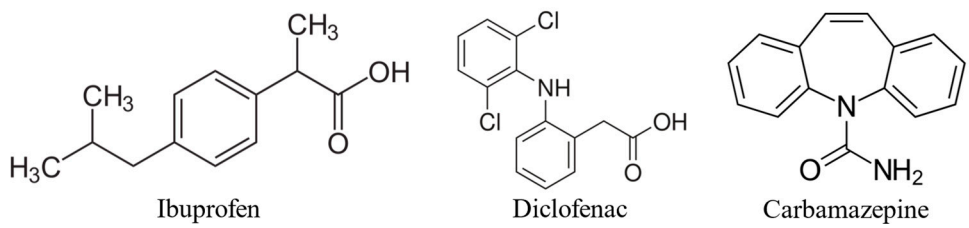


Figure 5. The chemical structures of the easily degradable ibuprofen, at times degradable diclofenac, and recalcitrant carbamazepine.

Considerable efforts have been devoted to identifying the degradation pathways and transformation products of individual micropollutants such as diclofenac (Jewell et al., 2016; Wu et al., 2020), and other compounds (Quintana et al., 2005; Helbling et al., 2010; Senta et al., 2017; Rich et al., 2022). Further identifying the microorganisms responsible for the degradation is difficult as the microbial communities in biological wastewater treatment are very diverse. The microorganisms responsible are largely unknown, but some microbial families have been suggested to be involved in the degradation of certain micropollutants (Wolff et al., 2018),

such as *Gammaproteobacteria* for naproxen and *Deltaproteobacteria* for diclofenac (Falås et al., 2018). Increased biodiversity of the microbial communities in biofilms has been shown to improve the degradation rates of several micropollutants, although the specific groups of organisms were not identified (Torresi, et al., 2016). Increased biodiversity may broaden the enzyme spectrum, thereby promoting the biological degradation of micropollutants. This could be achieved by combining different redox conditions (Alvarino et al., 2018) or decreasing substrate availability (Torresi et al., 2018).

According to Equation 1 above, the removal of micropollutants through biodegradation can be increased by increasing the biodegradation rate, the biomass concentration, or the HRT. A longer HRT means an increase in reactor sizes, and the biomass concentration is often limited by the capacity of the clarifiers in activated sludge processes and diffusion limitations in biofilm systems. As the biodegradation of micropollutants is affected by the microbial community, some micropollutants appear to be more readily degradable in biofilm processes such as MBBRs and integrated fixed film activated sludge (IFAS) systems, than in activated sludge processes (Jewell et al., 2016; Shreve & Brennan, 2019; Nguyen et al., 2021; Falås et al., 2012a; 2013). This may be attributed to the enrichment of slow-growing microorganisms in biofilms, similarly to increased degradation rates in activated sludge processes with long SRTs (Clara et al., 2005; Achermann et al., 2018a). Furthermore, the biodegradation rate can be affected by the substrate availability in the wastewater, as decreasing substrate availability tends to increase biodegradation rates (Escolà Casas et al., 2015a). However, as the substrate availability decreases, the biomass concentration in biofilm systems also tends to decrease (Paper I; Escolà Casas et al., 2015a; Mazioti et al., 2015). In order to improve the possibility of using biological micropollutant removal in full-scale WWTPs, processes that can combine high degradation rates, high biomass concentration, and low HRT must be developed.

Additional treatment technologies are currently required for efficient removal of a wide range of micropollutants. Some of the technologies being investigated are oxidation using agents such as ozone, hydrogen peroxide, chlorine, or ultraviolet radiation, and separation technologies, such as dosing or filtration with activated carbon, reverse osmosis, and nanofiltration. Ozonation and activated carbon are currently considered to be the most viable options (Eggen et al., 2014; Pistocci et al., 2022).

2.3.2 Ozonation

Ozonation is a process in which oxidation occurs via reactions with ozone or hydroxyl radicals at various reaction rates (Nöthe et al., 2009; von Sonntag & von Gunten, 2015). Ozone is a highly reactive but selective oxidant that reacts with electron-rich moieties (e.g., phenolic, amino, and olefinic groups), whereas

hydroxyl radicals are non-selective and highly reactive oxidants. The removal efficiency of micropollutants during ozonation is affected by the reaction rate of the specific micropollutant, as well as the characteristics of the wastewater; for example, increasing the concentrations of organic carbon and nitrite reduces the micropollutant removal rate (Paraskeva & Graham, 2002; Antoniou et al., 2013; Ekblad et al., 2019). To reduce ozone scavenging by the organic fraction in the wastewater, ozonation is usually applied after the biological treatment step (Hollender et al., 2009; Schaar et al., 2010). The organic fraction in the water is also considered when determining the ozone demand, as the ozone dose is usually normalized to the dissolved organic carbon (DOC) concentration (Reungoat et al., 2010; Lee et al., 2013; Altmann et al., 2014). Increasing the ozone dose increases the removal of micropollutants, and typical doses range from 0.3 to 1.0 mg O_3/mg DOC (Reungoat et al., 2010; 2012; Schaar et al., 2010; Kovalova et al., 2013).

Ozonation has been implemented for micropollutant removal in countries such as Switzerland, Germany, and Sweden (KomS, 2021; Svenskt Vatten, 2022; VSA, 2022b). Full-scale ozonation installations commonly employ HRTs between 15 and 60 min (Bourgin et al., 2018; Margot et al., 2013) to ensure oxidation of the micro-pollutants and the depletion of ozone to avoid emissions of residual gas to the atmosphere. Ozonation oxidizes micropollutants to transformation products and can form problematic by-products arising from other substances in the wastewater matrix, such as bromate from bromide and nitrosamines from organic precursors (Hollender et al., 2009; Marti et al., 2015; Wu et al., 2019). To address the problems resulting from by-products, and possibly transformation products, a biological post-treatment step is recommended to mitigate adverse effects in the recipient water (Zimmermann et al., 2011; Prasse et al., 2015). Sand filtration has been proposed as post-treatment following ozonation to reduce the levels of toxicity (Magdeburg et al., 2014; Stalter et al., 2010a, 2010b) and easily biodegradable micropollutants (de Wilt et al., 2018). Other post-treatment steps investigated also involve biofilms in fixed bed biofilm reactors, MBBRs, or GAC filters (Bourgin et al., 2018; Itzel et al., 2020; Gulde et al., 2021).

2.3.3 Activated carbon

In contrast to ozonation, removal using activated carbon is a separation technique in which micropollutants are adsorbed on the surface of the activated carbon. Activated carbon may be applied as PAC, with particle sizes typically between 10 and 100 µm, or as GAC, with granule sizes typically between 0.4 and 4 mm. Activated carbon is a porous material and the larger GAC granules are more susceptible to mass transfer limitations, such as pore-blocking effects (Corwin & Summers, 2010; Meinel et al., 2015). Increasing organic fraction in the wastewater increases the competition for adsorption sites on the activated carbon and reduces the removal of micropollutants.

Typical doses of PAC range between 10 and 30 mg/L (Boehler et al., 2012; Margot et al., 2013; Altmann et al., 2014; Mulder et al., 2015), which correspond to about 0.8-4.4 mg PAC/mg DOC when compensating for the organic fraction in the water. PAC can be dosed into or after the biological reactor, and there are several full-scale examples in Switzerland (VSA, 2022b) and Germany (Mulder et al., 2015). In integrated systems with direct dosing of PAC into activated sludge processes, the SRT of the biological treatment determines the retention time of the PAC in the system, and the used carbon is removed with the excess sludge. The effects of PAC addition in biofilm systems have been less explored.

Separate contact reactors after biological treatment are usually designed for HRTs of 30-40 min (Kosek et al., 2020), and therefore require greater footprint at the WWTP than direct dosing in the biological reactors. However, separate contact reactors may require lower doses of PAC for equivalent micropollutant removal due to lower competition from organic carbon in the water. Several studies have been carried out to evaluate the dosing of PAC in separate contact reactors with subsequent separation based on settling (Kårelid et al., 2017a), sand filtration (Altmann et al., 2015a, 2015b), and membrane filtration (Margot et al., 2013; Löwenberg et al., 2014). The separated PAC may be recirculated back to the biological treatment to maximize the utilization of the carbon (Boehler et al., 2012; Meinel et al., 2016; Kårelid et al., 2017b). However, recirculation and direct dosing of PAC in the biological treatment step increases the load on the subsequent separation processes, which may require additional capacity to allow adequate separation of the sludge and PAC from the water.

GAC, on the other hand, is used in filters after the biological treatment step, where GAC filters may replace existing sand filters (Böhler et al., 2020), or may be placed after sand or membrane filtration units (Fundneider et al., 2021a; Svenskt Vatten, 2021). The GAC can be used for several months or years, allowing colonization of a biofilm on the granules. The biofilm may limit the accessibility of adsorption sites but may, on the other hand, enable biodegradation of the organic fraction and certain micropollutants. The micropollutant removal efficiency is high in the initial stages of the service life of the GAC, but decreases with time as the number of treated bed volumes (BVs) increases. Prolonging the contact time between the water and GAC by reducing the flow of water through the filter increases the empty bed contact time (EBCT), and may temporarily improve the removal efficiency (Fundneider et al., 2021b). The EBCT generally ranges between 7 and 30 min (Kennedy et al., 2015; Böhler et al., 2020; Fundneider et al., 2021b).

Used GAC can be regenerated to regain the adsorption capacity. Regeneration typically results in a 10-20% loss of the GAC. Pilot-scale studies on GAC filtration with up to 60,000 BVs have been performed to evaluate the removal efficiency of micropollutants in wastewater (Altmann et al., 2016; Baresel et al., 2019; Fundneider et al., 2021a). Differences in removal efficiencies may, to some extent, be described by differences in DOC concentration in the wastewater, affecting the

competition for adsorption sites, as well as differences in the adsorption capacity of different GAC products (Fundneider et al., 2021b).

The number of full-scale installations of GAC filters at wastewater treatment plants is increasing (VSA, 2022b) as the technique is now considered to have comparable costs to PAC dosing and ozonation (Pistocchi et al., 2022). Used GAC is kept separate from the sludge at WWTPs and can be sent for regeneration and be reused, reducing the carbon footprint of the activated carbon. As PAC is removed with the sludge, the sludge cannot be used as fertilizer on farmland, while GAC filtration does not prevent the use of sludge for this purpose. GAC is for this reason currently considered more suitable than PAC in the Swedish context.

3 Methods

This chapter briefly describes the main methods used. Long-term pilot-scale studies were performed to capture natural variations in the wastewater and to mimic operating conditions similar to those used in large-scale installations. Lab-scale studies were carried out as a complement to the pilot-scale studies to allow systematic evaluation under more controlled batch conditions.

3.1 Pilot-scale setups

The papers describe process configurations on pilot-scale to allow the adaptation of biofilm on carriers (Papers I, II, III) and evaluation of the micropollutant removal efficiency in a GAC filter (Paper IV). The pilot-scale plants were operated at municipal WWTPs in southern Sweden.

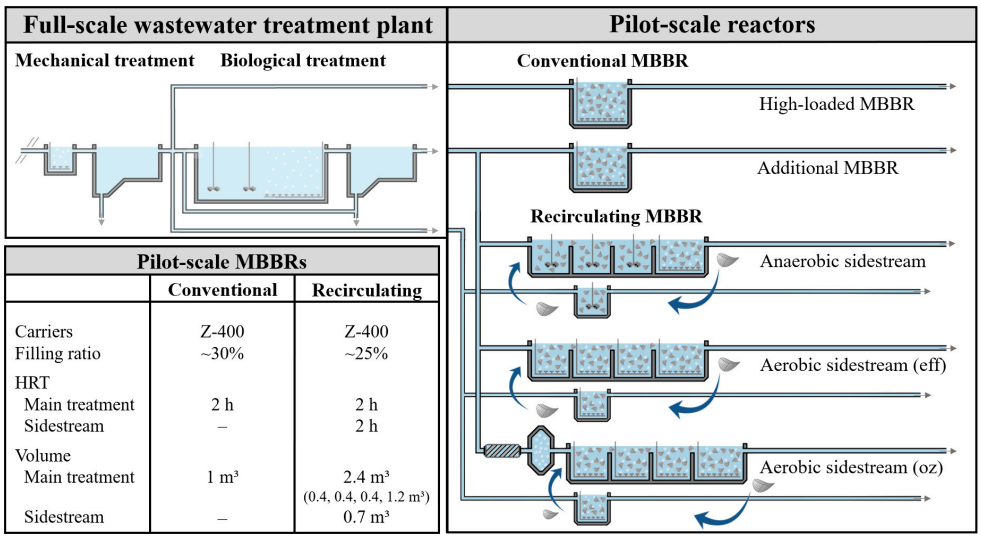
3.1.1 MBBR configurations

Two large and two small pilot-scale MBBR units were operated to adapt the biofilm on the carriers to the ambient environments, feeding strategies, and operating conditions of various process configurations (Papers I, II, III). The removal of micropollutants during continuous operation was determined by sampling influent and effluent water from the pilot-scale reactors.

The two large pilot-scale MBBR units, one conventional and one recirculating MBBR, were operated as for stand-alone treatment or post-treatment following pilot-scale ozonation. The conventional MBBR unit (1 m^3) was operated with primary or secondary treated wastewater (Paper I) according to Figure 6 and ozonated secondary treated wastewater in combination with intermittent feeding of primary treated wastewater (Paper II) according to Figure 7 to supply easily available substrate to the biofilm. Intermittent feeding was performed by alternating between an operational phase (12 h) with ozonated water and a feeding phase (6 h) with influent wastewater.

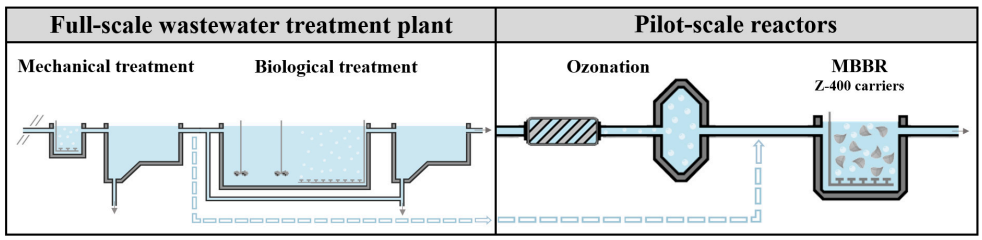
The recirculating MBBR unit (3 m^3) consisted of a mainstream and a sidestream treatment train. The main stream was operated with secondary treated wastewater or ozonated secondary treated wastewater, while the side stream was operated with

primary treated wastewater (Paper I) according to Figure 6. The biofilm carriers were moved between the mainstream and sidestream treatment trains by conveyor belts, and transported with the water flow in the main stream (Figure 8). Process configurations with a side stream minimize the risk of affecting the effluent quality of the main stream. Photographs of the pilot-scale MBBRs and ozonation unit are shown in Figures 9 and 10.



Pilot-scale MBBRs	Conventional	Recirculating
Carriers	Z-400	Z-400
Filling ratio	~30%	~25%
HRT		
Main treatment	2 h	2 h
Sidestream	–	2 h
Volume		
Main treatment	1 m³	2.4 m³ (0.4, 0.4, 0.4, 1.2 m³)
Sidestream	–	0.7 m³

Figure 6. Setup and operational characteristics of the pilot-scale units described in Paper I. The recirculating MBBR consists of a main treatment train and sidestream treatment to provide additional substrate for the biofilm carriers, and the carriers are moved between the main and sidestream treatment trains on conveyor belts. A pilot-scale ozonation unit was operated prior to the recirculating MBBR with an aerobic sidestream (oz). (Figure modified from Paper I.)



Ozonation				
Doses (g O_3/g DOC)	0.3	0.5	0.7	0.9

MBBR treatment	No additional load	Low additional load	High additional load
HRT of ozonated water (h)	2	2	2
Intermittent feeding	no	yes	yes
Influent wastewater (% of total flow)	0	2	9

Figure 7. Setup and operational characteristics of the pilot plant described in Paper II. (Modified figure from Paper II.)

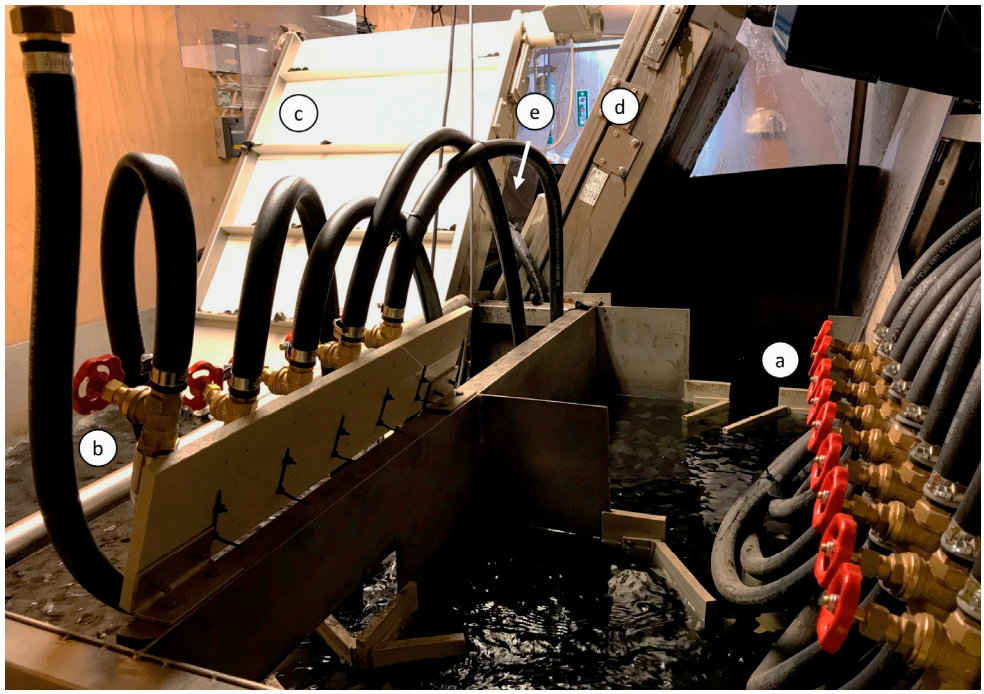


Figure 8. Photograph showing the recirculating MBBR unit described in Paper I. The mainstream treatment train received biologically treated wastewater in the top right compartment (a) and the water and biofilm carriers travelled through the baffles to the bottom left compartment (b). Carriers were moved by the conveyor belts (c and d) to the sidestream treatment with primary treated wastewater (e), and then transported back to the mainstream treatment train.

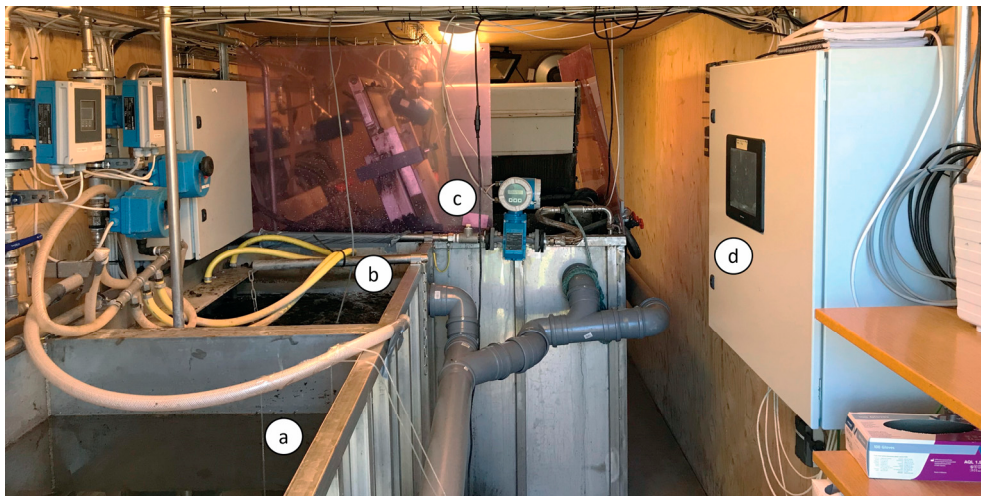


Figure 9. Photograph of the large pilot-scale MBBR units described in Papers I and II with an equalization tank (a), a conventional MBBR (b), a recirculating MBBR (c) and a control panel (d).

Figure 10. Photograph of the pilot-scale ozonation plant. Showing the oxygen generator units (a), ozone generator (b), control panel (c), ozone injection points (d) and reaction tanks (e).

Operation of the conventional and recirculating MBBR units proceeded for 13 months with a minimum of 1.5 months per feeding strategy, to allow for adaptation of the biofilm to the operating conditions. An HRT of 2 h was chosen in the MBBR units to reflect potentially realistic retention times in large-scale applications. However, the removal of micropollutants is often limited in continuous biological reactors with an HRT of 2 h. The potential of the developed biofilms to remove micropollutants was therefore also evaluated based on batch experiments in lab-scale with carriers from the pilot-scale MBBRs.

The biofilm carriers used in the two large pilot-scale MBBRs were Z-400 (AnoxKalndes, Sweden) as shown in Figure 11. Micropollutant removal with this type of carrier has previously been evaluated by Torresi et al. (2016; 2017) but Papers I and II are the first to describe this on large pilot-scale.

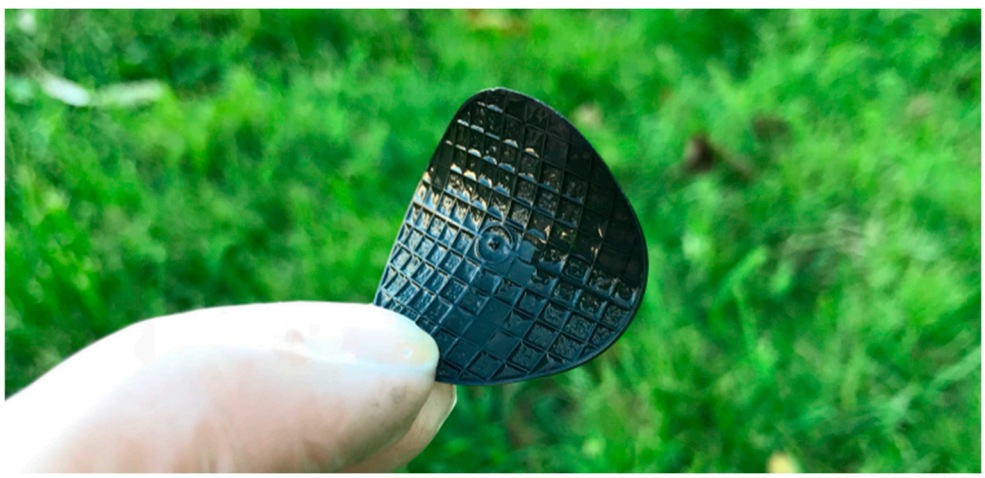
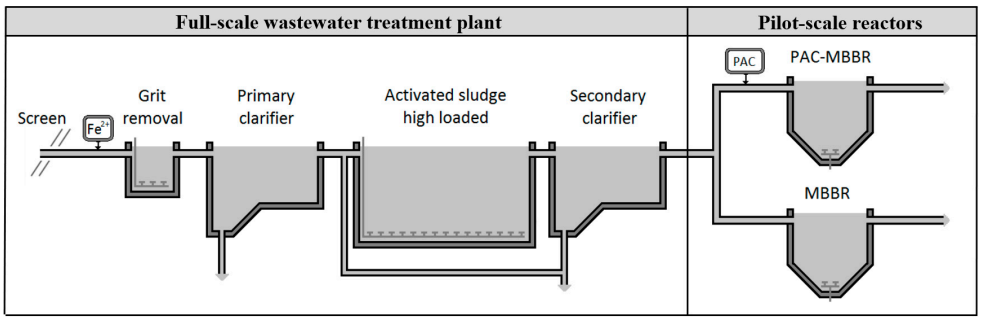


Figure 11. The Z-400 biofilm carrier used in the studies described in Papers I and II.

The small pilot-scale MBBR units are described in Paper III, and consisted of two 8-liter, parallel nitrifying MBBRs operated with wastewater from a high-loaded activated sludge process for five months (see Figure 12). One of the MBBRs was continuously dosed with PAC at various doses for simultaneous adsorption of micropollutants, while the other MBBR served as a reference with no dosage of PAC. PAC was integrated with the biofilm on the carriers in the MBBR with continuous dosing (Figure 13). The carriers (K5, AnoxKaldnes, Sweden) were collected from a full-scale nitrifying MBBR at Växjö WWTP and had an established nitrifying biofilm prior to the pilot-scale experiments. The parallel operation of the MBBRs allowed evaluation of the effects of PAC dosing on micropollutant removal, nitrification rates, and biofilm composition. A picture of the pilot plant is shown in Figure 14.



	Activated sludge treatment	MBBR treatment
Hydraulic retention time (h)	3	2
Solid retention time (d)	2	-
Carriers	-	K5 with a fill ratio of 40%
Specific surface area (m^2/m^3)	-	320
Oxygen concentration (mg/L)	1.5-2.5	4-6

		Sampling and PAC dosing
Days of operation (d)		0 25 50 75 100 125 150
Micropollutant sampling		
PAC dosage (mg PAC/L)	PAC-MBBR	0 5 10 15 20 30
PAC dosage (mg PAC/L)	MBBR	0

Figure 12. Setup and operational characteristics of the WWTP and pilot-scale plant described in Paper III. (Figure modified from Paper III.)

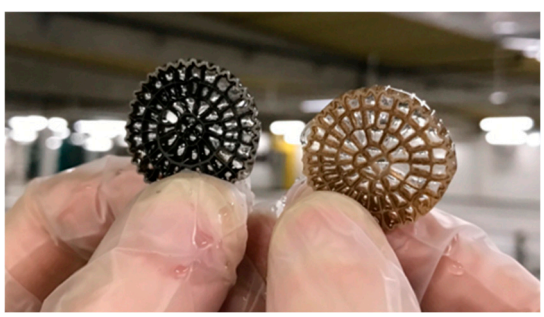


Figure 13. Biofilm carriers, K5, used in the study described in Paper III. The left carrier is from the MBBR dosed with PAC, and the right carrier is from the MBBR with no PAC dosage.

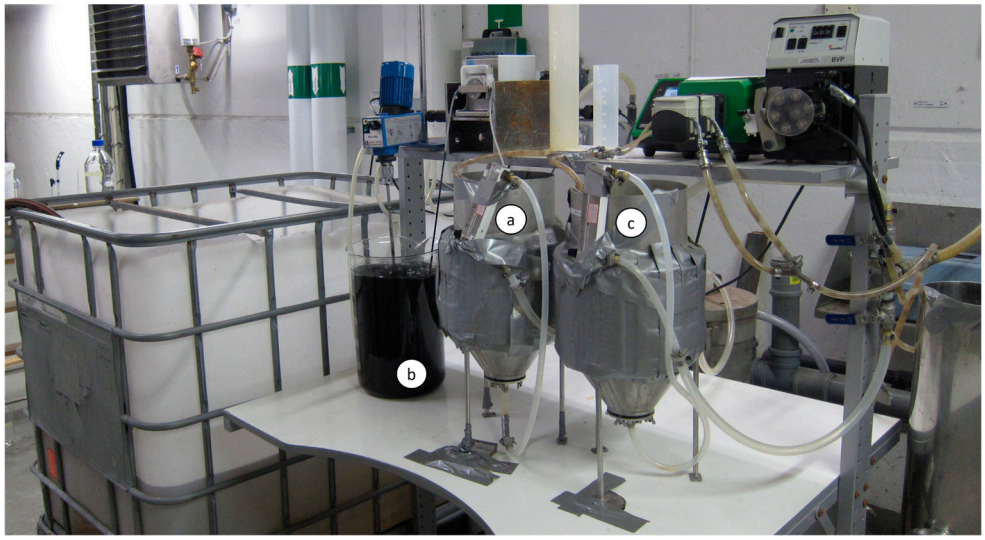


Figure 14. Photograph of the small pilot-scale MBBR units described in Paper IV. Both MBBRs contained nitrifying carriers, and one MBBR (a) was continuously dosed with PAC from a slurry (b), while the other MBBR (c) was not dosed with PAC.

3.1.2 GAC filter

Long-term pilot-scale operation of an ultrafiltration (UF) membrane unit and a GAC filter (Figures 15 and 16) for 12 months with municipal wastewater (Paper III). The GAC was sampled at four filter depths (10-20, 40-50, 70-80, and 100-110 cm) at several time points during the study and analyzed to elucidate the dynamics of micropollutant adsorption in the filter bed. Sampling was performed with a custom-made sampler from the top of the filter. The development of the biofilm throughout the filter was monitored by examining samples under a microscope, however, the biomass concentration was not assessed. Quantification of the biomass concentration in GAC filters is difficult. GAC cannot be washed as can biofilm carriers in MBBRs, and thus the solids cannot be determined according to the method used for biofilm carriers (Papers I, II, III). Using the volatile suspended solids as an approximation of the biomass content is not possible either because the method would not differentiate between biomass and the GAC. Adenosine triphosphate (ATP) activity can be used as a proxy for biomass activity (Velten et al., 2007), but this method was not available within this study.

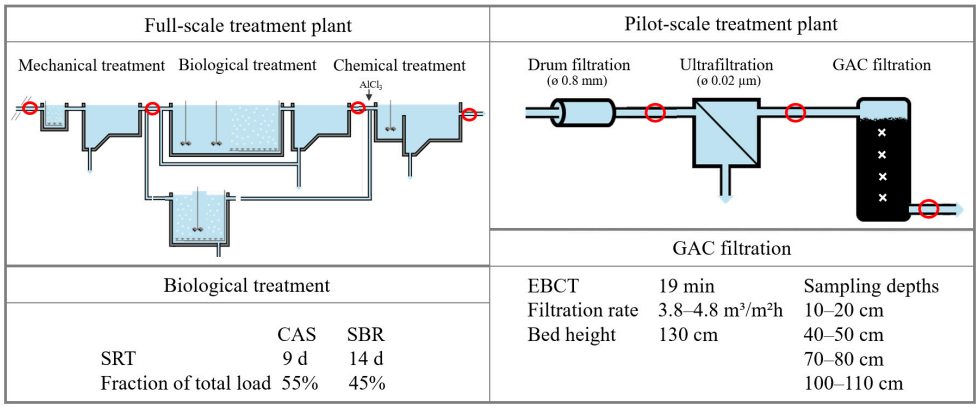


Figure 15. Process configuration of full-scale and pilot-scale treatment plants and operational parameters, including solids retention time (SRT) and empty bed contact time (EBCT). The biological treatment consisted of a conventional activated sludge (CAS) process, in parallel with an activated sludge process, using sequencing batch reactors (SBRs). Sampling points for water samples are indicated (o) and for GAC samples (x). (Figure from Paper IV.)

Figure 16. Photograph of the pilot-scale ultrafiltration (UF) and GAC filtration plant described in Paper III, showing the vertical hollow fiber UF membranes (a), control panel and collection tank (b), equalization tank (c), and the GAC filter (d).

3.2 Lab-scale experiments

Lab-scale batch experiments were performed in parallel with the pilot-scale studies (Papers I, II, and III) to evaluate the potential of micropollutant removal by the various systems. Batch experiments were used to determine the biological degradation rates of micropollutants (Papers I and II). In the study described in Paper III, batch experiments were used to study the dose–response relationship between the PAC dose and the removal efficiency of micropollutants, and the possible effects of different biomasses.

3.2.1 Biological degradation rate tests

Biological degradation rate tests were performed to assess the potential of various biofilms for the degradation of micropollutants (Papers I and II). The tests were performed by incubating biofilm carriers from the pilot-scale MBBRs in flasks with wastewater spiked with micropollutants and sampled over 3-6 days (as illustrated in Figure 17). The degradation rates were derived from the change in concentration of the micropollutants fitted to first-order kinetics, as in Equations (3)-(5):

$$C = C_0 \cdot e^{-k \cdot t} \qquad \text{(Equation 3)}$$

$$k_{bio} = \frac{k}{X} \qquad \text{(Equation 4)}$$

$$k_{surf} = \frac{k}{A} \qquad \text{(Equation 5)}$$

where C denotes the concentration of a dissolved compound (ng/L), C_0 is the initial concentration of the dissolved compound (ng/L), k is the degradation rate constant (1/d), t is time (d), X is the biomass concentration on the carriers (g/L), and A is the specific surface area of the carriers (m^2/L) generating k_{bio}, the degradation rate constant normalized to biomass concentration (L/($g_{biomass}$d)), and k_{surf}, the degradation rate constant normalized to carrier surface area (L/(m^2d)).

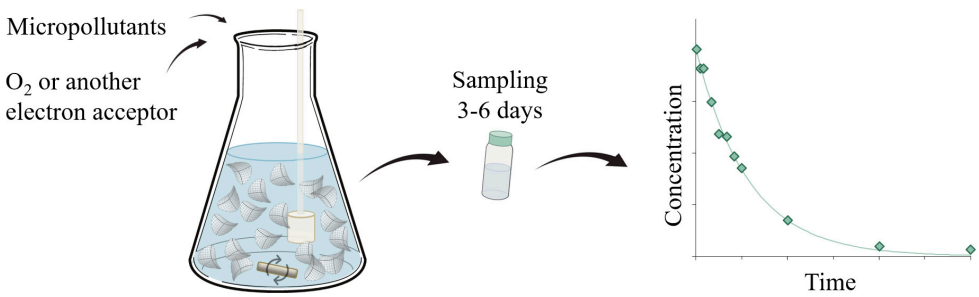


Figure 17. Illustration of the concept of the micropollutant degradation rate tests.

Micropollutant degradation rates for activated sludge and biofilm systems are commonly normalized to the biomass concentration (Joss et al., 2006; Falås et al., 2013). Normalization to the carrier surface area was discussed in Paper I, and introduced for the first time in Paper II. Biofilm systems are designed based on surface area rather than biomass concentration as oxygen diffusion can limit oxidation rates, as has been described for nitrification (Hem et al., 1992).

3.2.2 Adsorption potential of PAC

Dose–response experiments were conducted to determine the adsorption of micropollutants to PAC and the possible interference of biofilm carriers or suspended biomass (Paper III). Batch experiments were performed in mixed reactors (1 L) with wastewater, in the presence or absence of biofilm carriers from the small pilot-scale MBBR unit, or nitrifying activated sludge (Figure 18). The removal of micropollutants was determined at 6 doses of PAC (0-30 mg/L).

Based on the results at various PAC doses, the adsorption of certain micropollutants could be described by Freundlich isotherms, as expressed in Equation (6). Well-fitting isotherms allow prediction of the removal efficiency for these micropollutants.

$$\frac{x}{m} = \mathrm{k} \cdot C^{n} \qquad \text{(Equation 6)}$$

Here, x is the concentration of the adsorbed micropollutant (µg/L), m is the concentration of PAC (mg/L), k is the adsorption constant (µg/(mg(µg/L)^{n})), C is the concentration of the micropollutant in the liquid phase after 2 h (µg/L), and n is the intensity parameter (dimensionless).

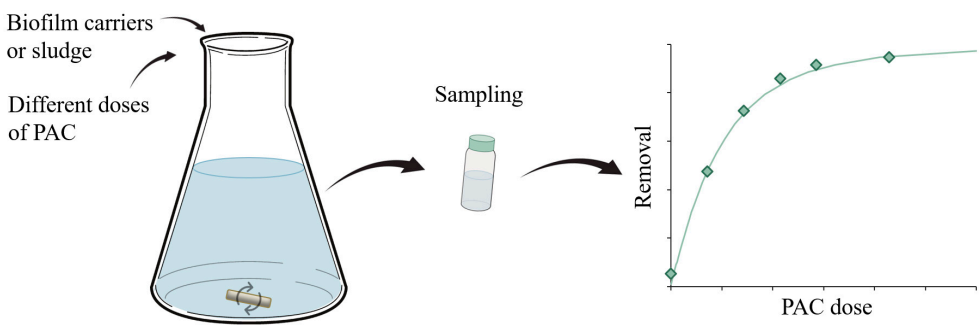


Figure 18. Illustration of the concept of the adsorption potential tests.

3.3 Differences between laboratory and pilot scale

Lab- and pilot-scale experiments both have strengths and weaknesses. Lab-scale experiments may be easier to perform due to their smaller size, and generally require less resources, water, and space, but may not reflect a large-scale process. Larger pilot-scale experiments may, on the other hand, be designed as a smaller version of a full-scale plant, and may therefore reveal practical aspects of the operation that may be relevant for further up-scaling.

The size and water demand of the pilot-scale experiments described in Papers I to IV required the units to be placed at WWTPs. Thus, the pilot-scale studies reflected natural variations in the water quality and temperature, allowing adaptation of the biomass to realistic wastewater conditions. However, such variations make it more difficult to draw conclusions regarding the reasons for changes in process performance. Lab-scale experiments allow for a more controlled environment, for example temperature, pH, and nutrients.

Another difference between the lab- and pilot-scale experiments is that the pilot-scale setups were operated in continuous mode, whereas batch experiments were performed in the laboratory. Continuous operation allows evaluation of the process performance under realistic conditions, whereas batch experiments provide a snap-shot of the potential removal under the conditions prevailing at a given time. A deeper understanding of a process may thus be obtained by combining batch and continuous experiments.

3.4 Analysis methods

In order to study the removal of a wide range of micropollutants in the treatment processes investigated, 34 environmentally relevant micropollutants were investigated (Table 1). The micropollutants vary in their chemical properties, such as size, charge, and aromaticity, and in use, such as pharmaceuticals (e.g., antibiotics, anti-inflammatory drugs, beta blockers, antiepileptics), X-ray contrast media, and biocides. The micropollutants were quantified using high-performance liquid chromatography via direct injection coupled with tandem mass spectroscopy (HPLC-MS/MS) in Papers I, II and III. In the final study (Paper IV), samples were prepared using solid phase extraction (SPE), and analyzed with ultra-performance liquid chromatography coupled with tandem mass spectroscopy (UPLC-MS/MS). The limit of quantification (LOQ) thus differed between the methods, generally from 0.2-2 ng/L with UPLC-MS/MS to 10-600 ng/L with HPLC-MS/MS.

Table 1. Micropollutants investigated and their classification, such as nonsteroidal anti-inflammatory drugs (NSAID) and angiotensin II receptor blockers (ARB).

Compound	Classification	Compound	Classification
Atenolol	Beta blocker	Losartan[2]	ARB
Benzotriazole	Corrosion inhibitor	Metoprolol[1, 2]	Beta blocker
Carbamazepine[1, 2]	Antiepileptic	Naproxen[2]	NSAID
Citalopram[1, 2]	Antidepressant	Oxazepam[2]	Sedative
Clarithromycin[1, 2, 3]	Macrolide antibiotic	PFOS[4]	Fluorosurfactant
Diclofenac[1, 2, 3, 4]	NSAID	Phenazone	NSAID
Erythromycin[2, 3]	Macrolide antibiotic	Propranolol	Beta blocker
Estrone[3]	Hormone	Roxithromycin	Macrolide antibiotic
Fluconazole[2, 3]	Antifungal	Sertraline[2]	Antidepressant
Gabapentin	Antiepileptic	Sotalol	Beta blocker
Ibuprofen[2]	NSAID	Sulfamethizole	Sulfonamide antibiotic
Imidacloprid[3, 4]	Neonicotinoid insecticide	Sulfamethoxazole[2, 3]	Sulfonamide antibiotic
Iohexol	Contract media	Tramadol[2]	Opioid analgesic
Iomeprol	Contract media	Trimethoprim[2, 3]	Antibiotic
Iopamidol	Contract media	Valsartan	ARB
Iopromide	Contract media	Venlafaxine[1]	Antidepressant
Ketoconazole[2]	Antifungal	Zolpidem[2]	Hypnotic

[1] Swiss indicator substance.
[2] Environmental indicator (*miljöindikator*) according to the Swedish Medical Product Agency.
[3] On EU watch list 1, 2, or 3.
[4] River-basin-specific pollutant (*särskilt förorenande ämnen, SFÄ*) according to the Swedish Agency for Marine and Water Management.

The methods used (HPLC-MS/MS and UPLC-MS/MS) are so-called targeted analytical techniques, meaning that a compound must be known to be analyzed. Transformation products may therefore only be detected if they are previously known and included in the analytical method, for example, four *N*-oxide transformation products described in Paper II. It is therefore possible to determine the concentration of certain micropollutants and the change in concentration during treatment, but it is not possible to identify the whole transformation pathway using only targeted mass spectrometry.

4 Biofilms for biological degradation of micropollutants

Increasing the removal of micropollutants in conventional biological treatment may be difficult, as the operating conditions and design parameters are often constrained by the existing infrastructure of the WWTPs. Integrating additional biological treatment steps at WWTPs may, however, improve the biodegradation of micropollutants.

Additional biological treatment for micropollutant removal has been referred to as tertiary treatment (Paper I; Abtahi et al., 2018), polishing (Escolá Casas et al., 2015b; Tang et al., 2017), and post-treatment (Liang et al., 2019) in the literature. The inconsistent use of terminology may be since the process is still being developed and the terminology has not been established. Tertiary treatment is more commonly applied to chemical or physical treatment of, e.g., phosphorus, while polishing often refers to filtration techniques used to remove particulate matter. Micropollutant removal, regardless of the technology, is sometimes referred to as quaternary treatment. However, the use of this term is not consistent due to variations in WWTP process configurations. In this dissertation, the use of MBBRs designed to remove micropollutants after the conventional biological treatment at WWTPs is referred to as additional biological treatment or additional MBBRs (Figure 19).

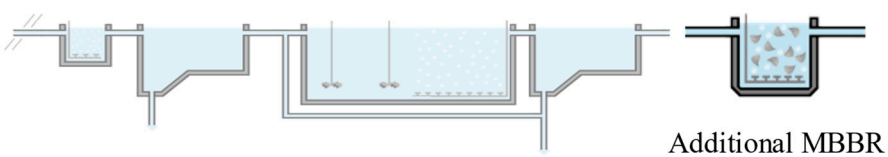


Figure 19. Schematic of additional treatment showing an MBBR for micropollutant removal. The process scheme used in the study described in Paper I.

The potential of biodegradation of micropollutants in additional MBBRs after an activated sludge process for biological phosphorus and nitrogen removal is presented in Paper I. Various operating conditions of the MBBRs were evaluated, such as substrate availability and redox conditions, in a single-stage MBBR, as well as a novel recirculating MBBR. To facilitate the evaluation of the differences between

operating conditions, the potential for biological degradation was discussed based on derived micropollutant degradation rates rather than removal in the pilot-scale MBBRs, as the removal in continuous reactors is limited due to generally low degradation rates and short HRTs. The degradation rate experiments also allowed prolonged exposure times.

4.1 Substrate availability and biomass concentration

An additional MBBR fed with biologically treated wastewater was compared with a high-loaded MBBR fed with primary treated wastewater to evaluate the degradation rate of a starved and a well-fed biofilm (Paper I). The degradation rates per unit biomass, k_{bio}, for several of the micropollutants, such as the beta blockers atenolol and metoprolol, the macrolide antibiotics clarithromycin and erythromycin, and the iodinated contrast media iohexol, iomeprol, and iopromide, were higher in the biofilm in the additional MBBR than in the high-loaded MBBR (Table 2). Decreasing substrate availability thus appears to have a positive effect on the degradation rate per unit biomass for several micropollutants, but at the expense of biomass concentration, in agreement with previous studies (Escolà Casas et al., 2015a; Mazioti et al., 2015). The lack of easily available substrates and phosphorus in the additional MBBR led to a low biomass concentration, 0.1 g/L, compared to that in the high-loaded MBBR, 1.5 g/L. Although the degradation rates of the biofilm were higher in the additional MBBR, the overall removal of micropollutants was lower due to the low biomass concentration. Predicting the biomass concentrations in the MBBRs presented in Paper I proved to be difficult as the substrate availability and load affect biofilm growth.

Table 2. Degradation rate constants normalized to biomass concentration, k_{bio}, (L/(g_{SS}d)) including the 95% confidence intervals (±) of selected micropollutants (< indicates rate constants below the experimental resolution).

	k_{bio} (L/(g_{SS}d))	
Compound	**High-loaded MBBR**	**Additional MBBR**
Atenolol	0.4 ± 0.1	5 ± 1
Carbamazepine	<0.02	<0.3
Clarithromycin	0.7 ± 0.3	3 ± 2
Diclofenac	0.1 ± 0.0	<0.3
Erythromycin	0.2 ± 0.2	2 ± 0.8
Ibuprofen	23[1]	15 ± 2
Iohexol	0.2 ± 0.1	1 ± 0.4
Iopromide	0.3 ± 0.2	1 ± 0.4
Metoprolol	0.1 ± 0.1	2 ± 0.2
Sulfamethoxazole	0.5 ± 0.2	<0.3
Trimethoprim	0.03 ± 0.04	0.3 ± 0.1

[1] Removed below the LOQ within 2 h of starting the experiment. Degradation rate estimated from only 2 data points.

4.2 Normalization of degradation rates

Conventional MBBRs are commonly designed based on nitrification rates and substrate loading rates per unit biofilm carrier surface area (Ødegaard et al., 2000). Evaluation of the degradation rates of micropollutants in MBBRs may also benefit from normalization to carrier surface area rather than biomass concentration, and this was introduced for the first time in Paper II, as k_{surf} (L/(m^2d)). Diffusion limitations in thick biofilms may limit aerobic degradation of micropollutants. Aerobic conditions have been shown to give faster degradation rates than in the absence of molecular oxygen under anoxic conditions with nitrate, or under anaerobic conditions without nitrate, for many micropollutants (Paper I; Phan et al., 2014; Xue et al., 2010; Suárez et al., 2010; 2012; Falås et al., 2013).

Additional MBBRs operated after the conventional biological treatment may not be susceptible to diffusion limitation in the biofilm due to low substrate availability and biomass growth, but evaluating micropollutant degradation rate constants normalized to carrier surface area, k_{surf}, may still be advantageous when comparing MBBR processes. The available carrier surface area is a design parameter that is controlled in MBBRs, whereas the biomass concentration rather reflects the operating conditions of the MBBR. The high-loaded and additional MBBRs described in Paper I were operated with the same carrier surface area, and the degradation potentials in the reactors are expressed as the degradation rates normalized to the surface area in Table 3. The degradation potentials were higher for the majority of the micropollutants in the high-loaded MBBR. Normalization to the biomass concentration may overestimate the degradation potential in reactors with thin biofilms (Table 2). The comparison of biofilm processes may therefore be more useful if it is based on a parameter that can be controlled. However, normalization of the degradation rate to biomass concentration is still useful when comparing biofilm processes to activated sludge systems.

Table 3. Biological degradation rate constants of selected micropollutants normalized to carrier surface area, k_{surf} (L/(m^2d)), including 95% confidence intervals (±).

	k_{surf} (L/(m^2d))				
	High-loaded MBBR	**Additional MBBR**		**High-loaded MBBR**	**Additional MBBR**
Atenolol	3.6 ± 1.0	2.8 ± 0.8	Iomeprol	1.7 ± 1.4	0.39 ± 0.18
Clarithromycin	6.2 ± 2.8	1.9 ± 1.3	Iopromide	2.6 ± 1.6	0.85 ± 0.22
Erythromycin	1.8 ± 1.6	1.2 ± 0.5	Metoprolol	1.2 ± 0.6	1.1 ± 0.1
Iohexol	2.0 ± 1.3	0.65 ± 0.22			

4.3 A novel recirculating MBBR configuration

A novel recirculating MBBR process configuration was introduced to combine the increased degradation capacity of starved biofilms with increased biomass concentration by supplying additional substrate. The recirculating MBBR was operated as an additional biological treatment step after conventional treatment, and additional substrate was supplied by circulating the biofilm carriers through a sidestream MBBR with primary treated wastewater. Three operating conditions were investigated, an aerobic or anaerobic sidestream with biologically treated wastewater in the main stream, and ozonated wastewater in the main stream with an aerated sidestream. The biomass concentrations under the above three operating conditions were 0.9, 1.8, and 2.3 g/L, respectively, i.e., significantly higher than in the additional conventional MBBR (0.1 g/L). The increased biomass enabled higher degradation rates of micropollutants normalized to the carrier surface area, k_{surf}, (Figure 20). Tang et al. (2020) proposed that increasing nutrient loads of organics (chemical oxygen demand, COD) and ammonium could increase the degradation rate. As the biomass tends to increase with increasing nutrient load, intermittent feeding with primary treated wastewater in additional MBBRs will increase the potential for biological degradation of micropollutants. However, further process development is needed to obtain an MBBR process that has an efficiency comparable to that of ozonation or activated carbon treatment in terms of targeting a wide range of compounds.

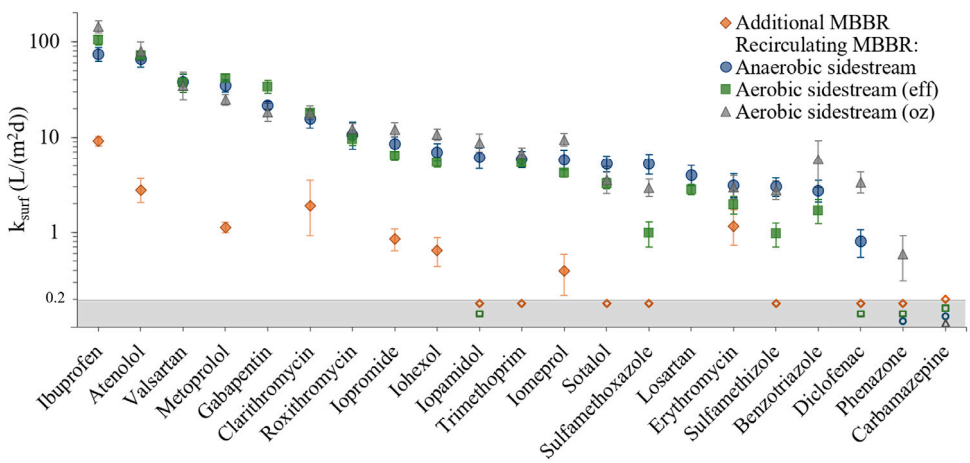
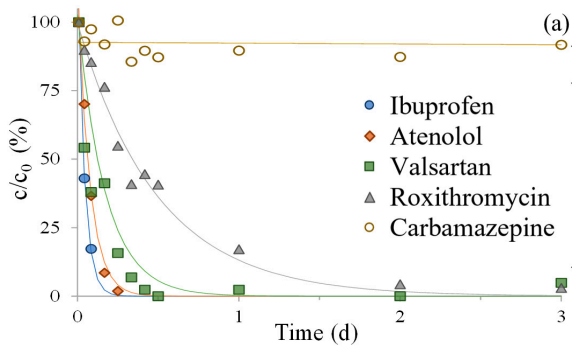


Figure 20. Biological degradation rate constants normalized to carrier surface area, ksurf, under four different operating conditions and feeding strategies in MBBRs. The recirculating MBBR was operated with secondary treated effluent (eff) or ozonated effluent (oz), while providing additional feeding in a sidestream with primary treated wastewater under different redox conditions. Error bars represent the 95% confidence intervals. The gray shaded bar and empty symbols represent degradation rates constants below the experimental resolution of 0.2 L/(m2d). (Figure modified from Paper I.)

The removal of micropollutants in the conventional biological treatment at Lundåkra WWTP, where the pilot-scale study described in Paper I was performed, was highest for ibuprofen (100%), sulfamethoxazole (75%), losartan (65%), gabapentin (64%), atenolol (47%), and valsartan (47%) (see Figure 4 in Chapter 2). Four of these compounds, ibuprofen, gabapentin, atenolol, and valsartan, had among the highest degradation rates in the additional MBBRs (Figure 20). The degradation of sulfonamides such as sulfamethoxazole appears to be associated with bacterial growth (Achermann et al., 2018b), and the removal is therefore expected to be lower in the additional MBBRs than in the conventional biological treatment. The removal of losartan varies between 20 and 60% in conventional biological treatment (Figure 4; Matsuo et al., 2011; Gurke et al., 2015), but degradation rates in additional MBBRs suggest low removal (Figure 20; Liang et al., 2021). Carbamazepine was not degradable in the conventional biological treatment (Figure 4), or in any of the additional MBBR process configurations evaluated (Figure 20). Biodegradation of carbamazepine is limited due to the low availability of moieties for biological reactions in its chemical structure (Kosjek et al., 2009).

Although the degradation rates per unit carrier surface area in the recirculating MBBR were significantly increased, only the easily degradable ibuprofen and atenolol showed values of removal exceeding 50% within 2 h of starting the batch experiments (Figure 21), which correspond to a degradation rate constant per unit carrier surface area greater than 50 L/(m^{2}d). The degradation of roxithromycin was slower, and 50% removal was only achieved after about 8 h in the batch experiments (Figure 21); the majority of the micropollutants showed even lower degradation rates (Figure 20). MBBRs in operation can be considered as a continuous stirred tank reactors and to achieve 50% removal with carriers from the recirculating MBBR with an HRT of 2 h, k_{surf} must exceed 70 L/(m^{2}d), which was only seen for ibuprofen and atenolol (Figures 20 and 21). Degradation rates of >290 L/(m^{2}d) would be needed to achieve 80% removal.



(b)

Micropollutant	k_{surf} (L/(m^{2}d))
Ibuprofen	143 ± 21
Atenolol	80 ± 18
Valsartan	35 ± 12
Roxithromycin	12 ± 2
Carbamazepine	<0.2

Figure 21. (a) Relative change in concentration (c/c_0) for selected micropollutants in degradation experiments with biofilm carriers from the recirculating MBBR, when the main stream was fed with ozonated wastewater. The lines show the fits to degradation according to first-order kinetics. (b) Degradation rate constant normalized to carrier surface area, k_{surf}.

5 Biofilms after ozonation

A biological post-treatment step is recommended following ozonation at WWTPs to mitigate possible adverse effects on the recipient water (Zimmermann et al., 2011; Prasse et al., 2015). Biofilm processes such as sand filters are a common choice (VSA, 2022b), although MBBRs have also been used (Baresel et al., 2019; Itzel et al., 2020). Pilot-scale ozonation and post-treatment with an additional MBBR (Figure 22) were used to investigate the removal of micropollutants and the formation of *N*-oxide transformation products and bromate during ozonation, as well as the potential for further biodegradation of micropollutants and *N*-oxides in the MBBR (Paper II). As the research presented in this dissertation was focused on engineering aspects of wastewater treatment, no ecotoxicological studies were included in the evaluation of process performance.

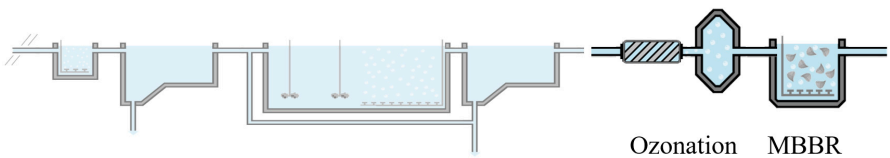


Figure 22. Schematic of the process configuration with ozonation and post-treatment additional MBBR described in Paper II.

5.1 Removal of micropollutants

The removal of micropollutants during ozonation was evaluated at 4 ozone doses (Paper II), and the results are presented in Figure 23. One-fifth of the micropollutants, including e.g., carbamazepine, diclofenac, sulfamethoxazole, and trimethoprim, were removed below the LOQ at the lowest ozone dose, 0.3 g O_3/g DOC. The removal of the other micropollutants increased with increasing ozone dose. At an ozone dose of 0.5 g O_3/g DOC, over 60% of most micropollutants was removed, in good agreement with the results of previous studies on ozone treatment of effluent wastewater (Reungoat et al., 2012; Lee et al., 2014; Bougin et al., 2018). However, other micropollutants were more persistent during ozone treatment, such as the iodinated contrast media iomeprol, iopamidol, and iohexol, as also reported by Margot et al. (2013) and Altmann et al. (2014).

Also, less than 50% of the antiepileptic drug gabapentin was removed at 0.5 g O_3/g DOC and higher ozone doses are required for improved removal (Kovalova et al., 2013).

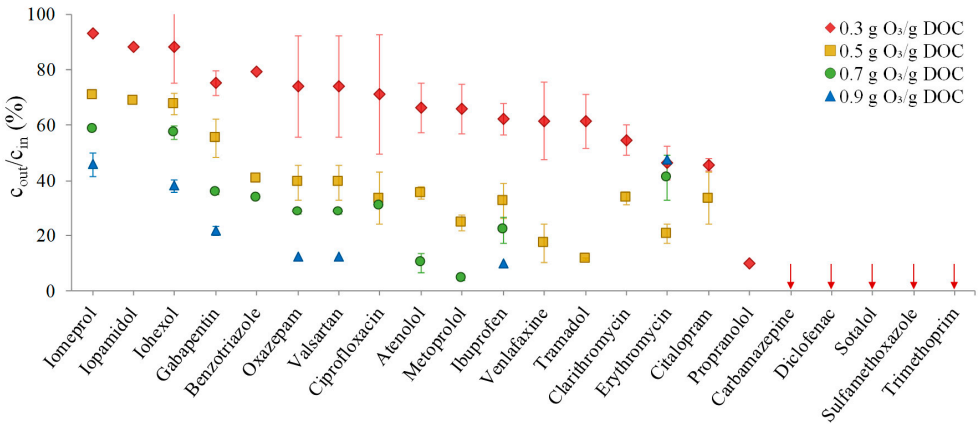


Figure 23. Relative change in concentration of micropollutants (c_{out}/c_{in}) after ozonation at four ozone doses. Error bars represent the standard deviation (n=3). The red arrows indicate removal below the LOQ at the lowest ozone dose. (Figure modified from Paper II.)

The pilot-scale MBBR presented in Paper II was operated as post-treatment to a pilot-scale ozonation plant. Three feeding strategies (no, low, and high additional load) were used to investigate the impact of biologically available substrates through intermittent feeding with influent wastewater from the primary settler. Increasing the substrate availability was expected to increase the biofilm growth, and thus possibly the degradation potential of the micropollutants. The biomass concentration on the carriers increased with increased substrate availability, from 0.3 g/L with no additional load to 1.0 g/L with high additional load (Paper II).

5.2 Substrate availability and biomass concentration

Increased values of the degradation rate, k_{surf}, were seen for about half of the micropollutants, e.g., atenolol, iohexol, iomeprol, and sulfamethoxazole, as the substrate availability was increased from no, to high, additional feeding (Table 4). However, the degradation rate decreased with increasing substrate availability for some of the micropollutants, such as metoprolol, iopamidol, and gabapentin (Table 4). No apparent trends were seen between the degradation potential and the chemical structure of the micropollutants. This could have been because the difference in the feeding strategies was not sufficiently great to cause significant changes in the micropollutant degradation rate. However, it is unlikely that large

volumes of influent wastewater would be directed to an additional MBBR treating ozonated effluent wastewater in practice, as this could lead to excessively high values of nitrogen, phosphorus, and BOD in the effluent of the WWTP. Other, unexplored factors, such as the microbial composition of the biofilm, may also explain the changes in the degradation rate constants.

Table 4. Degradation rate constants normalized to carrier surface area, k_{surf} (L/(m^{2}d)), including the 95% confidence intervals (±). The limit of experimental resolution was 0.2 L/(m^{2}d). No degradation kinetic data obtained (-). Degradation does not follow first-order kinetics (◊).

Compound	No additional feeding (L/(m^{2}d))	Low additional feeding (L/(m^{2}d))	High additional feeding (L/(m^{2}d))
Atenolol	38 ± 3.9	48 ± 5.1	48 ± 3.6
Carbamazepine	<0.2	0.2 ± 0.1	<0.2
Ciprofloxacin	-	1.2 ± 0.3	1.9 ± 2.1
Clarithromycin	◊	2.5 ± 0.4	13 ± 2.6
Diclofenac	1.6 ± 0.2	1.1 ± 0.2	1.2 ± 0.1
Gabapentin[1]	20 ± 6.4	5.8 ± 0.9	-
Ibuprofen	186[2]	190[2]	219[2]
Iohexol	9.6 ± 1.4	5.5 ± 0.7	23 ± 1.5
Iomeprol	5.7 ± 1	3.4 ± 0.6	16 ± 1.1
Iopamidol	5.6 ± 0.8	<0.2	<0.2
Metoprolol	24 ± 3.8	20 ± 1.5	17 ± 1.4
Oxazepam[1]	<0.2	0.3 ± 0.1	-
Sotalol	1.8 ± 0.5	1.2 ± 0.2	◊
Sulfamethoxazole	<0.2	0.2 ± 0.1	0.5 ± 0.2
Trimethoprim	2.0 ± 0.2	1.9 ± 0.2	4 ± 0.4

[1] Compound not spiked in batch experiments.
[2] Removed below LOQ within 2 h of starting the batch experiments. Degradation rate estimated from only 2 data points.

When the MBBR described in Paper II was operated with 2 h HRT and with no additional substrate load, significant removal was only observed for ibuprofen, while the indicated removal of iopamidol and iomeprol was about 20% (Figure 24). Degradation of the iodinated contrast media, such as iopamidol and iomeprol, could have an impact on the overall removal at WWTPs as these compounds are poorly removed in conventional wastewater treatment (Kormos et al., 2011) and by ozonation (Figure 23; Margot et al., 2013; Altmann et al., 2014; Lee et al., 2014). MBBRs designed for post-treatment following ozonation, as an alternative to sand filtration, would probably have short HRTs to limit the footprint of the treatment. A full-scale MBBR has been run with about 10 min HRT (Itzel et al., 2020) and a pilot-scale plant with 21 min HRT (Bourgin et al., 2018), however, such short times would limit the potential for the degradation of micropollutants. Simultaneous post-treatment and post-nitrification & denitrification as implemented on full scale at Nykvarns WWTP, Sweden, after a pilot-scale study (Baresel et al., 2016), may offer HRTs long enough to allow biodegradation of certain micropollutants. As the

purpose of the biological post-treatment is foremost to degrade by-products and reduce toxicity, it is expected that ozonation will be responsible for the main removal of the micropollutants.

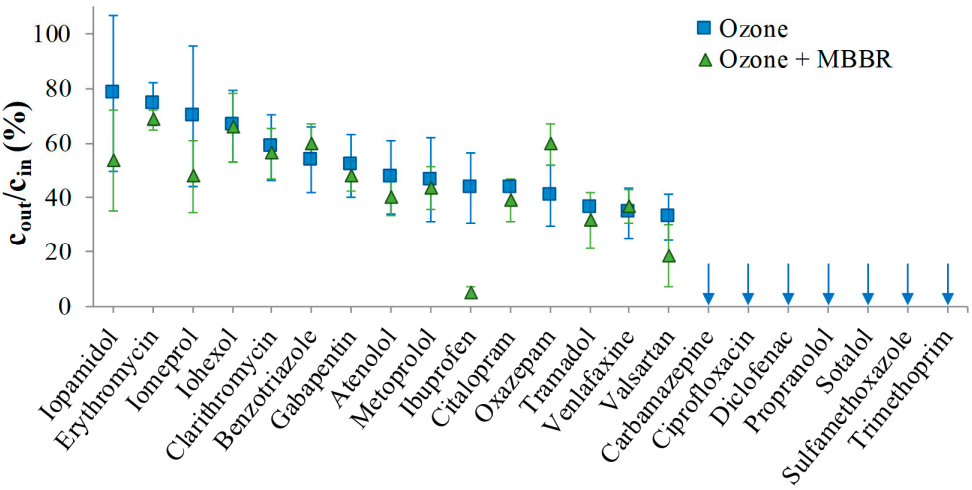


Figure 24. Relative change in concentration (c_{out}/c_{in}) of micropollutants after ozonation and subsequent MBBR treatment. Pilot-scale ozonation was operated with 0.5 g O_3/g DOC and the MBBR was operated with no additional load of influent water and 2 h HRT. Error bars show the standard deviation (n=3). Arrows indicate removal below the LOQ during ozonation. (Figure modified from Paper II.)

5.3 Formation and removal of *N*-oxide transformation products

The removal of micropollutants during ozonation results in oxidation to transformation products. The tertiary amines erythromycin, tramadol, clarithromycin, and venlafaxine are transformed into their corresponding *N*-oxide transformation products during ozonation, and these were investigated (Paper II). The results are shown in Figure 25. The *N*-oxide formation peaked at an ozone dose of 0.5 g O_3/g DOC, and was up to 80% of the influent concentration of the parent compound, consistent with previous studies suggesting *N*-oxides to be the main transformation products for tertiary amines (Lange et al., 2006; Zimmerman et al., 2012, Kharel et al., 2020). At higher ozone doses the concentration of *N*-oxides decreased, in agreement with results presented by Bourgin et al. (2018), Zucker et al. (2018), and Kharel et al. (2020), probably due to further oxidation.

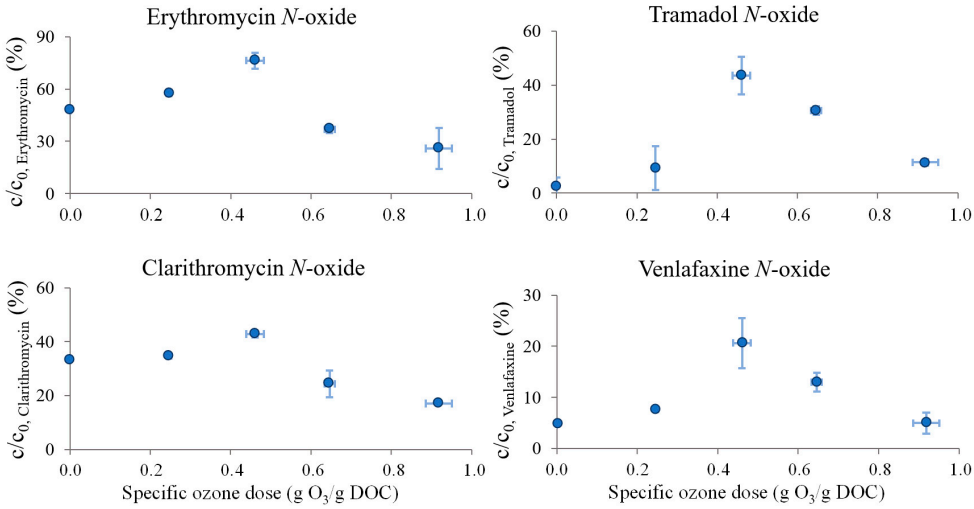


Figure 25. Relative change in concentrations (c/c_0) of four *N*-oxide transformation products after ozonation at various ozone doses. Error bars show the standard deviation (n=3). (Figure from supporting information of Paper II.)

The targeted *N*-oxides (erythromycin *N*-oxide, clarithromycin *N*-oxide, tramadol *N*-oxide, and venlafaxine *N*-oxide) underwent no or minor biodegradation during batch experiments, regardless of the operational conditions of the pilot-scale MBBR. The biodegradation rates were generally <0.2-0.35 L/(m^2d) (Paper II). Comparable degradation of venlafaxine *N*-oxide has been reported with activated sludge (Zucker et al., 2018). Biological degradation of erythromycin *N*-oxide and clarithromycin *N*-oxide have previously been observed in contact with biofilm carriers with higher biomass concentration (6.1 g/L; El-taliawy et al., 2018, compared to a maximum 1.0 g/L in the present work; Paper II), possibly facilitating increased removal rates. The *N*-oxides studied here were persistent in the pilot-scale post-treatment MBBRs after ozonation, consistent with the findings of Bourgin et al. (2018).

It is currently not known whether the *N*-oxide transformation products are toxic. The results and conclusions of ecotoxicological studies are in some ways more complex than those in engineering-oriented studies. Determining whether certain transformation products affect the toxicity may be useful in targeting specific groups of compounds and their fate in wastewater treatment and in the recipient water bodies. But as the identification and quantification of transformation products can be as challenging as evaluating the toxicity of specific compounds, it is sometimes more useful and practical to evaluate the toxicity of the wastewater before and after treatment, considering all the compounds present in the water. The effects on toxicity of wastewater after ozonation has been reported to vary depending on the evaluated organisms, the end point, and the wastewater being treated (Stalter et al., 2010a; 2010b; Gerrity & Snyder 2011; vom Eyser et al., 2013; Völker et al., 2019).

Post-treatment with sand filters has been reported to reduce (Stalter et al., 2010a; 2010b) or partly reduce toxicity (Magdeburg et al., 2014) after ozonation of wastewater, which highlights the need for biological post-treatment, although engineering studies may not fully reveal which compounds are removed in the post-treatment. Ozonation increases the biodegradability of the organic fraction in the wastewater (Phan et al., 2022), which may facilitate the degradation of some of the transformation and by-products formed. However, of the wide range of micropollutants, an even wider range of transformation products are formed during ozonation, some of which will be biodegradable, while others will be recalcitrant to biological degradation.

5.4 By-products produced by ozonation

Ozonation can lead to the formation of problematic by-products, such as bromate and NDMA (see, e.g., Hollender et al., 2009, Gerrity et al., 2015; Marti et al., 2015), by reactions with substances in the wastewater matrix. The formation of bromate during ozonation was studied on pilot-scale, and the results presented in Paper II.

Bromide is the primary precursor of bromate during ozonation, and the influent concentrations of bromide to the ozonation pilot ranged from 0.3 to 0.5 mg/L (Paper II). Lundåkra WWTP, where the pilot-scale study was performed, is situated close to the sea, and the bromide concentrations were in the range of those at other costal WWTPs, according to Falås et al. (2022), but considerably higher than at most non-costal WWTPs (Soltermann et al., 2016; Falås et al., 2022). Less than 10% of the bromide was oxidized to bromate, and the yields of bromate shown in Figure 26 are comparable to those reported by Soltermann et al. (2016). The elevated bromide concentrations resulted in bromate levels of 15-32 µg/L at 0.7 and 0.9 g O_3/g DOC (Figure 26). These bromate concentrations exceed the drinking water standard of 10 µg/L in several countries (USEPA 2006; EPA, 2012), and are not much less than the proposed environmental standard of 50 µg/L (Oekotoxzentrum, 2015), which limits the use of elevated ozone doses at Lundåkra WWTP. Full-scale ozonation of bromide-rich wastewater is not recommended, to avoid the formation of bromate (Schindler Wildhaber et al., 2015; Wunderlin & Gerlot, 2021).

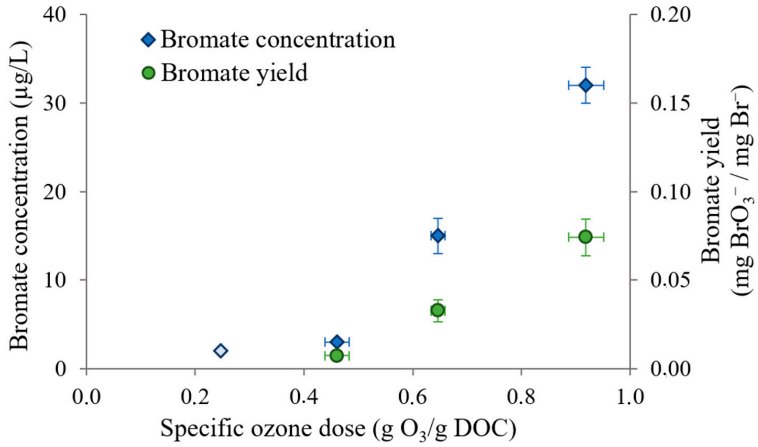


Figure 26. Bromide concentrations and yields after ozonation at various ozone doses. The empty symbol indicates a value below the LOQ (2 µg/L). Error bars show the standard deviation (n=3). (Data presented in Paper II.)

Bromate is not degraded during aerobic post-treatment following ozonation (Zimmermann et al., 2011; Bourgin et al., 2018). The reduction of bromate by denitrifying biofilms has been demonstrated in MBBRs at nitrate concentrations below 2 mg N/L, reaching 80% removal of bromate in 60 min (Falås et al., 2022). To achieve denitrifying conditions, the elevated oxygen concentration in the ozonated wastewater must be reduced. One way of achieving this is to use two-step post-treatment, as used at Nykvarns WWTP, Sweden (Barelsel et al., 2016), utilizing MBBRs with nitrification to consume the oxygen, followed by denitrifying conditions to achieve nitrogen removal. The potential for biological degradation of by-products as well as transformation products can be increased by prolonged HRTs (in the range of 1-2 h) in process configurations with post-nitrification and post-denitrification (Rusten et al., 1995; Ødegaard 2006), compared to sand filtration where the HRT is in the range of 10-26 min (Bourgin et al., 2018; Böhler et al., 2020), as discussed in Section 5.2.2.

The current recommendation is to employ biological post-treatment after ozonation to reduce the toxicity, but the design criteria that should be used to ensure adequate post-treatment are not well-defined. Increasing our knowledge of the fate of transformation and by-products, in combination with an improved understanding of the ecotoxicological benefits of various kinds of biological post-treatment, may facilitate tailored solutions depending on the needs of the WWTP.

6 Biofilms integrated with activated carbon processes

Integrated biofilm and activated carbon processes are in the subjects of Papers III and IV. These studies were carried out to evaluate the removal of micropollutants and increase our understanding of the role of the biofilm in these systems. The study presented in Paper III is the first in which simultaneous nitrification and micropollutant adsorption in a biofilm system was studied by dosing PAC into an MBBR.

Microbial colonization of GAC during operation turns the filters into biofilm systems. The effects of the biofilm in GAC filters have been studied using several approaches (Rattier et al., 2012; Paredes et al., 2016; Sbardella et al., 2018; Barelsel et al., 2019; Zhiteneva et al., 2020; Betsholtz et al., 2021), discussed in section 6.2.2. A novel approach was used in this work, in which the adsorption profiles of micropollutants were evaluated after pilot-scale operation of a GAC filter, as illustrated in Figure 27 (Paper IV).

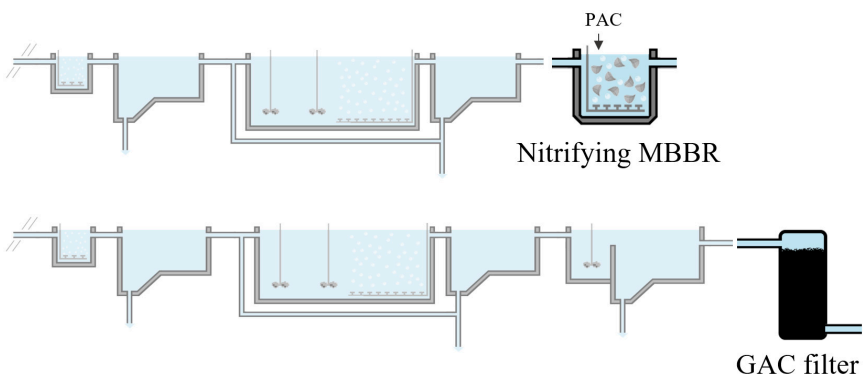


Figure 27. Schematics of the process configurations employing PAC dosing in a nitrifying MBBR and a GAC filter, described in Papers III and IV.

6.1 Integrating PAC dosing into MBBR treatment

Two pilot-scale MBBRs were operated in parallel, one with PAC dosing and one without, to determine the effects of PAC dosing on nitrification and micropollutant adsorption in biofilm systems (Paper III). The dosing of PAC was increased stepwise from 0 to 30 mg/L. The removal of micropollutants was evaluated in the two MBBRs, and lab-scale experiments were used to investigate possible effects of biomass. Changes in the microbial communities and nitrification rates were studied to elucidate possible effects on the biofilm composition.

6.1.1 Micropollutant removal

The removal of micropollutants in the pilot-scale MBBRs was due to adsorption on the PAC, as no significant removal was observed in the reference reactor without PAC (Figure 28). Furthermore, increasing the PAC dose increased the micropollutant removal. The insignificant removal of micropollutants in the reference MBBR is most likely due to the low sorption constants (k_d) and degradation rates (k_{bio}) of the micropollutants, as discussed previously (Section 2.3 and Chapter 4), in combination with low biomass concentration (1.5 g/L), sludge production (2.8 mg/L), and an HRT of 2 h, as presented in Paper III.

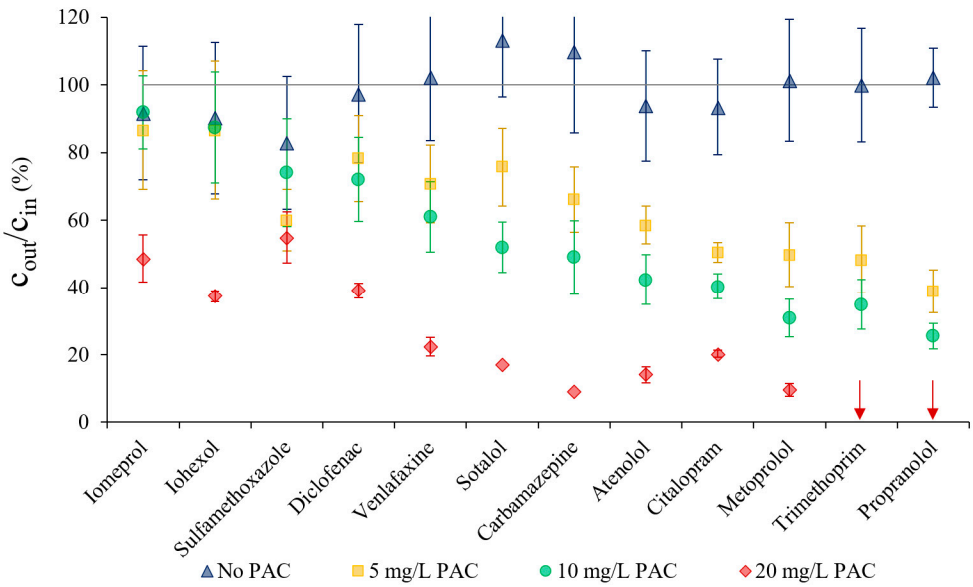


Figure 28. Relative change in concentration of micropollutants (c_{out}/c_{in}) in the MBBRs at various PAC doses. Error bars show the standard deviation (n=3 for 5, 10, and 20 mg/L PAC; n=12-18 for the reference reactor with no PAC). The arrows indicate micropollutant removal below the LOQ. (Figure modified from Paper III.)

The extent of adsorption to PAC differs between the micropollutants (Figure 28). The removal of the contrast media iomeprol and iohexol was poor, consistent with previous studies (Boehler et al., 2012; Margot et al., 2013; Altmann et al., 2014), whereas the removal of the beta blockers propranolol, metoprolol, and atenolol, and trimethoprim and carbamazepine was more extensive. Similar removal patterns have been reported in previous studies on PAC dosing in wastewater (Boehler et al., 2012; Margot et al., 2013; Altmann et al., 2014; Kårelid et al., 2017a), but lower PAC doses (mg/L) were generally needed to achieve removal rates similar to those found in the present work.

The average influent DOC concentration to the MBBRs in the present work was relatively high, 16 mg/L, compared to that in previous studies (Boehler et al., 2012; Margot et al., 2013) due to the process configuration of the WWTP. The removal rates of several micropollutants, such as atenolol, carbamazepine, diclofenac, and sotalol, were more comparable to those in other studies when the PAC dose was normalized to the DOC concentration (Margot et al., 2013; Kovalova et al., 2013; Altmann et al., 2014).

Lab-scale batch experiments showed that the adsorption of micropollutants to PAC was not affected by the presence of biomass or carriers (Paper III), indicating low interference with adsorption by suspended solids, supporting the findings of Streicher et al. (2016), who reported only slightly lower micropollutant removal in the presence of activated sludge than in wastewater without solids.

Freundlich isotherms were derived based on the results of the batch experiments with the PAC dose normalized to the DOC concentration. The removal of four model micropollutants (atenolol, metoprolol, carbamazepine, and venlafaxine) in the pilot-scale MBBR could be predicted with good precision using the derived isotherms (Figure 29). The good agreement suggests that batch adsorption experiments can be used to predict micropollutant removal on full scale. Although dosing of PAC may be integrated in a biofilm system, such as an MBBR, the removal of micropollutants can be predicted without considering the presence of biomass and carriers.

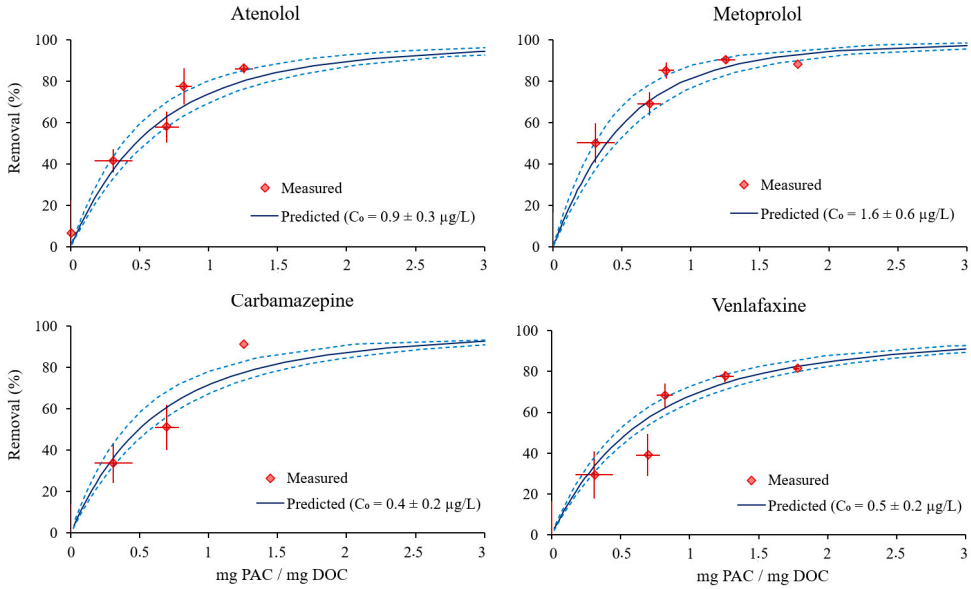


Figure 29. Measured and predicted removal of organic micropollutants in the pilot-scale MBBR. The predictions are based on Freundlich isotherms obtained from batch experiments and the average influent micropollutant concentration into the pilot plant (solid lines). Dotted lines indicate the standard deviation of the influent concentration (C0). (Figure modified from Paper III.)

6.1.2 Role of the MBBR

The MBBRs described in Paper III contained nitrifying biofilm carriers and were operated after a high-loaded activated sludge process. Micropollutant removal was attributed to adsorption to the PAC, and was not significantly influenced by the biofilm, as described in the previous section. The PAC was integrated to some extent into the biofilm, and the nitrification rate and microbial composition of the biofilm were investigated to evaluate the effects on the biofilm of the dosing of PAC. The nitrification capacity of the biofilm increased over time, but remained comparable in the two MBBRs, indicating continuous adaptation of the biofilms to the operating conditions, but no effect of PAC dosing (Table 5). An HRT of 2 h was sufficient to achieve almost complete nitrification in both MBBRs (Table 5).

Table 5. Nitrification rate and average effluent concentration with standard deviations (±) in the pilot reactors. MBBR denotes the reference reactor without PAC dosing, and PAC-MBBR denotes the reactor with doses of 5, 10, 15, 20, or 30 mg PAC/L (n=3). (Table modified from Paper III.)

PAC dose	**5 mg PAC/L**		**10 mg PAC/L**		**15 mg PAC/L**		**20 mg PAC/L**		**30 mg PAC/L**	
Duration	Day 47-69		Day 69-92		Day 92-121		Day 121-141		Day 141-155	
	MBBR	PAC-MBBR	MBBR	PAC-MBBR	MBBR	PAC-MBBR	MBBR	PAC-MBBR	MBBR	PAC-MBBR
NH_4-N (mg/L)	1.9 ± 1.3	1.6 ± 1.2	1.7 ± 1.4	3.2 ± 3.0	0.6 ± 0.0	0.8 ± 0.1	0.5 ± 0.3	0.5 ± 0.2	0.8 ± 0.2	0.6 ± 0.1
Nitrification rate (g NH_4-N/(m^2d))	0.8	0.7	1.3	1.0	2.0	1.7	1.8	1.6	2.0	2.0
Nitrification rate (g NO_3-N/(m^2d))	0.7	0.7	1.6	0.7	1.8	1.5	1.6	1.4	1.9	1.8

The microbial communities in both MBBRs were dominated by nitrifiers (*Nitrospira* spp. and *Nitrosomonas* spp.) in the biofilms (Paper III corrigendum). The relative abundance of *Nitrospira* spp. increased from 8.2% to 20% and *Nitrosomonas* spp. from 4.8% to 16%, supporting the increase in nitrification rate during the operation of the MBBRs (Table 5). Further assessment of the composition of the microbial community, presented in Paper III, showed that the development of the microbial communities in the two MBBRs followed the same trajectory over time. The statistical analysis suggested that the influence of PAC dosing on the microbial community was small, and differences between the biofilms were mainly attributed to microorganisms with low relative abundance.

Nitrification was the main function of the biofilm, and it was unaffected by the addition of PAC to the MBBR. However, other biological functions, such as the degradation of micropollutants, could have been affected, but this was not observed in the study. Microorganisms with low relative abundance, <1%, could be important for the degradation of certain micropollutants, such as ibuprofen, naproxen, and diclofenac (Vuono et al., 2016; Falås et al., 2018). Identifying the microorganisms responsible for the degradation of micropollutants is difficult due to the complex composition of the biomass in biofilms and activated sludge in wastewater treatment, but it has been proposed that certain organisms are linked to the degradation of micropollutants (Harb et al., 2016; Falås et al., 2018; Gallardo-Altamirano et al., 2019; Liang et al., 2021). An improved understanding of the microbial communities may be necessary to understand the differences in micropollutant removal in biological wastewater treatment.

The potential effects of the addition of PAC to an MBBR on micropollutant degradation rates could have been studied using batch incubations of the biofilm carriers, similarly to the degradation experiments presented in Papers I and II. However, the degradation capacity must be significantly increased for biodegradation to have any practical relevance in MBBRs with an HRT of 2 h.

When integrating dosing of PAC into an MBBR, the role of the biofilm will be to perform the biological removal of nutrients such as nitrogen and phosphorus, and organic fractions, whereas micropollutants will be removed mainly by adsorption onto the PAC. The biofilm is likely to affect the removal of micropollutants indirectly by degrading organics and decreasing the DOC concentration, thus decreasing the PAC dose required to achieve equivalent micropollutant removal.

Recirculation of the PAC in biological wastewater treatment has been reported to increase the utilization of the adsorption capacity of the PAC (Boehler et al., 2012; Meinel et al., 2016; 2016b; Kårelid et al., 2017b). In activated sludge processes, recirculation is built into the system with the return sludge, and the retention time of the PAC is determined by the SRT. The process configurations of MBBRs differ, and the recirculation of water or sludge is not required to maintain the biological function. The retention time of PAC in MBBRs would therefore be determined by the HRT, and could be significantly shorter than in activated sludge processes, except for a small portion of the PAC being integrated into the biofilm and retained in the MBBR. Recirculation of separated PAC in an MBBR would increase the retention time of PAC in the system and likely increase the carbon utilization, but would not affect the utilization of the biofilm as the HRT is unaffected.

Increasing recirculation increases the concentration of suspended solids in a system and, at some point, this may affect the subsequent separation of PAC. Separation of the suspended solids was not included in the study described in Paper III, and it was not expected to be a problem as several separation techniques are available, such as sand filters (Altmann et al., 2015b), sedimentation and sand filters, with and without flocculation (Boehler et al., 2012; Meinel et al., 2016; Kårelid et al., 2017b), and UF (Löwenberg et al., 2014).

Integrating PAC dosing into MBBRs may allow compact process configurations for the simultaneous adsorption of micropollutants and conventional biological treatment, such as nitrification and denitrification. This combination of treatment methods may be particularly convenient at WWTPs where space is limited.

6.2 Biofilms in GAC filters

Biofilms can be found on the granules of GAC filters. Micropollutants are mainly removed via adsorption in GAC filters, but it is not known how, biodegradation may contribute to the removal of micropollutants. Micropollutant removal in GAC filters is commonly described in terms of breakthrough curves, as illustrated in Figure 30 (e.g. Nguygen et al., 2013; Kennedy et al., 2015; Zietzschmann et al., 2016; Fundneider et al., 2018; Merle et al., 2020). The GAC filter is considered to be a black box, and the influent and effluent concentrations are used without considering the removal mechanisms. Breakthrough curves have indicated some biological

degradation (Fundneider et al., 2021a). Several other approaches have also been used to distinguish between adsorption and biodegradation in GAC filters (Rattier et al., 2012; Paredes el al., 2016; Sbardella et al., 2018; Barelsel et al., 2019; Zhiteneva et al., 2020; Betsholtz et al., 2021), increasing our understanding of the role of the biofilm.

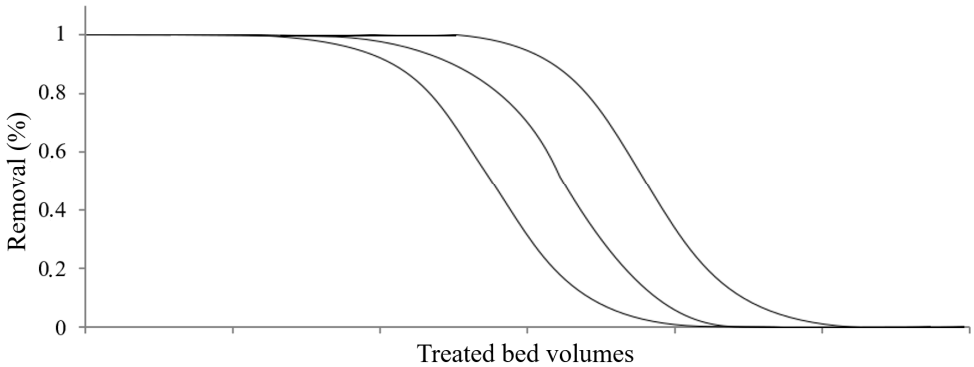


Figure 30. Illustration of breakthrough curves for micropollutants in GAC filters. The curves represent different micropollutants.

The adsorption profiles of micropollutants in a GAC filter were obtained by extracting adsorbed micropollutants from GAC samples from four filter depths (Paper IV). Biodegradation by the biofilm was considered to explain the spatial and temporal development of the adsorption profiles of certain micropollutants.

6.2.1 Adsorption profiles of micropollutants

Adsorption profiles, expressed as the amounts of various micropollutants extracted at several filter depths, have not previously been extensively studied in large-scale wastewater applications. The adsorption profiles were evaluated at four filter depths at 2600, 7300, and 15,500 BVs and the results are shown in Figure 31. Stratification of the micropollutant abundance in the filter bed was evident at 2600 BVs. Several compounds with positive charge and high adsorption affinity to activated carbon (Moreno-Castilla 2004; Guillossou et al., 2020; Gidstedt et al., 2022), such as propranolol, metoprolol, and citalopram, were found primarily in the top layer (10-20 cm). Uncharged and negatively charged compounds with lower affinity to activated carbon (Paper III; Boehler et al., 2012; Margot et al., 2013; Mailler et al., 2015; Kårelid et al., 2017b; Gidstedt et al., 2022), such as sulfamethoxazole and PFOS, were observed in the deeper layers of the filter, corresponding to three-quarters of the filter depth.

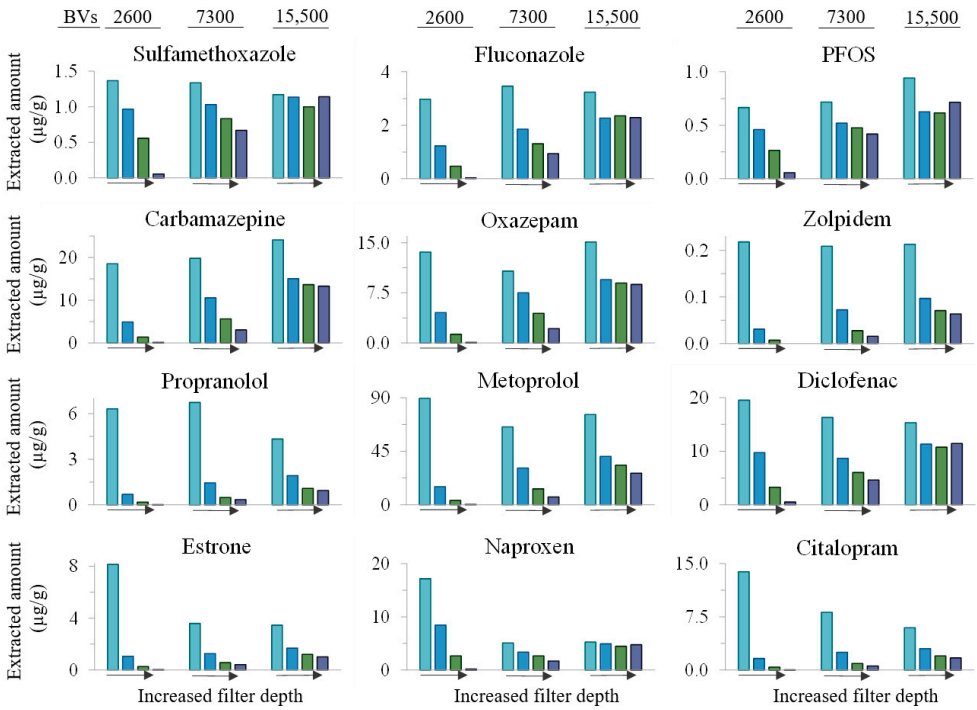


Figure 31. Adsorption profiles of selected micropollutants through the GAC filter, expressed as the amount of micropollutant extracted per amount of GAC (µg/g), at three occasions, 2600 BV, 7300 BV, and 15,500 BV. Darker color of the bar represents deeper sampling point of the GAC filter. (Figure from Paper IV.)

Higher amounts of the micropollutants were extracted from the deeper layers of the filter at 7300 and 15,500 BVs (Figure 31), as seen, for example, for carbamazepine and oxazepam, which are persistent in conventional wastewater treatment (Wick et al., 2009; Luo et al., 2014; Tran & Gin., 2017; Ejhed et al., 2018). Increasing amounts of adsorbed micropollutants were expected as micropollutants were continuously removed from the treated wastewater.

For certain micropollutants, such as estrone, naproxen, and citalopram, the amount extracted decreased over time (Figure 31), although the GAC filtration resulted in continuous removal of > 75% of the influent concentrations of these micropollutants. Estrone and naproxen were degraded in the full-scale WWTP (see Figure 4 in Chapter 2). Degradation is also possible in biofilm systems (Miège et al., 2008; Zorita et al., 2009; Suárez et al., 2010; Ejhed et al., 2018; Shreve & Brennan 2019), which suggests that the biofilm in the GAC filter contributed to the degradation of these micropollutants. Biodegradation may therefore explain the decrease in the extracted amounts of the micropollutants over time.

6.2.2 Biodegradation in GAC filters

Biological degradation of naproxen, estrone, and citalopram was proposed based on the temporal variations in the adsorption profiles of extracted micropollutants, as discussed in the previous section (Paper IV). A comparison of the amounts of micropollutants extracted and estimates of the accumulated amount removed, based on the influent and effluent concentrations in the GAC filter, also indicated biological degradation of diclofenac, sulfamethoxazole, ibuprofen, clarithromycin, and venlafaxine, for which the amounts extracted corresponded to 28%, 38%, 11%, 22%, and 17% of the estimated accumulated amount removed at 15,500 BV, respectively. Sulfamethoxazole is mainly degraded in activated sludge processes (see Figure 4 in Chapter 2; Fernandes-Fontaina et al., 2016), whereas the other compounds are also biodegradable in biofilm processes (Paper I; Torresi et al., 2016; Falås et al., 2016; Liang et al., 2019).

Degradation of naproxen, diclofenac, and ibuprofen in GAC filters has been suggested by the detection of transformation products (Fundneider et al., 2021a) or other end-products (Betzholts et al., 2021). Others have differentiated between micropollutant adsorption and biodegradation by inhibiting the biological activity of the biofilm in batch incubations (Rattier et al., 2012) or in lab-scale filters (Paredes et al., 2016; Sbardella et al., 2018). Both increased (Rattier et al., 2012; Sbardella et al., 2018) and decreased (Paredes et al., 2016) removal of certain micropollutants e.g., sulfamethoxazole, by GAC filters with an active biofilm, have been reported. The presence of a biofilm may limit the accessibility of the adsorption sites on the GAC but may, on the other hand, continuously degrade organic matter (Reungoat et al., 2011; Altmann et al., 2016; Benstoem et al., 2017) and micropollutants, possibly increasing the number of adsorption sites available for micropollutants.

Biodegradation of DOC in GAC filters is supported by the fact that the breakthrough curves reached a steady state at 10-15% removal (Paper IV; Altmann et al., 2016), and similar reasoning suggests the biodegradation of metoprolol (Fundneider et al., 2021a). Rapid small-scale column tests have also been used to estimate the degree of biodegradation in GAC filters (Zhiteneva et al., 2020). However, the need to validate the results, by, for example, the measurement of transformation products, was highlighted as there were also indications of biodegradation of the non-degradable carbamazepine.

Although the biodegradation of certain micropollutants may be indicated by studies such as that described in Paper IV, it is difficult to determine the extent and long-term effects of biological degradation in GAC filters. Biodegraded micropollutants (transformation products) may be adsorbed onto the GAC or may exit the filter with the water. However, it is difficult to determine the fate and effects of the transformation products as all the major biodegradation pathways may not yet be elucidated. Quantifying the amounts of micropollutants adsorbed on used GAC may

also be challenging. The recovery rates of adsorbed micropollutants can be determined by extraction in batch experiments with new GAC. However, these recovery rates are unlikely to be valid when the GAC has been used for several months, as covalent bonds may form between the GAC surface and micropollutants (Moreno-Castilla 2004). This phenomenon may not have been considered in a previous study where a different extraction method to that described in Paper IV was used (Baresel et al., 2019). They proposed that biological degradation accounted for most of the removal, as <32% of e.g., carbamazepine, citalopram, diclofenac, oxazepam, and propranolol were retrieved in the extraction. As carbamazepine and oxazepam are difficult to biodegrade in any biological process, it is likely that other mechanisms are responsible for the differences seen between the extracted and removed amounts in the GAC filter.

It was concluded in Paper IV and shown in Figure 32 that increased levels of an adsorbed micropollutant in the bottom layer of the filter bed resulted in decreasing removal efficiency of the micropollutant in the treated wastewater for the majority of the compounds. However, this was not the case for naproxen, ibuprofen, or venlafaxine, for which the adsorption profiles in Figure 32a indicate biological degradation, as discussed above. Although low amounts of these compounds were found in the bottom layer of the filter bed (Figure 32b), their removal efficiency decreased over time. Adsorption of the transformation products may affect the adsorption capacity of the GAC, but this must be verified in future studies.

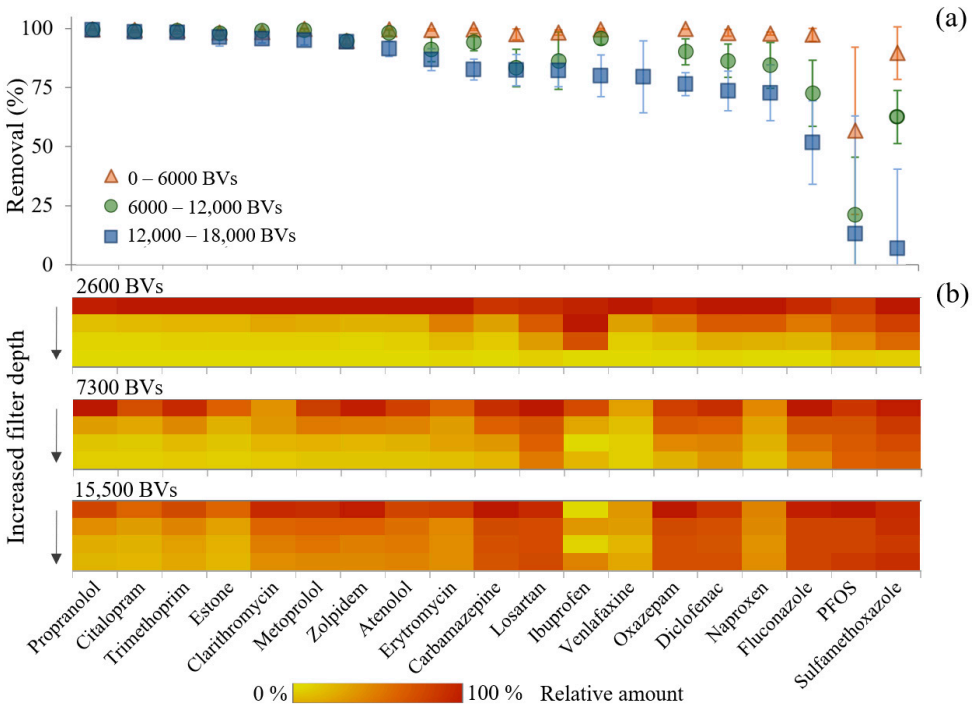


Figure 32. (a) Micropollutant removal efficiencies in the treated wastewater (0-6000 BVs, n=10; 6000-12,000 BVs, n=8; 12,000-18,000 BVs, n=7) and (b) relative adsorption profiles in the GAC filter. The relative adsorption profiles are depicted as the amount of micropollutant extracted from each filter depth, expressed as the relative amount of the highest amount extracted per micropollutant. (Figure from Paper IV.)

The development of biofilms on large-scale GAC filters is inevitable. The use of various approaches to evaluate the effects of biofilms on GAC filters may contribute to our overall understanding of the process. Such a biofilm may have positive or negative effects on several aspects of the operation of GAC filters. Biofilm growth shortens backwashing intervals (Fundneider et al., 2021a), increasing the need for maintenance of the filters. However, a biofilm may contribute by the removal of residual fractions of DOC and nitrification (Yapsakli & Çeçen, 2010), increasing the quality of the effluent wastewater, not only in terms of micropollutants. The way in which we approach and value such a biofilm in GAC filters will probably evolve as our understanding of the biofilm increases.

7 Conclusions

The research described in this dissertation focuses on how biofilms can be utilized to improve micropollutant removal in WWTPs. The pilot-scale studies provided the possibility to adapt biofilms to ambient wastewater conditions and to evaluate the performance of the processes in continuous experiments. The complementary lab-scale studies provided systematic approaches to gain a deeper understanding of the processes.

Part 1 of this work was focused on biofilms for the biological degradation of micropollutants in additional MBBR treatment processes. Normalization of the degradation rates to the biofilm carrier surface area, k_{surf}, was suggested as a better reflection of design and operational parameters in diffusion-limited biofilm systems, such as MBBRs, than the more common normalization to biomass concentration, k_{bio}.

In the additional biological treatment, the degradation rate of most micropollutants increased with increasing biofilm growth, by providing additional substrate from primary treated wastewater as a complement to the biologically treated wastewater. Aerobic conditions were also needed to support the biological degradation of micropollutants with redox-sensitive degradation patterns, such as diclofenac, metoprolol, and valsartan.

Although the degradation rate of most micropollutants could be increased by development of the MBBR process, significant removal of a wide range of micropollutants would require HRTs that are probably unrealistic for full-scale implementation at WWTPs. Furthermore, some compounds, such as carbamazepine, are recalcitrant to biological degradation, regardless of the biological process. Nevertheless, biofilms may still play an important role in the removal of micropollutants, but as part of process configurations including ozonation or activated carbon.

Part 2 of this work highlighted some aspects of process configurations combining biofilms and ozonation or activated carbon. In the combination of ozonation and MBBR post-treatment, the micropollutants were predominately removed during ozonation. Several *N*-oxide transformation products that were formed were persistent in contact with the biofilm. To evaluate the relevance of degradation in post-treatment it may be useful to include toxicity studies or transformation products and by-products that may be a cause for concern.

When combining MBBR treatment with dosage of PAC, the biofilm was responsible for nitrification and micropollutants were removed by adsorption to the PAC. More importantly, nitrification had no negative influence on the removal of micropollutants, and vice versa. This combination of technologies allows compact solutions for simultaneous nitrification and micropollutant removal, which are particularly interesting for WWTPs with space limitations.

GAC filters evolve to provide a combined adsorption and biofilm process due to microbial colonization of the granules. Biological degradation of certain micropollutants, such as naproxen, diclofenac, and sulfamethoxazole, was suggested based on the temporal variations of the adsorption profiles and rough mass estimates. The extraction method used may be further developed to allow determination of the extent and long-term effects of biological degradation in the GAC filters.

The two studies in which biofilms and activated carbon were combined also highlighted aspects of micropollutant removal not associated with the biofilm. The extraction of micropollutants from four filter depths in the GAC filter allowed adsorption profiles to be obtained through the filter, verifying the theoretical adsorption theory. Initially, adsorption occurs in the top part of the filter. The adsorption fronts of the various micropollutants then progress through the filter bed at varying rates, where well-adsorbing compounds, such as propranolol and citalopram, advance slower than compounds with lower adsorption affinity, such as sulfamethoxazole, PFOS and fluconazole.

The removal of micropollutants with PAC in an MBBR could be controlled by the dose of activated carbon, where increasing the dose improved the removal efficiency. Removal could also be predicted using the results of batch experiments and Freundlich isotherms. Thus, rather simple batch studies may be useful when assessing the process performance prior to full-scale implementation, possibly reducing the need for continuous pilot-scale studies.

Micropollutant removal at WWTPs can be influenced by biofilm processes in several ways, as discussed in this dissertation. Whether the biofilm directly degrades the micropollutants or facilitates removal by ozonation or activated carbon depends on the process configuration. In the case of MBBRs the process is designed to make use of the biofilm, whereas in a GAC filter the biofilm will form regardless of engineering design. Increasing our understanding of the possibilities and applications of biofilms will help us take advantage of the properties of biofilms.

8 Future work

Biofilms in GAC filters may degrade part of the organic fraction and certain micropollutants, but the way in which this degradation affects the service life of the GAC is largely unknown. Further studies are required to reveal whether biological degradation increases the number of available adsorption sites, or if transformation products are adsorbed on the GAC. Since micropollutants are a diverse group of compounds their fate in GAC filters is likely to be compound-specific. The service life of GAC is also likely to be affected by the organic fraction in the water. Organics are present at concentrations of mg/L, whereas the levels of micropollutants are in ng-µg/L, yet the service life is determined by the removal of micropollutants. Methods to predict the service life of GAC would facilitate operation and cost estimates of GAC filters.

Targeting groups of transformation products, whether they arise from biological degradation or ozonation, using radiolabeled (^{14}C) micropollutants as a complement to targeted analysis, could improve our understanding of the fate of these compounds in wastewater treatment. Radiolabeling may allow us to differentiate between sorption, uptake, degradation, and reactions with specific moieties of the micropollutants, and could be applied to several treatment methods, such as biological processes, ozonation, and GAC filters, or a combination of these.

In addition to further studies to evaluate the removal of micropollutants and transformation products with different treatment processes, ecotoxicological studies should be carried out to evaluate the overall effects of micropollutant removal treatment. Ecotoxicological studies may also highlight compounds of concern with regards to potential effects on the aquatic environment.

Wastewater treatment in Sweden is facing many challenges as more stringent effluent demands are being placed on organics, nitrogen, and phosphorus, while loads are increasing from growing cities. The Swedish Water Association is also working towards a climate-neutral water and wastewater sector by 2030. Furthermore, the need to implement micropollutant removal at WWTPs would require substantial infrastructural investments. In the context of the subject of this dissertation, I believe that the choice of treatment method for micropollutant removal will be governed by the existing infrastructure and the challenges facing a particular WWTP. Future studies should therefore include the aspects of climate impact and possible synergies with stringent effluent demands.

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WATER DOESN'T COME FROM THE TAP, nor does it disappear with a toilet flush, it circulates. Wastewater treatment is critical to protect our aquatic environment from harmful substances such as pharmaceutical residues and other organic micropollutants. How treatment can be implemented is currently being developed and evaluated in terms of both technical and legislative aspects. This dissertation addresses some technical solutions for micropollutant removal. The findings can contribute to more efficient wastewater treatment so that the generations to come can continue to enjoy our open waters.

ELLEN EDEFELL holds a Master of Science in Engineering, Biotechnology. In 2017, she started her doctoral studies in Water and Environmental Engineering at Lund University as an industrial PhD student together with Sweden Water Research. Her research has been focused on the removal of organic micropollutants from wastewater using biofilm systems as stand-alone treatment or in combination with ozonation or activated carbon.

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