inside cover

Foulants in ultrafiltration of wwtp effluent

Sandy te Poele

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Front cover: Photograph of the ultrafiltration membrane module

FOULANTS IN ULTRAFILTRATION OF WWTP EFFLUENT

PROEFSCHRIFT

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voorzitter van het College voor Promoties,
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door Sandy TE POELE

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Summary

Water is the basic element for all living organisms on earth. Moreover, water fulfils a large number of different functions for human activities such as drinking water, in households, agriculture, industrial applications and transport. The latter also refers to transport our waste to treatment plants. This wastewater is mechanically and biologically treated in wastewater treatment plants (wwtp's) resulting in a good effluent water quality, whereby biodegradable organics, nitrogen, phosphate and suspended solids are removed to a large extent. The resulting wwtp effluent is normally discharged to surface water, but can also be used as a water source for other applications. One of the techniques to upgrade wwtp effluent to a higher water quality is membrane filtration. By using ultrafiltration membranes an excellent basic water quality can be achieved, without suspended solids, bacteria, large macro-molecules and mostly all pathogenic organisms. The advantages of ultrafiltration are the relatively high flux, low trans membrane pressure and low energy costs, applying the dead-end mode. A major drawback in the use and operation of ultrafiltration is membrane fouling, which is a natural consequence of the membrane separation process. Membrane fouling affects the filtration properties directly and therefore limits the overall process performance. In order to understand membrane fouling mechanisms, it is of great importance to know which components contribute to membrane fouling and how these foulants are attached to the membrane surface and connected to each other.

In this thesis the physical and chemical mechanisms of membrane fouling during dead-end ultrafiltration of wwtp effluent have been investigated in order to optimise process conditions, pre-treatment and membrane cleaning.

Filtration properties like filterability (: the increase of filtration resistance as a function of filtration time within a filtration period) and reversibility (: the extent within which the filtration resistance after applying a hydraulic cleaning is returned to the start value) have been used to evaluate the process performance. These parameters have been measured both on lab and pilot scale, using the same ultrafiltration membrane type (capillary ultrafiltration membranes of X-Flow with an internal diameter of 0.8 mm, a nominal pore size of 0.03 μm and prepared of polyether sulphone). With the pilot installation the filtration properties have been measured more realistically at different wwtp locations in the Netherlands. To characterise the filterability

on lab scale the Specific Ultrafiltration Resistance (SUR) parameter has been used. On pilot scale the change in filtration resistance over time has been monitored and in addition Clean Water Flux (CWF) measurements have been carried out to determine the actual resistance over the membrane. A new parameter, the maximum theoretical filtration resistance ($R_{max,th}$), has been introduced in order to evaluate the process performance by comparing the actual filtration resistance to the $R_{max,th}$. This parameter describes the filtration resistance at the maximum Trans Membrane Pressure (TMP) allowed, the applied constant flux and the feed water temperature (so including the dynamic viscosity of water).

The constituents in wwtp effluent revealed to be mainly of organic origin. They are originally present in the wastewater influent, but also they are produced during biological treatment and escaped final separation. These components are characterised as soluble biodegradable organics, suspended organic material and non biodegradable organics and are also known as effluent organic matter (EfOM). On their turn EfOM incorporates Natural Organic Matter (NOM) and extracellular polymeric substances (EPS). The EPS are present in biological treatment systems in relatively large quantities, because of their importance in the formation of sludge flocs. Based on these glue-like properties, EPS have been suggested to play an important role in membrane fouling. The main components of EPS are proteins and polysaccharides. In order to analyse proteins and polysaccharides in wwtp effluent an excising photometric measurement method has been developed further. In addition to proteins and polysaccharides, total organic matter, characterised by COD, colour components and humic substances (a major component of NOM) have been indicated as potential organic membrane foulants.

The influence of the size of wwtp effluent constituents and in particular the potential organic foulants on the filterability have been studied. On laboratory scale the effluent of different wwtp's has been fractionated by successively filtering over a 400 or 450 μm sieve, 0.45, 0.20 and 0.10 μm membrane filters. The filterability of these fractions has been characterised by the SUR and the potential organic foulants have been analysed in each fraction. The results showed that wwtp effluent constituents sized between 0.1 and 0.45 μm, which are colloids, are of major influence on the filterability during ultrafiltration, but could hardly be related to any of the measured potential foulants. On pilot scale the filterability of different feed waters (sieved wwtp effluent, multimedia filtrate and microfiltrate with or without coagulation) has been investigated and the amount of potential membrane fouling components retained has been analysed. The parameter $R_{max,th}$ has been found very useful in evaluating the filterability. The amount of measured foulants retained has been found independent of the feed water type, but can be influenced by coagulation. Furthermore, no clear relations between the filterability and amount of potential foulants retained were found.

The influence of different conditioning and pre-treatment methods on the filtration properties has been investigated by influencing the physical and chemical properties of the wwtp effluent constituents. By using pre-filtration techniques like sieving (<

450 μm), multimedia filtration (about < 50 μm) and microfiltration (< 0.2 μm) prior to ultrafiltration, the influence of the size of different wwtp effluent constituents on filterability and reversibility has been studied on pilot scale at two different wwtp's. The results show that multimedia filtration has been effective in removing particles. This increased both filterability and reversibility. Furthermore, a large increase in filterability has been found using microfiltrate as feed water instead of multimedia filtrate, suggesting that suspended material and colloids are of major influence on the filterability. The influence of the flux on the filtration properties has been studied during ultrafiltration of microfiltrate by increasing the flux from 28.5 to 50 L/m^2·h. As a result hardly no change in filterability has been observed, but the reversibility decreased significantly, indicating that membrane fouling by macro-molecules and dissolved material is depending on the applied flux. On pilot scale the effect of coagulation prior to ultrafiltration on the filtration properties has been studied. For the three pilot investigations at different wwtp's simular results have been obtained. The influence of Poly Aluminium Chloride (PACl) coagulation on the filterability revealed to be rather small. But, conditioning of wwtp effluent, sand filtrate and multimedia filtrate by coagulation of 2-2.5 mg Al^{3+}/L PACl was found to be very effective, resulting in a high reversibility. Temperature conditioning was studied by measuring the filterability at different feed water temperatures on lab scale. Due to the temperature dependency of the dynamic viscosity of water the ultrafiltration flux is expected to increase when the temperature increases. However, the results of the temperature conditioning experiments revealed that the filterability decreases with increasing temperature of the feed water. This could only be explained by a change of the retained components, that caused a higher filtration resistance. Therefore it is suggested not to normalise fluxes for temperature in case of ultrafiltration of wwtp effluent, but to always indicate the exact temperature of operation or measurement.

More insight in the membrane foulants were obtained by applying different cleaning agents and methods. The presence of protein fouling was indicated by comparing the results of the basic alkaline cleanings with and without the enzyme protease. Furthermore, the protease cleaning protocol used resulted in a complete recovery of the CWF at low temperature (25-30 °C). In contrast to that, no significant difference in cleaning performance was observed with and without the use of the enzyme amylase. Thus, polysaccharide fouling could not be indicated. In case metal complexes were formed during filtration of coagulated wwtp effluent, it is advisable to apply an acid cleaning previous to the enzymatic protease or alkaline cleaning.

Overall, (organic) colloids sized between 0.1 and 0.45 μm revealed to be of major influence on the filterability. They were not identified as proteins, polysaccharides, humic substances and colour, but might be cell fragments and large macro-molecules. On the other hand, (organic) macro-molecules < 0.2 μm revealed to be of major influence on the reversibility, whereby proteins were identified to adsorb on the membrane surface. Adsorption of polysaccharides was not clearly identified. In addition, proteins have been suggested to play an important role in crosslinking foulants to each other and attaching to the membrane surface, forming a network layer.

Samenvatting

Water is het basiselement voor alle levende organismen op aarde. Verder vervuld water een groot aantal functies voor menselijke activiteiten zoals drinkwater, in de huishouding, landbouw, industriële toepassingen en transport. Deze laatste toepassing heeft ook betrekking op het transport van ons afval naar zuiveringsinstallaties. In een rioolwaterzuiveringsinstallatie (rwzi) wordt dit afvalwater mechanisch en biologisch behandeld. Hierdoor wordt een goede water kwaliteit van het effluent bereikt, waarbij biologisch afbreekbare organische stoffen, stikstof, fosfaat en zwevende stoffen vergaand worden verwijderd. Dit rwzi effluent wordt gewoonlijk op het oppervlaktewater geloosd, maar zou ook kunnen worden gebruikt als een water bron voor andere toepassingen. Een van de technieken om rwzi effluent op te werken tot een betere water kwaliteit is membraanfiltratie. Door ultrafiltratie membranen te gebruiken, kan een uitstekende basis water kwaliteit worden verkregen dat vrij is van zwevende stof, bacteriën, grote macromoleculen en vrijwel alle pathogene organismen. De relatieve hoge flux, lage transmembraandruk en lage energiekosten indien "dead-end" filtratie wordt toegepast, worden als voordelen van ultrafiltratie gezien. Echter, een groot nadeel van deze techniek is de membraanvervuiling die optreedt tijdens filtratie en inherent is aan dit scheidingsprocecs. Membraanvervuiling heeft direct invloed op de filtratie eigenschappen en daardoor wordt het totale filtratieproces gelimiteerd. Om de achterliggende mechanismen van membraanvervuiling te begrijpen, is het van groot belang te weten welke componenten bijdragen aan membraanvervuiling en hoe deze vervuilende stoffen aan het membraan oppervlak hechten en zich aan elkaar binden.

In dit proefschrift zijn de fysische en chemische mechanismen van membraanvervuiling tijdens "dead-end" ultrafiltratie van rwzi effluent onderzocht met als doel de proces condities, voorbehandeling en membraanreiniging te optimaliseren.

Filtratie eigenschappen zoals filtreerbaarheid (: de mate waarin de filtratieweerstand toeneemt als functie van de tijd binnen een filtratieperiode) en reversibiliteit (: de mate waarin de filtratieweerstand terug komt op z'n startwaarde na toepassing van een hydraulische reiniging) zijn in dit onderzoek gebruikt om het filtratieproces te beoordelen. Deze parameters zijn zowel op laboratorium (lab) schaal als op pilot schaal gemeten, waarbij hetzelfde ultrafiltratie membraan type is gebruikt (capillaire ultrafiltratie membranen van X-Flow met een interne diameter van 0.8 mm, een nominale poriegrootte van 0.03 μm en bestaand uit polyether sulfon). Met de pilotinstallatie

zijn de filtratie eigenschappen meer realistisch bepaald op verschillende rwzi locaties in Nederland. De filtreerbaarheid op lab schaal is gekarakteriseerd door de Specifieke Ultrafiltratie Weerstand (SUR) te meten. Op pilot schaal is de verandering van de filtratieweerstand als functie van de tijd gemeten en zijn Schoon Water Flux (SWF) metingen uitgevoerd om de actuele weerstand over het membraan te bepalen. Een nieuwe parameter, waarmee de theoretisch maximaal haalbare weerstand tijdens filtratie wordt bepaald ($R_{max,th}$), is geïntroduceerd om het filtratieproces beter te kunnen beoordelen door de actuele filtratie weerstand te vergelijken met de $R_{max,th}$. Deze parameter beschrijft de filtratieweerstand bij de maximaal toegestaande Trans Membraan Druk (TMD), de toegepaste constante flux en de voedingswater temperatuur. Theoretisch is de dynamische viscositeit temperatuur afhankelijk.

De bestanddelen in rwzi effluent blijken voornamelijk van organische aard te zijn. Ze zijn deels uit het afvalwater influent afkomstig, zijn geproduceerd tijdens biologische behandeling en zijn niet afgescheiden tijdens de nabezinking. Deze componenten worden gekarakteriseerd als opgeloste biologisch degradeerbare organische stoffen, zwevend organisch materiaal en niet biologisch degradeerbare organische stoffen en zijn ook bekend als Effluent Organische Materiaal (EfOM). EfOM omvat ondermeer Natuurlijk Organisch Materiaal (NOM) en Extracellulaire Polymere Stoffen (EPS). De EPS zijn in relatief grote hoeveelheden aanwezig in biologische behandelingssystemen vanwege de belangrijke functie die deze stoffen hebben in de vorming van slibvlokken. Gebaseerd op de plakeigenschappen van deze stoffen wordt verondersteld dat EPS een belangrijke rol zouden kunnen spelen in de membraanvervuiling. De hoofdbestanddelen van EPS zijn proteïnen (tot 60 %) en polysachariden (40-95 %). Om deze componenten te kunnen analyseren in rwzi effluent is een bestaande fotometrische meetmethode verder ontwikkeld. Naast proteïnen en polysachariden, is de totale hoeveelheid aan organische materiaal, gekarakteriseerd als Chemisch Zuurstof Verbruik (CZV), kleurhoudende componenten en humusachtige stoffen (een belangrijke component van NOM) aangemerkt als potentiële membraanvervuilende stoffen van organische aard.

De invloed van de grootte van de rwzi effluent bestanddelen en meer specifiek de potentiële vervuilende organische stoffen op de filtreerbaarheid is onderzocht. Op lab schaal is effluent afkomstig van verschillende rwzi's gefractioneerd door te filtreren over een 400 of 450 μm zeef en achtereenvolgens over 0.45, 0.2 en 0.1 μm membraanfilters. De filtreerbaarheid van deze fracties is gekarakteriseerd door de SUR en de potentiël vervuilende organische stoffen zijn geanalyseerd in iedere fractie. De resultaten laten zien dat de rwzi effluent bestanddelen in de grootte orde tussen 0.1 en 0.45 μm, die als colloïden worden beschouwd, van grote invloed zijn op de filtreerbaarheid tijdens ultrafiltratie. Echter, deze deeltjes kunnen niet of nauwelijks worden gerelateerd aan de gemeten potentiële vervuilende organische stoffen. Op pilot schaal is de filtreerbaarheid van verschillend voedingswater (gezeefd rwzi effluent, multimedia filtraat en microfiltraat met en zonder coagulatie) onderzocht en is de hoeveelheid tegengehouden potentiële vervuilende organische stoffen geanalyseerd. De parameter $R_{max,th}$ is heel bruikbaar gebleken om het filtratieproces te kunnen beoordelen. De

hoeveelheid aan gemeten tegengehouden vervuilende stoffen is onafhankelijk van het type voedingswater gebleken, maar kan wel worden beïnvloed door coagulatie. Verder zijn er geen duidelijke relaties gevonden tussen de filtreerbaarheid en de hoeveelheid tegengehouden potentiële vervuilende stoffen.

De invloed van verschillende conditionerings- en voorbehandelingsmethoden op de filtratie eigenschappen zijn onderzocht door de fysische en chemische eigenschappen van de rwzi effluent bestanddelen te beïnvloeden. Door filtratietechnieken, zoals een zeefbocht (< 450 μm), multimedia filtratie (ongeveer < 50 μm) en microfiltratie (< 0.2 μm) voor ultrafiltratie toe te passen, is de grootte van verschillende rwzi effluent bestanddelen op de filtreerbaarheid en reversibiliteit op pilot schaal onderzocht op twee verschillende rwzi's. De resultaten laten zien dat multimedia filtratie een efficiënte techniek is om deeltjes te verwijderen, waardoor zowel de filtreerbaarheid als de reversibiliteit toeneemt. Verder is een grote toename in filtreerbaarheid gevonden bij de toepassing van microfiltraat ten opzichte van multimedia filtraat als voedingswater. Hiermee wordt verondersteld dat hoofdzakelijk gesuspendeerd materiaal en colloïdale deeltjes van invloed zijn op de filtreerbaarheid. De invloed van de flux op de filtratie eigenschappen is onderzocht door tijdens ultrafiltratie van microfiltraat de flux te verhogen van 28.5 naar 50 L/m^2·u. Hetgeen resulteerde in een verwaarloosbare verandering van de filtreerbaarheid, maar in een significante afname van de reversibiliteit. Hiermee wordt verondersteld dat membraanvervuiling door macromoleculen en opgelost materiaal (< 0.2 μm) afhankelijk is van de toegepaste flux. Op pilot schaal is tevens het effect van coagulant dosering voor ultrafiltratie op de filtratie eigenschappen onderzocht. Voor drie pilotonderzoeken die hebben plaats gevonden bij verschillende rwzi's zijn gelijkwaardige resultaten gevonden. De invloed van PACl coagulatie op de filtreerbaarheid blijkt slechts gering te zijn. Echter, conditionering van rwzi effluent, zandfiltraat en multimedia filtraat door coagulatie met 2-2.5 mg Al^{3+}/L PACl is erg effectief gebleken om een hoge reversibiliteit te behouden. Temperatuur conditionering is onderzocht door de filtreerbaarheid van voedingswater bij verschillende temperaturen te meten op lab schaal. In het algemeen wordt verwacht dat de flux tijdens ultrafiltratie bij constante TMD toe neemt naarmate de temperatuur van het voedingswater stijgt, als gevolg van de temperatuursafhankelijkheid van de dynamische viscositeit. Echter, de resultaten van de temperatuur conditioneringsexperimenten laten zien dat de filtreerbaarheid af neemt bij toenemende voedingswater temperatuur. Dit kan alleen worden verklaard door een verandering van de tegengehouden componenten waardoor de filtratieweerstand toeneemt. Daarom wordt aanbevolen de flux niet te normaliseren voor temperatuur in het geval van ultrafiltratie van rwzi effluent, maar altijd de exacte temperatuur aan te geven.

Meer gedetailleerde informatie over de membraan vervuilende stoffen is verkregen door toepassing van verschillende reinigingsmiddelen en methoden. Door de resultaten van de alkalische reinigingen met en zonder het enzym protease te vergelijken, is de aanwezigheid van proteïne vervuiling aangetoond. Verder heeft de toepassing van het protease reinigingsprotocol bij relatief lage temperatuur (25-30 °C) geresulteerd in een complete recovery van de SWF. Een tegengesteld resultaat is gevonden

bij de vergelijking van de reinigingen met en zonder het amylase enzym complex. Hierbij is geen verschil gevonden tussen beide toegepaste reinigingsoplossingen en polysacharide vervuiling kon daarmee niet worden aangetoond. Indien metaalcomplexen zijn gevormd tijdens filtratie van gecoaguleerd rwzi effluent, wordt aanbevolen eerst een zure reiniging toe te passen alvorens een protease of alkalische reiniging uit te voeren.

Samenvattend kan worden gesteld dat (organische) colloïden in de grootte orde tussen 0.1 en 0.45 μm van grote invloed zijn op de filtreerbaarheid, maar kunnen niet worden gerelateerd aan de gemeten proteïnen, polysachariden, kleurhoudende componenten en humusachtige verbindingen. Het zou kunnen zijn dat deze colloïden uit cel fragmenten en grote macromoleculen bestaan. Van de andere kant blijken (organische) macromoleculen < 0.2 μm van grote invloed te zijn op de reversibiliteit, waarbij proteïnen kunnen adsorberen aan het membraanoppervlak en de adsorptie van polysachariden niet kon worden aangetoond. Verder wordt verondersteld dat proteïnen een belangrijke rol spelen in de binding met andere vervuilende stoffen en de binding met het membraanoppervlak, zodat een netwerkachtige structuur van membraanvervuilende componenten zou kunnen ontstaan.

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Sandy te Poele

Eindhoven, 20 November 2005

Nomenclature

Symbols

A	membrane surface	$[m^2]$
A	absorption	[-]
COD	chemical oxygen demand	$[mg/l]$
CWF	clean water flux @ 20 $^\circ C$	$[L/m^2 \cdot h \cdot bar]$
C	concentration	$[mg/L]$
J	flux	$[L/m^2 \cdot h]$, $[m^3/m^2 \cdot s]$
ΔP	trans membrane pressure	$[bar]$
P	pressure	$[bar]$
$PUVA$	ratio of ultra violet absorption and proteins	$[L/mg \cdot m]$
R	resistance	$[1/m]$
$R_{max,th}$	maximum theoretical filtration resistance	$[1/m]$
SUR	specific ultrafiltration resistance	$[1/m^2]$
T	temperature	$[^\circ C]$
TMP	trans membrane pressure	$[bar]$
V	filtrated volume	$[m^3]$
l_p	permeability	$[m/Pa \cdot s]$
c_v	solids concentration in the feed water	$[kg/m^3]$
m	filtrated mass	$[kg]$
t	filtration time	$[s]$

Greek symbols

α_{av}	average specific cake resistance	$[m/kg]$
η	dynamic viscosity	$[Pa \cdot s]$
ρ	density	$[kg/L]$

Indices

254	wavelength of 254 nm
L	measured by Lowry et al. (1951)
a	adsorption
a, b	time indication
c	cake layer
h	humic acid
m	membrane
f	filtration
pb	pore blocking
$prot$	protein
tot	total

Abbreviations

Al	poly aluminium chloride
aPS	after Pond System
BF	Back Flush
BOD_5	Biochemical Oxygen Demand after 5 days
BSA	Albumin bovine
CA	Cellulose Acetate
CC	Chemical Cleaning
CN	Cellulase Nitrate
CST	Capillary Suction Time
DBP	Disinfection By-products
DMF	Multimedia Filtrate
DOC	Dissolved Organic Carbon
EF	Effluent
EPS	Extracellular Polymeric Substances
EWFD	European Water Framework Directive
EfOM	Effluent Organic Matter
Exp	Experiment
FF	Forward Flush
Fe	Ferric Chloride
HCl	Hydrogen Chloride
HvH	Hoek van Holland
KTP	pentapotassium-tri-phosphate
LC-OCD	Liquid Chromatography - Organic Carbon Detection
M	Methanol
MBR	Membrane BioReactor
MF	Microfiltration
MFI	Modified Fouling Index
MTR	"Maximaal Toelaatbaar Risico" (maximum admissible risk)

Abbreviations continued

MWCO	Molecular Weight Cut-off
mem	membrane
NF	Nanofiltration
NOM	Natural Organic Matter
NW4	"Vierde Nota Waterhuishouding" (Fourth National Policy Document on Water Management)
NaOCl	Sodium Hypochloride
PACl	Poly Aluminium Chloride
PAH	Poly-aromatic hydrocarbons
PES	Polyether sulphone
PS	Polysaccharides
PVP	Polyvinylpyrolidene
RF	Reversed Flush
RO	Reversed Osmosis
SMP	Soluble Microbial Products
SOC	Synthetic Organic Compounds
SRF	Specific Resistance Filtration
SS	Suspended Solids
T-N	Tilburg-Noord
TOC	Total Oxygen Demand
TSS	Total Suspended Solids
TTF	Time To Filtrate
UF	Ultrafiltration
UV	Ultra Violet
UVA	Ultra Violet Absorption
VIS	Visable
VSS	Volatile Suspended Solids
WVO	"Wet Verontreiniging Oppervlakte water" (Pollution of Surface Water Act)
WWTP	Wastewater Treatment Plant
wwtp	wastewater treatment plant

Contents

Chapter 1

Wastewater treatment: where are we and how far do we go?

1.1 wastewater treatment

The basic element for life is water. Water is needed in nature, more specifically in the aquatic environment, and for human activities such as drinking water, households, industrial applications, agriculture, fishery, transport and recreation.

Through human activity water is getting polluted and since this water is discharged to surface waters it also affects the water quality of rivers, channels and lakes. Therefore the polluted water needs to be treated before discharge. In the period of 1900 to 1970 the objectives of wastewater treatment were the removal of colloidal, suspended and flotable material, treatment of biodegradable organics and removal of pathogenic organisms. In the following period till 1980 the objective of wastewater treatment changed to more ethical and environmental concerns, Metcalf and Eddy (2003). In the Netherlands wastewater treatment started to develop rapidly since in 1970 the Pollution of Surface Waters Act (Wet Verontreiniging Oppervlaktewater, WVO) was introduced by the Dutch government. Here the focus was on the removal of biodegradable organics. Later in the '80-'90 the objective changed to the removal of nutrients such as nitrogen and phosphorous, Van der Graaf (2001a).

New treatment methods that are being developed are designed to deal with health and environmental concerns associated with findings of recent research. For example, the increasing interest of removing endocrine disruptors of wwtp effluents stems from the early '90 when reproductive abnormalities were found in fish living downstream of wastewater plant outfalls in the United States and the United Kingdom, Flamink et al. (2003). Other health and environmental concerns relate to the removal of heavy metals and poly-aromatic hydrocarbons (PAHs). These components are identified as priority and priority hazardous substances. In total 33 components are listed in the European Water Framework Directive (EWFD). The objective of the EWFD is to

achieve a water quality classified as good status, which means for surface water a good chemical and ecological status. The new aspect of the EWFD is the harmonisation of existing directives and legislation, and the focus on river basins crossing country boarders. The emission control of the priority and priority hazardous substances are then related to the river basin. The construction of the EWFD was started in 2000 and will be fully implemented in 2015. In the end the EWFD will provide a mechanism for renewing quality standards established for chemical substances at an European level, Broseliske and Verkerk (2004).

Meanwhile, in the Netherlands, the Fourth National Policy Document on Water Management (vierde Nota Waterhuishouding, NW4) is being established for the period 1998-2006. By this standards relating to nutrients and other water quality parameters are based on an area-specific approach, focusing on reducing emissions of substances. Priority will be given based to risk assessment. Water management authorities have a duty to strive to achieve the maximum admissible risk, (Maximaal Toelaatbaar Risico, MTR) level, NW4 (1998).

1.1.1 conventional wastewater treatment

Today, the sanitary and environmental infrastructure in the Netherlands is on such a level that nearly all households have drinking water supply and 98% of the houses are connected to sewer systems. In wastewater treatment plants, wwtp's, municipal and industrial wastewater and in case of combined sewer systems also rainwater are treated mechanically and biologically. To ensure protection of public health and the environment, certain treatment levels should be achieved. Currently, secondary treatment is prescribed in European legislation, UWWTD (1991), and has been implemented at all wwtp's in the Netherlands. In figure 1.1 a description is given of the different treatment levels. In addition, the operation processes are indicated.

In the Netherlands 98% of the biological treatment is performed by activated sludge processes, CBS (2004), and tertiary treatment is only applied at a few wwtp's. Due to health and environmental reasons disinfection is applied when the receiving surface water is used for recreation and in case of mussel banks, Van der Graaf (2001a). In general the effluent of a wastewater treatment plant, wwtp effluent, is discharged to surface water. The wwtp effluent quality after secondary treatment is listed in table 1.1.

Table 1.1: Characteristic data of wwtp effluent quality in the Netherlands in 2002, CBS (2004)

Parameter	Mean concentrations (mg/L)
BOD_5	5
COD	43
N_{tot}	10
P_{tot}	2

Treatment level	Description	Treatment process
		Influent ↓
Preliminary	Removal of rags, sticks, floatables, grit and grease	Screening and grit removal
Primary	Removal of a portion of the suspended solids and organic matter	sedimentation
Advanced primary	Enhanced removal of suspended solids and organic matter	chemical addition or filtration
Secondary	Removal of biodegradable organic matter, suspended solids and nutrients	activated sludge, trickling filters
		Effluent ↓
Tertiary	Removal of residual suspended solids and disinfection	granular media filtration and chlorination
Advanced	Removal of dissolved and suspended materials remaining after normal biological treatment	see 1.1.2

Figure 1.1: Description of treatment levels and examples of operating processes, Metcalf and Eddy (2003)

1.1.2 advanced treatment

Nowadays in the Netherlands wastewater treatment includes full biological treatment and nutrient removal, resulting in a good effluent quality. However, the amount of heavy metals and synthetic organic compounds in municipal wastewater increased. According to Metcalf and Eddy (2003) 10,000 new organic compounds are generated each year and many of these compounds are found in the wastewater. In addition the use of human medicine like hormones and β-blockers increased as well and after consumption these products, derivatives or by-products are discharged to wastewater via faeces. Therefore advanced treatment methods will be applied to meet future standards. For further treatment of effluent many processes can be applied, Van der Graaf (2001a) and Van der Graaf (1999):

Coagulation, flocculation: Removal of a broad spectrum of components by chemical precipitation. A broad range of coagulants and flocculants can be used. In general, ferric chloride and poly aluminium chloride are often applied.

General filtration techniques: Removal of suspended solids, fine particles and micro particles. In combination with coagulation and flocculation higher removal efficiencies can be obtained and phosphate concentrations can be reduced as well. With the addition of a carbon source and by applying low flow rates, the filter will function as a biological filter

and as a result nitrate can be reduced as well. Examples of well known filtration techniques are:

- sand filtration,
- multimedia filtration,
- deep bed filtration,
- flocculating filtration.

Membrane filtration: Removal of particles which are < 10 μm. Depending on the pore size of the applied membranes smaller components are retained:

- microfiltration: micro particles,
- ultrafiltration: colloids and macro-molecules,
- nanofiltration: macro-molecules and multivalent ions,
- reverse osmosis: di- and monovalent ions.

In section 1.3 a more detailed description of the different membrane filtration techniques is given.

Disinfection: The hygienic quality of effluent can be improved by applying disinfection techniques, like:

- chlorination,
- ozone,
- UV light.

Adsorption: Removal of dissolved components like (organic) micro-pollutants and some heavy metals. The most applied technique is the use of an activated carbon filter. This filter can also be function as a biological filter for the removal of nitrate.

Biological treatment: Removal of a broad range of components by biological treatment and sedimentation. Some examples are:

- polishing ponds,
- constructed wetlands,
- biofilms.

1.2 Water reclamation

In general, people should be aware of the fact that water is needed for all living organisms on earth. Therefore care should be taken to control the water quality of ground and surface water and to limit the quantity used for human activity. In this sense wwtp effluent should be considered as a water source rather than a waste stream.

Although over 3000 (municipal) wastewater reclamation sites exists all over the world, implementation problems like public acceptation, finance and legislation still have to be overcome, Bixio et al. (2004). Therefore Thomas and Durham (2003) plead for an integrated water resource management approach that can facilitate the acceptance of these projects. Key elements in this approach are participation of a large number of stake-holders in the decision making process and looking at the water cycle in relation to the urban area. Implementation of alternative water resources are driven by the recognition of the social and environmental impact of water scarcity and the advantages of integrated water resource solutions. Some examples of water reclamation projects in the world, including membrane filtration applications, are:

- Water reuse in Japan
  Due to frequent and severe droughts, rapid economic growth and concentration of population in urban areas new water resources with considerable economic and environmental costs are used, Ogoshi et al. (2001) and Levine and Asano (2004). Water reclamation in Japan involves non-potable urban applications like toilet flushing, industrial reuse and environmental water for landscaping. As early as in 1951 the first experiments on water reclamation and reuse based on conventional wwtp effluent for industrial water use in paper mill industry were performed. The first serious wastewater reuse efforts were carried out during the Tokyo Summer Olympics in 1964. Nowadays over 1500 on-site individual building and block-wide water reclamation and reuse systems are in operation.

- West Basin Water Recycling Plant, USA
  The probably most well known wastewater reuse project in the world is the West Basin Water Recycling plant in California (USA) which aims to increase the availability of water resources in the region. The effluent of the Los Angelos Hyperion wwtp is further treated by a Title 22 train for industrial and irrigation use, in parallel with the application of barrier treatment for groundwater recharge, Levine et al. (2001).

- WWTP effluent for drinking-water, Belgium
  In Koksijde (Belgium) wwtp effluent is used for the drinking water production via infiltration into the dunes, Van Houtte (2003). In this way an integrated water system is developed in which filtered wwtp effluent is introduced as an artificial water supply into the groundwater reservoir of the dunes to prevent natural groundwater mining, and to avoid salt water intrusion.

- NEWater project, Singapore
  Another argument to use wwtp effluent as a source of drinking water production is for political reasons. Singapore would like to be more independent of the drinking water supply of Malaysia, Volkskrant (2002). Therefore reclaimed water of wwtp effluent is used to produce NEWater which is supplied to wafer fabrication plants as ultrapure water, industries and commercial buildings for their process and air cooling systems, and to citizens as (bottled) drinking water, Bennett (2004).

- Tangshan Steel works, China
  Recently they started using coal mine wastewater as a water source for the production of high purity water for boiler feed water and steel plate cooling at the Tangshan steel works in China. Severe water shortages in this particular region of China was the main drive to use this wastewater as an alternative water source, Bennett (2004).

- Flag Fen sewage treatment works, UK
  The Flag Fen treatment plant is one of the first sites in Europe to use wwtp effluent for the production of high purity water which is used to generate steam for the Peterborough power station, AWG and TXU EP (2000). This unique partnership between Anglian Water group and TXU Europe Power combines high purity water production and power generation.

- The Virginia Pipeline, Australia
  In the area of Virginia in South Australia near Adelaide the need to reuse water became of great importance due to both environmental and economic considerations, Kracman et al. (2001). In this farming area a major ground water resource is being used as an irrigation water supply, but there the limits of sustainable exploitation are exceeded. On the other hand discharge of wwtp effluent to sea has unfavourable ecological impact. Combining these factors resulted to further treatment of the Adelaide wwtp effluent which is transported and introduced to the ground water resources near Virginia for irrigation of vegetable crops with minimal public health restrictions.

Interest in advanced treatment of wastewater is increasing due to stricter legislation in the near future and growing possibilities in the use of effluent as a source of water supply. The Dutch governmental policy aims to reduce the use of groundwater sources for water consumption and to close the water cycle, VROM (1995). Furthermore upgrading of wastewater treatment plant effluent involves European environmental laws and forms an alternative source for water production. Van der Graaf and Roorda (2000) suggested that membrane filtration appears to be a very promising method for upgrading wwtp effluent. After nutrient removal, wwtp effluent has an excellent quality for further improvement by flocculation filtration, membrane filtration and others, Van der Graaf (2001a).

1.3 Ultrafiltration of wwtp effluent

One of the techniques to upgrade wwtp effluent to improved water quality is membrane filtration. Depending on the membrane separation properties (structure and material) components can be rejected by the membrane, which is a perm-selective barrier. When particles of a diameter > 100 nm have to be retained, the membrane process is called microfiltration. To separate macromolecules with molecular weights in the range of 10^4-10^6 ultrafiltration membranes are used. By nanofiltration low molecule weight components and divalent ions can be separated and furthermore monovalent ions can be rejected by reverse osmosis. Going from microfiltration to ultrafiltration,

nanofiltration and reverse osmosis, the hydrodynamic pressure increases and consequently higher pressure differences are needed, Mulder (1996). Typical values of pore sizes and applied pressures are taken from Doyen (2003) and presented in table 1.2.

Table 1.2: Membrane filtration processes, Doyen (2003)

Membrane process	Pore size	Pressure range
Microfiltration	0.1 - 20 μm	0.1 - 3 bar
Ultrafiltration	2 - 100 nm	0.2 - 8 bar
Nanofiltration	$<$ 2 nm	5 - 20 bar
Reverse Osmosis	dense [a]	10 - 100 bar

[a]Membrane structure is so dense that no pores can be distinguished

With the development of asymmetric membranes in 1963 a breakthrough in industrial membrane applications was achieved. To improve the flux performance of these reverse osmosis membranes, thin film composite membranes were developed, which consists of an ultraporous membrane support base. This resulted in a development of ultrafiltration membranes, Mulder (1996) and Mallevialle et al. (1996). According to Doyen (2003) the use of ultrafiltration membranes in large scale applications depends on the membrane and operational costs. Only since the mid nineties these costs decreased through large scale applications. In water treatment ultrafiltration is applied to replace conventional clarification and filtration processes in drinking water production and as pre-treatment in reverse osmosis operations, because of its good and constant filtrate quality of the treated water in terms of particles and microbial removal, regardless the raw feed water quality.

By using ultrafiltration in upgrading wwtp effluent an excellent basic water quality can be achieved, without suspended solids, bacteria, large macro-molecules and mostly all pathogenic organisms. Ultrafiltrate can be used directly in reuse applications for agricultural, industrial and urban water, or can be treated further by reverse osmosis to produce ultrapure water. The advantages of ultrafiltration are the relatively high flux, low trans membrane pressure and low energy costs, applying dead-end mode (1.3.1). Compared to microfiltration, ultrafiltration membranes have an asymmetric structure with a denser toplayer and consequently a higher hydrodynamic resistance, Mulder (1996), resulting in higher energy costs. On the other hand ultrafiltration can be applied as a clarification and disinfection technique, whereas the primary application of microfiltration is particle removal, Mallevialle et al. (1996).

Low molecular weight components can not be retained by the ultrafiltration membranes. Therefore these membranes can not be used in upgrading wwtp effluent to meet the European Water Framework Directive standards for priority components, like removal of heavy metals and endocrine disruptors.

1.3.1 Membrane process design

In general, the following aspects for membrane process design should be considered: choice of membrane material, membrane module and mode of operation. In water treatment applications hydrophilic polymer membranes are normally used, because of their good wettability and the less tendency of hydrophobic components to foul the membrane, Mulder (1996). Inorganic materials, such as ceramic, have a high chemical and temperature resistance, but are much more expensive than polymeric materials.

Nowadays most available ultrafiltration membranes are prepared from polymeric materials by a phase inversion process, Mulder (1996). These membranes can be prepared in two configurations: flat or tubular. Flat membranes are relatively simple to prepare, but for industrial applications special module design is needed. Here feed and permeate flows are separated in two compartments by placing spacer material, resulting in a plate-and-frame module. The packing density of such modules is about 100-400 m^2/m^3. In order to increase the packing density spiral-wound modules are developed, which is in fact a plate-and-frame system wrapped around a central collection pipe. The packing density of this module is 300-1000 m^2/m^3. Due to the hydraulic design of such modules, many 'dead' areas are obtained which are hard to clean. Hollow fibers, capillary and tubular membranes are membranes of the tubular form prepared via spinning techniques and differ in internal diameter. Tubular membranes are not self-supporting and are placed inside a porous tube. Here the feed solution always flows through the centre of the tube and the permeate flows through the supporting tube into the membrane housing. The packing density of a tubular module is rather low: < 300 m^2/m^3, whereas the hollow fibre module has good process control and membrane cleaning conditions and is therefore suitable for feed streams with a high fouling tendency. Capillaries and hollow fibers are assembled together in a module by potting the ends of the membranes in the housing material. The feed can either flow through the lumen of the fibers: inside-out, or enter the fibre from the outside: outside-in, as illustrated in figure 1.2. A disadvantage of outside-in filtration is that channelling may occur. The difference between capillary and hollow fibre modules lies in the packing density, which is about 600-1200 m^2/m^3 and values of 30,000 m^2/m^3 respectively. The hollow fibre module is often used when the feed stream is relatively clean. In this research capillary membranes are used, because of their high packing density and the relatively dirty feed water, being wwtp effluent.

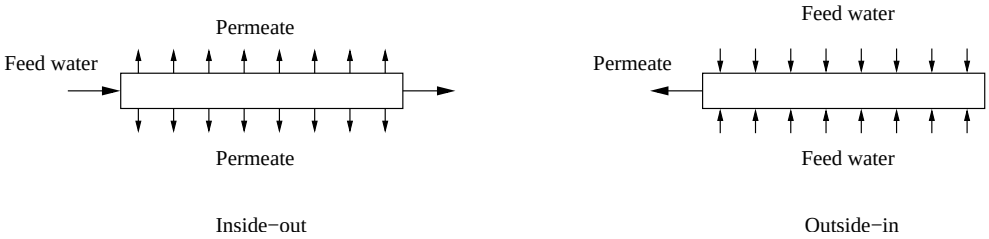

Figure 1.2: Schematic drawing of inside-out and outside-in filtration

Basically two modes of operation exists: dead-end and cross-flow filtration, as illustrated in figure 1.3. In dead-end filtration all feed water is filtered through the membrane which results in an accumulation of retained components at the membrane surface. In contrast, when cross-flow filtration is applied a part of the feed water flows along the membrane surface, so that the accumulation of retained components is limited. The advantages of both operation modes are combined in the hybrid dead-end/ cross-flow system, Mulder (1996), or semi dead-end system, Doyen (2003), in which the filtration is alternated by hydraulic flushes, mostly back flushes (1.3.2). Due to the relatively low energy costs of the semi dead-end operation mode, it becomes an attractive filtration system of wwtp effluent.

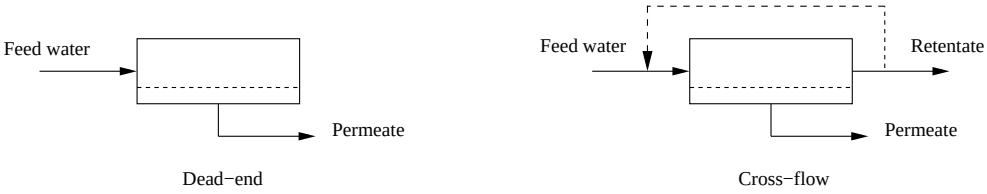

Figure 1.3: Schematic drawing of dead-end and cross-flow filtration

1.3.2 Process parameters

Transport in membranes can be described by the flux, trans membrane pressure (TMP) and the permeability according to Darcy's law. The flux through the membrane, J, is the flow per membrane surface area and is directly proportional to the applied pressure, ΔP:

$$J = L_p \cdot \Delta P \tag{1.1}$$

The permeability, L_p, contains membrane structural factors and the viscosity of the feed water. Furthermore the build up of retained components at the membrane surface is also included in this factor. The permeability is often described as:

$$L_p = \frac{1}{\eta \cdot R} \tag{1.2}$$

in which η is the dynamic viscosity of the feed water and R is the total resistance, formed by the membrane resistance R_m and the filtration resistance R_f, depending on the feed water properties:

$$R = R_m + R_f \tag{1.3}$$

In figure 1.4 the relation between flux and applied pressure is illustrated. When constant TMP is applied by ultrafiltration of wwtp effluent, the flux decreases over time as a result of increase in filtration resistance. The flux decline is caused by concentration polarisation and fouling, as illustrated in figure 1.5. During filtration retained components accumulate at the membrane surface. Concentration polarisation is described as the resulting concentration build-up, which generate a diffusive back flow to the bulk of the feed solution. According to Song and Elimelech (1995) the accumulation

of solutes includes colloids and particles, and concentration polarisation is inherent of all membrane processes. The concentration polarisation phenomena occurs fast and is a reversible process. In addition fouling occurs, which is defined as deposition of solutes inside the pores of the membrane or at the membrane surface. The fouling phenomenon takes place on a longer time scale and can be either reversible or irreversible.

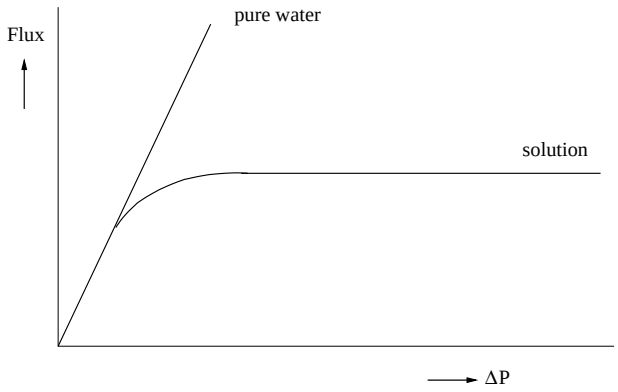

Figure 1.4: Flux as a function of the applied pressure for pure water and a solution, Mulder (1996)

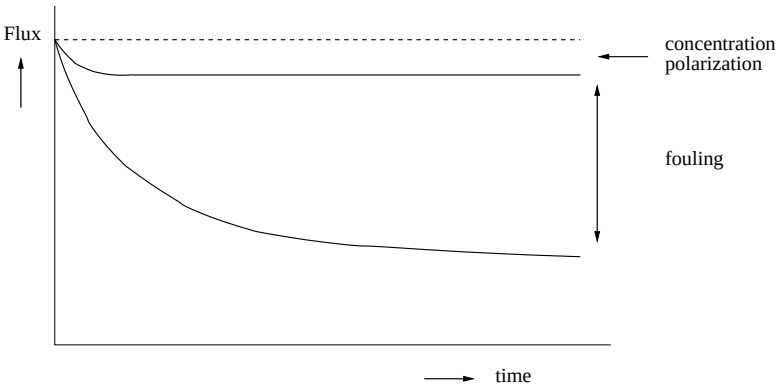

Figure 1.5: Schematic drawing of concentration polarisation and fouling, Mulder (1996)

In order to maintain a stable flux, the membranes should be cleaned periodically. Cleaning can be performed either hydraulically, mechanically, chemically or by electrical cleaning. Mechanical cleaning can only be applied in tubular systems using sponge balls. Electrical cleaning has not been applied in water treatment applications and will therefore not be discussed further. As hydraulic cleaning methods water and air flushes or a combination of both can be applied. Depending on the flow direction two

types of flushes are distinguished, as illustrated in figure 1.6:

- Forward Flush, FF,
  a complete cross-flow at high flow rates;

- Back Flush, BF,
  the flow is changed to the opposite direction, which means that permeate is flowing from the permeate side to the feed side of the membrane and discharged as retentate.

The forward flush can be improved by addition of air, which forms a flow pattern of water and air bubbles. This technique is patented as the AirFlush® and is investigated by Verberk et al. (2002). The period between two hydraulic cleanings is usually called a filtration period.

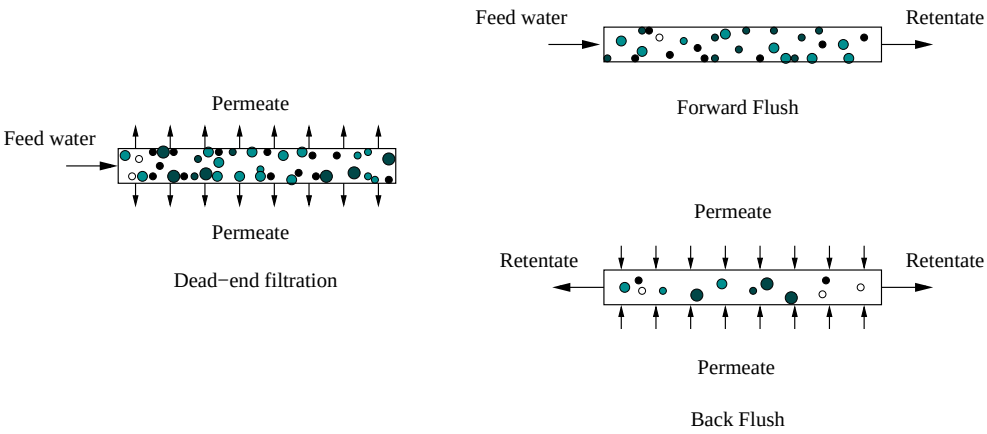

Figure 1.6: Schematic drawing of back flush and forward flush

If the average flux declines further, in spite of frequently applied hydraulic flushes, the only way to recover the flux to initial values is to clean the membranes chemically. Therefore the cleaning agent can be introduced to the membrane by a forward or back flush. Then the membranes are soaked for a certain period of time and finally the membranes are flushed with permeate, tap water or ultra pure water. As cleaning agents a broad range of chemicals can be used depending on the type of fouling.

In figure 1.7 the process parameters are summarised by giving a typical example of filtration curves.

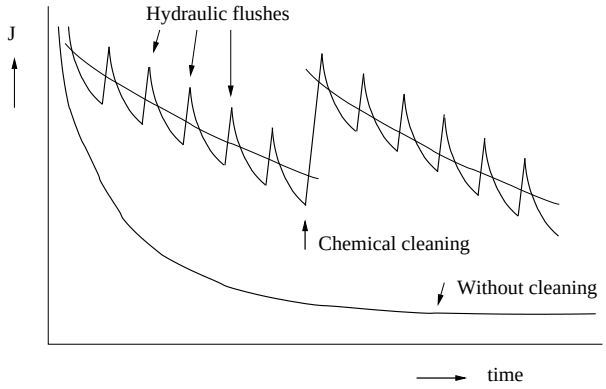

Figure 1.7: Example of the filtration process at constant TMP

1.3.3 Filtration curves and membrane fouling

Analysing the above described filtration curves two filtration phenomena can be distinguished: the filterability and the reversibility. In general, the increase of filtration resistance as a function of filtration time within a filtration period is described as the filterability, as illustrated in figure 1.8. If the increase in filtration resistance is rather slow (dotted line), than a good filterability is indicated.

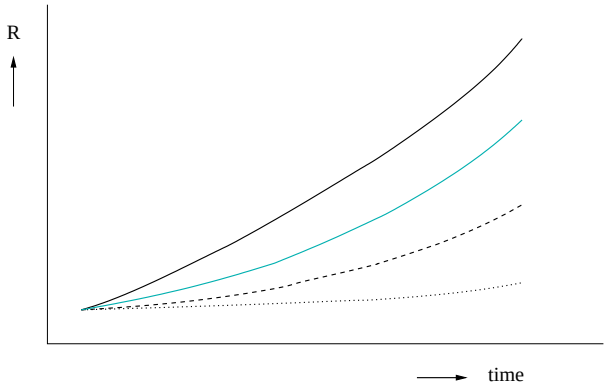

Figure 1.8: Typical filtration curves, illustrating filterability

In general, the extent within which the filtration resistance after applying a hydraulic cleaning is returned to the start value is described by the reversibility. In figure 1.9 the reversibility is illustrated. If the filtration resistance after hydraulic cleaning is equal to the filtration resistance at the start of the previous filtration period, than the fouling is considered to be complete reversible.

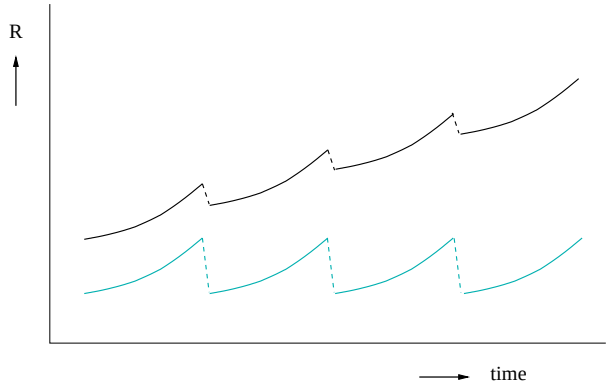

Figure 1.9: Typical filtration curves, illustrating reversibility

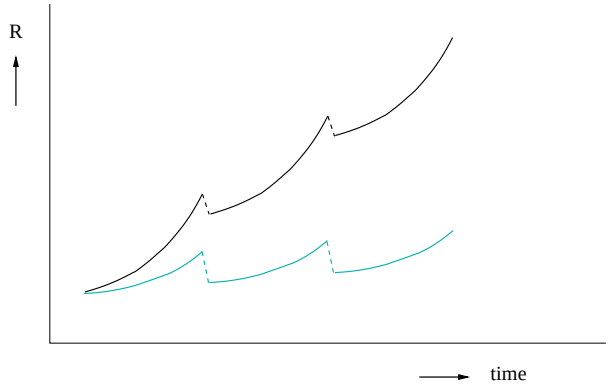

Figure 1.10: Related filterability and reversibility

According to Roorda (2004) in ultrafiltration of wwtp effluent filterability and reversibility are strongly related. A good filterability goes often hand in hand with a good reversibility, as illustrated in figure 1.10 bottom line. The increase in filtration resistance in time is caused by membrane fouling and is a consequence of the membrane separation process. Fouling mechanisms affect both filterability and reversibility and is therefore subject of many studies.

Membrane fouling in ultrafiltration of wwtp effluent is mainly caused by the water constituents. In this sense wwtp effluent differs from surface water since wwtp effluent contains compared to surface water relatively high concentrations of organic components. In addition these components strongly vary, due to influences of the weather, the efficiency of the biological treatment and changes in influent flow during day and night. In general, the membrane fouling can be classified by their nature, Flemming (1995): inorganic or mineral, organic, particles and biofouling. The interaction between the different types of fouling is complex and hardly investigated, Flemming

(1995) and Baker and Dudley (1998). It is of great importance to know which components contribute to membrane fouling in order to understand membrane fouling mechanisms. In ultrafiltration of wwtp effluent it is still unknown which components contribute mostly to membrane fouling.

1.4 Background, aim and outline of this thesis

The research described in this thesis was performed in the frame of the project "membrane filtration of effluent". The project is a cooperation between Witteveen+Bos, Rossmark Water Treatment and Delft University of Technology and is financially supported by the Dutch Ministry of Economic Affairs, Senter BTS 99112, Kramer et al. (1999). The overall objective of the project is to develop filtration techniques for the large scale distribution of reclaimed water, based on biologically treated effluent. The project aims among others, to get more insight into the interaction between wwtp effluent and the ultrafiltration membranes in order to improve the design at lower costs of ultrafiltration installations for wwtp effluent reuse options. Within this project dead-end ultrafiltration of wwtp effluent was a topic of a research project leading to two dissertations. The 1^{st} dissertation "Filtration characteristics in dead-end ultrafiltration of wwtp-effluent", published by Roorda (2004) deals with the determination of filtration characteristics of wwtp effluent in dead-end ultrafiltration. One of the main outcomes of his work was the development of the parameter Specific Ultrafiltration Resistance (SUR) based on the model of cake filtration. The 2^{nd} dissertation is this thesis, concerning the physical and chemical interactions of membrane fouling. The work of Roorda was performed partly in parallel and is closely connected to the research described in this thesis as schematic presented in figure 1.11.

An important part of the project is formed by pilot investigations. By this the possibilities of wastewater reclamation and reuse are investigated at different wwtp locations in the Netherlands. These studies include the use of wwtp effluent reclaimed by floc filtration and membrane filtration as industrial water and urban water for golf course irrigation. With this an integrated approach is chosen in which water boards and wastewater boards were involved. Results were published in Van der Graaf et al. (1999), Van der Graaf (2001b), Ruiters (1999) Maas (2003) and Te Poele et al. (2004). As an example of where pilot research can lead to, the involved authorities of the pilot investigations at wwtp Tilburg-Noord decided to proceed into a full-scale installation with a capacity of approximately 100 m^3/h. More details about the pilot investigations related to this thesis are described in Appendix A. In addition, more fundamental research was performed on the filtration and membrane fouling characteristics in dead-end ultrafiltration.

1.4.1 Aim of this thesis

The research described in this thesis is concerned with the physical and chemical mechanisms of membrane fouling during dead-end ultrafiltration of wwtp effluent to

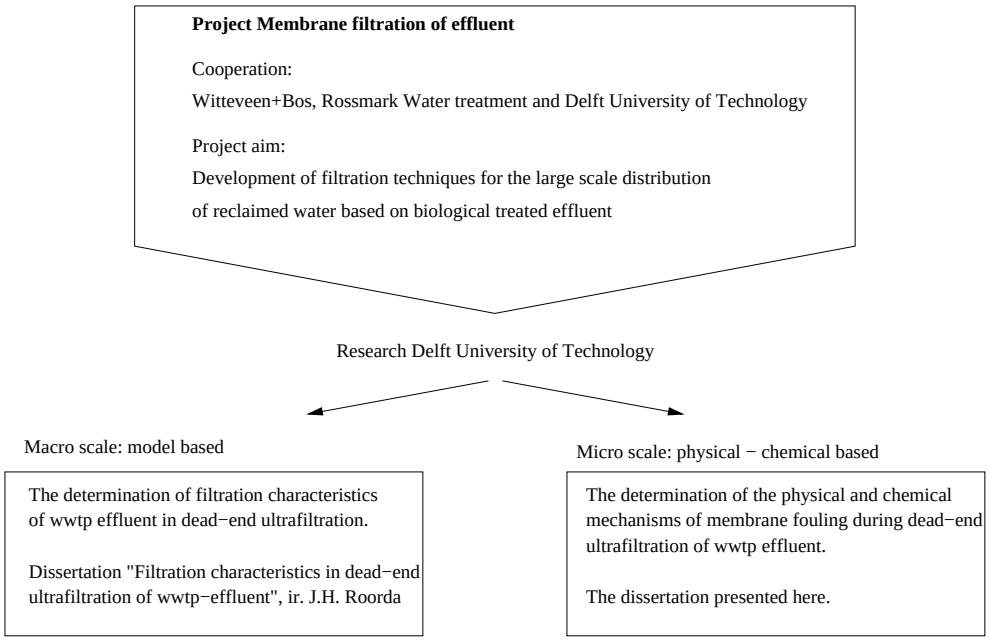

Figure 1.11: Project scheme

optimise process conditions, pre-treatment of wwtp effluent and membrane cleaning. To gain insight into this, the following aspects were investigated:

- Identification of membrane foulants in ultrafiltration of wwtp effluent. The wwtp effluent is characterised by fractionation and conditioning with pH and temperature changes in order to evaluate the physical and chemical properties of these foulants. A photometric measurement method is further developed in order to analyse polysaccharides and proteins as potential membrane foulants in wwtp effluent.

- The influence of different conditioning and pre-treatment methods on the filtration properties are investigated using a laboratory test set-up and a pilot scale installation.

- Analytical data of the foulants are compared with the actual filtration properties as filterability and reversibility.

- The use of different cleaning agents and methods in laboratory and pilot filtration tests to provide details of the membrane foulants in wwtp effluent and development of new membrane cleaning strategies.

1.4.2 Outline

In chapter 2 the filtration properties filterability and reversibility are described including the used measurement methods. Chapter 3 gives the theoretical background of foulants in ultrafiltration of wwtp effluent and their analytical measurement methods. The relations between the filterability and foulants in ultrafiltration of wwtp effluent were determined by both laboratory and pilot scale investigations and are presented in chapter 4. In chapter 5 the results of pre-filtration and coagulation as conditioning method are presented. Furthermore the results of pH and temperature conditioning of wwtp effluent on lab scale to investigate physical properties of foulants are presented in this chapter. The results of the enzymatic, alkaline and acid cleaning methods are presented in chapter 6. Here the relation between protein fouling and reversibility is discussed. In chapter 7 the results of the various filtration and cleaning experiments are reviewed and considerations are made about the fouling mechanisms occurring in ultrafiltration of wwtp effluent. Furthermore suggestions for further research are given.

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Chapter 2

Filtration properties

In the membrane filtration process of wwtp effluent different fouling mechanisms may occur, based on the formed filtration resistance (figure 2.1). The retained components can form a cake layer (R_c) on top of the membrane surface, block the membrane pores (R_{pb}) or adsorb (R_a) at the membrane surface or in the membrane pores, depending on their chemical and physical properties. In addition, concentration polarisation and biofouling may occur in specific situations. In dead-end ultrafiltration concentration polarisation is of minor importance than fouling. By concentration polarisation the solubility product of salts can be exceeded and as a result scaling may occur by deposition of salts on the membrane surface. According to Flemming (1995) biofouling is defined as growth of micro-organisms on the membrane surface and is explained in more detail in section 3.3.3. In general, the type of the dominant fouling mechanism is highly dependant on the filtration process, i.e. MF, UF, NF or RO. Other mechanisms which can influence the filtration resistance are compaction of the membrane, compression of the cake layer and capillary blocking, which may occur during the back wash when cake flocs can block the capillary completely.

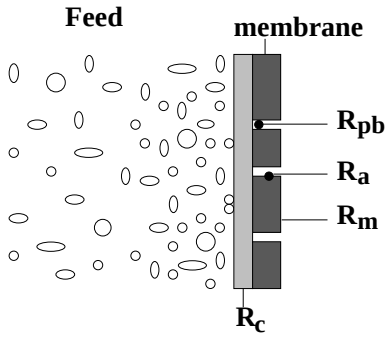

Figure 2.1: Schematic drawing of the filtration resistances, Mulder (1996)

The resistance to filtration, R, can be described by Darcy, according to Mulder (1996):

$$J \;=\; \frac{1}{A}\frac{dV}{dt} \;=\; \frac{\Delta P}{\eta \;\cdot\; R} \tag{2.1}$$

where J is the flux, V is the filtrated volume, t is the filtration time, A is the membrane surface, ΔP is the trans membrane pressure and η is the dynamic viscosity. With the resistance in series model:

$$R \;=\; R_{membrane} \;+\; R_{cake} \;+\; R_{pore\ blocking} \;+\; R_{adsorption} \tag{2.2}$$

The dynamic viscosity is depending on temperature, T, according to the empiric relation which is derived for water solutions by Janssen and Warmoeskerken (1997):

$$\eta \;=\; 10^{-3} \;\cdot\; exp^{0.580 \;-\; 2.520\ \theta \;+\; 0.909\ \theta^2 \;-\; 0.264\ \theta^3} \tag{2.3}$$

$$in\ which: \quad \theta \;=\; 3.6610 \;\cdot\; \frac{T}{273.1 \;+\; T} \qquad with\ T\ in\ ^\circ C \tag{2.4}$$

Over the past years it became evident that fouling is a complex phenomenon determined by the interaction of many of the previously described factors. In any case, a major impact on fouling can be expected by effective interactions between feed components and the membrane. In this sense, fouling is feed specific as it depends on the composition of the feed, but at the same time membrane system specific as the membrane material as well as module geometry and operation mode influence the possible type and extent of fouling. In analysing filtration data two parameters are very useful in characterisation of membrane fouling, which are the filterability and reversibility.

2.1 Filterability

The filterability as described in section 1.3.3 can be interpret by the specific contribution of constituents of wwtp effluent to the filtration resistance during filtration within a filtration period. By this the filterability only considers (actual) influences imposed by membrane material and feed characteristics like chemical composition, solids content, rheological influences and others. There have been attempts to establish tests and indices to describe the filterability of feed suspensions and solutions, Rosenberger et al. (2005):

- Time To Filter (TTF), Modified Fouling Index (MFI), Specific Resistance to Filtration (SRF) and Specific Ultrafiltration Resistance (SUR) are used to describe filterability. Capillary Suction Time (CST) is also used to describe filterability, although it derives from sludge dewaterability tests. TTF, MFI, SRF, and SUR are all based on the theory of cake filtration. These filtration tests are usually performed in dead-end in a small filtration set-up, Christensen and Dick (1985), Roorda (2004).
- On-line measurements of flux and TMP during continuous filtration can be used to calculate the fouling rate (slope of resistance over time). This can be done either in batch experiments (e.g. with side-stream modules) or in-situ.

2.1.1 Filtration indices

When cake filtration is the dominant filtration mechanism, the filtration resistance can be characterised by lab scale filtration tests. Here, the modified fouling index, which is often used as standard test and the SUR, which is especially developed for ultrafiltration membranes, are discussed.

Modified Fouling Index

According to the cake filtration model the following relation between filtration time, t, and filtrated volume, V, can be derived, assuming constant pressure Mulder (1996):

$$\frac{t}{V} = \frac{\eta \cdot R_m}{\Delta P \cdot A} + MFI \cdot V \tag{2.5}$$

where MFI is the Modified Fouling Index. This equation predicts a linear relationship between t/V and V during cake filtration. A high value of MFI indicates rapid fouling of the membrane. Fouling behaviour of different feed solutions can be compared by use of MFI. However, a microfiltration membrane (pore size of 0.45 μm) is used to characterise filtration behaviour and predict fouling in UF, NF and RO systems, Mulder (1996). Furthermore the applied pressure is 2 bar which is about 4 times more than usual in ultrafiltration applications.

The MFI is further developed by Boerlage et al. (2004) to the MFI-UF to measure and predict the particulate fouling potential for different feed waters in membrane filtration installations.

Specific Ultrafiltration Resistance

The Specific Ultrafiltration Resistance (SUR) is developed to measure the filterability of wwtp effluent and is measured over an ultrafiltration membrane at constant temperature (∼20 °C) and trans membrane pressure (TMP) of 0.5 bar, which is more or less simular as applied in ultrafiltration installations, Roorda (2004). The SUR is defined as the cake filtration resistance per unit of filtered feed water per membrane surface. A high SUR value indicates rapid membrane fouling, i.e. poor filterability. Under the conditions of constant TMP and particle fouling as the only additional filtration mechanism, the SUR can be derived by the cake filtration resistance, R_c:

$$R_c = \alpha_{av} \cdot c_v \cdot \frac{V}{A} \tag{2.6}$$

where α_{av} is the average specific cake resistance and c_v is the solids concentration in the feed water. Combination of equation 2.1, 2.2 and 2.6, and integration over t_0=0, t_t=t, V_0=0 en V_v=V gives:

$$\frac{t}{V} = \frac{\eta \cdot R_m}{\Delta P \cdot A} + \frac{\eta \cdot \alpha_{av} \cdot c_v}{2 \cdot \Delta P \cdot A^2} \cdot V \tag{2.7}$$

and

$$SUR = \alpha_{av} \cdot c_v = \frac{d(\frac{t}{V})}{d(V)} \cdot \frac{2 \cdot \Delta P \cdot A^2}{\eta} \qquad \left(\frac{1}{m^2}\right) \tag{2.8}$$

However there are some drawbacks since the MFI and SUR are based on cake filtration whereas also other factors contribute to membrane fouling. Furthermore it is assumed that cake resistance is independent of the pressure, Mulder (1996), which is not always the case. Nevertheless, these methods are useful to get a fast indication of the filterability.

2.1.2 On-line measurements

In full scale or pilot plant studies the filterability can be measured as fouling rate (dR/dt) which is the increase in filtration resistance over time, Rosenberger et al. (2005), and can be derived from the on-line measurements of flux, TMP and temperature:

$$\frac{dR}{dt} \tag{2.9}$$

with

$$R = \frac{TMP}{\eta(T) \cdot J} \tag{2.10}$$

Rabie et al. (2001) introduced the "Normalised Fouling Rate" (NFR), which is a parameter to analyse data from pilot and full scale installations. Nevertheless, in assessing filterability data the NFR parameter is found limited since only cake filtration is considered as occurring fouling mechanism under the condition that constant TMP is applied and has therefore no added value compared to the previously described fouling rate.

2.2 Reversibility

In general, the reversibility as described in section 1.3.3 can be indicated by two methods, which are illustrated in figure 2.2:

- ΔR/Δt, which is the increase of filtration resistance over time after a series of filtration periods including hydraulic cleaning and is measured by comparing the filtration resistance at the start of the first filtration period to the filtration resistance at the start of a filtration period after a serie(s) of filtration periods:

$$\frac{\Delta R}{\Delta t} = \frac{R_b - R_a}{t_b - t_a} \tag{2.11}$$

- Comparing the measurements of the clean water flux (CWF) at the start of the filtration and at the end of a filtration period after hydraulic cleaning. The clean water flux (CWF) is the flux of pure water expressed as L/m^2·h·bar and usually normalised to 20 °C in order to compare obtained results. By this the actual filtration resistance can be determined.

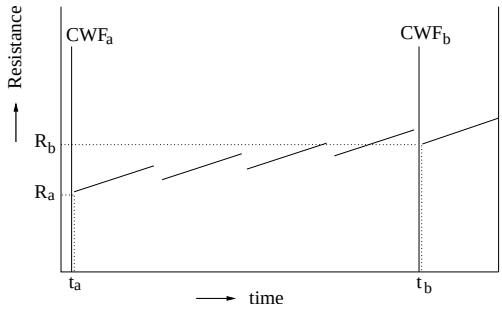

Figure 2.2: Determination of the reversibility by $\Delta R/\Delta t$ or CWF measurements

If the filtration resistance after hydraulic cleaning is equal to the filtration resistance at the start of a previous filtration period, then the filtration process is considered completely reversible. In case irreversible fouling occurred, the interactions between membrane material and feed constituents resulted in strong chemical/ physical bounds which are often related to adsorption phenomena.

Roorda and Van der Graaf (2000) reported the reversibility of a fouling layer as the relative increase of filtration resistance to the filtration resistance after applying a cleaning procedure, see figure 2.3. Here the reversibility is also calculated by the ratio of CWF measurements. However, the filtration period chosen by Roorda and Van der Graaf (2000) is rather long, a few hours, compared to about 30 minutes as applied in practise, Roorda (2004). Longer filtration periods can cause additional fouling mechanisms, which are related to changes in feed water quality and to more important changes in cake layer formation. Therfore this method is considered of limited use.

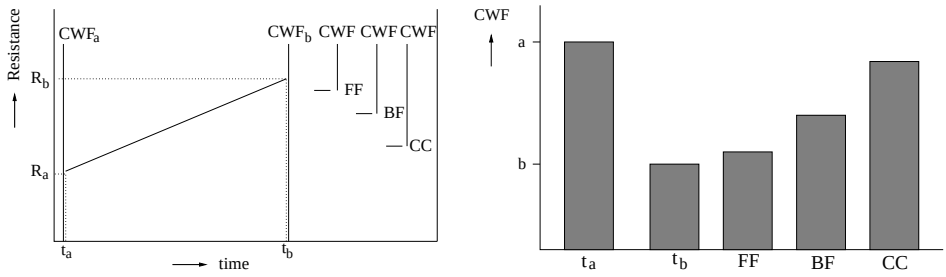

Figure 2.3: Example of reversibility calculations of Roorda and Van der Graaf (2000); filtration resistance as function of filtration time and applied Forward Flush (FF), Back Flush (BF), Chemical Cleaning (CC) (left); related CWF measurements (right)

2.3 Measuring filtration properties on lab scale

2.3.1 SUR measurement

Filtration curves were measured on a lab-scale test set-up, schematically shown in figure 2.4, providing a membrane area of about $10{\cdot}10^{-4}$ m^2. The membranes used for all experiments were capillary ultrafiltration membranes of X-Flow with an internal diameter of 0.8 mm, a MWCO of 150-200 kDa and prepared of PES(PVP). A small membrane module consisted of three membranes.

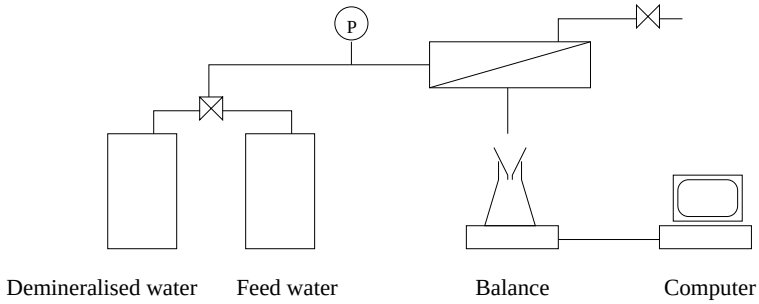

Figure 2.4: Schematic drawing of the laboratory test set-up

The membrane filtration process was operated in dead-end and was carried out at constant Trans Membrane Pressure (TMP) of 0.5 bar. The filtration time was set to 30 minutes. Two pressure vessels, with a volume of 10 litres each, were placed in parallel, in order to change the feed to demineralised water or to feed water, which was in this research wwtp effluent. A manometer indicated the pressure prior to the feed water enters the membrane. On the permeate side of the membrane, the pressure was equal to the atmospheric pressure. The pressure difference over the membrane was indicated as the TMP. The permeate is collected in an Erlenmeyer on a balance. The data of the balance and manometer (connected to a computer) were recorded continuously in time. The temperature of the feed is measured regularly.

The obtained data of filtrated volume (V), calculated from the mass (m) and the density of water (ρ), and filtration time (t) were plotted as t/V against V as shown in figure 2.5. The tan γ was used to to calculate the SUR value with use of the membrane surface area (A), TMP and feed water temperature, which was used to calculate the dynamic viscosity (η).

The accuracy of the SUR measurement is determined for demineralised water and effluent of wwtp Utrecht in three tests, resulting in 0.39 $\pm$ 0.10 $\cdot 10^{12}$ m^{-2} and 8.82 $\pm$ 1.29 $\cdot 10^{12}$ m^{-2} respectively.

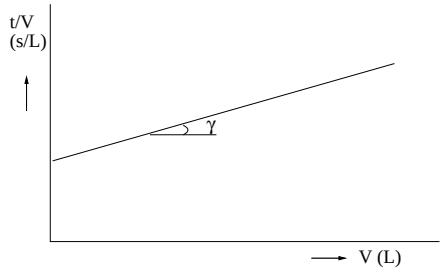

Figure 2.5: Relation between the ratio of filtration time (t) to filtrated volume (V) and filtrated volume (V) obtained during the SUR measurement

2.3.2 Measuring cleaning efficiency on lab scale

On laboratory scale the cleaning efficiency was evaluated by comparing the CWF after cleaning to the initial CWF at the start of each experiment. The CWF was measured with demineralised water at a constant TMP of 0.5 bar and approximately 20 °C until a stable flux was observed. An example of CWF measurements on laboratory scale is given in figure 2.6.

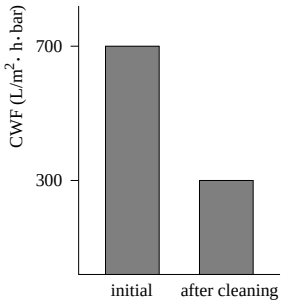

Figure 2.6: Example of CWF measurements before and after cleaning on laboratory scale to evaluate the cleaning efficiency

The cleaning efficiency was then calculated as:

$$cleaning\ \ efficiency\ =\ \frac{CWF_{after\ \ cleaning}}{CWF_{initial}}\ \cdot\ 100\ \% \tag{2.12}$$

2.4 Measuring filtration properties on pilot scale

In contrast to the hydraulic limitation of lab scale measurements, filtration properties are measured most realistically on pilot scale. On pilot scale the hydraulic conditions of a full scale plant is simulated, since it consists of one membrane module as used in full scale plants. Research was carried out at different wwtp locations in the Netherlands, as described in more detail in Appendix A.

2.4.1 Pilot scale ultrafiltration installation

The pilot ultrafiltration installation was especially designed to perform research at different wwtp's using wwtp effluent as main feed water. The ultrafiltration installation, as pictured in figure 2.7, contained X-flow membranes with a capillary diameter of 0.8 mm, a pore size of 0.03 μm (MWCO of 150-200 kDa) and prepared of PES(PVP). The installation capacity is 10 m^3/h and was equipped with two 8-inch modules type S-225 FSFC PVC, each with a length of 1.5 meter, providing a membrane area of 70 m^2. The module and membrane specifications are given in Appendix C. A detailed flow chart of the pilot installation is given in Appendix B.

Figure 2.7: Photograph of the pilot ultrafiltration installation

The installation was operated in dead-end at constant flux, which varied between 28.5 and 100 L/m^2·h, and with a filtration period between 10 and 60 minutes, followed by a back flush. Chemical cleaning strongly varied in frequency, time and cleaning agents.

2.4.2 Feed water

The filtration properties of wwtp effluent could be influenced by pre-treatment. To this purpose dual media filtration, microfiltration and coagulation were investigated in this research. A schematic overview of all tested configurations is presented in figure 2.8. The used configuration depended on the type of experiments performed.

As feed water effluents of different wwtp's in the Netherlands were used. The wwtp effluent was first filtered over a curved sieve with a mash size of 0.45 mm in order to protect the installations from non-separated organic and inorganic material from the secondary clarification. In figure 2.9 a picture of the used curved sieve is given.

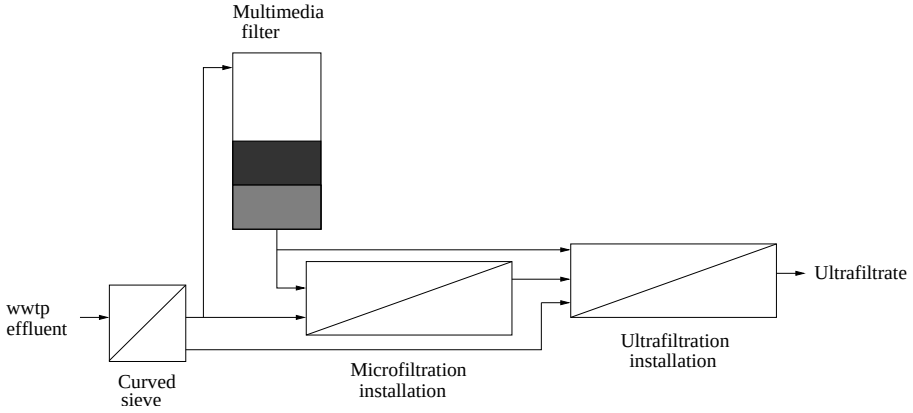

Figure 2.8: Overview of all tested configurations of the pilot installations

Figure 2.9: Photograph of the curved sieve, which is used in the pilot investigations

Multimedia filtration

In figure 2.10 a photo of the used multimedia filter is shown. The multimedia filter contained one layer of (0.8 m) anthracite and one layer of (0.4 m) sand and was operated with a fixed water level above the filter bed of 1.73 meter. In Appendix B a flow chart of the multimedia is shown. Coagulant could be dosed in-line to the feed water pipe and was mixed with the feed water in a static mixer before entering the filter column. Flocculation took place above and in the filter bed. The filtration rate, the filter run time and the coagulant concentration varied during the pilot investigations. The cleaning sequence was a combination of water and air flushing at high and low rates for the duration of 10 minutes in total.

Figure 2.10: Photograph of the multimedia filter, which is used in the pilot investigations

Microfiltration

The microfiltration installation used here, was a Memcor Continuously Microfiltration Installation (CMF), see figure 2.11. The installation contained 3 modules providing a total membrane surface area of 45 m^2. The pore size of the membranes was 0.2 μm. The installation was operated at constant flux, which varied between 50 and 105 $L/m^2 \cdot h$. It had a filtration period of 15 minutes and was followed by a back wash. Chemical cleaning was performed once or twice a week depending on the filtration resistance. Chemical cleaning was carried out by a Cleaning in Place procedure with Memclean C (a Memcor product) at a pH of 12. More detailed information of the Memcor microfiltration installation is given in Appendix B.

Coagulation

Coagulant could be dosed either directly in-line in front of the feed pump of the ultrafiltration installation or via in-line coagulation in a tube flocculator, see figure 2.12, which is placed in front of the ultrafiltration installation.

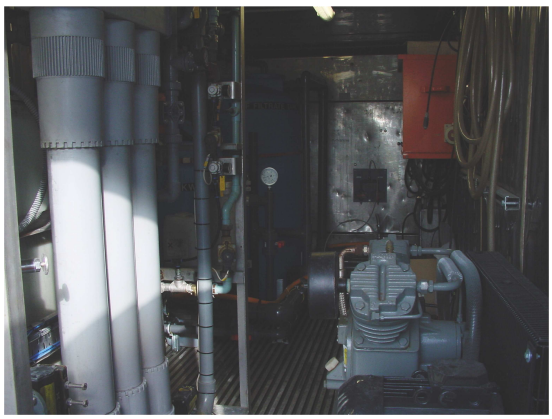

Figure 2.11: Photograph of the Memcor Continuously Microfiltration Installation (CMF), which is used in some of the pilot investigations

Figure 2.12: Photograph of the tube flocculator, which is used in some of the pilot investigations

2.4.3 Measuring filterability

The filterability is expressed as fouling rate (dR/dt) within a filtration period, which can be calculated by the obtained data of the pilot ultrafiltration installation. As an example typical filtration data are presented in figure 2.13. In the left graph the obtained filtration data of an ultrafiltration installation operating at constant flux are shown. In the right graph the calculated resistance is given as a function of time. The resistance increase in time can be calculated by tan γ as dR/dt.

By using this method, filterability of different feed waters of different wwtp locations can be easily compared. The filterability, dR/dt, is expressed in 1/m per hour.

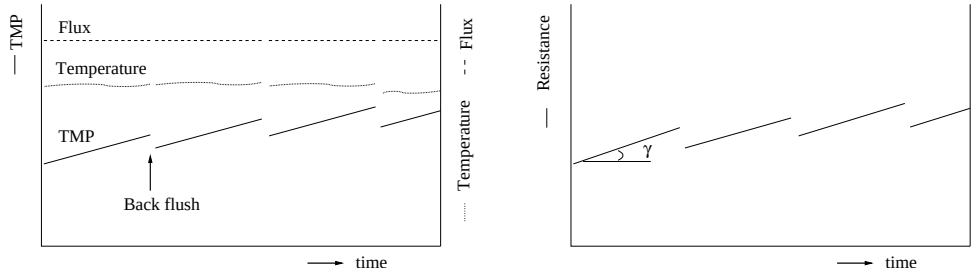

Figure 2.13: Example of filtration data of an ultrafiltration installation; flux, TMP and temperature as function of filtration time (left); calculated filtration resistance as function of filtration time (right)

Besides the influence of the process conditions and the feed water constituents on the filtration resistance the history of the filtration process should be considered as well. Measuring the filterability based on on-line data starts rather arbitrary at the beginning of a filtration period. In fact the remaining membrane fouling after (hydraulic) cleaning (back flush) at the beginning of a filtration period interacts with the feed water constituents and as a consequence is of influence during the resistance increase in this filtration period.

The membrane resistance of the used membrane type is approximately $0.8{\cdot}10^{12}$ 1/m (CWF of 450 L/m^2·h·bar and feed water temperature of 20 °C). At the start of the filtration the resistance is equal to the membrane resistance of a new membrane. Thereafter the start condition of following filtration periods is depending on the cleaning efficiency of the performed cleaning. For the membrane type used in this thesis the maximum TMP is 1 bar. At the applied process conditions, being constant flux and feed water temperature, the maximum theoretical filtration resistance, $R_{max,th}$ is calculated by equation 2.13.

$$R_{max,th} = \frac{\Delta P_{max}}{J \cdot \eta_{(T)}} \tag{2.13}$$

If the applied flux is increased, the $R_{max,th}$ decreases. Since the dynamic viscosity is related to the temperature (see section 2.1) $R_{max,th}$ will decrease with decreasing feed water temperature due to an increase of the dynamic viscosity. The $R_{max,th}$ is a useful parameter in evaluating the process performance during ultrafiltration. By comparing the actual filtration resistance with the $R_{max,th}$ an indication is given of the range in which the system can be operated.

The actual filtration resistance can also be determined by measuring the CWF. The overall fouling rate then is determined by measuring the CWF frequently.

2.4.4 Measuring reversibility

In this thesis the reversibility is determined by ΔR/Δt, which is the increase of filtration resistance over time after a series of filtration periods including back flushes and is measured by comparing the filtration resistance at the start of the first filtration period to the filtration resistance at the start of a filtration period after a serie(s) of filtration periods and is illustrated in figure 2.14:

$$\frac{\Delta R}{\Delta t} = \frac{R_b - R_a}{t_b - t_a} \tag{2.14}$$

A high value for ΔR/Δt indicates a low reversibility, whereas a high reversibility is indicated by a low value for ΔR/Δt.

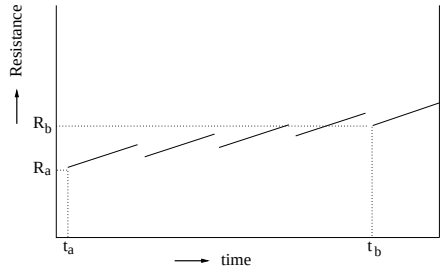

Figure 2.14: Determination of the reversibility by ΔR/Δt

2.4.5 Measuring cleaning efficiency on pilot scale

On pilot scale the effect of the cleaning was determined by measuring the CWF before and after cleaning. The cleaning efficiency was evaluated by comparing the CWF after cleaning to the initial CWF of a new membrane module:

$$cleaning\ \ efficiency = \frac{CWF_{after\ \ cleaning}}{CWF_{initial}} \cdot 100\ \% \tag{2.15}$$

Here, the CWF is measured either with ultrafiltrate or (breaker tank) tap water at the actual water temperature and at various constant fluxes, applying flow rates of: 2.8, 3.3, 3.8, 4.3, 4.8 and 5.8 m^3/h, until stable TMP is observed. Then the CWF is calculated as mean value and normalised to 20 °C. The accuracy of this CWF measurement is determined in 5 tests, resulting in a standard deviation of 2 L/m^2·h·bar.

If the CWF after cleaning is equal to the initial CWF, then the CWF is completely recovered by this cleaning.

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Chapter 3

Foulants in ultrafiltration of wwtp effluent

3.1 Characterisation of wastewater effluent

The constituents in wastewater treatment plant effluent are the components remaining in the effluent after mechanical, biological and often chemical treatment. This means that most of the constituents that are settable or biodegradable, have been removed in the previous processes. An overview of the different fractions, constituents and sizes of wastewater effluent is presented in figure 3.1. In this overview separation techniques and special membrane filtration techniques are included as well.

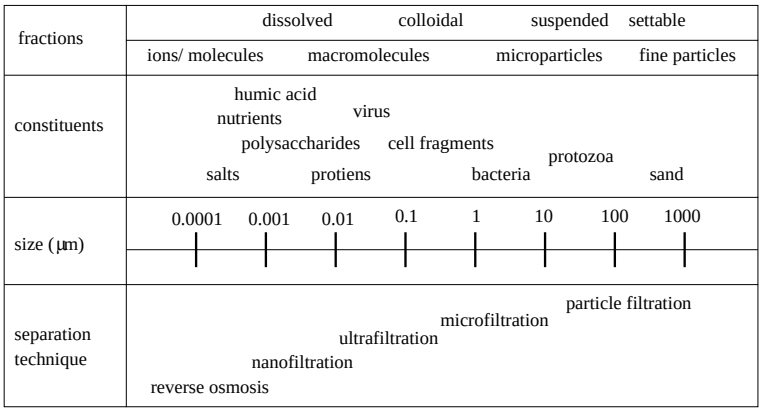

Figure 3.1: Characteristics of wastewater constituents

Wastewater is classified in different fractions by Van Nieuwenhuijzen (2002) into dissolved (< 0.1 μm), colloidal (0.45-1.2 μm), suspended (5-63 μm) and settable ($>$ 63 μm) fractions. In addition to the dissolved and colloidal fraction he defined a supra-dissolved fraction (0.1-0.45 μm) in between. Similar to this the supra-colloidal

fraction (1.2-5 μm) is defined between the colloidal and suspended fraction. However, different size ranges for the colloidal fraction have been reported in literature. Azema et al. (2002) and Levine et al. (1991) defined the colloidal fraction between 0.001 and 1 μm, whereas Levine et al. (1985) previously reported the size range of the colloidal fraction between 0.08 and 1.0 μm and Metcalf and Eddy (2003) considered the colloidal fraction between 0.01 and 1.0 μm. In table 3.1 the fractions distinguished in this thesis are given.

Table 3.1: Fractions distinguished in this thesis

Size (μm)	Fraction
> 0.45	particles (suspended and settable material)
0.1 - 0.45	colloids
< 0.10	dissolved material (macro-molecules)

According to Metcalf and Eddy (2003) wastewater can be characterised by:

- inorganic nonmetallic constituents,
  like chlorides, nitrogen, phosphorus, sulfur, various gases and odours;
- metallic constituents,
  such as cadmium, chromium, copper, iron, lead, manganese, mercury, nickel and zinc;
- aggregate organic constituents,
  comprising a number of organic constituents with similar characteristics, which are often measured by parameters as biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC);
- individual organic compounds,
  includes priority pollutants, volatile organic compounds, disinfection byproducts, pesticide and agriculture organics.

However, there is some overlap between the different groups. Nitrogen and phosphorous are also found in organic bound forms. Moreover organic nitrogen is a complex mixture of compounds including amino acids, amino sugars and proteins, whereas proteins and polysaccharides (carbohydrates) are also accounted as organic constituents. In fact, according to Metcalf and Eddy (2003), organic matter in wastewater typically consists of 40-60% proteins, 25-50% carbohydrates and 8-12% oils and fats. Levine et al. (1985) reported in more detail that the major group of organic macro-molecules in wastewater consists of proteins, polysaccharides, lipids and nucleic acids. More and more synthetic organic molecules are found in wastewater contributing to a few percent of the organic matter.

In activated sludge processes micro-organisms are used to oxidise or convert dissolved and particulate carbonaceous organic matter into end products and additional

biomass, Metcalf and Eddy (2003). During biological treatment particle size distributions in wastewater change as a result of new cell synthesis, flocculation, adsorption, enzymatic breakdown of macro-molecules and biochemical oxidation, Levine et al. (1985). Micro-organisms and biomass mainly contain cell components. The cytoplasm of cell components consists of DNA, RNA, nutrients, enzymes and small organic molecules. Cell enzymes determine the metabolic capability of micro-organisms in wastewater treatment and catalyse biological reactions necessary for cell functions. Protein is an essential component of cellular enzymes and is complicated with a co-factor such as a metal ion. Cells also produce enzymes for hydrolysis of particles and large molecules outside the cell wall, the so called extracellular enzymes, Metcalf and Eddy (2003). According to Levine et al. (1985) low molecular mass compounds, such as humic acids, are stable under normal treatment conditions because of kinetic limitations.

The biomass is usually removed from the biologically treated water by gravity in a secondary clarifier. By this more than 99 % of the suspended solids can be removed. The ratio of volatile suspended solids (VSS) and total suspended solids (TSS) in effluent found in literature is 0.85 by Metcalf and Eddy (2003). This implies that 85 % of the total suspended solids in wastewater effluent is organic matter. However, the nature of the BOD and suspended solids (SS) that remains after secondary treatment is quite different from that of untreated wastewater, Levine et al. (1985). The major parameters of interest that determine the effluent quality consist of organic compounds, suspended solids and nutrients, adopted from Metcalf and Eddy (2003):

- Soluble biodegradable organics
  - Organics that escaped biological treatment
  - Organics formed as intermediate products in the biological degradation of the waste
  - Cellular components as a result of cell death or lysis
- Suspended organic material
  - Biomass produced during treatment that escaped separation in the final settling tank
  - Colloidal organic solids in the wastewater plant influent that escaped treatment and separation
- Nitrogen and phosphorus
  - Contained in biomass in effluent suspended solids
  - Soluble nitrogen as NH_4-N, NO_3-N, NO_2-N and organic N
  - Soluble orthophosphates
- Non biodegradable organics
  - Those originally present in the wastewater influent
  - Byproducts of biological degradation

3.2 Fractionation of wwtp effluent

Fractionation of wastewater influent was applied by Van Nieuwenhuijzen (2002) as characterising technique. In this thesis as well as in Roorda (2004) the fractionation technique was used to investigate the influence of different fractions of wwtp effluent on the filterability of wastewater effluent.

The fractionation experiments were performed at the Laboratory of Sanitary Engineering at Delft University of Technology. The first fraction was either formed by a curved sieve with a mash size of 450 μm at the wwtp during pilot investigations or by effluent filtration over a sieve with a mash size of 400 μm. The other fractions were formed by filtrating this water over successively 0.45 μm cellulose acetate, and 0.2 μm cellulose acetate or cellulose nitrate and 0.1 μm cellulose nitrate filters of Sartorius. An overview of the applied fractionation methods is given in figure 3.2.

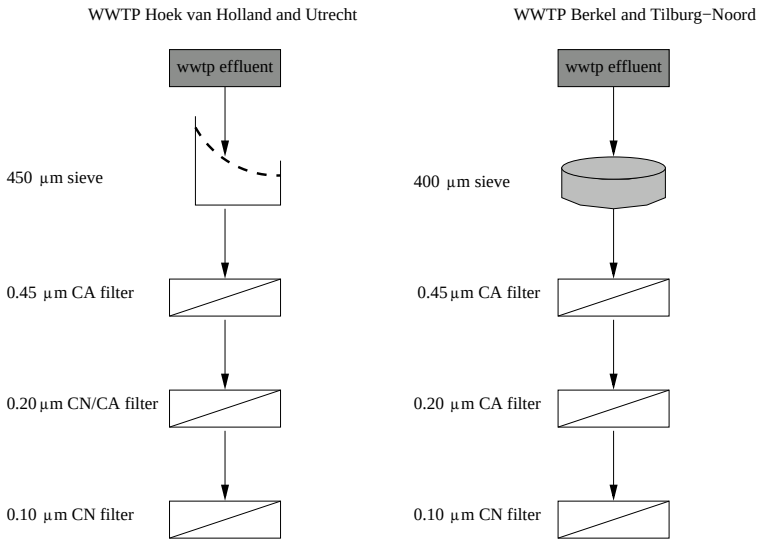

Figure 3.2: Schematic drawing of the fractionation, left as applied for effluent of wwtp Hoek van Holland and Utrecht, and right as applied for effluent of wwtp Berkel and Tilburg-Noord

3.3 Classification of membrane fouling

As explained in chapter 1 membrane fouling is a natural consequence of the membrane separation process. Membrane fouling can be classified into inorganic or mineral fouling, organic fouling, particles and biofouling, depending on the nature of the involved components, Flemming (1995). Since the major part of wwtp effluent consists of organic matter, in this thesis organic fouling is considered as major fouling occurring

in ultrafiltration of wwtp effluent. The role of organic matter in membrane filtration of wwtp effluent will be discussed in more detail in paragraph 3.4.

3.3.1 Particles

Particulate fouling is a persistent problem in all membrane filtration processes and refers to the deposition of suspended matter, colloids and micro-organisms on the membrane surface, whereas scaling mainly occurs in reverse osmosis (RO) and nanofiltration (NF) applications and refers to the deposition of hard scale on the membrane surface due to exceeding the solubility of soluble salts, Boerlage (2001).

Investigations of the fouling potential of colloidal particles in ultrafiltration of surface water and wastewater effluent are performed by several researchers. Boerlage (2001) developed the MFI-UF as a water quality test and monitor instrument to detect feed water changes over time. Roorda (2004) developed the SUR test based on the cake filtration model to measure the influence of particulate and colloidal fouling on the filterability. Pilot plant tests indicated that effluent constituents $<$ 5-10 μm mainly determined the filtration characteristics. Moreover SUR tests of fractionated wwtp effluent showed that the fraction between $<$ 0.2 and 0.1 μm predominantly determined the filtration characteristics. In addition, Thorson (1999) found that particles in the range of 0.2 - 3 μm need to be removed to alleviate the fouling problems with nanofiltration of surface water.

In ultrafiltration of filtered (Dynasand) primary effluent Bourgeous et al. (2001) found that this effluent contained large amounts of molecules with a similar or smaller size than the membrane pore size (0.01 μm) which likely became attached to the inside of the pores causing large resistance to flow and leading to rapid membrane fouling. Tchobanoglous et al. (1998) suggested that smaller particles in secondary wastewater have a disproportionately higher impact on membrane performance than larger particles. However, if the particle size distribution is preferentially to the larger particle size range ($>$ 20 μm) fibre plugging should be avoided to maintain high membrane productivity.

The results of these studies revealed that particles between 0.01 and 3 μm are important in membrane fouling.

3.3.2 Inorganic or mineral fouling

In a literature review by Laîné et al. (2002) only a few studies reported on irreversible fouling due to inorganic compounds such as aluminium, silica and iron, specially under specific conditions of concentration, temperature and pH.

Elemental analysis of the cake formed during ultrafiltration of NOM raw water indicated that circa half of the material deposits were inorganic such as clays, carbonates and hydroxides. Moreover analyses form scanning electron microscopy revealed

that clay particles were found bound by a NOM based gel, Laîné et al. (2002).

From the results of experimental tests of ultrafiltration of Japanese lake water Khatib et al. (1997) observed major irreversible fouling due to the formation of silicium-rich ferric gel directly deposited on the membrane surface and an amorphous alumina-silicate gel layer at a larger distance. The ferric gel adhesion to the membrane could be related to the surface charge of the membrane.

Laîné et al. (2002) stated that precipitation of iron, manganese and carbonate has often been observed as the cause for membrane fouling, specially when an oxidant like chlorine is applied during membrane cleaning. In addition, Boom (2001) found that oxidation of soluble manganese, Mn^{2+}, to solid manganese-oxide, MnO_2, may occur when oxygen is released by for example NaOCl, which often has been used as cleaning agent. The formed manganese-oxide particles resulted in pore blocking of ultrafiltration membranes.

So far no relation has been published between mineral precipitation and filtration characteristics in ultrafiltration of wwtp effluent. However, inorganic compounds may play a role in gel layer formation and bounding with the membrane material.

3.3.3 Biofouling

According to the "classical" theory based on reverse osmosis, Flemming (1995), biofouling is described as attachment of micro-organisms at the membrane surface, where they secrete slimy substances the so called extracellular polymeric substances, EPS. Furthermore the micro-organisms are embedded within the EPS structure which forms a three-dimensional tight matrix i.e. biofilm. In ultrafiltration of wwtp effluent biofouling is expected to play a minor role, due to the performance of hydraulic and chemical cleaning regimes. In these processes a back wash with addition of chlorine is frequently applied in cleaning procedures. Therefore it is expected that biofouling maybe only occurs to a minor extent. This idea is confirmed by Laîné et al. (2002).

3.4 Organic fouling in membrane filtration

Organic components, which are formed during activated sludge treatment, are expected to be the main foulants in ultrafiltration of wwtp effluent. In the filtration of wwtp effluents, fine and macro particles are expected to play a minor role. Considering comparable experiences with surface water filtration for drinking water production, mainly colloidal and dissolved organic compounds as humic substances are expected to cause fouling while filtering a feed source with low solids content.

Looking into more detail, effluent organic matter (EfOM) is the sum of natural organic matter (NOM), synthetic organic compounds (SOC), disinfection by-products (DBP), and soluble microbial products (SMP) as schematically shown in figure 3.3. These components are supposed to contribute to membrane fouling, Drewes and Fox

(1999). Drewes and Croue (2002) investigated differences and similarities between NOM and EfOM by characterisation techniques with respect to origin, size, structure and functionality. Jarusutthirak et al. (2002a) characterised EfOM and investigated the role of different EfOM fractions in fouling of UF and NF membranes revealing that particularly polysaccharides and colloids exhibited a high fouling potential. In addition, Cho et al. (1998) characterised clean and NOM fouled NF and UF membranes and indicated polysaccharides or polysaccharide-like substances as foulants.

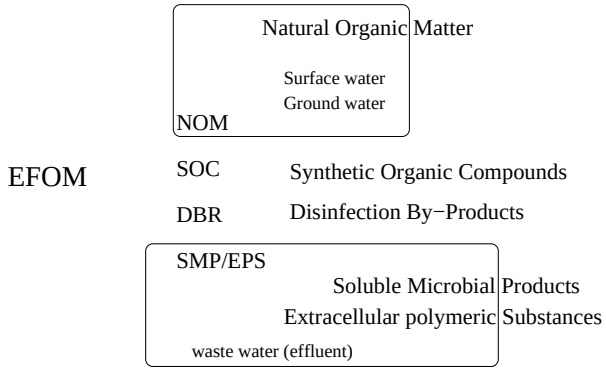

Figure 3.3: Contaminants of Effluent Organic Matter (EFOM) and main source

During filtration of wwtp effluent EfOM deposits on or in the membranes, reducing the permeate rate by cake filtration, pore blocking and adsorption. These processes are depending on both the characteristics of the membranes and foulants, Wiesner and Aptel (1996). More recently several researchers studied the interaction of organic compounds and membrane surface properties. Jarusutthirak and Amy (2001) found that EfOM rejection, flux decline and fouling mechanism were depending on the membrane surface charge. Both surface charge and hydrophobicity of the membrane play a significant role in the adsorption of EfOM.

Characterisation of EfOM of different EfOM-source waters combined with membrane filtration tests using different membrane types and materials resulted in more insight in fouling mechanisms during nano- and ultrafiltration of EfOM, Jarusutthirak et al. (2002b). They identified proteins and/ or polysaccharides as possible foulants, as components of SMP produced during microbial activities. An increase of flux decline was found with effluents derived from longer sludge ages. Furthermore flux decline by EfOM fouling was found affected by steric exclusion and electrostatic repulsion, depending on membrane properties as molecular weight cut-off, surface charge and hydrophobicity.

3.4.1 EPS and SMP

In wwtp effluent filtration, soluble substances seem to have a rather large impact on membrane performance. They can adsorb on the membrane surface and block

membrane pores as well as form a gel structure on the membrane surface where they provide a possible nutrient for biofilm formation.

EPS and SMP are substances produced by micro-organisms that are released into the liquid phase as part of the metabolism and due to biological or mechanical stress. Laspidou and Rittmann (2002) compared the concepts of EPS and SMP and concluded that soluble EPS and SMP are indeed identical. From an engineering point of view, it is impossible to differentiate between the concepts as long as only simple mechanisms for phase separation (e.g. filtration or centrifugation) and sum parameters for quantification (e.g. COD, TOC, polysaccharides, proteins) are applied.

The results given in literature are difficult to be compared as they depend very much on the analytical methods chosen. No unequivocal method for determination of the fouling potential exists, Rosenberger et al. (2005).

3.4.2 EPS characteristics

In activated sludge systems the production of EPS by bacteria is of importance in the forming of sludge flocs. Not all produced EPS contribute to the floc formation process, some remain as non-bound or soluble EPS in the wastewater. After sedimentation of the biological treated wastewater in the secondary clarifier these soluble EPS and escaped sedimentation parts of sludge flocs remain in the wastewater effluent. Wingender et al. (1999) determined bound EPS as capsular polymers, condensate gel, weakly bound monomers and organic material, whereas soluble EPS exist of soluble macro-molecules, colloidal substances and slime. The difference in structure of bound and soluble is presented in figure 3.4.

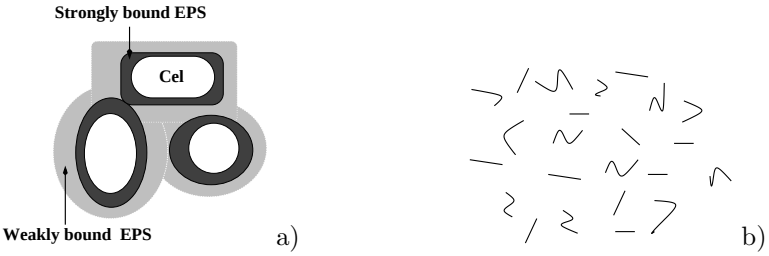

Figure 3.4: Structure of Extracellular Polymeric Substances, a) bound EPS, b) soluble EPS, Wingender et al. (1999)

The main components of EPS are the proteins (till 60 %) and polysaccharides (40-95 %), Flemming and Wingender (2001a):

- Polysaccharides,
  Constructed of mono saccharides, urine acids and amino sugars which are bound by ether bonds. The structure is linear with side chains and organic as well as inorganic substituents like acetyl, succinyl, pyruvyl, sulphate and phosphate;

- Proteins,
  Constructed of amino acids with peptide bounds formed of α-amino acids with amide bonds and have a linear structure with oligosaccharides and fatty acids as substituents.

Furthermore EPS consist of nucleic acid and lipids:

- Nucleic acids,
  Constructed of genetic material DNA and RNA, which are bound with phosphor-di-acids-bonds and form a linear structure;

- Lipids,
  Constructed of fatty acids, glycerol, phosphate, ethanol-amine, serine, choline and sugars, which are bound with ester bonds and form a structure with side chains.

Sometimes humic substances are accounted as well as EPS constituents.

- Humic substances
  Mainly the soluble humic and fulvic acids, which are constructed of phenol components, single sugars and amino acids and bound with ether, carbon and peptide bonds. The formed structure is cross-linked.

The concentrations of the individual components in the EPS matrix show a broad variation, depending on the sludge properties. In activated sludge systems the amount of proteins in soluble EPS is 4.5 times higher than the amount of polysaccharides, suggesting that proteins are the dominant foulants in wwtp effluent membrane filtration.

According to Wingender et al. (1999) EPS are mainly responsible for the structural and functional integrity of the biofilm and therefore dominate the physical, chemical and biological properties of the biofilm. A three-dimensional network structure is formed by the interactions between the individual macro-molecules. Because of the molecule structure and relatively high concentration in EPS, proteins and polysaccharides play an important role as structure polymers, Rosenberger (2003). The intra polymer bonds are covalent whereas the inter molecular bonds in the EPS matrix are Van der Waals forces, electrostatic interactions and hydrogen bonds. The physical and chemical properties are mainly dominated by the chain structure and linked substituents like phosphate and sulphate. This indicates that proteins and polysaccharides naturally intend to form a gel layer which is highly structured.

The EPS are predominantly negatively charged, Flemming and Wingender (2001a), which is important for the stabilisation of the EPS matrix. The mechanical properties of the biofilm are influenced by the precipitation of minerals, especially calcium carbonate, Flemming and Wingender (2001b). These cations are cross-linked in the EPS structure and as a result improve the mechanical properties of the biofilm by a higher elasticity coefficient. Furthermore EPS are often related to slimy substances and are highly hydrated. EPS tend to attach to surfaces and there form slimy films,

which is of importance in the formation of biofilms. Furthermore inorganic material or minerals have the potential to bind with EPS and are useful in the formation of a tighter and mechanical strong gel structure.

Proteins smaller than the pore size of the ultrafiltration membrane can be rejected by the following mechanisms, Noordman (2000):

- effect of the charge (negative),
- bounding with water molecules,
- bounding with anions (Ca^{2+})

by which the protein molecule becomes larger. In addition the proteins can form a network structure on the membrane surface. In this process the water molecules and anions have an important role.

According to Zouboulis et al. (2003) humic substances contain a main structure of phenol and phenolic acids. These aromatic groups are linked together by short saturated aliphatic chains. Humic acids are the alkali soluble and acid insoluble fractions. They have an anionic character and are capable of complex formation with metal ions.

Summarising, gel layer formation is a complex structure of proteins, polysaccharides, humic substances and inorganic material, metal ions or minerals.

3.5 Analytical methods

In general, the organic content can be measured by overall parameters like COD, BOD and TOC, Metcalf and Eddy (2003). The COD test is used to measure the oxygen equivalent of the organic material in wastewater that can be oxidised chemically. However, high and incorrect COD values can be obtained because inorganic substances can be oxidised as well. For the analyses of COD the colour test of Merck 14540, range 10-150 mg/L, is used. The colour is measured by a spectrophotometer (SQ 200, Merck). The sensitivity of this method is $\pm$ 2 mg/L COD.

Biodegradable organic matter can be measured by the 5-day BOD as dissolved oxygen used by micro-organisms in the biochemical oxidation. One of the limitations of the BOD test is that only the biodegradable organics are measured.

Total organic carbon, TOC, is measured as carbon dioxide by converting organic carbon. When a wastewater sample is filtered over a 0.45 μm filter paper then the dissolved organic carbon, DOC, can be measured by the same TOC test method. However, these overall parameters are not specific enough to determine membrane foulants, Te Poele (2003). Therefore the components with a high potential fouling rate like proteins, polysaccharides, colour and humic acids are measured individually.

The role of EPS in biofouling and biofilm systems have long been subject of many studies, Baker and Dudley (1998), Flemming et al. (1997), Flemming (1995) and Wingender et al. (1999). Rosenberger (2003) and Nagaoka et al. (1996) studied the role of EPS in Membrane Bioreactors (MBR) in relation to the overall process performance and the membrane separation process. Similar in these researches are the EPS characterisation by extraction of biomass and analysing the most important substances, being proteins and polysaccharides. Since wwtp effluent mainly consists of non bound or soluble EPS, the main components proteins and polysaccharides can be directly analysed in order to characterise EPS.

3.5.1 Proteins

Proteins are often measured by the method of Lowry et al. (1951) or Bradford (1976). The Lowry et al. (1951) method is based on a colour forming reaction between peptide bonds and copper. The formed copper bonds are reduced by Folin-Ciocalteu phenol reagent to a blue colour. By this method all proteins with two or more peptide bonds are analysed. In contrast to the Lowry et al. (1951) method the colour formation by the Bradford (1976) method is based on a colour binding with Coomassie Brilliant Blue G250. Proteins with more than 8-9 peptide bonds are analysed. The advantage of the Bradford (1976) method compared to the method of Lowry et al. (1951) is the less sensitivity of interfering compounds, specially compounds with phenol groups, which are frequently present in wastewater. In contrast to the method of Lowry et al. (1951) only macro-molecules with eight or more peptide bonds could be measured by the method of Bradford (1976) and the colour intensity as measured with this method is often developed for only 50%. Therefore the method of Lowry et al. (1951) is usually applied.

For the analyses of proteins the modified method of Rosenberger (2003) is used, which is based on the method of Lowry et al. (1951). In order to analyse proteins in wwtp effluent the method of Rosenberger (2003) is improved by using a 4 cm cuvett in stead of a 1 cm cuvett and a double amount of reagents, which increases the reliability of the analyses. By this the standard deviation becomes less than 3 %. A detailed description of the method is given in Appendix E.

3.5.2 Polysaccharides

By the Dreywood (1946) method the polymers are hydrolysed with concentrated sulphuric acid and the monomers formed are dehydrated to aromatic compounds. The aromatic compounds are determined after coloring with Anthron. The method of Dubois et al. (1956) is based on the same principle as the Dreywood (1946) method, but phenol is used as reagent for the colour development. In contrast to the Anthron method of Dreywood (1946) the colour intensity developed by the Dubois et al. (1956) method is the same for every kind of sugar. Although the method of Dubois et al. (1956) has a poor reproduction, most likely caused by an undefined reaction temperature and time, it is mostly used.

For the analyses of polysaccharides the modified method of Rosenberger (2003) is used, which is based on the method of Dubois et al. (1956). The method of Rosenberger (2003) is improved in order to measure lower concentrations of polysaccharides in the wwtp effluent. Therefore the volume of the sample is doubled and the volumes of reagents are not changed. In addition a 4 cm cuvett is used instead of a 1 cm cuvett to be able to measure an extinction value > 0.2. By this the reliability of the analyses is improved and the standard deviation becomes less than 7.5 % (mostly 5%). A detailed description of the method is given in Appendix E.

The photometric analysis of polysaccharides interferes linearly with nitrate-nitrogen, Rosenberger et al. (2005), which is illustrated in figure 3.5. This can easily be calibrated and substracted:

$$measured\ PS \quad = \quad real\ PS \quad + \quad f \cdot nitrate\ concentration \tag{3.1}$$

where PS is the concentrations of polysaccharides (mg/L) and the factor f depends on the spectrophotometer and is 0.19 for the photometer used in this research. For the investigated wwtp effluent and ultrafiltrate the nitrate concentration is 4-5 mg/L on average. Nitrate is not removed by ultrafiltration.

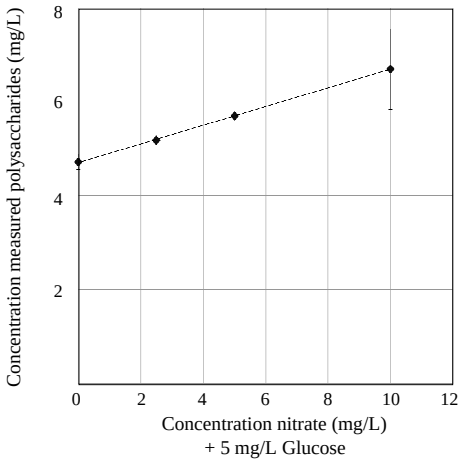

Figure 3.5: Standard addition of different nitrate concentrations added to 5 mg/L Glucose in demineralised water

3.5.3 Humic substances

Humic substances are characterised by UV-absorption at 254 nm. UV-absorption is measured at 254 nm in a 1 cm quarts glass cuvett by the UV-VIS spectrophotometer Perkin-elmer Lambda 16. The amount of humic substances is usually expressed in m^{-1} or cm^{-1}. The measured standard deviation is < 1 %.

3.5.4 Colour

For the determination of colour the NEN 1056 11.2 method was used. The absorption of colour at 455 nm in a 4 cm quarts glass cuvett is measured by the spectrophotometer milton roy spectromic 401. The amount of colour is expressed in mg Pt/L. The measured standard deviation is < 0.25 %.

3.6 Discussion

The photometric analyses of proteins by Lowry et al. (1951) mutually interfere by humic substances, Frølund et al. (1995) and Rosenberger et al. (2005). Apart from Frølund et al. (1995) and Frølund et al. (1996) no references were found where it was clear that they corrected their values. Frølund et al. (1995) used the Lowry et al. (1951) method to analyse both proteins and humic substances in one sample.

The mutual interference of proteins and humic substances in the Lowry et al. (1951) method was investigated by standard addition of humic acid (Jansen Chemica 12.086.58) solution to demineralised water and a standard protein solution (BSA) applying the correction method of Frølund et al. (1995). This correction method is described as follows:

$$A_{total} = A_{prot} + A_{humic} \tag{3.2}$$

$$A_{blind} = X \cdot A_{prot} + A_{humic} \tag{3.3}$$

$$A_{prot} = Y \cdot (A_{total} - A_{blind}) \tag{3.4}$$

where A_{total} is the total absorption measured by the Lowry et al. (1951) method using $CuSO_4$, A_{blind} is the absorption measured by the Lowry et al. (1951) method without addition of $CuSO_4$, A_{prot} is the absorption of proteins and A_{humic} is the absorption of humic acid.

Table 3.2: Results of the standard addition of different humic acid concentrations to 5 mg/L BSA in demineralised water

	Concentration BSA (mg/L) + Humic acid (mg DOC/L)			
	5 + 0	5 + 0.5	5 + 1	5 + 2
A_{blind}	0.049 ± 0.008	0.095 ± 0.001	0.153 ± 0.003	0.252 ± 0.004
A_{total}	0.198 ± 0.009	0.234 ± 0.008	0.298 ± 0.007	0.386 ± 0.003
A_{prot}	0.198 ± 0.017	0.185 ± 0.009	0.192 ± 0.010	0.178 ± 0.006
C_{prot}	5.24 ± 0.45	4.81 ± 0.24	5.06 ± 0.26	4.58 ± 0.16
A_{humic}	0.000 ± 0.026	0.049 ± 0.018	0.106 ± 0.017	0.208 ± 0.009
UVA_{254}	0.003 ± 0.000	0.067 ± 0.000	0.131 ± 0.000	0.257 ± 0.001

In table 3.2 the results of the standard addition of humic acid to proteins are presented. The factors X and Y can easily be calculated by the obtained results for A_{total} and A_{blind} of a the standard protein solution (5 mg BSA/L) without humic

acid, and are 0.25 and 1.33 respectively.

The relation between humic acid concentration and the total absorption measured by the Lowry et al. (1951) method is illustrated in figure 3.6 a), whereas in figure 3.6 b) the relation between humic acid concentration and the UVA at 254 nm is given. The results show a clear interference of humic acid to the protein concentration measured by the Lowry et al. (1951) method. Furthermore, the humic acid concentrations measured by UVA at 254 nm shows a neglectable interference of proteins.

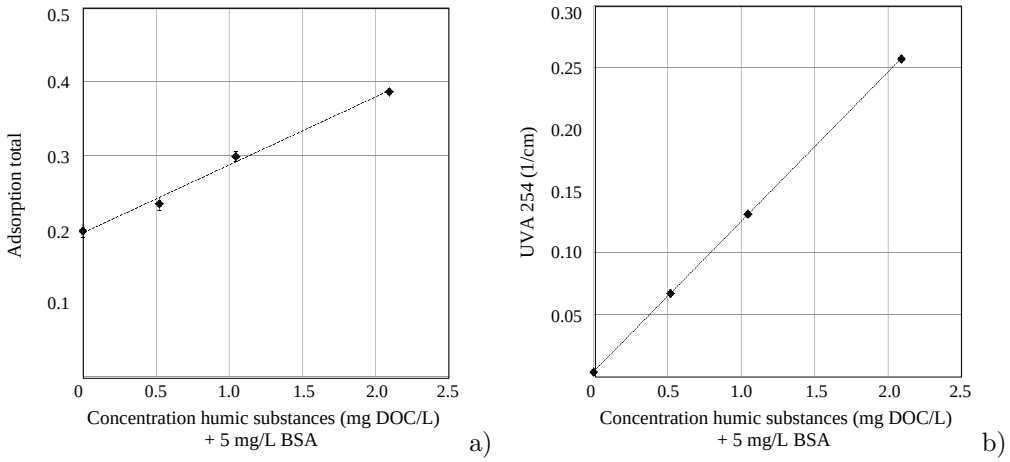

Figure 3.6: Relation between humic acid concentration added to 5 mg/L BSA in demineralised water and a) the total absorption measured by the Lowry et al. (1951) method and b) the UV-absorption at 254 nm.

However, when the correction by Frølund et al. (1995) of the Lowry et al. (1951) method was applied at different wwtp effluent samples, the concentration of proteins was less than expected. These results are presented in table 3.3. In one sample of wwtp effluent even negative values for the protein concentration were found. In addition, the absorbance of humic acid in these samples measured by the Frølund et al. (1995) method was found at least twice as high as the absorbance calculated by the relation between A_{humic} and the UV-absorption at 254 nm, obtained from the standard addition results as illustrated in figure 3.7:

$$A_{humic} = \frac{UVA_{254}}{1.214} \tag{3.5}$$

Since the UV-absorption at 254 nm is commonly used in practice, the obtained results of humic acid measured by the Frølund et al. (1995) method were found unreliable. These results suggest that the effluent matrix interfere with the measurement of A_{blind} in the corrected method of Frølund et al. (1995). Thus, measuring proteins in wwtp effluent by the Lowry et al. (1951) method can not be corrected for the mutual interference of humic substances by the Frølund et al. (1995) method.

Table 3.3: Results of the correction method of Frølund et al. (1995) of two different wwtp effluent samples

	effluent	
	wwtp 3 Ambachten	industrial wwtp Cerostar
A_{blind}	0.537 ± 0.009	0.911 ± 0.008
A_{total}	0.445 ± 0.008	1.015 ± 0.008
A_{prot}	- 0.119 ± 0.017	0.135 ± 0.016
$Conc._{prot}$	-2.57 ± 0.36	3.10 ± 0.36
A_{humic}	0.564 ± 0.025	0.880 ± 0.023
UVA_{254}	0.278 ± 0.001	0.598 ± 0.000
calculated A_{humic}	0.229 ± 0.001	0.492 ± 0.000

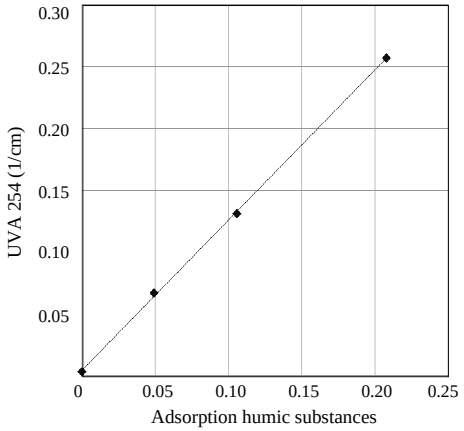

Figure 3.7: Relation between UV-absorption at 254 nm and A_{humic}, obtained from the standard addition results

In order to compare different water samples a new parameter is introduced: the ratio of ultraviolet absorption to proteins (PUVA). PUVA is in fact a measure of the amount of humic substances by UV-absorption at 254 nm relative to the protein concentration by Lowry et al. (1951) in the sample being analysed:

$$PUVA \quad = \quad \frac{UVA_{254}}{C_{prot,L}} \tag{3.6}$$

where PUVA is the ratio of ultraviolet absorption to proteins (L/m·mg), UVA_{254} is the UV-absorption at 254 nm (1/m) and $C_{prot,L}$ is the protein concentration by Lowry et al. (1951) (mg/L).

Low values for PUVA are related to relatively high concentrations of proteins. Whereas high values for PUVA indicate high concentrations of humic substances compared to proteins.

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Chapter 4

Foulants versus filterability

4.1 Fractionation of wwtp effluent

In order to investigate the influence of the size of foulants on the filterability of wwtp effluent fractionation experiments were carried out. To that purpose, the wwtp effluent is separated into several fractions. The potential organic foulants: polysaccharides, proteins, humic substances, colour and total organic matter measured as COD are analysed in these fractions. The filterability of each fraction is measured by the SUR. By comparing the SUR and foulant concentration in the different fractions a possible relation between the filterability and the size of the foulants may be derived.

4.1.1 Methods

The experiments were performed on effluent of wwtp Berkel, Hoek van Holland, Utrecht, Tilburg-Noord and effluent after the pond system at wwtp Tilburg-Noord. The first water was not used as feed water in pilot investigations. A sample was collected and fractionated as described in section 3.2 into four fractions: < 450 or < 400 μm, < 0.45 μm, < 0.20 μm and < 0.10 μm. For each fraction which was formed by fractionation of a wwtp effluent the same ultrafiltration membrane module was used to measure the SUR.

A SUR measurement was proceeded by measuring the clean water flux (CWF) in order to check if the membranes were clean. Then the fractionated feed water was filtrated to measure the filterability by the SUR. Thereafter the membrane module was flushed with demineralised water and cleaned with a solution of 400 mg/L NaOCl or 1.25 w/w-% Divos 120CL by flushing and soaking for 10 minutes; by this cleaning procedure an equal CWF is achieved as at the beginning of each SUR measurement. When new membranes were applied the cleaning protocol which is described in Appendix D was used. In each fraction the concentration of polysaccharides, proteins, humic substances, colour and COD was analysed. The methods used are described in section 3.5. The fractionation experiments of a wwtp effluent were repeated twice on different days.

4.1.2 Results

The results of a wwtp effluent are obtained from the fractionation experiments which were performed on different days, due to logistic reasons. Therefore the results are presented as mean values with the variation of the wwtp effluent during the different days. According to Roorda (2004), a SUR value smaller than $10{\cdot}10^{12}$ m^{-2} indicates a good filterability.

WWTP Berkel

The filterability of the fractionated effluent of wwtp Berkel, characterised by the SUR, and the amount of foulants as well as the calculated values for PUVA in each fraction are presented in table 4.1. In order to compare the decrease in SUR with the decrease of the measured foulants over the smaller fractions, the results in figure 4.1 are presented relatively to the largest fraction (< 400 μm), which is considered as the sum of all fractions.

Table 4.1: Results wwtp Berkel: mean values of SUR, COD, colour, polysaccharides, proteins, humic substances and PUVA per fraction

Measured parameter		Fraction (μm)			
		< 400	< 0.45	< 0.20	< 0.10
SUR	$\cdot 10^{12}$ m^{-2}	8.5 ± 1.1	7.3 ± 0.9	3.5 ± 0.5	2.7 ± 0.8
COD	mg/L	41 ± 2	39 ± 1	36 ± 3	36 ± 4
Colour	mg Pt/L	73 ± 19	42 ± 18	34 ± 14	35 ± 15
Polysaccharides	mg/L	3.5 ± 0.2	3.1 ± 0.4	2.8 ± 0.4	2.7 ± 0.3
Proteins	mg/L	11.7 ± 1.2	10.9 ± 0.6	10.4 ± 1.0	10.1 ± 0.9
Humic subst.	cm^{-1}	0.305 ± 0.002	0.293 ± 0.002	0.293 ± 0.002	0.286 ± 0.002
PUVA	L/mg·m	2.6 ± 0.5	2.7 ± 0.4	2.8 ± 0.5	2.8 ± 0.5

The SUR value found for the largest fraction (< 400 μm) is lower than $10{\cdot}10^{12}$ m^{-2}, which indicates a good filterability. The filterability is improved even further by fractionation and the largest increase in filterability is found between the fractions < 0.45 μm and < 0.20 μm. The SUR value of the smallest fraction is found rather low and is $2.7{\pm}0.8 \cdot 10^{12}$ m^{-2}.

In general, only small changes in potential foulant concentrations over the fractions were noticed and more than 75 % of the foulants remained in the smallest fraction. The concentration of colour components varied largely between the different samples of wwtp effluent and therefore a relation between filterability and colour components is difficult to give. The ratio between humic substances and proteins, characterised by PUVA, shows hardly any changes, which means that proteins are hardly removed by fractionation, because the humic substances measured by UVA_{254} changed only little.

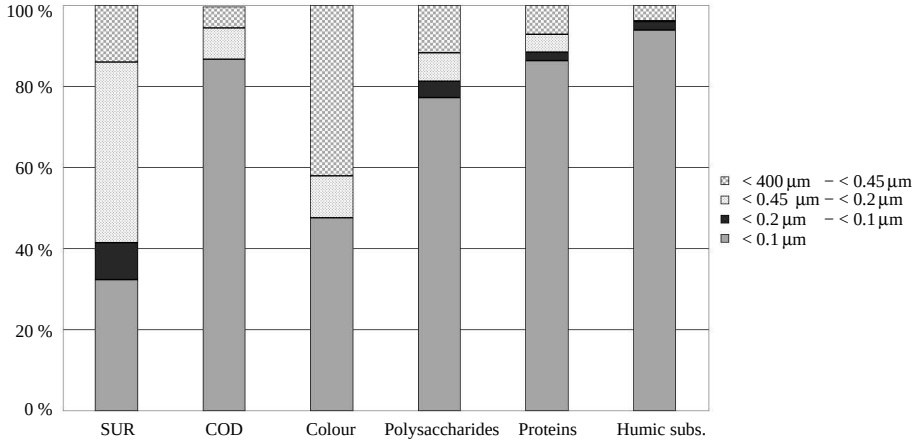

Figure 4.1: Overview of the fractionation results at wwtp Berkel; Relative presentation of the mean values of SUR, COD, colour, polysaccharides, proteins and humic substances to the largest fraction (< 400 μm)

The obtained mean values show a small decrease of colour components and polysaccharides between the fractions < 400 and < 0.45 μm, and a small decrease in SUR is observed between these fractions . The amount of humic substances shows a small decrease between the fractions < 400 and < 0.45 μm and therefore their contribution to filterability increase is small. The largest SUR decline is found between the fractions < 0.45 and < 0.20 μm, and is 45%. Here no decrease in humic substances, colour, COD, polysaccharides and proteins could be observed. The decrease of the SUR between the fractions < 0.20 and < 0.10 μm could not be related to any of the measured foulants.

WWTP Hoek van Holland

The results of the fractionation experiments of Hoek van Holland wwtp effluent are also published in Te Poele et al. (2004) and are here presented in table 4.2 and in figure 4.2.

Table 4.2: Results wwtp Hoek van Holland: mean values of SUR, COD, colour, polysaccharides, proteins, humic substances and PUVA per fraction

Measured parameter		Fraction (μm)			
		< 450	< 0.45	< 0.20	< 0.10
SUR	$\cdot 10^{12}$ m^{-2}	18.1 ± 6.7	15.6 ± 4.0	8.7 ± 2.0	5.1 ± 0.3
COD [a]	mg/L	72 ± 5	64 ± 2	61 ± 7	65 ± 12
Colour	mg Pt/L	173 ± 16	140 ± 18	138 ± 18	136 ± 19
Polysaccharides	mg/L	5.2 ± 0.9	4.5 ± 0.6	4.6 ± 0.8	3.8 ± 0.6
Proteins	mg/L	29.3 ± 1.8	26.3 ± 1.9	25.6 ± 1.6	25.3 ± 2.0
Humic subst.	cm^{-1}	0.630 ± 0.008	0.612 ± 0.009	0.610 ± 0.009	0.608 ± 0.009
PUVA	L/mg·m	2.1 ± 0.4	2.3 ± 0.5	2.4 ± 0.5	2.4 ± 0.5

[a] based on two measurements

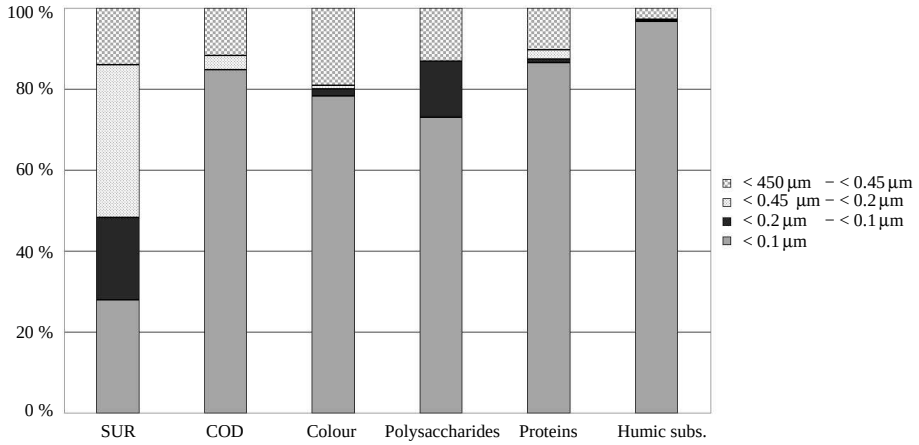

Figure 4.2: Overview of the fractionation results at wwtp Hoek van Holland; Relative presentation of the mean values of SUR, COD, colour, polysaccharides, proteins and humic substances to the largest fraction (< 450 μm)

The largest fraction here is < 450 μm and a relatively high SUR value, 18.1±6.7 $\cdot 10^{12}$ m^{-2}, is obtained resulting in a poor filterability i.e. the SUR value is significantly larger than $10 \cdot 10^{12}$ m^{-2}. The SUR value decreased below $10 \cdot 10^{12}$ m^{-2} when the feed water was fractionated over a 0.20 μm filter.

The measured foulant concentrations were relative high compared to the concentrations found in wwtp Berkel effluent; the concentrations were circa twice as high. Also here approximately 75 % of the measured foulants appeared to be smaller than 0.10 μm. The lower value for PUVA indicates that the concentration of proteins was relatively high compared to humic substances.

Furthermore the obtained mean values show a decrease in amount of colour components, polysaccharides, COD and proteins comparable with the decrease of the SUR between the fractions < 450 and < 0.45 μm. The largest SUR decline was found between the fractions < 0.45 and < 0.20 μm, and is 38%, but can hardly be related to any of the measured foulants. The decrease in SUR between the < 0.20 and < 0.10 μm fractions is 20 % and can only be related to a decrease in polysaccharide concentration.

WWTP Utrecht

In table 4.3 and figure 4.3 the results of the fractionation experiments of wwtp Utrecht are presented. The filterability of the first three fractions (< 450, < 0.45 and < 0.20 μm) were rather poor, indicated by the relatively high SUR values, which are all higher than $10{\cdot}10^{12}$ m^{-2}.

Table 4.3: Results wwtp Utrecht: mean values of SUR, COD, colour, polysaccharides, proteins, humic substances and PUVA per fraction

Measured parameter		Fraction (μm)			
		< 450	< 0.45	< 0.20	< 0.10
SUR	$\cdot 10^{12}$ m^{-2}	15.7 ± 1.3	14.3 ± 1.6	13.0 ± 1.0	7.7 ± 0.8
COD	mg/L	34 ± 4	29 ± 5	30 ± 4	29 ± 3
Colour	mg Pt/L	77 ± 10	50 ± 4	49 ± 5	49 ± 4
Polysaccharides	mg/L	5.7 ± 1.2	4.9 ± 1.0	4.9 ± 1.2	4.7 ± 1.0
Proteins	mg/L	15.2 ± 0.6	13.3 ± 0.4	13.2 ± 0.5	12.8 ± 0.4
Humic subst.	cm^{-1}	0.274 ± 0.002	0.253 ± 0.001	0.254 ± 0.001	0.252 ± 0.001
PUVA	L/mg·m	1.8 ± 0.2	1.9 ± 0.2	1.9 ± 0.2	2.0 ± 0.1

When comparing the concentrations of measured foulants with the results of Berkel wwtp, the values for COD, colour and humic substances are almost equal, but the concentrations for EPS (proteins and polysaccharides) are significantly higher. The obtained polysaccharide concentration are almost equal to wwtp Hoek van Holland, but the protein concentrations were twice as low. Relatively high protein concentrations were observed compared to humic substances, indicated by the low value for PUVA.

In figure 4.3 the obtained mean values show a decrease in all measured foulants

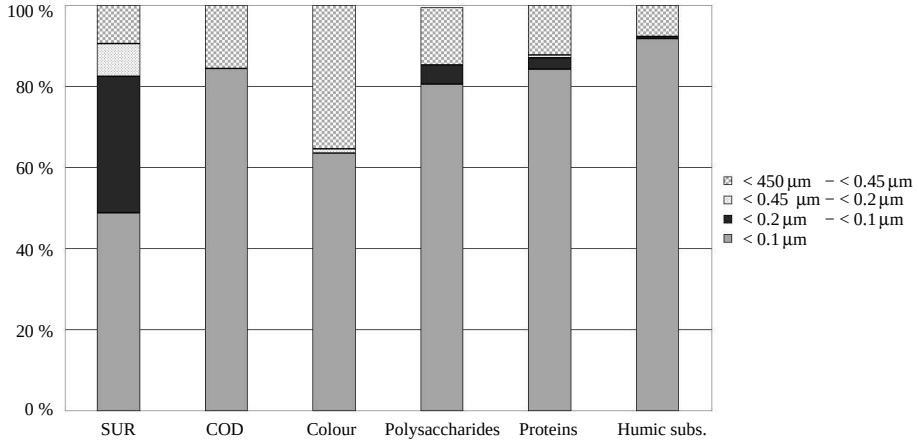

Figure 4.3: Overview of the fractionation results at wwtp Utrecht; Relative presentation of the mean values of SUR, COD, colour, polysaccharides, proteins and humic substances to the largest fraction (< 450 μm)

between the fractions < 450 and < 0.45 μm, and a small decrease in SUR is observed between these fractions. The decrease in SUR between the < 0.45 and < 0.20 μm fractions can not be related to any of the measured foulants. The largest SUR decline was between the fractions < 0.20 and < 0.10 μm, and is 34%, which can hardly be related to any of the measured foulants. Except for colour more than 80% of the measured foulants was < 0.10 μm.

WWTP Tilburg-Noord

During the pilot investigations at wwtp Tilburg-Noord two types of feed water were used: the effluent after secondary sedimentation and after the pond system. Therefor both feed waters here were used for the fractionation experiments.

The results of the fractionation experiments in which effluent after secondary sedimentation was used are given in table 4.4 and in figure 4.4. The SUR values obtained for all fractions were relatively low, i.e. $< 10{\cdot}10^{12}$ m^{-2}, and changed rather little during fractionation to smaller fractions. The measured concentrations of the foulants are comparable with or even lower than the results of wwtp Berkel. Approximately more than 80% of the measured foulants were < 0.10 μm.

Furthermore, a decrease in the amount of colour and polysaccharides between the fractions < 400 and < 0.45 μm was found and no significant decrease in SUR between these fractions was observed. The increase in filterability between the < 0.45 and < 0.20 μm fractions could not be related to any of the measured foulants. The largest SUR decline was found between the fractions < 0.20 μm and < 0.10 μm, and was 28%. This could hardly be related to any of the measured foulants.

Table 4.4: Results wwtp Tilburg-Noord: mean values of SUR, COD, colour, polysaccharides, proteins, humic substances and PUVA per fraction

Measured parameter		Fraction (μm)			
		< 400	< 0.45	< 0.20	< 0.10
SUR	$\cdot 10^{12}$ m^{-2}	8.3 ± 0.3	8.0 ± 0.3	7.3 ± 0.2	5.0 ± 0.2
COD	mg/L	27 ± 7	24 ± 7	25 ± 6	28 ± 5
Colour	mg Pt/L	61 ± 7	47 ± 6	48 ± 5	48 ± 5
Polysaccharides	mg/L	2.8 ± 0.1	2.5 ± 0.1	2.4 ± 0.1	2.4 ± 0.1
Proteins	mg/L	12.4 ± 2.3	11.8 ± 2.3	11.8 ± 2.2	11.4 ± 2.0
Humic subst.	cm^{-1}	0.307 ± 0.004	0.300 ± 0.004	0.299 ± 0.004	0.297 ± 0.004
PUVA	L/mg·m	2.5 ± 0.8	2.5 ± 0.8	2.5 ± 0.8	2.6 ± 0.8

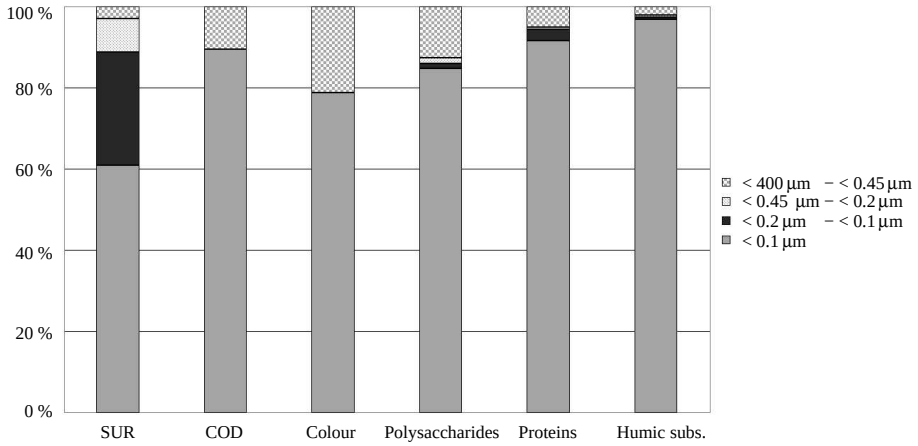

Figure 4.4: Overview of the fractionation results at wwtp Tilburg-Noord; Relative presentation of the mean values of SUR, COD, colour, polysaccharides, proteins and humic substances to the largest fraction (< 400 μm)

In table 4.5 and in figure 4.5 the results of the fractionation experiments, in which effluent after the pond system was used as feed water, are presented. The SUR value of the largest fraction (< 400 μm) is larger than $10 \cdot 10^{12}$ m^{-2} and therfore indicating a slightly poor filterability. The SUR value decreases slightly during fractionation and the largest decrease in SUR is between < 0.20 μm and < 0.10 μm fraction. This is 25% and can hardly be related to any of the measured foulants. Except for colour, approximately more than 90% of the measured foulants are < 0.10 μm. Compared to the results of the same wwtp in which effluent after secondary sedimentation is used, the SUR values and the measured foulants are relatively high.

Table 4.5: Results wwtp Tilburg-Noord after Pond System: mean values of SUR, COD, colour, polysaccharides, proteins, humic substances and PUVA per fraction

Measured parameter		Fraction (μm)			
		< 400	< 0.45	< 0.20	< 0.10
SUR	$\cdot 10^{12}$ m^{-2}	11.1 ± 1.2	9.9 ± 2.1	8.5 ± 2.1	5.8 ± 1.4
COD	mg/L	29 ± 4	29 ± 4	31 ± 2	28 ± 4
Colour	mg Pt/L	86 ± 7	47 ± 14	50 ± 18	51 ± 17
Polysaccharides	mg/L	3.1 ± 0.2	3.0 ± 0.0	2.9 ± 0.1	2.8 ± 0.2
Proteins	mg/L	14.4 ± 1.0	13.0 ± 0.6	12.7 ± 0.7	12.6 ± 0.5
Humic subst.	cm^{-1}	0.353 ± 0.002	0.320 ± 0.001	0.309 ± 0.003	0.309 ± 0.003
PUVA	L/mg·m	2.5 ± 0.3	2.4 ± 0.2	2.4 ± 0.4	2.5 ± 0.4

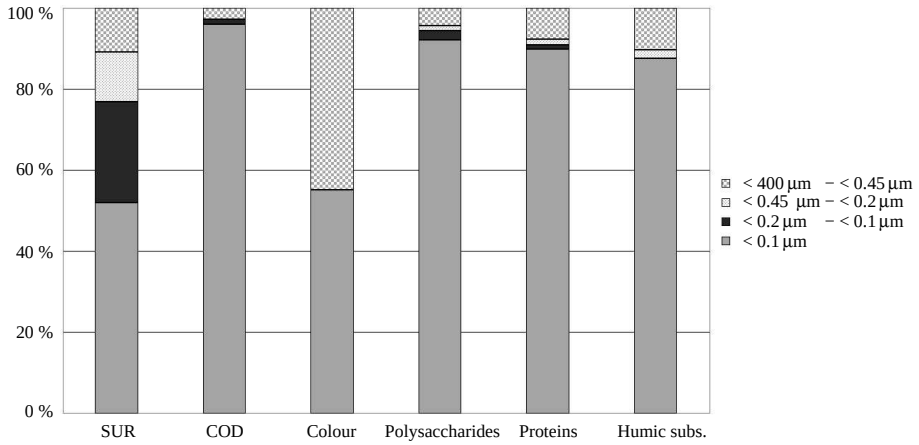

Figure 4.5: Overview of the fractionation results at wwtp Tilburg-Noord after Pond System; Relative presentation of the mean values of SUR, COD, colour, polysaccharides, proteins and humic substances to the largest fraction (< 400 μm)

4.1.3 Discussion fractionation experiments

In general, the increase in filterability between the $< 450/400$ and < 0.45 μm fraction is found relatively small and for some of the measured foulants a decrease in concentration between these fractions is observed. For colour the decline in concentration was in all cases larger than the decrease of the SUR value the $< 450/400$ and < 0.45 μm fraction. This could be a consequence of the used analytical method, which was a pure photometric measurement and could be disturbed by particles larger than 0.45 μm. The amount of polysaccharides and proteins retained by the 0.45 μm filter is probably related to the retained bacteria and biomass material, which contains

polysaccharides and proteins as intracellular material. The observed increase in filterability between the < 0.45 and < 0.20 μm fractions could hardly be related to any of the measured foulants. Except for colour, approximately more than 75 % of the measured foulants are < 0.10 μm. Thus for all investigated wwtp effluents a large decrease in SUR is found between the < 0.45 and < 0.1 μm fractions, which could not be related to a decrease in any of the measured foulants. This part is defined as the colloidal fraction. However, the distribution of foulants in effluents between the < 0.45 and < 0.1 μm, and < 0.20 and < 0.10 μm fractions may differ from wwtp to wwtp and from time to time.

It is remarkable that no decrease of COD is found in the part between the < 0.45 and < 0.1 μm fractions, since the total suspended solids in wwtp effluent consists for 85% of organic material, section 3.1. Either the increase of filterability may be related to inorganic or non COD organic constituents in the wwtp effluent or to an organic constituent that forms only a small contribution to COD and could therefore not be detected by COD. In addition Laabs (2004) showed that only a small percentage of the total DOC delivered to the membrane surface contributes to the fouling layer, approximately 10 % of EfOM measured as TOC. This indicates that only a small part of the organic fraction contributes to membrane fouling, which is hard to measure by parameters like COD and DOC.

In order to compare the filterability and potential foulant concentrations of the different investigated wwtp effluents an overview of the results of the largest ($< 450/400$ μm) and smallest (< 0.10 μm) fractions are summarised in tables 4.6 and 4.7 respectively. The SUR values of the filtered effluent by a sieve with a mesh size of 400 μm of wwtp Berkel and Tilburg-Noord were lower than $10{\cdot}10^{12}$ m^{-2}, which is according to Roorda (2004) a good filterability. For wwtp Hoek van Holland and Utrecht the effluent constituents < 0.1 μm and < 0.2 μm respectively need to be removed alleviating fouling problems during ultrafiltration of these wwtp effluents.

Table 4.6: Overall results $< 450/400$ μm fraction for the investigated WWTP's

		Berkel	HvH	Utrecht	T-N	T-N aPS
SUR	$\times 10^{12}$ m^{-2}	8.5	18.1	15.7	8.3	11.1
COD	mg/L	41	72	34	27	29
Colour	mg Pt/L	73	173	77	61	86
Polysacch.	mg/L	3.5	5.2	5.7	2.8	3.1
Proteins	mg/L	11.7	29.3	15.2	12.4	14.4
Humic sub.	cm^{-1}	0.305	0.630	0.274	0.307	0.353
PUVA	L/mg·m	2.6	2.1	1.8	2.5	2.5

Comparing the changes in concentrations of proteins and humic substances is possible by measuring both proteins (Lowry et al. (1951) method) and humic substances (UVA254). The new parameter PUVA can be used in order to compare different wwtp

Table 4.7: Overall results < 0.10 μm fraction for the investigated WWTP's

		Berkel	HvH	Utrecht	T-N	T-N aPS
SUR	$\times 10^{12}$ m^{-2}	2.7	5.1	7.7	5.0	5.8
COD	mg/L	36	65	29	28	28
Colour	mg Pt/L	35	136	49	48	51
Polysacch.	mg/L	2.7	3.8	4.7	2.4	2.8
Proteins	mg/L	10.1	25.3	12.8	11.4	12.6
Humic sub.	cm^{-1}	0.286	0.608	0.252	0.297	0.309
PUVA	L/mg·m	2.8	2.4	2.0	2.6	2.5

effluents regarding their protein and humic substance concentrations. For example, the PUVA value calculated for the < 400 μm fraction at wwtp Berkel contains a relatively high amount of humic substances compared to proteins, which is in contrast to the PUVA value calculated for the < 450 μm fraction at wwtp Utrecht. The concentration of humic substances found in these fractions was higher at wwtp Berkel than at wwtp Utrecht. Thus the protein concentration found in these fractions at wwtp Berkel was indeed lower than at wwtp Utrecht. In addition, the measured proteins by the Lowry method in the < 0.10 μm fraction of wwtp Utrecht and wwtp Tilburg-Noord after the pond system are equal, but the obtained value for PUVA indicates a higher concentration of proteins at wwtp Utrecht in this fraction compared to wwtp Tilburg-Noord after the pond system.

4.2 Pilot investigations

In order to further investigate the existence of a relation between filterability and membrane fouling components in ultrafiltration of wwtp effluent, research was performed on pilot scale at wwtp 'Nieuwe Waterweg' in Hoek van Holland and at wwtp 'Utrecht' in Utrecht.

4.2.1 Methods

The filterability in these experiments was measured as fouling rate (dR/dt), which is the increase in filtration resistance over time during one filtration period, see also section 2.4.3. The length of a filtration period strongly depended on the feed water quality, the filterability and applied flux. Therefore in these pilot investigations in which different types of feed water were used, the length of a filtration period varied between 10, 15 and 60 minutes, and the applied flux was in almost all cases 28.5 L/m^2·h.

In ultrafiltration of wwtp effluent the constituents causing membrane fouling are assumed mainly of organic origin. In addition, previous research investigations indicated the role of extracellular polymeric substances in membrane fouling, section 3.4.

Therefore polysaccharides and proteins were measured as main constituents of EPS, COD and colour were measured as two more general parameters indicating organic substances, and humic substances were measured separately as potential foulants in the feed water and ultrafiltrate. The used analytical methods are described in section 3.5. Furthermore, colloids revealed to be of large influence on the filterability, section 4.1.

Pilot investigations at wwtp Hoek van Holland

During the pilot investigations at wwtp Hoek van Holland multimedia filtrate and microfiltrate were used as feed water for ultrafiltration. A schematic overview of the pilot configuration is presented in figure 4.6. Multimedia filtrate was produced out of (coagulated) wwtp effluent. Here four different types of feed water are distinguished:

MF:	microfiltrate out of wwtp effluent;
MF(DMF):	microfiltrate out of multimedia filtrate out of wwtp effluent;
MF(DMF(EF+Al)):	microfiltrate of multimedia filtrate of coagulated wwtp effluent by 2.3/ 5 mg Al^{3+}/L PACl;
DMF(EF+Al):	multimedia filtrate out of coagulated wwtp effluent by 4.3/ 10.6 mg Al^{3+}/L PACl;
DMF+5Al:	coagulated multimedia filtrate by 4/5 mg Al^{3+}/L PACl.

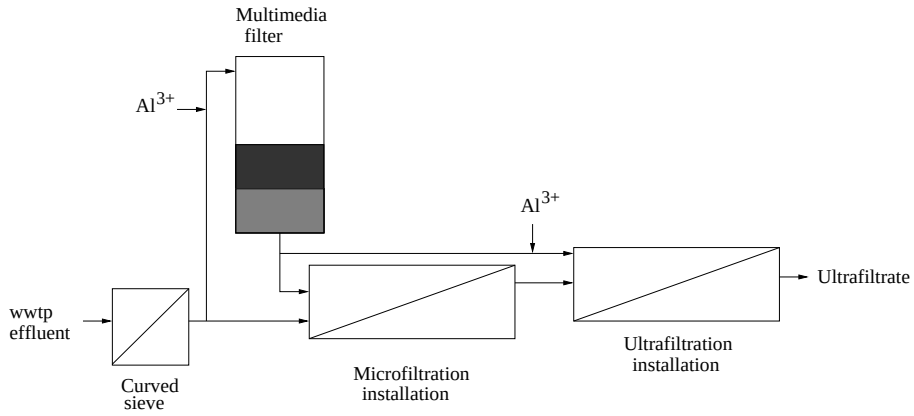

Figure 4.6: Scheme of the pilot plant at wwtp Hoek van Holland

Pilot investigations at wwtp Utrecht

During the pilot investigations at wwtp Utrecht (coagulated) wwtp effluent, (coagulated) multimedia filtrate and microfiltrate were used as feed water for ultrafiltration. In figure 4.7 a schematic overview of the used pilot installations is given. In some

cases methanol was dosed prior to the multimedia filter. Here six different types of feed water are distinguished:

MF:	microfiltrate out of wwtp effluent;
MF(DMF(EF+Al):	microfiltrate out of multimedia filtrate, which was produced out of coagulated wwtp effluent by PACl or $FeCl_3$;
DMF:	multimedia filtrate out of wwtp effluent with and without addition of methanol and/or $FeCl_3$;
DMF(EF+M):	multimedia filtrate out of wwtp effluent and methanol;
DMF(EF+Al):	multimedia filtrate out of coagulated wwtp effluent by 1.0/ 2.5 mg Al^{3+}/L PACl;
DMF+2.5Al:	coagulated multimedia filtrate by 2.5 mg Al^{3+}/L PACl, which was produced out of wwtp effluent and methanol;
EF:	wwtp effluent;
EF+2.5Al:	coagulated wwtp effluent by 2.5 mg Al^{3+}/L PACl.

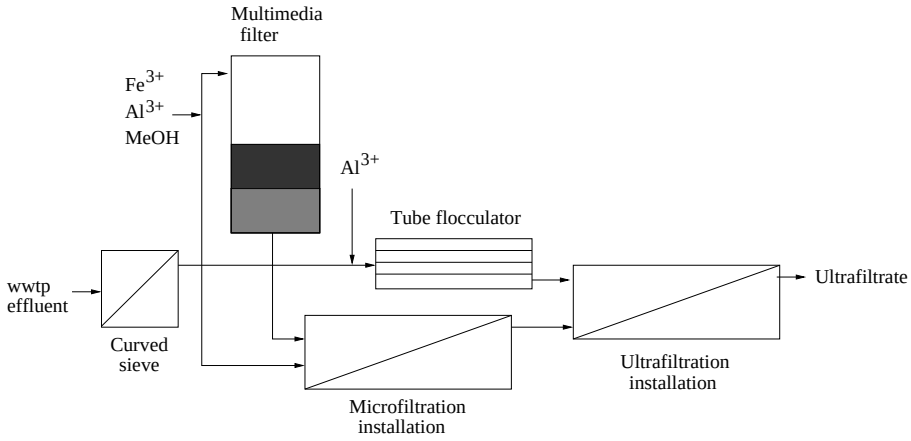

Figure 4.7: Scheme of the pilot plant at wwtp Hoek van Holland

4.2.2 Results

The results of the pilot investigations at wwtp Hoek van Holland and Utrecht are presented in tables 4.8, 4.9 and 4.10 respectively.

Table 4.8: Overview of the fouling rate and concentrations of measured foulants in the feed water, ultrafiltrate and amount retained by ultrafiltration at wwtp Hoek van Holland

Feed water	dR/dt	Proteins (mg/L)			Polysac.[c](mg/L)			Humic sub.[d](1/cm)			Colour (mg Pt/L)			COD (mg/L)		
	$\cdot 10^{12}$ (1/m·h)	Feed	UF[a]	Ret[b]	Feed	UF	Ret	Feed	UF	Ret	Feed	UF	Ret	Feed	UF	Ret
MF	3.10	33.5	11.1	22.5	5.6	5.4	0.2	0.84	0.48	0.36	221	56	165	73	53	21
MF	3.08	35.4	23.2	12.2	5.7	5.8	0.0	0.91	0.78	0.14	236	146	90	78	71	7
MF	1.76	29.3	16.8	12.5	5.2	4.1	1.0	0.74	0.61	0.13	186	89	97	68	61	8
MF	0.32	29.7	18.2	11.5	4.5	4.1	0.4	0.72	0.62	0.10	188	129	59	59	57	2
MF	0.05	13.9	12.4	1.5	2.8	2.5	0.3	0.44	0.41	0.03	105	86	19	42	43	0
MF	0.05	16.5	16.0	0.5	2.9	2.9	0.0	0.55	0.54	0.02	114	109	5	53	43	10
MF(DMF(EF+Al))	0.09	14.9	14.2	0.8	1.9	1.7	0.2	0.42	0.41	0.01	48	44	4	37	34	3
MF(DMF(EF+Al))	0.11	15.1	13.8	1.2	2.5	2.3	0.2	0.36	0.34	0.02	59	54	6	43	42	2
MF(DMF(EF+Al))	0.04	11.6	11.3	0.3	2.0	1.8	0.3	0.29	0.29	0.01	21	21	1	30	25	5
MF(DMF)	0.13	20.3	18.7	1.5	3.3	3.0	0.4	0.60	0.56	0.04	133	114	18	55	51	5
MF(DMF)	0.13	22.4	20.9	1.6	3.7	3.2	0.6	0.60	0.57	0.03	137	124	13	53	52	1
MF(DMF)	0.10	23.8	23.5	0.3	3.7	3.4	0.3	0.64	0.63	0.01	150	142	8	59	56	3
DMF+5Al[e]	13.85	31.9	14.5	17.4	6.5	4.0	2.5	0.82	0.52	0.30	237	78	159	73	46	27
DMF+5Al[e]	8.36	33.4	19.8	13.6	6.4	3.9	2.5	0.86	0.58	0.28	244	95	149	73	47	26
DMF+4Al[e]	12.92	33.6	15.0	18.6	6.3	3.4	2.9	0.86	0.50	0.36	231	66	165	86	62	24
DMF(EF+Al)	1.14	15.9	11.0	4.8	3.6	2.7	0.9	0.46	0.43	0.03	80	62	19	49	40	10
DMF(EF+Al)	0.40	22.1	18.6	3.5	4.7	3.6	1.1	0.59	0.58	0.01	118	106	13	55	51	4

[a] UF is ultrafiltrate

[b] Ret is amount retained

[c] Polysac. is polysaccharides

[d] Humic sub. is humic substances

[e] flux is 40 L/m^2·h

Table 4.9: Overview of the fouling rate and concentrations of measured foulants in the feed water, ultrafiltrate and amount retained by ultrafiltration at wwtp Utrecht

Feed water	dR/dt	Proteins (mg/L)			Polysac. (mg/L)			Humic sub. (1/cm)			Colour (mg Pt/L)			COD (mg/L)		
	$\cdot 10^{12}$ (1/m·h)	Feed	UF	Ret	Feed	UF	Ret	Feed	UF	Ret	Feed	UF	Ret	Feed	UF	Ret
MF	0.08	11.4	10.1	1.3	4.0	3.9	0.1	0.24	0.24	0.01	43	35	8	25	24	1
MF	0.08	13.0	12.4	0.6	4.7	4.4	0.3	0.25	0.25	0.01	48	43	5	25	22	3
MF	0.08	10.4	9.6	0.8	2.8	2.7	0.1	0.21	0.20	0.01	39	37	1	19	10	9
MF(DMF(EF+Fe)	0.06	12.4	12.0	0.4	2.9	2.6	0.3	0.23	0.22	0.01	40	36	4	24	24	0
MF(DMF(EF+Al)	0.05	11.2	10.1	1.1	3.1	3.0	0.1	0.20	0.20	0.01	32	27	5	13	16	0
MF(DMF(EF+Al)	0.07	13.0	12.2	0.8	2.8	2.8	0.1	0.22	0.22	0.01	38	36	2	17	17	0
DMF	0.04	9.2	8.8	0.3	3.5	3.3	0.2	0.20	0.20	0.01	27	27	0	18	15	4
DMF	0.22	9.8	9.3	0.5	4.0	3.6	0.3	0.20	0.19	0.01	32	26	6	17	16	2
DMF	1.33	9.1	9.0	0.1	2.4	2.4	0.1	0.19	0.20	0.00	31	31	0	19	13	6
DMF	0.34	8.8	8.3	0.5	3.2	2.8	0.4	0.19	0.19	0.01	29	26	3	18	15	4
DMF	0.26	8.9	8.6	0.3	4.0	3.6	0.4	0.18	0.18	0.01	26	23	2	18	13	5
DMF(EF+M+Fe)[f]	0.62	11.7	10.6	1.1	3.5	3.2	0.3	0.29	0.27	0.02	52	43	9	21	17	4
DMF(EF+M+Fe)	0.87	11.9	11.0	0.9	4.2	2.7	1.5	0.28	0.26	0.01	53	47	7	26	21	5
DMF(EF+M)	0.26	12.4	11.2	1.2	3.7	2.9	0.8	0.25	0.24	0.01	59	47	12	*[g]		
DMF(EF+M)	0.60	11.9	11.1	0.8	3.0	2.8	0.3	0.25	0.23	0.01	46	41	5	27	18	9
DMF(EF+M)	0.28	12.2	10.9	1.3	3.2	2.4	0.8	0.24	0.22	0.01	44	39	5	22	18	5
DMF(EF+M)	0.76	12.1	11.4	0.7	2.3	2.0	0.2	0.26	0.25	0.01	51	48	4	22	18	4
DMF(EF+M)+Fe[h]	0.59	11.3	9.7	1.6	2.8	2.2	0.6	0.23	0.22	0.02	42	34	8	20	12	8
DMF(EF+M)+Fe	0.91	10.5	9.1	1.5	2.9	2.5	0.4	0.23	0.21	0.02	44	34	10	19	13	6

[f] DMF(EF+M+Fe) is DMF(EF+M) including coagulation of wwtp effluent by 1.0 mg Fe^{3+}/L $FeCl_3$

[g] no COD values available

[h] DMF(EF+M)+Fe is coagulated DMF(EF+M) by 1.0 mg Fe^{3+}/L $FeCl_3$

Table 4.10: Continuation of table 4.9; Overview of the fouling rate and concentrations of measured foulants in the feed water, ultrafiltrate and amount retained by ultrafiltration at wwtp Utrecht

Feed water	dR/dt	Proteins (mg/L)			Polysac. (mg/L)			Humic acid (1/cm)			Colour (mg Pt/L)			COD (mg/L)		
	$\cdot 10^{12}$ (1/m·h)	Feed	UF	Ret	Feed	UF	Ret	Feed	UF	Ret	Feed	UF	Ret	Feed	UF	Ret
DMF+2.5Al	0.74	11.0	6.9	4.1	3.5	2.3	1.2	0.25	0.15	0.10	43	13	30	23	9	14
DMF+2.5Al	0.75	9.7	6.1	3.6	3.4	2.6	0.7	0.25	0.14	0.10	39	11	28	20	10	10
DMF+2.5Al	0.86	11.6	7.9	3.8	2.9	2.1	0.8	0.24	0.15	0.09	42	16	26	22	11	11
DMF+2.5Al	0.67	12.4	8.4	4.0	3.0	2.2	0.9	0.25	0.15	0.09	45	15	29	21	11	11
DMF(EF+Al)	2.11	6.9	6.4	0.6	2.6	2.2	0.4	0.22	0.21	0.01	21	19	3	16	15	1
DMF(EF+Al)	0.40	6.4	6.0	0.4	2.0	1.7	0.3	0.16	0.15	0.01	21	20	1	13	11	2
DMF(EF+Al)	0.57	8.0	7.6	0.4	2.4	2.1	0.3	0.17	0.17	0.01	22	21	1	13	13	1
DMF(EF+Al)	1.48	11.7	11.4	0.3	3.5	2.5	1.0	0.24	0.23	0.01	45	43	2	26	19	7
DMF(EF+Al)	2.59	11.2	10.4	0.8	2.3	2.1	0.2	0.23	0.23	0.01	43	36	7	20	17	4
EF	0.40	9.8	8.2	1.6	5.3	3.9	1.4	0.24	0.22	0.02	42	29	14	21	19	2
EF	1.04	9.0	7.5	1.5	3.3	2.7	0.7	0.23	0.21	0.03	42	30	12	17	12	6
EF	0.95	10.7	9.7	1.0	3.5	2.7	0.8	0.22	0.21	0.02	44	38	7	17	13	4
EF+2.5Al	0.71	11.8	7.6	4.2	3.8	2.6	1.2	0.23	0.14	0.09	47	14	32	20	9	11
EF+2.5Al	0.71	12.6	7.8	4.7	3.9	2.5	1.3	0.24	0.14	0.10	49	15	34	21	11	10

Furthermore, the obtained results are presented in two kind of graphs: one in which the foulant concentration in the ultrafiltrate is given as a function of the foulant concentration in the feed water. Secondly, one in which the fouling rate (dR/dt) is given as a function of the amount of a measured foulant retained by the ultrafiltration membrane.

The maximum filtration resistance, $R_{max,th}$, was used in evaluating the process performance during ultrafiltration. By comparing the actual filtration resistance with the $R_{max,th}$ an indication was given of the range in which the system could be operated. At a flux of 28.5 L/m^2·h, as used in these experiments, the $R_{max,th}$ is calculated by equation 2.13. The feed water temperature in these experiments was roughly between 10 and 20 °C. Thus the values for $R_{max,th}$ are between $9.7 \cdot 10^{12}$ and $12.6 \cdot 10^{12}$ 1/m. At a flux of 40 L/m^2·h $R_{max,th}$ is $7.9 \cdot 10^{12}$ 1/m at 15 °C. If $R_{max,th}$ was reached in 1 hour, the fouling rate was extremely high. This meant in these experiments that the filtration resistance, R, at a flux of 28.5 L/m^2·h and 15 °C as mean feed water temperature was equal to $R_{max,th}$ and is $11.1 \cdot 10^{12}$ 1/m after 1 hour of filtration. A good filterability here is defined if the increase in filtration resistance to the $R_{max,th}$ was reached after 24 hours of filtration. In other words, the fouling rate, dR/dt, should be smaller than $0.43 \cdot 10^{12}$ 1/m·h.

In figures 4.8, 4.9, 4.10, 4.11 and 4.12 the results obtained of wwtp Hoek van Holland are presented. In figures 4.13, 4.14, 4.15, 4.16 and 4.17 the results obtained of wwtp Utrecht are shown.

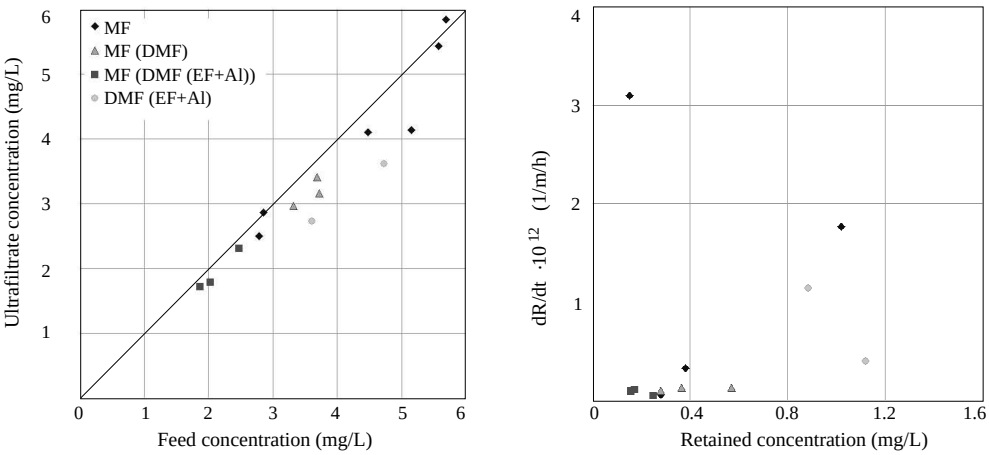

Figure 4.8: Relations between polysaccharide concentration in feed water and ultrafiltrate (left) and amount of polysaccharides retained and fouling rate (right) during ultrafiltration of Hoek van Holland wwtp effluent

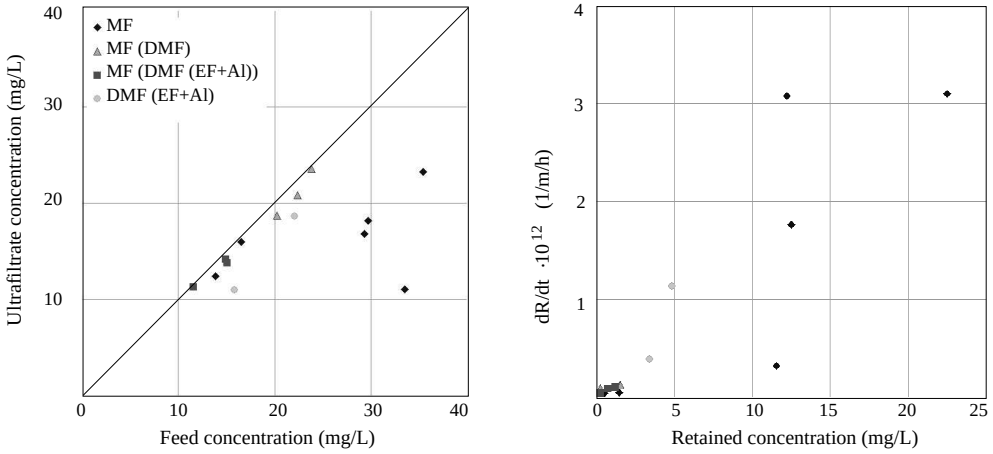

Figure 4.9: Relations between protein concentration in feed water and ultrafiltrate (left) and amount of proteins retained and fouling rate (right) during ultrafiltration of Hoek van Holland wwtp effluent

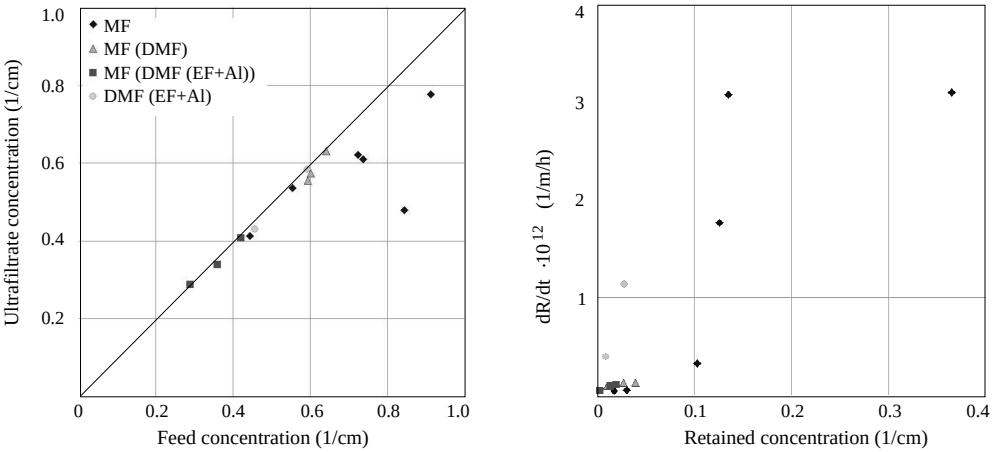

Figure 4.10: Relations between humic substance concentration in feed water and ultrafiltrate (left) and amount of humic substances retained and fouling rate (right) during ultrafiltration of Hoek van Holland wwtp effluent

In contrast to the results at wwtp Hoek van Holland, in case microfiltrate was used as feed water, no influence of the amount of the measured foulants retained on the fouling rate was found at wwtp Utrecht.

The relations between ultrafiltrate concentration and feed water concentration of a particular foulant, presented in the left graphs, show only in a few situations a partial removal of specific components.

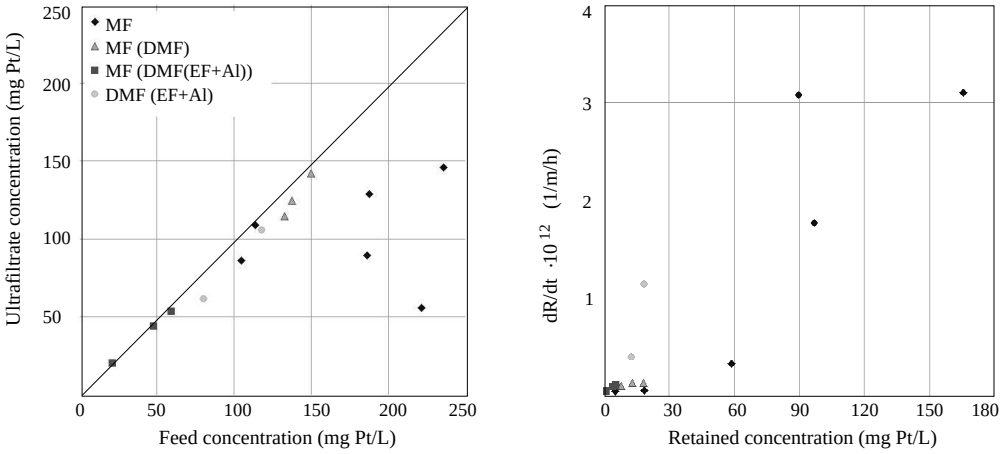

Figure 4.11: Relations between colour concentration in feed water and ultrafiltrate (left) and amount of colour retained and fouling rate (right) during ultrafiltration of Hoek van Holland wwtp effluent

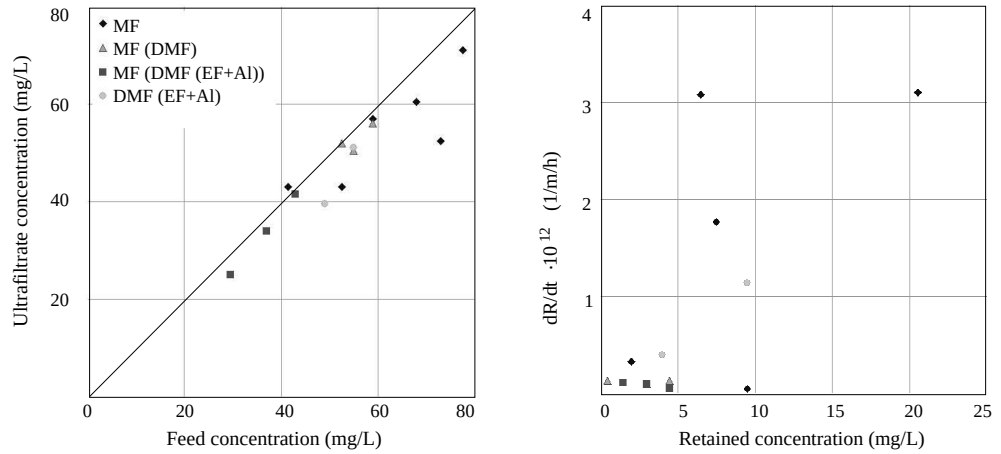

Figure 4.12: Relations between COD concentration in feed water and ultrafiltrate (left) and amount of COD retained and fouling rate (right) during ultrafiltration of Hoek van Holland wwtp effluent

At wwtp Hoek van Holland the results show that the amount of polysaccharides retained was 20 %; sometimes a higher amount of proteins retained was found (till 40 %), specially when MF was used as feed water; humic substances were retained in some cases in which proteins were retained as well and then colour was also retained. The amounts of measured potential foulants retained at wwtp Utrecht show rather simular results as found at wwtp Hoek van Holland; polysaccharides and proteins

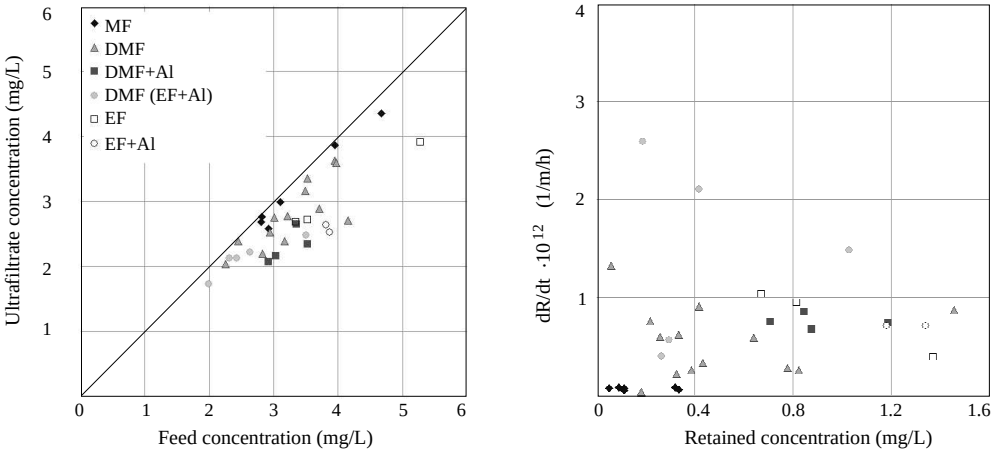

Figure 4.13: Relations between polysaccharide concentration in feed water and ultrafiltrate (left) and amount of polysaccharides retained and fouling rate (right) during ultrafiltration of Utrecht wwtp effluent

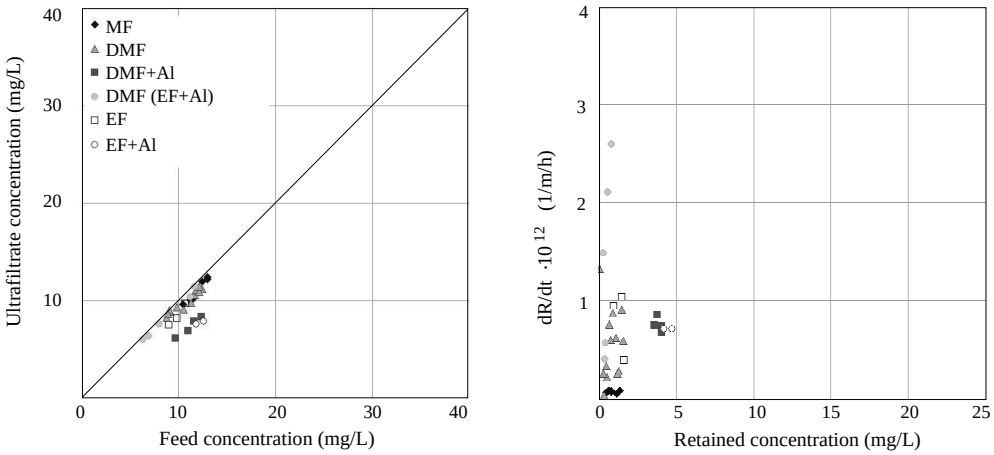

Figure 4.14: Relations between protein concentration in feed water and ultrafiltrate (left) and amount of proteins retained and fouling rate (right) during ultrafiltration of Utrecht wwtp effluent

were retained in some cases till 30 %; then also humic substances and colour were retained. In general, higher amounts of measured potential foulants retained were found when PACl was dosed prior to ultrafiltration.

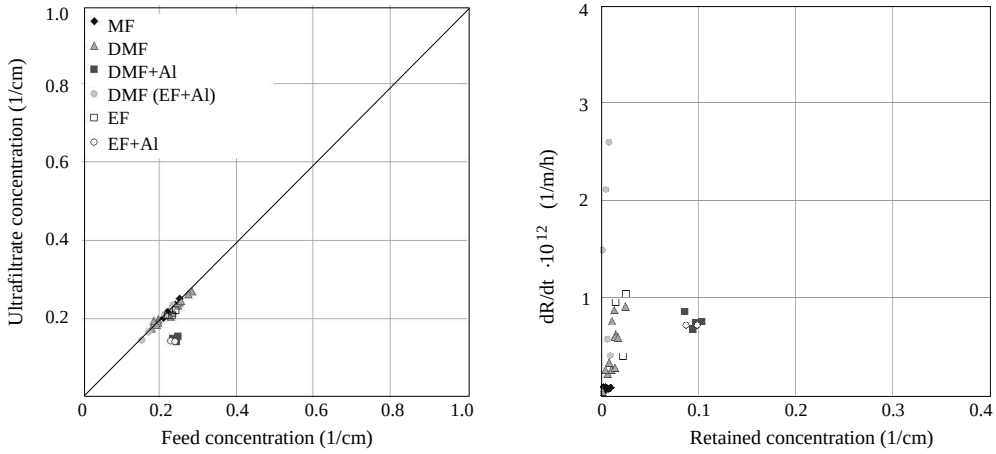

Figure 4.15: Relations between humic substance concentration in feed water and ultrafiltrate (left) and amount of humic substances retained and fouling rate (right) during ultrafiltration of Utrecht wwtp effluent

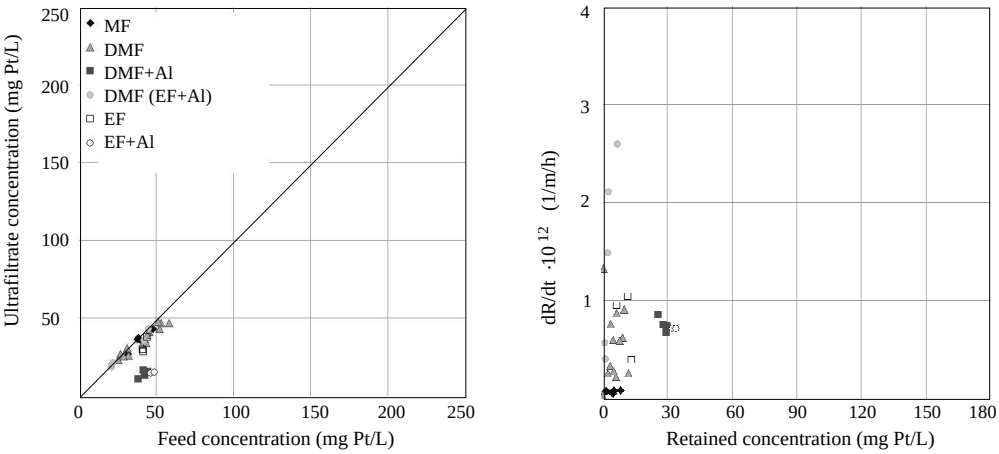

Figure 4.16: Relations between colour concentration in feed water and ultrafiltrate (left) and amount of colour retained and fouling rate (right) during ultrafiltration of Utrecht wwtp effluent

Polysaccharides

Polysaccharides were retained by the ultrafiltration membrane in relatively small concentrations: 0-1.5 mg/L. For all tested feed waters of both investigated wwtp's no relation was found between the amount of polysaccharides retained and the fouling rate.

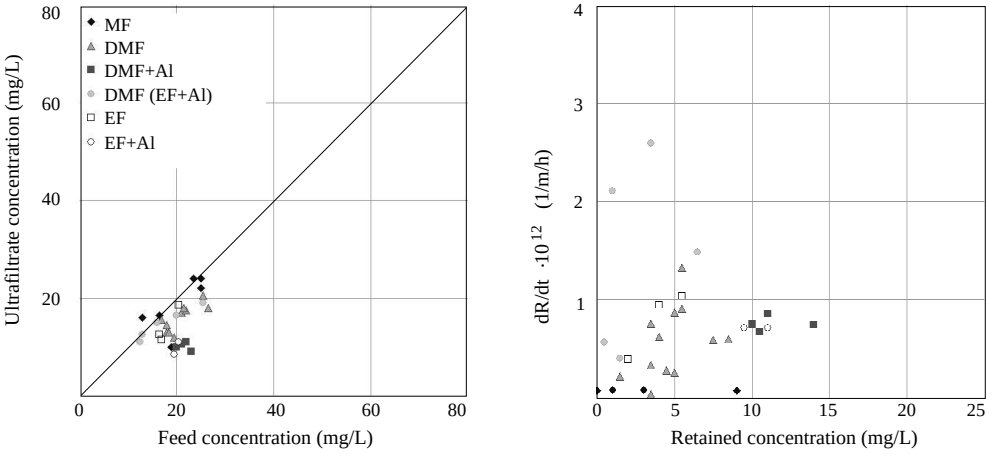

Figure 4.17: Relations between COD concentration in feed water and ultrafiltrate (left) and amount of COD retained and fouling rate (right) during ultrafiltration of Utrecht wwtp effluent

Proteins

The retained proteins by ultrafiltration was different at the two investigated wwtp locations. In case of wwtp Utrecht the amount retained was between 0-2 mg/L and increased when coagulant (PACl) was dosed to the feed water to 3-5 mg/L. The amount of proteins retained at wwtp Hoek van Holland was between 0-12 mg/L with an exception of 23 mg/L. For all tested feed waters of both investigated wwtp's no relation was found between the amount of proteins retained and the fouling rate. Nevertheless coagulation by PACl of the feed water influenced the amount of proteins retained and fouling rate: the amount retained increased whereby the fouling rate remained constant.

Humic substances

Small amounts of retained humic substances by ultrafiltration were found: 0-0.15 cm^{-1} at wwtp Hoek van Holland, 0-0.03 cm^{-1} at wwtp Utrecht and in case of coagulant (PACl) dosing the amounts of humic substances retained increased to 0.10 cm^{-1}. Only in case of wwtp Utrecht when DMF was used as feed water a relation could be derived between the amounts of humic substances retained and fouling rate, although the amounts retained were rather small.

Colour

Colour components are retained by the ultrafiltration membrane. At wwtp Hoek van Holland the amount of colour retained between were 0-100 mg Pt/L. Whereas at wwtp Utrecht the amount retained were between 0-20 mg Pt/L and could be increased by coagulant dosing (PACl) to 20-40 mg Pt/L. For both investigated wwtp's no relation

was found between the amount of colour retained and the fouling rate for all tested feed waters.

COD

The retained COD by the ultrafiltration membrane was found between 0-10 mg/L. When coagulant (PACl) was added to the feed water the amount of COD retained slightly increased to 10-15 mg/L. For all tested feed waters of both investigated wwtp's no relation was found between the amount of COD retained and the fouling rate.

4.2.3 Discussion pilot experiments

An overview of the obtained fouling rate per feed water type of wwtp Hoek van Holland is presented in table 4.11. Overall, microfiltration contributes to lower fouling rates. The highest fouling rates were obtained where DMF+Al was used as feed water at a flux of 40 L/m^2·h, which indicate a poor filterability since $R_{max,th}$ was reached within 1 hour. The lowest fouling rate, i.e. highest filterability, was found when MF(DMF(EF)) was used as feed water. Furthermore the fouling rate of DMF(EF+Al) and MF(EF) was rather high since dR/dt was in most cases larger than $0.43 \cdot 10^{12}$ 1/m·h.

Table 4.11: Summary of the fouling rate results of the different types of feed water applied at wwtp Hoek van Holland

Feed water	dR/dt ($\cdot 10^{12}$ 1/m·h)
MF(EF)	0.05 - 3
MF(DMF(EF))	0.04 - 0.1
MF(DMF(EF+Al))	0.1 - 0.13
DMF+4/5Al[a]	8 - 13
DMF(EF+Al)	0.4 - 1.1

[a]flux is 40 L/m^2·h

An overview of the obtained fouling rate per feed water type of wwtp Utrecht is presented in table 4.12. The lowest fouling rate was observed when MF was used as feed water. With the exception of one single measurement the fouling rate of DMF was low as well. For the feed waters DMF+Al, DMF(EF+Al), EF and EF+Al the fouling rate found was high, since dR/dt was in most cases larger than $0.43 \cdot 10^{12}$ 1/m·h.

These results indicate that particles and colloids need to be removed by multimedia filtration and microfiltration in order to increase the filterability, but pre-caution should be taken to introduce extra suspended solids as shown by DMF+Al and EF+Al as feed water.

In the pilot experiments the amount of measured foulants retained was independent of the feed water type i.e. microfiltrate, multimedia filtrate and wwtp effluent.

Table 4.12: Summary of the fouling rate results of the different types of feed water applied at wwtp Utrecht

Feed water	dR/dt ($\cdot 10^{12}$ 1/m·h)
MF	0.05 - 0.08
DMF	0.04 - 1.33
DMF+Al	0.67 - 0.86
DMF(EF+Al)	0.4 - 2.59
EF	0.4 - 1.04
EF+Al	0.71

However, these retained amounts were increased by addition of coagulant (PACl) to the feed water. By this the fouling rate for wwtp effluent as feed water decreased and for multimedia filtrate increased. Furthermore when microfiltrate was used as feed water no influence of the amount of measured foulants retained on the fouling rate was found at wwtp Utrecht, in contrast to at wwtp Hoek van Holland there was. In case of coagulant dosing, compared to the other measured foulants, the amount of colour retained was the highest.

In a study of Rosenberger et al. (2005), between two parallel operated membrane bioreactors a linear relation between fouling rate and polysaccharide concentrations of the sludge water phase was observed for both pilots at 8 days sludge retention time; for other sludge retention times no correlation could be observed. Compared to the results described in this chapter the concentration of polysaccharides in the water phase of the wwtp effluent was three times less and the fouling rate was a factor 1000 more. Here, only under certain process conditions with relative high polysaccharide concentration in the feed water phase and relative low fouling rates a correlation between fouling rate and polysaccharide concentration could be found.

4.3 Concluding remarks

In both lab scale and pilot scale experiments no clear relations between the filterability and amount of potential foulants retained: proteins, humic substances, colour and COD were found. The results of the pilot experiments revealed that particles and colloids are of large influence on the filterability. However, the results of the fractionation experiments showed that wwtp effluent constituents of size > 0.45 μm are of minor influence on the filterability. Thus, wwtp effluent constituents of size between 0.1 and 0.45 μm, which are defined as colloids, are found of major influence on the filterability during ultrafiltration.

These results were found in accordance to Laabs (2004). In her experiments organic colloids and polysaccharides accounted for the flux decline in stirred cell tests. In this research samples of feed water, permeate and retentate were analysed by size

exclusion chromatography using Liquid Chromatography - Organic Carbon Detection (LC-OCD). However, differences in the polysaccharide peaks between feed water (wwtp effluent) and permeate measured by the LC-OCD method could possibly be due to the contribution of polysaccharides originating from retained bacteria, since the feed water sample was pre-filtered over 2 μm instead of 0.45 μm as applied in this research. In addition no clear foulant as polysaccharides could be identified by the LC-OCD method, since so far it is not possible to discriminate between organic colloids and polysaccharides.

Nevertheless, a combination of fractionation and measuring potential foulants in these fractions gives a nice fingerprint of the filterability and leads to more insight in the filtration characteristics during ultrafiltration of wwtp effluent.

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Chapter 5

Conditioning methods

In the previous chapter relations between filtration properties and potential membrane foulants in ultrafiltration of wwtp effluent were subject of investigation. As a result of the laboratory fractionation experiments the size of wwtp effluent constituents was found to influence the filterability during ultrafiltration. Moreover, colloids were predominantly indicated. However, no clear relation between the filterability and amount of potential foulants retained could be determined. This displays that more information is needed for the interacting mechanisms during membrane fouling. Therefore the physical and chemical properties of wwtp effluent constituents are studied in this chapter by the following conditioning methods:

- pre-filtration,
- coagulation,
- temperature changes,
- pH changes.

Herewith the influence of the wwtp constituents and more specific potential membrane foulants at the feed side of the membrane on the filterability and in less extent the reversibility is investigated.

5.1 Pre-filtration of wwtp effluent

During ultrafiltration of wwtp effluent different sizes of constituents - particles, suspended solids, colloids, macro-molecules and dissolved components - are influencing the filterability, as described in section 4.1. By using pre-filtration techniques prior to ultrafiltration the influence of the size of the different wwtp effluent constituents on the filtration properties is investigated on pilot scale. Therefore sieving, multimedia filtration and microfiltration were applied as pre-filtration techniques. A detailed description of the used installations is given in section 2.4.2.

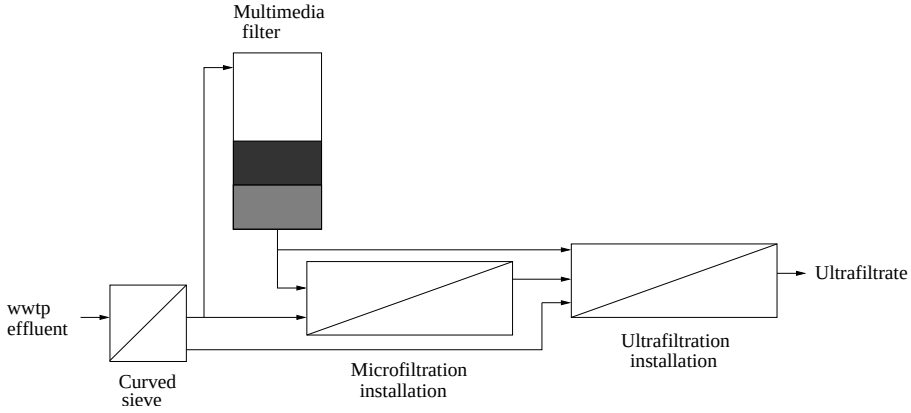

Figure 5.1: Scheme of the pilot plant at wwtp Hoek van Holland and Utrecht

Pilot plant studies regarding pre-filtration were performed at wwtp Hoek van Holland and Utrecht. A schematic overview of the used installations is presented in figure 5.1. By using a curved sieve with a mesh size of 0.45 mm the wwtp effluent constituents were smaller than 0.45 mm and thereby more comparable. Almost all suspended material and particles > 50 μm, Te Poele et al. (2003), and ≥ 90 % of the total particles in the size range 2-100 μm, Te Poele et al. (2004), are removed by multimedia filtration. The turbidity of the multimedia filtrate is usually below 2 NTU. The microfiltration membranes of Memcor used, had a pore size of 0.2 μm. Since the colloidal fraction is defined between 0.1 and 0.45 μm (section 3.1) a large part of the colloidal components were removed by microfiltration and therefore microfiltrate contains mostly macro-molecules and dissolved material. An indication of the different fractions formed by sieving, multimedia filtration and microfiltration is given in table 5.1

Table 5.1: Indication of the formed fractions by pre-filtration of wwtp effluent on pilot scale

Fraction (μm)	main wwtp effluent constituents
50 - 450	particles (settable material)
0.2 - 50	colloids and suspended material
< 0.2	macro-molecules and dissolved material

The obtained on-line data of the pilot ultrafiltration installation were analysed on the filterability and at wwtp Utrecht also on the reversibility. The filterability is expressed by the fouling rate, see section 2.1.2, which is determined as the mean value of three successive filtration intervals. The reversibility was calculated by the total resistance increase over time, $\Delta R/\Delta t$, comparing the filtration resistance at the beginning of two filtration periods over a certain time interval. Back washes are typically included in the reversibility calculations, whereas chemical cleaning is excluded.

In general, three types of resistances are important when analysing filtration data:

1. the membrane resistance of a new membrane, which depends on the membrane properties and is, for the used membrane, approximately $0.8 \cdot 10^{12}$ 1/m (CWF of 450 L/m^2·h·bar and feed water temperature of 20 °C),

2. the resistance at the start of the filtration period, which more or less depends on the feed water quality,

3. the maximum theoretical filtration resistance, $R_{max,th}$, which depends on the process conditions temperature and flux, and is calculated by equation 2.13.

5.1.1 WWTP Hoek van Holland

The first pre-filtration experiments were carried out during the pilot investigations at wwtp Hoek van Holland in the period of October 2002 to July 2003. The ultrafiltration installation was operated at a constant flux of 50 L/m^2·h with a filtration period of 15 minutes followed by a back flush during 100 seconds at a flow of 10 m^3/h, except in case that microfiltrate was used as feed water. Here the filtration period was set to 60 minutes followed by a back flush during 45 seconds at a flow of 17 m^3/h. The performance of a chemical cleaning depended on the used feed water. An overview of the different applied chemical cleaning methods is given in table 5.2.

Table 5.2: Performed chemical cleaning at wwtp Hoek van Holland

Feed	Chemical cleaning
sieved effluent	1 per 2 hours 200 mg/L NaOCl alternated by 1 per 2 hours 200 mg/L HCl; soaking time of 30 minutes
multimedia filtrate	1 per 2 hours 200 mg/L NaOCl; soaking time of 15 minutes
microfiltrate	none

Results

The filtration resistances during ultrafiltration of the sieved wwtp effluent, multimedia filtrate and microfiltrate are presented in figures 5.2, 5.3 and 5.4 respectively. In addition the temperature of the feed water is shown. The filterability was calculated after 11 hours of filtration, taking the last three filtration periods before chemical cleaning was applied. In table 5.3 the filterability, the maximum theoretical filtration resistance and feed water temperature is given.

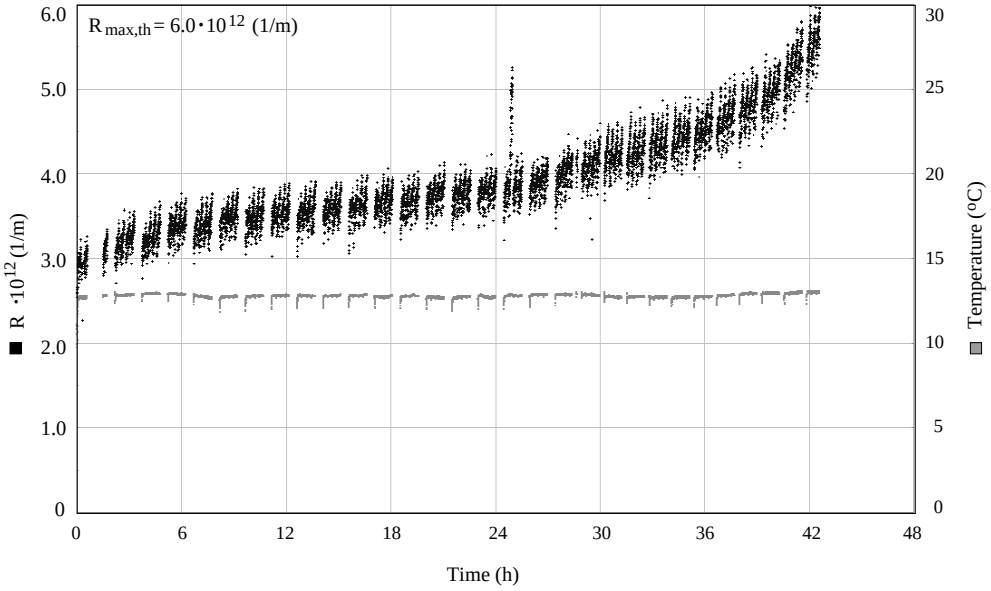

Figure 5.2: Filtration resistance during pilot ultrafiltration of sieved effluent of wwtp Hoek van Holland at a flux of 50 L/m^2·h

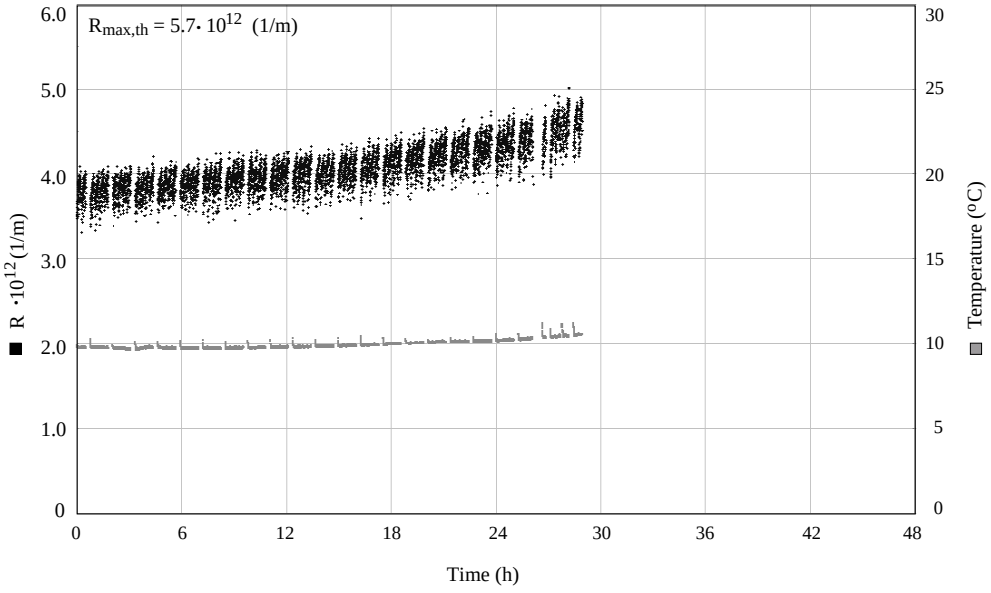

Figure 5.3: Filtration resistance during pilot ultrafiltration of multimedia filtrate at wwtp Hoek van Holland and a flux of 50 L/m^2·h

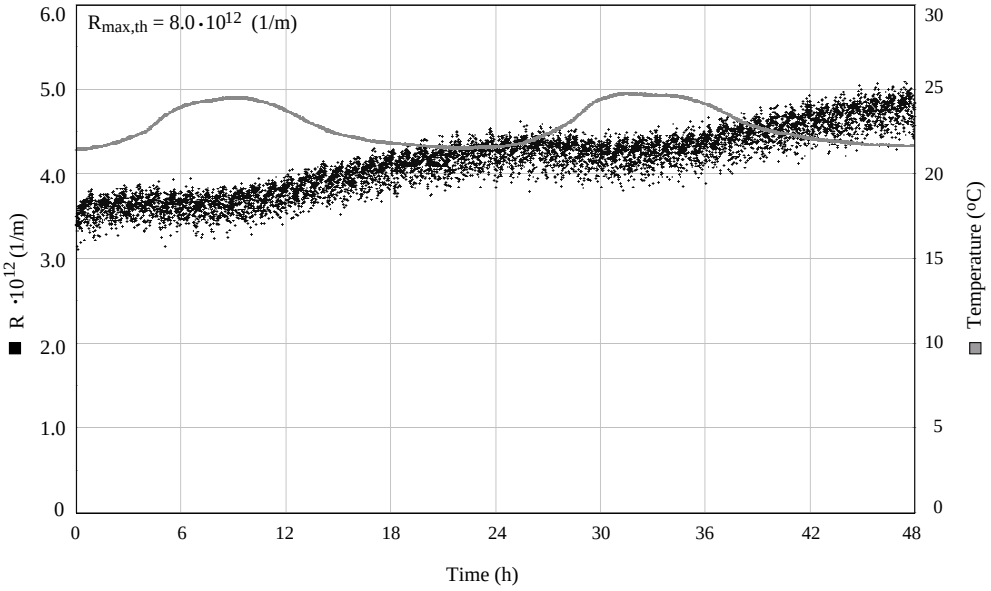

Figure 5.4: Filtration resistance during pilot ultrafiltration of microfiltrate at wwtp Hoek van Holland and a flux of 50 L/m^2·h

Table 5.3: Filterability of pre-filtered wwtp effluent during pilot ultrafiltration at wwtp Hoek van Holland, flux of 50 L/m^2·h

Feed		sieved wwtp effluent	multimedia filtrate	microfiltrate
dR/dt	($\cdot 10^{12}$ 1/m·h)	1.31 ± 0.08	1.00 ± 0.10	0.20 ± 0.04
Temperature	(°C)	9.7 - 13.1	9.6 - 11.2	21.4 - 24.7
$R_{max,th}$	($\cdot 10^{12}$ 1/m)	6.0	5.7	8.0

At the beginning of the filtration process the filtration resistance was between 3 and 4·10^{12} 1/m for the different applied feed waters. Taking into account the membrane resistance of a clean membrane (0.8·10^{12} 1/m) and the maximum theoretical filtration resistance. This indicates that the membranes were already fouled to a large extent. After 43 hours of ultrafiltration of sieved wwtp effluent the maximum theoretical filtration resistance under these specific process conditions was achieved. As a consequence the installation was shut down. As can be seen from the results presented in figures 5.2 and 5.3 the applied chemical cleaning was found not sufficient, since the filtration resistance increased further over time.

In general, a high filterability was found for low values of dR/dt. The results, presented in table 5.3, show that the filterability of microfiltrate as feed water was

significantly higher than for multimedia filtrate. The latter in its turn was higher than for sieved wwtp effluent.

Discussion

The small difference in filterability between sieved effluent of wwtp Hoek van Holland and multimedia filtrate indicated that a relatively small part of the filterability was influenced by particles. The largest increase in filterability was between multimedia filtrate and microfiltrate as feed water, suggesting that wwtp constituents between $\sim$ 50 - 0.2 μm and thus colloids and suspended material were of major influence on the filterability. Although the filtration period during ultrafiltration of microfiltrate was four times longer than for the other feed waters, the contribution of macro-molecules and dissolved material to the filterability was relatively low.

The applied flux in these experiments was relatively high, regarding the feed water temperature and thereby the maximum theoretical filtration resistance. It was not possible to operate the ultrafiltration installation with a stable process performance for a longer period of time ($>$ 48 hours), using wwtp effluent and multimedia filtrate as feed water and under the chosen process regimes.

Calculations of the reversibility were not carried out, since the intervals between two chemical cleanings were too short and therefore these calculations were judged not representative enough. In addition the applied back flush regimes differed between the used feed waters and therefore comparing results in reversibility was rather difficult.

5.1.2 WWTP Utrecht

The pre-filtration experiments were continued at wwtp Utrecht in the period of January 2004 to July 2004. Compared to wwtp Hoek van Holland more conservative process conditions were chosen in order to operate under stable process performance. The applied flux was lower than at wwtp Hoek van Holland and as a consequence higher values for maximum theoretical filtration resistance were obtained. The installation was operated at a constant flux of 28.5 L/m^2·h with a filtration period of 15 minutes followed by a back flush during 45 seconds at a flow of 17 m^3/h. In case sieved wwtp effluent and multimedia filtrate were used as feed water a chemical cleaning was applied once per 12 hours. The soaking time of the chemical cleaning was prolonged to 2.5 hours to increase the cleaning efficiency. An overview of the different applied chemical cleaning methods is given in table 5.4.

The multimedia filtrate used in this investigation was produced of sieved wwtp effluent with an addition of methanol. It is assumed that methanol had no influence on the filtration performance during ultrafiltration, since almost all dosed methanol was consumed by the denitrifying bacteria in the multimedia filter, Te Poele et al. (2004).

Table 5.4: Performed chemical cleaning at wwtp Utrecht

Feed	Chemical cleaning
sieved effluent	1 per 12 hours 1.25 %-w/w Divos 120Cl; soaking time of 2.5 hours
multimedia filtrate	1 per 12 hours 1.25 %-w/w Divos 120Cl alternated by 1 per 12 hours 0.18 %-w/w Divos 2; soaking time of 2.5 hours
microfiltrate	non

Results

In figures 5.5, 5.6 and 5.7 the filtration resistance during ultrafiltration of the sieved wwtp effluent, multimedia filtrate and microfiltrate respectively are presented together with the feed water temperature. The results show a stable process performance for all feed waters under the applied process conditions; the applied chemical cleaning was sufficient, although the applied acid cleaning after 25 hours during filtration of multimedia filtrate did not result in a decrease of the filtration resistance after cleaning.

In order to compare the filtration properties of the different applied feed waters, the filtration resistance of sieved wwtp effluent, multimedia filtrate and microfiltrate during the first 12 hours of ultrafiltration is illustrated in figure 5.8. The filterability was calculated after 11 hours of filtration, taking the last three filtration periods before chemical cleaning was applied. The reversibility was determined over the first 12 hours, comparing the filtration resistance at the beginning of the filtration periods. An overview of the obtained results is shown in table 5.5.

Table 5.5: Filtration properties of pre-filtered wwtp effluent during pilot ultrafiltration at wwtp Utrecht, flux of 28.5 L/m^2·h

Feed		sieved wwtp effluent	multimedia filtrate	microfiltrate
dR/dt	($\cdot 10^{12}$ 1/m·h)	1.31 ± 0.12	0.46 ± 0.13	0.08 ± 0.01
ΔR/Δt	($\cdot 10^{12}$ 1/m·h)	0.6	0.2	0.07
Temperature	(°C)	13.9 - 17.8	16.3 - 20.4	13.3 - 14.5
$R_{max,th}$	($\cdot 10^{12}$ 1/m)	11.9	12.7	10.9

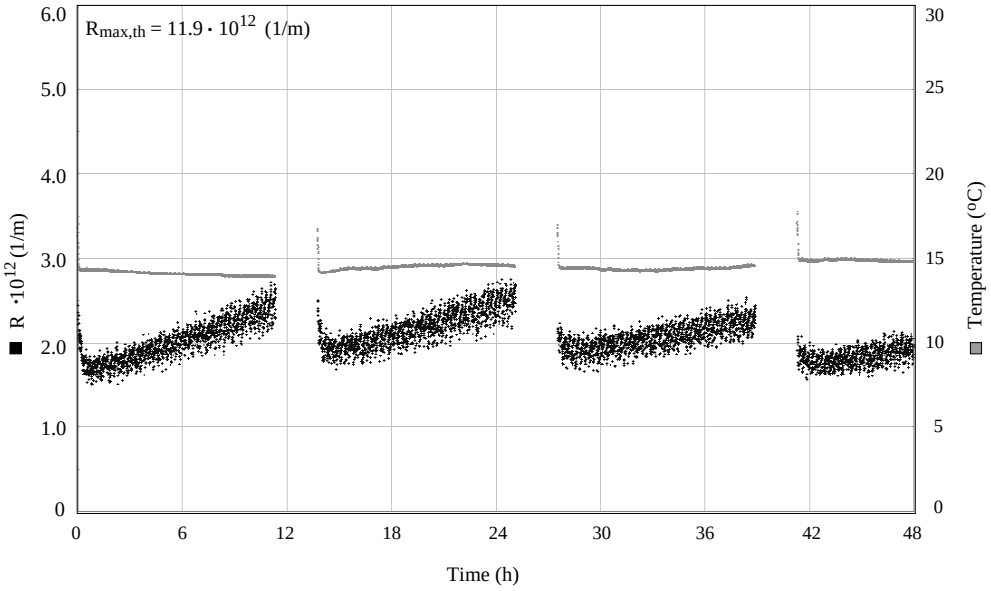

Figure 5.5: Filtration resistance during pilot ultrafiltration of sieved effluent of wwtp Utrecht and a flux of 28.5 L/m^2·h

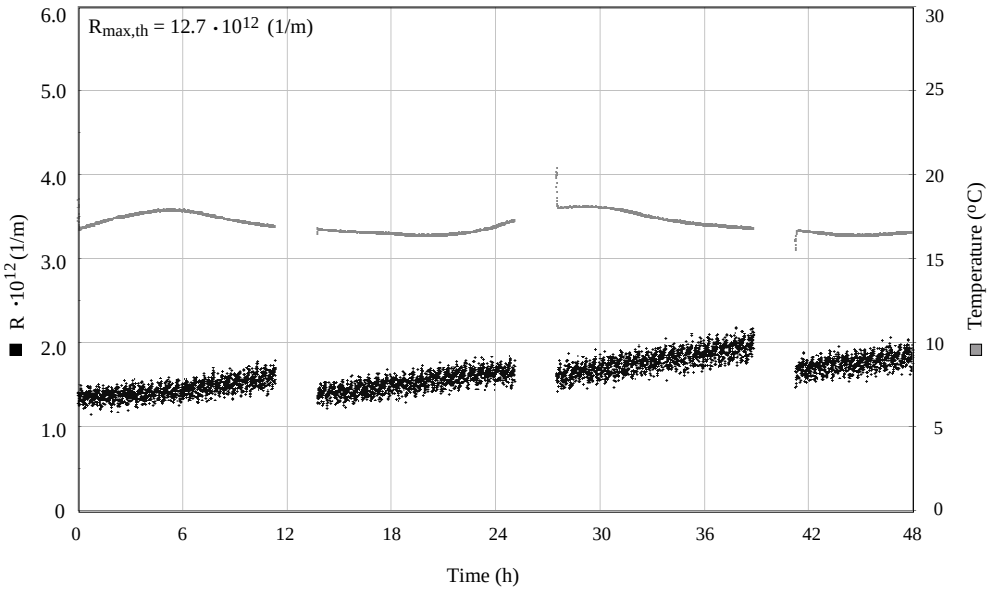

Figure 5.6: Filtration resistance during pilot ultrafiltration of multimedia filtrate of wwtp Utrecht and a flux of 28.5 L/m^2·h

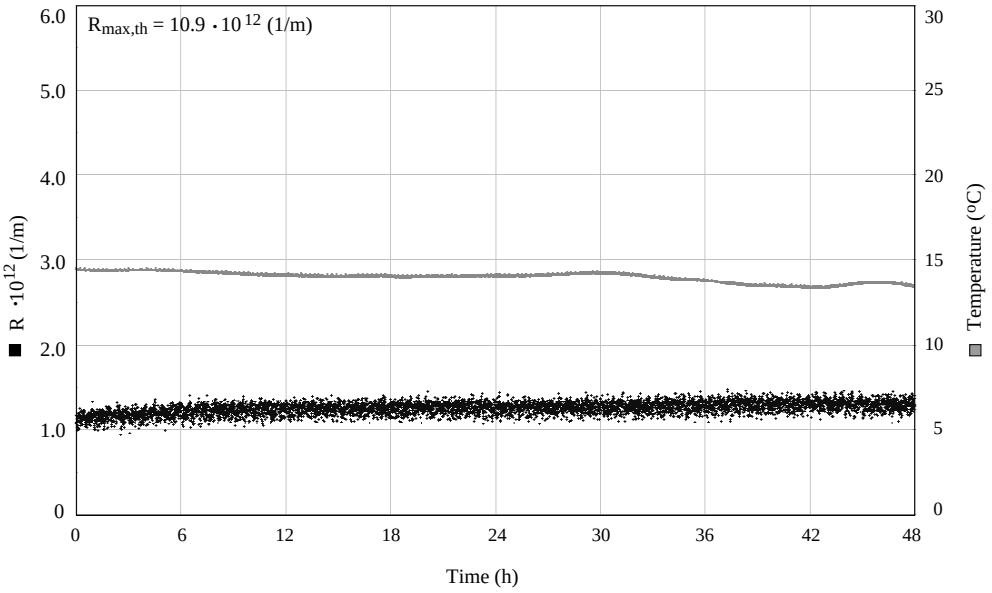

Figure 5.7: Filtration resistance during pilot ultrafiltration of microfiltrate at wwtp Utrecht and a flux of 28.5 L/m^2·h

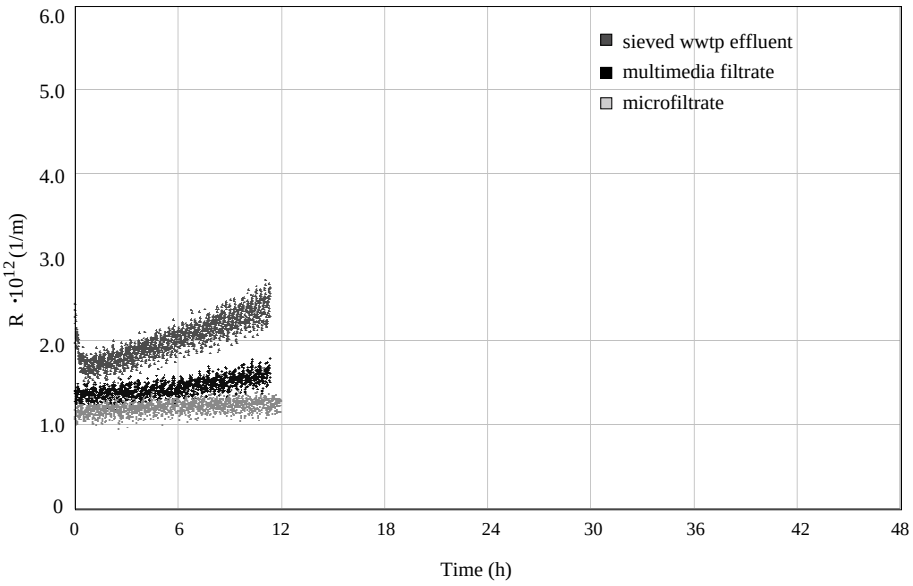

Figure 5.8: Filtration resistance during pilot ultrafiltration of sieved effluent, multimedia filtrate and microfiltrate and a flux of 28.5 L/m^2·h at wwtp Utrecht

The filterability and reversibility of microfiltrate as feed water were found significantly higher than for multimedia filtrate, which in its turn was significantly higher than for sieved wwtp effluent. With regard to the maximum theoretical filtration resistance, which depends on the feed water temperature and applied flux, both dR/dt and $\Delta R/\Delta t$ were relatively low for all applied feed waters. Looking at the resistance at the start of the filtration period it must be noted that the values found here (1.0-2.0 $\cdot 10^{12}$ 1/m) were lower than at wwtp Hoek van Holland (3.0-4.0 $\cdot 10^{12}$ 1/m).

Discussion

A significant increase in filterability and reversibility was found between sieved wwtp effluent and multimedia filtrate, suggesting that particles in the size range between $<$ 450 and $\sim$ 50 μm have a clear influence on both filterability and reversibility during ultrafiltration of sieved effluent at wwtp Utrecht. However, colloids and suspended solids revealed to be of even more influence on the filterability, based on the obtained relative differences in dR/dt of microfiltrate compared to multimedia filtrate and sieved wwtp effluent and multimedia filtrate. The results show that a good filterability goes hand in hand with a good reversibility.

5.1.3 Influence of the flux on filtration properties

In order to investigate the influence of the flux on the filtration properties, filtration experiments were performed at wwtp Hoek van Holland and Utrecht at different fluxes. Therefore microfiltrate was used as feed water and the ultrafiltration installation was first operated at a constant flux of 28.5 L/m^2·h with a filtration period of 1 hour followed by a back flush during 45 seconds at a flow of 17 m^3/h and without any chemical cleaning. At a filtration time of 170 hours the flux was increased to 50 L/m^2·h. In addition, at wwtp Utrecht the flux was decreased to 28.5 L/m^2·h after 265 hours of filtration.

Results

The filtration resistance and the feed water temperature during ultrafiltration of microfiltrate at wwtp Hoek van Holland and Utrecht are presented in figures 5.9 and 5.10 respectively. The results shows a stable process performance at a flux of 28.5 L/m^2·h, presented by a more or less constant filtration resistance over time. At the time the flux was increased to 50 L/m^2·h the filtration resistance showed a sharp rise ($\Delta R_{J28.5-50}$), which was followed by an upward trend. After the flux was decreased to 28.5 L/m^2·h at wwtp Utrecht, the filtration resistance first fell off and continued declining.

The filterability data calculated in sections 5.1.1 and 5.1.2 are used in this section. In addition at wwtp Hoek van Holland the filterability was calculated after 150 hours of filtration at a flux of 28.5 L/m^2·h over three successive filtration periods. Furthermore at wwtp Utrecht the filterability was calculated after 200 hours of filtration at a flux of 50 L/m^2·h over three successive filtration periods. The reversibility is

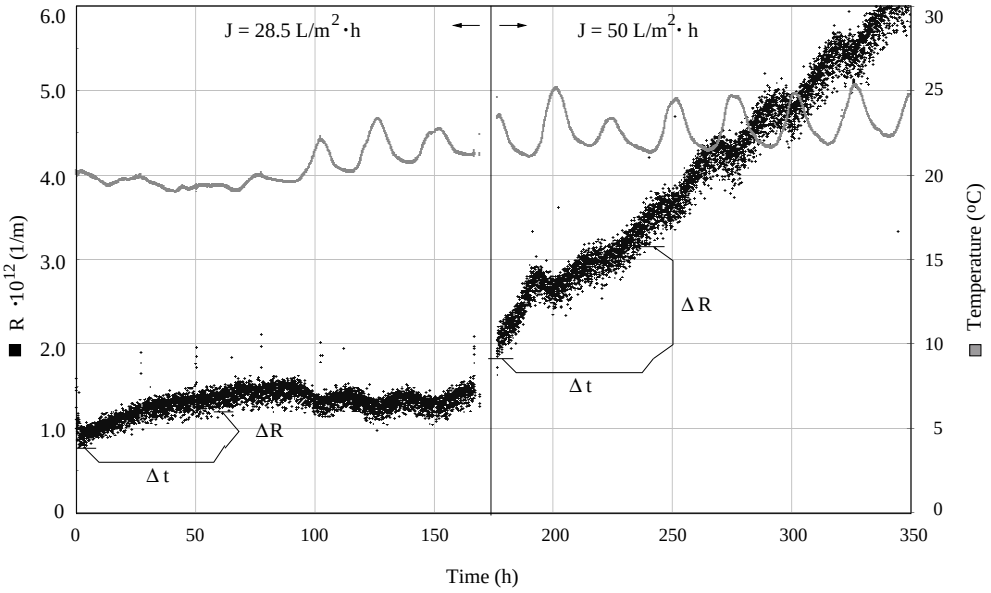

Figure 5.9: Influence of flux increase on the filtration resistance during pilot ultrafiltration of microfiltrate at wwtp Hoek van Holland

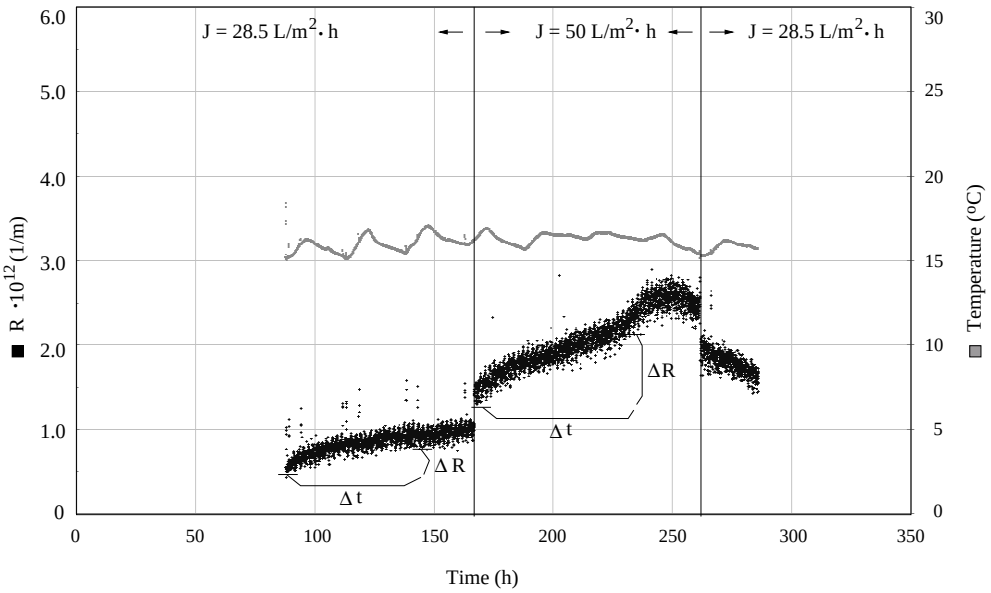

Figure 5.10: Influence of flux increase and decrease on the filtration resistance during pilot ultrafiltration of microfiltrate at wwtp Utrecht

determined over 60 hours, comparing the filtration resistance at the beginning of the filtration periods. The first filtration period started at 3 hours (flux of 28.5 L/m^2·h) and at 180 hours (flux of 50 L/m^2·h) at wwtp Hoek van Holland, and at wwtp Utrecht at 86 hours (flux of 28.5 L/m^2·h) and at 162 hours (flux of 50 L/m^2·h). An overview of the obtained results is shown in table 5.6.

Table 5.6: Filtration properties during pilot ultrafiltration of microfiltrate at two different fluxes

wwtp	Hoek van Holland		Utrecht	
Flux (L/m^2·h)	28.5	50	28.5	50
Temperature (°C)	19.0 - 25.5		14.5 - 22.4	
$R_{max,th}$ ($\cdot 10^{12}$ 1/m)	13.2	7.5	13.3	7.6
dR/dt ($\cdot 10^{12}$ 1/m·h)	0.06 ± 0.02	0.20 ± 0.04	0.08 ± 0.01	0.09 ± 0.01
ΔR/Δt ($\cdot 10^{12}$ 1/m·h)	0.42	1.26	0.43	0.76
$\Delta R_{J28.5-50}$ ($\cdot 10^{12}$ 1/m)	0.33		0.33	

The fouling rate at a flux of 28.5 L/m^2·h was almost equal for both wwtp's and was relatively low. After the flux was increased to 50 L/m^2·h the fouling rate remained almost constant at wwtp Utrecht, whereas at wwtp Hoek van Holland the value for dR/dt increased. The increase in flux resulted for both wwtp's in an instantaneous increase of the filtration resistance of 0.33 $\cdot 10^{12}$ 1/m. The results of ΔR/Δt were comparable for both wwtp's at a flux of 28.5 L/m^2·h. At both wwtp's the reversibility decreased, i.e. values for ΔR/Δt increased, after the flux was increased. In addition at wwtp Hoek van Holland the values for ΔR/Δt tripled and at wwtp Utrecht almost doubled.

Discussion

Based on the obtained results, the influence of the flux on the filterability was relatively small and was only shown to a small extent at wwtp Hoek van Holland. In contrast, the influence of the flux on the reversibility was significant, because the values for ΔR/Δt tripled at wwtp Hoek van Holland and at wwtp Utrecht almost doubled by an increase of the flux from 28.5 to 50 L/m^2·h. This can be explained by the larger amount of foulants passing along the membrane surface and therefore an increase of foulant adsorption can be expected. The resistance increase found directly after the flux increase from 28.5 to 50 L/m^2·h was maybe caused by a higher compressibility of the remained fouling. The latter could be explained by the higher amount of retained foulants due to the higher applied flux. Furthermore, increase of the flux from 28.5 to 50 L/m^2·h resulted in an unstable process performance, since the filtration resistance increased over time.

These results suggested that membrane fouling by macro-molecules and dissolved material depends on the applied flux, influencing the reversibility.

5.2 Coagulation by Poly Aluminium Chloride

In the production of drinking water coagulation of feed water as pre-treatment for ultrafiltration was investigated on pilot scale by several researchers, Doyen et al. (2002), Jang et al. (2002), Machenbach et al. (2002) and Minegishi et al. (2001). In all these studies the results showed a significant improvement in filtration performance and removal efficiency of dissolved organics. On the other hand in waste water treatment, coagulation was used as a chemical unit process for the removal of colloidal particles, Metcalf and Eddy (2003). By coagulation colloids are chemically destabilised and as a result particle growth can occur. Thereafter the formed particles can be removed by gravity sedimentation or by several filtration techniques. Overall, in ultrafiltration of wwtp effluent coagulation is suggested to have a positive effect as conditioning method on the filtration performance. In addition Shon et al. (2004) showed, in small filtration tests, that coagulation by $FeCl_3$ resulted in only a small flux decline and increased the removal efficiency of organic matter. However the dosage used was rather high, i.e. 40 mg Fe^{3+}/L. Furthermore, in previous pilot investigations, described in Roorda (2004), at wwtp Tilburg-Noord coagulation by 2 mg Al^{3+}/L PACl prior to ultrafiltration resulted in a stable process performance: flux of 100 L/m^2·h and TMP of 0.55 bar for one month.

In water treatment different types of coagulants are available and ferric chloride ($FeCl_3$), aluminium sulfate ($Al_2(SO_4)_3$), and poly aluminium chloride (PACl) are often used. A low pH decrease and the formation of more stable flocs are the advantages of PACl compared to aluminium sulfate. In addition the coagulation is less sensitive for low temperatures and larger removal efficiency for colour and humic substances are often obtained. Besides that lower concentrations of aluminium could be dosed in a broader pH range (6-9). In general, ferric chloride is less effective than aluminium sulfate, mainly in the reduction of NOM, but is more effective in a broader pH range (5-10) and high density flocs are formed. Research investigations conducted by Oschwald (2000) showed that ferric chloride is tending to form weak and fragile flocs, which are easy to break by shear forces occurring in filtration processes. When choosing a coagulant the advantages of PACl like short reaction time, formation of strong flocs and lower dosage concentrations should be balanced against the much lower costs of ferric chloride.

In this section the effect of coagulation by Poly Aluminium Chloride on the filterability and reversibility during ultrafiltration of wwtp effluent is studied more detailed.

5.2.1 Jar tests

A useful tool in choosing a coagulant type and concentration for specific process conditions is the jar test. The used jar test apparatus consisted of six beakers with a volume of 2 litres and stirrers, which could be adjusted under equally stirring conditions for all beakers. Coagulant was added simultaneously to all beakers. The applied mixing conditions depended on the process conditions of the investigated pilot plant. Coagulation and flocculation mixing was followed by sedimentation for 30

minutes. Thereafter the supernatant could be analysed for turbidity, pH, residual metal concentration and colour.

5.2.2 WWTP Emmtec

During the pilot investigations at the industrial wwtp Emmtec in the period of November 2001 to March 2002 filtration experiments were carried out to investigate the influence of in-line coagulation on the filterability and reversibility. The pilot plant consisted of a continuous sand filter of Astrasand (Paques Astraco), which was used as pre-treatment, followed by an ultrafiltration unit of Norit containing X-Flow membranes (UFC M5 0.8mm). Coagulant could be dosed in-line just before the feed water pump of the ultrafiltration installation. A schematic overview of this pilot is presented in figure 5.11. Jar tests were conducted to evaluate the coagulant type and dosage. As a result PACl was found to be a more effective coagulant than $FeCl_3$ at lower concentrations for removing turbidity and colour. The coagulant dosage was varied between 0, 2 and 4 mg Al^{3+}/L PACl.

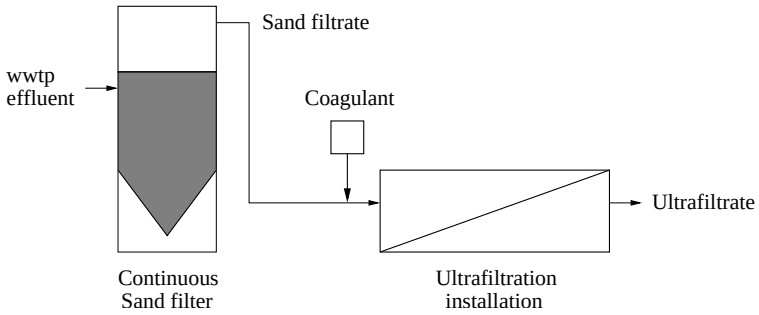

Figure 5.11: Scheme of the pilot plant at wwtp Emmtec

Methods

The feed water of the pilot was also used for filtration tests on lab scale. Filtration experiments were performed using the lab-scale test set-up, see figure 2.4. Instead of using a pressure vessel for the feed water supply, a peristaltic pump (Watson-Marlow 500 with a 505L low pulse and high accuracy peristaltic pump head) was used to operate at constant flux of 100 L/m^2·h. By this the obtained filtration curves could be compared with the on-line data obtained during the pilot experiments. The filtration period was 20 minutes on both lab scale and pilot scale. The filterability is expressed by the fouling rate, which was calculated as the slope of the resistance over time: dR/dt ($\cdot 10^{12}$ 1/m·h), see section 2.4.3. As feed water wwtp effluent and sand filtrate were used. In the laboratory 0, 2 and 4 mg Al^{3+}/L PACl was dosed to the feed water and mixed under simular conditions as in the pilot installation. The actual feed water of the pilot ultrafiltration installation at that time, which was coagulated sand filtrate by 2 mg Al^{3+}/L PACl, was tested as feed water as well. The filtration tests were carried out twice, whereby the feed water was collected on different days.

The fouling rate was calculated as mean value.

The pilot ultrafiltration installation was operated at a constant flux of 100 L/m^2·h with a filtration period of 20 minutes followed by a back flush during 30 seconds at 17 m^3/h. A chemical cleaning was applied once per 6 hours by 200 mg/L NaOCl alternated by once per 6 hours 200 mg/L Divos 2 with a soaking time of 10 minutes. The on-line data with regard to the filterability and reversibility was analysed. The filterability is expressed by the fouling rate, which was calculated as mean value of three successive filtration intervals. The reversibility was determined by the resistance increase over 4 hours, comparing the filtration resistance at the beginning of the filtration periods. As feed water (coagulated) sand filtrate was used by dosing 0, 2 and 4 mg Al^{3+}/L PACl.

Results

For the membrane type used the maximum TMP is 1 bar. At the process conditions applied: a flux of 100 L/m^2·h and a temperature of 20 °C, the maximum theoretical filtration resistance, $R_{max,th}$ was calculated by equation 2.13 and is 3.59 ·10^{12} 1/m.

The results of the laboratory filtration tests are presented in table 5.7. The fouling rate of the Emmtec wwtp effluent was a little higher than for sand filtrate and were relatively high compared to the maximum theoretical filtration resistance. Coagulation of this effluent reduced the fouling rate slightly, whereas coagulation of sand filtrate reduced the fouling rate significantly. Increasing the PACl dosage from 2 to 4 mg Al^{3+}/L didn't result in a lower fouling rate. The fouling rate of the actual feed of the pilot ultrafiltration installation at that time (sand filtrate and 2 mg Al^{3+}/L) is comparable with the fouling rate of coagulated sand filtrate by 2 mg Al^{3+}/L PACl and were relatively low compared to the maximum theoretical filtration resistance.

Table 5.7: Filterability of coagulated effluent and sand filtrate of wwtp Emmtec measured by laboratory filtration tests

Feed water	dR/dt (·10^{12} 1/m·h)
Effluent	1.47 ± 0.21
Effluent + 2 mg Al^{3+}/L	1.25 ± 0.31
Effluent + 4 mg Al^{3+}/L	1.31 ± 0.08
Sand filtrate	1.29 ± 0.18
Sand filtrate + 2 mg Al^{3+}/L	0.52 ± 0.04
Sand filtrate + 4 mg Al^{3+}/L	0.77 ± 0.18
Actual feed pilot (sand filtrate + 2 mg Al^{3+}/L)	0.47 ± 0.20

In table 5.8 the results of the filterability obtained from the on-line data of the pilot ultrafiltration installation are given. In-line coagulation by PACl resulted in a small

Table 5.8: Filterability of coagulated sand filtrate by PACl during pilot ultrafiltration at wwtp Emmtec

Feed	dR/dt ($\cdot 10^{12}$ 1/m·h)
Sand filtrate	0.64 ± 0.03
Sand filtrate + 2 mg Al^{3+}/L	0.52 ± 0.00
Sand filtrate + 4 mg Al^{3+}/L	0.43 ± 0.01

decrease of the fouling rate. The fouling rate of the (coagulated) sand filtrate were relatively low compared to the maximum theoretical filtration resistance. An overview of the results of both laboratory filtration tests and the on-line data is illustrated in figure 5.12. The obtained results show significant differences in fouling rate between the lab scale filtration tests and on-line data of the pilot installation. The sample of sand filtrate collected for the lab-scale filtration tests had been taken in the same period as the analyses of the on-line pilot data. Unfortunately, no explanation could be found for the difference in results. In contrast, the fouling rate of sand filtrate and 2 mg Al^{3+}/L obtained during the lab scale filtration and on-line data of the pilot are in good agreement.

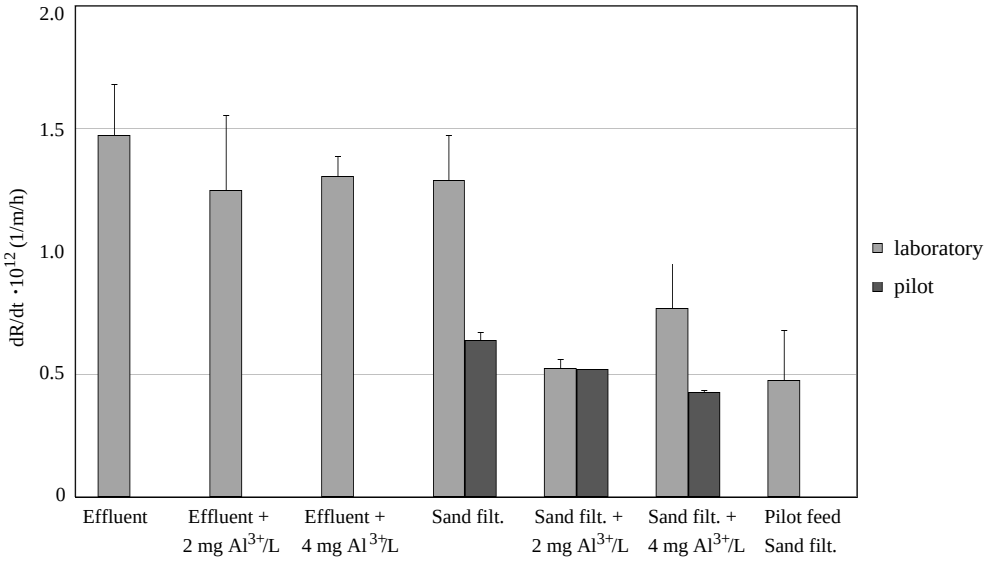

Figure 5.12: Filterability of coagulated effluent and sand filtrate of wwtp Emmtec measured on both lab-scale and pilot scale

In figures 5.13 and 5.14 the filtration resistance during pilot ultrafiltration is presented. The filtration started with sand filtered water that was coagulated with 2 mg Al^{3+}/L PACl. When the coagulant dosage was stopped, figure 5.13, the filtration resistance increased over time and the back flush was no longer sufficient. In case the

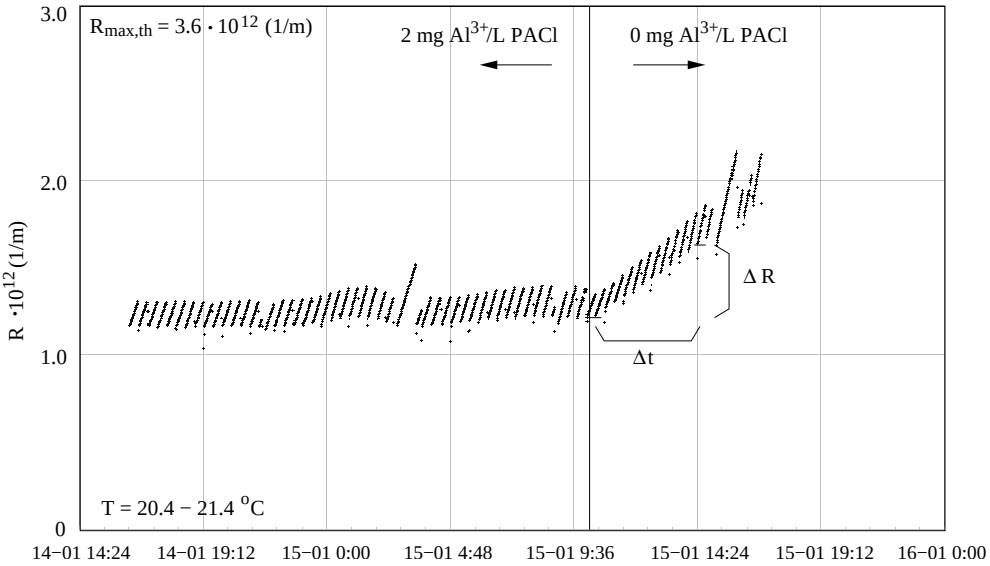

Figure 5.13: Filterability and reversibility of coagulated sand filtrate by 0 and 2 mg Al^{3+}/L PACl during pilot ultrafiltration tests at wwtp Emmtec

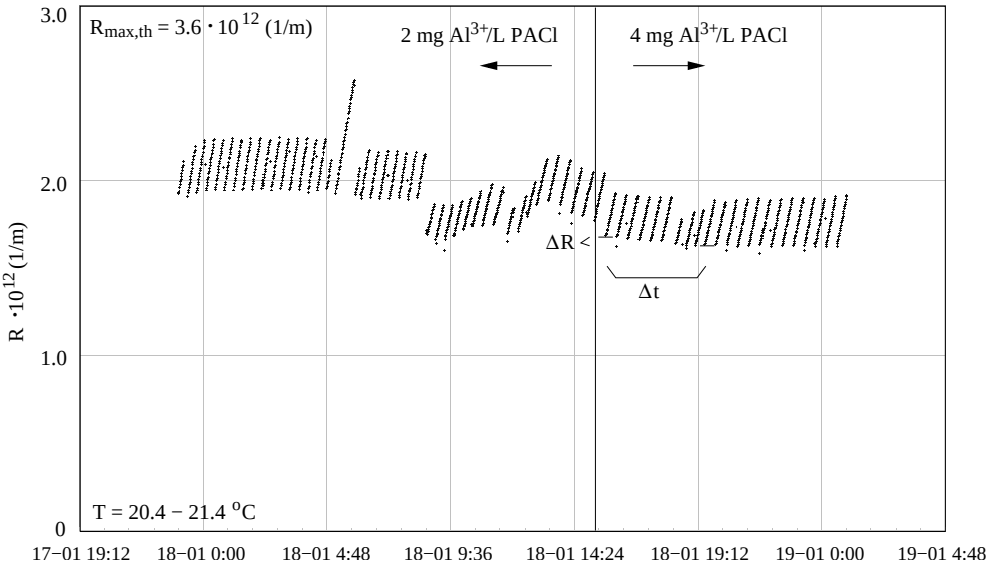

Figure 5.14: Filterability and reversibility of coagulated sand filtrate by 2 and 4 mg Al^{3+}/L PACl during pilot ultrafiltration tests at wwtp Emmtec

coagulant dosage was increased to 4 mg Al^{3+}/L PACl, 5.14, the filtration resistance decreased slightly over time. In general, if $\Delta R/\Delta t$ is 0, the filtration process is con-

sidered to be completely reversible. The results are presented in table 5.9. In case no coagulant was dosed to the sand filtrate $\Delta R/\Delta t$ was $0.4 \cdot 10^{12}$ 1/m.

Table 5.9: Reversibility of (coagulated) sand filtrate by PACl during pilot ultrafiltration at wwtp Emmtec

Feed	$\Delta R/\Delta t$ ($\cdot 10^{12}$ 1/m·h)
Sand filtrate	0.4
Sand filtrate + 2 mg Al^{3+}/L	0.0
Sand filtrate + 4 mg Al^{3+}/L	- 0.05

5.2.3 WWTP Hoek van Holland

In addition to the pre-filtration experiments at wwtp Hoek van Holland, as described in section 5.1, pilot experiments were performed to investigate the influence of coagulation on the process performance during ultrafiltration. As feed water multimedia filtrate was used. Coagulant was dosed in-line prior to ultrafiltration. Because of the low temperature ($\sim$ 10 °C) of the feed water and the formation of stronger flocs compared to $FeCl_3$, PACl was used as coagulant. The used concentration was 2 mg Al^{3+}/L. The ultrafiltration installation was operated at a constant flux of 50 L/m^2·h with a filtration period of 15 minutes followed by a back flush during 100 seconds at a flow of 10 m^3/h. A chemical cleaning was performed every hour with 200 mg/L NaOCl with a soaking time of 15 minutes.

Results

The filtration resistance during ultrafiltration of (coagulated) multimedia filtrate and feed water temperature at wwtp Hoek van Holland are presented in figure 5.15. During the first 26 hours no coagulant was dosed and the filtration resistance increased over time, in spite of applied chemical cleanings. After 26 hours of filtration PACl was dosed in-line with a concentration of 2 mg Al^{3+}/L. As a result the filtration resistance declined and decreased further over time.

Table 5.10: Filterability of (coagulated) multimedia filtrate during pilot ultrafiltration at wwtp Hoek van Holland, flux of 50 L/m^2·h

PACl concentration		0 mg Al^{3+}/L	2 mg Al^{3+}/L
dR/dt	($\cdot 10^{12}$ 1/m·h)	1.34 ± 0.25	1.25 ± 0.25

The filterability was calculated after 11 hours of filtration, taking the last three filtration periods before chemical cleaning. The results are presented in table 5.10. The feed water temperature was between 9 and 13 °C and the maximum theoretical filtration resistance, $R_{max,th}$, was $6.08 \cdot 10^{12}$ 1/m. Here, the reversibility was not

calculated, because of the frequently applied chemical cleaning and therefore calculations are considered not be representative enough. The filterability of (coagulated) multimedia filtrate was relatively high. Coagulation by PACl did not result in a significant change in of the fouling rate, but the efficiency of the chemical cleaning increased, indicated by the decrease of filtration resistance over time.

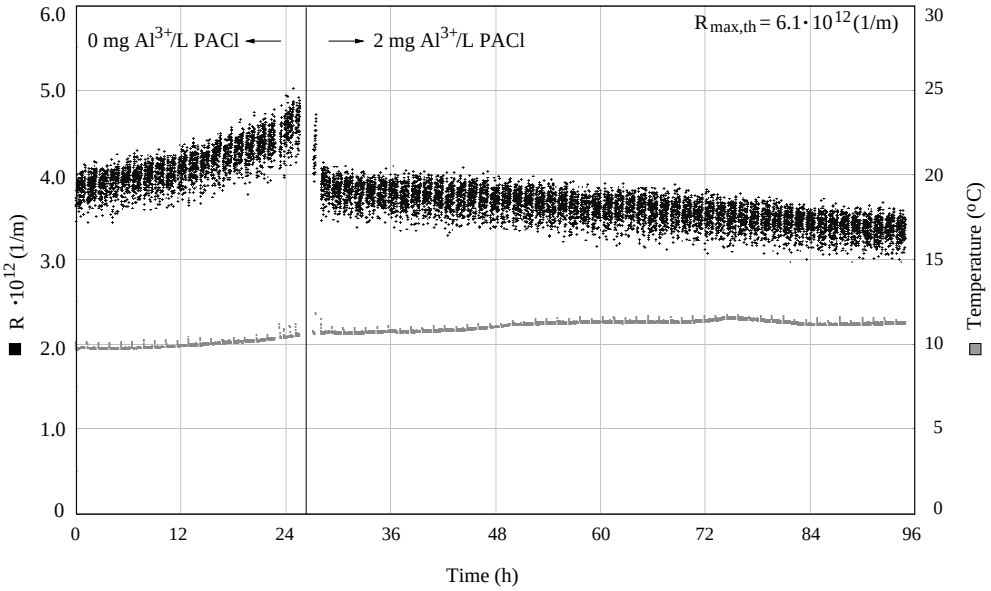

Figure 5.15: Filtration resistance during pilot ultrafiltration of (coagulated) multimedia filtrate of wwtp Hoek van Holland at a flux of 50 L/m^2·h

5.2.4 WWTP Utrecht

At wwtp Utrecht the pilot investigations, see section 5.1.2, were continued and here the influence of coagulation on the filtration properties during ultrafiltration was studied as well. In figure 5.16 a schematic drawing of the pilot plant is given.

As feed water sieved wwtp effluent was used. Coagulant was dosed in a tube flocculater, which was placed prior to the ultrafiltration installation. Jar tests were performed to select between PACl and $FeCl_3$ as coagulant. The results showed no floc formation and high residual metal concentration for $FeCl_3$ in contrast to PACl. Therefore PACl was selected as coagulant and the optimal dosage was found to be 2.5 mg Al^{3+}/L. The ultrafiltration installation was operated at a constant flux of 28.5 L/m^2·h with a filtration period of 15 minutes followed by a back flush during 45 seconds at a flow of 17 m^3/h. A chemical cleaning was performed every 12 hours with 1.25 %-w/w Divos 120 Cl alternated by once per 12 hours with 0.18 %-w/w Divos 2.

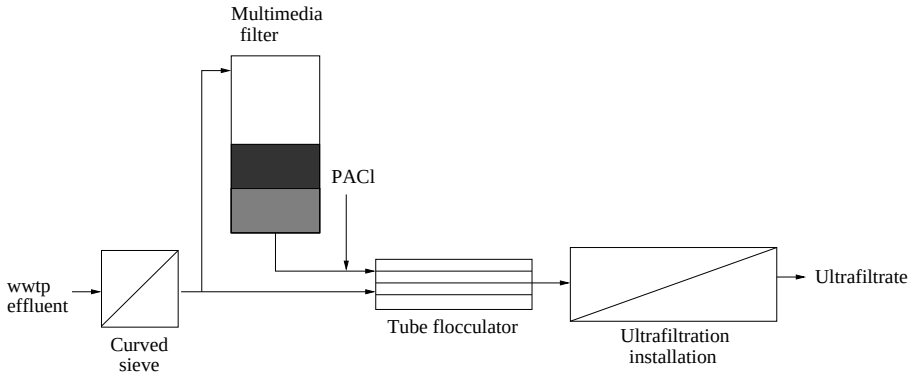

Figure 5.16: Scheme of the pilot plant at wwtp Utrecht

Results

In figure 5.17 the filtration resistance and feed water temperature during ultrafiltration of (coagulated) sieved effluent at wwtp Utrecht is presented. In the first 45 hours of filtration no coagulant was dosed. In this period the results show an increase in filtration resistance between the chemical cleanings. The applied chemical cleanings revealed to be sufficient enough, since the overall filtration resistance over the first 45 hours of filtration remained below $3.0 \cdot 10^{12}$ 1/m. The dosage of 2.5 mg Al^{3+}/L PACl was started after 45 hours of filtration. As a result the filtration resistance declined and decreased further over time. The applied chemical cleaning did not result in a further decline in filtration resistance.

After 11 hours of filtration the filterability was calculated as mean value over three successive filtration periods. In addition the reversibility was determined over the first 12 hours of filtration and after that the coagulant dosing was started over the next 12 hours before a chemical cleaning was applied. The results of the filtration properties are summarised in table 5.11. The feed water temperature was between 14.6 and 20.1 °C and the maximum theoretical filtration resistance, $R_{max,th}$ was $12.62 \cdot 10^{12}$ 1/m. With regard to $R_{max,th}$, dR/dt and $\Delta R/\Delta t$ were relatively low with respect to $R_{max,th}$. The results show a significant increase of both filterability and reversibility after the coagulation by PACl was started.

Table 5.11: Filtration properties of (coagulated) sieved effluent during pilot ultrafiltration at wwtp Utrecht, flux of 28.5 L/m^2·h

PACl concentration		0 mg Al^{3+}/L	2.5 mg Al^{3+}/L
dR/dt	($\cdot 10^{12}$ 1/m·h)	1.20 ± 0.26	0.76 ± 0.05
$\Delta R/\Delta t$	($\cdot 10^{12}$ 1/m·h)	0.34	- 0.10

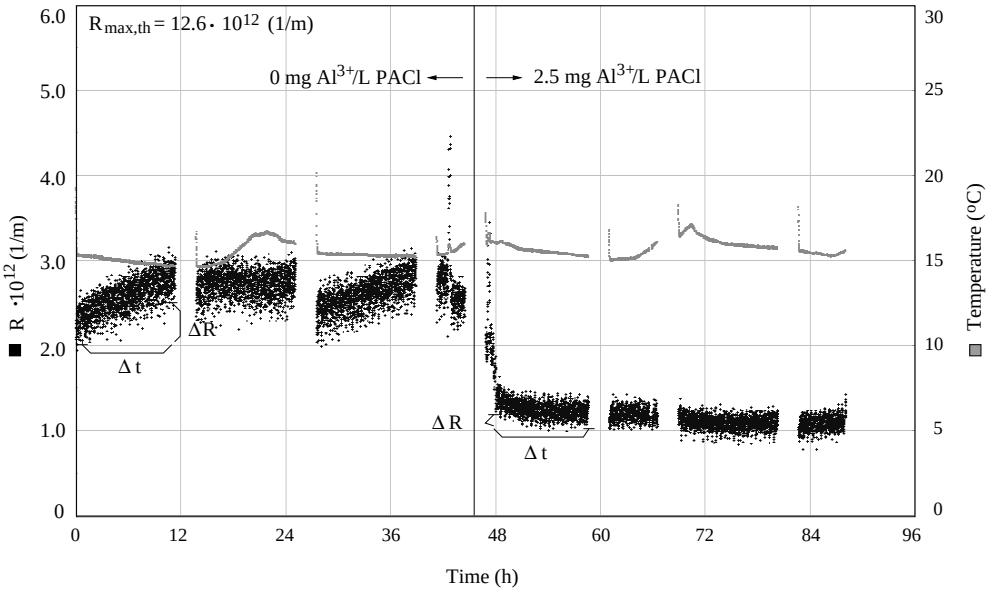

Figure 5.17: Filtration resistance during pilot ultrafiltration of (coagulated) sieved wwtp effluent of wwtp Utrecht at a flux of 28.5 L/m^2·h

5.2.5 Discussion

The effect of PACl coagulation on the filtration performance is simular for the three pilot installations investigated at different wwtp's. The influence of PACl coagulation on the filterability was rather small, since the fouling rate remained more or less the same. In contrast the effect of PACl coagulation on the reversibility revealed to be significant, since the results show a small increase of filtration resistance over time despite of applied back flushes.

The influence of on-line coagulation on the filtration performance of (semi) dead-end ultrafiltration was also subject of the studies performed by Doyen et al. (2002) and Qin et al. (2004). The optimal Alum dosage during ultrafiltration of wwtp effluent was studied by Qin et al. (2004) in pilot experiments (X-Flow membranes (UFC M5 0.8mm), flux of 70 L/m^2·h, filtration period of 20-30 minutes). As a consequence of reducing the coagulant dosage to 0.6 mg Al^{3+}/L, the TMP increased rapidly. The results showed an optimal dosage of 2.5 mg Al^{3+}/L. This level of coagulant was critical for the formation of flocs that gradually cumulated on the membrane surface and could easily be removed by a back wash. Doyen et al. (2002) investigated in-line coagulation with $FeCl_3$ in the semi dead-end ultrafiltration of surface water. During pilot studies (X-Flow membranes (UFC M5 0.8mm), flux of 100 L/m^2·h, filtration period of 60 minutes, 0.7 mg Fe^{3+}/L $FeCl_3$) they found simular results once the dosing was stopped: a sharp rise of the TMP in time. From these results it was concluded that cake layers formed with coagulation of $FeCl_3$ were less prone to adhere to the mem-

brane surface. In addition, from filtration tests they observed that by using $FeCl_3$ the cake layer thickness as well as the cake porosity was much higher.

The results of the pilot experiments by Doyen et al. (2002) and Qin et al. (2004) displays comparable effects of the reversibility of the formed cake layer during in-line coagulation of PACl to sand filtrate. Therefore it is suggested that the formed cake layer by PACl coagulation prevents sand filtrate constituents (colloids and suspended solids) to interact with the membrane surface, since this cake layer can easily be removed by a back wash.

5.3 Temperature

In order to investigated the relation between filterability and temperature, filtration test were performed of wwtp effluent at different temperatures. First the effect of large temperature changes on the wwtp effluent constituents and the filterability is studied. In addition the effect of these temperature changes on the membrane properties is investigated.

In the graphs presented in section 5.1 and 5.2 the temperature and filtration resistance during ultrafiltration is given. In figures 5.4 and 5.9 the filtration resistance show a inversely relation with the temperature. However, in figures 5.6 and 5.10 this relation is not shown at all. Therefore, the relation between filterability and temperature is investigated in more detail in this section.

5.3.1 Methods

The effluent used in these experiments was sampled at wwtp Berkel. The filterability was measured by the SUR, using the lab scale test set-up as described in section 2.3.1. First the SUR was measured of the feed water at initial temperature (raw feed water). Then the temperature of the feed was set to 30, 60 or 90 °C and kept constant by a water bath (conditioned feed water). A second SUR measurement was performed at this temperature. Thereafter the temperature of the feed water was reset to the initial temperature (restored feed water) and again the SUR of this feed water was measured. These filtration experiments were performed only once. For each filterability measurement with wwtp effluent as feed water a new membrane module was used, since the influence of temperature changes on the membrane properties were not known. When demineralised water was used as feed water one membrane module was used for the three successively performed SUR measurement to investigate the influence of temperature changes on the membrane properties.

A second set of filtration tests was carried out whereby the SUR of wwtp effluent was measured at different temperatures. The tested temperatures were 5, 10, 14, 20, 25 and 30 °C, based on the temperature of wwtp effluent that could occur in practice. The temperature was kept constant by a water bath during the SUR measurement. For these filtration tests one membrane module is used. After each SUR measurement

the membrane module was cleaned by circulating a solution of 1.25 %-w/w Divos 120 Cl for 10 minutes along the membrane surface to obtain a CWF simular to the CWF at the start of the measurement. This experiment was repeated five times. In table 5.12 an overview of the performed experiments on temperature conditioning is given.

Table 5.12: Overview of the filtration experiments on temperature conditioning

Experiment	Feed water	Temperature change	Initial temperature
1	effluent	30, 60 and 90 °C	13 °C
2	demiwater	30, 60 and 90 °C	22 °C
3	effluent	5, 10, 14, 20, 25 and 30 °C	14 °C

5.3.2 Results

In table 5.13 the results of experiment 1 and 2 are summarised and are presented in figures 5.18 and 5.19 respectively.

Table 5.13: Results of the filtration experiments on temperature conditioning to 30, 60 and 90 °C

Feed water	SUR ($\cdot 10^{12}$ 1/m^2)		
	Raw	Conditioned	Restored
wwtp effluent			
30 °C	14.9	18.3	14.6
60 °C	11.8	60.7	18.7
90 °C	10.9	75.0	8.4
demineralised water			
initial	0.3		
30 °C		-11.2	-10.3
60 °C		6.7	1.0
90 °C		7.1	1.1

In general, if the SUR value is $\leq 10 \cdot 10^{12}$ 1/m^2 the filterability is considered as high. The results show high SUR values for raw, temperature conditioned and restored wwtp effluent. Except for the restored wwtp effluent after temperature conditioning of 90 °C. The SUR values of conditioned wwtp effluent show a sharp rise with increasing conditioning temperature. After the temperature of the feed water was restored to the initial value, the SUR value of the restored effluent was found equal in case of temperature conditioning to 30 °C, increased in case of temperature conditioning to 60 °C and slightly decreased in case of temperature conditioning to 90 °C compared to the raw feed water. This indicates that the temperature changes resulted in changes in the filterability of the wwtp effluent.

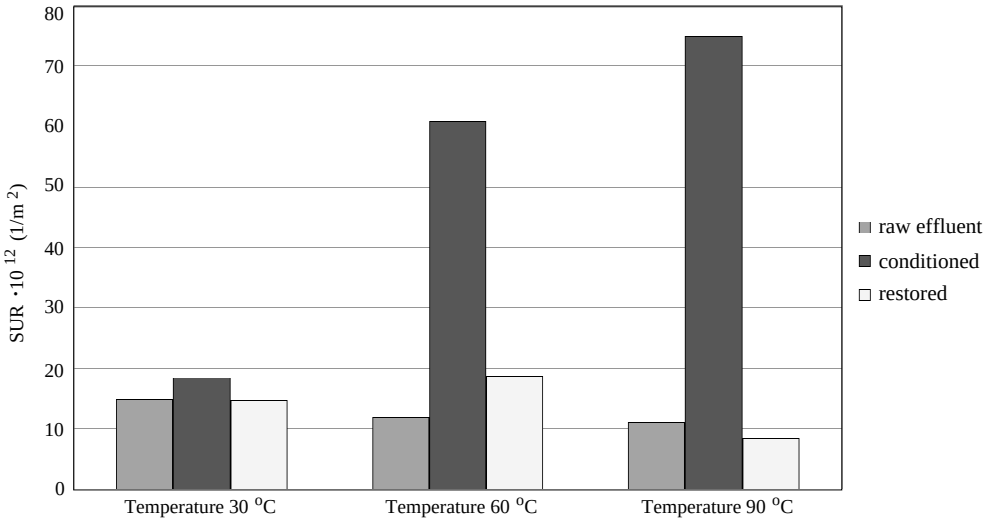

Figure 5.18: Results of SUR measurements of temperature conditioned, restored and raw effluent of wwtp Berkel

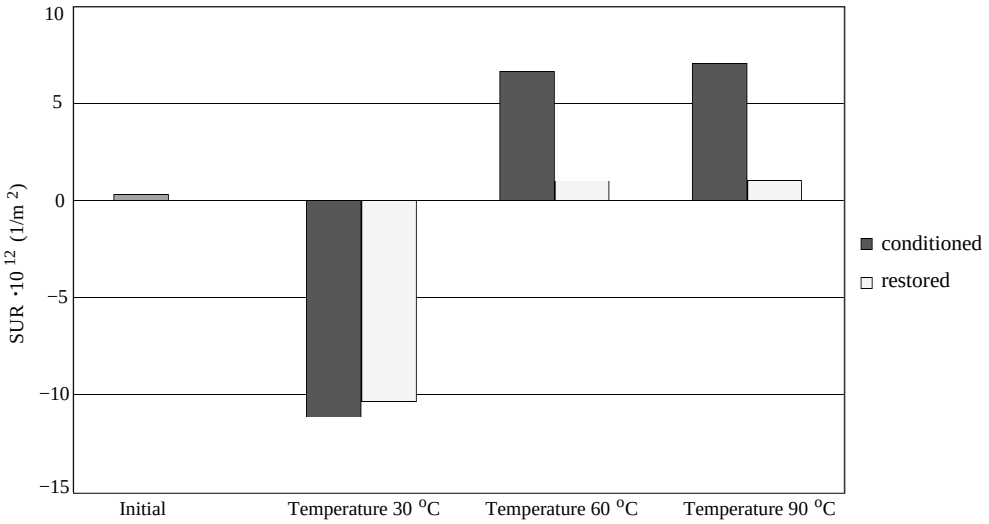

Figure 5.19: Results of SUR measurements of temperature conditioned, restored and untreated demineralised water

The results of temperature conditioned demineralised water show a negative SUR value at a temperature of 30 °C and positive SUR values at 60 and 90 °C. After restoring the temperature to the initial temperature the SUR value decreased compared to temperature conditioned water at 60 and 90 °C, but were higher than the SUR value of the initial temperature. On the other hand the SUR value of the re-

stored demineralised water at a temperature of 30 °C remained negative.

In figure 5.20 the results of the SUR measurements at different temperatures in the range of 5 to 30 °C are presented. At each temperature a mean value of the obtained SUR values of the five experiments was calculated, which is also given in this graph. Although the variation of the SUR values of the five experiments is rather large, the results show an upward trend in SUR values with increasing temperature. This indicates that the filterability decreases with increasing feed water temperature.

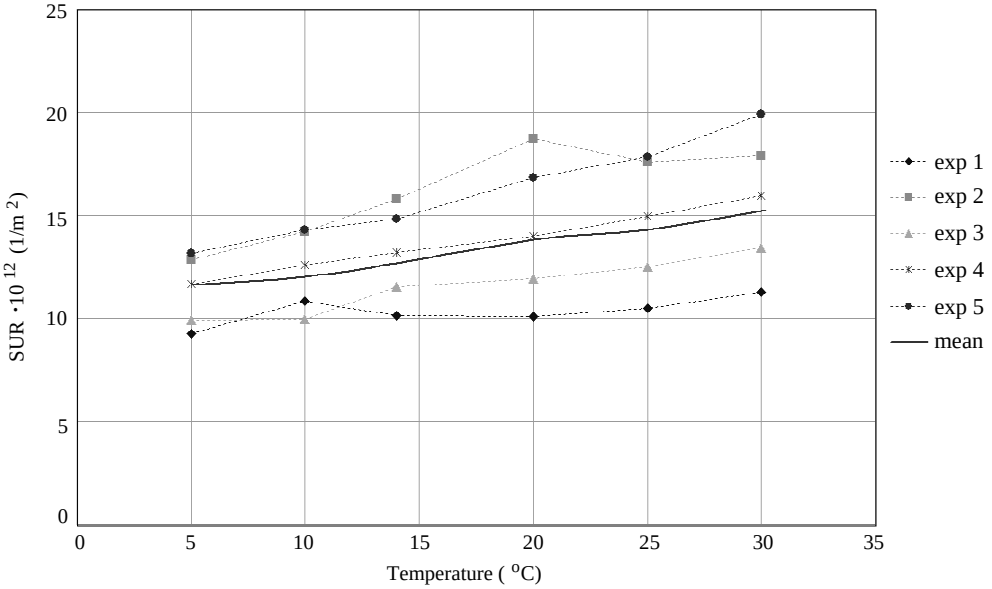

Figure 5.20: Results of SUR measurements of temperature conditioned effluent of wwtp Berkel

5.3.3 Discussion

As a result of temperature increase, a decrease in dynamic viscosity is expected, according to the empiric relation which is derived for water solutions by Janssen and Warmoeskerken (1997). If the filtration resistance is assumed to be independent of the feed water temperature, a temperature increase should then result in an increase of flux, when operating at constant pressure:

$$R = \frac{\Delta P}{J \cdot \eta} \tag{5.1}$$

In these experiments the filterability is characterised by the SUR, which is dominated by the resistance of the formed cake. The filtration resistance is then a sum of the membrane resistance and the resistance of the cake:

$$R = R_{membrane} + R_{cake} \tag{5.2}$$

When demineralised water is filtrated at constant pressure, the product of dynamic viscosity and flux is expected to be constant at any temperature, since the filtration resistance is dominated only by the membrane resistance. In other words, the SUR value is expected to be constant at any temperature indicating the membrane resistance. However, the results show a negative SUR value at a temperature of 30 °C and relatively high (positive) SUR values at temperatures of 60 and 90 °C compared to the SUR value at 20 °C. Therefore the membrane resistance revealed to be temperature depended. This might be explained by the idea that at high temperature the present PVP in the used membrane material may react with water. As a result membrane pores are narrowed and a higher membrane resistance is obtained, Boom (2002).

In general, wwtp effluent is considered a water solution, whereby the temperature dependence of the dynamic viscosity is valid. The results of temperature conditioning to 30, 60 and 90 °C of Berkel wwtp effluent shows extreme high SUR values compared to the SUR value at 20 °C and compared to demineralised water at these temperatures, suggesting that the temperature has some effect on the waste water constituents. In addition the results of temperature conditioning at ambient temperatures show an increase of the SUR values with increasing effluent temperature. This is also found by Roorda (2004). Thus, the temperature of wwtp effluent is not only of influence on the dynamic viscosity, but also on the retained components, resulting in an increase of filtration resistance.

Therefore it is suggested not to normalise fluxes for temperature in case of ultrafiltration of wwtp effluent, but always to indicate the exact temperature of operation or measurement.

5.4 pH

Chemical properties of the constituents in wwtp effluent can also be conditioned or changed by pH. The effect of pH conditioning on the interaction between potential membrane foulants in wwtp effluent and the filterability is subject of further investigation. Therefore the influence of pH changes on the filterability is studied in several filtration tests. Firstly, the influence of small and large pH changes on the filterability during ultrafiltration of wwtp effluent is investigated. In addition, the effect of these pH changes on the membrane properties is studied. Secondly, the influence of a pH change to 4.3 on the filterability of wwtp effluent is investigated, since pH 4.3 is the iso-electrical point of some proteins. This is illustrated by Noordman (2000), who investigated ultrafiltration of protein solutions and stated that fluxes are higher at pH values far away from the iso-electrical point, due to electrical repulsion between proteins, implying a lower filtration resistance.

5.4.1 Methods

Filtration experiments are performed using of the lab scale test set-up as described in section 2.3.1. The filterability here is characterised by the SUR. As feed water

effluent of wwtp Berkel and demineralised water were used. First the filterability of the raw feed water was measured at neutral pH. Then the pH of the feed water was changed by addition of HCl to pH 1 and 5 or NaOH to pH 9 and 13 and the filterability was measured. Finally the pH of the feed water was restored to the initial value by addition of NaOH or HCl and the filterability was measured again. For each filterability measurement with wwtp effluent as feed water a new membrane module was used, since the influence of temperature changes on the membrane properties are not known. When demineralised water was used as feed water one membrane module was used for the three successively performed SUR measurement to investigate the influence of temperature changes on the membrane properties. These filtration experiments were performed only once.

The filtration experiment in which the pH was changed to 4.3, is performed slightly differently. The filterability of the raw, conditioned and restored wwtp effluent were measured in the same way. However, for these filtration tests one membrane module was used. After each SUR measurement the membrane module was cleaned by circulating a solution of 1.25 %-w/w Divos 120 Cl for 10 minutes along the membrane surface to obtain a CWF simular to the CWF at the start of the measurement. This experiment was repeated three times. In addition the protein and humic substance concentration in the feed water and ultrafiltrate were analysed using the methods described in section 3.5. An overview of the performed experiments on pH conditioning is given in table 5.14.

Table 5.14: Overview of the filtration experiments on pH conditioning

Experiment	Feed water	pH change	initial pH
1	effluent	1, 5 ,9 and 13	8.2
2	demiwater	1, 5 ,9 and 13	5.9
3	effluent	4.3	7.6

5.4.2 Results

The results of experiment 1 and 2 are presented in table 5.15 and in figures 5.21 and 5.22 respectively. The filterability is characterised by the SUR. In general the results show a good filterability of the raw wwtp effluent. The SUR value slightly decreased when the wwtp effluent was conditioned to pH 5. Conversely the SUR value increased when the wwtp effluent was conditioned to pH 1. Comparing the obtained SUR values of the raw and restored wwtp effluent, the filterability decreased in case the effluent was previously conditioned to pH 1 and 5, the filterability slightly increased in case the effluent was previously conditioned to pH 9, and the filterability was not changed in case the effluent was previously conditioned to pH 13.

The results of the pH conditioned and restored demineralised water shows, with the exception of conditioned demineralised water to pH 13, negative values for the

Table 5.15: Results of the filtration experiments on pH conditioning to pH 1, 5, 9 and 13

Feed water	SUR ($\cdot 10^{12}$ 1/m^2)		
	Raw	Conditioned	Restored
wwtp effluent			
pH 1	9.8	13.1	14.1
pH 5	8.7	6.6	9.9
pH 9	12.8	13.6	10.5
pH 13	8.9	9.2	8.6
demineralised water			
neutral	0.3		
pH 1		-6.8	-2.9
pH 5		-3.0	-1.4
pH 9		-1.3	-1.0
pH 13		9.7	-2.8

SUR. This means that the ratio of filtration time and filtrated volume (t/V) decreases with the filtrated volume (V). In other words the filtration process goes faster when more water is filtrated. This effect remained after the pH of the conditioned demineralised water was restored to the initial value. Filtration of conditioned demineralised water to pH 13 resulted to an increase of the SUR value and therefore influenced the filterability negatively.

Table 5.16: Results of the filtration experiments on pH conditioning to pH 4.3

Parameter	Feed water effluent		
	Raw	Conditioned	Restored
SUR ($\cdot 10^{12}$ 1/m^2)	13.1 ± 2.4	12.1 ± 2.6	13.4 ± 2.7
proteins (mg/L)			
feed	13.4 ± 1.5	12.9 ± 1.5	
ultrafiltrate	11.3 ± 1.2	11.1 ± 1.1	
amount retained	2.1 ± 0.4	1.7 ± 0.8	
humic subst. (1/cm)			
feed	0.349 ± 0.026	0.352 ± 0.035	
ultrafiltrate	0.327 ± 0.021	0.323 ± 0.042	
amount retained	0.022 ± 0.006	0.029 ± 0.008	
PUVA (1/mg·m)			
feed	2.6 ± 0.2	2.8 ± 0.2	
ultrafiltrate	2.9 ± 0.2	2.9 ± 0.2	

The results of the filterability of pH conditioned wwtp effluent to pH 4.3 and the results of the analyses of the feed water and ultrafiltrate are presented in table 5.16.

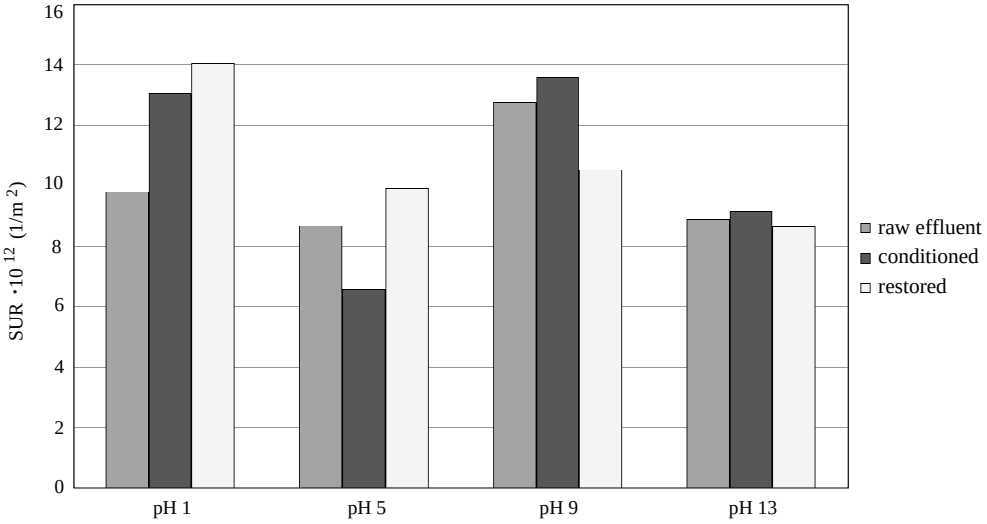

Figure 5.21: Results of the filterability measurements of pH conditioned, restored and raw effluent of wwtp Berkel

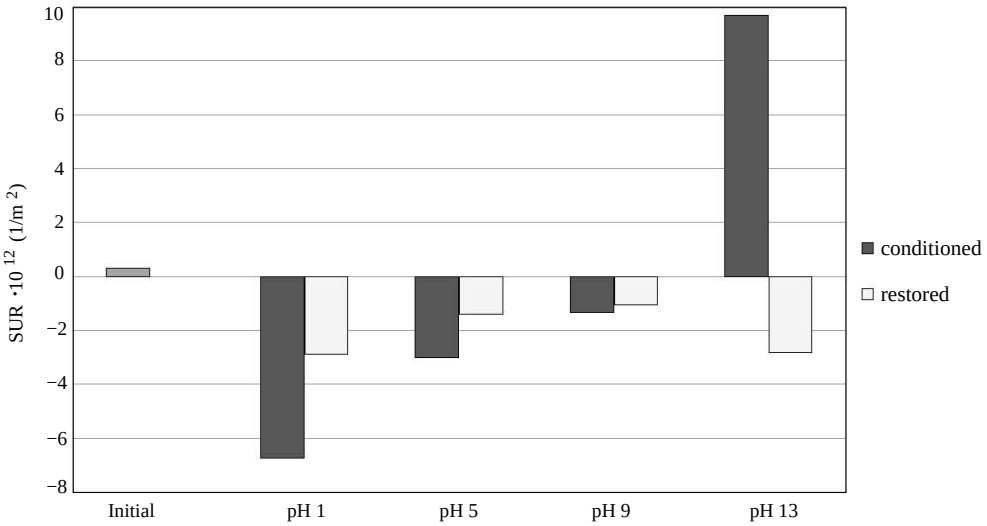

Figure 5.22: Results of the filterability measurements of pH conditioned, restored and untreated demineralised water

The results show relatively high values for the SUR of raw, conditioned and restored wwtp effluent. The SUR value hardly changed when the wwtp effluent was conditioned to pH 4.3. After the pH was restored to the initial value, the SUR value of the restored effluent was found simular to that of the raw effluent. As discussed in section

3.6 the protein analyses includes humic substances. Therefore, humic substances and the ratio between humic substances and proteins, PUVA, is given as well in table 5.16. In general, a higher value for PUVA indicates a higher concentration of humic substances compared to the protein concentration. The results show that the measured concentration of proteins and humic substances in raw wwtp effluent and conditioned wwtp effluent are almost equal. This means that the effect of pH conditioning to pH 4.3 on the filterability is neglectable.

5.4.3 Discussion

The results of pH conditioning of demineralised water show that the influence of the filtration process became faster during ultrafiltration of demineralised water at pH 1, 5 and 9 and even the restored demineralised water to the initial pH resulted in negative SUR values. On the other hand a high SUR value was found in case demineralised water at pH 13 was filtrated, which resulted in a negative influence of the membrane properties. Most likely the membrane surface charge, which is negative, became more and more neutral during filtration of low pH waters. As a consequence filtration of water became easier.

Conditioning of wwtp effluent to pH 4.3 and 5 resulted in a slightly increase in filterability. As a consequence the feed water constituents or membrane surface properties were positively influenced. Furthermore, changes of pH to 9 and restoring the pH to the initial value resulted in a small increase in filterability compared to the raw wwtp effluent. This results suggests that wwtp effluent constituents are permanently changed by the changes of pH which results in higher filterability properties. However, conditioning of wwtp effluent to pH 4.3 did not result in a higher amount of proteins retained.

5.5 Concluding remarks

The obtained results show that changing pH and temperature of wwtp effluent are not useful as conditioning methods.

The results of the temperature conditioning experiments revealed that the filterability decreases with increasing temperature of the feed water. This could only be explained by a change of the retained components, resulting in a higher filtration resistance.

Conditioning of wwtp effluent, sand filtrate and multimedia filtrate by coagulation with 2-2.5 mg Al^{3+}/L Poly Aluminium Chloride proved to be very effective to remain a high reversibility during ultrafiltration and therefore is a useful conditioning method.

Pre-filtration of wwtp effluent increased both the filterability and reversibility. Multimedia filtration is effective in removing particles, which increased both filterability and reversibility. On comparing multimedia filtrate and microfiltrate as feed water

for ultrafiltration a large increase in filterability was found in case of microfiltrate. This suggests that above all colloids are of major influence on the filterability. Increase of the applied flux from 28.5 to 50 L/m^2·h during ultrafiltration of microfiltrate indicates that macro-molecules and dissolved material influences the reversibility.

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Chapter 6

Membrane cleaning methods

Many approaches in applying a cleaning strategy to maximise flux recovery for organic fouled membranes have been investigated. The effectiveness of different chemicals, such as NaOH, NaOCl, HCl, citric acid and anionic surfactant has been studied often by short-term filtration tests, Lee et al. (2001), Mo and Huang (2003) and Maartens et al. (1999) and occasionally by pilot scale studies to investigate irreversible fouling, Kimura et al. (2004). However, more mechanistic studies of cleaning strategies for the removal of irreversible fouling, based on physicochemical properties of wwtp effluent foulants, are relatively rare.

The experiments described in this thesis suggest that during ultrafiltration of wwtp effluent mainly organic fouling occurs. This is indicated by the results of the fractionation and pre-filtration experiments, described in section 4.1 and 5.1 respectively, in which colloids were found of major influence on the filterability and in less extent on the reversibility. In addition size distribution found in literature, Metcalf and Eddy (2003), show that about 75 % of the waste water material consists of organic colloidal matter and the wastewater constituents organic matter contains 40-60 % proteins and 25-50 % carbohydrates. Furthermore in the activated sludge system EPS's (mainly proteins and polysaccharides) are produced by biological conversion and are released by cells. Thus, membrane fouling during ultrafiltration of wwtp effluent may probably be attributed to organic colloids and more specific adsorption of proteins and polysaccharides as main constituents of EPS.

In contrast to analyse components at the membrane surface, a different approach was chosen to investigate the membrane foulants. Different cleaning methods were applied in order to investigate how these components were attached to the membrane surface. Based on the previously made analysis of membrane fouling in ultrafiltration of wwtp effluent, alkaline cleaning was tested to investigate organic fouling in general and enzymatic cleaning was tested to investigate membrane fouling by proteins and polysaccharides specifically. In general, the mechanism of enzymes in membrane cleaning is to cut longer chains into smaller parts, but the enzymes do not have a cleaning function themselves. For practical reasons commercially available enzymatic

products were tested. Another aspect to consider is that enzymes work best at relatively high temperatures (50 °C), which is usually too high for the membrane modules in the pilot plant installation used in this research. Therefore a new enzymatic cleaning protocol based on low temperature was developed on lab scale and tested on pilot scale.

6.1 Membrane cleaning

Membranes can either be cleaned hydraulically or chemically. Hydraulic cleaning can be carried out with water or a combination of water and air. Chemical cleaning can be carried out by a variety of cleaning chemicals.

6.1.1 Hydraulic cleaning

In order to maintain an optimal flux, membranes are often cleaned by periodical hydraulic flushes. The filtration periods may vary between 10 and 60 minutes depending on the feed water quality, but a filtration period of 30 minutes is usually applied in practice. A hydraulic cleaning is performed by a flow of feed water, permeate or ultra pure water into the membranes. As explained in section 1.3.2 generally two types of flushes are distinguished depending on the flow direction: a Forward Flush (FF) and a Back Flush (BF). A mixture of water and air can be used to improve the FF, which is patented as the AirFlush® and further investigated by Verberk (2005). In addition a Reversed Flush (RF) can be applied, which is the opposite of a forward flush and is illustrated in figure 6.1.

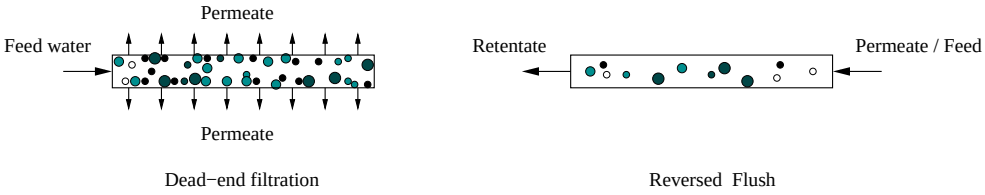

Figure 6.1: Schematic drawing of reversed flush

In spite of frequently applied hydraulic flushes the flux may decline further in time to a level which is no longer appropriate to maintain the flux specifications or stable process conditions. In this case the membranes need to be cleaned chemically in order to recover the flux to initial or acceptable values.

6.1.2 Chemical cleaning

Specific cleaning agents can provide information about the nature and physiochemical properties of the foulants. During chemical cleaning the interactions between foulants and membrane material are influenced by the use of specific cleaning agents

and therefore more details about the type of binding between the foulants and membrane material can be obtained.

Membrane chemical cleaning is usually carried out in several steps. First a back flush (BF) or forward flush (FF) is applied to remove the reversible fouling. The chemical cleaning solution can be introduced to the membrane surface by a BF or FF. Then the membranes are often soaked for a defined time. To introduce mechanical energy, the cleaning solution can be pumped along the membrane surface. By this shear stress is introduced to the boundary layer of the membrane surface. The last step is flushing the membranes with permeate, tap water or ultra pure water.

The global parameters that influence the cleaning performance are:

1. chemical reaction,
2. contact time,
3. temperature,
4. mechanical energy,
5. foulants: amount and type,
6. surface: type and roughness

The first four parameters can be changed depending on the fouling present and the cleaning agent. Temperature is an important parameter: the effect of temperature on chemical cleaning can be exponential. Most chemical cleaning is performed between 30 and 50 °C depending on the membrane module limitations.

The quality of the water and more specific the hardness of the water, which is used for chemical cleaning, is of importance for the concentration of cleaning agents. Soluble salts can disrupt the cleaning performance and in addition very often a higher concentration is needed. Important components in the water are metal-ions like manganese, iron and aluminium. These components can very easily form oxides and hydroxides during alkaline cleaning. Fouling of the membrane by pore blocking can be caused by the formation of metal complexes (oxides and hydroxides), Boom (2001), and can only be removed by acid cleaning. In case of manganese hydroxides formation even acid cleaning is very difficult, because manganese can easily transform into other configurations of oxide and hydroxide complexes. The formed pyrolusite can hardly be removed.

As cleaning solution bulk chemicals like hydrochloric acid and sodium hypochloride or detergents can be used. The advantages of using detergents instead of bulk chemicals are that these kind of products not only contain inorganic adsorbates, usually alkali's, phosphates and acids, but also contain surfactants and sequestering agents to establish the cleaning performance. Organic surfactants (anionics, cationics and non-ionics) are compounds used in detergents to form micelles, which keep foulants

in solution. Sequestering agents or sequestrants are compounds that prevent precipitation from hard water and dissolve precipitated calcium and manganese.

In general, six different types of cleaning agents can be distinguished by nature and mechanism:

Acid:	Removing of crystallised hardness salts, metal-oxides and metal-hydroxides.
Alkali:	Removing of general organic fouling.
Active chloride:	Active chloride as the active component to minimise organic fouling and micro-organisms.
Oxide:	Oxide as the active component to diminish mainly organic fouling and micro-organisms, but can also be used to minimise other types of fouling. Oxides are the strongest cleaning agents, but are often harmful to membranes and installations.
Organic solvent:	Removal of organics by solubility.
Enzyme:	Specific enzyme adsorb specific organic foulants. Removal is established by addition of alkali soap or additive. Temperature and pH are important parameters in enzymatic cleaning performance.

An overview of the used cleaning agents in this research and their major working mechanism are presented in table 6.1. A detailed description is given in the product data sheets of JohnsonDiversey (2003).

Prior to applying enzymatic cleaning the following aspects should be taken into account, Vreeman (2004):

- For the optimal performance of enzymes it is essential to choose the optimal temperature and pH conditions. For protease these conditions are: a temperature of 40-50 °C and pH between 8.5 and 9.5.
- For the removal of foulants when these are not Ca^{2+}, Fe^{2+}, Mg^{2+} salts, the pH should be as high as possible. However, membranes could seldom resist a pH higher than 11.
- For the removal of foulants, like in almost all chemical reactions, temperature should be as high as possible. However, membranes could seldom resist temperatures higher than 50 °C.
- Proteins are hard to remove above a certain temperature: 'the denaturisation temperature'. This temperature depends on the protein type, is within the range of 40 to 70 °C.

Table 6.1: Applied cleaning agents and their mechanisms

General Type	Cleaning agent	Mechanism
Acid	HCl	Bulk chemical and strong acid which removes carbonate scales and most mineral deposits. The disadvantage is that the chloride ion is very corrosive towards stainless steel
	Divos 2	Nitric acid and phosphoric acid are the main active substances. The cleaning is mainly acid as well as oxidising due to nitric acid. The solid foulants will be remained in solution by phosphoric acid.
	Divos 25	Divos 25 is a reducing acid cleaning agent. This product enables to remove metal-oxides (ferric and aluminium oxides) from membrane surfaces. A mixture of citric acid and glycol acid provides the acid cleaning and binds salts (Ca^{2+}, Fe^{2+}, Mg^{2+}). By addition of phosphoric acid solid foulants remain in solution.
	Divos 110	Divos 110 is a general alkali cleaning agent which contains different active substances. Potassium hydroxide is added to hydrolyse the foulants. KTP's (penta-potassium-tri-phosphates) are phosphates which prevent salts (Ca^{2+}, Fe^{2+}, Mg^{2+}) to precipitate on the membrane surface. In general phosphates keep solids in suspension. Amin-oxide is added as a membrane safe non-ionogenic surface active substance to lower the surfaces tension. The active component is 50 % NaOH
Active chlorine	NaOCl	Bulk chemical with active chlorine in strong alkali environment
	Divos 120Cl	Alkali cleaning agent with active chloride for the removal of organic as well as inorganic fouling.
Enzyme	Divos 80-2	Most important component is protease, an enzyme to separate proteins. Lauryldimethylbetaine is added as a membrane safe amphoteric surface active substance to lower the surfaces tension.
	IC0314	Amylase enzyme complex containing a wide range of carbohydrases including cellulase, which is an enzyme to hydrolyse cellulose.
Additive	Divos ADD1	Sodium-2-alkane-sulphonate is the basic component of this product and is a membrane friendly anionic surface active substance to lower the surface tension.

6.2 Laboratory experiments

On lab scale cleaning experiments were carried out in order to select different cleaning methods which could be potentially successfully applied on pilot scale. Moreover, the enzymatic cleaning was compared to a basic alkaline cleaning in order to investigate if this approach was selective enough to indicate protein adsorption as fouling mechanism. Important factors for membrane cleaning on pilot scale in this research were the low temperature, using ultrafiltrate for the preparation of the cleaning solution instead of ultrapure water and the concentration of the enzyme product.

The influence of ultrafiltrate in the cleaning solution, the concentration of the enzymatic product based on protease (Divos 80-2) and temperature were investigated. Then the enzymatic protease cleaning protocol was tested by applying pilot scale conditions and the effectiveness of the enzyme protease was studied by comparing the enzymatic protease cleaning with the alkaline cleaning. Furthermore the effect of temperature on the enzymatic cleaning by amylase and the effectiveness of the enzyme amylase was studied as well in simular experiments.

6.2.1 Methods

The lab scale test set-up, 2.3.1, was used to measure the clean water flux (CWF) with demineralised water and to foul the membrane by multimedia filtrate of the pilot installation at wwtp Hoek van Holland. To this purpose multimedia filtrate was used instead of wwtp effluent, because for these cleaning experiments the colloids, macro-molecules and dissolved material were subject of interest rather than particles and suspended solids.

A new membrane module was cleaned according to the cleaning procedure as described in Appendix D. Then the membranes were fouled by dead-end filtration of multimedia filtrate at 0.5 bar for 1 hour. Thereafter a back flush was applied with demineralised water at constant pressure of 2 bar for 1 minute or a forward flush at constant flow with 220 rpm for 1 minute. Finally a chemical cleaning was carried out depending on the performed experiment. After each step the CWF was measured at 0.5 bar and normalised to 20 °C. The cleaning performance was evaluated by comparing the CWF after a cleaning to the initial CWF at the start of each experiment. The experiments were repeated at least twice.

A chemical cleaning was carried out by putting the membrane module in a second filtration set-up with a peristaltic pump (Watson-Marlow 500 with a 505L low pulse and high accuracy peristaltic pump head) and by circulating the cleaning solution along the feed side of the membrane module for 20 minutes at a flux of 1.9 l/h, unless described otherwise.

The optimal cleaning solution for the enzymatic protease cleaning, according to the supplier, was prepared with ultrapure water and consisted of:

- 1%-w/w Divos 110 (alkaline cleaning solution),
- 1%-w/w Divos 80-2 (protease),
- adjustment of pH to 9.3 by addition of citric acid or HCl,
- temperature of 50 °C.

The influence of ultrafiltrate in the alkaline cleaning solution, the temperature and concentration of the protease solution (Divos 80-2) was first investigated in three experiments. Then the effectiveness of the enzyme protease was investigated in a fourth experiment by comparing the the enzymatic protease cleaning solution with and without addition of the protease enzyme product, applying pilot scale conditions:

- mixture of ultrafiltrate and tap water for preparation of the cleaning solution,
- temperature of 25 °C,
- cleaning procedure of a 1 hour circulation, followed by an overnight soak and again a 1 hour circulation via the feed side of the membrane modules.

The overnight soak was applied to compensate for the lower temperature and after having noticed that the membrane modules in the pilot installation had not been cleaned for half a year.

The enzymatic amylase cleaning solution was prepared in ultrapure water and consisted of:

- 1%-w/w Divos ADD1 (buffer solution),
- 1%-w/w IC0314 (amylase),
- adjustment of pH to 4.3 by addition of citric acid or HCl,

In experiment 5 the influence of the temperature on the cleaning performance was investigated and the effectiveness of the enzyme amylase was tested in experiment 6 by comparing the cleanings of the enzymatic amylase cleaning solution with and without the enzyme amylase product. Both experiments were carried out by applying pilot scale conditions. An overview of the performed experiments is given in table 6.2.

Table 6.2: Overview of the lab scale cleaning experiments

Exp.	Cleaning solution
1	1 %-w/w Divos110 + 0.3 %-w/w Divos 80-2 at 50 °C
a	in demineralised water
b	in ultrafiltrate
2	1 %-w/w Divos110 in ultrafiltrate at 50 °C
a	+ 1 %-w/w Divos 80-2
b	+ 0.3 %-w/w Divos 80-2
3	1 %-w/w Divos110 + 0.3 %-w/w Divos 80-2 in ultrafiltrate
a	at 50 °C
b	at 25 °C
4	1 %-w/w Divos110 in ultrafiltrate at 25 °C
a	+ 1 %-w/w Divos 80-2
b	-
5	1 %-w/w DivosADD1 + 1 %-w/w IC0314 in ultrafiltrate
a	at 50 °C
b	at 25 °C
6	1 %-w/w DivosADD1 in ultrafiltrate at 25 °C
a	+ 1 %-w/w IC0314
b	-

6.2.2 Results and discussion

The CWF of a new membrane as used in the modules for these laboratory experiments is, according to the manufacturer, approximately 600-700 L/m^2·h·bar at 20 °C, Appendix C. Each experiment started with a clean membrane, whereby the CWF varied between approximately 650 and 750 L/m^2·h·bar normalised to 20 °C.

The results of the protease cleaning experiments are presented as mean values of the measured CWF in table 6.3. After membrane fouling by multimedia filtrate the CWF declined to about 230 L/m^2·h·bar at 20 °C, indicating that the extent of fouling is simular in all experiments. Hydraulic cleaning by a back flush resulted in an increase in CWF to approximately 300-450 L/m^2·h·bar at 20 °C, but didn't result in a complete recovery of the CWF. More important are the results before and after the cleaning. Therefore the results of the cleaning experiments are presented relatively to the CWF of a new membrane in figure 6.2. The applied chemical cleaning methods resulted in almost all cases in a complete recovery of the CWF.

Comparing the chemical cleaning results between the protease cleaning solution prepared in demineralised water and ultrafiltrate (exp. 1), no significant differences were found. Moreover, in both cases a complete recovery of the CWF was found. Simular results were found when the 1 %-w/w and 0.3 %-w/w concentrations of Divos 80-2 were compared (exp. 2). Applying a lower temperature of 25 °C compared

Table 6.3: Results of protease cleaning experiments on lab scale

Exp.	Cleaning method	Clean Water Flux (L/m^2·h·bar) at 20 °C			
		Clean mem.[a]	Fouled mem.	after BF[b]	after CC[c]
1 a	demi water	682 ± 28	219 ± 14	451 ± 53	695 ± 42
b	ultrafiltrate	667 ± 22	231 ± 26	382 ± 11	660 ± 50
2 a	1 %-w/w Divos80-2	750 ± 45	219 ± 9	248 ± 8	775 ± 45
b	0.3 %-w/w Divos80-2	667 ± 22	231 ± 26	382 ± 11	660 ± 50
3 a	Temperature 50 °C	667 ± 22	231 ± 26	382 ± 11	660 ± 50
b	Temperature 25 °C	755 ± 25	207 ± 7	277 ± 80	729 ± 5
4 a	Divos110 + Divos80-2	726 ± 17	231 ± 30	352 ± 27	752 ± 11
b	Divos110	749 ± 12	264 ± 9	469 ± 90	658 ± 11

[a] membrane
[b] Back Flush
[c] Chemical Cleaning

to 50 °C of the protease cleaning solution (exp. 3) resulted in an almost complete recovery of the CWF. The results of the protease and basic alkaline cleaning (exp. 4) show a significant difference in recovery of the CWF. After applying this alkaline cleaning the CWF recovery was about 90 % (88 ± 3 %).

This indicates that the effectiveness of the applied enzymatic protease cleaning was independent of the water quality tested and was high at a Divos 80-2 concentration of 0.3 %-w/w and at a lower temperature of 25 °C. Furthermore the CWF after enzymatic cleaning is significantly higher than after the basic alkaline cleaning, indicating protein adsorption as fouling mechanism.

Table 6.4: Results of amylase cleaning experiments on lab scale

Exp.	Cleaning method	Clean Water Flux (L/m^2·h·bar) at 20 °C			
		Clean mem.[a]	Fouled mem.	after FF[b]	after CC[c]
5 a	Temperature 50 °C	686 ± 33	179 ± 22	331 ± 2	539 ± 3
b	Temperature 25 °C	647 ± 10	250 ± 7	404 ± 16	513 ± 17
6 a	DivosADD1 + IC0314	647 ± 10	250 ± 7	404 ± 16	513 ± 17
b	DivosADD1	725 ± 7	207 ± 5	326 ± 28	561 ± 32

[a] membrane
[b] Forward Flush
[c] Chemical Cleaning

In table 6.4 and figure 6.3 the results of the amylase cleaning experiments are presented. The CWF of the fouled membranes was about 220 L/m^2·h·bar at 20 °C. After hydraulic cleaning by a BF the CWF increased to 330-400 L/m^2·h·bar at 20 °C.

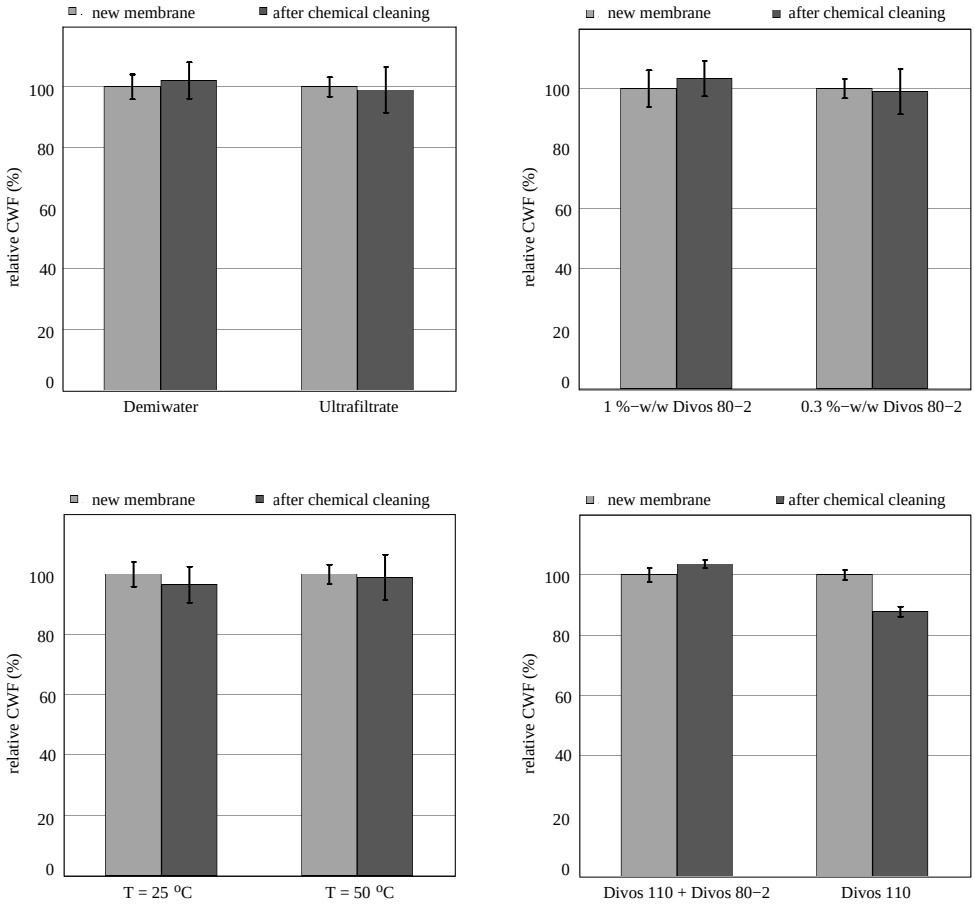

Figure 6.2: Results of the protease cleaning experiments 1 to 4, presented relative to the CWF of a new membrane

After chemical cleaning the CWF recovered to approximately 80 %. No differences were observed in the recovery of the CWF after enzymatic amylase cleaning between a temperature of 50 and 25 °C. The recovery of the CWF after enzymatic amylase cleaning (79 ± 4 %) was just a little higher than after cleaning with only the buffer solution (77 ± 5 %).

6.2.3 Conclusions

The protease cleaning method tested on lab scale at a low temperature of 25 °C and preparation in ultrafiltrate resulted in a 100 % recovery of the clean water flux. Moreover, the obtained different results between the protease cleaning method and the basic alkaline cleaning method could probably be an effective approach to discriminate between protein fouling and organic fouling.

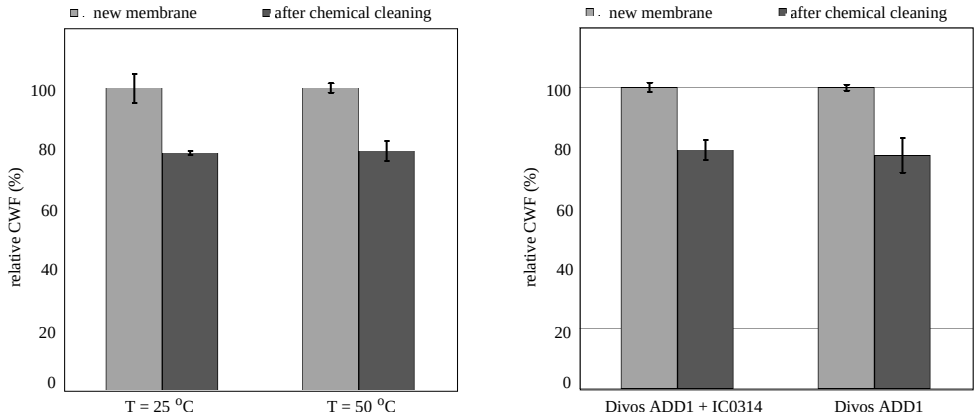

Figure 6.3: Results of the CWF measurements regarding to the amylase cleaning experiments 5 and 6

The results of the enzymatic amylase cleaning indicated hardly any difference in the recovery of the CWF between the enzymatic amylase cleaning and the cleaning with the buffer solution.

This leads to the conclusion that for this type of wastewater effluent proteins are indicated as irreversible foulant, whereas polysaccharides could not be indicated as irreversible foulant by this approach.

6.3 Enzymatic cleaning on pilot scale

During the pilot investigations at wwtp Hoek van Holland and Utrecht, several cleaning experiments were performed, which were based on the results of the laboratory experiments. On both wwtp locations an enzymatic cleaning with protease was compared to a basic alkaline cleaning. At wwtp Utrecht an amylase solution cleaning and a buffer solution cleaning were carried out.

The cleaning experiments were carried out according to the developed low temperature cleaning protocol:

- Forward flush with permeate
- Preparing cleaning solution at 25-30 °C
- 1 hour circulation
- Overnight soaking (24 hours)
- 1 hour circulation

- Flushing with tap water

The effect of the cleaning was determined by measuring the Clean Water Flux (CWF) before and after cleaning. The CWF is presented as mean value of the CWF measurements at different flow rates (2.8, 3.3, 3.8, 4.3, 4.8 and 5.8 m^3/h), at both flow directions (left and right) of the membrane module and normalised to 20 °C. For both pilot investigations the same membrane modules were used.

After membrane cleaning ultrafiltration took place during several days of pre-filtered wwtp effluent i.e. microfiltrate. The configuration of the pilot installations used in this research is schematically presented in figure 6.4. A detailed description of the used installations is given in section 2.4.2. The wwtp effluent was first filtered over a curved sieve with a mash size of 0.45 mm followed by microfiltration and then ultrafiltration successively. In some cases, the microfiltration installation was fed by multimedia filtrate.

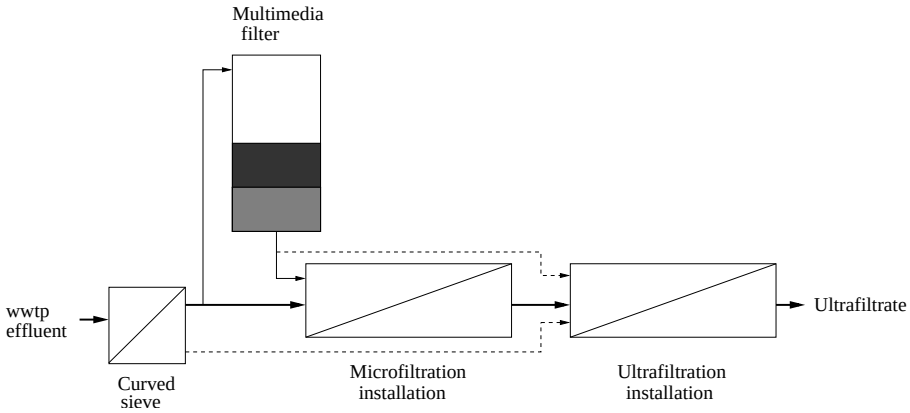

Figure 6.4: Schematic overview of the configuration of the pilot installations

The ultrafiltration installation was operated at a constant flux of 28.5 $L/m^2 \cdot h$ with a filtration period of 1 hour, which was followed by a back flush during 45 seconds at a flow of 17 m^3/h and without periodically chemical cleaning. The overall fouling rate was determined by measuring the CWF, which indicates the actual filtration resistance, frequently over time.

6.3.1 Enzymatic cleaning with protease

At the previous mentioned wwtp's, pilot experiments were performed regarding membrane cleaning based on the enzyme protease. In order to discriminate between fouling by organics and proteins cleaning experiments are performed with two different cleaning solutions:

- Basic alkaline cleaning:
  - 1 %-w/w Divos 110

  - pH adjustment to 9.3 by HCl (50 %)

- Enzymatic protease cleaning:
  - 1 %-w/w Divos 110
  - pH adjustment to 9.3 by HCl (50 %)
  - 1 %-w/w Divos 80-2

The cleaning was carried out according to the low temperature cleaning protocol. These cleaning experiments were performed twice. At wwtp Hoek van Holland, these experiments were performed after 8 months of operation. Thereafter the installations were moved to wwtp Utrecht and the cleaning experiments were carried out at the beginning of the period of the pilot investigations. The amount of proteins retained was measured by analysing the protein concentration in the feed water (microfiltrate) and ultrafiltrate. The used method is described in section 3.5.

Results and Discussion

The results of the first protease and basic alkaline cleaning experiments are presented in table 6.5 in a chronological order. The CWF of a new membrane module is approximately 400 and 500 L/m^2·h·bar at 20 °C, as stated by the membrane manufacturer, Molemaker (2003).

Table 6.5: Results of protease and basic alkaline cleaning methods

Cleaning method	Date	Clean Water Flux (L/m^2·h·bar) at 20 °C	
		Before	After
wwtp Hoek van Holland	2003		
Protease (1)	4-6	200	467
Protease (2)	16-6	138	411
Basic alkaline (1)	24-6	153	344
Basic alkaline (2)	30-6	165	271
wwtp Utrecht	2004		
Protease (1)	19-2	189	421
Basic alkaline (1)	28-2	237	445
Protease (2)	13-3	241	446
Basic alkaline (2)	27-3	231	413

The results clearly show that after applying the protease cleaning by the low temperature cleaning protocol, the CWF returned to its original value for a new membrane module. At wwtp Hoek van Holland, the effect of the protease cleaning was significantly larger than that of the basic alkaline cleaning. In fact, the effect of the basic alkaline cleaning decreased over time. This indicates that protein adsorption occurred as fouling mechanism. At wwtp Utrecht, the CWF after the protease cleaning step showed similar results as after the basic alkaline cleaning step. The effect

of the protease cleaning seems to be larger than that of the basic alkaline cleaning. Application of both cleaning methods resulted in a 100 % recovery of the CWF.

In figures 6.5 and 6.6, the results of these cleaning experiments, as well as the membrane fouling after cleaning at wwtp Hoek van Holland and wwtp Utrecht respectively, are presented as the clean water flux (CWF) normalised at 20 °C against time. The CWF decreases rapidly after starting ultrafiltration of microfiltrate, especially when the CWF starts above 400 L/m^2·h·bar. At wwtp Hoek van Holland, after 20 days the microfiltration unit was fed by floc filtrate. However, this did not seem to influence the results. Here, the CWF decreased after protease cleaning from around 440 to 220 L/m^2·h·bar in about 1 day and decreased further to approximately 160 L/m^2·h·bar in about 3 days. The CWF at wwtp Utrecht decreased from around 430 to 305 L/m^2·h·bar in about 1 day and decreased further to approximately 260 L/m^2·h·bar in about 3 days. At wwtp Hoek van Holland the CWF declined after 1 day of ultrafiltration of microfiltrate was around 50 % compared to around 30 % at wwtp Utrecht, which is 40 % less. After about 3 days of filtration the CWF was levelling off to 160 L/m^2·h·bar at wwtp Hoek van Holland, whereas at wwtp Utrecht this value was around 260 L/m^2·h·bar. In other words, the fouling of the ultrafiltration membrane by organic macro-molecules was more severe at wwtp Hoek van Holland than at wwtp Utrecht.

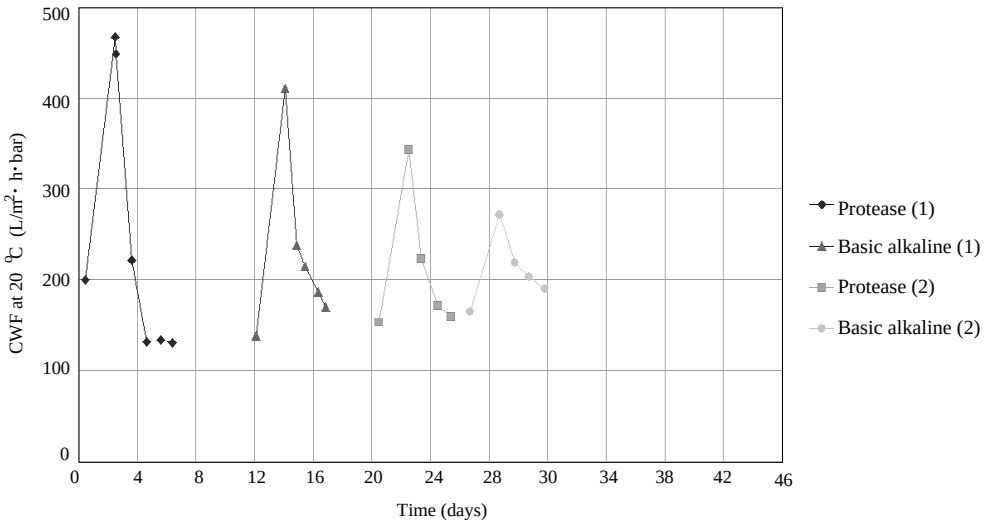

Figure 6.5: CWF measurements after protease or alkaline cleaning and of the fouled membranes by ultrafiltration of microfiltrate at wwtp Hoek van Holland

During the periods of ultrafiltration of microfiltrate, protein concentrations were analysed twice in one period. The mean protein concentrations in the feed water (microfiltrate) and ultrafiltrate over all periods are presented in table 6.6. The results may show an overestimation due to the interference of humic compounds in the Lowry

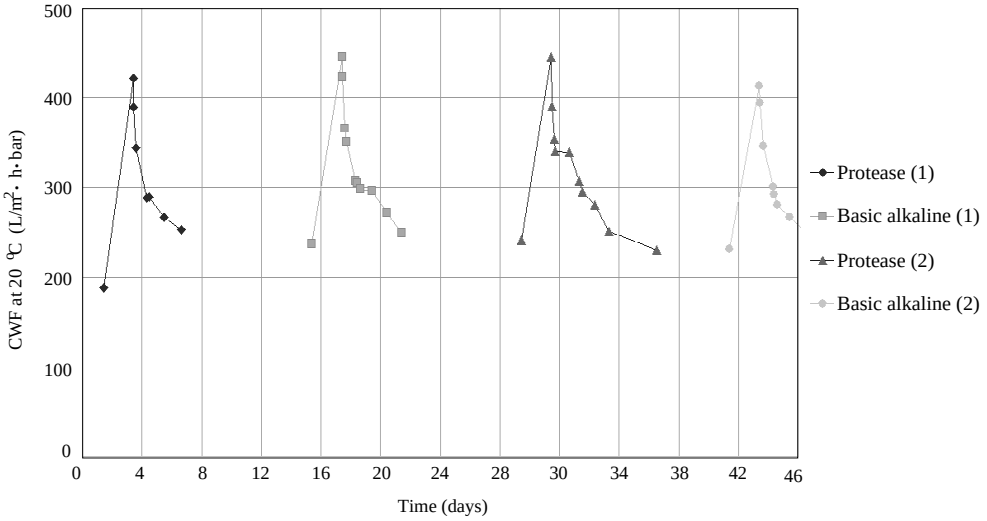

Figure 6.6: CWF measurements after protease or alkaline cleaning and of the fouled membranes by ultrafiltration of microfiltrate at wwtp Utrecht

et al. (1951) procedure, as explained in section 3.6. Assuming humic substances are hardly retained by the ultrafiltration membranes using microfiltrate as feed water, see section 4.2, the amount of proteins measured may be compared. The amount of proteins retained by the ultrafiltration membrane was relatively more for wwtp Hoek van Holland than for wwtp Utrecht. This indicates that the higher CWF decline found at wwtp Hoek van Holland may be related to the relatively higher amount of proteins retained by ultrafiltration of microfiltrate.

Table 6.6: Mean values of protein concentration in feed water (microfiltrate) and ultrafiltrate

Wwtp	Period	Protein concentration (mg/L)	
		Feed water	Ultrafiltrate
Hoek van Holland	4-6 till 6-7 2003	17.3 ± 4.4	16.3 ± 4.3
Utrecht	13-2 till 1-4 2004	11.4 ± 1.9	10.8 ± 1.8

6.3.2 Enzymatic cleaning with amylase

At wwtp Utrecht several cleaning experiments were performed on pilot scale in order to investigate membrane fouling by organic matter and more specific by polysaccharides. Cleaning experiments were performed with two different cleaning solutions:

- Buffer solution:

  - 1 %-w/w Divos ADD1
  - pH adjustment to 4.3 by HCl (50 %)

- Enzymatic amylase cleaning:
  - 1 %-w/w Divos ADD1
  - pH adjustment to 4.3 by HCl (50 %)
  - 1 %-w/w IC0314

The cleaning was carried out according to the low temperature cleaning protocol. These cleaning experiments were performed twice.

Results and discussion

In table 6.7 the results of the enzymatic amylase cleaning and cleaning with the buffer solution are presented in chronological order. After having applied both cleaning methods, the CWF remained lower than the CWF of a new membrane. In fact, the CWF after cleaning with these methods decreased over time. In addition, no significant differences could be observed when comparing the effect of the enzymatic amylase cleaning to the buffer solution cleaning.

Table 6.7: Results of amylase and buffer cleaning methods at wwtp Utrecht

Cleaning method	Date 2004	Clean Water Flux ($L/m^2 \cdot h \cdot bar$) at 20 °C	
		Before	After
Buffer (1)	14-5	222	323
Amylase (1)	26-5	138	271
Buffer (2)	12-6	88	237
Amylase (2)	26-6	79	165

The results of these cleaning experiments and the membrane fouling after cleaning are presented in figure 6.7 as the CWF against time. Here, the microfiltration installation was fed by multimedia filtrate. Especially after the first two applied cleanings, the results showed a rapid decrease in CWF during ultrafiltration of microfiltrate. In the end the membranes were fouled to a large extent, indicated by the measured CWF compared to the CWF of a new membrane.

6.3.3 Conclusions

The results of the protease cleaning compared to the basic alkaline cleaning shows an indication of protein fouling at wwtp Hoek van Holland. In this case the enzymatic cleaning by protease is preferred in order to restore the initial CWF completely.

The fouling of the membranes during ultrafiltration of microfiltrate was faster at wwtp Hoek van Holland than at wwtp Utrecht. In addition, this fouling was easier to

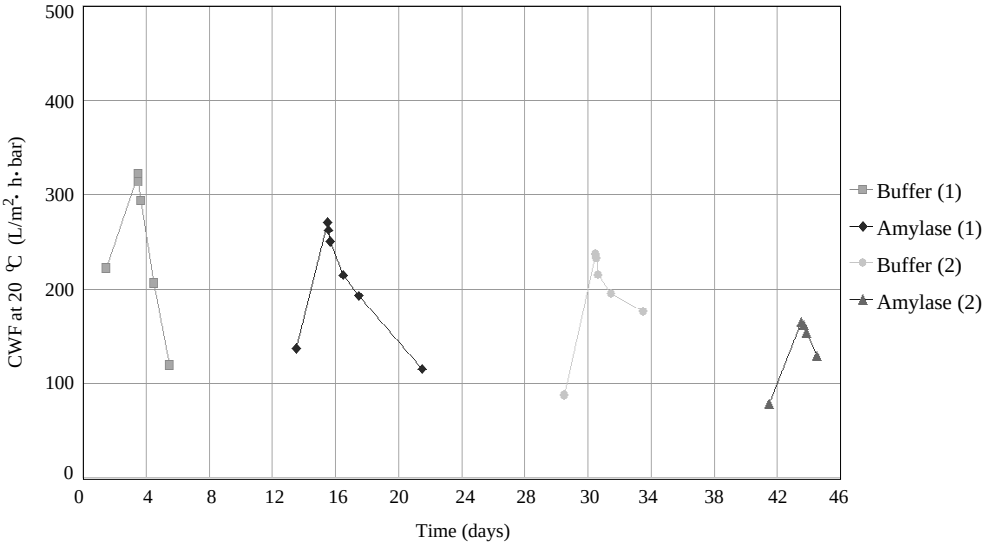

Figure 6.7: CWF measurements after amylase or buffer cleaning and of the fouled membranes by ultrafiltration of microfiltrate at wwtp Utrecht

remove by alkaline cleaning at wwtp Utrecht and an enzymatic cleaning by protease was not necessary.

Comparing the results of the cleaning with the cleaning of the buffer solution no indication was found for polysaccharides fouling. After applying these cleaning methods most of the fouling remained on the membranes.

6.4 Final cleaning of the pilot installation

After these first cleaning experiments, the ultrafiltration installation was fed by different feed waters: wwtp effluent, dual media filtrate and microfiltrate, with and without in-line coagulation of Poly Aluminium chloride (PACl) for other research purposes as described in chapters 4 and 5.

At the end of the pilot investigations the membranes were cleaned completely in order to continue the research at a different wwtp, starting with a CWF comparable to a new membrane. Therefore different cleaning methods were applied successively. The applied cleaning methods are presented in table 6.8. The enzymatic cleaning with amylase and the cleaning with the buffer solution were not applied, since the results presented in section 6.3.2 show that those cleaning methods are not very effective.

Table 6.8: Description of the different applied cleaning methods

Cleaning method	Cleaning agent(s)	pH	Protocol
Protease	Divos 110 + 80-2	9.3	Low temperature cleaning
Basic alkaline	Divos 110	9.3	Low temperature cleaning
Alkaline	Divos 110	12.5	Low temperature cleaning
Acid FF	Divos 2	1.5	FF[1]- 30 min soaking - flushing
Acid BF	Divos 2	1.5	BF[2]- 30 min soaking - flushing
Acid	Divos 2	1.5	Low temperature cleaning at 22 °C
Mild acid	Divos 25	2	Low temperature cleaning

[1]FF = Forward Flush
[2]BF = Back Flush

6.4.1 Results and discussion

After the first cleaning experiments at wwtp Hoek van Holland, the membranes were successfully cleaned by the protease cleaning protocol. This result is given in the first column of figure 6.8. Then other filtration experiments were performed, using different types of feed water in combination with coagulant (PACl) dosing. In order to start the pilot investigation at wwtp Utrecht the membranes were cleaned with several cleaning agents, the results are presented in figure 6.8. First the protease cleaning protocol was applied, resulting in a CWF of 120 L/m^2·h·bar. The membranes were not cleaned with acid over along period of time and metal salts were dosed in the pervious filtration period. Combining these factors it was suggested that an acid cleaning might work. The applied acid cleaning resulted in an increase in CWF to 200 L/m^2·h·bar. A last clean using the protease cleaning protocol was applied again, resulting in an increase of the CWF to almost 400 L/m^2·h·bar and a recovery of the CWF of 85 %. As stated before, the pilot investigations were continued at wwtp Utrecht. The result of the first applied protease cleaning protocol, given in table 6.5, shows a CWF of 421 L/m^2·h·bar and therefore it may be concluded that no irreversible fouling remained.

At the end of the pilot investigations at wwtp Utrecht, similar cleaning experiments were performed as at wwtp Hoek van Holland. In contrast to the results of the first cleaning experiments at Hoek van Holland, here the result of the last basic alkaline cleaning experiment of the enzymatic cleaning experiments described in section 6.3.1 is presented in the first column of figure 6.9. After a period of filtration tests with different types of feed water, including PACl dosing, first the basic alkaline cleaning protocol was applied, which resulted in a CWF of 145 L/m^2·h·bar. Secondly the protease cleaning protocol was applied resulting in an increase of the CWF to 210 L/m^2·h·bar. The previous results at wwtp Hoek van Holland indicated the usefulness of an acid cleaning. In order to investigate which type of inorganic fouling was present an acid forward flush, an acid back flush, an acid cleaning and a mild acidic cleaning

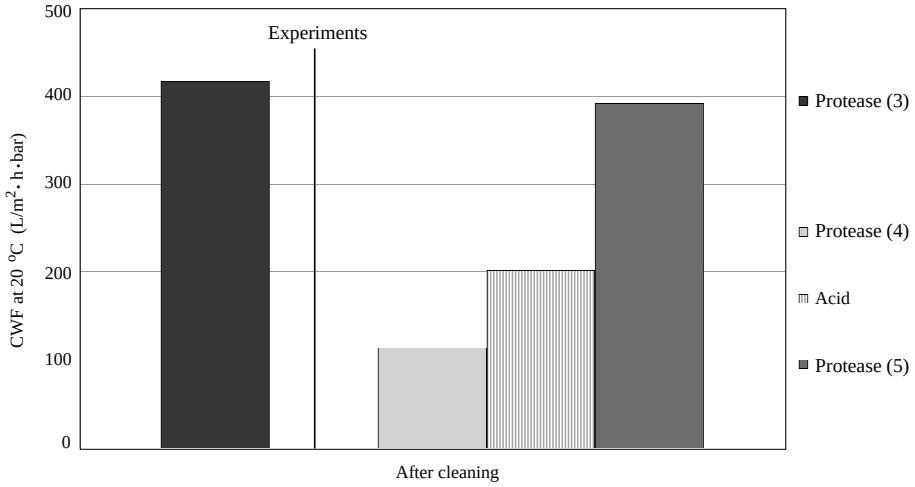

Figure 6.8: CWF measurements after cleaning by different applied cleaning methods at wwtp Hoek van Holland

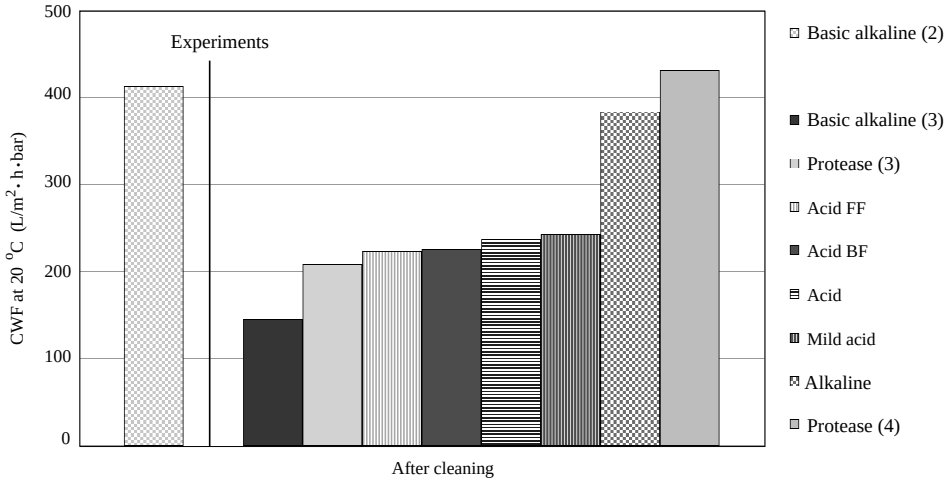

Figure 6.9: CWF measurements after cleaning by different applied cleaning methods at wwtp Utrecht

were carried out successively. The CWF increased in small steps of 15, 2, 12 and 7 L/m^2·h·bar respectively to 240 L/m^2·h·bar. Thereafter, an alkaline cleaning protocol was applied, a similar cleaning protocol to the one at wwtp Hoek van Holland, which resulted in an increase of CWF to 384 L/m^2·h·bar. A last cleaning with the protease cleaning protocol was applied, which resulted in an increase of CWF to 431 L/m^2·h·bar, indicating the presence of protein fouling.

6.4.2 Conclusions

In order to clean the membranes to a complete recovery of the CWF it is important to know the process conditions applied before cleaning, which dominate the build-up of the fouling and consequently define the cleaning methods that have to be applied.

6.5 Concluding remarks

The approach of comparing the results of the basic alkaline cleanings with and without the enzyme protease was found selective in indicating the presence of protein fouling. The used protease cleaning protocol resulted in a complete recovery of the CWF at low temperature (25-30 °C). The different results found at wwtp Utrecht and Hoek van Holland suggest that protein fouling is a relatively long term effect, i.e. building a protein network structure on the membrane surface costs time and depends upon the retained proteins.

In contrast to that, no significant difference in cleaning performance was observed with and without the use of the enzyme amylase. Thus, no polysaccharide fouling could be indicated.

Organic macro-molecules (< 0.2 m) like proteins contribute to rapid membrane fouling of a clean membrane, which is demonstrated by the rapid CWF decline flux during ultrafiltration of microfiltrate. The degree of CWF decline may be related to the amount of proteins retained by ultrafiltration. The applied enzymatic cleaning with protease did not contribute to maintain the performance of a clean membrane.

If metal complexes were formed during filtration of (pre-filtered) wwtp effluent it is suggested to apply an acid cleaning previous to the enzymatic protease or alkaline cleaning.

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Chapter 7

Review

7.1 Foulants in ultrafiltration of wwtp effluent

The research described in this thesis, titled "Foulants in ultrafiltration of wwtp effluent" can be summarized in three main questions:

Why? Membrane fouling is the main cause of limitations in use and operation of ultrafiltration (Chapters 1 and 2).

What? Which wwtp effluent constituents contribute to membrane fouling (Chapter 3)?

How? In which way are these foulants forming membrane fouling; how are these components attached to the membrane surface; are these foulants connected to each other, influencing the extent of fouling (Chapters 3, 4, 5 and 6)?

By answering these questions, solutions can be found to improve the ultrafiltration process of wwtp effluent in terms of process operation, pre-treatment and membrane cleaning.

The constituents in wwtp effluent revealed to be mainly of organic origin (Chapter 3). These compounds are soluble biodegradable organics, suspended organic material and non biodegradable organics, which are originally present in the wastewater influent, produced during biological treatment and escaped final separation. One specific group of these organic components had special attention, because of their relatively large quantities present in biological treatment systems and their properties which are important in the formation of sludge flocs: the Extracellular Polymeric Substances (EPS), which consist mainly of proteins and polysaccharides. Based on these glue-like properties, EPS were suggested to play an important role in membrane fouling: the interaction with retained components and the membrane surface. In figure 7.1 a sample of the constituents in wwtp effluent are schematically shown.

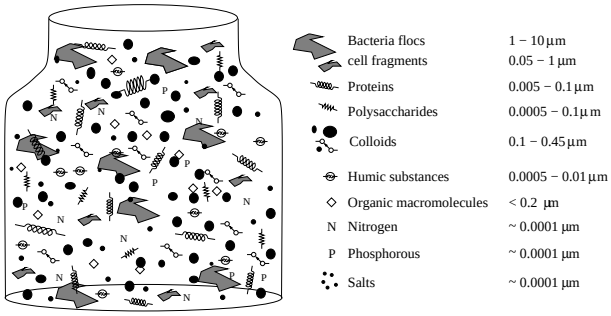


Figure 7.1: Main constituents of wwtp effluent and ultrafiltration membrane foulants with an indication of their sizes

The results obtained in chapters 4, 5 and 6 revealed that colloids of size between 0.1 and 0.45 μm and organic macromolecules smaller than 0.2 μm in the wwtp effluent play a significant role in the fouling of ultrafiltration membranes, influencing respectively the filterability and reversibility. This is schematically shown in figure 7.2.

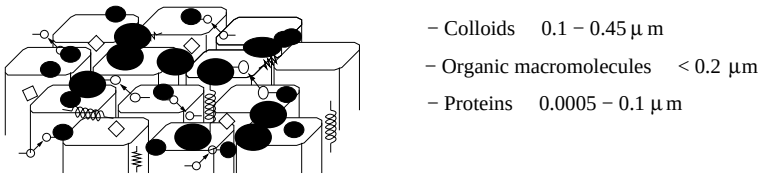


Figure 7.2: Main foulants in ultrafiltration of wwtp effluent. Colloids of size between 0.1 and 0.45 μm are suggested to form a cake layer on the membrane surface, influencing the filterability. Organic macromolecules < 0.2 μm (proteins) are suggested to adsorb in the membrane pores and at the membrane surface, influencing the reversibility

These foulants could hardly be influenced by pH and temperature changes (section 5.3 and 5.4), but could be conditioned by coagulation with 2 to 2.5 mg Al^{3+}/L Poly Aluminium Chloride (PACl) (section 5.2) resulting in a large increase of the reversibility and a small increase of the filterability, as pictured in figure 7.3.

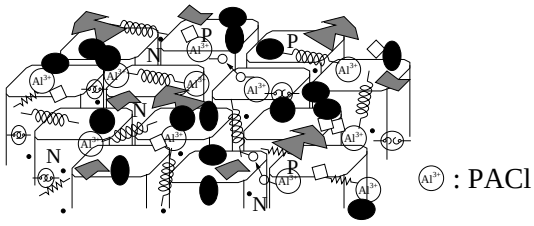


Figure 7.3: Role of PACl in membrane fouling during ultrafiltration of wwtp effluent. The Al^{3+} molecules are suggested to play an important role in binding bacterial flocs, cell fragments, colloids and organic macromolecules (proteins, polysaccharides and humic substances) resulting in a filterable cake, which improves the reversibility of the cake

Membrane cleaning experiments with alkali and enzymatic (protease) detergents (section 6.3.1) show a significant difference in cleaning performance between protease cleaning and the alkaline cleaning at wwtp Hoek van Holland, indicating proteins as foulants. In figure 7.4 this is illustrated.

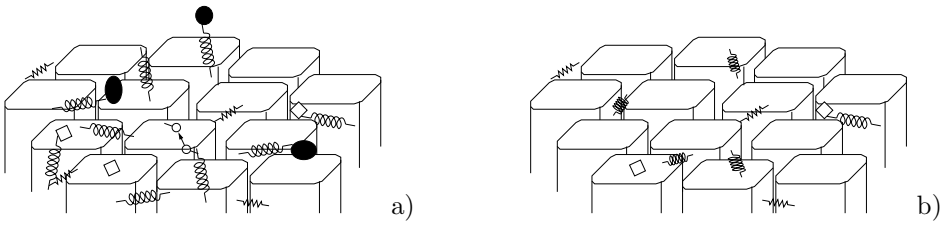
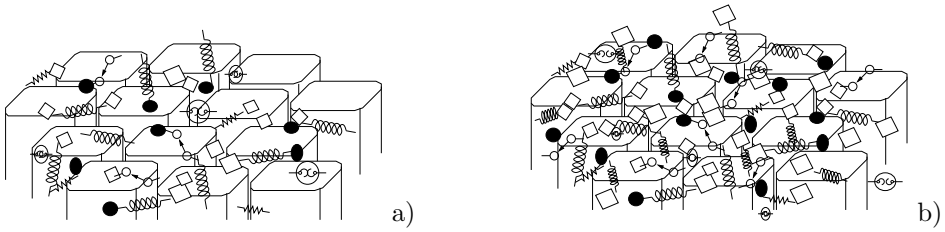


Figure 7.4: Membrane cleaning with a) alkaline and b) protease enzyme cleaning. After alkaline cleaning proteins and some other organic macromolecules are suggested not to be removed. On the contrary, after protease enzymatic cleaning organic macromolecules including proteins are suggested to be removed almost completely

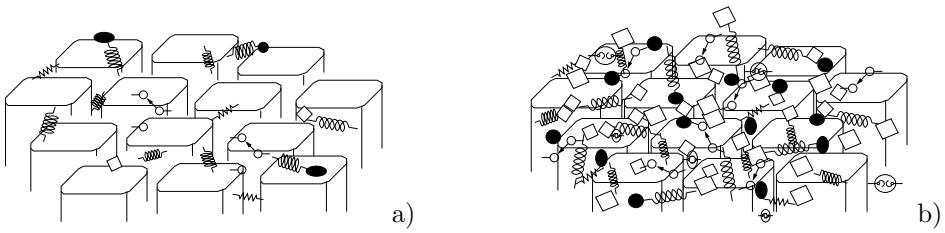
A complete recovery of the Clean Water Flux (CWF) was obtained at wwtp Hoek van Holland after enzymatic (protease) cleaning and at wwtp Utrecht after alkaline cleaning (section 6.3.1). However, in both cases a rapid flux decline followed during ultrafiltration of microfiltrate as illustrated in figure 7.5.



a) b)

Figure 7.5: Rapid membrane fouling by microfiltrate as feed water a) after 1 hour and b) after 1 day of filtration. The wwtp constituents after microfiltration are < 0.2 μm and are suggested to be mainly organic macromolecules, which are contributing to rapid membrane fouling due to adsorption

On the other hand, after alkaline cleaning and possibly also after enzymatic protease cleaning, the pores become wider, as shown in figure 7.6a. Thereafter the pores reduce slowly in size when filtrating feed water. This is illustrated in figure 7.6b. This might be explained by the observed rapid flux decline.



a) b)

Figure 7.6: Membrane surface a) just after alkaline cleaning, whereby the pores are suggested to become wider. Membrane surface b) after 1 day of filtration of microfiltrate as feed water, where the membrane pores are suggested to decrease to their original size and at the same time membrane fouling occurs due to adsorption of organic macromolecules

In case of coagulant dosing prior to ultrafiltration, alkaline and enzymatic (protease) cleaning (section 6.4) resulted in a poor cleaning performance. An acid cleaning revealed to be necessary before an alkaline or enzymatic (protease) cleaning. This acid cleaning resulted in a small increase in of the CWF as shown in figure 7.7. By removing the aluminium out of the formed (organic) complexes, it is suggested that essential linkages between aluminium and organic foulants are broken down, which allows alkaline or enzymatic (protease) cleaning solutions to attack the organic foulants.

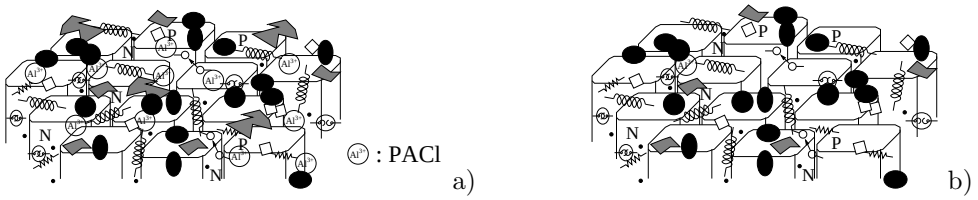


Figure 7.7: Results before a) and after b) acid cleaning. Due to acid cleaning Al^{3+} and other anions are dissolved and suggested to be removed from the fouling structure, which then is supposed to be more accessible for alkali and enzymatic cleaning agents

Thereafter the remained foulants could be removed to a large extent by an alkaline cleaning and could only be removed completely by an enzymatic protease cleaning (section 6.4). This indicates that protein fouling is a relatively long term fouling mechanism, see in figure 7.8. This is also displayed by the relative small amount of proteins retained during ultrafiltration of different feed waters: wwtp effluent, multimedia filtrate and microfiltrate (section 4.2).

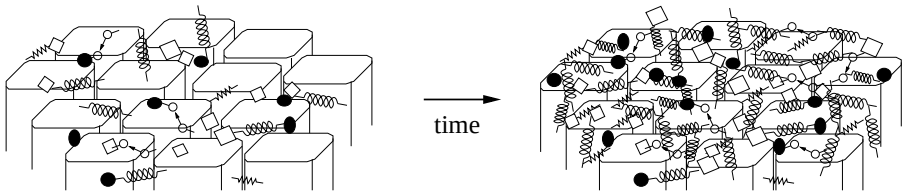


Figure 7.8: Membrane fouling by protein networking. Proteins are suggested to adsorb on the membrane surface and in the membrane pores, but also to each other in such a way that a network structure can be formed

Membrane fouling by polysaccharides could not be determined by enzymatic cleaning with amylase (section 6.3.2). However, during the fractionation experiments (section 4.1) polysaccharides are suggested to play a minor role in membrane fouling, influencing the filterability. In figure 7.9 the suggested role of polysaccharides in linking colloids is displayed.

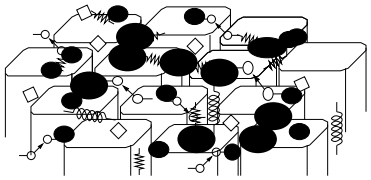


Figure 7.9: Role of polysaccharides in membrane fouling. Relatively low concentrations of polysaccharides are suggested to form linkages between colloids and therefore form a structured cake layer, which is less filterable and less reversible

The measured foulants in this thesis as COD, colour, proteins, polysaccharides and humic substances revealed to be to a large extent smaller than 0.10 μm (section 4.1) and were of minor influence on the filterability (section 4.1 and section 4.2). This was observed by individual measurements based on the amount retained by the 0.10 μm membrane filter and ultrafiltration membrane. It might be possible that only small amounts of these foulants are used for linking colloids to each other and as a consequence result in higher filtration resistances, as indicated by the relatively small retentions found for polysaccharides (chapter 4).

7.2 Overall Conclusions

The performed fractionation, pre-filtration, coagulation and cleaning experiments gave more insight in the fouling behaviour during ultrafiltration of wwtp effluent. Combining the results of these experiments resulted in the following conclusions:

- Particles $>$ 0.45 μm were of limited influence on the filterability and could be removed from the wwtp effluent by applying sand filtration or multimedia filtration as pre-treatment methods
- Colloids of size fraction $<$ 0.45 and 0.10 μm revealed to be of major influence on the filterability and to a less extent on the reversibility during ultrafiltration. These colloids can be influenced by coagulation with PACl, which mainly effects the reversibility.
- Macro-molecules and dissolved material $<$ 0.10 μm were of major influence on the reversibility and to a minor extent on the filterability. These components can be partly influenced by coagulation with PACl, but more effective pre-treatment methods should be investigated. Protein adsorption was indicated as fouling mechanism.

Filterability

Organic colloids of size fraction $<$ 0.45 and 0.10 μm revealed to be of major influence on the filterability during ultrafiltration of wwtp effluent. The filterability could be increased by pre-filtration. By using microfiltration as pre-filtration a stable process performance was achieved, but this is not attractive economically. Conditioning of wwtp effluent or multimedia filtrate by approximately 2 mg Al^{3+}/L PACl hardly resulted in an increase in filterability. The role of EPS on the filterability was only limited. The organic colloids of size fraction $<$ 0.45 and 0.10 μm might possibly be cell fragments and large macro molecules, which could not be measured by the used analytical methods in this thesis.

Reversibility

Reversibility is mostly influenced by organic macromolecules $<$ 0.10 μm as revealed by the membrane fouling experiments by microfiltrate in section 6.3 and more spe-

cific by protein adsorption. However, adsorption by polysaccharides was not clearly demonstrated.

Organic adsorption could be influenced by foulant loads, temperature, applied flux, hydraulics and possible membrane material and morphology. In addition, reversibility could be positively influenced by coagulant dosing with PACl as pre-treatment technique.

Cleaning

The protease cleaning protocol resulted in a complete recovery of the CWF at low temperature of 25-30 °C. If protein adsorption was less severe the alkaline cleaning protocol resulted in a complete recovery of the CWF as well. An acid cleaning did not result in a complete recovery of the CWF, but revealed to be necessary to apply previous to the protease or alkaline cleaning in case metal complexes were formed. Thus, mainly organic fouling revealed to be occur during ultrafiltration of wwtp effluent.

7.3 Suggestions for further investigations

There is a need for further investigations as outcome of this research:

- The influence of membrane properties, such as surface charge, membrane material and morphology on membrane fouling mechanisms.
- How to remain the CWF after (enzymatic) cleaning during filtration of (conditioned or pre-filtered) wwtp effluent and thus to postpone the chemical cleaning to a process acceptable time sequence.
- The influence of new pre-treatment methods on membrane filtration properties, including the amount of foulants retained, for example:
  - oxidation by organic peroxide, active chlorides or peracid in order to deactivate or reduce foulants.
  - activated carbon in order to adsorb foulants previous to membrane filtration.
  - addition of talc or other adsorbent in order to prevent foulants to adsorb at the membrane surface.
- Development of a time efficient cleaning protocol, where several cleaning methods are applied after each other.

Appendix A

Pilot investigations

WWTP Tilburg-Noord

The water supply company "N.V. Tilburgsche Waterleiding-Maatschappij", waterboard "de Dommel" and the local municipality of Tilburg were joined together in a convention "Samen stromen" with the aim to investigate the possibilities of an alterative water quality, Maas (2003). This alternative water quality could possibly be used as industrial water, extinguish water, infiltration water and/ or irrigation water. The effluent of wwtp Tilburg-Noord was investigated as a water source, because of the available quantity and the more constant and better quality as the alternative canal water in terms of suspended solids. The technical and financial feasibility of the production of this water was studied on pilot scale by Witteveen+Bos, Delft University of Technology and Rossmark Watertreatment in cooperation with waterboard "de Dommel" and the water supply company "N.V. Tilburgsche Waterleiding-Maatschappij". The investigated filtration techniques were multimedia filtration, ultrafiltration and nanofiltration in order to produce three different water qualities. The tested configurations are presented in figure A.1.

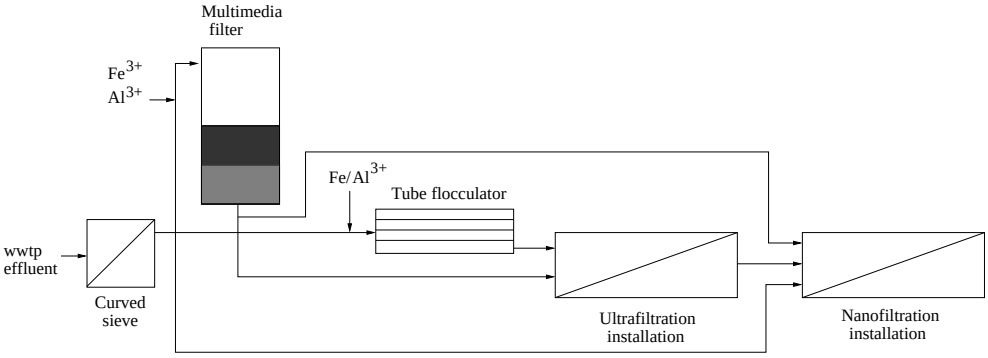


Figure A.1: Scheme of the pilot plant at wwtp Tilburg-Noord

The results showed stable process performances for multimedia filtration with in-line coagulation of 2 mg Al^{3+}/l PACl at a filtration velocity of 12.5 m/h and filtration period of 16 hours, followed by an efficient air/ water cleaning procedure. A stable operation, TMD < 0.6 bar, of the ultrafiltration installation at a constant flux of 110 L/m^2·h and a recovery of 92 % was achieved with wwtp effluent as feed water and in-line coagulation of 2 mg Al^{3+}/l PACl or with multimedia filtrate as pre-treatment before ultrafiltration. The nanofiltration installation resulted in a stable process performance with a recovery of 95 %. The water quality for multimedia filtrate and nanofiltrate were reasonable as defined beforehand, whereas for ultrafiltration for all important water quality parameters the previously defined quality requirements were achieved. The operational costs for ultrafiltration were relatively low and for multimedia filtration the costs were the lowest. For nanofiltration no reliable cost estimation could be made. Based on these results it was concluded that ultrafiltration showed the best performance on water quality with relatively low operational costs and was found technically and economically feasible. Therefore, the involved authorities decided to build an ultrafiltration plant on full scale. This water is produced and distributed by supervision of the water company "Samen stromen" and is named "werkwater", which means water to work with, Ekkelboom (2005). The installation with a capacity of 50 m^3/h is in operation since mid 2004 and produces 75 m^3/h on average "werkwater" at this moment. This "werkwater" is used as industrial water.

WWTP Emmtec

The technical and financial feasibility of the use of wwtp effluent as feed water for the production of demiwater and boiler feed water was investigated for Emmtec Services B.V., which is a company supplying electrical power and water utilities, including industrial wastewater treatment at an industrial area at Emmen, the Netherlands. Therefore, a pilot study was carried out by Witteveen+Bos in cooperation with Delft University of Technology and Nuon Water. The production of boiler feed water was tested on pilot scale by several filtration steps in series: a continuous sand filtration (Astrasand), ultrafiltration and reversed osmosis. This is illustrated in figure A.2. As coagulant PACl was used, which could be dosed before sand filtration and before ultrafiltration.

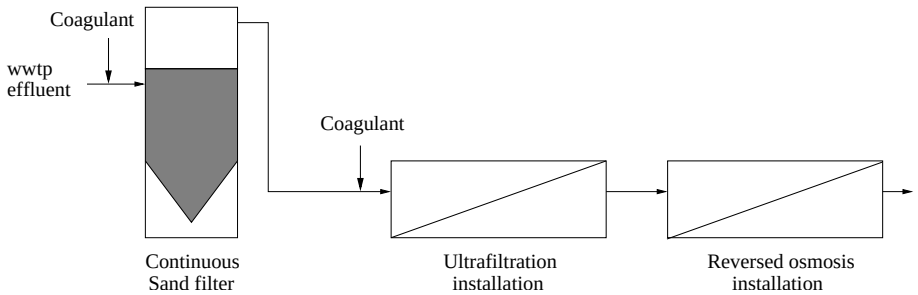


Figure A.2: Scheme of the pilot plant at wwtp Emmtec

The quality of the sand filtrate was classified as good, in terms of turbidity and suspended solids, for use as feed water for the ultrafiltration installation. A stable operation, TMD < 0.5 bar, of the ultrafiltration installation was achieved with in-line coagulation with 2 mg Al^{3+}/l PACl at a constant flux of 100 L/m^2·h, filtration period of 30 minutes followed by a back flush during 45 seconds and a chemical cleaning every 6 hours by alternating NaOCl and Divos 2. The coagulant dosing prior to sand filtration was of no influence on the process performance during ultrafiltration. The reversed osmosis installation resulted in a stable process performance with a recovery of 75 % when 7 mg/L anti-scalant was continuously dosed and once a week a biocide dosage. The quality requirements for boiler feed water were expected to be achieved after ion exchange, which had not been tested on pilot scale, since the reversed osmosis permeate was of good quality to use as feed water for ion exchange.

The financial investigations based on the results of this pilot research resulted in an estimation of the costs for the production of boiler feed water of 0.70 euro/m^3. More details can be found in Kooi (2002).

WWTP Hoek van Holland

Upgrading of the wastewater treatment plant effluent as a part of the Dutch governmental policy to close the water cycle has increasing interest now. The Water Board "Hoogheemraadschap van Delfland" together with the project team of Witteveen+Bos Consulting Engineers, Delft University of Technology and Rossmark water treatment investigated the reuse possibilities of wwtp effluent in the region of Delfland. Therefore, pilot research was carried out at wwtp Hoek van Holland applying different filtration techniques: multimedia filtration, micro- and ultrafiltration. A schematic overview of the pilot installations is presented in figure A.3.

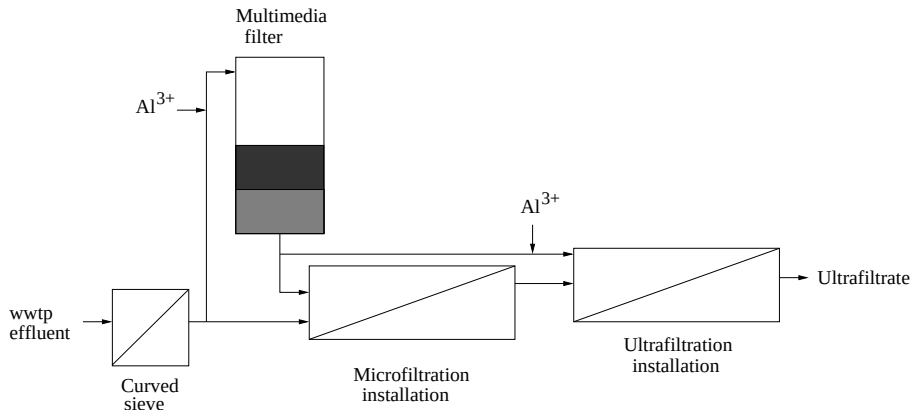


Figure A.3: Scheme of the pilot plant at wwtp Hoek van Holland

The results showed stable process performances of the different filtration techniques when proper pre-treatment was applied. For microfiltration the filtration

characteristics were strongly influenced by particles, which were not retained in the multimedia filter. For ultrafiltration the filtration characteristics were strongly influenced by organic components < 0.2 μm. The upgraded wwtp effluent could not directly be used as process water or for agriculture purposes, due to high concentrations of COD and salts in the wwtp effluent and filtrates. However, wwtp effluent or floc filtrate could be applied directly as water for the washing of sea-sand. More detailed results of the pilot investigations at wwtp Hoek van Holland are given in Bentvelsen (2003), Te Poele et al. (2004a), Menkveld et al. (2004), Te Poele et al. (2003) and Van der Veldt (2003).

WWTP Utrecht

The primary aim of the pilot research carried out at wwtp Utrecht was to investigate the advanced removal of phosphate and nitrogen out of the wwtp effluent by multimedia filtration, microfiltration, ultrafiltration and biological activated carbon. The main interest of the waterboard "Hoogheemraadschap De Stichtse Rijnlanden" (HDSR) was the further development of knowledge about innovative water treatment techniques to polish wwtp effluent in order to be prepared for stricter legislation in near future. This legislation includes the Dutch MTR quality for nitrogen, phosphate and suspended solids and the removal of endocrine disrupters. On the other hand the waterboard HDSR was obligated to investigate the advanced removal of phosphate and nitrogen out of the effluent of wwtp Utrecht to achieve MTR standards. Therefore at wwtp Utrecht pilot investigations were carried out by the Delft University of Technology in cooperation with Rossmark Water treatment and Witteveen+Bos. In figure A.4 a schematic overview of the pilot installations is given.

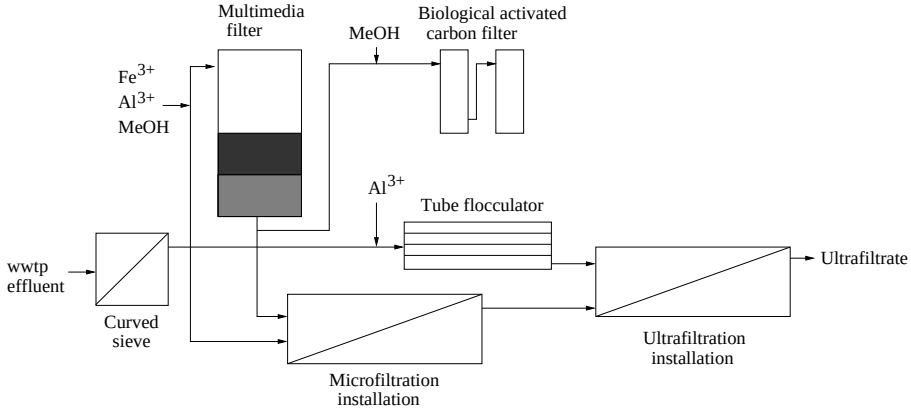


Figure A.4: Scheme of the pilot plant at wwtp Utrecht

Phosphate and nitrogen could be removed simultaneously in the multimedia filter by addition of methanol and coagulant, whereby MTR quality was not achieved. Although through further optimalisation this is expected to be possible. Phosphate

could be removed almost completely by coagulation prior to ultrafiltration and consequently MTR quality for phosphate and suspended solids were achieved, whereas nitrogen could hardly be retained by the ultrafiltration membranes. Simular results are expected for microfiltration, which had not been tested for this purposed. Application of biological activated carbon was successful in the removal of nitrogen and endocrine disrupters (17β-estradiol) to 99.9 % and therefore MTR quality for nitrogen was achieved. For further results is revered to Te Poele et al. (2004).

References

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Van der Veldt, D.J. (2003) "Effluent als bron voor 'ander' water en vervuilende stoffen bij de ultrafiltratie van effluent", in Dutch, Msc thesis, Delft University of Technology, Delft, the Netherlands.

Appendix B

Overview of the pilot installations

Ultrafiltration

The ultrafiltration installation used in this research is designed by Rossmark watertreatment and Witteveen+Bos, Geelen et al. (1996a), and is schematically shown in figure B.1.

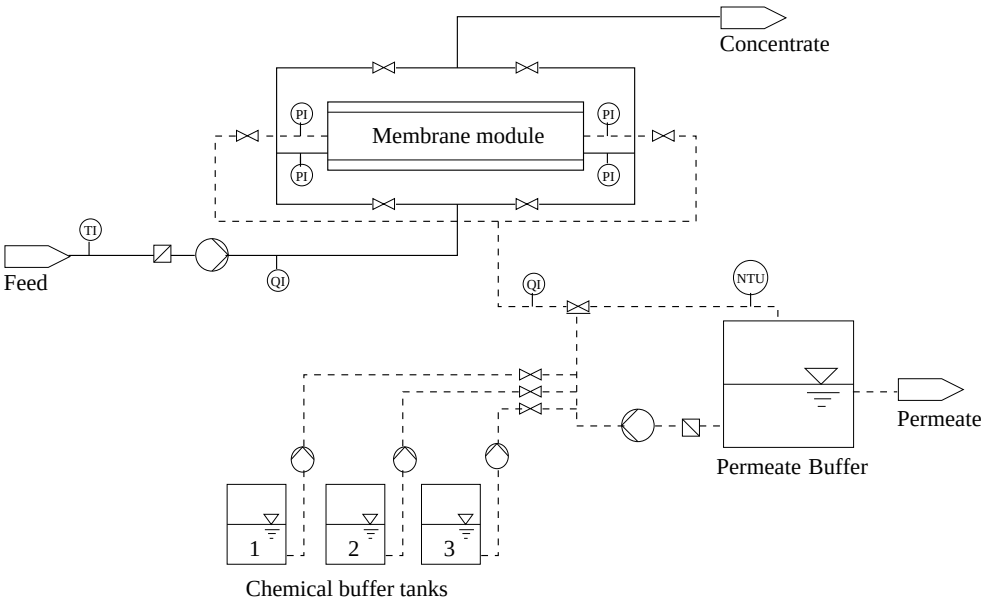

Figure B.1: Flow diagram of the ultrafiltration installation

Multimedia filtration

The multimedia filter used in this thesis is designed by Witteveen+Bos, Geelen et al. (1996b), and is schematically shown in figure B.2. The specifications of the filter bed are given in table B.1.

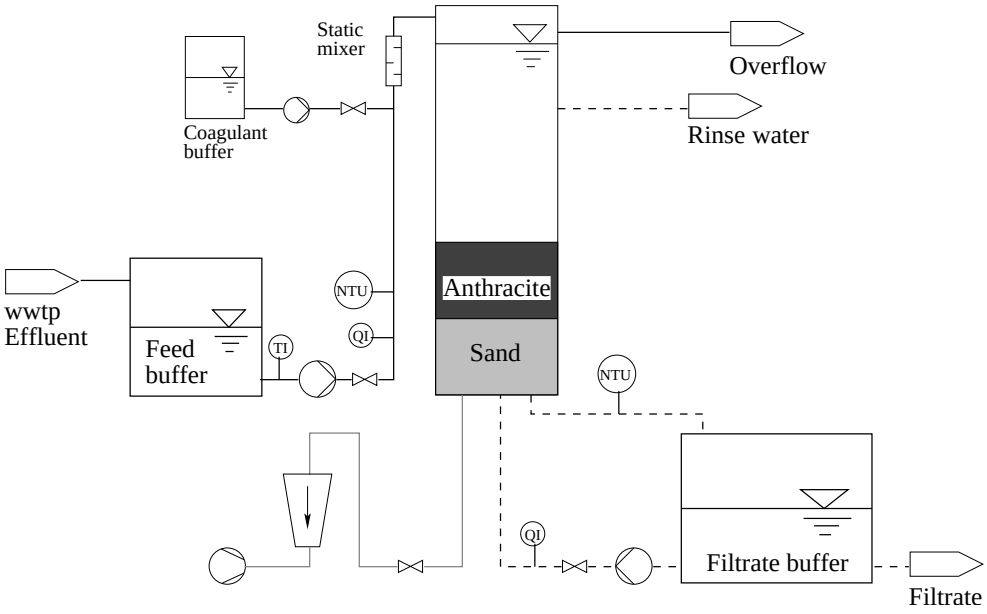

Figure B.2: Flow diagram of the multimedia filter

Table B.1: Multimedia filterbed specifications

Filter layer	Bed height (mm)	Material	Grain diameter (mm)	Density (kg/m^3)
top layer	800	Anthracite	2.0 - 4.0	1400
bottom layer	400	quarts sand	1.5 - 2.25	2600

Microfiltration

The microfiltration installation used in this thesis is designed by Memcor and is schematically shown in figure B.3. In table B.2 the membrane and module specifications are presented. The membrane material is polypropylene.

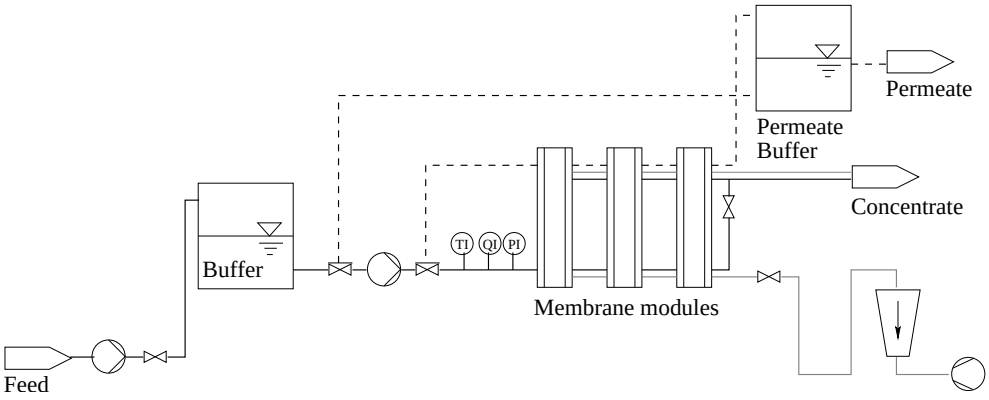

Figure B.3: Flow diagram of the microfiltration installation

Table B.2: Microfiltration module and membrane specifications

Parameter	Specification	
module element length	1.16	m
module element diameter	0.12	m
membrane area	15	m^2
hydraulic membrane diameter	0.5	mm
membrane pore diameter	0.2	μm

References

Geelen, N.M.H., Boersen, M.J.A., Kramer, J.F. (1996a) Flow chart "pilot-plant Membraanfiltratie", in Dutch, Witteveen+Bos, Deventer, the Netherlands, 25 May, ZZWA 5082.

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Appendix C

Membrane properties

Membrane module

The membrane module used in the ultrafiltration installation is the 8" Capfil Membrane element PVC, type S-225 FSFC of X-Flow, X-Flow (2004). A schematic picture of the element with the specifications is given in figure C.1 and table C.1.

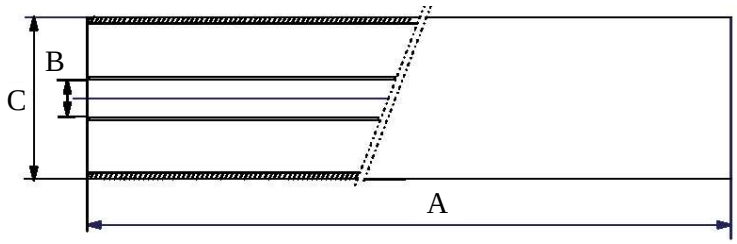

Figure C.1: Scheme of the 8" Capfil Membrane element PVC, type S-225 FSFC of X-Flow

Table C.1: Module specifications of S-225 FSFC (X-Flow)

Parameter	Specification	
hydraulic membrane diameter	0.8	mm
membrane area	35	m^2
element length A	1527.5	mm
permeate collector inner diameter B	42.6	mm
element outer diameter C	200	mm

Materials of construction are:

- PVC housing
- polyethersulfone or PVC flow distributor
- epoxy potting

The operating specifications are presented in figure C.2.

Table C.2: Module operating specifications of S-225 FSFC (X-Flow)[a]

Parameter	Specification		
maximum system pressure	0-20 °C:	600	kPa
	20-25 °C:	500	kPa
	25-30 °C:	400	kPa
	30-35 °C:	350	kPa
	35-40 °C:	300	kPa
maximum transmembrane pressure	0-40 °C:	300	kPa
maximum back flush pressure	0-40 °C:	300	kPa
maximum operating temperature		40	°C

[a]final maximum operating limits are determined by the lowest values of the membrane and element, and pressure and temperature specifications

Ultrafiltration membranes

The membranes used in the ultrafiltration pilot installation and lab scale test set-up are the Capfil ultrafiltration membranes, type UFC M5 of X-Flow, X-Flow (2001).

Basic characteristics:

- hydrophilic polyethersulfone membrane
- capillary membrane of 0.8 mm
- structure asymmetric/ microporous
- developed for inside-out filtration
- developed for use in large-scale processes for water purification
- high performance and a very good anti-fouling behaviour
- membrane elements can be back flushed for efficient membrane cleaning

Membrane composition:

- hydrophilic membrane composed of a blend of polyvinylpyrrolidone and polyethersulphone (patented)
- M5: contains glycerine for pore protection and bisulfite for prevention of microbiological growth.

The membrane performance data is presented in figure C.3.

Table C.3: Ultrafiltration membrane performance data

Parameter	Specification		Remarks
transmembrane pressure	-300 +300	kPa	
pore size	25-30	nm	
molecular weight cutoff	150-200	kDa	on 1 wt% PVP at 1 bar
pH feed	2-12		
temperature	1-80	°C	
chloride exposure	250000	ppm·h	500 ppm max. at 0-40 °C

The permeability of clean water (at least UF filtrate quality) as measured on a single membrane capillary is approximately 600-700 L/m^2·h·bar at 20 °C, X-Flow (2003). The permeability of clean water as measured on a module is approximately 300-400 L/m^2·h·bar at 20 °C, Molemaker (2003).

Since the resistance of the membrane to solvents strongly depends on the actual process conditions, the indications given in figure C.4 should be considered as guidelines.

Table C.4: Resistance of the ultrafiltration membrane to solvents

Solvent	Resistance [a]
Acids	++
Bases	++
Organic esters, ketones, ethers	–
Aliphatic alcohols	+
Aliphatic hydrocarbons	+
Halogenated hydrocarbons	–
Aromatic hydrocarbons	–
Polar organic solvents	–
Oils	++

[a] ++: no change in membrane properties; +: membrane properties may slightly change; -: significant changes in membrane properties

The cleaning agents which can be used are listed in table C.5.

Table C.5: Possible cleaning agents to use for the cleaning of the ultrafiltration membrane

Chemical	Specification
NaOCl (active chloride)	200 ppm max. at 40 °C and max. 30 minutes per day
H_2O_2	100-200 ppm at 40 °C
NaOH + EDTA	pH $\leq$ 12 + 1 wt%
HCl	pH $\geq$ 1
Citric acid	2 wt%
Enzymatic compounds	

It is recommended to keep the pH between 1 and 13 and not to exceed a temperature of 80 °C (depending on the module type) during cleaning and/ or disinfection.

References

Molemaker, F.J. (2003) Personal communication, X-Flow.

X-Flow (2004) CAPF-XIGA-225-PVC-0418, membrane module data sheet of X-Flow, 27 April 2004.

X-Flow (2003) CAPF-UFC SPEC-0346, Ultrafiltration fibre specifications UFC M5, membrane data sheet of X-Flow, 12 November 2003.

X-Flow (2001) CAPF-UFCM5-0143, membrane data sheet of X-Flow, 25 October 2001.

Appendix D

Cleaning of new membranes

For the cleaning of new membranes, which were applied in the laboratory test set-up, the used cleaning procedure was as follows:

- Flushing the membranes with demineralised water by a forward flush for a few minutes;
- A solution of 400 mg/L NaOCl was introduced by a forward flush into the membrane feed site for 2 minutes;
- The membranes were soaked for 30 minutes in the NaOCl solution;
- The NaOCl solution was flushed out by demineralised water for 5 minutes;
- Filtration with demineralised water for 10 minutes.

Appendix E

Measurement of EPS

Proteins

For the analysis of proteins the by Rosenberger (2003) modified method of Frølund et al. (1996), based on the method of Lowry et al. (1951) is used. For the calibration Albumin bovine, BSA, (Acros) fraction V, in a concentration range between of 0 - 25 mg/L is used. The concentration can be calculated with the measured extinction and calibration curve.

Reagents

A: 143 mM NaOH and 270 mM Na_2CO_3 in demineralised water

B: 57 mM $CuSO_4$ in demineralised water

C: 124 mM Na_2-tatrate, $C_4H_4Na_2O_6$, or Na-K-tatrate, $C_4H_4NaKO_6$, in demineralised water

D: mixture of reagents A, B en C in the relation of 100:1:1

E: Folin-Ciocalteu phenol reagent 1:2 dilution with demineralised water

Reagents A, B, C en E can be stored unlimited, reagent D has to be prepared daily.

Method

A sample of 5 mL and in addition 7 mL reagent D, is filled in a round tube and mixed in a tube mixer. After that the mixture is stored for 10 minutes at room temperature. Then immediately after addition of 1 mL reagent E the mixture must be mixed fast and powerful because the Folin-Ciocalteu phenol reagent is only for a short time stable in the alkaline environment. The formation of the colour complex will be finished before starting the measurement. The sample-solution mixtures must be incubated for 45 minutes at room temperature. The adsorption is then measured

in a 4 cm cuvett at a wavelength of 750 nm with a UV-VIS spectrophotometer against a reference sample of demineralised water. The formed colour complex will be stable for about 45-60 minutes. The samples should be measured twice and the mean value has to be calculated. The amount of proteins is expressed in mg/L.

Polysaccharides

For the analysis of polysaccharides the by Rosenberger (2003) modified method of Dubois et al. (1956) is used. For the calibration D(+)-glucose (J.T.Baker), in a concentration range between 0.5 - 10 mg/L is used. The concentration can be calculated with the measured extinction and calibration curve.

Reagents

A: 5 % Phenol solution in demineralised water

B: 95 - 97 % sulphuric acid

Method

A sample of 4 mL is filled in a round tube and 2 mL reagent A is added. After mixing 10 mL reagent B is added in a spout in order to get a proper mixing. Thereafter the mixture is stored for 10 minutes at room temperature, mixed again and incubated for 30 minutes at room temperature. The adsorption is then measured in a 4 cm cuvett at a wavelength of 487 nm with a UV-VIS spectrophotometer against a reference sample of demineralised water. The formed colour complex will be stable for a long time. The samples are measured twice and the mean value is calculated. The amount of polysaccharides is expressed in mg/L.

Materials

- VIS Photo-spectrometer: Milton Roy Spectronic 401
- Mass balance: Mettler AT261 Delta range, range 0 - 200 g $\pm$ 0.0001 g
- Tube mixer: Vortex-genie 2, scientific industries
- Glass test tubes: Schott duran 16$\times$160 mm with screw pod
- Plastic test tubes: 25 mL with screw pod
- Pipettes:
  $\odot$ 200 - 1000 μL $\pm$ 5 μL, Finnpipette Digital
  $\odot$ 1 - 5 mL $\pm$ 0.05 mL, Finnpipette Digital
  $\odot$ 2 - 10 mL $\pm$ 0.1 mL, Finnpipette
  $\odot$ 100 mL $\pm$ 0.08 mL, glass pipette, DIN AS, Hirschmann EM Techcolor
- 4 cm quarts or glass cuvett

References

Dubois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A., Smith, F. (1956) Colorimetric method for determination of sugars and related substances, Analytical Chemistry, Vol. 28, pp. 350-356.

Frølund, B., Palmgren, R., Keiding, P.H., Nielsen, K. (1996) Extraction of extracellular polymers from activated sludge using a cation exchange resin, Water Science & Technology, Vol. 30, no. 8, pp. 1749-1758.

Lowry, O.H., Rosebrough, N.J., Farr, A.L., Randall. R.J. (1951) Protein measurement with the Folin phenol reagent, Journal of Biological Chemistry, Vol. 193, pp. 265-275.

Rosenberger, S. (2003) "Charakterisierung van belebtem Schlamm in Membranbelebungsreaktoren zur Abwasserreinigung", in German, PhD thesis, University of Berlin, Germany.

List of Figures

List of Tables

Curriculum Vitae

Identification

Name	Poele, te
First name	Sandy
Date of birth	14 June 1973
Place of birth	Deventer, the Netherlands

Education

1986 – 1991	Higher General Secondary Education, 'Geert Grootte College', in Deventer.
1991 – 1996	Chemical Engineering, 'Hogeschool Enschede', in Enschede, bachelor degree in environmental engineering.
1996 – 1999	Chemical Engineering, University of Twente, in Enschede, master degree in process engineering.

Work experience

May '05 – recent	Research & Development manager Food & Beverage Europe Middle East and Africa at JohnsonDiversey GmbH & Co. oHG, Mannheim, Germany.
Sept. '00 – Feb. '05	PhD student at the Delft University of Technology, faculty of Civil Engineering and Geoscience, department of Sanitary Engineering under supervision of prof. ir. J.H.J.M. van der Graaf.
Nov. '99 – Aug. '00	Consultant in 'Occupational Safety and Health' (OSH) related 'Risk Inventory and Evaluation' (RI&E) studies at the Dutch Ministry of Defence via 'Randstad' Staffing Agency.