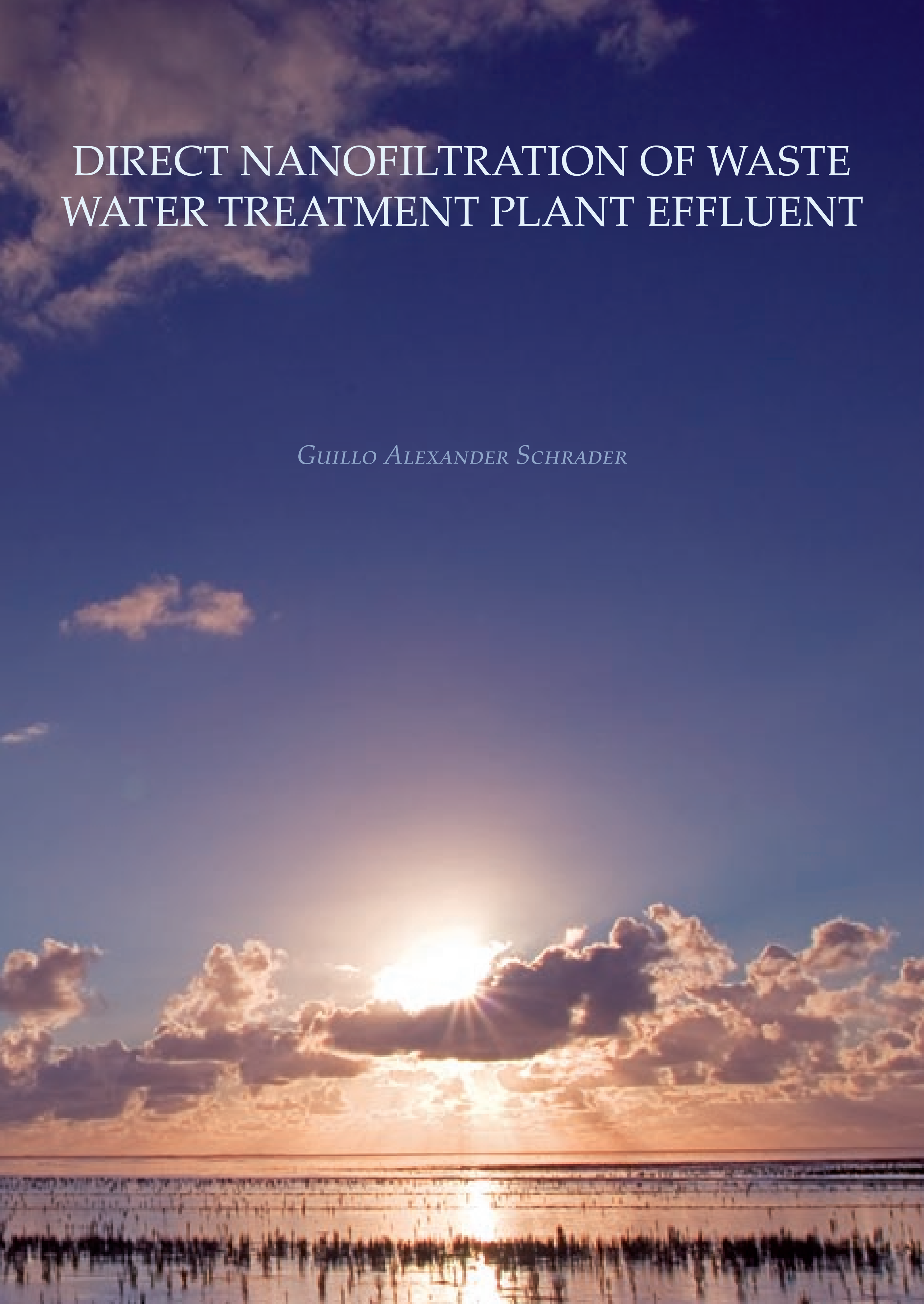
DIRECT NANOFILTRATION OF WASTE WATER TREATMENT PLANT EFFLUENT

Guillo Alexander Schrader



STELLINGEN BEHORENDE BIJ HET PROEFSCHRIFT: *"DIRECT NANOFILTRATION OF WASTE WATER TREATMENT PLANT EFFLUENT"* DOOR GUILLO SCHRADER.

1. Milieutechnologie en chemische technologie zijn nauw verwant al geldt dat zeker niet voor het jargon. Dit kan geïllustreerd worden met het begrip 'colloïdaal'.

2. Te vaak wordt membraanfiltratie beschreven als een schoonmaaktechnologie, terwijl het een pure scheidingstechniek is en er niets wordt veranderd aan de vuillast.

3. Het succes van nanofiltratie als behandelingstechniek voor effluent hangt niet zozeer af van de verwachte vervuilingsproblematiek, maar valt of staat met een geschikte behandelingsmethode voor het membraanconcentraat.
   - Hoofdstuk 5 en 6 van dit proefschrift.

4. De noodzaak van verregaand zuiveren van effluent teneinde het milieu te beschermen tegen verstorende stoffen wordt het best geïllustreerd door de problematiek rond het vinden van een geschikte methode tot verwerking van het membraanconcentraat.
   – Hoofdstuk 6 van dit proefschrift.

5. Veel rapporten over verbeterde zuivering van effluent bekijken alle beschikbare technieken op zichzelf zonder naar gunstige combinaties te kijken. Juist het toepassen van een combinatie van adsorptietechnieken en membraanfiltratie kan leiden tot optimale oplossingen.
   – Hoofdstuk 6 en 7 van dit proefschrift.

6. Het voldoen aan de normen van de Kader Richtlijn Water en de daarin beschreven prioritaire stoffen dwingt tot het leveren van een drinkwaterkwaliteit rioolwaterzuiveringseffluent.
   - Hoofdstuk 7 van dit proefschrift.

7. Sir Winston Churchill once said: "Success consist of going from failure to failure without loss of enthusiasm". For many experiments this is true, if the experimenter recognizes that the failure itself illuminates the path to success.

8. Kernenergie zou geen enkel probleem zijn als het radioactief afval dezelfde halfwaarde tijd had als pennen, scharen, gereedschap en maatbekers in een laboratorium.

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The research described in this thesis was carried out at the van Hall Institute and WETSUS *'Centre for Sustainable Water Technology'*, Leeuwarden, The Netherlands under supervision of the department of Membrane Process Technology, University of Twente, Enschede, The Netherlands.

Vitens Water, Landustrie Sneek and Wetterskip Fryslân are highly acknowledged for their co-operation in and financial support for the work described in this thesis.

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Direct Nanofiltration of Wastewater Treatment Plant Effluent
Ph.D. Thesis, University of Twente, The Netherlands
ISBN 90-365-2332-X

Printed by PrintPartners Ipskamp B.V., Enschede, The Netherlands
Cover by Hillebrand Breuker Photography, Warten, The Netherlands

DIRECT NANOFILTRATION OF WASTEWATER TREATMENT PLANT EFFLUENT

PROEFSCHRIFT

ter verkrijging van
de graad van doctor aan de Universiteit Twente,
op gezag van rector magnificus,
prof.dr. W.H.M. Zijm,
volgens besluit van het College voor Promoties
in het openbaar te verdedigen
op vrijdag 31 maart 2006 om 16.45 uur

door

Guillo Alexander Schrader

geboren op 10 juni 1974
te Willemstad, Curaçao

Dit proefschrift is goedgekeurd door de promotoren:
Prof.dr.-ing. M. Wessling
Prof.dr.ir. W.G.J. van der Meer

en de assistent promotor:
Dr. A. Zwijnenburg

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CHAPTER 1

THE NEED FOR AN UPGRADED WASTE WATER TREAMENT PLANT EFFLUENT QUALITY

This chapter gives a short overview of the historical and current problematic issues regarding the disposal of (treated) sewage on surface waters. Analogously, the historical development of membrane technology is described. Both historical developments culminate in the introduction of industrial membrane technology after World War II in the drinking water sector. A few decades later, membranes are seen as a possible technology for enhanced treatment of effluents of wastewater treatment plants. With the further progress in membrane development a new kind of membrane emerges, the nanofiltration membrane. This membrane seems ideally suited for the application in wastewater reuse schemes, especially for advanced treatment of effluent from domestic wastewater treatment plants. Advanced treatment of WWTP effluent utilizing nanofiltration membranes is the topic of this Ph.D-thesis. The chapter concludes with a brief outline of the work presented in this thesis.

1 The need for an upgraded WWTP effluent quality

1.1 Historical context from a Dutch perspective

Surface water quality problems related to discharge of human originated waste have been reported since the founding of the Dutch cities. In 1530 the Amsterdam city council described the quality of the canal water as 'costelijck' (Old Dutch for 'well drinkable'). In reality, the same city council had to cancel the visit of Emperor Charles V in the year 1540. The Amsterdam water quality was so bad that the Emperor 'de doedt drinken soeden', i.e. would drink himself to death with Amsterdam canal water [1]. It took until 1960-1970 before public and governmental awareness led to the first piece of Dutch environmental legislation, the Pollution of Surface Water Act [2].

Figure 1 - An Amsterdam canal in the mid sixties.

By that time, untreated sewage discharge has led to acute problems such as oxygen deprivation, disappearance of indigenous species and sediment pollution. The accumulation of hazardous species in the aqautic environment became a treat to the water supply for human, agriculture and recreational purposes. Figure 1 shows a clear example of uncontrolled discharge, a picture hard to imagine in present times. From the seventies onwards, the Dutch sewers were gradually connected to central sewage treatment facilities aimed at reducing the nutrient load to the receiving surface water to a minimum.

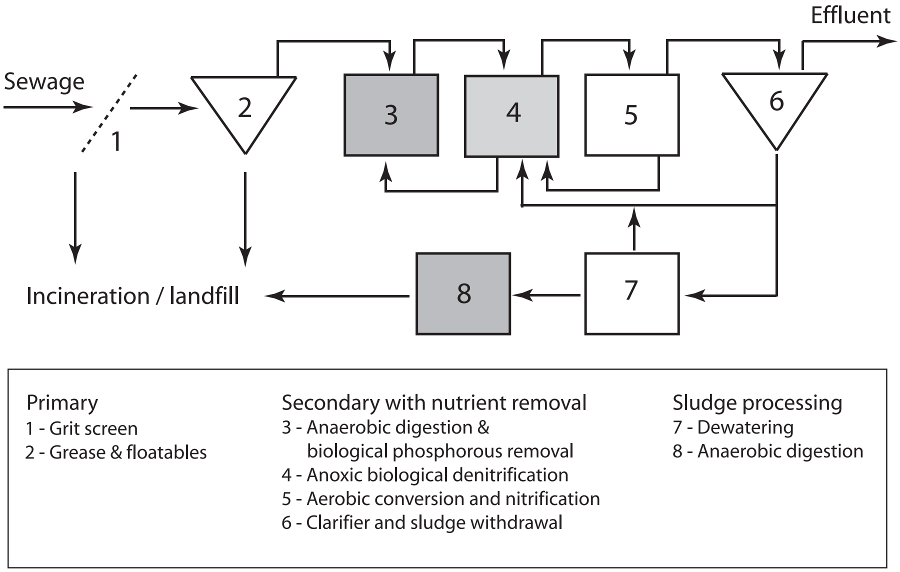

Figure 2 - Modern wastewater treatment facilities

A modern sewage treatment plant, often referred to with the more generic term wastewater treatment plant (WWTP), is able to remove most nutrients up to ppm level. Figure 2 shows a schematic flow chart of most basic parts of a WWTP.

In time, surface water acts became more stringent and as result, some signs of partial restoration of the Dutch waters, in respect to nutrient load, were reported in the beginning of this century [3]. Unfortunately, surface water quality still deteriorated due to emission of other substances than (organic) nutrients, such as heavy metals and organic micro-pollutants, for instance pharmaceutical and personal care products (PPCPs).

With the development of new analytical tools it became evident in the 1990's that wastewater treatment plants (WWTP) were a major source in spreading of PPCPs and other micro-pollutants in receiving surface waters [4-6].

In recent years, researchers have uncovered environmental effects linked to the discharge of PPCPs, such as feminization of fish by (xeno-)estrogens [7, 8]. Some researchers have attributed the decrease in human sperm quality [9] and increase in breast, testicular and prostate cancer [10, 11] to the occurrence of endocrine disrupting compounds in the environment.

Many effects are still unknown; however the occurrence of PPCPs in water has trigged new research in the direction of identification, occurrence and effects of trace contaminants in WWTP effluent.

Beside scientific awareness, public awareness was triggered by newspaper headlines as 'Stay calm - Prozac™ in your drinking water' [12] and 'Fish on Prozac™ - how depressing' [13]. Consequently, the latest European Directive on Surface Waters (2000)[14] lists a number of PPCPs, together with other species, as 'propriety hazardous substances' for which a zero-discharge level is set in 2021.

It is in this perspective that, since the turn of the century, research has been initiated focused on new technologies to remove PPCPs and other micro-contaminants from effluent as the removal efficiency of current WWTPs were proven to be inadequate.

1.2 RECLAIMING WATER FROM WWTP EFFLUENT

Fresh water resources in the world are limited and water stress in dry or highly urbanized regions is rather common. Currently, about one third of the world's population lives in areas with moderate to severe water shortages [15]. WWTP effluent is therefore seen as a potential source for water reclamation to alleviate water stress whether used for irrigational, recreational or potable use.

Around 65% of the fresh water resources are used for irrigational purposes. In a non-Dutch perspective, municipal wastewater has been a source in (semi)-arid regions for agricultural and/or gardening purposes for many decades. Reuse of effluent can be beneficial in raising crop production [16], but is not without risks. Studies in the last decade have shown correlations between human health effects and consumption of raw salads grown from sewage irrigated fields [17, 18]. Irrigation of agricultural fields with effluent can also lead to the accumulation of heavy metals and/or salinization of the top-soil rendering agricultural grounds barren [19, 20].

Removal of micro-bacterial contaminants (e.g. *Giardia, Cryptosporidium*) and heavy metals are therefore essential for sustainable irrigation. In recent years, concern has grown whether the occurrence of PPCPs and endocrine disruptive compounds in or on crops irrigated with WWTP effluent has health effects. Especially the accumulation of pharmaceuticals in the soil is suspected to become problematic. Micro-organisms and pests associated with soil life could grow antibiotic-tolerant [21]. In analogy with the previous paragraph, an enhanced effluent treatment is needed for safe and sustainable use of effluent as irrigational water. In the past years new effluent reclamation plants, capable of (partly) removing mentioned hazardous species, have been constructed in areas of water stress such as Australia [22] and Mediterranean countries [23, 24]. The technology used in safe reclamation schemes are membranes, often a combination, such as microfiltration – reverse osmosis.

Beside agricultural use, several initiatives have been launched in the past years for (in)direct potable use of WWTP effluent. The only reported direct usage of WWTP effluent for drinking water purposes is in Windhoek, Namibia. Daily, 21.000 m^3 of WWTP effluent is treatedby a complex treatment train of pre-ozonation, coagulation, dual media filtration, main ozonation, biological activated carbon sorption, dual granular activated carbon sorption, ultrafiltration and chlorine disinfection [25].

Examples for indirect use of WWTP effluent for drinking water are also limited. In Wulpnen (Belgium), Orange County (USA) and Singapore dual membrane processes (microfiltration-reverse osmosis) and a final disinfection step (ultraviolet radiation/H_2O_2) are used for effluent infiltration for aquifer replenishment [22, 26, 27]. Again, all these new reclamation schemes rely heavily on membranes.

1.3 MEMBRANE TECHNOLOGY

1.3.1 *A short history*

As early as 1748 the French cleric Jean Nollet was able to observe osmotic pressure using animal guts and bladders [28]. In 1861 membrane technology started when Thomas Graham (1805-1869) used synthetic membranes (vegetable parchment coated with albumin) to extract urea from urine [29].

The first working membrane applications were in the field of dialysis. In 1913, Abel, Rowntree, Turner and colleagues constructed the first artificial kidney. However, no patients were treated with this device. The German scientist Georg Haas performed the first successful human dialysis in autumn 1924. The dialysis was performed on a patient with terminal uraemia “because this was a condition against which the doctor stands otherwise powerless”. The dialysis lasted for 15 minutes, and no complications occurred. The first practical human haemodialysis machine, was developed by Willem Kolff and Hendrick Berk from the Netherlands in 1943 [30].

As a result of the major disruption of the water supply in Europe after World War 2, water filters were urgently needed. US army sponsored research for large scale water purification kick-started the already established microfiltration industry, a process which later led to the establishment of the Millipore Corporation [28]. In the USA, as population numbers were growing in the semi-arid region of California the need for fresh water from alternative sources became a necessity. This led to the first research on the membrane technology we now know as ‘reverse osmosis’. The major breakthrough came in 1961 with the Loeb-Sourirajan membrane which made desalination economically possible [31].

Presently, the membrane industry is a well established industry which is expanding rapidly. In the USA, the turnover for water and wastewater related membrane activities totaled over US$750 million in 2003 and is projected to reach US$1.3 billion in 2010 [32].

1.3.2 Nanofiltration

In the 30 years after the development of the first modern cellulose acetate membrane by the Loeb-Sourirajan process a whole range of membranes was available, as shown in Figure 3. At one side of the spectrum, seawater desalination membranes (reverse osmosis RO) with sodium chloride rejections higher than 99.9% and on the other side microfiltration (MF) membranes without any salt rejection. The membranes between RO and UF were classified as either loose RO, low pressure RO (LPRO) or tight UF. Unfortunately, the cellulose acetate membranes had quite some operational limitations, e.g. limited pH range and sensitivity to biological fouling, preventing widespread use in industry.

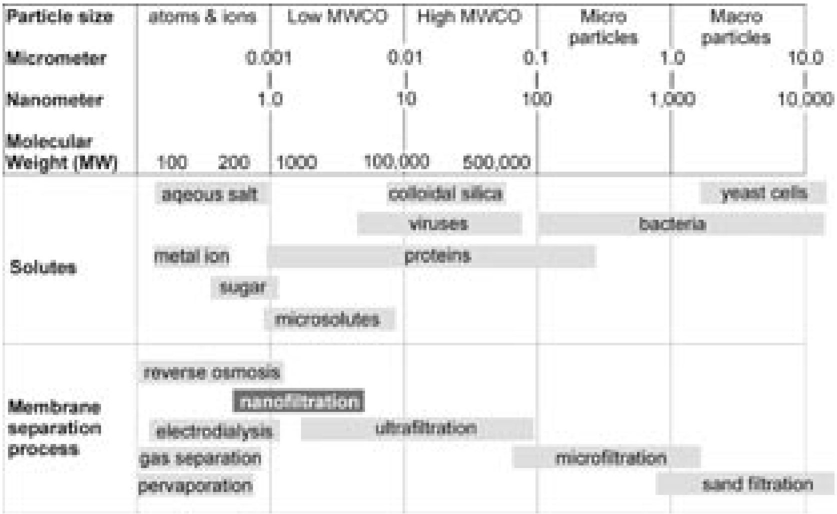

Figure 3 – Membranes classification based on typical rejection values

From the 1970s the modern generation of membranes emerged, thin film composite membranes. The base of this kind of membrane was an UF support membrane on which a very thin layer (submicron scale) of another polymer, often a polyamide, was coated. Optimization of the top layer (or selective layer) to accommodate for more demanding environments continued and in the mid 1980s the first commercially available membranes became available bearing the name: *Nanofiltration* (NF).

Such membranes in general pass mono-valent ions to a larger extent than divalent ions. Nanofiltration membranes can pass small organic molecules and reject organic with higher molecular weight. A typical molecular weight cutoff for a NF membrane, e.g. the level at which more than 90% of a certain molecule is rejected, lies in the region of 200-500 Dalton.

1.3.3 *Module design*

Next to the development of new membrane materials, module concepts were developed. Presently, membranes are installed in modules as; flat sheet, spiral wound, tubular, capillary, hollow fiber and even module-less configurations. Table 1 lists the (dis)-advantages of the various systems.

Table 1 - Various module concepts for NF membranes. Adapted from [33].

	Plate & Frame	*Spiral Wound*	*Tubular / Capillary*	*Hollow Fiber*
Packing density	200-500	500-1000	100-3600	500-5.000
Energy usage	Low-Moderate	Moderate	High	Low
Flow regime	Laminar	Laminar	Turbulent - Laminar	Laminar
Fouling	Moderate	Good (no solids)	Good	Moderate - Good
	Good	Poor (solids)	Physical cleaning possible Back flush	Back flush
Typical applications	Niche markets	Potable water Wastewater Paper / Pulp	Potable water Wastewater Paper / Pulp	No applications yet

1.3.4 *Fouling*

Membranes can be seen as molecular sieves retaining part of the feed. As a consequence, deposits of the retained material will accumulate at the feed side of the membrane. In time this might hamper the selectivity and productivity of the separation process. This process is called fouling. A widely accepted definition for fouling is given by Koros et al. [34] "The process resulting in loss of performance of a membrane due to deposition of suspended or dissolved substances on its external surfaces, at its pore openings, or within its pores". Other definitions of fouling extent Koros's definition and include concentration polarization. Concentration polarization is the increased gradient of feed material in the region near the membrane. Such a gradient develops when the speed of mass transfer to the membrane exceeds the back diffusion for certain feed components to the bulk of the feed. Another fouling concept frequently used is the so called "critical flux". The critical flux is defined as "the limiting flux value below which a flux decline over time does not occur" [35]. Figure 4 depicts a number of fouling processes which might happen in membrane filtration

Another fouling process not incorporated in Koros's definition is the growth of micro-organisms and their metabolic products on a membrane surface, so called biofouling. A membrane is an ideal place for the formation of biological activity. All bacteria, fungi, algae and most viruses are retained and accumulate at the feed side of the membrane. At the membrane surface nutrients are supplied to the micro-organisms at higher concentrations compared to the bulk feed due to their rejection.
Furthermore, the water temperature in membrane systems might be elevated due to the energy losses of the feed and circulation pumps. Once developed biofouling is very hard to remove as incomplete removal of (dead) micro-organisms will spawn re-establishment of new biological activity.

All mentioned processes are likely to occur when membranes are applied in treatment of domestic wastewaters [36]. Fouling and membranes are thus linked together just like catalysts and catalyst inactivation.

Fouling will always occur and a cleaning strategy is therefore an essential part a membrane process design. When a cleaning strategy is not successful in restoring the original membrane performance, the loss in performance is attributed by so-called ‘irreversible fouling’. The irreversible fouling often determines membrane lifetime and the economy of the chosen application [37].

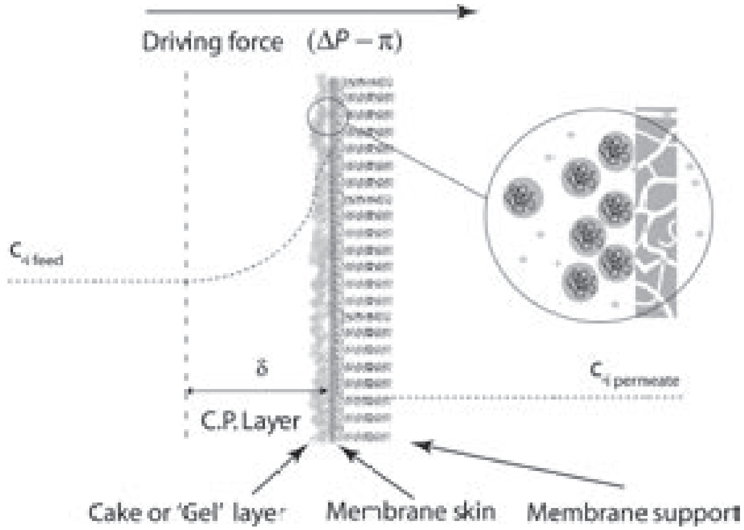

Figure 4 - Schematic diagram of a composite membrane with several kinds of fouling depicted; concentration polarization, deposition on the feed side of the membrane (cake) and internal fouling of the membrane skin void space (top layer).

1.4 Membrane filtration of WWTP effluent

As mentioned in the first paragraphs membrane technology is often seen as the appropriate technology for reclamation of WWTP effluent. Research in the 70s showed that reverse osmosis would be a suitable candidate for effluent reclamation [36]. At that time (1973) the first major installation of reverse osmosis membranes in a reclamation scheme were installed at Orange County Water factory 21[38]. These first membrane applications relied on an extensive pretreatment process, see Figure 5, to keep fouling of the membranes within tolerable levels.

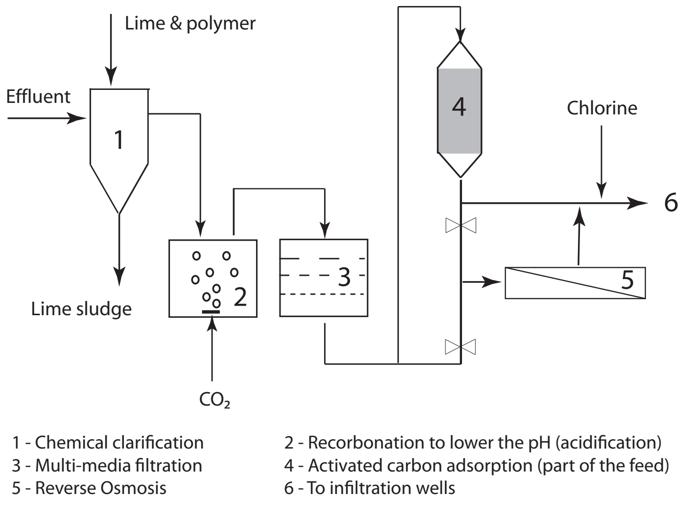

Figure 5 – Pretreatment for effluent reclamation by RO membranes at Orange County Water Factory 21. Adapted from Mills et al. [38]

In the decades following, new materials for membrane formation, other module concepts led to a drastic decrease in investment and operational costs for membrane related processes. Furthermore, new hybrid concepts were introduced as membrane assisted biological reactors, the so called membrane bioreactor (MBR). Studies in the 90s showed that reclamation of effluent might be achieved by other means than the proven but expensive reverse osmosis (including pre-treatment) option [39-44].

1.5 Direct Nanofiltration of WWTP Effluent

In 1999, a new promising membrane technique was introduced for reclamation of effluent with the arrival of capillary nanofiltration modules [45]. Conventional spiral wound modules required often pretreatment with conventional techniques or another membrane process like, micro- or ultrafiltration. With the more favorable hydrodynamics and new cleaning strategies applicable, such as back flush and air enhanced forward flush (Airflush®), a direct treatment of WWTP effluent seemed possible using capillary modules.
Early field tests showed that these new capillary nanofiltration membranes showed superior operational stability compared to ultrafiltration membranes [46, 47]. The successful trial tests with capillary nanofiltration modules showed the potential of the new concept as the nanofiltration membranes were able to achieve nearly all target for the Maximum Achievable Risks (MAR) targets as specified in the EU Water Framework Directive (see §1.1).

Albeit the successful trials, little was known about the fouling behavior of nanofiltration membranes in a direct filtration scheme. Furthermore, one started to realize that in a NF/RO reclamation scheme a solution should be found to deal with the waste stream of the process, the concentrate.

At the same time, a PhD-project was initiated at the department of Membrane Process Technology (University of Twente), to investigate the applicability of nanofiltration membranes in a direct effluent filtration scheme. The project started in February 2002 under the supervision of the late prof.dr.ing. Marcel Mulder and culminated in this thesis. The goal of the project was to study the reuse possibilities of WWTP effluent by using nanofiltration as polishing technique. Focal points of the study were to be the fouling behavior of the membranes and to investigate possible options for concentrate disposal.

1.6 Outline

This thesis deals with various topics in five main chapters. The chapters (2-5) deal with various aspects of fouling and anti-fouling strategies.
Chapter 2 is a study on the role of the colloidal stability of the feed in relationship to fouling behavior. Aspects of cake layer development and reversibility of the cake layer on flat sheet membrane samples are investigated as function of the colloidal stability.
The next chapter (3) deals with alteration of the feed by coagulant addition as an anti-fouling strategy. Main question in this chapter is; can coagulant addition alter the structure of the fouling layer such that a more favorable membrane performance is obtained.

Chapters 4 and 5 contain experiments on pilot plant scale using spiral wound nanofiltration modules.
In Chapter 4 the influence of temporary feed exposure to a high voltage static electric field device is investigated on the pilot plant performance. In theory such an electric field device is able to alter the electro-kinetic characteristics of the feed. Such an alteration could be beneficial as Chapter 2 showed a clear correlation between system performance and colloidal stability.

Chapter 5 explores several operation modes in which the pilot plant could be operated. The role of dissolved oxygen on system performance is explored, as well as the addition of coagulants and a more intensive pretreatment by ion-exchange. Finally a long term test is performed and the results are compared to reported studies utilizing capillary nanofiltration membranes.

The penultimate chapter (6) discusses various treatment and disposal options for the nanofiltration concentrate. The focus is to investigate under which conditions the concentrate could be returned to the head of the WWTP. The work presented in this thesis is evaluated in the final chapter (7) resulting in an outlook for the possibilities of WWTP effluent reuse utilizing nanofiltration membranes.

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CHAPTER 2

THE EFFECT OF WWTP EFFLUENT ZETA-POTENTIAL ON DIRECT NANOFILTRATION PERFORMANCE

Laboratory scale filtration tests utilizing WWTP effluent were conducted to investigate fouling and filtration performance of nanofiltration membranes. The focus of this research is to assess the influence of the zeta-potential of the colloidal fraction in WWTP effluent on nanofiltration performance. As the work presented in this study is conducted on a real effluent rather than model water, a statistical design method has been used to account for effluent composition variations and to obtain valid and significant results. The results show that in direct filtration (NF/RO) of water with NOM, maintaining a high zeta-potential is imperative to keep cake layer resistance to a minimum. The reversibility of the fouling process was shown to be independent from the changes in zeta-potential. Fouling was shown to be promoted by acidification (pH 5) of the effluent, whereas coagulant addition resulted in an increase in the reversibility of the fouling layer. The work presented in this paper suggests that selection of a proper coagulant to suppress fouling problems should be based on the interaction between membrane and coagulant, while the interaction of coagulant-NOM should be minimal to maintain a high (negative) zeta-potential.

This chapter has been published in the Journal of Membrane Science, volume 266 (2005) 80-93

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The effect of WWTP effluent zeta-potential on direct nanofiltration performance

2.1 Introduction

Reuse of water from wastewater treatment plants (WWTP) utilizing membrane technology has received a lot of attention in the past decade, especially microfiltration (MF) and ultrafiltration (UF). It has been proven that membrane technology is a successful technique for production of effluents free of micro-organisms and suspended solids. Even higher quality of permeates can be achieved by use of nanofiltration (NF) or reverse osmosis (RO) by additional removal of soluble organics and salts. Residual organics in WWTP effluent are often characterized by less bio-degradable compounds. Associated with these bio-inert compounds are humic substances and micro-contaminants like endocrine disrupters, pesticides and trace metals which are often adsorbed to humic substances. These micro-contaminants have been shown to accumulate in the environment threatening water resources [1, 2].

Apart from the environmental need for enhanced treatment of WWTP effluent for water reuse programs, future change in legislation might trigger the need for effluent polishing techniques. An example would the screening of WWTP effluent on priority substances, as proposed in the EU Wastewater Framework Directive [3].

Previous pilot studies showed that direct nanofiltration could be a suitable technique for polishing WWTP effluent [4, 5]. A key component in a successful sustainable and economical implementation of NF/RO in wastewater polishing is to find a disposal strategy for the resulting concentrates [6, 7]. Concentrates from NF effluent polishing can most likely not be discharged due to legislational and environmental aspects as mentioned before. For any discharge concept, apart from dilution to meet discharge levels, it is imperative to minimize the concentrate volume [8]. Minimization of the concentrate is often hampered by severe fouling effects. The main fouling constituents in the effluent are (biologically) inert dissolved organics originating from the WWTP influent and biological residue products from the activated sludge process.

A significant number of theoretical and experimental studies on model waters have been conducted to identify the main fouling mechanism of natural organic matter (NOM) in membrane filtration. Physical-chemical interactions between NOM, feed water matrix and the membrane have been found to play a significant role. The most important parameters are considered to be:

1. Colloid stability (related to zeta-potential); decreased stability leads to loss in cake layer void space resulting in higher filter cake resistance [9].
2. NOM - membrane bridging under influence of divalent cations, especially calcium; Divalent ions are shown to act as bridging material between carboxylic active groups present in many NOM and the negatively charged functional groups present at the membrane surface [10, 11].
3. Hydrophobicity of the feed water constituents. The hydrophobicity of feed water constituents, expressed in their octanol-water partitioning coefficient was shown to be a relatively robust parameter in predicting the fouling potential. Components with a higher partition coefficient show more hydrophobic interactions and cause more flux decline [11-13].

4. Membrane surface properties as surface roughness, contact angle and charge density [14,15].

The observed membrane performance appears to be a complex function of the feed water characteristics and the chemical and physical properties of the membrane itself. These complex interactions make process control in direct membrane filtration of WWTP effluent difficult as the feed water mixture changes rapidly (within hours to minutes). One parameter within the effluent, the zeta-potential of its colloidal matter, seems to be a good and robust indicator in operational control of a WWTP [17].

The authors hypothesized that the zeta-potential of the colloidal matter in the WWTP effluent could be a suitable parameter to assess filtration and fouling performance as the zeta-potential is directly linked to the most important fouling mechanism described before. It is important to notice that the term 'colloids' used in this paper refers to the components in the effluent which show colloidal behavior, i.e. show electrophoretic mobility as measured in visible light. This 'chemcentric' approach includes the colloidal pool such as coiled proteins and humic substances if they include interacting exterior charges best treated with double layer theories. Ergo, the term 'colloids' does not refer to the terminology often used in wastewater engineering in which colloids are classified as particles with a range between 0.01-1.0 μm [17].

In contrast to all previous studies, we have chosen to analyze the influence of the colloidal properties of real feed water, expressed in zeta-potential of the colloidal matter, on direct nanofiltration performance. To cope with the complexity of the changes in the feed water composition, we have chosen a design of experiment, to obtain statistically valid and meaningful conclusions.

2.2 METHODS AND MATERIALS

2.2.1 *Design of experiment*

To assess the influence of the stability of the NOM in a real effluent matrix we have to cope with three difficulties; control of the zeta-potential during the experiment, the variance in effluent matrix composition between experiments and possible interactions of the various factors (§2.2.4) chosen in the experimental design.

Paragraph 2.2.3 shows the zeta-potential to be a relatively robust parameter of the effluent which can be controlled by pH adjustment and coagulant dosage. Choosing a NF membrane with low salt rejection (§2.2.5) helps to reduce the effect of the ionic strength on the zeta-potential during the experiment.

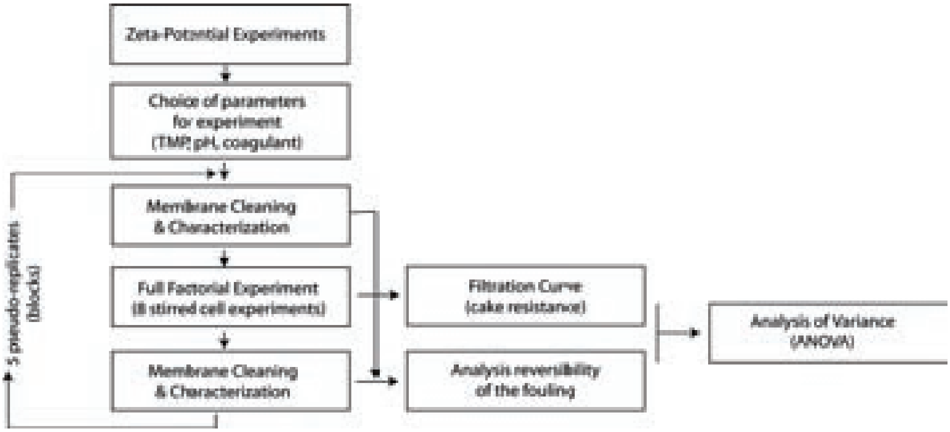

Figure 7 – Block diagram of the experimental design

To account for the variance between effluents and to detect interaction effects between chosen parameters a statistical method, full factorial design (FFD) with blocking was employed (see the appendix). A total of 40 stirred cell filtration experiments (§2.6.4) was run overnight at ambient room temperate (18-20 ºC). Total duration for each experiment varied from 15-20 hours to achieve, if possible, equal recoveries of around 95%. Nanofiltration performance was evaluated in terms of filtration resistance of the effluent and reversibility of the fouling. Figure 7 gives a schematic overview of the required sequences of experiments and data processing needed.

2.2.2 *Effluent characteristics*

Effluent from the municipal wastewater treatment plant at Leeuwarden, the Netherlands was used in this experiment. The Leeuwarden plant consists of an activated sludge system combined with phosphate removal by chemical pre-cipitation. Samples were drawn from the overflow of the secondary clarifiers and stored prior to analysis in dark at 5º C. Total storage time was kept below 24h to prevent change in effluent characteristics. General characteristics of the effluents used in the full factorial experiment are listed in Table 2.

Table 2 - General parameters for the WWTP effluents used for the experiments

Effluent sample ID	*TOC*	*DOC*	*UVA_{254}*	*SUVA*	*Conductivity*	*pH*	*Ca^{2+}*	*Na^+*	*Cl^-*
	$mg.L^{-1}$	$mg.L^{-1}$	cm^{-1}	$L.cm^{-1}.mg^{-1}$	$mS.cm^{-1}$		$mg.L^{-1}$	$mg.L^{-1}$	$mg.L^{-1}$
E1	14	14	0.37	0.026	1.55	7.8	38	270	240
E2	15	13	0.37	0.028	1.04	7.9	46	175	150
E3	21	19	0.41	0.022	1.63	7.7	62	295	230
E4	17	15	0.37	0.025	1.65	7.8	19	289	240
E5	14	13	0.31	0.024	0.84	7.8	9.0	156	120

1) TSS concentrations effluents E1-E5 always < 2 mg/L which is detection limit for Standard Methods 2540D [33]

2) Proteins (monthly average) 3.6 ± 1.0 mg/L analyzed by BioRad ©-assay according to Bradford Method

3) Polysaccharide content (monthly average) 2.4 ± 3.0 mg/L by phenol/ sulfuric acid method by Dubois et al. [34]

The effluent of the Leeuwarden sewage treatment plant has some site-specific characteristics:

Firstly, the moderate Specific Ultraviolet Absorption (SUVA) (> 0.02 $L.cm^{-1}.mg^{-1}$) of the effluent shows the aromatic nature of the effluent, which is not surprising as the drinking water of Leeuwarden contains a large amount of humic substances. The drinking water of Leeuwarden contains around 8 mg/L TOC with a SUVA of 0.026 $L.cm^{-1}mg^{-1}$ and a BOD_{28}-value of < 5 mg $O_2.L^{-1}$ [18].

Secondly, the effluent has a high conductivity due to a nearby dairy factory which discharges large amounts of sodium chloride in the sewer.

As the majority of organic components in the effluent are soluble, e.g. < 0.45 μm, GPC has been performed to determine the average molecular weight distribution of these compounds, as shown in Figure 8.

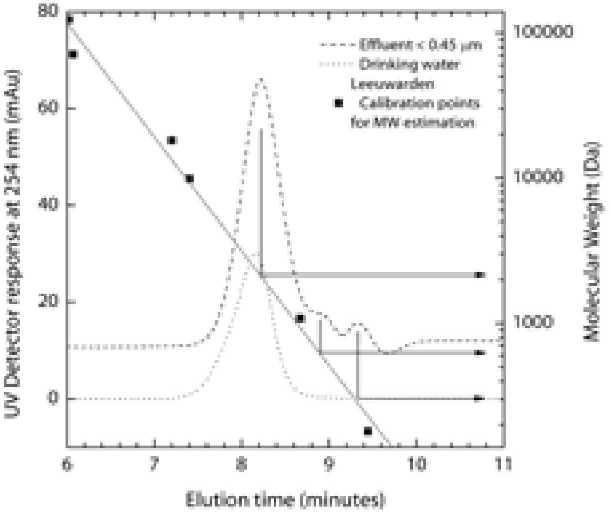

Figure 8 - GPC results for the fraction < 0.45 μm of WWTP effluent and potable water of Leeuwarden. The analysis shows three distinct groups of different MW (≈ 2100, 600 & 200). The group of 2100 MW is the dominant group responsible for around 90% of the DOC present in the effluent.

The GPC analysis was performed on a Metrohm HPLC setup with a PSS MCX-1000Å GPC column. A Bisschoff Lambda 1010 was used as UV-VIS detector. The mobile phase was an aqueous solution of 0.1 M Na_2HPO_4. Calibration of the GPC column was based on dextrans and pullulans of known molecular weight. A quantitative analysis was obtained with at detector setting of 254 nm. Ultraviolet absorption at 254 nm has been shown to have good correlation with DOC concentrations [19]. On the other hand, the detector setting at 254 nm might overestimate the aromatic species as the detector at 254 nm is less sensitive to non-aromatic compounds like polysaccharides and partially aromatic compound like proteins [20]. Due to the site-specific characteristics of the effluent, low protein and polysaccharide content versus a high amount of refractory organic material, a detector setting of 254 nm was chosen.

2.2.3 Zeta- potential determination

WWTP effluent contains a wide range of colloidal matter; humic acids, biological residue, metabolism products, dissolved organics, etc… The authors hypothesized that such a complex mixture can be characterized by an average zeta-potential. The average zeta-potential of the colloidal matter was measured by a Malvern Zetasizer 3000HS. The Zetasizer 3000HS has a resolution between 3 μm and 2 nm. The upper boundary of 3 μm is not a problem as most of the effluent organic content is present in the fraction smaller than 0.45 μm (DOC, see Table 2 & 3).

Gel Permeation Chromatography (§ 2.2.2) showed that the vast majority of the DOC content was present in the size fraction of 2100 Da. Literature [21, 22] estimates the average radius of randomly colloid organic matter of 2000 Da to be around 2.5-6 nm which is well within the detectable range of the Zetasizer 3000HS. It should be stressed that the fraction of average molecular weight around 2100 Da do not have to possess colloidal properties. However, if macromolecules present in this fraction do possess colloidal behavior they will be detected by the Zetasizer.

Table 3 - General parameters for the WWTP effluents used for zeta-potential determinations

Effluent sample ID	*TOC*	*DOC*	*UVA$_{254}$*	*SUVA*	*EC*	*pH*	*Ca^{2+}*	*Na^{+}*	*Cl^{-}*
	mg.L^{-1}	mg.L^{-1}	cm^{-1}	L.cm^{-1}.mg^{-1}	mS.cm^{-1}		mg.L^{-1}	mg.L^{-1}	mg.L^{-1}
E6	15	14	0.47	0.034	2.04	8.0	46	309	490
E7	9.4	9.3	0.36	0.038	0.94	7.8	51	160	310

Samples from the Leeuwarden WWTP plant were taken during rainy and dry weather periods to assess the variability of the zeta-potential due to dilution effects (Table 3). Dilution effects alter the ionic strength of the effluent which can have an effect on the electric double layer thickness and therefore influence zeta-potential according to the DLVO theory. Dilution effects can also alter the organic composition of the effluent as sludge might be destabilized as hydraulic retention time decreases [23].

To influence the zeta-potential, samples were adjusted by addition combinations of hydrochloric acid, inorganic and organic coagulants while being stirred vigorously for 2 minutes before sample injection. This made it possible to measure at initial coagulation conditions were only charge neutralization had taken place and no aggregation had occurred. Aggregation will result in a large shift in particle size distribution, with a size fraction above the detection limit of the ZetaSizer (> 3 μm), influencing the accuracy of the measurement.

Aluminum chloride was chosen as it showed to be more effective in neutralization of the zeta-potential than other tested coagulants. The results, presented in Figure 9, show that for the tested samples aluminum chloride addition at pH values between 7-8 did not influence the zeta-potential whereas at mild acidic condition (pH 4-6), a dose of 5 ppm Al^{3+} is sufficient to neutralize the zeta-potential of the effluent NOM.

It is important to notice that the effluent's zeta-potential does not alter significantly between diluted and non-diluted effluent within tested dilution ranges. This result makes it possible to control the zeta-potential and therefore NOM stability by pH adjustment and aluminum chloride addition in our experiment, independently of the variations in the effluent.

The authors are aware of the fact that the value of the zeta-potential is measured at the initial coagulation conditions whereas the filtration experiments

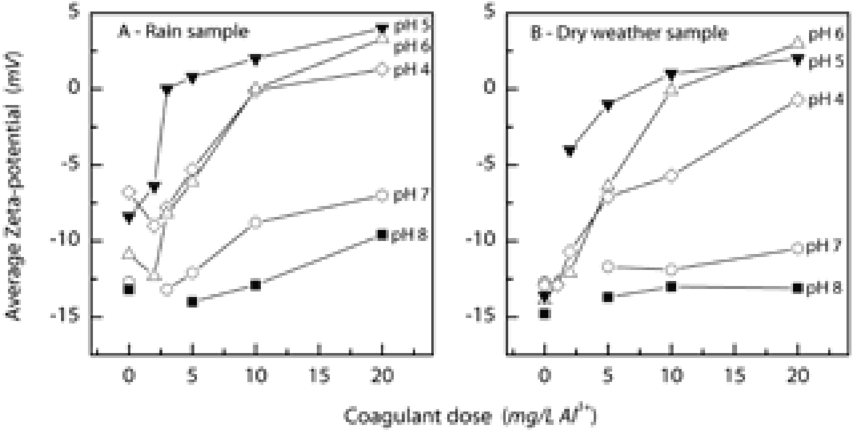

Figure 9 - Average zeta potential of the colloidal matter of WWTP effluent as function of pH and Al^{3+} dose: (A) WWTP effluent E6 with electrolyte background conductivity of 2.04 mS/cm, dry weather. (B) WTTP effluent E7 with electrolyte conductivity of 0.94 mS/cm, typically for a period rainy weather.

are performed on solutions which have reached coagulation equilibrium. Nonetheless, this paper demonstrates that there exists a very strong correlation between the zeta-potential at initial coagulation conditions and the observed filtration performance.

2.2.4 *Factors in the experimental design*

To influence the zeta-potential of the effluent, pH and coagulant dose were chosen as factors for the experiment. The values (levels) for both pH and coagulant were chosen such that 4 sets (a,b,c,d see Table 4) were created.

Table 4 - Full Factorial Experimental Design

Run	*Set*	*Factors*			*Legend*	*Factors levels*	
		ΔP	pH	Al^{3+}			
1	a	-	-	-		*Low (-)*	*High (+)*
2	b	-	-	+	ΔP (kPa)	300	600
3	c	-	+	-	pH	5	8
4	d	-	+	+	Al^{3+} (mg/L)	0	5
5	a	+	-	-	Set (a) acidified effluent		
6	b	+	-	+	Set (b) neutral zeta-potential		
7	c	+	+	-	Set (c) blank		
8	d	+	+	+	Set (d) alum spiked effluent		

Instead of choosing only set b (zeta-potential ≈ neutral) and set c (unaltered effluent) as design points to investigate the influence of the zeta-potential of colloidal matter on nanofiltration performance set a and set d were added as well. In set a, only pH is lowered which has little effects on the zeta-potential. This makes it possible to investigate the role of pH adjustment on the performance as well. This might be interesting as some membrane plants acidify their feed in order to decrease scaling effects at high recoveries. The same applies for set d in which only coagulant is added. Zeta-potential of the colloidal matter is hardly influenced due to the addition, whereas in industry coagulant is often added as anti-fouling strategy.

A third factor, transmembrane pressure (TMP), was added to the design to check on cake compression phenomena. TMP low and high level were set at 300 and 600 kPa. Choosing these three factors at two levels leads to a FFD of $2^3 = 8$ runs per effluent sample (Table 3 & appendix).

2.2.5 Choice of membrane & membrane characteristics

For this study a relatively open NF membrane was chosen for two reasons:

A NF membrane with high salt retention would increase the ionic strength on the retentate side, which would alter the zeta-potential of the organics. This is one of the experimental parameters which we like to keep as constant as possible.

Secondly, from a zero-discharge perspective in which the retentate is returned to the head of the WWTP plant, a salt rejecting membrane is a poor option. As the majority of salts are relatively inert material in a WWTP, accumulation effects are likely to occur. This could hamper the operation of the WWTP due to scaling effects and changes in the activated sludge process.

The membrane used in this study, the NF270 by DOW Filmtec, is polyamide composite NF membrane with high organic retention and low salt retention. The specifications according manufacturer and literature data [24, 25] are summarized in Table 5. Prior to each experiment, membranes were screened on performance according to manufacturer's specifications on $MgSO_4$ retention and permeability (see also §2.2.7). Outliers (more than 15% difference from manufacturer's specifications) were discarded.

Table 5 - Reported characteristics for the DOW Filmtec NF270 membrane

Source	*Zeta-potential* (mV)	*Contact Angle*	*Perme-ability* (L/m^2.bar.h)	*Membrane Roughness* (nm)	*Organic rejection* (%)	*CaCl$_2$ rejection* (%)	*Sulfate rejection* (%)
DOW Filmtec[†]	-	-	11.1	-	94	40-60	99
Mänttäri[‡]	-16	30º	15.6	-	94.9	48.2	99.0
Freger	-	-	-	1-2	-	-	-

† Test conditions: Permeability: 4.8 bars, 25º C, 2000 ppm MgSO4. Organic rejection based on Lake Mead pilot plant, Overton, Nevada, USA.

‡ Test conditions: Permeability: 7.8 bar, 35º C, pH 7. Background solution for zeta-potential 0.01M KCl. Data on salt and organic rejection based on paper mill effluents.

2.2.7 *Cleaning procedure*

Cleaning of the membranes consisted of a rinse with 1mM HCl for 10 minutes to remove possible inorganic foulants. After the acid cleaning, an alkaline (pH 11) enzymatic cleaning step was performed at 35º C for 30 minutes for the removal of organics. The cleaning solution was made up from demineralized water with 0.5w% P3- Ultrasil 67 and 1.0w% P3- Utrasil 69 (Ecolab). The enzymatic part (P3-67) of this product is biodegradable which might help in waste handling minimization of used cleaning solutions. Cleaning conditions were performed within the given range (pH, temperature) by the suppliers' membrane data sheet. After cleaning, the membranes were soaked for 10 minutes in pH neutral demineralized water prior to performance analysis on the $MgSO_4$ solution.

2.2.8 *Fouling analysis*

Filtration curve analysis was performed on the data to determine the dominating fouling behavior. Earlier experiments, not reported, with this type of effluent and membrane showed that the filtration behavior could be described with a resistance in series model based on membrane resistance and cake resistance according to standard cake filtration theory [26] represented by Equation (1):

$$\frac{t}{V} = \frac{\eta R_m}{A \Delta P} + \frac{r_c c_b}{c_c} \frac{\eta}{2A^2 \Delta P} V \tag{1}$$

In equation 1, filtration time (*t*) divided by permeated volume (*V*) is plotted against permeate volume.

The first term, consisting of the liquid viscosity (η); membrane resistance (R_m); filtration Area (*A*) and transmembrane pressure (ΔP), refers to membrane characteristics and is independent of the filtrated volume.

The second term is a resistance term caused by cake formation due to the feed water constituents and is a function of the amount of filtrated volume of feed water. The cake resistance term is a function of particle size radius (r_c) in the feed, particle concentration in the feed (c_b) and particle concentration in the cake (c_c).

At constant pressure filtration, assuming constant viscosity (η) and ideal cake behavior, i.e. no cake compression or cake collapse occurs, the resistance term is a constant and is represented by the slope of the function of *t*/*V* plotted against the permeated volume (*V*). Equation (1) can be simplified to Equation (2) in which K_C is the cake resistance term.

$$\frac{t}{V} = K_M + K_C V \tag{2}$$

In this study the resistance term K_C is used for evaluation of the filterability of the effluent as a function of the selected design factors.

To assess the reversibility of the fouling, permeability and retention tests were performed prior to the effluent filtration experiment on the fresh membranes and after the cleaning procedure. Test conditions were based on the membrane supplier fact sheet and consisted of filtering a 2000 mg/L $MgSO_4$ solution at 480 kPa and 15% recovery. Stirring speed for the cells was chosen at 900 rpm. Both reduction of permeability and retention were calculated according to:

$$Loss_{\mathrm{PERM}\ or\ \mathrm{R}}(\%) = \left(1 - \frac{\mathrm{PERM}\ or\ \mathrm{R}\ (after\ cleaning)}{\mathrm{PERM}\ or\ \mathrm{R}\ (initial)}\right) \times 100 \tag{3}$$

To assess the influence of the different parameter settings on the general performance of the membrane, the overall organic and salt rejection were measured after the filtration cycle. Organic rejection was based on the rejection of UVA_{254} whereas salt rejection was based on the rejection of conductivity.

2.2.9 Data analysis

After collecting all data from the experiments, Analysis Of Variance (ANOVA) was performed to validate the significance of the main factors and interaction effects. Factors with a P-Value of less than 0.05 were regarded as significant. The factors were considered to be categorical (discrete) rather than numerical (continuous) as this kind of statistic design (2-level full factorial) is not suited for model building. The results should therefore be treated as qualitative effects rather than quantitative effects. More background information about Design of Experiments (DOE) and ANOVA can be found in the appendix.

2.3 RESULTS AND DISCUSSION

Table 9, see the appendix page 54-55, displays the results of the performed experiments. Missing values were due to experimental error. Values marked with an asterisk (*) denote values which were pointed out as outliers during statistical data processing. Outliers were discarded as experimental error. The outcome of the ANOVA is presented in three separate paragraphs; filterability, reversibility and general performance.

2.3.1 Filterability of the effluent

As pointed out in §2.2.8, ideal cake filtration theory can be used to assess the filterability of the effluent by determination of the cake resistance term K_C. An example for the determination of K_C is given in Figure 10.

ANOVA (Table 8, page 48-49) shows that pH and coagulant dose and their interaction are the significant factors affecting the cake resistance. Together these factors explain around 60% ($R^2 = 0.64$) of the variation observed in the experiments. The ratio of variation between the experiments conducted on different effluent and the overall mean error (MS_{blocks} / MS_{error}) shows that the response is robust in relation to effluent effects (see appendix). This means that the factors and interactions responsible for the variation in cake resistance are not significantly affected due to feed water variation.

Comparison of the treatments involving pH and coagulant dose with the blank treatment (neither acidification nor coagulant addition) using Dunnett's test (appendix) showed a highly significant difference between the treatments with low (no) zeta-potential and other treatments, see Table 6.

Figure 11 illustrates the variance and difference of the treatment means using a

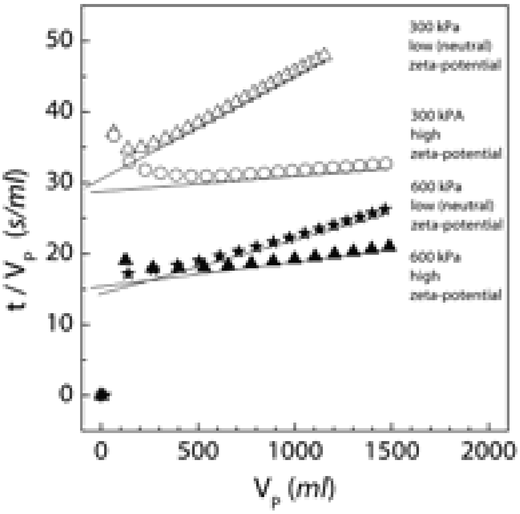

Figure 10 - Graphical illustration showing the determination procedure for assessment of the cake resistance in this research. The results depicted were obtained from experiment with effluent E4. The figure illustrates the increase in slope (resistance) for the filtration sets at low (neutral) zeta-potential.

Box-whisker plot. Apparently, decreased zeta-potential of colloidal NOM leads to a significant increase (on average 4-5 times) in the resistance of the filter cake.

Monte-Carlo simulations on dead-end filtration of latex particles, based on the DLVO theory, showed the zeta-potential to be of importance in affecting the porosity of formed cake [9].

Table 6 - Results for Dunnett's test for comparison of treatment means in Cake Resistance

Factor levels	*ID*	*Mean treatment difference (ID – blank)* (s/ml^2)	*Std. Error* (s/ml^2)	*P-Value*
pH 5, 0 ppm Al^{3+}	pH	0.0002	0.00367	0.769
pH 5, 5 ppm Al^{3+}	Neutral zeta-potential	0.0230	0.00357	< 0.001
pH 8, 5 pmm Al^{3+}	Coagulant	0.0001	0.00367	0.742
pH 8, 0 ppm Al^{3+}	Blank	0	-	1

At higher absolute values of the zeta-potential the porosity increased due to electrostatic repulsion between the particles. This result supports the finding in this study as the cake resistance increases at decreased zeta-potential.
However a second mechanism might contribute to the increase in cake resistance. A changed cake structure can have a profound effect on the resistance of a cake. This might be best illustrated by the particle size distribution (PSD) in a cake layer. Specific cake resistance (r_c) is inversely proportional to the square of the particle diameter (d_s) and inversely coupled to the porosity (ε) (Eq.(4), Kozeny-Carman).

$$r_c = \frac{(1-\varepsilon)^2}{\left(d_s^{\,2}\varepsilon^3\right)} \tag{4}$$

Neutralization of the zeta-potential of colloidal organic material results in coagulation of the colloids, altering the original PSD. GPC measurements (Figure 12) confirmed that on average 30% of the soluble organics of high MW were aggregated to a size fraction > 0.45 μm at neutral zeta-potential. Only the groups with smallest MW were unaffected. Assuming that the fraction greater than 0.45 μm does not play a role in cake formation due to the high surface shear created by the stirred cell, GPC (Figure 12) did not show a decrease in average MW for the all fractions.

This does not mean that the size distribution in the cake is not altered. The mixture of organic macro molecules which did not coagulate are likely to be of a different nature, e.g. non-colloidal but dissolved, and might have complete different spatial behavior. Removing the easy to coagulate organic material from the bulk of the organic material in the effluent could very well alter the structure of the cake, resulting in an increased resistance.
The zeta-potential of the colloidal NOM plays an important role in affecting

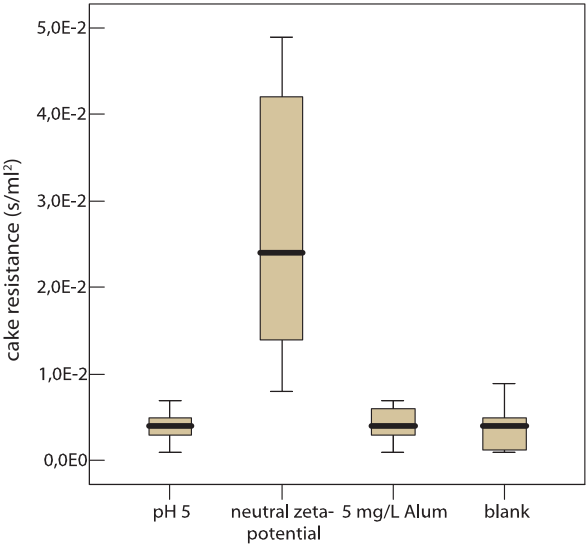

Figure 11 - Comparison of the treatments involving pH and coagulant addition against the blank treatment (unaltered wastewater). Black line denotes the mean value, boxes denote ¾ percentile and whiskers show the 95% confidence interval.

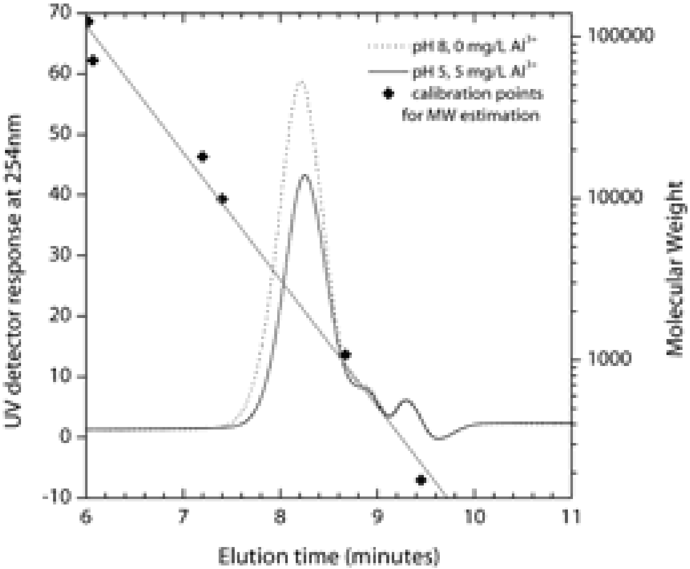

Figure 12 - GPC analysis of 0.45 µm filtered untreated effluent and coagulated effluent. A small part of the dominant group around 2100 MW has been coagulated whereas the other groups remain unaffected.

cake resistance as neutralization of the zeta-potential lead to an average 4-5 fold increase in cake resistance. Whether this increase is due to;

- loss in electrostatic repulsion between the cake constituent resulting in void space reduction;
- change in cake structure by taking out a specific colloidal fraction;
- or a combination of both is uncertain.

More research is needed to positively identify the major mechanisms behind the increase in cake resistance at neutral zeta-potential of the effluent constituents.

2.3.2 *Reversibility of the fouling*

Both changes in permeability and retention of the membrane were assessed after a full filtration cycle, including the cleaning cycle.

For changes in retention, ANOVA selected TMP, pH and their interaction as significant parameters (Table 8, page 48-49). Comparison of the relevant treatments (Table 7) showed that pH adjustment at low TMP had a significant effect on decreasing the membrane performance by an average 18%.

Table 7 - Results for Dunnett's test for the decrease in retention

Factor levels & ID	*Mean treatment difference (ID- Blank)* (% retention loss)	*Std. Error* (% retention loss)	*P-Value*
3 bar TMP & pH 5	18.6	4.64	< 0.001
3 bar TMP & pH 8	1.31	4.64	0.633
6 bar TMP & pH 5	1.95	4.64	0.576
6 bar TMP & pH 8	0.86	4.64	0.673

The factors responsible for decrease in permeability were identified to be the main parameters (TMP, pH, Al^{3+} dose) by ANOVA (Table 8, page 48-49). In Figure 13 a graphical illustration is presented of all mean permeability's after treatment compared to the initial permeability (blank).

Al^{3+} dosage has a clear positive effect on returning to original permeability whereas lowering the pH has a profound adverse effect. The effect of TMP is less distinct. Test conditions which resulted in a non-significant difference (*P* > 0.05, Dunnett's test) from the blank were all performed at pH 8. Within these treatments the ones with alum dosage consistently outperform the rest.

On average, combining the results of permeability and retention, reversibility is hampered by lowering the pH. A plausible explanation could be the decrease in membrane surface charge at lowered pH due to protonation of the functional groups (carboxylic, [27]) at the membrane skin. This could facilitate enhanced absorption of organics due to reduced electrostatic repulsion between membrane and organics. Recent studies on the NF270 membrane show similar trends of reduced permeability, decreased UVA and sugar retention at low pH values, especially in combination with saline feed [24, 25].

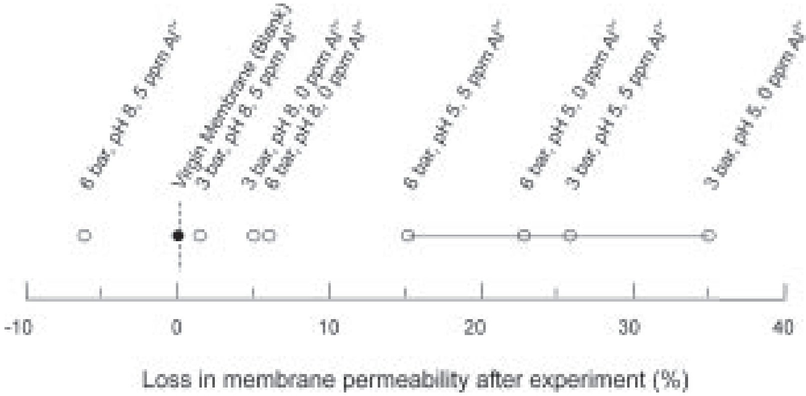

Figure 13 - Representation of all treatment combinations with corresponding mean loss in permeability. Connected treatments show significant (P < 0.05) difference with the blank.

Adding Alum to the feed has a positive effect in the removal of the cake layer and restoring original conditions after cleaning. Two major mechanisms or a combination of both reported in literature might explain this behavior:

1. Preferential adsorption of Al^{3+}/$Al(OH)^{2+}$ instead of bivalent cations like Ca^{2+} or Mg^{2+} to humic like organics in the feed water [28]. This could result in less 'sticky' fouling layers caused by humic – calcium – membrane surface interactions [10].
2. Alum coagulant residuals (esp. $Al(OH)_3$(am)), e.g. the fraction not adsorbed to the organics, form a hydrated aluminum layer on the membrane. Such a layer is shown to be completely removable [29].

Looking at the theoretical solubility of aluminum in water, depicted in Figure 14, aluminum is predominantly present in the form of $Al(OH)_3$(am), $Al(OH)_3$(aq) and $Al(OH)_4^-$ at pH 8. Preferential replacement of calcium or magnesium by negative charged aluminum hydroxides is therefore not likely to occur. This hypothesis is further strengthened by the zeta-potential measurements at pH 8. Aluminum dosage does not affect the zeta-potential, so interaction between NOM and Al^{3+} seems unlikely.

On the other hand, the formation of especially $Al(OH)_3$(am) might create a 'protective' layer on the membrane resulting in a more removable cake layer. This hypothesis might be supported by the salt rejection (§ 2.3.3) of the membrane, in which a significant decrease in retention is observed when dosing Alum at pH 8. A protective film of aluminum hydroxides deposits could very well result in decreased membrane surface potential. Such events will result in a decrease in rejection of salts due to the loss of electrostatic repulsion.

Dosing aluminum at low pH does also result in enhanced reversibility. Around pH 5-6, aluminum is mainly present as Al^{3+}/ $Al(OH)_2^+$ (Figure 14) and interaction

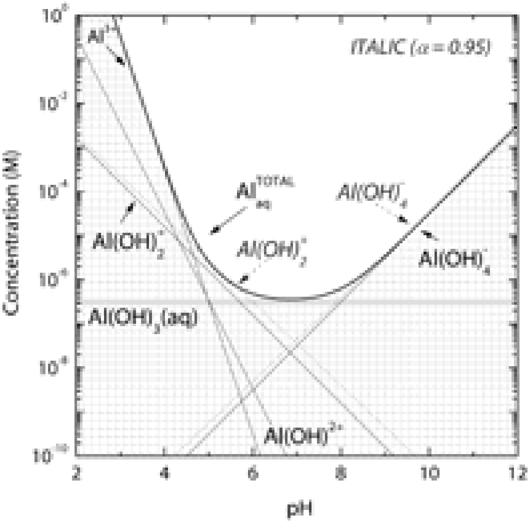

Figure 14 - Theoretical solubility of amorphous $Al(OH)_3$ in water at zero ionic strength and at 298 K, poly nuclear complexes not included.

with the NOM is optimal (Figure 9). If these Al-NOM complexes and/or Al-residuals are responsible for the enhanced reversibility is difficult to assess. At these conditions dense cake layers are also formed, which could also protect the membrane from further fouling.

2.3.3 General performance

Membrane performance was analyzed on average MWCO by GPC measurements, UVA rejection at 254 nm and retention of conductivity. MCWO measurements were not coupled to ANOVA as the fraction of organics passing the membrane were very low in concentration (< 2 mg/L TOC). Distinction between treatments based on GPC analysis became therefore impossible. Figure 15 shows a representative qualitative GPC measurement.

Organic species belonging to the group of 2100 average MW are almost fully retained by the membrane whereas, the smaller size fraction of 600 and 200

MW are not (completely) retained by the membrane. The apparent MWCO of 800 Da for the NF270 membrane from these measurements seems quite large compared to reported values for the NF270 membranes of around 200-300 MWCO [30]. However, standard MWCO measurements are performed at well controlled non-fouling conditions using diluted standard molecules, incomparable to the results presented. Under these test conditions, the NF270 membranes shows a tendency to permeate organic molecules of substantial larger molecular weight. If this tendency applies for condition at pilot scale test this might become a major issue. Most of the health hazardous suspected organics fall within the category of molecular weight less than 800 Da.

As mentioned in previous paragraph, alum addition did influence the rejection characteristics for the NF270 membrane significantly both for UVA_{254} and conductivity (Table 8, page 48-49). For the rejection on UVA_{254}, aluminum addition leads to a significant (P = 0.0002) decrease from 98.5% to 96% in rejection of UVA_{254}. Although significant, the difference between treatments is very small. As dosing alum generally leads to better reversibility, the higher retention at treatments without alum, i.e. at more fouling conditions, might very well be due to adsorption effects. The observed retention characteristics on UVA_{254} are according to earlier studies with this membrane (Table 5).

The results (Figure 16) of the factors affecting rejection of conductivity show an interesting effect. Treatments with aluminum dosage at pH 8 lead to a significant decrease (P < 0.0012, LSD method [31]) in retention. This observation supports the hypothesis, proposed in section 3.2, that aluminum hydroxides accumulate at the membrane surface. Such a layer could lead to a decrease in surface potential resulting in a decreased salt retention. Especially for more open nanofiltration membranes, surface charge is important parameter to maintain retention [32].

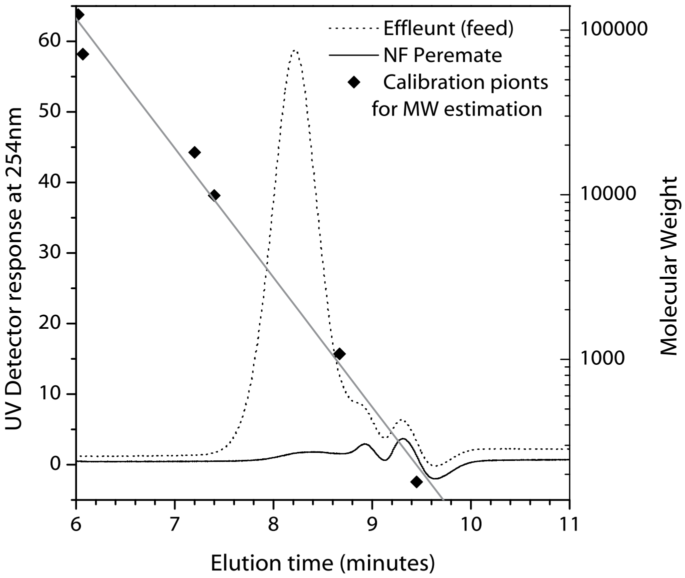

Figure 15 - GPC measurement showing elution times for effluent and permeate for filtration conditions at 6 bar TMP, pH 8 and 0 ppm Al^{3+} for the NF270 membrane.

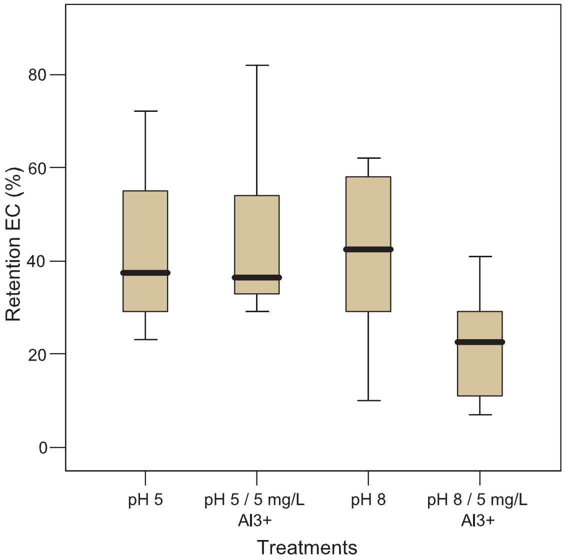

Figure 16 - Box & Whisker plot showing means, ¾ percentile and 95% significance intervals for the effect of pH and coagulant dose on the average conductivity retention. Data constructed by lumping high and low TMP data by neglecting the pressure effects.

Table 8 - ANOVA tables for all response parameters

Cake resistance (KC)

Source	*Sum of Squares (SS)*	*Degrees of Freedom (DF)*	*Mean Square (MS)*	*F_0-Value*	*Probability (P-Value)*
Block	0.52	4	0.13		
Selected Factors	27.1	3	9.03	17.59	<0.0001
B	7.89	1	7.89	15.37	0.0005
C	10.5	1	10.49	20.42	<0.0001
BC	7.55	1	7.55	14.70	0.0006
Error	15.4	30	0.51		
MS_{blocks}/MS_{error}				0.255	

Change in retention (Loss, R)

Source	*Sum of Squares (SS)*	*Degrees of Freedom (DF)*	*Mean Square (MS)*	*F_0-Value*	*Probability (P-Value)*
Block	11.1	4	2.76		
Selected factors	38.4	3	12.8	9.76	0.0001
A	8.25	1	8.25	6.29	0.0174
B	19.2	1	19.2	14.6	0.0006
AB	11.0	1	11.0	8.36	0.0068
Error	42.0	32	1.31		
MS_{blocks}/MS_{error}				2.11	

Change in permeability (loss, PERM)

Source	*Sum of Squares (SS)*	*Degrees of Freedom (DF)*	*Mean Square (MS)*	*F_0-Value*	*Probability (P-Value)*
Block	12.1	4	3.03		
Selected factors	62.7	3	20.9	17.2	< 0.0001
A	8.50	1	8.50	7.01	0.0134
B	40.5	1	40.5	33.4	< 0.0001
C	10.6	1	10.6	8.73	0.0064
Error	32.8	27	1.21		
MS_{blocks}/MS_{error}				2.50	

Rejection (retention) of conductivity of the NF270 membrane

Source	*Sum of Squares (SS)*	*Degrees of Freedom (DF)*	*Mean Square (MS)*	*F_0-Value*	*Probability (P-Value)*
Block	1004	4	251		
Selected factors	4216	5	843	3.77	0.0091
A	449	1	449	2.01	0.1668
B	723	1	723	3.23	0.0823
C	1232	1	1232	5.51	0.0257
AC	792	1	792	3.54	0.0695
BC	1020	1	1020	4.56	0.0409
Error	6707	30	224		
MS_{blocks}/MS_{error}				1.12	

Rejection (retention) of UVA254nm of the NF270 membrane

Source	*Sum of Squares (SS)*	*Degrees of Freedom (DF)*	*Mean Square (MS)*	*F_0-Value*	*Probability (P-Value)*
Block	8.48	4	2.12		
Selected factors	40.0	1	40.0	17.1	0.0002
C	40.0	1	40.0	17.1	0.0002
Error	77.2	33	2.34		
MS_{blocks}/MS_{error}	126	38		0.91	

2.4 CONCLUSIONS

Laboratory stirred cell filtration experiments on WWTP effluent were performed using the NF270 Nanofiltration membrane. Membrane performance was analyzed based on a statistical evaluation of three parameters; cake resistance, restorability (reversibility) of the initial membrane performance after the test and general performance.

In direct filtration (NF/RO) of water with NOM, maintaining a high zeta-potential is imperative to keep cake layer resistance to a minimum. One should therefore be very careful when dosing acids or coagulant to prevent scaling or fouling. Neutralizing the average zeta-potential of the colloidal fraction in the effluent led to the formation of cake layers with a very high resistance.

At neutral zeta potential conditions, the larger molecular weight fraction was partially aggregated to particulate matter. It was theorized that both loss in electrostatic repulsion between cake forming constituents and change in cake structure led to the formation of the observed dense cakes.

Addition of alum as coagulant at pH 8 seems to improve the reversibility of the fouling process. It was theorized that at slightly alkaline conditions an aluminum hydroxide layer forms a 'precoat' on the membrane surface. Such a layer is shown to be completely removable from polyamide membranes. At all conditions, lowering the pH results in more irreversible fouling. The zeta-potential was proven not to play a part in the restoration of original membrane properties (reversibility).
Adding aluminum to the feed has a side-effect. General performance of the membrane decreased noticeably for average salt rejection and only minor for UVA_{254} rejection.

The work presented in this paper suggests that selection of a proper coagulant to suppress fouling problems should be based on the interaction between membrane and coagulant, while the interaction of coagulant-NOM should be minimal to maintain a high (negative) zeta-potential. Further research will be conducted to evaluate and test these hypotheses in both laboratory as well as pilot plant scale.

2.5 Acknowledgements

The authors like to thank Vitens Water, Landustrie Sneek B.V. and the Frysian Waterboard (Wetterskip Fryslân) for the financial support of this project. Dow FilmTec is acknowledged for donation of the NF270 membranes used in this study. Ecolab® donated the membrane cleaning solutions (Ultrasil P3-67 & P3-69) used in this study for which the authors like to express their gratefulness.

2.6 Appendix

In this research, a full factorial design experiment was employed to study the effects of several factors on the filtration of WWTP effluent by nanofiltration. In a full factorial experiment all levels of every factor are combined with all levels of every other factor in the experiment. This way the experimental data can be used more effectively than in a 'one factor at a time' experiment for two main reasons. Interaction effects are accounted for and a better average effect of each effect can be obtained from fewer experiments [31]. In this case, a two-level full factorial block design was performed to evaluate the effect of three factors, pH, $AlCl_3$ dose and TMP. The full factorial experiment consisted of $2^3 = 8$ experiments (runs) and randomization was performed between runs. As effluent sampled for experimentation changed in composition, blocking was used to eliminate the effect that effluent variation could have on the statistical comparison among treatments. For each effluent sample (block), all 8 randomized factorial treatments were performed. The assumption for the validation of the effects, blocking technique and comparison between effects are discussed shortly.

2.6.1 *Validation of effects by ANOVA*

In this experiment we have three fixed factors; TMP, pH and Al3+-dose. These factors are analyzed using a linear fixed effects model in which the sum of squares (SS) methods is used to analyze the variance of the experimental factors (A, B & C), interactions (AB, AC, BC, ABC), blocks and experimental error;

$$SS_T = SS_A + SS_B + SS_C + SS_{AB} + SS_{AC} + SS_{BC} + SS_{ABC} + SS_{Blocks} + SS_{Error} \qquad (5)$$

This method is useful for qualitative analysis in search for influential values. Assuming an adequate model, e.g. normally and independent distribution of the error, the ratio (F_0) of mean squares (MS) versus the mean square error (MS_E) can be used for screening out the significant factors using the F-distribution. The principle is shown in equations (6)-(8), in which the SS for factor A and error are converted to mean squares (MS) by diving them by the degrees of freedom. The found F_0-value can be compared with standard tables for the F-type distribution for a specified accuracy (α = 0.05). In this study, a confidence level of 95% has been used to screen out significant factors.

$$MS_A = \frac{SS_A}{a-1} \qquad \{a = \text{number of levels factor A}\} \qquad (6)$$

$$MS_{error} = \frac{SS_{error}}{(a-1)(b-1)} \qquad \begin{Bmatrix} a = \text{number of treatments} \\ b = \text{number of blocks} \end{Bmatrix} \qquad (7)$$

$$F_0 = \frac{MS_A}{MS_{error}} \qquad (8)$$

By comparing the ratio (R^2) of total SS for the significant factors with the total SS, an interpretation can be made about the proportion of variability in the data explained by ANOVA.

2.6.2 Validation of blocking

To validate the assumption that the variance between effects is largely due to the variance of the effluent, the test statistic (Eq.(9)) was uses to test the hypothesis's H_0 and H_1. The use of an F-test in this case might not be justifiable due to the randomization restriction (the blocks itself are not randomized). However, it is reasonable to use the F-test as an approximate procedure.

$$F_0 = \frac{MS_{blocks}}{MS_{error}} \tag{9}$$

$$\begin{aligned} H_0 :\quad & MS_{blocks} = MS_{error} \\ H_1 :\quad & MS_{blocks} \neq MS_{error} \end{aligned} \tag{10}$$

If H_0 is not rejected, the block means do not differ significantly compared to the mean error. Therefore blocking might not be necessary to reduce the noise (error) within the experiment. In this study, accepting H_0 would lead to the conclusion that the observed effects are relatively robust towards effluent variation. Choosing a confidence interval of 95%, H_0 will be rejected if $F_0 > (F_{0.05,\,4,\,30}) = 2.69$ for the experiment presented in this paper.

2.6.3 Comparison between treatments

ANOVA can show relevant differences between factors and interactions, it is however interesting to make comparisons between the relevant factors and interactions to see which factors or combinations contribute most and how they differ compared to a control. Such a test is Dunnett's test [31]. Dunnett's test declares means significantly differ from a control value (a) if the absolute value of their difference exceeds;

$$|\mu_i - \mu_a| = d_\alpha (a-1, f)\sqrt{MS_E\left(\frac{1}{n_i}+\frac{1}{n_a}\right)} \quad (11)$$

In which value of d_α is based the on a standard T-test. The value of f is associated with the degrees of freedom of MS_E, α is the confidence interval of the T-test. μ represents the mean, subscript 'i' denotes the means tested against the mean of the control with subscript 'a'. n denotes the number of observations (experiments).

In this study, no replicates are present as each experiment was performed on a unique effluent and therefore consequently blocked in the statistical analysis. Therefore Dunnett's test can not be performed straightforward. However if the validation of blocking is rejected, one might assume that the 5 blocks become 5 replicates and Dunnett's test can be performed.
The same line of argumentation holds for the Least-Significant-Distance (LSD) method used in section 2.3.3.

2.6.4 Experimental data for ANOVA

Table 9 - Experimental results grouped by treatment. Actual experiment was randomized. Values denoted with an asterisk (*) were identified as Outliers.

Effluent	*Block*	*Factors*			*Responses*				
		A	*B*	*C*	*Cake Resistance (s/ml^2) x 10^{-3}*	*Loss, R (%)*	*Loss, PERM (%)*	*Rejection, UVA$_{254}$ (%)*	*R, conductivity (%)*
E4	Block 4	-	-	-	5,0	14	34	97	29
E5	Block 5	-	-	-	5,0	46	39	97	23
E1	Block 1	-	-	+	46	27	4	95	35
E2	Block 2	-	-	+	49	3	48	98	58
E3	Block 3	-	-	+	8,0	35	60	98	59

Effluent	*Block*	*Factors*			*Responses*				
		A	*B*	*C*	*Cake Resistance (s/ml^2) x 10^{-3}*	*Loss, R (%)*	*Loss, PERM (%)*	*Rejection, UVA$_{254}$ (%)*	*R, conductivity (%)*
E4	Block 4	-	-	+	14	6	13	97	29
E5	Block 5	-	-	+	12	28	5	98	10
E1	Block 1	-	+	-	5,0	0	5	99	31
E2	Block 2	-	+	-	6,0	-2	10	99	54
E3	Block 3	-	+	-	1,0	8	20*	97	29
E4	Block 4	-	+	-	1,0	3	5	99	46
E5	Block 5	-	+	-	4,0	22	0	99	33
E1	Block 1	-	+	+	1,0	0	4	93	17
E2	Block 2	-	+	+	14*	-2	-5	98	29
E3	Block 3	-	+	+	3,0	-4	-1	98	41
E4	Block 4	-	+	+	6,0	3	5	95	26
E5	Block 5	-	+	+	6,0	11	7	96	26
E1	Block 1	+	-	-	3,0	2	20	99	46
E2	Block 2	+	-	-	4,0	5	21	97	23
E3	Block 3	+	-	-	7,0	3	24	99	55
E4	Block 4	+	-	-	6,0	7	28	99	72
E5	Block 5	+	-	-	1,0	4	-17*	99	67
E1	Block 1	+	-	+	16	2	0	96	37
E2	Block 2	+	-	+	27	1	5	93	48
E3	Block 3	+	-	+	35	10	26	97	49
E4	Block 4	+	-	+	21	10	30	97	62
E5	Block 5	+	-	+	42	6	-39*	97	25
E1	Block 1	+	+	-	4,0	10	15	99	36
E2	Block 2	+	+	-	9,0	3	10	97	36
E3	Block 3	+	+	-	5,0	24	40*	98	54
E4	Block 4	+	+	-	4,0	-1	5	99	37
E5	Block 5	+	+	-	1,0	2	-7	99	82
E1	Block 1	+	+	+	4,0	-2	-5	99	11
E2	Block 2	+	+	+	3,0	-1	-2	92	19
E3	Block 3	+	+	+	7,0	-3	-10	97	40
E4	Block 4	+	+	+	3,0	2	-2	n.a.	7
E5	Block 5	+	+	+	4,0	9	-14	98	10

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CHAPTER 3

COAGULANT ADDITION FOR FOULING CONTROL IN DIRECT NANOFILTRATION OF WWTP EFFLUENT

Laboratory scale filtration tests were performed to assess the effects of coagulant addition to municipal wastewater treatment plant effluent on direct nanofiltration performance. Four different commercially available coagulants were tested. The focus of the research was to assess whether coagulant addition was beneficial for the development of the fouling layer on the membrane. The results in this study show that coagulant addition prevents cake collapse at higher pressures. Addition of coagulants did not influence rejection properties of the membrane, except for the tested aluminum chloride which caused a decrease in rejection of organic species. Autopsy and measurements in performance changes showed residual fouling to be minimal or absent when aluminum or a vegetable derived polymer was dosed. Addition of ferric chloride showed negative results as poor soluble ferric salts could not be removed by the applied cleaning regime. Coagulant addition might therefore be beneficial for improving filterability and cleaning behavior in filtration of WWTP effluent. A careful screening of coagulant, membrane and feed is necessary to avoid increases in residual fouling.

3

Coagulant addition for fouling control in direct nanofiltration of WWTP effluent

3.1 INTRODUCTION

Advanced treatment of wastewater treatment plant (WWTP) effluent for agricultural, industrial, or (in)direct potable purposes could be beneficial in areas of water stress. Moreover, regulatory agencies have shown to broaden their surface water quality regulation acts to include additional public and environmental protection, e.g. the new EU directive on bathing water [1]. The latter will force an upgraded quality of WWTP effluent in receiving surface waters. Nanofiltration (NF) could be used as such advanced treatment for effluents. Pilot and full scale studies [2-4] have proven direct NF to be a suitable technique for the production of a high quality permeate, free of bacteria and viruses, with low hardness and very low organic content.

The advantage of tertiary treatment of WWTP effluent by direct nanofiltration is the high recovery rate, typically 90-95%, compared to the classical ultrafiltration – reverse osmosis systems which operate at 50-80% recovery. The main disadvantage of direct nanofiltration is the higher fouling rate; however some of the previous reported pilot studies [2, 4] reported that direct nanofiltration showed superior operational stability compared to direct ultra and microfiltration. Nonetheless, fouling will occur and hamper recovery rates, lower the permeate quality and decrease membrane lifetime. It is therefore imperative to find strategies to control and limit fouling.

In previous work by the authors [5], investigating the influence of colloidal stability of effluent organic matter, some interesting results were found in terms of improved removal of the fouling layer when adding 5 mg/L Al_{3+} (as $AlCl_3$) to the feed solution. Based on the results of this study two hypothesizes were formulated (H_1 & H_2) and these hypothesizes are further investigated and explored in this paper.

H_1: Adding coagulants to the feed solution results in formation of a protective layer on the membrane surface.
H_2: The resulting protective layer alters the performance of the membrane in terms of rejection, filterability and cleanability.

In this study these hypothesizes are explored using four commercially available coagulants. The behavior of the individual coagulants, interaction effects with the feed water, membrane performance and membrane autopsy are studied to elucidate the effect of coagulants addition on fouling. As real WWTP effluent is used, design of experiment (DOE) is used to discriminate between experimental parameters and feed water composition to obtain statistically valid and meaningful conclusions.

3.2 Materials and Methods

3.2.1 *Design of experiment*

To test the postulations a protocol was designed, see Figure 16, to assess the interaction of the selected coagulants with the feed water and the selected membrane. The first part of the protocol has the objective of studing the colloidal behavior of the coagulants in order to predict effluent-coagulant interactions. Gel Permeation Chromatography (GPC) was used to obtain information of the molecular weight (MW) of the supplied polymers by Nalco. Interactions of coagulants and the feed water (aggregation/complexation) were analyzed by changes in feed water zeta-potential, feed water chemical analysis (ICP & IC) and shifts in molecular weight distribution by Gel Permeation Chromatography (GPC).

The second part of the protocol consist of a series of filtration tests in which cake resistance was recorded during filtration as a function of transmembrane pressure (TMP) and coagulant addition. After the filtration tests, membranes were analyzed in respect to their change in permeability and retention. To account for the variance between effluents and to detect interaction effects between chosen parameters a statistical method, full factorial design (FFD) with blocking was employed for the filtration tests. More information on the background of this type of statistically aided experimentation can be found in the appendix.

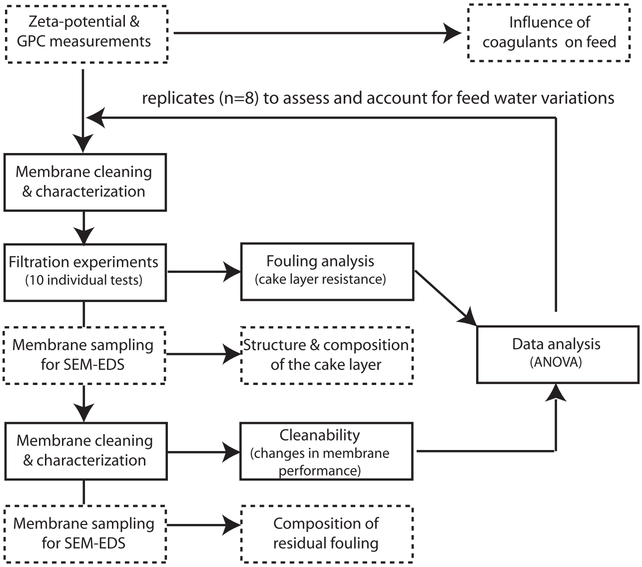

Figure 16- Block diagram of the experimental design. Experimental procedures boxed in dotted lines were not part of the ANOVA to correct for feed water variations.

Additionally, membrane samples of fouled and cleaned membranes of the filtration tests were selected for element analysis by SEM X-ray microanalysis.

3.2.2 *Selection of coagulants*

Four different coagulants were chosen: Two salts based on their widespread use in coagulation processes, aluminum and ferric chloride, and two cationic coagulants provided by Nalco: a proprietary blend of poly-aluminum chloride and poly-DADMAC (Nalco Ultrion® 71231) and a vegetable derived aromatic 3-D polymer (Nalco 77135). These two polymers were selected out of a product range of polymers supplied by Nalco. The mixture of PACl and DADMAC will be referred to as PACl in this paper.

3.2.3 *Zeta-potential measurements*

The zeta-potential of the individual coagulants, effluent and effluent-coagulant mixtures were measured as function of pH and coagulant dose using a NICOMP 380/ZLS system by Particle Sizing Systems (Santa Barbara, CA). Individual coagulant behavior was assessed by adding 5 $mg.L^{-1}$ of the selected coagulant to MilliQ water with a background electrolyte concentration of 1mM NaCl. The electrolyte's pH was adjusted with either hydrochloric acid or sodium hydroxide. Samples of effluent and coagulants were mixed at high speed (1000 rmp) for 10 minutes using a magnetic stirrer prior to analysis.

3.2.4 *GPC*

Gel permeation chromatography experiments were performed on effluent and coagulant treated effluent to assess changes in the molecular weight distributions due to coagulation. The same GPC setup is used to gain information about the molecular weight of both Nalco products. GPC analysis was performed on a Metrohm HPLC setup with a PSS MCX-1000Å GPC column. A

Bisschoff Lambda 1010 was used as UV-VIS detector. The mobile phase was an aqueous solution of 0.1M Na_2HPO_4. The UV detector was set at 240nm to get a high resolution without interference of the mobile phase. An UV detector will exaggerate the aromatic species in the Effluent Organic Matter (EfOM) while underestimating (or not detecting) single carbon bond based species like polysaccharides. The elution diagrams should therefore be interpreted as qualitative data rather than quantitative.

3.2.5 Visual and SEM-EDS

For analysis of the nature and structure of the fouling, membrane samples were obtained after the filtration tests for visual and element analysis. Elemental analysis was performed on a low vacuum (50 kPa) electron microscope (JEOL type JSM-6480LV, Thermo NORAN System Six). Membranes pieces from two different filtration tests were analyzed. The membranes were cut in three pieces. One piece was washed with demineralized water, one piece was cleaned as described in § 3.2.9 and one piece was left unaltered. Out of every piece, two samples were cut for element analysis. The results presented in this paper are the averaged data obtained from these samples.

3.2.6 Fouling Analysis

Filtration curve analysis was performed on the data to determine the dominating fouling behavior. Earlier experiments with this type of effluent [5] and membrane showed that the filtration behavior could be described with a resistance in series model based on membrane resistance and cake resistance according to standard cake filtration theory [6].

$$\frac{t}{V} = \frac{\eta\, R_m}{A\, \Delta P} + \frac{r_c\, c_b}{c_c}\, \frac{\eta}{2 A^2\, \Delta P}\, V \tag{12}$$

In Equation (12), filtration time (t) divided by total permeated volume (V) is plotted against permeated volume. The first term, consisting of the liquid viscosity (η), membrane resistance (R_m), filtration Area (A) and transmembrane pressure (ΔP), refers to membrane characteristics and is independent of the filtrated volume. The second term is a resistance term caused by cake formation due to the feed water constituents and is a function of the amount of filtrated volume of feed water. The total cake resistance is a function of the specific cake resistance (r_c), particle concentration in the feed (c_b) and particle concentration in the cake (c_c). At constant pressure filtration, assuming constant viscosity (η) and ideal cake behavior, i.e. no cake compression or cake collapse occurs (c_c = constant), the resistance term is a constant and is represented by the slope of the function of t/V plotted against V. Eq. (12) can be simplified to (Eq. (13)) in which K_C is the cake resistance term.

$$\frac{t}{V} = K_M + K_C V \tag{13}$$

In this study the resistance term K_C is used for evaluation of the filterability of the effluent as a function of the selected design factors.

To assess the reversibility of the deposits, permeability and retention tests were performed prior to the effluent filtration experiment on the fresh membranes and after the cleaning procedure. Test conditions were based on the membrane supplier fact sheet and consisted of filtering a 2000 mg.L^{-1} MgSO$_4$ solution at 480 kPa and 15% recovery. Stirring speed for the cells was chosen at 900 rpm. Reduction of permeability and retention were calculated according to:

$$Loss_{\mathrm{PERM}\ or\ \mathrm{R}}(\%) = \left(1 - \frac{\mathrm{PERM}\ or\ \mathrm{R}\ (after\ cleaning)}{\mathrm{PERM}\ or\ \mathrm{R}\ (initial)}\right) \times 100 \tag{14}$$

Were *t=0* denotes the performance of the cleaned membrane before the filtration cycle and t=end indicates the performance after the filtration cycle and cleaning procedure.

To assess the influence of the different parameter settings on the general performance of the membrane, the overall organic and salt rejection were measured after the filtration cycle. Organic rejection was based on the rejection of UVA_{254} whereas salt rejection was based on the rejection of conductivity.

3.2.7 Membrane characteristics

In this study an NF membrane with a moderate salt retention was chosen for two reasons. An NF membrane with high salt retention would increase the ionic strength on the retentate side, which would alter the zeta-potential of the effluent. This is one of the experimental parameters which should be kept as constant as possible to prevent the formation of dense fouling layers. Secondly, from a zero-discharge perspective in which the retentate is returned to the head of the WWTP plant, a high salt rejecting membrane is a poor option. As the majority of salts are relatively inert material in a WWTP, accumulation effects are likely to occur. This could hamper the operation of the WWTP due to scaling effects and changes in the activated sludge process.

The membrane used in this study, the NF270 by DOW Filmtec, is a polyamide composite NF membrane with high organic retention and low salt retention. The specifications are well reported in literature [5, 7-9]. Prior to each experiment, membranes were screened on performance according to manufacturer's specifications on $MgSO_4$ retention and permeability (see also §3.2.9). Outliers (more than 15% difference from manufacturer's specifications) were discarded.

3.2.8 Effluent characteristics

Effluent from the municipal wastewater treatment plant at Leeuwarden, the Netherlands was used in this experiment. The Leeuwarden plant consists of an activated sludge system combined with phosphate removal by chemical precipitation. Samples were drawn from the overflow of the secondary clarifiers and stored in dark at 5º C prior to analysis. Total storage time was kept below 24h to prevent change in effluent characteristics. General characteristics of the effluents used in the full factorial experiment are listed in Table 10.

The effluent of the Leeuwarden sewage treatment plant has some site-specific characteristics:

Table 10 - General parameters of the secondary effluent used during this study.

Components	Mean	Min	Max	Unit
COD	36	14	51	mg O_2/L
BOD	< 3	< 3	5	mg O_2/L
TOC	13	6	22	mg/L
UVA_{254}	0.37	0.32	0.60	1/cm
Proteins†	3.8	0.6	6.3	mg/L
Polysaccharides‡	4.6	1.2	7.3	mg/L
TSS	< 5	< 5	13	mg/L
Phosphate (aq)	0.8	0.1	1.5	mg/L
Total P	1.0	0.4	2.2	mg/L
Nitrate	1.7	0.2	6.9	mg/L
Total N	1.9	0.6	4.2	mg/L
pH	8.0	7.1	8.2	mg/L
Chloride	187	106	349	mg/L
Sulfate	35	27	44	mg/L
Sodium	187	112	305	mg/L
Calcium	57	19	46	mg/L
Potassium	24	15	27	mg/L
Magnesium	11	8	12	mg/L
Silica	12	7	13	mg/L
Cu, Fe, Al, Zn	Variable < 1.0	mg/L		

† Phenol/sulfruirc acid method by Dubois et al. [24]

‡ as analyzed by the Bradford method (BioRad©-assay)

- The moderate Specific Ultraviolet Absorption (SUVA) (>0.02 $L.cm^{-1}.mg^{-1}$) of the effluent shows the aromatic nature of the effluent, which is not surprising as the drinking water of Leeuwarden contains a large amount of humic substances. The drinking water of Leeuwarden contains around 8 mg/L TOC with a SUVA of 0.026 $L.cm^{-1}.mg^{-1}$ and a BOD_{28}-value of < 5 mg O_2/L [10].
- The effluent has a high conductivity due to a nearby dairy factory which discharges large amounts of sodium chloride in the sewer.

3.2.9 Cleaning procedure

Membranes were cleaned according to the manufacturer's specifications. The first cleaning consisted of an alkaline (pH 11) enzymatic cleaning step at 35º C (308 K) for 30 minutes. The cleaning solution was made up from demineralized water with 0.5w% P3- Ultrasil 67 and 1.0w% P3- Utrasil 69 (Ecolab). The enzymatic part (P3-67) of this product is biodegradable which might help in waste handling minimization of used cleaning solutions. The alkaline step was followed by acidic cleaning of the membranes with 1mM HCl for 30 minutes. After cleaning, the membranes were soaked in pH neutral demineralized water for 10 minutes prior to performance analysis on the $MgSO_4$ solution.

3.2.10 Stirred cell setup

Eight identical stainless steel stirred cells with effective filtration area of 40 cm^2 were used. Each cell was coupled to a 5L pressure vessel and tests were conducted under 'dead end' conditions, with pressures varying from 300 to 600 kPa (3-6 bar) according to the experimental design. Stirrer speed was kept constant at 800 rpm. Permeate was collected on an electronic weight balance for the purpose of filtration curve analysis. All experiments were performed with a total feed water recovery of 95%.

3.2.11 Data analysis

The data from all fouling tests were analyzed by Analysis Of Variance (ANOVA) to validate the significance of the main factors and interaction effects. Factors with a *P*-Value of less than 0.05 were regarded as significant. The factors were considered to be categorical (discrete) rather than numerical (continuous) as this kind of statistic design (multi-level full factorial) is not suited for model building. The results should therefore be treated as qualitative effects rather than quantitative effects. Data from the zeta-potential tests and SEM-EDS analysis are presented as mean values with 95% confidence interval.

3.3 RESULTS AND DISCUSSION

The results of the test are discussed in three sections; first, the results are presented for the behavior of the different coagulants in demineralized water and effluent. The second part describes the filtration performance of the effluent, comparing effluent against coagulant-added effluent. The last section deals with the description of the (residual) fouling as analyzed by electron microscopy.

3.3.1 Coagulant behavior

Coagulant properties in water

Figure 17 shows the colloidal behavior of the selected coagulants in water as function of the pH. At the ambient pH (7.8-8.0) of the feed water, the hydrated Al^{3+}-complexes and polyaluminumchloride (PACl) are close to their iso-electric point. Both the hydrated iron-complexes and the biodegradable polymer show a negative zeta-potential at pH 8.

Based on the observed electro-kinetic behavior it seems unlikely that any of the selected coagulants will cause charge neutralization effects with the negatively charged EfOM in the MSTP effluent.

Molecular weight estimation of the mixture PACl by GPC, see appendix for details, showed a MW around 2.7 kDa. The estimated MW for the biopolymer is 10 kDa. The elution diagram, see appendix, shows that the biopolymer is very polydisperse and might have a tendency to aggregate to species with MW well above the size exclusion range measurable in this column (> 100 kDa).

Coagulants and effluent

Addition of the coagulants to the effluent at 5 mg.L^{-1} (Figure 18) shows little

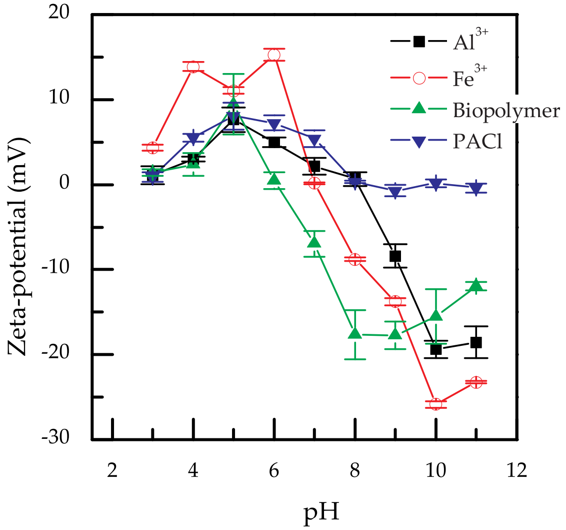

Figure 17 - Zeta-potential measurements for the tested coagulants as function of the pH at constant concentration of 5 mg.L^{-1} in demineralized water. Whiskers denote 95% confidence interval.

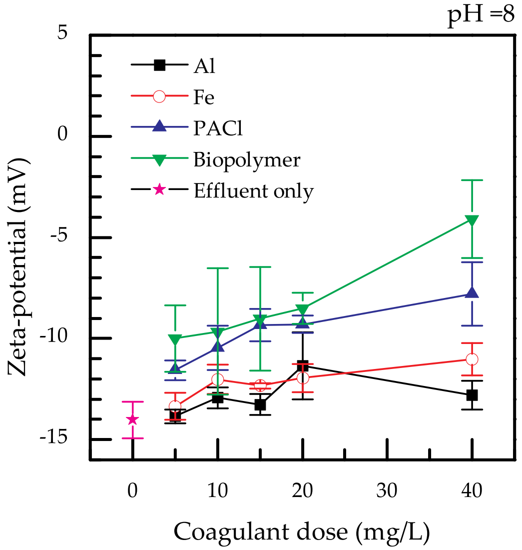

Figure 18 - Zeta-potential of the effluent as function of added coagulant at constant pH. Average data from 3 different effluents to account for feed water variations. Whiskers denote 95% confidence interval.

interaction between feed and coagulants. Both polymers do influence the measured zeta-potential slightly, but the overall zeta-potential remains negative indicating coagulation is not likely to occur. GPC measurements of the effluent and coagulant added effluent (Figure 19) confirm that coagulation effects were minimal. A very small change in molecular weight distribution was observed by additions of salt whereas the polymer added effluent did not show any changes. Based on these observations, it seems unlikely that the added coagulants interact significantly with the EfOM.

3.3.2 *Fouling and cleaning tests*

Influence of coagulant addition on the filterability

A total of 8 replicates of the filtration experiments were performed on freshly sampled effluent. The background on the statistic data processing of these 80 individual experiments can be found in the appendix. The results presented are shown by Analysis of Variance (ANOVA) to be significant with probability values (P-Value) below 5%.

ANOVA showed that transmembrane pressure, coagulant addition, their interaction and the variation of the feed water had a significant effect on the observed cake resistance. The resulting means for the experiments are plotted in Figure 20 and show that addition of coagulants has a beneficial effect on the filter cake resistance at 600 kPa (6 bar).

Without coagulant addition, filter cake resistance will almost double when increasing the TMP from 300 to 600 kPa. The results at 600 kPa confirm that the addition of coagulant does alter the nature of the cake by decreasing the cake's compressibility.

Reversibility of the fouling layer

Before and after a full filtration cycle including cleaning, permeation and

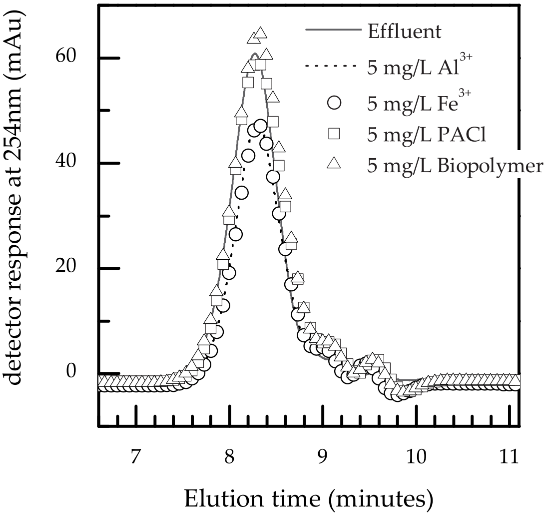

Figure 19 - Elution diagram of 0.45 μm filtered MSTP effluent and coagulant added MSTP effluent (dose 5 mg/L).

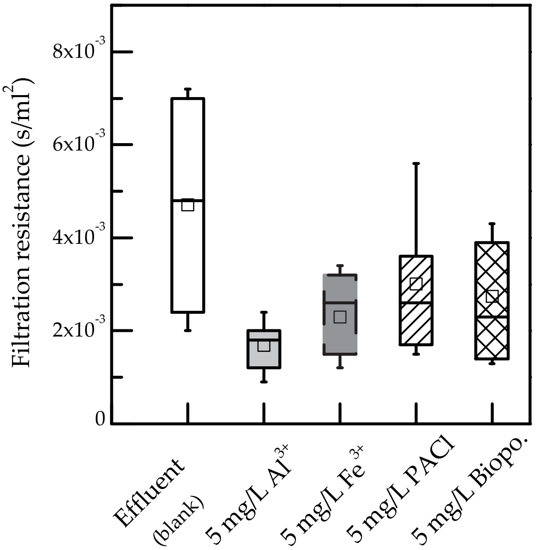

Figure 20 - Comparison of the filter cake resistance as function of pressure and pretreatment method. At 3 bars (300 kPa) no significant difference between treated and untreated effluent was observed, therefore the all experiments are displayed in a single box. Boxes mark the 25/75 percentile, median (50% value), mean value (□) and the whiskers denote the 95% confidence interval.

retention experiments on a magnesium sulfate solution were performed to check the presence of residual fouling. Residual fouling was expressed in decreased rejection and permeability on a standard test solution. ANOVA showed no correlation between rejection and the experimental parameters. ANOVA showed that the effluent composition was solely responsible for the recovery of the retention. On average, the decrease in rejection after each experiment was 9.2 ± 7.9 % compared to the original overall rejection of 93 ± 4.6 %.

ANOVA showed a very significant correlation for the change in permeability with TMP, coagulant addition and feed water composition. On average, see Figure 21, a slight decrease in membrane permeability could be observed at higher transmembrane pressures. Adding aluminum or biodegradable polymer to the effluent showed increased membrane permeability when compared to all other experiments.

An observed increased permeability compared to the original state might indicate damage to the top-layer, however retention values stayed stable. The cause of the increased permeability was the insufficient removal of preservatives in the membrane during of the initial cleaning and characterizing protocol. Increased permeability is thus an indication of less residual fouling.

The last influential parameter selected by ANOVA, the feed water composition, was shown to determine how much the permeability could be restored, independent of coagulant addition.

Changes in rejection due to coagulant addition

Rejection characteristics of the membrane for organic species, is altered significantly when dosing aluminum ($P << 0.01$). When dosing aluminum the

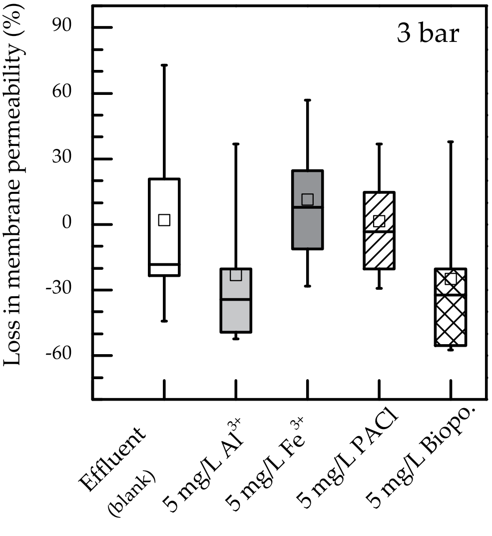

Figure 21 - Comparison the change in membrane permeability due to the different pre-treatments and pressure conditions. Boxes mark the 25/75 percentile, median (50% value), mean value (□) and the whiskers denote the 95% confidence interval.

rejection on UVA_{254} decreases from 95% to 92%. Addition of the other tested coagulants did not lead to any significant change in rejection characteristic for organic species measured by UVA_{254} absorption. An explanation for differences in retention might be found in cake enhanced concentration polarization effects [11]. As a result of cake deposition on the membrane, dissolved solutes might be entrapped in the cake, leading to a decline in solute rejection [11, 12]. The latter studies show that the hydrodynamic cake resistance can be very low compared to the enhanced build-up of solutes inside the cake. The findings of decreased cake resistance when dosing aluminum might therefore not result in increased rejection of solutes. More favorable accumulation of organic solutes in cakes formed under aluminum dosing conditions could lead to decreased rejection.

3.3.3 Morphology and composition of fouled and cleaned membranes

Visual analysis

After the filtration experiment, membrane pieces were sampled for visual and elemental analysis by SEM-EDS. Figure 22 gives a typical representation of the visual analysis of the fouling layers. Readers are recommended to observe this figure in the electronic version of this document (higher quality).

Filtration experiments with effluent and PACl added effluent gave gel-like fouling layers which could not be removed (e.g. by rubbing with a finger) from the membrane (see top, 12 o'clock position, on the membrane, fig. 8A).

Aluminum or ferric addition did improve the mechanical structure of the fouling layer as can be seen in figure 8B. A slight rub or a slight rinse with water resulted in the complete visual removal of the fouling layer, although the membranes samples remain slightly yellowish colored. The fouling layers for aluminum and ferric treated effluent were thinner and more translucent than the fouling layers observed for the biopolymer treated samples.

The biopolymer treated samples (fig. 8C) showed to be very homogeneous but could not be removed with a water rinse. Rubbing with a finger did remove the complete layer and no visual fouling could be detected and no residual color could be detected.

The corresponding electron micrographs in Figure 22, right column, show the structure of the fouling layer of the untreated effluent to be very different compared to the coagulant treated samples. In the aluminum and ferric treated samples, shown for aluminum (middle picture), a kind of two-phase mixture in the fouling layer can be observed. The biopolymer gives a very homogenous fouling layer.

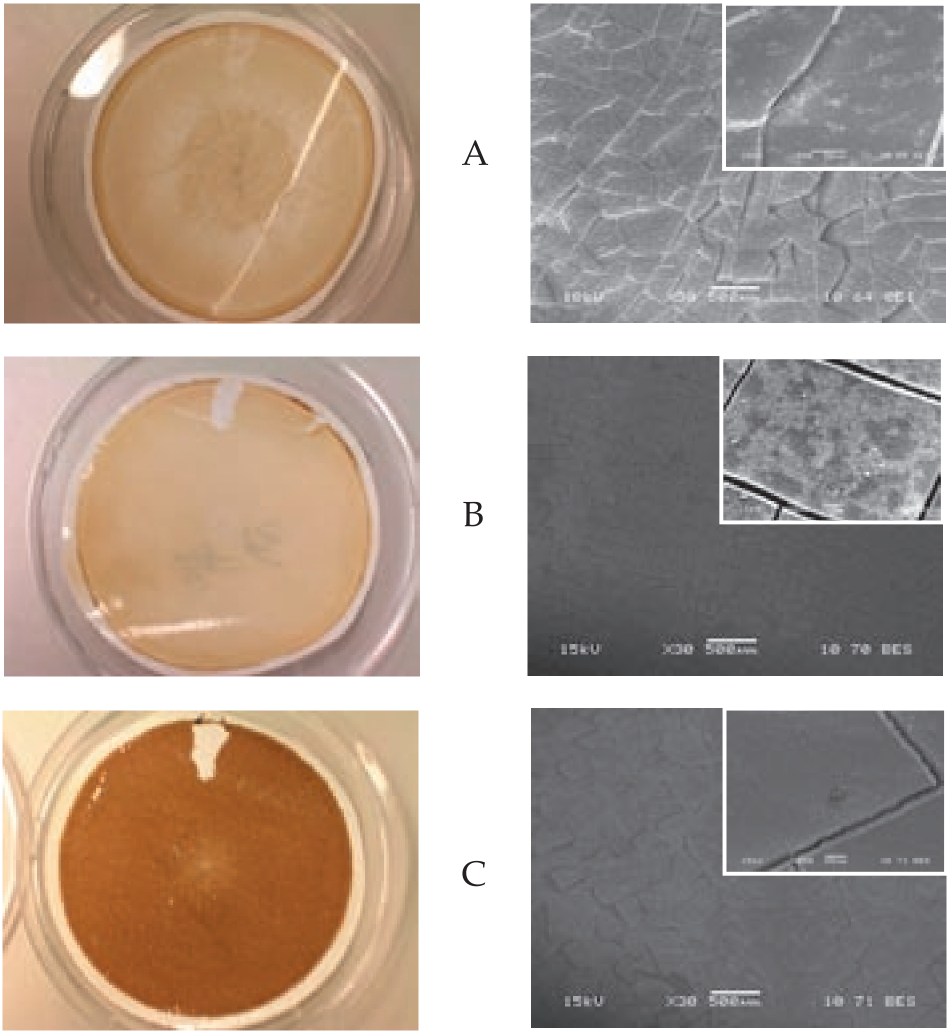

Figure 22 - Left to right: Membrane pieces fouled after the filtration experiment and their corresponding electron micrographs (magnification x30, insert x600). From top to bottom: Effluent only, effluent and Al^{3+} and effluent and biodegradable polymer.

SEM-EDS Results

Element analysis was performed on fouled membranes, water rinsed membranes and chemically cleaned membranes. The averaged data are displayed in Figure 23. Some trace elements such as copper, magnesium and sodium were detected on the fouled membrane. As these elements failed to show up in any cleaned membrane sample they were omitted from the figure.

Figure 23-A shows the results for the fouled membranes compared to the blank. The DOW Filmtec™ NF270 consists of a polyamide top layer with a polysulfone (PSf) support. The EDS result show the presence of the polysulfone support (sulfur) but is unable to detect the nitrogen in the amide group in the unused membranes.

A general trend is the steep decline in carbon and sulfur content while the oxygen and nitrogen content increases sharply for all samples. This change can be attributed to the accumulation of protein- or humic-like organics (C,H,O,N) and inorganic precipitation (O) products on the surface of the membrane. Furthermore, all samples show accumulation of multivalent inorganic salts in the fouling layer. The EDS result confirms that for the aluminum and ferric treated samples their hydroxides are heavily accumulated in the fouling layer.

The EDS result for the washed membranes show (rinsed with demineralized water) that the majority of the precipitated aluminum and ferric hydroxides are removed easily, see Figure 23-B. This is in agreement with the visual observation. Nonetheless, residual fouling is profound and seems to be made up out of inorganic-organic (humic/protein –like) complexes. It seems that the first layer(s) of fouling material behaves in the same way as observed in many papers by different groups [13-16] on model waters: Fouling layers made up of complexes of organic material, multivalent ions and membrane. Coagulant addition seems to enhance this complexation behavior.

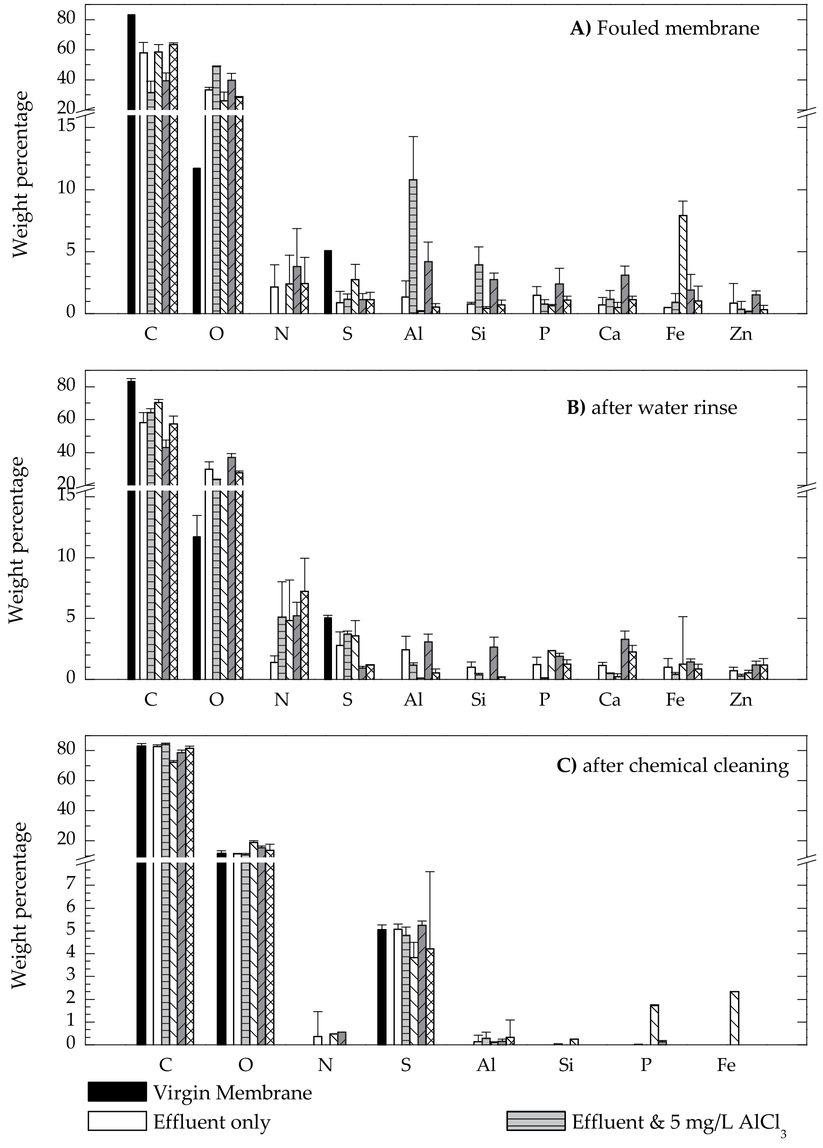

Figure 23- Elemental analysis of fouled (top), washed (middle) and cleaned membranes (bottom) by SEM-EDS

For the biopolymer treated samples an exception must be made. The nitrogen detected by EDS could be contributed to the biopolymer itself as it contains nitrogen. Unfortunately, Nalco could not disclose detailed specifications for this product.

The EDS-spectra (Figure 23-C) for the cleaned membranes show that residual fouling can be removed to great extent. The results for the Al^{3+} and biopolymer treated water are excellent. No residual fouling could be detected, although some Al^{3+} (0.21-0.33 w%) traces were still found on the membrane. Aluminum is present in the feed water in small quantities, see Table 10. As in all cleaned samples aluminum was detected, aluminum is most likely preferentially adsorbed to the carboxylic groups of the polyamide top-layer compared to sodium (present on all unused membranes). These results are in good agreement with the ANOVA analysis for the permeability data.

EDS analysis showed that all other samples remained fouled with residual organic material. On membranes fouled with effluent and PACl-treated effluent minor traces for nitrogen, aluminum and phosphor could be detected. This is surprising for the PACl-treated effluent as the initial fouling layer of the PACl-treated samples showed the highest number of all inorganic salts in the residual fouling layer.

The least promising results are obtained from the Fe^{3+}-treated effluent. The residual iron and phosphor content is significant, however the iron content varies greatly across the membrane; the 95%-confidence interval over 4 samples was of the same magnitude as the mean value (2.3 ± 4). The other residual fouling constituents detected were silica, aluminum and nitrogen. It seems that the applied cleaning regime is not effective enough in case of Fe^{3+}-treated effluent. The EDS data suggests a stronger binding mechanism between the membrane and the residual ferric-complexes.

The EDS data are in good agreement with the observed results for permeability changes. The ferric treated effluent showed the highest mean value for decreased permeability (Figure 21). ANOVA could not discriminate ($P > 0.05$) between the ferric pretreated effluent and the unaltered and PACl treated effluent due to the large confidence interval.

3.3.4 *Why aluminum and biopolymer treated effluent fouls less*

The results of the three previous paragraphs support the hypothesis that the added coagulants do accumulate in the fouling layer, resulting in a less compressible cake. In case of Al^{3+}/Fe^{3+} addition, the bulk of the fouling layer could be washed away easily. The residual fouling as analyzed by EDS does look rather the same for all coagulants. The EDS results seem to indicate that the first layer(s) of fouling are caused by complexation of the feed water constituents. However, the cleaning procedure was shown to be significantly more successful in case of the aluminum and biopolymer treated water.

An interpretation for this behavior might be found in the transport behavior, affinity and solubility of the added coagulants at the membrane surface.

If coagulant derived species are transported preferentially into the fouling layer, fouling due to complexation of the feed water constituents and the membrane might be partially prevented or the first fouling layer might be less thick. Such a mechanism would make the removal of the residual fouling easier. This kind of fouling prevention by ‘coating’ the membrane is found in a study were activated carbon (AC) is added to the feed [17].

A study by Thorsen [18] modeled the effect of concentration polarization based on molecular mass of aquatic macromolecules, flux and cross-flow. It was shown that species of larger MW were faster accumulated near the membrane, especially web-like structures. If we look at the estimated MW of the coagulants, the following sequence is observed.

$$\text{Biopolymer} \gg \text{PACl} \approx \text{EfOM} > [\text{Me(OH)}_3]_n\text{(am)}$$

The MW of the Al^{3+}/Fe^{3+} complexes were estimated based on the formation of amorphous (am) $[Me(OH)_3]_n$ in the effluent. Monomeric substances ($n = 1$) are most likely to be considered [19, 20], however polymeric forms ($n = 2\text{-}12$) can be present as well.
Such a model would support the hypothesis of the build up of an initial fouling layer rich in biopolymer. The visual data support this behavior for the biopolymer treated samples as these layers were thick and were definitely enriched biopolymer conglomerates. As the biopolymer was not washed away with demineralized water, it remains unclear, whether the biopolymer or other (in) organic structures fouled the membrane initially.

The other coagulants do not differ in MW in such extremities as the biopolymer. Another mechanism must be responsible for the different behavior. In general the residual fouling consists of a complex mix of inorganic and organic structures. The easiness of removal of the fouling seems very dependant on the coagulant type.

In case of aluminum treated effluent the residual fouling could be easily removed. The observed affinity of aluminum for the membrane and key fouling components might play an important role in this behavior. Aluminum has shown to be easily removed from polyamide top-layer, [21]. Furthermore, aluminum has been shown to be preferentially absorbed to humic like structures instead of multi-valent ions like iron, calcium or magnesium, [22]. Other studies have shown that especially the aromatic compounds in EfOM together with calcium are capable of the formation of persisting fouling layers. Addition of aluminum might therefore lead to other and more removable fouling layers. It is noteworthy to see that although the PACl treated effluent seems to have more residual fouling, cleaning is quite successful.

The same analogy as for aluminum can be held for the ferric treated effluent, with two exceptions:

- Ferric iron is less preferentially adsorbed to humic-like structures;
- Some ferric complexes have a very low solubility. Once precipitated, these complexes might not dissolve under the cleaning regime applied (pH 3-11).

3.4 Conclusions

This study set out to prove the following hypothesizes:

H_1: Adding coagulants to the feed solution results in formation of a protective layer on the membrane surface.

H_2: The resulting protective layer alters the performance of the membrane in terms of rejection, filterability and cleanability.

The results presented in this paper do not fully support the first hypothesis. Evidence was found that all tested coagulants accumulated in the fouling layer. This layer is not made up of coagulant species alone but of an intricate mixture of feed water species and coagulants. An exception has to be made for the vegetable derived coagulant (biopolymer) which seemed to be heavily accumulated on the membrane confirming the first hypothesis. The mechanism behind the formation of coagulant dominated fouling was hypothesized to be the difference in molecular weight of the coagulant and effluent organic matter.

Although no direct proof could be found for a protective layer, coagulant addition does have a profound effect on for filterability, cleanability and rejection. Addition of coagulant enhances the strength of the cake layer preventing cake collapse at high pressure. Addition of certain types of coagulant improved the cleanability of the residual fouling layer. The results imply that a careful screening should be made whether the feed water, membrane and selected coagulant are compatible.

The membrane used in this paper, Dow Filmtec™ NF270, showed good compatibility with $AlCl_3$ and the vegetable derived polymer (Nalco 77135) compared to all other treatments. The addition of $FeCl_3$ resulted in problematic residual fouling.

Soluble organic matter rejection was reduced when dosing aluminum. The mechanism behind this phenomenon was hypothesized to be the difference in cake enhanced polarization for the cakes formed under aluminum dosed conditions. For all other coagulant treated samples no significant changes in rejection were observed.

3.5 ACKNOWLEDGEMENTS

The authors like to express there gratitude to Christelle Tuchagues and Zélia Chaptal of the Ecole Nationale Supérieure d'Ingénieurs de Limoges (France) who contributed to this paper by their practical work during their student internship placement during the summer of 2004. Norit MT co-financed this internship through the EU Leonardo-da-Vinci exchange program. Vitens Water, Landustrie Sneek B.V. and Wetterskip Fryslân (Frisian waterboard) are kindly acknowledged for funding this study.

3.6 Appendix

3.6.1 Full factorial design & ANOVA

In this research, a full factorial design experiment was employed to study the effects of several factors on the filtration of WWTP effluent by nanofiltration. Factorial designs excel in finding relationships between several experimental factors accounting for inter-factor effects. Furthermore, the design can be altered to account for and discriminate between un-controllable factors, such as effluent quality. More detailed information about factorial design and the validation method can be found in [5, 23]. For this study a two-level, five factor factorial design was used, see Table 11.

Table 11- Full factorial multi-level design

Run	*ΔP (kPa)*	*Coagulant type (5 mg/L)*
1	300	None
2	300	Al^{3+}
3	300	Fe^{3+}
4	300	PACl
5	300	Biopolymer
6	600	None
7	600	Al^{3+}
8	600	Fe^{3+}
9	600	PACl
10	600	Biopolymer

The experimental design was performed eight times to obtain a sufficient confidence level as each design could not be treated as a true replicate due to feed water variations (blocking of the factor 'feed'). Thus, in total eighty (8 x 10) individual filtration experiments were performed. The results for the ANOVA analyses are given in Table 12.

Table 12 - ANOVA for the experiments performed

Source *(SS)*	*Sum of Squares (SS)*	*Degrees of Freedom (DF)*	*Mean square (MS)*	*F0-value*	*Probability (P-value)*
Cake resistance (log10 transform)					
Feed	1.2	7	0.17		
Selected factors	0.83	9	0.093	5	< 0.0001
Pressure	0.075	1	0.075	4.05	0.0488
Coagulant	0.37	4	0.093	5.03	0.0015
Pressure – Coagulant	0.39	4	0.098	5.27	0.011
Residual	1.1	60	0.019		
Change in retention (overall mean best predictor)					
-	-	-	-	-	-
Change in permeability (no transform)					
Feed	40013	7	5716		
Selected factors	11799	5	2360	8.54	< 0.0001
Pressure	3836	1	3836	13.88	0.0004
Coagulant	7927	4	1982	7.17	< 0.0001
Residual	17965	65	276		

3.6.2 *Molecular weight estimation*

Samples of both polymers obtained from Nalco were injected in the GPC column. The elution diagram is shown in Figure 24.

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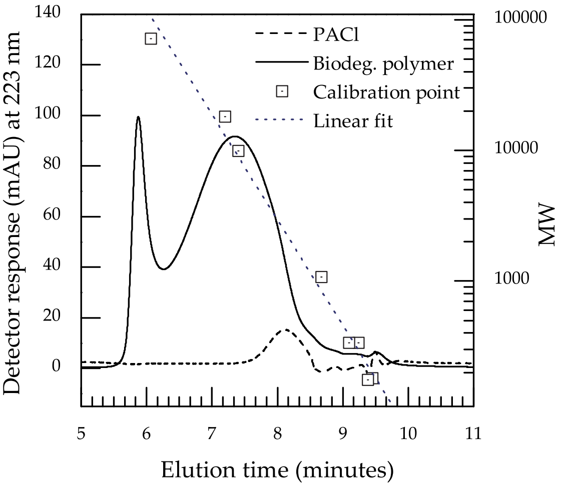

Figure 24 - Elution diagram for both Nalco products.

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CHAPTER 4

FOULING CONTROL IN NANOFILTRATION USING A HIGH VOLTAGE STATIC ELECTRIC FIELD DEVICE

Pilot scale tests were performed to assess the influence of temporary feed exposure to a high voltage static field device on nanofiltration performance. It was shown for both a model and real feed (WWTP effluent) that exposure to the field had the beneficial effect of increasing the initial membrane permeance. The electric field device was shown to elevate the electrophoretic mobility of the feed, an effect that lasted for 6 minutes after passage through the field. Elevation of the electrophoretic mobility of colloidal matter was interpreted as enhanced dissociation of weak acid groups associated with the humic-like material in the feed.

The rate of membrane fouling, when occurring, was shown to be independent of the application of the electrostatic device. The application of an electrostatic device seems therefore beneficial in membrane filtration of feeds with organic content, enabling an on average higher production rate during a filtration cycle.

4

Fouling control in nanofiltration using a high voltage static electric field device

4.1 INTRODUCTION

Advanced treatment of wastewater treatment plant (WWTP) effluent for agricultural, industrial, or (in)direct potable purposes could be beneficial in areas of water stress. Moreover, regulatory agencies have shown to broaden their surface water quality regulation acts to include additional protection of public and environment, e.g. the new EU directive on bathing water [1]. The latter will force an upgraded quality of WWTP effluent in receiving surface waters. Nanofiltration (NF) could be used as such advanced treatment for effluents. Pilot and full scale studies [2-5] have proven direct NF to be a suitable technique for the production of a high quality permeate, free of bacteria and viruses, with low hardness, low organic content and good removal rates for most micro-contaminants.

The advantage of tertiary treatment of WWTP effluent by direct nanofiltration is the high recovery rate, typically between 90-95%, compared to the classical ultrafiltration – reverse osmosis systems which operate at 50-80% recovery. The main disadvantage of direct nanofiltration is the higher fouling rate; however some of the previous reported pilot studies [3, 5] reported that direct nanofiltration showed superior operational stability compared to direct ultra and microfiltration. Nonetheless, fouling will occur and hamper recovery rates, lower the permeate quality and decrease membrane lifetime. It is therefore imperative to find strategies to control and limit fouling.

In our previous study [6] the relationship between the colloidal properties of the effluent organic matter (EfOM) and fouling behavior was studied. The results showed that maintaining a stable colloidal system is imperative to prevent the formation of dense non-permeable fouling layers. Keeping a stable colloidal system is very hard in case of NF/RO filtration. At increased recovery rate, the ionic strength of the feed solution increases as salts are rejected, especially the multivalent species in case of NF. The increased ionic strength will cause compression of the electric double layers surrounding many organic macromolecules leading to colloidal destabilization. The latter is shown to cause fouling layers with high resistance to permeation[7, 8].

A non-conventional method to mitigate fouling is by exposure of the feed solution to an external electric field. Electric fields are able, see the theory section, to influence dielectric and polar media in the feed solution. This principle is used for instance in electro-coagulation, capacitive deionization and electro-filtration applications. In case of electro-filtration, fouling could be prevented when an alternating electric field was imposed over the membrane surface [9-11].

In this study, the feed solution is exposed for a limited period of time to a high voltage non-uniform static field. The field stems from an electrode assembly integrated into the feed piping system. The feed flow rate and the volume of the electrode assembly determine the time of exposure. As the feed is only temporary exposed to the electric field, it is uncertain whether and how long the effect on the colloidal matter lasts. Once out of the field possible effects will dissipate. The effect of the exposure of the feed solution is measured by analyzing the electrophoretic mobility before and after passage through the external field as function of time. Pilot-scale filtration tests are conducted to see if the temporary exposure of the feed to the high voltage field has any effect on the system performance. A model and a real feed is used in this study.

4.2 Theory

When a solution containing water, salts, solids and macromolecules (polar and non-polar) is passed through a charged capacitor, numerous charge related effects take place, see Figure 25. The most relevant will be discussed briefly.

In presence of an external non-uniform static electric field, polarization of almost every surface between solvent and dissolved or colloidal species occurs assuming that the dielectric constants of the dissolved materials is different from the solvent. Water has a very high dielectric constant (ε_r = 78 F/m) compared to many organic molecules, e.g. ε_r paraffin/ sugar = 2-3. Polarization happens very fast with time scales in the order of 10^{-6}-10^{-9} seconds. Polarized matter is accelerated in the electric field and the resulting hydrodynamics resistance (drag) changes the arrangement of free charge (ions) around polarized matter [12]. As water itself is a very strong dielectric, water molecules at an interface might contribute to enhanced ‘wetting’ of surfaces, a principle used in inverse electro spray [13].

Apart from polarization and orientation of surfaces two other important effects take place. Due to the distance between the charge centers of ion-pairs in macro-molecular structures, deformation, rotation and alignment will take place along the electric field lines. At sufficient field strength structural-conformational changes can take place. It has been shown that collapsed charged polymers can be distorted due to induced motion of ions and alignment of

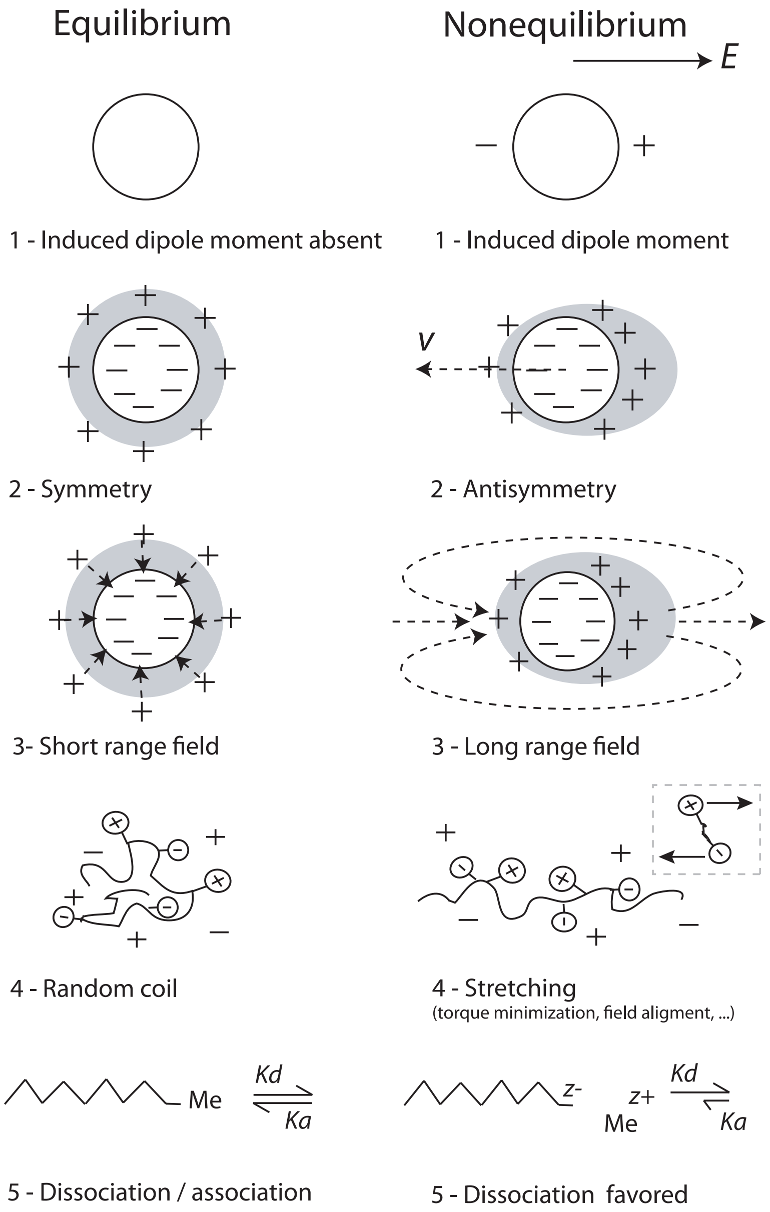

Figure 25 - Changes in behavior of dielectrics when placed in an external electric field. **1)** Induced dipole moment in a non polar material due to rearrangement of electron cloud and proton nuclei. **2)** Displacement of the DL surrounding uniform sphere with fixed surface charges. **3)** Formation of electric field gradients beyond the DL near surfaces due to non-equilibrium distribution of charge. **4)** Stretching and alignment of macromolecules with active surface charges due to minimization of the induced torque on the charged groups in the external electric field or due to imposed velocity gradients. **5)** Enhanced dissociation

fixed charged surface groups [14]. Secondly, an external electric field increases the dissociation of weak acids and base and promotes the separation of ion-pairs into the corresponding free ions (dissociation field effect; second Wien effect) [15, 16].

Once outside the electric field, polarization effects will dissipate rapidly. It is however plausible that some electric field effects could have some temporary influence on the colloidal stability of the feed solution. Especially the disruption of the charge distribution around the colloidal material, the stretching/ distortion of the macro-molecules and the enhanced dissociation could play an important role.

4.3 MATERIALS AND METHODS

4.3.1 Measuring colloidal stability

Electrophoretic light scattering (NICOMP 380/ZLS, Particle Sizing Systems) was used to estimate the electrophoretic mobility of the colloidal material of the feed water. The apparatus used has a detection range of 20 μm to 5 nm. From the electrophoretic mobility the corresponding zeta-potential was calculated using the Smoluchowski equation (15);

$$\mu = \frac{\zeta \varepsilon_0 \varepsilon_r}{\eta} \qquad (15)$$

in which μ denotes the measured electrophoretic mobility, ζ is the zeta-potential, ε_0 ε_r are the dielectric constants of vacuum and feed and η denotes the viscosity of the feed. The Smoluchowski equation is well applicable for systems in which the thickness of the double layer is small compared to the radius of the particle, i.e. $\kappa a > 100$ with κ the inverse Debye length and a the particle radius.

The inverse Debye length can be calculated as;

$$\kappa^{-1} = \sqrt{\frac{F^2 \sum_i z_i^2 c_i}{\varepsilon_0 \varepsilon_r RT}} \tag{16}$$

with F Faradays constant, R the gas constant, T temperature and $z_i^2 c_i$ the ionic strength in the feed water. As the ionic strength of the feed water, see Table 15, is between 0.01 – 0.02, κ-values are in the order of 1x10^8 m^{-1}. The colloidal material in the effluent is estimated to be below micrometer size. Gel permeation chromatography results [6] indicate a maximum molecular weight of the aquatic colloids of 2000-2500 Da, resulting in estimated radii of 30-50 nm [17]. The validity of the Smoluchowski equation is therefore unsure as $O(\kappa a) = 10^8 \times 10^{-8} = 1$. In the region below $\kappa a < 100$ serious distortion of the double layer due to polarization effects occurs and the zeta-potential will be underestimated using the Smoluchowski equation [18]. Therefore colloidal stability will be presented in terms of electrophoretic mobility instead of the more usual zeta-potential.

4.3.2 Application of the external electric field

The feed solution was passed through a charged capacitor (Zeta Rod®) constructed by the Zeta Corporation, Tucson, U.S.A. This device consists of a rod-shaped dielectric ceramic insulator as high voltage electrode inside a grounded stainless steel cylinder. Dimensions and schematics are given in Figure 26. The high voltage wire connected to the ceramic electrode is fed by a DC power supply capable of charging and keeping the electrode up to a potential of 30 kV. This will create a non-uniform static field inside the chamber with field lines radiating from the electrode to the grounded cylinder. It is important to notice that the system is 'open', hence no current flows are possible. The only power consumption is due to energy losses in the AC-DC converter.

4.3.3 Pilot plant description

A membrane filtration pilot plant constructed by Norit MT, Enschede, NL was used. The pilot was capable of holding a 4 inch module (spiral or capillary configuration) and was fully automated. The pilot design schematics are given in Figure 27. The pilot was connected to a 1 m^3 feed tank (indoor) with level control. To replenish the feed tank a low levels and facilitate continuous filtration test, the feed tank was connected to an outdoor underground storage room capable of holding 8 m^3. This storage container was replenished with secondary effluent drawn from the clarifiers of the Leeuwarden WWTP. Inside the intermediate feed tank an aerator was constructed for nitrogen aeration to keep the oxygen levels in the feed under 1 mg/L O_2. This was essential to mimic the feed conditions as when drawing feed directly from the overflow of the secondary clarifiers. Besides suppressing the dissolved oxygen levels, aeration supplied the necessary mixing to prevent sedimentation in the tank.

A strainer (0.5 mm) and the electrostatic device were placed directly after the intermediate feed tank. The pilot was fitted for this study with a 4″ spiral wound module, type NF270-4040, supplied by DOW Filmtec®, having a total effective filtration area of 7.6 m^2. General characteristics for this membrane can be found in Table 13.

Table 13 - Reported characteristics for the DOW Filmtec NF270 membrane

Source	*Zeta Potential* (mV)	*Contact Angle*	*Permeability* (L/m^2.bar.h)	*Organic rejection* (%)	*$CaCl_2$ rejection* (%)	*Sulfate rejection* (%)
DOW Filmtec[†]	-	-	11.1	94	40-60	99
Mänttäri[‡] [32]	-16	30º	15.6	94.9	48.2	99.0

[†] Test conditions: Permeability: 4.8 bars, 25º C, 2000 ppm MgSO4. Organic rejection based on Lake Mead pilot plant, Overton, Nevada, USA

[‡] Test conditions: Permeability: 7.8 bar, 35º C, pH 7. Background solution for zeta-potential 0.01M KCl. Data on salt and organic rejection based on paper mill effluents.

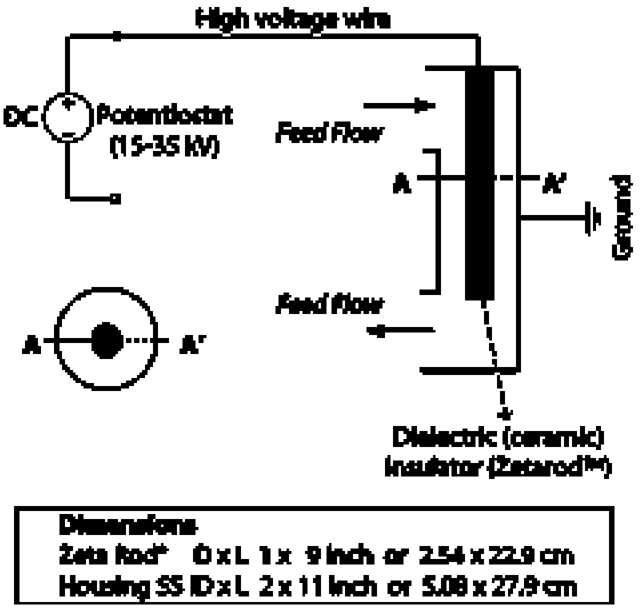

Figure 26 - Schematics of the apparatus used for the application of the external electric field.

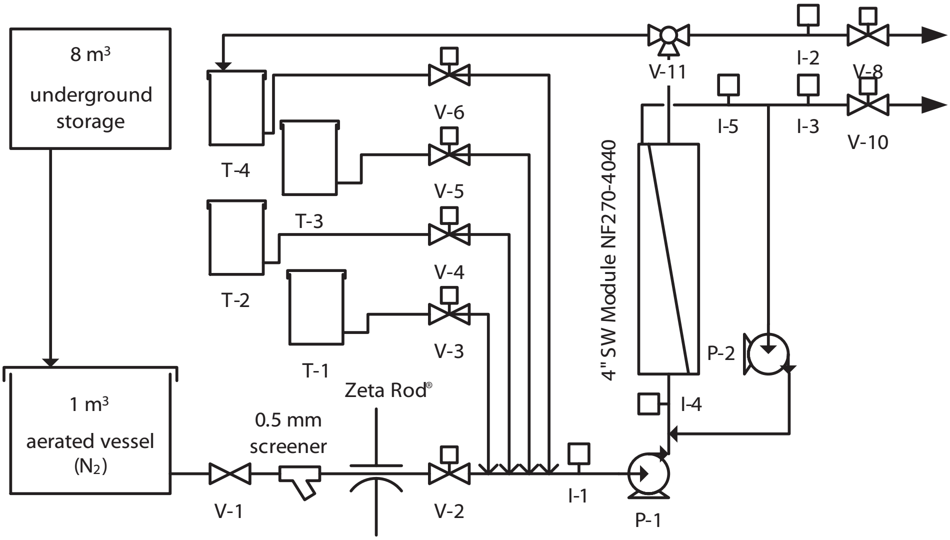

Figure 27 - PID for the setup used. T1 to T4 indicate 50L storage vessels for cleaning and flushing solutions. Automated valves v-1 to v-11 for process control. P-1: Feed pump, P-2: Circulation pump. I-1 to I-5 denotes automated indictors for flow, temperature, pH, pressure and conductivity.

4.3.4 System performance benchmarks

To assess the influence of the electrostatic device, mass transfer coefficient (MTC) and rejection characteristics for the used membranes will be analyzed during filtration runs in batch and cross flow modus. The mass transfer coefficient (or permeance) is defined as:

$$MTC = \frac{Q_p \cdot TCF}{A_{mem} \cdot NDP} \tag{17}$$

$$TCF = (1.03)\exp(T - T_{ref}) \tag{18}$$

$$NDP = \frac{P_{f,in} + P_{f,out}}{2} - \left(\frac{(\pi_{f,in} + \pi_{f,out})}{2} - \pi_p \right) \tag{19}$$

$$\pi = x_\pi \cdot EC \cdot \frac{T}{T_{ref}} \tag{20}$$

The MTC represent the permeate flux (Q_p), corrected for feed water viscosity changes by the temperature correction factor (TCF) and the net driving pressure (NDP). The NDP is obtained from the pressure difference between the transmitters at the entrance and exit of the module and is corrected for osmotic pressure.

The osmotic pressure is related to the electrical conductivity by the factor x_π and is corrected for temperature. The factor x_π was determined experimentally for the feed waters used in this paper. The reference temperature (T_{ref}) used is 298 K.

Rejection on TOC and most common salts will be analyzed. After each test run the module was cleaned and characterized on permeability (expressed in MTC) and rejection on magnesium sulfate. Cleaning consisted of an alkaline based rinsing (pH 10, 35° C) and soaking step of 30 minutes, followed by an acid washing (pH 3, ambient temperature) and soaking step of 30 minutes. Alkaline cleaning solution was made from permeate and an alkaline enzymatic cleaning product (Ultrasil P3-67 & P3-69) supplied by Ecolab, whereas the acid solution consisted of permeate and hydrochloric acid. If the cleaning did not suffice to restore original permeability and rejection characteristics of the module (based on 2000 mg/L $MgSO_4$ MilliQ solution) a new cleaning cycle was initiated until original conditions were restored.

Table 14 - Experimental protocol

ID	*Feed*	*Operational mode*	*Zetarod™* (Yes/No)	*Feed/ Perm. Flow* (L/hour)
A	Tap water	Batch	N	235 / 200
A′	Tap water	Batch	Y	235 / 200
B	Tap water	Continuous	N	235 / 200
B′	Tap water	Continuous	Y	235 / 200
C	Effluent 1	Batch	Y	118 /100
C′	Effluent 1	Batch	N	118 /100
D	Effluent 2	Batch	N	212 / 180
D′	Effluent 3	Batch	Y	212 / 180
E	Effluent 4	Batch	Y	165 / 140
E′	Effluent 5	Batch	N	165 / 140
F	Effluent 6	Continuous	N	140 / 120
F′	Effluent 6	Continuous	Y	140 / 120
G	Effluent 7	Continuous	Y	235 / 200
G′	Effluent 7	Continuous	N	235/ 200

4.3.5 *Experimental protocol*

The testing protocol followed is given in Table 14. Both for 'model' feed and secondary effluent different tests were conducted based on operation mode: continuous or batch. In the continuous mode the installation was run with 85% recovery over the single module with return of concentrate and permeates to the intermediate feed tank (full recycle). Batch operation consisted of the production of permeate with only concentrate return to the intermediate feed vessel. When a recovery of 95% was reached the system was flushed to remove the concentrate and a new filtration cycle was started. For both the continuous and batch operation a constant flow of 1.6 m^3/h (approx. 0.1 m/s cross flow velocity) over the module was maintained. The use of the electric field was randomized between the different tests runs. The trans-membrane pressure over the membrane was adjusted by setting a desired product flow. The maximum achievable feed pressure of the pilot installation was 400 kPa (4 bars). A trial test revealed that the pilot was able to produce 250-260 L/hour of permeate at maximum feed pressure based on tap water when a non-fouled module was used. Test setting was therefore chosen around 80% (200 l/hour) of the maximum permeate production rate. For the test with effluent different settings were used, ranging from 40%-80% of the maximum production rate depending on effluent quality.

4.3.6 Feed water characteristics

Potable water, as supplied by the regional water supplier (Vitens Water), was used as a model water because of its characteristics. Beside moderate hardness and constant quality, it contains a fair amount of humic substances due its ground well characteristics. General characteristics of the potable water can be found in Table 15, whereas a more detailed information can be found in a Ph.D.-thesis by the University of Twente dealing with these humic substances [19].

The real feed used is secondary effluent from the local waste water treatment plant in Leeuwarden (NL). Effluent was drawn from the overflow of the secondary settlers and transported to the test site (WETSUS laboratory, Leeuwarden, NL). The effluent was stored in an underground outdoor storage tank with mixing facility, prior to use. Effluent storage time was less than 3 days to prevent major changes in quality due to possible biological re-growth. The effluent has some site-specific characteristics:

- The moderate Specific Ultraviolet Absorption (SUVA) (>0.02 L.cm^{-1}.mg^{-1}) of the effluent shows the aromatic nature of the effluent, which is not surprising as the drinking water of Leeuwarden contains a large amount of humic substances.
- A high conductivity due to a nearby dairy factory which discharges large amounts of sodium chloride in the sewer.

The general characteristics of the effluents used in this study can be found in Table 15.

Table 15- General feed water properties

Feed	*TOC*	*Na^+*	*K^+*	*Mg^{2+}*	*Ca^{2+}*	*Cl^-*	*NO_3^-*	*SO_4^{2-}*	*μ*
				(mg.L^{-1})					(μm.cm.V^{-1}.s^{-1})
Tap water	9.0	78	3.0	10	30	34	10	< 3†	n.d.
Effluent 1	12	231	32	14	62	154	n.d.	59	-0.11 (± 0.03)
Effluent 2	7.1	101	13	7.4	42	102	3	24	-0.13 (± 0.15)
Effluent 3	11	174	22	10	48	125	7	70	-0.18 (±0.07)
Effluent 4	16	178	24	12	52	123	7	71	-0.14 (± 0.06)
Effluent 5	10	175	10	10	52	129	3	33	-0.17 (± 0.10)
Effluent 6	17	260	20	13	56	166	4.	74	-0.10 (± 0.05)
Effluent 7	8.3	90	14	11	44	110	n.d.	25	-0.32 (±0.04)

† Fluctuations in sulfate concentration 0.5-3 mg/L

n.d. = not detected or below sensitivity of analysis method (HPLC-IC)

4.3.7 *Analytical*

Total organic compounds (TOC) of the feed were analyzed using a Shimadzu TOC-V CPH TOC analyzer. Most common cationic species (Na^+, K^+, Mg^{2+} and Ca^{2+}) were determined using inductively coupled plasma - optical emission spectroscopy (ICP-OES – Perkin Elmer Optima 3000XL). An IC (Metrohm, Herisau, Switserland, type: 761 Compact IC) was used to measure most common anions (Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}).

4.4 RESULTS AND DISCUSSION

4.4.1 *Temporal effect of the electric field on the feed*

Feed solutions were exposed to the electric field and the electrophoretic mobilities were assessed prior to entering the electric field and after passage as function of time. Depending on the chosen feed flow, contact time with the electric field was between 5 and 10 seconds. As sampling for measurements takes time, the first measurement is obtained approximately 2 minutes after passage of the electric field. Measurements are grouped around 2 minute's intervals and are displayed in Figure 28.

Data for all effluents samples are presented together as no significant difference in behavior was found between the tested effluents samples. It was impossible to obtain meaningful electrophoretic mobilities for the potable water used, as colloid concentrations were below the detection limits of the apparatus used.

As Figure 28 shows, exposure of the effluent to the external electric field has a significant influence on the electrophoretic mobility of the colloidal matter in the effluent. As expected, the influence is time dependent. After a period of 6 minutes, no significant difference ($P > 0.05$, Dunnet's test) in electrophoretic mobility can be observed between the initial and exposed feed solution. To interpret this experimental observation, let us consider the parameters influencing the electrophoretic mobility. The electrophoretic mobility is a characteristic constant given by Eq. (21) [20];

$$\mu = \frac{qe}{f}\,\mathrm{f}'(\kappa) \tag{21}$$

in which q is the number of charges on a surface, e the value of a unit charge, f the hydrodynamic friction coefficient and $\mathrm{f}'(\kappa)$ is a function which accounts for

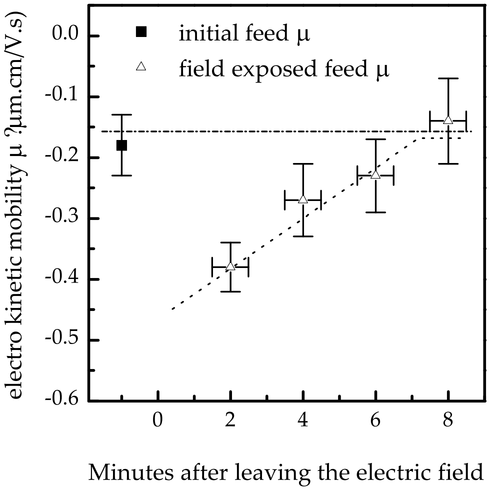

Figure 28 - Electro kinetic mobility as function of time after leaving the electrostatic device. Averaged data from tests C, D′, E and F′, total number of samples per data point > 35, whiskers denotes 95% confidence interval.

the screening by counter ions in the double layer.

The screening factor f′(κ) dependents on the distribution of the ions around a surface. Inside the electric field this distribution can be distorted, see Figure 25, due to ion migration and induced dipole moments. The typical reaction time of the electrolyte entering an electric field is almost instantaneous, with time scales in order of nanoseconds [21]. If we assume that relaxation times for the electrolyte leaving an electric field are in the same order, the screening factor will not differ between the original feed and the exposed feed in the time scale of the electrophoretic mobility measurements.

Other parameters which may be affected on the time-scale of 5 minutes are the hydrodynamic friction coefficient f′(κ) and the charge density *q*.

As the macro-molecules could be stretched, distorted and aligned in the electric field, their shape and might be different when leaving the electrostatic field. Shape has a direct effect on the hydrodynamic radius and therefore electrophoretic mobility. A comparison of the electrophoretic mobility of various peptides and proteins of different molecular weight (MW) [22] showed that more asymmetric and open structured proteins and peptides have a higher mobility ($\mu \sim MW^{-1/3}$) than randomly shaped proteins and peptides ($\mu \sim MW^{-1/2}$). However it seems unlikely that shape distortion is the key factor in causing prolonged elevated electrophoretic mobility as relaxation time of stretched polymers are in the timescale of milliseconds [23].

The net charge density q of most aquatic organic matter is highly dependent on the feed water matrix as complexation of their reactive groups (carboxylic, phenolic…) occurs depending on solution pH, cation competition, etc… [24]. An electrostatic field has a profound effect on the dissociation of multivalent ions involved in ionic equilibria, especially when counterion-polymeric dissociations are involved [16]. Assuming that dissociation occurs in the electric field, the net charge density will be affected. Once outside the electric field the association of metals – organic complexes will occur. This is a process controlled by kinetics depending on their association /dissociation constants. Complexation reactions of aquatic organic material have been shown to take place with time scales in the order of seconds to hours [24, 25]. Dissociation of weak acidic groups of the organic material (most probably humic-like substances) could therefore be the cause of the observed time-effect in electrophoretic mobility.

4.4.2 System performance

A total of 14 tests were performed to assess the influence of temporary exposure of the feed to the applied electric field (see Table 14, Figure 29 and Figure 30). Six out of seven tests show a significant ($P < 0.05$) difference in total averaged MTC when the feed was exposed to the field. For the tests with tap water

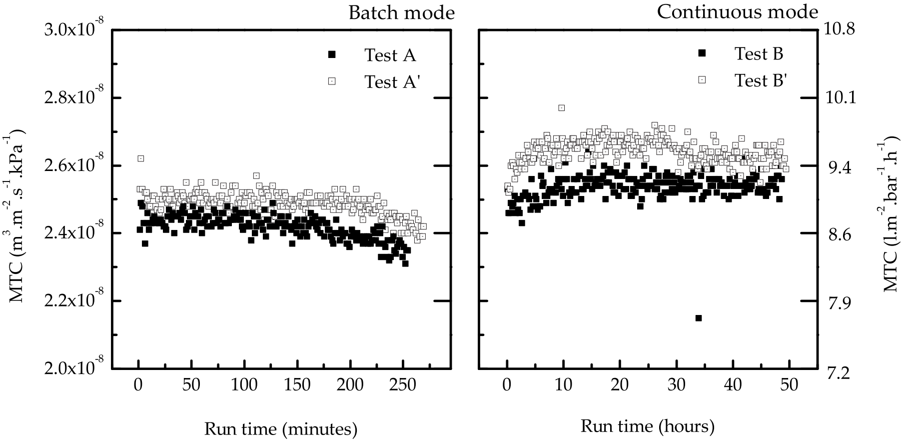

Figure 29 - Mass transfer coefficient during filtration of tap water in batch mode (left) and continuous mode (right). Open symbols denote the test with the electrostatic device.

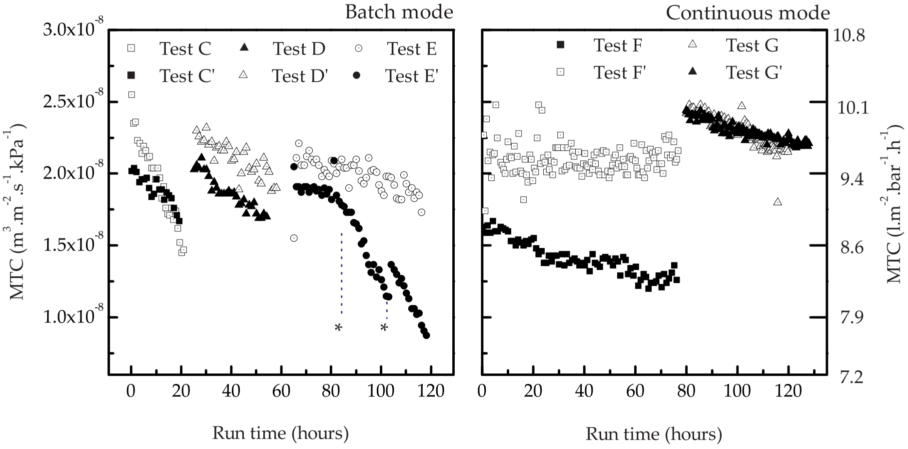

Figure 30 - Mass transfer coefficient for the test using effluent in batch (left) and continuous mode (right). Open symbols denote the tests with the electrostatic device. Between the asterisk (*) the cross-flow pump failed.

an average increase of +5% in MTC was observed.
The tests on WWTP effluent showed an increase in MTC of 10-20%. In all situations were the electric field was applied the initial MTC was higher, indicating that initial (quick) fouling of the membrane was prevented.

Nevertheless, exposure of the feed to the electric field could not prevent fouling entirely as most tests showed a gradual decrease in MTC. An earlier study by the Orange County Water District [26] utilizing the same technology in attempt to alleviate fouling on the RO membranes installed in their advanced wastewater reclamation plant, showed similar results. During pilot tests (5000 hours) initial increases in MTC, varying from -2 to 53%, were reported. In time fouling did occur on all modules to an extent in which the MTC between the control and electric field exposed membranes were similar.

The observed higher MTC could be attributed to the larger net charge distribution of the colloidal material in the feed. A higher net (negative) charge distribution could have a twofold effect:

Firstly, an increase of the electrostatic repulsion between the negatively charged membrane surface and negatively charged colloidal matter will decrease the possibility of sorption of organic molecules on the membrane. However, in a complex feed such as secondary effluent, multiple interactions will occur such as; cation-organic complexation with the membrane[8, 27] and sorption of hydrophobic parts of organic molecules and membrane [7, 28, 29]. The ionic strength of the feed solution and the resulting salts gradient near the membrane will determine whether electrostatic interactions play a major role. For feeds with a high salt content (or systems with high concentration polarization) the importance of electrostatic interactions between feed and membrane are less profound due to compression of the double layers. At sufficient ionic strength, electrostatic repulsion effects become negligible and fouling due to electrostatic repulsion can not be prevented. It is therefore noteworthy to see that test F′ shows non-fouling behavior when the feed was exposed to the electric field. Apparently, the increase in surface charge of colloidal matter was able to prevent fouling during the operational conditions encountered in test F′; low ionic strength of the feed and low trans-membrane pressure due to low permeate flux.

Secondly, surface charge of macromolecules has an effect on the properties of the fouling layer. Earlier research [6] by the same authors showed that effluent colloidal matter with a high zeta-potential forms less compact and more permeable fouling layers compared to effluent colloidal matter with neutral zeta-potential. Utilizing the standard cake filtration theory for incompressible (ideal) cakes [30], we plotted the inverse MTC as function of permeated volume {Eq.(23)} in Figure 31:

$$\frac{t}{Qt} = \frac{\eta R_m}{Q} MTC + \frac{\eta R_c}{2A} MTC \frac{V_p}{Q} \quad \Rightarrow \quad \frac{1}{MTC} = \eta R_m + \frac{\eta R_c}{2A} V_p \tag{23}$$

With R_m, R_c and V_p respectively the membrane resistance, cake resistance and produced permeate.

Figure 31 shows that for most tests, the cake resistance (slope) between the control and treated feed is comparable or even worse for the treated feed with exception of runs F and F′. The steep increase observed in test E can be contributed due to a hardware control failure in the pilot. During the run (see asterisk * in Figure 30) the cross-flow pump controller failed, the problem was corrected during the same run but failed to restore the MTC. Based on these results it is unlikely that the observed increase in electrophoretic mobility has any beneficial effects on the structure (resistance) of the cake layer.

It is noteworthy that for all tests with electric field the initial resistance is lower than the corresponding blank. The increased electrophoretic mobility alleviates fouling of the membrane during the start-up of filtration, resulting in an initial decreased resistance. Once a cake starts to form on the membrane, the application of the electrostatic device does not differ from the control.

Big differences in performance between the tests can be observed, but these differences could not be related to feed water quality parameters. For instance, one of the most concentrated effluents (dry weather effluent 7, test G and G′) showed one of the highest MTC's with no significant difference between the control and treated effluent, whereas test F shows the lowest averaged MTC with rain diluted effluent (effluent 6). Interestingly, the only trend (no statistical correlation due to too few tests) is that the initial MTC of the system seems to be determining if the electric field will have a large impact on the MTC. At initial high values (> 2.2 x 10^{-8} $m^3.m^{-2}.s^{-1}.kPa^{-1}$) the application of an electric field has little effect, possibly due to the already high mobility of the colloidal matter in the feed.

Although the spiral wound membrane fouled considerably, original MTC and retention values based on magnesium sulfate solutions could be restored after a cleaning cycle, except for the fouling observed in tests E′ and F′, which required several (2 respectively 4) cleaning cycles.

The severe fouling behavior in test E′ could be attributed to the mentioned hardware failure of the cross-flow pump. Test F′ showed a distinct low initial MTC which seems untypical compared to all other tests. The fouling rate is however not excessive compared to the other tests (Figure 31).

The application of the electric field showed no significant effect on the rejection characteristics (Table 16) of the membrane, which were in general agreement with the manufacturer's specifications. Table 16 shows the NF270 membrane to

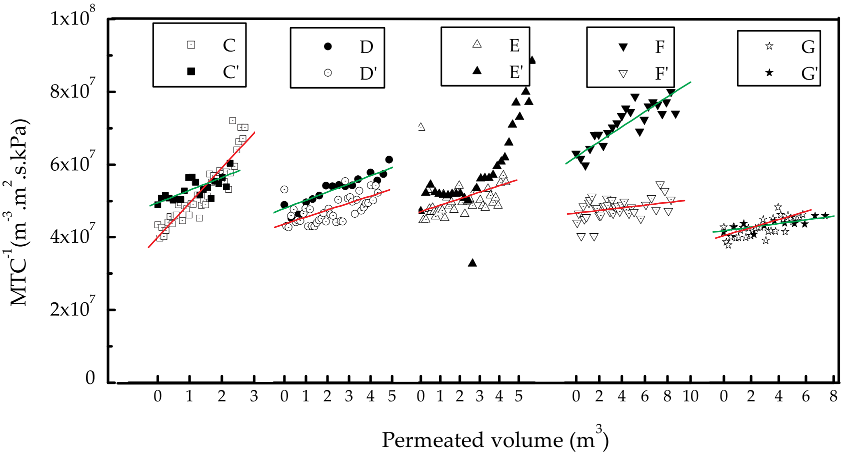

Figure 31 - Evolution of filtration resistance in time for the test conducted with effluent. Open symbols denote the test with applied electric field, straight lines are linear fits.

be a typical nanofiltration membrane with regard to the dependency on rejection of multivalent cat-ionic species on Donnan exclusion of their corresponding counter-ion in the feed [31].

Table 16 - Averaged retention for the NF270 membrane

	Tap water	*Effluent*
	Rejection (%)	
TOC	> 97†	96 (±3)
Na^+	27 (±15)	6 (±2)
K^+	29 (±6)	6 (±3)
Ca^{2+}	74 (±15)	12 (±1)
Mg^{2+}	66 (±6)	16 (±1)
Cl^-	-2 (±6)	1 (±2)
NO_3^-	4 (±3)	-2 (±1)
SO_4^{2-}	96 (±2)	84 (±2)
PO_4^{3-}	>90‡	>90‡

† concentration in permeate below detection limit of TOC analyzer (<0.2 mg/L)

‡ phosphate concentration below detection limit IC (< 0.5 mg/L) in permeate or feed

4.5 CONCLUSIONS

Temporary exposure of the solutions used in this study to a high voltage electric static field showed a marked increase in the mass transfer coefficient (MTC). It was shown that the electrophoretic mobility of the feed was raised after passage trough the electric field. The electrophoretic mobility remained significantly elevated for the duration of 6 minutes after leaving the electric field.
We interpret the increase in electrophoretic mobility to be related to the dissociation of weak acid groups of the organic materials in the feed under influence of the electric field. Dissociation of such groups leads to an increase in net surface charge distribution and hence electrophoretic mobility.
The increased electrophoretic mobility might help to prevent early deposition of material on the membrane, hence resulting in a higher initial MTC. When cake layer depositions starts, no beneficial effects from the increased electrophoretic mobility could be observed.

Apart from an increased average MTC, no differences were detected in membrane performance in terms of salt or organic rejection, between the control and electrostatic treated feed.

The application of an electrostatic device seems therefore beneficial in membrane filtration of feeds with organic content, enabling an average higher production rate during a filtration cycle.

4.6 ACKNOWLEDGEMENTS

The authors like to thank Vitens Water, Landustrie Sneek B.V. and the Frysian Waterboard (Wetterskip Fryslân) for the financial support of this project. Dow

FilmTec and Ecolab® are acknowledged for donation of the NF270 membranes and membrane cleaning solutions (Ultrasil P3-67 & P3-69) used in this study. The authors like to express their gratefulness to Mr. Rodrigo Romo from Zeta Corporation, Tuscon U.S.A. for constructing, shipping and borrowing of the electrostatic device (Zeta Rod®) used in this study.

4.7 Symbols & abbreviations

symbol		*Unit*
$\varepsilon0$	permittivity of vacuum	Fm^{-1}
εr	relative permittivity	-
ζ	zeta-potential	V
η	Viscosity	Nsm^{-2} (Pa.s)
κ	inverse Debye length	m^{-1}
μ	electrophoretic mobility	m^{2}s^{-1}V^{-1}
π	osmotic pressure	Pa (Nm^{-2})
A	area (filtration)	m^{2}
F	Faraday's constant	Cmol^{-1}
P	pressure	Pa (Nm^{-2})
Q	volume flux	m^{3}s^{-1}
R	gas constant	Jmol^{-1}K^{-1}
Rx	resistance of phase 'x'	
T	temperature	K
a	radius	m
c	concentration	mol.l^{-1}
e	elementary charge	C
q	charge density	eq.mg^{-1}
t	filtration time	s
z	charge number	-
DL	Double Layer	
EfOM	Effluent Organic Matter	
WWTP	Wastewater Treatment Plant	
MTC	Mass Transfer Coefficient / permeance	
NDP	Net Driving Pressure	
TCF	Temperature Correction Factor	
TOC	Total Organic Content	

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CHAPTER 5

DIRECT NANOFILTRATION OF WWTP EFFLUENT USING SPIRAL WOUND MEMBRANES: FOULING AND AUTOPSY

Pilot scale tests were performed to assess the fouling behavior of spiral wound modules on a direct nanofiltration application on wastewater treatment plant (WWTP) effluent. The results show that suppressing the dissolved oxygen (DO) levels in the feed prevents the formation of biofouling on the membrane. Additional tests showed that forward flush had a beneficial effect on the systems performance whereas coagulant addition led to clogging of the feed spacer decreasing system performance. At DO concentration below 1 mg.L^{-1} a stable performance could be reached at 50% of the initial permeability, using forward flush only. Autopsy revealed that the residual fouling responsible for the decrease in permeability consisted of silt like material. Comparison with earlier studies on direct nanofilration of WWTP effluent utilizing capillary membranes show that spiral wound modules perform as well in regard to fouling and have a better permeance and rejection.

5

Direct nanofiltration of WWTP effluent using spiral wound membranes: fouling and autopsy

5.1 INTRODUCTION

Advanced treatment of wastewater treatment plant (WWTP) effluent for agricultural, industrial, or (in)direct potable purposes could be beneficial in areas of water stress. Moreover, regulatory agencies have shown to broaden their surface water quality regulation acts to include additional public and environmental protection, e.g. the new EU directive on bathing water [1]. The latter will force an upgraded quality of WWTP effluent in receiving surface waters.

Nanofiltration (NF) could be used as such advanced treatment for effluents. Pilot studies [2, 3] have proven direct NF to be a suitable and robust technique for the production of a high quality permeate, free of bacteria and viruses, with low hardness, low organic content and good removal rates for most micro-contaminants.

All these studies used capillary nanofiltration modules for direct (no pretreatment) [2] and indirect filtration [3] of secondary effluent. Capillary nanofiltration membranes have more favorable hydrodynamics along the membrane surface and can cleaned by backwashing and air enhanced forward flush (Airflush®) compared to spiral wound membranes. However, capillary nanofiltration membranes are expensive in contrast to spiral wound membranes.

In 2000, capillary nanofiltration modules (Stork/ X-Flow) were priced at 180 €/m^2 [4], in 2005 the commercial price is still 200 €/m^2 which is more than five times the price of spiral wound membranes 15-25 €/m^2 [3]. In the cost calculations reported in the mentioned studies, the membrane investment costs are a major part (50-70%) of the total investment and operational costs (0.23-0.60 €/m^3). It would be therefore interesting to see how spiral wound modules perform in a direct nanofiltration application compared to the previous studies.

If spiral wound modules could be used and operational performance does not differ significantly compared to capillaries, operational costs might fall below the estimated lower end of 0.23 €/m^3. If permeate is of sufficient quality, reuse might become attractive from a Dutch perspective as the ground-water tax in the Netherlands is € 0.20/m^3 [3].

In this study, pilot plant trial tests were performed to assess the fouling behavior of spiral wound nanofiltration membranes in a direct effluent filtration application.

Earlier tests [5] with the same pilot installation revealed that the spiral wound membranes were susceptible to fouling but mild chemical cleaning (pH 3-10, soaking time 30 min - 1 hour) was sufficient to achieve a stable performance. In this study the authors explore the limiting conditions for operation and the influence of parameters as forward flush and feed pre-treatment. The membrane performance is compared to the results of the previously published studies on direct nanofiltration using capillary membranes. At the end of the tests, autopsy was performed on the different membranes modules to analyze residual fouling components.

5.2 Material and methods

5.2.1 *Experimental protocol*

The goal of the experimental protocol is twofold. The first series of tests are designed to intentionally foul the membrane. In the second series of experiments different operational conditions were tested to find their effect on membrane performance. All tests are listed in Table 17.

Table 17 - General parameters for the experiments performed in this study

Tests ID	*Total run-time*	*Permeate flow*	*Cross-flow*	*Forward Flush*	*Coagulant*	*Aeration*
	hours	L/hour	m^3/hour	Yes /No (interval)	Yes /No	N$_2$/Air)
A	93	120	0	N	N	N$_2$
B	68	120	0	N	N	Air
C	95	120	0	N	N	Intermittent
Autopsy on module 1						
D	51	150	1.6	N	N	N$_2$
E	69	150	1.6	N	Y	N$_2$
F	53	150	1.6	Y / 2 hours	N	N$_2$
G	52	150	1.6	Y / 2 hours	Y	N$_2$
H	77	150	1.6	Y / 2 hours	N	N$_2$
I	223	180	1.6	Y/ 2 hours	N	N$_2$
J	25	200	1.6	Y / 2 hours	IEX	N$_2$
Z	25	250	1.6	Y/ 2 hours	N	N$_2$
Autopsy on module 2						

5.2.2 Fouling tests

During earlier tests with the same setup, membranes and feed (effluent) a stable membrane performance (permeability, retention) was obtained during 470 hours of operation [5]. This was unexpected as the feed (see section 5.2.4) has large fouling potential in terms of colloidal matter, dissolved substances, hardness and has all the necessary nutrients for biological growth (BOD_{28} concentrate = 30-40 mg $O_2.L^{-1}$).

It was hypothesized that the lack of dissolved oxygen present in the feed plays a major role in suppressing biological growth in the system. Secondary effluent leaving the settlers in a conventional activated sludge plant does have dissolved oxygen levels of less than 1 mg $O_2.L^{-1}$ due to the biological activity (uptake of O_2) of the settling sludge.

To investigate this hypothesis, the feed of the pilot was aerated intermittent with N_2 and air during continuous filtration. During filtration the feed was monitored on dissolved oxygen concentration, total organic content (TOC), protein and polysaccharide content (see analytical section). To enhance the concentration gradient of nutrients close to the membrane surface, the crossflow pump was switched off during filtration. The pilot was run under 85% recovery over the module with full recycle of permeate and concentrate to the intermediate feed tank. At 1 day intervals, the feed was refreshed with new effluent. Between each test the module is cleaned and tested on performance according to the protocol listed in Table 18. At the end of the tests, autopsy was performed on the module to analyze residual fouling.

Table 18 - Cleaning and performance protocols

Protocol	*Solutions*	*Operational parameters*
Alkaline cleaning (1st)	P3 Ultrasil 67 & 69	pH 10, 35° C, 1hour
Acid cleaning (2nd)	Hydrochloric Acid	pH 3, 20° C, 1 hour
Performance check (3rd)	2 g/L $MgSO_4$	pH 6, 15.8 m^3/h perm. flux, 2 hours

Ultrasil is an Ecolab product

All solutions made out of demineralized water

5.2.3 *Anti-fouling tests*

Earlier laboratory tests on flat sheet membranes samples [6] revealed that the addition of coagulants could have a beneficial effect on the performance of the membrane. To test whether the same holds for tests in a spiral wound module, an experiment was performed with one of the coagulants previously tested, a vegetable derived polymer (Nalco 77135). The coagulant was dosed prior to the feed pump to a level of 5 $mg.L^{-1}$ feed.

Forward Flush (FF), i.e. a temporal regime of high feed flow without filtration resulting in enhanced cross-flow shear, might be beneficial when the fouling (cake) layer is loosely attached to the membrane. In spiral wound modules, forward flush regimes are restricted by hydrodynamic resistance. Too high cross-flows might lead to a high pressure drop (> 100 kPa) over the module damaging the module(telescoping)[7]. Due to the limitations mentioned, a maximum FF of 5-6 m^3/h (0.4 m/s cross-flow) could be used. The duration of a FF was chosen at 2 minutes.

Application of a forward flush could be beneficial in the combination when combined with coagulants. Earlier tests [6] showed that the mechanical strength of the cake was improved by adding coagulants. A mechanically stronger cake will hold itself together and might therefore be removed to a greater extent compared to more gel-like cakes formed without coagulant.

Besides coagulant addition and forward flush a more intensive pre-treatment was employed to minimize fouling. Prior to filtration the feed was led through an ion-exchange (IEX) column. The function of the IEX column is to remove to majority of humic and humic-like material which has been shown to be the major foulants in secondary effluent [8].

All tests (D-I) were preformed at 85% recovery over the membrane module without recirculation of the concentrate and permeate, except for test J when concentrate and permeate were returned to the intermediate feed tank to achieve a higher total recovery (95%). After test J the module was fed again with un-pretreated effluent (test Z) prior to the autopsy.

5.2.4 *Feed water characteristics*

Effluent from the municipal wastewater treatment plant at Leeuwarden, NL was used in this experiment. The Leeuwarden plant consists of an activated sludge system combined with phosphate removal by chemical precipitation. The effluent of the Leeuwarden sewage treatment plant has some site-specific characteristics.

Firstly, the moderate Specific Ultraviolet Absorption (SUVA) (> 0.02 L.cm^{-1}.mg^{-1}) of the effluent shows the aromatic nature of the effluent, which is not surprising as the drinking water of Leeuwarden contains a large amount of humic substances. The drinking water of contains around 8 mg.L^{-1} TOC with a SUVA of 0.026 L.cm^{-1}.mg^{-1} and a BOD$_{28}$-value of 0 mg O$_2$/.L^{-1}[9].

Secondly, the effluent has a high conductivity due to a nearby dairy factory which discharges large amounts of sodium chloride in the sewer. The general characteristics of the effluent are listed in Table 19.

Table 19 - General feed water characteristics

Components	*Mean*	*Min*	*Max*	*Unit*
COD	36	14	51	mgO$_2$/L
BOD5	< 3	< 3	5	mgO$_2$/L
TOC	13	6	22	mg/L
UVA$_{254}$	0.37	0.32	0.60	1/cm
Proteins†	3.8	0.6	6.3	mg/L
Polysaccharides‡	4.6	1.2	7.3	mg/L
TSS	< 5	< 5	13	mg/L
Phosphate (aq)	0.8	0.1	1.5	mg/L
Total P	1.0	0.4	2.2	mg/L
Nitrate	1.7	0.2	6.9	mg/L
Total N	1.9	0.6	4.2	mg/L
pH	8.0	7.1	8.2	mg/L
Alkalinity (as CaCO$_3$)	330	204	400	mg/L
Chloride	187	106	349	mg/L
Sulfate	42	33	49	mg/L
Sodium	187	112	305	mg/L
Calcium	53	19	64	mg/L
Potassium	24	15	27	mg/L
Magnesium	11	8	12	mg/L
Silica	12	7	13	mg/L
Cu, Fe, Al, Zn	Variable < 1.0	mg/L		

† Phenol/sulfruirc acid method by Dubois et al.

‡ as analyzed by the Bradford method (BioRad©-assay)

5.2.5 *Pilot plant description*

A membrane filtration pilot plant constructed by Norit MT, Enschede, NL was used. The fully automated pilot holds 4 inch pressure vessels for spiral wound or capillary configuration. The pilot design schematics are given in Figure 33. The pilot is connected to a 1 m^3 feed tank (indoor) which is in turn connected to an outdoor underground storage room capable of holding 8 m^3. This storage container was replenished on the demand with secondary effluent drawn from the clarifiers of the Leeuwarden WWTP. Inside the intermediate feed tank an aerator was constructed for nitrogen aeration to keep the oxygen levels in the feed under 1 mg/L O_2. This was essential to mimic the feed conditions as encountered when drawing feed directly from the overflow of the secondary

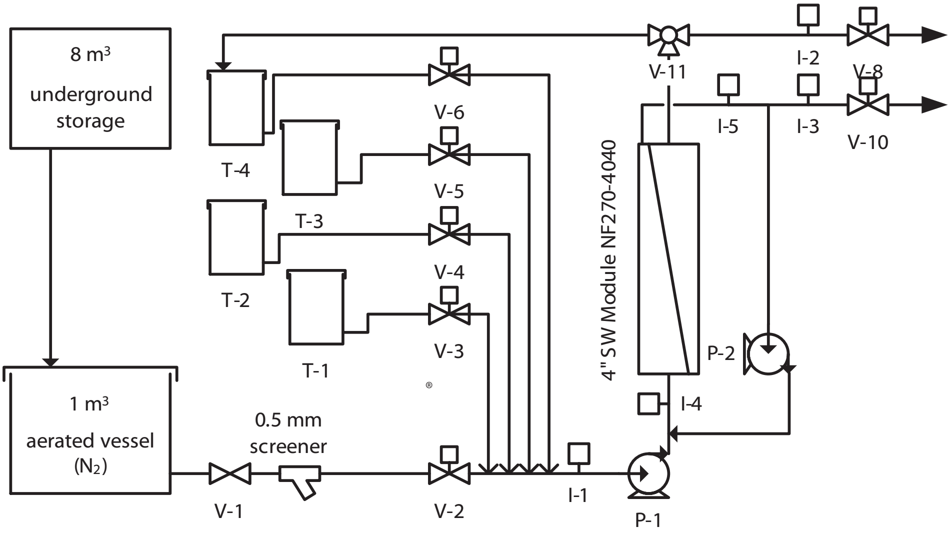

Figure 33 - Design and instrumentation of the pilot plant and auxiliaries. P-x for pumps, T-x for auxiliary tanks (cleaning, characterization and coagulant solutions), V-x for all automated valves and I-x for automated recording instrumentation (pressure, pH, flow, conductivity & temperature)

clarifiers. Besides suppressing the dissolved oxygen levels, aeration also supplied the necessary mixing to prevent possible sedimentation in the tank.

A strainer (0.5 mm) was placed directly after the intermediate feed tank. The pilot was fitted for this study a 4″ spiral wound module, type NF270-4040, effective membrane area 7.6 m^2, supplied by DOW Filmtec®. General characteristics for this membrane are listed in Table 20.

The ion exchange column for effluent pre-treatment consisted of a packed bed filled with an anion-exchange resin of polystyrene macro-porous beads with quaternary ammonium functionality (Purolite A806S). This type of resin has proven to be very adequate in the removal of humic-like substances [9].

Table 20 - Reported characteristics for the DOW Filmtec NF270 membrane

Source	*Zeta Potential* (mV)	*Contact Angle*	*Permeability* (L/m2.bar.h)	*Organic rejection* (%)	*$CaCl_2$ rejection* (%)	*Sulfate rejection* (%)
DOW Filmtec†	-	-	11.1	94	40-60	99
Mänttäri‡ [21]	-16	30º	15.6		48.2	99.0

† Test conditions: Permeability: 4.8 bars, 25º C, 2000 ppm MgSO4. Organic rejection based on Lake Mead pilot plant, Overton, Nevada, USA.

‡ Test conditions: Permeability: 7.8 bar, 35º C, pH 7. Background solution for zeta-potential 0.01M KCl. Data on salt and organic rejection based on paper mill effluents.

5.2.6 System benchmarking

As the feed water composition (temperature, salt content, etc…) is not constant in time, the flux needs to be normalized, e.g. to permeance or mass transfer coefficient (MTC), according to equations (24-27):

$$MTC = \frac{Q_p \cdot TCF}{A_{mem} \cdot NDP} \tag{24}$$

$$TCF = (1.03)\exp(T - T_{ref}) \tag{25}$$

$$NDP = \frac{P_{f,in} + P_{f,out}}{2} - \left(\frac{(\pi_{f,in} + \pi_{f,out})}{2} - \pi_p \right) \tag{26}$$

$$\pi = x_\pi \cdot EC \cdot \frac{T}{T_{ref}} \tag{27}$$

The MTC represents the permeate flux (Q_p), corrected for feed water viscosity changes by the temperature correction factor (*TCF*), and the net driving pressure (*NDP*). The NDP is obtained from the pressure difference between the transmitters at the entrance and exit of the module and is corrected for the osmotic pressure. The osmotic pressure is related to the electrical conductivity by the factor x_π and is corrected for temperature. The factor x_π was determined experimentally for the effluent and characterizing solution used in this paper, see the appendix. Reference temperature (T_{ref}) used is 298 K.

To investigate the fouling rate, the common relationship for cake filtration under constant pressure, Equation (28), was rewritten to accommodate for filtration under constant permeate production. If cake filtration is the dominant fouling mechanism the plot of Equation (29) would give a straight line in which the slope denotes the cake filtration resistance.

$$\frac{t}{V_p} = \frac{\eta R_m}{A\Delta P} + \frac{\eta R_c}{2A^2\Delta P} V_p \tag{28}$$

$$\frac{t}{Qt} = \frac{\eta R_m}{Q} MTC + \frac{\eta R_c}{2A} MTC \frac{V_p}{Q} \quad \Rightarrow \quad \frac{1}{MTC} = \eta R_m + \frac{\eta R_c}{2A} V_p \tag{29}$$

With R_m, R_c and V_p respectively the membrane resistance, cake resistance and produced permeate volume.

5.2.7 Analytical

Total organic compounds (TOC) of the feed were analyzed using a Shimadzu TOC-V CPH TOC analyzer. The chemical oxygen demand (COD) was determined colorimetric using standardized test kits; (COD) cuvette test LCK 014 , XION 500 spectrophotometer, Dr. Lange Nederland B.V., The Netherlands. Polysaccharide content was determined colorimetric by the phenol/sulfuric acid method, first described by [10]. Protein content was analyzed colorimetric utilizing a standard test kit based on the Bradford method [11], obtained from Bio-Rad Laboratories GmbH (Germany). Biological oxygen demand (BOD) was analyzed using the OxiTop®-C systems from WTW (Weilheim, Germany).

Most common cat-ionic species (Na^+, K^+, Mg^{2+} and Ca^{2+}) were determined using inductively coupled plasma - optical emission spectroscopy (ICP-OES – Perkin Elmer Optima 3000XL). An IC (Metrohm, Herisau, Switserland, type: 761 Compact IC) was used to measure most common anions (Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}).

GPC analysis for determination of the molecular weight (MW) distribution of the feed was performed on a Metrohm HPLC setup with a PSS MCX-1000Å GPC column. A Bisschoff Lambda 1010 was used as UV-VIS detector. The mobile phase was an aqueous solution of 0.1 M Na_2HPO_4. The calibration diagram of the GPC column was based on the elution of standard polymers (Polymer

Standard Service GmbH, GE) of known molecular weight. The UV detector was set at 223 nm to get a maximum resolution. An UV detector will exaggerate the aromatic species in the Effluent Organic Matter (EfOM) while underestimating (or not detecting) single carbon bond based species like polysaccharides. The elution diagrams should therefore be interpreted as qualitative data rather than quantitative

5.2.8 Autopsy

At the end of each test series the modules were cut open for visual inspection. To assess the average amount of residual fouling on the membrane, part of the membrane area (1.6 m^2) was scraped with a wiper to collect all removable material (slime). The mass of the slime was analyzed in wet state, after 24 hours of drying at 105 degrees Celsius and as ashes after heating the sample to 550 degrees Celsius for over 2 hours. Elemental analysis was performed on the dried sample and ash residue. From the membrane leafs, samples were cut prior and after wiping. These samples were inspected by element analysis with Low Vacuum (50 kPa) electron microscopy (JEOL type JSM-6480 LV, Thermo NORAN System Six).

5.3 RESULTS AND DISCUSSION

5.3.1 *Fouling tests*

The MTC and cake resistance plot for tests A-C are plotted in Figure 34. The plots show a very steep decline in MTC and simultaneously increase in resistance in both experiments aerated with air after a certain 'conditioning' period. Filtration tests under anoxic conditions do not differ in respect to fouling behavior.

The oxygen level during the air-aerated periods proved to be constant around 7.4-7.9 mg $O_2 .L^{-1}$. However, the levels in TOC, protein, sugar and pH changed significantly in the aerated tanks, especially in the end periods of tests B and C, as can be observed in Figure 35. These results are indication for major biological activity due to aerobic digestion. In time, see Figure 35, nutrients are consumed at a faster rate, indication accelerated growth in time. Apart from the chemical analysis, pieces of fouling material detached from the membrane at the end of the tests. This material (brownish color) was collected and analyzed in the electron microscope, see Figure 36, revealing the biological nature of the material. Comparison with reference books [12, 13] listed algae of the *Chrysophyta* group (brown, golden algae) as likely candidates. Algae belonging to the *Chrysophyta* group are not obligate phototropic. In absence of light they can turn heterotrophic, assimilating organic compounds as growth medium.

Both chemical and visual analysis showed proof for the hypothesis that effluent is an ideal source for biological fouling. Furthermore, re-growth of the biology takes less time in test C compared to test B which is an indication that some biomass was still present on the membrane.

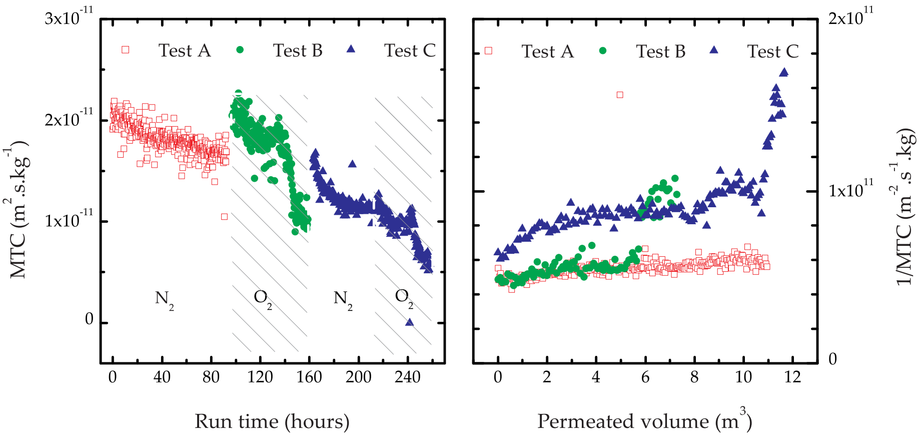

Figure 34 - MTC (left) and Cake resistance plot (right) for test A, B and C. Arched areas denote the time when the feed tank was aerated with air.

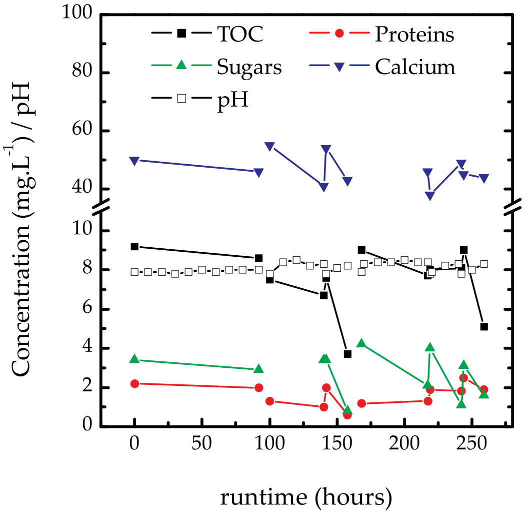

Figure 35 - Change in pH, TOC, sugars, proteins and calcium for tests A, B and C.

Autopsy of the module after the final cleaning procedure of test C revealed the presence of rod shaped material in the resulting fouling cake (Figure 37).

The cake itself was very difficult to remove (with wiper) from the membranes and consisted mainly of calcium-carbonate, see Table 21. This observation shows that besides biological fouling, carbonate scaling was responsible for part of observed fouling. Carbonate scaling is expected as the pH in the feed tank increased to 8.4, as shown in Figure 35. The change in pH is the cause for calcium carbonate scaling as the maximum solubility for calcite ($CaCO_3$) is well exceeded for both the Langelier and Ryzner saturation indexes at pH 8.4 (see the appendix).

The cause of the raise in pH is the removal of CO_2 in the feed water. The aeration strips the CO_2 from the feed, as can be observed in the slow but steady increase in pH after the aeration with air is turned on (Figure 35). Initially, the feed is oversaturated with CO_2 compared to the equilibrium ratio of water/air. Based on initial pH and alkalinity the effluent CO_2 concentration was approximately 0.12 mmol (as H_2CO_3), which is well above the equilibrium saturation of effluent and air 10^{-2} mmol (as H_2CO_3). In the appendix more detailed information is given about the carbonate system.

During the test period, the cleaning cycle was not sufficient to restore previous MTC and retention values, except after test A. Both a change in retention (91% to 86%) and MTC (1.64 $x10^{-8}$ to 7.25 x 10^{-9} $m^2.m^{-3}.s^{-1}.kPa^{-1}$) was observed. In the

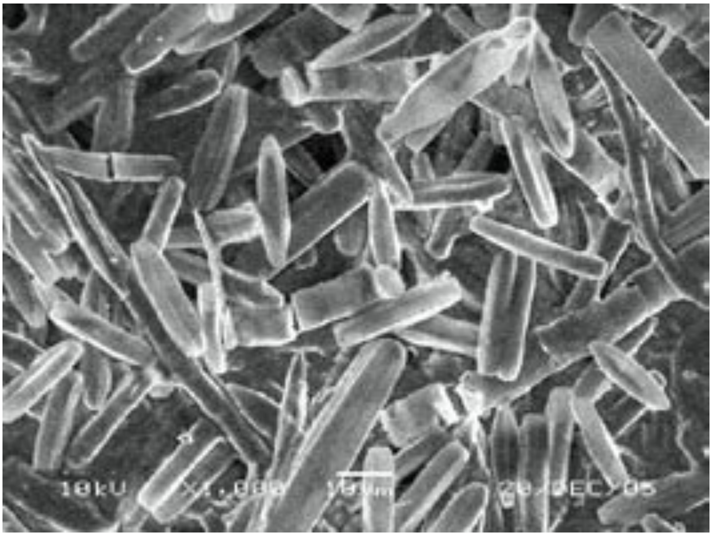

Figure 36 - Low vacuum SEM photograph of the material sloughed from the membrane during filtration under aerobic conditions. Image shows the majority of material to be of the Chrytosphyta group (diatoms) (compared to reference pictures from [12, 13],) combined with unknown species.

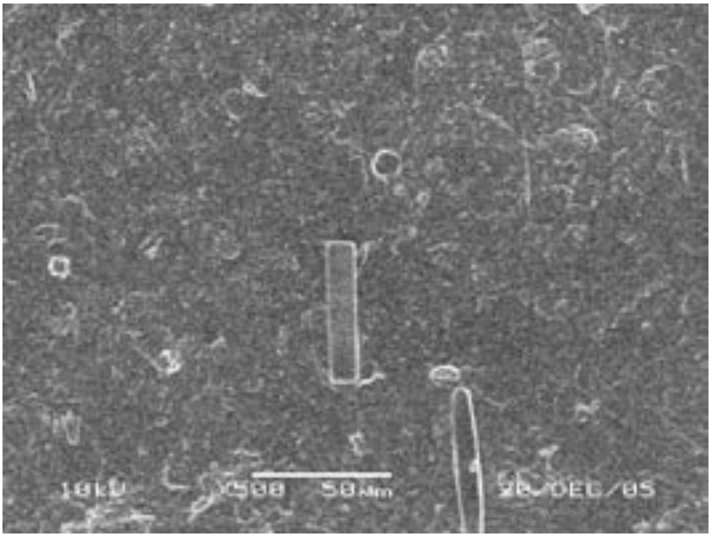

Figure 37 - Residual fouling at the feed side of the membrane of module 1 used in test A-C. Picture shows some algae on a bed of calcium carbonate.

appendix a detailed cleaning history can be found. Based on the membrane autopsy results, the decline in MTC after cleaning can be attributed to the incomplete removal of mainly calcium carbonate and some residual magnesium, silica and alumina (silt) on the membrane (Table 21).

The fouling tests show that the microbial activity in the secondary settlers in a conventional WWTP has two major consequences for membrane filtration. The consumption of oxygen leads to inhibition of (aerobic) biofouling. This might be the reason why chlorine addition is necessary in MBR-RO applications to suppress biofouling, like the NEWater project, Singapore [14]. The consumption of oxygen might lead to elevated CO_2-levels in the effluent which might trigger carbonate scaling.

Table 21 - EDS results for the autopsy on module 1

	Fresh membranes	Module 1		slime (dry)	slime(ashes)
	weight %	residual	rinsed	378 K	823 K
C	83	47	77	21	14
N		0.4	-		
O	12	36	16	42	44
Mg		0.6	-	0.5	0.6
Al		1.6	0.3	1.2	1.4
Si		4.3	0.6	2.8	3.7
P		0.3	-	0.3	0.4
S	5	3.0	5.2	0.4	0.4
K		0.4	-	0.3	
Ca		5.6	1.3	31	34
Fe		1.2	-	-	1.9
			wet	dry	ash
total slime mass in mg/m^2			1503	1479	1358

5.3.2 *Anti-fouling tests*

Coagulant addition & forward flush

Laboratory tests have shown that coagulant addition can be beneficial in protecting the membrane from irreversible fouling [6]. Dosing the proper coagulant leads to the formation of a 'protective' film on the membrane. Whether coagulant addition would be benificial in spiral wound modules was assessed in tests D to G. The results of these tests are shown in Figure 38.

Test D (blank) and test E (5 ppm coagulant) differ substantially. Test E exhibits a sharp drop in MTC, which coincides with a drop in cross-flow shear rate until a kind of equilibrium is reached. The cause for the decrease in cross-flow was evident when the module was inspected visually. Near the end of test E, filtration was stopped for a short moment to take the module out of the pressure housing to seek answers why the cross-flow went down. The reason was evident as the area between the spacers (as observed from the feed spacer) was clogged with coagulated matter. The cross-flow pump, running on constant power output, could not maintain its original flow rate due to the increase in resistance in the module clogged with coagulant. After reinsertion, a quick flush with feed (see test E, 902 hours) removed most of the coagulant restoring MTC and cross-flow.

A second series of tests (F & G) was performed in which a forward flush was given to the system at a 2 hours interval. As can be observed in Figure 38, forward flush was effective in raising the MTC of both the blank (test F) and the coagulant test (G). Like observed in test E, the original cross-flow values could not be maintained by the pump in test G. Forward flush was helpful in restoring MTC and cross-flow for a short time. After the FF rapid fouling with the coagulant took place creating a saw-tooth in the filtration resistance graph, see Figure 39. The same figure shows that the resistance for both experiments with coagulant reaches a stable plateau with no further increase in resistance.

Thus, the poor MTC in the tests with coagulant are due to a thicker cake on the membrane. Unfortunately, a test with constant cross flow equal to the blank tests could not be performed due to pilot plant system limitations.

The cleaning of the module, under the specified cleaning regime was successful for all tests.

The test with coagulant proved that the coagulant exhibits affinity for the membrane leading to the formation of a thick cake layer of coagulant. Maintaining a MTC comparable to the blank tests required a higher power input in the cross-flow pump to keep the cake thickness to a minimum. As the blank tests could be cleaned as easily as the coagulant added tests, it is questionable whether the required additional energy for cross-flow compensates for the possible less stringent cleaning regime. In all tests, forward flush showed a positive effect on the MTC.

Long term tests & IEX pretreatment

Based on the previous results two long term tests (H & I) were performed with

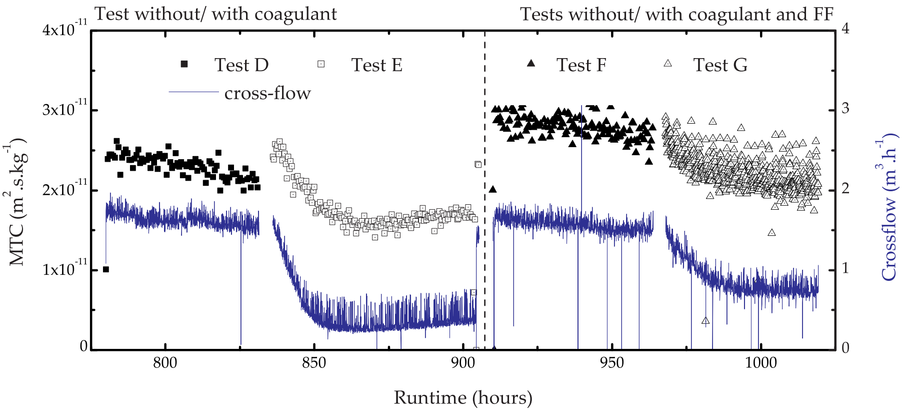

Figure 38 - MTC and cross-flow for the tests with coagulants and forward flush

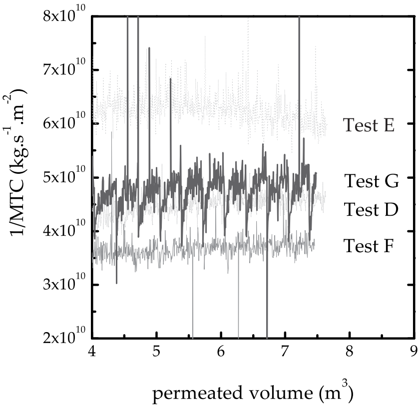

Figure 39 - Part of the cake resistance plot for tests D-G.

forward flush only. Tests were run continuously (neither permeate nor concentrate return) at 85% recovery over the module. Initially, a constant production rate of 150 l/h was set (test H). As this did not seem problematic in regard to fouling, the production rate was increased to 180 l/h, leading to an average

TMP of 340 to 370 kPa. The results are shown in Figure 40. After 220 hours of continuous filtration (test I) the MTC had dropped with 15%, after which the test was stopped and a cleaning protocol was initiated. Cleaning restored the MTC and rejection on the standard $MgSO_4$-solution (see appendix).

Samples drawn during the test period of feed and permeate showed rejections as listed in Table 22.

Table 22 – Average retention values for tests K, I and J

Species	*Average rejection during tests (%)*		
	K	*I*	*J*
UVA_{254}/ COD	96	93	>99
TOC	85-90	80-90	69
Na^+	-1	0	1
K^+	5	4	3
Mg^+	19	21	7
Ca^{2+}	16	31	8
SO_4^{2-}	70-90†	70-90†	38
PO_4^{3-}	>99‡	>99‡	n.d.
Cl^-	-1	-2	1
NO_3^-	1	-1	2
Conductance	28	29	34

† fluctuating values, well above normal standard deviation

‡ permeate concentration below detection limit (0.1 mg.L-1)

n.d. not detected in feed

The discrepancy between the high observed rejections in UVA_{254} and considerably lower rejection values for TOC can be explained by the lack of absorbance of UVA_{254} for the low molecular weight species which pass the membrane. The permeate contained 1.0-1.5 $mg.L^{-1}$ TOC. Gel permeation chromatography was performed to estimate the molecular weight of the

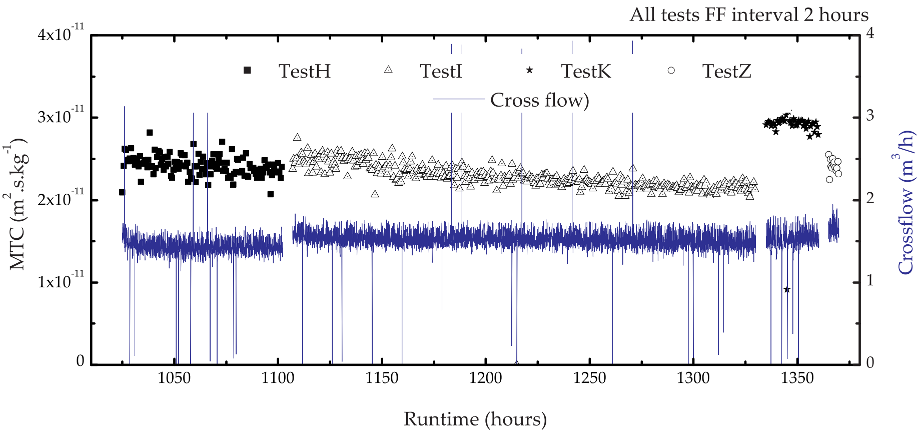

Figure 40 - MTC and cross-flow for the long term filtration runs (H & I) and the test with IEX pretreated effluent (J).

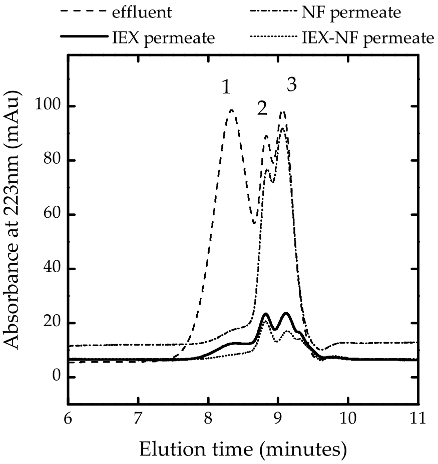

Figure 41 - Gel permeation diagram for the feed (effluent and IEX pretreated effluent) and corresponding NF permeates.

species passing the membrane; the diagram is shown in Figure 41. Peak 1 was estimated to have a MW of 2150 Da whereas peak 2 and 3 were estimated on 590 and 370 Da.

To see if the system's performance could be enhanced further, the feed was led through and IEX column before filtration (test J). On average the IEX column removed 60-70 percent of TOC and almost all sulfate and phosphate.
As can be observed in Figure 40 the MTC was considerably higher compared to all other tests. At the end some fouling could be observed as the system was run on a high total system recovery (>98%). The average rejection for organic species and salts can be found in Table 22.

Although permeate of the IEX-NF contained less TOC (0.5 $mg.L^{-1}$) the chloride content was considerably higher. The IEX column binds the majority of organics, see Figure 41, and chloride is exchanged for feed TOC. An additional amount of chloride is exchanged due to the binding of multi-valent anions in the feed with the IEX column. On average the chloride concentration increased by 150 $mg.L^{-1}$ in feed and permeate, reaching finite permeate concentrations up to 400 $mg.L^{-1}$. This renders discharge or reuse of permeate impossible as surface water and irrigation standards for chloride are exceed ed (<200[15] and <178[16] for sensitive crops). Therefore, ion exchange as a pretreatment does not seems feasible in this particular application.

5.3.3 *Autopsy*

Autopsy on the membrane revealed the presence of a gel layer on the feed side. The permeate side of membrane and permeate spacer were clean. The residual fouling could be removed easily with a wiper or a rinse of water. The membrane looked clean without any coloration after wiping/rinsing. Both cake and membrane were analyzed by SEM-EDS (Table 23). The cake contained organic and inorganic species. The total organic volatile fouling was around 70 mg/m^2. This amount is in reasonable agreement with values (11 mg.L^{-1}) found by Shon and co-workers [17] who used a sodium hydroxide extraction procedure to isolate effluent organic matter from the membrane. Total inorganic residue (170 mg/m^2) consisted mainly of silica, alumina and magnesium oxides, which points towards the accumulation of fine silts/clay on the membrane. Electron microscopy of the un-wiped membrane and scrape sample (Figure 42) showed the presence of silt-like material. Inspection of the wiped and rinsed membrane showed to be clean of residual fouling.

Table 23 - EDS results for the autopsy on module 2

	Fresh membranes	*module 2*		*Slime*	
		residual	rinsed	(wet) 298 K	(ashes) 828 K
			weight %		
C	83	67	81	37	5.4
N	-	1.6	-	2.8	-
O	12	24	12	39	49
Mg	-	0.3	-	1.4	2.9
Al	-	2.1	-	4.3	9.1
Si	-	2.0	-	11	21
P	-	0.2	-	-	0.5
S	5.1	3.6	5.9	0.7	1.9
K	-	0.9	-	1.3	2.9
Fe	-	1.2	-	1.7	6.8
			wet	dry	ash
total slime mass (mg/m^2)			2185	243	172

Inorganic scaling of fine silts seems to be the dominant fouling species in direct nanofiltration of effluent. A study by Molinari et al. [18] on the fouling behavior of NF/RO membranes in a model effluent showed similar results. As silt is inert, the chemical cleaning applied or chemical cleaning in general will not be able to remove these particles. The inorganic foulants may be removed with a high cross-flow (high turbulence) regime by sweeping the silt from spacer and membrane surface. With removal of the silt most organic fouling will be removed as well as no residual organic species were detected on the wiped membrane surface.

Apparently, the applied cross-flow regime and FF that could be achieved with this type of module were insufficient to remove the residual fouling. Perhaps residual fouling could be alleviated by use of a different feed spacer (thicker), making a more turbulent FF regime possible or by specialized sanitation protocols.

5.3.4 Comparison to reported pilot tests

To compare this study to the reported pilot studies, data from test I will be used. Table 24, see page 149, summarizes the most important parameters. As can be observed, direct nanofiltration using spiral wound modules do perform as well as the reported pilot studies. Compared to the capillaries, the spiral wound module performs slightly better in the removal of salt and organic matter. This is not surprising as the reported values for the molecular weight cut-off between X-flow capillaries and the Filmtec NF270 differ significantly (1000 vs. 200 Da).

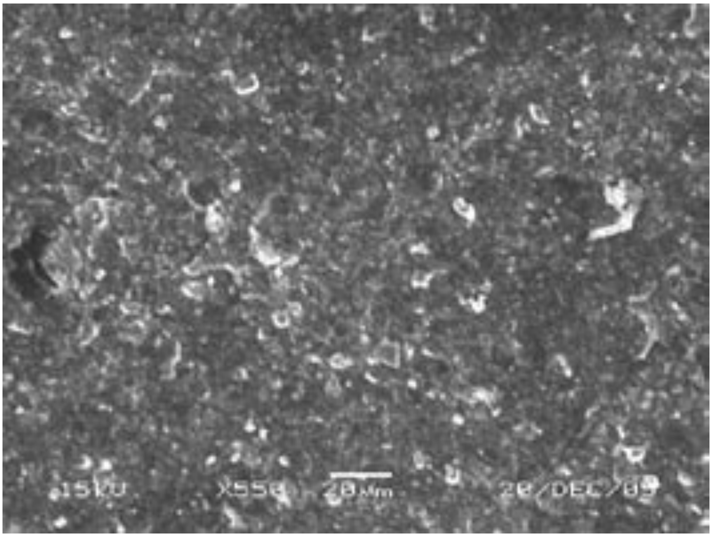

Figure 42 - SEM picture of a dried slime scrape sample from module 2.

As no autopsy was reported on the modules used in other tests no detailed comparison can be made about the residual fouling on the capillary modules. The flux-history data reported by Duin et al. [2] show that during the trial as stable performance was reached after an almost instantaneous decline in flux of 50%. Regular cleaning was able to maintain these flux values but could not restore the flux to initial values indicating residual fouling on the membranes. Flux could be restored to initial flux levels after a hydrogen peroxide based cleaning, indicating an organic nature of the residual fouling.

In this study similar fouling behavior was observed. After a comparable initial decline in MTC of 40-50%, a stable performance could be achieved. Initial

MTC could not be restored with the cleaning protocols followed in this study. Both results show that in the first hours of operation residual fouling develops which causes a significant drop in flux performance. After the initial drop a stable plateau in performance can be reached depending on operational conditions. Attempts to enhance permeate flux and therefore minimize installed membrane area should therefore focus on frequent short term cleaning regimes that would restore original permeance. However, it may be beneficial to cope with the residual fouling and operate at lower fluxes with less frequent cleaning providing that [19]:

- Residual fouling does not comprise retention/ intergrity of the membrane to unacceptable levels;
- Residual fouling can be removed by a sanitizing regime as residual fouling layers can compress in time compromising performance.

Both targets seem to be easier achievable with capillary modules compared to spiral wound modules.

The results from this study show that spiral wound module performances in direct effluent filtration are similar, even slightly better, than capillary modules. However, if the observed residual fouling can not be removed; system integrity might be compromised in longer operational periods.

Table 24 - Comparison between different pilot studies on secondary effluent

	Duin (2000)	Roorda (2005)	This study
pretreatment	none	Absorbent	none
Membranes	3″ capillary Stork	8″ capillary X-flow	4″ SW NF270 DOW Filmtec
Recovery	80%	94%	85%
Cross flow (m/s)	0.5	1.0	0.1
Operational Pressure (kPa)	400	400	350
permeability (l/m^2.bar.h)	6.25	7.0	8.2
Cleaning			
- Airflush / FF	2 hour	30-45 min	2 hour
- Acid	1/ week	1/ day	1/ week
- Alkaline /other	1/ week	1/ 3 weeks	1/ week
Total runtime module	3 months	1-2 months	1 month
Reported rejection (%) (n.a. = not avalaible)			
COD	75-80	n.a.	90-95
TOC	n.a.	n.a.	80-90
PO_4^{3-}	50-55	n.a.	>99
NO_3^-	5-10	n.a.	-1
EC (conductance)	±25	n.a.	±30
Zinc	75-80	n.a.	>99‡
Copper	70-75	n.a.	>98†
Durion	±25	n.a.	n.a.

‡ Below detection limit < 10 μg.L^{-1} in permeate, detected in feed 30-130 μg.L^{-1}.

† Below detection limit < 10 μg.L^{-1} in feed or permeate, however detected in concentrate with concentrations of 40-160 μg.L^{-1}.

5.4 CONCLUSIONS

In this study two kinds of trails were performed when filtering WWTP effluent through spiral wound modules. In the first trial the effluent, dissolved oxygen levels were raised to show that lack of dissolved oxygen is the key factor in suppressing biological fouling. It was shown that after an incubation period rapid biofouling took place, resulting in a sharp decrease in the mass transfer coefficient (MTC). The aeration had a second effect by stripping CO_2 from the effluent, raising the pH of the effluent, resulting in carbonate scaling.

The second trail was designed to assess the influence of coagulant addition, ion-exchange pretreatment and forward flush on the performance.

Forward flush had an overall beneficial effect on the performance whereas coagulant addition proved to cause a thick coagulant based fouling layer on the membrane. This cake caused an increase in resistance over the module resulting in a decreased cross-flow velocity as the cross-flow pump could not maintain original flux. Hence the MTC dropped considerably. The cake could be removed by the forward flush regime restoring original MTC.

Ion-exchange pretreatment was shown to be beneficial in maintaining a high MTC even at high recoveries rates (>98%). Unfortunately, the exchange of TOC and multi-valent anions in the IEX column caused a raise in the permeate chloride content well above permissible levels for reuse or discharge in surface waters.

A long term test proved that spiral wound membranes have similar performances as the reported pilot tests utilizing capillary modules. The used spiral wound module outperformed the capillary modules in terms of TOC and multi-valent salt rejection.

Autopsy revealed that residual fouling consisted of silt like material with organic material attached to the silt.

5.5 ACKNOWLEDGEMENTS

The authors like to thank Vitens Water, Landustrie Sneek B.V. and the Frysian Waterboard (Wetterskip Fryslân) for the financial support of this project. Dow FilmTec and Ecolab® are acknowledged for donation of the NF270 membranes and membrane cleaning solutions (P3 Utrasil 67 & P3 Ultrasil 69) used in this study.

5.6 USED SYMBOLS AND ABBREVIATIONS

symbol		Unit
η	Viscosity	Nsm^{-2} (Pa.s^{-1})
π	osmotic pressure	Pa (Nm^{-2})
A	area (filtration)	m^2
P	pressure	Pa
Q	volume flux	m^{3}s^{-1}
R_x	resistance of phase 'x'	
T	temperature	K
c	concentration	mol.l^{-1}
t	filtration time	s
BOD	Biological Oxygen Demand	
DO	Dissolved Oxygen	
EfOM	Effluent Organic Matter	
GPC	Gel Permeation Chromatography	
MBR	Membrane Bioreactor	
MTC	Mass Transfer Coefficient	
NDP	Net Driving Pressure	
SUVA	Specific UltraViolet Absorbance	
TCF	Temperature Correction Factor	
TOC	Total Organic Content	
WWTP	Wastewater Treatment Plant	

5.7 APPENDIX

5.7.1 *Determination of the conductance-osmotic pressure factor (x_π)*

Samples were taken of feed, permeate and concentrate. Electric conductivity was measured and the major ionic species (Na^+,K^+,Mg^{2+},Ca^{2+}, Cl^-, SO_4^{2-}) were analyzed by ICP-EOS and IC (see analytical). Osmotic pressure was calculated by van Hoff's law (30):

$$\pi = \sum_{n}^{1} \frac{c_n}{M_n} RT \tag{30}$$

Electric conductance was plotted against the calculated osmotic pressure to find x_π, as can be seen in Figure 43. The relationship between effluent conductance and osmotic pressure is not very accurate ($R^2 < 0.95$), but accurate enough ($R^2 = 0.91$) to use for corrections. The difference in osmotic pressure between feed, concentrate and permeate are small (max. calculated 20 kPa) compared to the operating pressure of the pilot (300-400 kPa). One can argue if the correction for osmotic pressure difference is necessary for continuous nanofiltration of effluent. It is necessary to corrected for osmotic pressure during characterization on $MgSO_4$ as the osmotic difference between permeate and concentrate easily reaches 50-100 kPa. In the case for the $MgSO_4$ solution, van Hoff's law suffices to give an accurate relation between conductance and osmotic pressure (Figure 43).

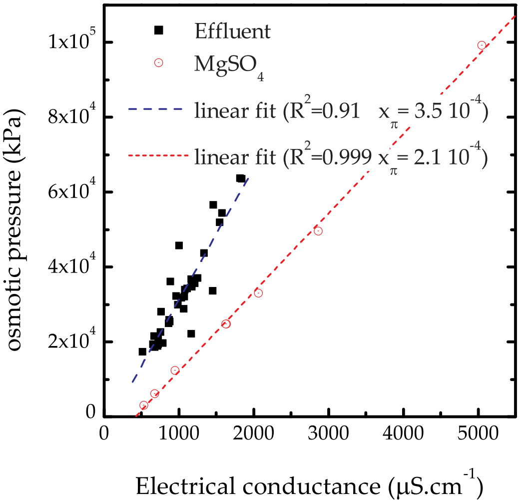

Figure 43 - Experimental determination of the factor x_π (Pa.cm.µS^{-1}) relating osmotic pressure to the conductivity of the feed.

5.7.2 Carbonate system

Figure 44 represents the relationship between bicarbonate and calcium concentrations. The following reactions correspond to the diagram shown:

$$CaCO_3(s) \rightleftarrows Ca^{2+} + CO_3^{\,2-}; \qquad K_{s0} = 10^{-8.4} \qquad (298K) \qquad (31)$$

$$CO_3^{\,2-} + H^+ \rightleftarrows HCO_3^{\,-}; \qquad K_2^{-1} = 10^{10.3} \qquad (32)$$

$$CO_2(g) + H_2O \rightleftarrows H_2CO_3; \qquad K_H = 10^{-1.5} \qquad (33)$$

$$H_2CO_3{*} \rightleftarrows H^+ + HCO_3^{\,-}; \qquad K_1 = 10^{-6.3} \qquad (34)$$

The * in Equation (11) denotes that the concentration of H_2CO_3 is a composite value between the equilibrium between CO_2(s) and H_2CO_3(true). Data for the construction of Figure 44 were taken from Stumm et al. [20]. The figure shows that for the given alkalinity and pH the effluent is already slightly super-saturated at initial conditions. Calculation of both the Langelier stability index (*LSI*)(12) and the Ryzner Index (*R*I)(13);

$$LSI = pH - pH_s \tag{35}$$

LSI > 0	Water is super-saturated and scaling may occur
LSI < 0	Water is under-saturated and has a tendency to dissolve calcium

$$RI = 2pH_s - pH \tag{36}$$

RI < 5.5	Heavy scale will form
5.5 < RI < 6.2	Scale will form
6.2 < RI < 6.8	No difficulties
6.8 < RI < 8.5	Water is corrosive
RI > 8.5	Water is very corrosive

The results for both LSI and RI are shown in Table 25. According to the LSI scaling will occur in at all conditions, whereas the RI shows scaling potential at the higher feed pH and high calcium concentrations. At the membrane surface the calcium concentration can be higher than the feed concentrations, especially at the concentrate end of the module. However under effluent filtration conditions the rejection of calcium lays around 10-15%, which would in theory lead to an increase of around 20% in calcium concentration near the concentrate side.

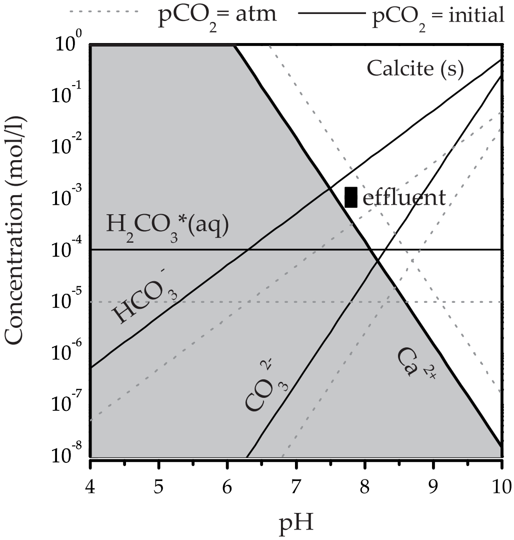

Figure 44 - Calcium-carbonate equilibrium. The shaded area represents the area in which calcium is soluble at initial conditions. The dotted lines indicate equilibrium conditions of the effluent with the atmosphere ($pCO_2=1 \times 10^{-3.5}$).

Table 25 - Stability criteria for calcium-carbonate

$[Ca^{2+}]$ (mg.L^{-1})	pH	LSI	RI
max (64)	7.8	0.6*	6.6
min (19)	7.8	0.1*	7.7
max	8.4	1.2*	6.0*
min	8.4	0.7*	7.1

*values denote over-saturation

5.7.3 Cleaning history

The cleaning history and values for the rejection and MTC on the 2000 mg.L^{-1} magnesium sulfate solution can be found in Table 26.

Table 26 - Cleaning and characterizing history

	Cleaning time (runtime hours)	MTC x 10^8 ($m^3m^{-2}.s^{-1}.kPa^{-1}$)	Rejection (%)
Manufacturer's specs.†		3.08	> 97
Initial module 1	0	4.01	94
before test A	472	1.64	89
after A	570	1.13	89
after B	636	1.15	86
after C	735	0.73	93
Initial module 2	0	3.42	93
before D	778	1.75	90
after D	834	1.84	92
after E	908	1.96	92
after F	966	1.67	90
after G	1023	1.58	87
after H	1105	1.72	90
after I	1333	1.89	91
after J	1363	1.75	89
after Z	1402	1.71	91

†Specifications given are measured at higher TMP and lower recovery (see Table 20)

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CHAPTER 6

ZERO LIQUID DISCHARGE DIRECT NANOFILTRATION OF WWTP EFFLUENT

CONCENTRATE CHARACTERIZATION AND DISPOSAL OPTIONS

During nanofiltration, apart from producing permeate, a concentrate (retentate) is produced as well. This concentrate consists of typically fifteen volume percent of the original feed and contains the rejected feed component up to 10 times their original concentration. In case of WWTP effluent nanofiltration, the concentrate contains heavy metals, most of the organic micro-pollutants, and multivalent ions. As this concentrate can not be discharged due to environmental reasons, a proper solution has to be found. Nanofiltration concentrate management is therefore the topic of chapter 6.

This chapter shows that the only feasible alternative is to return the concentrate back to the WWTP. Accumulation of rejected species in the WWTP will occur to such levels that the microbiology of the WWTP is seriously compromised. Tests on nitrifying bacteria (sludge from the WWTP) show an inhibition effect above two times the original concentration of refractory matter. Further concentrate treatment is therefore necessary before recycling concentrate back to the WWTP. A possible alternative technique for concentrate treatment is ion exchange. Ion exchange removes the vast majority of refractory organic material, while minimizing the residual waste stream to approximately 0.5 liter per 1000 m^3 of treated effluent.

Long term recirculation tests are necessary to assess whether ion-exchange or an alternative concentrate treatment technique is sufficient to safeguard the microbial population in the WWTP against toxicity or inhibition effects.

6 Zero liquid discharge direct nanofiltration of WWTP effluent:

concentrate characterization & disposal options

6.1 INTRODUCTION

Reclamation of municipal wastewater treatment plant (WWTP) effluent by means of membrane filtration is seen as a possibility to alleviate water stress in (semi) arid or densely populated regions. Beside the opportunities for reuse of WWTP effluent, new legislations, such as the new European Water Framework Directive [1], demand an enhanced effluent quality. In both situations, nanofiltration (NF) or reverse osmosis (RO) have shown to be capable of reaching the desired quality standard in pilot [2-4] and full scale applications [5].

Despite these success stories, effluent polishing by NF/RO membranes is in its infant state and is not widely accepted by many water regulating offices. In a recent report by the cooperating Dutch wastewater boards (STOWA) nanofiltration was assessed as the most appropriate technology to comply with future standards but considered unfeasible due to the lack of knowledge how to manage the produced concentrate fraction [6].

Recent publications show that concentrate management is becoming a major issue as disposal of concentrates from seawater desalination plants and groundwater polishing plants receives more attention from local water boards in regard to their environmental effects [7-9].

Concentrates from a NF plant have a volume of typically 10-15 volume % of the feed and contain all rejected species up to 10 times their feed water concentrations. In case of WWTP effluent this results in a concentrate with a total dissolved solids (TDS) concentrations of typically less than 1 gram per liter. This concentrate has to be dealt with as it contains all trace contaminants, like organic micro-pollutants, heavy metals and (biologically) inert material. Concentrate disposal could be expensive or even unfeasible, especially if the NF concentrate is classified as chemical waste and has to be transported to a waste handling site.

The lack of knowledge how to deal with concentrates from effluent polishing has to be overcome before NF/RO will be seen as an alternative compared to established techniques such as sand-filtration and sorption based technologies.

In this study, one of the options for concentrate disposal of WWTP NF concentrates is investigated: recirculation of the concentrate to the WWTP. To assess the feasibility of this option a detailed characterization of a NF concentrate originating from a municipal WWTP is performed. The NF concentrate is analyzed on chemical composition and residual biodegradability. As accumulation of certain organic and inorganic concentrate species might occur, an assessment is made of the concentrate toxicity on the nitrifying bacteria in the activated sludge. The nitrifying bacteria are one the most sensitive micro-organisms in the activated sludge [10] and have shown to be good indicators for the presence of toxic organic and inorganic compounds [11].

Based on the experimental findings, the need for concentrate treatment is assessed and discussed with various options from literature and experimental data.

6.2 Materials and methods

6.2.1 *Concentrate source*

Effluent from the municipal wastewater treatment plant at Leeuwarden, NL was used in this experiment. The Leeuwarden plant consists of an activated sludge system combined with phosphate removal by chemical precipitation. The effluent of the Leeuwarden sewage treatment plant has some site-specific characteristics.

Firstly, the moderate Specific Ultraviolet Absorption (SUVA) (>0.02 L/cm.mg) of the effluent shows the aromatic nature of the effluent, which is not surprising as the drinking water of Leeuwarden contains a large amount of humic substances. The drinking water contains around 8 mg/L TOC with a SUVA of 0.026 L/cm.mg and a BOD_{28}-value of 0 mg O_2/L [12].

Secondly, the effluent has a high conductivity due to a nearby dairy factory which discharges large amounts of sodium chloride in the sewer. The general characteristics of the effluent are listed in Table 27, page 169.

To produce concentrate, a membrane filtration pilot plant constructed by Norit MT, Enschede, NL was used. The fully automated pilot holds a 4 inch pressure vessel loaded with a Dow Filmtec NF270 spiral wound membrane. Details about the installation and used membrane can be found in our previous work [13, 14]. The NF pilot operated at an average recovery of 85%. Concentrate samples were obtained every week and processed for further analysis. The data presented in this study are the averaged values of the concentrate characteristics over a 5 week period.

6.2.2 *Analytical*

Dissolved organic compounds (DOC) of the feed were analyzed using a

Shimadzu TOC-V CPH TOC analyzer. Polysaccharide content was determined colorimetrically by the phenol/sulfuric acid method, first described by Dubois [15]. Protein content was analyzed colorimetrically utilizing a standard test kit based on the Bradford method [16], obtained from Bio-Rad Laboratories GmbH (Germany). Biological oxygen demand (BOD) was analyzed using the OxiTop®-C systems from WTW (Weilheim, Germany).

Ammonium concentrations were photometrically determined using standardized test kits (ammonium cuvette test LCK303, XION 500 spectrophotometer, Dr. Lange Nederland B.V., The Netherlands).

Metals were determined using inductively coupled plasma - optical emission spectroscopy (ICP-OES – Perkin Elmer Optima 3000XL). An IC (Metrohm, Herisau, Switserland, type: 761 Compact IC) was used to measure most common anions (Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-}).

GPC analysis for determination of the molecular weight (MW) distribution of the feed was performed on a Metrohm HPLC setup with a PSS MCX-1000Å GPC column. A Bisschoff Lambda 1010 was used as UV-VIS detector. The mobile phase was an aqueous solution of 0.1 M Na_2HPO_4. The calibration diagram of the GPC column was based on the elution of standard polymers (Polymer Standard Service GmbH, GE) of known molecular weight. The UV detector was set at 223 nm to get a maximum resolution. An UV detector will exaggerate the aromatic species in the Effluent Organic Matter (EfOM) while underestimating (or not detecting) single carbon bond based species like polysaccharides. The elution diagrams should therefore be interpreted as qualitative rather than quantitative results.

6.2.3 *Concentrate fractionation*

A typical NF concentrate contains the major portion of the higher molecular weight organic components present in the effluent. NF membranes have a high rejection for higher molecular weight organic compounds often associated with the humic / more aromatic fraction of the organics in the effluent [14, 17, Schrader, 2005 #1217]. According to literature, nitrification could be inhibited by high concentration of aromatic compounds [10]. Removal of the aromatic compounds in the NF concentrate might be beneficial to prevent accumulation and inhibition or toxicity effects. To remove the majority of the aromatic species, the NF concentrate was passed over a column filled with an ion-exchange resin (Purolite A806S). This resin has quaternary ammonium function groups and was shown to be very effective in the removal of humic substances from water [12]. The NF concentrate depleted in organic species was further analyzed on chemical content, BOD_{28}-value and molecular weight distribution based on gel permeation chromatography (see analytical section).

6.2.4 *Nitrification rate assessment*

Endogenous respiration rate determination

Mixed liquor from the WWTP of Leeuwarden was sampled and sieved over a 5 mm screen and an amount of 20 liter was put in an aerated container. Sludge was analyzed on total volatile suspended solids (VSS), Standard Methods 2540E [18]. The sludge was aerated overnight (17-18 hours) to deplete the nutrients available for aerobic digestion in the mixed liquor. Before tests, the supernatant was tested on residual ammonia. If necessary the pH was adjusted with a NaOH solution to restore the original pH (7.8). From the container containing the nutrient depleted mixed liquor, for each tests 700 ml was placed in a stirred and aerated 1 L glass beaker with pH and DO-meter (Hach HQ10 portable DO meter) to assess the oxygen depletion under endogenous and ammonia rich conditions. The endogenous oxygen consumption was measured by monitoring the dissolved oxygen (DO) concentration after stopping the aeration in the beaker. At the moment that the level of 4 mg O_2/L DO was reached, aeration was switched on again to restore original conditions.

Nitrification rate determination

After assessment of the endogenous oxygen consumption and restoration of original DO levels to 8.5-9.0 mg O_2/L, approximately 50 mg of ammonium bicarbonate was added to the vessel to induce nitrification activity. After 5 minutes the aeration was stopped and oxygen consumption was monitored, till a level of 4 mg/L DO was reached. Below this level, nitrification rates decrease due to O_2 limitations [10].

Nitrification rate is calculated by speed of oxygen consumption corrected for endogenous respiration Equation(36) and the stochiometric relation ship for ammonia oxidation according to Equation(37) neglecting ammonia utilization for biomass growth as the test time (maximum 1 hour) is small compared to normal nitrifying growth rates (8 – 38 x 10^{-3} g VSS/ g VVS.h [10])

$$\frac{\left(\frac{dO_{NH_4}}{dt} - \frac{dO_{endogenous}}{dt}\right)}{VSS} = kO_{2-NH_4} \quad \left(\frac{mg\,O_2}{VSS.s}\right) \tag{36}$$

$$NH_4^+ + 2HCO_3^- + 2O_2 \rightarrow NO_3^- + 2CO_2 + 3H_2O \tag{37}$$

Nitrification toxicity/ inhibition assessment

The procedure as described above was followed to assess the endogenous respiration and respiration under ammonia rich conditions of the nitrifying biomass. At the end of these tests ample ammonia is present (> 45 mg/L). After reestablishing DO values, 200 ml NF retentate in various concentrations or a sodium sulfate solution (as Na_2SO_4) were added to the mixed liquor. After aeration for 5 minutes the air supply was stopped and oxygen concentration monitored till a level of 4 mg/L DO was reached. The rate of oxygen consumption was compared to the initial nitrification rate to assess toxicity/inhibition effects on the nitrifying biomass as function of the rising levels of concentrate species, represented by the concentration factor (CF).

$$CF = \frac{level\,of\,species\,'x'}{original\,level\,in\,effluent\,of\,species\,'x'} \tag{38}$$

6.3 Results and discussion

This section contains three parts. First, possible alternatives for disposal of the NF concentrate other than disposal by return to the sewer are discussed. The second part deals with the inevitable accumulation of (in)organic species within the WWTP as a consequence of the return of concentrate based on a mass-balance computation. After assessment of the most accumulated species, the validity and possible effects of accumulation on the activated sludge system are discussed. The third section present the results of the concentrate's inhibiting/toxicity effects on the nitrifying bacteria. It shows that inhibition will take place above a critical concentration factor demonstrating the need for concentrate treatment. Consequently some possible concentrate treatment techniques are discussed to overcome accumulation effects.

6.3.1 Other concentrate disposal alternatives

There is only a limited amount of papers describing membrane concentrate disposal options [9, 19-24]. In most cases concentrate is disposed of by sewer discharge, surface water discharge or deep-well injection. The first option is essentially the scenario presented in this study and the second option is unfeasible as one of the aims of effluent polishing is to safeguard release of harmful substances to the aquatic environment. Deep-well injection is often seen as the most viable option for larger scale applications; however local geology and water board permits might prevent this option [9, 25]. Therefore disposal of NF concentrate by deep-well injection is not considered.

All other options are zero-liquid discharge scenarios which require extensive dewatering for further processing, generally up to 20 w/w% dried solids (DS).

Dewatering of membrane concentrates by natural evaporation is an unfeasible option for wet climates and even in arid areas the costs for evaporation might be high due to little economy of scale [25]. Dewatering concentrates by high pressure reverse osmosis (RO) followed by evaporation is often suggested utilizing excess heat from possible local excess heat sources (e.g. power plants). The remaining dewatered concentrate might be further treated by wet air oxidation, biogas treatment (anaerobic digestion of organic degradable waste) or incineration.

The nature of the WWTP NF concentrate, as described in the following paragraphs, makes further dewatering problematic. The NF concentrate consist of 0.1 w/w% DS (as TDS) and some salts ($CaCO_3$, $Mg/CaSO_4$) are already close to their saturation levels. Further processing with high pressure RO membranes seems therefore unfeasible as severe scaling is likely to occur. Scaling might be prevented by pH adjustment and addition of anti-scalents, however this increases the waste load.

The option of dewatering (RO or excess heat) followed by spay drying and incineration is estimated to costs close to 38 €/m^3 concentrate [22], rendering this kind of disposal for the NF concentrate economically unfeasible, compared to the operational costs (0.20-0.60 €/m^3 permeate [2, 4]).

Therefore, disposal to the sewer might be the only option which might result in an economically viable solution. However accumulation effects are to be expected and the NF concentrate has to be treated depending on the concentrate composition to safeguard the operational stability of the WWTP.

6.3.2 Accumulation

Return of NF concentrate to the WWTP, as shown in Figure 45 will cause accumulation of species retained by the membrane until equilibrium is reached. The equilibrium concentration in the WWTP for a species *'i'*, neglecting scaling, sorption to the sludge or biological mineralization can be calculated using Equation(39);

$$c_{WWTP}^{\infty} = \frac{c_{IN}}{1-R} \tag{39}$$

with $c_{i,WWTP}$ the equilibrium concentration, $c_{i,IN}$ the original concentration and R_i the retention of the membrane. For the derivation of equation(39), consult the appendix.

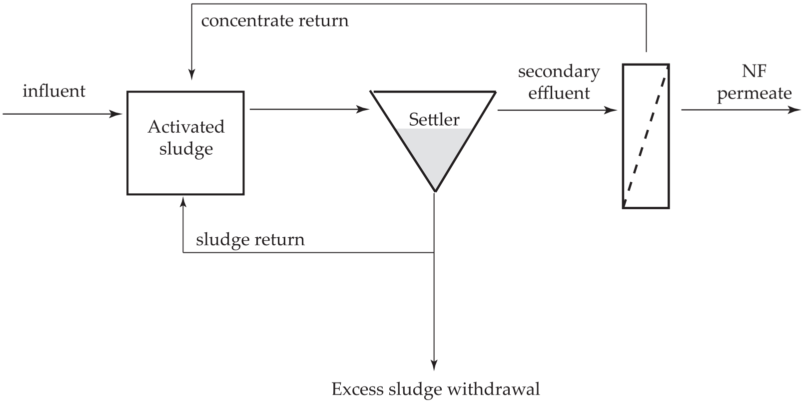

Figure 45 – Schematic representation of a WWTP-NF plant

Table 27 gives the calculated retentions and final equilibrium concentrations within the WWTP based on observed effluent and pilot data.

Table 27 – Content of effluents, concentrates and Ion Exchange treated concentrates

	Effluent	*Concentrate*	*Retention**	*Final equilibrium***	*NF-IEX Concentrate*
	mg/L	*mg/L*	*(%)*	*mg/L*	*mg/L*
DOC	*13*	*81*	*91 (100 for MW > 1000)*	∞	*16*
UVA$_{254}$ (cm^{-1})	0.37	2.44	> 97	-	0.34
SUVA	0.028	0.030	-	-	0.021
Sugars	4.7	21	60	≈ 10	9.2
Proteins	3.9	15	50	≈ 8	3.2
Na^{+}	122	211	10	≈ 135	225
K^{+}	17	26	10	≈ 19	21
Ca^{2+}	50	164	40	≈ 80	153
Mg^{2+}	8.6	41	60-70	≈ 25	38
Zn^{2+}	< 0.1	< 0.1	-		< 0.1
Cu^{2+}	< 0.1	max 0.26†	> 99‡	∞	< 0.1
Al^{3+}	< 0.1	< 0.1	-		< 0.1
Fe$^{2+/3+}$	< 0.1	< 0.1	-		< 0.1
B^{3+}	< 0.1	3.0	> 99‡	∞	3.5
Si^{4+}	n.a.	11	-		12
Cl^{-}	178	164	0	≈ 178	380
NO_3^-	5.16	7.5	10	≈ 6	3.4
HCO_3^-	270	430	10	≈ 300	420
SO_4^{2-}	35.4	280	70-80	≈ 140	18
PO_4^{3-}	0.71	5.7	80-90	≈ 5	<0.05
M/D-ratio	1.8	0.9		≈ 0.8	1.0
BOD$_{28}$	< 5	35	-	-	10
BOD$_{28}$/DOC ratio	0.43	-	-	0.63	

** Averaged typical observed retention during pilot plant trails (see chapter 5) ± 5%*

*** As based on mass balance computation (see appendix)*

† in 3 of the 5 concentrates detected

‡ found in concentrate, below detection limit in permeate and effluent (<0.05 mg/L)

n.a. = not analyzed

The general trend is an increase in ionic content within the WWTP at equilibrium conditions. These elevated salt concentrations could promote scaling which might be problematic in maintaining a stable NF performance. Furthermore, Equation(39) shows that a problematic increase in species which are fully retained by the membrane, like high molecular weight organics and trace contaminant like copper and boron, is to be expected.

Scaling

In Figure 46 the scaling potential for the most common least soluble salts is shown. Based on the retention characteristics of the membrane, scaling of gypsum ($CaSO_4$), calcium phosphate and magnesium carbonate is very unlikely to occur.

Scaling of calcium and especially calcium-magnesium carbonate might be expected. This is not surprising as effluent was shown to be close to the saturation point for calcium carbonate scaling in chapter 5 (appendix). The increase in scaling potential of the effluent might give problems with the nanofiltration modules, however returning a feed rich in calcium and magnesium back to the WWTP might have beneficial effects on the (biomass)sludge properties.

By increasing the di-valent cation concentration compared to the monovalent cation concentration (the M/D-ratio) in the WWTP, sludge properties as settleability and dewaterability can be improved [26, 27]. The decreased ratio leads to increased inorganic content (scaling onto the biomass) of the sludge and a decreased repulsion between organic surfaces (collapse of the double layers). The M/D-ratio of the Leeuwarden WWTP is 1.8 showing a just sufficient amount of bivalent ions to keep a stable sludge, a ratio of 2 and greater is believed to be undesirable [26]. Decreasing the M/D-ratio even further as consequence of the concentrate return could be beneficial. The total milli-equivalent concentration of Mg^{2+} and Ca^{2+} (1.6 meq/L) at initial conditions is lower than the reported

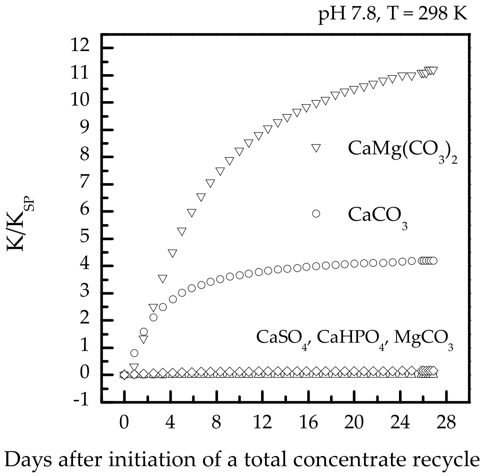

Figure 46 - Scaling potential within the WWTP with full concentrate return and without sorption of inorganic salts to available biomass. Y-axis shows the ratio between calculated concentration product (K) and solubility product (K_{SP}). A ratio greater than 1 could lead to scaling.

limiting value (10 meq/L) above which no further beneficial effects could be observed [27]. Concentrate return would result in a decrease in the M/D-ratio to 0.8 with a total equivalent concentration for Mg^{2+} and Ca^{2+} of 5 meq/L.

There seems to be a sufficient bleed in the system for calcium and magnesium which might prevent severe carbonate scaling at the membrane surface. If this is not the case, a membrane with a lower retention value for Ca^{2+} and Mg^{2+} or addition of acid to lower the alkalinity might be necessary to maintain stable operation. Both options might compromise permeate quality.

Phosphates and sulfates

The increase in sulfate and phosphate content might be problematic. The nanofiltration membrane has a manufacturer reported rejection of more than 97% for sulfate and phosphate (70-90% in real practice).

Excess sulfate and phosphate might be reduced by sulfate reducing bacteria (SRB) and phosphate accumulating bacteria present in many anaerobic systems. The WWTP of Leeuwarden does not contain an anaerobic stage in which sulfate and phosphate are removed.

Excess phosphate might be removed by precipitation with ferric chloride as is standard practice for WWTPs without biological phosphorous removal. As most plants add an excess of $FeCl_3$ or $FeClSO_4$ accumulation of phosphate to levels as calculated in Table 27 are not to be expected.

Sulfate on the other hand has no bleed in the WWTP. The elevated sulfate level might cause an unwanted effect. Increased sulfate content in the plant waters will have an effect on the efficiency in the sludge digestion towers (to degrade excess sludge) by increasing H_2S production and decreasing CH_4 production which is undesirable.

Trace components

It is noteworthy to see that boron and copper were present in the effluent and accumulated in the concentrate to levels above the detection limit. The concentrations copper and boron are small and a recycle to the WWTP might be sufficient for further removal by additional metal uptake by the activate sludge.

An increase in hydraulic residence time has shown to increase the amount of copper bound to activated sludge [28]. The uptake of boron to activated sludge is limited (26 mg/kg Dried Solids (DS)) compared to other metals, like copper (300 mg/kg DS) [29]).

Figure 47 shows that the boron sorption of 2.0 mg/kg DS activated sludge is sufficient to ensure a constant level of boron in the WWTP. For copper no accumulation is to be expected as the reported sorption of copper to activated sludge is a magnitude higher that for boron.

Calculation shows that it is possible to create a sufficient bleed by sorption to the activated sludge for trace components such as boron and copper. However a careful analysis on the WWTP sludge prior to initiating the recycle should be performed to assess remaining sorption capacity for copper and boron to safeguard against accumulation.

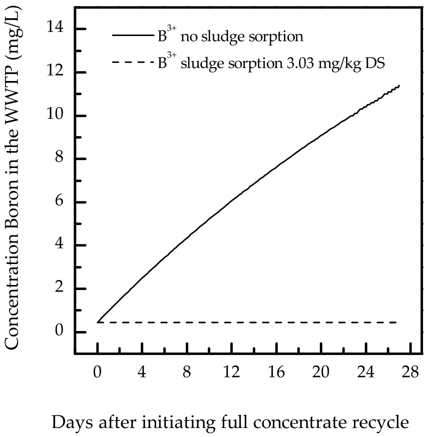

Figure 47 – Calculation of the Boron concentration in the WWTP as function of time after initiating a total recycle of NF concentrate.

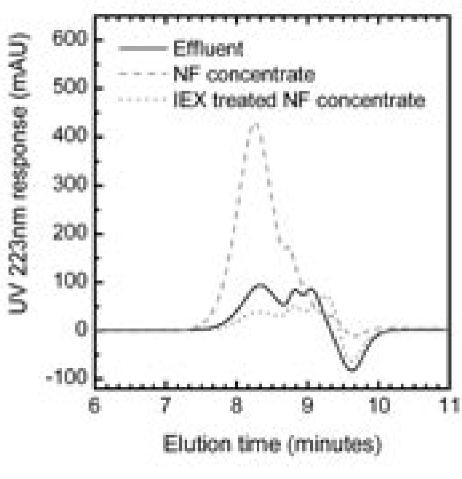

Figure 48 – GPC elution diagram for NF effluent, NF concentrate and NF-IEX treated concentrate

Inert organic species

The organic species of higher molecular weight are accumulated in the NF concentrate as is shown in the GPC elution diagram displayed in Figure 48. Organic species with an elution time less than approximately 8.8 minutes (700 Dalton) are accumulated in the retentate and are absent in the permeate (not shown in figure, see previous work [30]).

These compounds of higher MW are most likely to be associated with humic-like substances and might be refractory (i.e. not biodegradable) in nature. BOD_{28} tests with the effluent showed that the species present are either too diluted or of refractory nature as no significant ($BOD_{28} < 5$ mg O_2/L) biodegradability was detected. A long term (BOD_{28}) biological degradation test on the NF concentrate shows that on average 40 percent of the DOC in the concentrate might be degraded. This percentage might increase even further at longer residence times as the BOD-tests did not reach a plateau value after 28 days. However, standard practice would classify the concentrate as difficult degradable as the BOD/DOC-ratio is less than 0.5 [10].

The result implies that return of the concentrate to the WWTP might be feasible as not all material is of refractory nature. The remaining organic content might be removed by biosorption, as at higher calcium and humic concentrations in the mixed liquor biosorption of humic and fulvic components is enhanced [31].

The main question is whether biodegradation and sorption will keep up with the speed of accumulation. It might be very well possible that a final equilibrium between refractory material and biosorption reaches concentration levels problematic to part of the micro-organisms in the sludge. It might therefore be necessary to partly remove refractory material.

6.3.3 *Nitrification toxicity test*

Nitrification inhibition was assessed on sludge from the Leeuwarden WWTP as function of increased concentrate inert matter (organic and inorganic) and inorganic content (as Na_2SO_4). Figure 49 shows that with increasing sulfate content (the most predominantly accumulating inorganic species) nitrification rates do not decrease significantly.

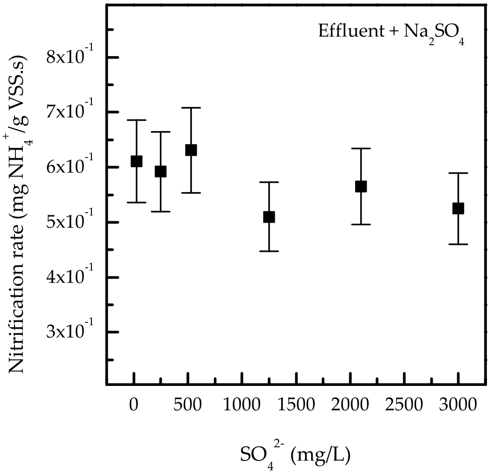

Figure 49 – Nitrification rate versus increasing sodium sulfate concentration

However, by increasing both organic material and inorganic material nitrification rates decrease significantly above a concentration factor of 2 as shown in Figure 50. The results shown in Figure 50 imply that the mixture of species with a retention of > 50% for the used NF membrane cause a serious inhibition of the nitrifying bacteria in the sludge.

Long-term tests will be necessary to assess whether the measured effect is due to an inhibition effect which might be temporary of nature (adaptation of the biomass in time) or that the observed decrease in nitrification speed is caused by death of the nitrifying bacteria in the sludge due to toxicity effects.

It is difficult to pinpoint the reason for the observed decrease in nitrification rate. Tests with sodium sulfate show that the increased ionic strength does not have a significant impact. Possible sources for the observed decrease can be found in the increased copper content when adding concentrate. It was shown that ammonium oxidation can be inhibited by a copper concentration as low as 100 $\mu g.L^{-1}$ [32]. Beside copper, nitrifiers are sensitive to a wide range of organic toxic compounds at low concentrations [11] which could be very well be present in elevated levels in the concentrate. A Dutch survey [33] showed that most effluents from domestic WWTPs contain a vast array of organic micro-contaminants which are well retained by a NF membrane.

The results of the nitrification tests show that treatment of the concentrate should be considered to prevent accumulation of inhibiting or toxic components within the WWTP.

6.3.4 Additional concentrate treatment

The previous paragraphs illustrated that concentrate treatment is necessary to safeguard the WWTP against accumulation of heavy metals and (toxic) organic components. Two options for concentrate treatment will be discussed in more detail, ion-exchange and granular activated carbon, as these well-established techniques seem most feasible in respect to (partial) removal of the targeted components. Two other options should be mentioned as well as they might be promising but require further research.

The first option for additional concentrate treatment are so called ‘low cost

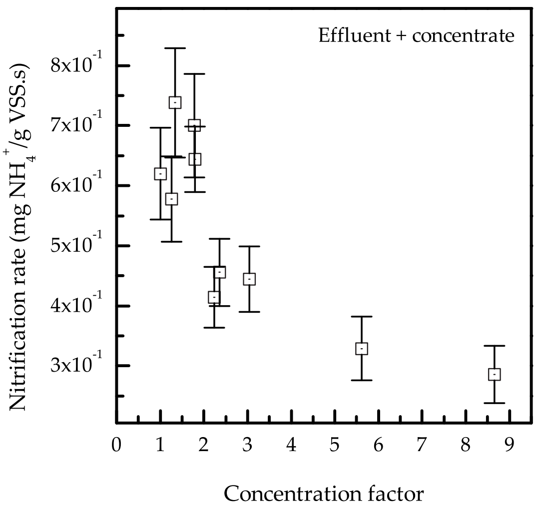

Figure 50 – Nitrification rate as function of increased concentrate matter

adsorbents' as chitosan, zeolite, lignin and seaweed. These adsorbent might be attractive alternatives as they are able to remove heavy metals. However little is known about their actual performance and costs [34] and are therefore not discussed further.

The second option, anaerobic processing of the NF concentrate, might be a possibility to remove toxic organic components, phosphate, sulfate as well as heavy metals by biosorption [10]. As the biodegradable organic content present in the NF concentrate is insufficient for complete anaerobic digestion of sulfate and phosphate, organic waste has to be supplied (e.g. beet-root pulp).

Ion-exchange

Removal of the humic-like and refractory material, excess sulfate and phosphate can be achieved by ion-exchange treatment of the NF concentrate as a shown in Table 27 and Figure 48. The NF-IEX treated concentrate (Table 27) is enriched in polysaccharides/TOC ratio and depleted of aromatic organic species (decreased SUVA). This change improved the biodegradability of the concentrate. On average, more than 60 percent of DOC could be degraded in de BOD_{28} test. Noteworthy, no copper or zinc could be detected in the IEX treated concentrate implying that copper was associated with the humic-like components. However, this was not the case for boron. Accumulation of boron could therefore occur if no further sorption with the sludge takes place.

In practice, removal of aromatic compounds with an ion-exchange method could be problematic. If all the concentrate has to be treated by IEX, the chloride content in the concentrate will be increased significantly, see Table 27, for the type of ion-exchange resin used. Accumulation effects of chloride are not to be expected as the chloride will exit the WWTP through the NF membranes. However, the elevated chloride content (+ 30 mg/L) in the NF permeate might hamper reuse possibilities.

Furthermore, the IEX column has to be regenerated with a high strength alkaline sodium chloride solution, typically 10 w/w% NaCl and 1 w/w% NaOH, creating a highly concentrated organic and sulfate rich waste product. However, the IEX-regeneration solution is a far more concentrated stream.

Previous research [35] showed that concentrations of around 30 gram $TOC.L^{-1}$ could be reached in the IEX-regeneration solution with the type of resin used in this study. This means that per 460 m^3 of NF concentrate 1 m^3 has to be disposed of. For the load of wastewater treated per day at the WWTP of Leeuwarden, this would result in waste stream of 20 m^3 per day of IEX regeneration fluid, see Figure 51. This is a reasonable daily waste stream, compared to other waste streams (excess sludge) generated at the WWTP. Further concentration might be possible by evaporation (natural or using an excess heat source) prior to transportation and incineration.

Activated carbon

Another possibility for concentrate clean-up would be the use of granular activated carbon to adsorb most of the organic species. The majority of the heavy metal load is assumed to be associated with the humic-like (high molecular weight) organic components in the feed and would be removed by the PAC as well. Special attention to the pore size distribution must be paid as a study by Ernst et al. [36] reported poor loading of PAC due to the presence of a mixture of high MW effluent organic matter coating the outside of the pores, reducing effective sorption area and effective loading time.

A disadvantage for this kind of system is that the activated carbon has to be regenerated by heat treatment, a process often not possible on-site. This means transport of spent carbon and regenerated carbon vice versa to the reactivation plant, which might increase costs unfavorably. Furthermore, the amount of activated carbon to be dealt with on a daily based (≈ 800 m^3/day [32]) is an order of magnitude higher than for the IEX process.

A complete process scheme for an integrated WWTP-NF system with concentrate handling technique is depicted in Figure 51.

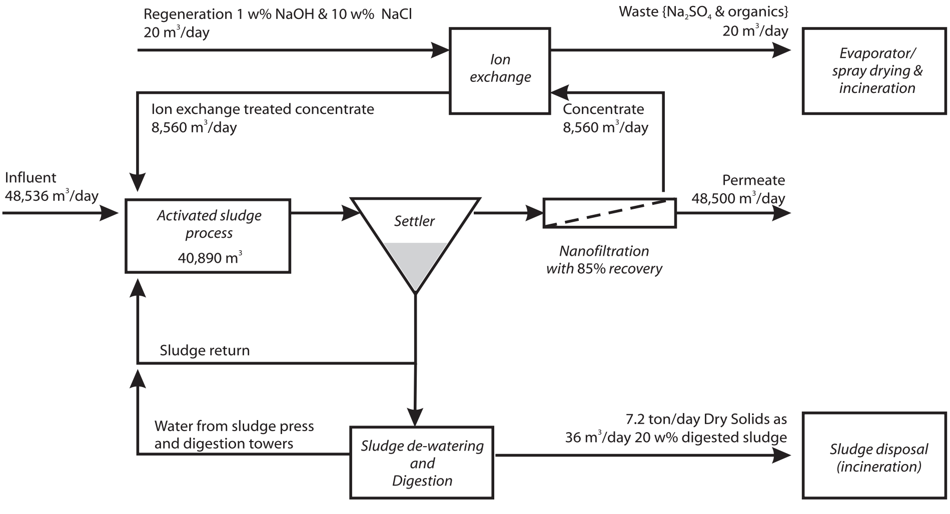

Figure 51 – Proposed flow scheme for an integrated WWTP-NF installation with concentrate return

6.4 CONCLUSIONS

In this paper the possibility was investigated to return WWTP NF concentrate back to the WWTP. Comparison with other disposal alternatives showed that return to the WWTP is the only feasible option to deal with the concentrate due to the volume and composition of the concentrate.

Exposure of the nitrifying bacteria in the activated sludge to increasing concentration of WWTP-NF concentrate showed inhibition/ toxicity effects above a twofold concentration of retained species within the WWTP.

Based on literature reported and experimental observed retention values for nitrification inhibiting components (heavy metals, organic micro-pollutants) a two-fold concentration factor will be well exceeded, demonstrating the need for a tailored concentrate treatment process prior to return to the WWTP.

Such a treatment process should aim at the removal of refractory organics and heavy metals while minimizing residual (liquid) waste streams caused by additional concentrate treatment.

Two options for concentrate treatment were investigated, ion-exchange and granular activated carbon of which ion exchange showed the most promising potential in respects to residual waste management and accumulation prevention within the WWTP. Further studies are necessary for selection of a tailored ion-exchange resin for optimal performance.

6.5 ACKNOWLEDGEMENTS

The authors like to express there gratitude to Noémie Maurin of the Ecole Nationale Supérieure d'Ingénieurs de Limoges (France) who contributed to this paper by her practical work during their student internship placement during the summer of 2005. Vitens Water co-financed this internship through the EU Leonardo-da-Vinci exchange program. Vitens Water, Landustrie Sneek B.V. and Wetterskip Fryslân (Frisian waterboard) are kindly acknowledged for funding this study.

6.6 APPENDIX

6.6.1 *Mass balance WWTP*

The assumptions and symbols for creating the mass balance used for the flow chart represented in Figure 52 are listed in Table 28.

The mass balances, equations (I to IV), can be substitued and rewritten to give Equation (40) which can be used to calculate the concentration of species '*i*' as function of time after concentrate recycling starts. The final equilibrium concentration (t^{∞}) can be calculated using Equation(41).

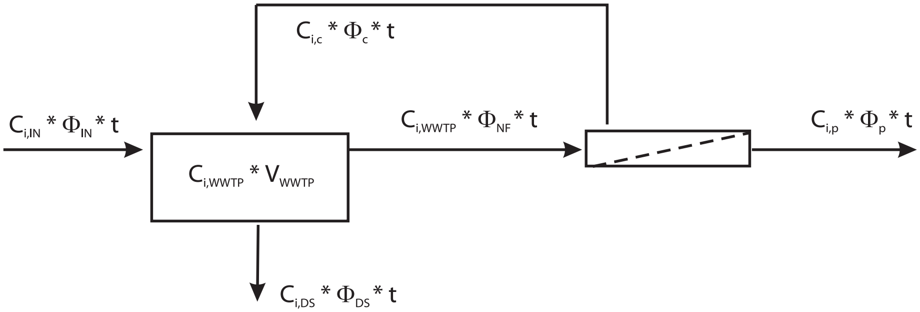

Figure 52 – Flow scheme for the mass balance and accumulation calculations

I) $c_{i,wwtp}V_{wwtp} = c_{i,in}.V_{in} + c_{i,c}.V_c - c_{i,wwtp}.V_{NF} - c_{i,DS}.DS$

II) $c_{i,wwtp}.V_{NF} = c_{i,c}V_c + c_{i,p}V_p$

III) $V_{in} = V_p$

IV) $c_{i,p} = c_{i,wwtp}(1-R)$

$$c_{i,wwtp} = \frac{\phi_{in} \cdot c_{in} \cdot t - c_{i,DS} \cdot \phi_{DS} \cdot t}{V_{wwtp} + \phi_{in} \cdot (1-R) \cdot t} \tag{40}$$

$$c^{t=\infty}_{i,wwtp} = \frac{\phi_{in} \cdot c_{in} - c_{i,DS} \cdot \phi_{DS}}{\phi_{in} \cdot (1-R)} \tag{41}$$

Table 28 – Symbols and data for constructing the mass balance over the WWTP

Symbols		*Units*
c	concentration	g/m^3
t	time	hours
R	Retention	-
V	Volume	m^3
Φ	Flow	m^3/hour
C_{DS}	Sorption factor to the sludge	mg/ gram DS
DS	Sludge bleed as Mass Dried Solids (DS)	gram DS/hour
subscript c	concentrate	
subscript p	permeate	
subscript i	species ‘i’	
Data used for the mass balance (based on actual data WWTP Leeuwarden)		
Volume WWTP	40890	m^3
DS exit	300	kg/hour
Recovery NF	0.85	
Influent flux	2021	m^3/hour
Retention values	see Table 27	

6.6.2 Solubility data

Table 29 lists the data used for the construction of Figure 46.

Table 29 – Data from [37]

Component	*Solubility product (K_{SP})*
$CaHPO_4$	2.51 * 10^{-7}
$CaCO_3$	5.00 * 10^{-9}
$CaSO_4$	7.10 * 10^{-5}
$MgCO_3$	3.46 * 10^{-8}
$CaMg(CO_3)_2$	1.00 * 10^{-17}
Ion	*Activity coefficient (I = 0.05 M)*
Ca^{2+}, Mg^{2+} & SO_4^{2-}	0.40
CO_3^{2-}	0.88
HPO_4^{2-}	0.16

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CHAPTER 7

CONCLUSIONS & FUTURE OUTLOOK

The concluding chapter shows that for a successful implementation of nanofiltration as an effluent reclamation technique two conditions have to be met.

The produced permeate is of such a high quality that it should be reused for a high quality purpose (e.g. potable water). To achieve potable water quality further treatment is necessary but achievable using conventional techniques. This way the permeate can be valorized.

Further studies should focus on developing a tailored concentrate handling technique as the costs for concentrate handling will determine economic feasibility.

7 Conclusions and future outlook

This study was initiated to investigate further treatment of WWTP effluent using nanofiltration membranes. Focuses of study were process options for water reuse, fouling behavior of the membranes and to investigate possible options for concentrate disposal. In the next paragraphs the main findings of this study are presented related to three major themes. Paragraph 7.1 discusses the permeate quality and its applicability for reuse. In § 7.2 the results from the laboratory and pilot plant scale experiments are compared and evaluated. Additional concentrate treatment will alter the economy of polishing WWTP effluent by nanofiltration, a topic discussed in §7.3. In the final paragraph a general conclusion is drawn about the future applicability of nanofiltration as effluent polishing technique.

7.1 PERMEATE QUALITY & POTENTIAL REUSE

7.1.1 General NF performance in relation to the Water Framework Directive

Whether nanofiltration of WWTP effluent would be a suitable technique to meet the European Water Framework Directive (WFD) targets for surface water was the main interest for the combined Dutch water boards (STOWA), represented in this study by Wetterskip Fryslân (the Frisian water board). Nanofiltration of WWTP effluent should prevent the accumulation of six groups of pollutants in surface waters, which were all detected on a regular basis in Dutch WWTP's and listed in the EU WFD (Table 30).

Table 30 – A selection of listed substances found in WWTP effluent and listed in the EU Water Framework Directive and WHO Guidelines for potable water.

	MW (g/mole)	*WWTP effluent period 2000-2004 [1]*	*Recreational waters Directive*	*EU WFD/ Dutch surface water directive (NW4)*	*WHO drinking water guidelines*
			µg/L		
Nutrients					
Total nitrogen	-	1.400-61.000	2.200	-	n.a
Total phosphorous	-	120-29.000	150	-	n.a.
Micro-organisms & viruses					
E.Coli	-	$2 * 10^5$ cnts/L	250	-	none
viruses	-	$1\text{-}10^5$ cnts/L	none	-	none
Organic micro pollutants					
Diethylhexyl phthalate	390	0-20		0.33	-
Anthracene	178	0-0.1		0.063	-
Naphthalene	128	0-0.2		2.4	-
Pesticides					
Lindane	290	0-0.01		0.042	2
Atrazine	215	0-0.12		-	20
Diuron	233	0-1.4		0.046	
Heavy metals & metalloids					
Arsenic	75	0-11	32		0.1
Chromium		0-43	84		30
Lead		0-50		2	10
Mercury		0-0.14		none	10
Nickel		0-37		1.3	20
Copper		0-95		3.8	2000
Zinc		0-210		40	5
PPCPs					
Bisfenol A	> 228	0.04-4.1		none	none
Ibuprofen	> 206	0.12-0.76		none	none
Sotalol	> 272	0.97-1.60		none	none
Prozac	> 356	n.a.		none	none

This study and related research by other groups [2-10] showed nanofiltration to be a suitable technique for the removal of almost every listed substance in Table 30. Only for the uncharged low molecular weight components (typically < 200 Da) nanofiltration does not suffice.

For complete removal of all listed WFD components further clean-up of the nanofiltration permeate would be required. This could be achieved by means of a second stage membrane process (RO) or by a combination of advanced oxidation (AOP) and activated carbon. Consequently, this would result in a final permeate of drinking water quality.

7.1.2 Permeate quality, concentrate management and reuse

As mentioned in the previous paragraph, utilizing RO membranes with lower molecular weight cut-offs would improve the permeate quality even more. Permeates from WWTP– reverse osmosis systems are of such a high quality that reuse as (indirect) potable water is possible [11]. However increased permeate quality has its price. Energy demands for RO systems are higher and effluent recoveries are significantly lower than for NF systems (typically 60 versus 85 percent) increasing the concentrate volume and salinity. The concentrate volume and salinity would prevent a return of the concentrate to the WWTP as plant capacity would be decreased significantly and excessive salt accumulation would occur due to the high retention values for salts (typically >99%). Without the option of concentrate return to the sewer, omitting the options for discharge on large surface water bodies and deep-well injection, concentrate handling would become very expensive (see §7.3).

On the opposite side, effluent polishing with ultrafiltration (UF) membranes (e.g. membrane bioreactors) would result in an effluent quality which would reach the EU directives for recreational waters but fails to meet standards as described in the EU WFD. Concentrate management for an UF system is practically a non-issue as such systems reach a recovery of almost 100%. Due to the UF retention characteristics no salt accumulation takes place and the only waste stream of concern are the chemicals used for the maintenance cleaning of the membranes. However further treatment of the WWTP-UF effluent would be required to meet WFD standards.

Further processing of UF effluents with other than membrane techniques, could be more problematic compared to NF permeates. UF effluents still contain some heavy metals and soluble organic matter of high and low molecular weight. These characteristics would limit the use of techniques like AOP, chlorination due to disinfection by-product formation. Furthermore, the wide molecular range distribution of the organic load in the UF effluents would reduce effectiveness of the loading rate of activated carbon compared to nanofiltrated effluents [12].

Nanofiltration is therefore a good compromise by achieving a high quality in the effluent, while producing a manageable volume of concentrate. If necessary, further cleanup of the effluent to WFD (or drinking water) quality is relatively easy by means of standard techniques with a minimum of residual waste streams. Furthermore, the concentrate of the WWTP-NF process is of such a volume and composition that it might be dealt with in a zero-discharge process scheme as was shown in chapter 6.

As the quality of the nanofiltration permeate is close to drinking water standards the most appropriate reuse option is to use the NF treated effluent as source for potable water production, whether as a direct water source or indirect water source (infiltration in existing aquifers).

7.2 Factors influencing nanofiltration performance

7.2.1 *Colloidal stability*

Chapters 2 and 4 dealt with the influence of electro-kinetic stability on nanofiltration performance.

In chapter 2, laboratory scale experiments showed a strong correlation between colloidal instability of the effluent and the formation of irreversible fouling layers with low permeability, regardless of effluent composition variations. To alter the colloidal stability of the effluent, acidification combined with the addition of a coagulant ($AlCl_3$) was used to neutralize the electrophoretic mobility (expressed in the zeta-potential) of the constituents of the WWTP effluent. During experimentation it was noticed that adding coagulant at non-neutralizing conditions was beneficial to minimize residual fouling, a finding further explored in chapter 3 (see also §7.2.2).

As lowering the electrophoretic mobility showed to have a negative impact on the nanofiltration performance, increasing the colloidal stability might have a positive effect. Increasing the effluent constituents electrophoretic mobility might be achieved by adding surfactants to the feed or continuous exposure of the effluent to an electric field. Adding surfactants to the WWTP effluent would possibly hamper concentrate management options.

Temporary exposure of the WWTP effluent to a high voltage static electric field proved to be possible and this option was validated on pilot-plant scale. The outcome of this test, as described in chapter 4, showed that the electrophoretic mobility of the WWTP effluent could be (temporary) raised utilizing an electric field device. Although fouling could not be prevented entirely, a significant decrease in filtration resistance was observed.

Chapters 2 and 4 illustrate the importance of the electro-chemical interactions of the feed components and the nanofiltration membrane, illustration the major role charge repulsion plays in nanofiltration performance.

7.2.2 Fouling prevention by coagulant addition

Laboratory scale experiments in which different coagulants were added to the WWTP effluent to prevent irreversible fouling showed variable results (chapter 3). Addition of any coagulant proved to be beneficial in strengthening the fouling cake, preventing collapse and resistance increase of the cake layer under high pressure. Prevention of irreversible fouling was shown to be highly dependant on coagulant type; coagulant addition could even worsen fouling behavior. Best results compared to the blank tests were obtained when adding a high molecular weight vegetable derived polymer to the WWTP effluent at high pressure conditions. The variation in effluent quality showed to be significant, indicating that coagulant addition could only be beneficial to a limited extent.

During pilot trial tests with a spiral wound NF module, as described in chapter 5, a test was performed with the vegetable derived polymer. Coagulant addition showed to be incompatible with the hydrodynamics as encountered in the feed spacers of the spiral wound module, clogging the feed side of the membrane within minutes with the added polymer. Forward flush cycles showed that these layers could be removed easily by increasing the shear stress along the membrane feed side. Cleaning of the spiral wound module proved to be non-problematic.

No further test with coagulants were performed as normal operation of the pilot plant proved to be less problematic (see also §7.2.3) than expected from the earlier performed laboratory scale experiments.

Reasons for this discrepancy can be attributed to the different hydrodynamic conditions (stirred cell, dead-end versus spiral wound semi dead-end) and the trans-membrane pressure (TMP) in the pilot tests (< 400 kPa) compared to the laboratory test (300 < TMP < 600 kPa). As mentioned before, coagulant addition showed to be most beneficial at high TMP. Coagulant addition might therefore be considered in applications with both higher operational TMP and more favorable hydrodynamics (tubular/ capillary modules) to prevent excessive build up of fouling layers.

7.2.3 The role of dissolved oxygen and fouling

The pilot trial tests utilizing spiral wound modules proved to be less problematic in respect to fouling as initially expected (chapter 4 and 5). Considering the composition of the effluent, scaling, organic and biological fouling would be expected, especially as spiral wound modules are often found to be more susceptible to fouling as tubular or capillary modules. However, during the first month of operation, regular cleaning cycles utilizing a relatively mild cleaning regime was shown to be sufficient to maintain operational stability. The main factor determining whether severe (bio)fouling would develop was shown to be the dissolved oxygen level in the WWTP effluent. Effluent drawn from the secondary clarifiers of the WWTP does not contain dissolved oxygen as the respiration of the settling sludge in the clarifiers consumes all oxygen. The lack of oxygen was shown to prevent (aerobic) biological activity within the pilot plant. In time, anaerobic biological activity might occur, however the growth rates of anaerobic bacteria are magnitudes smaller than for aerobic bacteria [13]. It is therefore not likely that anaerobic communities could develop within the normal cleaning cycles, assuming that these cycles disrupt the development of biofilms.

7.3 Concentrate management & economic assessment

The findings presented in chapter 6 showed that returning concentrate to the WWTP is probably the only feasible economic option to manage the produced concentrate. Analysis of the concentrate showed that the organic content is partly biodegradable, the majority however consists of refractory organic and inorganic material. Return of the concentrate will therefore cause accumulation of organic and inorganic species within the WWTP. Although beneficial effects on the WWTP performance might be expected by the resulting increase of divalent cations concentration in the WWTP, it was shown that accumulation has serious inhibition/ toxicity effects on the WWTP's nitrifying bacteria. It is therefore necessary to treat the concentrate stream prior to the return. Such a treatment should be aimed at the removal of heavy metals, organic-micro pollutants and refractory organic matter to safeguard the WWTP's performance. For the concentrate treatment options discussed, ion-exchange is seen as the most promising technique in terms of:

- refractory organics removal, favorably changing the biodegradability of the concentrate
- (partial) removal of most heavy metals
- additional removal of sulfates and phosphates
- resulting volume of waste (ion-exchange regeneration solution)

A disadvantage of using ion-exchange as a concentrate treatment technique is the release of the corresponding co-ions (chloride) in the concentrate, elevating the chloride level of the final permeate, which might complicate reuse possibilities.

Taking into account the necessity of concentrate treatment and subsequent handling of waste streams, the economics of WWTP effluent polishing will differ from the reported operational costs between 20-60 €-cent/m^3 [7, 16].

Table 2 gives a list of estimated operational costs per produced m^3 of permeate assuming different scenarios based on the operation data as reported in chapter 6. As the reported operation costs were calculated based on application of the more expensive capillary nanofiltration membranes, the lower end (20 €-cents) is used for the calculations in Table 31.

Table 31 – Different scenarios for concentrate handling and effect on operational costs

Option number	Scenario	Comments	Total costs† (€/m^3)
1	Concentrate is shipped for anaerobic digestion and incineration to a sludge handling facility: costs 28 € / 1w% DS m^3 concentrate [14]	Sludge handling facility should be nearby and accept the concentrate (as non-toxic waste)	5.1
2	Concentrate is shipped for hazardous waste disposal: costs 215 €/m^3 [14]	Transport over water seems necessary due to daily concentrate volume	38
3	Concentrate is returned to the head of the WWTP using GAC treatment: costs 0.35-90 €/m^3 [1, 14]	Large difference in reported treatment costs depending on transport costs and efficiency	0.28-16
4	Concentrate is returned to the head of the WWTP using IEX treatment (0.02 €/m^3) [15] and IEX-regeneration fluid is classified as toxic waste (see option 2)	Reference scenario (chapter 6)	0.30

†Costs per produced m^3 of permeate. Based on a permeate to concentrate volume ratio of (8560/48500 m^3)

7.4 Final conclusion

Nanofiltration of WWTP effluent proved to be a very successful technique in producing a high quality effluent, meeting almost all WFD qualifications. The NF treated effluent is of such high quality that additional treatment to produce potable water would seem a suitable option, valorizing the NF permeate.

Operational stability of performing direct (e.g. no pre-treatment) nanofiltration on WWTP effluent using conventional spiral wound modules proved to be successful as long as the effluent dissolved oxygen levels were minimal (< 1 mg O_2/L).
Operational stability could be further enhanced by using a high static electrical field device enhancing the effluent's colloidal stability reducing fouling.

The key factor whether nanofiltration will be regarded as feasible technology for effluent polishing was shown to be the options available for concentrate treatment when recycling the concentrate back to the WWTP. A total recycle of the concentrate to the WWTP would lead to accumulation and results in inhibition effects on the microbial population of the WWTP. Therefore a tailored concentrate 'clean-up' strategy has to be developed aimed at reduction of accumulation while minimizing further waste streams.

Ion-exchange was tested and assessed as the technology most suitable for concentrate clean-up in this study. However, only a long term pilot experiment will reveal whether ion-exchange or another concentrate treatment technique suffices to prevent problematic accumulation of trace components in the long run.
Beside the challenges to prevent accumulation, benefits might be gained as well

by recycling the concentrate back to the WWTP. Sludge properties as biodiversity, settleability and dewaterability might be improved and the sludge might adept to elevated concentrations of refractory material.

Future application of nanofiltration for advanced treatment of effluent will therefore depend on finding the ideal combination between membrane rejection properties and concentrate handling technique. Developing such a system will require collaboration between the disciplines of separation-, process- and bio-technology in order to create the prefect symbiosis between separation, concentration, extraction and the activated sludge biology. Nanofiltration seems to be the ideal separation technique within such a scheme, facilitating processes required for permeate clean-up and further concentrate handling.

7.5 References

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SUMMARY

DIRECT NANOFILTRATION OF WASTEWATER TREATMENT PLANT EFFLEUNT

Summary

The need for an enhanced treatment of wastewater treatment plant (WWTP) effluent was shown to be a necessity in chapter 1 for a three-fold reason.

The first being the European Water Framework Directive (EU WFD), which sets a series of standards for the surface water quality in 2021. As many of the priority standards listed in the EU WFD, such as pharmaceutical and personal care products (PPCPs), originate from WWTP effluent discharge, removal of those substances from the WWTP effluent is a priority.

The second reason is related to the first as the uncontrolled release of PPCPs, non-biodegradable organic compounds and heavy metals in our surface water threaten the ecological quality of the surface water and our water supply.

A third reason relates to the growing need for fresh water resources of high quality due to increasing demand for fresh water as population density and welfare increases.

Membrane technology, especially nanofiltration, is seen as a suitable technology to polish WWTP effluent to EU WFD standards and consequently produce an effluent quality suitable for agricultural or (in)direct potable usage.

The objective of this study was to assess the potential of direct nanofiltration as technique for effluent reclamation.

Chapter 2 and 3 describe the effect of the WWTP effluent colloidal properties on membrane performance during laboratory stirred cell experiments. In contrast to other studies, a real feed was used.

Chapter 2 showed the importance of maintaining a stable colloidal system in order to maintain a high permeability. Neutralizing the WWTP effluent's zeta-potential resulted in a significant loss in permeability. Reversibility of fouling was shown to be related to the pH and presence of coagulant. A low pH (5) residual fouling was promoted whereas spiking the feed with coagulant at non-coagulating conditions (i.e. maintaining a colloidal stable system) residual fouling was decreased.

The relationship between coagulant addition and residual fouling prevention was the topic of chapter 3. Four different coagulants (two salts, two cationic polymers) were tested. Results showed that all coagulants proved effective in maintaining a constant permeability during filtration at high pressure (max 600 kPa) compared to the blank by preventing cake collapse. Whether coagulant addition was effective in reducing residual fouling was shown to be dependant on the coagulant type. Both an organic coagulant of high molecular weight (> 10 kDa) and alum showed to be most effective in decreasing residual fouling, whereas ferric addition increased residual fouling. Furthermore, the beneficial effect of coagulant addition on residual fouling was shown to be of the same order as the effect of feed water variation on residual fouling. Coagulant addition might therefore considered in applications operating at high pressure to prevent cake collapse. A careful screening of coagulant-feed-membrane compatibility is necessary as the effect on residual fouling is coagulant dependent.

Chapter 4 and 5 discusses experiments on nanofiltration performance behavior during pilot-plant tests, using spiral wound modules.

In chapter 4 a high voltage electrostatic device is tested, which causes a temporal exposure of the feed (WWTP effluent) to a high strength electric field. After passage through the electric field the electrophoretic mobility of the feed was shown to have increased significantly. This effect dissipated in time and after six minutes original electrophoretic mobility was restored. The increase in electrophoretic mobility enhances the colloidal stability of the effluent which

could result in a better filtration performance (see also chapter 2).
The increased electrophoretic mobility was hypothized to originate in enhanced dissociation of complexes due to the electric field exposure. It was shown for both a model feed (tap water with humic content) and WWTP effluent that the increase in electrophoretic mobility improved initial permeability.
The fouling rate was shown to be independent of the application of the electrostatic field device. Due to the increase of initial permeability, on average higher production rates can be achieved using the electrostatic field device.

The objective of chapter 5 was to test various parameters influencing nanofiltration performance during pilot plant tests using conventional spiral wound modules.
The results show that suppressing the dissolved oxygen (DO) levels in the feed prevents the formation of biofouling on the membrane. Additional tests showed that forward flush had a beneficial effect on the systems performance whereas coagulant addition led to clogging of the feed spacer decreasing system performance. At DO concentration below 1 mg/L a stable performance could be reached at 50% of the initial permeability, using forward flush only. Autopsy revealed that the residual fouling responsible for the decrease in permeability consisted of silt like material.
Comparison with earlier studies on direct nanofiltration of WWTP effluent utilizing capillary membranes show that spiral wound modules perform as well in regard to fouling and have a better permeability and rejection.

During nanofiltration, apart from producing permeate, a concentrate (retentate) is produced as well. This concentrate consists of typically fifteen volume percent of the original feed and contains the rejected feed component up to 10 times their original concentration. In case of WWTP effluent nanofiltration, the concentrate contains heavy metals, most of the organic micro-pollutants, and multivalent ions. As this concentrate can not be discharged due to environmental reasons, a proper solution has to be found. Nanofiltration concentrate management is therefore the topic of chapter 6.

This chapter shows that the only feasible alternative is to return the concentrate back to the WWTP. Accumulation of rejected species in the WWTP will occur to such levels that the microbiology of the WWTP is seriously compromised. Tests on nitrifying bacteria (sludge from the WWTP) show an inhibition effect above two times the original concentration of refractory matter. Further concentrate treatment is therefore necessary before recycling concentrate back to the WWTP.

Ion exchange (IEX) was shown to be a possible technique for concentrate treatment. The vast majority of refractory organic material and heavy metals can be removed from the concentrate by IEX , while minimizing the residual waste stream to approximately 0.5 liter per 1000 m^3 of treated effluent.

Long term recirculation tests are necessary to assess whether ion-exchange or an alternative concentrate treatment technique is sufficient to safeguard the microbial population in the WWTP against toxicity or inhibition effects.

The concluding chapter (chapter 7) shows that for a successful implementation of nanofiltration as an effluent reclamation technique further investigation in two research areas is needed.

The produced permeate is of such a high quality that it should be reused for a high quality purpose (e.g. potable water). To achieve potable water quality further treatment is necessary but achievable using conventional techniques. This way the permeate can be valorized.

Further studies should focus on developing a tailored concentrate handling technique as the costs for concentrate handling will determine economic feasibility.

SAMENVATTING

DIRECTE NANOFILTRATIE VAN RWZI EFFLUENT

Samenvatting

De huidige kwaliteit van het geloosde gezuiverde rioolwater (het effluent) is ontoereikend. Het effluent bevat na de biologische en chemische zuivering in een rioolwaterzuiveringinstallatie (RWZI) nog een verscheidenheid aan stoffen die een negatief effect hebben op de kwaliteit van het oppervlaktewater (zware metalen, medicinale stoffen, weekmakers, pathogenen…). Naast de schade op lange of korte termijn, wordt ook het gebruik van oppervlaktekwater voor recreationele en drinkwaterwinning toepassingen bemoeilijkt. In dit perspectief is de Europese Kaderrichtlijn Water (KRW) tot stand gekomen in het jaar 2000. Om te voldoen aan de in de KRW gestelde eisen zal RWZI effluent verder gezuiverd moeten worden. Hiertoe zullen de RWZI's moeten worden voorzien van één of meerdere nageschakelde technieken.

Naast het veiligstellen van ons toekomstige aquatisch milieu en onze drinkwater bronnen is hergebruik van RWZI effluent zeer aantrekkelijk als bron voor irrigatie- en drinkwater in droge of dichtbevolkte gebieden.

Één van de technieken die voor borgstelling van een hoge kwaliteit effluent in relatie tot de KRW en/of hergebruik opties geschikt lijkt is membraan filtratie, in het bijzonder nanofiltratie.

Directe nanofiltratie is het onderwerp van deze dissertatie. Direct betekent in dit geval dat de membranen zonder verdere voorbehandeling worden ingezet na de slibbezinkingbassins van een RWZI.

Het doel van het onderzoek was het bestuderen van het vervuilingsgedrag van de membranen, de kwaliteit van het gefilterde effluent (permeaat) en onderzoek naar de behandeling van de reststroom tegengehouden door het membraan (brijn of concentraat).

Het onderzoek als beschreven in hoofdstukken 2 en 3, richtte zich op het verkrijgen van kwalitatieve informatie over de parameters van belang in effluent filtratie. Hiertoe werden een groot aantal testen op laboratorium uitgevoerd.

De stabiliteit van het colloïdale materiaal in het effluent, d.w.z. de neiging van de stoffen in het effluent om in oplossing te blijven, bleek een belangrijke parameter. Hoofdstuk 2 toont aan dat de filtratie eigenschappen van effluent negatief worden beïnvloedt wanneer het colloïdale materiaal instabiel is. Een instabiel colloïdaal systeem leidt tot een significante weerstandverhoging van de vuillaag op het membraanoppervlak. Om deze instabiele toestand te verkrijgen werd aan het effluent een combinatie van zoutzuur (pH verlaging) en vlokmiddel (aluminium chloride) toegevoegd. Het bleek dat de toevoeging van vlokmiddel alléén, zonder het effluent te destabiliseren, een positief effect had op het verwijderen van de vuillaag op het membraan ontstaan tijdens filtratie.

In hoofdstuk 3 is daarom onderzocht wat de invloed is van 4 verschillende vlokmiddelen op de prestaties van het membraan gedurende het filtratie proces en op de verwijderbaarheid van de ontstane vuillaag. De resultaten tonen aan dat alle vier de geteste vlokmiddelen een positief effect hebben of het voorkomen van verhoogde weerstand in de vuillaag bij hoge operationele druk (6 bar). Elektronenmicroscopie en elementen analyse van de verschillende vuillagen tonen aan de vlokmiddelen in hoge mate vertegenwoordigd zijn in de ontstane vuillaag. De oorzaak van de niet verhoogde weerstand bij hogere druk kan worden verklaard doordat de vlokmiddelen in de vuillaag de mechanische sterkte verhogen en daarmee samendrukking en verlies in porositeit voorkomen bij hogere druk.

De verwijderbaarheid van de vuillaag blijkt zeer afhankelijk van het gebruikte vlokmiddel. Aluminium chloride en een uit een biologisch materiaal geëxtraheerd polymeer gaven goede resultaten terwijl ijzer chloride een zeer slecht resultaat gaf. De verwijderbaarheid bleek ook sterk af te hangen van de variabiliteit van het effluent, hetgeen aangeeft dat vlokmiddel niet de belangrijkste factor in het vervuilingsgedrag is, maar eerder de genoemde voedingskarakteristiek.

Het toevoegen van een vlokmiddel kan nuttig zijn in applicaties die opereren op hoge drukken, mits een zorgvuldige selectie is gemaakt gebaseerd op vlokmiddel, membraan en voedingswater interacties.

De hoofdstukken 4 en 5 richten zich op het testen van de informatie verkregen in de vorige hoofdstukken op proefinstallatie niveau. De proefinstallatie bevatte conventionele spiraal gewonden membraan modules.

In hoofdstuk 4 is de mogelijkheid onderzocht om met behulp van een extern aangebracht statisch elektrisch veld van hoge sterkte de colloïdale stabiliteit van het effluent te beïnvloeden. Hiertoe werd het effluent vlak voor filtratie door een hoog geladen condensator geleidt. Het kortstondig blootstellen van het effluent aan het elektrische veld zorgde voor een tijdelijke verhoging van de stabiliteit van het colloïdale systeem. De reden voor deze tijdelijke verhoging kan worden toegeschreven aan het door het elektrische veld opgewekte verhoogde dissociatie van gecomplexeerd materiaal in het effluent. Na verlaten van het elektrische veld blijft dit effect nog enkele minuten (< 6 minuten) naijlen.

Nanofiltratie van kraanwater (met een hoge humuszuur concentratie) en RWZI effluent toonde aan dat blootstelling aan het elektrische veld een verhoogde initiële productiviteit oplevert. De snelheid van vervuiling gedurende de filtratie testen was onafhankelijk van blootstelling aan het elektrische veld. Doordat de initiële productiviteit hoger lag bij gebruik van het elektrostatische veld kon gemiddeld een hogere productiviteit bereikt worden.

In hoofdstuk 5 is de invloed van een aantal operationele parameters zoals opgeloste zuurstof concentratie in het effluent en vlokmiddel toevoeging getest.

De resultaten laten zien dat bij lage zuurstof concentraties (typisch < 1 mg O_2/L) biologische vervuiling van het membraan wordt tegengegaan.

Testen met een kortstondige verhoogde langstroom snelheid (z.g. forward flush) lieten een positief effect op de productietijd zien terwijl vlokmiddel toevoeging een negatief effect had. Het toevoegen van vlokmiddel leidde, onder de hydraulische condities voorkomend in een spiraal gewonden membraanmodule, tot verstopping van het voedingskanaal.

Een stabiele productiviteit kon worden bereikt in een langdurige test, gebruik makend van optimale condities (geen opgelost zuurstof en forward flush). Vergelijkend onderzoek ten opzichte van eerdere studies toonde aan dat conventionele spiraal gewonden modules geen mindere productiviteit hebben dan capillaire modules in directe nanofiltratie van RWZI effluent en qua retentie zelfs beter presenteerden.

Zoals eerder vermeld produceert een nanofiltratie installatie ook een brijn of concentraat. Het concentraat volume is typisch 15 procent van de behandelde voeding. De samenstelling van het concentraat bestaat uit de niet (of slechts deels) doorgelaten stoffen in de voeding tot concentraties van tien maal de originele waarde. In het geval van RWZI effluent worden in het concentraat onder andere de zware metalen, organische microverontreiniging (bijv. weekmakers), pesticiden en medicijnresten verzameld. Het concentraat kan daarom niet geloosd worden. Het vinden van een oplossing voor de afvoer van het concentraat is het onderwerp van hoofdstuk 6.

Het hoofdstuk toont aan dat de enige geschikte oplossing voor concentraat afvoer, terugvoer van het concentraat naar de RWZI is. Dit heeft als gevolg dat de door het membraan tegenhouden stoffen zich in meer of mindere mate zullen ophopen in de RWZI. Laboratorium proeven met verhoogde concentraties van stoffen aangetroffen in het concentraat wijzen uit dat ernstige remming van de nitrificerende bacteriën in het slib van de RWZI is te verwachten als gevolg van accumulatie effecten. Concentraatbehandeling is daarom noodzakelijk voordat het concentraat teruggevoerd kan worden naar de RWZI. Van de verschillende besproken technieken, lijkt ionen wisseling een veelbelovende techniek. Ionen wisseling verwijdert een zeer groot deel van de lastig af te breken organische stoffen uit het concentraat. Bovendien is de residuele reststroom als gevolg van de ionen wisseling zeer beperkt.

Langdurige proeven zullen nodig zijn om vast te stellen of ionen wisseling of een andere alternatieve techniek voldoende is om accumulatie en remmende effecten op de biologie in de RWZI te voorkomen.

Het laatste hoofdstuk (no. 7) concludeert dat voor een succesvolle implementatie van directe nanofiltratie in ieder geval twee onderwerpen nader onderzocht moeten worden.

1. Het geproduceerde permeaat is van zulk hoge kwaliteit dat de mogelijkheden voor hergebruik als drinkwater overwogen moeten worden. Verdere permeaat behandeling is dan noodzakelijk maar bereikbaar met conventionele technieken. Dit maakt het mogelijk een economische waarde te verbinden aan het geproduceerde permeaat.
2. De nadruk bij toekomstige studies naar de mogelijkheden van nanofiltratie van RWZI effluent zal moeten liggen bij het ontwikkelen van geschikte concentraatbehandelingstechnieken. Concentraat management is daarmee de bepalende factor in de economische haalbaarheid voor het toepassen van nanofiltratie als RWZI effluent behandelingstechniek.

Dankwoord

Dankwoord

De allerlaatste pagina's van het proefschrift. Het werk is af, mijn vier jaar als promovendus in Leeuwarden zitten erop en ik wacht op het "Hora Est". Het dankwoord, waar te beginnen. Dit proefschrift draagt dan wel mijn naam maar zonder de hulp van vele mensen om mij heen was dit resultaat er niet gekomen.

Ten eerste dank ik Marcel Mulder die mij binnenhaalde binnen zijn jonge groep promovendi (Ronald en Ellen) in Leeuwarden. Ondanks dat ik Marcel niet lang heb mogen meemaken, ben ik blij dat ik deze markante en enthousiasmerende persoonlijkheid nog heb leren kennen.

In Leeuwarden leerde ik mijn collega's van het eerste uur kennen: Ronald, Ellen en later Win. Samen hebben we er een erg plezierige en memorabele periode van gemaakt.

Een speciaal woord van dank naar het management team in Enschede. Matthias en Greet, in de onzekere periode na het wegvallen van Marcel hebben jullie ons goed opgevangen en in het voorjaar van 2003 een begeleider uit duizenden uit de hoge hoed getoverd in de vorm van Arie.

Arie het was fijn om je als begeleider te hebben. Bedankt voor je scherpe kritiek en je algemene betrokkenheid bij de groep.

Er is ook een grote groep mensen van het van Hall Instituut die onlosmakelijk verbonden zijn met dit proefschrift. De medewerkers van de milieuhal en technische dienst die ons hielpen met onze eerste opstellingen en analyses. Sameh, Leo, Aldert, Geert, Henk, Lolle, Jan en Johan bedankt voor alle adviezen en hulp.

In de eerste maanden van 2004 werd het duidelijk dat de groep versterkt ging worden. Met de komst van Wetsus en de aanstelling van Walter als hoogleraar kwamen er nieuwe energie, apparatuur en menskracht in het onderzoek in Leeuwarden.

Dat maakte de laatste twee jaar van het onderzoek bijzonder prettig. Aan alle Wetsianen, dank voor jullie collegialiteit en veel voorspoed in de komende jaren.

Dank aan mijn kamergenoten (Maxime, Perry, Tim, Ellen, Ronald en Paula) voor het creëren van het meest vibrerende kantoor van Wetsus.

Janneke en Naomi, bedankt voor het geduld dat jullie toonden als ik weer eens binnenkwam met een lading monsters om te laten analyseren.

Special thanks to my French trainees starting with Zélia and Christelle. The two of you initiated the start of an increasing amount of trainees of the 'Ecole Nationale Supérieure d'Ingénieurs de Limoges' visiting Wetsus each summer since 2004. Noémie thank you for your enthusiasm during your internship period, your presence was a great addition to this project and the Wetsus team in general.

Een speciaal woord van dank voor Rianne de Leeuw van het Cartesius Instituut. Rianne, bedankt voor de fijne samenwerking gedurende drie jaar van lesgeven, eerst in Franeker en daarna in Leeuwarden. Veel succes voor de toekomst!

Speciale dank voor mijn twee paranimfen. Ellen, bedankt voor je collegialiteit, het meeslepen naar Friese les en het inwijden van deze mijnbouwer in de wondere wereld van de bio-beestjes. Perry, het was fijn om de cursus aan de studenten van het Cartesius instituut aan iemand over te dragen die er net zoveel plezier aan beleeft als ik.

Nynke, mede dankzij jouw vertrouwen in mij dat "AIO-schap" wel iets voor mij was ligt er nu dit proefschrift, iets waarvoor ik heel dankbaar ben. Straks lekker op vakantie! En namens alle Wetsianen bedankt voor de Hertog en Ben&Jerry ijsjes gedurende de zomer!