Demonstration of Hybrid Ceramic Membrane Filtration for the Removal of Organic Micropollutants from Municipal Wastewater Treatment Plant Effluent

The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under Grant Agreement no. 308339 for the research project DEMEAU

www.demeau-fp7.eu

Title: Demonstration of Hybrid Ceramic Membrane Filtration for the Removal of Organic Micropollutants from Municipal WWTP Effluent

Summary: This deliverable presents the outcomes of pilot studies carried out to investigate the removal of organic micropollutants by the use of Hybrid Ceramic Membrane Filtration (HCMF) systems in field conditions of full scale municpal waste water treatment plants in the Netherlands and Switzerland.

Both studies demonstrated that the combination of PAC (powdered activated carbon) and ceramic membrane filtration is able to remove emerging pollutants up to 90 %. The level of removal was determined mainly by the level of PAC dosage. In both cases, stable operation could be achieved.

Grant agreement no:	308339
Work Package:	WP22
Deliverable number:	D22.1
Partner responsible:	KWR and FHNW
Deliverable author(s):	Arslan Ahmad (KWR), Wolter Siegers (KWR), Jan Svojitka (FHNW), Jonas Löwenberg (FHNW)
Quality assurance:	Emile Cornelissen (KWR) and Emiel Nijhuis (RWB)
Planned delivery date:	September 1st, 2015
Actual delivery date:	September 1st, 2015
Dissemination level:	PU = Public

KWR
Watercycle Research Institute

n|w
University of Applied Sciences
Northwestern Switzerland

WATERSCHAP
vechtstromen

Rwb

Table of contents

LIST OF FIGURES III

LIST OF TABLES V

ABBREVIATIONS VI

SUMMARY 1

1 INTRODUCTION 2

1.1 Project background 2

1.2 Ceramic MF/UF in water and wastewater treatment 3

1.3 Hybrid MF/UF membrane filtration 4

1.4 Organic micropollutants in the aquatic environments 4

1.5 Aim and layout of this deliverable 5

2 HCMF PILOT TESTS AT WWTP ALMELO IN THE NETHERLANDS 6

2.1 Material and methods 6

2.1.1 Feed water characteristics 6
2.1.2 Organic micropollutants 7
2.1.3 Membranes 7
2.1.4 Powdered activated carbon 7
2.1.5 Pilot plant layout 7
2.1.6 Pilot tests 8
2.1.7 Sampling and analysis 14
2.1.8 Bio assay measurements 14

2.2 Results and discussion 14

2.2.1 Removal of organic micropollutants 14
2.2.2 Measurements with different Bio assays 21
2.2.3 Process performance of HCMF 21

2.3 Conclusions 23

2.4 Recommendations for further research 23

2.5 References 24

3 HCMF PILOT TESTS AT WWTP BIRSFELDEN IN SWITZERLAND 28

3.1 Introduction and objectives 28

3.2 Experimental setup and methods 28

3.2.1 Hybrid ceramic membrane process 29
3.2.2 Analytical methods 33

3.3 Results and Discussion 35

3.3.1 Reference run 35
3.3.2 PAC 1 37
3.3.3 PAC + Fe 1 40
3.3.4 PAC + Fe 2 44
3.3.5 PAC 2 47

3.4 Conclusions 49
3.5 References 49

List of Figures

Figure 1.1: Overview of the DEMEAU Project. 3
Figure 2.1 Aerial view of WWTP Sumpel at Almelo. 6
Figure 2.2: Process scheme of PAC-CMF pilot setup operated at WWTP Almelo. 9
Figure 2.3: Photographs of the PAC-CMF pilot setup operated at WWTP Almelo. 11
Figure 2.4: Average removal (±standard deviation) of the OMPs by pilot-scale HCMF system at permeate flux of 60 L/m^2.h. 15
Figure 2.5: Average removal (±standard deviation) of the OMPs by pilot-scale HCMF system at permeate flux of 100 L/m^2.h. 16
Figure 2.6: Average removal (±standard deviation) of the OMPs by pilot-scale HCMF system at permeate flux of 100 L/m^2.h. 16
Figure 2.7: Influence of permeate flux on average removal of OMPs at 15 mg/L PAC dose 17
Figure 2.8: Influence of permeate flux on average removal of OMPs at 30 mg/L PAC dose 18
Figure 2.9: Removal of the OMPs (sorted on the basis of charge) at permeate flux of 60 L/m^2.h. 19
Figure 2.10: Removal of the OMPs (sorted on the basis of charge) at permeate flux of 100 L/m$^{2.}$h. 19
Figure 2.11: Removal of the OMPs as a function of solute LogD$_{pH7,4}$ values at 60 L/m^{2}h flux. 20
Figure 2.12: Removal of the OMPs as a function of solute LogD$_{pH7,4}$ values at 100 L/m^2.h flux. 21
Figure 2.14: TMP build up during a longer term experiment with a flux of 100 L/m^2.h with PAC dosing. 22
Figure 2.15: TMP build up during a longer term experiment with a flux of 100 L/m^2.h without PAC dosing. 23
Figure 3.1 View on the WWTP Birsfelden 29
Figure 3.2 – Schematic of double HCMP 30
Figure 3.3 – Photo of the PAC + UF pilot plant 31
Figure 3.4 – View of contact and filtration tank with the ceramic membrane 31
Figure 3.5 – Trans-membrane pressure and suspended solids during the reference run (arrows indicate recovery cleanings) 35
Figure 3.6 Trans-membrane pressure and fouling rate during the reference run 36
Figure 3.7 Concentration of micropollutants in the influent and permeates from the HCMP systems during the reference run 36
Figure 3.8 Removal of micropollutants during the reference run 37
Figure 3.9 LC-OCD analysis of the influent and HCMP effluents during the reference run 37
Figure 3.10 Trans-membrane pressure and suspended solids during the PAC 1 phase (arrows indicate recovery cleanings) 38
Figure 3.11 Trans-membrane pressure and fouling rate during the PAC 1 phase 39
Figure 3.12 Concentration of micropollutants in the influent and permeates from the HCMP systems during the PAC 1 phase 39
Figure 3.13 Removal of micropollutants during the PAC 1 phase 40
Figure 3.14 LC-OCD analysis of the influent and HCMP effluents during the PAC 1 phase 40

Figure 3.15 Trans-membrane pressure and suspended solids during the PAC + Fe 1 phase (arrows indicate recovery cleanings) 41
Figure 3.16 Trans-membrane pressure and fouling rate during the PAC + Fe 1 phase 42
Figure 3.17 Concentration of micro pollutants in the influent and permeates from the HCMP systems during the PAC + Fe 1 phase (day 14-26)..... 42
Figure 3.18 Removal of micro pollutants during the PAC + Fe 1 phase (day 14-26)..... 43
Figure 3.19 Concentration of micro pollutants in the influent and permeates from the HCMP systems during the PAC + Fe 1 phase (day 14-26)..... 43
Figure 3.20 Removal of micro pollutants during the PAC + Fe 1 phase (day 14-26)..... 44
Figure 3.21 Trans-membrane pressure and suspended solids during the PAC + Fe 2 phase (arrows indicate recovery cleanings) 45
Figure 3.22 Trans-membrane pressure and fouling rate during the PAC + Fe 2 phase 45
Figure 3.23 Concentration of micropollutants in the influent and permeates from the HCMP systems during the PAC + Fe 2 phase 46
Figure 3.24 Removal of micropollutants during the PAC + Fe 2 phase 47
Figure 3.25 Trans-membrane pressure and fouling rate during the PAC 2 phase (arrows indicate recovery cleanings) 48
Figure 3.26 Trans-membrane pressure and cleaning efficiency of CEB in HCMP 1 during the PAC 2 phase 49

List of Tables

Table 2.1 Quality of the effluent of WWTP Almelo during OMP removal tests. 7

Table 2.2: Background and dosed concentrations of selected organic micropollutants in the effluent of WWTP Almelo. 10

Table 2.3: Ceramic membrane characteristics. 12

Table 2.4: Process parameters during pilot tests. 12

Table 2.5: Experiments to investigate OMP removal. 13

Table 2.6: Experiments to investigate process stability. 13

Table 2.7: The average removal and physicochemical properties of selected OMPs. 20

Table 2.8: The results of the Bio assay measurements and calculated removal rates 22

Table 3.1 WWTP effluent quality from 2011[n= 12–127] 28

Table 3.2 – Summary of design technological parameters during different operational phases 32

Table 3.3 Average concentration of selected pollutants in influent to the HCMP systems 34

Abbreviations

BZT – Benzotriazole
CBZ – Carbamazepine
CEB – Chemical enhanced backwash
DCF – Diclofenac
DOC – Dissolved organic carbon
MEC – Mecoprop
PAC – Powdered activated carbon
SBR – Sequencing-batch-reactor
SMX – Sulfamethoxazole
TMP – Transmembrane pressure
TSS – Total suspended solids
UF – Ultrafiltration
WWTP – Wastewater treatment plant
HCMP – Hybrid ceramic membrane process
LMH – $L \cdot m^{-2} \cdot h^{-1}$
LC-OCD – liquid chromatography – organic carbon detection

Summary

The objectives of current study were (i) to demonstrate the hybrid ceramic membrane filtration (HCMF) systems for the effective removal of organic micropollutants (OMPs), (ii) to demonstrate that HCMF can be applied to waste water treatment and (iii) to optimize the ceramic membrane operation by piloting the hybrid configurations. This report presents the findings of the pilot scale investigations that were undertaken in the Netherlands (WWTP Almelo) and in Switzerland (WWTP Birsfelden).

A powdered activated carbon – ceramic membrane filtration (PAC-CMF) pilot plant was operated at WWTP Almelo in the Netherlands for investigation of the removal of 18 OMPs and the stability of the hybrid process by short and long term experiments. Firstly, the removal of OMPs was studied at three PAC dosages (15, 30 and 60 mg PAC/L) and at two permeate fluxes (60 and 100 L/m^2.h) by short term tests. Secondly, long term experiments were conducted to investigate the stability of the hybrid PAC-CMF process. These tests aimed at studying the effect of PAC dosing on the development of transmembrane pressure (TMP) at different permeate fluxes during continuous pilot plant operation. In general, the removal of OMPs increased with PAC dosage. The highest OMPs removal (70-90 %) was achieved with 60 mg PAC/L. With a relative low dose of 15 mg PAC/L only 0-20 % OMPs removal was measured, while with 30 mg PAC/L about 20-70 % removal of OMPs could be achieved. A stable flux of 100 L/m^2.h was achieved during the long term experiments. CEB with NaOCl was adequate to maintain a stable PAC-CMF process. No significant correlations were found between OMPs removal percentages and physicochemical properties of the OMPs such as electrostatic charge, $\log K_{OW}$ or $\log D_{pH\ 7,4}$.

In addition to the pilot study in the Netherlands, another HCMF pilot plant was carried out at the municipal wastewater treatment plant (WWTP) ARA Birs (Basel-Landschaft, Switzerland) to investigate removal of OMPs. The pilot unit consisted of two identical HCMF process units, so that the influence of different operational parameters could be compared. The pilot operation comprised five operational phases with different doses of PAC (sorbent), $FeCl_3$ (coagulant), filtration flux or chemical cleaning frequency. The total operation time was approximately 300 days. During all operational phases filtration parameters (flux, fouling rate etc.) were recorded continuously; while the concentration of selected OMPs in the influent and effleunts from the HCMF units was determined during the 5 measurement campaigns. Four of the campaigns covered five substances: sulfamethoxazole, mecoprop, diclofenac, benzotriazole and carbamazepine; additional 60 pharmaceutical compounds were analysed during the fifth campaign. Further analyses included the dissolved organic carbon (DOC) profiles in the influent and effluent samples by liquid chromatography – organic carbon detection (LC-OCD). Most of the detected OMPs were removed from the municipal wastewater by the tested PAC-UF process with 60 to 95% efficiency, although the removal of some compounds was <10 % (e.g. hydroxy ibuprofen). Especially the non-polar compounds (benzotriazole, carbamazepine and diclofenac) were removed with 80 to 95 % efficiency. Negligible removal of the target compounds was observed during the reference phase, i.e. without PAC addition into the system. Lower fouling was observed during the operational phase with PAC addition compared to the reference phase. After stabilization of the PAC concentration the average fouling rate decreased from 3-4 kPa/d to 2-2.5 kPa/d. The enhancement of PAC separation by coagulation by Fe^{3+} addition could not lead to stable operation, possibly due to high mixing gradients in the compartments of the HCMF units, which did not provide proper conditions for flocculation.

1 Introduction

1.1 Project background

DEMEAU in a nut-shell

The water and wastewater sector worldwide is facing tremendous challenges to assure safe, cost-effective and sustainable water supply and sanitation services. Policy makers are calling for sustainable solutions for existing and emerging challenges. For many previous years emerging pollutants in the water cycle have been the subject of many European research projects. Within these projects a suite of novel technologies and practices have been developed, however, these technologies have not yet reached the status of widespread uptake in practices and policies.

DEMEAU aims at promoting the uptake of knowledge, prototypes and practices from previous EU research to enable the water cycle sector to face emerging pollutants and thus securing water and waste water services and public health. The project exploits four groups of promising technologies from previous EU research (Figure 1.1).

- Managed aquifer recharge
- Hybrid ceramic membrane filtration and automatic neural net control
- Advanced oxidation processes
- Bioassays

Exploitation of knowledge takes place through action research with universities, research institutions, innovative SME's, water utilities as launching customers and policy makers. Existing and improved methodologies are used to assess performance of the novel technologies and to demonstrate their suitability and cost-effectiveness. Moreover, drivers and barriers regarding implementation of the innovations are explored within various cases by means of social scientific methods. To foster a broader impact and market penetration of the technologies, DEMEAU seeks cooperation with relevant policy makers, regulators and standardization bodies on Member State and European level in order to address the identified implementation drivers and barriers.

Work Package 22

Whilst polymeric membranes are extensively used in water treatment to remove pathogens, particles and (partly) organics from surface, ground, process and filter backwash water, ceramic membranes are currently limited in use for these purposes. Lab-scale research in TECHNEAU showed that hybrid processes with ceramic membranes (combinations of ceramic membranes with processes such as in line coagulation, pre-coats of powdered activated carbon, ion exchange pre-treatment etc.) are promising cost effective candidates for many tasks in future water treatment schemes. Coupling ceramic membranes with other processes (such as activated carbon, ion exchange) into hybrid ceramic membrane filtration systems (HCMF) can effectively contribute towards achieving the overall DEMEAU goal, i.e. stimulating the application of promising technologies – in this case HCMF. The objective of WP22 (WA2) was to demonstrate HCMF systems for the effective removal of dissolved compounds (e.g. emerging substances) and to optimize ceramic membrane operation by piloting hybrid configurations.

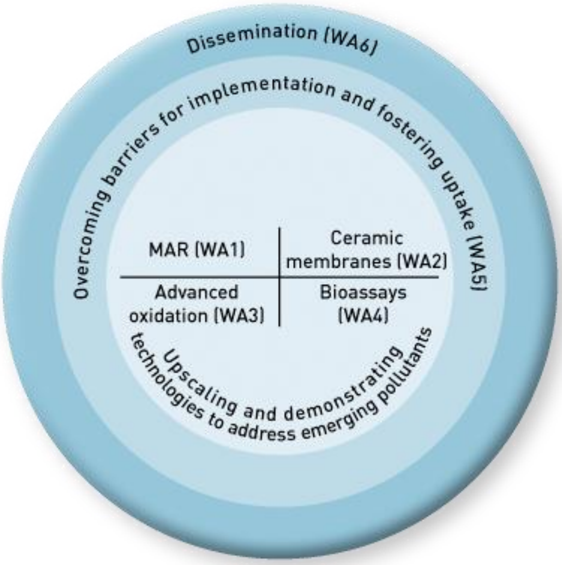

Figure 1.1: Overview of the DEMEAU Project.

1.2 Ceramic MF/UF in water and wastewater treatment

Microfiltration (MF) and ultrafiltration (UF) processes offer the possibility to remove particles, colloids, microorganisms (bacteria and viruses) and precursors for disinfection by-products (e.g. organic matter) in drinking water production and waste water treatment. Compared to alternative separation processes, such as coagulation/flocculation and sand filtration, MF/UF processes are compact, modular, require only a moderate amount of chemicals and can be easily automated. Commercial MF and UF membranes are either polymeric or ceramic, however, the application in water treatment is still dominated by polymeric membranes. Ceramic MF/UF membranes are applied in industrial processes such as clarification of natural fruit juices (Fokumoto et al., 1998), waste water filtration from pulp and paper production (Luonsi et al., 2002; Park et al., 2006), waste water treatment in textile industry (Voigt et al.,2001; Weber and Seidel 2003) and dairy processing (Grangeon and Lescoche 2000; Zapata-Montoya et al., 2006). Ceramic MF /UF membranes offer a better mechanical, chemical and thermal stability compared to polymeric MF/UF membranes resulting in a longer lifetime (Tsuru, 2001). Furthermore, compared to polymeric MF/UF membranes, ceramic MF/UF membranes can be operated at higher fluxes and higher recoveries (Kanaya et al.,2007) and can be cleaned with more extreme cleaning agents for a better fouling control.

Ceramic MF/UF membranes used in water treatment are aluminum oxide (Bottino et al., 2001; Lerch. et al., 2005; Matsui et al., 2005; Shirasaki et al., 2009), titanium dioxide (Lee and Cho, 2004), zirconium dioxide (Ericsson and Tragardh, 1997) and a titanium dioxide/zirconium dioxide combination (Bodzek and Konieczny 1998; Klomfas and Konieczny, 2004; Konieczny et al., 2006). The most commonly applied ceramic membrane material is aluminum oxide (α- Al_2O_3) because of the stability in alkaline and acidic environments. Alternative ceramic membrane materials are silicon carbide (SiC), silicon nitride (Si_3N_4) and aluminum nitride (AlN), although the application of these materials in ceramic MF/UF membranes is limited.

The charge of ceramic MF/UF membranes not only plays an important role in removal mechanisms, but also in fouling by particles, micro-organisms, organic matter and precursors for disinfections by-products. Membrane fouling and deposition of silica particles of uncharged ceramic MF/UF membranes was found to be higher than for charged ceramic MF/UF membranes (Nazzal and Wiesner, 1994). The charge of the membrane is pH dependent and can be determined by zeta-potential measurements (de la Rubia et al., 2006) and membrane surface titration. The water chemistry, the presence of particles, micro-organisms and organic matter, and membrane fouling will untimely alter the membrane charge during ceramic membrane filtration.

Commercial ceramic MF/UF membrane modules are available as monoliths, plate membranes and hollow fiber membranes (Chan and Brownstein, 1991; Strathmann, 2000). Ceramic monolith membranes are produced in one part by extrusion and have a low surface area. For full scale applications multiple ceramic elements are inserted within stainless steel housings. Ceramic monolithic membranes have considerable higher packing densities (e.g. up to 25 m^2) compared to the alternative ceramic membrane modules (Chan and Brownstein, 1991). Ceramic plate membranes are produced as discs and are housed in a plate-and-frame configuration. The membrane discs can be individually inspected or replaced which facilitates a better fouling control. Flow distribution in plate membranes is, however, not optimal and the packing density is relatively limited. Ceramic hollow fiber membrane modules have the highest packing density (Peters et al., 2005).

Ceramic MF/UF membranes are operated either in cross-flow or in (semi) dead-end mode. In cross-flow operation the feed flow is tangential to the permeate flow. While in (semi) dead-end operation the feed flow is perpendicular to the permeate flow. In dead-end mode retained solutes accumulate on the membrane surface to form a cake layer with an additional resistance to feed flow. A periodic back wash will temporarily revert the negative effects of the build-up of the cake layer. In ceramic MF/UF both operational modes are applied, cross-flow operation with a different cross-flow velocities ranging from 0.1 to 4 m/s (Bodzek and Konieczny, 1998; Lee and Cho, 2004) and dead-end operation with different back wash frequencies ranging from 20 minutes to 17 hours (Ericsson and Tragardh, 1997; Klomfas and Konieczny, 2004; Lerch. et al., 2005; Matsui et al., 2005; Konieczny et al., 2006; Shirasaki et al., 2009) were found.

1.3 Hybrid MF/UF membrane filtration

The pore size of MF/UF membranes is larger than the size of many pollutants (e.g. viruses, dissolved heavy metals, OMPs etc.). Therefore, pretreatment is generally applied before the membranes to retain these (smaller) solutes and the combined process is regarded as “hybrid membrane filtration (HMF)”. The application of pre-treatment processes is also an effective measure to control membrane fouling (Brink et al., 1993; Jacangelo et al., 1995). Depending on the pollutant to be treated, a variety of processes can be applied as pre-treatment, for example, coagulation, flocculation, sedimentation, sand filtration, ozonation, activated carbon treatment etc. Cornelissen et al., 2009 showed that hybrid processes with ceramic membranes (combinations of ceramic membranes with processes such as in line coagulation, pre-coats of powdered activated carbon, ion exchange pre-treatment etc.) are promising cost effective candidates for many tasks in future water treatment schemes. Löwenberg et al., 2015 compared two PAC-UF processes for the removal of OMPs from a wastewater treatment plan effluent and found efficient removal of selected OMPs in both systems.

1.4 Organic micropollutants in the aquatic environments

Organic micropollutants (OMPs) include any organic compounds that occur in concentrations ranging from microgram per liter to nanogram per liter in water. These typically include pesticides, pharmaceutical residues, hormones, personal care products, flame-retardants, plasticizers, perfluorinated compounds etc. Organic micropollutants are sometimes also described as emerging pollutants, priority contaminants or trace organic contaminants. Toxicology studies have shown that aquatic organisms (e.g. fish) in natural waters that receive wastewater effluents containing organic micro-pollutants can exhibit adverse effects that are directly attributable to OMPs. The accumulation of OMPs in natural waters, wastewaters and drinking water is a societal challenge that needs to be addressed as a priority (Kolpin et al., 2002; Gälli et al., 2009; Goetz et al., 2011). The metabolites and degradation by-products of certain OMPs may pose higher risks than the parent compounds.

Micropollutants are introduced into the natural environment through municipal or industrial wastewater**,** agriculture, traffic, and direct emissions (Heberer, 2002). The main source has been identified to be the effluents of WWTPs (Gälli et al., 2009). Reducing the discharge of OMPs to natural water bodies has been an active research area for past many years (van Beelen, 2007). In the EU Water Framework Directive 2008 33 substances or groups of substances are on the list of priority substances. The monitoring of these substances is mandatory in EU member states. In the 1980s, Dutch and Flemish drinking water companies were confronted with the issue of elevated pesticide concentrations in surface waters. To counter that, pressure was exerted by the government on farmers and producers to develop alternatives for the use of pesticides, and also drinking water barriers were improved by implementing activated carbon filtration. Subsequently, attention was also drawn to other OMPs as a result of more accurate analyzing methods and/or higher discharge of these pollutants to the environment (Verliefde et al., 2007). In Switzerland, legislative changes are underway which will force 100 of the currently 700 operating WWTP to be upgraded with an additional treatment step to remove OMPs (Gälli et al., 2009).

Several treatment methods are available to remove OMPs from water. Most widely applied techniques include membrane treatment (Verliefde et al., 2007), advanced oxidation processes (Altmann et al., 2014) and activated carbon adsorption (Margot et al., 2013). Latest research is focused on the development of new energy-efficient treatment technologies and to optimize existing treatment practices to remove OMPs from water and wastewater in a sustainable way.

1.5 Aim and layout of this deliverable

This report presents the findings of pilot scale investigations that were carried out in the Netherlands (WWTP Almelo) and in Switzerland (WWTP Birsfelden). The aim of pilot testing was to demonstrate the OMPs removal and field scale implementation potential of HCMF systems.

In section 1 of this report (current section), a brief introduction of ceramic membrane technology has been provided followed by a description of the importance of OMPs in aquatic environments and water and wastewater treatment research.

Section 2, describes the pilot tests carried out at WWTP Almelo in the Netherlands. The logistics involved, materials, methods and outcomes are discussed.

And, Section 3 describes the pilot tests carried out at WWTP Birsfelden in Switzerland. The logistics involved, materials, methods and outcomes are discussed.

.

2 HCMF pilot tests at WWTP Almelo in the Netherlands

The WWTP Almelo in the Netherlands (coordinates: 52.341542, 6.639701) has a design capacity of 1530 m^3/h during dry weather conditions and 5200 m^3/h during rainy conditions. The biological capacity is designed at 115,000 pollution equivalents at 54 g of BOD. It has been managed and operated by Waterschap/waterboard Vechtstromen. The full scale treatment process includes mechanical pre-treatment with screening, grit removal and fine screening as well as an activated sludge treatment with nutrient removal by nitrification-denitrification and simultaneous biological phosphorous removal.

From January to June 2015, a HCMF using PAC pilot plant was operated at WWTP Almelo in the Netherlands for investigating the removal of OMPs and the stability of hybrid process. Throughout the pilot testing, the pilot plant was operated by KWR Watercycle Research Institute. In this section PAC-CMF and HCMF will be used interchangeably to refer to the pilot setup.

2.1 Material and methods

2.1.1 Feed water characteristics

During all the tests, actual effluent of WWTP Almelo was used to feed the PAC-CMF pilot. The average pH of the pilot plant feed (WWTP effluent) was determined at 7.4. Measurements of WWTP effluent quality, performed in 2014, showed average total N concentration of 6.2±4.7 mg/L (n=57), total P concentration of 1.7±1.2 mg/L (n=57), COD of 33.7±8.5 mg/L (n=50) and BOD of 2.3±1.5 mg/L (n=50). The tests to determine the removal of OMPs at different PAC dosages and permeate fluxes were investigated during 3 days (16-04-2015, 23-04-2015 and 30-04-2015). The WWTP effluent water quality on the given dates varied and is illustrated in Table 2.1.

Figure 2.1 Aerial view of WWTP Sumpel at Almelo.

Table 2.1 Quality of the effluent of WWTP Almelo during OMP removal tests.

Date	Total N mg/L	Total P mg/L	BOD mg/L	COD mg/L
16-04-2015	10	1.2	2	46
23-04-2015	4.6	0.57	2	41
30-04-2015	3.6	0.35	2	37

2.1.2 Organic micropollutants

Since the background concentrations of OMPs were relatively low in the WWTP effluent, a cocktail of 18 pre-selected OMPs was dosed to the WWTP effluent to produce the feed for the OMP removal experiments (Table 2.2). The cocktail was prepared at KWR Watercycle Research Institute to achieve approximately 1 µg/L of each OMP in the cocktail. This would allow to quantify the removal up to >99 %.

2.1.3 Membranes

The pilot plant consisted of two METAWATER ceramic membrane (2x0.4m^2, 0.1µm) modules. The membranes were operated in dead-end mode (i.e. no concentrate circulation) throughout the pilot testing period.

2.1.4 Powdered activated carbon

The NORIT® CA1 PAC, supplied by Cabot Norit Nederland B.V., was used during the entire period of pilot testing. The median size d_{50} and specific surface area of PAC was reported as 30 µm and 1400 m^2/g respectively by the supplier.

2.1.5 Pilot plant layout

The schematic diagram of the PAC-CMF pilot is shown in Figure 2.2. The cocktail of OMPs was dosed in-line to the feed stream by using a dosing pump (Grundfos ALL DOSE). The pilot plant contained 2 ceramic membranes (please note: Figure 2.2 shows only 1 membrane) which were fed from the bottom using a feed pump (0.5 m^3/h maximum flow at 3.5 bar). Produced permeate (i.e. filtrate) left the membrane modules at the top and was collected in a 10 L permeate storage tank (PVC material). Table 2.3 presents further details of the membrane modules and design (operating) parameters. PAC was dosed in-line in the form of a slurry (10 g/L slurry in demineralized water) using a peristaltic pump (Masterflex® Model 7519-10). The PAC slurry was dosed from a separate container where it was continuously being mixed to avoid settling of activated carbon particles.

The pilot setup offered the possibility of in-situ cleaning of the membranes. Approximately 3 L of the permeate produced in each filtration cycle was stored in a backwash tank (material: stainless steel) that could be pressurized by a compressor unit. The stored permeate was used for backwashing.

For collecting the feed and permeate samples, taps were available at different points in the pilot setup (indicated in Figure 2.2). Transmitters for turbidity, flow, pH, temperature, level and pressure were available on both feed and permeate sides. Data from the transmitters was logged continuously.

For the control of the HCMF process a Siemens S7 PLC was provided within the pilot container. Process operation and programming was done using a Siemens MP377 touch screen multi-panel. Dosing of PAC, filtration and membrane cleaning was therefore fully adjustable.

2.1.6 Pilot tests

Pilot tests were designed to investigate the removal of OMPs at different PAC dosages and PAC-CMF process performance. The filtration time, hydraulic backwash strategy (frequency and duration) and chemical cleaning strategy (chemical choice, frequency, soaking duration) were optimized before starting the actual experiments. Table 2.4 includes the process parameters that were kept stable throughout the pilot testing period.

The removal of OMPs was studied at three PAC dosages (15, 30 and 60 mg PAC/L) and at two permeate fluxes (60 and 100 L/m^2.h). The tests were performed at 3 separate days. Since the feed water was pumped directly from the effluent reservoir of the WWTP, considerable variation in feed quality was encountered (see Table 2.1). Each short term experiment (for investigating the OMPs removal efficacy of the PAC-CMF process) started at the beginning of the day and included starting the pilot installation , adjusting the permeate flux to a required level (60 or 100 L/m^2.h), checking the process stability (flux, TMP) during 2 filtration cycles and finally collecting the feed and permeate samples during the 3rd filtration cycle. The duration of each filtration cycle was kept at 900 sec. The permeate samples were collected between 200 and 800 sec of the filtration cycle. The feed samples were collected from the tap that was installed before the in-line dosing point of PAC in order to avoid contamination of samples with PAC.

Table 2.5 provides dates and details of the experiments performed to study OMPs removal. The feed was pumped directly from the WWTP effluent reservoir, therefore the OMPs had to be dosed in-line continuously to increase the OMPs concentration in the influent. PAC was dosed in-line in the pre-coat mode, i.e. only for a short interval (7-21 sec depending upon the PAC dose) in the beginning of the filtration cycle so that a cake layer was formed at the surface of the membranes. PAC dosing solution (10 g/L slurry in demineralized water) was continuously mixed with a stirring speed of about 500 rpm to avoid settling of PAC particles in the bottom of PAC solution tank. No tests were performed with continuous PAC dosing.

Most experiments were performed three times, except the test at a dosage of 60 mg PAC/L which was performed only one time . For this test, samples were also taken for bio-assay measurements, with and without OMP dosing (see 2.1.8).

Longer term experiments were conducted to investigate the long term stability of the hybrid PAC- CMF process (Table 2.6). These tests aimed at studying the effect of PAC dosing on TMP development at different permeate fluxes during a continuous pilot operation. PAC dosage of 30 mg/L was used in these experiments and permeate flux values of 60, 80, 100 and 120 L/m^2.h were investigated. These tests also evaluated the CEB strategy adopted for the pilot tests. Unfortunately, because of difficulties in maintaining a continuous feed flow to the pilot, not all stability experiments could be performed for the targeted 5 days of continued pilot operation. The uncontrolled biological growth and frequent clogging of pipes and the pump were the main reasons that continuous experiments had to be stopped before completing the targeted period.

Cleaning of the membranes was done by a pressurized back wash with permeate water and air (BackWash or BW) and by a combination of permeate and sodium hypochlorite (Chemical Enhanced Backwash or CEB). CEB was performed before the start of experiments on each day and it was assured that the initial TMP was similar for each test. After every CEB, the installation was operated for at least 2 filtration cycles without any test being performed to ensure the removal of all traces of chemicals from the system.

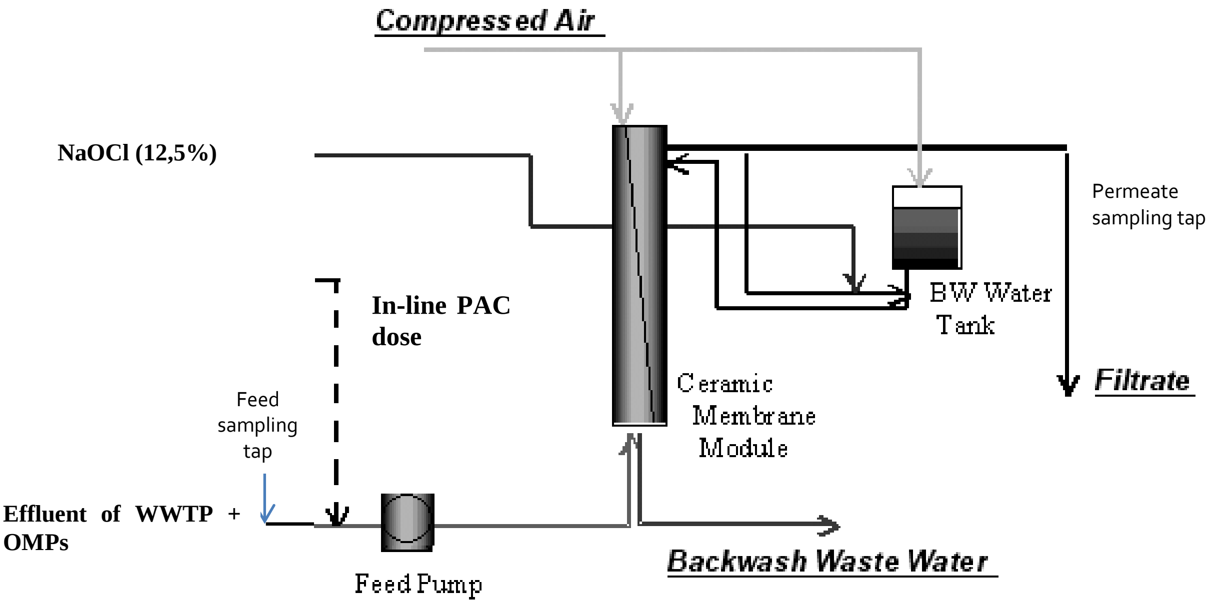

Figure 2.2: Process scheme of PAC-CMF pilot setup operated at WWTP Almelo.

Table 2.2: Background and dosed concentrations of selected organic micropollutants in the effluent of WWTP Almelo.

Organic micropollutant	Background Concentration (µg/L) n=3	Concentration in the dosed cocktail (µg/L)
Atenolol	0.539 ± 0.08	0.972
Bezafibrate	0.016 ± 0.005	0.918
Carbamazepine	0.464 ± 0.050	0.962
Cyclophosphamide	<0.01	0.797
Diatrizoic acid	<0.01	1.02
Diclofenac	0.489 ± 0.061	1.03
Phenazon	<0.01	0.997
Gemfibrozil	0.774 ± 0.163	0.953
Ketoprofen	0.023 ± 0.003	0.999
Metoprolol	3.310 ± 0.276	0.936
Metronidazole	0.036 ± 0.005	1.01
Pentoxifylline	<0.01	0.97
Propranolol	0.090 ± 0.032	0.849
Sotalol	1.597 ± 0.035	0.901
Sulfamethoxazole	0.315 ± 0.028	0.98
Tramadol	0.937 ± 0.163	0.951
Trimethoprim	0.176 ± 0.019	0.973
Venlafaxine	0.418 ± 0.07	0.881

Figure 2.3: Photographs of the PAC-CMF pilot setup operated at WWTP Almelo.

Table 2.3: Ceramic membrane characteristics.

Supplier	METAWATER
Number of elements	2
Dimensions (element)	Ø 0.03 m x l 1.0 m
Nominal pore size	0.1 µm
Membrane surface area per element	0.4 m^2
Cell inner diameter	Ø 2.5 mm
Number of cells	55
Filtration condition	Dead-end mode
Material	
Element	Ceramic
Housing	Stainless Steel 316

Table 2.4: Process parameters during pilot tests.

Filling tubes and filters	1.5 min
Filtration time	15 min
Backwash frequency	4 times per hour
Backwash with	Air + water (5 bar)
Backwash duration	10 sec
CEB frequency	1 time per 6 hour
CEB duration	300 sec
Chemical used	NaOCl (12.5 wt%)

Table 2.5: Experiments to investigate OMP removal.

PAC dose (mg/L)	Flux (L/m^2.h)	Trials	Date
0	60	Triplicate	16-04-2015
0	100	Single	30-04-2015
15	60	Triplicate	23-04-2015
15	100	Triplicate	30-04-2015
30	60	Triplicate	16-04-2015
30	100	Triplicate	30-04-2015
60	60	Single	23-04-2015
60	100	Single	30-04-2015

Table 2.6: Experiments to investigate process stability.

Flux (L/m^2.h)	PAC dose (mg/L)	Test period (h)
60	0	80
60	30	48
80	0	70
80	30	130
100	0	12
100	30	90
120	30	8

2.1.7 Sampling and analysis

Influent samples (500 mL) for OMP analysis were collected before the PAC dosing. This eliminated the possibility of PAC presence in the collected samples. After 100 sec of starting the filtration cycle, effluent was collected during the whole filtration period. This ensured that PAC film was deposited on the membrane surface when the effluent was being collected. A 500 mL sample was taken from the collected effluent for the analysis of OMP. Samples were stored in a dark and cold environment.

Samples were analyzed at KWR laboratory with reversed phase UHPLC (ultrahigh performance liquid chromatography) or normal phase (HILIC) chromatography with MS (mass-selective) detection.

2.1.8 Bio assay measurements

For the Chemical Activated LUciferase gene eXpression (CALUX) bioassay measurements extra samples were taken during the experiment with 60 mg PAC/L dosing. After performing a blank experiment (without PAC and without dosing OMPs) the experiments with PAC dosing were performed. The samples were transported to and measured by the BDS laboratory (BioDetection Systems, Amsterdam). For the measurement of bio assays about 500 mL of sample was extracted with SPE (Solid Phase Extraction). The extracts were solved in 100 µL DMSO (dimethylsulfoxide) and 5 dilution series (1 – 100) of the final extracts in DMSO were prepared. The agonistic potencies of the sample extracts were determined using the estrogenic responsive (ERα), androgenic responsive (AR), glucocorticoid responsive (GR), progestin responsive (PR) and peroxisome proliferator responsive (PPARγ2) CALUX bioassays. In addition, the anti-androgenic and anti-estrogenic potency of the sample extracts was determined using the anti-androgenic (anti-AR) and anti-estrogen (anti-ERα) CALUX bioassay. Furthermore, the genotoxic potency of the sample extracts was evaluated using the P53 CALUX bioassay in the presence and absence of rat liver S9-fraction for metabolic activity. All CALUX cells were seeded in 96 well plates and pre-incubated for 24 hours in a humidified atmosphere at 37°C under 5% CO_2. Following pre-incubations, the 10 serial dilutions of the sample extracts were added to the CALUX cells in triplicate and further incubated for 24 hours. On each 96-well plate, a complete calibration curve for each respective bioassay was also added. During incubation the final concentration of DMSO was 0.1% for the (anti-) ERα, (anti-)AR, PR, GR, and PPARg CALUX assays. Both P53 CALUX assay's (with and without S9 for metabolism) were performed with an DMSO percentage of 1%. After 24 hours, the medium was removed, the cells were lysed and luminescence was measured with a luminometer after addition of the substrate luciferine. Analysis result were interpolated in the respective calibration curve for quantification of the (anti-)estrogenic, (anti-) androgenic, glucocorticoid, progestin, peroxisome proliferator and genotoxic potency of the sample extracts.

2.2 Results and discussion

2.2.1 Removal of organic micropollutants

The efficacy of PAC-CMF to remove 18 OMPs was determined by pilot scale tests at WWTP Almelo, using the actual effluent of WWTP as the feed water for the pilot plant.

Figure 2.3 illustrates the average removal (± standard deviation) of given OMPs at permeate flux of 60 $L/m^2.h$. Figure 2.5 is another depiction of the same removal data, formulated to understand the OMP removal as a function of PAC dose. It is evident that the removal of OMPs increased with an increase in PAC dosage. When no PAC was present the removal of solutes ranged from <5 to 20 %. At a PAC dose of 15 mg/L, the removal slightly increased to 10-30 %. At a PAC dose of 30 mg/L, OMPs removal in the range of 20-65% could be achieved. And finally, the highest OMPs removal rates of 70-90% could be achieved at 60 mg/L PAC dose (the highest PAC dose tested in this study).

The efficacy of PAC-CMF process to remove the selected OMPs was also determined at a permeate flux of 100 L/m^2.h. Figure 2.6 illustrates the average removal (± standard deviation) of OMPs at permeate flux of 100 L/m^2.h. Again, it can be seen that the removal increased with an increase in PAC dosage. The PAC dose of 15 mg/L could not significantly increase the OMPs removal compared to no PAC dose. However, at a PAC dose of 30 mg/L, OMPs removal increased significantly and ranged between 25-70%.

Although the effluent of WWTP Almelo was used in all the experiments as the feed water for the pilot installation, the feed water quality in terms of N, P and COD varied during the OMP removal experiments (Table 2.1). All the OMPs removal tests at permeate flux of 100 L/m^2.h were performed on one day (30-04-2015). The OMPs removal tests at 60 L/m^2.h, however, were conducted on two different days (16-04-2015 and 23-04-2015). This may be a possible explanation of relatively high standard deviation marked in Figure 2.4 in comparison to Figure 2.6.

Diatrizoic acid showed a different removal behavior compared to other OMPs taken into account in this study (Figs 2.4 and 2.6) Compared to other solutes, diatrizoic acid showed a relatively high removal (≈38%) even at no PAC dosing. However, its removal decreased to about 20% when 15 and 30 mg/L of PAC was dosed. The removal increases to 50 % when 60 mg/L of PAC was dosed. The molecular weight of diatrizoic acid (614 g/mol) is much higher than other solutes used in this study (<300 g/mol). It seems that the rejection of diatrizoic acid was governed by its size, i.e. sieving effect. When 60 mg/L of PAC was dosed, the layer of PAC deposited on membranes perhaps acted like a secondary membrane and aided the separation, as proposed by Kuberkar and Davis, 2000. In general, diatrizoic acid was the least removed OMP by PAC-CMF system at both permeate fluxes. Trimethoprim, propranolol, metropolol, venlafaxine, pentoxyfilline and carbamazepine consistently showed higher than 80% removal.

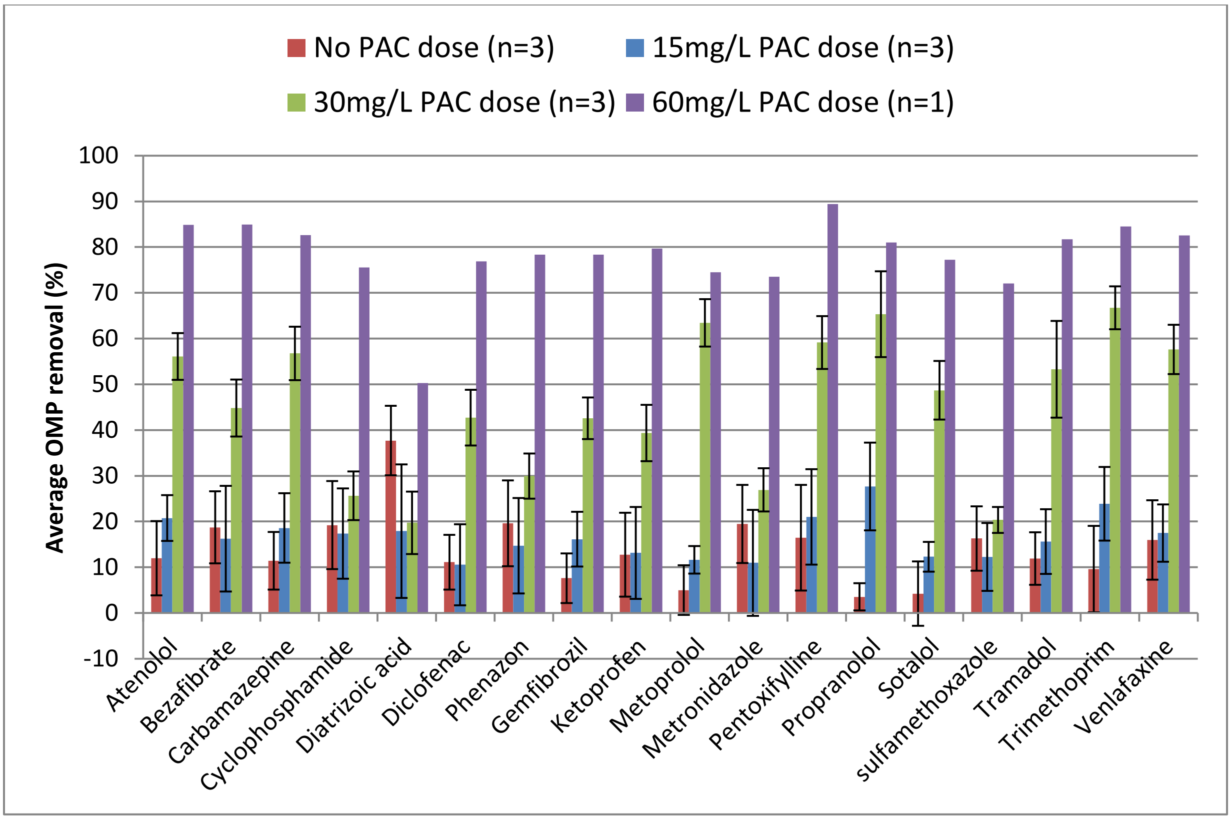

Figure 2.4: Average removal (±standard deviation) of the OMPs by pilot-scale HCMF system at permeate flux of 60 L/m^2.h.

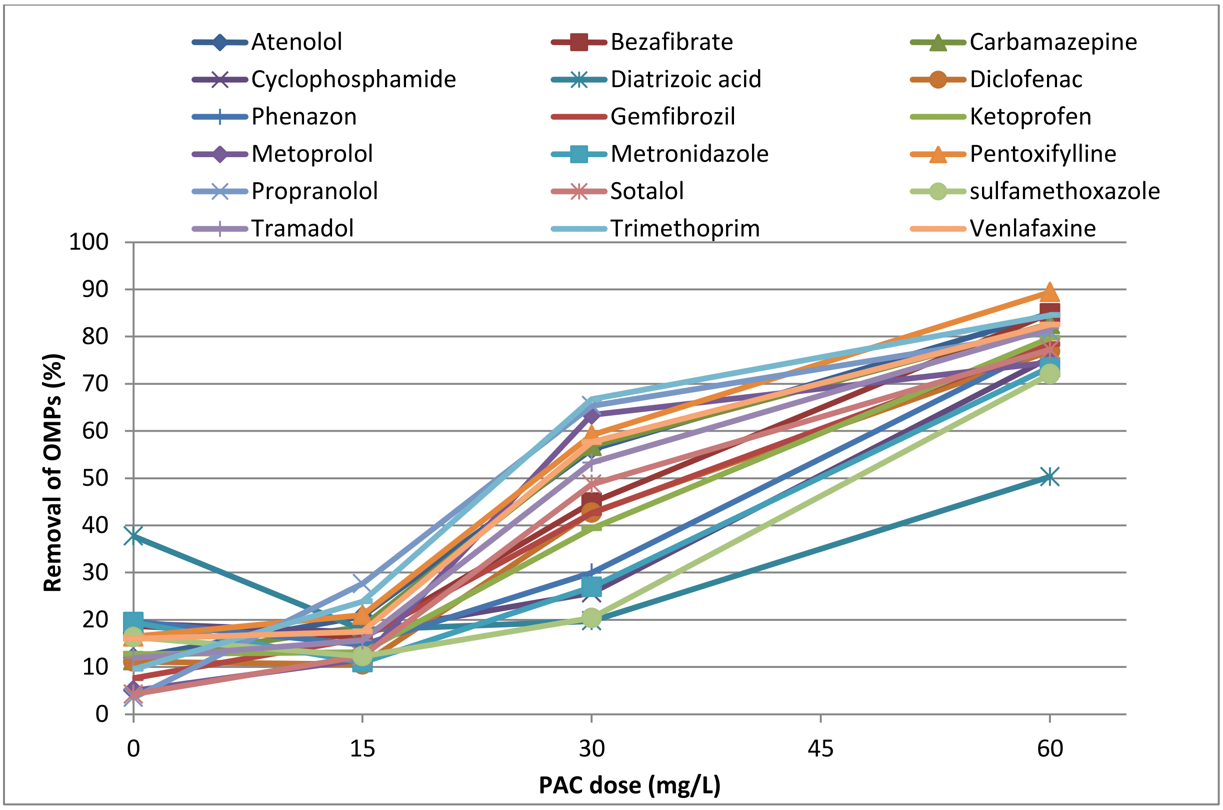

Figure 2.5: Average removal (±standard deviation) of the OMPs by pilot-scale HCMF system at permeate flux of 100 L/m^2.h

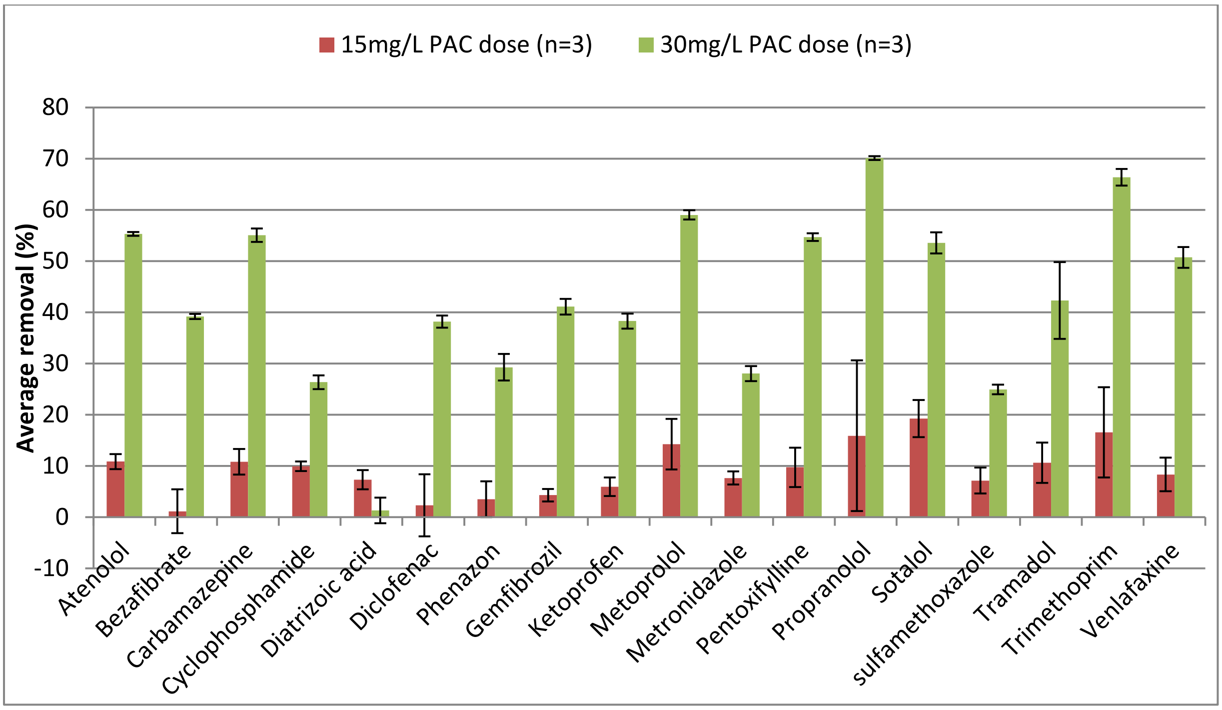

Figure 2.6: Average removal (±standard deviation) of the OMPs by pilot-scale HCMF system at permeate flux of 100 L/m^2.h.

Figure 2.7 and Figure 2.8 show a comparison between the removal of OMPs at permeate fluxes of 60 and 100 L/m^2.h respectively. It can be noticed that at 15 mg/L PAC dose, a significant decrease in the removal of OMPs occurred when the flux was increased from 60 to 100 L/m^2.h. On the other hand, at 30 mg/L PAC dose, the removal remains more or less the same at both permeate fluxes. It might be the case that the surface of ceramic membranes was not completely covered and/or inhomogeneously covered with PAC at 15 mg/L PAC dose, explaining the lower OMPs removal at 15 mg/L PAC dose. Unfortunately, this aspect could not be checked during the pilot tests. If it is assumed that the membrane surface was completely and evenly covered with a layer of PAC at both 15 and 30 mg/L PAC doses. This would mean that the PAC layer thickness deposited at 15 mg/L PAC was not sufficient to remove OMPs at an increased filtration velocity resulting in (an earlier) breakthrough of solutes. The layer (thickness) deposited by 30 mg/L PAC dose seemed to be sufficient for OMPs removal at increased flux (filtration velocity), resulting into similar removal rates at both fluxes. It would be interesting to investigate the breakthrough phenomenon at a wider flux and PAC dosing range. A systematic approach and well-controlled experiments are needed to evaluate the distribution (area) and thickness of PAC on the membrane surface at each setting.

The properties of the activated carbon and OMPs, feed water quality and the operating conditions influenced the PAC-CMF process performance. The adsorption of OMPs on activated carbon is central in this process and is governed by electrostatic attraction/repulsion, hydrophobic partitioning, hydrogen bonding and attraction by van der Waals forces (De Ridder et al., 2010; Löwenberg et al., 2015). In order to explain why some OMPs were removed better than others in this study, it is attempted to find correlations between OMPs removal and solute charge, molecular weight, hydrophobicity of the OMPs. Furthermore the energy of adhesion between OMPs and PAC is calculated using the XDVLO approach. The OMPs properties were obtained from literature sources. Unfortunately, the properties of PAC used in this study could not be determined. De Ridder et al., 2013 have reported properties of various PAC types which were used for calculations in this study. One should keep in mind that the PAC type remained the same for all the removal tests.

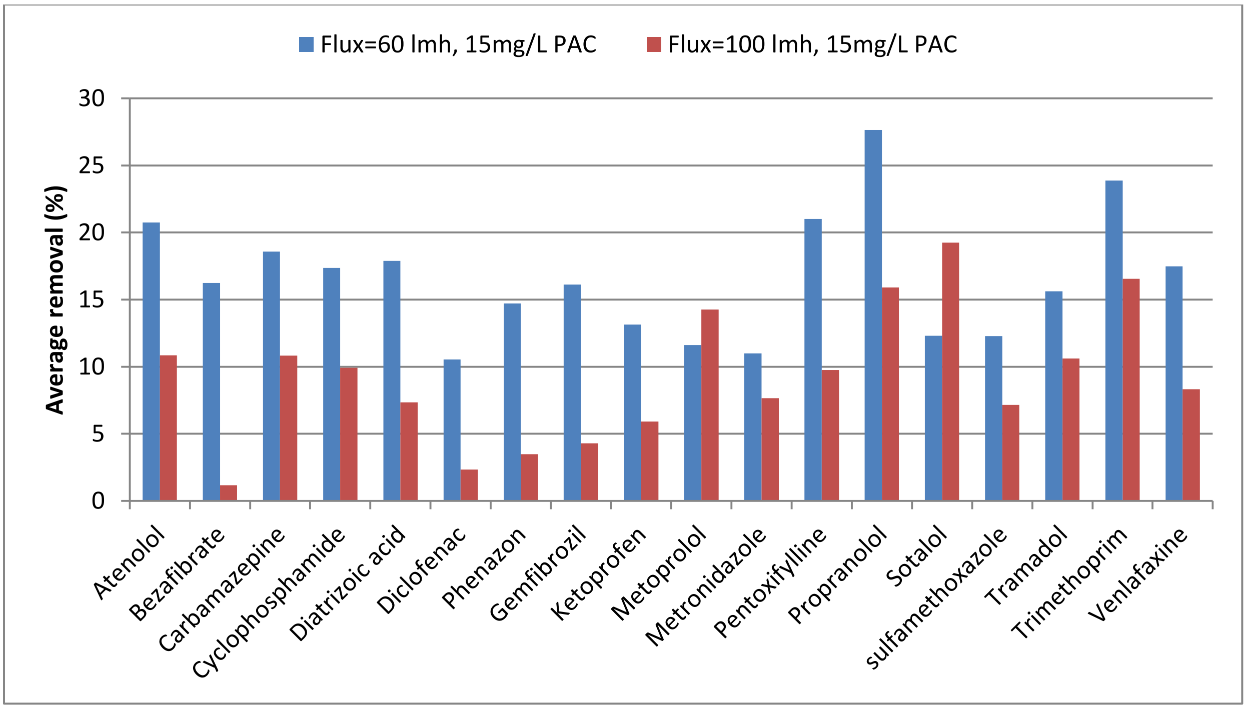

Figure 2.7: **Influence of permeate flux on average removal of OMPs at 15 mg/L PAC dose**

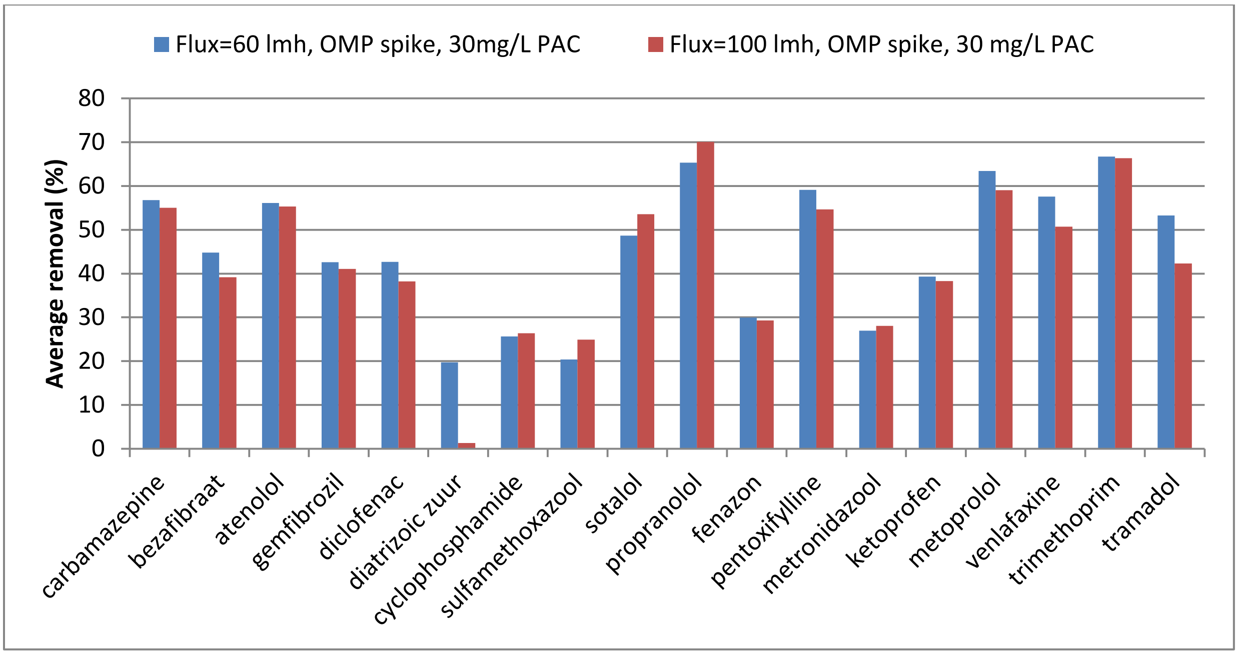

Figure 2.8: **Influence of permeate flux on average removal of OMPs at 30 mg/L PAC dose**

In Figure 2.9 and Figure 2.10, OMPs removal is plotted in function of charge of OMPs (grouped in different charge groups i.e. positive, neutral and negative) (also see Table 2.7). It can be seen that Positively charged solutes show a slightly better adsorption onto PAC compared to negatively charged OMPs. This trend is more pronounced at 30 mg/L of PAC dosing and for both permeate fluxes, i.e. 60 and 100 L/m^2.h. Considering the assumption that at 30 mg/L PAC dose the surface of membranes was completely covered with PAC, it seems that electrostatic interactions might have played some role in the retention of certain OMPs. Since the feed water contained NOM and the adsorption of NOM on PAC might have rendered the PAC surface with a negative charge. This should lead to repulsion of negatively charged solutes and attraction of positively charged solutes. Unfortunately, the surface charge of virgin and loaded PAC used in this study at (the operating pH of 7.4) was not determined. Therefore, this hypothesis remains unproven.

The efficacy of activated carbon to remove solutes from water is often attributed to the hydrophobicity of the solutes and activated carbon. Hydrophobicity of a solute is often expressed as log$_{kow}$ and logD$_{pH\ 7,4}$. Table 7 shows the logk$_{ow}$ and logD$_{pH\ 7,4}$ values of all the 18 OMPs investigated in this study. Figure 2.11 and Figure 2.12 show the removal of the OMPs as a function of solute LogD$_{pH7,4}$ values at 60 and 100 L/m^{2}h flux respectively. It can be observed that most OMPs included in this study were hydrophobic and that the increase in PAC dosing increased their removal. It remains unclear whether the hydrophobicity was the governing mechanism of OMPs adsorption to PAC or not, because there is only a slight correlation between logD and removal (%) (Figure 11 and 12). According to thermodynamics, adsorption onto activated carbon is more than only hydrophobic interactions (electrostatic interactions are not considered here).

The adsorption energy depends upon solute-water interactions, carbon-water interactions, solute-carbon interactions and water cohesion (Israelachvili, 1992; de Ridder et al., 2010). Therefore, calculating the energy of adhesion based on the surface tension component approach (XDVLO approach) shall also be considered to gain further insights into the OMPs adsorption on PAC. In summary, there seem to be slight correlations between electrostatic charge and OMP removal and hydrophobicity and OMP removal, however these mechanisms cannot be concluded as governing yet.

The influence of work of adhesion needs to be evaluated in a more systematic study to gain further insights.

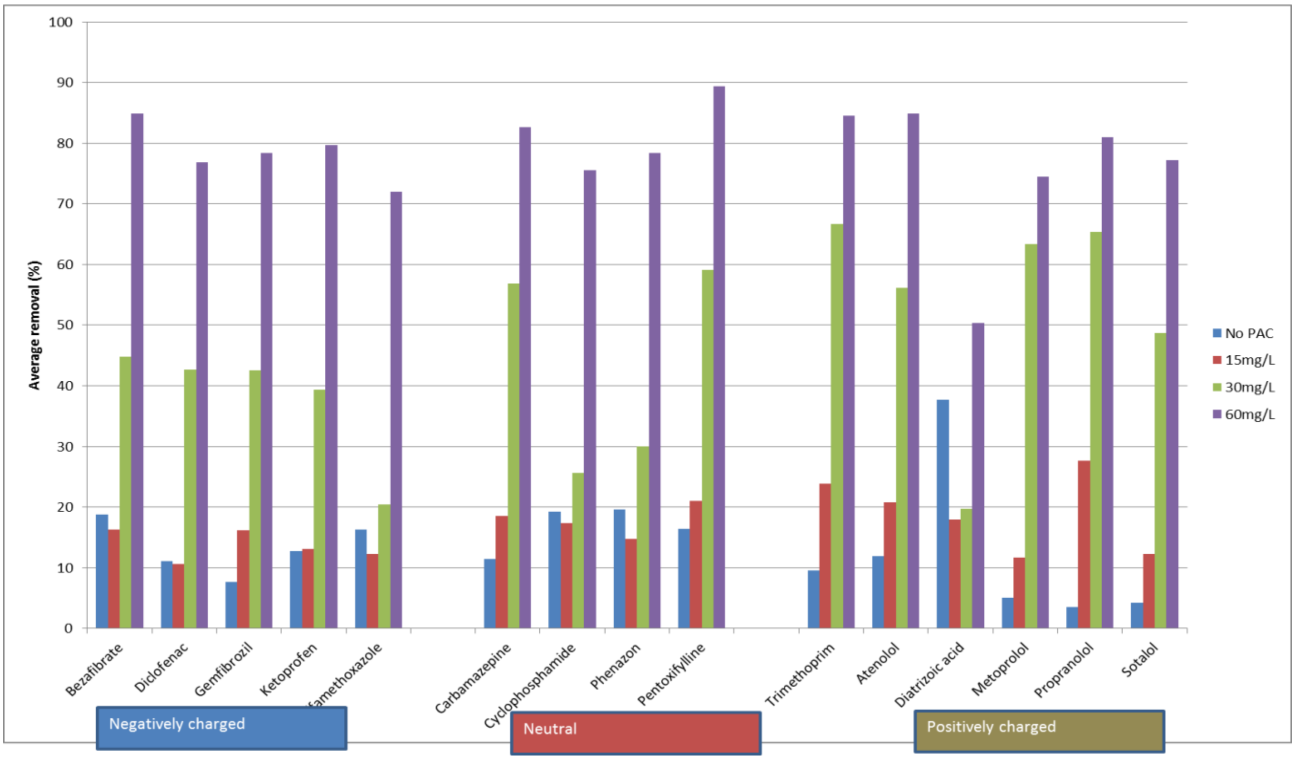

Figure 2.9: Removal of the OMPs (sorted on the basis of charge) at permeate flux of 60 L/m^2.h.

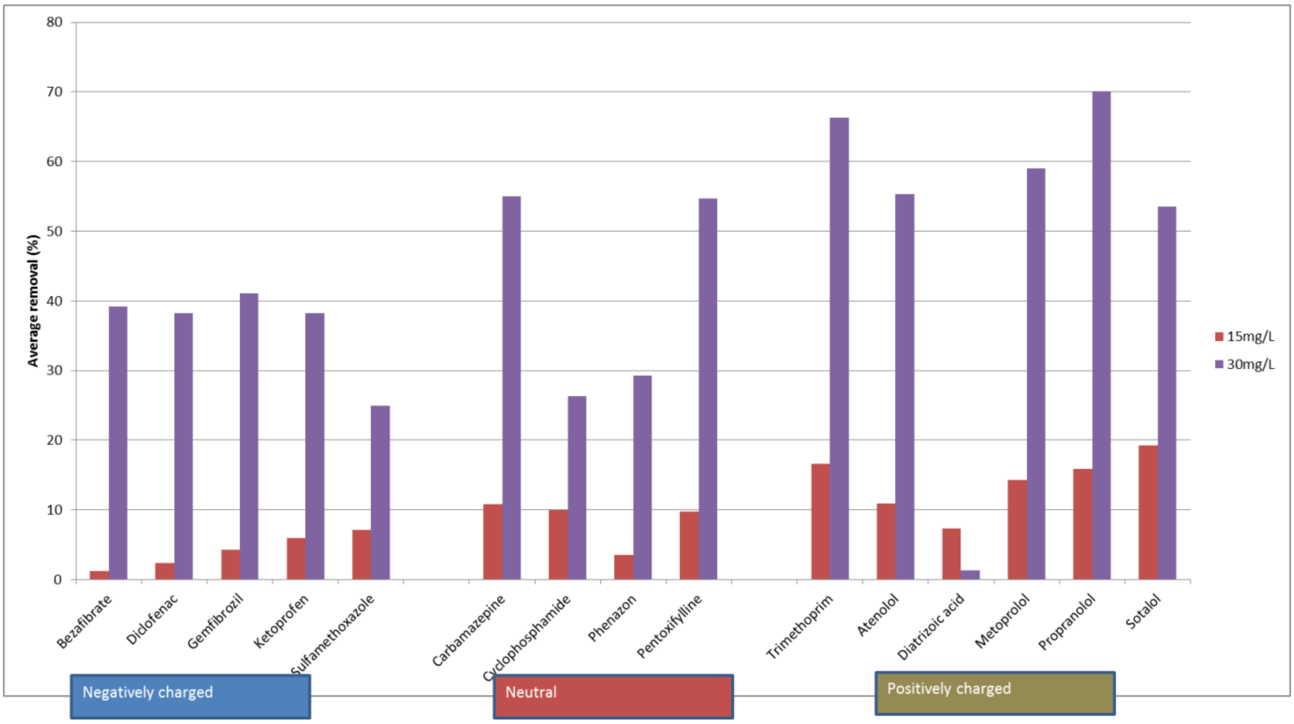

Figure 2.10: Removal of the OMPs (sorted on the basis of charge) at permeate flux of 100 L/m^{2}·h.

Table 2.7: The average removal and physicochemical properties of selected OMPs. Source of physicochemical properties: De Ridder et al., 2013; Hofman-Caris and Bauerlein, 2014; Chemispider (www.chemispider.com).

	Flux=60 lmh				Flux= 100lmh		Physico-chemical properties				
OMPs	Blank	PAC 15 mg/L	PAC 30 mg/L	PAC 60 mg/L	PAC 15 mg/L	PAC 30 mg/L	MW	log Kow	log D 7,4	pKa	charge
	%	%	%	%	%	%	g/mol				
Bezafibrate	18,7	16,2	44,8	84,9	1,2	39,2	361,8	4,25	0,7	3,44	-
Diclofenac	11,1	10,6	42,7	76,9	2,3	38,2	296,2	4,51	1,0	4,08	-
Gemfibrozil	7,6	16,1	42,6	78,3	4,3	41,1	250,3	4,77	1,8	4,45	-
Ketoprofen	12,7	13,1	39,3	79,7	5,9	38,3	254,3	3,12	-0,3	4,29	-
Sulfamethoxazole	16,3	12,3	20,4	72,0	7,2	24,9	253	1,3	-0,2		-
Carbamazepine	11,4	18,6	56,8	82,7	10,8	55,0	236,3	2,45	2,7		0
Cyclophosphamide	19,2	17,4	25,7	75,6	9,9	26,3	261,1	0,63	0,2	0, 12,8	0
Phenazon	19,6	14,7	30,0	78,4	3,5	29,3	188,2	0,38	0,3	1,4	0
Pentoxifylline	16,5	21,0	59,1	89,4	9,8	54,7	278,3	0,29	0,3	0,3	0
Metronidazole	19,5	11,0	26,9	73,5	7,7	28,0	171,2	-0,02	0,05		0
Trimethoprim	9,6	23,9	66,7	84,5	16,6	66,3	290	0,91	0,6	7,2	0/+
Atenolol	12,0	20,8	56,1	84,9	10,9	55,3	266,3	0,16	-1,7	9,43	+
Diatrizoic acid	37,7	17,9	19,7	50,3	7,3	1,3	614	1,37	-2,7	2,17	+
Metoprolol	5,0	11,6	63,4	74,5	14,3	59,0	267,4	1,88	-0,1	9,49	+
Propranolol	3,5	27,6	65,3	81,0	15,9	70,1	259,4	3,48	1,3	9,58	+
Sotalol	4,2	12,3	48,7	77,2	19,2	53,5	272,4	0,24	-1,6	9,44	+
Tramadol	11,9	15,6	53,3	81,7	10,6	42,3	263,4	2,51	0,5		+
Venlafaxine	16,0	17,5	57,6	82,5	8,3	50,7	277,4	3,28	1,4		+

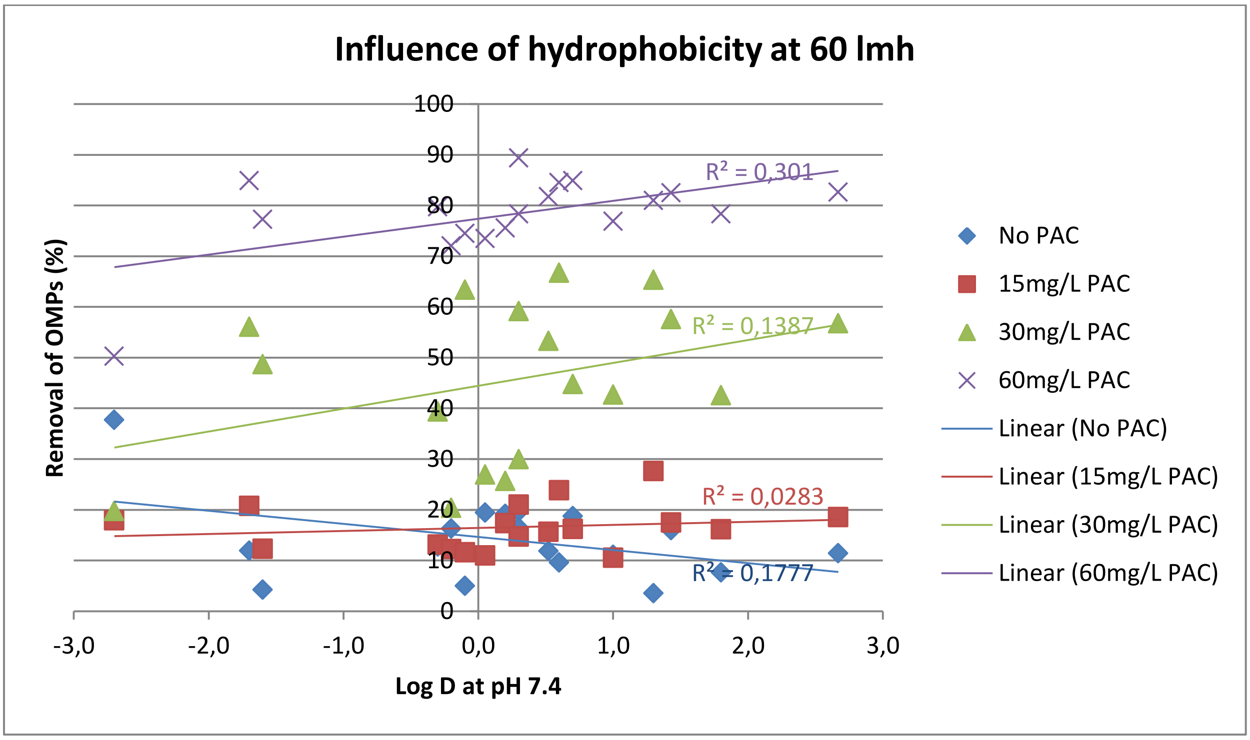

Figure 2.11: Removal of the OMPs as a function of solute LogD$_{pH7,4}$ values at 60 L/m^{2}h flux.

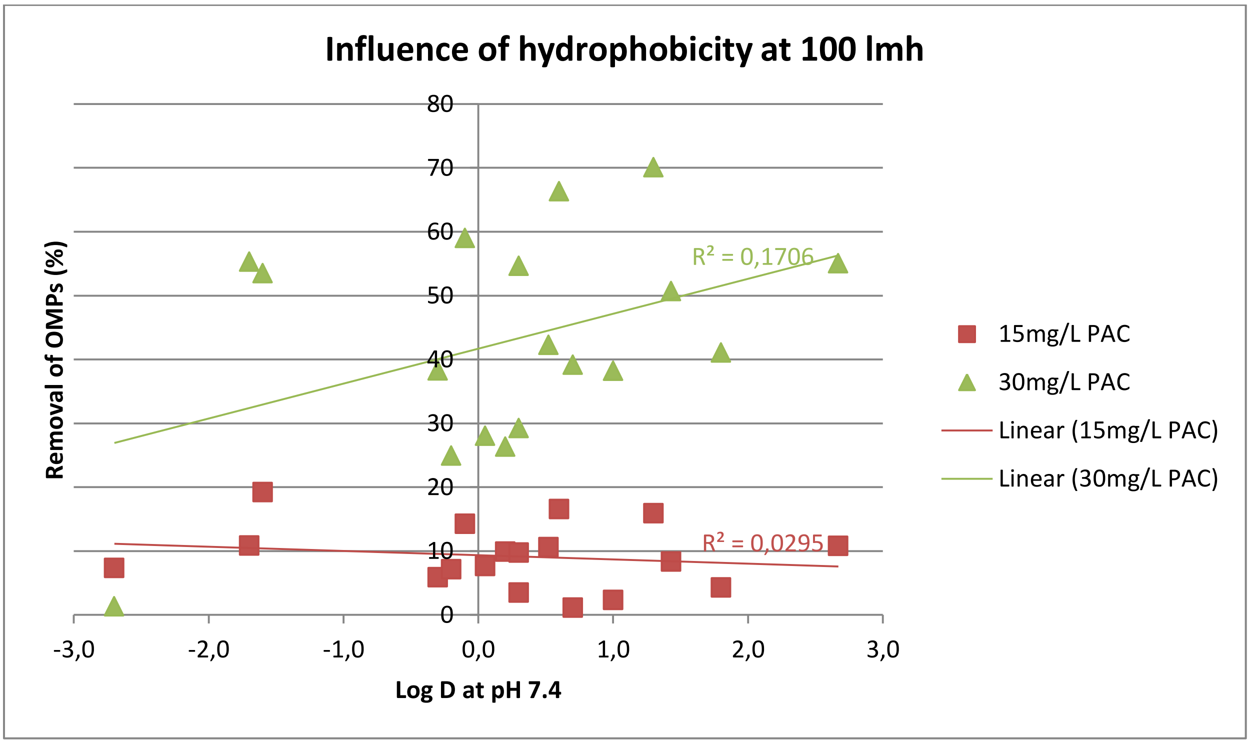

Figure 2.12: Removal of the OMPs as a function of solute LogD$_{pH7,4}$ values at 100 L/m^2.h flux.

2.2.2 Measurements with different Bio assays

In Table 2.8 the results are given from CALUX bioassay measurements. No androgenic, anti-estrogenic, peroxisome proliferator or mutagenic activity was observed in any of the feed and permeate samples tested. In contrast, all other bioassay analysis results showed high levels of removal (up to approximately 90%). Interestingly, the reduction of bio-activity was already observed after MF filtration only. This suggests that by removing particulate matter also the compounds that trigger the Bio assay are removed as well. Only grucocorticoid activity was only reduced following PAC dosing.

The removal of some bio assays could not be established because the measurements were below the detection limit.

2.2.3 Process performance of HCMF

The PAC-CMF process remained quite stable in terms of permeate flux and OMP removal tests could be easily performed with effluent water of WWTP Almelo. However, because of difficulties in transport of the effluent water to the pilot, long term experiments could not be performed thoroughly. Due to uncontrolled biological growth in various parts of the pilot installation, it became difficult to operate the pilot continuously. Furthermore, the water quality of the effluent water changed quite drastically during the duration of the experiment (from cold water with green algae to warmer water with brownish slimy sludge). Therefore, the outcomes of the stability experiments are not compared in this report. It is suggested that longer term experiments need to be performed to gain further insights into the impact of seasonal changes. Nevertheless, in Figure 2.14 and Figure 2.13 it can be seen that only by the use of NaOCl for CEB, the TMP of the CMF was adequately recovered (reversible fouling) and that it was possible to maintain a stable flux (at least) during the experiment.

Table 2.8: The results of the Bio assay measurements and calculated removal rates

Experiment	ERa CALUX	AR CALUX	PR CALUX	GR CALUX	anti-ERa CALUX	anti-AR CALUX	PPARy 2 CALUX	P53 (-S9) CALUX	P53 (+S9) CALUX
Blank influent	2	<0,22	1,2	94	<270	53000	<47	<0,04	<29
Blank effluent	<0,04	<0,25	<0.10	100	<270	<1600	<48	<0,03	<30
Removal (%)	**90,0**	**-**	**91,7**	**-6,4**	**-**	**96,2**	**-**	**-**	**-**
60 mg/LPAC influent	1,5	<0,40	2,7	93	<280	54000	<50	<0,06	<30
60 mg/LPAC effluent	0,27	<0,22	0,43	11	<270	15000	<48	<0,05	<29
Removal (%)	**82,0**	**-**	**84,1**	**88,2**	**-**	**72,2**	**-**	**-**	**-**
60 mg/L PAC and OMP's influent	1,1	<0,21	1,2	44	<260	44000	<46	<0,08	<28
60 mg/L PAC and OMP's effluent	<0,04	<0,22	<0,13	<4,8	<270	11000	<48	<0,07	<29
Removal (%)	**81,8**	**-**	**91,7**	**93,2**	**-**	**75,0**	**-**	**-**	**-**

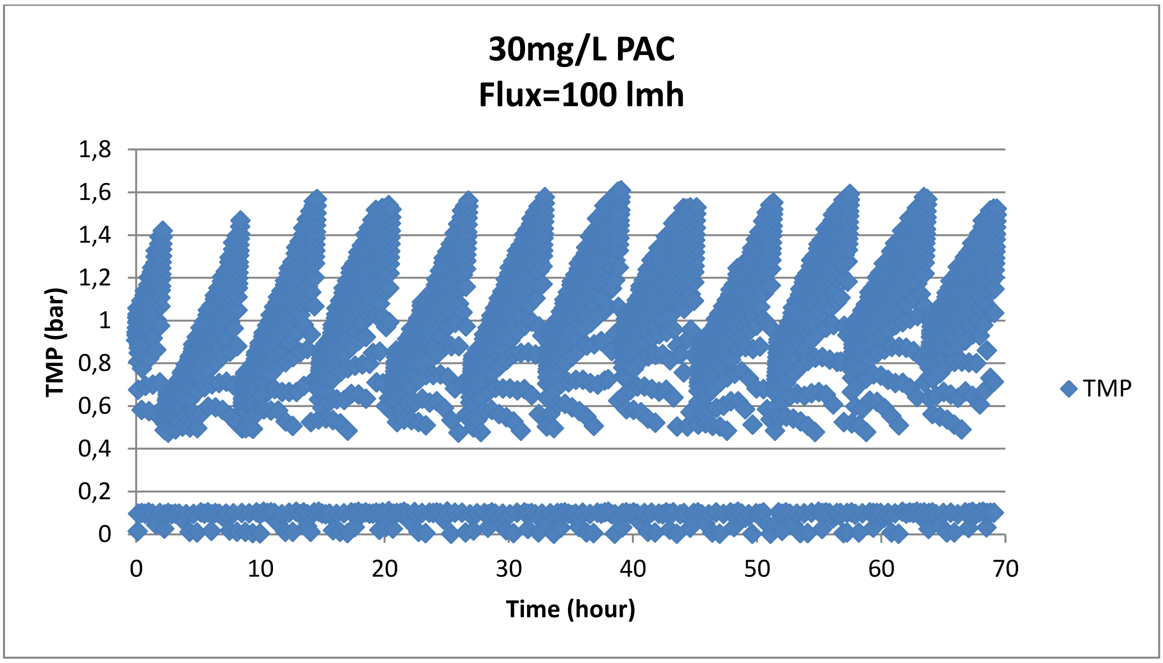

Figure 2.13: TMP build up during a longer term experiment with a flux of 100 L/m^2.h with PAC dosing.

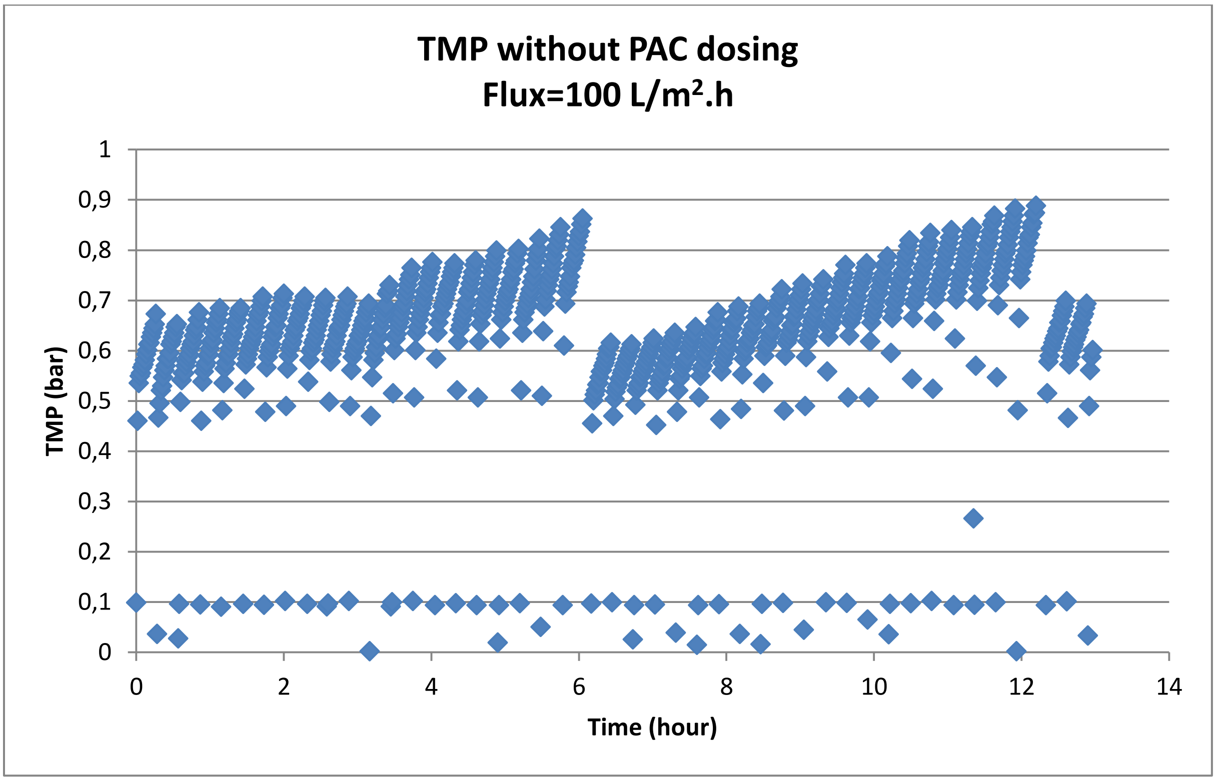

Figure 2.14: TMP build up during a longer term experiment with a flux of 100 L/m^2.h without PAC dosing.

2.3 Conclusions

On the basis of the PAC-CMF pilot research performed at WWTP Almelo, the following can be concluded:

- In general, the use of higher PAC doses leads to increasing removal of the selected OMPs. Depending on the solutes and PAC dose (tested 0-15-30-60 mg PAC/L) up to 90 % OMPs removal could be achieved. The highest removal (70-90 %) was achieved with 60 mg PAC/L. A relative low dose of 15 mg PAC/L showed only 0-20 % OMPs removal while with 30 mg PAC/L about 20-70 % could be achieved.
- A stable flux of 100 $L/m^2.h$ was achieved as the highest possible maximum value under the given field conditions. There is no significant effect measured due to PAC dosing for the stability of the MF process in terms of TMP. Due to difficulties with the influent water transport, no representable long term experiments (up to 5 days of stable performance) could be performed.
- CEB with NaOCl was adequate to maintain a stable PAC-CMF process.
- No significant relations were found between OMPs removal percentages and physicochemical properties of the OMPs such as charge, $\log K_{OW}$ or $\log D_{pH\ 7,4}$.
- The Bio assay measuring methods that gave interpretable results, showed that MF was capable to remove up to 90 % of Bio assay triggering compounds. Only one Bio assay method (GR CALUX) showed an effect of using PAC in the process. There was no significant increase of Bio assay values by the dosed OMPs, which could not be explained.

2.4 Recommendations for further research

On basis of the PAC-CMF pilot research performed at Sumpel the following can be recommended:

- Investigation with different water quality are recommended at different locations: to show that the PAC-CMF hybrid system functions also at other locations, this work should be repeated elsewhere.
- For higher possible flux values the pilot needs to be adjusted with a pump system that allows higher pressures and flows.
- Other types of PAC may lead to higher or lower removal of OMPs, this should be investigated in further research.
- It would be interesting to investigate the breakthrough phenomenon at a wider flux and PAC dosing range. A systematic approach and well-controlled experiments are needed to evaluate the distribution (area) and thickness of PAC on the membrane surface at each setting.
- Calculating the energy of adhesion based on surface tension component approach shall also be considered to gain further insights into the OMPs adsorption on PAC.
- More research is needed to gain more insight in the adsorption phenomenon of compounds in waste water effluent with PAC as the adsorption medium.

2.5 References

Altmann , J. Ruhl, A. S., Zietzschmann, F. and Jekel, M. 2014. Direct comparison of ozonation and adsorption onto powdered activated carbon for micropollutant removal in advanced wastewater treatment. Water Res. 55. 185-193.

Bodzek, M. and Konieczny, K. (1998). Comparison of various membrane types and module configurations in the treatment of natural water by means of low-pressure membrane methods. Separation and Purification Technology, 14 (1-3). 69-78

Bottino, A., Capannelli, C., Del Borghi, A., Colombino, M. and Conio, O. (2001). Water treatment for drinking purpose: ceramic microfiltration application. Desalination, 141(1), 75-79

Brink, L.E.S., Elbers, S.J.G., Robbertsen, T. and Both, P. 1993. The anti-fouling action of polymers preadsorbed on UF and MF membranes. Membrane Science. 76: 281.

Chan, K. and Brownstein, A.M. (1991). Ceramic membranes- growth prospects and oppurtunities. Am. Cer. Soc. Bul., 70(4), 703-707.

Ciora, R. J. and Liu, P.K.T. (2003). Ceramic membranes for environmental related applications. Fluid. Part. Sep. J., 15(1), 51-60.

Cornelissen, E.R., Hofs, B., Muller, U., Beerendonk, E. F. and Heojman, S.G.J. 2009. Direct and hybrid ceramic membrane filtration in water treatment. In: (Eds.) van der Hoven, T. and Kazner, C. TECHNEAU: Safe Drinking Water from Source to Tap. State of the Art and Perspective. IWA Publishing. London, UK. ISBN: 9781843392750.

de la Rubia, A., Rodriguez, M. and Prats, D. (2006). pH, Ionics strength and flow velocity effects on the NOM filtration with TiO2/ZrO2 membranes. Separation and Purification Technology, 52(2), 325-331

De Ridder, D.J. Villacorte, l., Verliefde, A. R. D., Verberk, J.Q.J.C., Heijman, S.G.J., Amy, G.L., Van Dijk, J. C. 2010. Modeling equilibrium adsorption of organic micropollutants onto activated carbon. Water res 44, 3077-3086. De Ridder et al., 2013 De Ridder, D.J., Verliefde, A.R.D., Schoutteten, K., Van Der Linden, B., Heijman, S.G.J., Beurroies, I., Denoyel, R., Amy, G.L., Van Dijk, J.C. 2013. Relation between interfacial energy and adsorption of organic micropollutants onto activated carbon. Carbon. Volume 53, March 2013, Pages 153-160.

Endter, A., Schleifenheimer, M. and Voigt, I. (2004). Nanofiltrationsanlage zur dezentralen Trinkwasseraufbereitung. Filtrieren und separieren, 18(1), 12-15

EPA- Environmental Protection Agency (2001). Low-pressure membrane filtration for pathogen removal: application, implementation, and regulatory issues. Environmental Protection Agency, Office of Water: Cincinnati.

Ericsson, B. and Tragardh, G. (1997). Treatment of surface water rich in humus – Membrane filtration vs conventional treatment. Desalination, 108(1-3), 117-128.

Fokumoto, L.R., Delaquis, P. and Girard, B., (1998). Microfiltration and ultrafiltration ceramic membranes for apple juice clarification. J. Food. Sci., 63(8), 845-850

Gälli, R. , Ort, C., Schärer, M., 2009. Mikroverunreinigungen in den Gewässern. Bewertung und Reduktion der Schadstoffbelastung aus der Siedlungsentwässerung (Micropollutants in the water bodies. Evaluaton and reduction of contaminant load from urban drainage). Umwelt-Wissen Nr. 0917. Federal Office of the Environment, Bern.

Götz, C.W., Abegglen, C., McArdell, C.S., Koller, C.S., Siegrist, H., Hollender, J., Schärer, M., 2010. Mikroverunreinigungen - Beurteilung weitergehender Abwasserreinigungs-verfahren anhand Indikatorsubstanzen (Micropollutants – Evaluation of additional sewage treatment processes based on indicator substances). gwa 4/2010: 1-9.

Grangeon, A. and Lescoche, P. (2000). Flat ceramic membranes for the treatment of dairy: comparison with tubular ceramic membranes. Lait. 80, 5-14

Heberer, T. 2002. Occurance, fate and removal of pharmaceutical residues in the aquatic environment: a review of recent research data. Toxicology Letters. 131:5-17.

Heijman, S.G.J., Hamad, J.Z., Kennedy, M.D., Schippers, J. and Amy, G. (2008). Submicron powdered activated carbon used as a pre-coat in ceramic micro-filtration, in Membranes in Drinking Water Productionand Waste Water Treatment, AWWA/EDS: Toulouse, p. 8.

Hofman-Caris, R. and Baurlein, P. 2014. Affinity adsorption for specific removal of pharmaceuticals. BTO 2014.003

IDA (2006). 19th IDA worldwide desalting plant inventory, Oxford: Media analyst Ltd.

Israelachveli J.n. 1992. Intermolecular and surface forces. 2nd ed. Academic press.

Jacangelo, J. G., Adham, S. S., Laine, J. M. 1995. Mechanism of cryptosporidium, giardia and MS 2 virus removal by MF and UF. AWWA. 87:107-121.

Kanaya, S., et al. (2007). The world largest ceramic membrane drinking water treatment plant, in AWWA conference on membrane technology. Tamba Bay

Kimura, K., Hane, Y., Watanabe, Y., Amy, G. and Ohkuma, N. (2004). Irreversible membrane fouling during ultrafiltration of surface water. Water Research, 38(14-15), 3431-3434.

Klomfas, G. Konieczny, K. (2004). Fouling phenomena in unit and hybrid processes for potable water treatment. Desalination, 163(1-3), PII S0011-9164(04)00101-8

Kolpin, D. W., Furlong, E. T., Meyer, M. T., Thurman, E. M., Zaugg, S. D., Barber, L. B., Buxton, H. T., Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999−2000: A National Reconnaissance, Environ. Sci. Technol, 36, 1202, 2002.

Konieczny, K. Bodzek, M. and Rejca, M. (2006). A coagulation – MF system for water treatment using ceramic membranes. Desalination, 198(1-3), 92-101.

Kuberkar, V. and Davis, R.H. 2000. Modeling of fouling reduction by secondary membranes. J. of Membrane Science. 168:243.

Lee, S., Cho, J. (2004). Comparison of ceramic and polymeric membranes for natural organic matter (NOM) removal. Desalination, 163(3), 663-665

Lerch, A., Panglisch, S., Buchta, P., Tomita, Y., Yonekawa, H., Hattori, K., and Gimbel, R. (2005). Direct river water treatment using coagulation/ceramic membrane microfiltration. Desalination, 179(1-3), 41-50.

Löwenberg, J., Zenker, A., Beggenstos, M., Koch, Gerhard, Kazner, C. and Wintgens, T. 2015. Comparison of two PAC/UF processes for the removal of micropollutants from wastewater treatment plant effluent: Process performance and removal efficiency. Water Research 56: 26-36.

Luonsi, A., Laitinen, N., Beyer, K., Levänen, E., Poussade, Y., and Nyström, M. (2002). Separation of CTMP mill-activated sludge with ceramic membranes. Desalination, 146(1-3), 399-404.

Margot, J., Kienle, C., Magnet, A., Weil, M., Rossi, L., Felippe de Alencastro, L., Abegglen, C., Thonney, D., Chèvre, N., Schärer, N., Barry, D.A., 2013. Treatment of micropollutants in municipal wastewater : Ozone or powdered activated carbon. Science of the Total Environment 461-462, 480-498.

Matsui, Y., Fukuda, Y., Inoue, T. and Matsushita, T. (2003). Effect of natural organic matter on powdered activated carbon adsorption of trace contaminants: characteristics and mechanism of competitive adsorption. Water Research, 37(18), 4413-4424.

Matsui, Y., Murase, R., Sanogawa, T., Aoki, N., Mima, S., Inoue, T. and Matsushita, T. (2005). Rapid adsorption pretreatment with submicrometer activated carbon particles before microfiltration. Water, Science and Technology, 51(6-7), 249-256.

Matsushita, I., Matsui, Y., Shirasaki, N. and Kato, Y. (2005). Effect of membrane pore size, coagulation time and coagulant dose on virus removal by a coagulation- ceramic micro filtration hybrid system. Desalination, 178(1-3), 21-26.

Nazzal, F.F. and Wiesner, M.R. (1994). PH and ionic-strength effects on the performance of ceramic membranes in water filtration. Journal of Membrane Science, 93(1), 91-103.

Park, J.Y., Choi, S.J. and Park, B.R. (2006). Effect of N2-back-flushing in multi channels ceramic microfiltration for paper wastewater treatment. Desalination, 202, 207-214.

Peters, T.A., Fontalvo, J., Vorstman, M.A.G., Benes, N.E., van Dam, R.A., Vroon, Z.A.E.P., van Soest-Vercammen, E.L.J. and Keurentjes, J.T.F. (2005). Hollow fiber microporous silica membranes for gas separation and pervaporation. Synthesis, performance and stability. Journal of Membrane Science, 248, 73-80.

Schippers, D., Bakker, S.H., Brummel, D. and Heijman, S.G.J. (2007). Particle removal from surface water with ceramic microfiltration, in particle separation 2007 – from particle characterization to separation processes, IWA: Toulouse, France, p. 8.

Shirasaki, N., Matsushita, T., Matsui, Y., Kobuke, M. and Ohno, K. (2009). Comparison of removal performance of two surrogates for pathogenic waterborne viruses, bacteriophage Q beta and MS2, in a coagulation-ceramic microfiltration system. Journal of Membrane Science, 326(2), 564-571.

Strathmann, H. (2000). Membrane separation processes: current relevance and future opportunities. Aiche Journal, 47(5), 1077-1087.

Tsuru, T. (2001). Inorganic porous membranes for liquid phase separation. Separation and Purification Methods, 30(2), 191-220.

van Beelen, E., 2007. Municipal Waste Water Treatment Plant (wwtp) Effluents - a Concise Overview of the Occurrence of Organic Substances, RIWA, NL.

Verliefde, A., Cornelissen, E., Amy, G., Van der Bruggen, B. and Van Dijk, H. 2007. Priority organic micropollutants in water sources in Flanders and the Netherlands and assessment of removal possibilities with nanofiltration. Environmental Pollution. 146:281-289.

Voigt, I., Stahn, M., Wöhner, St., Junghans, A., Rost, J. and Voigt, W. (2001). Integrated cleaning of colored waste water by ceramic NF membranes. Separation and Purification Technology, 25, 509-512.

Weber, J. and Seidel, T. (2003). Characteristics and application of ceramic nanofiltration membranes. Annals NY Acedam Sci, 984, 178-193.

Yuasa, A. (1998). Drinking water production by coagulation-microfiltration and adsorption-ultrafiltration. Water Science and Technology, 37(10), 135-146.

Zapata-Montoya, J.E., Gaudix, E.M. and Gaudix, A. (2006). Long term effects of chemical cleaning in the performance of ultrafiltration ceramic membranes. Desalination, 200(1-3), 316-31.

3 HCMF pilot tests at WWTP Birsfelden in Switzerland

3.1 Introduction and objectives

In Switzerland, legislative changes are underway which will force 100 of the currently 700 operating WWTP to be upgraded with an additional treatment step to remove micropollutants (Gälli et al., 2009). Ozonation as well as powdered activated carbon (PAC) adsorption have been identified as suitable processes to remove certain micropollutants from the effluent (Margot et al., 2013).

Since adsorption is most efficient when applied on the effluent from a biological step, an additional separation step has to be installed for the removal of the sorbent from the treated water. In case of using the activated carbon in powdered form (PAC) the separation is usually realized by sedimentation and/or sand filtration. Membrane processes offer several advantages over competing processes for the removal of PAC from the effluent. Amongst these advantages are total suspended solids removal (including PAC), lower footprint and partial virus and bacteria removal. Membrane processes may be operated in different ways and different process set-ups result in different operating conditions for the membrane. Differences in membrane operations are submerged configuration in contrast to dead-end or cross-flow operation as well as inside-out filtration in comparison to out-side in. The different operating conditions are believed to influence membrane performance as well as micropollutants removal efficiency due to different retention times in different process set-ups (Löwenberg et al., 2014).

Within the scope of WP22 a submerged hybrid ceramic membrane filtration (HCMF) process was investigated in a small pilot-scale system. Beside the removal of selected micropollutants from wastewater, the influence of different operational parameters (e.g. flux, addition of coagulant or cleaning strategy) on the membrane filtration performance was demonstrated.

3.2 Experimental setup and methods

Within the scope of the Demeau project, two HCMF processes were operated on WWTP effluent at the municipal WWTP ARA Birs (Basel-Landschaft, Switzerland). Both membrane processes are operated in submerged mode and incorporate flat sheet membranes.

The scope of the experiments included the demonstration of the membrane operation with PAC on WWTP effluent as well as the removal efficiency for certain micropollutants in the chosen process set-up.

The municipal WWTP ARA Birs is operated as a sequencing batch reactor (SBR) and has a capacity of 150,000 population equivalent. Some standard effluent water quality parameters are given in Table 3.1 and a view on the WWTP is given in Figure 3.1.

Table 3.1 WWTP effluent quality from 2011[n= 12–127]

	pH	N_{tot} [mg/L]	P_{tot} [mg/L]	DOC [mg/L]	TSS [mg/L]
Average ± standard deviation	7.6 ± 0.3	6.0 ± 1.5	0.7 ± 0.3	8.8 ±1.2	10.2 ±10.5

Figure 3.1 View on the WWTP Birsfelden

3.2.1 Hybrid ceramic membrane process

Pilot units

The experiments included the investigation of both operating conditions of the processes as well as their efficiency for micro pollutant removal.

The demonstration trials were carried out in a pilot scale filtration system with submerged membranes. The pilot system consists of two identical units (HCMF 1 and HCMF 2) which were operated independently from each other with the same feed, so that different technological parameters can be compared.

Both units were used for the post-treatment of the effluent from the WWTP ARA Birs. Before entering the HCMF units, the incoming water was passing through a buffer tank in order to overcome the periods without any discharge from the WWTP. Each of the filtration units consisted of a 35 L contact zone, where the PAC slurry and Fe^{3+} solution were continuously dosed into the incoming wastewater. PAC slurry with a concentration of 3.6 g PAC/L was prepared in a mixed tank and pumped into the HCMF contact zone with a multi-channel peristaltic pump. The PAC slurry consisted of tap water and PAC SAE Super (Norit Activated Carbon, The Netherlands). The PAC dose was set to 20 mg/L as this has been determined to be a sufficient dosage to achieve the target removal of 60-80% for the investigated micropollutants over the HCMP (Löwenberg et al., 2014). The aim of the Fe^{3+} dosing was to provide coagulation and agglomeration of PAC particles into bigger agglomerates. The target dose of Fe^{3+} was 4 mg/L.

The mixture subsequently proceeded to a filtration unit (150 L) with a submerged membrane module, where the PAC was separated from the treated water (Figure 3.2, Figure 3.3, **Error! Reference source not found.**). Permeate, which was the final product of the tested process, was extracted by means of a gear pump. At regular intervals (300 s) the flow direction of the permeate pump was reversed for 30 s in order to backwash the membrane. Chemically enhanced backwash (CEB) of the membranes was carried out every 1 – 2.5 days and included the addition of sodium hypochlorite (1000 ppm) and subsequently citric acid (1500 ppm) into the permeate. The retentate was discharged from the filtration tank at regular intervals. The target recovery of the system was 92.5 to 95%.

Recovery cleaning of the membranes was performed when the TMP exceeded 0.5 bar or when a new operation phase was initiated. Recovery cleaning was carried out externally by submersing the membrane module into the solution of sodium hypochlorite (500 or 1000 ppm at pH 10.5) and subsequently citric acid (1200 ppm at pH 3.5 or 1.8) for about 1 hour.

The pilot system was placed indoor and the water temperature varied between 10 and 24 °C. Trans-membrane pressure (TMP), permeate flow as well as other operational parameters were continuously recorded.

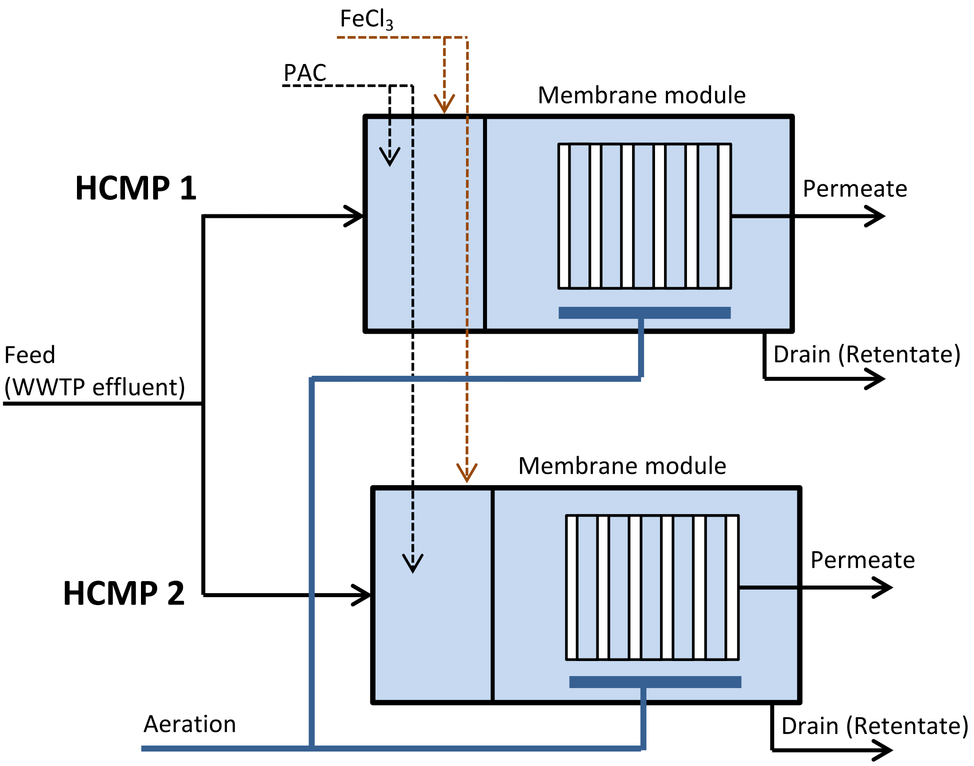

Figure 3.2 – Schematic of double HCMP

Figure 3.3 – Photo of the PAC + UF pilot plant

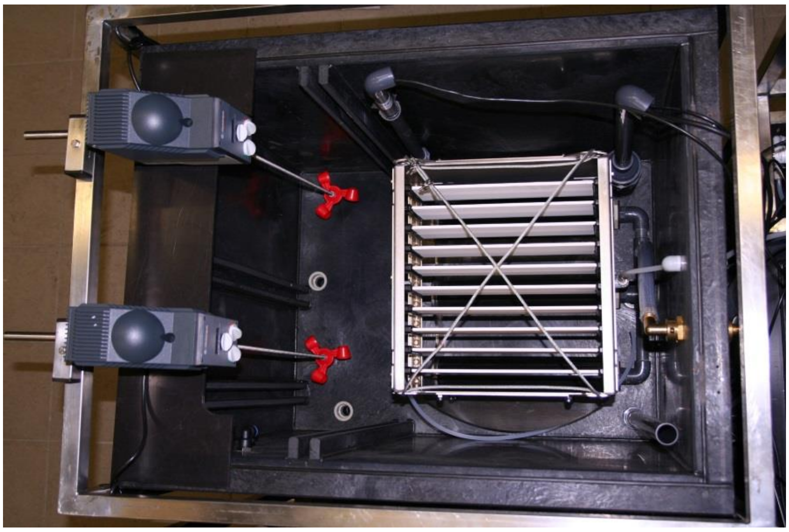

Figure 3.4 – View of contact and filtration tank with the ceramic membrane

One submerged G-LM type membrane module from ItN Nanovation was installed in each HCMF unit. The module consisted of flat sheet ceramic membranes with a total active area of 0.8 m^2. The membrane material was α-Al_2O_3; the nominal pore size was 200 nm (ultrafiltration range). Scouring of the membrane surface and mixing of the membrane tank was induced by aeration below the membrane sheet.

The filtration performance was evaluated by the transmembrane pressure development (TMP) and the efficiency of chemical cleaning. The permeate flux, backwash flux, chemical cleaning interval and its protocol were the parameters to be adjusted during the operation to increase the membrane permeability and stabilize the process with respect to TMP evolution.

Micropollutant removal is mainly depending on the PAC dosage and the PAC contact time and mixing conditions in the filtration tank as well as the effluent DOC concentration. The PAC retention time in the system is thereby linked to the recovery rate which itself is mainly determined by the combination of filtration flux, filtration time and adjusted drain volume.

The investigation of the chemical cleaning strategy included the testing of different protocols of chemically enhanced backwashing (CEB) and different CEB intervals.

Phases of operation

The HCMP systems were operated for a period of approx. 300 days. The operation was divided into five operational phases with different process parameters (**Error! Reference source not found.**).

Table 3.2 – Summary of design technological parameters during different operational phases

Phase	Run time [d]		Filtration flux [LMH]		Backwash flux [LMH]		CEB interval [d]		PAC [mg/L]		Fe^{3+} [mg/L]	
	H1	H2	H1	H2	H1	H2	H1	H2	H1	H2	H1	H2
Reference	43	43	26.2		37.5		2.5		0		0	
PAC 1	82	88	26.2		37.5/45	37.5	2.5		20		0	
PAC+Fe 1	82	83	26.2		37.5		2.5		20		4/0	0/4
PAC+Fe 2	57	57	18		33		1		20		0	0/4
PAC 2	29	29	18		33		1		20		0	

1) Reference run

The aim of the first operational phase was to gather reference data about the removal of micropollutants and the filtration performance of the system without PAC addition. Both units were operated under the same parameters. One measurement campaign focusing on the removal of micropollutants was carried out during the reference phase.

2) PAC 1

In the second operational phase the filtration parameters (flux, CEB etc.) remained unchanged, however, 20 mg/L of PAC was dosed to the influent into both HCMP units. During most of this phase both units were operated under the same parameters; a higher backwash flux was tested in HCMF 1 during the second half of the phase. The aim of the phase was to evaluate the removal of micropollutants with the PAC addition and study its effect of the filtration performance.

3) PAC + Fe 1

During the third operational phase $FeCl_3$ solution was dosed into the HCMP 1 unit in addition to PAC; the other HCMP 2 was still receiving only PAC. After approx. 30 days of operation the tanks of both HCMPs were emptied and the dosing point of $FeCl_3$ was moved from HCMP 1 to HCMP 2. Filtration parameters were identical to the reference phase and the beginning of PAC 1 phase. The goal of this phase was to evaluate the effect of prior coagulation by Fe^{3+} on the membrane performance.

4) PAC + Fe 2

Since accelerated fouling was observed at the end of the third phase, the filtration parameters were set to milder conditions – filtration and backwash flux was lowered and CEB interval was shortened to 1 d. The PAC was still dosed into both HCMP systems; Fe^{3+} was dosed only for a limited time during this phase. PAC and Fe^{3+} were dosed directly into the filtration tank instead of the contact tank for a certain period of time.

5) PAC 2

During this phase the addition of coagulant was stopped and both HCMP units were operated with PAC dosing only. The aim of this phase was to test development of TMP with a modified CEB protocol.

Calculation of fouling rate and cleaning efficiency

The fouling rate (in kPa/d) was calculated from the slope of TMP over the runtime between two chemical cleanings (CEB or recovery cleaning). If the interval between two cleanings was lower than 0.7 d or if the runtime was lower than 0.5 d within 24 hours (i.e. high share of membrane relaxation), the calculated values were excluded.

The cleaning efficiency of the CEB was calculated from the extrapolated TMP values based on the slopes of TMP in the intervals before and after the CEB. The cleaning efficiency is the difference of the two extrapolated TMP values at the point of the CEB. If the interval between two cleanings was lower than 0.7 d or if the runtime was lower than 0.5 d within 24 hours (i.e. high share of membrane relaxation), the calculated values were excluded. The cleaning efficiency of the recovery cleaning is not presented in the graphs either.

3.2.2 Analytical methods

Micropollutant analysis

The removal of certain micropollutants relevant in Switzerland was investigated in the HCMP systems. Switzerland represents a special case, since in the near future 100 WWTP will be upgraded with an additional treatment step for the removal of micropollutants. Legislative changes are in progress and significant research on the presence of certain micropollutants as well as on possible process combinations to reduce the discharge through WWTPs has been carried out (Zwickenpflug et al. 2011, Margot et al. 2013, Löwenberg et al., 2014).

Within the Demeau project 5 micro pollutants have been selected for this investigation based on previous studies on relevant micropollutants in Switzerland (Götz et al., 2010). These micropollutants are sulfamethoxazole (SMX), mecoprop (MEC), diclofenac (DCF), benzotriazole (BZT) and carbamazepine (CBZ). These micropollutants are present in the WWTP effluent at the ARA Birs in concentrations from 200 ng/L (SMX) to 8 µg/L (BZT) (Löwenberg et al., 2014); similar concentrations were found during the measurements in the frame of the Demeau project.

During the operational period samples of the HCMP feed (WWTP effluent) and the permeate streams were taken as 48 – 72 h mixed samples. The samples were taken continuously during the sampling period with a peristaltic pump. Three to ten samples from each stream were taken during each measurement campaign.

Samples were stored on site at 6 °C during sampling. Immediately after the sampling period the samples will be transported to the Institute of Ecopreneurship for storage at 4 °C until prepared by solid phase extraction (SPE) for HPLC-MS/MS analysis. The pH of the samples was adjusted to 7.5 prior to the SPE, which was done according to Hummel et al. (2006). Methanol was used as extraction medium. The same methodology as described by Löwenberg et al. (2014) was used for the liquid chromatography – mass spectrometry (LC-MS) analysis.

LC-OCD analysis

Besides micropollutant analysis, composite samples of influent and HCMP effluents as well as grab samples from the filtration tanks were collected for liquid chromatography – organic carbon detection (LC-OCD) analysis and the determination of the concentration of suspended solids. The LC-OCD method was used for the characterization of organic matrix in samples from different profiles and for the quantification of different fractions based on the size exclusion (molecular weight). The LC-OCD device (DOC Labor Huber, Germany) used for the analyses was equipped with a separation column Fractogel® TSK HW-50 S. The sum of fractions in the LC-OCD measurement was for the quantification of total DOC of the samples.

Summary of the analyses of WWTP Birs effluent

The average values measured during all campaigns in the incoming wastewater are summarized in **Error! Reference source not found.**. Large variations in concentration were observed for some parameters, especially sulfamethoxazole (resulting in high calculated standard deviation). This might be due to occasional discharge from an industrial source. Such observation was also experienced in previous studies within different projects, where the same wastewater was analyzed.

Table 3.3 Average concentration of selected pollutants in influent to the HCMP systems

Parameter	Average ± standard deviation
Suspended solids	5.5 ± 3.6 mg/L (n = 19)
DOC	8.0 ± 1.7 µg/L (n = 17)
Benzotriazole [µg/L]	4.1 ± 1.4 µg/L (n = 31)
Sulfamethoxazole [µg/L]	0.74 ± 3.05 µg/L (n = 31)
Carbamazepine [µg/L]	0.38 ± 0.12 µg/L (n = 31)
Mecoprop [µg/L]	0.18 ± 0.18 µg/L (n = 31)
Diclofenac [µg/L]	6.8 ± 6.6 µg/L (n = 31)

3.3 Results and Discussion

3.3.1 Reference run

During the reference run the two HCMP systems were operated with a constant influent of treated wastewater. The goal of the reference run was to collect data about filtration and OMPs removal without PAC addition into the system. Identical operation parameters were set in HCMP 1 and 2 to confirm the comparability of the two systems.

Filtration

Since both HCMP systems were operated at constant flux, the TMP was the main parameter for the assessment of the filtration performance (**Error! Reference source not found.**). It can be seen that the CEB frequency (every 2.5 d) could not ensure a stable TMP and that three recovery cleanings were necessary (indicated by arrows in the graph). Except the period between first and second recovery cleaning, the two HCMP systems showed an almost identical evolution of TMP. The reason for the mentioned discrepancy is unclear, it might have resulted from differences during recovery cleaning (i.e. mechanical washing step). The suspended solids concentration in the membrane tank was between 10 – 25 mg/L in both tanks, which is lower than the expected value. Although no PAC was dosed at this stage, the influent itself contains between 5-10 mg/L suspended solids. With 95 % recovery rate of the filtration, the equilibrium concentration in the filtration tank should be well above 100 mg/L. The reason might be partial sedimentation of solids in the membrane tank.

The observed fouling rate in both HCMPs was mostly between 2 and 7 kPa per day (average 4.1 in both units) with slightly decreasing trend towards the end of the phase (**Error! Reference source not found.**).

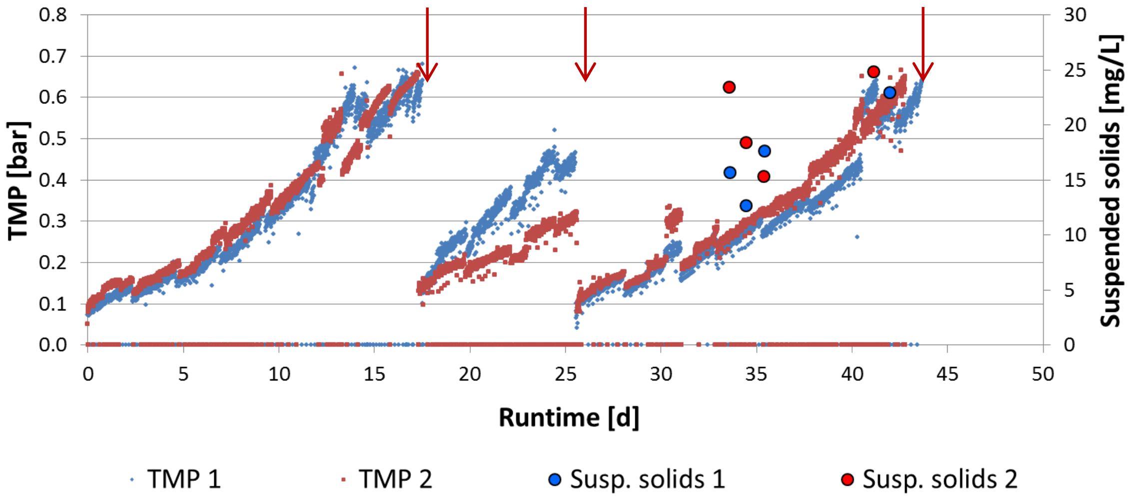

Figure 3.5 – Trans-membrane pressure and suspended solids during the reference run (arrows indicate recovery cleanings)

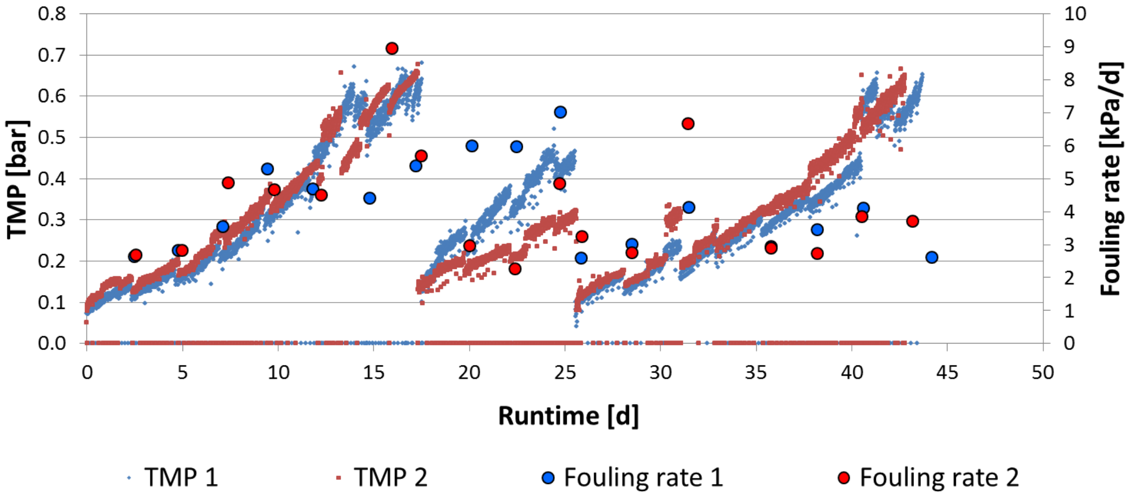

Figure 3.6 Trans-membrane pressure and fouling rate during the reference run

<u>Removal of micropollutants and DOC</u>

The OMPs concentration in the feed and permeate samples collected during the reference phase (6 samples collected within 12 days) is shown in **Error! Reference source not found.**. Large variations were observed for diclofenac, whose concentration varied between 3 and 33 µg/L. Other micro pollutants were found in relatively stable concentrations.

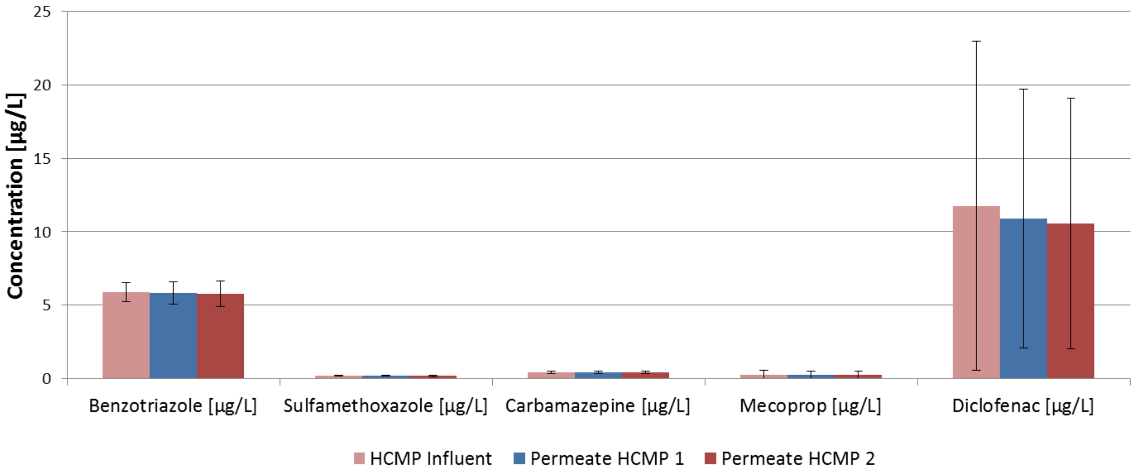

Figure 3.7 Concentration of micropollutants in the influent and permeates from the HCMP systems during the reference run

The removal rate of the target compounds merely by ultrafiltration without any addition of PAC was close to zero (**Error! Reference source not found.**). Observed removal of some compounds (on average up to 6%) probably resulted from variations in incoming concentration combined with hydraulic effect in the HCMP systems.

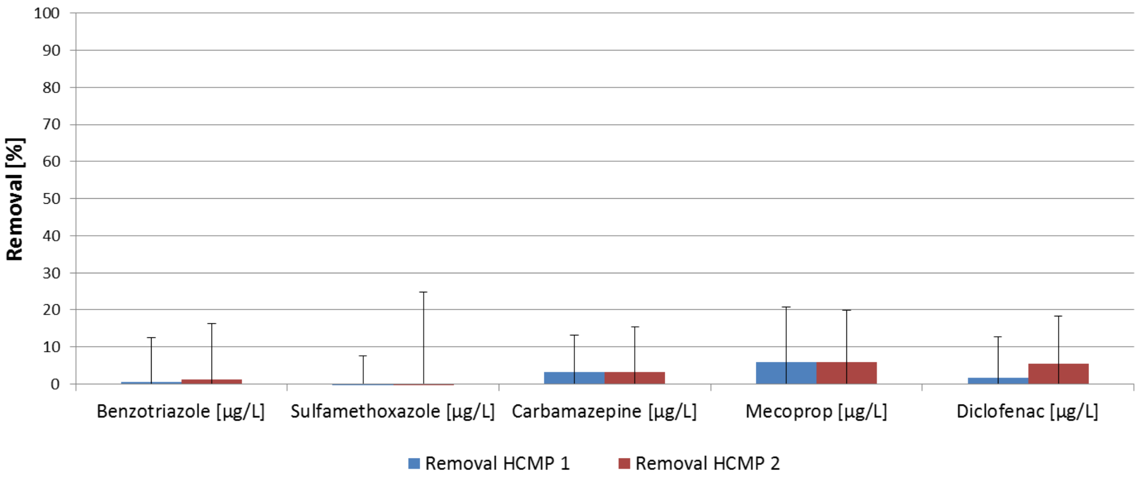

Figure 3.8 Removal of micropollutants during the reference run

The LC-OCD analysis of the influent and permeates (**Error! Reference source not found.**) showed that only the fraction of biopolymers were retained by the ultrafiltration. This was due to their high molecular weight close to the cut-off of the used membrane.

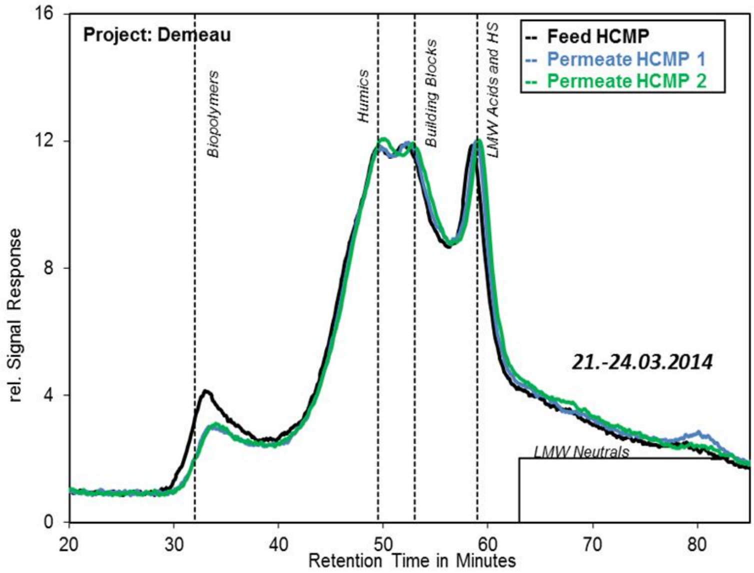

Figure 3.9 LC-OCD analysis of the influent and HCMP effluents during the reference run

3.3.2 PAC 1

The PAC 1 phase was initiated after the last recovery cleaning of the reference phase without emptying and cleaning the contact and membrane tank. The PAC slurry was dosed into both HCMP units with a target concentration of 20 mg/L of incoming wastewater. Three recovery cleanings were performed during this phase. Until the second recovery cleaning the HCMP units were operated under identical operational parameters; after that the backwash flux was increased from 37.5 to 45 LMH in HCMP 1 in order to test the influence of the fouling rate.

Filtration

Similar as in the previous phase the course of TMP of the two units showed a similar development, except for the period between runtime 6 – 15 d, when problems with inflow stability were experienced and the filtration pattern of the membranes included longer periods of relaxation (**Error! Reference source not found.**). In the first half of the PAC 1 phase a general increase in TMP was observed, which could not be fully compensated by the regular CEB, therefore a recovery cleaning was necessary. A different course was observed at the end of the phase – TMP stabilized at a constant level between 0.2 and 0.3.

Highly varying concentrations of suspended solids were present in the two HCMP units ranging from 50 to 350 mg/L. Taking into consideration the 95 % recovery rate of the filtration, these values are lower than the expected values and indicate partial settling of the solids in the system.

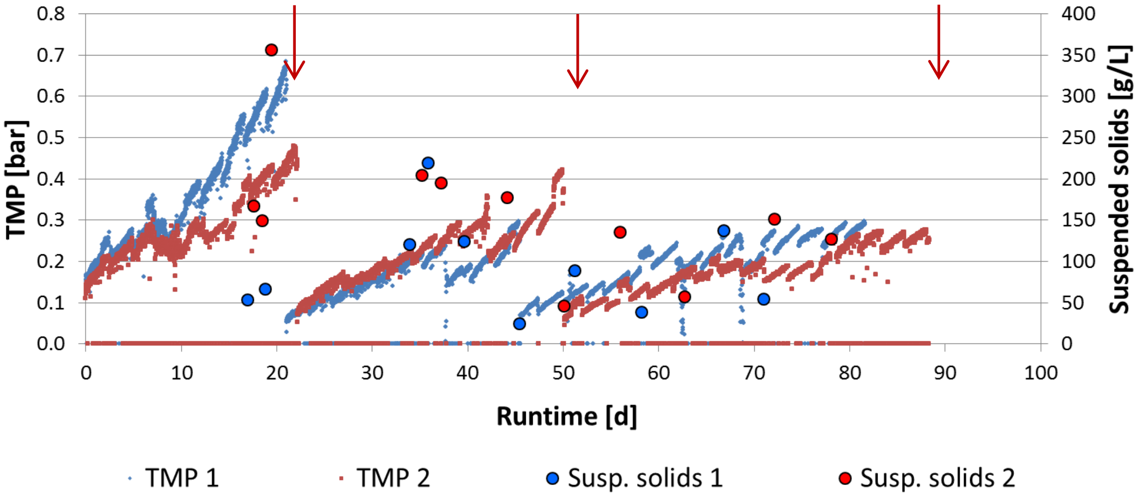

Figure 3.10 Trans-membrane pressure and suspended solids during the PAC 1 phase (arrows indicate recovery cleanings)

The analysis of fouling rate showed a decreasing trend, which allowed a stable operation of the filtration at constant TMP in the last third of the operational phase (**Error! Reference source not found.**). This positive trend can be attributed to gradual accumulation of the PAC suspension in the system, which contributed to more efficient cleaning of membrane surface. The average fouling rates in the periods between recovery cleanings were 4.4, 2.2 and 2.4 kPa/d in HCMP 1 and 2.8, 2.1 and 2.0 kPa/d in HCMP 2.

In the last third of the phase PAC 1 the HCMP 1 system was operated under higher backwash flow, however, no substantial improvement of fouling behavior was observed in HCMP 1 compared to HCMP 2.

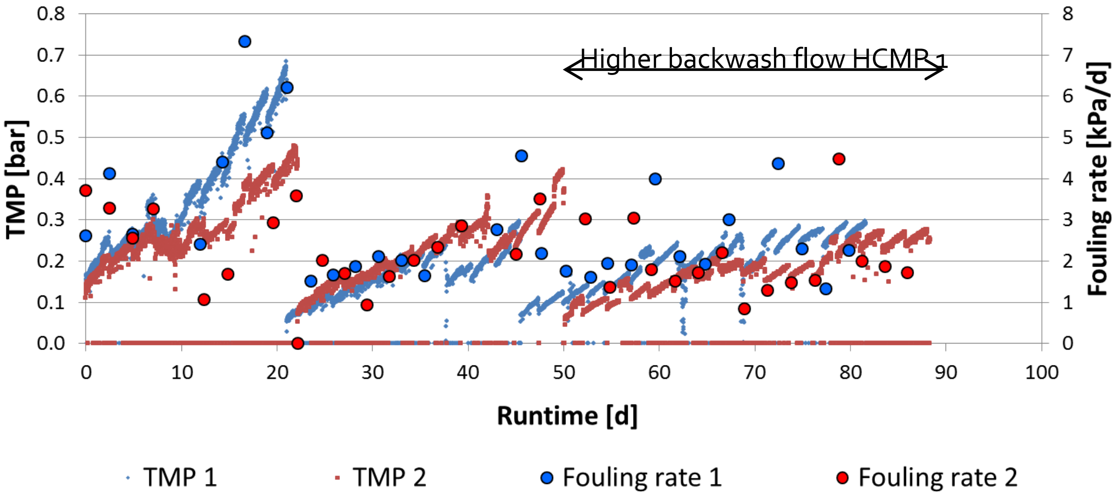

Figure 3.11 Trans-membrane pressure and fouling rate during the PAC 1 phase

Removal of micro pollutants and DOC

The micro pollutants were analyzed in 10 samples collected within 33 days during the PAC 1 phase. The results of the campaign illustrated the effect of PAC sorption on the removal of micro pollutants in the HCMP systems (**Error! Reference source not found.** and **Error! Reference source not found.**). Especially the non-polar compounds (benzotriazole, carbamazepine and diclofenac) were removed with 85 to 95 % efficiency. The lowest removal (around 25 %) was observed in case of sulfamethoxazole. The removal efficiencies measured in HCMP 1 and HCMP 2 were almost identical. Largely varying concentrations in the influent were recorded for some compounds, especially sulfamethoxazole and diclofenac.

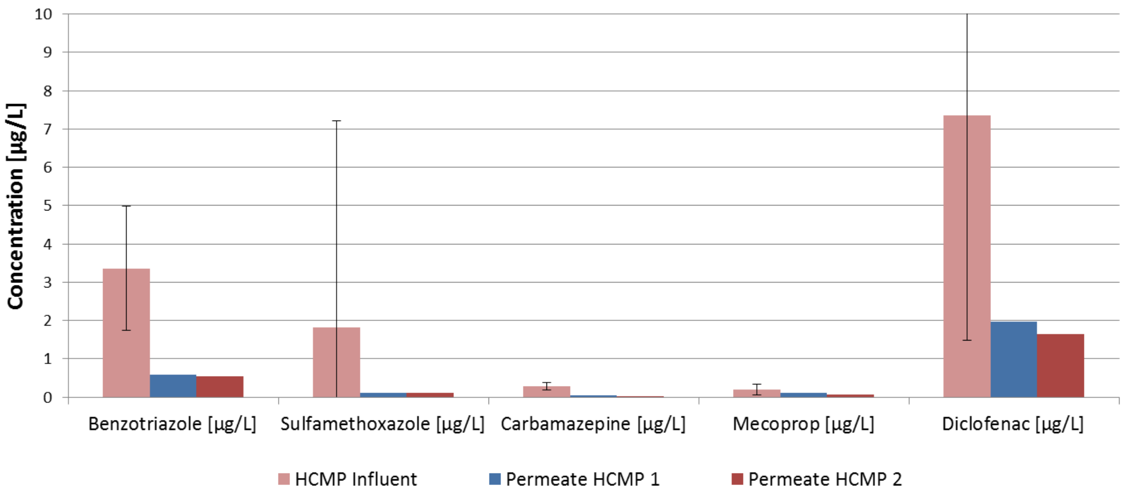

Figure 3.12 Concentration of micropollutants in the influent and permeates from the HCMP systems during the PAC 1 phase

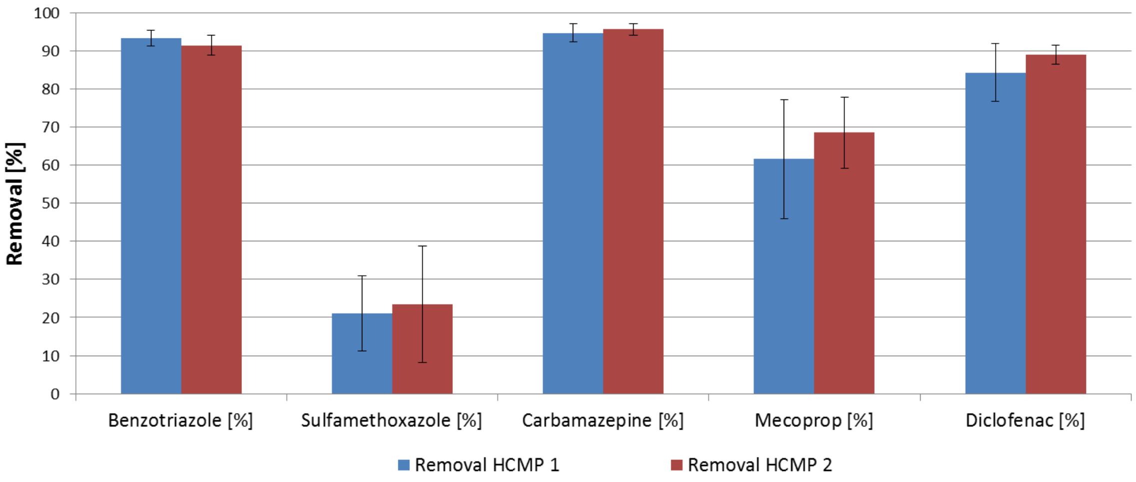

Figure 3.13 Removal of micropollutants during the PAC 1 phase

The LC-OCD analysis of the influent and permeate samples collected during the PAC 1 phase is shown in **Error! Reference source not found.**. Compared to the reference phase, a portion of all DOC fractions is removed in addition the biopolymers due to the adsorption on the PAC.

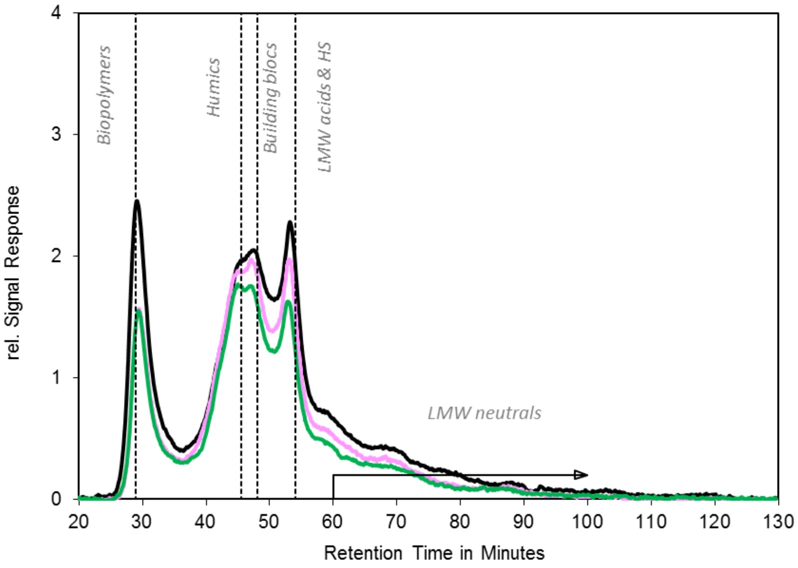

Figure 3.14 LC-OCD analysis of the influent and HCMP effluents during the PAC 1 phase

3.3.3 PAC + Fe 1

The PAC + Fe 1 phase was initiated after the last recovery cleaning of the previous phase without cleaning the tanks. Fe^{3+} (4 mg/L influent) was continuously dosed into the contact tank of HCMP 1 during the first 25 days of the operation. After 25 days a recovery cleaning of the membranes was carried out and the operation of the HCMPs had to be interrupted and the tanks were emptied and cleaned due to technical reasons. In the rest of the phase the Fe^{3+} was dosed into HCMP 2.

Filtration

The TMP course during the PAC + Fe 1 phase is illustrated in **Error! Reference source not found.**. During the first 15 days of operation, no difference was observed between HCMP 1 and HCMP 2, except for a short period, when HCMP 2 was accidentally operated at a flux of 60 LMH for 3 days. From day 15 onwards, a rapid increase in TMP was observed in HCMP 1. It is not clear whether this phenomenon was caused by the dosing of Fe^{3+} or by problems with aeration in HCMP1, which led to low cross flow velocities along the membrane surface and were observed starting from this day. Synergistic effects between the two effects cannot be excluded. The contact tank was not optimized for the formation of large flocs and as shown later in the description of Phase PAC + Fe 2, improper conditions for floc formation can lead to rapid fouling of the membrane.

When the system was restarted after the first recovery cleaning the dosing point of $FeCl_3$ solution was moved from HCMP 1 to HCMP 2. Stabilization of TMP in neither of the two systems was observed; on the contrary, a rapid increase in TMP requiring chemical cleanings was observed. The TMP increase was faster in HCMP1, which was only receiving PAC at this stage of operation.

The analysis of suspended solids showed varying results in the first half of the phase; more consistent data were recorded at the end of the phase. The stable concentration of suspended solids in HCMP 1 was around 100 mg/L, i.e. similar as in the Phase PAC 1. The concentration in HCMP 2 was between 500 to 700 mg/L due to the accumulation of iron hydroxides in the membrane tank.

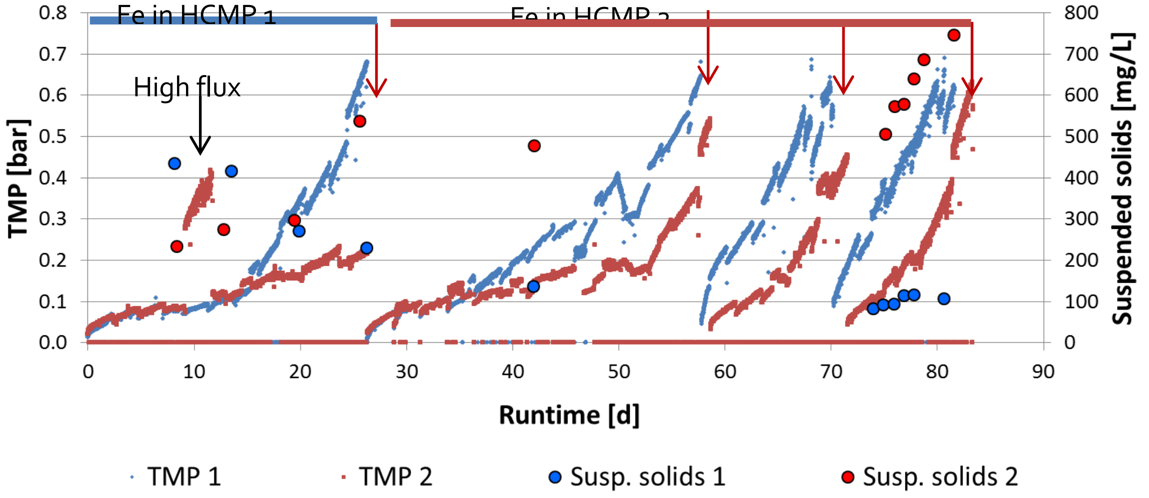

Figure 3.15 Trans-membrane pressure and suspended solids during the PAC + Fe 1 phase (arrows indicate recovery cleanings)

The analysis of the fouling rates recorded during the phase PAC + Fe 1 shows opposing trend compared to the previous phases: gradually increasing values (**Error! Reference source not found.**). Whereas during the first weeks of the operation the average values were between 1 and 2 kPa/d at the beginning of the phase, they reached 5.8 and 3.7 kPa/d in HCMP 1 and HCMP 2, respectively. It is not clear, what caused such an increase in both HCMP systems, no matter whether Fe^{3+} was dosed to the unit or not.

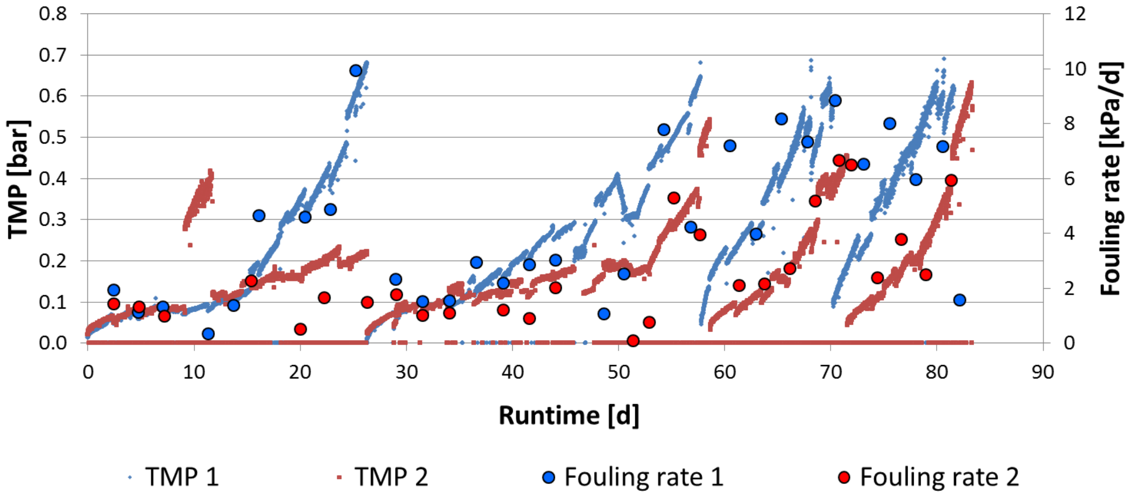

Figure 3.16 Trans-membrane pressure and fouling rate during the PAC + Fe 1 phase

Removal of micro pollutants

Two measurement campaigns focusing on the micro pollutants were conducted during the phase PAC + Fe 1. The first campaign included five samples collected between days 14 – 26 of operation. The results did not differ substantially between the two HCMP (**Error! Reference source not found.** and **Error! Reference source not found.**) and were generally similar to those observed in the previous phase.

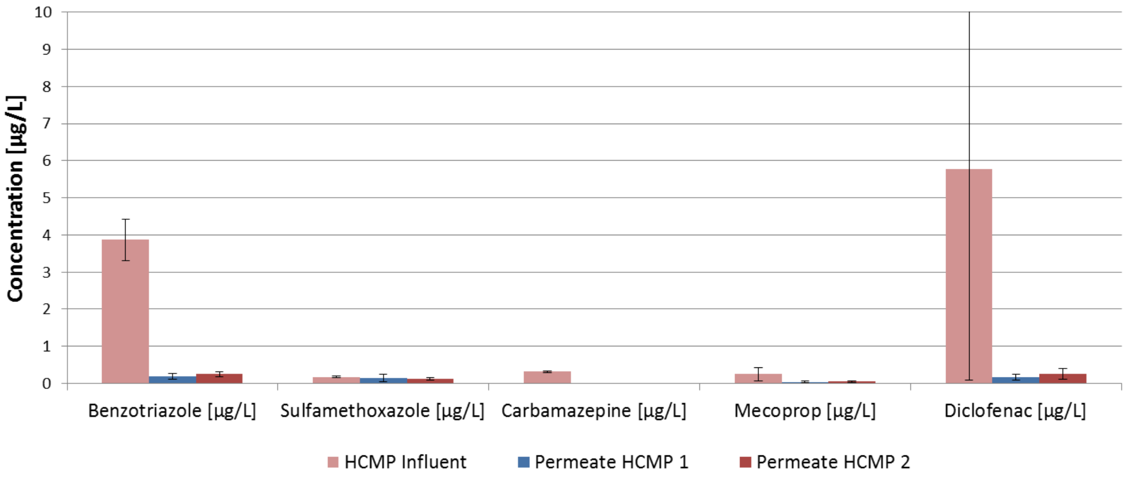

Figure 3.17 Concentration of micro pollutants in the influent and permeates from the HCMP systems during the PAC + Fe 1 phase (day 14-26)

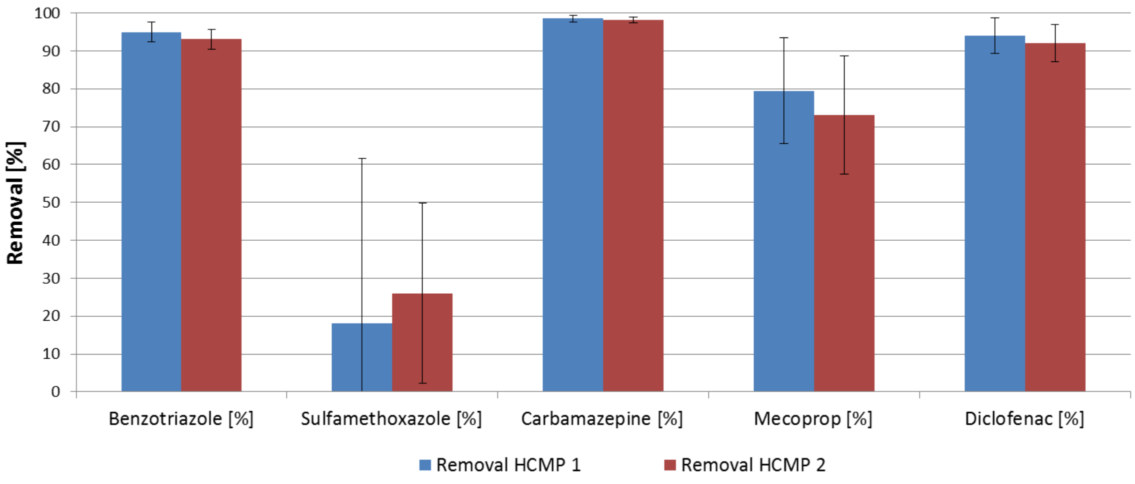

Figure 3.18 Removal of micro pollutants during the PAC + Fe 1 phase (day 14-26)

The second measurement campaign was conducted between days 74 – 81 of the operation. Significantly better removal efficiencies were observed in HCMP 2 (i.e. the system with Fe^{3+} dosage) compared to HCMP 1 (**Error! Reference source not found.** and **Error! Reference source not found.**), which achieved similar results as in the previous two measurement campaigns. HCMP 1 showed a lower sorption efficiency than in the previous two phases. Although the different removal efficiencies in the two parallel systems probably resulted from the difference in overall concentration of suspended solids (**Error! Reference source not found.**), this cannot fully explain the deterioration of sorption efficiency in HCMP 1, since the dose of sorbent was identical in both pilot systems (20 mg/L). Besides that the concentration of solids in HCMP 1 (approx. 100 mg/L) was comparable to the values during the phase PAC 1.

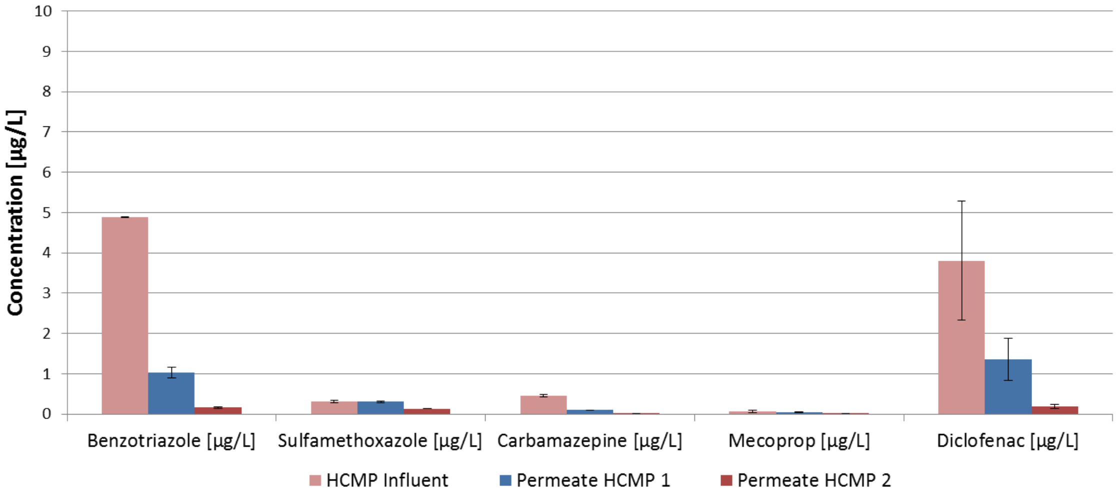

Figure 3.19 Concentration of micro pollutants in the influent and permeates from the HCMP systems during the PAC + Fe 1 phase (day 14-26)

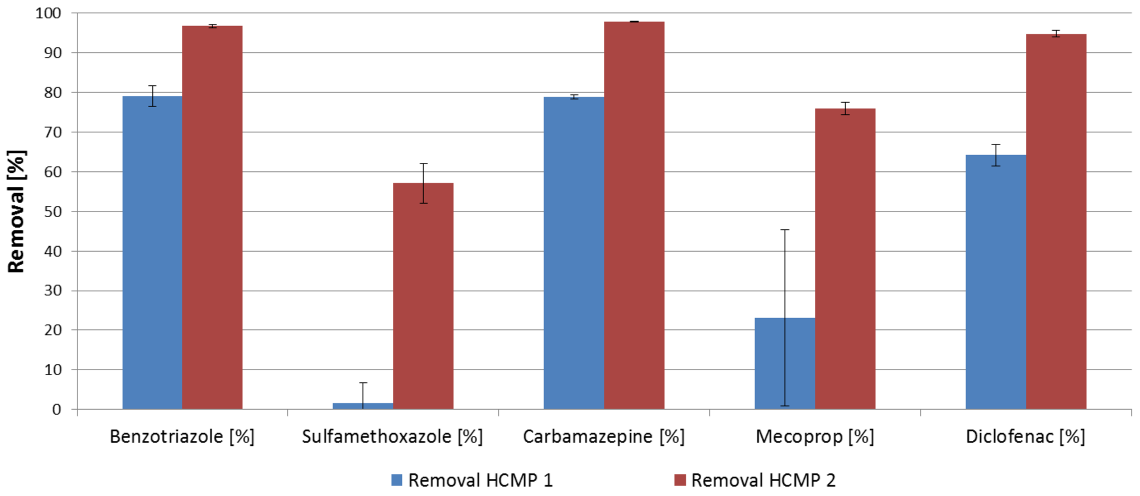

Figure 3.20 Removal of micro pollutants during the PAC + Fe 1 phase (day 14-26)

3.3.4 PAC + Fe 2

Since rapid fouling of both HCMP systems was experienced in the previous phase, which could not be compensated by the CEB, several measures were adopted before the PAC + Fe 2 phase was initiated. It was assumed that the poor performance was caused by the addition of Fe^{3+} which was dosed into both HCMP systems during the previous phase. The resulting compounds might have been attached to the membrane surface or membrane pores and to some extent resistant to the chemical cleaning protocol. Thus, the tanks were emptied and cleaned and a recovery cleaning procedure was carried out using more concentrated chemicals: alkali step with 1000 mg/L NaOCl (instead of 500 mg/L) and acidic step at lower pH (1.8 instead of 3.5). The filtration parameters were adapted towards lower filtration flux and more frequent CEB.

Filtration

The filtration flux was set to 18 LMH in both HCMP at the beginning of the phase. Besides that, the CEB interval was shortened to 1 d. PAC suspension (20 mg/L) was dosed into both HCMP; the dosing of Fe^{3+} (4 mg/L) into HCMP 2 only started after 17 days of operation, when the concentration of suspended solids in the tanks reached 50-100 mg/L (**Error! Reference source not found.**).

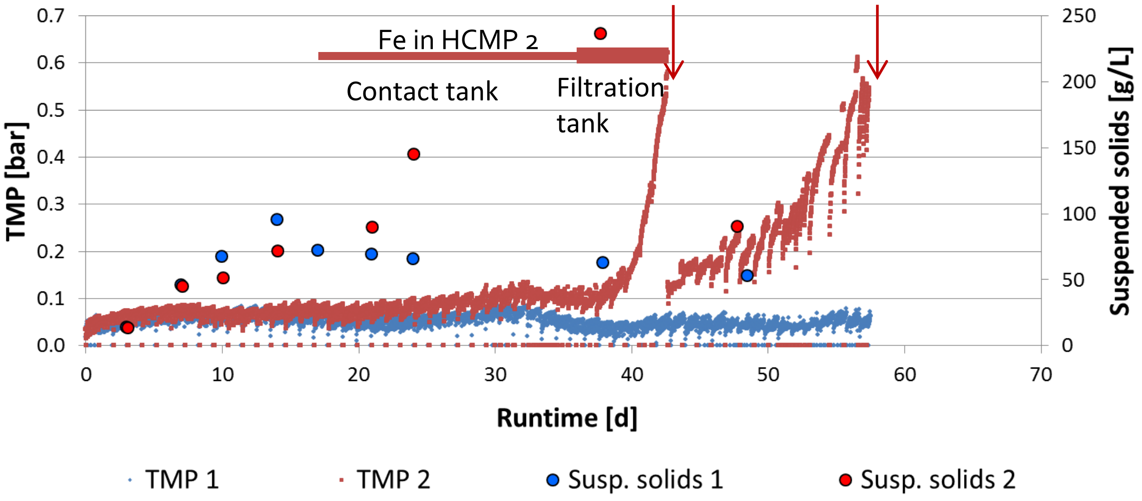

Figure 3.21 Trans-membrane pressure and suspended solids during the PAC + Fe 2 phase (arrows indicate recovery cleanings)

The intensive recovery cleaning, low filtration flux and frequent CEB contributed to stable filtration with low TMP (<0.1 bar). Both HCMPs showed identical TMP course in the first 17 days of operation; however, slightly higher TMP was observed in HCMP 2 after the Fe^{3+} dosing was initiated. A rapid increase in TMP (and fouling rates up to 20 kPa/d - **Error! Reference source not found.**) was observed after the dosing point of Fe^{3+} was moved from the contact tank into the membrane tank. Despite the addition of Fe^{3+} into HCMP 2 was stopped after a recovery cleaning of the membrane, substantially higher fouling rates were recorded compared to HCMP 1.

This experiment pointed out the need for optimized conditions for flocculation, when coagulant is dosed to the PAC-UF process. Formation of small flocs of iron hydroxides without their agglomeration into larger particles will not lead to the expected increase in filterability of the PAC; on the contrary, it can cause rapid fouling of the membranes. The effect of improper dosing of the coagulant on the filtration can also persist for extended period of time, even if the source of the coagulant is removed. This effect might have contributed to the relatively poor filterability in both HCMP units observed in the previous phase.

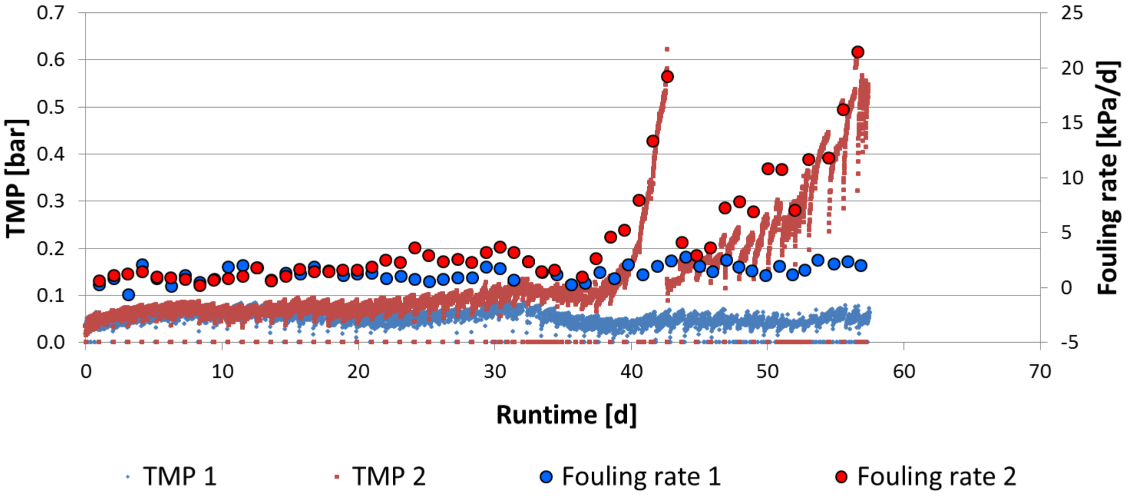

Figure 3.22 Trans-membrane pressure and fouling rate during the PAC + Fe 2 phase

Removal of micro pollutants

The concentration of a number of different pharmaceuticals was analyzed by KWR in the samples (n = 5) collected during the measurement campaign of the phase PAC + Fe 2. The samples were collected during the period following the recovery cleaning of HCMP 2 between day 44 and 57. The results are summarized in **Error! Reference source not found.** and **Error! Reference source not found.**. Only samples with concentrations above the detection limit in at least two samples from each profile are shown in the graphs.

Most of the tested pharmaceutical micro pollutants were removed in the HCMP systems with > 50 % efficiency, although low or no removal was observed for some compounds, such as hydroxy ibuprofen or sulfamethoxazole. The latter observation is not consistent with the measurement campaigns from the previous phases with PAC addition, where approx. 20 % removal of sulfamethoxazole was observed. The observed removal of diclofenac was lower as well, which might be due to lower influent concentration during the last campaign compared to previous phases (2.8 µg/L vs. 6.8 µg/L). On the other hand, the measured concentrations and removal efficiency of carbamazepine was consistent with previously measured values.

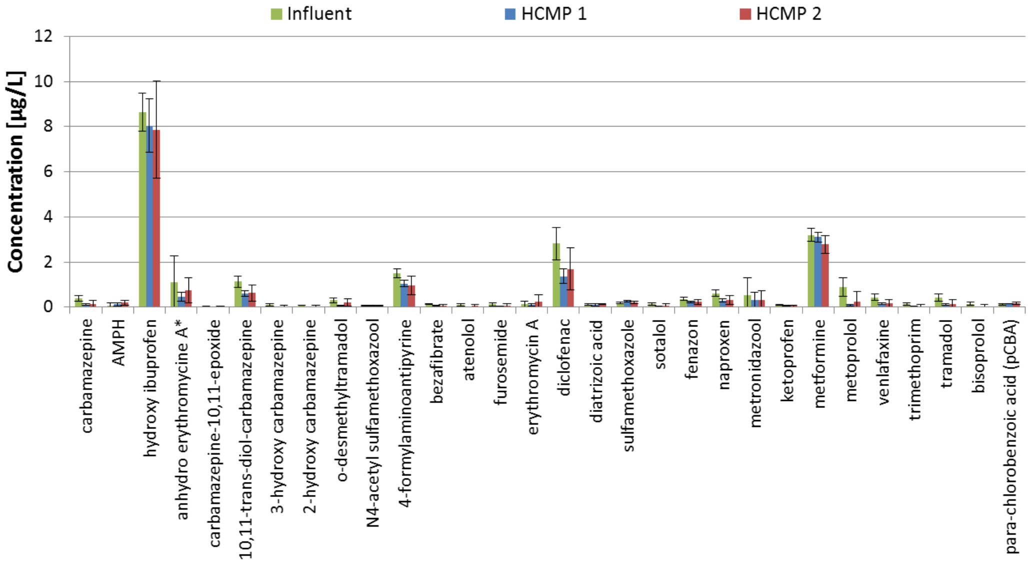

Figure 3.23 Concentration of micropollutants in the influent and permeates from the HCMP systems during the PAC + Fe 2 phase

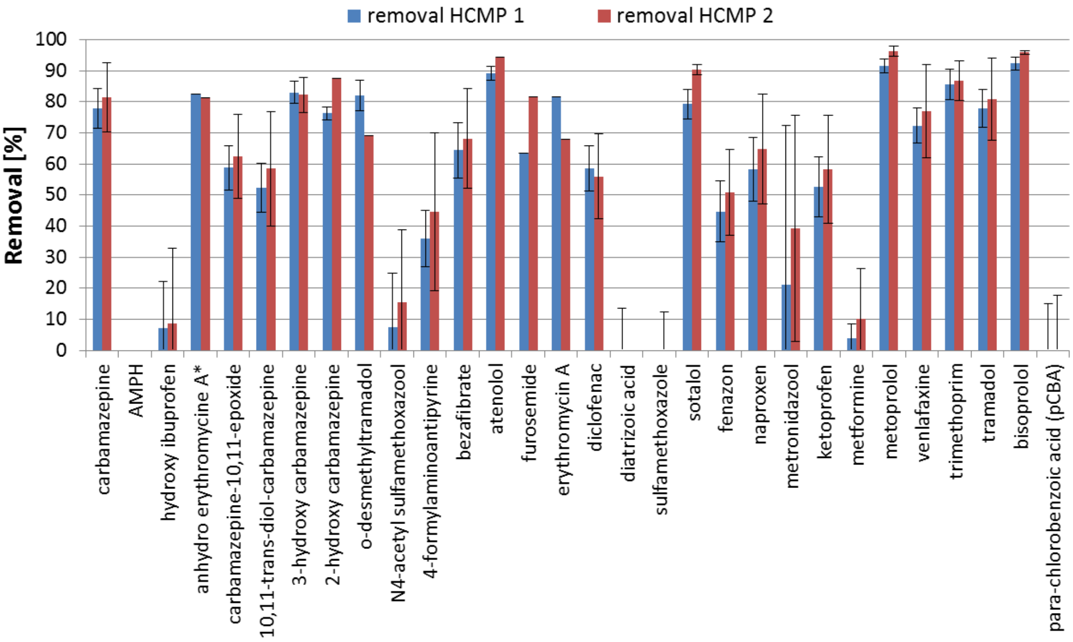

Figure 3.24 Removal of micropollutants during the PAC + Fe 2 phase

3.3.5 PAC 2

At the beginning of the phase both tanks were emptied and cleaned and recovery cleaning of both membrane modules was performed using the protocol with higher concentration of cleaning chemicals. Both HCMPs were operated at identical parameters, which were kept unchanged from the previous phase: filtration flux 18 LMH, CEB interval 1 d, 20 mg/L PAC, no Fe^{3+} dosing. The aim of the phase was to restore the original filtration properties in HCMP 2, which deteriorated after incorrect dosing of $FeCl_3$, and to study the effect of modified CEB protocol on the cleaning efficiency.

Filtration

The TMP and calculated fouling rate is plotted in **Error! Reference source not found.**. Despite the recovery cleaning and cleaning of the tanks HCMP 2 showed substantially higher TMP and fouling rate compared to the HCMP 1 (5.1 vs. 1.5 kPa/d) (**Error! Reference source not found.**). Unlike the beginning of the previous PAC + Fe 2 phase, stable TMP was only reached in HCMP 1. Additional recovery cleaning of the membrane in HCMP 2, which was carried out on day 11 of the operation, did not change the increasing difference between the TMP profiles in the two units. This observation confirms persistent binding of the particles arising from improper dosing of Fe^{3+} during the previous phase, possibly inside of the membrane pores.

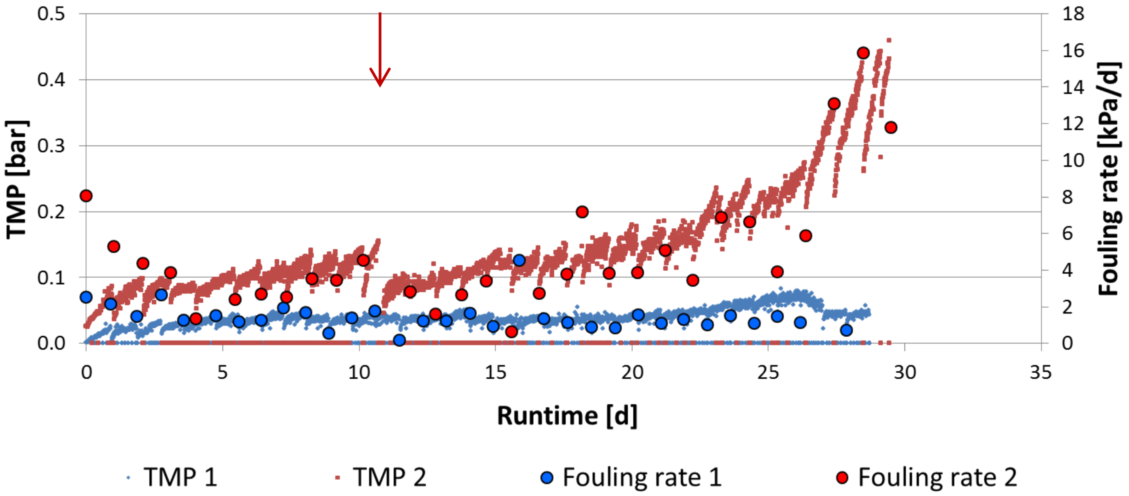

Figure 3.25 Trans-membrane pressure and fouling rate during the PAC 2 phase (arrows indicate recovery cleanings)

Another aim of the phase was to test the influence of the CEB on the efficiency of membrane cleaning. The CEB protocol in the previous operation consisted of:

- 5x backwash with 1000 mg/L NaOCl –duration of each backwash 45s, pause between backwash 5 min
- Backwash with permeate without chemicals
- 5x backwash with 1000 mg/L citric acid –duration of each backwash 45s, pause between backwash 5 min
- Backwash with permeate without chemicals

After day 16 of the phase PAC 2 the duration of each backwash in HCMP 1 was reduced from 45 s to 30 s, which would mean 30 % reduction in chemical consumption. In order to evaluate the efficiency of the CEB sequence, the cleaning efficiency was calculated for each CEB (**Error! Reference source not found.**). A decrease in CEB efficiency was observed in the period following the change of the CEB protocol: while before day 16 the average TMP drop after each CEB was 1.1 kPa (0.011 bar), from day 17 until the end of operation the average TMP drop was 0.73 bar (0.0073 bar). The decrease in efficiency (33%) roughly corresponds to the reduction of chemical consumption.

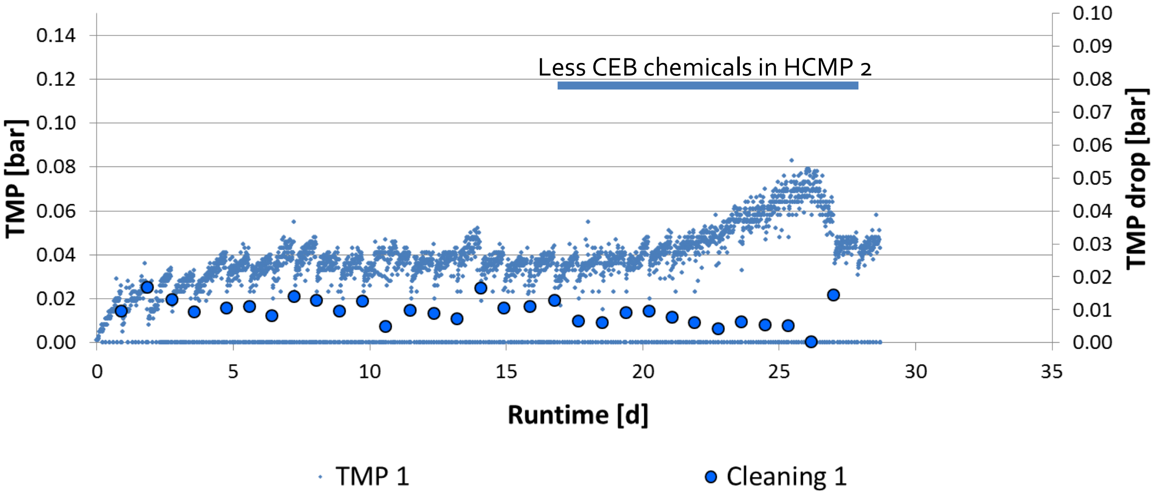

Figure 3.26 Trans-membrane pressure and cleaning efficiency of CEB in HCMP 1 during the PAC 2 phase

3.4 Conclusions

Most of the target micro pollutants were removed from the municipal wastewater by the tested PAC-UF process with 60 to 95% efficiency. Especially the non-polar compounds (benzotriazole, carbamazepine and diclofenac) were removed with 80 to 95 % efficiency. Negligible removal of the target compounds was observed during the reference phase, i.e. without PAC addition into the system.

Lower fouling was observed during the operational phase with PAC addition. In comparison to the reference operation the fouling rate after the stabilization of PAC concentration decreased from 3-4 kPa/d to 2-2.5 kPa/d.

The enhancement of PAC separation by coagulation by Fe^{3+} addition could not return expected results, possibly due to high mixing gradients in the compartments of the HCMP units, which did not provide proper conditions for flocculation.

3.5 References

Gälli, R. , Ort, C., Schärer, M., 2009. Mikroverunreinigungen in den Gewässern. Bewertung und Reduktion der Schadstoffbelastung aus der Siedlungsentwässerung (Micropollutants in the water bodies. Evaluaton and reduction of contaminant load from urban drainage). *Umwelt-Wissen* Nr. 0917. Federal Office of the Environment, Bern.

Götz, C.W., Abegglen, C., McArdell, C.S., Koller, C.S., Siegrist, H., Hollender, J., Schärer, M., 2010. Mikroverunreinigungen - Beurteilung weitergehender Abwasserreinigungs-verfahren anhand Indikatorsubstanzen (Micro pollutants – Evaluation of additional sewage treatment processes based on indicator substances). gwa 4/2010: 1-9.

Löwenberg, J., Zenker, A., Baggenstos, M., Koch, G., Kazner, C., Wintgens, T., 2014. Comparison of two PAC/UF processes for the removal of micropollutants from wastewater treatment plant effluent: process performance and removal efficiency. *Water Research*, 56, 26–36.

Margot, J., Kienle, C., Magnet, A., Weil, M., Rossi, L., Felippe de Alencastro, L., Abegglen, C., Thonney, D., Chèvre, N., Schärer, N., Barry, D.A., 2013. Treatment of micro pollutants in municipal wastewater : Ozone or powdered activated carbon. *Science of the Total Environment* 461-462, 480-498.

Zwickenpflug, B., Böhler, M., Sterkele, B., Joss, A., Siegrist, H., Traber, J., Gujer, W., Behl, M., Dorusch, F., Hollender, J., Ternes, T. and Fink, G., 2010. *Einsatz von Pulveraktivkohle zur Elimination von Mikroverunreinigungen aus kommunalem Abwasser* (Use of powdered activated carbon for the removal of micropollutants from municipal wastewater). Final report of the MicroPoll project, EAWAG on behalf of the Swiss Federal Office for the Environment, Dübendorf, CH, http://www.eawag.ch/forschung/eng/schwerpunkte/.

Hummel, D., Loffler, D., Fink, G., Ternes, T.A., 2006. Simultaneous determination of psychoactive drugs and their metabolites in aqueous matrices by liquid chromatography mass spectrometry. *Environ. Sci. Technol.* 40 (23), 7321 – 7328.