Major Organic Foulants in Ultrafiltration of Treated Domestic Wastewater and their Removal by Bio-filtration as Pre-treatment

Acknowledgements

Abstract

Ultrafiltration (UF) membranes can be used after conventional wastewater treatment to produce particle free and hygienically safe water for reuse. However, membrane fouling affects UF performance to a large extent. Without suitable pre-treatment and optimized operational conditions, the membrane can loose its permeability quickly. Althogh hydraulic backwashing is periodically used to remove the foulants, the accumulation of hydraulically irremovable fouling reduces the efficiency of the membrane permanently. Thus, qualitative and quantitative identification of the major foulants is necessary to understand and control fouling.

This research investigated the variation of fouling potential of domestic wastewater applying bio-filtration as a pre-treatment process. The aim is to identify and quantify the major foulants and understand fouling control effects using bio-filtration. Pilot-scale bio-filtration processes were used to treat secondary effluent prior to UF. The fouling potential of various water samples was assessed by lab-scale stirred cell experiments. An UF pilot plant was used to verify the correlation between the feedwater characteristics and membrane fouling.

The lab-scale stirred cell experiments demonstrated that the dissolved substances larger than or comparable to the UF pore size are major foulants, in either secondary effluent or in bio-filtrate. These substances were detected as biopolymers using liquid chromatography with online organic carbon detection, UV absorption and organic nitrogen detection (LC-OCD-UV-OND) which were characterized as macromolecular protein-like and polysaccharide-like substances. The content of biopolymers influenced the filterability of water samples in UF proportionally. It affected the reversibility of formed fouling crucially. The correlation between the biopolymer content in feedwater and the performance of UF was verified to be reproducible by pilot-scale UF experiments.

Bio-filtration was demonstrated to be able to improve the performance of the downstream connected UF due to the removal of particles, colloids and especially biopolymers from the secondary effluent. The elimination of biopolymers was observed mainly within the upper active filter layer and was revealed to be relevant to biological processes. The operational conditions of bio-filtration, e.g. temperature, biopolymer concentration in feedwater and filtration rate, influenced biopolymer removal efficiency.

After bio-filtraton, although the fouling potential of secondary effluent could be significantly reduced, operational conditions of UF plant affected fouling development to a large extent. Backwash interval and filtration flux were identified as the most important operational parameters affecting the severity of fouling. Severe fouling can appear due to the extension of filtration time and/or the increase of filtration flux. To control fouling development under these critical conditions, different chemicals were used to perform chemically enhanced backwash. The results showed that NaClO and H_2O_2 were effective reagents in controlling irreversible fouling. Chemical cleaning was carried out to restore the permeability of a fouled UF membrane. In the present study, the combination of NaOH and NaClO as cleaning reagent was identified as an effective choice.

Zusammenfassung

In der weitergehenden Aufbereitung von Kläranlagenablauf bietet der Einsatz von Ultrafiltrationsmembranen eine Energie schonende Aufbereitungsmöglichkeit bezüglich pathogener Keime und Partikeln. Bei der Membranfiltration führen jedoch Ablagerungen auf der Membran sowie in den Membranporen (Fouling) sukzessive zu einer Reduzierung der Filtrationsleistung. Für einen stabilen Betrieb der Ultrafiltration sind daher eine geeignete Vorbehandlung des Rohwassers und die optimale Betriebsführung der Filtration erforderlich, um den Permeabilitätsverlust zu reduzieren. Eine qualitative und quanitative Analyse der für das Fouling primär verantwortlichen Substanzen ist notwendig, um die dominierenden Foulingmechanismen zu verstehen und das Fouling kontrollieren zu können.

Im Rahmen dieser Arbeit wurde die Biofiltration zur Vorbehandlung von Kläranlagenablauf und deren Auswirkung auf das Ultrafiltrationsverhalten untersucht. Dafür wurde eine Pilotanlage betrieben, die Biofiltration mit anschließender Ultrafiltration für die Aufbereitung von Kläranlagenablauf kombinierte. Mit Hilfe von Laborfiltrationsversuchen wurde das Foulingpotential des biologisch behandelten Abwassers vor sowie nach Durchlaufen der Biofiltration betrachtet. Parallel konnte über das Filtrationsverhalten der UF-Pilotanlage der Zusammenhang zwischen den Rohwassereigenschaften und dem Membranfouling verifiziert werden.

Die Ergebnisse der Laborfiltrationsversuche zeigten, dass sowohl im Kläranlagenablauf als auch im Biofiltrat gelöste Substanzen größer oder im Größenbereich einer Membranpore das Fouling hauptsächlich beeinflussen. Bei der Analyse mittels Größenausschlusschromatographie und anschließender Detektion des organischen Kohlenstoffs, der UV-Absorption sowie des organischen Stickstoffs (LC-OCD-UV-OND) eluierten diese Stoffe als Biopolymere. Steigende Biopolymerkonzentrationen im Rohwasser führten zu einer proportional sinkenden Filtrationsleitung und wirkten sich ebenfalls auf die Reversibilität der Foulingschicht aus.

Die Biofiltration zeigte sich aufgrund der Entfernung von Partikeln, Kolloiden und insbesondere Biopolymeren aus dem Ablauf der Kläranlage geeignet für die Verbesserung der Leistungsfähigkeit der nachgeschalteten UF. Die Reduzierung von Biopolymeren fand hierbei hauptsächlich in der oberen aktiven Filterschicht statt und ist damit auf biologische Prozesse zurückzuführen. Betriebsparameter wie beispielsweise die Temperatur, die Biopolymerkonzentration im Rohwasser sowie die Filtrationsgeschwindigkeit beeinflussten die Effizienz der Biopolymerentfernung.

Die Biofiltration reduzierte das Foulingpotential des Kläranlagenablaufs signifikant. Weiter wirkten sich optimale Betriebsbedingungen der UF positiv auf ihre Leistung aus. Der Filtrationsflux sowie das Rückspülintervall erwiesen sich als wichtigste Betriebsparameter für eine Reduzierung des Foulings. Um einen stabilen Betrieb auch unter diesen kritischen Bedingungen zu erreichen, wurden verschiedene Reinigungschemikalien für die Realisierung einer chemisch unterstützten Rückspülung untersucht. NaOCl und H_2O_2 erwiesen sich als am effektivsten, um dem irreversiblen Fouling entgegenzuwirken. Sobald die Filtrationsleistung der UF auf ein Minimum sank, wurden die Membranmodule chemische gereinigt, um die Ausgangspermeabilität wiederherzustellen. Die effektivste Reinigungsleistung erreichte die Kombination der Chemikalien NaOH und NaOCl.

Abbreviations

AFM	atom force microscopy
BAC	biological activated carbon adsorption
BC	biopolymer concentration, mg C/L
BOD	biological oxygen demand
BSA	bovine serum albumin
BSF	biological rapid sand filtration
BW	backwash
BWF	backwash flux, L/(m·h), LMH
BWI	backwash interval, min
BWT	backwash time, sec
CEBW	chemically enhanced backwash
CIP	cleaning in place
COD	COD chemical oxygen demand
COP	cleaning out place
DB	delivered biopolymer load , mg C/m^2
DBPs	disinfect by-products
DCB	divalent cation bridging
DIN	Deutsches Institut für Normung (German Institute for Standardization)
DO	dissolved oxygen, mg/L
DOC	dissolved organic carbon, mg/L
DOM	dissolved organic matter
EBCT	empty bed contact time, h
EDTA	polyamino carboxylic acid
EfOM	effluent organic matter
EPS	extracellular polymeric substances
FF	forward flush
GAC	granular activated carbon adsorption
GFH	granular ferric hydroxide
HMW	high molecular weight
HS	humic substances
LBF	lake bank filtratoin
LMH	L/(m^2·h)
LC-OCD-UVD-OND	liquid chromatogram with online organic carbon detector, UV detector

	and organic nitrogen detector
LMW	low molecular weight
LOQ	limit of quantification
MBR	membrane bioreactor
MF	Microfiltraton
MW	molecular weight, Da
MWCO	molecular weight cut-off, Da
NF	Nanofiltration
NOM	natural organic matter
PACl	poly aluminium chlorine
PE	Polyethylene
PES	Polyethylsulphone
POM	particular organic matter
PP	Polypropylene
PVDF	polyvinylidene difluoride
RBF	river bank filtration
RNA	ribonucleic acid
RO	reverse osmosis
SAT	soil aquifer treatment
SE	secondary effluent
SMP	soluble microbial products
SOC	synthetic organic compounds
SSF	slow sand filtrate
SSFr	slow sand filter
SSFn	slow sand filtration
SUVA	specific UV absorbance, L/(m·mg)
SWITCH	EU Project: Sustainable Urban Water Management Improves Tomorrow's City's Health
TDS	total dissolved solids, mg/L
TMP	trans-membrane pressure, mbar, bar
TMP$_{end}$	TMP at the end of each experiment, mbar
TMP$_{start}$	TMP at the beginning of each experiment, mbar
TN	total nitrogen, mg/L
TP	total phosphorus, mg/L

UF	ultrafiltration
UV	ultraviolet
WWTP	wastewater treatment plant

Latin Symbols

A	membrane filtration area	m^2
C_b	biopolymer concentration	mg C/L
C_f	concentration of the subjected substance in the feed water	mg/L
C_p	concentration of the subjected substance in the permeate	mg/L
C_s	foulant concentration	kg/m^3
Da	atomic mass unit	
d_h	hydrodynamic diameter of organic molecule	µm
H	height	m
J	linear fluid velocity	$m^3/(m^2{\cdot}s)$, $L/(m^2{\cdot}h)$
J_{20}	flux normalized to 20 °C	$m^3/(m^2{\cdot}s)$, $L/(m^2{\cdot}h)$
k	rate constant depending on n	
K_w	permeability of a membrane	$L/(m^2{\cdot}h{\cdot}bar)$
K_{w0}	permeability of a membrane at the beginning of filtration	$L/(m^2{\cdot}h{\cdot}bar)$
$K_{w\text{-}c}$	permeability after chemical cleaning	$L/(m^2{\cdot}h{\cdot}bar)$
$K_{w\text{-}end}$	permeability after five days filtration	$L/(m^2{\cdot}h{\cdot}bar)$
$K_{w\text{-}start}$	permeability before filtration	$L/(m^2{\cdot}h{\cdot}bar)$
L	length	m
M_b	biopolymer mass loading per unit membrane area	mg/m^2
m_c	dry weight of foulants per unit membrane area	kg/m^2
n	flow behaviour index characterizing fouling mechanisms	
P_r	permeate recovery	%
R	resistivity	mΩ·cm
R_c	hydraulic resistance of cake/gel layer	1/m
R_f	total hydraulic resistance	1/m
R_{fi}	hydraulic fouling resistance due to fouling component i	1/m
R_m	hydraulic resistance of the membrane	1/m
R_p	restoration of permeability	%
R_r	retention rate	%
R_{TMP}	TMP increase per unit permeate	$mbar/m^3$

s	compressibility coefficient	
t	time	sec
T	temperature	℃
V	product volume of permeate	m^3
V_{bw}	permeate volume used for backwash	m^3
W	width	m

Greek symbols

α	specific cake/gel resistance	m/kg
α_0	specific cake/gel resistance at reference pressure	m/kg
ΔP	TMP, the pressure difference between feed water and permeate in dead-end filtration	N/m^2,bar or mbar
η	viscosity of the fluid	$N·s/m^2$
Σ	summation	

Table of Contents

1 Low-pressure Membrane Filtration in Wastewater Reclamation

1.1 Application of Low-pressure Membrane in Wastewater Reclamation

Wastewater Reuse and Low-pressure Membrane Filtration

Over the past decades there has been an increasing interest for wastewater reclamation and reuse in the world, particularly in arid and semi-arid regions, to meet growing demand on available water supplies. Driving forces of this trend arise from and are being strengthened through water shortage caused by climate change or pollution, through increasing demand of fresh water for urbanization, industrialization and increasing population (Jimenez and Asano, 2008). Different from long distance water transfer or exploitation of limited natural water resources, large numbers of wastewater treatment plants (WWTP) can be utilized as reliable and economical alternative water sources (Chu et al., 2004). After suitable treatment process, treated wastewater can be used either for indirect potable purposes (Ernst et al., 2007), or even for direct potable reuse (Wintgens et al., 2005).

In wastewater reclamation, suitable treatment processes are chosen fundamentally based on water quality requirement, economical issues and reliability of the technique. As an innovative technique, low-pressure membranes like microfiltration (MF) and ultrafiltration (UF) have got more interest in this area due to the high water quality effluent, reliability in operation and small footprint (Wintgens et al., 2005). With the decrease of membrane prices, more membrane equipments have been and will be set up for water reclamation (Sullivan, 2007). Since the removal of contaminants through low-pressure membranes is predominantly due to size exclusion of membrane pores in the lower μm range (Crittenden et al., 2006), MF and UF have the ability to separate suspended solids, large dissolved organic compounds and pathogens like protozoan cysts, bacteria and/or viruses from reclaimed water for indirect water reuse, such as urban purpose reuse (e.g., toilet flushing, auto washing and green irrigation, de Koning et al., 2008). They can also be used to reduce fouling on the downstream high-pressure membranes to produce high quality reuse water (U.S.EPA, 2004).

Based on a report about global perspective of low-pressure membranes (Furukawa, 2008), in December 2006 the installed treatment capacity using MF and UF reached $13 \cdot 10^6$ m^3/d, 25% of which has been used in wastewater treatment and pre-treatment prior to reverse osmosis membranes (RO).
Tab. 1-1 shows some current projects with large-scale low-pressure membrane facilities for water reuse. More projects or studies on advanced treatment and reuse using low-pressure membranes combined with other treatment processes e.g. flocculation, high-pressure membrane filtration (NF and RO), soil aquifer treatment (SAT) can be found all over the world (Fan et al., 2008; Kim et al., 2008; Jarusutthirak et al., 2002). With the increasing demand for wastewater reclamation and more stringent water quality regulatory standards, the low-pressure membrane technology exhibits as a reliable post-treatment choice after the conventional treatment approaches (Furukawa, 2008).

Tab. 1-1 Case projects of wastewater reclamation applying low-pressure membrane filtration

Reuse purpose	Location	Capacity (m³/d)	Treatment process	Literature
Direct potable reuse	Windhoek (Namibia)	21 000	Pre-O_3 + coagulation + dual media filtration + O_3 + BAC + GAC + UF + chlorine	Wingtens et al., 2005
Indirect potable reuse	Newater Project (Singapore)	91 000	MF + RO + UV disinfection	Qin et al., 2006
Groundwater recharge	Factory 21 California (U.S.A.)	265 000	MF + RO + UV/ H_2O_2	Water21, 2008
Irrigation, water fountains, domestic uses	Olympic park 2000 Sydney (Australia)	7 500	cross-flow MF	de Koning et al., 2008
Domestic uses	Olympic Park 2008 Beijing (China)	80 000	PACl flocculation + MF + GAC	Ernst et al., 2007

BAC: biological activated carbon adsorption, GAC: granular activated carbon adsorption, PACl: poly aluminium chlorine

Fouling Problem in Low-pressure Membrane Filtration

Along with the wide spreading utilization of low-pressure membranes in wastewater reclamation, the fouling problem has always been considered as one of the major limitations to increase the acceptance of the process (Haberkamp, 2008). Fouling is 'the process resulting in loss of performance of a membrane due to the deposition of suspended or dissolved substances on its external surfaces, at its pore openings, or within its pores' (Crittenden et al., 2006). In fouling phenomena, all of the constituents in feed water that can be retained on the membrane surface or in the membrane pores are called foulants (fouling materials). Due to fouling, the productivity of membrane processes is reduced, membrane lifespan is shortened and operation costs are increased. Therefore, the scientific understanding and control of membrane fouling is of particular concern.
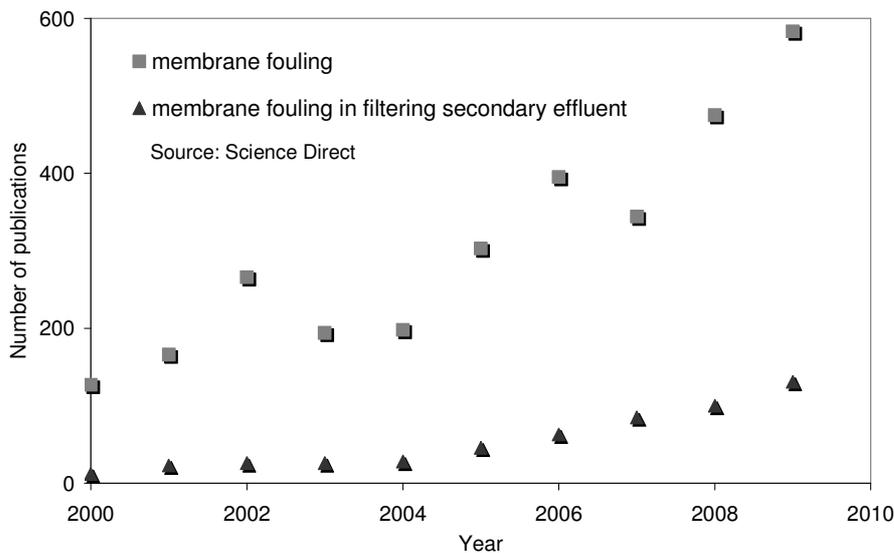
Fig. 1-1 Annual publications on membrane fouling (source: Science Direct)

During the last several years, with the expotential growth of installed MF and UF treatment capacity (Furukawa, 2008), a considerable number of papers have been published about low-pressure membrane fouling. According to Science Direct, the annual publication increased from 200 by 2004 to over 600 by 2009. The number of studies investigating fouling in low-pressure membrane processes filtering secondary effluent (SE) increases with a similar trend (Fig. 1-1). The significant increase of publications indicates the increasing importance of understanding fouling phenomenon in wastewater reclamation using low-pressure membranes, and moreover, the requirement of correspondingly suitable fouling control strageties.

In practice, biologically treated domestic wastewater always shows high fouling potentials in membrane filtration. Direct filtration is identified as an unreasonable operational strategy as the low-pressure membranes can be fouled seriously and loose its permeability quickly (Xie et al., 2006; Fan et al., 2008). During long-term operation, hydraulically irremovable interactions between foulants and membrane result in a continuous reduction of the membrane permeabilitiy although different fouling control methods, e.g. hydraulic flushing, are performed periodically. Numerous studies have shown that effluent organic matters (EfOM) are the major foulants in membrane filtration of SE (e.g. Jarusutthirak and Amy, 2006). In several previous studies, it is evident that a specific fraction of organic compounds in EfOM are principle foulants in UF of treated domestic wastewater (Laabs, 2004; Haberkamp, 2008). Nevertheless, EfOM represents a combination of various components. In terms of chemical nature they could be proteins, polysaccharides, humic substances, lipids, nucleic acids, etc. During membrane filtration these substances interact with the membrane in different manners. Due to the complexity of fouling phenomenon and also conflicting results on the nature of the foulants (Li et al., 2008), further studies on EfOM fouling in low-pressure membrane process are necessary. To control EfOM fouling, different pre-treatment processes prior to membrane filtration are commonly used, e.g., coagulation, adsorption, preoxidation and biofiltration (Huang et al., 2009; Lehman and Liu, 2009; Sperlich et al., 2008). Althoug the foulants removal effect can be evaluated by comparing the performance of a downstream membrane unit, a fundmental understanding of the character of major foulants and a quantitative assessment of their content is necessarily required to assess the fouling control effect of different strategies, and further more, to understand their removal mechanisms.

1.2 Research Objectives

The primary objectives of the present study are to identifiy the major foulants in UF of treated wastewater and understand their removal in bio-filtration processes. Specially, the main objectives were:

1) Identify major foulants based on the quantitative correlation between the content of foulants in feedwater and their fouling effect.
2) Compare the suitability of different foulant quantifying methods.
3) Understand fouling mechanisms during UF.
4) Demonstrate the effect of bio-filtration on the performance of UF.
5) Study foulant removal processes within a bio-filter.
6) Investigate operational factors of bio-filtration on its performance in foulant removal.

To support the major objectives in understanding fouling phenomena, additional objectives were as follows:

7)   Investigate the influence of operational conditions on fouling development in UF and suggest sustainable operating strategy.

8)   Understand fouling development in long-term membrane operation based on pilot-scale experiments.

9)   Develop membrane cleaning methods.

The study has been carried out within the scope of the German – Chinese cooperation project entitled 'Sustainable water management for Olympia Park 2008' (Contract no.: 02WA0524, 02WA1016) subproject 4 'Wastewater treatment and reuse' and within the European research project 'Sustainable Urban Water Management Improves Tomorrow's City's Health (SWITCH)'. SWITCH is supported by the European Commission under the 6th Framework Programme and contributes to the thematic priority area of "Global Change and Ecosystems" [1.1.6.3] Contract n° 018530-2.

1.3 Structure of the Dissertation

This dissertation continues in **chapter 2** with an introduction to UF membranes and a description of UF in water treatment. In relevance to membrane fouling, a review about the characteristics of different foulants and their removal are presented. **Chapter 3** introduces the material and analysis applied in the study. In the present work pilot-scale bio-filtration (short-term bank filtration) prior to UF was carried out in WWTP Beixiaohe (Beijing, China) in 2005. From 2006 to 2008 fouling control effects of pilot-scale bio-filtration (slow sand filtration) were investigated in WWTP Ruhleben in Berlin (Germany). For the pilot-scale experiments the same UF pilot plant and the same type of membrane module was used. The water quality analysis includes bulk water quality parameters and common organic foulant parameters, e.g. proteins, polysaccharides and biopolymers.

Chapter 4 identifies firstly the attribution of size fractionated foulants on fouling in UF filtering treated domestic wastewater. Subsequently, a quantitative correlation between specific fractional substances and fouling is presented based on lab-scale experimental results. The correlation is further validated based on pilot-scale membrane filtration results. Additionally, the relationship of different methods determining fouling potential is quantitatively compared. In **Chapter 5**, the fouling control effect by bio-filtration prior to UF is demonstrated. The removal of different foulants within slow sand filter and factors affecting the removal effect has been investigated. Although foulants are significantly removed by slow sand filtration, pilot-scale UF results show that operational conditions play also an important role in fouling development. In **Chapter 6** several operational variables, e.g. filtration flux, back wash interval (BWI) and back wash time (BWT) on fouling development in the UF pilot plant are investigated. In particular, the effect of filtration flux on fouling is quantitatively interpreted using lab-scale results.

Finally, the main findings of the current study are discussed and presented in **Chapter 7**. In this chapter some suggestions are also made for further studies.

2 Ultrafiltration Process and Fouling Phenomenon

2.1 Classification of Membrane Processes in Water Treatment

Membrane filtration is a filtration process in which membrane material acts as a selective barrier between two phases (Mulder, 2000). As a result of the driving force and due to the selectivity of the membrane, components transported to the membrane can pass through (in which case they become the permeate stream) or be rejected by it (in which case they become the retentate or concentrate stream, Fig. 2-1).
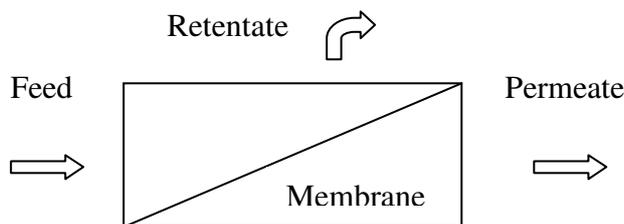
Fig. 2-1 Schematic illustration of a membrane separation process

For water and wastewater treatment, pressure is generally used as the driving force to push water through the membrane; the degree of the selectivity of the applied membrane depends on the membrane pore size. Based on the pore size range, the pressure driven membrane can be subdivided into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). In respect of driving pressure range, MF and UF are classified as low-pressure membrane processes and high-pressure membranes include NF and RO membrane. Tab. 2-1 shows an overview of the classification of membrane processes available in water treatment.

Tab. 2-1 Membranes applied for water treatment (Mulder, 2000; Judd, 2006)

Membrane process	Pressure (bar)	Pores (nm)	Removable components in water treatment	Major separation mechanism
Microfiltration	0.1 - 2	100 - 1000	Suspended solids, bacteria	Sieving
Ultrafiltration	0.1 - 2	10 - 100	Macromolecules, viruses,	Sieving
Nanofiltration	4 - 20	1- 10	Micropollutants, bivalent ions	Charge rejection, solution-diffusion and sieving
Reverse Osmosis	10 - 30	< 1	Monovalent ions	Solution-diffusion

2.2 Ultrafiltration in Water Reclamation

Based on water quality requirements and energy consumption specifications, the use of low-pressure membranes (MF/UF) in water and wastewater treatment has exploded since mid-1990s. In which, UF is considered to be able to produce hygienically safe permeate compared to MF due to its smaller pore size (Mulder, 2000). In the present dissertation UF process is investigated in relation to wastewater reclamation.

Ultrafiltration Membranes

UF membranes typically consist of a thin surface layer (pore size: 0.01 to 0.1 µm, Mulder, 2000) which provides the required selectivity on the top of a more porous support layer (pore size to 100 µm), and which provides mechanical stability. Different polymeric (organic) and ceramic (inorganic) materials are used to form membranes to get the desired physical properties and reasonable thermal and chemical resistance. The most suitable and commonly used polymers are polyvinylidene difluoride (PVDF), polyethylsulphone (PES), polyethylene (PE) and polypropylene (PP, Judd, 2006). For inorganic membranes, alumina (α-/γ-Al_2O_3), zirconia (ZrO_2), titania (TiO_2) and even metal like stainless steel are suitable membrane materials (Li et al., 2008).

Membrane Properties

Pore size and pore size distribution

For low-pressure membranes, the separation character can be given as a relevant pore size, normally in µm for MF, or as molecular weight cut-off (MWCO) in Daltons (Da, one Da represents one g/mol) for UF. The nominal MWCO of a UF membrane is defined as the molecular weight of a certain solute which is 90% rejected by the membrane (Mulder, 2000). The retention rate R can be calculated according to Eq. 2-1.

$$R_r = \frac{C_f - C_p}{C_f} \times 100\% \quad \text{Eq.2-1}$$

Where

R_r = retention rate, %
C_p = concentration of the subjected substance in the permeate, mg/L
C_f = concentration of the subjected substance in the feed water, mg/L

R ranges from 0 to 100% to express no rejection (0%) to complete rejection (100%). Based on the rejection curve using model solutes (frequently dextrans, Wickramasinghe et al., 2009), the membrane pore size and its distribution can be obtained. For specific substances, the rejection rate by a membrane depends on the molecular size. However, the shape of the molecules, their electrical charge and the pH of the feed solution play also important roles (Baker, 2004).

Pure water flux

Another important property of a membrane is its flow rate/flux operated at corresponding pressures (Eq.2-2).

$$K_w = \frac{J}{\Delta P} \quad \text{Eq.2-2}$$

where
K_w = permeability of a membrane, $m^3/(m^2 \cdot s \cdot Pa)$ or in practice $L/(m^2 \cdot h \cdot bar)$
J = the linear fluid velocity, $m^3/(m^2 \cdot s)$ or in practice $L/(m^2 \cdot h)$

ΔP = TMP = the pressure difference between feed water and permeate, N/m^2, Pa; in practice bar or mbar is commonly used)

The flow rate (J) of liquid passing through a membrane can be calculated according to Darcy's law (Eq.2-3).

$$\frac{dV}{Adt} = J = \frac{\Delta P}{\eta R_m} \quad \text{Eq.2-3}$$

where
V = the product volume of permeate, m^3
t = the filtration time, s
A = the membrane filtration area, m^2
η = viscosity of the fluid, N·s/m^2
R_m = hydraulic resistance of the membrane, 1/m

The dynamic viscosity η is related to feed water temperature T (ºC) which can be determined using the following equation (Roorda, 2004).

$$\eta = \frac{497 \cdot 10^{-3}}{(T + 42.5)^{1.5}} \quad \text{Eq.2-4}$$

where

T = temperature of the feed water, ºC

Membrane Configuration and Operation

Membrane module configuration

For practical operation, membranes are encapsulated in membrane modules. The term 'membrane module' is used to describe a complete unit comprised of membranes, a pressure support structure, a feed inlet, a concentrate outlet and an overall support structure (Roorda, 2004). The principal types of membrane modules applied in water treatment at an industrial scale are as following (Li et al., 2008):

Hollow fibre or capillary membranes: the most common configuration of MF and UF for water treatment. The hollow fibres are 0.5 – 1.5 mm in diameter, several hundreds to thousands of fibres are packed in a membrane module.
Tubular membranes are an extension of the hollow fibre configuration with a larger diameter (up to 25 mm). This kind of module is suitable to treat feed water with a high level of suspended solids.
Spiral wound membranes: two flat sheets of membrane are separated with a permeate collector channel material to form a leaf. The assembly is sealed on three sides and the forth side is open to exit permeate.
Plate and frame membranes: are comprised of a series of flat membrane sheets and support layers. Membranes sandwich support plates which are arranged in stacks. Permeate is collected from each support plate.

The flow direction in tubular and hollow fibre membranes can be inside-out or outside-in. In inside-out mode the feedwater flows from the inside of the membrane tube to the outside of the tube. The outside-in configuration shows the opposite flow direction. Generally, the outside-in scheme of hollow fibre membranes offers a larger filtration area compared to a similar model operated in inside-out mode (Crittenden et al., 2006).

Contained (pressurized) and submerged (suction) modules

In water and wastewater treatment processes, membrane modules can be classified into contained pressure vessels or submerged membranes. Contained pressure vessel is the traditional approach filtering water through low-pressure membranes. Permeate can be obtained due to significant positive pressure from the feedwater side to the membrane. Trans-membrane pressure (TMP) is developed by a feed pump that increases the feedwater pressure, while the permeate stays at a near-atmospheric pressure. Submerged membranes are an assembly of membranes positioned in a feedwater tank typically open at the top. The liquid to be filtered is fed to the tank and permeate is removed under suction, either by a pump or by a gravity effect. While the contained pressure vessels can be operated in inside-out and/or outside-in mode, filtering water using submerged membranes is always in outside-in mode (Li et al., 2008).

Operation of UF

Membrane systems can be operated at either constant flux or constant pressure. Operated at constant flux mode TMP is increased to maintain the constant permeate flux as the membrane fouls. During constant pressure filtration, the TMP is maintained constant but the productivity decreases continuously as a result of fouling. In practical operation, membrane systems are commonly operated at constant flux.

Considering feed water flux direction, UF and MF systems can be operated in cross-flow or dead-end filtration. In cross-flow configuration, the feed water is supplied in parallel with the membrane surface. A portion of the feed water passes through the membrane and forms permeate, the rest forms concentrate and is recirculated with additional feed water for filtration. To control the concentration of the solids in the recirculation loop, the concentrate is discharged at a specific rate. In dead-end filtration, all the feed water is forced pass through the membrane. In practical operation, a fraction of permeate is used for periodical backwashing to maintain the permeability of the membrane. As the energy consumption in dead-end mode with backwashing is lower than that in cross-flow mode (Li et al., 2008), most of the low-pressure membrane systems are operated in dead-end.

Application of Low-pressure Membranes in Wastewater Relamation

For wastewater reclamation, low-pressure membranes are being used either as a polishing step after secondary/tertiary treatment (Fig. 2-2 a) or as a part unit of membrane bio-reactors (MBR, Fig. 2-2 b). As a post-treatment process, MF/UF is considered primarily as a water quality improvement unit, e.g. as a physical disinfection process removing bacteria and particles. In MBR systems, besides effluent quality control, low-pressure membranes are used to concentrate up the biomass within the biological wastewater treatment unit. Subsequently, it reduces the necessary tank size and increases the effciency of the biotreatment process. MBRs thus tend to generate treated waters of higher purity with respect to dissolved constitutents.

Moreover, by removing the requirement for biomass sedimentation, the flow rate through a MBR cannot affect product water quality through impeding solids settling, as is the case for an activated sludge process (Judd, 2006). Currently, MBR has been actively employed for wastewater treatment and reclamation and efforts have been mainly addressed on the improvement of its performance while decreasing treatment costs (e.g. Meng et al., 2009).
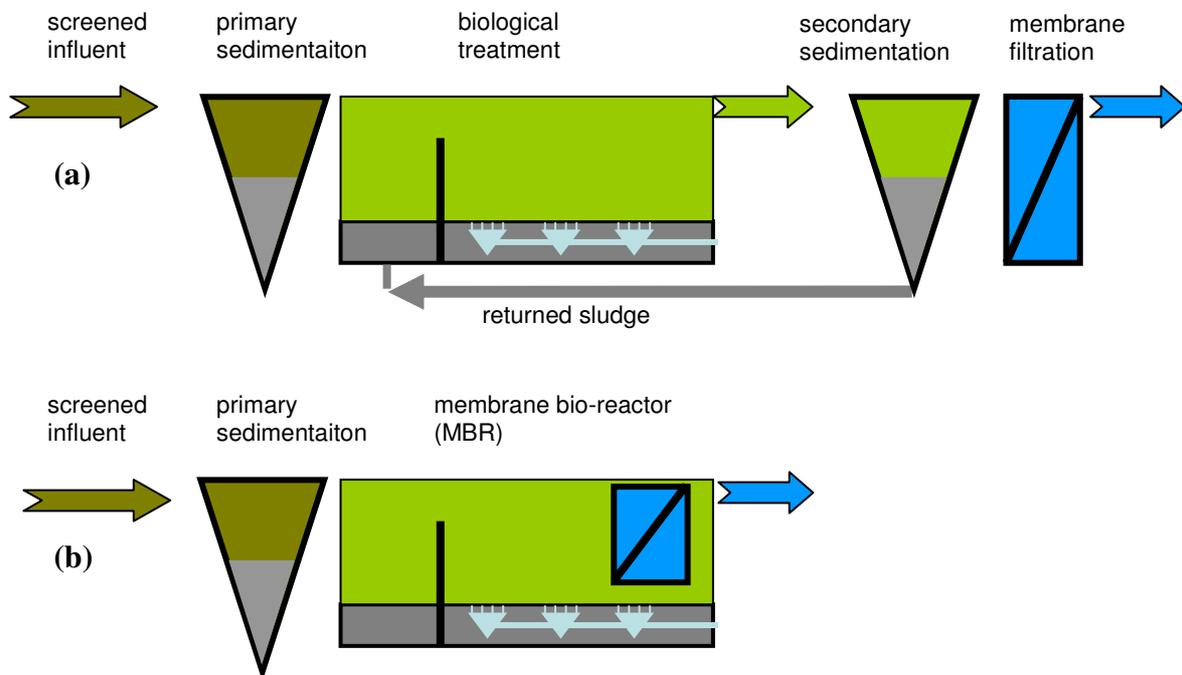
Fig. 2-2 Application of low-pressure membranes (a) as a post-treatment unit after conventional biological wastewater treatment processes for water reclamation, (b) in a MBR system to produce reuse wate**r**

2.3 Fouling Phenomenon and Fouling Mechanisms in UF Process

During membrane filtration the flux declines over time although all operating parameters are kept constant. This phenomenon is caused by fouling. Fouling refers to the blockage of membrane pores during filtration due to the combination of sieving and adsorption of particulates and dissolved compounds. The accumulation of foulants can appear either on the membrane surface which forms a cake/gel layer or within the membrane pores (Li et al., 2008). As fouling decreases membrane performance and shortens membrane life, it is one of the most important issues hindering the widespread application of membrane filtration.

Classification of Fouling

Fouling can be broadly classified into reversible and irreversible fouling (Fig. 2-3). Reversible fouling in this dissertation refers to the fouling that can be removed by backwashing or flushing after each filtration cycle. Irreversible fouling is the fouling that cannot be removed by hydraulic processes. This item can be further classified into chemically reversible and irreversible fouling, in which the chemically irreversible fouling is defined as the fouling that cannot be removed through chemically enhanced backwash (CEBW) or chemical cleaning.
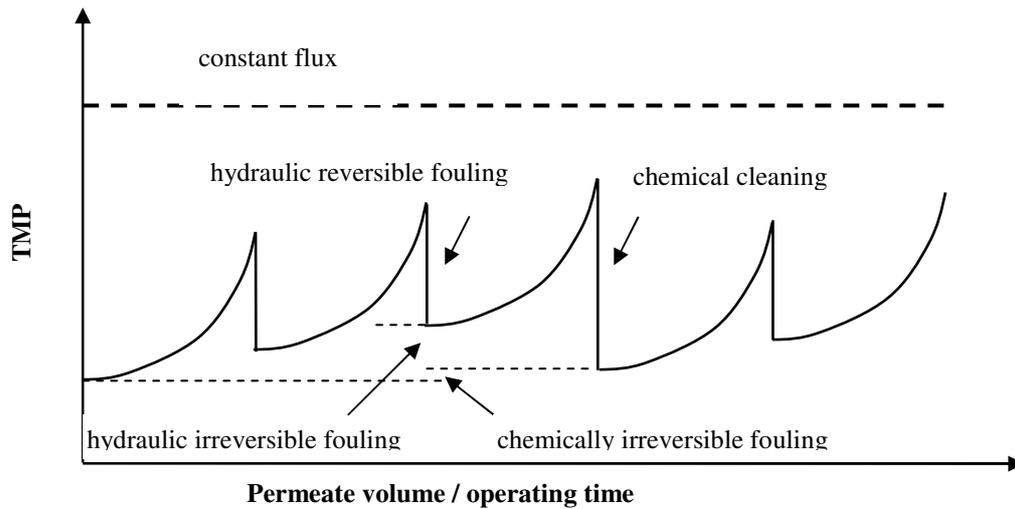
Fig. **2**-**3** Illustration of reversible and irreversible fouling in UF operated at constant flux

Based on the way the foulants accumulate, different fouling mechanisms can appear individually or simultaneously (Roorda, 2004; Bowen and Jenner, 1995; Böddeker, 2007; Foley, 2006). The following descriptions are the major fouling mechanisms in UF (Fig. 2-4):
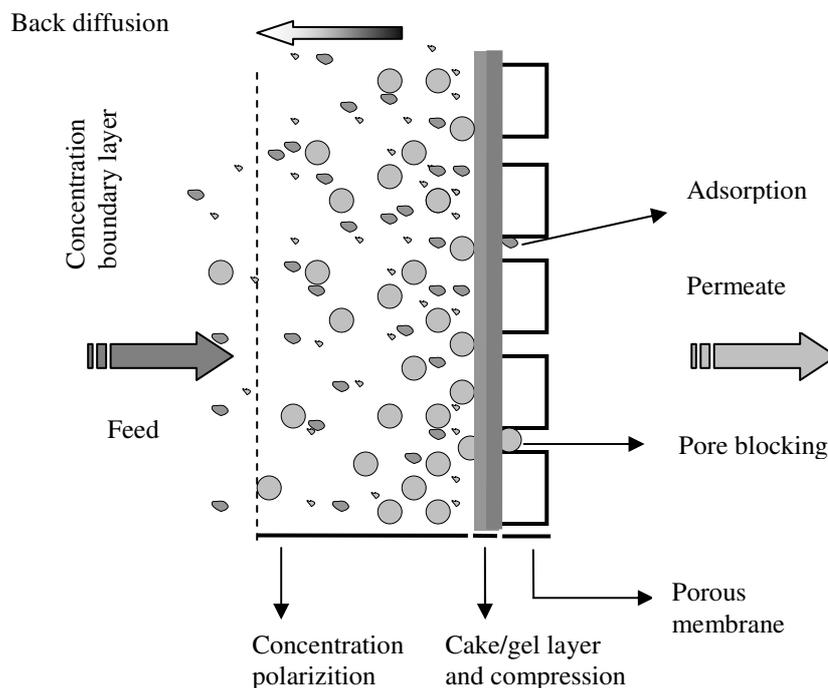
Fig. 2-4 Schematic diagram of a fouled membrane by various fouling mechanisms (adapted from Roorda, 2004, revised**)**

Concentration polarisation due to high concentration of foulants (macromolecules) near to the membrane surface (reversible) and/or subsequent solidification due to gel-polarization (less reversible);
Adsorption inside the membrane pores (less reversible);

Blocking of the membrane pores due to sieving effect and followed by cake/gel layer formation (more reversible) and compression.

Quantification of the hydraulic resistance caused by these fouling types can be obtained based on resistance-in-series model. The model applies a resistance value to each component of membrane fouling with the assumption that each contributes to hydraulic resistance and they act independently from one another (Crittenden et al., 2006). Eq. 2-5 presents the resistance-in-series relationship to describe the relationship of flux and the resistance of a fouled membrane:

$$J = \frac{\Delta P}{\eta(R_m + \Sigma R_{fi})} \quad \text{Eq.2-5}$$

where
R_m = the hydraulic resistance caused by membrane, 1/m
R_{fi} = hydraulic fouling resistance of fouling component i, e.g., reversible and irreversilbe fouling, or due to adsorption, cake layer and gel layer, 1/m

Analysis of Fouling Mechanisms

Fouling caused by concentration polarization

During membrane filtration, the separation of solute and solvent takes place at the membrane surface where the solvent passes through the membrane and the retained solute causes the local concentration to increase, this effect is defined as concentration polarization (Bowen and Jenner, 1995). The localized accumulation on the membrane could be either particle polarization or concentration polarization (applies to dissolved species) which leads to an osmotic counter-pressure against the driving force. The basic equation describing the relationship between flux and driving force is as following:

$$J = \frac{\Delta P - \Delta \Pi}{\eta(R_m + R_d)} \quad \text{Eq. 2-6}$$

where
R_d = hydraulic resistance due to reversible or irreversible deposition of solute onto the membrane surface, 1/m
$\Delta \Pi$ = $\Pi(c_m) - \Pi(c_p)$, the osmotic pressure difference across the membrane, mbar
$\Pi(c_m)$ = the osmotic pressure at the membrane surface, mbar
$\Pi(c_p)$ = the osmotic pressure in the permeate, mbar

In low-pressure membrane processes for water and wastewater treatment, the osmotic pressure is in general negligible. Therefore, osmotic effects are frequently ignored by calculation (Bowen and Jenner, 1995). However, the concentration polarization effect is important in respect to the formation of membrane fouling. During filtration, the solutes accumulated at the membrane surface have a tendency to diffuse back into bulk solution according to Fick's law of diffusion. At a steady state condition the solute mass balance above the membrane surface can be achieved which gives the rate of convective transport of solute towards the membrane surface equal to the rate of solute leakage through the membrane plus the rate due to back-

diffusion. Withdrawing feed force leads to back-diffusion of foulants into the solution. When the hydraulic resistance disappears after feed force withdrawing, the fouling is considered reversible. However, under certain conditions concentration polarization can lead to an irreversible buildup. For instance, when the concentration of macrosolutes at the membrane surface reaches its solubility limit and precipitates to form a solid or thioxotropic gel layer, the consolidated structure is slow in diffusing into water and leads to a flux reduction, a fraction of which could be irreversible. Current analysis (Wang and Waite, 2009) has revealed that the formed gel layer in filtering wastewater effluent is a cross-linked three-dimensional network consisting of macromolecular compounds. The interactions among these organics with membrane are assisted or strengthened by bridging via multivalent metals and/or specific molecules.

Fouling caused due to pore blocking

Based on the pore sealing effect a theoretical description of the fouling behaviour in dead-end membrane filtration was introduced by Hermia (1982). In the physical model the pressure applied is set constant. The membrane pores are assumed as straight cylindrical with identical pore diameter and length. The flow through the pores is assumed as laminar. Based on the modes in which the foulants accumulate (Fig. 2-5), the following four basic filtration laws can be used to describe the fouling phenomena:
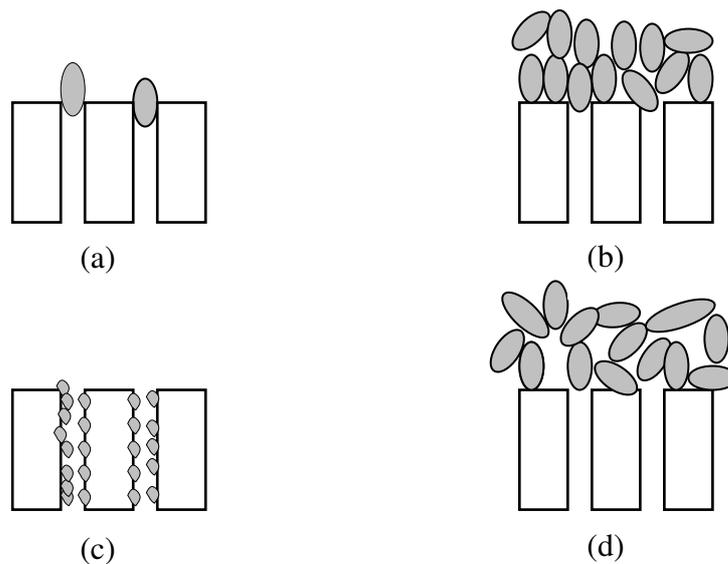
Fig. 2-5 Fouling mechanisms related with blocking laws (a) complete blocking, (b) intermediate blocking, (c) standard blocking, (d) cake filtration

Complete pore blocking law: For complete blocking it is assumed that each particle reaching the membrane participates in the blocking phenomenon by pore sealing (Fig. 2-5 a, i.e. no flow at all through the pore), the particles are not superimposed upon another (i.e. the particles form a single particle layer).

Intermediate blocking law: Based on the complete blocking law and considering the probability for a particle to block a pore, this law describes the filtration behaviour that the following particles (the second particle layer) have an equal probability to settle on the first layer as on the membrane surface which was left free (Fig. 2-5 b).

Standard blocking filtration law: It is assumed that pore volume decreases proportionally to the filtrate volume by particles depositing/adsorption on the pore walls (Fig. 2-5 c). This implicates a reduction of the pore diameter.

Cake filtration law: Assuming resistance in series and a constant superimposition, the resistance of the fouling layer increases proportionally to the accumulated particle mass (Fig. 2-5 d).

In relevance to these possible physical phenomena, a unified equation describing the blocking filtration laws was derived to represent the filtration characteristics (Eq.2-7, Hermia, 1982):

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \quad \text{Eq.2-7}$$

where
t = filtration time
V = the total permeate volume
k = rate constant depending on n
n = flow behaviour index characterizing fouling mechanisms

Depending on the exponent n, the dominant fouling mechanism is:
$n = 2$ complete pore blocking
$n = 1.5$ standard blocking
$n = 1$ intermediate blocking
$n = 0$ cake filtration

Similar derivations for constant flux filtration (Huang et al., 2008a; Bolton et al., 2006) or for varying flux and TMP filtration (Augstin Suarez and Veza, 2000) have also been presented. The model has been successfully used to explain some fouling phenomena in dead-end membrane filtration processes (Yuan et al., 2002; Costa et al., 2006; Roorda, 2004).

However, what the model describes is the behaviour of rigid, spherical and neutrally charged particles in dilute solutions during filtration through straight cylindrical pores. The effects of foulant-foulant and foulant-membrane interactions and fouling layer (cake/gel layer) compression, which are significantly influenced by the physical and chemical characteristics of foulants, are generally ignored. Nevertheless, these factors are considered to be important to fouling phenomena in practical operation (Zhang et al., 2008; Roorda, 2004; Huisman et al., 2000). To get a better understanding of fouling phenomena, it is necessary to characterize the foulants and understand their interactions in detail.

2.4 Classification of Foulants

 According to the type of foulants, the corresponding fouling in wastewater treatment and reclamation can be generally classified into organic, inorganic, biological and particular/colloidal fouling (Amy, 2008; Li et al, 2008).

2.4.1 Organic Fouling – Effluent Organic Matters (EfOM)

In wastewater reclamation, organic fouling is considered to be a major constraint for the application of UF. The EfOM which are considered as major organic foulants have been investigated intensively (Jarusutthirak et al., 2002 ; Laabs et al., 2006; Shon et al., 2006; Amy, 2008). Generally, EfOM in wastewater effluents originate from three different sources: 1) natural organic matters (NOM) present in the drinking water, 2) synthetic organic compounds (SOC) discharged by consumers and disinfection by-products (DBPs) generated during disinfection processes, and 3) soluble microbial products (SMP) generated during biological wastewater treatment (Amy, 2008; Barker and Stuckey, 1999; Drewes and Fox, 1999). Typical organic constituents in treated domestic wastewater and their size ranges are shown in Fig. 2-6.
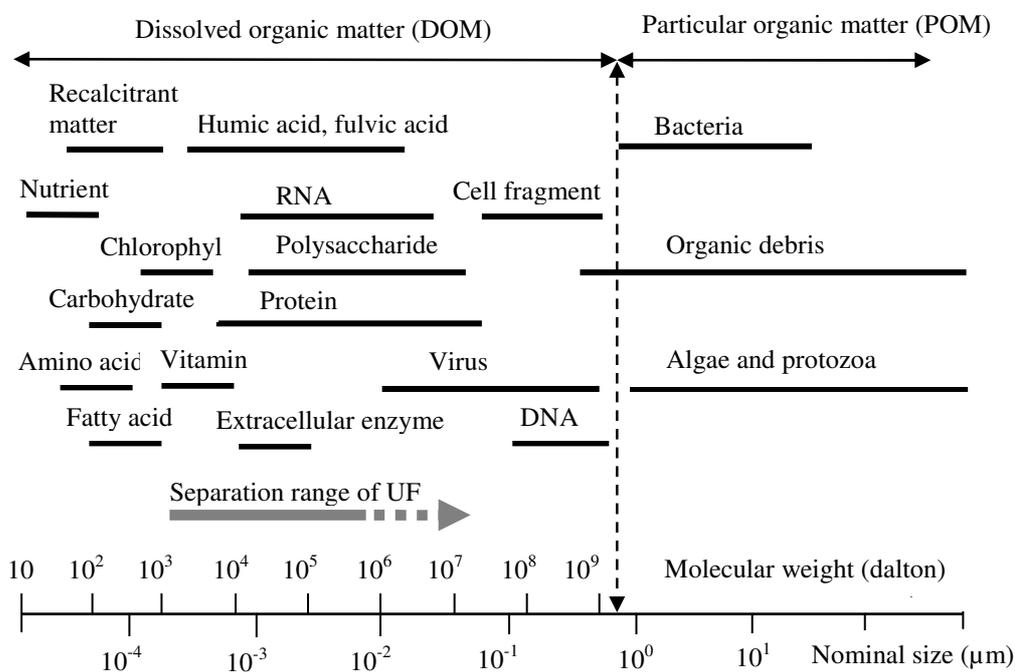
Fig. 2-6 Typical organic constituents in biological treated domestic wastewater and their size ranges (Adapted from Levine et al., 1985)

Although NOM in drinking water (surface water as a source) attributes to fouling in low-pressure membrane filtration (Hallé et al., 2009; Kennedy et al., 2008; Huang et al., 2007), recent evidences have shown that the EfOM foulants in membrane filtration of treated domestic wastewater are different to NOM foulants in drinking water. Huang (2007) compared the fouling effect of UF treating surface water and biologically treated wastewater. It is evident that the foulants from SE reduce the permeability of UF more significantly than that from surface water but the formed fouling shows a higher reversibility. Further more, the high molecular organic compounds demonstrate much more severe fouling effect than other organic fractions. This result coincides with the result reported by previous studies (Jarusutthirak, 2002; Laabs et al., 2006). These substances, based on the study made by Jarusutthirak and Amy (2006), are mostly SMP and/or extracellular polymeric substances (EPS) which are

mainly formed during biological wastewater treatment processes (Jarusutthirak and Amy, 2007).

SMP is defined as 'the pool of organic compounds that result from substrate metabolism (usually with biomass growth) and biomass decay during the complete mineralization of simple substrates' (Barker and Stuckey, 1999). This definition concerns soluble cellular components in relation to different activities of micro-organisms e.g. excreted by micro-organisms due to their interaction with the environment, produced as a result of substrate metabolism and bacteria growth or released during the lysis and degradation of micro-organisms (Chudoba, 1985). Some of SMP have been identified as humic and fulvic acid, polysaccharides, proteins, nucleic acids, amino acids, structural components of cells and products of energy metabolism (Barker and Stuckey, 1999; Jarusutthirak and Amy, 2006).

EPS is used as a general term which encompasses all classes of autochthonous macromolecules such as carbohydrates, proteins, nucleic acids, phosphorous lipids and other polymeric compounds found at or outside the cell surface and in the intercellular space of microbial aggregates (Flemming and Wingender, 2001). Typically, the EPS solution is characterised according to its relative content of proteins and polysaccharides. Although there is some difference between the definitions of SMP and EPS, it is now widely accepted that the concepts of soluble EPS and SMP in treated domestic wastewater are identical (Judd, 2006).

The fouling effect of SMP/EPS in UF of EfOM-containing wastewater has been intensively investigated (Haberkamp, 2008; Laabs et al., 2006). Laabs et al. (2006) compared the fouling potential of treated wastewater after different pre-treatment processes prior to UF. Using liquid chromatography with online detectors (LC-OCD) they found that the macromolecules play a more crucial role in fouling than other dissolved fractions smaller than the membrane pore size. Such substances block membrane pores, form cake/gel layer on membrane surface and reduce membrane permeability seriously (Laabs and Amy, 2006). In terms of chemical nature they can be characterized as polysaccharide-like and protein-like substances (Amy, 2008; Her et al., 2003; Huber, 1998). Studies investigating characteristics of foulants in both conventional biological treatment processes and MBR systems support this conclusion (Rosenberger et al., 2006; Jarusutthirak and Amy, 2006; Liang et al., 2007; Geng and Hall, 2007). Using inline attenuated total reflection (ATR) – fourier transform infrared (FTIR) spectrometry, proteins and polysaccharides have been identified as the major organic foulants in irreversible fouling (Shon et al., 2004). The important role of protein-like and polysaccharide-like substances can be further confirmed using other analysis methods, e.g., fluorescence excitation-emmison-matrix (EEM) for proteins (Her et al., 2003). Using these advanced methods, Haberkamp (2008) investigated fouling phenomenon in a PVDF UF membrane filtering treated domestic wastewater. Besides the identification of macromolecular protein-like and polysaccharide-like compounds as primary foulants, protein-like substances have been shown to play a more crucial role in irreversible fouling than other compounds (Haberkamp, 2008).

To understand fouling mechamisms, the fouling effect of model substances which have similar character like SMPs has also been investigated (Wang and Waite, 2008a; Torrestiana-Sanchez et al., 2007). Frequently, dextran and alginate are used to represent polysaccharides

while bovine serum albumin (BSA), pepsin and myoglobin and are used to represent proteins. It is evident that during membrane filtration, these organic compounds can accumulate and/or be adsorbed on the membrane surface and/or in membrane pores. The interaction between these organics and membranes leads to irreversible fouling (Susanto et al., 2007; Susanto and Ulbricht, 2005). In long-term operation, model substances such as alginate can form irreversible fouling which results in continuous increase of hydraulic fouling resistance (Ye and Chen, 2005).

2.4.2 Biofouling

Biofouling is defined as the undesired development of microbial layers (biofilms) on membrane surfaces (Li et al., 2008). Biofilm is an expression which applies to microbial life in aggregates combined through EPS which contains mainly polysaccharides and proteins (Flemming, 2002). Generally, biofouling mechanisms in membrane processes include the adsorption of soluble and suspended EPS on membrane surfaces and in membrane pores, the clogging of membrane pore structure by fine colloidal particles and cell debris, and the adhesion and deposition of sludge cake on membrane surfaces (Liao et al., 2004). As bacteria alone cannot foul the membrane seriously, the far more important foulants are the EPS secreted from them (Xu and Chellam, 2005). Due to the accumulation of EPS and their reaction with solute ions, mass transfer coefficient in the water phase can be reduced and this contributes significantly to permeate flux decline in membrane filtration (Kim et al., 2006). Moreover, the secreted EPS decrease the effectiveness of backwashing and lead to irreversible fouling (Xu and Chellam, 2005). The EPS gel structure protects also bacterial cells from hydraulic shearing and from chemical attack of biocides such as chlorine (Li et al., 2008). Based on the characteristics of the active substances in biofouling, the classification of biofouling is overlapping within organic fouling. Biofouling can then be considered as a biotic form of organic fouling (Amy, 2008). The severity of biofouling in wastewater reclamation is greatly related to the characteristics of the feedwater, such as nutrient availability, turbulence, temperature, particles, etc. The structure of microbial community and the surface condition of the membrane surface influence the process also to some degree (Melo and Bott, 1997; Ahmed et al., 2007; Huang et al., 2008b).

2.4.3 Inorganic Fouling

Inorganic fouling is caused by the accumulation of inorganic precipitates (such as metal hydroxides and carbonates) and scales on membrane surfaces or within the pore structure (Li et al., 2008). Precipitates are formed when the concentration of these chemical species exceed their saturation concentrations, which is a major concern for RO and NF as they reject most of the solved inorganic species. For UF and MF, inorganic fouling due to concentration polarization is much less profound, but can exist most likely due to interactions between ions and other fouling materials, e.g. organic foulants via chemical bonding (Liang et al., 2008; Costa et al., 2006). If pre-treatment processes for membrane filtration such as coagulation or oxidation are not designed or operated properly, it may introduce metal hydroxides into fouling matrix (Zhao et al., 2005). Inorganic fouling/scaling can be a significant problem for make-up water of caustic solutions prepared for chemically enhanced backwash or chemical cleaning (Liu et al., 2006).

2.4.4 Particulate and Colloidal Fouling

In UF of water or wastewater, dissolved and colloidal organic matters lead to the most severe fouling (Howe et al., 2006; Jarusutthirak and Amy, 2006). Fan (2008) showed that the colloidal substances in the SE are major foulants to UF as the fouling potential of the water could vary only a little after a pre-filter with a pore size of 1.5 µm prior to UF. Howe (2006) demonstrated that the size of major foulants to UF is within the range of MW of 100 k Da to 1 µm in diameter. In a pilot-scale study, Poele (2006) compared the fouling control effect using a curved sieve with a mesh size of 0.45 µm and a MF with a nominal size of 0.1 µm prior to UF. The results indicated that the major foulants in the SE to UF are within the size range of 0.1 to 0.45 µm. Particles are considered to have little influence on the fouling phenomenon in UF as flux decline due to their accumulation is largely reversible by hydraulic cleaning processes (Liu et al., 2006). In conjunction to this statement, flocculation/coagulation processes can be used to improve the filterability of water sample by enlarging the size of the foulants. Several studies showed that after flocculation the water samples can be easier filtered, the formed fouling layer can be more readily backwashed (Fan et al., 2008; Cho et al., 2006). This leads to a better performance of the UF (Huang et al., 2009).

Although it is indicated that inorganic particles and colloids do not really foul the membrane because of the better reversibility, under certain operational conditions the inorganic colloids can also lead to irreversible fouling due to deposits and fouling layer compression (Bessiere et al., 2005; Li et al., 2008). In drinking water treatment or wastewater reclamation, the colloidal inorganic foulants could be irreversible adhered on the membrane surface through organic foulants and lead to a complex irreversible fouling layer (Jermann et al., 2008; Zhang et al., 2003). Zhang (2003) showed the effect of colloidal and particulate SiO_2 (d = 0.5 to 10 µm) and powdered active carbon (PAC, d = 1 to 80 µm) on the TMP development of UF filtering NOM-containing water. It was illustrated that the dosage of both kinds of fine particles led to more severe fouling. The combined particle-NOM layer at the membrane surface could not be effectively back washed. Simultaneously, it was observed that although PAC is able to adsorb much more NOM than SiO_2 does in the feedwater, it reduces the reversibility of the fouling more severely than the latter one at a similar dosage. After systematic investigation on the co-effect of organic and inorganic colloidal foulants in dead-end UF, Jermann (2008) stated that the combined fouling effect is determined by the characteristics of NOM and its interaction with the particles in the feed water.

2.5 Complexity of Fouling Phenomena

2.5.1 Influence of Membrane Property

The previous studies indicate that in fouling phenomena organic foulants play a crucial role in membrane filtration. In reality, although the physical and chemical interactions between organic foulants and membrane and among various types of foulants add the complexity of fouling, the severity of fouling is primarily determined by the interaction between foulants and the membrane (Yamamura et al., 2007a). Therefore, besides the characterization of foulants, the

property of membranes needs also to be identified (Huang et al., 2009). Based on the review made by Wyart et al. (2008), the property of membranes can be described by two classes of parameters which are membrane structure parameters (roughness, porosity, pore size, pore shape, pore size distribution) and membrane/effluent coupling parameters (membrane material, surface charge, hydrophobicity, etc.).

Influence of Membrane Structure

In respect to membrane structure, one important parameter relevant to fouling is the roughness which is used to describe the surface topology of a membrane. Generally, rough surfaces can be easily fouled because roughness increases surface area and affects macroscopic properties like zetal potential that can also influence fouling rates (Wong et al., 2009). This correlation is always reproducible in either MF/UF processes (Zhang et al., 2008; Evans et al., 2008) or in RO and NF membrane filtration (Li et al., 2007; Peng et al., 2004), during membrane filtration of either wastewater effluent, surface water or model substances (Lee et al., 2005; Vrijenhoek et al., 2000).

For membranes made of identical material, pore size and its distribution are important parameters affecting membrane performance. It is suggested that a suitable pore size and a narrow pore size distribution are preferred to control membrane fouling (Kimura et al., 2006; Meng et al., 2009). For instance, in filtering SE, Huang (2007) observed that the membrane with a larger pore size (0.1 µm) is more prone to irreversible fouling than that with a smaller pore size (0.02 µm) although they are both made of PVDF. This phenomenon could be attributed to the severe adsorption and pore blocking in the membrane with a larger pore size as colloids penetrate more readily into the pores and interact with the membrane matrix (Costa et al., 2006). Similar conclusion has been made by Fu et al. (2008). In their study it was simultaneously revealed that the membrane with a lower porosity, which indicates the ratio between pore volume and that of the material, demonstrates much severe fouling. This phenomenon is attributed to the fact that at similar delivered foulant load, the membrane with a higher porosity can offer more spare void for the solutes.

Influence of Hydrophobicity and Charge

In relevance to the chemical characteristics of the membrane material, membrane surfaces show hydrophilic or hydrophobic properties which reflect the interfacial tension between water and the membrane material. To estimate the hydrophobicity of a membrane, contact angle can be measured using the sessile drop method (Li et al., 2008). A membrane with a higher contact angle indicates that it is of higher hydrophobicity. Hydrophobic membranes are regarded to be more prone to fouling than hydrophilic ones. That is because the constituents in water that are sparingly soluble, nonpolar, or hydrophobic will accumulate readily at the hydrophobic surface to minimize the interfacial tension between the water and membrane (Li et al., 2008). At this point, numerous studies have highlighted the correlation, either by filtering surface water and wastewater effluent (e.g., Huang et al., 2007; Kim and Dempsey, 2008) or using model substances (e.g., Susanto et al., 2007). The hydrophobicity of components in water on fouling has also been intensively investigated (Xiao et al., 2009; Zularisam et al., 2007a; Zularisam et al., 2007b). XAD-8 and XAD-4 resins have been used to separate and isolate the hydrophobic and hydrophilic portions (Kim and Dempsey, 2008). Kim and Dempsey (2008) claimed that hydrophobic/hydrophilic acid in EfOM attributes mostly to the

fouling of a PES UF membrane (more hydrophobic). Jarusutthirak et al. (2002) observed a severe gel layer fouling caused by hydrophobic and transphilic components in EfOM by UF using a polyamide (PA) membrane (more hydrophilic). But in a later study (Jarusutthirak and Amy, 2006), major foulants in EfOM to a PA UF membrane were considered to be hydrophilic macromolecules. In MF (hydrophobic PVDF) filtering wastewater effluent, Liang and Song (2007) reported that the most important foulants in SMP are hydrophobic humic substances and hydrophilic neutrals.

Contrasting experimental results indicate that the interactions between membrane and foulants are far more complicated than that can be interpreted only based on hydrophobic interacions. For instance, the fouling phenomenon can also be impacted by electrostatic conditions of NOM/EfOM foulants and membranes (Liang et al., 2008). Similar to hydrophobicity, electrostatic charge is also a membrane/effluent coupling parameter impacting fouling. As NOM/EfOM in water is commonly negatively charged at neutral pH (Li et al., 2008; Schrader et al., 2005), membranes are negatively charged or modified to be negatively charged to generate repulsive forces against organic fouling. Knowledge of the electrokinetic properties of membranes can be obtained by zeta potential (ζ) measurement (Li et al., 2008). Numerous studies have investigated the effect of electrostatic charge on fouling by changing the pH, ionic strength of the solutions (e.g., Bouzid et al., 2008). Generally, it is believed that solutions with a high ionic strength or in a certain range of pH reduces the electrostatic double layer thickness of both membrane surface and foulants and leads to more severe fouling (Ahn et al., 2008; Narong and James, 2006).

2.5.2 Solution Chemistry

The interacton between foulants and membrane is also influenced by solution chemistry, e.g., solution pH, ionic strength as reviewed in the previous section. In addition to the general ionic strength effect, the divalent cations, especially calcium, have also been considered to be able to enhance NOM/EfOM fouling due to bridging effects (Herzberg et al., 2009; Yamamura et al., 2007b). For calcium ions, they alone play little effect in fouling during low-pressure membrane filtration, but are shown to act as bridging material between carboxylic active groups present in many NOM/EfOM and the negatively charged functional groups present at the membrane surface. Additionally, they can promote the aggregation of organic compounds in solution and lead to more severe pore blocking (Ahn et al., 2008). Using AFM the adhesion force of model organic compounds, e.g., proteins (BSA, Ang and Elimelech, 2007), polysaccharides (Alginate) and humic substances (Lee and Elimelech, 2006) on RO membranes at different feed solution chemistry were compared. The results showed that Ca^{2+} concentration influence the interaction between foulants and the membrane proportionally. The correlation has been confirmed in RO filtering EPS-rich wastewater effluent (Herzberg et al., 2009). Nevertheless, in different low-pressure membrane filtration processes calcium ions impact fouling development in different manners. In contrast to a significant correlation between calcium concentration and fouling development in a MBR system (Liang et al., 2008), no obvious effect can be observed in MF/UF filtering surface water (Yamamura et al., 2007b). In UF of wastewater effluent, Hamberkamp (2008) observed a slight reduction of irreversible fouling when the Ca^{2+} concentration increased from 2 to over 80 mg/L. It seems that in low-pressure membrane filtration, within its typical concentration range, calcium does not to be an

influential factor in NOM/EfOM fouling as it performs in high-pressure membrane filtration (Amy, 2008).

2.5.3 Co-effect of different Organic Foulants

When various foulant types are present in wastewater effluents, the possibility of one foulant type binding to another will change the physical (size and molecular weight) and chemical (charge and hydrophobicity) characteristics of the combined foulant type (Ang and Elimelech, 2008). Jermann et al. (2007) investigated the interaction effect between humic acid and polysaccharide (alginate) in dead-end UF. The results showed that the addition of humic acid into polysaccharide solution led to more severe irreversible fouling due to the adsorption of humic acid onto the membrane. Based on the finding that alginate (polysaccharide) can cause more severe fouling compared to other substances in MF (Negaresh et al., 2006), Nagaresh (2007) investigated the co-effect of polysaccharides (alginate) and proteins (bovine serum albumin – BSA) and showed that the addition of protein results in different fouling behavior as filtering polysaccharide samples alone.

This short review indicates that the fouling phenomena in UF membrane filtration for wastewater reclamation are highly complicated. The interaction between foulants and membrane depends on the characteristics of the foulants, membrane and solution chemistry. This suggests that for the investigation of fouling phenomena, the experimental condition (e.g. membrane material, source water) in either lab-scale or pilot-scale tests should be comparable. On the other side, it has also been illustrated that organic foulants, in EfOM-containing water referred to SMPs, which are mainly characterized as polysaccharides and proteins, play a central role in fouling phenomenon.

2.6 Quantification of Fouling Potential

The content of proteins and polysaccharides can be quantified using different photometric methods (Raunkjaer et al., 1994). Some methods have been widely used in MBR systems to indicate the fouling potential of treated wastewater (e.g. Rosenberger et al., 2005). A good correlation between the content of polysaccharides and/or proteins and fouling development has also been reported by several studies (Al-Halbouni et al., 2008; Rosenberger et al., 2006). Based on Lowry method (Lowry et al., 1951) and Dubois method (Dubois et al., 1956), an automatic online measurement system has also been developed (Mehrez et al., 2007).

In contrast to that in a MBR system, little relationship between the content of the photometrically determined SMP foulants and fouling has been found in membrane filtration of SE (e.g. Poele et al., 2004). Poele et al. (2004) compared the filterability of pre-filtered SE and the content of proteins and polysaccharides. It is evident that the improvement of filterability after size fraction is mainly attributed to the the removal of macromolecules within the size range of 0.1 to 0.45 μm. However, the photometrically quantified SMP cannot reflect a proportional variation of the content of these organic compounds after size fraction. To test the usability of photometrically quantified proteins and polysaccharides in presenting the fouling potential of wastewater effluent, further investigations need to be performed.

The content of colloidal foulants can be reflected by the modified fouling index (MFI) which is based on the filtration curve filtering colloid-containing water using a membrane with a pore size of 0.45 µm under constant pressure (Schippers and Verdouw, 1980, Eq. 2-8). The MFI is the slope of the linear regression between t/V plotted against V (t: filtration time, V: permeate volume) during cake/gel filtration. Originally, MFI is used to assess the colloidal fouling in RO systems. A similar method was used to quantify the content of high molecular polymers in surface water lower than the µg/L range (Jekel and Boeckle, 1982). Compared to the traditional silt density index (SDI, also known as fouling index, Dupont de Nemours and Co. 1977) which can be poorly interpreted theoretically, this method is based on well defined cake/gel filtration theory (Schippers and Verdouw, 1980).

$$MFI = \frac{d(\frac{t}{V})}{d(V)} = \frac{\eta \cdot R_f}{2 \cdot \Delta P \cdot A^2} \quad \text{Eq. 2-8}$$

Where
MFI = membrane fouling index
t = filtration time, s
V = cumulative permeate volume, m^3
R_f = resistance of the fouling, 1/m
A = area of the membrane, m^2
ΔP = trans-membrane pressure, N/m^2

Adapted to UF membrane filtration, MFI is altered as MFI-UF and specific ultrafiltration resistance (SUR) to fit the pore size of the correspondingly used UF membranes (Boerlage et al., 2003; Roorda, 2004). Actually, these indicators present the hydraulic fouling resistance plotted vs. permeate volume under different operational conditions (Roorda, 2004). Using SUR as a parameter, it was identified that the major foulants in wastewater effluents are within the size range of 0.1 to 0.2 µm. The water with a higher SUR value, which indicates a lower filterability, is related to a more severe irreversible fouling problem (Roorda and van der Graaf, 2005). Recently, a unified membrane fouling index (UMFI) has been developed to assess the fouling potential of NOM-containing water in MF and UF processes operated at constant flux (Huang et al., 2008a). Using this indictor, Amy (2008) showed a significant positive correlation between the UMFI value and irreversible fouling. These results indicate that under certain conditions the increase of major foulant content can be reflected by fouling indicators.

Simultaneously, it should be noted that the nature of foulants play also an important role in determining the interaction between foulants and the membrane (Amy, 2008; Haberkamp, 2008). When organic matter is the primary cause of membrane fouling, the indicators are lacking in information about their properties. An understanding of the characteristics of major organic foulants and their quantity in feedwater is otherwise required for fouling control and selection of cleaning strategies. Therefore, a simultaneous characterization of these colloidal organic foulants is necessarily required. This calls for a comprehensive parameter reflecting size distribution, characteristics and quantity of organic foulants simultaneously.

Liquid chromatography with high sensitive and online multi-detectors, e.g. online organic carbon detection, UV_{254} absorption detection and organic nitrogen detection (LC-OCD-UVD-OND), can be applied to identify major organic foulants in treated domestic wastewater considering molecular size, aromatic characteristics and magnitude of organic carbon and nitrogen simultaneously (Huber, 1998). It has been reported that the fraction of large dissolved organic molecules defined as biopolymers contribute more significantly to permeability reduction of a UF membrane than other DOC fractions in filtering wastewater effluent (Laabs et al., 2006). They may be organic colloids, e.g. polysaccharides, proteins (Laabs, 2004; Her et al., 2003). A significant correlationship between biopolymer content and hydraulic fouling resistance in UF of treated wastewater was presented by Haberkamp (2008). In respect to irreversible fouling, it is stated that the content of protein-like substances may play a more important role than other compounds. As the fouling potential of organic foulants is not universal but membrane-specific (Huang et al., 2007), further investigations are needed to get more insight into fouling phenomena in UF of wastewater effluents.

2.7 Fouling Control

2.7.1 Fouling Control by Pre-treatment Processes

Along with the fouling problem in membrane filtration for wastewater reclamation, different pre-treatment processes have been investigated to remove foulants and improve the performance of the downstream membrane processes (Li et al., 2008). The pre-treatment processes can briefly be classified into coagulation / flocculation (pre-coagulation / sedimentation, in-line coagulation, pre-flocculation), adsorption, oxidation, ion exchange, pre-filtration (rapid sand filtration, sieve filtration), bio-filtration and their combinations. An overview of these pre-treatment processes in respect to foulants removal prior to UF is shown in Tab. 2-2.

As simple and cost effective measure, bio-filtration demonstrates the potential to remove foulants prior to membrane filtration (Huck and Sozanski, 2008; Hallé et al., 2009). Natural bio-filtration processes such as river bank filtration (RBF) and soil aquifer treatment (SAT) have been verified as effective processes reducing foulant content in SEs and improving the performance of membrane filtration (Sperlich et al., 2008; Jarusutthirak, 2002). To reduce area requirements bio-filtration can be operated at higher filtration rates. However, although biological (rapid) sand filtration (BSF, filtration rate > 5 m/h) can improve the performance of MF in wastewater reclamation (Xie et al., 2008), it showed little effect on the improvement of the performance of UF (Roorda, 2004; Poele, 2006). The foulant removal effect has been determined to be influenced by the filtration rate. A suitable filtration rate range needs to be identified to operate bio-filtration as fouling control process prior to UF.

Tab. 2-2 Overview of fouling control pre-treatment processes prior to membrane filtration for wastewater reclamation

Technical process	Process description	Possible fouling control mechanisms	Shortages of the process in practice	references
Coagulation /flocculation	Addition of chemicals (coagulants) into feed water / sedimentation	Increase size of particles and colloids, promote cake layer formation and reduce irreversible fouling	Coagulate residual in membrane matrix Increase of solid loading to membrane Requirement of sludge disposal	Haberkamp et al., 2007 Bagga et al., 2008
Advanced oxidation	Dosing oxidants into feed water	Break up large organic molecules into smaller ones	Requirement of anti-oxidation membrane Possible generation of disinfection by-products	Wang et al., 2007 Huang et al., 2008c
Adsorption	Feed water flow through adsorbent filter or dosing adsorbents into feed water	Adsorb organics onto adsorbents	Reduction of foulants removal efficiency due to competitive adsorption Disposal or regeneration of adsorbents	Haberkamp et al., 2007 Fan et al., 2008
Ion exchange	Feed water flow through ion exchange bed	Remove low and medium MW fraction molecules	Low removal rate of large molecules Sensitive to water quality Regeneration and disposal of resins	Fan et al., 2008 Zhang et al., 2006b
Pre-filtration	Filtering feed water using sand filter or sieve-filter	Remove suspended and large colloids, protect membrane module from clogging	Little effect on irreversible fouling control	Roorda, 2004 Poele, 2006 Fan et al., 2008
Bio-filtration	Filtering feed water using bio-filter	Remove particles, colloids and dissolved substances through straining, adsorption and biological degradation	Requirement of filtration area	Huck and Sozanski, 2008 van der Hoek et al., 2000 Jarusutthirak, 2002

Compared to bank-filtration processes, slow sand filtration is an engineered bio-filtration unit with higher filtration rate and shorter residence time (Tab. 2-3). In advanced wastewater treatment it can be used as a tertiary filtration section for removing suspended solids or turbidity, total microorganisms, biological oxygen demand (BOD), chemical oxygen demand (COD) and ammonia nitrogen (Ellis, 1987). Although slow sand filtration decreases the colloidal fouling potential in membrane filtration (Downing et al., 2002; van der Hoek et al., 2000), little is known about its effect on organic foulants removal and subsequent influence on the performance of UF. To eliminate this knowledge gap is one of the major objectives of the present research.

Tab. 2-3 Design/Operational Parameters/Conditions for biological (rapid) sand filtration (BSFn), slow sand filtration (SSFn), river bank filtration (RBFn) and SAT (Adapted from Amy et al., 2006)

Condition/Process	BSFn	SSFn	RBFn	SAT
Travel Distance	≤2 m	≈1 m	≥10 m	≥30 m
Travel Time	≤10 min	≥2 hours	≥1 day	≥ 2 weeks
Filtration Rate	≥ 5 m/h	≤ 0.5m/h	≤ 1m/day	≤ 1m/day
Schmutzdecke*	no	yes	yes	yes
Fouling Control Effect to UF	poor (Roorda, 2004 Poele, 2006)	good (Zheng et al., 2009b)	very good (Sperlich et al., 2008)	excellent (Jarusutthirak, 2002)
Flow Regime	saturated	saturated	un/saturated	un/saturated
Redox	oxic (aerobic)	oxic (aerobic)	an/oxic (aerobic)	an/oxic (aerobic)

Schmutzdecke*: the so-called filter skin (dirt layer in German) on the sand bed which consists of sediment and adjusted organic and inorganic particles, a biofilm made of different microorganisms, protozoa and mesozoa (Ellis, 1985)

As a bio-filtration process, the performance of slow sand filtration is affected by operational conditions. A study in advanced wastewater treatment using slow sand filtration (Ellis, 1987) showed that filtration rate influences contaminant removal and the length of operational run time for sand scraping. Investigations on slow sand filtration in drinking water treatment show that temperature, source water characteristics, filtration rate and the extent of surface ripening have the most significant effect on the performance in terms of water quality control (Amy et al., 2006). So far, the influence of operational conditions on the removal of organic foulants by slow sand filtration has little been investigated.

2.7.2 Influence of Operational Conditions on Fouling

Impact of Operational Conditions on Fouling Development

Besides the quality and quantity of foulants, properties of membranes and chemical circumstances, fouling extent in membrane filtration is also influenced by operational conditions (Huang et al., 2007; Wang et al., 2008; Amy and Cho, 1999). The interactions between foulants and membrane and among foulants in the fouling layer can be significantly changed in terms of resistance and reversibility under different operating conditions (Le-Clech et al., 2006). For instance, flux affects the development of fouling: 'there exists a flux below which a decline of flux with time does not occur; above this flux, fouling is observed. This flux is

termed as the critical flux' (Field et al., 1995). Although in long-term operation fouling is inevitable such as by filtering treated wastewater (Pollice et al., 2005), fouling development can be mitigated by means of operating membrane filtration at a sustainable flux which is defined as 'the flux for which the TMP increases gradually at an acceptable rate, such that chemical cleaning is not necessary' (Ng et al., 2005). Choosing suitable operational strategies is helpful to control the development of fouling and maintain membrane processes operated in an economically acceptable level.

In dead-end UF membranes operated at constant flux, operational conditions such as flux and duration of filtration (backwash interval: BWI) and relaxation time are the main parameters investigated. Decarolis (2001) showed that BWI in dead-end UF of tertiary effluent could be set between 15 to 30 minutes. The extension of BWI led to higher foulant load on the membrane and more severe fouling. Based on the water quality of SE, the filtration flux was suggested to be maintained at 50 to 60 LMH (Roorda, 2004; Poele, 2006). Higher flux results in a higher foulant load on the membrane and leads to a more compact fouling layer (due to higher pressure applied) which is more difficult to be removed (Kim and DiGiano, 2006; Decarolis et al., 2001).

The removal of reversible fouling can be improved by membrane relaxation which can be achieved by withdrawing pressure during filtration. Membrane relaxation is also called as non-continuous operation of membrane (Le-Clech et al., 2006). Under relaxation, back transport of foulants is naturally enhanced as non-irreversibly attached foulants can diffuse away from the membrane surface through the concentration gradient. During UF of treated wastewater the effect of relaxation was affected by the magnitude of solids and solvable fractions accumulated at the membrane surface and the applied pressure during filtration (Smith et al., 2006). Although combined with cross-flow and/or backwashing relaxation can mitigate fouling phenomena, this type of operation is considered as economically unfeasible under certain conditions (Le-Clech et al., 2006).

Characterization of Fouling Layer

The structure of a fouling layer is considered to play a significant role in the stability of the fouling (Wang and Waite, 2008b). To characterize the fouling layers under pressure, the specific fouling resistance and the compressibility of the layer can be investigated based on cake filtration theory. It is assumed that the macrosolutes rejected by the membrane form a solid cake/gel layer, which causes fouling resistance to increases in proportion to the magnitude of the delivered foulants to the membrane surface. According to this definition fouling layer resistance can be calculated using Eq.2-9:

$$R_c = \alpha \cdot m_c = \alpha \cdot c_s \cdot V \quad \text{Eq.2-9}$$

where
R_c = resistance of cake/gel layer, 1/m
α = specific cake/gel resistance (fouling resistance per unit dry weight of foulants), m/kg
m_c = dry weight of foulants per unit membrane area, kg/m^2
c_s = foulant concentration, kg/m^3
V = permeate volume, m^3

Tab. 2-4 Specific fouling resistance and compressibility of fouling layer in low-pressure membrane filtering EPS, activated sludge or NOM content waters

reference	Membrane type	Feed water and operating conditions	Specific fouling resistance α (m/kg)	Compressibility s
Torrestiana-Sanchez et al., 2007	Polysulphone UF MWCO 500 k Da	Xanthan solution Constant TMP 3.45 bar	$11\text{-}63 \times 10^{15}$ (Variation due to concentration of KCl and isopropanol)	-
Ye et al., 2005	Hydrophilic PVDF MF Pore size 0.22 µm	Sodium alginate solution Constant TMP 0.8 bar Constant flux 50 LMH	$5.6\text{-}8.9 \times 10^{15}$ $5.9\text{-}16 \times 10^{15}$	0.28 0.41
Ho and Zydney, 2001	Four kinds of MF membranes Pore size 0.16-0.2 µm	Bovine serum albumin (BSA) solution Constant pressure 0.02 - 0.7 bar	$0.2\text{-}190 \times 10^{15}$	0.97
Furukawa et al., 2008	Two types of Polysulphone UF MWCO 50 and 750 k Da	MBR treating soy sauce lees Constant TMP 0.5 – 2 bar	$1.53 \times 10^{13} - 1.77 \times 10^{14}$ (Variation due to pressure and membrane type)	1.81
Lodge et al., 2004	Hydrophilic PES UF MWCO 150-200 k Da	Biologically treated wastewater TMP 0.125-1 bar	$3.95\text{-}9.3 \times 10^{15}$ (Depends on TMP)	0.68
Chellam et al., 1998	Hydrophobic polypropylene MF Pore size 0.2 µm	MBR treating domestic wastewater	$0.46\text{-}8.22 \times 10^{14}$	0.65
Mousa, 2007	Six types of UF MWCO from 10 to 150 k Da	Humic acid solution Constant TMP 0.35 bar	$1.3\text{-}4.7 \times 10^{14}$	-
Costa et al., 2006	Cellulose acetate UF MWCO 10 k Da	Humic acid solution Constant 1.4 bar	3.7×10^{15}	-

Many foulants are highly compressible, higher pressure therefore results in an increasing density of the cake/gel layer and thereby increases α. The effect of compressibility can be estimated assuming specific fouling resistance to increase as a power law function with pressure (Eq.2-10).

$$\alpha = \alpha_0 \cdot \Delta P^s \quad \text{Eq.2-10}$$

where

α_0 = specific cake/gel resistance at reference pressure, m/kg

ΔP = TMP, N/m^2

s = compressibility coefficient (s = 0: no compression, increasing value of s represents increasing compressibility)

The compressibility coefficient can then be calculated as following:

$$s = \frac{d(\log \alpha)}{d(\log \Delta P)} \quad \text{Eq.2-11}$$

The specific cake resistance and its compressibility depend on the character of the foulants. Foulants in SE have a biological background (EPS or SMP) and may behave similar to the fractions of microorganims (Roorda, 2004). Tab. 2-4 presents a short summarisation of calculated specific fouling resistance and compressibilities of different organic foulants in low-pressure membrane filtration.

Membrane Cleaning

Membrane cleaning is an integral part of the operation of membrane filtration and has significant impact on the performance of membrane systems. Based on the usage of chemical cleaning reagents, membrane cleaning can be classified into hydraulic cleaning (permeate backwashing) and chemical cleaning.

Backwashing involves reversing the flow through the membrane using the product water (permeate) to remove the foulants accumulated on the membrane surface and clogging the membrane pores. Under certain conditions, air can also be injected in the backwashing permeate in MF to enhance backwashing effect (Li et al., 2008). Normally, backwashing is considered to be effective in removing particulate and colloidal foulants (Liu et al., 2006). The effect of backwashing is significantly correlated with the amount of solids and solvable fractions deposited on the membrane surface (Wu et al., 2008).

Investigations on the effect of backwash strength and duration on the restoration of membrane flux were conducted by several studies (Huang et al., 2007; Kim and DiGiano, 2006; Kennedy et al., 1998). It is stated that either the extension of backwashing time or the enhancement of backwashing flux can improve fouling control effect. The efficiency of backwashing is shown to be more dependent on duration than flux. However, due to the complexity of fouling and in situ operational conditions, determination of backwashing conditions needs considering fouling control effect and permeate recovery rate (P_r, Eq. 2-12, used for dead-end filtration processes). They are generally obtained by trial and error procedure based on suggestions of the membrane manufactures.

$$P_r = \frac{V - V_{bw}}{V} \times 100\% \quad \text{Eq.2-12}$$

P_r = permeate recovery, %
V = permeate volume, m^3
V_{bw} = permeate volume used for backwash, m^3

As irreversible fouling is inevitable, after some operating time the membrane must be chemically cleaned to restore its permeability. In practice, chemical cleaning can be conducted either in place/in-line (CIP: the membrane module is cleaned without removing it from the installation) or out of place/off-line (COP: the membrane module is cleaned from the system and soaked in chemicals). A generally used CIP measure is chemically enhanced backwash (CEBW). Chemicals can be added into backwash water (with soaking 3 – 5 minutes, (Teodosiu et al., 1999)/ or recirculation for 10 – 15 minutes, Li et al., 2008) to improve/enhance foulant removal effect through backwashing. In practice, different chemicals can be used as backwashing reagents based on different foulant removal mechanisms (Tab. 2-5). Considering the components in feed water, chlorine (Decarolis et al., 2001; Roorda, 2004), sodium hydroxide or critic acid (Teodosiu et al., 1999; Panglisch et al., 2007) can be chosen. The major removal mechanisms are listed in Tab. 2-5. Recently, demineralised water has also been tested as backwash water in UF filtering NOM-containing water (Li et al., 2009). TMP development can be effectively controlled using demineralised water for backwashing compared to using permeate. This is attributed to the reduction of charge-screening effect around the negatively charged membrane and NOM due to the absence of cations. The calcium-bridging effect between membrane and NOM can also be reduced, simultaneously.

Tab. 2-5 Major categories of membrane cleaning chemicals (Liu et al., 2006; Poele, 2006; Tian et al., 2009)

Category	Major functions	Typical chemicals	Removed foulants
Caustic solutions	Hydrolysis, solubilization, Increase negative charges of functional groups of membrane	NaOH	Polysaccharide, protein, fats, oils, humic substances
Oxidants	Oxidation, disinfection Generate more oxygen containing function groups to improve hydrophilicity	NaClO, H$_2$O$_2$, peroxyacetic acid	Humic substances and other organic foulants
Acids, chelating agents	Solubilization, chelation	Citric acid, nitric acid and EDTA	Scales, metal oxides and also organic foulants
Surfactants	Emulsifying, dispersion, surface conditioning	Surfactants and detergents	Fat, oil, protein and biofilms
Enzymes	Hydrolyse specific functional groups, cut long chains to samller parts	Protease or carbohydrases	Organic foulants (protein, polysacchride, etc.)

In selecting chemical reagents used for membrane cleaning, different reagents have been investigated. Poele (2006) tested the cleaning effect of alkaline, acid, enzyme protoase and amylase on a fouled UF membrane after filtering SE. It is reported that using the combination of alkaline and enzyme protease the permeability of a fouled membrane can be largely restored. In contrast, the use of enzyme amylase after alkaline cleaning results in little further

improvement. The results suggested that a combination of alkaline and suitable enzyme is an effective method to remove the foulants. A consecutive use of NaOH (1%) and ethanol has been developed by Tian et al. (2009) in removing NOM foulants in UF of surface water. For a fouled membrane, the use of ethanol after alkaline cleaning can improve the cleaning effect significantly. Additionally, ethanol shows positive effect in reducing the hydrophobicity of the fouled polyvinyl chloride (PVC) membrane. Although the cleaning strategies of fouled low-pressure membranes have been also investigated in other several studies (Yamamura et al., 2007a; Kimura et al., 2004), the utilization of cleaning agents are mostly based on the recommendations from membrane manufactures due to the limited understanding of fouling mechanisms. Liu et al. (2006) made an attempt to explain the interactions between foulants and the membrane, among different foulants and between foulants and cleaning chemicals. Their interpretation is based on the electrostatic and hydrophobic/hydrophilic interactions theory. A summarization of the effects of different cleaning reagents and the removed foulants is shown in detail in Tab. 2-5. These advances may help membrane operators to find out suitable cleaning reagents.

3 Material and Analysis

3.1 Lab and Pilot-scale UF Membrane Filtration Test

Membranes used in Lab and Pilot-scale UF Experiments

In the present work, lab and pilot-scale membrane filtration tests have been carried out to study the fouling potential of different wastewater effluents. To make the results more comparable, UF membranes with similar properties in lab and pilot-scale experiments have been applied. Important characteristics of the membranes are shown in Tab. 3-1.

Tab. 3-1 Properties of applied UF membranes in lab and pilot-scale membrane filtration tests

UF membrane property	Used in lab-scale test	Used in pilot-scale plant
Manufacturer	Microdyn-Nadir GmbH	Inge AG
Material	Hydrohilized PES	Hydrophilized PES
MWCO (Da) / pore size (µm)	150 k Da[a] / 0.026 µm[b]	100 k Da[a] / 0.02 µm[b]
Average permeability (L/(m²·h·bar)) @20ºC	650	530
Zeta Potential (mV)	-42[c]	-20[a]
Contact angle	53 ± 2.5[c]	n.m. (total wetting)[a]
Membrane configuration	flat membrane (UP150)	multi-bore hollow fibre membrane (for module dizzer® 450)
Operational conditions	Constant pressure Dead-end	Constant flux Dead-end

a: offered by the membrane manufacturers
b: calculated based on the relationship between the hydrodynamic diameter of a molecule (dextran) and its MWCO (Crittenden et al., 2006)
c: measured by Haberkamp (2008)
n.m.: not measured

Lab-scale UF Tests

A filtration cell with a volume of 200 mL (Amicon 8200, Millipore, U.S.A) and UP150 membrane (Microdyn-Nadir GmbH, Germany) with an effective filtration area of $2.87 \cdot 10^{-3}$ m² have been used to determine the fouling potential of different waters. As shown in Fig. 3-1, due to an attached feed reservoir, up to 4 litres of water could be filtered in each experiment in dead-end mode under a certain pressure offered by a nitrogen cylinder. The flux was measured using a balance (Sartorius-basic) connected to a computer. The weight of the collected permeate is automatically stored by data loggers in a minute frequency.
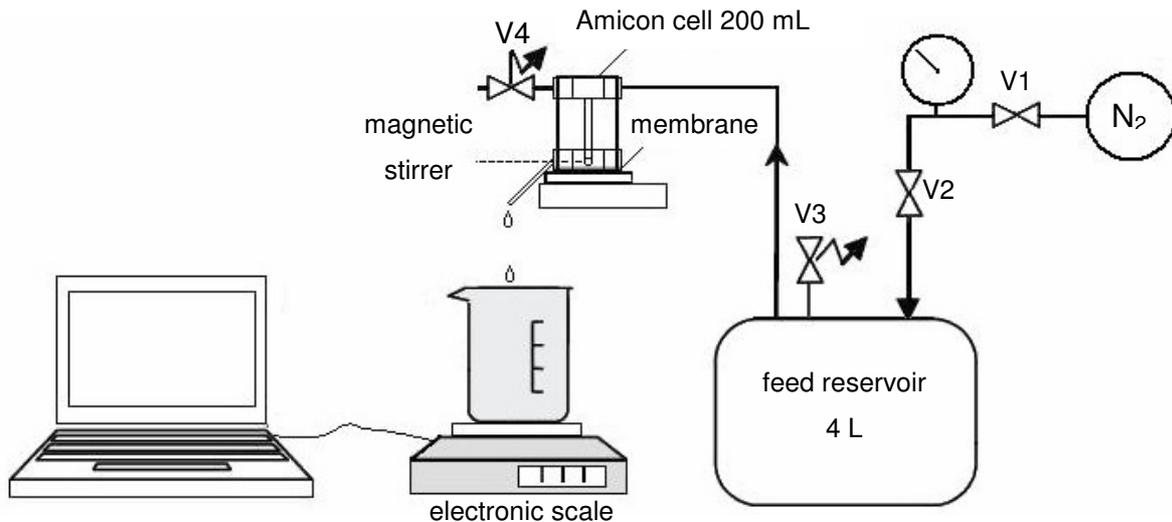
Fig. 3-1 Schematic illustration of the Amicon system (V1: nitrogen gas valve, V2: pressure reducer valve, V3: relief valve of the feed reservoir, V4: relief valve of Amicon cell)

The fouling potential test includes the determination of the filterability of a water sample and the reversibility of the correspondingly formed fouling. The filterability is determined by one cycle filtration test which is standardized in the present work as the normalized flux decline over 500 mL cumulative permeate volume using a clean membrane. The operation is carried out under a trans-membrane pressure of 1 bar and at a stirring speed of 120 rpm. All experiments are conducted at room temperature around 22°C. For each filtration test a new UP150 membrane is used.

Before commencing determination of the filterability, each membrane is soaked in pure water (R >17.4 mΩ·cm, Elga) at least 24 hours and then filtrated with pure water (1m^3 water / m^2 membrane area) under 1 bar (water filled in the water reservoir is pressurized using nitrogen gas, the pressure is measured using a pressure gauge and the variation of the pressure is controlled within 5% using a valve) to remove wetting agents and production residues. Immediately before the stirred cell test the pure water flux of the membrane is determined by filtering 500 mL pure water. Only membranes within 20% pure water flux variation are chosen for the experiment.

The reversibility of formed fouling in UF using Amicon cell system is defined as normalized flux after several filtration cycles which has already been used in other studies (Jermann et al., 2007; Jermann et al., 2008). The membrane is prepared in the same way as described for the filterability test. Then the water sample is filtered in several filtration cycles. Each filtration cycle included: filtration of 500 mL water sample using the prepared membrane, backwash with 50 mL salt solution at one bar (CaCl$_2$ 2.8 m mol/L, NaCl 5.4 m mol/L in pure water, conductivity around 1200 µS/cm), then filtration of 200 mL pure water at one bar to determine pure water flux. The ratio between the pure water flux at the last cycle and that of the clean membrane is defined as flux recovery. Higher flux recovery indicates that the fouling layer could be more easily removed by backwashing and represents higher fouling reversibility.

Pilot-scale UF Plant
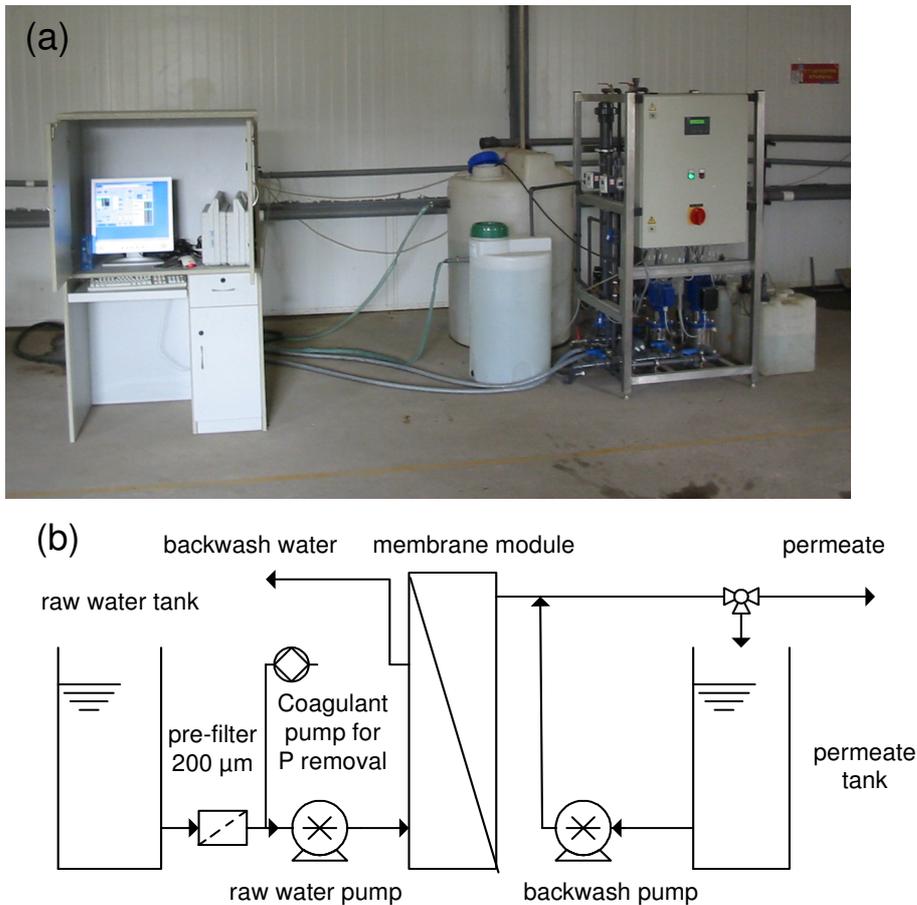
Fig. 3-2 (a) The photo of the W.E.T UF pilot plant system equipped with Inge Dizzer® 450 module and (b) the schematic diagram of the UF system

An UF pilot plant (W.E.T, Germany) with a hydrophilized PES membrane (Dizzer® 450, Inge AG, Germany) is used to filter different effluents (Fig. 3-2). The membrane module has a filtration area of $4.5m^2$ and the MWCO of the membrane is around 100 kDa. The specific permeability of the membrane at 20°C is about 530 L/(m^2·h·bar) (tested with tap water). It is operated in dead-end filtration mode. Based on the water quality of the feed water, the pilot plant is suggested to be operated at 50 - 140 LMH with a filtration time from 10 – 60 minutes and a backwash time of 15 – 60 seconds. The membrane is able to withstand pH range 1-13 and has a high tolerance to free chlorine (200 ppm) and hydrogen peroxide (500 ppm). The arrangement of seven capillaries in one fiber results in high mechanical strength against fiber breaking during intensive hydraulic backwash at a flux as high as 260 LMH (per Inge AG).

3.2 Pilot-scale Bio-filtration Systems

### 3.2.1 Short-term Bank-filtration in WWTP Beixiaohe-Beijing
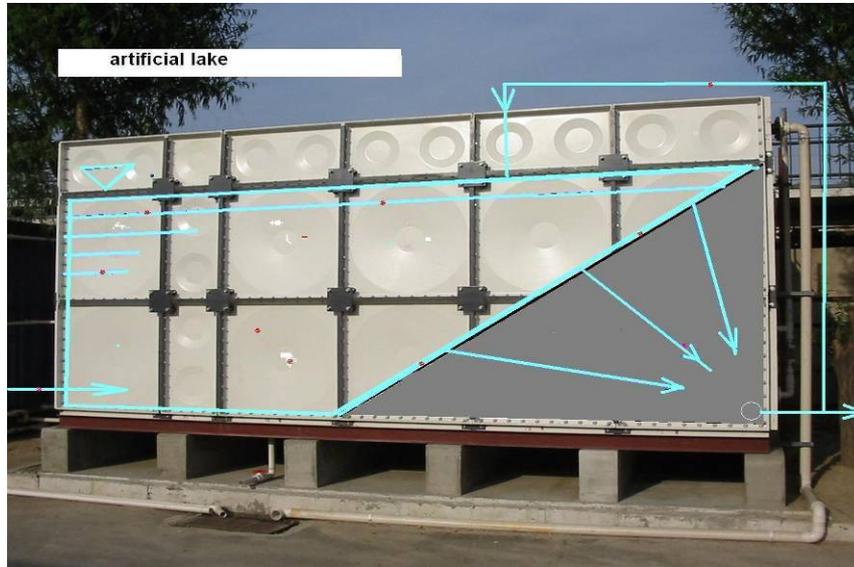
Fig. 3-3 Illustration of short-term bank filtration in the artificial lake in WWTP Beixiaohe

The WWTP Beixiaohe is the first domestic wastewater treatment plant in Beijing, China. With a treatment capacity of 70 000 m^3/d it serves for more than 0.4 millions inhabitants. In 2008, it was decided to integrate a membrane bioreactor (MBR) system in the extension of the plant. Based on the plans for the Olympic Green (Olympic Game 2008, Beijing) and the extension plan for the WWTP Beixiaohe, a wastewater reuse concept has been developed (Ernst et al., 2007). Effluent of a MBR with in-situ P-precipitation would be treated to two different qualities, depending on the reuse purpose. In the first treatment step, phosphate as an essential nutrient is removed by adsorption onto granular ferric hydroxide (GFH) and the water is pumped into an artificial lake for scenic impoundment. The lake water is then filtered using lake-bank filtration for further removal of organic compounds as a fouling control step for a downstream operated UF.

Tab. 3-2 Average water quality of the lake water in WWTP Beixiaohe in 2005

Parameter	COD	Turbidity	TN	NH_4^+-N	TP	pH
	mg/L	NTU	mg/L	mg/L	mg/L	
Average	11	0.6	10	0.8	< 0.05	7.9

The concept was realized in 2005. More information about the whole treatment process was introduced in a previous study (Sperlich et al., 2008). For bank filtration, an artificial lake (L×W×H: 5.5m×5.5m×2.5m) was constructed and was put into operation in 2005 (Fig. 3-3). The applied filtration materials are sand (grain size 2 – 4 mm) and limestone (grain size 3 – 6 mm) which were set up in two separated containers to form embankments. At start-up, the lake was filled with 95 % drinking water, supplemented by 5% treated waste water. In order to facilitate the settlement of planktonic organisms, plankton samples were taken from four

lakes in Beijing and the lake was inoculated. On the surface of each bank, a layer of textile was situated to ensure stability. The bank filtration was operated with a filtration passage in a depth of 1.7 m, a filtration velocity of 1.55 m/d and a travelling time of about 1.1 to 1.5 days. The lake water was the effluent from a MBR pilot plant (Toray, Japan) after flocculation and GFH adsorption. The lake water quality during the experiment period is summarized in Tab. 3-2.

3.2.2 Slow Sand Filtration in WWTP Ruhleben-Berlin

WWTP Ruhleben

With a treatment capacity of 240 000 m^3/d the WWTP Ruhleben is the largest sewage treatment plant in Germany. Raw water, including 20 - 30% industrial wastewater is treated using a conventional activated sludge treatment process with biological/chemical phosphorous removal and biologic nitrification/denitrification (Laabs, 2004). Its annual average effluent quality is summarized in Tab. 3-3.

Tab. 3-3 Wastewater effluent quality of the WWTP Ruhleben (Bahr et al., 2007)

| Parameter	COD mg/L	BOD mg/L	DOC mg/L	TN mg/L	NH_4^+-N mg/L	NO_3^- mg/L	TP mg/L	pH
Average	40±7	3.8±0.5	11.4±0.9	10.3±2.1	0.9±0.6	6.9±1.7	0.28±0.1	7.4±0.2

Slow Sand Filtration
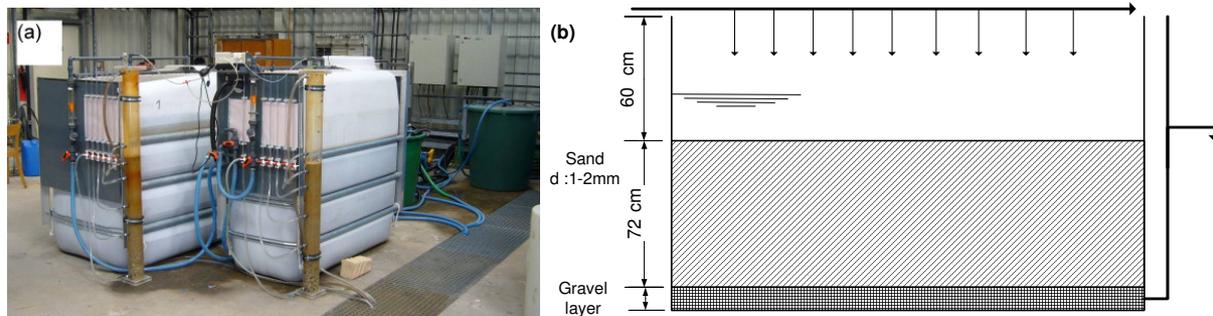
Fig. 3-4 (a) The photo of the slow sand filtration system in WWTP Ruhleben, (b) the schematic diagram of a slow sand filter

Two pilot scale slow sand filters (SSFrs, Fig. 3-4) were operated from September 2006 to December 2007 to treat SE after sieve filtration (pore size 100 μm) from the WWTP Ruhleben Berlin. The filters are operated in down flow mode with a filtration area of 2 m^2 (SSFr Nr. 1) and 1 m^2 (SSFr Nr. 2) respectively. Each filter is filled with silica sand (grain size 1 – 2 mm) for a layer with sickness of 0.7 m. Two gravel layers are placed below it as supporting layer, each with a height of 0.1 m, consisting of gravel with grain size 4-8 mm and 8-12 mm, respectively. The height of the supernatant is 0.6 m. On the outside wall of each filter there are 6 probe sites vertically distributed, the distance of each probe site to the sand surface is 0, 0.1, 0.2, 0.4, 0.6 and 0.8 cm, respectively. In addition to the pilot scale filters, two lab-scale

filters (SSFr Nr. 3 and 4, each with a filtration area of 0.008 m^2 at a filtration rate of 0.05 m/h and 0.1 m/h, respectively) were run simultaneously from September 2006 to July 2007 to investigate the influence of the filtration rate on the performance of slow sand filtration. From August 2007 till to March 2008 SSFr. Nr. 3 and 4 were operated with a protection layer consisting of BioNet (Fig. 3-5 b) to improve the performance of slow sand filtration. The BioNet carriers are porous compressible synthetic materials used in bioreactors. They offer large surface area for adherence and growth of microorganisms and large void volumes for the retention of colloids and particles.
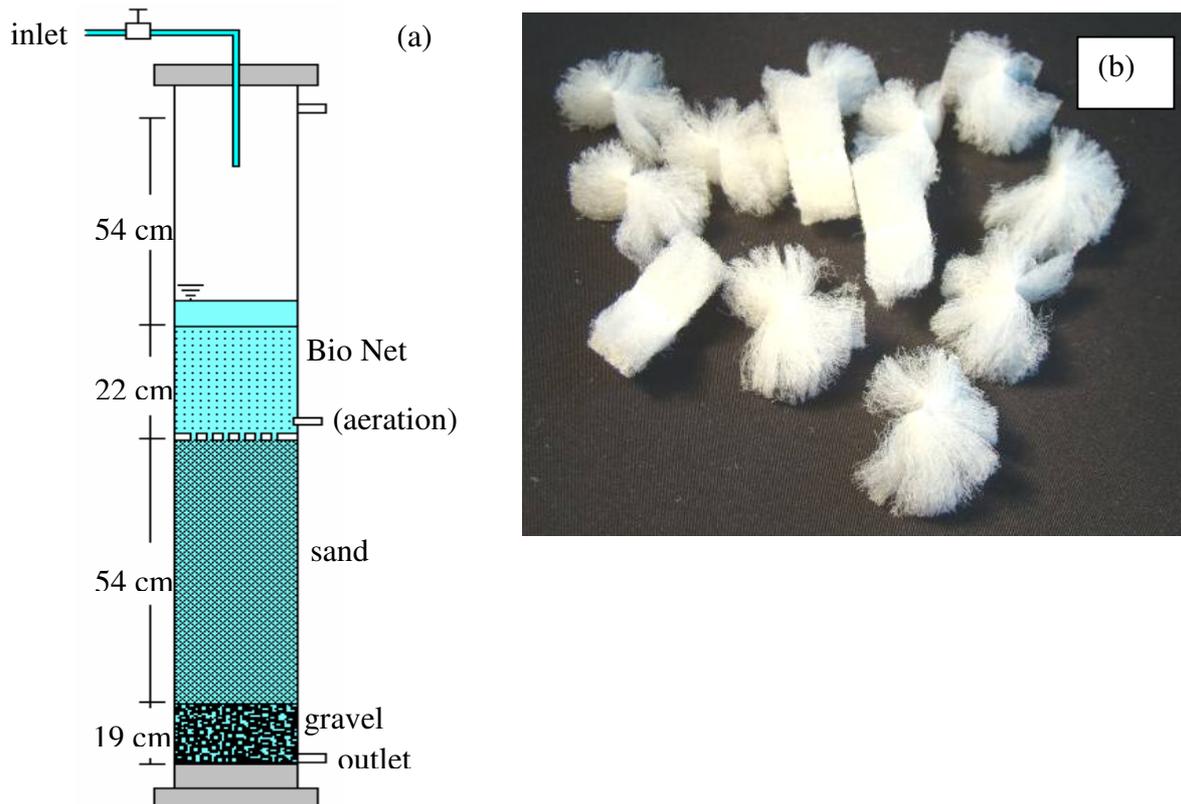

Fig. 3-5 (a) Diagram of a slow sand filter using BioNet as a protect layer (b) foto of BioNet carriers

3.3 Analysis

3.3.1 LC-OCD-UVD-OND

Biopolymer concentration in water samples is analyzed using liquid chromatography (LC, manufacturer DOC-LABOR Dr. Huber, Karlsruhe, Germany) with a dissolved organic carbon detector (OCD) using nondispersive infrared absorption (Ultramat 6, Siemens, Germany), with a dissolved organic nitrogen detector (OND) using UV_{220} absorption (Well Chrom fixed wavelength detector K2001- UV220 Knauer, Germany), with a UV_{254} detector (UVD, K-200-UV254) and a size exclusion chromatography HW55S (GROM Analytik + HPLC GmbH, Germany). The LC unit separates organic compounds according to their molecular size through the size exclusion column. The underlying principle is the diffusion of molecules into the resin pores. The larger molecules elute first as they cannot penetrate into the pores very deeply, while the smaller molecules take more time to diffuse into the pores and out again. The separated compounds are then detected by online detectors and corresponding content

could be converted into concentrations in mg C/L, mg N/L and SUV 1/m respectively. The unit of the concentration in the present thesis is mg C/L (more detail information in appendix 8.1).

3.3.2 Fluorescence Exitation Emission Matrix

Additional identification of the presence of protein-like substances in biopolymer is conducted by fluorescence measurement. Fluorescence of organic matter occurs when a loosely held electron in an atom or a molecule is excited to a higher energy level by the absorption of energy, and fluorescence occurs when energy is lost as light when the electron returns to its original energy level (ground state). The wavelength at which absorption (excitation) and emission occur is specific to the molecules. For protein-like substances, three fluorescent amino acids (tryptrophan, tyrosine and phenylalanine) which contain aromatic ring structure are specific indicators (Hudson et al., 2007).

The excitation emission matrix (EEM) spectroscopy is the state-of-the-art technique in fluorescence measurement. The principal of EEM is that excitation, emission and fluorescence intensity can be scanned over a range of wavelengths synchronously and plotted on a single chart, developing a 'map' of optical space, an EEM. Recent advances in fluorescence spectrophotometry permit the collection of fluorescence data from waters at high optical resolution and the generation of excitation and emission data in the form of excitation-emission wavelengths.

To minimize the influence of the free amino acids and matrix effect in wastewater effluent (Hudson et al., 2007), biopolymers used for the measurement of fluorescence EEM are fractioned using SEC HW55S as following: a 2 mL water sample is injected into the size exclusion column H55 and transported by eluent (consistent see A-Tab. 1). From elution time 20 minutes to the significant increase of UV_{254} signal (around elution time 50 to 55 minutes) the fractioned water sample is collected. The sample is then analyzed using a JYHoriba/Spex Fluoromax-2 fluorometer with a xenonlamp as the excitation source. EEM spectra are a collection of a series of emission spectra over a range of excitation wavelengths. In this experiment, EEM spectra are collected with subsequent scanning emission spectra from 240 to 500 nm at 2 nm increments by varying the excitation wavelength from 300 to 500 nm at 10 nm increments. The presence of lower energy of the emitted photon than that of the excitation energy is due to energy loss from the excited electron by collision, non-radiative decay and other processes prior to emission. Spectral subtraction is performed to remove blank spectra mainly caused by Raman scattering. The data is then treated by a program developed at the Institute for Water Education (UNESCO-IHE, the Netherlands) based on MathLab[®].

3.3.3 Photometric Protein and Polysaccharide Analysis

Measurement of Protein Concentration

Proteins are analysed according to the method developed by Rosenberger (2003) based on the Lowry method (Lowry et al., 1951). Protein concentration is expressed in mg/L using bovine serum albumin (BSA) as a standard. According to the calibration result (within the range of 0 to 30 mg/L) and DIN 32645, the limit of quantification (LOQ) of this method is 1.7 mg/L.

Reagents:

Reagent A: 143 mmol/L NaOH and 270 mM Na_2CO_3 in distilled water

Reagent B: 57 mmol/L $CuSO_4$ in distilled water

Reagent C: 124 mmol/L Na_2-Tartat in distilled water

Reagent D: mixture of reagent A, B and C in a ratio of 100:1:1 (shortly before the measurement)

Reagent E: Folin-Cioucalteau-reagent. 1:2 diluted with dist. water

Reagent A, B, C and E are stable for around 30 d at 4 ℃. Reagent D was prepared shortly before the measurement. The reagents and water samples were slowly warmed to room temperature when needed.

Execution (duplicate determination)

1. 2.5mL water sample and 3.5 mL reagent D are placed into a test tube and quickly mixed for 5 seconds. The mixture stays for 10 minutes at room temperature.
2. 0.5 mL Reagent E is then added quickly into the tube and stirred strongly for 5 seconds
3. The mixture is in still at room temperature for 45 minutes.
4. The wave absorption of each sample is measured in a photometer at the wave length of 750nm (Perkin Elmer UV/VIS Spectrometer Lambda 12, Perkin-Elmer, U.S.A.).
5. The protein concentration is calculated based on the calibration.

Measurement of Polysaccharide Concentration

Polysaccharide were determined using the method developed by Rosenberger (2003) based on the Dubois method (Dubois et al., 1956). The method is based on colour labelling, the absorption of the formed colour is measured at 490 nm in a 4 cm quartz cuvet by a photo spectrometer. The concentration of polysaccharide is expressed in mg/L using D-glucose as a standard. Chemical reagents are 5% phenol solution (in demineralized water) and 95% -97% sulphuric acid (H_2SO_4). According to the calibration result (within the range of 0 to 10 mg/L) and DIN 32645, the LOQ of this method is 0.7 mg/L.

Execution (duplicate determination)

1. 2 mL water sample is added into a test cube and mixed with 2 mL phenol solution by shaking for 10 seconds. The mixture is then in still for 10 minutes at room temperature.
2. 10 mL sulphuric acid is added into the mixture. After in still for 5.5 minutes at room temperature the mixture is shaken for 10 seconds and then in still for 25 minutes at room temperature.
3. The wave absorption of the sample is measured in a photometer at the wave length of 490 nm (Perkin Elmer UV/VIS Spectrometer Lambda 12, Perkin-Elmer, U.S.A.).
4. The polysaccharide concentration is calculated based on the calibration result.

3.3.4 DOC Measurement

A High TOC II (Elementar Analysensysteme GmbH, Germany) is used to measure the DOC concentration of treated wastewater. The DOC content is the difference of carbon content between total carbon (TC) and total inorganic carbon (TIC) measured based on the thermal catalytic method. For TC measurement, the water sample (0.45 µm filtered) is injected into a

cartridge which is heated from 700 ° – 750 ℃ to 850 ° – 920 ℃. The combustion products are then transported by CO_2-free pressure air to the catalyst (CuO at 950 ℃) and oxidized. After the removal of water vapour and halogens, the CO_2 content is quantified by a nondispersive infrared (IR) detector. To measure TIC, the water sample is acidified to lower than pH 2 when it is injected into a sparger. After the removal of water vapour and halogens, the driven out CO_2 is transported by CO_2-free pressure air to the IR detector. The difference of the two carbon contents is the DOC of a water sample. For the standardized measurement of TOC, the detection limit is lower than 0.5 mg/L.

The DOC concentration can also be quantified using LC-OCD using by-pass operting mode based on photochemical oxidation. During measurement, the injected water sample (after 0.45 µm filter) is firstly acided by ortho phosphoric acide to remove inorganic carbons. Subsequently, the water sample is transported by the eluent flow to a rotating Gräntzel thin-film reactor. While being transported along the surface of the reactor, organic contents in water sample are oxidized by UV radiation at a wave length of 185 nm (generated by a low-pressure mercury-vapor lamp). The formed CO_2 is blowed by pure nitrogen gas to the IR detector. Corresponding carbon content can be calculated with the sofeware FIFIKUS® (DOC Labor Dr Huber, Karlsruhe) according to the signal intensity. For DOC measurement, the detection limit is lower than 0.5 mg/L. Compared to the thermal catalytic method which is assumped to have almost 100% oxidation efficiency, the photochemical method demonstrates a DOC recovery over 90% with respect to secondary effluent. This suggests a requirement for improving the oxidation efficiency of the photochemical oxidation process.

3.3.5 On-line Measurement of Oxygen

The oxygen concentration in SE and slow sand filtrate (SSF) is measured using the oxygen meter OXY-4 (Precision Sensing GmbH, Germany). The major components of the instrument are a light source, a photodetector and optical fibers each connected with an oxygen-sensitive minisensor. The principle of the measurement is based on the effect of dynamic luminescence quenching by molecular oxygen. The collision between the luminophoren (on minisensors) in its excited state (caused by light source) and the quencher (oxygen) results in radiationless deactivation. After collision, energy transfer takes place from the excited indicator molecule to oxygen which is consequently transferred from its ground (triplet state) to its excited singlet state. As a result, the indicator molecule does not emit luminescence and the measurable luminescence signal descreases. Based on a proportional correlation between the luminescence intensity and oxygen concentration, the detected luminescence intensity by the photodetector indicates the concentration of oxygen. Calibration of oxygen minisensors is performed using a two-point calibration in oxygen free water (1 g sodium sulfite in 100 mL water) and air-saturated water (20 min air blowing and 10 min stirring in 100 mL water).

3.3.6 Analysis of Bulk Water Quality Parameters

During the experiment, some other bulk water quality parameters were also tested. Tab. 3-4 exhibits the parameters and correspondingly used measurement equipments.

Tab. 3-4 Bulk water quality parameters and corresponding applied measurement equipments

Parameter	Equipment	Producer
UV_{254} (1/m)	Perkin Elmer UV/VIS Spectrometer Lambda 12	Perkin-Elmer GmbH U.S.A.
Turbidity (NTU)	2100 NIS Turbidimeter	HACH
pH	WTW pH 537	WTW, Germany
Temperature (ºC) and conductivity (µS/cm)	WTW LF340	WTW, Germany

4 Identification and Quantification of Major Organic Foulants

In UF of treated domestic wastewater SMP/EPS have been identified as major foulants (Jarusutthirak and Amy, 2006; Laabs et al., 2004; Amy, 2008). Different analysis methods have been applied to quantify the content of these substances and to correlate the results with fouling development (Rosenberger et al., 2005; Laabs, 2004; Roorda, 2004). Nevertheless, due to the high complexity of the fouling phenomenon in UF there has no universal parameter been found reflecting the fouling potential. To detect foulants, the analysis method should be capable of presenting their size, basic chemical characteristics and also quantity, simultaneously.

In this section the influence of size fractioned substances on the filterability of water sample and the reversibility of correspondingly formed fouling layers are quantitatively identified in lab-scale experiments. Based on these results, the major organic foulants have been identifed. The conclusion is verified to be reproducible according to pilot-scale UF results. Fouling mechanisms due to organic foulants in UF of treated domestic wastewater are interpreted using the pore-blocking model. Based on quantitative results, different methods detecting the fouling potential of treated wastewater are compared.

4.1 Identication of Major Foulants

4.1.1 Impact of the Size of Foulants on Filterability

It is considered that in low-pressure membrane filtration colloids and dissolved organic substances in treated wastewater are major foulants. In the current work the substances with a nominal size larger than 1 µm are classified as particles, those with a diameter less than 1 µm are classified as colloids and the materials able to pass through a filter with pore size of 0.45 µm are defined as dissolved substances (Haberkamp, 2008). In this section, the impact on filterability of size fractioned substances is firstly tested (size-fraction using cellulose nitrate filter with nominal pore size of 1.2 µm, 0.45 µm and PES UF membrane (UP150, nominal pore size 0.026 µm)) and the results are displayed in Fig. 4-1. Fig. 4-1(a) shows that direct filtration of SE causes a steep flux decline which indicates the low filterability of the water sample. After the removal of suspend particles (due to pre-filtration with 1.2 µm filter), the filterability is slightly improved. A further removal of the large colloids (due to pre-filtration with 0.45 µm filter) results in an increasing improvement of the filterability. When the UF permeate is filtrated using a new UF again, the normalized flux is significantly increased. The results imply that compared to particles, large colloids and substances smaller than UF pore size, the substances within the size of 0.45 – 0.026 µm have the most significant influence on the filterability of SE. Similar result can be obtained by filtering slow sand filtrate (SSF).
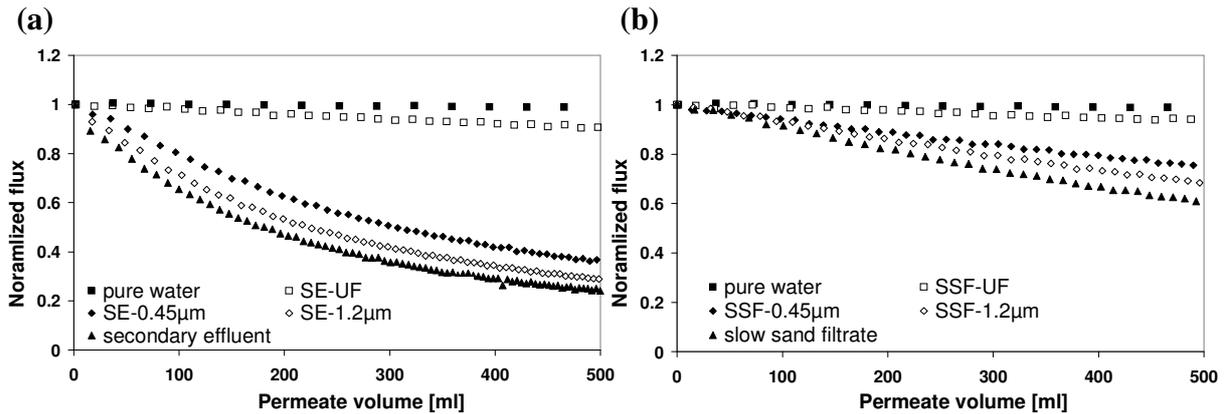
Fig. 4-1 Influence of size fraction in SE and its SSF on filterability. (a) SE, SE after 1.2 µm filter, after 0.45 µm filter and after UP150; (b) SSF at filtration rate 0.25m/h, SSF after 1.2 µm filter, after 0.45 µm filter and UP150

Fouling resistance (calculated based on Eq.2-3) contributions of different fractioned substances are shown in Fig. 4-2. As displayed, in either SE or SSF all fractions (particles, larger colloids and organic residuals) lead to fouling resistance. But, the most pronounced fouling was caused by dissolved substances within the fraction of 0.45 – 0.026 µm. This fraction contributes to more than 50% of the total fouling resistance in both water samples. Although the fractionation neglects the coupling or synergistic effect which may influence the interaction among different compounds, it reflects the importance of dissolved substances in respect to fouling resistance during membrane filtration.
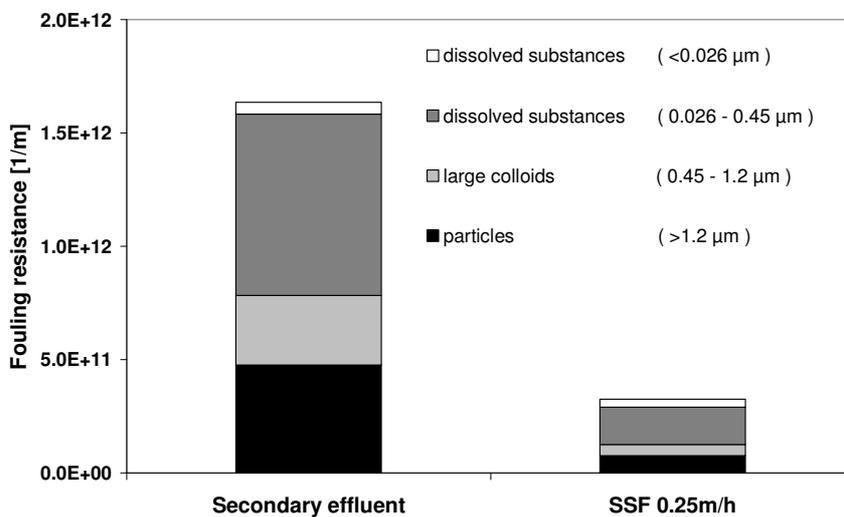
Fig. 4-2 Fouling resistance attributed from different fractioned substances in SE and its SSF

The filterability results show that in treated domestic wastewater the dissolved substances larger than or comparable to UF membrane pore size (0.45 – 0.026 µm) have a predominant influence on the water filterability. These substances play an important role in the fouling phenomenon and need to be identified. In subsequent sections, fouling tests and analytical investigations were focused on these dissolved substances (water sample after 0.45 µm filtration).

4.1.2 Influence of Foulant Content on Water Filterability

Detection of Major Dissolved Organic Foulants Using LC-OCD-UVD-OND

As the DOC concentration in treated domestic wastewater was reduced by around 8% after UF in a Amicon cell (Tab. 4-2), the removed DOC played a major role in the fouling phenomenon and this part of organic matters must be characterized in more details. LC-OCD-UVD-OND was used to determine the removed dissolved substances through UF.

Tab. 4-1 DOC and biopolymer content of SE, permeate of SE and SSFs

Water sample	DOC	Biopolymer peak of LC-OCD-UVD		
		DOC	UV $_{254}$	SUVA
	mg/L	mg C/L	1/m	L/(m·mg)
SE	12.2	0.48	0.31	0.65
Permeate of SE	11.2	< 0.05	n.d.	-
SSF 0.25 m/h	10.0	0.23	0.14	0.61
SSF 0.5 m/h	10.5	0.26	0.16	0.62

SUVA: specific UV absorbance
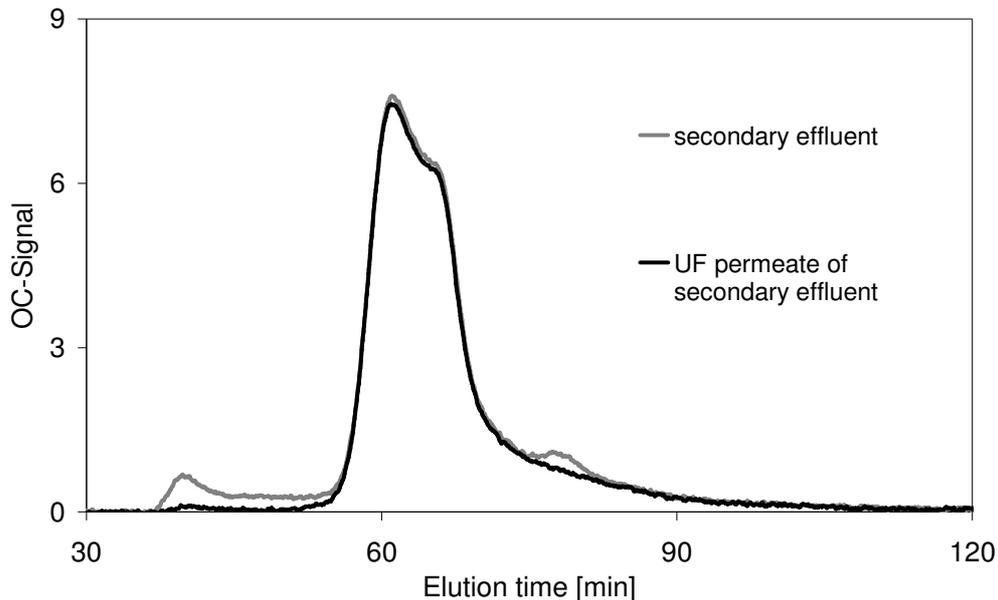
Fig. 4-3 Liquid chromatography (LC-OCD) of SE and its UF permeate

A comparison of the chromatograms of SE and its UF permeate show that the most significant difference appeared at the first peak after an elution time of about 40 minutes (Fig. 4-3). While the SE exhibited a clearly detectable peak, in the UF permeate the peak was mostly removed. As the difference after a retention time of 55 minutes was much smaller than that in this peak, the substances detected in the first peak, which is called biopolymer peak, should

present much higher responsibility for the fouling phenomenon than other organic fractions. Similar results can be obtained by comparing the chromatograms of SSF and its corresponding UF permeate. Based on the calibration results, most detectable substances in the biopolymer peak are considered as large organic molecules. They show comparatively high organic carbon content and low UV absorption (low aromaticity, Tab. 4-1). Organic nitrogen was also detected (data not quantified). They are normally regarded as polysaccharide-like and protein-like substances (Huber, 1998; Her et al., 2003; Amy, 2008).

Correlation between Biopolymer Content and Filterability

Filterability of SE, SSF (at filtration rate of 0.25 and 0.5 m/h) and UF permeate of SE was compared (Fig. 4-4 (a)). It is shown that filtering SE (after 0.45 μm) led to a 87% flux decline for a cumulative permeate volume of 500 mL, while filtering SSFs (after 0.45 μm) at filtration the rate of 0.25 m/h and 0. 5 m/h showed 75% and 78% flux declines, respectively. After UF when the permeate of the SE was filtrated again, it showed a strikingly high permeability compared to SE and SSFs as the normalized flux showed only a 16% decline.
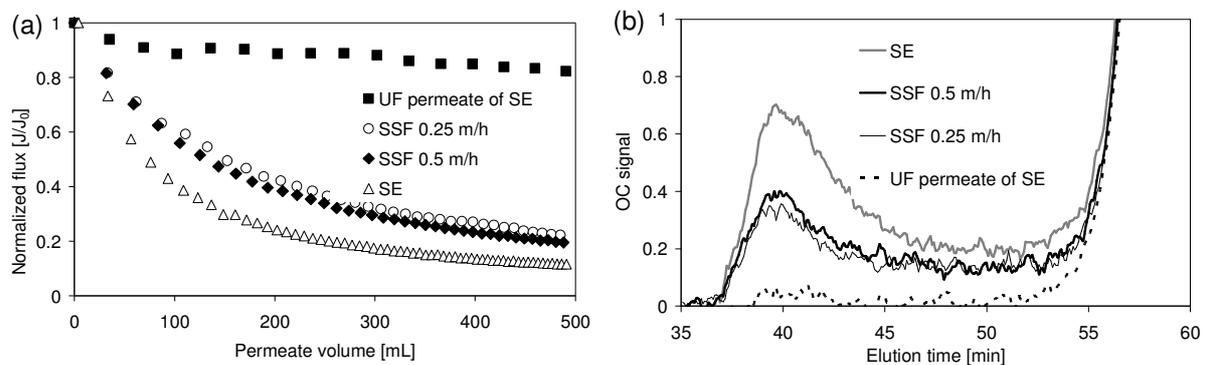
Fig. 4-4 Correlation of filterability and biopolymer peak of different water samples (a) Normalized stirred-cell UF flux decline curves using SE, SSFs and UF permeate over cumulative permeate volume of 500 mL. (b) Biopolymer peaks of SE, UF permeate of SE and SSFs

The biopolymer peaks of corresponding water samples are shown in Fig. 4-4 (b). It is illustrated that SE was of the lowest filterability and it showed the largest biopolymer peak. After slow sand filtration at a filtration rate of 0.5 m/h the filterability was to some extent improved and the peak was reduced to some degree; the SSF at a filtration rate of 0.25 m/h showed a higher filterability and it exhibited a further reduced biopolymer peak; the UF permeate of SE exhibited a much higher filterability and there was much fewer biopolymer detected in it. The comparison suggests that the content of biopolymer in dissolved fractions is negatively correlated with the filterability of corresponding water samples using a UP150 membrane.

Quantitative Relationship between Biopolymer Concentration and Filterability

Since the concentration of biopolymers influences the filterability, water samples with a broader range of biopolymer concentration are tested to quantify the relationship. Fig. 4-5 (a) shows the biopolymer peaks of different water samples. Larger biopolymer peak areas represent higher biopolymer concentrations; Fig. 4-5 (b) displays the filterability of corresponding water samples. Comparison of the results demonstrates that the larger the area of the biopolymer peak is, i.e. the higher the biopolymer concentration in the water sample, the lower the filterability. The fouling resistance results in Fig. 4-5 (c) is in agreement with the filterability performance, water samples with higher biopolymer concentration lead to higher hydraulic resistance and show lower filterability.
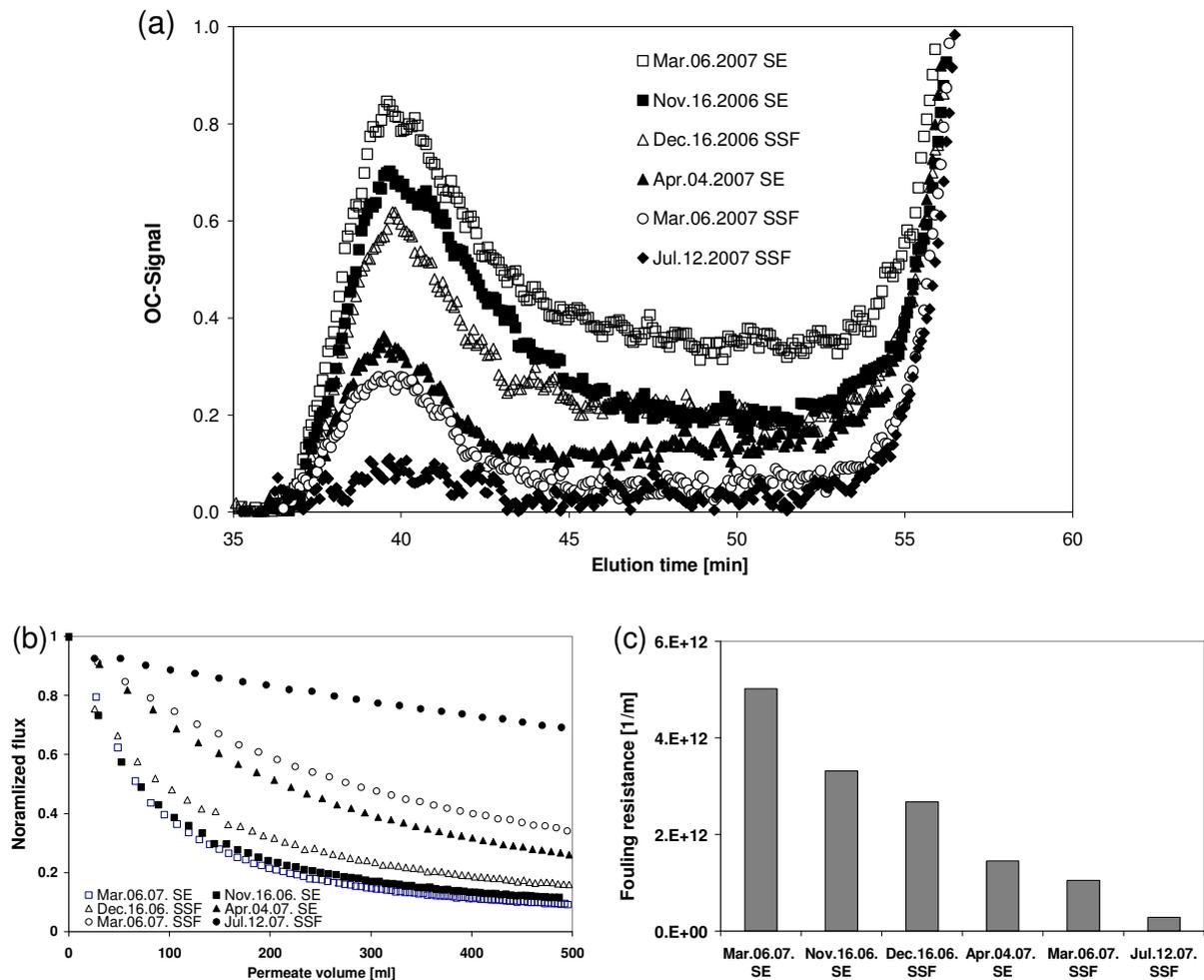
Fig. 4-5 (a) Biopolymer concentration of different water samples, (b) normalized flux of corresponding water samples, UP150, TMP 1 bar, (C) fouling resistance of corresponding water samples (flux data in detail see section 8.3, A-Tab.2)

To derive the relationship between biopolymer concentration and filterability or fouling resistance, results of more water samples are plotted under permeate volume 150 ml, 250 ml and 500 ml and are displayed in Fig. 4-6. Fig. 4-6 (a) and (b) show that for each permeate volume, the relationship shows the same trend: in the range of biopolymer concentrations between 0.05 to 0.58 mg C/L in the present work, water samples with higher biopolymer concentrations show a lower filterability and lead to higher fouling resistance in UF. The rela-

tionship between biopolymer concentration and fouling resistance during the whole filtration process is very striking as the R^2 is higher than 0.95.
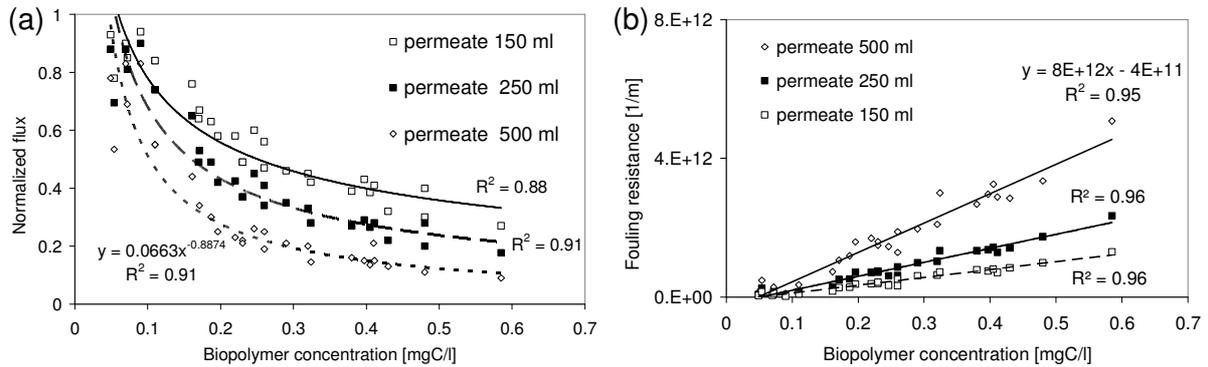

Fig. 4-6 Relationship between biopolymer concentration and (a) filterability (b) fouling resistance under permeate volume 150 mL, 250 mL and 500 mL. (n=26, water samples were taken randomly from Nov.2006 to July 2007 in WWTP Ruhleben, Berlin, Germany)

Verification of the Proportional Correlation

As biopolymers have been demonstrated as major foulants, it is reasonably to deduce that under a similar delivered biopolymer load the normalized flux decline during UF of different water samples should be comparable. To verify this hypothesis, different water samples were filtrated with the same biopolymer load calculated based on Eq.4-1.

$$M_b = C_b \times V \quad \text{Eq. 4-1}$$

where
C_b = biopolymer concentration, mg C/L
V = permeate volume, L
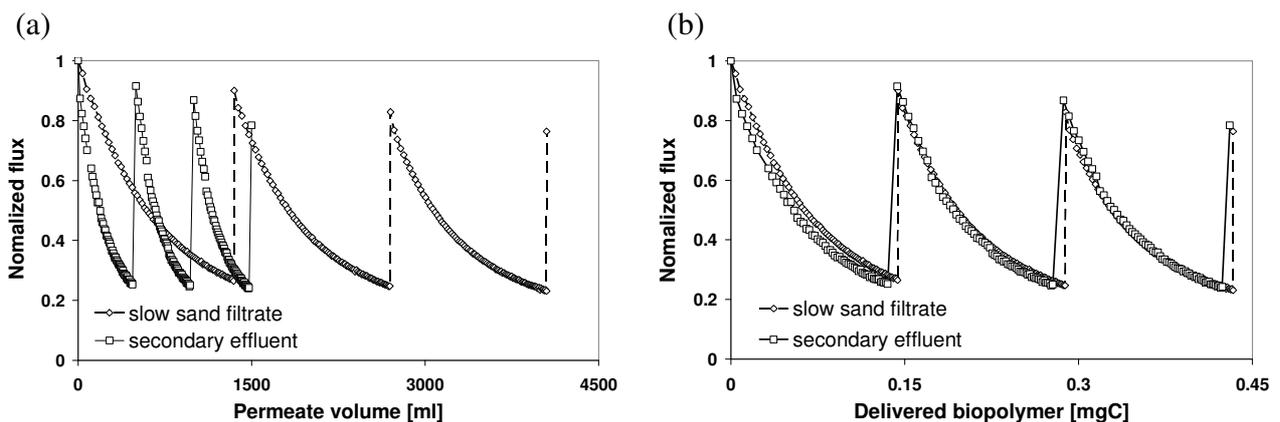
Fig. 4-7 Influence of delivered biopolymer amount on the normalized flux decline of SE and SSF. (a) Normalized flux decline under the same permeate volume; (b) Normalized flux decline under the same delivered biopolymer amount

Relying on Eq.4-1 filtrating 500 mL SE (biopolymer 0.29 mg C/L) or 1350 mL SSF (0.11 mg C/L) result in similar biopolymer loads to the membrane surface. The corresponding results are shown in Fig. 4-7. Under the same permeate volume the normalized flux of SE is much lower than that of SSF since under these conditions filtrating SE leads to more biopolymer

load to the membrane surface (Fig. 4-7 (a)). But for the same load, the normalized flux decline of the two different water samples is almost identical (Fig. 4-7 (b)), after approximately 0.145 mg C (50.5 mg C/m^2 membrane area) delivered biopolymer to the UF membrane surface in each filtration cycle, the normalized fluxes are always similar. The comparison verifies that similar biopolymer load delivered to the membrane surface causes similar fouling effects.

4.1.3 Effect of Foulant Content on the Reversibility of Fouling

Although the hydraulic fouling resistance impacts the efficiency of membrane filtration, for a long-term operation, the reversibility of the formed fouling layer plays a more crucial role on the performance. To investigate the influence of biopolymer concentration on the reversibility of the formed fouling layer in UF membranes, water samples with different biopolymer concentrations were filtered using Amicon cells with five filtration cycles. The results (Fig. 4-8 (a)) show that all of the treated wastewater lead to a flux decline – a permeability reduction during the filtration process. As expected, in each cycle the water samples with higher biopolymer concentrations lead to a more severe flux decline. It was further observed that after each backwash, the higher the biopolymer concentration in the feed water, the lower the reversibility the corresponding fouling was (Fig. 4-8 (b)). Although most of the biopolymers are reversible as most of them are present in the backwash water under the present experimental condition (Fig. 4-9), the results indicate that the more biopolymers are delivered to the membrane surface, the more irreversible the fouling is.

(b)
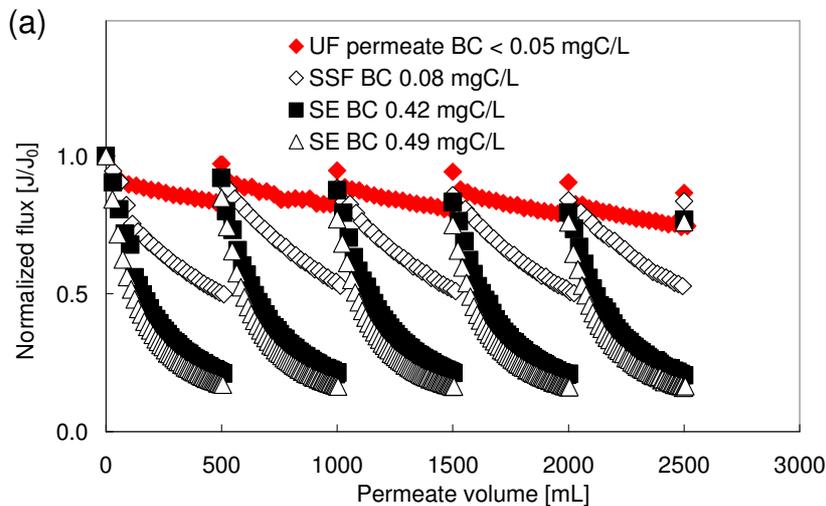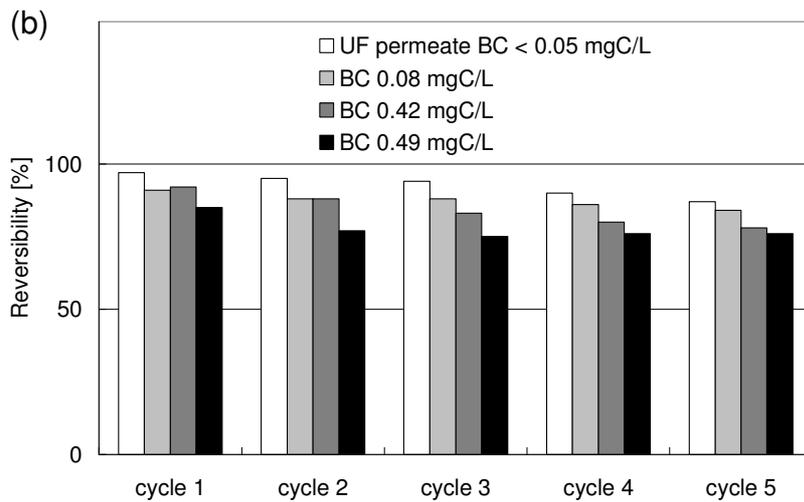
Fig. 4-8 (a) Influence of biopolymer concentration on fouling effect, (b) flux recovery at different biopolymer concentrations (BC: biopolymer concentration, Feed water is SE, SSF and SE UF permeate, operating pressure 1 bar, permeate volume 500 mL; back wash using salt solution 50 mL at 1 bar)

From October 8th 2007 to May 8th 2009 ten water samples (SE, SSF and also UF permeate) were randomly sampled and tested using Amicon cells with five filtration cycles. The correlation between biopolymer concentration and the reversibility of correspondingly formed fouling is displayed in Fig. 4-10 (a). As shown, with an increasing biopolymer concentration in feed water the reversibility of the fouling decreases. This phenomenon is confirmed by Fig. 4-10 (b) which shows that the increase of irreversible fouling resistance is related to the rise of biopolymer concentration. This phenomenon indicates that the more biopolymers delivered to the membrane, the more difficult they can be removed by backwashing. Biopolymers play thus a crucial role in the formation of irreversible fouling.
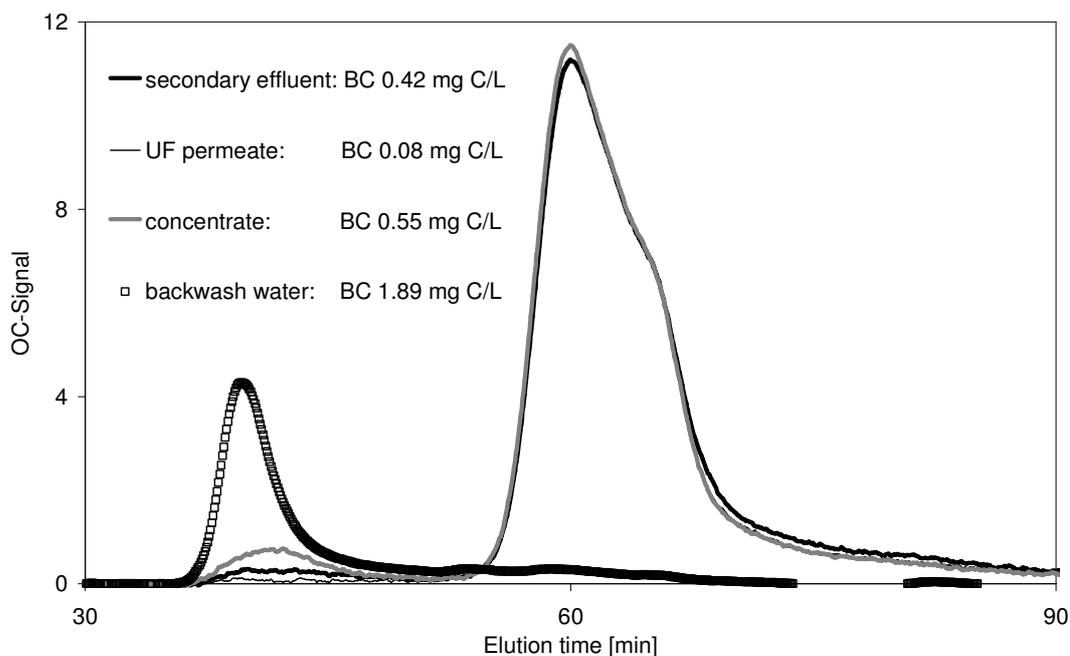
Fig. 4-9 Comparison of the LC-OCD chromatograms of SE, permeate after UP150, supernatant and back wash water (Permeate volume 500 mL, concentrate 200 mL, backwash water volume 50 mL, Dilution effect of different water samples was regulated)
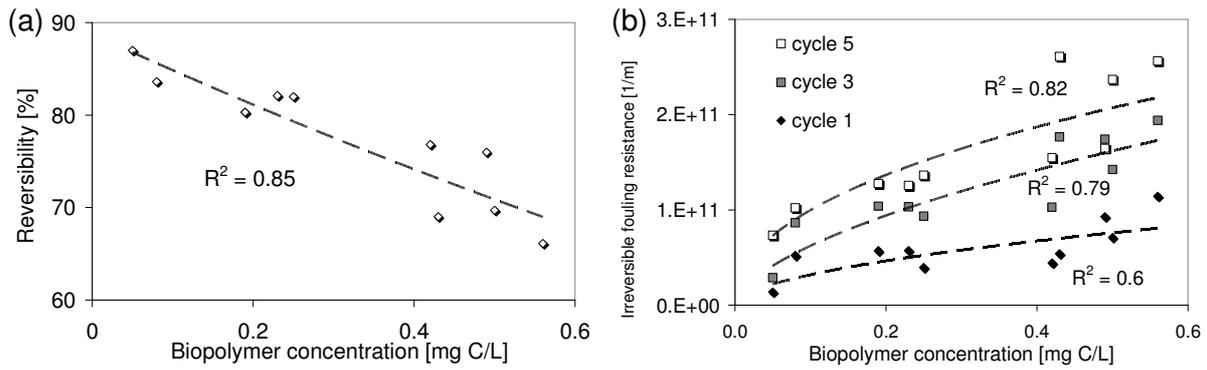
Fig. 4-10 (a) linear correlation between biopolymer concentration and reversibility after filtration cycle 5, (b) potential correlation between biopolymer concentration and irreversible fouling resistance after different filtration cycles (from October 8th 2007 to May 8th 2009, n=10, biopolymer concentration from 0.05 to 0.56 mg C/L).

To verify the influence of biopolymers on the performance of UF observed in the Amicon experiment, TMP development of the UF pilot plant operated at identical operational conditions (flux 50 LMH, BWI 10 minutes, BWT 10 seconds and BWF 260 LMH) was tested filtering SE or SSF at different biopolymer concentrations. Results taken from filtering SE and SSF were compared separately to minimize the influence of colloids and particles. Fig. 4-11 (a) shows the TMP development filtering SE at different biopolymer concentrations. It was exhibited that filtering SE with a biopolymer concentration of 0.79 mg C/L resulted in a TMP increase from 220 mbar to 700 mbar within 12 hours. The operating time with a biopolymer concentration of 0.56 mg C/L was extended to 14 hours. When the biopolymer concentration in the feed water was around 0.17 mg C/L, within the similar TMP increase scope, the operating time was extended to around 8 days. The comparison showed that in SE the biopolymer concentration affects the performance of UF processes decisively, lower biopolymer concentrations lead to a slower TMP development.
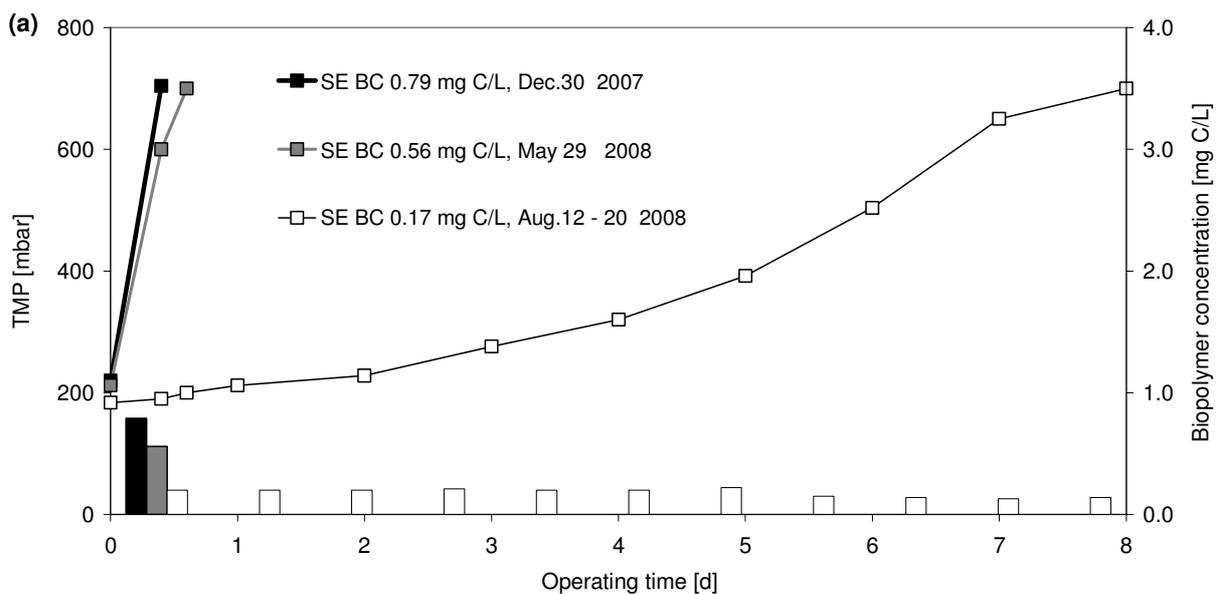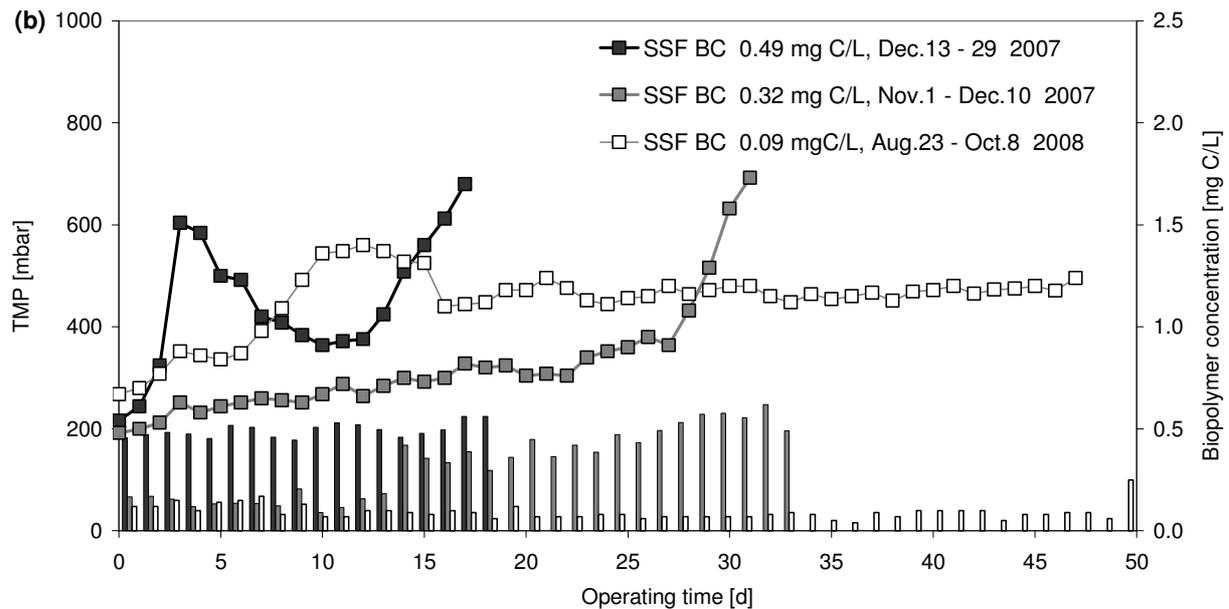
Fig. 4-11 TMP increase of UF pilot plant filtrating (a) SE and (b) SSFs at different biopolymer concentrations (BC: biopolymer concentration. Operational condition of UF: flux 50 LMH, BWI 10 minutes, BWT 10 seconds, BWF 260 LMH).

The results filtering SSFs are shown in Fig. 4-11 (b). It can be seen that filtering SSF with a biopolymer concentration of 0.49 mg C/L (on average) can be operated without chemical cleaning for about 15 days. With a biopolymer concentration of 0.09 mg C/L in SSF the operating time was 47 days with a TMP increase only from 280 to 490 mbar. The results indicate that in either SE or SSF, biopolymer content in the feed water influences the performance of UF process crucially. Higher biopolymer loads on the membrane surface lead to more irreversible fouling.

4.2 Fouling Mechanisms in UF

4.2.1 Fouling Mechanisms in Dead-end Filtration

Relying on the results acquired by determining filterability and biopolymer concentration, attempts were made to analyze the fouling mechanisms of biopolymers during dead-end UF process. Mechanisms within filtration of water containing colloidal matter through a low pressure membrane are well studied (Schippers and Verdouw, 1980; Roorda, 2004; Costa et al., 2006; Katsoufidou et al., 2007). It is generally regarded that in dead-end ultrafiltration the predominant filtration mechanisms are pore blocking and cake/gel filtration.

Fouling mechanisms relevant to constant pressure dead-end filtration experiments can be analyzed based on the approach summarized by Hermia (1982). Four major fouling mechanisms are described as complete blocking, standard blocking, intermediate blocking and cake filtration. Different mechanisms can be present simultaneously and the flow behaviour index n (section 2.3, Eq.2-7) may present a combination of different mechanisms by ranging in between given values (Crittenden et al., 2006).

The experimental data of permeate volume versus time in Fig. 4-5 (b) and Fig. 4-7 (a) is analyzed to generate plots of $\log(d^2t/dV^2)$ versus $\log(dt/dV)$, the formed curve is regarded as a characteristic curve reflecting fouling mechanisms as its slope is the flow behaviour index n. Since the derivations depends strongly on the smoothness of t-V curves, fitting polynomials of degree of six (Bowen et al., 1995) was conducted in each filtration process.

Fig. 4-12 presents characteristic curves reflecting fouling mechanisms under different biopolymer concentration ranges by filtrating 500 mL (standard condition in the present study) or 1350 mL water samples. Under standard condition, at high biopolymer concentrations (> 0.28 mg C/L) n starts within the range of 0.2 - 1 to 0 along the filtration process. Based on blocking laws, the fouling process can be explained as following: during filtration processes, biopolymers are firstly delivered to the membrane open pores. As the biopolymer concentration is comparatively high, all of the pores can be blocked in a short time, successive delivered biopolymers can only arrive on the biopolymers already present; this is the intermediate blocking process. With more biopolymers accumulating on the membrane surface, a gel layer then forms and cake/gel filtration dominates the following filtration process. As displayed in Fig. 4-12, the characteristic curve transforms from intermediate blocking (or combination of intermediate blocking) to cake filtration under the given operational condition.
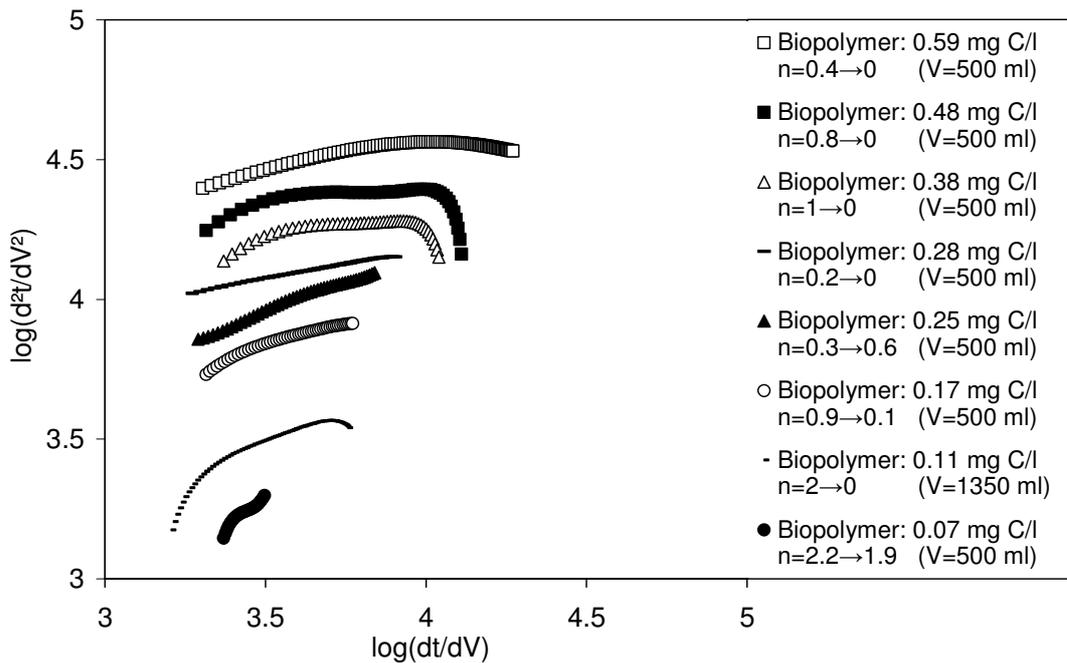

Fig. 4-12 Characteristic curves reflecting fouling mechanism for biopolymer fouling in UF at different biopolymer concentrations (Data are taken from Fig. 4-5 (b) and Fig. 4-7 (a), treated with polynomials of degree of six and analyzed with Eq.2-7. V: filtration volume. An example determining fouling mechanisms is shown in detail by section 8.3 A-Tab.3).

When biopolymer concentration in influents is in the medium range (0.17 – 0.25 mg C/L), n exhibits a value in the scope of 0.1 to 0.9 during filtration of 500 mL water samples. Fouling mechanism can be assumed as a combination of intermediate blocking and cake filtration. In filtrating waters containing a low concentration of biopolymers (< 0.11 mg C/L), n is always around 2 at the beginning. This complies well with the behaviour predicated by the complete

blocking model. The fouling process can be described as follows: Each delivered biopolymer molecule arriving to the membrane participates firstly in blocking an open membrane pore. As biopolymer concentration in the influent is comparatively low, after filtrating 500 mL water sample the biopolymers are not sufficient to cover all of the membrane pores/area. However, an increase of biopolymer load results in an alteration of fouling mechanism. As shown by filtering a 1350 mL water sample with a biopolymer concentration of 0.11 mg C/L, n changes from 2 to 0. This demonstrates that at low biopolymer concentrations sufficient biopolymers delivered to membranes surface results in a transition of fouling mechanisms from pore blocking to cake/gel filtration.

4.2.2 Fouling Mechanisms in Multi Cycle Filtration

In multifiltration cycles (section 4.1.3) it is shown that after the filtration process the formed biopolymer cake/gel layer can be readily backwashed. Nevertheless, irreversible fouling develops continuously along with the increase of filtration cycles. The influence of irreversible fouling on fouling mechanism is further investigated based on the blocking laws.
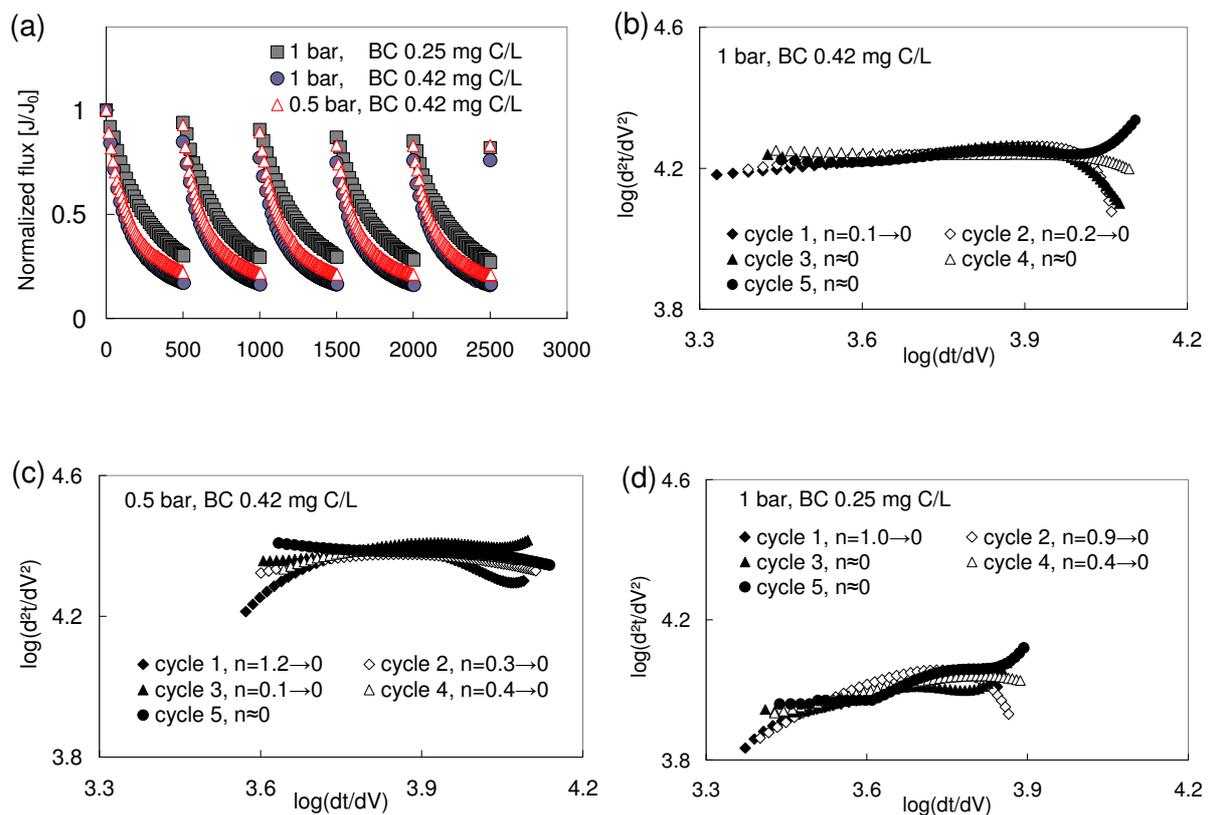

Fig. 4-13 (a) Multifiltration of water under different conditions, characteristic curves in UF of water (b) with a biopolymer concentration of 0.42 mg C/L under 1 bar, (c) with a biopolymer concentration of 0.42 mg C/L under 0.5 bar, (d) with a biopolymer concentration of 0.25 mg C/L under 1 bar

Fig. 4-13 (b) presents the characteristic curves filtering a water sample with biopolymer concentration of 0.42 mg C/L in five filtration cycles. It is shown that n changes from 0.1 to 0 during the first cycle. The variation of n indicates the shift of fouling mechanisms from pore blocking to cake/gel formation. After backwashing, in the second filtration cycle the alteration of fouling mechanism is similar to that in the previous. Nevertheless, from filtration cycle

three n presents around zero at the beginning of the filtration. This indicates that at the very beginning of the filtration there is no open pore for biopolymers to block, they can only cumulate at the surface of a fouling layer. In subsequent filtration cycles, the major fouling mechanism is identified as cake/gel filtration. This phenomenon indicates that although the formed cake/gel layer is readily backwashed, the irreversible attachment among biopolymers and membrane is further promoted due to the interactions among them (Zhang et al., 2006a). This leads to a further cumulation of biopolymers and subsequently the increase of irreversible fouling resistance. Similar trend can be observed filtering water at a lower operating pressure (Fig. 4-13 b) or with a lower biopolymer concentration (Fig. 4-13 c).

4.3 Comparison of Fouling Potential Measurements

As biopolymers quantified using LC-OCD-UVD-OND are identified as major foulants, further investigations were undertaken to find out a possible correlation between biopolymer content and fouling potential parameters quantified by other measurement methods, e.g., protein and/or polysaccharide concentration analysed using photometric methods and fouling index measured based on filtration curves.

4.3.1 Photometric Measurement of Polysaccharide and Protein

Several water samples analysed using LC-OCD-UVD-OND were also tested using the photometric methods to determine the relevant concentration of polysaccharides and proteins (Tab. 4-2).

Tab. 4-2 DOC, protein, polysaccharide concentration and biopolymer content of SE, permeate of SE and SSFs

| Water sample	DOC	Protein	Polysaccharide	Biopolymer	Filterability	Fouling resistance
	(mg/L)	(mg/L)	(mg/L)	(mg C/L)		$(10^{11}\ 1/m)$
SE	12.2	10.9	4.6	0.48	0.12	3.41
Permeate of SE	11.2	10.4	4.3	< 0.05	0.82	0.1
SSF 0.25 m/h	10.0	9.4	3.2	0.23	0.22	1.63
SSF 0.5 m/h	10.5	9.6	3.7	0.26	0.20	1.92
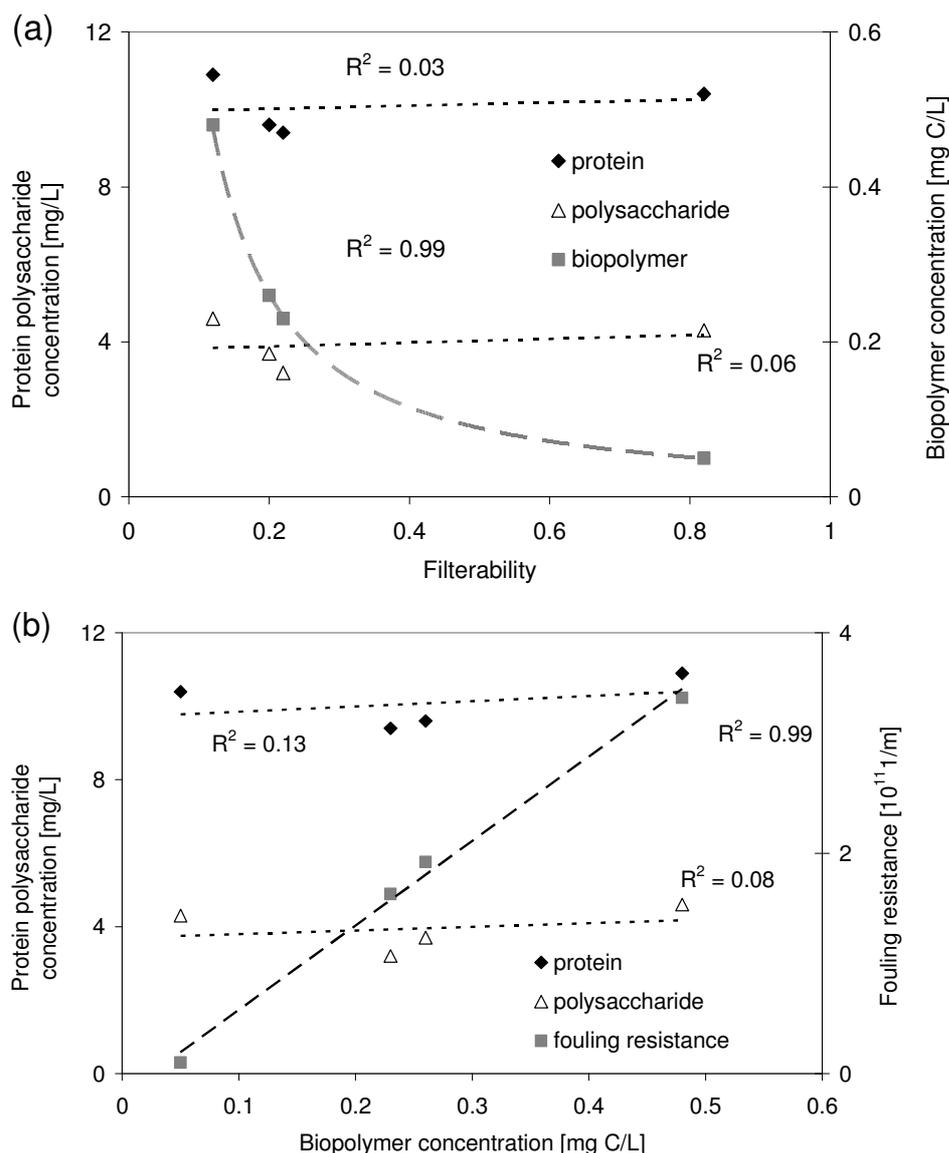
Fig. 4-14 (a) Correlation between filterability and content of foulants (potential relationship with bio-polymers), (b) correlation between fouling resistance and content of foulants (PR: protein, PS: polysaccharide, BC: biopolymer concentration)

It is shown that after UF the content of polysaccharides and proteins in the SE was reduced from 4.6 mg/l and 10.9 mg/l to 4.3 mg/l and 10.4 mg/l, respectively. These substances were removed by UF and seemed to be potential foulants. However, the concentration of polysaccharides and proteins in the UF permeate of SE was higher than that in SSFs, although the UF permeate showed a much higher filterability (Fig. 4-14 a). No quantitative correlation between biopolymer and protein and polysaccharides can be observed (Fig. 4-14 b). The comparison indicated that the photometrically detectable concentrations of polysaccharides and proteins are not in accordance with the foulant content detected with LC-OCD-UVD-OND. They show little information about the filterability of the water. In low-pressure membrane filtration processes the rejection of foulants is primarily due to size exclusion (Amy and Cho, 1999), the substances which are larger than membrane pore size contribute predominantly to the flux decline. The analysis using LC-OCD-UVD-OND can reflect the size distribution of organics and the amount of detectable foulants which show a correlation with filterability of water sample. Photometric methods reveal no information about molecular size distribution

and the results show no correlation with filterability. This result is consistent with the observations in several other studies (Poele et al., 2004; Kimura et al., 2009). When the content of biopolymers and photometricly quantified polysaccharides and proteins are plotted together with more measurements (Fig. 4-15), as expected, little correlation can be found between these two types of analysis methods.
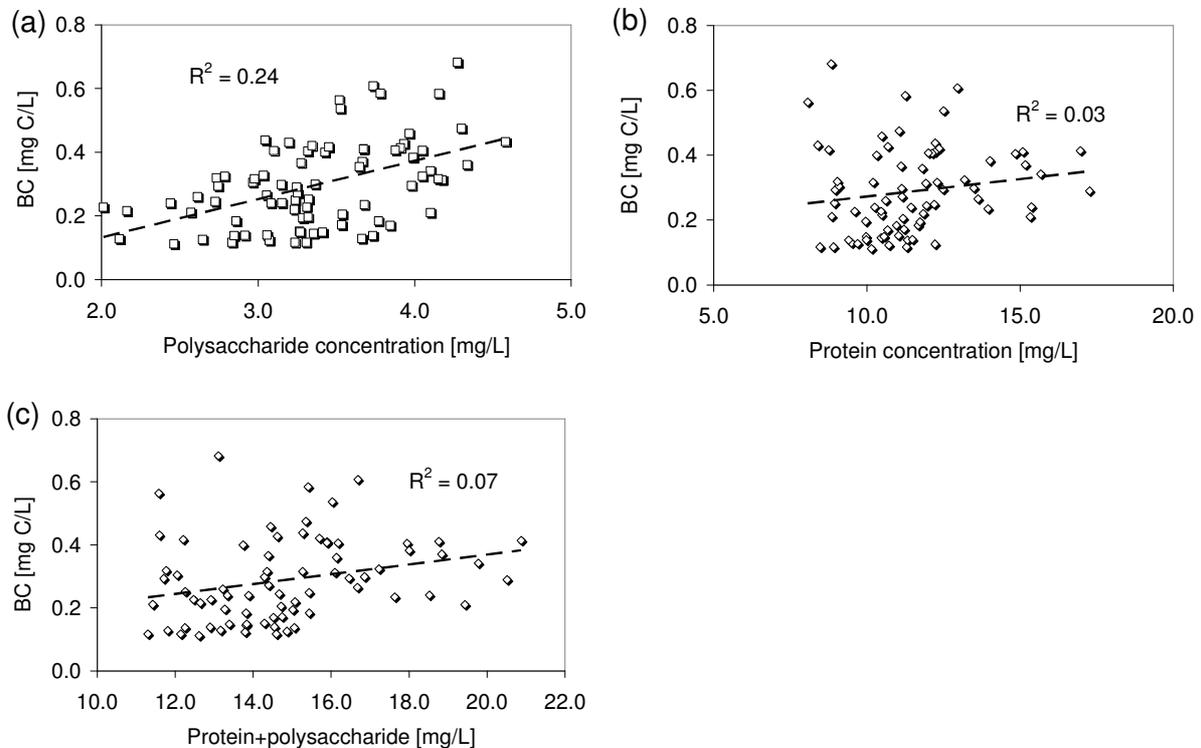

Fig. 4-15 Correlation between biopolymers and photometric measured polysaccharide (Dubois method) and protein (Lowry method) (a) polysaccharide and organic carbon in biopolymers, (b) protein and organic carbon in biopolymers, (c) polysaccharide+protein and carbon in biopolymers (n = 82, BC: biopolymer concentration)

4.3.2 Fouling Index and Hydraulic Fouling Resistance

It is demonstrated that there is a proportional correlation between biopolymer concentration and fouling resistance (Zheng et al., 2009a). This relationship suggests a possible connection between fouling resistance measured in a filtration cycle and the fouling potential of the corresponding water sample. To validate this deduction, the filtration resistance of the ten water sample taken from October 8th 2007 to May 8th 2009 (used in section 4.1.3) are plotted with irreversible fouling resistance. As expected, Fig. 4-16 (a) shows a significant correlation between them. The result indicates that the higher the fouling resistance in a single filtration cycle, the higher the irreversible fouling resistance is. Due to the presence of biopolymers, the fouling resistance measured in a filtration cycle can reflect the fouling potential of the feed water. Additionally, the correlation between biopolymer concentration and fouling resistance shown in Fig. 4-16 (b) is similar to that investigated in a previous study between November 2006 and July 2007 (Fig. 4-5, Zheng et al., 2009a). The reproducible relationship indicates that this correlation is constant throughout the whole experimental period (2006 – 2009).
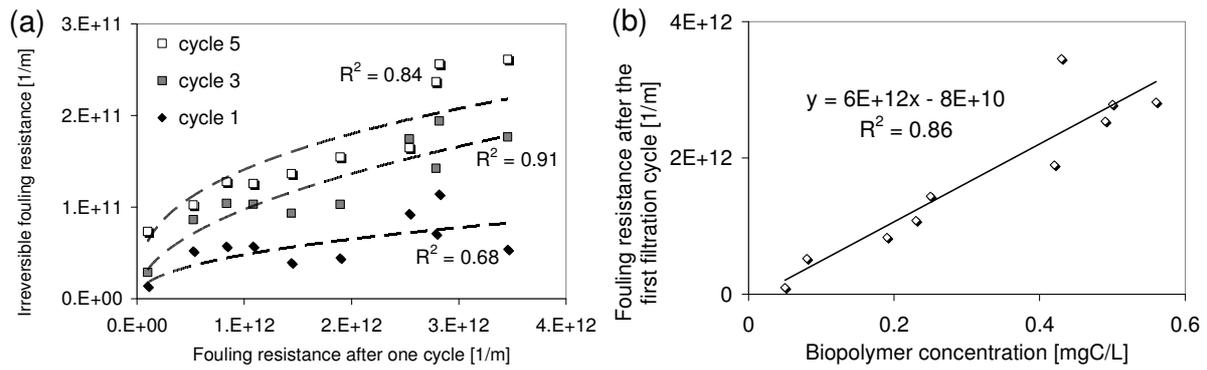
Fig. 4-16 (a) Correlation between fouling resistance and development of irreversible fouling, (b) correlation between biopolymer concentration and fouling resistance (from November 5. 2007 to May 08. 2009, n=10, flux and hydraulic resistance data in detail see section 8.3, A-Tab.4)

Tab. 4-3 Comparison of the operational conditions measuring SUR and fouling resistance in the present work

	SUR (Roorda, 2004)	Fouling resistance
Feedwater	SE	pre-filtered SE (0.45μm)
Temperature effect	nomalized to at 20 ºC	nomalized to at 22 ºC
Operating pressure	0.5 bar	1 bar
Membrane type	hollow fibre	flat sheet membrane
Filtration configuration	dead-end	dead-end
Membrane material	PES/PVP	PES
MWCO	70 – 150 kDa	150 kDa
Treatment of the membrane	NaOCl soaking and pure water flushing, permeability variation within 10%	flushing with pure water, variation of permeability within 10%
Specific permeate volume	based on the applied membrane area and permeate volume after 30 min filtration	174 L/m^2
Filtration time	30 min	varies from 30 to 90 min, depends on biopolymer content
Fouling mechanism	cake filtration	cake/gel filtration

The measurement process of hydraulic resistance caused by biopolymer is compared with the procedure determining the SUR of SE (Tab. 4-3). It is evident that the measurement of the both parameters is based on cake/gel filtration in dead-end filtration mode. Besides minor differences in operation, the operational conditions are also comparable. Similarity of determining biopolymer fouling resistance and SUR suggests a possible correlation between the two parameters. In the Amicon UF cell filtration of biopolymer-containing water under constant pressure at 1 bar, the predominant filtration mechanism is identified also as cake/gel filtration, the duration of the filtration is generally longer than 30 min which fulfils the requirement of the measurement of SUR value (Roorda, 2004). Based on the definition of SUR, the specific fouling resistance per unit feedwater per m^2 membrane area caused by biopolymers in Amicon UF can be calculated according to Eq. 4-2. A significant relationship between SUR and biopolymer concentration can be observed (Fig. 4-17). The result indicates that the concentration of biopolymers can be proportionally reflected by SUR. Further more, com-

pared to the slope of the linear relationship between fouling resistance and biopolymer concentration presented on Fig. 4-16 b, that presented on Fig. 4-17 is five times higher, which is consistent with the theoretical relationship between these two slopes (Eq. 4-2).

$$SUR = R_{cake} \frac{A}{V} = R_f \times \frac{28.7 \times 10^{-4}}{0.5 \times 10^{-3}} = R_f \times 5.74 \quad \text{Eq. 4-2}$$

where

$R_{cake} = R_f$ = hydraulic resistance of the biopolymer fouling, 1/m
V = the product volume of permeate, m^3
A = the membrane filtration area, m^2
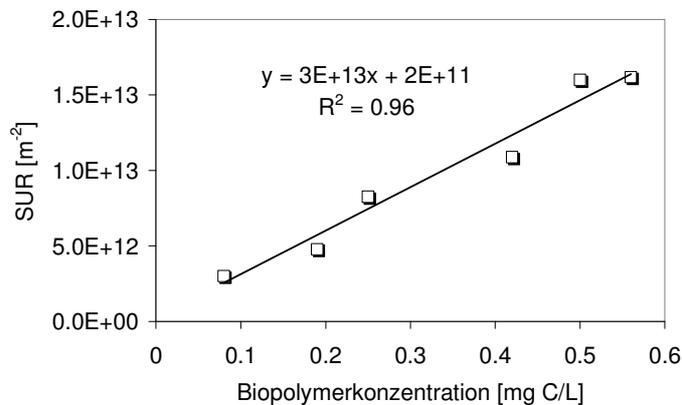
Fig. 4-17 Correlation between SUR and biopolymer concentration

Originally, SUR presents the total fouling resistance caused by particles, colloids and dissolved substances which can be retained by correspondingly used UF membranes (Roorda, 2004). The parameter has already been used in several studies and it shows a good correlation with the fouling phenomena in UF of treated domestic wastewater (Roorda and van der Graaf, 2005). However, it is stated that no other water quality parameter is found to have a quantitative correlation with it (Janssen and Van der Graaf, 2008). Considering that water quality generally reflects the content of specific substances within a certain size range, the measurement of SUR is however, conducted without any pre-treatment of the water sample. This may be one of the reasons interpreting the absence of a correlation to other parameters. As dissolved substances (< 0.45 µm) are identified as major foulants (Zheng et al., 2009a; Poele, 2006), a pre-filtration of water samples with 0.45 µm filter prior to the determination of SUR is therefore recommended. The SUR can be thereby defined as $SUR_{0.45}$, indicating the measurement of fouling potential of dissolved substances.

4.4 Discussion and Summary

Major organic foulants

In the present section, biopolymers are quantitatively identified as major organic foulants in UF of treated domestic wastewater. Their mass load leads to a proportional increase of hy-

draulic fouling resistance. Although most of them can be removed by backwashing, they impact the development of irreversible fouling in the applied PES membrane crucially.

The crucial fouling effect of biopolymers is based on their size and chemical characteristics. As shown in this section, biopolymers are with a nominal size larger than or comparable to the UF pore size. They attribute to a much higher fouling resistance than that caused by partculate and large colloidal substances. In respect to fouling effects of different size fractioned substances, Poele (2006) showed that using a 0.45 µm sieve prior to a pilot-scale UF couldn't improve its performance in filtering SE. By contrast, the application of a MF with a nominal size of 0.1 µm led to a significant improvement in fouling control. It was concluded that the major foulants in SE to UF are within the size range of 0.1 to 0.45 µm. The importance of dissolved substances in UF membrane fouling is supported by other studies (Fan et al., 2008; Laabs et al., 2006).

Despite the crucial role of dissolved biopolymers, the role of particulate and large colloidal substances in fouling phenomena should not be ignored. For instance, it was observed that direct UF of SE resulted in a much faster TMP development compared to treating SSF with a similar biopolymer concentration (Fig. 4-11). It seems that particles and large colloids also play an important role in fouling phenomenon. Jermann et al. (2008) investigated the influence of particles on the irreversibility of fouling by NOM. The results showed that the dosage of inorganic particles (kaolinite) into polysaccharide (alginate) or other NOM (humic acid) solutions could accelerate the development rate of irreversible fouling. A similar effect was observed by the addition of PAC or SiO_2 particles into NOM-containing water for UF (Zhang et al., 2003). It is interpreted that the strong connection between particles (depends on their nature and amount, Lohwacharin et al., 2009) and membrane through NOM binding results in a continuous cake layer, which reduces the effectiveness of backwashing. Otherwise, a cake layer formed by particles alone could be effectively backwashed and led to little irreversible fouling (Zhang et al., 2003). The settlement of particular foulants on the membrane surface was considered to reduce the available filtration area for dissolved foulants (Zhang et al., 2003). The subsequent increase of local flux resulted in a more compacted fouling layer which presented a lower reversiblility (Kim and DiGiano, 2006).

Based on the understanding of the role of particles, colloids and biopolymers in fouling phenomenon, it is evident that biopolymers are the crucial foulants. They can adhere to membanes strongly and bind other foulants with the membrane. Particles and large colloids are entrapped in the sticky biopolymer fouling layer. The synergy effect of these foulants results in a cake/gel layer which is stable against hydraulic backwashing or flushing.

Characterization of these dissolved large molecular foulants shows that biopolymers present a low SUVA value and contain organic nitrogen, particularly identified as polysaccharides (Huber, 1998) and proteins (Her et al., 2003). These organics have been stated as typical components in irreversible fouling in low-pressure membrane filtering waters containing effluent organic matters (EfOM) (Jarusutthirak and Amy, 2006; Kimura et al., 2005). More recently, Haberkamp (Haberkamp et al., 2008) compared the performance of a PVDF UF filtering SE and its UF permeate dosed with a kind of extracted bacterial EPS. The more severe fouling caused by SE than the prepared water was attributed to the higher content of protein-

like substances in effluent biopolymers. Based on the investigation on the spatial components of fouling on a PVDF membrane surface, Zhang (2009) stated that protein-like substances attributed to more fouling than polysaccharide-like foulants in the fouling layer adjacent to the membrane surface. Their adhesion increases the stickness and roughness of the membrane surface and encourages the attachment of other foulants. At the outer fouling layer polysaccharides were otherwise identified as the most important foulants. In contrast, Chen et al. (2006a) investigated the foulant distribution on a cellulose ester membrane surface. Alpha polysaccharide was revealed as the most concentrated EPS close to the membrane surface which attributed to a high hydraulich resistance, although proteins and other polysaccharides were also present in the feedwater. Filtering EPS-rich water with a hydrophilized PVDF MF membrane, Shen et al. (2010) found that compared to other organic fractions in water, the hydrophilic polysaccharides led to the steepest flux decline. The correspondingly formed fouling showed also the lowest reversibility. It seems that in relevance to membrane properties, different foulants play a different role in the formation of a fouling layer (Huang et al., 2007).

In general, biopolymers are considered to interact with the membrane and with each other through hydrogen bonding (for polysaccharides) or dipole interactions (for proteins), and also due to the contribution to the formation of a cake/gel layer (Amy, 2008). Variation of their mass cumulated on the membrane surface can change the number of binding sites available (Flemming and Wingender, 2001), and therefore, the total binding strength among foulants and membrane.

Evaluation of Fouling Potential

Although fouling potential of treated wastewater can be reflected by the concentration of biopolymers, their carbon content alone may not be a general fouling indicator because the components in terms of polysaccharides and proteins in different effluents can vary (Haberkamp, 2008). But, in regard to the effluent from a single wastewater treatment plant, as the case in the present study, biopolymer content can represent its fouling potential. This result implies that the variation of the components in biopolymers is within a certain ratio. Thus, it does not impact the fouling phenomenon significantly.

Under the same assumption, the proportional correlation between hydraulic fouling resistance (and also $SUR_{0.45}$) and biopolymer concentration may be used to present the fouling potential roughly. Nevertheless, as the indictor generally represents the filtration resistance caused by dissolved substances, it is lacking in information about the nature and components of foulants. The content of proteins and polysaccharides quantified by photometrical methods cannot reflect the fouling potential of treated domestic wastewater in UF, although typical function groups of irreversible foulants have been always related to protein-like and polysaccharide-like substances (Jarusutthirak and Amy, 2006; Shon et al., 2004). This is attributable to the intrinsic property of the method which has no consideration of the size distribution of the foulants despite the fact that these organic compounds have various molecular weight (size) distributions in different waters (Her et al., 2003; Garnier et al., 2005).

5   Removal of Organic Foulants in Bio-filtration Processes

Bio-filtration is considered as a promising pre-treatment option to control membrane fouling (Huck and Sozanski, 2008). In the present section the fouling control effects of short-term bank filtration and slow sand filtration prior to UF are tested. Under varied operational conditions the removal of biopolymers by slow sand filtration has been intensively investigated.

5.1 Fouling Control by Short-term Bank-filtration

To demonstrate fouling control effect using short-term bank-filtration, the UF pilot plant equipped with the Inge module (Dizzer® 450) was set up behind an artificial lake to filter bio-filtrate from July to November in 2005. Within this period the UF was operated at a flux of 89 LMH. Backwash interval (BWI) and backwash time (BWT) were 45 minutes and 30 seconds, respectively. The backwash flux (BWF) was set at 260 LMH according to the instruction of the membrane manufacturer. During each backwash, NaClO solution was dosed into the backwash permeate to keep the concentration of active chlorine at around 10 mg/L.
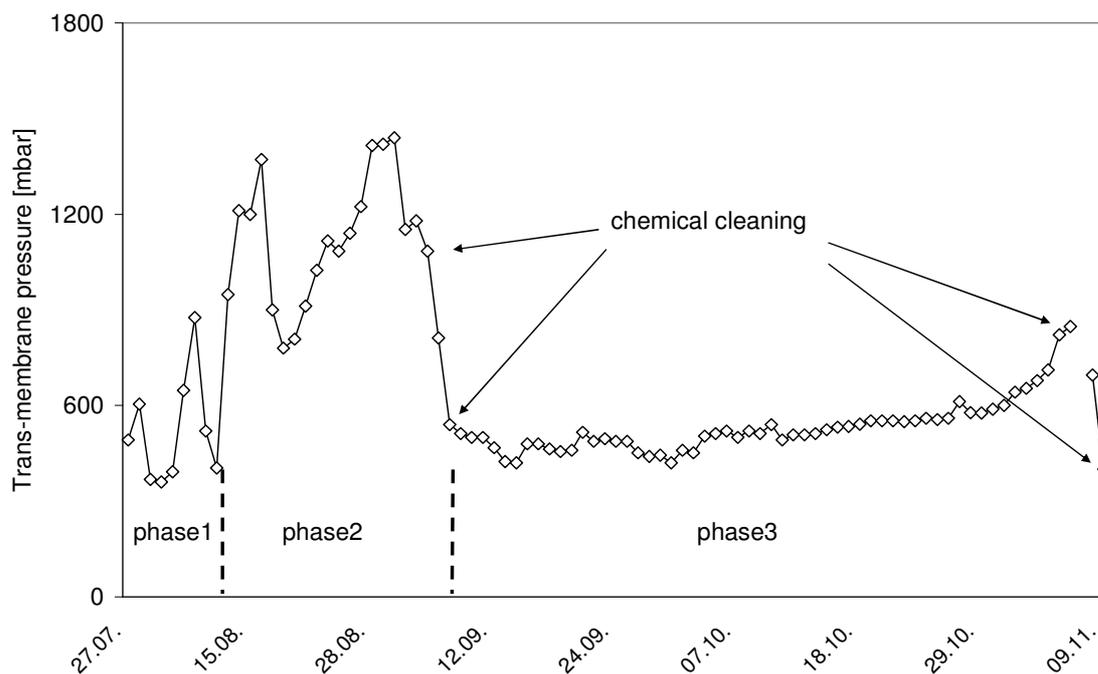
Fig. 5-1 Trans-membrane pressure development during the experimental period in WWTP Beixiaohe (July 27th to November 09th in 2005)

In the experimental period, TMP of the UF varied in different patterns depending on the characteristics of influents through different filtration media (Fig. 5-1). In the first phase (July 27th to August 15th) of the experiment, the influent to UF was a 1:1 mixture of sand and limestone filtered water. Because of the impurity of limestone, effluent pH after limestone filtration was always higher than ten and serious scaling was observed on the pipe wall to UF. Simultaneously, limestone filtration can only partly decrease humic substances (HS, retention time from 55 to 65 minutes, Fig. 5-2). The biopolymers (retention time from 35 to 55 minutes) could be

hardly removed. In this phase scaling and organic fouling caused a steep TMP increase. As shown in Fig. 5-1, TMP increased from 300 mbar to over 800 mbar within three days.

In phase 2 (August 16th to September 12th, 2005), the influent to UF was only sand filtrate. Since the lake water contained high concentration of biopolymers (Fig. 5-2) and the biological process in the sand seemed not totally adapt to removing them, TMP also increased quickly. TMP increased much slower in phase 3 (September 12th to November 7th, 2005) compared to phase 1 and 2. During this period, influent to UF was the effluent from sand filtration only. A comparison of LC-OCD chromatogram of different water samples confirmed that in this phase the biopolymer peak in the lake water was greatly reduced through sand bank filtration prior to UF. With a low biopolymer concentration in the influent, UF could run more sustainably under identical operational conditions. In this phase TMP increased around 400 mbar within 55 days.

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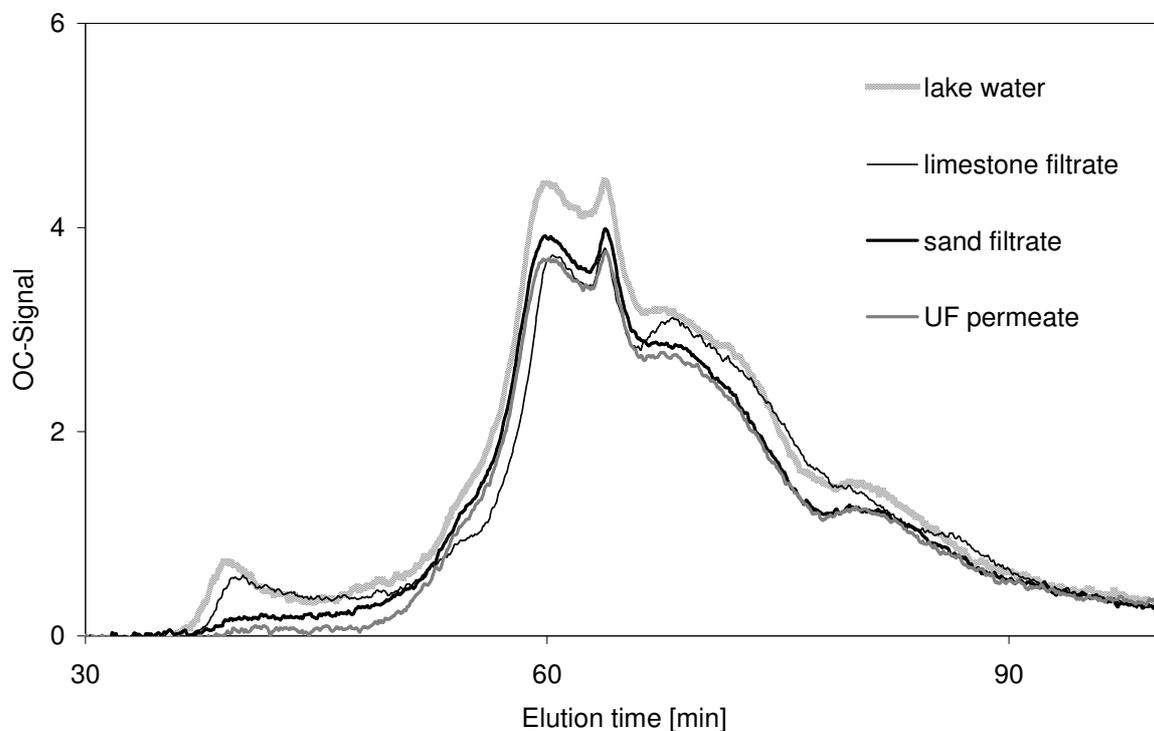
Fig. 5-2 LC-OCD diagram of lake water, effluent after limestone and sand filtration and UF permeate (dilution 1:5)

These results demonstrate that the short-term bank filtration with silicate material performs better than that with limestone material and can serve as an effective pre-treatment in fouling control for UF. As it is operated at a comparatively low filtration rate (< 0.06 m/h), bio-filtration with higher filtration rates (till to 0.5 m/h) was tested to identify the effect of filtration rate on fouling control. The experiments were conducted in WWTP Ruhleben (Berlin, Germany).

5.2 Fouling Control by Slow Sand Filtration

In WWTP Ruhleben the feedwater to the UF pilot plant was the filtrate from the slow sand filter (SSFr) operated at a filtration rate of 0.25 m/h. After installation in September 2006, the filter was continuously operated for about three months filtering SE to stabilize its bacterial community and ensure constant removal of organic compounds. Since November 2006, the treatment process showed a constant DOC removal.
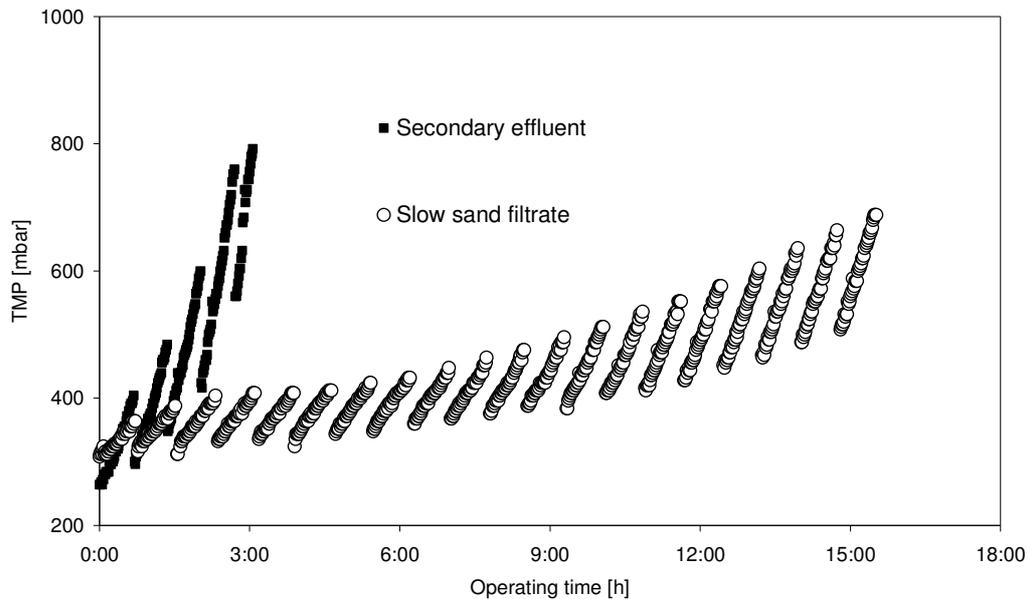

Fig. 5-3 TMP development filtrating SE and SSF at a filtration rate of 0.25 m/h (Operational condition: flux 89 LMH, BWI 40 minutes, BWT 50 seconds, BWF 260 LMH)
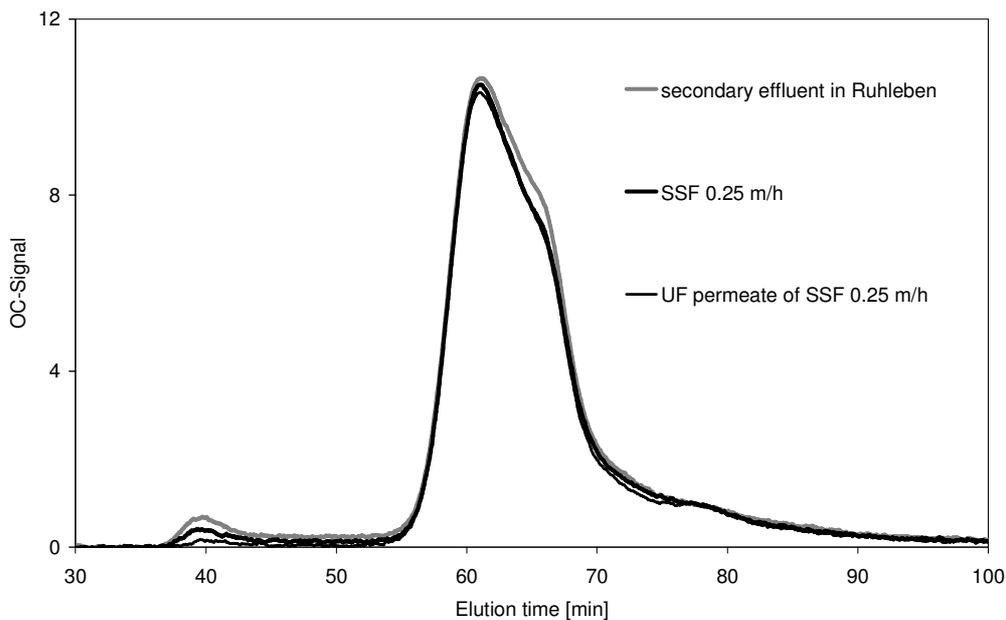
Fig. 5-4 LC-OCD diagram of SE, SSF (filtration rate at 0.25 m/h) and UF permeate of SSF (dilution 1:4)

The effect of slow sand filtration on the performance of UF was investigated (Fig. 5-3). The result exhibits that operated at identical operational conditions filtering SSF led to a slower TMP improvement compared to treating SE. Due to the removal of particular, colloidal and dissolved foulants (Fig. 4-1) - particularly the removal of biopolymers (Fig. 5-4), slow sand filtration can improve the performance of UF significantly.

5.3 Organic Foulants Removal in Slow Sand Filtration

5.3.1 Operation of Pilot-scale Slow Sand Filters

The investigation of foulant removal during slow sand filtration was carried out from September 2006 to December 2007. In this period, SSFr Nr. 1 was continuously operated at a filtration rate of 0.25 m/h; SSFr Nr. 2 was operated at a filtration rate of 0.5 m/h except the period from February to July 2007, during which the filtration rate was 0.1 m/h. To recover the permeability of slow sand filters, the top sand layer was removed by 3 to 5 cm and filled with new sand after the water level in the supernatant was higher than 0.55 m. The time range between sand change was defined as cycle time (days). To extend the cycle time of slow sand filtration, a textile layer was put on to the surface of the filters and the influent was aerated with a ratio between air and water at $1.4 : 1$ Nm^3/m^3.

5.3.2 General Water Quality of Secondary Effluent and Slow Sand Filtrates

Tab. 5-1 Water quality of SE and SSFs on average (December 2006 to December 2007, SSF at 0.5 m/h: except February to July 2007)

	Biopolymer mg C/L	DOC mg/)	UV_{254} 1/m	SUVA L/(m·mg)	DO mg/L	pH	Turbidity NTU
SE	0.40±0.17 (n=54)	11.7±1.4 (n=40)	27.7±3 (n=45)	2.36±0.17 (n=36)	7.1±1 (n=30)	7.2±0.3 (n=35)	1.5±1.3 (n=44)
SSFr Nr.1 0.25 m/h	0.21±0.13 (n=47)	10.5±1.4 (n=40)	26.2±3 (n=45)	2.48±0.19 (n=34)	0.4±0.3 (n=30)	6.9±0.3 (n=35)	0.3±0.1 (n=44)
SSFr Nr.2 0.5 m/h	0.22±0.14 (n=25)	10.6±1.3 (n=19)	26.4±3 (n=25)	2.51±0.18 (n=15)	1.5±1.2 (n=14)	6.9±0.3 (n=17)	0.3±0.1 (n=23)

DO: dissolved oxygen

The two SSFrs began to operate in September 2006. After three months adaptation time both showed constant DOC removal. The average water quality of SE and slow sand effluents from December 2006 to December 2007 is shown in Tab. 5-1. The results show that during the operation period slow sand filters removed biopolymers and DOC around 47 % and 10% at both filtration rates, respectively. Humic substances were also removed as the UV_{254} absorption decreased about 5 - 6%. In contrast, specific UV absorption (SUVA) increased from 2.4 to around 2.5 L/(m·mg). The slight rise of SUVA indicates that after slow sand filtration the proportion of humic substances in DOC increased. A significant decrease of dissolved oxygen (DO) concentration (from 7.1 mg/L to 0.4 mg/L and 1.5 mg/L at filtration rates of 0.25 m/h and 0.5 m/h, respectively) after SSFn was observed. During the whole period SSFrs

demonstrated effective removal of turbidity, the turbidity in SSF was always around 0.3 NTU despite the large variations in influent.

5.3.3 Removal of Organic Compounds in Slow Sand Filtration

Removal Profile of Organics in Slow Sand Filter

To study the removal process of foulants in SSFrs different parameters next to biopolymer concentration were measured simultaneously. The results investigated from March to November 2007 by SSFr. Nr.1 are shown in Fig. 5-5. The profile of biopolymer concentration (Fig. 5-5 a, mean value (diamond) and standard deviation (horizontal line)) shows that in SSFr the biopolymers were removed significantly in the upper 20 cm sand layer. In the filter zone below this region they were also removed but to a much lower degree. The significant reduction of DOC and humic substances (measured as UV_{254}) occured also in the upper layer (Fig. 5-5 b and d). In contrast, in this region SUVA increased from 2.33 to 2.42 L/(m·mg) (Fig. 5-5 f) which indicates that the relative content of humic substances increases. The reduction of biopolymer concentration and the improvement of SUVA imply that in all of the DOC fractions macromolecular polysaccharides and proteins are more preferentially removed than aromatic and double-bond substances. Investigation on other parameters showed that in the upper zone dissolved oxygen concentration decreased from around 7.5 mg/L to less than 0.5 mg/L (Fig. 5-5 b) and pH dropped also to some degree (Fig. 5-5 c). As conventional depth filtration cannot remove dissolved substances effectively (Metcalf & Eddy, 2003), the correlation of these phenomena implies that the removal of dissolved organic matters is related to biological processes. The readily degradable organic substances are biologically oxidized with the consumption of oxygen and lead to the formation of carbon dioxide and thus, the reduction of pH. The humic substances which are normally considered as non-readily biodegradable organics are comparably persistent and this leads to only a slight increase of SUVA.

The LC-OCD diagram confirms the removal of different DOC fractions. As shown in Fig. 5-6, the comparison between the chromatograms of the SE and its SSF indicates that the most fundamental change during slow sand filtration takes place within the fraction of biopolymers (elution time at 35 – 55 min). They are significantly removed through slow sand filtration. Also, a part of humic substances (second peak) could be removed which is consistent with the results measured using UV_{254} (Fig. 5-5 d). Moreover, the chromatograms of the sand filtrate and the water sample taken from 20 cm below the filter surface are almost identical, which indicates that the removal of organic compounds takes place mostly at the upper sand zone. This is consistent with the DOC measurement (Fig. 5-5 b).
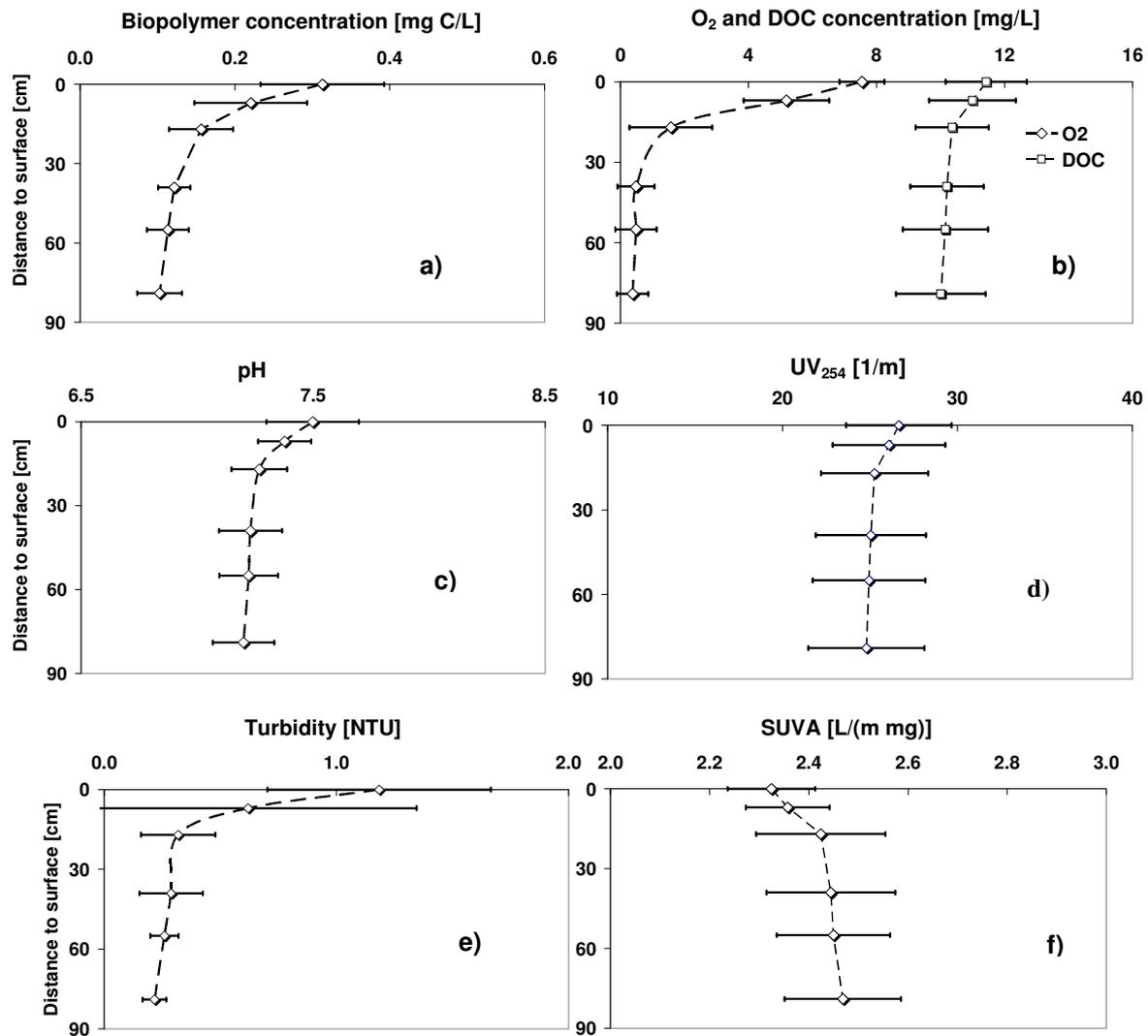
Fig. 5-5 Removal profile of a) biopolymer (n=13), b) dissolved oxygen and DOC (n=10), c) pH (n=10), d) UV_{254} (n=12) and e) turbidity (n=12) f) SUVA (n=10) in slow sand filter operated at filtration of 0.25 m/h, period: March 2007 to November 2007, removal profile at filtration rate of 0.5 m/h is shown in section 8.3, A-Fig. 5).

The significant removal of organics and turbidity (Fig. 5-5 e) in the upper sand layer is similar to the phenomenon in slow sand filtration for drinking water treatment (Ojha and Graham, 1996). In slow sand filtration it is normally considered that the schmutzdecke (thickness < 25mm) in association with the upper active layer plays an important role in removing contaminants (Amy et al., 2006). Head loss, maximum bio-film growth and fine particles removal occur normally in this zone. Compared to slow sand filters used for drinking water treatment, the removal of contaminants in treating SE also mostly occurred in the upper active layer despite the high organic load and utilization of coarser sand (sand for drinking water treatment ususally with grain size < 0.4 mm) (Rachwal et al., 1996). In this zone the macromolecular proteins and polysaccharides can be effectively removed. The phenomenon is similar to that taking place in water reclamation using bank-filtration or SAT system (Gruenheid et al., 2005; Amy and Drewes, 2007). In those studies, the sustainable removal of macro organic molecules was attributed to biodegradation.
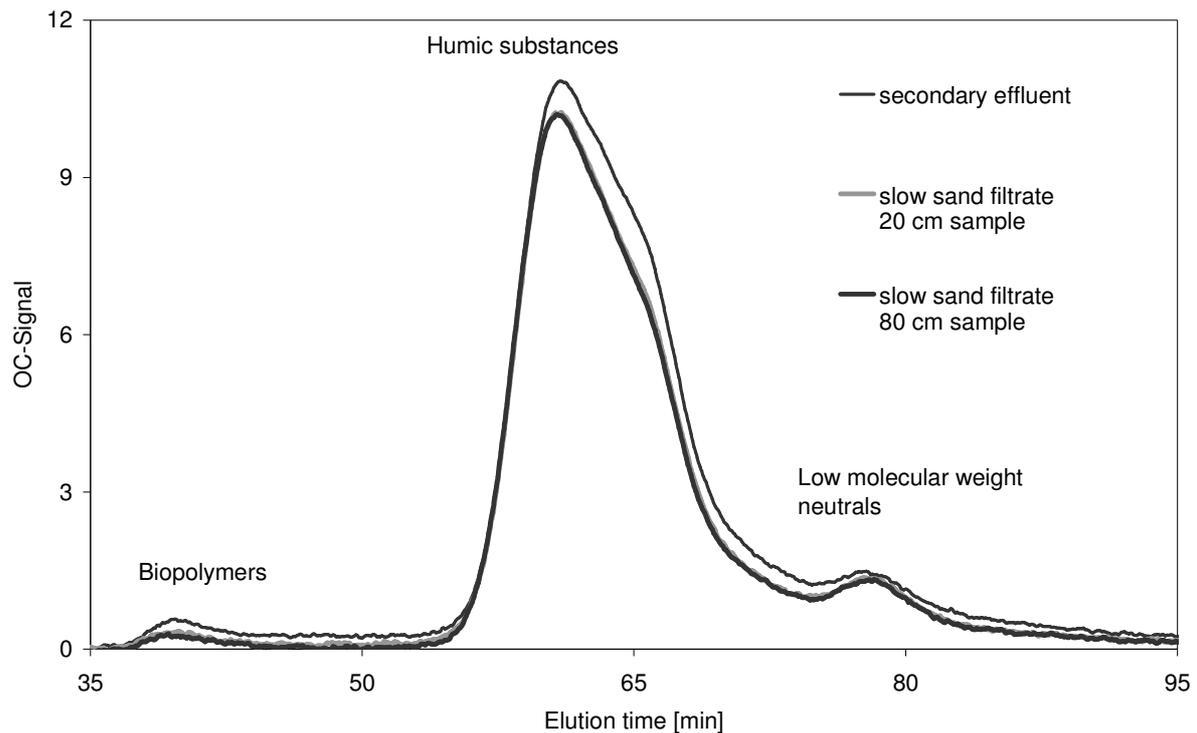
Fig. 5-6 LC-OCD chromatograms in different SSFr probe sites (SSFr 20 cm: the probe site 20 cm below the sand filter surface)

Identification of Biological Degradation of Biopolymers

The biodegradability of biopolymers and humic substances was tested using the method developed by Servais et al. (1987) and Block et al. (1992) (detail information see section 8.4). Fig. 5-7 shows the result of the biodegradability test. As displayed, after 30 days of inoculation, around 45% of biopolymers (initial biopolymer concentration 0.4 mg C/L) can be biologically degraded; simultaneously, humic substances were also degraded as the absorption signal of UV_{254} (initial absorption 26.5 1/m) decreased around 8%. The reduction of these organics is in good agreement with the result shown in (Tab. 5-1).

During the test, the degradation of biopolymers can be subdivided into three stages (Fig. 5-7). In the initial stage, the biopolymer concentration decreased sharply - around 25% of the initial value within one day of inoculation. Thereafter, the concentration increased from 0.3 to 0.37 mg C/L. Subsequently, it was decreasing continuously until the end of the test. The phenomenon is similar to that in a biodegradability test of biofilm extracellular polymeric substances (Zhang and Bishop, 2003). The initial decrease of the concentration of biopolymers can be contributed to a fast degradation of easily degradable substances or biosorption (Esparza-Soto and Westerhoff, 2003). Due to the production of extracellular biopolymers of inoculants (microorganisms) or desorption of absorbed substances, their concentration could rise to some degree. Finally, biopolymers are consumed as substrates for microorganisms as they are under a starvation situation (Zhang and Bishop, 2003; Flemming and Wingender, 2001) which leads to the continuous decrease of biopolymer concentration.
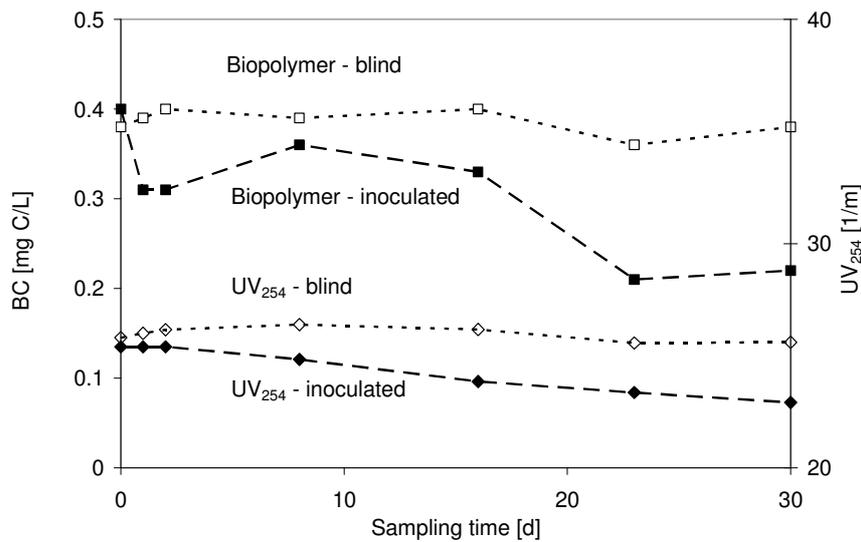
Fig. 5-7 Biological degradation test of biopolymers and UV$_{254}$-absorbing substances

Removal of the Protein-like Biopolymers

Next to the quantitative reduction of biopolymers, the impact of slow sand filtration on the qualitative change of biopolymers, in terms of nitrogen to carbon ratio (N/C), is also investigated. The N/C ratio of SE and SSF is within the range of 0.16 to 0.25 (n=10) and is altered little after slow sand filtration. This implies that the nitrogen and carbon-containing compounds are in general evenly removed by slow sand filtration. Suppose that the organic nitrogen is mostly from protein-like substances, the reduction of nitrogen content indicates their removal. The EEM measurement of SE and corresponding SSF confirms the deduction. As shown in Fig. 5-8, in both waters an obvious peak at 285-350 nm (Ex-Em) can be observed which suggests the presence of protein-like substances (Henderson et al., 2009; Her et al., 2003). Compared to that in the SE, the intensity of the peak in the SSF is significantly reduced. The decrease of the intensity reflects the removal of protein-like substances which is in accordance with the reduction of organic nitrogen content in biopolymers detected using LC-OCD-OND.
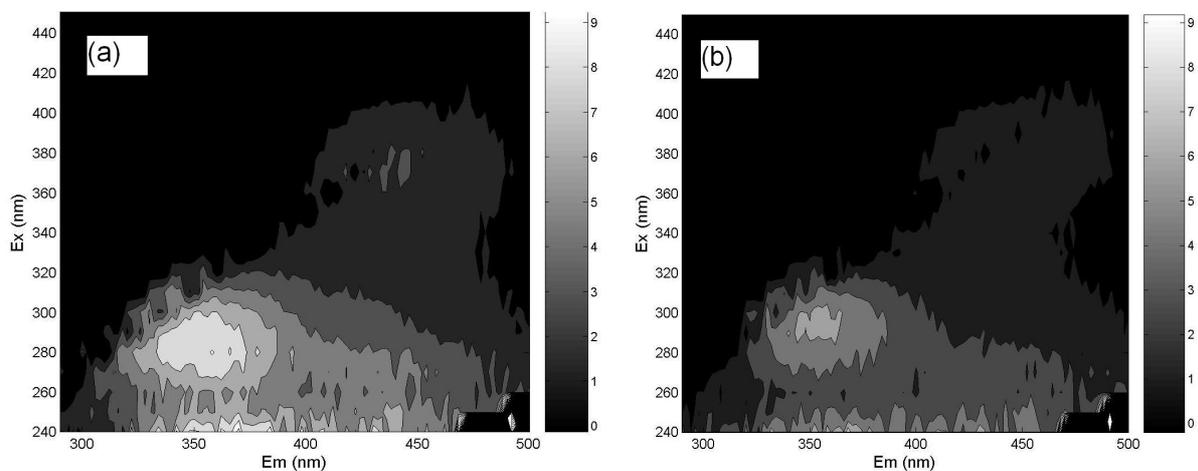
Fig. 5-8 Fluorescence EEM of fractioned biopolymer in (a) SE (b) corresponding SSF at a filtration rate of 0.25 m/h (Em: Emission, Ex: Excitation)

5.4 Factors Affecting the Performance of Slow Sand Filtration

5.4.1 Filter Ripening

As a biological and physical process, the ripening extent of slow sand filtration impacts its performance (Amy et al., 2006). In terms of duration, filter ripening may take weeks to months based on the influent water quality and the desired effluent quality (Weber-Shirk and Chan, 2007). In the present work the filter ripening stage (adaption time) was three months (September – November 2006). Within this period, slow sand filters achieved a comparatively constant DOC removal.

Filter ripening can also be evaluated in regard to certain water quality parameters. With respect to biopolymer removal, after three months adaption time SSFr.1 (0.25 m/h) achieved a removal ratio around 30% from December 2006 to Feberary 2007. After a significant fluctuation appeared from March to July 2007, the removal was constant at around 70% in warm seasons. An extreme temperature drop appeared at the end of 2007 (Fig. 5-10), during which the ratio fell to about 30%. It was indicated that under similar temperature conditions, the ratio achieved after three months ripening time was comparable to that after one year of operation. This result demonstrated that three months filter ripening time were sufficient for the microorganisms to adapt to biopolymers. Concerning turbidity control, SSFr.1 presented a constant removal effect. The turbidity in the effluent was never higher than 0.6 NTU which was independent of that in the influent (Fig. 5-9 b) throughout the experimental period.
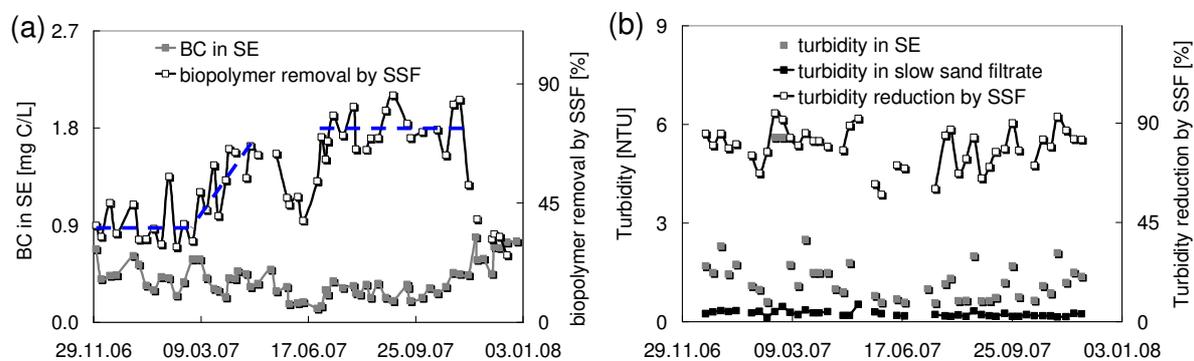
Fig. 5-9 Removal effect by SSFr.1 in terms of (a) biopolymer, (b) turbidity due to slow sand filtration (0.25 m/h)

5.4.2 Temperature and Biopolymer Concentration in Secondary Effluent

Variation of biopolymer concentrations in the SE was investigated within fifteen months (October 2006 to December 2007, Fig. 5-10). It is shown that the biopolymer concentration is generally higher in winter time than in warmer seasons. In winter (November 2006 – February 2007, November 2007 – December 2007) the concentration was 0.55 mg C/L on average, in warmer seasons (March – October 2007) it was around 0.31 mg C/L. In contrast to the variation of biopolymer concentration, the DOC was comparatively constant during this period. Throughout the whole sample period the variation of biopolymer concentration appears to be associated with temperature change. As shown in Fig. 5-11, by trend biopolymer concentration decreased generally as the temperature increased.
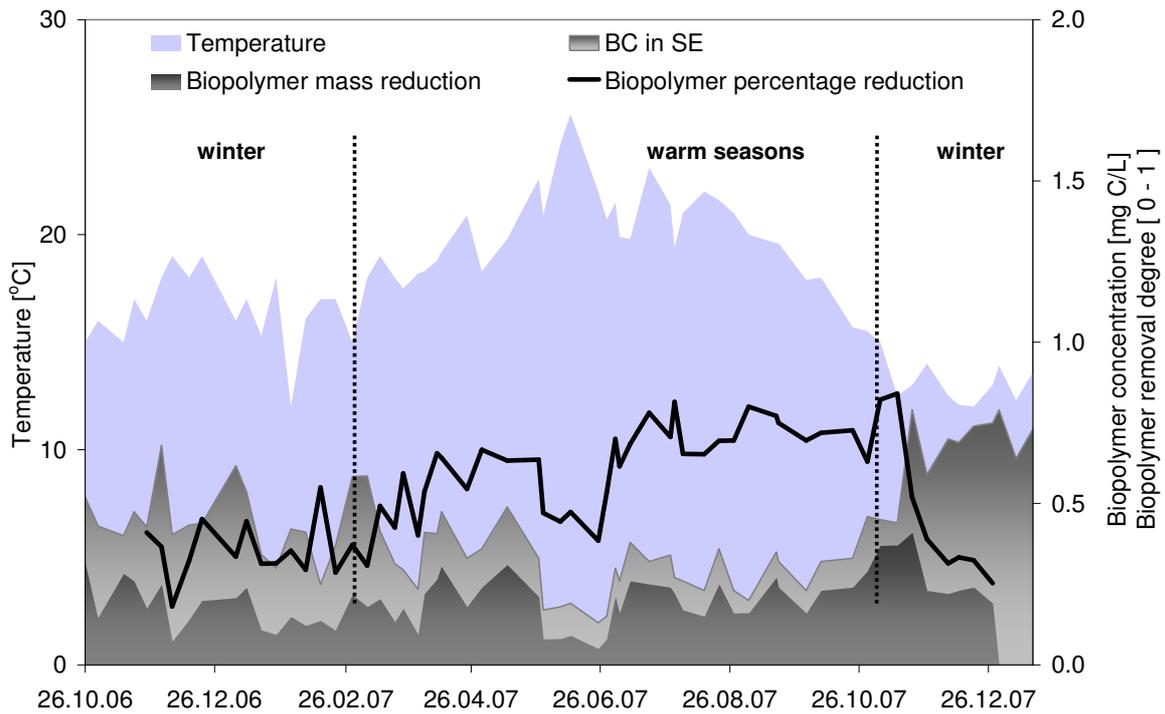
Fig. 5-10 Variation of temperature, biopolymer concentration in SE (October 2006 – December 2007) and removal effect by SSFr.1 (filtration rate 0.25 m/h, December 2006 – December 2007, removal degree: 0 - 1 represents 0 - 100%)
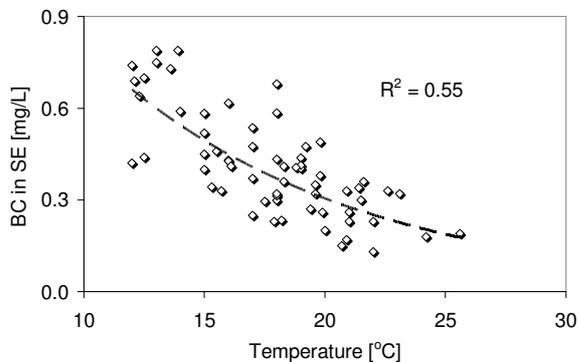

Fig. 5-11 Trend of biopolymer concentration in association with temperature in SE (October 2006 – December 2007, n=63)

Similar effects on the variation of biopolymer concentration by temperature was observed by Laabs (2004) operating two MBR systems treating domestic wastewater. Al-Halbouni et al. (2008) noted seasonal variations of bound EPS content in a MBR treating municipal wastewater. Since either proteins, polysaccharides or biopolymers are mostly SMP (Jarusutthirak and Amy, 2006) or synthetic/waste organic substances from wastewater (Barker and Stuckey, 1999; Al-Halbouni et al., 2009; section 8.3, A-Fig. 6) variation of temperature may put stress on bacteria to produce more EPS/SMP and release them into the water phase or influence the activity of microorganisms to degrade them.

The influence of temperature and biopolymer concentration on biopolymer removal by SSFr Nr. 1 is depicted in Fig. 5-10. The results show that from February to June 2007 the removal of biopolymers was increased from around 34% to 65% while the temperature increased from 16 °C to 22 °C and the average biopolymer concentration decreased from 0.5 mg C/L to around 0.4 mg C/L. During the period from July to November 2007, the biopolymer concentration in the SE was around 0.3 mg C/L – even though the temperature decreased from 21 °C to 15 °C – and the removal was rather constant at about 75 %. From the end of November to the end of December 2007, as the temperature dropped to lower than 13 °C and the biopolymer concentration jumped to over 0.6 mg C/L, the removal fell from 74% to below 35%. Simultaneously, the cycle time of the SSFr. 1 was dramatically reduced from around 80 days to shorter than 18 days (Tab.5-2).

Based on the results shown in Fig. 5-10, temperature or biopolymer concentration results are separately plotted versus biopolymer removal (Fig. 5-12). The results show that either temperature or biopolymer concentration in the SE impacts the biopolymer removal in slow sand filtration. Higher temperatures (Fig. 5-12 a) or lower biopolymer concentrations (Fig. 5-12 b) result in higher biopolymer removal. In general, SSFr Nr. 1 could control biopolymer effectively, with a removal over 65% on average during warm seasons (Fig. 5-12 c, around 20 °C, n=30) and comparatively low biopolymer concentrations (0.15 – 0.45 mg C/L). At lower temperatures (Fig. 5-12 c, on average 15 °C, n=16) and higher biopolymer concentrations (> 0.4 mg C/L), the removal was lower than 40%.
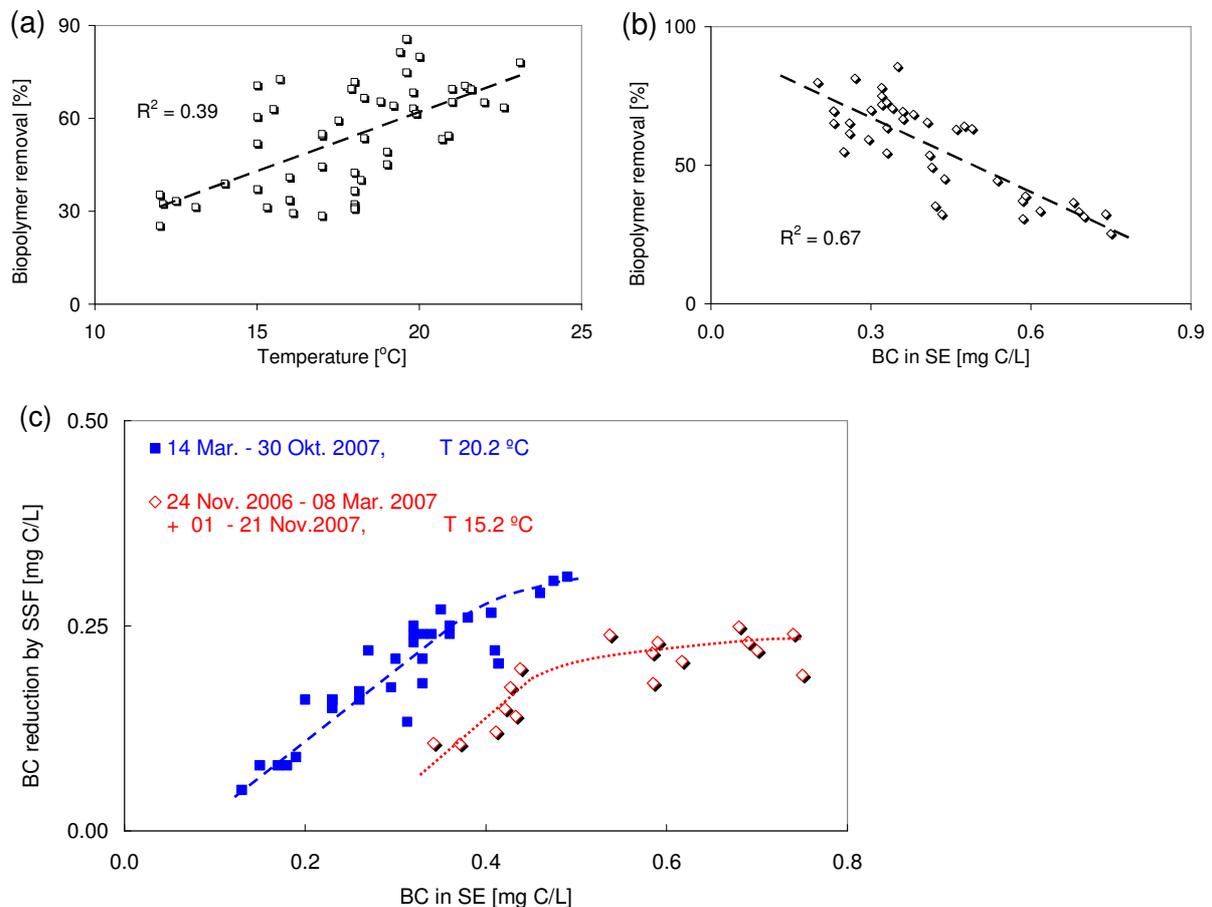
Fig. 5-12 Influence of a) temperature, b) biopolymer concentration and c) temperature and biopolymer in the SE on biopolymer removal by SSFn (filtration rate 0.25 m/h, Dec. 2006 – Dec. 2007, n=46)

As the percentage removal of biopolymers depends highly on the feedwater quality, a further investigation on their mass reduction under different conditions was carried out (Fig. 5-10 and Fig. 5-12 c). It is evident that with a similar feedwater quality higher temperature promotes more biopolymers removal (Fig. 5-12 c). The results indicate that increasing temperature can create a more suitable circumstance to the microorganism and therefore, they can remove more biopolymers. Furthermore, it is observed that an increase in biopolymer content in the feedwater within a certain scope results in an almost proportional rise in their mass removal (Fig. 5-11 c). Nevertheless, the rise is much less than linear when the biopolymer concentration is beyond a certain value. For instance, at the end of 2006 and 2007 the variation of biopolymer content from 0.5 to 0.8 mg C/L resulted in a similar mass removal by 0.21 mg C/L, which is also similar to the mass removal in April and July 2007 (Fig. 5-10). These phenomena suggest that overloaded biopolymers cannot be effectively degraded, which is attributable to a restricted degrading activity of microorganisms. At this point, environmental factors, e.g., available oxygen, surface area available for biofilms (Metcalf & Eddy, 2003; Huck and Sozanski, 2008) may play an important role.

Tab. 5-2 Performance of bio-filtration operated under different temperature and biopolymer concentration in SE

		Dec.01.2006 -Feb.07.2007	Feb.10.2007 -Jul.10.2007	Jul.17.2007 -Nov.13.2007	Nov.20.2007 -Dec.28.2007
Average temperature (^{o}C)		16.8 (n=11)	19.6 (n=25)	19.1 (n=19)	13.1 (n=9)
Average BC in SE (mg C/L)		0.46 (n=11)	0.33 (n=25)	0.3 (n=19)	0.68 (n=9)
Biopolymer removal	SSFr Nr.1 (0.25 m/h)	37% (n=6)	58% (n=15)	73% (n=15)	32% (n=5)
	SSFr Nr.2 (0.5 m/h)	24% (n=8)	--	67% (n=17)	28% (n=3)
	BioN+SSFn (0.5 m/h)	--	--	45% (n=6)*	31% (n=5)**
Cycle time (days)	SSFr Nr.1 (0.25m/h)	~ 40	~ 80	~ 80	~ 18
	SSFr Nr.2 (0.5 m/h)	~ 20	--	~ 30	~ 8
	BioN+SSFn (0.5 m/h)	--	--	> 120 (test till March 2008)	

BC: biopolymer concentration
BioN: BioNet as filter material
Cycle time: the period between upper sand layer cleaning
*Water samples from September to November 2007
**Water samples from November 2007 to January 2008

Filtration Rate

Tab. 5-2 shows the biopolymer removal and cycle time of SSFr Nr. 1 (filtration rate 0.25 m/h) and SSFr Nr. 2 (filtration rate 0.5 m/h) during the experimental period. The results indicate that during winter time in 2006, biopolymer removal at a filtration rate of 0.25 m/h and 0.5 m/h was around 37% and 24%, in the warmer seasons in 2007 the removal was 73% and 67%, respectively. As lower filtration rates lead to longer empty bed contact times (EBCT), higher organic removal effects can be achieved (Huck and Sozanski, 2008; Urfer et al., 1997). The comparison of biopolymer removal profile within slow sand filters operated at different filtration rates is shown in Fig. 5-13 (a) and (c). It is evident that at lower filtration rates the

active layer in slow sand filter can remove more biopolymers due to the prolonging of EBCT. At similar EBCT similar biopolymer removal efficiency can be achieved (Fig. 5-13 b and d).
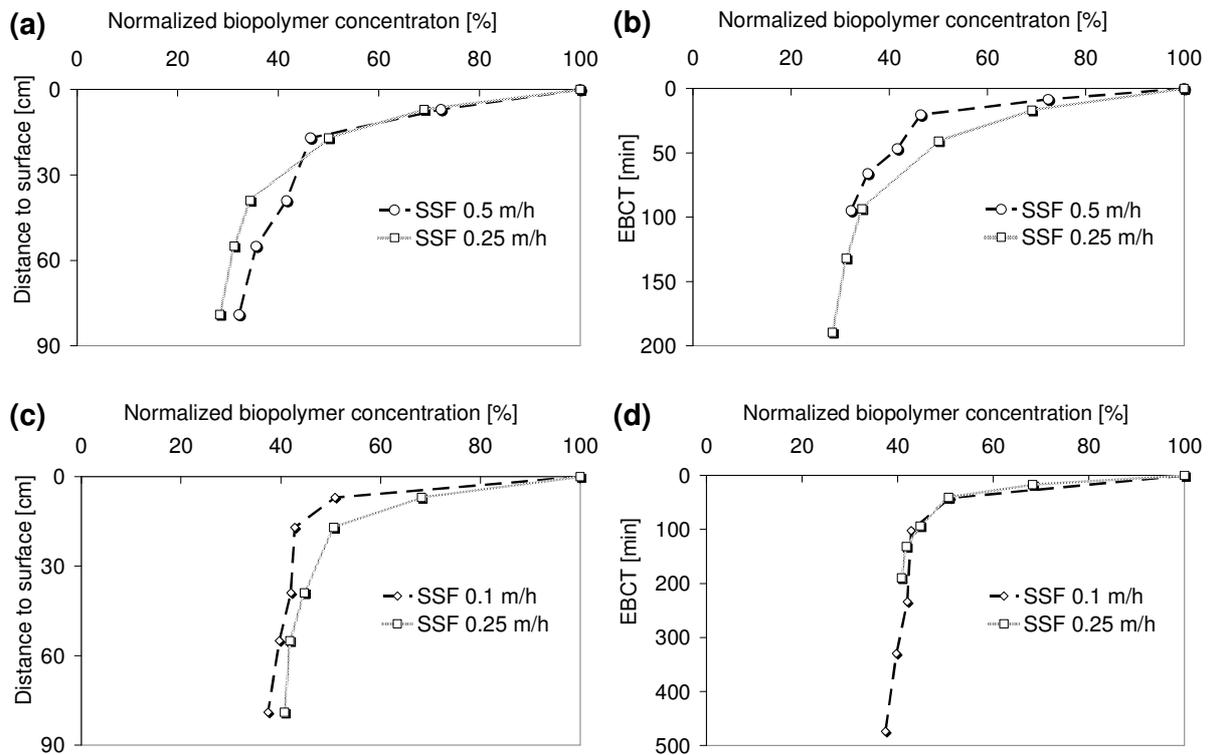

Fig. 5-13 Normalized biopolymer concentration profile within slow sand filters operated at filtration rate of 0.5 and 0.25 m/h in terms of (a) depth and (b) contact time (test period: July to November 2007, biopolymer n=13 for SSF 0.5 m/h and n= 6 for SSF 0.25 m/h), operated at filtration of 0.25 and 0.1 m/h in terms of (c) depth and (d) contact time (test period: April to June 2007, n = 6 for both filters)

Although a higher biopolymer removal effect can be obtained by reducing the filtration rate, a decrease of filtration speed cannot lead to a proportional increase of the removal efficiency. The investigation carried out at filtration rates from 0.05 m/h to 0.5 m/h from November 2006 to July 2007 (Fig. 5-14) shows that biopolymer removal rates are improved from 32 % to 50 % when filtration rates are decreased from 0.5 m/h to 0.25 m/h. But if filtration rates are reduced from 0.1 m/h to 0.05 m/h, corresponding biopolymer removal rate increases only from 62 % to 65 %. It has been indicated (Zhang and Huck, 1996) that although the filtration rate (based on EBCT) is a key parameter determining organics removal effect in bio-filtration processes, other factors, e.g. reactor specific surface area, biomass density, substrate diffusivity and kinetic parameters, are also important. The variation of one parameter cannot result in a proportional change on the performance of the bio-filtration. Therefore, an unified parameter, e.g. dimensionless contact time, which contains other factors important for biofiltration performance is more suitable to describe and optimize the bio-filtration process (Huck and Sozanski, 2008).
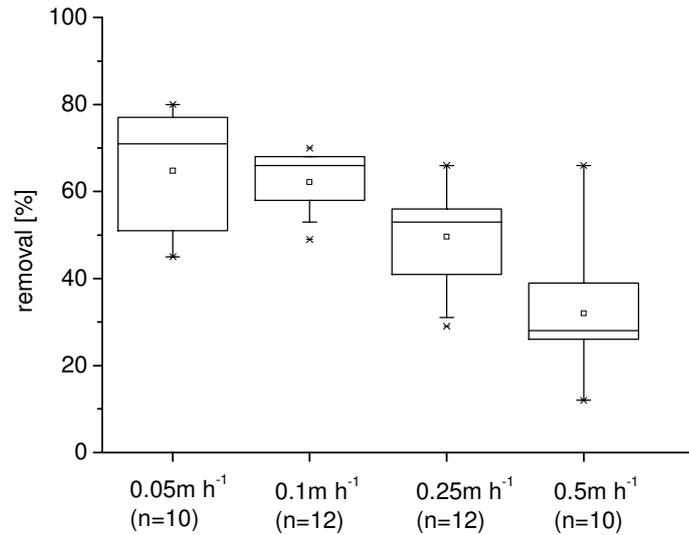
Fig. 5-14 Biopolymer removal at different filtration rates (November 2006 to July 2007 in WWTP Ruhleben, Median value (horizontal centre line), average value (the square in box), the 25%- and 75%-quartiles (box) and the minimum and maximum values (vertical line))

The influence of filtration rates on the cycle time was much more significant than on bio-polymer removal. In the investigated period, the cycle time of SSFr Nr. 2 was always around 50% of that of SSFr Nr. 1 (Tab.5-2). During operation, the increase of hydraulic resistance is observed mainly in the upper sand layer (Fig. 5-15) and is considered generally as a result of the accumulation of particles and the growth of microorganisms (Leverenz et al., 2009; Maelzer and Gimbel, 2006). Compared to the active upper sand layer, the layer deeper than 0.2 m presents little variation in terms of water headloss during the operational period (Fig. 5-15). It implies that due to the removal of particles and biopolymers in the upper layer, the deeper layer works more like a support layer than as a foulants removal layer. The difference of cycle time at different filtration rates indicates that higher filtration rates lead to higher surface loading rate within the top zone. This results in subsequently more accumulation of substances (Leverenz et al., 2009) pre unit filtration area and leads to a faster increase in hydraulic resistance.
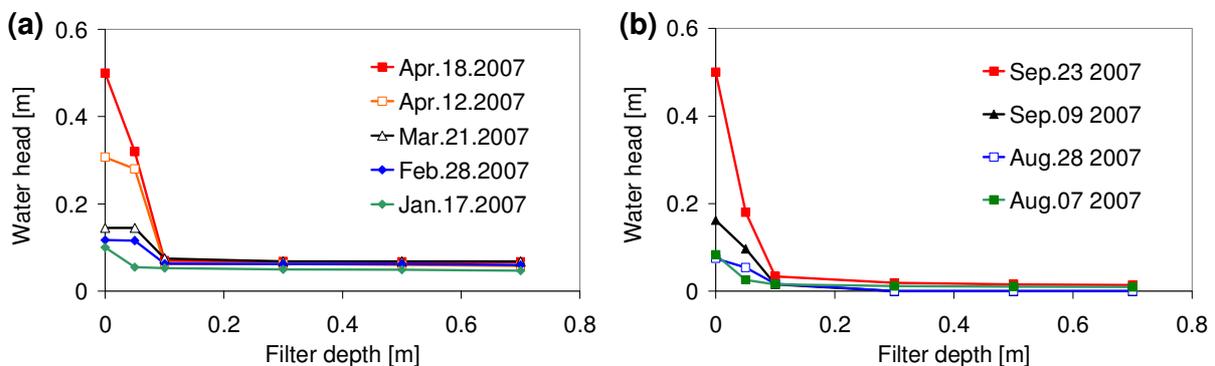
Fig. 5-15 Water head in (a) SSFr Nr. 1 operated at a filtration rate of 0.25 m/h during a cycle time from Jan.17 to Apr.18 2007 (b) SSFr Nr. 2 operated at a filtration rate of 0.5 m/h during a cycle time from Aug.07 to Sep.23 2007

5.4.3 Protective Layer

To extend the cycle time of slow sand filtration at high filtration rates, e.g., 0.5 m/h, a protective layer consisting of BioNet was put on the sand layer surface (Maelzer and Gimbel, 2006) in SSFr Nr. 3. A 0.2 m thick BioNet layer is constructed above a 0.5 m sand layer. The dual-media filter was operated from July 2007 to March 2008. After two months adaption time, the biopolymer removal effect was noted (Tab.5-2).

The operational results show an astonishing extension of the cycle time due to the protect layer. During the experiment period (July 2007 to March 2008), the filter was only cleaned once. The cycle time is longer than four months under the present operational condition. Compared to a slow sand filter, the combined BioNet and sand filter can remove biopolymers to an extent of about 45 % from September to November 2007. The removal rate is lower than that achieved by the SSFr Nr. 2 at the same filtration rate. This might be due to the much shorter operation time of the filter. After several months of operation, the combined BioNet and sand filter achieved similar biopolymer removal effect as the SSFr Nr. 2 during the cold season (November to December 2007). As BioNet carriers are made of porous compressible material, they can offer large surface areas for adherence and growth of microorganisms and also large void volumes for the retention of colloids and particles. With the removal of biopolymers, colloids and particles in the BioNet layer, the loads to the sand layer could be significantly reduced. Therefore, the permeability of the sand layer can be maintained for a longer time.

5.5 Discussion and Summary

5.5.1 Biopolymer Removal in Slow Sand Filtration

Slow sand filtration removed particles, colloids and biopolymers from SE and improved the performance of UF to a large extent. Within the slow sand filter, the removal of biopolymers was demonstrated to be related to the reduction of oxygen concentration and the decrease of pH. As dissolved substances cannot be retained due to straining by the filter material, their removal was attributable to biological processes (Morales et al., 2007). Further tests demonstrated that biopolymers are biodegradable. It indicated that the removal of biopolymers within slow sand filter depended on biodegradation. Nevertheless, it should be noted that in biological processes biosorption of high molecular weight substances to live biomass is a preliminary step previous to enzymatic hydrolysis breakdown and biological uptake (Esparza-Soto and Westerhoff, 2003). Therefore, organic compounds are also removed from water phase due to biosorption. But, due to the exhaustion of adsorption capacity no adsorption system can offer a sustainable removal effect. In an investigation on macromolecular organics removal through bioadsorbtion to live biomass (Esparza-Soto and Westerhoff, 2003), it was observed that within several hours the bioadsorption reached a steady state and no more removal effect could be achieved. By contrast, the biofilters could remove biopolymers continuously for hundred to thousand hours at a constant rate. This phenomenon indicated that although biosorption is a necessary step transporting biopolymers from water phase to biomass, the ultimate elimination of these substances was biodegradation.

Due to biological removal, biopolymer content can be reduced in terms of organic carbon or nitrogen. The N/C ratio of biopolymers showed little variation after slow sand filtration. It seemed that the carbon and nitrogen-containing compounds were mostly evenly removed. The removal of nitrogen compounds by slow sand filtration was further validated based on the EEM spectra measurement of fractioned biopolymers in feedwater and effluent. Nevertheless, several studies reported that the protein-like substances (generally organic nitrogen-containing organics) are preferably removed by biofiltration than polysaccharides. For instance, based on the comparison of EEM spectra and LC-OCD chromatograms of SE and SSF, Haberkamp (2008) stated that protein-like substances were more significantly removed by slow sand filtration than other biopolymer compounds. This phenomenon was attributed to their higher biodegradability compared to polysaccharides (Flemming and Wingernder, 2002). According to this deduction, the N/C ratio of biopolymers after slow sand filtration should decrease, which is inconsistent to the observation in the present work. The conflicting results may lie on the difference in protein measurement scope. In the present study, the measurement focused only on the proteins within biopolymers as water sample fractionation using chromatography was conducted prior to LC-OCD-OND and fluorescence EEM. In the study undertake by Haberkamp (2008), all the proteins removed by slow sand filtration were detected by the fluorescence EEM measurement, which were considered as a component of biopolymers. Therefore, a higher removal ratio of proteins can be deduced.

5.5.2   Influencing Factors on the Performance of Slow Sand Filtration

The removal of biopolymers as well as other DOC fractions took place mostly in the active upper sand layer. In the deeper sand layer, they could be further reduced, but to a much slower rate. This phenomenon is similar to that in several studies investigating DOC removal in bank filtration and/or artificial recharge (Gruenheid et al., 2005; Brinkmann et al., 2004; Hua et al., 2003). Having identified biopolymer removal mainly due to biological processes, the factors such as temperature, biopolymer concentration in feedwater and filtration rate (depends on EBCT) are considered to influence its performance.

As a primary environmental factor, temperature affects the microbial growth and activity in slow sand filter. Generally, a higher temperature leads to a more suitable circumstance to the microorganism and therefore, can result in a higher biopolymer removal. Additionally, it was evident that temperature impacted the biopolymer concentration in SE, an increase of temperature led to a decrease of biopolymer concentration. To understand the end effect of temperature on biopolymer removal, a more direct indicator is the removed biopolymer mass. As shown in Fig. 5-12 (c), it is evident that under higher temperature more biopolymer can be removed when biopolymer concentration in SE is similar.

Besides biopolymer removal, temperature seemed to influence the cycle time of the filters. Lower temperature led always to a shorter running time due to filter clogging at the upper sand layer. A similar phenomenon was observed by Le Binhan and Lessard (2000) while they studied biofilter clogging in treating snowmelt wastewater. The reduction of the operating time was primarily attributed to a weakened hydrolytic activity of the bacteria due to low temperature. This led to the abundance of EPS in biofilm which had a clogging effect in the biofilter. In the present work, slow sand filter received more biopolymers (EPS) in cold time

than in warm seasons. It has been shown that the accumulated biopolymer cannot be removed by bacteria as quickly as under higher temperatures. Thus, filter clogging appears more frequently in winter.

To control slow sand filter clogging at low temperatures, the application of a protective layer, e.g., BioNet, was identified as an effective method. The use of BioNet could not improve the removal effect of biopolymers, but offers large void space for the accumulation of bacteria as well as biofilm and particles. Therefore, the biofilm inhabited not only in the sand layer, but also in BioNet structure. This leads to a partial removal of biopolymers before they reach the sand filter, and may reduce the accumulation of biofilm. The permeability of the upper sand zone can thus be maintained for a much longer time. A further verfication of the effect of a protective layer consisting of BioNet has been conducted in pilot-scale. Operated at a filtration rate of 0.25 m/h, the biofilter has worked from Febrary 2009 to February 2010 without sand scraping.

Despite the fluctuation of biopolymer concentration throughout the whole experimental period, a significant correlation between the concentration in the feedwater and the amount removed by slow sand filtration (0.25 m/h, Fig. 5-12 b) could be observed when biopolymer content is within a certain range, such as lower than 0.4 mg C/L observed in the present work. This correlation is reproducible at different temperature scopes (Fig. 5-12 c). The proportional relevance suggests that the removal of biopolymer may be a first order process (Rooklidge et al., 2005; Huck and Anderson, 1992). Nevertheless, there was no unified apparent first order constant found suitable to describe the biopolymer removal rate. The major reason for this phenomenon is that biopolymers contain components with different properties, e.g., proteins, polysaccharides, etc. During biodegradation they present different removal rates. A first order constant describing the removal rate of a signal substance cannot be adapted to present the rate of a mixture with different biodegradation characteristics (Gruenheid et al., 2008). An overload of biopolymer mass to the filter changes the removal to a zero order process. As the substrates (biopolymers) are always available, the almost exhaustion of oxygen after active layer suggests that oxygen availability may restrict the biomass activity significantly.

The performance of slow sand filtration is also impacted by operating variables in which EBCT is considered to be a key parameter controlling the removal effect (Huck and Sozanski, 2008; Urfer et al., 1997). The EBCT in the present work was changed by the variation of hydraulic loading (filtration rate) for the filters had a similar filter depth. For a given EBCT, as shown in Fig. 5-13 (b and d), biopolymer removal was little dependent on hydraulic loading in the range of applied filtration rates (0.1 to 0.5 m/h). This empirical finding suggests that external mass transfer may play a minor role in biopolymer removal under conditions applied in the present work because for a given EBCT the increase in flow velocity did not increase the percentage of removal (Urfer et al., 1997). Moreover, the decrease of filtration rates from 0.5 to 0.05 m/h resulted in an improvement in biopolymer removal. This is mainly attributed to the manipulation of the duration of interaction between biofilm and organic substance (Simpson, 2008). Nevertheless, the correlation was less than proportional (Fig. 5-14). It seems that over a certain level, further increase of EBCT offers only a very limited improvement of biopolymer removal.

6 Pilot-scale Ultrafiltration of Bio-filtrate

Although the application of biofiltration prior to UF improved the performance of membrane to a large extent, it was observed that TMP development in UF was significantly influenced by operational conditions. The effect of filtration force (flux), filtration duration (backwash interval: BWI), backwash duration (backwash time: BWT) and chemically enhanced backwash (CEBW) were investigated using a pilot-scale UF plant. The impact of filtration flux on fouling was further explored in lab-scale tests. Several cleaning reagents were tested to restore the permeability of the fouled membrane.

6.1 Overview of the Experiments

In the previous chapter it is evident that due to the reduction of foulant content by biofiltration the performance of UF can be improved significantly. Nevertheless, UF treating slow sand effluent leads to a fast TMP increase when the plant was operated under high permeate flux and long BWI, e.g., flux 89 LMH, BWI 40 minutes, the TMP increased from 300 to 700 mbar within 16 hours (Fig. 5-3). Subsequent chemical cleaning had to be carried out to restore the permeability of the membrane. To slow down TMP development, the effect of operational conditions needs to be investigated.

The investigation was carried out from November 2006 to August 2007. An overview of the tests is displayed in Tab. 6-1. During this period, the effect of flux, BWI, BWT and CEBW on TMP development rate were tested. In each experiment, a test ended as soon as the TMP reached a specific level (maximum 800 mbar per manufacturer's guidelines). The time the plant operated from the beginning until the TMP increased to the specific value is defined as operating time. The corresponding TMP development rate is calculated in terms of per unit permeate volume using Eq.6-1:

$$R_{TMP} = \frac{TMP_{end} - TMP_{start}}{V} \quad \text{Eq.6-1}$$

where
R_{TMP} = TMP increase per m^3 permeate, mbar/m^3
V = permeate volume, m^3
TMP_{end} = TMP at the end of each experiment, mbar
TMP_{start} = TMP at the beginning of each experiment, mbar

The TMP data used in the present work was the TMP value (mbar) after 5 minutes filtration in each filtration cycle at identical times on each operating day. After each experiment the module was subsequently cleaned using NaClO (active chlorine 50 mg/L) and NaOH (pH 12) / H$_2$SO$_4$ (pH 2) solution until the permeability (tested with tap water) was recovered to over 90% of the initial value.

Tab. 6-1 Influence of operational conditions on the performance of UF filtering SSF (BWF was always 260 LMH during the whole experiment)

Comprison	Experiment date	Flux (LMH)	TMP increase (mbar)	BWI (min.)	BWT (s)	BWT arrangement (FF/BW/FF/still - s)	Permeate volume (m^3)	Produc-tivity (%)	R_{TMP} (mbar/m^3)	Biopolymer Concentration (mg C/L)	Turbidity (NTU)
Flux	02 15 - 02 26 2007	50	228 - 280	10	20	10 / 20 / 10 / 0	51	83	1.2	0.19	0.22
	07 29 - 08 04 2007	65	259 - 709	10	20	10 / 20 / 10 / 0	40	87	13.1	0.12	-
	04 18 - 04 20 2007	80	284 - 708	10	20	10 / 20 / 10 / 0	12	89	39.1	0.17	0.2
BWI	02 15 - 02 26 2007	50	228 - 280	10	20	10 / 20 / 10 / 0	51	83	1.2	0.19	0.22
	02 28 - 03 10 2007	50	216 - 676	20	20	10 / 20 / 10 / 0	58	92	8.7	0.32	0.38
	04 03 - 04 05 2007	50	268 - 712	40	20	10 / 20 / 10 / 0	11	96	43.7	0.19	0.27
BWT	03 14 - 04 02 2007	50	250 - 570	20	40	10 / 40 / 10 / 0	57	83	6.8	0.18	0.29
	02 28 - 03 10 2007	50	216 - 676	20	20	10 / 20 / 10 / 0	58	92	8.7	0.32	0.38
	04 03 - 04 05 2007	50	268 - 712	40	20	10 / 20 / 10 / 0	11	96	43.7	0.19	0.27
	04 12 - 04 14 2007	50	300 - 720	40	60	10 / 60 / 10 / 0	11	87	46.1	0.17	0.3
CEBW Permeate	11 07 2006	89	308 - 660	40	50	10 / 50/ 10 / 300	6	94	78.3	0.2	-
NaOH	08 22 – 08 29 2007	89	300 - 658	40	50	10 / 50/ 10 / 300	61	94	7.5	0.1	0.28
H_2O_2	09 17 – 10 18 2007	89	195 - 405	40	50	10 / 50/ 10 / 300	270	94	1.7	0.11	0.2
NaClO	11 20 2006 – 01 23 2007	89	210 - 390	40	50	10 / 50/ 10 / 300	561	94	0.8	0.29	0.31

BWI: backwash interval
BWT: backwash time
CEBW: chemically enhanced backwash
FF: forward flush
BW: backwash

6.2 Influence of Flux on Fouling

6.2.1 Pilot-scale Investigation

The effect of operating flux was investigated by filtering SSF at 50, 65 and 80 LMH. Each experiment was performed at BWI 10 minutes and BWT 20 seconds, the permeability of the membrane at the beginning of each experiment (Kw_0) was around 260 L/(m^2·h· ·bar) (tested with tap water, normalized to at 20°C) which was lower than that of a new membrane as it was chemically cleaned in previous tests. Fig. 6-1 (a) shows the result of TMP development with respect to operating time at different fluxes. At 80 LMH TMP increased from 284 to 708 mbar within 40 hours. At 65 LMH the operating time was extended to longer than 120 hours. When the flux was reduced to 50 LMH, TMP increased only 50 mbar within 240 hours. In terms of permeability reduction, the declining slopes indicate clearly that K_w decreased with time/permeate volume at each flux. The comparison of permeability decline rates at different operational conditions illustrated that the permeability decreased steadily as operating flux increased, either due to operating time (Fig. 6-1 b) or permeate volume (Fig. 6-1 c).
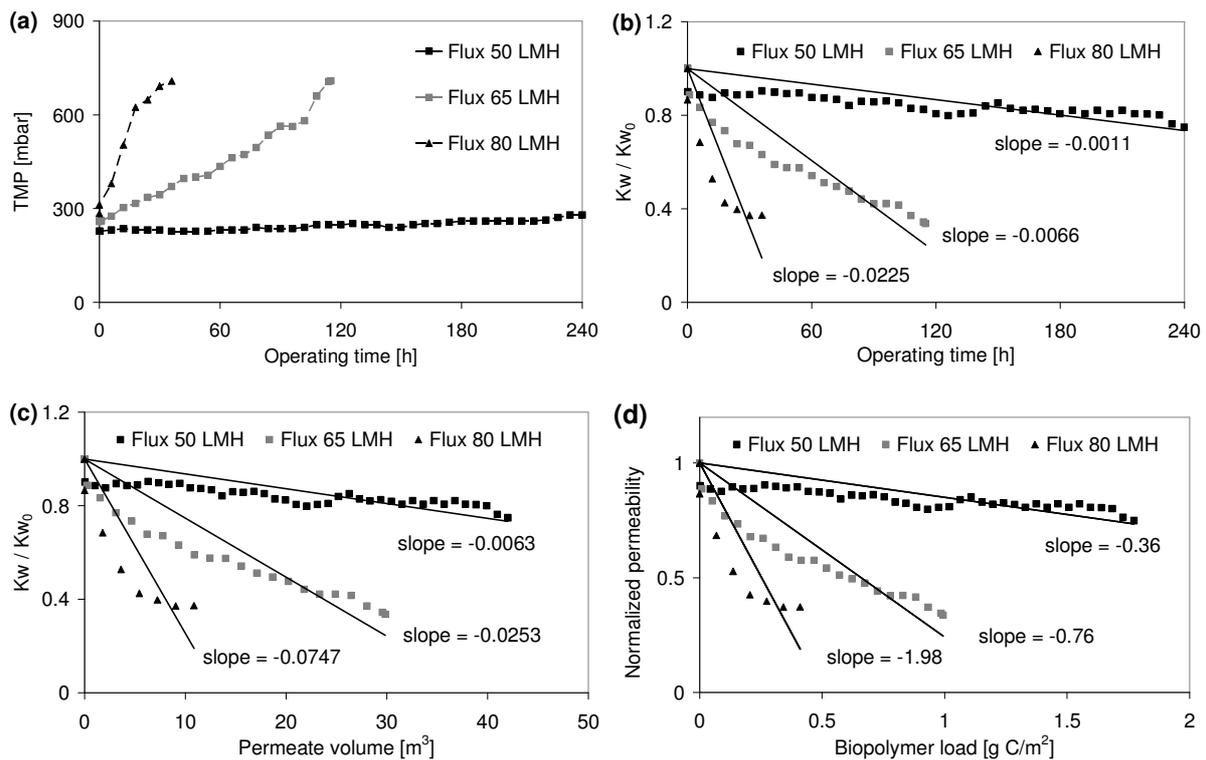
Fig. 6-1 (a) TMP development vs. operating time at different fluxes, (b) Kw/Kw$_0$ vs. operating time, (c) Kw/Kw$_0$ vs. permeate volume, (d) Kw/Kw$_0$ vs. biopolymer load mass

The more severe decrease of permeability at higher flux is primarily attributed to a higher foulant mass load (biopolymers mass load) during a filtration cycle which can lead to more irreversible fouling. According to the water quality data shown in Tab. 6-1, more biopolymer was delivered to the membrane at a flux of 80 LMH than at 50 LMH within a filtration cycle. The more severe fouling can be attributed to the biopolymer mass load.

However, compared to operation at a flux of 50 LMH, filtering SSF at a flux of 65 LMH delivered less biopolymer to the membrane in each filtration cycle due to a lower biopolymer concentration in the feed water (Tab. 6-1), the permeability of the membrane decreased sharper, either versus operating volume or biopolymer load mass (Fig. 6-1 c and d). This phenomenon cannot be interpreted according to biopolymer load mass. Therefore, lab-scale experiments were carried out investigating flux on fouling development.

6.2.2 Effect of Filtration Flux on Biopolymer Fouling

Influence of TMP on Biopolymer Fouling Effect
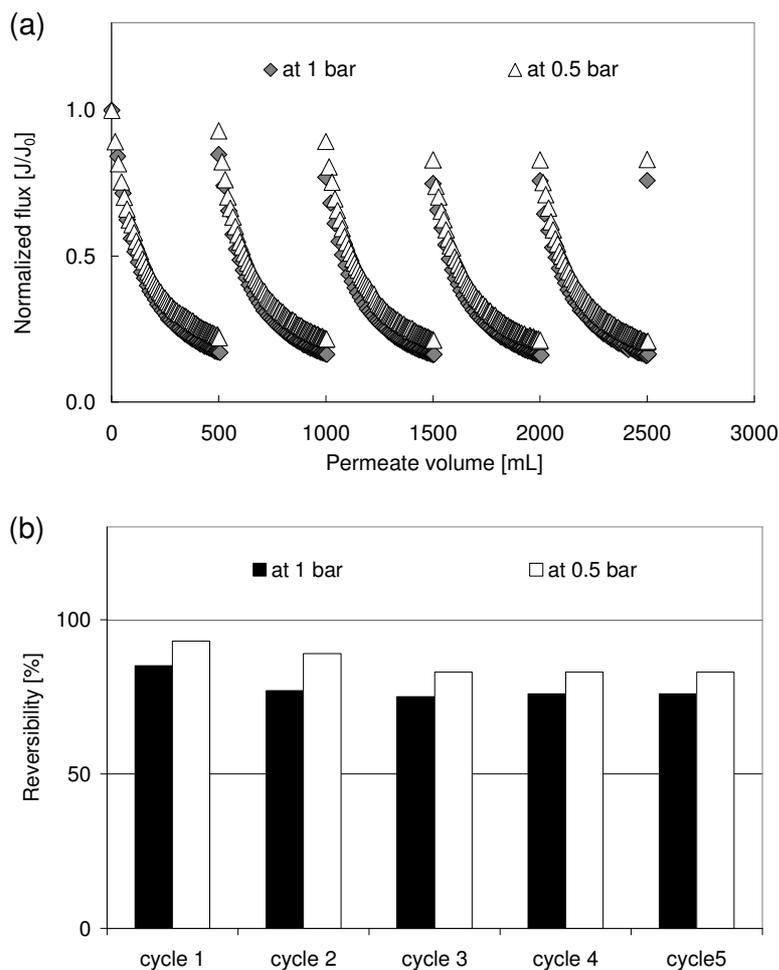

Fig. 6-2 (a) Influence of operating pressure on fouling effect, (b) flux recovery at different operating pressures (feed water is SE after 0.45μm filter with a biopolymer concentration of 0.42 mg C/L, operating pressure at 1 bar and 0.5 bar, permeate volume 500 mL; back wash using salt solution 50 mL at 1 bar)

Lab-scale multi cycle filtration tests, each operated at constant pressure throughout the test, were used to investigate the effect of different operating pressures. The operation was conducted by filtering identical SE samples at 1 bar and 0.5 bar. The results in Fig. 6-2 (a) show that each filtration cycle operated at 1 bar leads to a more serious flux decline than at 0.5 bar; the correspondingly formed fouling is also more irreversible as the reversibility is always lower than that formed at lower operating pressure (Fig. 6-2 b). As the feedwater is identical, the difference in performance of the UF was interpreted by comparing the biopolymer mass in

the fouling layer under the two different pressures. Based on a mass balance, the biopolymer mass in each fouling layer can be calculated (the dry weight of biopolymers is assumed to be twice their carbon content as carbon accounts for around 50 % of the mass of the protein-like and polysaccharide-like substances (Thullner et al., 2002)). The comparison (Tab. 6-2) shows little difference in biopolymer mass at the two operating pressures. Further analysis was then focused on the fouling mechanisms at different filtration pressures. The results shown in Fig. 4-13 (c) indicated that during each filtration at 0.5 bar the predominant fouling mechanism was cake/gel filtration which was similar to that at a filtration pressure of 1 bar (Fig. 4-13 d). The difference in the performance of the UF thus needs to be further investigated, taking into consideration the structure of the fouling layer as influenced by the filtration pressure.

Tab. 6-2 Calculated biopolymer mass content in formed cake/gel layer and the corresponding specific fouling resistance (biopolymer concentration in SE is 0.42 mg C/L, permeate volume 0.5 L, supernatant 0.2 L).

	cycle1	cycle2	cycle3	cycle4	cycle5	Average
Biopolymer in fouling layer at 1 bar(mg)	0.27	0.28	0.27	0.30	0.27	0.28
Biopolymer in fouling layer at 0.5bar (mg)	0.27	0.29	0.29	0.25	0.26	0.27
Specific resistance α_1 at 1.0 bar (10^{16} m/kg)	1.97	1.93	2.0	1.83	2.13	1.98
Specific resistance $\alpha_{0.5}$ at 0.5 bar (10^{16} m/kg)	1.40	1.26	1.25	1.58	1.51	1.40

Based on the experimental results displayed in Fig. 6-2 (a), the specific fouling resistance of the biopolymer fouling layer was calculated according to Eq.2-5 and Eq.2-9. The calculated results (Tab. 6-2) show that under the present experimental conditions the specific fouling resistance of the biopolymer fouling layer is about 1.4×10^{16} and 2.0×10^{16} m/kg at operating pressure 0.5 bar and 1 bar, respectively. The formed biopolymer fouling layer is moderately compressible as the calculated compressibility was around 0.54 at corresponding pressure range (calculation according to Eq.2-11 based on the results shown in Fig. 6-2 (a). The values are similar to the results presented by Lodge et al. (2004). In their research a UF membrane similar to the one used in the present study was operated to treat wastewater effluent.

The comparison of the reversibility of fouling formed at TMP 1 bar and 0.5 bar is shown in Fig. 6-2 (b). As displayed, during the five cycles of the filtration process the declined membrane permeability at 1 bar can always be restored to a lower extent than that under 0.5 bar. The phenomenon indicates that the permeability reduction caused at a higher filtration pressure is more difficult to be recovered. As higher operating pressure leads to a more condensed fouling layer and results in a higher α, the stronger compressed biopolymer fouling layer leads to a more serious normalized flux decline and a decrease of the reversibility.

Validation of the Effect of Compression on Biopolymer Fouling

Further tests filtering SSF with a biopolymer concentration of 0.51 mg C/L were conducted to validate the reproducibility of the effect of operating pressure. The filtration was carried out at 1.0, 0.8, 0.6 and 0.4 bar, using five filtration cycles (Fig. 6-3).
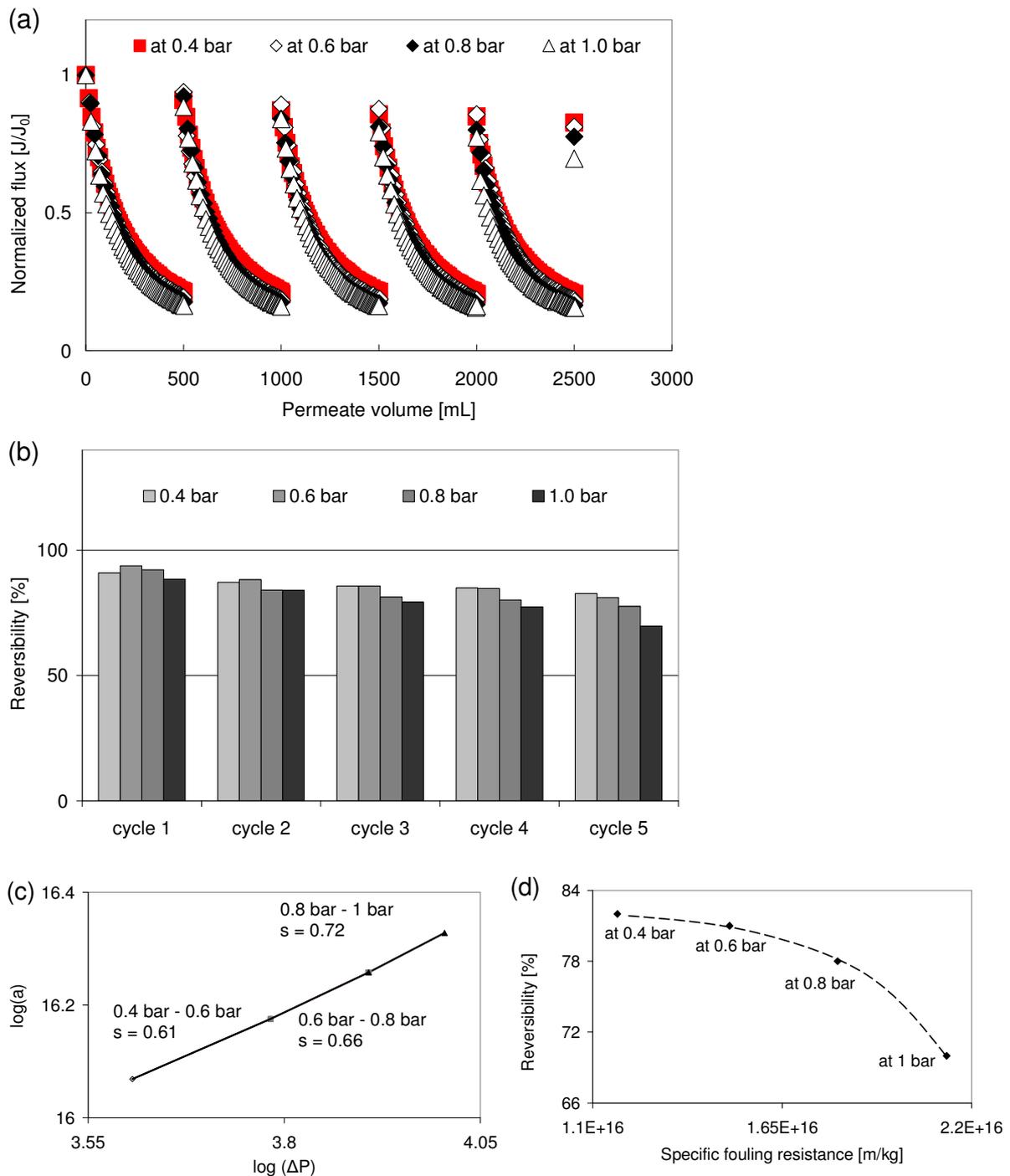
Fig. 6-3 (a) Influence of operating pressure on fouling effect, (b) flux recovery at different operating pressures, (c) compressibility under different pressure ranges, (d) correlation between specific fouling resistance and reversibility of corresponding fouling (feed water is slow sand effluent with biopolymer concentration of 0.51 mg C/L, operating pressure at 1.4 bar, 1 bar and 0.5 bar, permeate volume 0.5 L; back wash using salt solution 0.05 L at 1 bar)

As expected, the results show that the calculated α (Fig. 6-3 c) is comparable to the value shown in the previous experiment (Tab. 6-2) at operating pressure from 0.5 bar to 1 bar. Simultaneously, α values also show a correlation with the reversibility (Fig. 6-3 d). This correlation verifies the observation that more compact biopolymer fouling layers decrease the efficiency of backwash and the layer is less reversible. More over, the compressibility calculated at 0.4 to 0.6 bar, 0.6 to 0.8 bar and 0.8 to 1 bar increased with the increase of operating pres-

sures (Fig. 6-3 c). This indicates that at higher pressures the biopolymer fouling layer can be further compressed (Foley, 2006). This is also consistent with the increase of specific fouling resistance results.

6.3 Influence of Biopolymer Load Mass on Fouling Development

6.3.1 Impact of Backwash Interval

The foulant load mass can be changed by backwash interval or due to the variation of foulant concentration in feedwater. The influence of BWI on TMP development was tested at a flux of 50 LMH and a backwashing time of 20 seconds. In each experiment, BWI was set at 10, 20 or 40 minutes. At the beginning of a test the specific permeability of the membrane was around 260 $L/(m^2 \cdot h \cdot bar)$ (tested with tap water, normalized to at 20°C). Operational conditions, average biopolymer concentration and turbidity in feed water are shown in Tab. 6-1.
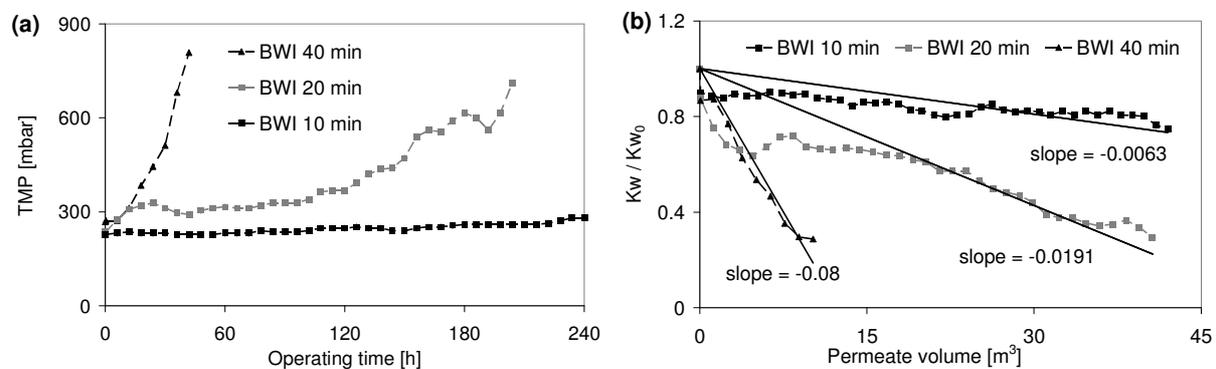
Fig. 6-4 (a) TMP development vs. operating time at different BWI (b) Kw/Kw_0 vs. permeate volume at different BWI (Other operating parameters were identical: BWI 10 minutes, BWT 20 seconds, BWF 260 LMH)

The comparison of TMP increase with respect to operating time is displayed in Fig. 6-4 (a). As shown, TMP increased more quickly when BWI was extended from 10 to 40 minutes. At BWI 10 minutes TMP increased 50 mbar within 240 hours, the extention of BWI to 20 minutes led to a TMP increase of 600 mbar in 210 hours. When the BWI was 40 minutes, TMP raised over 600 mbar after 40 hours operation. Fig. 6-4 (b) shows the slopes of permeability reduction versus permeate volume under these conditions. It is indicated that at a longer BWI the membrane suffers more severe fouling while treating similar water volume. As the feedwater quality in each experiment was similar to each other (Tab. 6-1), the severity of fouling was therefore mainly caused by the variation of BWI. The extention of BWI leads to more foulants accumulating at the membrane surface. This decreases the efficiency of backwashing and results in more severe fouling.

6.3.2 Effect of Foulant Concentration in Feedwater

Considering biopolymers as major organic foulants in UF of treated domestic wastewater, it is expected to find a connection between the variation of biopolymer concentration in feed water

and TMP development along membrane filtration. A logical correlation can offer useful information in fouling control.

Correlation between Biopolymer Concentration and TMP Development

The investigation on the relationship was conducted in three tests. In each test, the UF pilot plant was used to filter slow sand effluent. During the first two succession tests (test 1 and 2), the UF was operated at a flux of 50 LMH, BWI of 20 minutes (Fig. 6-5 a, b). In test 3, the operational conditions were flux at 75 LMH and BWI in 14 minutes. Comparison of the TMP development in these tests indicates that TMP proceeded in a similar pattern. After a rise at the beginning of filtration, TMP increased slowly for several days. Thereafter, it increased more quickly.

A significant correlation between biopolymer concentration and TMP variation was observed in operating day 16 to 17 by test 1 (Fig. 6-5 a), during which TMP decreased sharply while biopolymer concentration fell in the feedwater. During the end phase of test 3 (from operating day 9 to 11, Fig. 6-5 c), a slower than expected TMP increase was related to a very low biopolymer concentration in the SSF. Thereafter, TMP rose significantly in parellel to an increase of biopolymer content in feedwater.

In contrast, no significant relevance between these two parameters was found when TMP development was in the slow increase phase. For instance, at day 7 by test 2 (Fig. 6-5 b) and day 6 by test 3 (Fig. 6-5 c) a significant variation of biopolymer concentration in the feedwater led no immediate change in TMP variation.
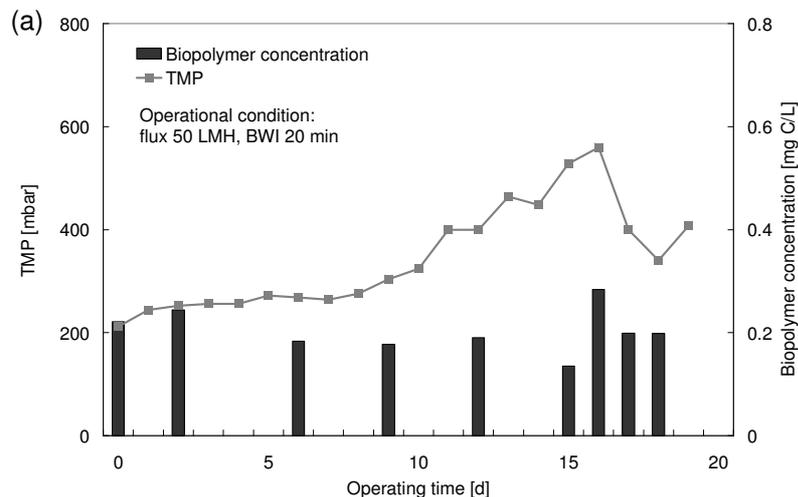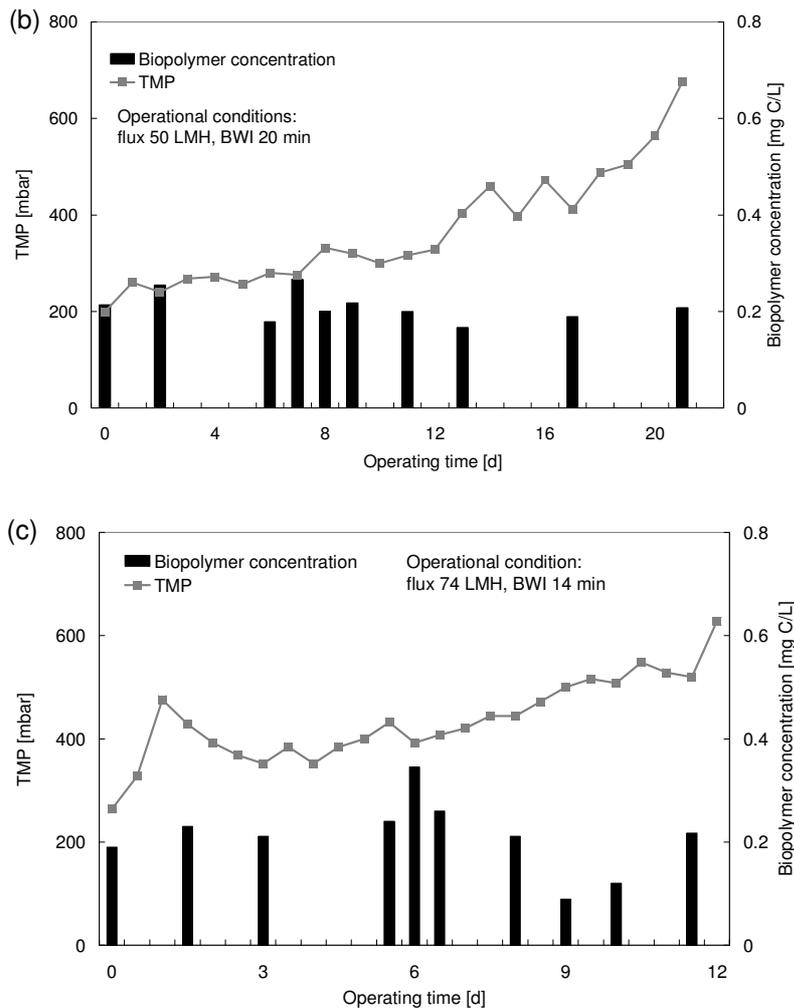
Fig. 6-5 Correlation between biopolymer concentration and TMP development in (a) test 1 at flux 50 LMH, BWI 20 min, (b) test 2 at flux 50 LMH, BWI 20 min and (c) test 3 at flux 74 LMH, BWI 14 min

6.3.3 Fouling Development Processes

Multi-phase Fouling Development

It is evident that although an increase of biopolymer load mass in each filtration cycle leads to generally more severe fouling (Fig. 4-11), a correlation between biopoylmer concentration in feedwater and TMP variation cannot always be observed in daily operation. Particularly, no relevance was found when the operation was in the TMP slow increase phase. It implies that the interactions between foulants and membrane and between foulants vary over the whole period of membrane operation. The effect of biopolymer load mass on fouling development may be different at different TMP development phases.

Based on pilot-scale results, a similar TMP development pattern at different operational conditions can be observed. It contains an initial rise of TMP, followed by a steady TMP increase. In the end of a test there is a sudden TMP rise. A similar fouling development has been observed by Ye et al. (2005) and Zhang et al.(2006a) while operating membrane filtration at sustainable operational conditions and in constant flux mode. A three-stage fouling process in MBR was well summarized by Zhang et al. (2006a). Although the conditions are

not identical to that in this work, the similar organic fouling behaviour in MBR and in low-pressure membrane processes of treated wastewater (Amy, 2008) render their research helpful to understand the fouling phenomenon in UF as a post treatment process.
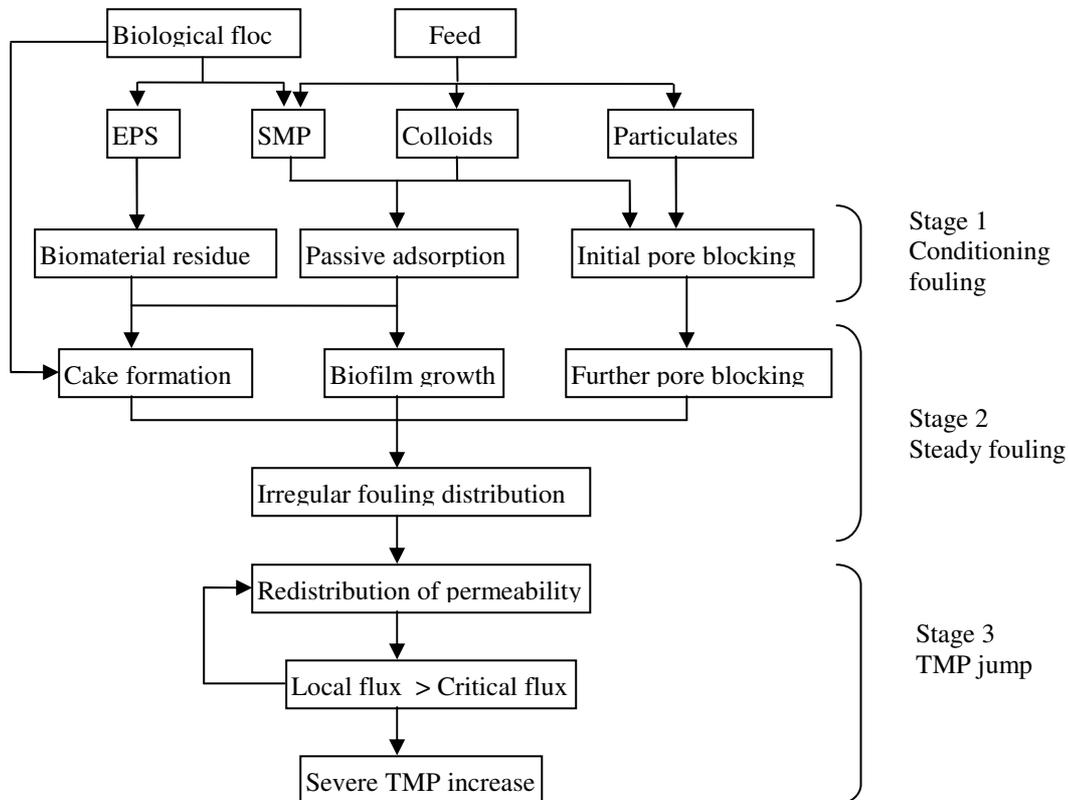
Fig. 6-6 Fouling mechanisms for MBR operation at constant flux (adapted from Zhang et al., 2006a)

Fig. 6-6 shows an overview about the TMP development stage and correspondingly related fouling mechanisms. Based on their report the initial fouling stage is defined as conditioning fouling which appears at the beginning of the filtration when strong interactions take place between the membrane surface and the SMP/EPS. The fouling is mainly due to pore blocking or adsorption (Jiang et al., 2005). This leads to an initial TMP increase. In the following steady fouling stage the membrane surface is expected to be mostly covered by SMP/EPS, promoting further attachment of particulates, colloids and dissolved substances. Although the membrane filtration is operated at sustainable conditions, adsorption and/or deposition of organics may also occur during this stage. As these effects take place also across the whole membrane surface besides directly on the membrane pores, the accumulation of foulants may not affect TMP significantly. Therefore, TMP develops more slowly compared to the conditioning fouling phase. Because of the uneven distribution of the delivered foulants along a membrane fibre, the fouling layer is assumed to develop from location to location alternatively (Wang and Waite, 2008b). At last, most of the fibres are covered with a fouling layer to a critical extent. The critical fouling level would lead to a jump of TMP when the membrane is operated at a constant flux mode. Judd (2006) summarized several mechanisms to explain the TMP jump condition. Based on this summary, the jump would be a result of filtration area loss (in a macroscopic view) or pore loss (in a microscopic view) and the structure modifica-

tion of the fouling layer due to increasing driving force effects. Above the critical fouling level, the permeability of the membrane is difficult to be restored by hydraulic cleaning.

Fouling Development in UF

Based on the proposed mechanisms of the fouling effect of biopolymers and the above mentioned review on fouling phenomena, a three-stage fouling process (Fig.6-8) is used to interpret fouling development in UF of treated domestic wastewater. The experimental result of UF of SSF displayed in Fig. 4-11 (b) (operated at 50 LMH, BWI 10 minutes, BWT 10 seconds, biopolymer concentration is around 0.32 mg C/L on average) is recalled and analyzed as an example (Fig. 6-7).
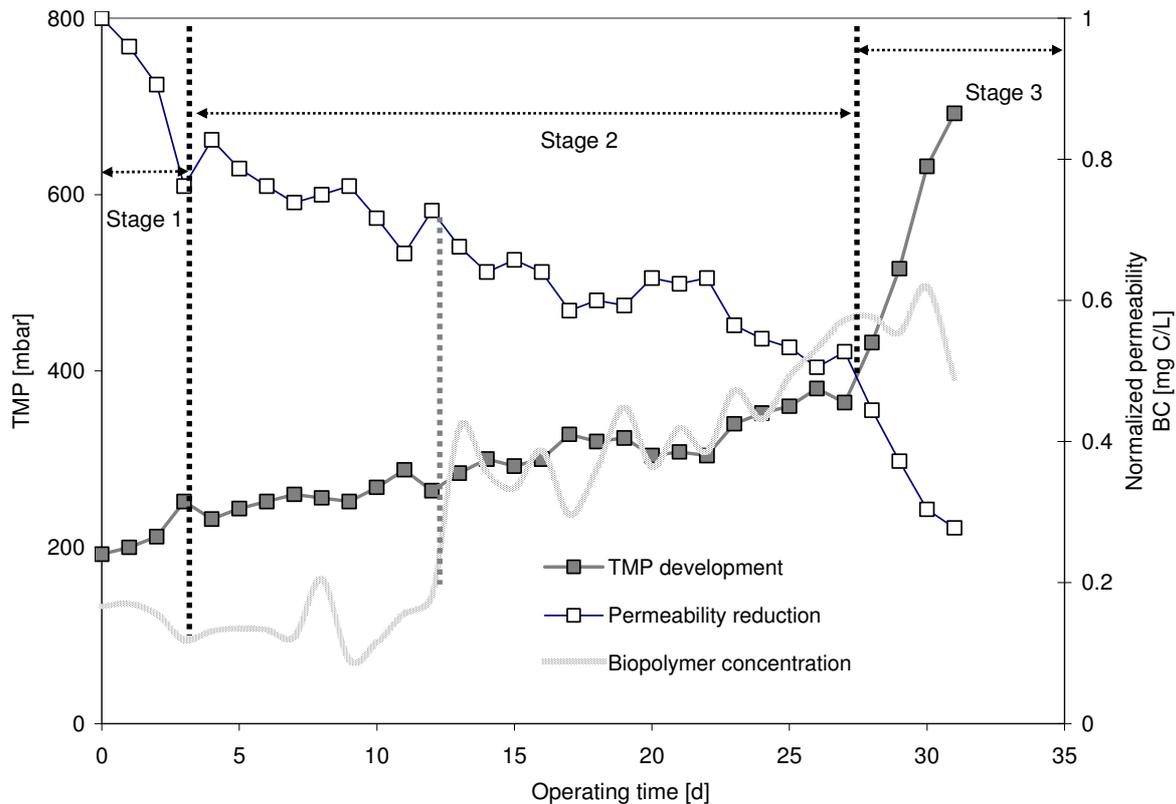
Fig. 6-7 Three-stage fouling development process during UF of SSF (0.5 m/h)

As shown, an increase of TMP (TMP increase rate 20 mbar/day) occurred within the initial three days. Correspondingly, the permeability of the membrane was reduced by 24%. This phase can be classified as conditioning fouling phase, during which rapid irreversible fouling occurs due to pore blocking by biopolymers (Fig. 4-12 a) and/or passive adsorption (Haberkamp, 2008; Susanto et al., 2007).

After the initial significant rise, TMP increased steadily at an average rate of 5.5 mbar per day from day four to day 27. During this period, the permeability was reduced continuously from 76% to 52% of the initial value. It is observed that although from day 14 to day 27 the biopolymer concentration is much higher than before, the variation of TMP was not significant. During this phase the TMP increased averagely 6 mbar per day. This phenomenon could be

attributable to the sustainable operational conditions. As shown in section 6.2.1, operated at a flux of 50 LMH, BWI of 10 minutes, TMP could be kept stable for a long period. Under these conditions, it can be supposed that the biopolymer load mass is under a critical level, most of the accumulated foulants can be effectively backwashed. Therefore, the increase of biopolymer concentration may not affect TMP to a large extent. At this point, TMP development in this phase does not seem to reflect the change of biopolymer concentration in the feedwater.

When the biopolymer concentration could be maintained at lower levels, e.g. lower than 0.1 mg C/L in SSF, the operating time could be extended significantly (Fig. 4-11 b). However, as the concentration was above 0.5 mg C/L from day 27, the high biopolymer load to UF led to a TMP jump. Within four days the TMP increased from 364 mbar to around 700 mbar (TMP increase rate 82 mbar/d). The permeability decreased from 53% to 28% of the initial capacity.
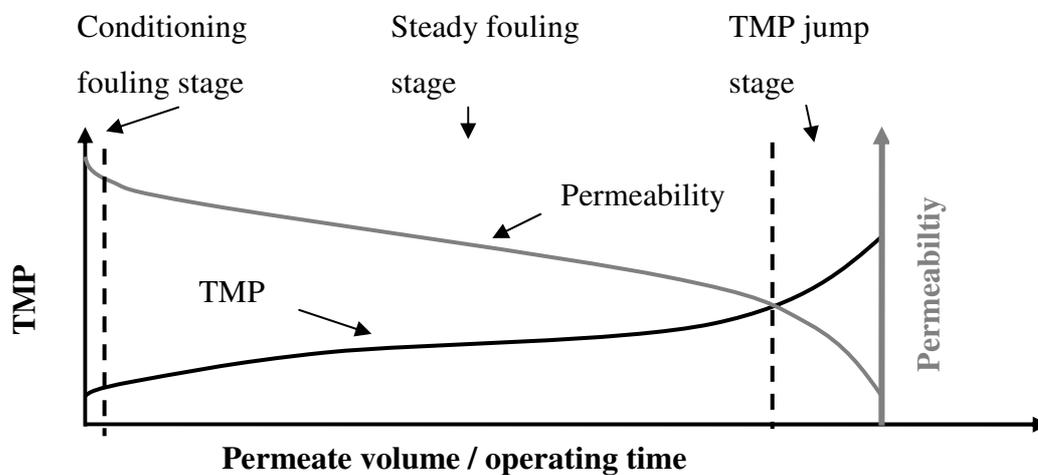
Fig.6-8   Illustration of an ideal three-stage fouling process in UF of treated domestic wastewater (adapted from Zhang et al., 2006a)

Based on the above case study and previous observation, a graphic illustration of the fouling process in UF of treated domestic wastewater is suggested (Fig.6-8). In general, fouling processes include conditioning fouling, steady fouling and TMP jump phase when the UF is operated in constant flux mode and under sustainable operational conditions. In UF of SSF, due to the removal of particles, colloids and biopolymers, the three-stage fouling process can be readily identified. Nevertheless, due to the high fouling potential of SE, the three-stage process can only be observed at very low biopolymer concentrations in feed water (Fig. 4-11 a, biopolymer concentration in SE is 0.1 mg C/L). The reduction of the foulant load mass and/or optimization of operational conditions can extend the duration of these phases significantly. Otherwise, the distinct differences between the different fouling phases cannot be identified (Fig. 6-1 a, Fig. 6-4 a, Fig. 4-11 a).

6.4 Influence of Backwash Time on Fouling Control

Since the backwash flux was set at 260 LMH which is significantly higher than the filtration flux (from 50 to 90 LMH) in the present work, a shorter BWT is preferred to improve the

permeate recovery (P_r, Eq.2-12). Therefore, it is necessary to investigate the influence of BWT on fouling control effects.
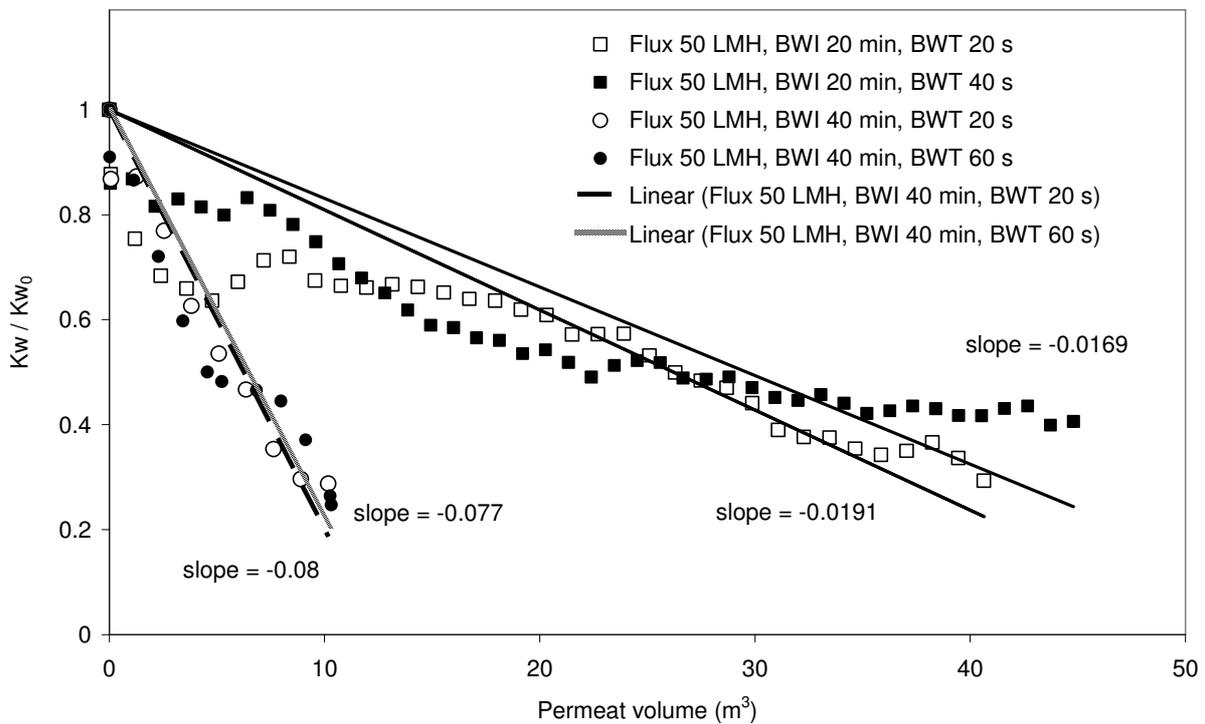
Fig. 6-9 Comparison of the influence of BWT on the performance of UF

The comparison was conducted by filtering slow sand effluent at a flux of 50 LMH. The effect of BWT of 20 and 40 seconds at BWI of 20 minutes, effect of BWT 20 and 60 seconds at BWI 40 minutes were investigated, respectively. The biopolymer concentration on average throughout the experiments was similar (Tab. 6-1). Fig. 6-9 displays the permeability reduction at corresponding operational conditions. In the case of BWI at 20 min, the BWT at 20 s and at 40 s demonstrates no significant influence on the performance of UF, although longer BWT led to a slightly slower permeability reduction. The extension of BWT from 20 s to 40 s resulted in, however, an approximate eight percent decrease of permeate recovery. When BWI was set at 40 min, an extention of BWT from 20 s to 60 s led to no improvement in fouling control but a significant reduction in respect of permeate productivity. The result implies that most of the hydraulic reversible fouling can be removed at the beginning of a backwashing. Based on the experimental results, the backwash time in filtering SSF in the present work was set to around 20 seconds.

6.5 Chemically Enhanced Backwash

In practice, membrane filtration is preferred to be operated at high flux and long BWI to reduce the membrane area and improve the permeate productivity. Under these conditions, as shown previously, fouling develops quickly. Therefore, chemically enhanced backwash is necessary to stabilize the performance of membrane systems. Based on the chemical characteristics of fouling and feed water quality different reagents can be used (Decarolis et al., 2001; Teodosiu et al., 1999; Liu et al., 2006).
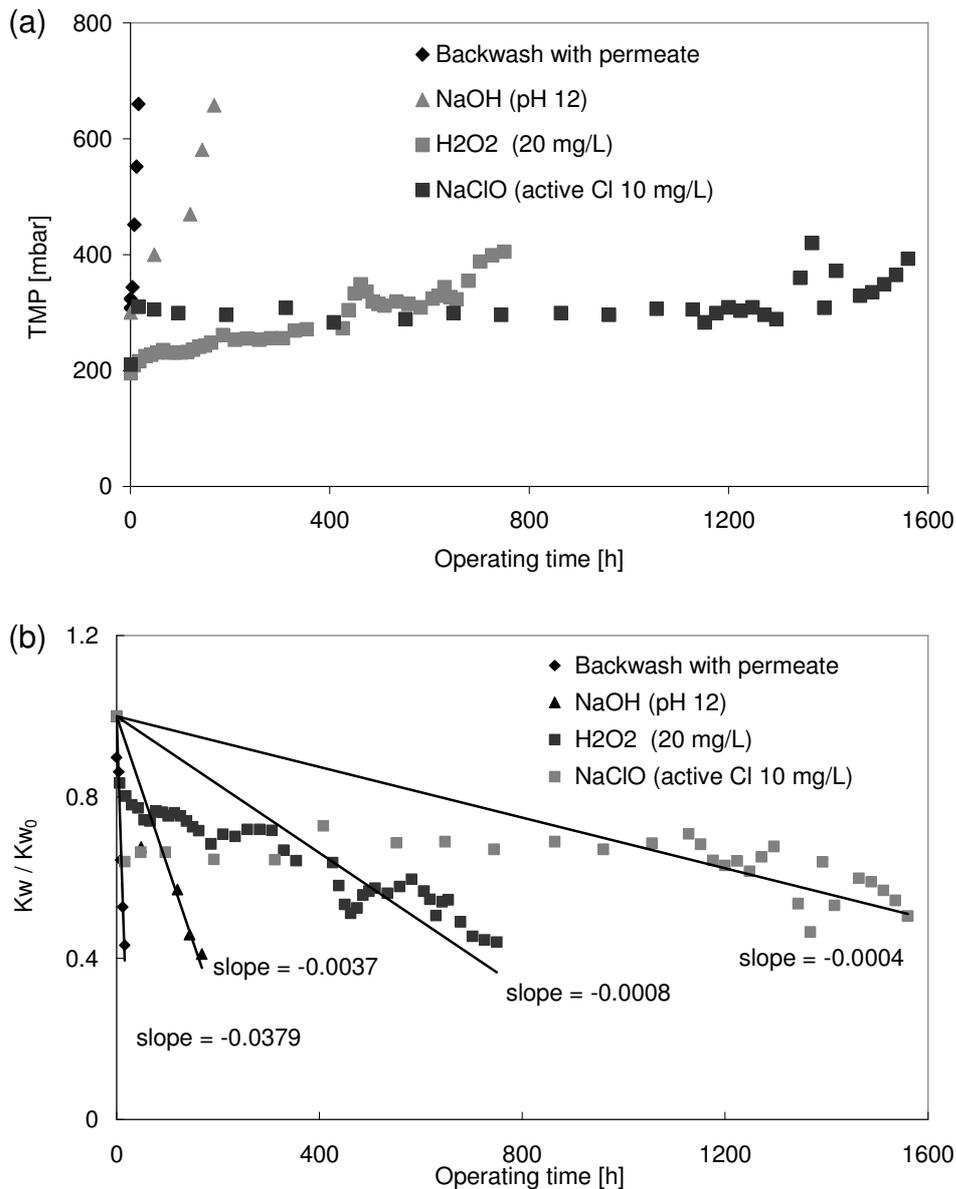
Fig. 6-10 (a) TMP development vs. operating time using permeate backwash and enhanced backwash reagents (b) Kw/Kw$_0$ vs. operating time using permeate backwash and enhanced backwash reagents

In the present work sodium hydroxide, hydrogen peroxide and sodium hydrochloride were tested individually as enhanced backwash reagents. The UF was operated at flux 89 LMH, BWT 40 minutes. To improve backwash effect, CBWT was set at 50 seconds followed by a soaking time of 5 minutes. During each chemically enhanced backwash, the dosage was controlled by keeping the backwash permeate at pH of 12 or by holding the concentration of H_2O_2 at 20 mg/L or active chlorine at 10 mg/L. Each experiment was conducted until the TMP increased to 700 mbar. The operational conditions and water qualities are shown in Tab. 6-1.

TMP control results using different chemicals are shown in Fig. 6-10 (a) and Tab. 6-1. The results show that dosing different backwash reagents extends the operating time of the pilot

plant in different patterns. Within the same TMP increase scope, the dosing of NaOH into the backwash permeate extended the operating time of the UF pilot plant from 16 hours to around 150 hours. It is indicated that the hydraulic irreversible fouling can be removed by bases. However, after several days the pilot plant was out of operation due to serious scaling in the membrane module and dosing system. The inorganic precipitates scaled the outside of the membrane surface so seriously that the whole system was stopped due to high pressure losses. Best TMP control effects were achieved by using NaClO (active Cl concentration 10 mg/L). The TMP rose from 200 to 450 mbar after 1600 hours operation. In detail, Fig. 5-3 shows the effect of NaClO. It can be seen that each time after enhanced backwash using NaClO, the TMP was almost back to its original level. This result indicated that NaClO removed most of the hydraulic irreversible fouling during backwashing. In contrast, backwash using permeate resulted in continuous increase of TMP. Althoug it recovered the permeability to some extent, it was unable to remove the hydraulic irreversible fouling.

Dosing H_2O_2 (concentration 20 mg/L) into backwash water was also identified as an effective fouling control method. This led to a TMP increase from 200 to 500 mbar after about 800 hours operation. Normalized permeability reduction versus time (Fig. 6-10 b) shows that the usage of NaClO leads to the flattest permeability reduction compared to other enhanced backwash reagents. Although using H_2O_2 shows a sharper permeability decreases, it is presented as a reliable chlorine-free fouling control reagent compared to the usage of chlorine which causes disinfection by-product problems in water treatment (Hua and Reckhow, 2007).

6.6 Membrane Cleaning

As an integrated part of membrane operation, chemical cleaning is important to recover the permeability of a fouled membrane. Based on the characteristics of major foulants in membrane filtration, different cleaning reagents can result in different cleaning effects. For UF of SSF in the present work, cleaning effects of acid (H_2SO_4 pH 2), caustic (NaOH pH 12), oxidants (NaClO active Cl 50 mg/L, H_2O_2 125 mg/L) and different waters (UF permeate, tap water and demineralised pure water) on the permeability restoration were tested (Tab. 6-3).

Tab. 6-3 Cleaning effect of different chemical reagents on permeability restoration of UF of SSF

Experiment date (2007)	Flux (LMH)	TMP$_{start}$ (mbar)	TMP$_{end}$ (mbar)	Chemical reagents	TMP$_c$ (mbar)	Permeability Restoration
23.05.~27.05	60	220	680	H_2SO_4 pH 2	520	15%
01.06.~06.06	60	240	688	NaOH pH 12	312	65%
08.06.~13.06	60	270	468	NaClO active Cl 50 mg L^{-1}	324	61%
15.06.~20.06	60	224	400	Tap water	336	24%
22.06.~27.06	60	240	576	Permeate	460	18%
29.06.~04.07	60	260	708	H_2O_2 125 mg/L	500	24%
06.07.~11.07	60	280	600	Pure Water	396	45%

To compare the cleaning effect of different reagents, membrane filtration of SSF (filtration rate at 0.25 m/h) was operated at a flux of 60 LMH, BWI 20 minutes and BWT 20 seconds for five days. After that, the membrane was cleaned using a single cleaning reagent. During cleaning, 10 L cleaning reagent was firstly backwashed into the membrane module to remove the cake layer on the membrane. The membrane was then soaked for 24 hours. Subsequently, 10 L cleaning reagent was backwashed again to remove irreversible foulants. Thereafter, tap water was used to forward flush the membrane for two minutes. At the end, the TMP was tested by filtering tap water at 60 LMH for five minutes. All the cleaning procedures were performed at room temperature (around 20 ºC). After cleaning the corresponding permeability restoration was calculated according to Eq.6-2. In the present study cleaning conditions would not damage the membrane since the concentration studied was within the ranges recommended by the membrane manufacturer.

$$R_p = \frac{K_{w-c} - K_{w-end}}{K_{w-start} - K_{w-end}} \times 100\% \quad \text{Eq.6-2}$$

where
R_p = restoration of permeability, %
$K_{w-start}$ = permeability before filtration, L/(m²·h·bar)
K_{w-end} = permeability after five days operation, L/(m²·h·bar)
K_{w-c} = permeability after cleaning, L/(m²·h·bar)

The results are shown in Fig. 6-11. It can be seen that the highest permeability recovery was obtained by using NaOH (pH 12) while acid (H_2SO_4, pH 2) exhibited the lowest cleaning effect. This result indicates that inorganic foulants (scales and metal dioxides) play a minor role in hydraulic irreversible fouling during UF of treated wastewater. The fouling is mainly of organic property. Caustic reagents can hydrolyze the organic binding more readily than acids and solve them into the solution (Liu et al, 2006).

Although the concentration of NaClO (active Cl 50 mg/L, fourfold diluted as the recommended concentration per the membrane manufacturer) used in the present work was much lower than the recommend value, it presented also a capacity restoring the membrane permeability. At a higher concentration NaClO is expected to perform better (Kimura et al., 2004; Liu et al., 2006). H_2O_2 (125 mg/L, fourfold diluted as the recommended value) was also a recommended cleaning reagent, but it showed a permeability recovery lower than 30% at the present concentration. The result suggests that with respect to removing EfOM fouling, chlorine performs better than hydrogen peroxide.

A significant permeability restoration was obtained by using demineralized pure water in membrane cleaning. After 24 h soaking, the permeability of the fouled membrane was recovered by 50%. In contrast, tap water and permeate showed a recovery by 20% (Fig. 6-11). The DOC content in these waters before and after membrane was measured. It is evident that (Tab. 6-4) using pure water more organic substances can be removed from the fouled membrane. Considering that calcium in backwash water influences the fouling control efficiency (Li et al., 2009), calcium content in these waters before and after membrane cleaning was measured (Atom Absorption Spectrometry, GBC Secientific Equipment, Australia). In the used pure

water it reached 106 mg/L. In the tap water and permeate the concentration was little changed after membrane cleaning.

As no single reagent can recover the permeability to over 90%, a mixture of NaOH, NaClO in demineralised water (pH 12, active Cl 50 mg/L) was then tested to remove organic foulants. The result (Fig. 6-12) showed that using this mixture reagent the permeability of a fouled membrane can be restored to 90 – 95 %. It suggests that a cleaning strategy utilizing the co-effect of different reagents can improve the cleaning effect to a large extent.
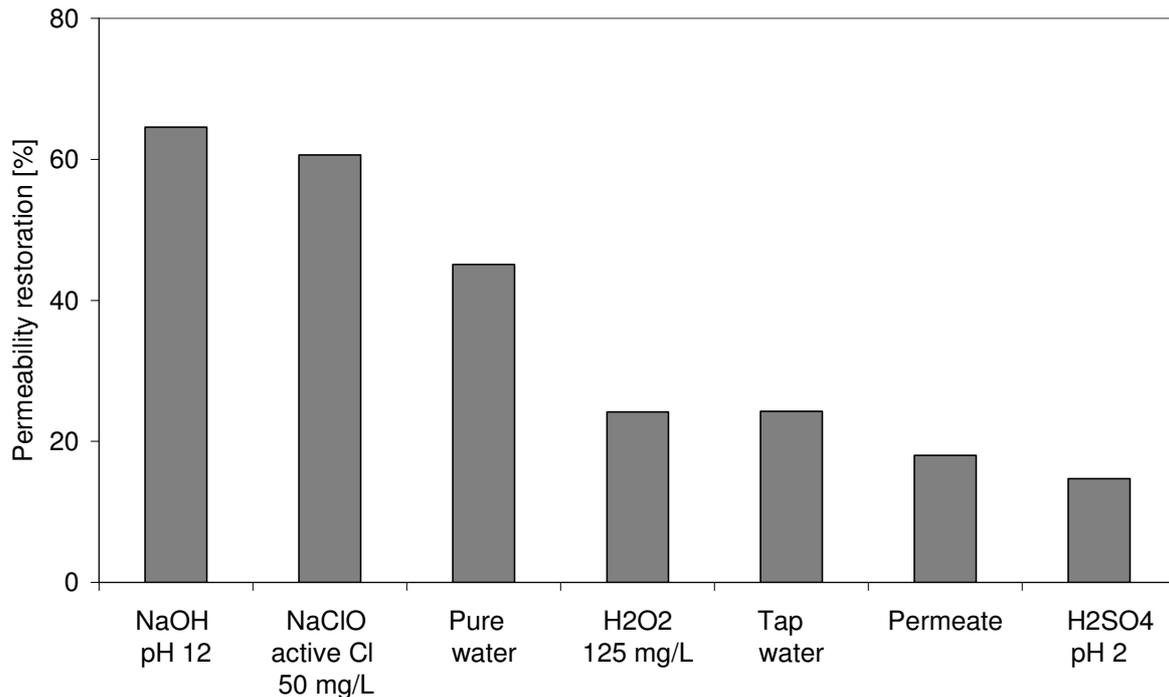
Fig. 6-11 Comparison of permeability restoration effect of UF using different cleaning reagents

Biopolymer content in feedwater (SSF) to UF and in cleaning water after membrane cleaning was quantified (Tab. 6-4). The results show that in feedwater to UF biopolymers contributed to around 1.1 - 2.4% carbon of the total DOC. In the dissolved fraction in cleaning water, their contribution increased to 30 – 63%. The significant enrichment of biopolymers in cleaning water indicates that biopolymer fraction is preferred to be retained by UF and forms irreversible fouling.

The biopolymer concentration in different cleaning waters shows an apparent correlation with the membrane permeability restoration (Fig. 6-12). Generally, the higher the biopolymer concentration in the cleaning water – the more biopolymers are removed and/or solubilized in the solution, the higher the permeability of the membrane can be recovered. It suggests that the understanding of the property and fouling mechanisms of biopolymers can improve the effectiveness of membrane cleaning. Simultaneously, it is noted that other fractions with a size smaller than biopolymers play also a role in irreversible fouling. Within the increased DOC fraction, which represents the removed organics from the fouled membrane, these nonbiopolymer organics attributed to over 37% of the DOC increase (except the case using permeate as cleaning reagent, Tab. 6-4).

Tab. 6-4 Comparison of biopolymer content in SSF to UF and that in cleaning water using different cleaning reagents

Cleaning reagent	BC in SSF	DOC of SSF	Ratio BC/DOC	BC in cleaning water	DOC increase in cleaning water	Ratio BC/DOC increase
	(mg C/L)	(mg/L)	(%)	(mg C/L)	(mg/L)	(%)
H_2SO_4 pH 2	0.14	12.4	1.1	0.9	2.9	32
NaOH pH 12	0.1	8.5	1.1	11.3	26.7	42
NaClO active Cl 50 mg/L	0.1	8.6	1.2	1.4	4.0	34
Tap water	0.08	7.1	1.1	0.7	2.2	30
Permeate	0.08	7.3	1.1	0.3	0.31	97
H_2O_2 125 mg/L	0.09	7.8	1.2	-	-	-
pure water	0.11	7.5	1.5	2.1	5.2	40
Standard cleaning reagent*	0.32	13.3	2.4	19.4	30.5	63

Standard cleaning reagent*: NaOH pH 12 + NaClO active Cl 50 mg/L + demineralized water; BC: biopolymer concentration, DOC increase: DOC increase in cleaning water after membrane cleaning
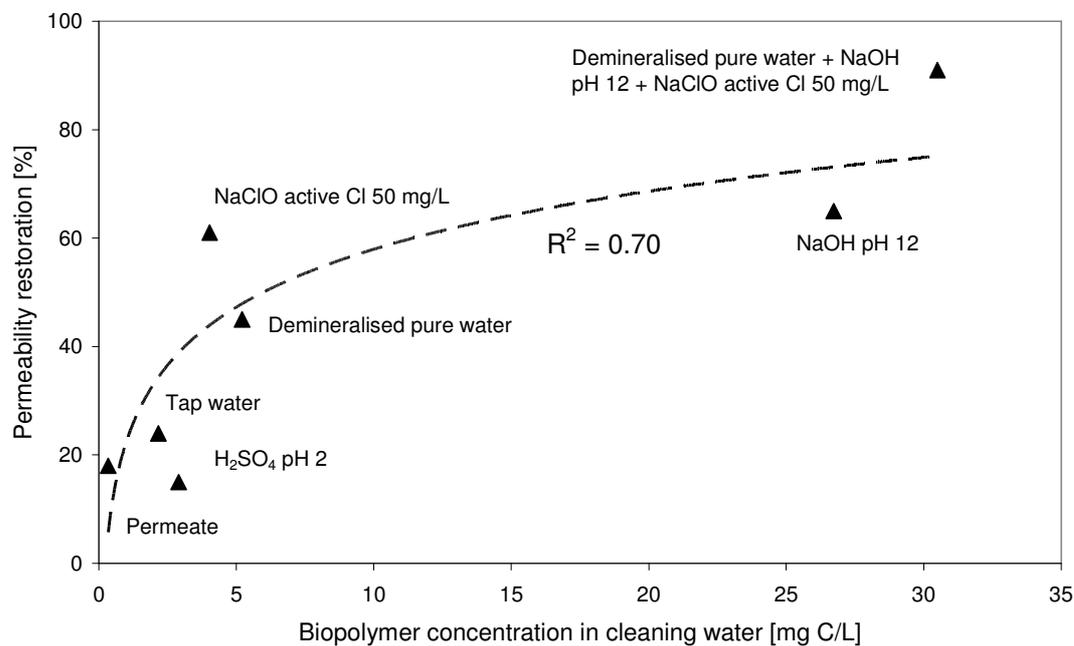
Fig. 6-12 Relation between permeability restoration using different cleaning reagents and biopolymer concentration in corresponding cleaning waters (same volume of cleaning water was used in all the experiments)

Optical impressions of several cleaning water samples are shown in Fig. 6-13 (a) and (b). Generally, suspended tender fragments can be seen in cleaning waters. In NaClO solution large numbers of fragments were observed (Fig. 6-13 b). The breadth of a compact fragment on a slide glass (Fig. 6-13 c) was measured as 1.4 mm (Microscopy ALTRA 20, Zeiss, Ger-

many). The diameter of the corresponding fragment was calculated as 0.9 mm. It was identical to the diameter of a single UF fibre (Fig. 6-13 d, Dizzer 450, Inge AG). As the result was reproducible, it can be logically proposed that the tender fragments are mainly irreversible cake/gel layers which are formed by aggregated or compacted foulants on the membrane surface.
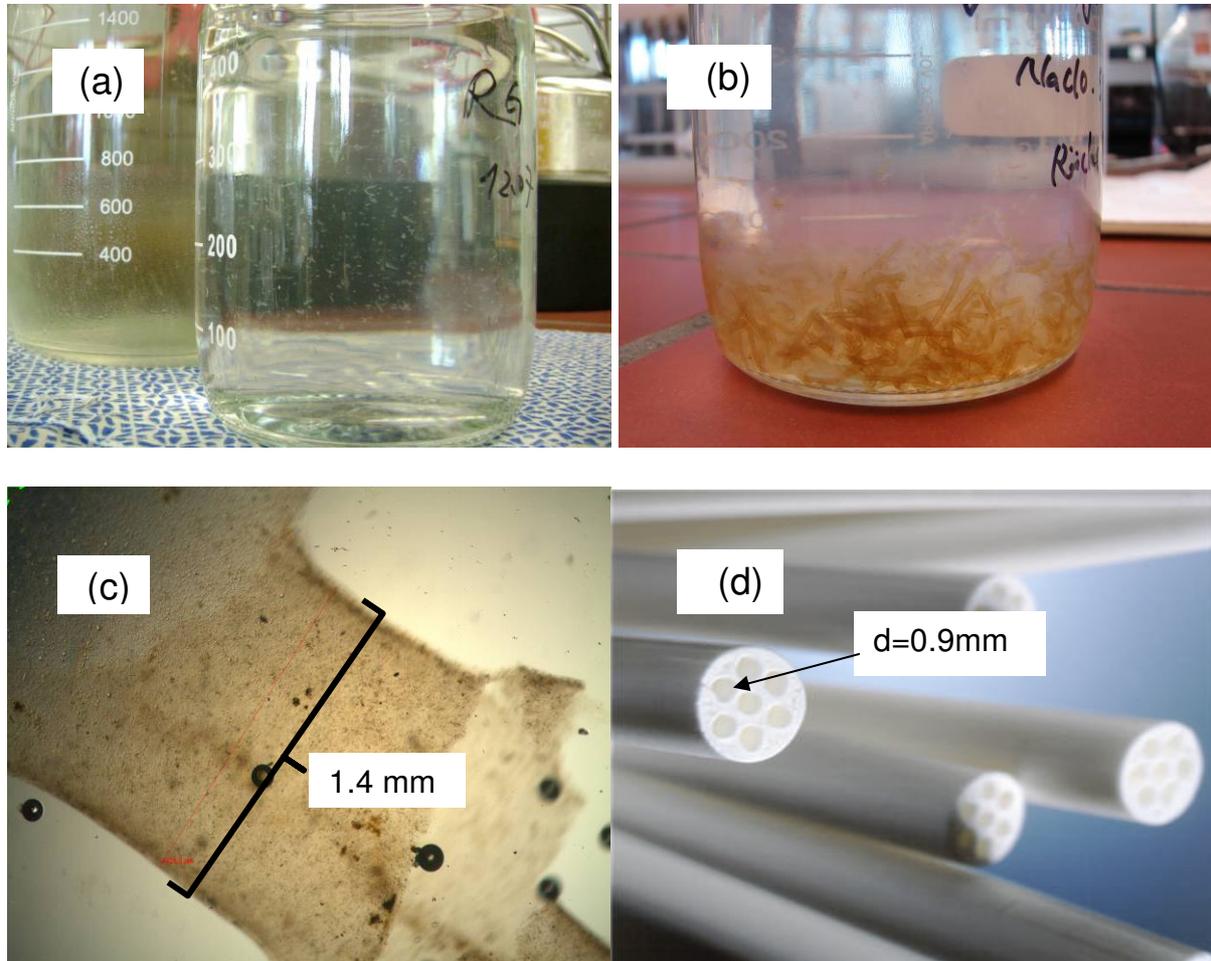
Fig. 6-13 (a) Optical impression of demineralised water after membrane cleaning, (b) optical impression of NaClO solution (active Cl 50 mg/L) after membrane cleaning, (c) diameter measurement of the suspended orbicular fragment in NaClO solution after membrane cleaning, (d) diameter of a membrane fibre of Inge membrane (dizzer® 450, source: Inge AG)

6.7 Discussion and Summary

Influence of BWI and Flux

The present section shows that operational conditions, in particular BWI and flux, impact the performance of UF to a large extent. Under similar feedwater quality, they affect the extent of fouling by influencing foulant mass load and/or the structure of the fouling. In lab-scale tests (section 4.1) it is evident that an increase of biopolymer mass load to a membrane leads to more fouling. The increase of the interaction between foulants and membrane and between foulants is primarily attributed to the multiplication of binding sites available of the macromolecules. Although the interactions are based on weak physico-chemical adhesion and cohesion, the total binding energies of weak interactions between EPS molecules multiply with the

increase of binding sites and add up to binding values exceeding those of strong covalent C-C bonds (Flemming and Wingender, 2001). The strengthened interaction due to load mass increase can be used to interpret the promotion effect on fouling caused by the extension of BWI by the UF pilot plant.

The increase of filtration flux can also lead to more fouling. It is evident that an increase of flux results in a more than proportional TMP development. The main reason has been identified as the alteration of the fouling layer structure. Under a higher filtering flux, which is caused by a higher filtration pressure, the biopolymer layer is further compressed. The fouling layer induces higher specific fouling resistance and lower reversibility. In membrane filtration compressibility is presented as an intrinsic property of the deposited foulants (Singh and Song, 2006). Deformable colloids (soft colloids) e.g. biopolymers are more compressible than rigid ones. While for rigid colloids the compression is mainly due to closer packing and rearrangement, biological colloids can be significantly deformed under filtration pressures. The deformation can increase the contact area among foulants, fluid and membrane (Foley, 2006). Thus, both the available binding sites and the cross-linked network structure of the fouling layer can be subsequently changed (Wang and Waite, 2008b). In particular, the foulants adjacent to the membrane are exposed to the highest pressure, present the highest specific fouling resistance and induce the severest fouling effect (Tansel et al., 2006; Ye et al., 2005). For a membrane filtration operated at constant flux mode, the pressure on newly delivered foulants in each cycle is similar (based on flux applied). According to pressure gradients within the fouling layer, the TMP measured for the membrane module is acting mainly on the existing fouling, instead of the newly accumulated foulants (Chen et al., 2006b; Ye et al., 2005).

Main Fouling Mechanisms and Fouling Development

In this section, the fouling mechanisms discussed in section 4.2 are integrated to the fouling development investigated by a UF pilot plant to get an overview of the fouling phenomenon. In lab-scale experiments (section 4.2) it is evident that during the initial filtration phase the major fouling mechanism during is pore blocking. This leads to a significant permeability reduction. Simultaneously, adsorption is regarded to play also an important role. In an adsorption experiment, Haberkamp (2008) showed that adsorption of biopolymer onto a membrane surface resulted in a permeability reduction by 5 %. Continuous delivering biopolymers to the membrane surface alters the fouling mechanisms from pore blocking to the formation of a cake/gel layer (section 4.2).

Lab-scale multi cycle filtration experiments (section 4.1) show that backwashing can recover the permeability of a fouled membrane to a large extent, which indicates the high reversibility of the fouling layer. Nevertheless, irreversible fouling increases continuously. As the major fouling mechanism is identified as cake/gel filtration, this implies a constant growth of a cake/gel layer along the operation. The development of the fouling layer is caused by the increase of the biopolymer mass and also due to the change of the fouling structure under pressures (Wang and Waite, 2008b; Ye et al., 2005). Considering that major foulants are protein-like and polysaccharide-like substances, an increase of their accumulated mass promotes the interaction among them and with the membrane significantly (Amy, 2008). As a result, the development of the cake/gel layer impacts the effectiveness of hydraulic backwashing.

In practical operation of a UF pilot plant, the variation of biopolymer concentration in feed-water cannot always result in a consequent TMP alteration. This can be partly attributed to the high complexity of fouling phenomenon in the reality. In addition, the influence of the fouling development phase on the relationship should also be taken into consideration. Fouling mechanism analysis in previous studies has been generally focused on the initial interactions between foulants and membrane (Listiarini et al., 2009; Susanto et al., 2008), little has been addressed on fouling development during a long-term UF operation. Under this condition, the fouling mechanism is different to that in the initial phase. Ye et al. (2005) found that fouling presented in a long-term membrane filtration, even under subcritical flux, showed a lower reversibility compared to that presented in a short-term dead-end experiment.

According to the concept describing fouling development in MF of model EPS (Ye et al., 2005) and in MBR systems (Zhang et al., 2006a), and based on the pilot-scale experimental results in the present work, the fouling process in UF of treated domestic wastewater is suggested to be separated into three stages. It is evident that in the first stage, which is called conditioning fouling stage, the development of irreversible fouling is mainly caused by pore blocking and adsoption due to a direct interaction between foulants and membrane. In general, the fouling in this stage is formed within a short time. It presents a limited fouling resistance (Haberkamp, 2008) but is of low reversibility. During the second stage, the deposition of foulants may take place mostly on the fouling layer already present on the membrane surface. Although small foulants can pass through this layer and be transported into the pores, the adsorption capability of the pore wall could be exhausted due to saturation (Xiao et al., 2009; Haberkamp, 2008; Susanto et al., 2007). Therefore, the main mechanism in this stage is considered to be cake/gel filtration. The cake/gel layer shows a high reversibility. This has been revealed by the lab-scale experiment (section 4.1). In pilot-scale plant the high reversibility of the fouling can be detected by the slow increase of TMP. This phenomenon indicates that most of the newly cumulated foulants are hydraulically removable. In a more detailed investigation, Wessling (2001) visulized that in cake/gel filtration the density of the fouling layer above the pore opening is lower than that above the flat adsorption surface. This kind of fouling can be readily removed by backflushing when its density is lower than a critical level. In this phase, a short term variation of foulant load may not influence TMP development significantly. But, when biopolymer concentration in feedwater is kept high for a longer time, the accumulation of irreversible fouling can accelerate the TMP increase rate significantly. Otherwise, a long-term operation under sustainable conditions offers also time for the relocation of foulants and consolidation of the links between foulants and membrane (Chen et al., 2006b; Ye et al., 2005). This leads to a chronic accumulation of irreversible fouling until a sudden TMP increase, which indicates the appearance of the third stage. In this phase, the accumulation of irreversible fouling is over a critical condition. The effectiveness of backwashing is reduced to a large extent. Therefore, the variation of foulants content in feedwater can be immediately reflected by TMP development.

The results based on pilot-scale tests suggest that an overview of fouling development phases is helpful to understand the correlation between foulants in feedwater and TMP development. At critical operational conditions, e.g. at high flux, the duration of the three-stage TMP development can be largely influenced. The correlation between flux and the severity of fouling indicates that the compression of a cake/gel fouling layer plays an important role in fouling phenomenon.

Membrane Cleaning

Backwashing was used as a physical cleaning process to maintain the permeability of the UF. Generally, key parameters in the design of backwashing are frequency (presented by back-wash interval), duration and intensity. Based on the previous discussion, it is evident that the frequency impacts the severity of fouling mainly due to the variation of the accumulated foulant mass. At a fixed backwash intensity (flux), section 6.4 demonstrated that an extension of backwashing duration from 20 to 60 s led to only a very limited improvement of permeability recovery. By contrast, it reduced the productivity of the membrane system significantly. In addition, the result suggested that at a high backwashing flux, e.g. 260 LMH in the present case, most of the removable foulants were backwashed within a short time. As backwashing is mainly used to remove more reversible foulants, e.g. particles or pore blocking foulants, an extension of its duration is not expected to improve irreversible fouling removal. Thus, an optimization of backwashing is suggested to be undertaken with regard to reversible fouling control and energy or permeate consumption.

The irreversible fouling can be effectively mitigated by chemically enhanced backwash during operation, as shown in section 6.5, or by chemical cleaning which is investigated in section 6.6. In coincidence to the results of other studies (Guo et al., 2009; Le-Clech et al., 2006; Kimura et al., 2004), caustic reagents and oxidants are effective membrane cleaning chemicals. The effective separation of fouling and membrane is considered to be due to the functions of the agents when they interact with fouling meterials. According to the report presented by Liu et al. (Liu et al., 2006), the functions of caustics are hydrolysis and solubilization. Organic materials including polysaccharides and proteins can be hydrolyzed by caustics. For humic substances, caustic can improve their negative charge as well. Therefore, the binding between membrane and these organics can be weakened. This results in a more reversible fouling.

In either CEBW or in membrane chemical cleaning experiments, oxidant performs effectively in removing fouling. Besides the function of hydrolization (Le-Clech et al., 2006), another major fouling removal mechnism of an oxidant is considered as generation of oxygen-containing functional groups, e.g. carboxylic acids, during oxidation of organic polymers (Liu et al., 2006). The existence of these functional groups generally increases hydrophilicity of their parent compounds. Therefore, oxidation reduces the adhesion of fouling materials to membranes. As a prevalent oxidant, NaClO appears in most of the cleaning recipes (Le-Clech et al., 2006). However, the selection of a suitable reagent is not only based on its fouling removal effect and economic items, its influence on the environment needs also to be taken into consideration. Due to the disinfection by-products caused by chlorine, other chlorine-free oxidants, e.g. H_2O_2 , are more recommended to be used.

Using demineralized water in membrane cleaning can recover the permeability of a fouled membrane more significantly than using tap water or UF permeate. In the used pure water a higher biopolymer content and a much more significant increase of calcium concentration than that in tap water or UF permeate was observed (section 6.6). These phenomena indicated that the removal of irreversible fouling was relevant to the release of cations into pure water. Demineralized water has been used as backwash water in several studies to reduce fouling in

UF membranes (Li et al., 2009; Abrahamse et al., 2008). It was found that due to the absence of cations, either divalent or monovalent, the removal efficiency of irreversible fouling was largely improved. These results suggested that the absence of cations leads to a weakened link between fouling and membrane (Abrahamse et al., 2008). Therefore, more irreversible fouling could be backwashed. The mechanisms are considered similar to that in membrane cleaning using demineralised water. The function of demineralised water in fouling removal was summarized by Li et al (2009) in detail. It is stated that during membrane filtration, due to the screen effect caused by cations organic foulants can easily deposit on the membrane surface and cause fouling. The absence of cations in cleaning water reduces the charge-screening effect. The repulsion force between the negatively charged membrane and organic compounds can be increased. This subsequently results in a more removable fouling layer. In particular, due to dissolution of calcium into pure water, the calcium-bridging strength between membrane and organic foulants can also be partly reduced. The weakened cohesion of organic compounds on the membrane improves the reversibility of the fouling layer.

7 General Conclusions

This study aims at relating the content of principal organic foulants to the fouling phenomena in ultrafiltration of treated domestic wastewater and investigating fouling control effects using bio-filtration as a pre-treatment process. In lab and pilot-scale UF experiments, the fouling potential of various water samples was assessed. A quantified correlation between the content of biopolymers and fouling in UF has been set up and verified. Pilot-scale bio-filtration processes (bank-filtration, slow sand filtration) were operated to reduce the fouling potential of wastewater effluent prior to UF. Foulants removal mechanisms and factors affecting the performance of biofiltration process have been investigated.

7.1 Major Organic Foulants in UF and related Fouling Mechanisms

The identification of major foulants in UF of treated domestic wastewater is undertaken in lab and pilot-scale experiments. In either secondary effluent or slow sand filtrate, the fraction of dissolved organics larger than or comparable to the correspondingly used UF pores (hydrophilized PES UF membrane, MWCO 100-150 k Da, nominal pore size 0.026 µm) have been identified as major foulants affecting the filterability of the water sample and the reversibility of the fouling in UF. These organics can be roughly characterized using LC-OCD-UVD-OND. The measurements show that they are large organic molecules with low UV absorbance and some organic nitrogen content, commonly regarded as macromolecular polysaccharide-like and protein-like biopolymers.

Using the carbon content to represent the concentration of biopolymers, it is evident that the biopolymer concentration affects the filterability of water proportionally. In lab-scale multi cycle filtration experiments it is further shown that the higher the biopolymer load to the membrane, the lower the restoration of the membrane permeability by hydraulic backwashing, although most of the cumulated biopolymers can be backwashed. A significant negative correlation between biopolymer concentration in feedwater and the reversibility of fouling layer is identified. Based on the quantified correlation, it can be stated that the content of biopolymers in treated wastewater can reflect its fouling potential in UF. The statement is verified to be reproducible using pilot-scale UF filtering secondary effluent or slow sand filtrates. Further tests show that the fouling potential of treated wastewater cannot be quantified using photometric methods for proteins and polysaccharides. But, under certain conditions fouling index parameters, e.g. SUR, show a reasonable correlation with it.

Besides the effect of biopolymer load mass on fouling development, the structure of the biopolymer fouling layer influences the extent of fouling as well. Pilot-scale UF experiments show that an increase of flux leads to a more than proportional development of fouling. Lab-scale experiment results demonstrate that enhanced flux (due to increasing TMP in constant pressure tests) leads to a further compression of biopolymer fouling layer which presents higher specific cake/gel layer resistance. The more compact fouling decreases the backwashing efficiency.

Fouling mechanism analysis is carried out based on the filtration curves in lab-scale experiments. The analysis indicates that according to the delivered biopolymer mass, fouling

mechanisms vary from pore blocking to cake/gel filtration. Although the fouling layer is hydraulically reversible, cake/gel filtration is identified as the primary fouling mechanism in multi cycle filtration test. Based on the observation of TMP development in a UF pilot-plant, fouling processes can be devided into conditioning fouling, steady fouling and TMP jump phase when the UF is operated at sustainable operational conditions. The three stages can be significantly influenced by foulant load mass and/or filtration flux. High foulant load mass or filtration force (caused by flux) increases the severity of fouling.

7.2 Removal of Organic Foulants in Bio-filtration Processes

In the present work bio-filtration (short-term bank filtration: filtration rate around 0.06 m/h, retention time around 24 h; slow sand filtration: filtration rate from 0.1 to 0.5 m/h, retention time from 2 to 8 h) of treated domestic wastewater can remove the particulate, colloidal and soluble foulants effectively. The performance of the downstream UF can be improved to a large extent.

The removal mechanism of biopolymers within slow sand filters is investigated in pilot-scale tests. The removal is observed mainly taking place at the top layer of slow sand filters. In this active zone, the decrease of biopolymer concentration is found to be relevant to the reduction of oxygen concentration and pH. Biological processes appear to be important during the removal. Tests on the bio-degradability of biopolymers show that these macromolecular polysaccharide-like and protein-like substances can be biologically degraded. Compared to humic substances they are more readily removed by bio-filtration processes.

Several factors, e.g., filter ripening, filtration rate, temperature, biopolymer concentration in feedwater and the application of a protective layer are investigated in terms of biopolymer removal in slow sand filtration processes. It is evident that three months ripening time suffices for a constant biopolymers removal effect. However, the removal efficiency is not stable under temperature fluctuations. A one-year pilot-scale investigation demonstrated a positive influence of temperature on the removal. As temperature impacts the biopolymer concentration in secondary effluent negatively, the winter season leads to a poor performance of slow sand filter in terms of both biopolymer removal and cycle time. To improve the performance, lowering filtration rate or constructing a protective layer on the filter surface can be applied. A lower filtration rate extends the contact time between biopolymers and biofilms in sand filter, and thus leads to a higher removal effect. Nevertheless, the filtration rate and the removal efficiency are of a less than proportional relationship. To extend the cycle time of a filter, the effect of BioNet as protective layer material is tested in the present work. Although the protective layer cannot improve biopolymer removal efficiency, it offers large void space for foulants and bacteria and mitigates the treatment load in the sand surface layer. Therefore, the cycle time of a biofilter is extended significantly.

In general, low filtration rates, high temperatures, low biopolymer concentrations in the feedwater and the application of suitable protective layers can improve the performance of slow sand filtration.

7.3 Optimization of Operational Conditions

Although the performance of UF is higher in filtering bio-filtrate compared to treating secondary effluent, the operational conditions (filtration flux, filtration duration) influence fouling development to a large extent. It has been demonstrated that unsuitable filtration durations or high filtration fluxes lead to a fast TMP increase. The severe fouling is attributed to an increased foulant mass load or more compressed fouling layers, respectively. Based on the pilot-scale tests, a sustainable operation of UF treating slow sand filtrate is achieved using the Inge Dizzer® 450 module at a filtration flux of 50 $L/(m^2 \cdot h)$, backwash interval of 10 minutes, backwash flux of 260 $L/(m^2 \cdot h)$ and backwash time of 10 -15 seconds.

Different chemicals are used as enhanced backwash reagents in UF. Considering fouling control and also environmental protection, operational conditions of UF treating slow sand filtrate can be suggested as following: filtration flux at 90 $L/(m^2 \cdot h)$, backwash interval of 40 minutes, backwash flux at 260 $L/(m^2 \cdot h)$, backwash time around 30 seconds using H_2O_2 (active H_2O_2 20 mg/L) as an enhanced backwash chemical. After each backwash the disinfection time can be set to around 5 minutes. Different cleaning reagents are also used to clean the fouled membrane filtering treated domestic wastewater. Based on the effect on permeability restoration, the most effective reagent for the removal of irreversible organic fouling is a combination of base (NaOH, pH 12) and NaClO (active Cl 50 mg/L).

7.4 Research Recommendations

The present work shows a coincidence between the fouling potential tested in lab-scale multi cycle filtration experiments and that obtained based on pilot-scale UF tests. It indicates that the lab-scale test can reflect the fouling potential of different water samples in the reality, although it presents mainly the fouling developed in the initial filtration phase. Compared to a pilot-scale experient, this method is a simple, time saving and cost-effective approach determining fouling potential. As irreversible fouling depends on the qualitative composition of biopolymers (Haberkamp, 2008), a multi cycle filtration test is suggested to be used to test the fouling effect caused by different biopolymers, e.g., proteins, polysaccharides and biopolymers from treated wastewater. Based on the results, a further understanding of fouling mechanisms by biopolymers is expected to be achieved.

Although several studies investigated the fouling potential of model substances using a similar method (Jermann et al., 2008; Ye et al., 2005), the organic compounds used were always bovine serum albumin for proteins, dextran or alginate for polysaccharides with an assumption that these substances are representative in fouling phenomenon. This may lead to a negligence of other important foulants. In addition, certain compounds may play a specific role in fouling development. For instance, using a confocal laser scanning microscopy (CLSM) Zhang et al. (2009) identified the important role of proteins adjacent to the membrane surface. In another study, Chen et al. (2006a) showed that a certain type of polysaccharides played a more crucial role in fouling than proteins. Thus, several kinds of proteins and polysaccharides are suggested to be tested using multi cycle tests to evaluate their fouling potential and the function in fouling development.

The second prospect is to optimize the chemical cleaning procedure (choice of suitable reagents). In the present work, a combination of NaOH and NaClO soaking of membrane module for 24 h is demonstrated as an effective method removing irreversible fouling. However, due to the disinfection by-products using chlorine, the cleaning water can be a source of new contaminants. Based on the understanding of the contribution from biopolymers in irreversible fouling, more environmental friendly and specialized reagents, e.g., enzymes (Poele, 2006) and ethanol (Tian et al., 2009), are suggested to be tested in further membrane cleaning experiments. To improve foulant removal efficiency, circulating cleaning solutions through the system instead of soaking is also suggested for dynamic cleaning promotes more mass transfer of chemicals to the fouling layer and of the reaction products back to the bulk liquid phase than static soaking.

8 Appendix

8.1 LC-OCD-UVD-OND System and LC-OCD Chromatogram
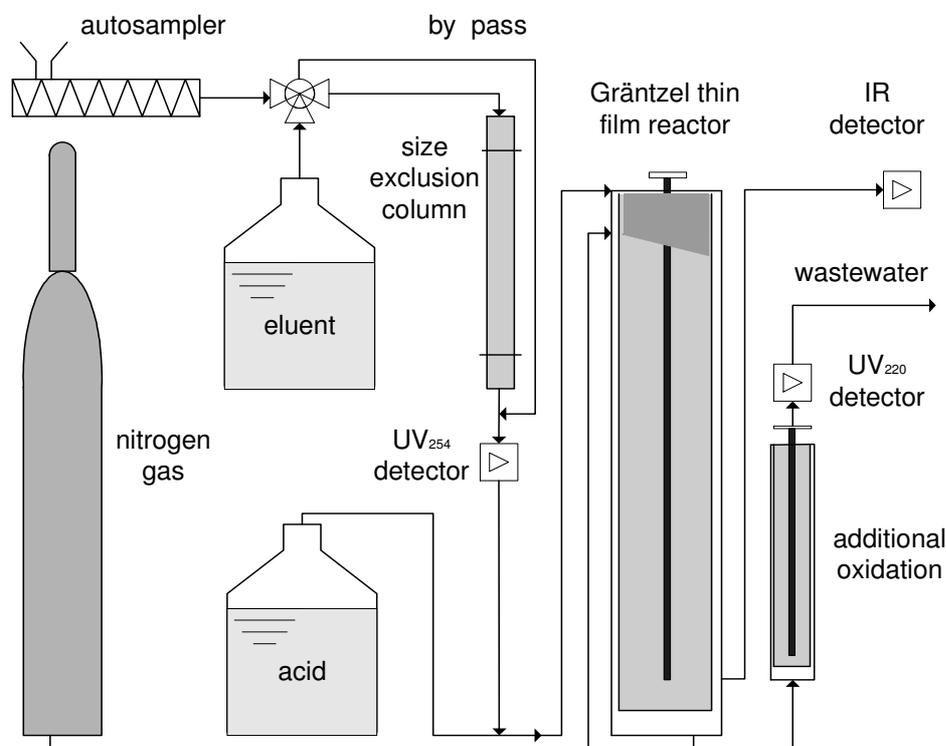
A-Fig. 1 Set-up of the LC-OCD-UVD-OND system

Measurement Process

During the chromatogram measurement one mL water sample is injected into the eluent flow (A-Fig. 1) and is carried into the size exclusion column (Alltech-Grom GmbH, resin material: Toyopearl® HW-55s which are synthesized by co-polymerization of ethylene glycol and methacrylate-type polymers, Tosoh Bioscience, Tokio/Japan). The separated organic compounds in the column are transported into the UV_{254} detector (Wellchrom K-200, Knauer GmbH, Berlin) to measure the UV absorbance. Subsequently, the eluent flow and acid flow enter the reactor at the upper end where they are thoroughly mixed by means of the Teflon pins in the rotor. The upper third of the reactor is UV-shielded and the carbon dioxide from inorganic source is stripped out upwards using the carrier gas (nitrogen). The residence time of the liquid in this area is about 20 seconds. The liquid continues way down due to gravity. The UV oxidation ($\lambda = 185$ nm) forms carbon dioxide from the dissolved organic compounds. This carbon dioxide is carried downwards stripped through the nitrogen gas and is measured in a no-dispersive infrared detector cuvette (SIEMENS ULTRAMAT 6E, Siemens AG, Munich). The residence time of the liquid in the reactor is about 60 seconds. During the oxidation process, the thinness of the liquid film ($10 - 20$ µm) and the active stirring by the Teflon pins (500 rpm) guarantees a rapid oxidation and stripping process. The wastes after the thin film oxidation is collected in a small reservoir and then pumped to the additional oxidation process (185 nm, Well chram K-2000). The oxidized N-content organic form nitrate (NO_3^-) and the

corresponding nitrogen content can be quantified measuring the absorbance at λ of 220 nm (Wellchrom K-2000, Knauer GmbH, Berlin). Besides the measurement of a chromatogram, the total C, N contents and UV absorbance of a water sample can be determined by injecting 0.1 mL water sample into eluent flow through by pass (A-Fig. 1).

A-Tab. 1 Eluent and acid solution used in LC-OCD system

Eluent	di-sodium hydrogen phosphate dehydrate (Na$_2$ HPO$_4$·2H$_2$O)	8.4 mmol/L
	Potassium di-hydrogen phosphate KH2PO4	18.4 mmol/L
	pH	6.6
	flux	1 mL/min
Acid	Ortho-phosphoric acid	60 mmol/L
	pH	1.8
	flux	0.5 mL/min

Quantification of Biopolymer Content

Biopolymers generally consist of organics with high molecular weights (HMW), e.g. polysaccharides, proteins and other organic colloids. The fractions after the biopolymer peak are humic substances, building blocks, acids and low molecular weight (LMW) humics and LMW neutrals (A-Fig. 2). For LC-OCD analysis water samples are pre-filtered using cellulose nitrate (Sartorius Stedim Biotech GmbH) with a pore size of 0.45 µm. The DOC concentration in the water sample is suggested to be diluted using pure water into the range of 2 to 5 mg/L (per manufacturer).
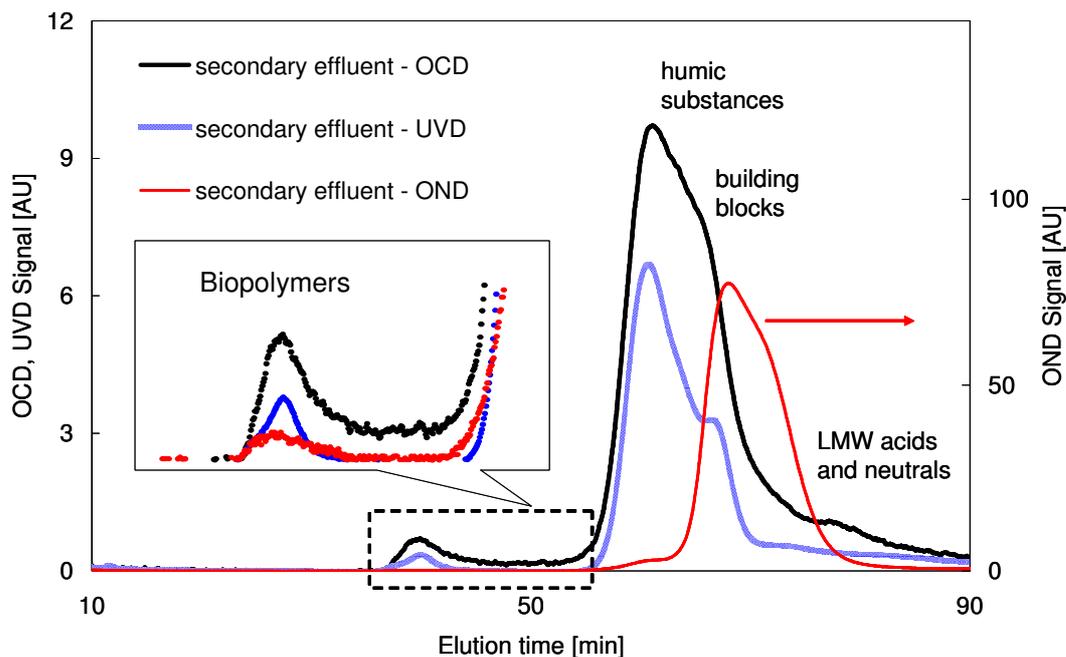
A-Fig. 2 LC-OCD-UVD-OND chromatogram of treated domestic wastewater

Using the software FIFIKUS® (DOC Labor Dr Huber, Karlsruhe) the acquired data can be integrated to quantify the content of biopolymers. In the present dissertation the biopolymer peak begins at elution time of 20 minutes till to the time point where UV_{254} signal jumps (A-Fig. 2). As in the biopolymer peak there is only a weak UV_{254} signal peak, the jump of the absorbance strength indicates the presence of humic peak due to the high contents of UV_{254} active substances in the corresponding region. The carbon, nitrogen content and UV_{254} absorbance strength of biopolymers can then be integrated in the determined boundary.

Calibration of the Detectors and Size Exclusion Column
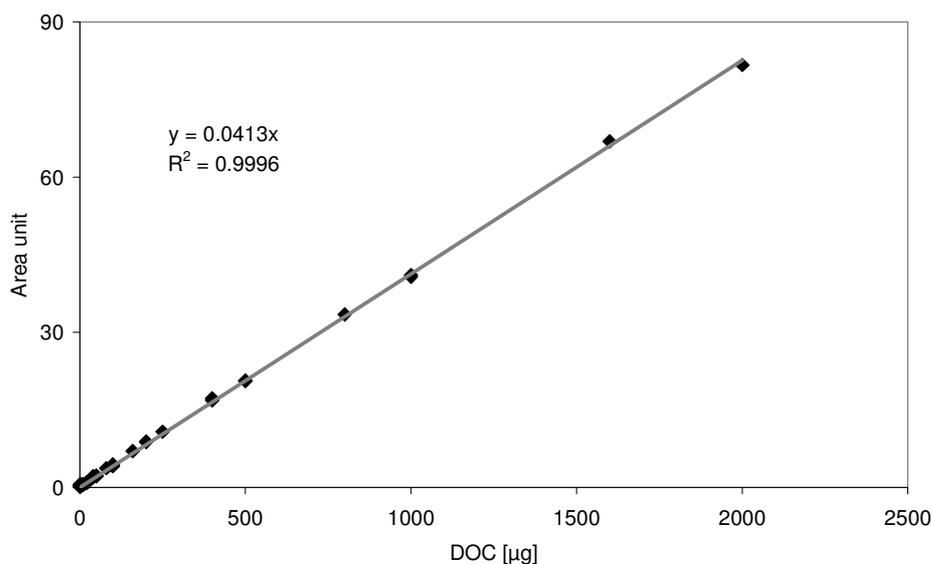
A-Fig. 3 Calibration of the carbon detector of the LC-OCD system (standard solution of potassium hydrogen phthalate: 2.1254g/L = 1000mg DOC/L, injection volumes are 0.05, 0.1 and 0.2 mL within concentration range of 0.005 to 10 mg/L)

The organic carbon, nitrogen and UV254 absorbance detectors can be calibrated using potassium hydrogen phthalate (PHP, $C_8H_5KO_4$), potassium nitrate (KNO_3) and standard humic acid (HA) and fulic acid (FA) from international humic substance society (IHSS). The calibration can be carried out using by-pass with injecting specific volume of corresponding standard solutions. In A-Fig. 3 is the DOC content and corresponding area unit of the OCD chromatogram.
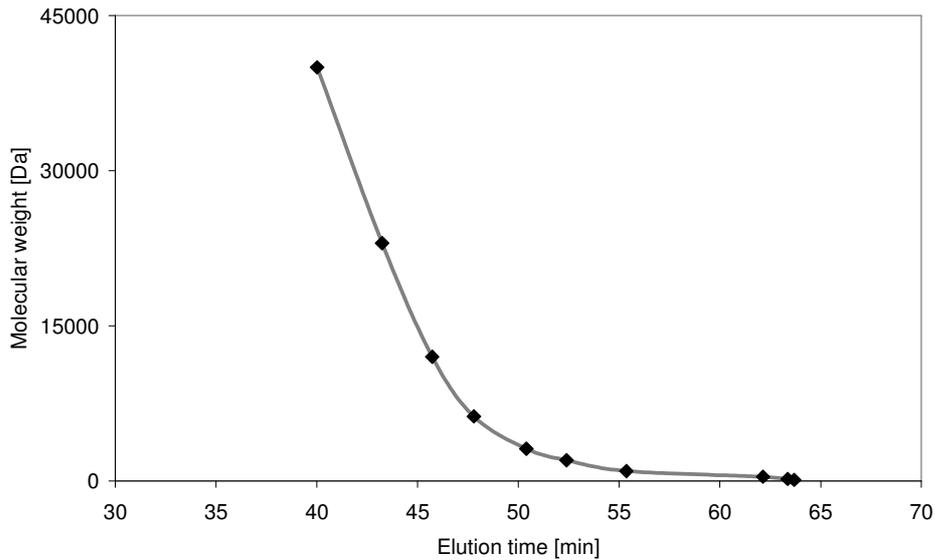
A-Fig. 4 Molecular weight distribution and corresponding elution time of polyethylenglycol (MW range of 106 to 40 000 da) using size exclusion column HW 55s

The size exclusion effect the column HW 55s can be calibrated using polyethylenglycol (PEG) with a molecular weight range from 106 to 40 000 da (g/mol). A-Fig. 4 demonstrates that there is a negative correlation of molecular weight and elution time using the corresponding PEG standard. Since in treated domestic wastewater the characteristics of molecules are different to that of the PEG standards, in the present work the biopolymers are preferred to be presented using elution time instead of molecular weight. Simultaneously, it should be stated that within the elution time of biopolymer peak the detected organics are generally large molecules.

8.2 Amicon Cell Results

A-Tab. 2 Amicon cell filtration determining the filterability of water samples (corresponding to Fig. 5-8)

Date	Mar.06.2007	07.08.2007	Nov.16.2006	Dec.16.2006	Apr.08.2007	Apr.04.2007	Mar.06.2007	July 12 2007
BC [mg C/L]	0.59	0.11	0.48	0.38	0.28	0.25	0.17	0.07
water sample	SE	SSF	SE	SE	SE	SE	SSF	SSF
filtration time [s]	V [mL]	V [mL]	V [mL]	V [mL]	V [mL]	V [mL]	V [mL]	V [mL]
0	0	0	0	0	0	0	0	0
60	27.36	38.11	29.37	25.83	31.76	30.65	29.05	25.71
120	48.82	74.13	52.42	48.56	59.08	58.35	56.04	51.43
180	66.38	108.9	72.05	68.27	83.38	83.82	81.27	76.5
240	81.4	142.61	89.3	86.03	105.17	107.09	105.04	101.14
300	95.05	174.91	104.8	102.48	125.26	128.77	127.42	125.44
360	107.59	206.01	119.21	117.75	143.7	149.23	148.78	149.3
420	119.16	236.09	132.58	131.98	161.13	168.43	168.95	172.83
480	129.9	265.05	144.53	145.9	177.41	186.69	188.34	196.05
540	140.07	293.1	156.45	158.31	192.83	204.07	206.92	218.84
600	149.68	320.3	167.59	170.52	207.77	220.62	224.74	241.46
660	158.82	346.52	178.28	182.21	222.13	236.42	241.96	263.64
720	167.47	372.22	188.4	193.33	235.92	251.7	258.67	285.52
780	175.86	396.99	198.06	204.18	249.14	266.25	274.78	307.03
840	183.82	421.09	207.44	214.57	261.62	280.39	290.35	328.32
900	191.55	444.56	216.46	224.72	273.76	294.02	305.53	349.28
960	198.93	467.52	225.24	234.25	285.61	307.15	320.27	370.02
1020	206.12	489.75	233.69	243.9	297.11	319.98	334.56	390.52
1080	213.14	511.62	241.96	253.18	308.25	332.46	348.59	410.69
1140	219.93	532.92	249.98	262.16	319.16	344.52	362.25	430.72
1200	226.58	553.76	257.84	270.98	329.77	356.29	375.57	450.44
1260	233.05	574	265.58	279.49	340.13	367.76	388.59	469.85
1320	239.21	593.91	273.03	287.82	350.23	378.96	401.32	489.07
1380	245.35	613.41	280.39	296.06	360.13	389.94	413.86	508.11
1440	251.39	632.6	287.64	304.1	369.78	400.68	426.02	
1500	257.25	651.3	294.66	311.81	379.24	411.12	438.11	
1560	262.97	669.75	301.49	319.53	388.53	421.42	449.89	
1620	268.64	687.78	308.32	327.14	397.63	431.4	461.38	
1680	274.16	705.71	314.9	334.59	406.51	441.26	472.78	
1740	279.62	723.36	321.43	341.96	415.32	450.98	484	
1800	284.92	740.59	327.89	349.23	423.86	460.43	494.87	
1860	290.19	757.52	334.14	356.18	432.41	469.79	505.81	
1920	295.33	774.22	340.43	363.17	440.71	478.97		
1980	300.42	790.69	346.43	370.12	448.86	488.02		
2040	305.38	806.85	352.42	376.88	456.99	496.84		
2100	310.36	822.88	358.46	383.58	464.87	505.61		
2160	315.23	838.65	364.28	390.13	472.77			
2220	320.05	854.14	369.97	396.65	480.44			
2280	324.7	869.52	375.71	403	488.04			
2340	329.37	884.55	381.25	409.32	495.54			
2400	333.94	899.46	386.82	415.58	503			
2460	338.51	914.15	392.32	421.74	510.3			
2520	343.04	928.66	397.69	427.92				
2580	347.46	943.1	403.03	433.93				
2640	351.92	957.19	408.34	439.9				
2700	356.19	971.2	413.51	445.69				
2760	360.5	985.06	418.71	451.66				
2820	364.7	998.77	423.88	457.4				
2880	368.9	1012.35	428.89	463.04				
2940	373.04	1025.76	434.01	468.77				
3000	377.19	1039.01	438.98	474.49				
3060	381.28	1052.09	443.88	480.17				
3120	385.22	1065.24	448.81	485.71				
3180	389.23	1077.95	453.72	491.21				
3240	393.24	1090.67	458.59	496.67				
3300	397.1	1103.32	463.4	502.11				
3360	400.97	1115.86	468.14					
3420	404.88	1128.12	472.89					
3480	408.67	1140.29	477.54					
3540	412.45	1152.45	482.2					
3600	416.19	1164.46	486.84					
3660	419.89	1176.46						
3720	423.59	1188.31						
3780	427.31	1199.93						
3840	430.93	1211.59						
3900	434.54	1223.18						
3960	438.11	1234.55						
4020	441.69	1245.98						
4080	445.15	1257.23						
4140	448.67	1268.42						
4200	452.19	1279.44						
4260	455.59	1290.44						
4320	459.01	1301.38						
4380	462.42	1312.16						
4440	465.83	1323.01						
4500	469.24	1333.79						
4560	472.52	1344.33						
4620	475.9							
4680	479.17							
4740	482.46							
4800	485.74							
4860	488.94							
4920	492.22							
4980	495.36							
5040	498.58							

A-Tab. 3 Analysis of fouling mechanisms during a dead-end filtration (corresponding to Fig. 5-10)

Mechanism analysis based on pore blocking model
Experiment date: November 16.2006
Biopolymer concentration in secondary effluent: 0.48 mg C/L, filtration volume 500 mL

Filtration in the test		calculated for simulation		calculation				
time: s	volume: L	t (s)	v (L)	dt/dv	d2t/dv2	log(dt/dv)	log(d2t/dv2)	n
0	0	0.0E+00	0					
60	0.03	1.9E+01	0.01	1889.71				
120	0.05	4.0E+01	0.02	2066.32	17661.01	3.32	4.25	
180	0.07	6.2E+01	0.03	2255.76	18943.73	3.35	4.28	0.80
240	0.09	8.7E+01	0.04	2456.10	20034.52	3.39	4.30	0.66
300	0.10	1.1E+02	0.05	2665.63	20952.46	3.43	4.32	0.55
360	0.12	1.4E+02	0.06	2882.78	21715.66	3.46	4.34	0.46
420	0.13	1.7E+02	0.07	3106.20	22341.34	3.49	4.35	0.38
480	0.14	2.1E+02	0.08	3334.65	22845.77	3.52	4.36	0.31
540	0.16	2.4E+02	0.09	3567.10	23244.31	3.55	4.37	0.26
600	0.17	2.8E+02	0.1	3802.61	23551.38	3.58	4.37	0.21
660	0.18	3.2E+02	0.11	4040.42	23780.50	3.61	4.38	0.16
720	0.19	3.6E+02	0.12	4279.86	23944.24	3.63	4.38	0.12
780	0.20	4.1E+02	0.13	4520.40	24054.26	3.66	4.38	0.08
840	0.21	4.6E+02	0.14	4761.61	24121.29	3.68	4.38	0.05
900	0.22	5.1E+02	0.15	5003.17	24155.14	3.70	4.38	0.03
960	0.23	5.6E+02	0.16	5244.81	24164.68	3.72	4.38	0.01
1020	0.23	6.1E+02	0.17	5486.39	24157.88	3.74	4.38	-0.01
1080	0.24	6.7E+02	0.18	5727.81	24141.77	3.76	4.38	-0.02
1140	0.25	7.3E+02	0.19	5969.03	24122.46	3.78	4.38	-0.02
1200	0.26	7.9E+02	0.2	6210.09	24105.12	3.79	4.38	-0.02
1260	0.27	8.6E+02	0.21	6451.03	24094.02	3.81	4.38	-0.01
1320	0.27	9.2E+02	0.22	6691.95	24092.48	3.83	4.38	0.00
1380	0.28	9.9E+02	0.23	6932.98	24102.93	3.84	4.38	0.01
1440	0.29	1.1E+03	0.24	7174.25	24126.84	3.86	4.38	0.03
1500	0.29	1.1E+03	0.25	7415.90	24164.77	3.87	4.38	0.05
1560	0.30	1.2E+03	0.26	7658.06	24216.36	3.88	4.38	0.07
1620	0.31	1.3E+03	0.27	7900.86	24280.31	3.90	4.39	0.08
1680	0.31	1.4E+03	0.28	8144.41	24354.41	3.91	4.39	0.10
1740	0.32	1.5E+03	0.29	8388.76	24435.53	3.92	4.39	0.11
1800	0.33	1.5E+03	0.3	8633.96	24519.59	3.94	4.39	0.12
1860	0.33	1.6E+03	0.31	8879.97	24601.61	3.95	4.39	0.12
1920	0.34	1.7E+03	0.32	9126.73	24675.67	3.96	4.39	0.11
1980	0.35	1.8E+03	0.33	9374.08	24734.93	3.97	4.39	0.09
2040	0.35	1.9E+03	0.34	9621.80	24771.64	3.98	4.39	0.06
2100	0.36	2.0E+03	0.35	9869.57	24777.11	3.99	4.39	0.01
2160	0.36	2.1E+03	0.36	10116.98	24741.71	4.01	4.39	-0.06
2220	0.37	2.2E+03	0.37	10363.53	24654.92	4.02	4.39	-0.15
2280	0.38	2.3E+03	0.38	10608.59	24505.27	4.03	4.39	-0.26
2340	0.38	2.4E+03	0.39	10851.39	24280.37	4.04	4.39	-0.41
2400	0.39	2.5E+03	0.4	11091.06	23966.92	4.04	4.38	-0.59
2460	0.39	2.7E+03	0.41	11326.57	23550.67	4.05	4.37	-0.83
2520	0.40	2.8E+03	0.42	11556.73	23016.47	4.06	4.36	-1.14
2580	0.40	2.9E+03	0.43	11780.21	22348.22	4.07	4.35	-1.54
2640	0.41	3.0E+03	0.44	11995.50	21528.93	4.08	4.33	-2.06
2700	0.41	3.1E+03	0.45	12200.91	20540.65	4.09	4.31	-2.77
2760	0.42	3.3E+03	0.46	12394.55	19364.52	4.09	4.29	-3.74
2820	0.42	3.4E+03	0.47	12574.36	17980.76	4.10	4.25	-5.15
2880	0.43	3.5E+03	0.48	12738.05	16368.66	4.11	4.21	-7.26
2940	0.43	3.6E+03	0.49	12883.11	14506.59	4.11	4.16	####
3000	0.44							
3060	0.44							
3120	0.45							
3180	0.45							
3240	0.46							
3300	0.46							
3360	0.47							
3420	0.47							
3480	0.48							
3540	0.48							
3600	0.49							

The relationship between filtration time and permeate volume used to analyse fouling mechanism

y = -128434x6 + 178046x5 - 96934x4 + 26761x3 + 8092.9x2 + 1806.2x
R2 = 1

flow behavior index n
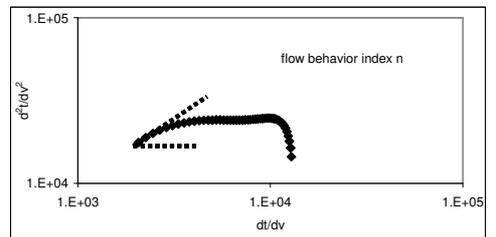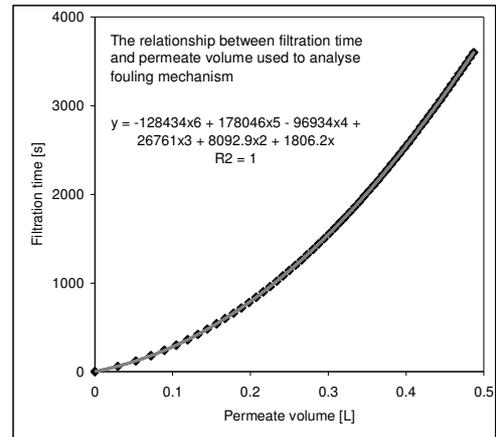
A-Tab. 4 Amicon cell test with five filtration cycles for setting up the relationship between biopolymer concentration in the influent and irreversible fouling filtering corresponding water sample (corresponding to Fig. 4-16)

Experiment date	May 8 2009	April 29 2009	April 17 2009	Mar. 17 2009	Feb. 25 2009	Dec. 31 2008	Dec.05 2008	April 1 2008	Nov. 5 2007	Oct. 8 2007
Water sample	SSF	SE	SSF	SE	SE	SE	SE	SSF-UF permeate	SSF	SE
Biopolymer concentration (mg C/L)	0.19	0.56	0.5	0.43	0.23	0.25	0.49	0.05	0.08	0.42
filtration TMP (bar)	1	1	1	1	1	1	1	1	1	1
Flux filtering pure water (LMH)	698.3	725.9	666.8	625.9	630.4	583.3	696.1	765.9	695.8	706.9
Flux of pure water (m3/m2S)	1.94E-04	2.02E-04	1.85E-04	1.74E-04	1.75E-04	1.62E-04	1.93E-04	2.13E-04	1.93E-04	1.96E-04
Filtration temperature ((°C)	21	21	21	21	21	21	21	21	21	21
Water viscosity (η)	9.82E-04	9.82E-04	9.82E-04	9.82E-04	9.82E-04	9.82E-04	9.82E-04	9.82E-04	9.82E-04	9.82E-04
Filterability	0.38	0.15	0.16	0.14	0.35	0.30	0.17	0.83	0.50	0.21
Flux recovery (%)	80.3	66.1	69.7	69.0	82.1	82.0	76.0	87.0	83.6	76.8
R mem (1/m)	5.30E+10	5.10E+10	5.55E+10	5.91E+10	5.87E+10	6.35E+10	5.32E+10	4.83E+10	5.32E+10	5.24E+10
Flux after 500 mL (LMH)	268.0	109.3	108.9	89.9	218.9	176.0	118.5	634.5	347.0	150.7
R total (fouling after 500+ R mem) (1/m)	1.38E+11	3.39E+11	3.40E+11	4.12E+11	1.69E+11	2.10E+11	3.12E+11	5.83E+10	1.07E+11	2.46E+11
R fouling after 500 mL (1/m)	8.51E+10	2.88E+11	2.84E+11	3.53E+11	1.10E+11	1.47E+11	2.59E+11	1.00E+10	5.35E+10	1.93E+11
Pure water flux after backwashing (500mL)(LMH)	629.0	590.8	589.8	572.5	573.2	548.5	590.8	744.3	632.5	650.7
Irreverble fouling after 500 mL (1/m)	5.84E+09	1.17E+10	7.25E+09	5.51E+09	5.86E+09	4.02E+09	9.48E+09	1.41E+09	5.32E+09	4.53E+09
Flux after 1000 mL (LMH)	258.8	106.2	106.8	91.6	212.4	171.0	113.9	627.2	368.6	147.6
R total (fouling after 1000+ R mem) (1/m)	1.43E+11	3.49E+11	3.47E+11	5.77E+11	5.77E+11	5.77E+11	3.25E+11	5.90E+10	1.00E+11	2.51E+11
R fouling after 1000 mL (1/m)	9.00E+10	2.98E+11	2.91E+11	4.94E+11	4.94E+11	4.94E+11	2.72E+11	1.07E+10	4.72E+10	1.98E+11
Pure water flux after backwashing (1000mL) (LMH)	604.4	554.4	560.0	532.3	561.9	528.5	536.7	725.3	615.3	619.1
Irreverble fouling after 1000 mL (1/m)	8.23E+09	1.58E+10	1.06E+10	1.04E+10	7.16E+09	6.58E+09	1.58E+10	2.71E+09	6.96E+09	7.43E+09
Flux after 1500 mL (LMH)	250.2	103.3	108.5	89.9	203.2	171.4	113.7	616.5	355.2	150.5
R total (fouling after 1500+ R mem) (1/m)	1.48E+11	3.58E+11	3.41E+11	4.12E+11	1.82E+11	2.16E+11	3.26E+11	6.00E+10	1.04E+11	2.46E+11
R fouling after 1500 mL (1/m)	9.49E+10	3.07E+11	2.86E+11	3.53E+11	1.23E+11	1.52E+11	2.72E+11	1.17E+10	5.10E+10	1.94E+11
Pure water flux after backwashing (1500mL) (LMH)	581.7	523.0	528.4	479.7	534.6	507.0	521.6	722.0	596.9	588.7
Irreverble fouling after 1500 mL (1/m)	1.06E+10	1.98E+10	1.45E+10	1.80E+10	1.05E+10	9.54E+09	1.78E+10	2.94E+09	8.82E+09	1.05E+10
Flux after 2000 mL (LMH)	249.8	102.0	108.1	85.9	205.3	163.9	112.1	602.3	352.7	145.7
R total (fouling after 2000+ R mem) (1/m)	1.48E+11	3.63E+11	3.43E+11	4.31E+11	1.80E+11	2.26E+11	3.30E+11	6.15E+10	1.05E+11	2.54E+11
R fouling after 2000 mL (1/m)	9.52E+10	3.12E+11	2.87E+11	3.72E+11	1.22E+11	1.62E+11	2.77E+11	1.31E+10	5.18E+10	2.02E+11
Pure water flux after backwashing (2000mL) (LMH)	574.4	490.3	515.7	478.4	515.8	496.8	528.3	692.6	584.2	562.1
Irreverble fouling after 2000 mL (1/m)	1.14E+10	2.45E+10	1.63E+10	1.82E+10	1.30E+10	1.10E+10	1.69E+10	5.11E+09	1.02E+10	1.35E+10
Flux after 2500 mL (LMH)	243.1	101.2	104.1	84.9	200.5	156.6	111.6	571.4	367.5	144.5
R total (fouling after 2500+ R mem) (1/m)	1.52E+11	3.66E+11	3.56E+11	4.36E+11	1.85E+11	2.36E+11	3.32E+11	6.48E+10	1.01E+11	2.56E+11
R fouling after 2500 mL (1/m)	9.92E+10	3.15E+11	3.00E+11	3.77E+11	1.26E+11	1.73E+11	2.78E+11	1.65E+10	4.75E+10	2.04E+11
Pure water flux after backwashing (2500mL) (LMH)	560.6	479.8	464.6	431.5	517.4	478.4	528.9	663.2	581.7	543.2
Irreverble fouling after 2500 mL (1/m)	1.30E+10	2.62E+10	2.42E+10	2.67E+10	1.28E+10	1.39E+10	1.68E+10	7.49E+09	1.04E+10	1.58E+10

A-Tab. 5 Calculation of biopolymer mass in fouling layer and corresponding specific fouling resistance during UF

Pressure	Cycle	Biopolymer concentration (mg C/L)			Biopolymer mass (mg)	Fouling resistance (10^{11} 1/m)	Specific fouling resistance (10^{16} m/kg)
		Feedwater (0.7 L)	Concentrate (0.2 L)	Permeate (0.5 L)			
(bar)							
0.5	1	0.42	0.54	0.1	0.27	1.35	1.43
	2	0.42	0.52	0.09	0.29	1.30	1.28
	3	0.42	0.50	0.1	0.29	1.29	1.27
	4	0.42	0.52	0.1	0.28	1.37	1.41
	5	0.42	0.54	0.11	0.26	1.42	1.54
	1	0.42	0.44	0.14	0.27	1.91	2.01
1.0	2	0.42	0.52	0.1	0.28	1.92	1.97
	3	0.42	0.55	0.1	0.27	1.94	2.07
	4	0.42	0.44	0.11	0.30	1.96	1.87
	5	0.42	0.50	0.12	0.27	2.03	2.18

8.3 Investigation of Slow Sand Filtration on Biopolymer Removal
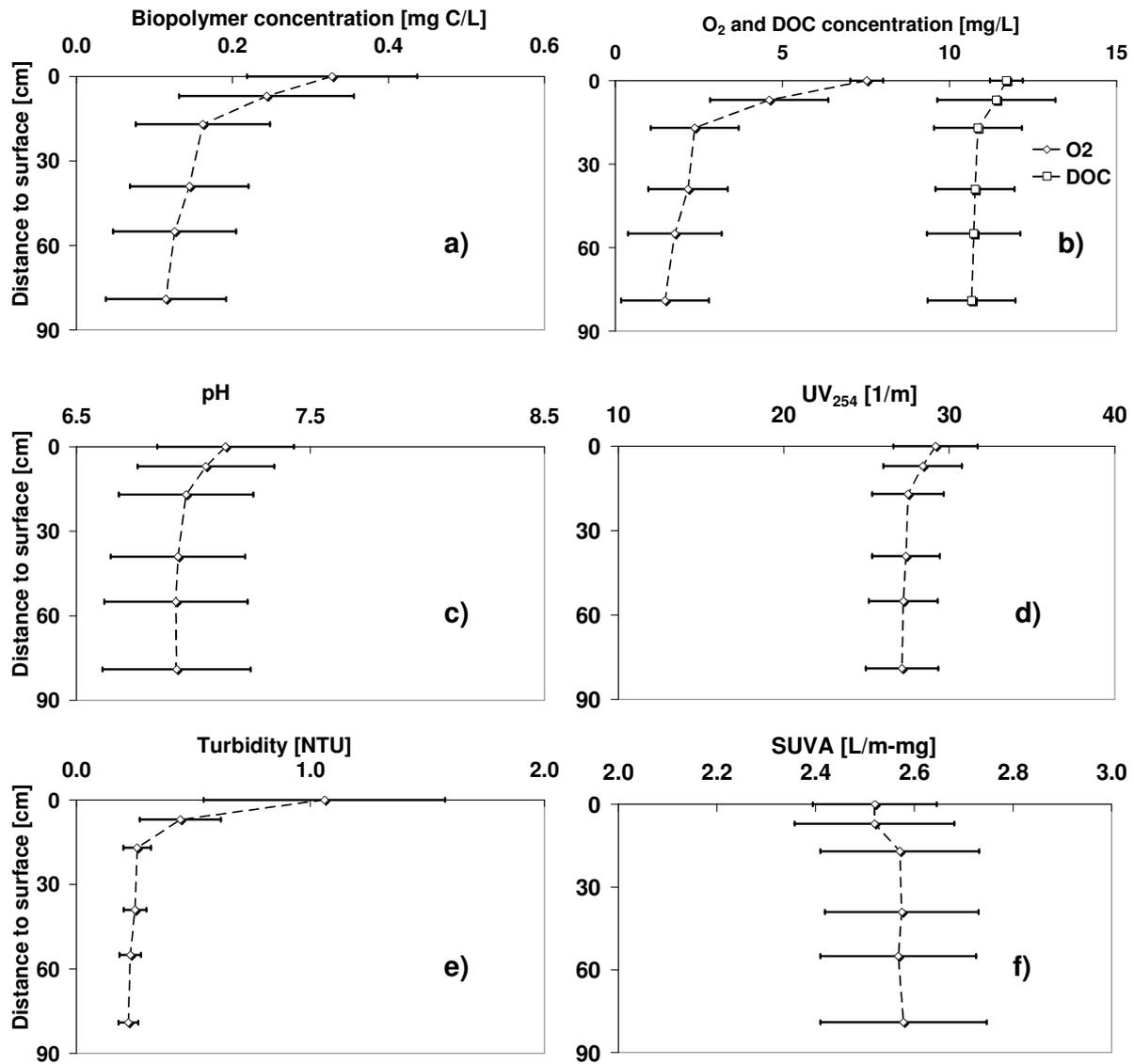
A-Fig. 5 Removal profile of a) biopolymer (n=14), b) dissolved oxygen and DOC (n=10), c) pH (n=14), d) UV_{254} (n=14) and e) turbidity (n=14) f) SUVA (n=10) in slow sand filter operated at filtration of 0.5 m/h, period: July 10 2007 to November 20 2007)
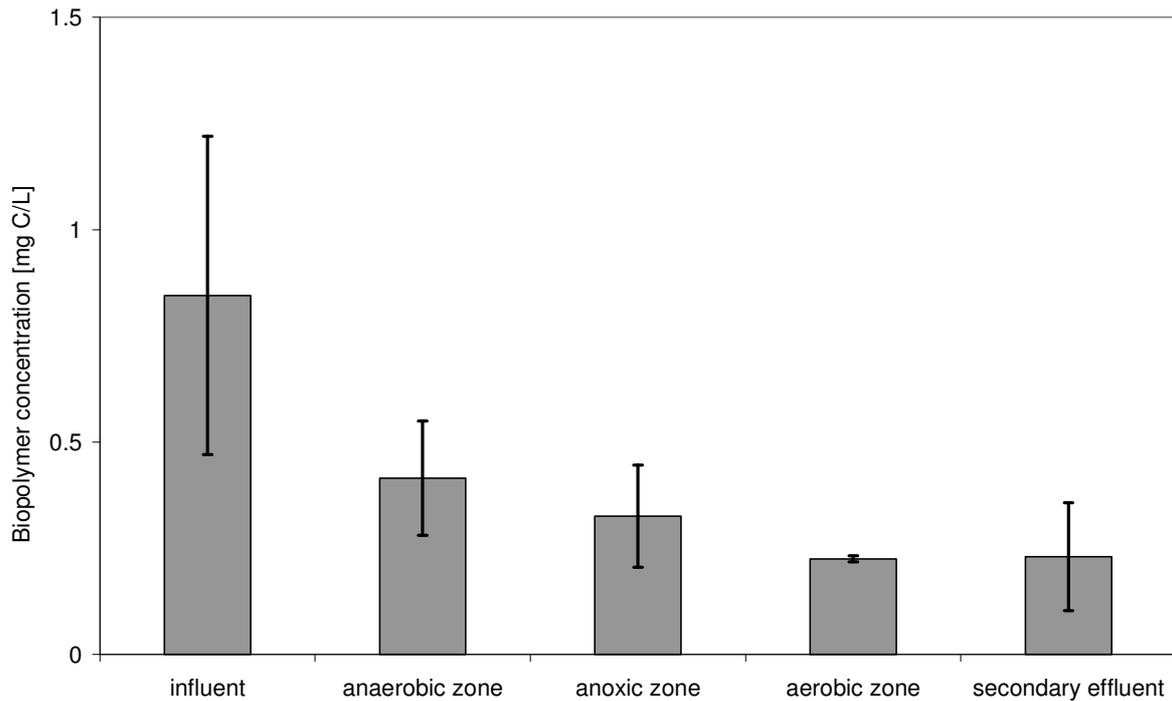
A-Fig. 6 Biopolymer concentration variation in water phase along wastewater treatment procedure in WWTP Ruhleben (Average value of three series of water samples, July 2007 and November 2007)

A-Fig. 6 presents the variations of biopolymer concentration along the wastewater treatment process in WWTP Ruhleben. The biopolymer concentration is always higher in the influent than in the effluent. The results imply that part of the biopolymers detected in the SE could be biopolymers from untreated wastewater.

Measurement of Biological Degradability Biopolymers

Biological degradability of biopolymers and humic substances was tested using BDOC determination method developed by Servais et al., 1987 and Block et al., 1992 with some revisions. Suspended biomass inoculation (SBI) and blinds test were conducted simultaneously. SE 900 mL is sterilized by filtration through 0.2 µm cellulose acetate membrane (Sartorius). Inoculation was undertaken as following: 300 g sand was taken from sand filter at depth 10 cm and strongly shaked in 900 mL SE. After 1 hour sedimentation, 9 mL supernatant was filtered through 1.2 µm cellulose nitrate membrane (Sartorius) and then added to the sterilized water sample. Incubation and blind test occurred in darkness at 20 ± 1 ^{o}C for a period of 30 days, during which biopolymer concentration and UV_{254} was measured daily at the first two days and then weekly.

A-Tab. 6 Biopolymer concentration in SE and SSFs (Oct.26 2006 to Dec. 31 2007)

Date	Temperature °C	BC in SE mg C/L	BC in SSF 0.1 m/h mg C/L	BC in SSF 0.2-0.25m/h mg C/L	BC in SSF 0.4-0.5m/h mg C/L
10.26.06	15	0.52	0.24	0.21	0.25
11.01.06	16	0.43	0.33	0.29	0.294
11.13.06	15	0.40	0.23	0.12	0.14
11.18.06	17	0.48	0.23	0.22	0.26
11.24.06	16	0.43	0.31	0.25	0.32
12.01.06	18	0.68	0.56	0.43	0.42
12.06.06	19	0.40	0.35	0.33	0.32
12.14.06	18	0.43	0.38	0.29	0.32
12.20.06	19	0.44	0.25	0.24	0.32
01.05.07	16	0.62		0.41	0.46
01.10.07	17	0.54	0.36	0.30	0.49
01.17.07	15.3	0.34	0.32	0.24	0.3
01.24.07	18	0.30	0.21	0.21	0.21
01.31.07	12	0.42	0.24	0.27	0.31
02.07.07	16.1	0.41	0.24	0.29	
02.14.07	17	0.25	0.13	0.11	
02.21.07	17	0.37	0.13	0.27	
03.01.07	15	0.58	0.18	0.37	
03.08.07	18	0.59	0.22	0.41	
03.14.07	19	0.41	0.19	0.21	
03.21.07	18	0.31	0.12	0.18	
03.25.07	17.5	0.30		0.12	
04.01.07	18.2	0.23	0.10	0.14	
04.04.07	18.3	0.41	0.14	0.19	
04.10.07	18.8	0.41	0.17	0.14	
04.12.07	19.2	0.48		0.17	
04.24.07	20.9	0.33	0.13	0.15	
05.01.07	18.3	0.36	0.12	0.12	
05.13.07	19.8	0.49	0.19	0.18	
05.28.07	22.6	0.33	0.09	0.12	
05.30.07	20.9	0.17	0.08	0.09	
06.07.07	24.2	0.18	0.11	0.10	
06.12.07	25.6	0.19	0.08	0.10	
06.25.07	22	0.13	0.09	0.08	
06.29.07	20.7	0.15		0.07	
07.03.07	21.5	0.30	0.10	0.09	
07.05.07	19.9	0.26		0.10	
07.10.07	19.8	0.38		0.12	0.25
07.19.07	23.1	0.32		0.07	0.11
07.29.07	21.4	0.34		0.10	0.16
07.31.07	19.4	0.27		0.05	0.1
08.04.07	21	0.26		0.09	0.09
08.14.07	22	0.23		0.08	0.07
08.21.07	21.6	0.36		0.11	0.14
08.28.07	21	0.23		0.07	0.05
09.04.07	20.0	0.20		0.04	0.05
09.17.07	19.6	0.35		0.08	0.08
09.18.07	19.6	0.32		0.08	0.09
10.01.07	17.9	0.23		0.07	
10.08.07	18	0.32		0.09	0.12
10.23.07	15.7	0.33		0.09	
10.30.07	15.5	0.46		0.17	0.09
11.05.07	15	0.45		0.08	0.17
11.13.07	12.5	0.44		0.07	0.15
11.20.07	13	0.79		0.38	0.31
11.27.07	14	0.59		0.36	0.43
12.07.07	12.5	0.70		0.48	0.62
12.12.07	12.1	0.69		0.46	
12.19.07	12	0.74		0.50	
12.28.07	13	0.75		0.56	
12.31.07	13.9	0.79			
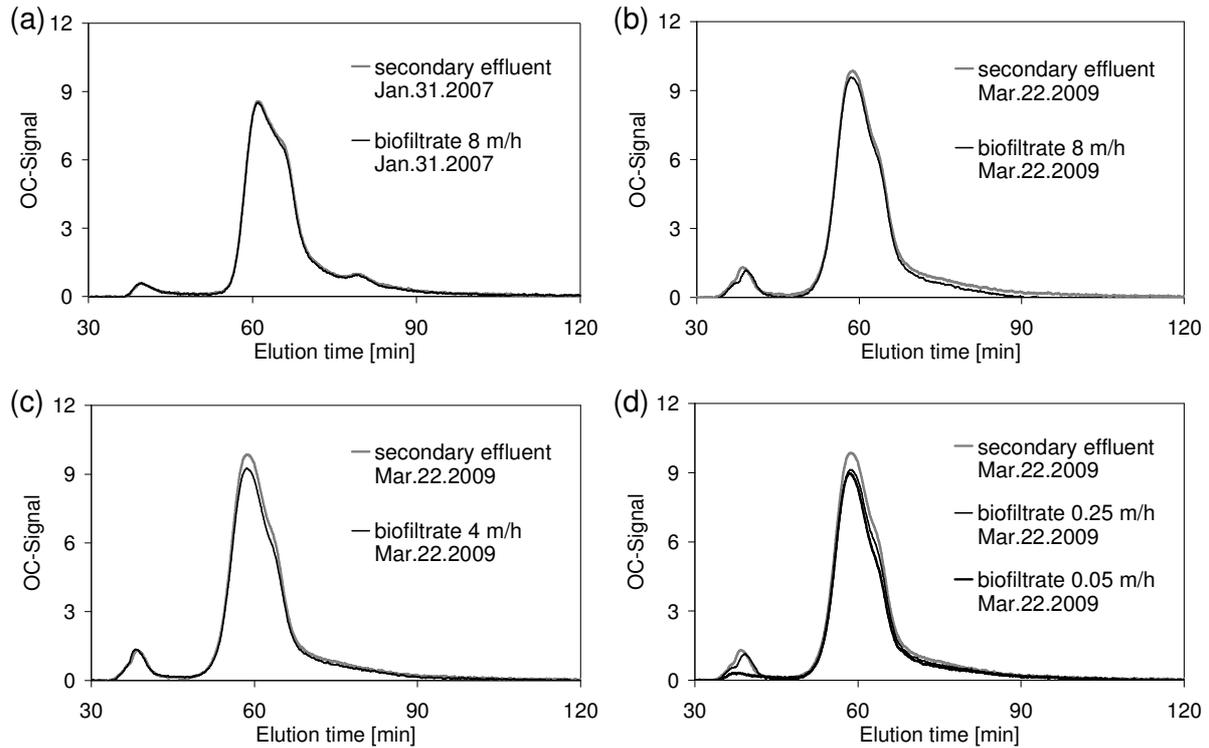
A-Fig. 7 Influence of filtration rate on biopolymer removal effect (a) LC-OCD chromatogram of SE and bio-filtrate operated at filtration rate of 8 m/h (Jan. 31 2007, start up November 2007), (b) LC-OCD chromatogram of SE and bio-filtrate operated at filtration rate of 8 m/h (March 22 2009, start up November 2007), (c) LC-OCD chromatogram of SE and bio-filtrate operated at filtration rate of 4 m/h (March 22 2009, start up April 2008), (d) LC-OCD chromatogram of SE and bio-filtrate operated at filtration rate of 0.25 m/h (March 22 2009, start up March 1 2009) and 0.05 m/h (March 22 2009, start up Jan. 1 2009)

A-Fig. 7 shows biopolymer removal effect using bio-filtration operated at filtration rates from 0.05 m/h to 8 m/h. The bio-filters operated at filtration rate of 8 m/h and 4 m/h were operated within the project 'Barrieren' which was supported by Berliner Wasser Betriebe (BWB). The bio-filter operated at 8 m/h is consisted of 1 m anthracite layer (size: 1.4 – 2.5 mm) and a 0.8 m sand layer (size: 0.7 – 1.1 mm). During operation the filter was periodically backwashed using filtrate. The comparison of A-Fig. 7 (a) and (b) show that after longer than 16 months operation, bio-filter operated at the corresponding conditions cannot remove biopolymers effectively although they show effective removal of turbidity (on average the turbidity in SE was 2 – 4 NTU, in bio-filtrate it was lower than 0.6 NTU). The bio-filter operated at 4 m/h was filled with filtralite (Maxit group, Norway) which is expended clay with a core size of 2 – 5 mm. The filter layer was around 0.9 m high. In the filter was operated in anoxic condition. A-Fig. 7 (c) shows that after longer than half year operation, the filter exhibited little effect in biopolymer removal. A-Fig. 7 (d) displays the biopolymer removal effect of slow sand filtration operated at filtration rate of 0.25 m/h (started from Feb. 01 2009, filter material BioNet 0.2 m in depth, sand 0.6 m in depth (core size: 2 – 4 mm)) and 0.05 m/h (started from Jan. 01 2009, sand layer 0.6 m with sand core size of 2 – 4 mm)).

8.4 Figure contents

8.5 Table contents

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