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Role of organic substances in tertiary treatment via oxidation and membrane filtration

Project acronym: OXERAM 2

by

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Abstract (English)

In work package 4 the influence of different treatments (ozonation, coagulation) on macromolecular organic substances (biopolymers) in secondary effluent and the effects on subsequent ultrafiltration were investigated at lab-scale. Furthermore, fouling mechanisms were intensively investigated and an analytical method was developed to observe the formation of ozonation by-products.

Analyses with LC-OCD showed a significant reduction of major organic foulants (biopolymers) for coagulation while ozonation appears to transform macromolecules into compounds smaller than approx. 50 nm. With ultrafiltration tests (PES membranes) it could be shown that coagulation is capable to reduce total fouling resistance to some extent and additional ozonation can further enhance the membrane filtration process. However ozonation as a pretreatment step caused more irreversible fouling. The lowest irreversible fouling was achieved with coagulation. LC-OCD analyses showed that the transformation of organic matter by ozonation is mainly responsible for the observed increased irreversible fouling of ultrafiltration membranes. Tests with different membranes showed comparable results for pretreated secondary effluent concerning total fouling resistance. Total fouling resistance was reduced with additional ozonation compared to coagulation without ozonation. In contrast to the observations with all tested UF membranes, for the tested microfiltration membranes irreversible fouling was reduced with additional ozonation. In general, the pore size seems to be strongly influencing irreversible fouling if ozonation is used for pretreatment of membrane filtration.

Intensive investigations of fouling mechanisms using filtration laws identified cake filtration as the dominant filtration process for coagulation while additional ozonation leads to increased pore blocking/in pore fouling.

Experiments with secondary effluents from different sewage treatment plants in Berlin showed comparable fouling behavior for all observed pretreatments. Thus membrane filtration results generated with samples from WWTP Ruhleben seem to be transferable to other WWTPs in Berlin.

MALDI-TOF-MS analyses of secondary effluent were not suitable to identify major organic foulants, neither in solution nor on top of the membrane after filtration. Consequently, MALDI-TOF-MS was primarily used for investigations of theoretical aspects of fouling by using model fouling substances.

An analytical procedure for bromate was successfully developed with LC-MS/MS at TUB. With the procedure it was possible to quantify samples up to a limit of quantification of 0.5 µg bromate per liter. Higher concentrations of bromate (> 10 µg/L) were produced only at specific ozone consumptions higher than 0.9 $mgO_3/mgDOC_0$.

Abstract (Deutsch)

Im Arbeitspaket 4 (AP4) wurde der Einfluss verschiedener Verfahrensschritte (Ozonung, Flockung) auf makromolekulare organische Substanzen (Biopolymere) im Ablauf kommunaler Kläranlagen und die Effekte auf eine nachgeschaltete Ultrafiltration in Laborversuchen untersucht. Darüber hinaus wurden die auftretenden Foulingmechanismen durch Modellrechnungen bestimmt und eine Analysemethode zur Bestimmung von Oxidationsnebenprodukte entwickelt.

Mit Hilfe der LC-OCD Analytik konnte eine deutliche Entfernung der Biopolymere durch eine Flockung festgestellt werden. Hingegen werden bei der Ozonung die Makromoleküle in Stoffe kleiner als ~50 nm zerlegt. Durch Ultrafiltrationsexperimente mit Membranen aus Polyethersulfon (PES) konnte gezeigt werden, dass eine Flockung vor der Filtration den Gesamtfoulingwiderstand signifikant verringert und eine zusätzliche Ozonung die Filtrationseigenschaften weiter verbessert. Das geringste irreversible Fouling wurde durch eine Flockung erreicht, währenddessen die Vorozonung verstärktes irreversibles Fouling verursachte. Die LC-OCD Analyse zeigte, dass die Transformation der organischen Makromoleküle hauptsächlich für das erhöhte irreversible Fouling der Ultrafiltrationsmembranen verantwortlich ist. Untersuchungen mit verschiedenen Niederdruckmembranen zeigten vergleichbare Ergebnisse im Hinblick auf den Gesamtfoulingwiderstand. Durch die Ozonung konnte der Gesamtfoulingwiderstand im Vergleich zur alleinigen Flockung stärker reduziert werden. Im Gegensatz zu den Ultrafiltrationsmembranen wurde das irreversible Fouling durch eine Ozonung bei der getesteten Mikrofiltrationsmembran zusätzlich reduziert. Generell kann die Porengröße einer Membran als entscheidender Faktor für die Vorozonung und das irreversible Fouling der Membranen gesehen werden.

Mit Hilfe von Modellrechnungen konnten die Foulingmechanismen näher beschrieben werden. Nach der Flockung konnte eine Kuchenfiltration und bei zusätzlicher Ozonung eine Porenverblockung bzw. In-Pore-Fouling als vorherrschender Foulingmechanismus ermittelt werden.

Versuche mit Abläufen verschiedener Kläranlagen zeigten vergleichbare Filtrationseigenschaften durch die untersuchten Vorbehandlungsschritte. Folglich können die Ergebnisse der umfassenden Experimente mit Proben aus der KA Ruhleben weitestgehend auf die anderen Berliner Kläranlagen übertragen werden.

Mittels MALDI-TOF-MS konnten die organischen Makromoleküle weder in Lösung noch auf der Membranoberfläche bestimmt werden. Folglich wurde das MALDI-TOF-MS hauptsächlich zur Untersuchung theoretischer Aspekte des Foulings durch Einsatz von Modellösungen verwendet.

Eine Methode zur Bestimmung von Bromat mittels LC-MS/MS wurde erfolgreich an der TU Berlin entwickelt. Mit dieser Methode ist es möglich Bromat bis zu einer Bestimmungsgrenze von 0,5 µg/L zu quantifizieren. Erhöhte Bromatkonzentrationen (>10 µg/L) wurden nur bei spezifischen Ozondosen von mehr als 0,9 $mgO_3/mgDOC_0$ im Kläranlagenablauf gebildet.

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Thank you!

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Abbreviations & quantities

Abbreviations

AU	area unit
BP	biopolymer
DOC	dissolved organic carbon
Fe	iron
$FeCl_3$	iron(III) trichloride
H_2O	water
LC	liquid chromatography
LMH	liter per square meter per hour
MW	molecular weight
MWCO	molecular weight cutoff
OCD	organic carbon detection
OND	organic nitrogen detection
PES	polyethersulfone
PVDF	polyvinylidene fluoride
R^2	coefficient of determination
SEC	size exclusion chromatography
SI	international system of units
TMP	trans-membrane pressure

Quantities

Greek symbols

α	specific resistance	$[m \cdot kg^{-1}]$
α_0	specific resistance at reference pressure	$[m \cdot kg^{-1}]$
α_i	specific resistance at pressure *i*	$[m \cdot kg^{-1}]$
Δp	trans membrane pressure	$[N \cdot m^{-2}]$
Δp_i	trans membrane pressure *i*	$[N \cdot m^{-2}]$
κ	conductivity	$[\mu S \cdot cm^{-1}]$
η	dynamic viscosity	$[N \cdot s \cdot m^{-2}]$
σ	standard deviation	

Latin symbols

A	area	$[m^2]$
c	concentration	$[mg \cdot L^{-1}]$
c_i	concentration in entity *i*	$[kg \cdot m^{-3}]$
c_{feed}	concentration in feed	$[mg \cdot L^{-1}]$
c_{perm}	concentration in permeate	$[mg \cdot L^{-1}]$
d_h	hydrodynamic diameter	[nm]
η	dynamic viscosity	$[N \cdot s \cdot m^{-2}]$
J	flux	$[m \cdot s^{-1}]$
J_M	measured flux	$[m \cdot s^{-1}]$
J_0	pure water flux	$[m \cdot s^{-1}]$

J_S	standardized flux	$[m \cdot s^{-1}]$
k	filtration coefficient, units depending on filtration exponent n	
m	mass	[kg]
m_i	mass in entity i	[kg]
M	molecular weight, equivalent to Da (dalton)	$[g \cdot mol^{-1}]$
n	filtration exponent, dimensionless	
p	pressure, also given in bar $[10^5 \cdot N \cdot m^{-2}]$	$[N \cdot m^{-2}]$
R	resistance	$[m^{-1}]$
R_m	resistance by membrane	$[m^{-1}]$
$R_{f,rev}$	resistance by reversible fouling	$[m^{-1}]$
$R_{f,irr}$	resistance by irreversible fouling	$[m^{-1}]$
s	compressibility, dimensionless	
t	time	[s]
T	temperature	[°C]
T_M	measured temperature	[°C]
T_S	standardized temperature	[°C]
V	volume	[L]
V_i	volume of entity i	$[m^3]$
Z	specific ozone consumption	$[mgO_3/mgDOC_0]$

1 Introduction

1.1 Background

There are especially two new regulations which lead to a new challenge for environmental agencies and water disposal companies. One the one hand, the European Water Framework Directive demands a “good” ecological and chemical status for all artificial and natural water bodies. On the other hand, the European Bathing Water Framework specifies minimum requirements for official bathing areas especially concerning their microbial status.

In particular, it is the discharge of treated waste water from municipal sewage plants which has strong negative effects on the quality of surface waters and, thus, endangers the sufficient implementation of these regulations. This leads to considerations of an upgrade of municipal sewage plants with a tertiary treatment step in Berlin. This should improve effluent quality and reduce negative impacts on surface waters. Concerning these new challenges mentioned above the main goals of a possible tertiary treatment are the reduction of phosphorus to avoid eutrophication and the disinfection to reduce microbial contamination in the receiving water bodies.

To reach these goals there are, in general, different treatment processes available, which are appropriate for tertiary treatment. One possibility is the implementation of a low pressure membrane filtration system. Due to its pore size it is able to retain and reduce microorganisms. In combination with a pre-flocculation it is also an appropriate process to remove phosphorus.

One important weak point of this process is the fouling of the membrane which leads to a lower efficiency, higher downtimes, higher operational costs and shorter lifetimes of the membranes. Previous studies indicate that it is the fraction of so-called biopolymers which are mainly relevant for fouling of secondary effluent [Haberkamp 2008; Zheng 2010]. Nevertheless, the effects of fouling are have not been investigated in a sufficient way so that fouling is the main inhabitation of a stronger implementation of membrane systems.

Additionally to flocculation, pre-ozonation is another promising pretreatment step for membrane processes. Previous studies indicated a reduction of fouling after such a pretreatment [Genz et al. 2011; Van Geluwe et al. 2011] and an increase of filtration efficiency.

At the same time, ozonation can cause high concentrations of harmful oxidation-by-products like bromate or N-Nitrosodimethylamine (NDMA). Thus, there is a need for detailed and comprehensive investigations of this possible pretreatment step.

1.2 Aim of the project

A main objective of the OXERAM project is the comparison of different pretreatment and filtration processes as tertiary treatment step in the sewage plant and the evaluation of their ecological and economical impacts. Especially a possible implementation of a low pressure membrane system should be investigated.

Besides pilot plant investigations at wastewater treatment plant Ruhleben, which are implemented in work package 2, lab experiments and analyses at TU Berlin should be conducted to get more precise information about the phenomenon of fouling and the effects of different pretreatments. The main objectives of work package 4 include the following main aspects and questions:

- Further identification and characterization of substances in secondary effluent causing fouling during low pressure membrane filtration.
- Effects of pretreatment by flocculation, ozonation and flocculation with subsequent ozonation on these substances.
- Effects of these pretreatment procedures on filtration performance of low pressure membranes.
- Investigations on fouling mechanisms.
- Influence of membrane material and pore size on fouling and filtration performance.

Furthermore, work package 4 includes analyses and assessment of formation of oxidation-by-products by ozonation of secondary effluent. In the following report results and conclusions of the conducted investigations in work package 4 are presented.

2 Experimental

2.1 Water samples and pretreatment

2.1.1 Secondary effluent

Secondary effluent samples were obtained from effluent of the wastewater treatment plant (WWTP) *Ruhleben*, Berlin. The plant has a capacity of about $2.5 \cdot 10^5$ m^3/d (dry weather) and is equipped with mechanical/biological treatment steps (sedimentation, denitrification/nitrification and secondary sedimentation). In general, for each performed experiment new secondary effluent water samples were collected from the WWTP at the same day of the experiments. Before pretreatment/filtration experiments the samples were tempered (18 – 22 °C) to have comparable conditions.

For comparison of different secondary effluents samples from four different wastewater treatment plants in Berlin (Ruhleben; Muenchehofe; Wassmansdorf; Schoenerlinde) were taken at the same time after 3 days of dry weather and used for these specific experiments.

2.1.2 Pretreatment of secondary effluent in the lab

Ozonation

The ozonation of the water in the lab was performed using an ozonation unit that produces gaseous ozone from pure oxygen by an ozone generator from WEDECO (type Modular 8HC, ITT WEDECO GmbH, Germany). The gaseous oxygen/ozone-mixture was directly introduced into a 4-L-semi-batch stirred tank reactor filled with the water sample and stirred at 500 rpm. In-gas and off-gas ozone concentration, dissolved ozone and gas flow rate were measured continuously and recorded by a computer. Ozone dosage/consumption of the water samples was automatically calculated by the computer (mass balance of ozone) and specific ozone consumption was calculated manually after dissolved organic carbon (DOC) measurement.

Coagulation

Coagulation was performed according to DVGW worksheet W 218 (DVGW, 1998) in the same 4-L stirred tank reactor as used for ozonation. The coagulant was introduced directly into the batch and mixed for 10 seconds at 500 rpm (G = 1580 s^{-1}) followed by 5 min stirring at 60 rpm (G = 70 s^{-1}).

Pre-ozonation with subsequent coagulation

For combination of ozonation and coagulation the same 4-L stirred tank reactor was used. Right after the ozonation process the coagulant was dosed direct into the reactor followed by mixing according to DVGW worksheet W 218.

2.1.3 Treated effluent samples from the pilot plant (Ruhleben)

Besides ozonation and coagulation in the lab, pretreated samples from the pilot plant at the WWTP Ruhleben were obtained for batch filtration experiments. In general, samples were taken at different sampling points of the treatment process for further experiments in the lab. Table 2.1 summarizes the sampling points at the pilot plant in Ruhleben.

Table 2.1: Sampling points at the pilot plant.

Sampling point	Treatment
1	Pre-filtration (300 µm)
2	Ozonation
3	Coagulation
4	Ozonation with subsequent coagulation
5	Permeate after microfiltration
6	Permeate after ultrafiltration

Further details of the different treatment units (ozonation/coagulation unit and membrane filtration pilots) you can find in the report of Johan Stueber (KWB; Deliverable 2.2).

2.1.4 Model solutions

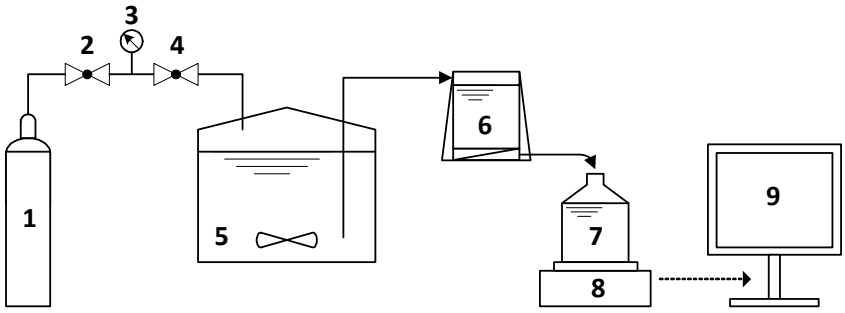
Model solutions were prepared using as protein bovine serum albumin (BSA, MW ~67 kDa, *Sigma-Aldrich*, USA) and as humic matter Suwannee River NOM from RO isolation (*International Humic Substances Society*, USA). Concentrations of 5 mg/L (BSA) and 2 mg/L (humic matter) were spiked into a salt solution that was made solving calcium dichloride dihydrate ($CaCl_2 \cdot 2\ H_2O$) and sodium chloride (NaCl) in ultrapure water. Concentrations were 411 mg/L $CaCl_2 \cdot 2\ H_2O$ and 316 mg/L NaCl, which resulted in a conductivity similar to the one of effluent from the WWTP Ruhleben (~ 1200 µS/cm). pH was adjusted before the filtration using sodium hydroxide (NaOH) and/or hydrochloric acid (HCl) to 3 (pH < IEP (isoelectronic point) of BSA) and 7 (pH > IEP of BSA).

2.2 Lab membrane filtration units

2.2.1 Type 1: Amicon®

Setup

Figure 2.1 shows a scheme of the experimental setup used for Amicon® filtration tests. A feed water reservoir (5) is pressurized using nitrogen (1). The outlet of the feed water tank is connected to a filtration cell (6) with the membrane positioned at the bottom of the cell. Permeate leaves the cell at its bottom, dripping into a beaker/bottle (7) on an electronic scale (8). The scale is connected to a computer (9) that periodically (every 20 seconds) records the weight on the scale. Flux can then be obtained by subtracting a value from its successor. The model of the used filtration cell was *Amicon® Stirred Cell 8200* (*Millipore*, USA) with a volume of 200 mL and an effective filtration area of $2.87 \cdot 10^{-3}$ m^2.



1 Pressurized nitrogen bottle
2 Pressure regulator
3 Manometer
4 Valve
5 Feed water tank (V = 4L)
6 Cell with flat-sheet membrane (V = 200 mL)
7 Permeate tank
8 Electronic balance
9 Computer with weight-recording software

Figure 2.1: Schematic illustration of the Amicon® filtration unit.

Procedure

All feed waters were adjusted to room temperature before starting an experiment (18 – 22 °C). A filtration cycle comprised filtration of 500 mL feed water, backwash with 50 mL permeate and flux measurement with ~200 mL ultrapure water. The reference pressure for filtration and backwash was 1 bar. For some filtration tests (compressibility tests, membrane comparison, etc.) the pressure was modified for the different approaches.

Membranes

The membranes used in all Amicon® filtration tests were taken from flat sheets and stamped using a custom die cutter fitted for the applied filtration cells. For storage the membranes were stored at least 24 h in ultra pure water at < 6 °C and not longer than 14 days. All membrane slices were rinsed with 2 L ultra pure water prior to any experiment to remove production remainders. [Jermann et al. 2007; Zheng 2010]

The membrane type generally applied was UP 150 (MWCO of ~150 kDa, *Microdyn Nadir GmbH*, Germany) made of hydrophilized polyethersulfone (PES). For membrane comparison experiments further membranes were used. Some membrane types were not able to operate at reference transmembrane pressure (TMP; 1 bar) so that the TMP had to be modified. For all conducted experiments a backwash pressure of 1 bar was used. Table 2.2 summarizes the membranes and applied TMPs that were used in the Amicon® filtration experiments.

Table 2.2: Membrane characteristics and corresponding TMPs for Amicon® filtration tests; PES = polyethersulfone, PVDF = polyvinylidene fluoride; * = manufactors data, ** = calculated, * = average experimental data.**

Parameter	Unit	UP150	MP005	UV150	MVT020
Membrane material	[-]	hydrophilized PES	hydrophilized PES	PVDF	PVDF
MWCO*	[kDa]	150	600	150	-
Pore size**	[µm]	0.026	0.05	0.026	0.2
TMP	[mbar]	1000 / 500	1000 / 500	1000 / 500	500
Permeability (20 °C)***	[L $m^{-2}h^{-1}bar^{-1}$]	930	1080	510	4200

2.2.2 Type 2: Semi-automatic Siemens® (Memcor)

Setup

A membrane unit for bench-scale filtration tests using outside-in polyvinylidene fluoride (PVDF) hollow-fibre membranes (max. pore size = 100 nm) by Memcor (*Memcor/Siemens® Water Technologies*, Windsor, NSW, Australia) developed by Haberkamp [2011] was modified for dead-end filtration tests within this project. Figure 2.2 shows the flow scheme of the semiautomatic membrane filtration unit.

The feed water tank is equipped with a static mixer (1) to avoid sedimentation of particulate water constituents. An adjustable gear pump (2) operates as filtration pump and also as backwash pump (produced permeate is used as backwash water). The membrane fibres are potted into plexiglas mountings and fixed in a membrane module (4). The filtration plant could be operated with one or optional with two membrane modules. The permeate flux was continuously measured by an electronic balance (10).

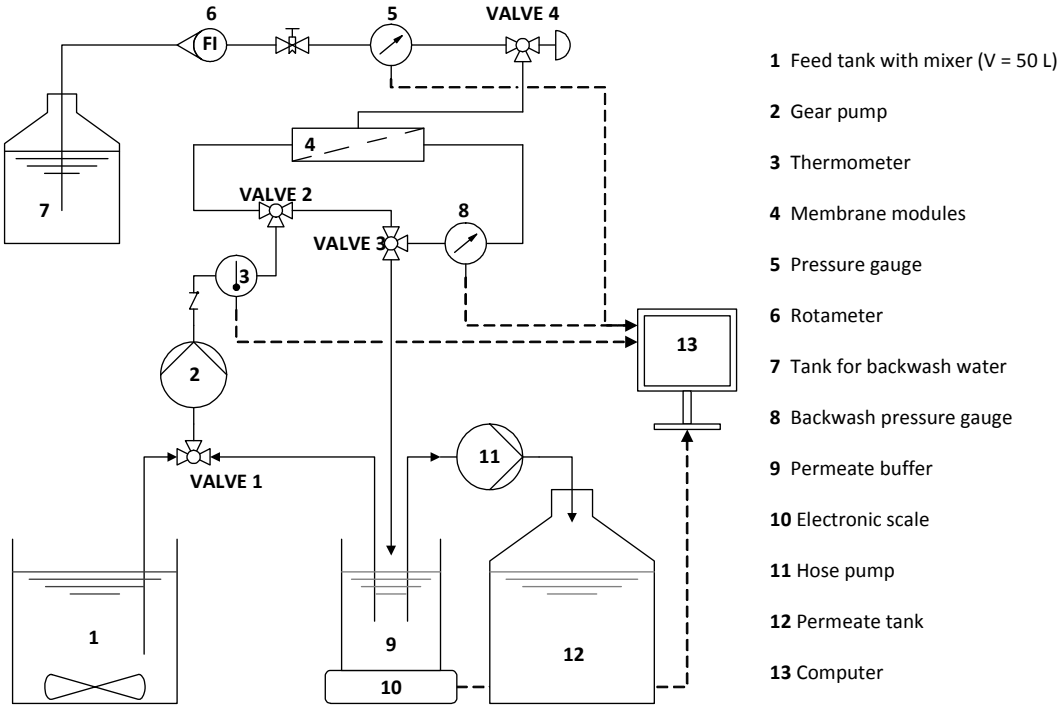


Figure 2.2: Flow scheme of semi-automatic Siemens® (Memcor) filtration unit.

Permeate (12) and backwash water (7) is collected separately in different beakers. Data recording (temperature, pressure, flux) and operational control (valve and pump controlling) is carried out by a computer (13) equipped with self programmed controlling software on *LabView* basis. Temperature correction for flux measurement and calculation of filtration resistance is done online additionally by the software.

Procedure

For all trials the same membrane fibres were used. Prior to each test, the membrane fibres were chemically cleaned with sodium hypochlorite (5%) and rinsed afterwards with ultrapure water. The cleaning procedure was repeated until the initial ultrapure water permeability was reached to have comparable initial conditions. The initial permeate flux J_0 of the membrane module was determined immediately before starting the test using ultrapure water.

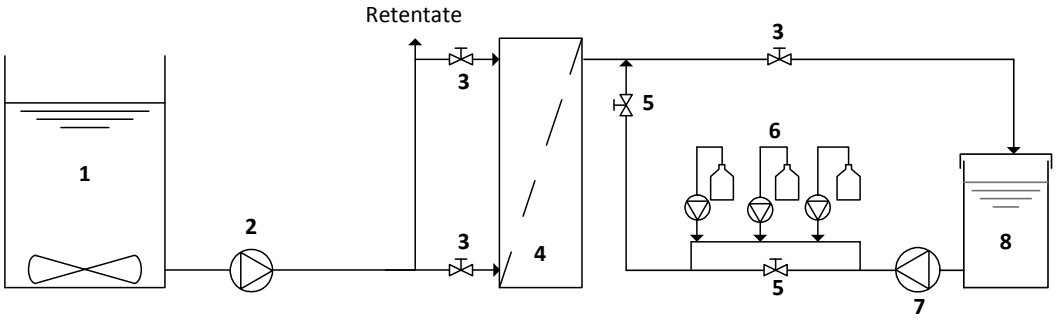
For all trials pretreated effluent from the pilot plant in Ruhleben was obtained (see chapter 2.1.3) on the day of the experiments. During the tests, the filtration cycles consisted of 1 L of feed water filtration at a TMP of 0.5 bar, followed by 0.2 L of permeate backwashing at a TMP of 1 bar.

2.2.3 Type 3: Inge® "PUE10"

Within the "OXERAM II" project a lab/pilot membrane filtration unit was built up. The filtration unit is nearly completely comparable to the UF membrane pilot plants at WWTP Ruhleben according to operation, controlling software, membrane module, etc..The major difference is the smaller membrane area of the used membrane modules resulting in lower flow rates at comparable fluxes.

Setup

Figure 2.3 shows the flowchart of the filtration pilot plant (PUE10). The feed water tank (1, V = 100 L) is equipped with a static mixer for continuous mixing of the feed water to avoid sedimentation of particulate water constituents. A feed pump (2) supplies the membrane module (4; A = 0.2 m^2) with feed water. Permeate is collected in a separate permeate tank (8; 15 L) for backwash carried out with a backwash pump (7).



1 Feed tank with mixer (V = 100 L)
2 Feed pump
3 Filtration valves
4 Membrane module
5 Backwash valves
6 Chemicals for CEB
7 Backwash pump
8 Permeate tank (V = 15 L)

Figure 2.3: Flowchart of INGE® filtration unit.

Besides hydraulic backwash the system is equipped for chemical enhanced backwash (CEB) procedures. The chemical dosing systems (6) consists of different chemicals like NaOCl, NaOH, HCl, and H_2SO_4, which can additionally be dosed into permeate before backwash.

Procedure

Two different membrane modules were tested during the experimental phase. Both membranes are made of hydrophilized PES material and have different maximal pore sizes (20 nm vs. 150 nm). Prior the filtration test the membrane modules were cleaned until the initial pure water permeability was reached to have comparable start conditions. For all trials pretreated effluent from the pilot plant in Ruhleben was obtained (see chapter 2.1.3) on the day of the experiments.

All experiments were performed at a constant flux of 60 LMH ($L*m^{-2}*h^{-1}$). Each filtration cycle consisted of 30 min filtration and mechanical backwash for 30 seconds with permeate and a flux of 250 LMH. Alternating the filtration of the feed water was from the top followed by the bottom.

2.2.4 Overview of the used membrane filtration units

The following Table 2.3 summarizes the used membrane filtration units and the corresponding operational parameters.

Table 2.3: Summary of the experimental filtration units and corresponding operational parameters.

Parameter	Unit	AMICON®	SIEMENS®/MEMCOR	INGE® *"Besenstil"*
Configuration	[-]	flat sheet	hollow fiber (outside-in)	hollow fiber (inside-out)
Operation	[-]	constant pressure (1 bar)	constant pressure (0.5 bar)	constant flux (60 $L*m^{-2}*h^{-1}$)
Backwash	[-]	1 bar	1 bar	250 $L*m^{-2}*h^{-1}$
Flow regime	[-]	dead-end	dead-end	dead-end
Membrane module	[-]	AMICON®-cell	self-made	dizzer
Membrane area	[m^2]	$2.87 \cdot 10^{-3}$	2 x 0.02	0.2
Application	[-]	lab-scale	lab-scale	lab/pilot-scale
Pretreatment	[-]	lab/pilot	pilot	pilot

2.3 Analyses

2.3.1 Bulk parameter

Turbidity, pH and temperature

For turbidity detection a *Hach 2100N IS Turbidimeter* (*Hach Lange GmbH*, Germany) was used. Temperature and pH were measured using a *pH 537 Microprocessor pH Meter* (*WTW Wissenschaftlich-Technische Werkstätten GmbH*, Germany).

Suspended solids (SS)

Suspended solids were measured according to the standard weight method. The weight of flushed and dried (105 °C) cellulose nitrate filters (*Stedim Biotech GmbH*, Germany; pore size = 0.45 µm) was determined after conditioning at room temperature in the desiccator. A defined volume of the sample was then filtered onto the filter. After repeating the drying and conditioning protocol the filters were weight once again. Suspended solids were then calculated by weight difference.

Pre-filtration and storage

After the determination of raw water characteristics water samples were pre-filtered by 0.45 µm (cellulose nitrate) prior to further analysis and stored at 4 °C until measurement.

Dissolved organic carbon (DOC)

DOC was measured using a thermal catalytic oxidation followed by infrared (IR) detection of carbon dioxide. The device in use was a *Vario TOC CUBE* (*Elementar Analysensysteme GmbH*, Germany). The method purges inorganic carbon out of the previously acidified (80 µL of 3-molar HCl) sample. The remaining organic carbon is then combusted (catalyzed-oxidized) and can be referred to as DOC because the sample was pre-filtered by 0.45 µm. DOC of any sample was measured in triplicate.

Ultraviolet (UV) absorption

UV absorption at 254 and 436 nm of water samples (0.45 µm pre-filtered) was analyzed using a *UV-vis spectrometer Lambda 12 (Perkin-Elmer*, USA), using quartz *Spurasil* 10 mm cuvettes (Type No. 100-QS, *Hellma GmbH & Co. KG*, Germany). All measurements were done in triplicate.

2.3.2 LC-OCD

Water sample constituent fractionation and analysis were conducted using a liquid chromatography (LC) with a size exclusion chromatography column (SEC, *HW50S/HW55S/HW65S*, *Alltech-GROM GmbH*, Germany), followed by a detector for ultraviolet absorption at 254 nm (UV, *Smartline UV Detector 200*, *Knauer*, Germany), and a Grätzel thin-film reactor for dissolved organic carbon oxidation, with a subsequent infrared detector for carbon dioxide (*Ultramat 6*, *Siemens*, Germany). Parts of the sample are sent to a nitrogen oxidation reactor, followed by a UV detector for nitrate (*WellChrom K2001 Filter Photometer* with 220 nm filter, *Knauer*, Germany), without entering the Gräntzel reactor. In addition to the chromatographic separation, a part of the water sample is directly sent to the detector, bypassing the chromatography column to measure dissolved organic carbon

(DOC), UV and dissolved organic nitrogen (DON) of the full sample. Samples were 0.45 µm pre-filtered and diluted (in general 1:4) with ultra pure water to obtain DOC concentrations in the range of 2 – 5 mg/L.

SEC columns and biopolymer analyses

Three SEC columns (HW50S/HW55S/HW65S) with different separation character were used for DOC fractionation and biopolymer analyses. The HW50S column has a higher resolution for the smaller organic compounds like humic substances and acids. For biopolymer analyses in general the HW55S and HW65S columns were used, which have better resolutions for the high molecular substances like proteins and polysaccharides.

For comparison Figure 2.4 shows the effluent LC-OCD chromatograms for different SEC columns. The chromatograms display the different retention times for the biopolymers. Further the very good resolution for the biopolymers but comparable bad resolution for the smaller compounds of the HW65S column is clearly visible. For biopolymer quantification (integration of the first peak) the retention times listed in Table 2.4 were used for the appropriate column.

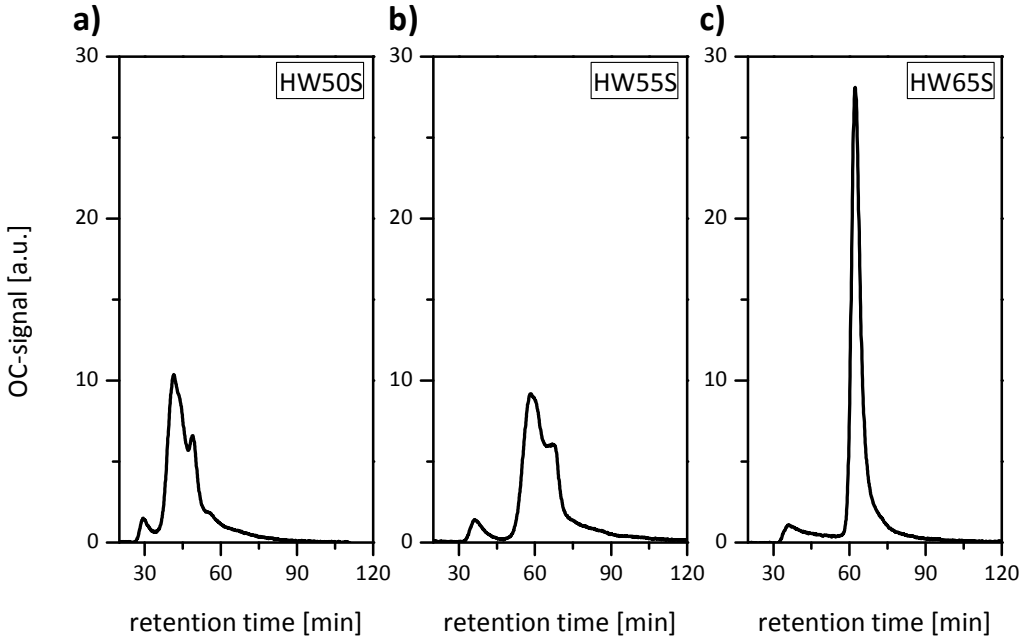


Figure 2.4: Comparison of WWTP effluent LC-OCD chromatograms measured with a) HW50S, b) HW55S and c) HW65S SEC column.

The different SEC columns were calibrated with dextran (dextran200, dextran70, dextran35) and polyethylene glycol (PEG40, PEG23, PEG12) standard solutions. The retention times of the different standard solutions were measured (see appendix) and the equivalent hydrodynamic diameter of the molecules (in nm) can be approximated by using empiric Equation 2.1. [Crittenden et al. 2005]

$$d_h = 0.11 \cdot M^{0.46}$$ **Equation 2.1**

where

d_h = hydrodynamic diameter of dextran molecule [nm]

M = molar mass [g · mol^{-1}]

The following Table 2.4 summarizes the retention times for biopolymers and respective molecule sizes for the used SEC columns.

Table 2.4: Retention time of biopolymers and selected organic molecule sizes for different SEC columns.

SEC column	Retention time for biopolymers [min]	Retention time for different molecule sizes [min]			
		30 nm	20 nm	15 nm	10 nm
HW50S	25 - 35	30.5	31.0	34.0	38.0
HW55S	30 - 50	40.0	42.5	45.0	51.0
HW65S	30 - 60	50.0	53.0	54.5	57.0

2.3.3 Particle analyses with Nanoparticle Tracking Analysis (NTA)

The method applied for submicron particle measurement is Nanoparticle Tracking Analysis (NTA) with the Nanosight NS500 (UK). It uses a laser light source to illuminate nano-scale particles. Particles appear individually as point-scatters, moving under Brownian motion. The motion is visualized via a microscope objective with 20-fold magnification mounted on a camera. 500 µl of sample of suitable concentration (10^7 – 10^{10} particles/mL) are introduced into the viewing unit by a peristaltic pump. After capturing a video of the sample, the average distance covered by each particle is automatically calculated by image analysis software and, knowing the temperature and viscosity of the sample, the hydrodynamic diameter is calculated by the program.

Pre-filtration (5 µm) of the sample is necessary to remove larger particles, otherwise they would disturb the measurement of submicron particles (below 1 µm).

2.3.4 Direct analysis of membranes with MALDI-TOF-MS

The analysis of membranes after filtration of model solution was done with matrix-assisted-laser-desorption-ionization time-of-flight mass-spectrometry (MALDI-TOF-MS) after preparation of the membranes direct on the MALDI-TOF-MS target plate.

Preparation method

The MALDI-TOF-MS preparation method used in this work is a modification of the dried droplet method introduced by Karas and Hillenkamp [1988] and the so-called redissolution sample preparation method developed by Leize et al. [1999]. Similar methods have been used by Chan et al. [2002] and Petrus et al. [2008].

3,5-Dimethoxy-4-hydroxycinnamic acid (*Fluka*, Switzerland), also referred to as sinapinic acid (SA), was used as matrix, oversaturated in a 1:2 mixture of acetonitrile (*Fisher*, USA) and 0.1 % trifluoroacetic acid (*Merck*, Germany). SA was stored in vials at -18 °C. On the day of the preparation, it was defrosted at room temperature and thoroughly vortexed.

Before MALDI-TOF-MS analysis, the membranes have to be stored for conditioning after filtration in a desiccator for at least 12 h. SA was then pipetted on the membrane in 2 µL spots; six spots were placed in a row. After crystallization at room temperature the membrane was cut with a scalpel and fixed with adhesive tape on the MALDI-TOF-MS target plate. Figure 2.5 shows the preparation of the membrane on the MALDI-TOF-MS target plate.

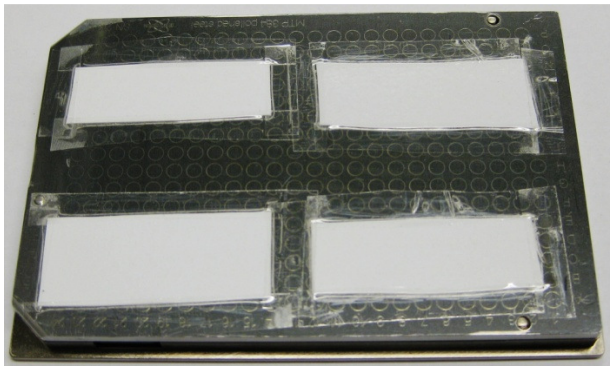


Figure 2.5: Membrane preparation on MALDI-TOF-MS target plate.

MALDI-TOF-MS

After preparation of the membranes on the target plate they were analyzed with a MALDI-TOF-MS. The MALDI-TOF-MS used was an autoflex III smartbeam (*Bruker Daltonics*, USA) equipped with an additional HM2 high mass detector (*CovalX AG*, Switzerland). The device operates with a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser emitting a wavelength of 355 nm for desorption-ionization process [Holle et al. 2006]. Detection was

done in positive-ion and linear TOF mode. Laser power of 55 % was selected for all experiments. Analysis of the membrane and acquisition of the mass spectra were carried out using flexControl software version 3.0 (*Bruker Daltonics*, USA).

Via a built-in camera, the crystallized spots on the membrane could be observed. The laser was operated manually to identify sweet spots with ideal crystallization and the sample was shot at 1000 times with a frequency of 100 Hz. This was done several times on all spots, and in each case the spectra with the highest intensities were selected for further evaluation.

2.4 Methods

2.4.1 Calculations for fouling analyses

Flux

Flux through the membrane is dependent on TMP, viscosity of solvent (water in the case of water treatment) and resistance of filtration. It can be derived from the Darcy-Law, written in the form of Equation 2.2. [Haberkamp 2008; Zheng 2010]

$$J = \frac{\Delta p}{\eta \cdot R} \qquad \textbf{Equation 2.2}$$

where

J = flux [$m^3 \cdot m^{-2} \cdot s^{-1}$] or [$m \cdot s^{-1}$]

Δp = TMP [$N \cdot m^{-2}$] or [Pa]

η = dynamic viscosity of solvent [$N \cdot s \cdot m^{-2}$]

R = resistance of filtration [m^{-1}]

Permeability of a membrane is flux per pressure. The dynamic viscosity of water at a given temperature can be calculated with the empirical Equation 2.3. [Roorda 2004; Haberkamp 2008; Zheng 2010]

$$\eta = \frac{0.497}{(T + 42.5)^{1.5}} \qquad \textbf{Equation 2.3}$$

where

η = dynamic viscosity of solvent [$N \cdot s \cdot m^{-2}$]

T = given temperature of water [°C]

The flux was measured with an electronic scale (Amicon® and Siemens®) or with a flowmeter (Inge®). Viscosity of water affects flux and itself is affected by temperature. Therefore the empirical formula in Equation 2.4 was applied to correct flux to 20 °C. [Crittenden et al. 2005]

$$J_S = J_M (1.03)^{T_S - T_M}$$ **Equation 2.4**

where

J_S = standardized Flux [$m \cdot s^{-1}$]
J_M = measured Flux [$m \cdot s^{-1}$]
T_S = standard Temperature [°C], 20 °C in the current case
T_M = measured Temperature [°C]

Resistance

Resistance is defined as the counteracting of the membrane and the fouling against feed water flux. Total resistance includes membrane resistance, reversible fouling resistance and irreversible fouling resistance and was calculated according to Darcy´s law (see Equation 2.2).

Total fouling resistance occurs at the end of a filtration cycle, when the initial membrane resistance (determined by filtration of pure water through the clean membrane) is subtracted. It encompasses reversible and irreversible fouling resistance; they are measured by determination of pure water flux after backwashing: Irreversible fouling resistance is the remainder of total fouling resistance after backwashing the membrane; accordingly it describes resistance of fouling that is irreversibly attached to the membrane.

Rejection

Rejection was calculated for biopolymers and represents the part of biopolymers that are removed from the feed water by the membrane during filtration. It is expressed as the difference between biopolymer concentrations of feed water and permeate, divided by feed water concentration, see Equation 2.5.

$$R = \frac{c_{feed} - c_{perm}}{c_{feed}} = 1 - \frac{c_{perm}}{c_{feed}}$$ **Equation 2.5**

where

R = rejection
c_{feed} = concentration of substance in feed [$mg \cdot L^{-1}$]
c_{perm} = concentration of substance in permeate [$mg \cdot L^{-1}$]

Specific resistance

Specific resistance is a measure for resistance per mass of foulant and area in the fouling layer on the membrane. Dry mass of foulants in the fouling layer can be calculated using a mass balance of feed water foulant inflow, permeate foulant outflow and retentate foulant concentration, according to Equation 2.6. In the present study, the mass of the biopolymer fraction and the suspended solids (SS) will be accounted for in the calculation of specific resistance.

$$m_l = m_f - m_p - m_r = c_f \cdot V_f - c_p \cdot V_p - c_r \cdot V_r \qquad \textbf{Equation 2.6}$$

where

m_i = dry mass of foulants in entity *i* [kg]

c_i = foulant concentration in entity *i* [kg · m^{-3}]

V_i = volume of entity *i* [m^3]

indices: l: layer (fouling layer), f: feed water, p: permeate, r: retentate

Fouling resistance of the gel/cake layer can be calculated using Equation 2.7:

$$R = \frac{\alpha \cdot m}{A} \qquad \textbf{Equation 2.7}$$

where

R = resistance of the fouling layer [m^{-1}]

α = specific fouling resistance at experiment pressure [m · kg^{-1}]

m = mass of dry foulants in the fouling layer [kg]

A = membrane filtration area [m^2]

Note that this parameter can be calculated if the mass of foulants of feed, permeate and retentate are known. Thus it depends on the measurement used for foulant determination. Specific resistance is thus barely comparable between studies that apply different methods for foulant detection which are not comparable.

Compressibility

Equation 2.7 can be solved for specific resistance α, since resistance of the fouling layer (R), dry mass of foulants in the fouling layer (m), and membrane filtration area (A) are determinable parameters. Specific fouling resistance is a measure of resistance of the fouling layer per unit of mass and unit of area.

At a given pressure it can be calculated according to Equation 2.8:

$$\alpha = \alpha_0 \cdot \Delta p^s$$ **Equation 2.8**

where

α = specific fouling resistance at given pressure [m · kg^{-1}]
α_0 = specific fouling resistance at reference pressure [m · kg^{-1}]
Δp = TMP [N · m^{-2}] (unit omitted when raised to the power of s)
s = compressibility, dimensionless

Influence of pressure difference is rising with compressibility *s*. As specific resistance is determinable at different operating pressures and pressure difference results from these, compressibility can be calculated using Equation 2.9:

$$s = \frac{\log_{10}\alpha_1 - \log_{10}\alpha_0}{\log_{10}\Delta p_1 - \log_{10}\Delta p_0}$$ **Equation 2.9**

where

s = compressibility, dimensionless
α_i = specific fouling resistance at TMP *i* [m · kg^{-1}]
Δp_i = TMP *i* [N · m^{-2}] (unit omitted when logarithmized)

Note that compressibility calculation relies on specific resistance. The latter is not comparable between studies that use different methods of foulant detection.

Fouling mechanisms

For constant pressure filtration in dead-end mode fouling mechanisms could be analyzed according to the filtration blocking laws postulated by [Hermia 1982]. He demonstrated that different fouling mechanisms can be assessed by Equation 2.10:

$$\frac{d^2t}{dV^2} = k \cdot \left(\frac{dt}{dV}\right)^{\varphi}$$ **Equation 2.10**

where

t = time [s]
V = volume [L]
k = filtration coefficient
φ = filtration exponent, dimensionless

The time and the associated volume increase were recorded by the flux analyzing software. The recorded time difference (dt) was divided by the corresponding volume increase (dV) for subsequent pairs. This results in the terms dt/dV, which were subtracted and divided by the appropriate volume increase dV. The terms dt/dV and d^2t/dV^2 were logarithmized to the basis 10 and could be plotted on abscissa and ordinate, respectively. The resulting slope of the curve is expressed by the filtration exponent ϕ representing the predominant fouling mechanism:

- ϕ = 2.0: complete pore blocking
- ϕ = 1.5: pore narrowing, pore constriction
- ϕ = 1.0: pore sealing with superposition (intermediate blocking)
- ϕ = 0.0: cake filtration

The change of the slope during ongoing filtration accounts for different mechanisms with changing time. Additionally, there always is an overlapping of different mechanisms.

2.4.2 Data evaluation

LC-OCD

LC-OCD measurement data were analyzed using the software *Fiffikus/ChromCalc* (*DOC-Labor Dr. Huber*, Germany) and the different DOC fractions were quantified by manually integration. Plotting of chromatograms was done after baseline subtraction and normalization with *OriginPro 8.5 software (OriginLab Corporation, USA)*.

MALDI-TOF spectra

The spectra were analyzed and background-substracted using *flexAnalysis software (Bruker Daltonics, USA)*. For further processing of the spectra, *OriginPro 8.5* was used. The mass spectra were smoothed by a Savitzky-Golay algorithm [Savitzky et al. 1964].

3 The role of organic substances in fouling of low pressure membranes

3.1 Biopolymers as major organic foulants

In previous studies the impact of organic substances in fouling processes of UF membranes was intensively investigated. Haberkamp [2008], Zheng [2010] and Tian et al. [2013] studied the strong role of biopolymers in the process of fouling. Especially Zheng [2010] showed a significant impact of biopolymers in secondary effluent on UF performance by illustrating high total fouling resistance of this fraction. In comparison, the proportion of larger colloids (> 0.45 µm) and particles (> 1.2 µm) as well as smaller compounds (smaller than the pore size of the membrane) on total fouling resistance is lower. Further he showed that lower biopolymer concentrations result in lower total fouling resistances. Thus, a removal of biopolymers can affect improved UF performance.

Biopolymer fouling

The conducted experiments within the OXERAM II project certify the results of Haberkamp [2008], Zheng [2010] and Tian et al. [2013]. Figure 3.1a) shows exemplary LC-OCD chromatograms of a secondary effluent from WWTP Ruhleben and the corresponding permeate after ultrafiltration.

Nearly no difference between the chromatograms concerning humic substances and lower molecular weight substances is visible whereas the biopolymer concentration in permeate is significantly lower as in secondary effluent (see circle in Figure 3.1a). This indicates very low permeation of biopolymers through the membrane but a high deposition on or in the membrane which can cause membrane fouling.

The effect of this deposition is shown in Figure 3.1b) which displays total fouling resistance in relation to biopolymer concentration of secondary effluent for all effluent filtration experiments carried out during project runtime. A correlation between these two parameters is clearly visible. The higher biopolymer concentration the higher is the total fouling resistance. Concentrations of biopolymers in secondary effluent of WWTP Berlin are in the range between 0.4 – 1.0 mgC/L (see Figure 3.1).

These results are similar to Zheng (2010). In comparison to his investigations there was no pre-filtration (0.45 µm) of feed samples before membrane filtration in the current research which leads to a lower coefficient of determination but respects synergetic effects of particular matter and dissolved organic matter.

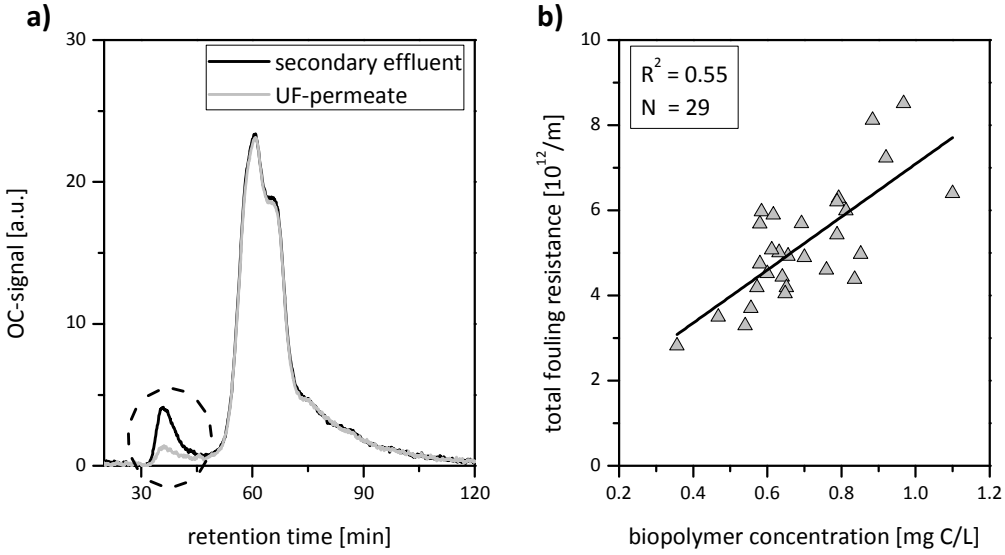


Figure 3.1: Exemplary LC-OCD chromatograms of secondary effluent and ultrafiltration permeate and correlation between total fouling resistance and biopolymer concentration; a) LC-OCD chromatograms (HW55S column, UP150 membrane filtration, circle = biopolymers), b) total fouling resistance over biopolymer concentration (effluent membrane filtration (UP150) during project runtime).

Due to this strong influence of biopolymers on low pressure membrane filtration performance investigations of TU Berlin focused on biopolymers as major organic foulants and their behavior towards different pretreatments and filtration conditions.

3.2 Influence of different pretreatments on biopolymers

3.2.1 Ozonation

Transformation of biopolymers

The effect of ozonation on dissolved organic substances was investigated in several previous studies. On the one hand, a decomposition of large organic molecules into smaller ones due to oxidation by ozone could be observed. One the other hand, this oxidation effect can also lead to transformation of hydrophobic organic molecules into more hydrophilic ones. [These et al. 2005; Song et al. 2010; Genz et al. 2011; Van Geluwe et al. 2011]

The present study focuses on effects of different pretreatments on biopolymers as major organic foulants. In Figure 3.2 LC-OCD chromatograms of secondary effluent as well as ozonated secondary effluents (dosages of 6 mgO_3/L and 12 mgO_3/L) are shown.

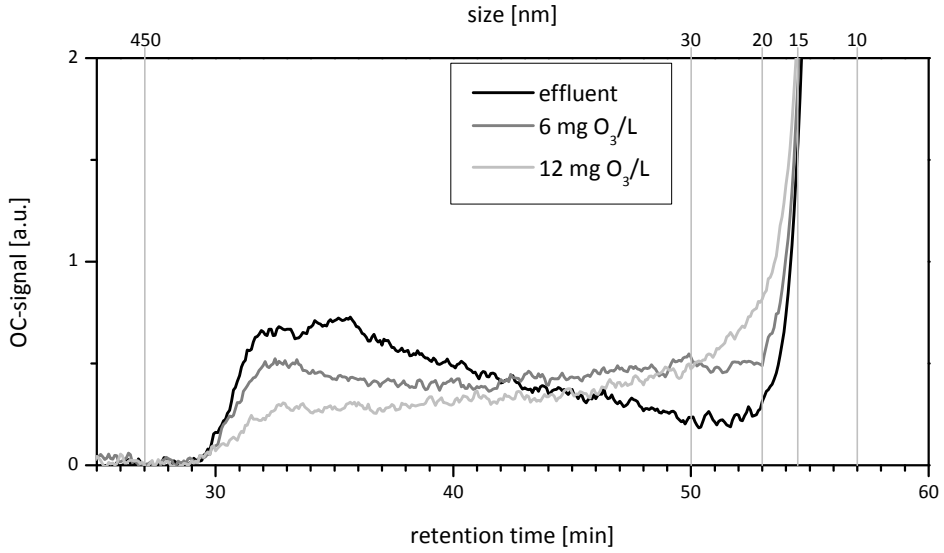


Figure 3.2: Transformation of biopolymers for different ozone dosages; (exemplary LC-OCD chromatograms, column HW65S, focus on biopolymers).

A detailed view on biopolymer peak shows that ozonation affects a transformation of this fraction resulting in a shift of molecular size. It can be seen that in comparison to untreated secondary effluent there is a decrease of biopolymers in the range of 450 nm to approximately 50 nm after ozonation. At the same time there is an increase of substances in the range of 50 nm to 15 nm due to ozonation. This leads to the presumption that biopolymers react with ozone and get partly decomposed into smaller molecules. This effect depends on ozone dosages. The higher the ozone dosage the higher is the transformation of large biopolymers into smaller compounds.

Transformation of particulate matter

Due to the observation of transformation of biopolymers it was investigated if there are further shifts in molecular size of secondary effluent compounds by ozonation and if there are also reactions with particulate matter.

For these investigations two ozonated samples of the same secondary effluent were analyzed. One was pre-filtrated (0.45 µm, particle free) before ozonation, the other one was not pre-filtrated (with particles). Figure 3.3a) shows the LC-OCD chromatograms of untreated secondary effluent, ozonated secondary effluent and pre-filtrated ozonated secondary effluent (HW50S columm).

In comparison to untreated secondary effluent a decrease of biopolymer concentration of pre-filtered ozonated secondary effluent and an increase of humic and low molecular substances in this chromatogram (below 10 nm) are visible. It indicates that without particles ozone induces a transformation of biopolymers into substances smaller than 10 nm. DOC analyses for both samples (pre-filtered secondary effluent DOC = 12.2 mg/L and DOC = 12.0 mg/L after additional ozonation) confirm that ozone induces only minor

mineralization of dissolved compounds but transformation into smaller substances < 10 nm as visible in the LC-OCD chromatograms (Figure 3.3).

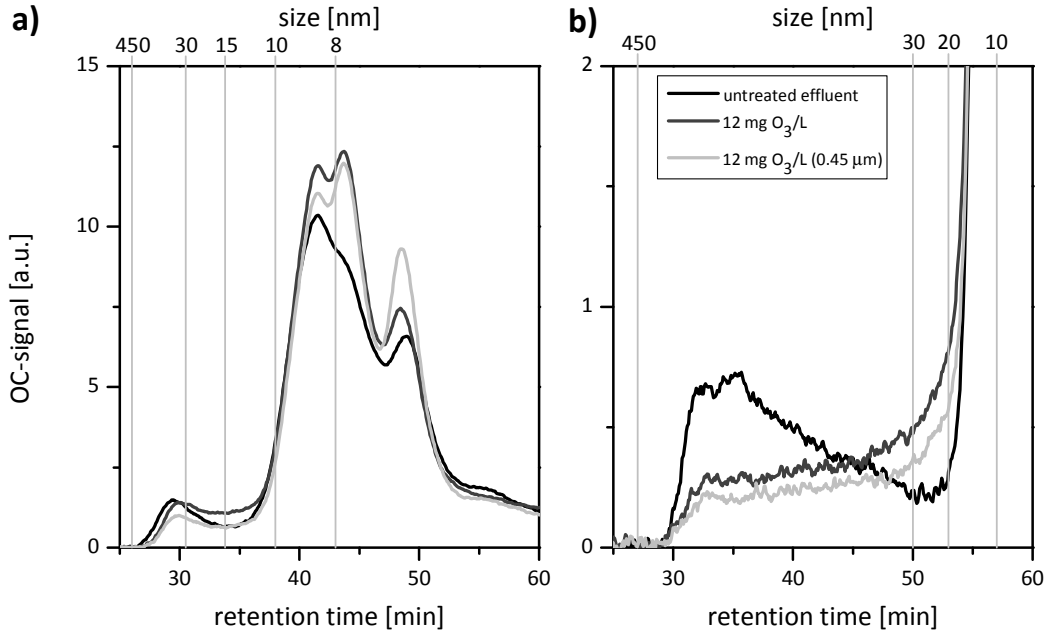


Figure 3.3: Transformation of the DOC by ozone with and without pre-filtration; a) HW50S column, b) HW65S column (focus on biopolymers) for untreated effluent and after a dosage of 12 mg O_3/L with and without filtration (0.45 µm) prior ozonation.

Comparing chromatograms of the pre-filtrated sample (light-grey line) and the sample without any pre-filtration prior ozonation (dark-grey line) with focus on biopolymers (see Figure 3.3b)) a similar trend but higher concentrations of compounds between 450 nm and 10 nm for the sample without pre-filtration prior ozonation are clearly visible. This leads to the presumption that biopolymers, especially in the range between 50 nm and 10 nm are formed by transformation of particulate matter due to interactions with ozone.

The transformation by particulate matter > 450 nm into dissolved compounds < 450 nm is supplementary confirmed by DOC analyses. The sample without pre-filtration has a higher DOC (DOC = 12.9 mg/L) after ozonation than untreated secondary effluent (DOC = 12.2 mg/L) which indicates a formation of dissolved organic substances out of particular matter by ozonation.

3.2.2 Biopolymer removal with coagulation

Coagulation experiments with secondary effluent were carried out using three different common coagulants ($FeCl_3$, $AlCl_3$, PACl) at comparable dosages and afterwards analyzed with LC-OCD to investigate the removal of biopolymers by coagulation. In Figure 3.4a) the

removal of biopolymers and b) for the low molecular substances (humics, acids, etc.) is shown for different dosages of the three investigated coagulants.

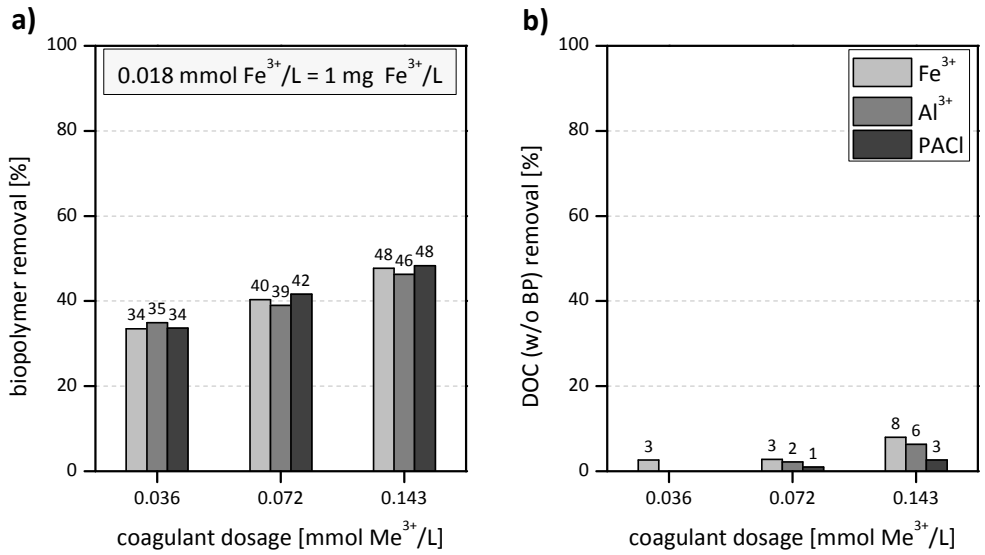


Figure 3.4: Removal of biopolymers and the DOC (without biopolymers) for different coagulants and coagulant dosages; a) removal of biopolymers, b) removal of DOC without biopolymers (other fractions like humics or organic acids).

Coagulation leads to a significant decrease of biopolymers. The rate of removal depends on coagulant dosage. The higher the dosage the higher is the removal, even comparable low coagulant dosages remove more than 30% of the biopolymers. Further there is nearly no difference between coagulation with ferric, aluminum and poly-aluminum. Thus, the removal of biopolymers is independent from the used coagulant.

The removal of smaller compounds (approximately compounds below 10 nm like humic, building block, acids, etc.) of the DOC by coagulation is shown in Figure 3.4b). The percentage removal is comparable low so that even high coagulant dosages achieve only a small percentage removal (below 10%) of these low molecular weight substances.

3.2.3 Ozonation with subsequent coagulation

There are several studies, which investigated the effect of pre-ozonation and subsequent coagulation on water quality. With focus on particle removal a multitude of these studies showed a synergetic effect of this combination which leads to a higher removal of particles respectively a lower necessary coagulant dosage due to pre-ozonation. [Jekel 1983; Jekel et al. 2007]

Ozonation and coagulation experiments at the TUB lab investigated the effect of this pretreatment on the main organic foulants by analyzing biopolymers with LC-OCD after treatment. Figure 3.5a) summarizes the biopolymer removal rates for the different

pretreatments for the experiments carried out during the project runtime. Ozonation indicates removal of the biopolymers but detailed LC-OCD analyses (see chapter 3.2.1) show rather a transformation of the macromolecules into smaller organic compounds than a removal of the biopolymers by ozonation. A clear removal of the biopolymers could be achieved by coagulation (around 40%). The combination of ozonation and coagulation leads to a lower biopolymer removal compared to coagulation without pre-ozonation.

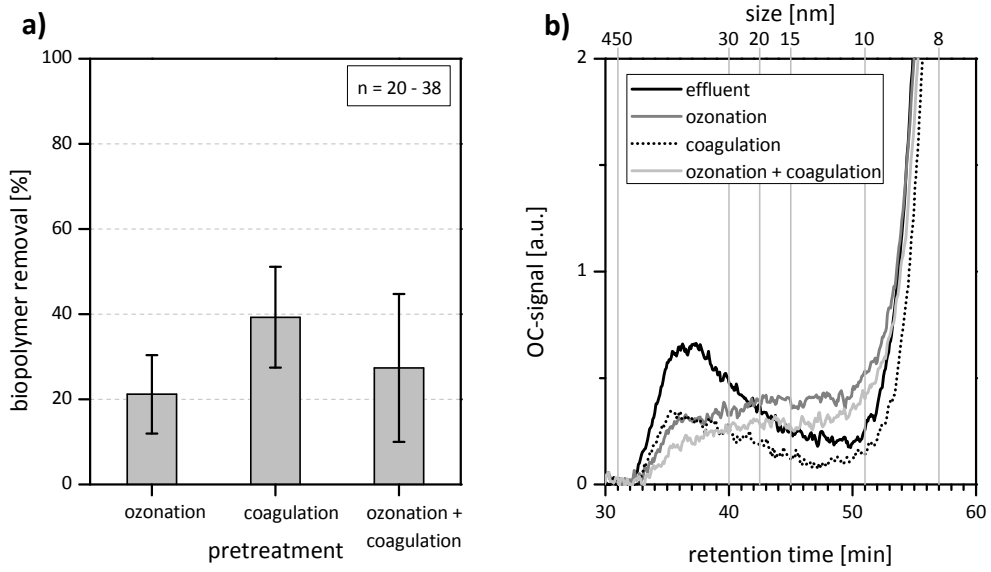


Figure 3.5: Removal and transformation of biopolymers by different pretreatments; a) removal (mean values with standard deviation for all pretreatment experiments carried out during project runtime) of biopolymers by ozonation (Z_{spez} = 0.4 - 1.6 mgO_3/DOC_0), by coagulation (0.036 - 0.216 mmol Me^{3+}/L), by combination of pre-ozonation and coagulation (Z_{spez} = 0.4 - 1.6 mgO_3/DOC_0 and 0.036 - 0.216 mmol Me^{3+}/L) and b) exemplary LC-OCD chromatograms (HW55S column, focus on biopolymers) for the pretreatments.

Figure 3.5b) displays a detailed view of biopolymer removal in LC-OCD chromatograms for the different pretreatments compared to the untreated secondary effluent (black line). Coagulation shows nearly a parallel shift of biopolymers to lower concentrations over the whole range with relatively high removal in the range between 450 and 30 nm. Exactly this part of the biopolymers and additional the particulate matter (see chapter 3.2.1) is decomposed into compounds smaller than 20 nm during the ozonation process (compare black and dark-grey line).

Coagulation after ozonation is not completely capable to remove the DOC fraction produced by ozonation (compare dark-grey and light-grey line between 50 and 10 nm in Figure 3.5b)). Consequently ozonation of secondary effluent produces a fraction of organic compounds between 50 and 10 nm which could be removed only to a certain amount by subsequent coagulation resulting in lower overall removal of biopolymers compared to coagulation as a single treatment step.

Summary

- Biopolymers are identified as major organic foulants with high impact on total fouling resistance.
- Ozonation leads to a transformation of biopolymers into compounds smaller than approx. 50 nm.
- Ozonation decomposes particular matter which leads to additional formation of compounds within the biopolymer fraction.
- Coagulation significantly reduces biopolymers independent of the used coagulation agent and shows only minor removal of compounds smaller than 10 nm.
- Even with low dosages of 0.036 mmol Me^{3+}/L over 30% of the biopolymers are removed by coagulation.
- Ozonation with subsequent coagulation has no synergetic effect on biopolymer removal.
- Compounds with a size between approx. 50 and 10 nm produced by ozonation could not significantly be removed by subsequent coagulation.

3.3 Amicon® filtration tests

The results in this chapter (chapter 3.3) were done all with the Amicon® filtration unit and UP 150 membranes (PES, MWCO = 150 kDa, pore size = 26 nm, comparable to the UF membranes at the pilot plant in Ruhleben) except for chapter 3.3.3 where further membranes with different character were tested.

3.3.1 Influence of the pretreatment on membrane filtration

Ozonation

Filtration experiments with ozonated secondary effluent were carried out for several times during the project runtime. In general, ozonation showed only minor improvement for the membrane filtration process and further the irreversible fouling resistance rises tremendously compared to the untreated effluent. A possible explanation is the formation of polar organic substances by ozonation (see chapter 3.2.1) which are in the range of membrane pore size and finally lead to enhanced irreversible fouling. As a consequence, ozonation as a single pretreatment step should not be considered for pretreatment of the ultrafiltration process.

Coagulation

Different coagulants ($FeCl_3$, $AlCl_3$, PACl) at comparable dosages (0.072 mmol Me^{3+}/L) were tested as pretreatment for ultrafiltration. The results for total and irreversible fouling resistance of the filtration process are summarized in Figure 3.6 for an exemplary experiment. Compared to the untreated effluent coagulation prior ultrafiltration reduces total fouling resistance independently of the used type of coagulant (see Figure 3.6a)). Ferric and aluminum chloride achieve comparable results while the use of poly-aluminum chloride leads to higher total fouling resistance. Polymeric structures of this coagulant could be a possible reason for a more dense cake layer on the membrane surface causing higher filtration resistance.

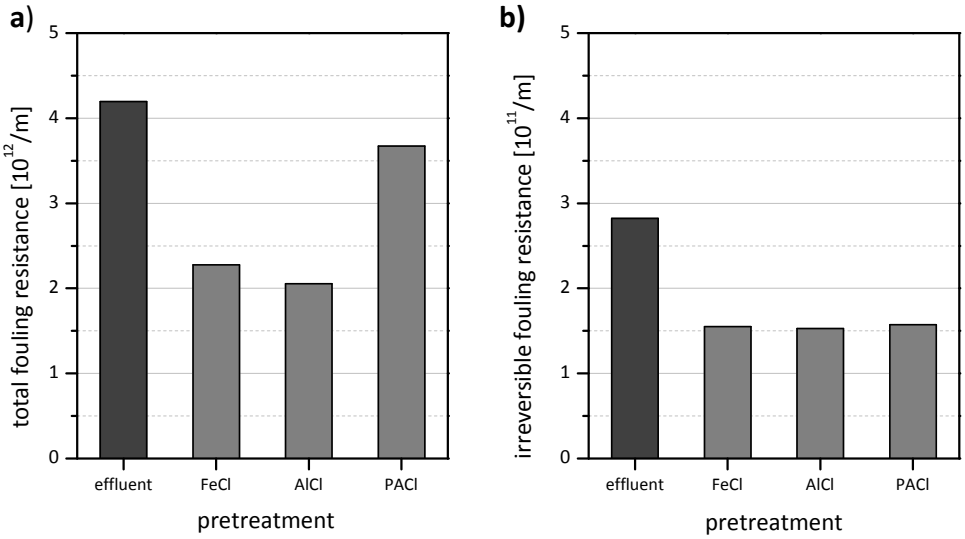


Figure 3.6: Influence of coagulation on total and irreversible fouling resistance; a) total fouling resistance, b) irreversible fouling resistance; pretreatment with 0.072 mmol Me^{3+}/L (FeCl = ferric chloride, AlCl = aluminum chloride, PACl = polyaluminum chloride); membrane filtration (UP150, V = 500 mL, TMP = 1.0 bar, 1st filtration cycle).

Concerning irreversible fouling resistance for all three tested coagulants the irreversible fouling resistance is nearly equal and much lower than for the untreated effluent (see Figure 3.6b)). Coagulation is capable to remove a certain amount of biopolymers (see chapter 3.2.2) and consequently leads to a reduction of total and irreversible fouling resistance.

Preozonation with subsequent coagulation

For comparison the effects of different pretreatments (coagulation and ozonation with subsequent coagulation) on fouling resistance (total and irreversible fouling resistance) during filtration tests are shown in Figure 3.7 for an exemplary single membrane filtration

experiment. Coagulation can reduce up to 50% of total fouling resistance compared to the untreated effluent (see also Figure 3.6a)). This effect is enhanced if ozone is applied to the secondary effluent before coagulation, especially for the very high ozone dosage of 15 mgO_3/L.

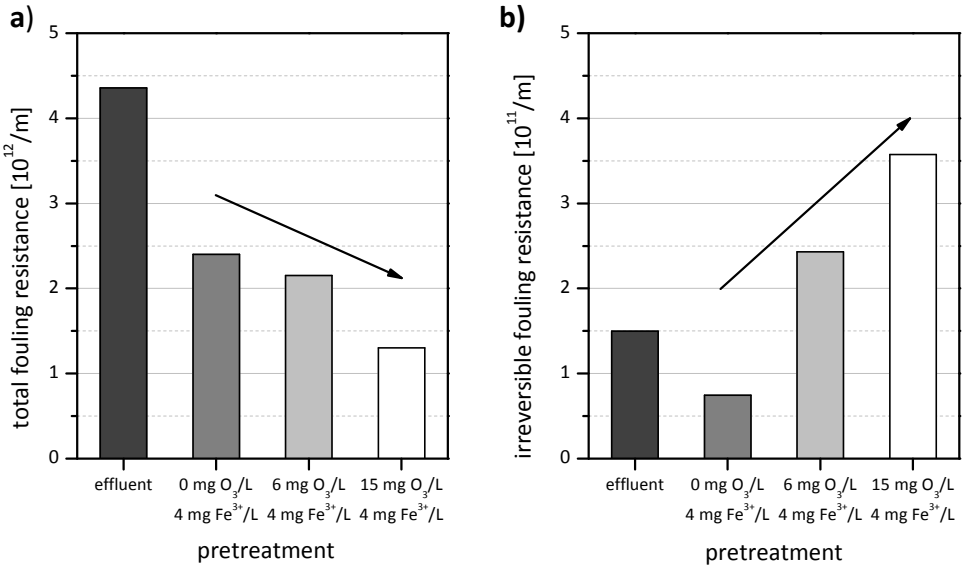


Figure 3.7: Influence of different pretreatments on total and irreversible fouling resistance; a) total fouling resistance, b) irreversible fouling resistance; membrane filtration (UP150, V = 500 mL, TMP = 1.0 bar, 1st filtration cycle).

In contrast to the total fouling resistance the irreversible fouling resistance rises with ozonation. Comparable results were also achieved by Genz et al. [2011] during the Oxeram I project.

Ozonation without coagulation produces the highest irreversible fouling resistance (data not shown) indicating a production of organic compounds by ozonation which interact specifically with the membrane or are in the range of the pore size of the membrane (see chapter 3.2.1). Coagulation can compensate this effect only to a certain extent (compare also Figure 3.5b)). Coagulation without pre-ozonation results in the lowest irreversible fouling resistance of all investigated samples (see Figure 3.7b)).

As mentioned above the data in Figure 3.7 are results from an exemplary single experiment. During the project runtime further filtration experiment were done with different dosages of coagulant and different dosages of ozone. The results of these experiments are shown as boxplots in Figure 3.8.

The trends of all filtration experiments (see Figure 3.8) are the same as for the exemplary single filtration experiment (see Figure 3.7). The lowest total fouling resistance could be achieved with ozonation and subsequent coagulation (see Figure 3.8a)). Unfortunately, this combination produces the highest irreversible fouling resistance, even higher than the irreversible fouling resistance of the untreated effluent (see Figure 3.8b)).

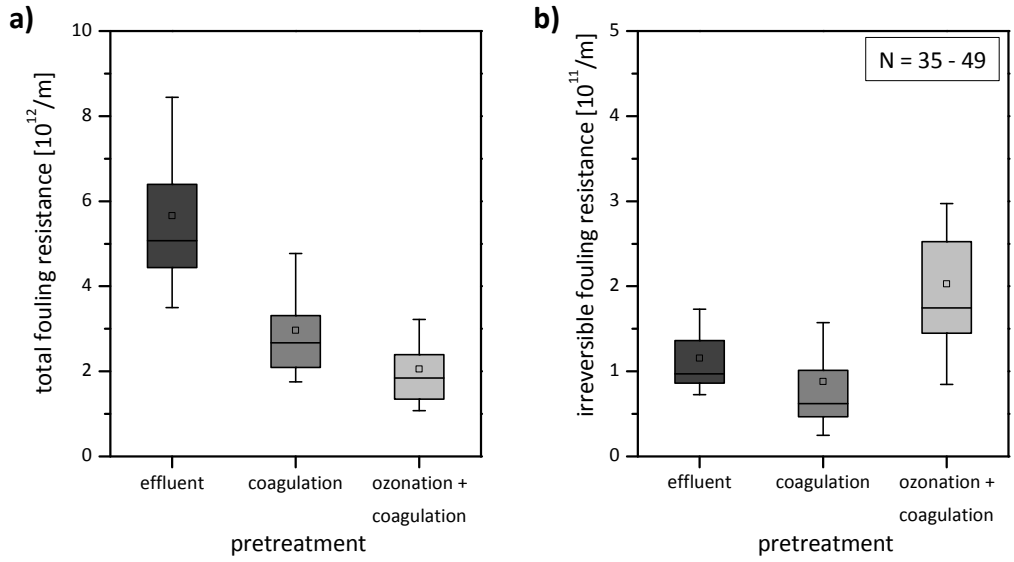


Figure 3.8: Boxplots of total and irreversible fouling resistance for different pretreatments; coagulation (0.072 - 0.216 mmol Me^{3+}/L), combination of pre-ozonation and coagulation (Z_{spez} = 0.2 - 1.6 mgO_3/DOC_0 and 0.072 - 0.216 mmol Me^{3+}/L); results for all membrane filtration experiments carried out during project runtime (UP150, V = 500 mL, TMP = 1.0 bar, 1st filtration cycle).

As a consequence the highest removal of biopolymers by coagulation (see Figure 3.5a)) results also in lowest irreversible fouling resistance while the transformation of the biopolymers by ozone leads to lowest total fouling resistance but highest irreversible fouling resistance.

A possible explanation for this phenomenon could be a better passage of biopolymers through the membrane after ozonation. Transformation of biopolymers into smaller compounds (see chapter 3.2.1 and 3.2.3) which are in the pore size range of the membrane (26 nm) can pass the membrane more easily and as a consequence decrease total fouling resistance. Contrary an improved passage means the compounds could enter the pores of the membrane which means they are also able to block the pores and finally are able to produce higher irreversible fouling resistance.

Rejection and biopolymer concentration in the permeate

Measuring the concentration of biopolymers in feed and permeate allows the calculation of biopolymer rejection by membrane filtration. Low rejection of biopolymers symbolizes a good passage of the biopolymers through the membrane and results in higher permeate concentrations of biopolymers. Figure 3.9 summarizes the biopolymer rejection by ultrafiltration and the permeate concentration of the biopolymers for all membrane filtration experiments (UP150 membrane; coagulation and ozonation + coagulation as pretreatments) during the project runtime.

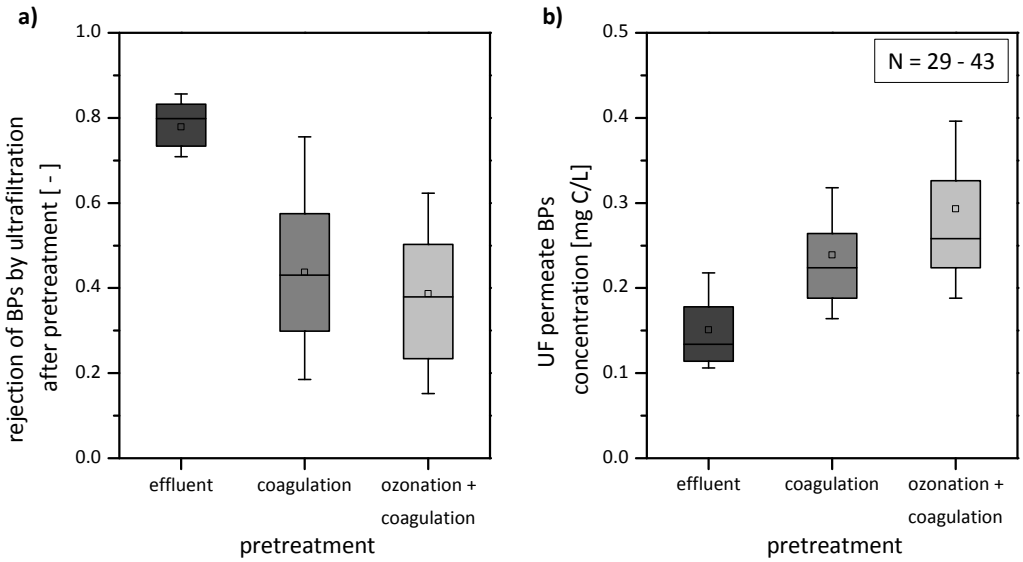


Figure 3.9: Rejection of biopolymers by ultrafiltration and permeate biopolymer concentration for different pretreatments; coagulation (0.072 - 0.216 mmol Me^{3+}/L), combination of pre-ozonation and coagulation (Z_{spez} = 0.4 - 1.6 mgO_3/DOC_0 and 0.072 - 0.216 mmol Me^{3+}/L); results for all membrane filtration experiments carried out during project runtime (UP150, V = 500 mL, TMP = 1.0 bar, 1st filtration cycle).

In general, permeate concentrations of the biopolymers are higher (implies lower percentage rejection) if additional ozone was applied before membrane filtration compared to coagulation without ozonation. These findings once again indicate an improved passage of organic foulants through the membrane resulting in the observed lower total fouling resistance (compare Figure 3.7 and Figure 3.8).

Higher passage of foulants necessarily means movement of substances through or into the membrane pores. During this process they could interact with the membrane surface and finally are not completely removable with hydraulic backwash procedures leading to increasing irreversible fouling resistance.

LC-OCD analyses of the backwash water

The backwash water of Amicon filtration tests was analyzed with LC-OCD to gather further information of the organic fouling causing substances. Backwash water generally comprises high amounts of (reversible) fouling substances compared to feed water. Figure 3.10 shows the chromatograms of the backwash water for membrane filtration experiments with different pretreatment.

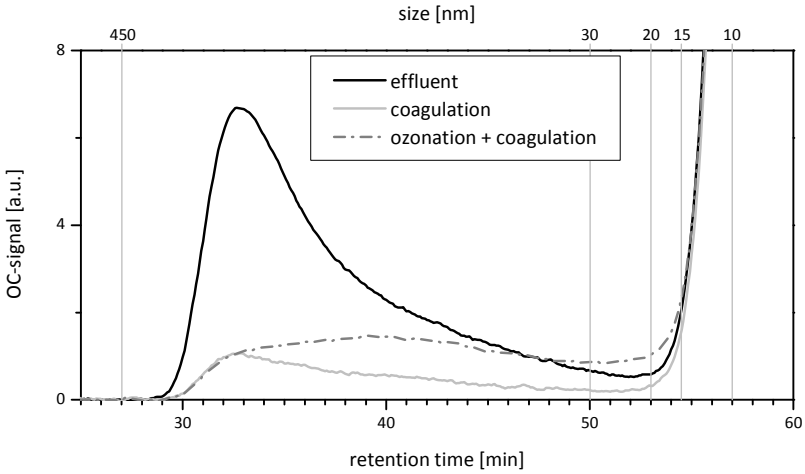


Figure 3.10: Backwash water analyzes for ultrafiltration after different pretreatments; untreated effluent, coagulation (4 mgFe^{3+}/L), ozonation + coagulation (12 mgO_3/L + 4 mgFe^{3+}/L); LC-OCD column HW65S, focus on biopolymers.

Backwash water analyses of the untreated secondary effluent shows a qualitative similar composition of water constituents in comparison to the feed water sample (compare Figure 3.5), but in contrast higher concentrations of biopolymers. There is especially a high concentration of substances in the range of ~50 to 450 nm. Having a bigger size than the membrane pores, it can be expected, that they form a dense cake layer on the membrane which causes a high total fouling resistance. A high concentration indicates that this cake layer is easily removable by backwash which results in low irreversible fouling resistance (see Figure 3.7).

The backwash water after filtration of coagulated secondary effluent shows very low concentration of biopolymers over the whole range of molecular sizes. In combination with the chromatogram of the feed sample (see Figure 3.5) it can be assumed that a high percentage of biopolymers are bound in the particulate flocks (bigger than 450 nm) during filtration and thus not able to attach to the membrane. Therefore only low concentrations of (dissolved) biopolymers are in feed as well as in backwash water resulting in lowest total fouling resistance and, especially, lowest irreversible fouling resistance.

As discussed above in chapter 3.3.1 pre-ozonation leads to a transformation of high molecular substances into compounds within the range of 10 to 50 nm, which are only marginal removable by coagulation. Especially a comparably high concentration of biopolymers in the range of the membrane MWCO around 15 to 30 nm could be analyzed. Concerning that ozonated samples produce highest irreversible fouling resistance it can be assumed that biopolymers in this range are partly removable by backwash, but certain amounts of these compounds still block pores after backwash and produce irreversible fouling.

The backwash water analyses for different treatments confirm the findings and assumptions previously discussed and show the high impact of transformed biopolymers by ozonation on fouling during ultrafiltration.

Summary

- Ozonation as a single pretreatment step is inappropriate for ultrafiltration.
- Coagulation is capable to reduce total fouling resistance up to 50% and shows lowest values for irreversible fouling resistance.
- Additional pre-ozonation leads to further reduction of total fouling resistance but causes higher irreversible fouling resistance.
- Higher ozone dosages increase the upper described effect.
- Rejection and permeate concentrations of biopolymers point to an increased passage of biopolymers for ozone treated secondary effluent.
- Analyses of the backwash water show a different composition for the observed pretreatments and confirm the high impact of transformed biopolymers by ozonation on irreversible fouling.

3.3.2 Treated effluent samples from the pilot

During the project runtime water samples at different sampling points were taken at the pilot plant and were further used for filtration experiments at the lab. Consequently, in this case the pretreatment was not conducted in the lab. In addition to the pretreatments (coagulation, ozonation and ozonation with subsequent coagulation) permeate samples from the pilot membrane filtration units were taken. The following figure (Figure 3.11) shows exemplary the results of the lab membrane filtration test for one sampling day in October 2011. In this case the pilot membrane filtration units were operated as follows: the pretreatment for the ultrafiltration (polymeric membrane, pore size = 20 nm) was coagulation (dosage of 4 mgFe^{3+}/L) and for microfiltration (ceramic membrane, pore size = 100 nm) ozonation (15 mgO_3/L) with subsequent coagulation (4 mgFe^{3+}/L).

Generally, the results confirm the findings generated with the pretreatment in the lab (compare chapter 3.3.1). The lowest total fouling resistance could be achieved by a pretreatment with ozonation and subsequent coagulation and the lowest irreversible fouling is produced with coagulation (except for the filtration of membrane permeates). Ozonation (as a single pretreatment step) reduces only a small amount of total fouling resistance but produces the highest irreversible fouling resistance.

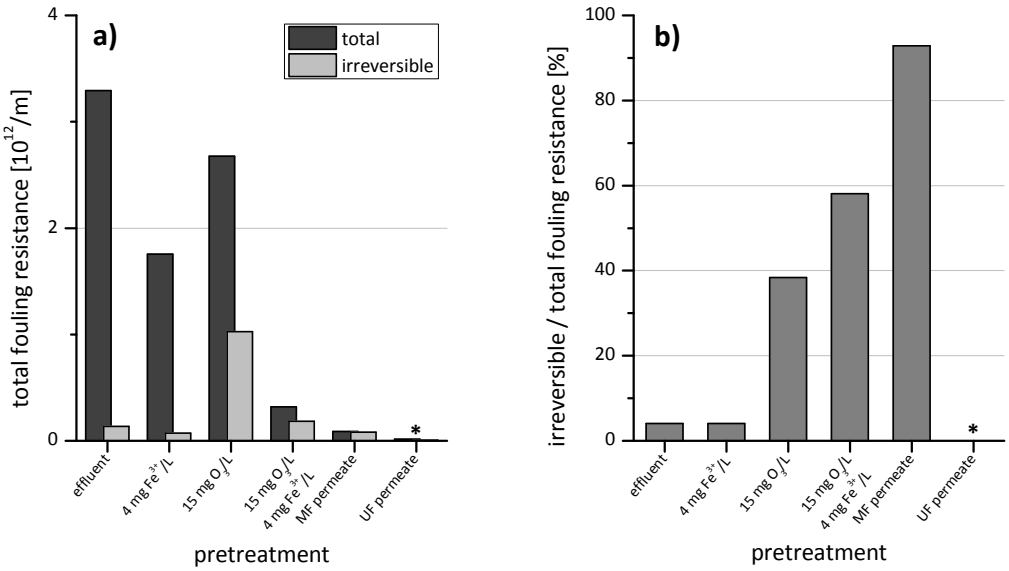


Figure 3.11: Fouling resistance for water samples from different sampling points of the pilot plant; a) total and irreversible fouling resistance, b) amount of irreversible on total fouling resistance; membrane filtration (UP150, V = 500 mL, TMP = 1.0 bar, 1st filtration cycle); MF permeate = ceramic membrane (pore size = 100 nm), UF permeate = PES membrane (pore size = 20 nm), * = reliable values were not possible because only negligible decrease of flux was analyzed after filtration of 500 ml.

Figure 3.11b) shows the amount of irreversible fouling on total fouling resistance for the different samples. For the three samples that were treated with ozone the amount of irreversible fouling in total fouling resistance is comparably high. For the microfiltration permeate nearly 100 percent of the produced fouling resistance during filtration process is not reversible by backwash procedures.

The filtration of the MF permeate confirm that during the ozonation process organic compounds were produced which can pass the microfiltration membrane but cause high irreversible fouling at subsequent ultrafiltration. This is further confirmed by LC-OCD analysis discussed in chapter 3.2.1 and 3.2.3 that show a production of compounds especially below 50 nm if ozone was applied to secondary effluent.

3.3.3 Further tests with different membranes

To get a more detailed understanding of the effects of different pretreatments on foulants and interactions between foulants and membrane, Amicon filtration experiments with different membranes were conducted. On the one hand, the used membranes differ in material and, thus, in their hydrophilic character. PES membranes are more hydrophilic than the ones made of PVDF (see pure water permeability Table 2.2). On the other hand, the investigated membranes have different pore sizes: 26 and 50 nm (calculated by MWCO), which are typical UF pores sizes, as well as 200 nm, which is more in the range of microfiltration.

Figure 3.12 shows total and irreversible fouling resistance of filtration tests with pretreated secondary effluent (coagulation and ozonation with subsequent coagulation) for the different membranes that were tested in Amicon filtration tests.

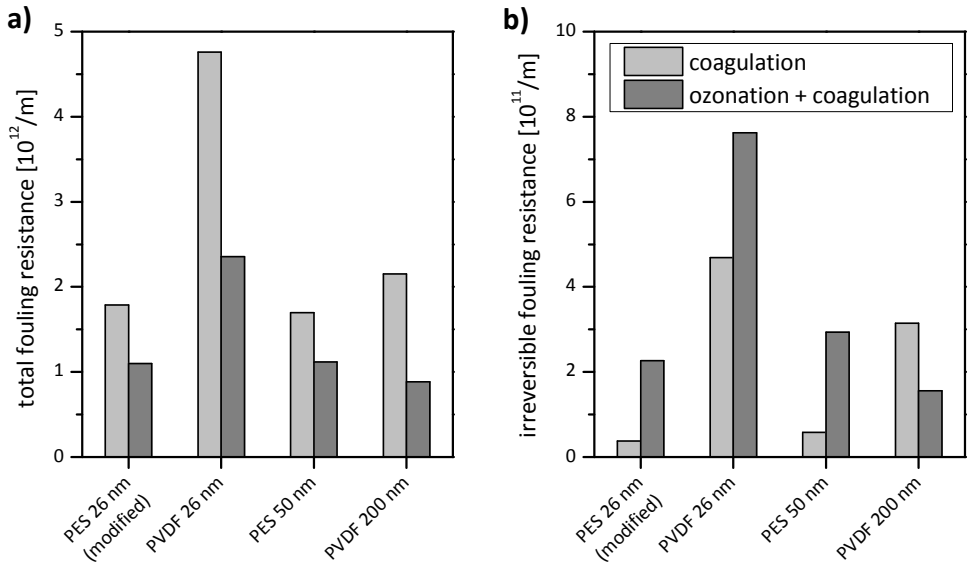


Figure 3.12: Fouling resistance for different membranes and coagulation and ozonation with subsequent coagulation as pretreatments; a) total fouling resistance, b) irreversible fouling resistance; pretreatment: coagulation (8 mg Fe^{3+}/L), ozonation + coagultation (15 mg O_3/L + 8 mg Fe^{3+}/L); membrane filtration (V = 300 mL, TMP = 0.5 bar, 1st filtration cycle).

Comparing fouling resistance of the two PES membranes having different pore sizes it can be seen that they are very similar for samples after coagulation as well as after ozonation with subsequent coagulation. Additional ozonation reduces total fouling resistance but produces higher irreversible fouling resistance. The small difference in pore size (26 vs. 50 nm) seems to have no meaningful effect on fouling behavior.

Comparing membranes with same pore size (26 nm) but different material (PES and PVDF), the same effect of pretreatment is visible. In both cases ozonation with subsequent coagulation leads to a lower total, but a higher irreversible fouling resistance in comparison to samples after sole coagulation. But in general, PVDF membrane excites higher total and irreversible fouling than PES. This leads to the presumption that foulants in (pretreated) secondary effluent have stronger interactions with PVDF than with PES and, thus, has a lower suitability for ultrafiltration of secondary effluent concerning fouling due to higher fouling effects.

Considering microfiltration membrane with a pore size of 200 nm, the tendency in total fouling resistance is similar as before. Ozonation with subsequent coagulation leads to best results. But in contrast to all other membranes with smaller pores sizes, ozonated sample also shows better results concerning irreversible fouling than sample after sole coagulation. This indicates that irreversible fouling is a matter, which strongly depends in membrane pore size. This can be illustrated with the effects of pretreatments on biopolymers. Ozone leads to

a shift of molecular sizes and a transformation of compounds bigger than 50 nm into compounds between 50 to 10 nm (compare Figure 3.2). In ultrafiltration these substances have a similar size as membrane pores so they are able to block them, partly irreversibly.

Due to the transformation of biopolymers during ozonation, concentration of substances bigger than 50 nm decreases (compare Figure 3.2). This may lead to lower irreversible fouling of ozonated samples in microfiltration because lower concentrations of substances which are able to block the pores are present after ozonation. Samples after sole coagulation have comparable higher concentration of compounds bigger than 50 nm (see Figure 3.5b)) leading to higher irreversible fouling due to possibly increased pore blocking.

Summary

- Pretreated samples from the pilot plant show comparable membrane filtration behavior like the pretreatment in the lab.
- Ozonated samples produce highest irreversible fouling.
- The amount of irreversible in total fouling resistance is nearly 90% for the filtration of microfiltration permeate.
- Ozonation products are able to pass the ceramic microfiltration membrane of the pilot plant and lead to enhanced irreversible fouling at further ultrafiltration.
- Tests with different membranes show comparable result for pretreated secondary effluent concerning total fouling resistance.
- In general, PES membranes are more suitable for the filtration of secondary effluent than PVDF membranes.
- For membranes with a pore size smaller than 200 nm the irreversible fouling is enhanced after ozonation.
- For the tested microfiltration membrane total and also irreversible fouling is reduced with additional ozonation.

3.3.4 Fouling mechanisms

The transformation of biopolymers by ozonation seems to be a possible reason for increased irreversible fouling of ultrafiltration membranes during filtration of secondary effluent. To gather further information of the fouling process, fouling mechanisms were investigated with the help of filtration laws described by Hermia [1982].

Fouling mechanisms for different pretreatments and ultrafiltration (UP150 membrane) were investigated using the filtration blocking laws [Hermia 1982]. With the help of this law filtration coefficients could be calculated to describe the fouling mechanisms for the

membrane filtration of the different water samples. In Figure 3.13 the filtration coefficient is plotted against filtration time for the different water samples and consequently the graph describes the development of the filtration mechanisms over filtration time. The initial phase of the filtration process is the point of interest because usually every filtration process ends up with cake filtration. Consequently only the first 10 minutes of the filtration are plotted in the graph.

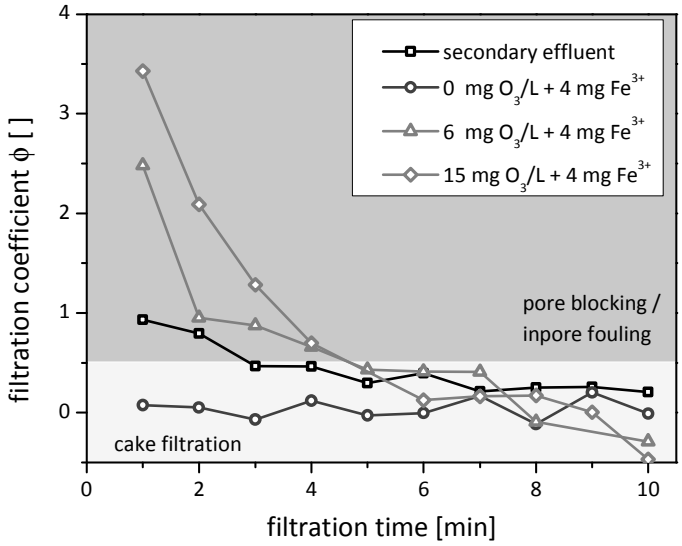


Figure 3.13: Filtration coefficient over filtration time for different pretreatments; membrane filtration (UP150, V = 500 mL, TMP = 1.0 bar, 1st filtration cycle).

Untreated secondary effluent initially tends to cause in-pore fouling changing to cake filtration during ongoing filtration. Effluent water constituents enter the membrane pores at the start of the filtration process and finally form a cake layer. Coagulation prior to membrane filtration immediately leads to the formation of a cake layer by the flocs and accordingly, the dominant filtration mechanism is cake filtration. For the combination of ozonation and coagulation the initial fouling mechanism is pore blocking, changing to in-pore fouling which remains the dominant fouling process for a comparatively long filtration time. For a higher ozone dosage (15 mgO_3/L) before coagulation the observed effect is enhanced.

The analyses of the fouling mechanisms confirm the assumption of the previous chapters concerning the influence of different pretreatments on membrane filtration. Additional ozonation before coagulation results in enhanced in pore fouling during membrane filtration (confirmed by the filtration laws) which causes an increase of irreversible fouling (see chapter 3.3.1).

3.3.5 Character of the fouling layer

Different filtration experiments were carried out to characterize the fouling layer and the influence of ozonation/coagulation on the character of fouling layer. The influence of the transmembrane pressure and parameters like specific fouling resistance and compressibility of the fouling layer was determined for the different pretreatments (no treatment, coagulation and ozonation with subsequent coagulation).

Influence of the TMP on the filtration process

To test the influence of the TMP on the filtration process two membrane filtration experiments were done parallel with same water samples but with different filtration pressure. One with a TMP of 1 bar and the other one with a TMP of 0.5 bar. Backwash was done with a TMP of 1 bar in both experiments. After filtration the total and the irreversible fouling resistance was analyzed. Figure 3.14 shows the results of this filtration experiment.

In general the previous observed trends for the different pretreatments could be observed for both TMPs. The combination of ozonation and coagulation achieves lowest total fouling resistance but highest irreversible fouling resistance independent of the TMP. The comparison of the results for the different TMPs shows especially for coagulation and the combination of ozonation and coagulation slightly lower total fouling resistances at a TMP of 0.5 bar. A possible explanation is the compressibility of the fouling layer. If the cake layer is compressible then higher pressure forms a denser fouling layer which is less porous resulting in higher filtration resistance.

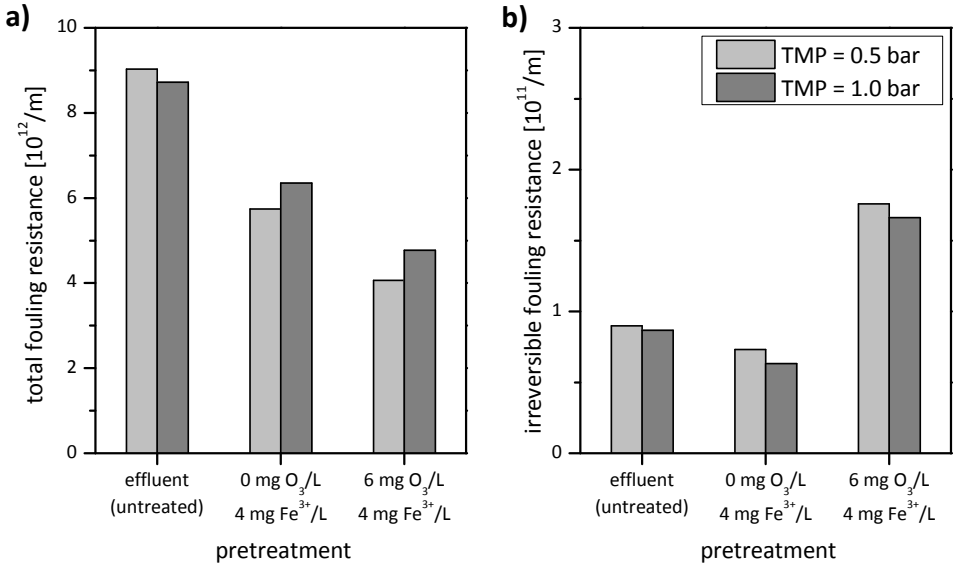


Figure 3.14: Fouling resistance for different pretreatment and different TMPs; a) total and b) irreversible fouling resistance; membrane filtration (UP150, V = 500 mL, TMP = 0.5 and 1.0 bar, 1st filtration cycle).

In contrast to total fouling resistance the irreversible fouling resistance is slightly lower for the filtration at a higher TMP. The faster formation of a cake layer at higher fluxes (higher

TMP results in higher fluxes and higher load of foulants per time onto the membrane) might reduce enhanced in pore fouling.

In conclusion the differences in the fouling behavior between filtration with a TMP of 0.5 bar and 1.0 bar are nearly negligible and consequently the filtration at 1.0 bar (reference TMP; filtration TMP for most of the filtration experiments carried out at TU Berlin) is a good compromise to generate results within a short time at the lab.

Specific fouling resistance

To gather additional information of the fouling layer specific fouling resistance was analyzed for different pretreatments during the project time. Specific fouling resistance gives information about the fouling resistance per mass of foulant and area in the fouling layer on the membrane. In this study foulants were measured by LC-OCD (dissolved organic foulants = biopolymers) and suspended solids (particulate matter, coagulation flocs).

Figure 3.15a) shows the mass of foulants on the membrane for the different pretreatments as boxplots (note: constant coagulant dosage). The mass of foulants on the membrane is higher after coagulation because besides the foulants of the untreated effluent (biopolymers + suspended solids/particulate matter) the flocs of the coagulation process are in the fouling layer as well. In comparison, with ozonation and subsequent coagulation a minor mass of foulants on the membrane could be observed. This is probably due to improved passage of biopolymers through the membrane after ozonation (compare chapter 3.3.1).

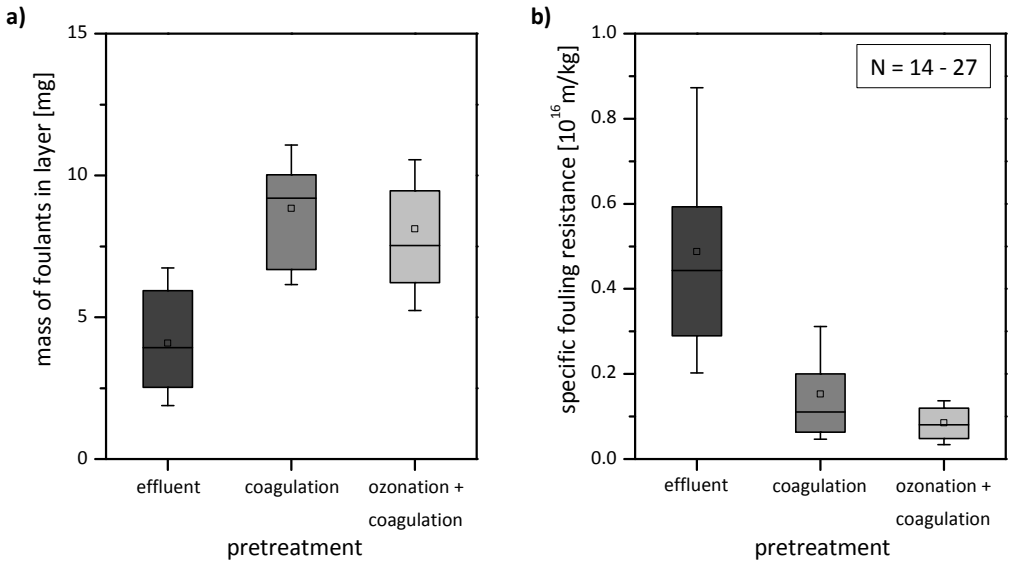


Figure 3.15: Fouling layer characteristics for different pretreatments; a) mass of foulants in the layer, b) specific fouling resistance; pretreatment: coagulation (0.072 mmol Me^{3+}/L), combination of pre-ozonation and coagulation (Z_{spez} = 0.3 – 0.6 mgO_3/DOC_0 and 0.072 mmol Me^{3+}/L); results for all membrane filtration experiments carried out during project runtime (UP150, V = 500 mL, TMP = 1.0 bar, 1st filtration cycle).

For the untreated effluent a comparable small amount of foulants produces a high filtration resistance resulting in a very high specific fouling resistance (see Figure 3.15). Pore blocking

and the formation of a dense fouling layer by effluents constituents are possible reasons for the high specific fouling resistance. If additionally coagulant is supplied to the effluent the character of the fouling layer changes. Even if the mass of foulants increases with coagulation the fouling resistance decreases resulting consequently in lower specific fouling resistance. In this case the fouling layer is porous and the pore blocking is reduced further due to the additional cake layer made out of coagulation flocks and removal of biopolymers which might enter/block the pores of the membrane (compare chapter 3.2.2 and 3.3.1.). Ozonation with coagulation yields in lowest specific fouling resistance. This indicates a very porous fouling layer.

Compressibility of the fouling layer

With specific fouling resistance determined at different operation pressures the compressibility of the fouling layer could be calculated. Figure 3.16 shows the specific fouling resistance at different filtration pressures (1.0 and 0.5 bar) and the compressibility for the observed pretreatments (no pretreatment, coagulation and ozonation + coagulation).

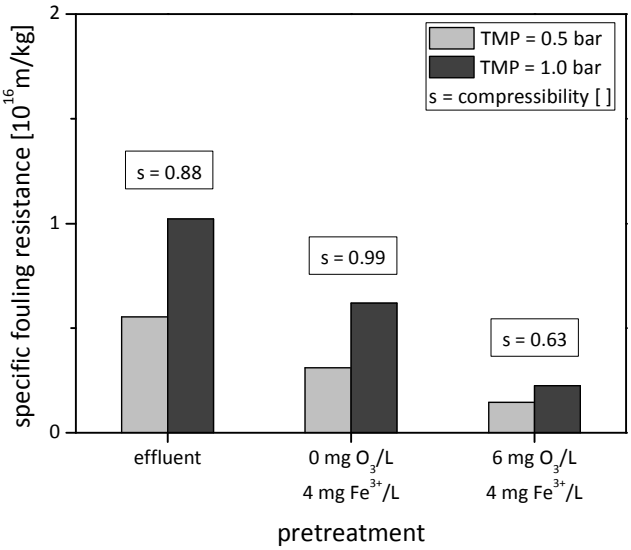


Figure 3.16: Compressibility of the fouling layer and specific fouling resistance for different pretreatments; s = compressibility; membrane filtration (UP150, V = 500 mL, TMP = 0.5 and 1.0 bar, 1st filtration cycle).

Lower values for the compressibility s point to a stable fouling layer while higher values indicate a soft fouling layer. The highest compressibility was determined for coagulation as pretreatment. The coagulation flocks seem to create a fluffier fouling layer which is highly compressible. The combination of ozonation and coagulation shows the lowest value for compressibility which indicates a comparable stable fouling layer. Showing the lowest total fouling resistance (compare chapter 3.3.1) and also the lowest compressibility, the pretreatment including ozonation and coagulation creates a stable but also very porous fouling layer.

Summary

- Cake filtration is the dominant filtration process for coagulation while additional pre-ozonation leads to increased pore blocking/in pore fouling.
- The filtration TMP has only minor effects on the fouling behavior of pretreated secondary effluent.
- Coagulation creates a very fluffy cake layer while ozonation + coagulation lead to a stable but also very porous fouling layer.

3.3.6 Comparison of different WWTP effluents

In previous parts of this report detailed effects of pretreatments on composition and filtration behavior of secondary effluent from WWTP Ruhleben were shown and discussed (compare chapter 3.2 and 3.3.1). For assessment of the transferability of these findings on other effluent water samples similar experiments were conducted with effluents from three additional WWTP in the Berlin area. These investigated WWTP were Schoenerlinde (SCH), Muenchehofe (MUE) and Wassmannsdorf (WAS).

In Figure 3.17 fouling relevant parameters like biopolymers and in this case also the particle concentration (for particles between 100 and 200 nm) of the four samples are shown. In Figure 3.17a) biopolymer concentration of untreated samples as well as after coagulation and coagulation with pre-ozonation are illustrated. Comparing biopolymers of the untreated secondary effluents Wassmannsdorf shows highest concentration whereas Schoenerlinde has the lowest. This order is also the same after every of the two pretreatment procedures. Thus, pretreatment has a similar effect on every of these secondary effluents. At the same time the observed effect of coagulation as well as coagulation with pre-ozonation is the same for every single effluent: coagulation results in a significant removal of biopolymers whereas additional pre-ozonation does not cause an additional removal compared to single coagulation (see also chapter 3.2).

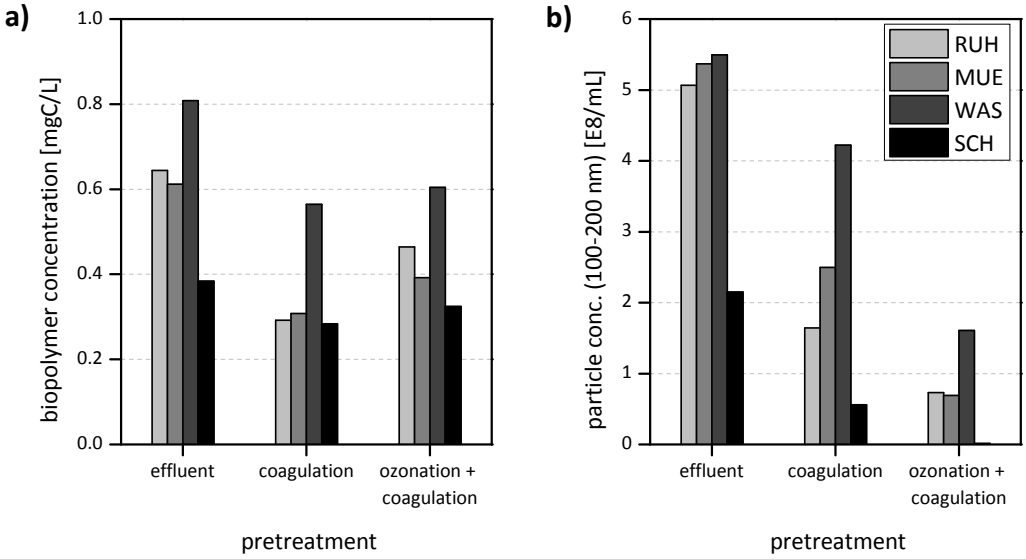


Figure 3.17: Biopolymer and particle concentrations of different WWTP effluents for different pretreatments; a) biopolymer concentration, b) particle concentration (fraction between 100 – 200 nm); pretreatment: coagulation (4 mg Fe^{3+}/L), ozonation + coagultation (6 mg O_3/L + 4 mg Fe^{3+}/L).

A similar trend for particles between 100 and 200 nm shown in Figure 3.17b) is visible. Also in this case Wassmannsdorf shows highest, Schoenerlinde lowest values. After coagulation there is a decrease of these particles for every sample. In contrast to biopolymers pre-ozonation leads to an additional removal of particles for all investigated effluents.

In Figure 3.18 filtration parameters of these samples are shown. Values in total fouling resistance (Figure 3.18a)) show a parallel trend to biopolymer concentration. Secondary effluent from Wassmannsdorf shows highest resistance, without pre-treatment as well as after pretreatment procedures. At the same time effluent from Schoenerlinde shows lowest resistances in all of the three cases. This indicates once again the role of biopolymers as major organic foulants. Besides this there is a very good correlation between particle concentration (100 – 200 nm) and total fouling resistance (compare Figure 3.17a) and Figure 3.18a)). This effect was previously shown by Schulz [2012] for the effluent of Berlin Ruhleben.

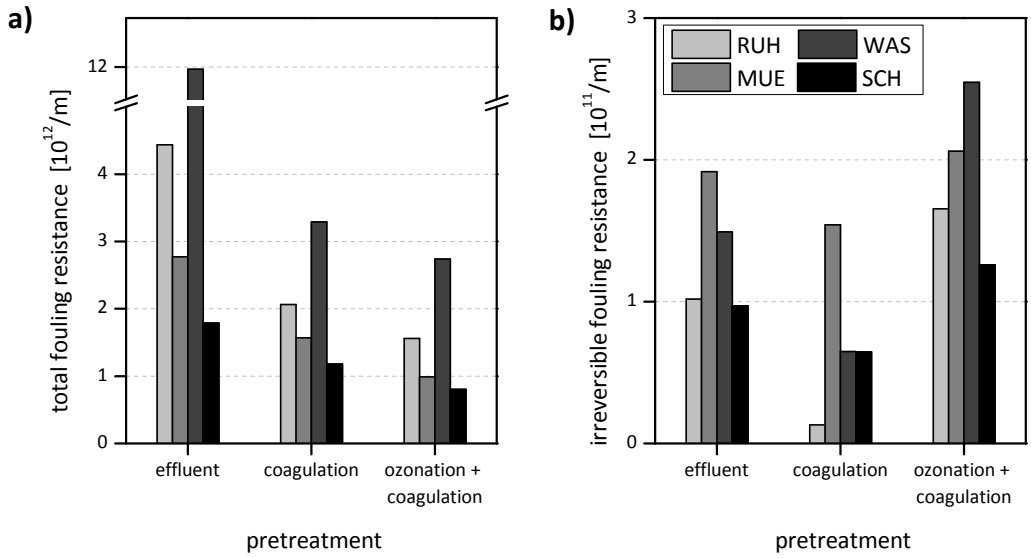


Figure 3.18: Fouling characteristics of different WWTP effluents for different pretreatments; a) total fouling resistance, b) irreversible fouling resistance; pretreatment: coagulation (4 mg Fe^{3+}/L), ozonation + coagultation (6 mg O_3/L + 4 mg Fe^{3+}/L); membrane filtration (UP150, V = 500 mL, TMP = 1.0 bar, 1st filtration cycle).

Pretreatment for all observed effluents results in a similar effect on membrane filtration that was already described in previous parts for the effluent of Berlin Ruhleben (compare chapter 3.3.1). Coagulation leads to a significant decrease of total fouling resistance. Additional pre-ozonation shows even lower values.

For irreversible fouling resistance (Figure 3.18b)) it can be seen that for all of the four effluent samples the irreversible fouling resistance increases after ozonation with subsequent coagulation resulting in highest overall values. Thus, the effect of ozone is the same that was already observed in previous experiments with secondary effluent from Ruhleben.

In summary, investigations with different secondary effluents show the same fouling behavior that was already observed with samples from WWTP Ruhleben. On the one hand, it is shown that biopolymer concentration significantly affects fouling behavior of a secondary effluent. On the other hand, in all cases ozonation results in low total, but significantly high irreversible fouling. The parallel trend of all samples indicates that the results with samples from WWTP Ruhleben, shown in this work, are also transferable to other WWTP in Berlin.

Summary

- Different secondary effluents from sewage treatment plants in Berlin show comparable fouling behavior for all observed pretreatments.
- Membrane filtration results generated with samples from WWTP Ruhleben are transferable to other WWTPs in Berlin.

3.4 Siemens® Memcor

A semi-automatic membrane unit for bench-scale filtration tests using outside-in polyvinylidene fluoride (PVDF) hollow-fibre membranes (max. pore size = 100 nm) was modified for dead-end filtration tests to gather additional information of fouling.

3.4.1 Setup

Filtration experiments with Siemens® Memcor lab filtration unit were conducted with three different feed samples: untreated secondary effluent, secondary effluent after coagulation, secondary effluent after ozonation and subsequent coagulation. Experiments were repeated four times at different days but with same dosages of ozone/coagulant. The experiments were carried out as semi-batch experiments (pretreatment at the pilot plants and membrane filtration in the lab).

3.4.2 Results

Figure 3.19 shows total and irreversible fouling resistance for the three different samples after every filtration circle. The illustrated values are mean values of the four repetitions of the experiment.

For total fouling resistance in Figure 3.19a) independently from pretreatment an increase from one circle to the next is clearly visible. Comparing the different pretreatments it is obvious that untreated secondary effluent induces the highest total fouling resistance whereas coagulation and, more largely, ozonation with subsequent coagulation affect a strong decrease of this parameter. This positive effect of pretreatment is similar to the one observed in lab filtration tests with Amicon filtration unit and a PES membrane with a pore size of 26 nm. (compare chapter 3.3.1).

In Figure 3.19b) mean values for irreversible fouling resistance are plotted for the different pretreated samples. The comparison of pretreatment procedures shows a parallel trend to total fouling resistance. Pretreatment by ozonation with subsequent coagulation induces best results due to lowest irreversible fouling resistance. Compared to results of Amicon filtration tests there is an opposite trend visible. In Amicon filtration tests ozonated samples show the highest irreversible fouling resistance and, thus, a completely different fouling behavior.

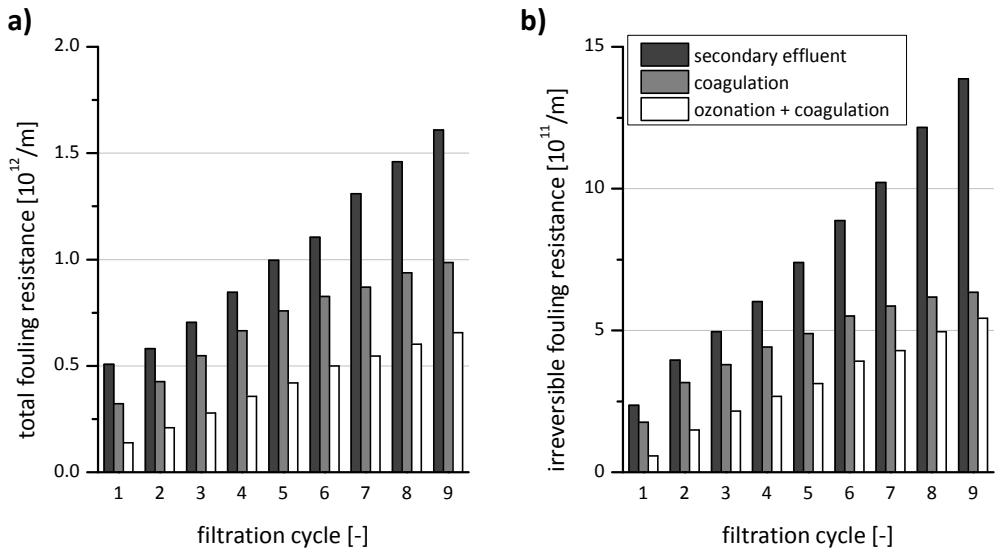


Figure 3.19: Fouling resistance of the semi-automatic lab filtration unit (SIEMENS®) for different pretreatments; 9 filtration cycles, TMP = 500 mbar, filtration volume = 1000 ml; a) total fouling resistance, b) irreversible fouling resistance; pretreatment: untreated effluent, coagulation (8 mg Fe^{3+}), ozonation + coagulation (9 mg O_3/L + 8 mg Fe^{3+}).

Reason for this different fouling behavior for ozonated samples could be explained by the differences of these two membrane units. The used membranes differ in pore sizes. While the UP 150 membranes in Amicon filtration tests have a calculated pore size of 26 nm the used membranes in the Siemens unit have a nominal pore size of 40 nm and a maximal pore size of 100 nm. As shown in chapter 3.2.1 and 3.2.3 ozonation leads to a decomposition of biopolymers into substances having sizes mainly between 30 and 10 nm. This could affect higher irreversible fouling in smaller pores of UP 150 membrane due to a more pronounced pore blocking of the formed compounds whereas for bigger pore sizes they rather pass pores without blocking them.

Another possible explanation could be the difference in membrane material. The material of UP 150 membranes used at the Amicon filtration unit is PES, which is comparatively hydrophilic. Membranes used in Siemens Memcor unit are made out of PVDF, which has a lower hydrophilicity than PES [Haberkamp 2008]. One effect of ozonation is polarization of water constitutions which results in the formation of more hydrophilic substances. This could lead to stronger interactions of these formed compounds with hydrophilic PES than with more hydrophobic PVDF, which could affect more irreversible fouling in Amicon filtration tests due to higher adsorption on surface or in pores of the membrane.

For further investigations permeate samples of Siemens Memcor filtration tests were used for proceeding filtration experiments with Amicon filtration unit.

3.4.3 Permeate filtration

For filtration of permeate of Siemens Memcor filtration experiments with Amicon filtration unit a UVT 150 flat sheet membrane was used. The membrane is also made out of PVDF, but has a MWCO of 150 kDa, which is according to a calculated pore size of 26 nm and, thus, smaller than the pore size of the membrane used in the Siemens Memcor filtration system.

In Figure 3.20 total and irreversible fouling resistance for permeate filtration tests are shown. In comparison to Figure 3.19 the trend in total fouling resistance is the same. Pretreated samples show lower values than untreated sample. Comparing irreversible fouling resistance both figures differ. Filtration of permeate after ozonation and subsequent coagulation with Amicon filtration unit show highest irreversible fouling resistance after it showed the lowest value for filtration with Siemens Memcor filtration unit. This indicates that permeate (respectively feed for Amicon filtration unit) after ozonation contains substances which lead to strong irreversible fouling at Amicon filtration unit whereas they did not do at Siemens Memcor filtration unit. This irreversible characteristic of ozonated samples was also observed with PES membranes of the same MWCO. This indicates that irreversible fouling of ozonated samples is not a question of membrane material. If it would be like this, experiments with ozonated samples at Amicon filtration unit should also show lowest irreversible fouling resistance like they did at Siemens Memcor filtration unit with the same membrane material.

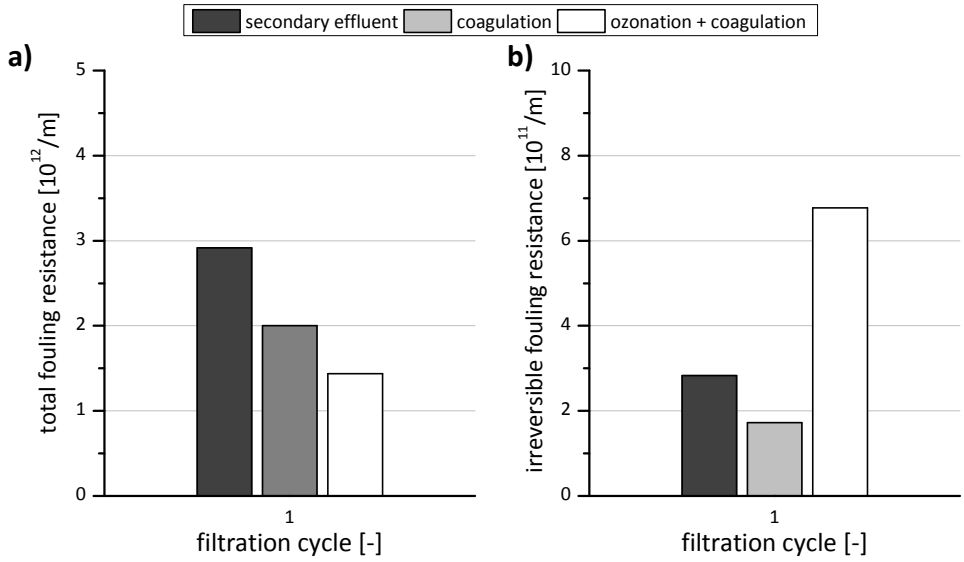


Figure 3.20: Total and irreversible fouling resistance for filtration of Siemens Memcor permeate samples; a) total fouling resistance, b) irreversible fouling resistance.

It shows on the other hand, that irreversible fouling by ozonation is probably a question of pore size due to pore blocking of formed substances. Like written before, ozonation of secondary effluent leads to a significant formation of compounds in the range of 10 to 30 nm in comparison to untreated respectively coagulated samples. Results indicate that

these formed substances are able to pass the bigger pores of Siemens Memcor filtration unit largely without blocking so that they end up in permeate. Filtration of permeate with UVT 150 membrane results in stronger irreversible fouling, which leads to the presumption, that these substances, which passed bigger pores, now block the smaller pores of this membrane.

Summary

- A semi-automatic membrane unit for bench-scale filtration tests including a PVDF membrane (max. pore size = 100 nm) was successfully modified for dead end filtration test.
- Filtration tests show the same trend like previously observed in Amicon filtration tests for the different pretreatments concerning total fouling resistance.
- Ozonation + coagulation results in lowest total and also irreversible fouling resistance.
- Additional permeate filtration test with a PVDF membrane (pore size = 26 nm) confirm a passage of products produced by ozonation through the membrane with bigger pore sizes (100 nm).
- Irreversible fouling by ozonation is probably a question of pore size.

3.5 Inge® “PUE10”

During the project a lab/pilot membrane filtration unit was successfully constructed, which is nearly completely comparable to the UF membrane pilot plants at WWTP Ruhleben according to operation, controlling software, membrane module, etc.. The major difference is the smaller membrane area of the used membrane modules resulting in lower flow rates at comparable fluxes.

3.5.1 Setup

After some test procedures after construction of the filtration unit two different membrane modules were tested during the experimental phase. Both membranes are made of hydrophilized PES material but have different maximal pore sizes (20 nm (UF) vs. 150 nm (MF)). For all trials (batch experiments) pretreated effluent (coagulation and ozonation + coagulation) from the pilot plant in Ruhleben was obtained (see chapter 2.1.3) on the day of the experiments. With a sample volume of 80 liters it was possible to perform 5 filtration cycles.

3.5.2 Results

Fouling resistance

The conducted experiments with pretreated secondary effluent showed a comparable trend concerning total fouling resistance for both membranes (UF and MF). Additional ozonation results in lower total fouling compared to coagulation as a single pretreatment (data not shown). For irreversible fouling no clear trend could be observed with the short term lab trails. Within 5 filtration cycles the effects for irreversible fouling of both membranes were only negligible. Long term experiments (filtration for 1 or 2 days) are necessary to achieve trustworthy results in the context of irreversible fouling.

LC-OCD

Nevertheless LC-OCD analyses of feed and permeate of the UF and MF membrane predict a different fouling behavior. The results of the LC-OCD analyses are plotted in Figure 3.21 for coagulation and ozonation with subsequent coagulation.

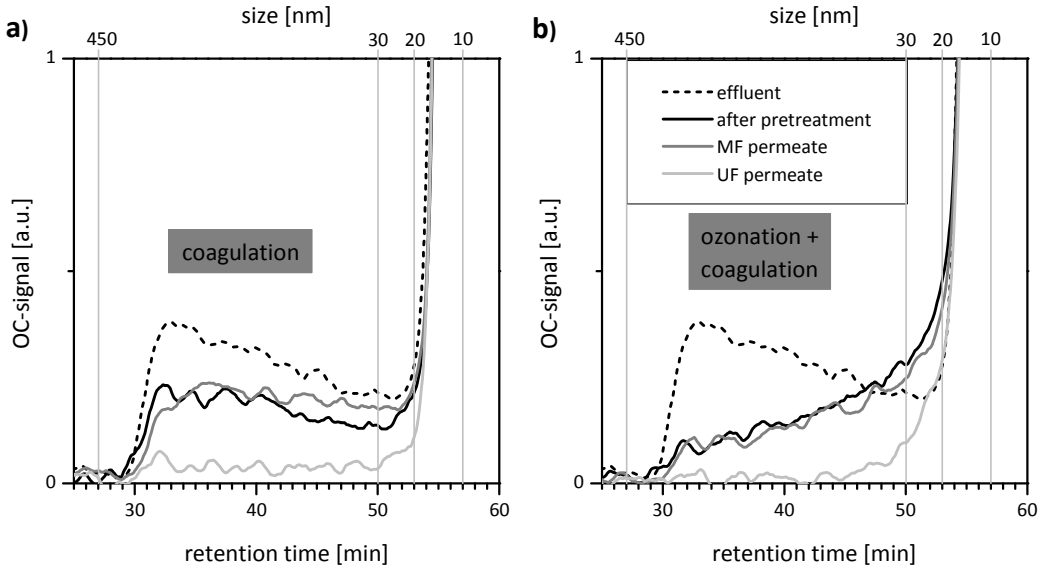


Figure 3.21: Exemplary LC-OCD chromatograms of MF and UF permeate samples for different pretreatments; LC-OCD: HW65S column, focus on biopolymers; a) pretreatment coagulation, b) pretreatment ozonation + coagulation.

In general, no difference of feed and permeate samples is visible for the microfiltration process independently of the pretreatment. This indicates a good passage of the foulants through the MF membrane. The membrane pore size seems to be big enough and only small interaction between ozonation products and the membrane could be expected. If this results in lower irreversible fouling has to be verified in long term experiments.

In contrast the UF membrane (calculated pore size = 20 nm) rejects nearly everything above 30 nm. In long term experiments enhanced irreversible fouling could be expected for the

combination of ozonation + coagulation pretreatment and ultrafiltration because a certain amount of ozonation products are in the pore size range of the membrane and could therefore block or enter the pores which consequently results in irreversible fouling like Amicon filtration tests showed previously.

In conclusion the experiments carried out within the project time point to the same trend observed in the upper experiments. For verification the experiments with Inge lab unit should be repeated in long term experiments.

Summary

- A small lab/pilot membrane filtration unit was successfully constructed which is comparable to the UF membrane pilot plants at WWTP Ruhleben.
- Total fouling resistance could be reduced with additional ozonation for both observed membrane modules having different pore sizes (20 nm and 150 nm).
- To generate reliable results for irreversible fouling of this filtration unit long term experiments are necessary.
- LC-OCD analyses indicate a lower interaction of ozonation products and the observed microfiltration membrane.

4 Fouling analyses with MALDI-TOF-MS

With the aim of a more detailed mass fingerprint MALDI-TOF mass spectrometry was used to analyze fouling affecting substances. In general, MALDI-TOF-MS is capable to analyze high molecular organic substance like proteins and polysaccharides. Therefore, two experimental methods were conducted: analysis of solutions as well as direct analysis of fouled membranes after filtration of solutions.

MALDI-TOF-MS analyses of secondary effluent did not show any evaluable signals, neither in solution nor on membrane after filtration (data not shown). Different cleaning and enrichment procedures of the fouling causing DOC fraction were tested without any success. In the end it can be surmised that due to a high diversity of the biopolymer fraction single substances are present in a concentration, which is below detection limit of MALDI-TOF-MS. Another reason is the high sensitivity of this method regarding matrix effects. It could be shown that humic and low molecular substances as well as macromolecular substances of secondary effluent have a strong negative effect on MALDI-TOF analyses (data not shown). Accordingly, also analyses of extracted biopolymers of secondary effluent did not show any evaluable signals.

Thus, MALDI-TOF-MS was primarily used for investigations of theoretical aspects of fouling by using model fouling substances (see chapter 2.1.4). Fouling behavior of single protein solutions under different conditions was investigated by direct analyses of membranes before and after backwash.

4.1 Setup

To compare the state of a membrane before and after backwash each experiment consisted of two parallel filtrations of the same model solution and resulted in two membranes, of which one was backwashed and the other one was not. Both of them were analyzed with MALDI-TOF-MS.

4.2 Results

Using this method, the influence of different solution parameters (e.g. pH, humics and Ca^{2+} concentration) on fouling of several proteins was investigated. In the following part the influence of humic substances on fouling of BSA is presented exemplary.

In Figure 4.1a) the spectrum of BSA on UF membrane (UP150) after filtration of a BSA salt solution before backwash is shown. Several peaks are visible. The highest peak at m/z of around 67k represents the single charged BSA molecule. With rising m/z oligomer peaks of BSA at m/z of 135k and 200k are present. This presence of oligomeres illustrates the aggregation of protein molecules on the membrane.

The mass spectrum after backwash (data not shown) shows the presence of the monomer peak but the absence of oligomer peaks. Consequently proteins can affect fouling in two ways. On the one hand they can produce mechanically reversible fouling by aggregation on the membrane. On the other hand they interact as monomers with the membrane which is mechanically irreversible.

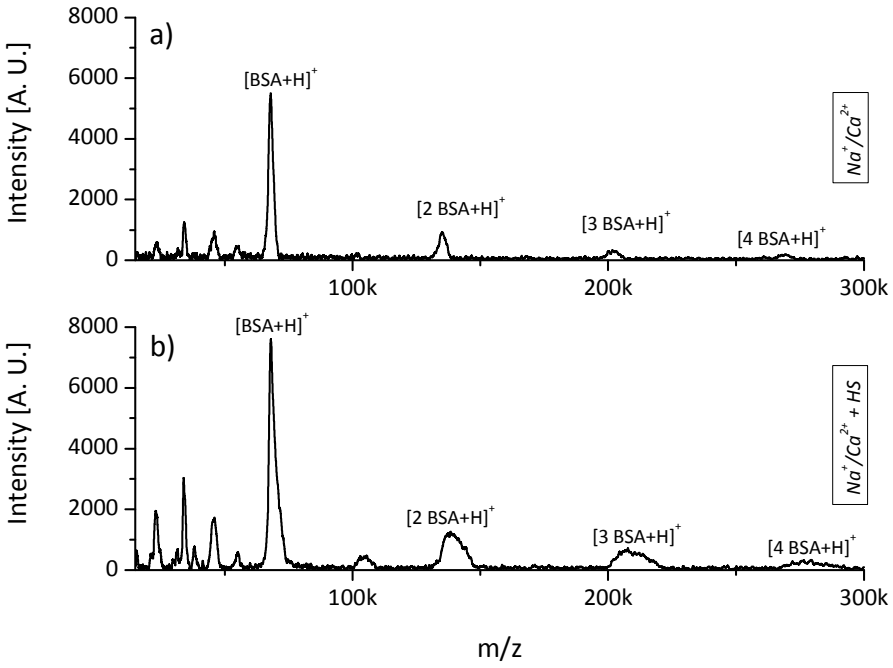


Figure 4.1: MALDI-TOF mass spectra of BSA on the membrane before backwash under the presence of humic substance and without humic substances; a) BSA in salt solution, b) BSA in salt solution with addional humic substances; filtration on UP150 membrane.

Figure 4.1b) shows the mass spectrum of a similar filtration test. In this case humic substances were added to the solution used in Figure 4.1a). This results in a similar mass spectrum. In comparison to figure a) especially the oligomer peaks are broadened to higher m/z. This leads to the assumption that there is an additional aggregation of humic

substances and proteins. This results in a lower filterability but also in a lower irreversible fouling resistance in comparison to filtration test without humic substances (data not shown). One possible explanation could be that humic substances support formation of a cake layer (lower filterability) and avoid interaction between membrane and proteins (lower irreversible fouling resistance).

Summary

- Due to matrix effects and high diversity of fouling substances direct MALDI-TOF-MS analyses of secondary effluent were not successful.
- With model solutions and direct analyzes of membranes MALDI-TOF-MS is able to show the state of foulants directly on the membrane even at comparatively low concentrations.
- Effects of different chemical conditions on fouling behavior of model substances can be shown.
- High potential in further investigations of theoretical aspects of fouling formation.

5 Oxidation by-products

A major drawback of applications with ozone is the formation of oxidation by-products. The most discussed by-products from ozonation are bromate and N-nitroso-dimethylamine (NDMA). One aim of the OXERAM II project was the development of reliable analytical procedures for bromate and NDMA to analyze the formation of these oxidation by-products and further to monitor the ozonation pilot unit in Berlin Ruhleben.

5.1 Bromate

5.1.1 Analytical setup

The oxidation by-product bromate was analyzed using the HPLC-MS/MS method described by Snyder et. al [2005]. All samples were measured after filtration with a 0.45 µm cellulose nitrate filter. No additional cleanup was applied before analysis for bromate. Analysis was conducted using a TSQ-Vantage LC-MS/MS from Thermo Fisher Scientific. As internal standard $Br^{18}O_3$ was used. Identification and quantification was accomplished using m/z of 110.9 and 112.9 (loss of one oxygen atom).

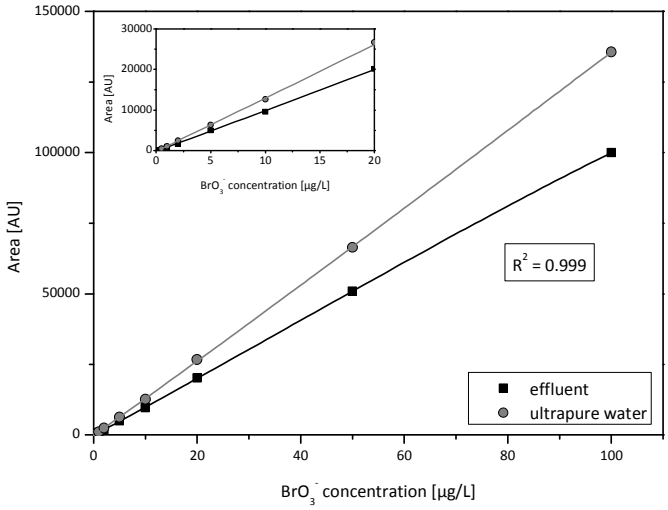


Figure 5.1: Calibration of bromate in effluent and ultra pure water.

Figure 5.1 shows very good calibration curves (R^2 = 0.99) of bromate in ultrapure water and in effluent. Even at very low concentrations (< 5 µg/L) the curves show a linear correlation

between concentration and area. Additionally, only minor signal suppression could be observed in the matrix of the effluent. In conclusion, a limit of quantification at a concentration of 0.5 µg/L bromate could be determined by direct analysis without any further pretreatment of the samples.

5.1.2 Bromate formation

To analyze the formation of bromate ozonation batch experiments were done with secondary effluent and increasing ozone dosages. The following Figure 5.2 shows the results of these experiments and additionally the data for the formation of bromate in surface water are plotted into the graph.

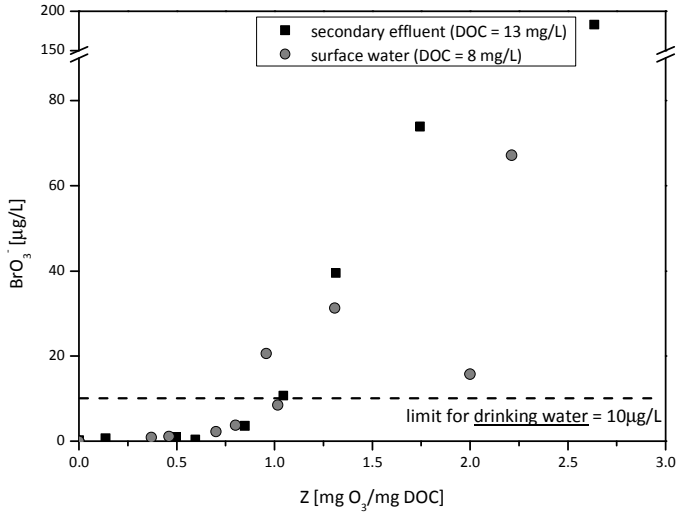


Figure 5.2: Formation of bromate in secondary effluent and surface water; (data for surface water were generated within the OXIRED II project [2011]).

According to Figure 5.2 in both waters the concentration of bromate increases with higher specific ozone consumption. In untreated samples (without ozone) bromate was not detectable and with rising specific ozone consumption higher bromate concentrations were analyzed (up to 180 µg/L for Z = 2.5 mgO3/mgDOC_0).

Bromate is declared as a potential human carcinogen [von Gunten 2003] and a limit value of 10 µg/L is set in the German drinking water directive. To avoid the formation of bromate in concentrations above the limit value of 10 µg/L water (secondary effluent and surface water) should be ozonated with specific ozone consumption below 0.9 – 1.0 mgO_3/mgDOC_0.

5.1.3 Monitoring

Besides batch ozonation experiments in the lab the ozonation pilot unit in Berlin Ruhleben was monitored for bromate during the operational time ones a week. Figure 5.3 summarizes the bromate formation for different applied ozone concentrations at the pilot plant and for the lab experiments during the experimental phase (March 2011 – December 2012).

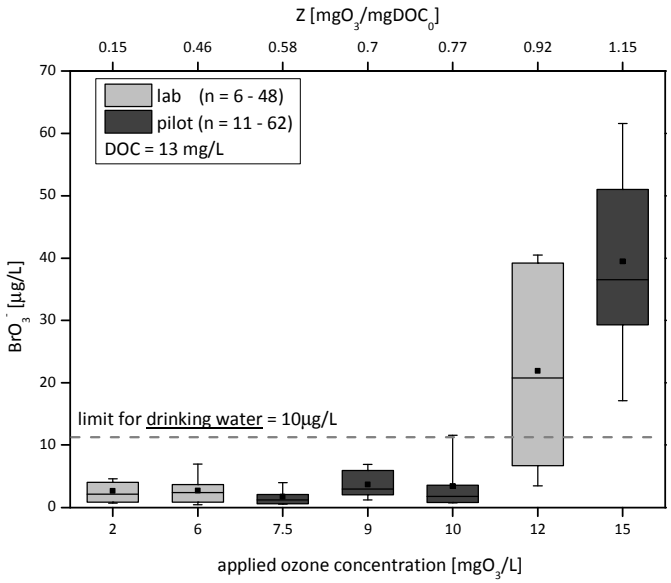


Figure 5.3: Bromate formation during the experimental phase in the lab and at the pilot plants for different ozone consumptions; experimental phase from March 2011 – December 2012; specific ozone consumption is calculated for DOC = 13 mg/L.

The boxplots of the bromate monitoring in Figure 5.3 show the same trend like in the single ozonation batch experiments (see chapter 5.1.2). Only for applied ozone concentration above 10 mgO_3/L (Z ~ 0.8 $mgO_3/mgDOC_0$) bromate concentrations > 10 µg/L could be observed.

However, the formation of bromate is influenced by many parameters, such as natural organic matter, bromide concentration, ammonium concentration or temperature [von Gunten 2003a; Legube et al. 2004]. This could be a possible explanation for the slight higher formation of bromate during the long experimental phase compared to the single batch experiment (see chapter 5.1.2, for Z = 0.9 – 1.0 $mgO_3/mgDOC_0$ bromate concentration > 10 µg/L).

5.2 N-Dimethylnitrosamine (NDMA)

Besides the development of a bromate analytical procedure the aim of the project was to establish an analytical method for N-Nitrosodimethylamine (NDMA) at TUB. After several months of testing and tuning it was impossible to measure NDMA at TUB. The analysis of (NDMA) is difficult and for reliable results, especially at very low concentrations, it has to be done with an orbitrap mass spectrometer [Krauss et al. 2008]. As a consequence the analysis of NDMA was carried out at Rheinisch-Westfaelisches Institut Fuer Wasser (IWW). The limit of quantification for this substance was 0.005 µg/L.

5.2.1 NDMA formation

Two sampling campaigns for NDMA formation were done at the ozonation pilot unit. Different specific ozone consumptions between 0 and 1.2 $mgO_3/mgDOC_0$ were investigated and the samples were sent to IWW immediately after sampling for further analyses of NDMA. Figure 5.4 shows the results of the two sampling campaigns.

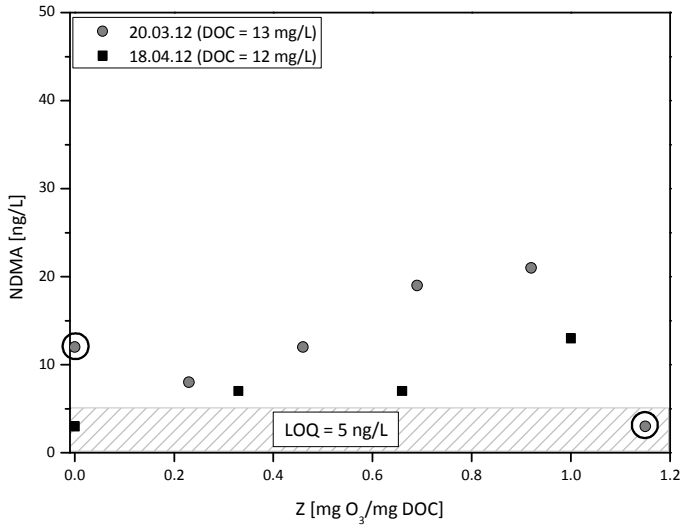


Figure 5.4: Formation of NDMA at the pilot plant.

The results show that only very small amounts of NDMA are formed during ozonation of secondary effluent. The NDMA concentrations are for all observed specific ozone consumptions below 20 ng/L and near the limit of quantification (LOQ) of the method.

Besides very low formation of NDMA during ozonation of secondary effluent photolysis and degradation in surface water as well as degradation in soil column experiments is reported in the literature [Drewes et al. 2006; Plumlee et al. 2007; Krauss et al. 2009]. Consequently the very low formation of NDMA by ozonation has only a minor influence on further water bodies.

Summary

- Successful development of an analytical procedure for bromate leading to a LOQ = 0.5 µg/L without any further pretreatment of the samples.
- Lab experiments and monitoring of the pilot plant shows a formation of bromate during ozonation of secondary effluent below 10 µg/L with specific ozone consumption of less than 0.9 $mgO_3/mgDOC_0$.
- Formation of NDMA during ozonation of secondary effluent was very low (< 20 ng/L) for all observed specific ozone consumptions.

6 Conclusions

6.1 Influence of ozonation and coagulation on biopolymers as major organic foulants

The important role of biopolymers in low pressure membrane fouling was investigated in different studies (Haberkamp [2008], Zheng [2010], Tian et al. [2013]) and could be confirmed within the OXERAM II project. In lab scale membrane filtration experiments a clear correlation between biopolymer concentration of the secondary effluent and total fouling resistance of the ultrafiltration process could be observed.

As a consequence the influence of ozonation and coagulation on biopolymers was analyzed. LC-OCD measurements pointed to a transformation of biopolymers into compounds smaller than approx. 50 nm by ozonation. Further the presence of particular matter results in additional formation of compounds within the biopolymer fraction. Coagulation experiments showed a significant reduction (up to 50%) of biopolymers independent of the used coagulation agent while only minor removal of compounds smaller than 10 nm could be achieved. Even with low dosages of 0.036 mmol Me^{3+}/L over 30% of the biopolymers were removed by coagulation. The combination of ozonation and subsequent coagulation showed no synergetic effect on biopolymer removal and LC-OCD analyzes indicated that compounds with a size between approx. 50 and 10 nm produced by ozonation could not significantly be removed by subsequent coagulation.

6.2 Influence of the different pretreatments on low pressure membrane filtration

The ultrafiltration membrane tests at the TUB lab (PES membrane, pore size = 26 nm) showed that ozonation as a single pretreatment step is inappropriate for ultrafiltration. With coagulation up to 50% of total fouling resistance could be reduced. Coagulation with additional pre-ozonation showed further reduction of total fouling resistance compared to coagulation without any pre-ozonation. With higher ozone dosages this effect could be increased furthermore.

Despite the good results that were achieved with the combination of ozonation prior coagulation for total fouling resistance the irreversible fouling resistance was enhanced and

even higher as for the untreated effluent. With coagulation the lowest irreversible fouling for ultrafiltration could be achieved.

Intensive investigations of the fouling mechanisms indicate cake filtration as the dominant filtration process for coagulation while additional pre-ozonation leads to increased pore blocking/in pore fouling. With compressibility test it could be shown that coagulation creates a very fluffy cake layer whereas ozonation + coagulation leads to a stable but also very porous fouling layer.

Experiments with different secondary effluents from sewage treatment plants in Berlin showed comparable fouling behavior for all observed pretreatments. Membrane filtration results generated with samples from WWTP Ruhleben seemed to be transferable to other WWTPs in Berlin.

Tests with different membranes showed comparable results for pretreated secondary effluent concerning total fouling resistance. Total fouling resistance was reduced with additional ozonation compared to coagulation without ozonation. In contrast to the observed UF membranes for the tested PVDF microfiltration membrane (pore size = 200 nm) irreversible fouling was reduced with additional ozonation.

A semi automatic membrane unit for bench-scale filtration tests including a PVDF membrane (max. pore size = 100 nm) was successfully modified for dead end filtration test and filtration tests showed the same trend like previously observed in Amicon filtration tests for the different pretreatments concerning total fouling resistance. In contrast, ozonation with coagulation resulted in lowest total but also in lowest irreversible fouling.

LC-OCD analyses showed that the transformation of organic matter by ozonation is mainly responsible for enhanced irreversible fouling of ultrafiltration membranes. In general, the pore size seems to be a crucial factor if ozonation is used for pretreatment of membrane filtration.

6.3 Fouling analyses with MALDI-TOF-MS

MALDI-TOF-MS is capable to analyze high molecular organic substances like proteins and polysaccharides and the idea within the OXERAM II project was to use it as a tool to have a more detailed mass fingerprint of the fouling affecting substances.

It can be concluded that MALDI-TOF-MS analyses of secondary effluent did not show any evaluable signals, neither in solution nor on membrane after filtration. Due to a high diversity of the biopolymer fraction the concentration of single substances is below the detection limit of the MALDI-TOF-MS. Another drawback is the high sensitivity of the analytic regarding matrix effects. Humic and low molecular substances as well as macromolecular substances of secondary effluent showed a strong negative effect on

MALDI-TOF analyses. Accordingly, also analyses of extracted biopolymers of secondary effluent did not show any evaluable signals.

Consequently, MALDI-TOF-MS was primarily used for investigations of theoretical aspects of fouling by using model fouling substances. With model solutions and direct analyzes of membranes MALDI-TOF-MS is able to show the state of foulants directly on the membrane even at comparable low concentrations and further effects of different chemical conditions on fouling behavior of model substances can be shown. In conclusion, MALDI-TOF-MS has a high potential in further investigations of theoretical aspects of fouling formation.

6.4 Formation of oxidation by-products

A major drawback of applications with ozone is the formation of oxidation by-products. A task of the OXERAM II project was the development of reliable analytical procedures for bromate and NDMA to analyze the formation of these oxidation by-products and further to monitor the ozonation pilot unit in Berlin Ruhleben.

On the one hand an analytical procedure for bromate was successful developed with LC-MS/MS at TUB. With the procedure it is possible to quantified samples without any further pretreatment. The limit of quantification for this procedure is 0.5 µg bromate per liter. On the other hand it was not possible to setup an analytical method for NDMA with the LC-MS/MS at TUB. For reliable results and quantification of very low concentrations, this has to be done with an orbitrap mass spectrometer. As a consequence the analysis of NDMA was carried out at Rheinisch-Westfaelisches Institut Fuer Wasser (IWW).

Lab experiments and further the monitoring of the pilot plant in Ruhleben during the project runtime showed a formation of bromate during ozonation of secondary effluent. Higher concentrations of bromate (above 10 µg/L; limit value in the drinking water directive) were produced only at specific ozone consumptions higher than 0.9 $mgO_3/mgDOC_0$. To avoid the formation of bromate in concentrations above the limit value secondary effluent and also surface water should be ozonated with specific ozone consumptions below 0.9 – 1.0 $mgO_3/mgDOC_0$.

Only very small amounts of NDMA are formed during ozonation of secondary effluent. The NDMA concentrations are for all observed specific ozone consumptions below 20 ng/L and near the limit of quantification (LOQ) of the method.

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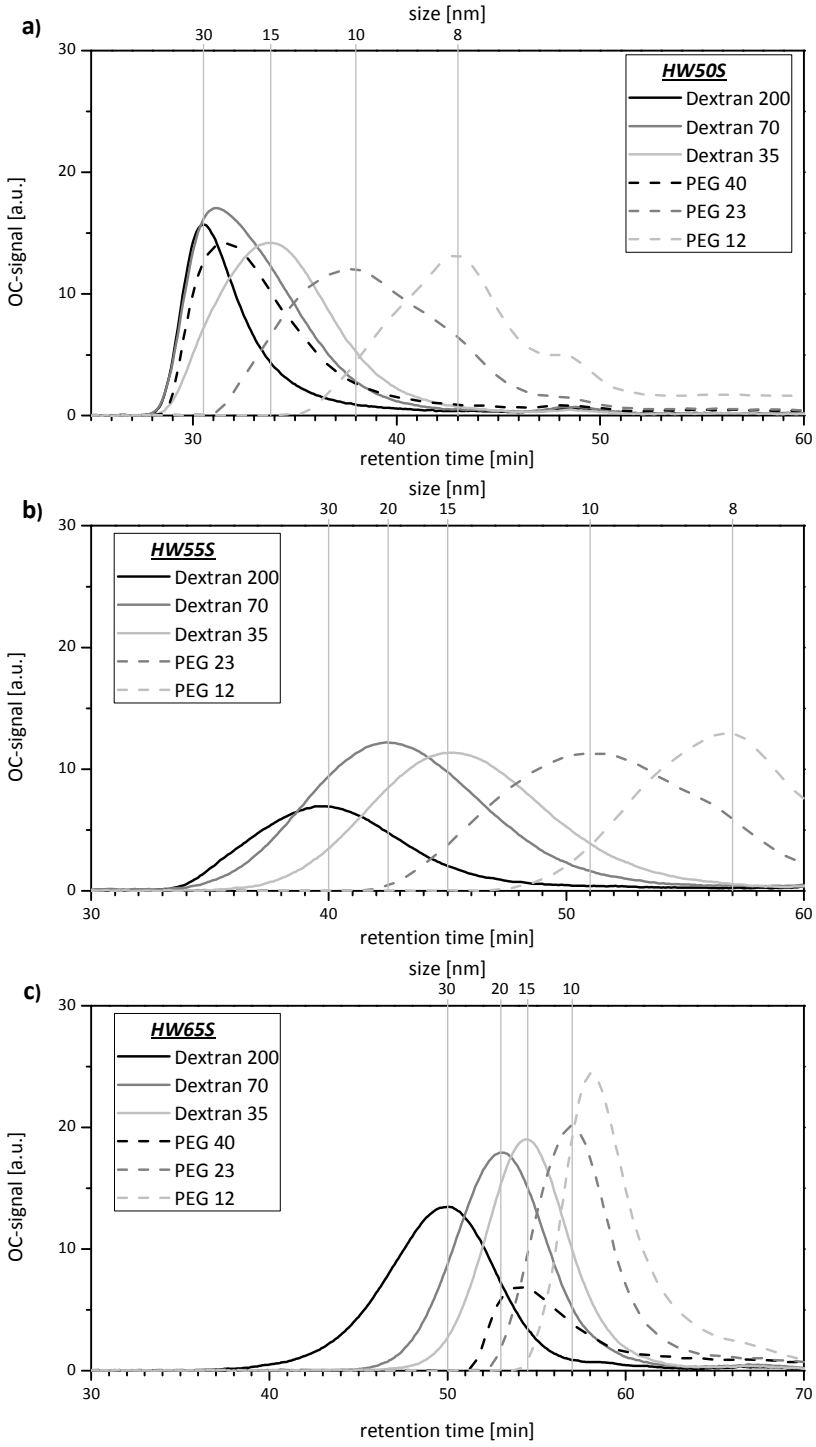
Appendix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