

# NANOFILTRATION AS A REFINING PHASE IN SURFACE WATER TREATMENT

Riina Liikanen

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Abstract <p>The residual organic matter in conventionally treated drinking waters may be sufficient for the formation of harmful disinfection by-products, and for supporting bacterial growth in distribution networks. Thus, nanofiltration has been proposed as an option for enhancing the organic matter removal from high organic load containing source waters. Given that little is known of the success of nanofiltration in removing residual organic matter from chemically pre-treated and rather pure surface waters, further research was required. In addition, more information was needed regarding fouling, operation, cost and environmental impact of nanofiltration process as a refining phase in surface water treatment. Long-term pilot-scale studies at an operating water treatment plant as well as laboratory-scale test runs using real and model feed waters were employed to evaluate the applicability of the nanofiltration process.</p> <p>Nanofiltration resulted in high and stable removal of organic matter after conventional surface water treatment in all circumstances that were studied. However, the nanofiltered water showed surprisingly high potential for microbial growth, and contained enough microbially available carbon and phosphorus for bacterial growth. Thus, disinfection using small dosage of chlorine is recommended as a safety barrier and for suppressing microbial growth in distribution systems after nanofiltration. In the cases studied, the use of nanofiltration membranes with high organic matter, and lowered inorganic matter retention, optimally met the requirements for treated water quality, as well as for the productivity and fouling of the membranes. However, the studied pre-treated feed waters caused intense flux decline of nanofiltration membranes and required short membrane cleaning intervals at the studied operational parameters. The results of the study also indicate that most feed water constituents, organic material, inorganic precipitates and micro-organisms, affect membrane fouling. Accordingly, it seems impossible to remove the membrane fouling tendency from surface waters.</p> <p>The study supports the consideration of nanofiltration as an efficient and reliable option for improving the quality of conventionally treated surface water in varying circumstances. However, in applications not requiring substantial improvement of organic matter or ion removals other process options may be more suitable and cost effective compared to nanofiltration.</p>			
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<b>Tiivistelmä</b> Juomaveden sisältämän orgaanisen aineksen pitoisuus voi olla riittävä haitallisten desinfiointin sivutuotteiden syntymiseksi sekä tukemaan mikrobien kasvua verkostossa. Nanosuodatus on yksi vaihtoehto orgaanisen aineksen poiston tehostamiseksi, ja lisätietoja tarvittiin nanosuodatuksen tehosta poistaa orgaanista ainesta kemiallisesti esikäsitellyistä ja suhteellisen puhtaista pintavesistä. Tutkimuksessa etsittiin tietoa myös nanosuodatusprosessin tukkeutumisesta, operoinnista, kustannuksista ja ympäristövaikutuksista pintavedenkäsittelyn viimeistelevänä vaiheena. Nanosuodatusprosessin toimivuutta arvioitiin vesilaitoksella pilot-mittakaavan laitteistoilla sekä laboratoriomittakaavan kokeilla suodattaen oikeilta esikäsitelyjä vesiä ja mallivesiä.  Nanosuodatus poisti orgaanista ainesta tehokkaasti ja vakaasti esikäsitellyistä syöttövesistä kaikissa tutkituissa tilanteissa. Mikrobien kasvukyky nanosuodatetussa vedessä oli kuitenkin yllättävän korkea ja nanosuodatettu vesi sisälsi mikrobikasvulle riittävän määrän mikrobeille käyttökelpoista hiiltä ja fosforia. Nanosuodatetun veden desinfiointi pienellä klooriannoksella onkin suositeltavaa vedenlaadun varmistamiseksi sekä mikrobien verkostokasvun hillitsemiseksi. Tutkituissa tilanteissa korkean orgaanisen aineksen ja alennetun epäorgaanisen aineksen pidätyskyvyn omaavat nanosuodatuskalvot toimivat tuoteveden laatuvaatimusten sekä kalvojen tuoton ja tukkeutumisen kannalta parhaiten. Kaikki tutkitut esikäsitellyt syöttövedet aiheuttivat kuitenkin käytetyillä operaatioparametreilla merkittävän kalvojen tuoton laskun ja vaativat tiheitä kalvojen pesuvälejä. Tutkimuksen tulokset myös osoittavat, että useimmat syöttöveden ainesosat, orgaaninen aines, epäorgaaniset saostumat ja mikro-organismit, aiheuttavat kalvojen tukkeutumista. Tutkimustulosten perusteella vaikuttaakin mahdolliselta poistaa pintavesistä nanosuodatuskalvoja tukkeuttavat ainekset.  Tutkimuksen perusteella nanosuodatus parantaa perinteisin menetelmin käsitellyn pintaveden laatua tehokkaasti ja luotettavasti. Sovelluksissa, joissa ei tarvita merkittävän tehokasta orgaanisen aineksen tai ionien poistoa muiden prosessivaihtoehtojen käyttö voi olla kuitenkin tarkoituksenmukaisempaa ja edullisempää.	
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## PREFACE

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Riihimäki, October 2006

Riina Liikanen





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## LIST OF ABBREVIATIONS AND SYMBOLS

AOC	assimilable organic carbon
DBP	disinfection by-product
FTIR	Fourier transform infrared
HPC	heterotrophic plate count
HPSEC	high performance size exclusion chromatography
MFI	modified fouling index
NDP	net driving pressure
NF	nanofiltration
NOM	natural organic matter
SDI	silt density index
SEM	scanning electron microscopy
SEM-EDS	scanning electron microscopy-elementary analysis
TOC	total organic carbon
UV <sub>254</sub>	UV absorbance at wavelength of 254 nm
XPS	x-ray photoelectron spectroscopy



## LIST OF ORIGINAL PUBLICATIONS

The experimental part of this thesis is based on the following six articles, which are referred to by their roman numerals throughout the text. The author's contribution in each article is indicated.

- I Liikanen R., Yli-Kuivila J. and Laukkanen R. (2002) Efficiency of various chemical cleanings for nanofiltration membrane fouled by conventionally treated surface water, *Journal of Membrane Science*, 195, 265-276.  
*The author was responsible for planning and conducting the study. The other authors supervised the work and commented on the authors's manuscript.*
- II Liikanen R., Yli-Kuivila J., Tenhunen J. and Laukkanen R. (in press) Cost and environmental impact of nanofiltration in treating chemically pre-treated surface water, accepted for publication in *Desalination*.  
*The author's contribution was the same as in I.*
- III Liikanen R., Miettinen I. and Laukkanen R. (2003) Selection of NF membrane to improve quality of chemically treated surface water, *Water Research*, 37, 864-872.  
*The author's contribution was the same as in I.*
- IV Liikanen R., Kiuru H., Tuhkanen T. and Nyström M. (2003) Nanofiltration membrane fouling by conventionally treated surface water, *Water Science and Technology: Water Supply*, 3, 183-190  
*The author's contribution was the same as in I.*
- V Matilainen A., Liikanen R., Nyström M., Lindqvist N. and Tuhkanen T. (2004) Enhancement of natural organic matter removal from drinking water by nanofiltration, *Environmental Technology*, 25, 283-291.  
*The author was responsible for planning and conducting the pilot runs. A. Matilainen conducted the high performance size exclusion chromatography analysis and wrote the manuscript in co-operation with the author. The other authors supervised the work and commented on the manuscript.*
- VI Liikanen R., Kiuru H., Peuravuori J. and Nyström M. (2005) Nanofiltration flux, fouling and retention in filtering dilute model waters, *Desalination*, 175, 97-109.  
*The author's contribution was the same as in I.*



# 1. INTRODUCTION

## 1.1 Background

The requirement for safe and high quality drinking water supply is evident. In boreal region the high content of naturally occurring organic compounds, mainly humics, in surface waters is problematic in drinking water treatment. Generally, the conventional chemical surface water treatment cuts the level of organic matter to comply with current drinking water quality standards. However, the remaining organic matter is still sufficient for formation of toxic, carcinogenic and/or mutagenic disinfection by-products (DBP) at disinfection with chlorine. In addition, the organic matter can support bacterial growth in distribution networks.

As the knowledge of drinking water quality hazards increases and the availability of high quality source waters diminishes, the demand for more efficient water treatment processes intensifies. The quality of drinking water can be improved either by enhancing the present processes by a refining treatment phase, or by adopting totally new treatment methods. One promising option for enhanced organic matter removal from conventionally treated surface water is the introduction of nanofiltration (NF) as a refining treatment phase (Jacangelo *et al.*, 1993; Siddiqui *et al.*, 2000).

## 1.2 Research problem

The advantage of NF for improving drinking water quality has been proven in many applications. However, most studies have concentrated on the removal of organic matter from natural untreated surface waters (Amy *et al.*, 1990; Siddiqui *et al.*, 2000), ground waters (Taylor *et al.*, 1987; Amy *et al.*, 1990; Fu *et al.*, 1994; Alborzfar *et al.*, 1998) and model waters (Schäfer *et al.*, 1998) by NF, while very little is known about the success of NF in removing organic matter from chemically pre-treated and rather pure surface waters. Also, due to the lack of knowledge of operating NF process as a refining phase in surface water treatment further research was required. Generally, the fouling of NF membranes and a consequent decrease in productivity limits the applicability of the process. Thus, understanding and control of membrane fouling are crucial for a more widespread use of NF in water treatment. In addition, information is needed of the operation and costs of the process, as well as of its environmental impacts.

## 1.3 Objective

The main objective was to critically evaluate the overall applicability of the NF process as a refining surface water treatment phase. This required evaluation of the effects of NF on treated water quality, as well as a search for an economical and sustainable way to operate the NF process by varying membranes and operating parameters. The fouling and cleaning of the membranes was studied in detail in order to characterise the critical foulants in pre-treated surface water. The cost and environmental impacts of a refining NF unit were also evaluated.

#### **1.4 Research methods**

Both long-term pilot-scale studies at an operating water treatment plant and laboratory-scale test runs with real and model feed waters were used in the research. The cost and environmental impact evaluations were mainly based on the calculations made according to a pilot study.

#### **1.5 Scope**

The research focused on the evaluation of NF applied as a refining surface water treatment phase and on the optimisation of the process operation. No emphasis was placed on the membrane or process configuration development. In other words, the research was conducted from the operators' point of view, and within the commercially available NF process options.

#### **1.6 Contribution**

The results indicate that NF clearly improves the quality of chemically treated surface water. The performance and economy of the process may be enhanced by the optimal operation of the process and the right choice of membranes and cleaning chemicals. The coagulation pre-treatment of surface water was insufficient to totally limit the fouling of NF membranes. The additional cost from installation of NF to enhance conventional surface water treatment seems high, and acceptable only in cases requiring very efficient water treatment. The installation of NF also increases the adverse environmental effects of water treatment considerably and further development should be done to minimise these effects.



## 2 LITERATURE REVIEW

### 2.1 Natural organic matter and drinking water quality challenges

#### 2.1.1 Natural organic matter in drinking waters

Surface water sources used for drinking water purposes always contain dissolved natural organic matter (NOM), a complex mixture of organic compounds derived from the decay of plant and animal material. NOM can be divided into humic and non-humic fractions. The humic fraction is more hydrophobic and comprises humic and fulvic acids and the non-humic fraction is less hydrophobic in character and comprises hydrophilic acids, proteins, amino acids and carbohydrates. The character and properties of NOM in water of different origin differs considerably (Gjessing *et al.*, 1999). Particularly in the boreal region the NOM is mainly characterised by humic substances. The heterogeneous mixture of aquatic humic substances contains various aromatic and aliphatic components and carboxylic and phenolic functional groups that determine the intensity of the charge of these macromolecules. The reported molar masses of NOM vary from a few hundred to greater than 100,000 g/mol, with molar masses lower than 10,000 g/mol being most likely. (Collins *et al.*, 1986; Martin-Mousset *et al.*, 1997; Pelekani *et al.*, 1999)

NOM can adversely affect water treatment and distribution and cause several drinking water quality problems. NOM challenges the water treatment process by transporting metals and hydrophobic organic chemicals, thus making their removal difficult, as well as by reacting with disinfectants and thus increasing their demand. The major water quality concern, however, relates to residual NOM reacting with chlorine forming toxic, carcinogenic, and/or mutagenic disinfection by-products (DBPs). Halogenated trihalomethanes and haloacetic acids are two major classes of DBPs commonly found in waters disinfected with chlorine, whereas bromate ions ( $\text{BrO}_3^-$ ) form during ozonation. Concerns regarding the potential health effects of DBPs have resulted in the following maximum contaminant levels in drinking waters in the European Union region: 100  $\mu\text{g/L}$  and 10  $\mu\text{g/L}$  for total halogenated trihalomethanes and bromate ions, respectively (European drinking water directive).

Another major concern with residual NOM in drinking water is its ability to support bacterial growth in the drinking water distribution network. Bacterial growth may lead to pathogen multiplication, can cause undesirable taste, colour and odour and contributes to corrosion of pipe materials. The ability of residual NOM to support bacterial growth is connected to the biodegradable fraction of NOM. Biodegradable NOM is generally measured either as biodegradable dissolved organic carbon or as assimilable organic carbon (AOC). In natural waters biodegradable dissolved organic carbon forming compounds typically consist of large organic macromolecules such as humic and fulvic acids as well as of small organic carbon compounds (Hong and Elimelech, 1997). AOC is the most readily degradable fraction of NOM, which tends to be composed of low molar mass compounds (Hem and Efraimsson, 2001).

#### 2.1.2 Elimination of problems associated with natural organic matter in drinking waters

The removal of DBP precursors is the most common and the most effective approach to minimise the DBP formation in drinking water treatment (Clark *et al.*, 1994),

whereas disinfection by chlorine is the most common approach to guarantee the hygienic quality of drinking water and to suppress bacterial growth. The elimination of growth promoting substances from water entering the distribution system should also be considered as a way to control bacterial growth (Chandy and Angles, 2001). The nutrient limitation approach may also result in lower effective disinfectant dosages, lower DBP formation and better disinfectant permanence in the distribution network.

Recent studies have shown that if water contains high loads of NOM, as is generally the case in the boreal region, phosphorus can be, instead of organic carbon, the nutrient limiting bacterial growth in drinking water (Miettinen *et al.*, 1996; Sathasivan *et al.*, 1997; Lehtola *et al.*, 2002). In these kinds of waters the removal of phosphorus has to be considered in addition to removal of NOM to control bacterial growth.

NOM is generally removed from surface waters by conventional treatment processes consisting of coagulant addition, flocculation, sedimentation/flotation and filtration. The studies indicate that conventional coagulation processes remove high molar mass and humic NOM more efficiently than low molar mass and non-humic NOM, i.e. the share of lower molar mass and readily biodegradable NOM increases after coagulation (Collins *et al.*, 1986; Amy *et al.*, 1992; Owen D.M. *et al.*, 1995; Hem and Efraimsson, 2001; Matilainen *et al.*, 2001). Accordingly, coagulated waters often contain considerable AOC concentrations even if high removal of total NOM is seen (Miettinen *et al.*, 1996; Hu *et al.*, 1999; Volk *et al.*, 2000; Lehtola *et al.*, 2002; Liu *et al.*, 2002).

After coagulation, NOM molecules can be transformed by ozonation into lower molar mass compounds that may be less reactive with chlorine and cause less problems with colour, odour or taste, or the NOM removal can be improved by granulated activated carbon filtration or nanofiltration (NF) (Jacangelo *et al.*, 1995). The drawback of ozonation is that it actually makes NOM more biodegradable (Owen D.M. *et al.*, 1995; Lehtola *et al.*, 2002). However, especially NF has proven to be an efficient option for high NOM removal (Jacangelo *et al.*, 1995).

## **2.2 What is nanofiltration?**

### **2.2.1 Nanofiltration process**

NF is a pressure-driven process where pressure forces part of feed water through a semi-permeable membrane (Figure 1). The filtered product water is called permeate. Retentate, the part of the water stream that does not pass through the membrane, contains a concentrated amount of feed water constituents that cannot pass through the membrane.

Membranes used in drinking water treatment are usually made of multiple-layer thin-film composites of polymers (Taylor and Jacobs, 1996). Membrane surface materials like cellulose acetates or polyamides give a negative charge to most commercial NF membranes. Polyamide membranes have higher permeabilities and better chemical tolerance than cellulose acetate membranes, which, in turn, have a low price and a low fouling tendency (Thorsen, 1999). Generally the NF plants used for drinking water treatment are designed for a five-year membrane life-time, but in Norwegian applications cellulose acetate membranes have been used for more than nine years (Ødegaard *et al.*, 2000).

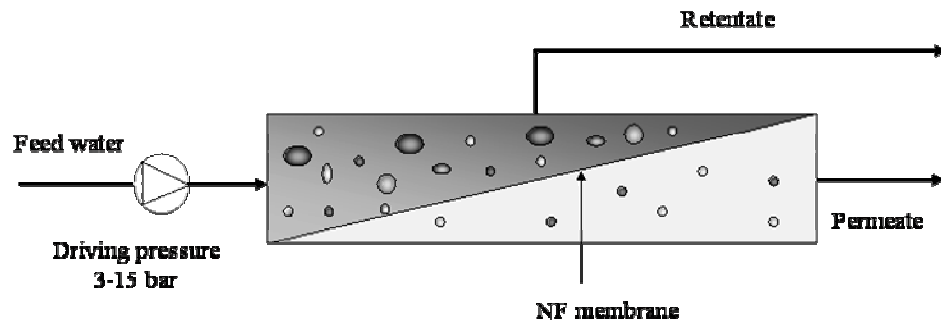


Figure 1. Principle of nanofiltration.

In drinking water treatment, NF membranes are generally packed as cylindrical spiral-wound modules (Figure 2), where feed/retentate water flows from one end of the module to another in feed spacers parallel to the membrane surface. In one module 10-15% of the feed water passes through the membrane leafs into the permeate spacer. The permeate spacer collects the permeate into a tube in the middle of the membrane module for discharge at the end of the module.

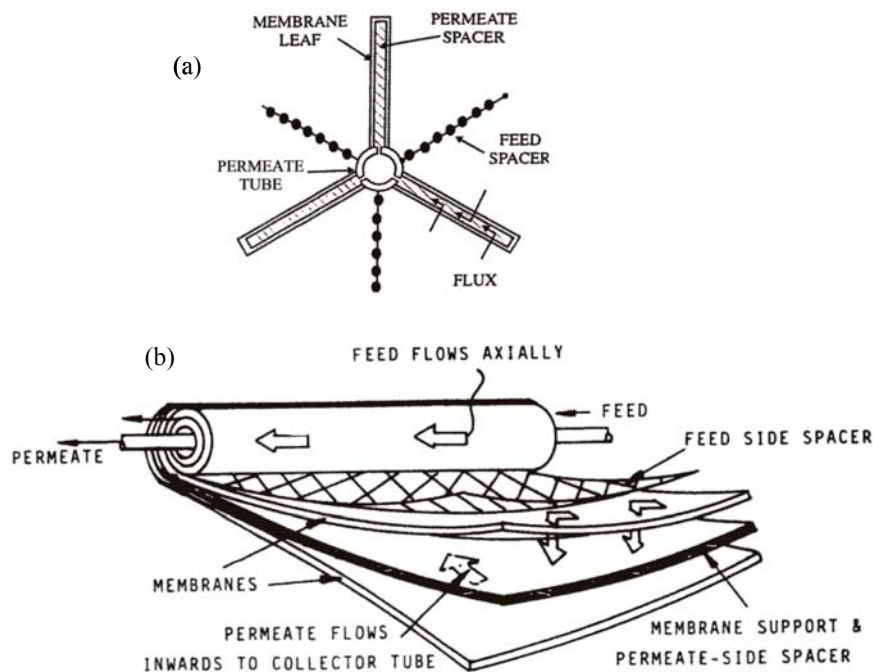


Figure 2. Basic elements (a), structure and flow paths (b) of spiral-wound membrane module (Fane, 2005).

Membrane modules are housed in cylindrical pressure vessels where several modules, generally six, are installed in series. The recovery of the NF process can be increased up to 90% by installing pressure vessels in several stages, generally as a tapered cascade (Figure 3). Retentate from the previous module or stage serves as the feed water for the next.

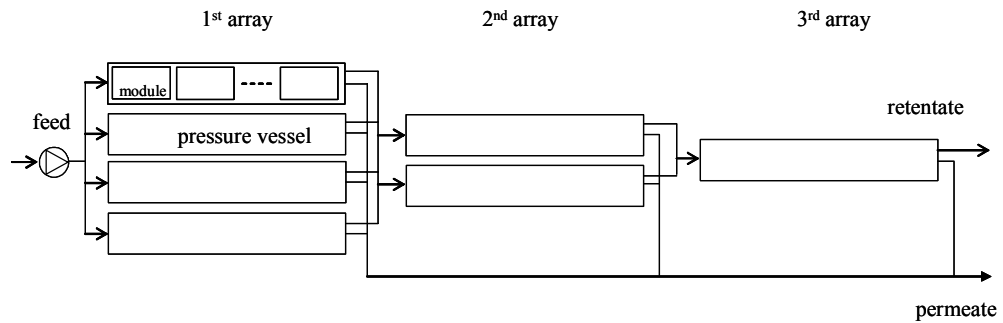


Figure 3. Typical module arrangement of NF process.

The operation of the NF process is controlled by the net driving pressure (NDP), the efficient pressure forcing the water through the membrane, by the recovery, a ratio of permeate flow to feed flow and by the feed flow rate. NDP, recovery, flow rate, membrane characteristics and feed water characteristics altogether affect flux (permeate flow per membrane area) and permeability (flux per applied NDP) of the membrane. The operation of the spiral-wound NF modules should be optimised considering the following constraints: Minimum feed flow to prevent concentration polarisation, maximum recovery and flux rate to prevent membrane fouling and maximum feed flow to prevent damaging high axial pressure drops (Wittman and Thorsen, 2005).

In Norway, the NF plants used for NOM removal are operated at pressures of 3-5 bar and recoveries are kept between 70-80%, since higher recoveries would result in decreased NOM removals (Ødegaard *et al.*, 2000). Fluxes not higher than 12-18 L/(m<sup>2</sup> h) are reported to result in stable operation of the NF process (Ødegaard *et al.*, 2000). At the Méry-sur-Oise NF plant in the suburbs of Paris the NF process is used as a refining phase in treating polluted river water (Ventresque *et al.*, 2000). There the recovery of the process is held steadily at 85% and the permeability of 6.0 L/(m<sup>2</sup> h bar) remains stable for 10-15 months.

The entire NF process consists of a pre-treatment unit for foulant removal from feed water, an NF unit, a cleaning unit for NF membranes, a retentate and cleaning solutions treatment unit and an NF permeate post-treatment unit (Figure 4). The unit operations are discussed in greater detail in the following chapters.

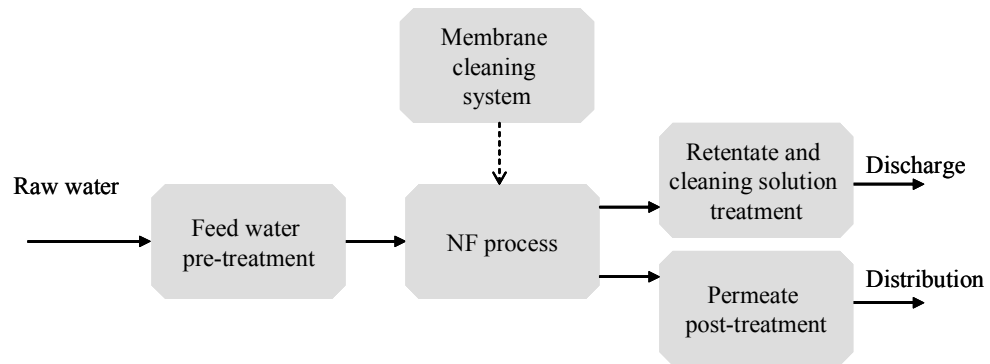


Figure 4. Schematic view of entire NF process.

### 2.2.2 Retention of nanofiltration membranes

According to their characteristics, NF membranes are effective in retaining particulate matter, dissolved organic matter, multivalent ions, bacteria, parasites, algae and viruses. Depending on the spaces in the membrane through which the molecules pass, the NF membranes retain material bigger than 1 nm in diameter or 200-1000 g/mol of molar mass (Taylor and Jacobs, 1996; AWWA M46, 1999). However, in NF the retention not only depends on the sieving effect, but also on charge and hydrophobicity interactions between the membrane and the compounds (Wiesner and Buckley, 1996). Differences in the diffusivity of feed water constituents and in the molecule configuration, as well as the electrostatic equilibrium across the membrane, also affect retention (Wiesner and Buckley, 1996).

Feed water constituents bigger than the membrane cut-off are retained mainly by a sieving mechanism while charge repulsion and diffusion are more important for small molecules (Van der Bruggen *et al.*, 1999). NF membranes also show selectivity based on the charge densities of the ions (Linde and Jönsson, 1995), a phenomena known as the Donnan effect. In maintaining the electrostatic equilibrium across the membrane, this Donnan effect can even lead to negative retention of less charged ions that pass the membrane easily. The importance of the different retention mechanisms depends on the molecule and membrane characteristics and higher or lower retentions can be obtained than expected according to molecular sizes (Fu *et al.*, 1994; Van der Bruggen *et al.*, 1999).

### 2.3 Quality of nanofiltered water

In addition to organic matter removal, NF applications in drinking water treatment include disinfection, softening of hard waters (Duran and Dunkelberger, 1995), removal of pesticides (Agbekodo *et al.*, 1996b), heavy metals (Linde and Jönsson, 1995) and nitrate (Santafé-Moros *et al.*, 2005) from polluted sources, as well as uranium (Raff and Wilken, 1999), arsenic (Vrijenhoek and Waypa, 2000) and fluoride (Härmä, 1999). NF has been proved efficient technique also in the removal of cyanotoxins (Gijbertsen-Abrahamse *et al.*, 2006) and recently emerged endocrine disrupting compounds, pharmaceuticals and personal care products (Yoon *et al.*, 2006).

### 2.3.1 Removal of organic matter by nanofiltration

NF has proved to be reliable and efficient in removing NOM from water sources with different characteristics: dissolved organic carbon removals between 51-98% (Taylor *et al.*, 1987; Amy *et al.*, 1990; Tan and Amy, 1991; Fu *et al.*, 1994; Alborzfar *et al.*, 1998; Siddiqui *et al.*, 2000; Ventresque *et al.*, 2000) have been reported. The efficiency of organic matter removal in NF varies between different source waters, different membranes and different operating conditions.

DBP precursor removals as high as 98% have been achieved by NF (Amy *et al.*, 1990; Tan and Amy, 1991; Blau *et al.*, 1992; Visvanathan *et al.*, 1998; Siddiqui *et al.*, 2000), indicating the potential of NF in controlling DBPs in treated water. However, several studies have indicated that the high removals of NOM coupled with low removals of bromide ion result in a considerable formation of brominated trihalomethane and haloacetic acid species in NF treated waters upon chlorination (Lainé *et al.*, 1993; Chellam, 2000; Siddiqui *et al.*, 2000). Thus, when treating bromide containing waters NF membranes with sufficient bromide removal capacity (membrane cut-offs 200-300 g/mol) should be used (Lainé *et al.*, 1993).

High reported removals of biodegradable dissolved organic carbon by NF (73-97%) (Escobar and Randall 1999; Laurent *et al.*, 1999; Escobar *et al.*, 2000) suggest that nutrient deprivation limits bacterial growth in NF permeate. On the contrary, Escobar and Randall (1999) and Escobar *et al.* (2000) reported rather insignificant removal of AOC by NF. Poor AOC removal is supported by the fact that the NF membranes efficiently retain high and moderate molar mass fractions of NOM, while the fraction with a molar mass smaller than 500 g/mol is only slightly retained (Amy *et al.*, 1990; Van der Bruggen *et al.*, 1999; Ozaki and Li, 2002). Also, the NOM characterisation of an NF permeate indicated the presence of AOC forming compounds in the permeate: NOM consisted of amino acids (60%), sugars (18%), formaldehyde and acetaldehyde (7%) and other identified low molar mass organic matter (15%) (Agbekodo *et al.*, 1996a).

Despite the efficient NOM removal in NF the permeate may contain a sufficient concentration of organic material to support bacterial growth. However, Laurent *et al.* (1999) found that on the real distribution network fed by a mixture of 80% NF permeate and 20 % granulated activated carbon filtrate, chlorination dosages could be reduced and a low level of chlorine residual stayed constant even in the areas of long residence times. The stability of the chlorine residual suggests that NF lessened the chlorine demand of treated water due to high NOM removal. The experiments of Sibille *et al.* (1997) with a previously colonised experimental distribution network suggest that the introduction of NF permeate to an existing distribution network does not prevent the colonisation of the distribution system, but the bacterial growth in the distributed water remains very low.

### 2.3.2 Post-treatment of nanofiltration permeate

The ability of NF membranes to retain hardness causing cations is generally undesirable in applications treating soft waters. In these conditions, permeate remineralisation (Alborzfar *et al.*, 1998; Ødegaard *et al.*, 1999), use of NF membranes designed for high organic matter and low inorganic matter retention (Ikeda *et al.*, 1988; Ventresque *et al.*, 1997) or mixing of NF permeate and less treated water (Laurent *et*

*et al.*, 1999) are the solutions to produce chemically stable, non-corrosive water. In the case of mixing NF permeate with clarified water from coagulation treatment, the hygienic quality of the blending water has to be secured (Glucina *et al.*, 2000; Ventresque *et al.*, 2000). The disinfection of NF permeate either by chlorination or by UV-irradiation is also recommended as a safety precursor (Ødegaard *et al.*, 1999; Ventresque *et al.*, 2000).

In applications where NF is used as a barrier against pathogens the performance of the process fails if the integrity of the membranes is compromised. Thus, the membrane integrity monitoring must be applied to detect potential breakthrough of microbes. On line integrity monitoring for NF systems may include sulphate ion detection (Ventresque *et al.*, 2000) or UV absorbance analysis either for organic components or by using dye challenge (Chapman Wilbert and Linton, 2001; Kruithof *et al.*, 2001). Vacuum tests for integrity check are recommended before installation of the membranes (Kruithof *et al.*, 2001).

## **2.4 Fouling of nanofiltration membranes**

In addition to the ability of the NF membranes to retain the required constituents, their operational performance, i.e. flux, fouling tendency and durability are important. In an optimal case, a membrane is capable of retaining a stable and high flux for long periods. Membrane fouling increases operational costs due to the requirement of higher pumping energy to produce equal treated water flow, need for more frequent membrane cleanings and shorter membrane life-time.

Fouling of the NF membranes depends on the foulant - membrane and foulant - foulant interactions. These interactions are controlled by the chemical characteristics of foulants and membranes, solution chemistry, operational environment, permeation drag force and cross flow shear.

### **2.4.1 Foulants**

A wide spectrum of feed water constituents, e.g. dissolved macromolecular organic compounds, weakly soluble inorganic compounds, colloidal and suspended particles and micro-organisms contribute to membrane fouling. Several studies have demonstrated that organic matter plays an important role in membrane fouling in water treatment applications (Childress and Elimelech, 1996; Hong and Elimelech, 1997; Alborzfar *et al.*, 1998; Schäfer *et al.*, 1998; Her *et al.*, 2000). However, the roles of organic matter adsorption, inorganic precipitation and biological growth in membrane fouling vary from application to application (Alborzfar *et al.*, 1998; Speth *et al.*, 1998; Kaiya *et al.*, 2000; Her *et al.*, 2001). The findings of Vrouwenvelder and van der Kooij (2001) indicated that many of the studied NF plants suffered from biofouling, and that highest membrane flux declines were related to severe biofouling.

The characteristics of both organic matter and the NF membrane strongly affect the adsorption tendency of organic matter on a membrane. The high molar mass and hydrophobic fractions of NOM have generally been found to be mostly responsible for NF membrane fouling (Childress and Elimelech, 1996; Nilson and DiGiano, 1996; Hong and Elimelech, 1997; Schäfer *et al.*, 1998; Violleau *et al.*, 2005), but in some applications also the role of hydrophilic NOM may be important (Amy and Cho, 1999).

The best and the most reliable method for foulant identification is the analysis of the foulants accumulated on the membrane. This method, however, requires membrane autopsies which are destructive, expensive and difficult to conduct. Thus, other sources of information are generally used to identify possible foulants. The knowledge of the feed water source is often enough to make a good guess about the type of fouling that is likely to occur, but a thorough feed water analysis gives better tools for foulant identification. Analysis of the material accumulated on the pre-filters can be of considerable help in determining what may foul the system: Deposits of organic matter, metals, silica or biomass indicate the probable membrane foulants. (Graham *et al.*, 1989)

#### **2.4.2 Effect of operational environment on fouling**

The operational environment during NF affects the charge and other characteristics of the membrane and the fouling material, and thus membrane fouling. Several studies indicate that the fouling of polymer membranes decreases at higher pH and low salt content of the feed water (Nyström *et al.*, 1995; Childress and Elimelech, 1996; Braghetta *et al.*, 1997; Hong and Elimelech, 1997) due to an increased negative charge of both membrane and organic matter and the consequent increase in mutual electrostatic repulsion. The increased charge also increases the repulsive forces between the functional groups of the NOM molecules making their appearance more stretched and linear, and consequently the fouling layer becomes more permeable (Childress and Elimelech, 1996; Braghetta *et al.*, 1998; Hong and Elimelech, 1997). In addition, membranes become more open as increased internal electrostatic charge repulsion increases the pore volume. Increasing pH also makes the humic substances more hydrophilic and thus less prone to attach on the membrane.

The adsorption of organic matter on the membrane surfaces increases in the presence of divalent cations (Hong and Elimelech, 1997; Schäfer *et al.*, 1998; Zander and Curry, 2001; Seidel and Elimelech, 2002; Li and Elimelech, 2005). Divalent cations act as bridges between the membrane surface and the free negatively charged functional groups of organic matter, and also between the free functional groups of organic matter (Hong and Elimelech, 1997; Yoon *et al.*, 1998). This leads to a formation of dense foulant layers that have been observed to cause higher flux decline than higher deposition of looser foulant material (Schäfer *et al.*, 1998).

#### **2.4.3 Effect of operating parameters on fouling**

In addition to characteristics of feed water, membrane, module and operating parameters affect the solution chemistry on the membrane surface, and consequently membrane flux decline, fouling and reversibility of fouling. Concentration polarisation, i.e. concentration of feed water constituents unable to pass through the membrane on the feed stream close to the membrane surface, may reduce membrane flux and lead to membrane fouling. High cross flow on the membrane surface has been observed to reduce concentration polarisation and membrane flux decline (Mänttari *et al.*, 1997; Alborzfar *et al.*, 1998; Braghetta *et al.*, 1998; Seidel and Elimelech, 2002) by enhancing foulant transport away from the membrane surface. Process operation and module design that decrease concentration polarisation on the membrane surface can be used in fouling mitigation of NF (Al-Bastaki and Abbas, 1999; Vrijenhoek *et al.*, 2001). Low operating pressures and low fluxes also reduce membrane flux decline (Alborzfar *et al.*, 1998) by decreasing the permeation drag through the membrane, and



consequently the contacts between fouling material and membrane (Hong and Elimelech, 1997; Seidel and Elimelech, 2002).

#### **2.4.4 Effect of membrane characteristics on fouling**

Studies indicate that a rough membrane surface (Zhu and Elimelech, 1997; Hobbs *et al.*, 2001; Boussu *et al.*, 2006), a low membrane surface charge (Hobbs *et al.*, 2001; Boussu *et al.*, 2006) and a high membrane hydrophobicity (Zander and Curry, 2001; Mänttari *et al.* 2002a; Boussu *et al.*, 2006) generally increase membrane fouling.

When considering the membrane characteristics one should bear in mind that operation, mainly fouling and cleaning, affects the membrane and may cause considerable changes in flux and retention with time (Childress and Elimelech, 1996; Yoon *et al.*, 1998; Schäfer *et al.*, 2000a). A fouled membrane may, for example, become more or less charged as the membrane surface is coated by foulants with higher or lower charge than a clean membrane surface (Childress and Elimelech, 1996; Cho *et al.*, 1998; Yoon *et al.*, 1998; Amy and Cho, 1999; Childress and Elimelech, 2000; Shim *et al.*, 2001; Xu *et al.*, 2006).

## **2.5 Nanofiltration feed water pre-treatment**

Efficient control of NF membrane fouling generally requires pre-treatment in order to lower the fouling tendency of the feed water. In surface water applications microfiltration and ultrafiltration have proved to be very efficient pre-treatments for NF processes (Chellam *et al.*, 1997; Lozier *et al.*, 1997; Glucina *et al.*, 2000), but a conventional chemical treatment also improves NF performance (Glucina *et al.*, 2000; Schäfer *et al.*, 2000b; Ventresque *et al.*, 2000). In an existing surface water treatment plant the present chemical water treatment process is the most probable pre-treatment option.

Cartridge filters with pore sizes ranging from 5-50  $\mu\text{m}$  are almost always installed to precede the NF unit (AWWA M46, 1999; Ventresque *et al.*, 2000; Ødegaard *et al.*, 2000). The purpose of these pre-filters is to guard the susceptible membrane modules and membranes against clogging by particles.

Due to the complexity of the membrane and feed water interactions, water quality parameters such as turbidity, total organic carbon (TOC) content and particle count do not necessarily give much information about the fouling tendency of a given water. Specific fouling indices, the silt density index (SDI) and the modified fouling index (MFI), can be used to evaluate the membrane fouling tendency and the need for pre-treatment of the given water more accurately (Schippers and Verdouw, 1980; Taylor and Jacobs, 1996; ASTM D 4189-95, 1997).

It has been proposed that SDI values smaller than 5 and MFI values smaller than 10  $\text{s/L}^2$  are low enough for NF feed waters (Taylor and Jacobs, 1996). MFI values have been observed to predict membrane fouling more precisely than SDI values, although both values are only rough estimates about the fouling tendency of the water (Reiss and Taylor, 1995; Taylor and Jacobs, 1996; Chellam *et al.*, 1997). At some plants, automatic SDI and MFI analysators are used to monitor the quality of water feeding the NF or RO treatment unit. Since biofouling seems to be a general problem in NF

plants (Vrouwenvelder and van der Kooij, 2001), analysing the biofilm formation rate of the feed water is also advisable when evaluating the membrane fouling tendency.

## 2.6 Cleaning of nanofiltration membranes

Adequate pre-treatment, membrane and module selection and optimal operation conditions may slow down fouling, but the membranes eventually become fouled. Membrane fouling may first require the application of increased feed pressure to maintain a constant permeate flow rate through the membrane, but at some stage the membranes have to be cleaned to maintain the production capacity of the plant. Therefore, membrane cleaning has an essential role in maintaining the performance of the membrane process.

According to general guidelines, NF membranes should be cleaned in any of the following cases: when there is a 10% drop in the normalised permeate flow, when the salt content of the permeate increases by 10% or when the NDP increases by 15% from the reference conditions (AWWA M46, 1999). The cleaning interval of the NF membranes is strongly site-specific ranging from days to months in drinking water applications. To prevent the accumulation of an irremovable foulant layer on the membranes, it is advisable to clean the membranes routinely after a certain period of operation, even if no above mentioned condition has been realised (Peplow and Vernon, 1987).

Chemical cleaning is the most common method of NF membrane cleaning. The cleaning procedure should be effective against the foulants and in restoring the membrane flux, as well as in maintaining membrane retention characteristics. The choice of the cleaning agents and conditions depends not only on the type of foulants, but also on the chemical and thermal resistance of the membrane, the module and the rest of the equipment (Mulder, 1998). Other aspects of chemical cleaning concern mainly temperature, concentration and pH of the cleaning solution, pressure, flow and cleaning time (Trägårdh, 1989; Krack, 1995).

### 2.6.1 Cleaning agents

Different cleaning agents are used to attack different foulants. Alkaline cleaners are generally effective in removing biofilms, colloidal silts and organic foulants, whereas acidic cleaners are used to dissolve inorganic precipitates from the membranes (Trägårdh, 1989; Anselme and Jacobs, 1996). Surfactants and detergents, generally combined with chelating agents, are used to lower the surface tension and adsorption forces of the foulants, to disrupt foulant layer structure and to make complexes of metals and calcium (Trägårdh, 1989; Anselme and Jacobs, 1996). Enzymatic cleaners are able to react with specific protein and lipid foulants by disrupting their structure (Trägårdh, 1989; Muñoz-Aguado *et al.*, 1996).

Disinfectants are needed to kill and remove micro-organisms from the membrane modules and to prevent biofouling resulting from attachment of micro-organisms on membrane modules (Trägårdh, 1989). In controlling biofouling it is more important to apply chemicals capable of removing biomass than to kill the micro-organisms in it (Flemming *et al.*, 1997; Vrouwenvelder and van der Kooij, 2001). Also, a disinfection of the permeate side of the module should be performed (Vrouwenvelder and van der Kooij, 2001). Chlorine-based disinfectants are not recommended for most polymeric

membranes, but peracetic acid based products are compatible with nearly all membranes (Krack, 1995). Sensitive membranes can be disinfected with nonoxidising chemicals such as formaldehyde, sodium bisulfite, EDTA and benzoic acid (Ridgway and Flemming, 1996).

For some fouling layers it is necessary to apply different chemicals after one another in order to obtain satisfactory cleaning results. Variations in effectiveness of cleaning can be achieved by altering the formulation of the cleaning solution, the frequency of cleaning and the cleaning protocol. For example, in the Norwegian NF applications for NOM removal the cleaning protocol generally includes daily cleaning with disinfecting solution and a more thorough cleaning carried out a couple of times a year (Ødegaard *et al.*, 2000). Both cleaning solutions are typically alkaline, but the compositions are different and vary from application to application.

The selection of the appropriate agent for a particular cleaning situation is critical. Fu *et al.* (1994) observed that two NF membranes with different characteristics required different cleaning procedures even when fed by the same feed water. Thus, the characteristics of the membranes affected the characteristics of the foulant layer. Some cleaning agent-membrane combinations are incompatible, and will result in irreversible loss of flux or retention. In addition, the use of non-optimal cleaning agents and conditions incurs unnecessary costs through over-use of chemicals or through shortening the membrane life-time.

### **2.6.2 Cleaning procedures**

The findings of Bartlett *et al.* (1995) suggest that there is a certain cleaning agent concentration and temperature for optimal cleaning. Generally, increased temperatures also increase the cleaning efficiency. However, the sensitivity of membrane materials usually prohibits the use of high temperatures. An increased cross flow of the cleaning agent on the other hand seems to have no effect on cleaning performance, and increasing the trans-membrane pressure may even decrease cleaning efficiency (Bartlett *et al.*, 1995).

The time required for efficient cleaning varies depending on the foulant, membrane and cleaning procedure applied. In a study conducted by Pontié *et al.* (1997) it was found that a cleaning for 5 minutes was sufficient to restore the initial permeability of the ultrafiltration membrane, but the streaming potential measurement indicated that 20 minutes was required to recover the membrane characteristics. In the study of Nyström and Zhu (1997), however, even a cleaning for 30 minutes was insufficient to restore the membrane characteristics according to streaming potential measurements.

Membrane cleaning generally includes two main stages: rinsing and chemical cleaning. The first rinsing phase is conducted to displace the feed water by clean water, and to remove as much as possible of the deposited layer from the membrane surfaces (Kulozik, 1995). Cleaning solutions are introduced gradually to the system under recirculating conditions. After cleaning, the cleaning agents are removed by rinsing with clean water (Kulozik, 1995). Membrane manufacturers generally recommend the use of high quality water, such as filtered and demineralised water for cleaning solutions and for rinsing. Any impurities contained in cleaning solution or in rinsing water may block the membranes rather than clean them, or at least can adversely affect the cleaning efficiency (Krack, 1995; Tran-Ha and Wiley, 1998).

In order to evaluate the cleaning performance, the characteristics of the cleaned membranes have to be compared with some reference state, e.g. to the characteristics of the new, pre-cleaned membranes. The main argument of membrane cleanliness is the pure water flux. Pure water flux is measured at defined operation conditions, i.e. pressure, temperature and feed water cross flow, before and after cleaning, and compared with the reference values of clean membranes (Trägårdh, 1989; Howell, 1993). In order to get a wider perspective of the cleaning performance, flux measurements can be complemented with other measurements such as streaming potential measurement (Nyström and Zhu, 1997; Pontié *et al.*, 1997), cleaning solution analysis (Graham *et al.*, 1989) or even microscopic analysis (Trägårdh, 1989).

The disposal of the used cleaning solutions and the rinsing water has to be solved as a part of the membrane cleaning procedure. The treatment of cleaning disposals depends on the volume of the solutions produced and the chemicals used. On-site treatment requires the implementation of complex treatment lines, the complexity of which depends on the chemicals used. On-site treatment is sensible only when the volume of the disposals generated is big enough. The problem with off-site treatment may be the cost of transportation to a municipal wastewater main or treatment plant. (Anselme and Jacobs, 1996)

## 2.7 Nanofiltration retentate discharge

The disposal of the retentate stream is an integral part of the NF process. The characteristics of the retentate reflect the characteristics of the source water, but the pre-treatment and the recovery of the system also affect the retentate quality considerably. The retentate disposal methods include direct disposal to receiving water, disposal to receiving water after treatment, disposal to wastewater treatment system or reuse as irrigation water (Squire, 2000; Nederlof *et al.*, 2005). Solutions are site-specific and depend on the quality and volume of the retentate, availability of the receiving site, dilution factors, regulatory requirements, public acceptance and cost of discharge (Squire, 2000). In the Méry-sur-Oise water treatment plant in the Paris suburbs, the retentate stream has a negligible environmental effect and therefore discharge into the local river is possible (Ventresque *et al.* 1997). Cleaning solutions are also discharged into the river after neutralisation. The experiences in the Netherlands, in turn, suggest that the retentate disposal may become a true problem hindering the use of membrane processes in the areas without suitable receiving waters (Nederlof *et al.*, 2005).

## 2.8 Cost of nanofiltration

The high expected overall cost of the NF process is one of the main barriers that arise when NF is considered as a water treatment option. Despite the lack of comprehensive data from the operating NF water treatment plants, some knowledge about the costs can be obtained from studies based on both data collected from the real operating plants (Bergman, 1996; Elarde and Bergman, 2001), and on pilot-scale operational data complemented with empirical cost calculations (Pickering and Wiesner, 1993; Wiesner *et al.*, 1994; Owen G. *et al.*, 1995; Chellam *et al.*, 1998).

The cost of the NF process is largely a function of the membrane flux: a higher flux corresponds to higher pressures and higher energy consumption, smaller required membrane area, less membrane modules and less associated equipment. Thus, the

estimates of the NF process cost require accurate flux estimates for specific application from pilot tests. Both Wiesner *et al.* (1994) and Chellam *et al.* (1998) observed that the cost of NF was extremely sensitive to the changes of flux, but the recovery had a relatively small effect on the cost of NF.

The cost of membrane modules is proportional to the design capacity and flux of the membrane plant, but the data collected from the real operating plants indicate that the other components of investment costs have a significant economy of scale (Bergman, 1996; Elarde and Bergman, 2001). The proportion of the membrane-related investment costs has been reported to be 20-30% of the total investment costs at smaller plants (plant capacity 4,000-8,000 m<sup>3</sup>/d), and the proportion increases to near 50% as the plant size increases (plant capacity 53,000-125,000 m<sup>3</sup>/d) (Bergman, 1996; Elarde and Bergman, 2001). To conclude, the membrane module cost becomes a more important factor of cost and smaller economy of scale is realised at larger plants (Bergman, 1996; Elarde and Bergman, 2001).

Operation and maintenance costs of a membrane plant can be separated into fixed and variable costs (Bergman, 1996). Fixed costs include labour and general maintenance that are not dependent on plant operation, whereas variable costs vary proportionally with plant production and include energy, pre-filter replacements, chemicals and retentate treatment. Membrane replacement, which is generally a major factor of the operation and maintenance costs (Bergman, 1996) can be classified as fixed costs, if the membranes are replaced according to a certain fixed schedule or as variable costs, if the membranes are replaced according to need.

In some cases the cost of membrane treatment can be lowered by mixing membrane filtered water with less treated water to produce drinking water for distribution. The degree of possible blending is controlled by the required quality of treated water and the quality of less treated blending water. The plant operation rate also affects the cost of membrane treatment. The operation rate should be as high as possible to minimise the effect of amortised annual investment costs and fixed operation and maintenance costs that are not influenced by the operation rate.

Studies indicate that NF may be economically competitive with other treatment options mostly at small water treatment plants with a low capacity (Wiesner *et al.*, 1994; Chellam *et al.*, 1998). The cost estimates of Wiesner *et al.* (1994) suggest that NF is more cost effective in enhancing DBP removal after conventional treatment than ozonation and granulated activated carbon adsorption at least at facilities with capacities lower than 80,000 m<sup>3</sup>/d. Pianta *et al.* (2000), in turn, suggested that treatment of karstic spring water with a combination of microfiltration or ultrafiltration and NF is approximately twice the cost of conventional treatment with ultrafiltration and powdered activated carbon.

## **2.9 Evaluation of nanofiltration performance**

When the degree of chemical complexity of feed water constituents is combined with the aspects of the membrane characteristics and the filtration process it is very difficult to predict NF performance. Several mathematical models have been developed to simulate the performance of the NF process (Bowen and Mukhtar, 1996; Van der Meer and van Dijk, 1997; Wang *et al.*, 1997; Tay *et al.*, 2002; Shetty and Chellam, 2003; Shetty *et al.*, 2003; Peng *et al.*, 2004). However, pilot studies with real feed waters are required to verify the quality of the treated water, to identify the optimal process

parameters, to evaluate different membranes, and as a whole to establish design criteria for full-scale plants. The study by Mulford *et al.* (1999) indicated that the performance of pilot-scale NF plants predicted the performance of a full-scale plant well. However, not all studies have produced such a good correlation (Hobbs *et al.*, 2001), and emphasis must be put on proper design of pilot tests. Laboratory-scale batch tests with simplified membrane apparatuses can be used for rapid pre-evaluation of the process suitability and performance at a relatively low cost (Allegier and Summers, 1995; DiGiano *et al.*, 2000).

## 3 MATERIALS AND METHODS

### 3.1 Outline of experimental procedures

In the first part of the research, the operation of a pilot-scale NF process was studied as a refining phase in a real surface water treatment plant. Different operational parameters, cleaning procedures and NF membranes were tested for optimal operation of the NF process. Permeate qualities, permeabilities, fluxes, flux declines and durability of the NF membranes as well as cleaning efficiencies and membrane foulants were evaluated.

In the second part of the study, a closer look at the membrane fouling was taken in the laboratory-scale NF process. Both real pre-treated surface waters and model waters were used as NF feed waters for different membranes. The effect of feed water characteristics was evaluated for permeate quality, permeabilities, fluxes and flux declines of the NF membranes and foulants deposited on the membranes.

The experimental procedures are summarised in the following chapters, and a more detailed description of the experiments is found in the corresponding articles.

#### 3.1.1 Pilot-scale studies (I, II, III)

The performance of NF as a refining phase in surface water treatment was studied with two parallel NF pilots (Figure 5) using the same NF membrane during a one-year pilot-scale study at a real surface water treatment plant between August 1999 and September 2000. In the beginning of the study, new unused NF membranes were run with NF permeate until the membrane flux stabilised.

The pure water fluxes of the NF membranes were measured with permeate water using 5 bar NDP and 50% recovery at 20°C at different phases during the one-year study. The pure water fluxes of fouled and cleaned NF membranes were compared with the pure water fluxes of unused membranes in order to evaluate the membrane fouling and the effectiveness of cleanings, as well as the membrane wear during the study.

During the first four months of the one-year study the efficiency and effects of different cleaning chemicals and procedures were evaluated with one NF membrane (I). In this cleaning comparison study, the fouled membranes were cleaned weekly with different alkaline and acidic chemicals at different combinations. Each cleaning was performed twice, once with the both running NF pilots. After all cleanings, care was taken to ensure the standard membrane condition before the following test run. Fouling of the membranes was assured by heavily loaded operation of the pilot processes (NDP = 7.3 bar, recovery = 80%, cross flow = 1.3 m<sup>3</sup>/h). Cleaning efficiencies of the tested chemicals were compared in terms of flux recoveries and foulant removals.

In the following phases of the one-year study the membranes were cleaned with a well performing cleaning found in the comparison study: An acidic cleaning phase with 0.8% citric acid and 0.1% oxalic acid was followed by an alkaline cleaning solution of 0.2% Na<sub>4</sub>EDTA and 0.1% Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub>. The cleaning solutions were made of permeate water, the cleaning time with each solution was 30 minutes and membranes were rinsed carefully with permeate after application of each cleaning solution.

Driving pressures ranging from 4 to 7 bar were compared at 12% and 18% recoveries per membrane module (corresponds to 40% and 55% pilot-scale recoveries, respectively) at the parallel NF pilots during cold feed water temperature ( $T=0.5-1.0^{\circ}\text{C}$ ) in the operation optimisation study (II). The cost and environmental impacts of NF installed to enhance the conventional surface water treatment was calculated based on these experiments (II).

In addition to cleanings and operating parameters, some other aspects of the NF process were studied during the one-year pilot study, but these tests are not presented here. However, retentions and permeabilities of the membranes are presented for the whole one-year experiment to give a more reliable picture of the long-term performance of the process. These results are referred to as 'one-year' in the text.

Six different NF membranes were compared with regard to improving the quality of real chemically pre-treated surface water in the membrane comparison study (III). The tested membranes were operated for 136-142 hours with two membranes being run in parallel in a pilot-scale NF process. During the experiments the NDP and recovery were kept constant at 3.5 bar and 15%, respectively, or as close to these parameters as each situation allowed. The performance of the membranes was evaluated by the quality of permeates and by membrane fluxes and fouling.

### **3.1.2 Laboratory-scale studies (IV, V, VI)**

The permeate quality, permeabilities, fluxes and flux declines of different NF membranes as well as membrane foulants were studied with different real pre-treated surface waters with the laboratory-scale NF pilot (Figure 6) (IV, V). Three different NF membranes were compared at parallel flat-sheet modules when filtering the same feed water. With all the tested feed waters the NF process was operated in a retentate circulation mode until 60 litres of permeate was produced as a sum of all the membrane modules. The process parameters were kept constant in the different test runs (cross flow velocity = 0.65 m/s, NDP = 10 bar,  $T = 20^{\circ}\text{C}$ ). Since the purpose of the study was to evaluate membrane fouling, the operating conditions were chosen to favour rapid fouling of the membranes.

The retentions, permeabilities, fluxes and flux declines of different NF membranes were also studied with model feed waters using the laboratory-scale NF pilot (VI). Three different NF membranes were compared at parallel flat-sheet modules when filtering the same feed water. The pilot process was operated in a circulation mode for one hour with each feed water combination. The process parameters were kept constant in the different test runs (cross flow velocity = 1.0 m/s, NDP = 7 bar,  $T = 25^{\circ}\text{C}$ ).

## **3.2 Feed waters**

The pilot-scale NF studies (one-year, I, II, III) were conducted at Espoo Waterworks, which draws its raw water from a small humus-rich lake (average TOC 6.9 mg/L). The process at Espoo Waterworks consisted of periodical ozonation, chemical coagulation, dissolved air flotation, rapid sand filtration and post-treatment with chloramine and lime. The coagulation chemical was polyaluminium chloride during the studies I and II, but was changed to ferric chloride in the study III, and both coagulants were used during the course of the one-year study. Some characteristics of the Espoo feed water



during the different studies are presented in Table 1. The feed water for the NF pilot was drawn from the Espoo process before the post-treatment.

The real pre-treated surface water samples were collected from five surface water treatment plants and from one artificial ground water treatment plant for the laboratory-scale NF study (IV, V). The feed water samples were collected after the conventional water treatment train, but before post-treatment. Some characteristics of the feed water samples are presented in Table 1.

The model feed waters for filtration at the laboratory-scale NF unit were chosen to resemble real chemically pre-treated surface waters (VI). Organic and inorganic constituents alone and at different combinations were used as feed water constituents.

Table 1. Some characteristics of real pre-treated feed waters. Parameters are presented as averages  $\pm$  standard deviation during one-year, I, II and III studies and in the beginning of study IV/V.

Feed water	pH	TOC mg/L	UV <sub>254</sub> 1/cm	AOC $\mu\text{g eq-C/L}$	Conductivity mS/m	Alkalinity mmol/L	Hardness mmol/L	HPC CFU/mL	Study
Espoo	6.2 $\pm$ 0.2	2.7 $\pm$ 0.3	0.039 $\pm$ 0.016		14.6 $\pm$ 2.8	0.15 $\pm$ 0.04	0.19 $\pm$ 0.16	4100 $\pm$ 5300	one-year
Espoo	6.3 $\pm$ 0.1	2.7 $\pm$ 0.3	0.035 $\pm$ 0.019		14.8 $\pm$ 3.2	0.18 $\pm$ 0.03	0.08 $\pm$ 0.06	4100 $\pm$ 4100	I
Espoo	6.3 $\pm$ 0.1	2.9 $\pm$ 0.1	0.046 $\pm$ 0.007		13.7 $\pm$ 2.5	0.15 $\pm$ 0.01	0.41 $\pm$ 0.06		
Espoo	5.9 $\pm$ 0.1	2.2 $\pm$ 0.1	0.024 $\pm$ 0.002	63 $\pm$ 26	14.3 $\pm$ 0.7	0.09 $\pm$ 0.01	0.10 $\pm$ 0.01	5000 $\pm$ 1300	III
Espoo	5.7	2.2	0.043		15.5	0.10	0.49		IV, V
Kotka	6.8	3.4	0.058		9.2	0.38	0.33		IV, V
Pietarsaari	9.3	4.2	0.068		20.5	0.45	0.77		IV, V
Raisio-Naantali	7.1	3.2	0.049		17.4	0.48	0.58		IV, V
Tampere	7.6	2.9	0.040		14.1	0.66	0.55		IV, V
Turku	7.9	2.0	0.023		24.3	0.62	0.91		IV, V

### 3.3 Apparatus

#### 3.3.1 Pilot-scale nanofiltration units

Two similar pilot-scale NF units were used in the studies conducted at Espoo Waterworks (one-year, I, II). A schematic view of the NF pilot is presented in Figure 5. The 5- $\mu\text{m}$  cartridge pre-filters precede the NF process. The array of the plant is two-staged, and part of the retentate from the final stage can be circulated back to the feed stream of the pilot to enhance the recovery of the plant. The pressure vessels in the both stages house two spiral-wound membrane modules with nominal dimensions of 9.9 cm in diameter and 101 cm in length. The total membrane area of the NF pilot plant is 4\*7.7m<sup>2</sup>. Pressures and flows as well as feed water temperature and permeate conductivity were measured from the locations indicated in Figure 5.

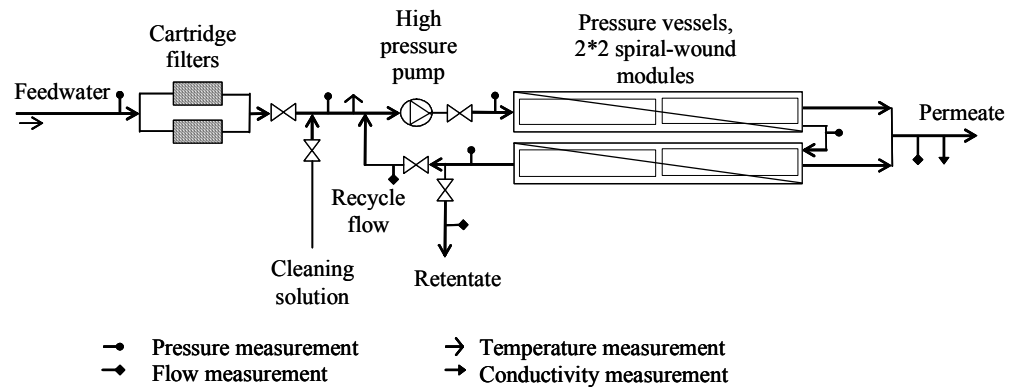


Figure 5. Schematic view of NF pilot-scale process.

The NF pilot process used in the membrane comparison study at Espoo Waterworks (III) has two parallel spiral-wound membrane modules with nominal dimensions of 6.1 cm in diameter and 101 cm in length (corresponding to a membrane surface area of 2.6 m<sup>2</sup>) as a one-stage process. The feed water is filtered by a 5- $\mu\text{m}$  cartridge filter before it enters the pressure vessels housing the membrane modules.

#### 3.3.2 Laboratory-scale nanofiltration units

The NF units (Figure 6) used in the laboratory-scale studies have three cross flow flat-sheet NF modules run in parallel with the same feed water. The membrane area in each NF module was either 46.0 cm<sup>2</sup> (IV, V) or 53.0 cm<sup>2</sup> (VI), and the channel height was 2 mm. Operation pressures and flows were measured from the locations indicated in Figure 6.

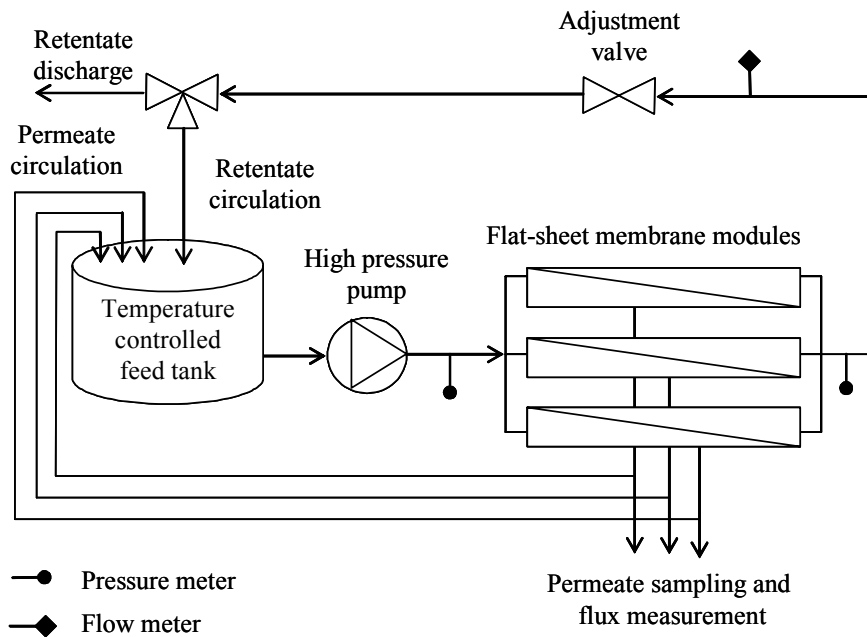


Figure 6. Schematic view of laboratory-scale NF process.

### 3.3.3 Nanofiltration membranes

In the pilot-scale experiments (one-year, I, II, III) the spiral-wound membrane modules were used. The tested NF membranes are listed in Table 2 with their representative characteristics. Both used and new modules were used and the comparability of the results, despite the different histories of the membranes, was considered to be good.

New pre-treated flat-sheet membranes were used in each laboratory-scale experiment (IV, V, VI). The tested membranes are listed in Table 2 with their representative characteristics.

Table 2. Characteristics of studied NF membranes. Information from manufacturers if not indicated otherwise.

Membrane	Manufacturer	Material	Cut-off, g/mol	Operating pH range	CaCl <sub>2</sub> retention, %	MgSO <sub>4</sub> retention, %	Studies
Desal-5 DL	Osmonics	PPZ	150-300	2-11		96	III, IV, V, VI
Desal-51 HL	Osmonics	PPZ	150-300				VI
NF70	Filmtec	PA	200-300			95	III
NF255	Filmtec	PPZ	300	3-10	>50		one-year, I, II, III, IV, V
NF270	Filmtec	PPZ	300	3-10	40-60	>97	IV, V, VI
NTR-7410	Nitto Denko	SPS	20 000 <sup>1)</sup>			9	III
NTR-7450	Nitto Denko	SPS	600-800 <sup>2)</sup>			32	III
TFC-S	Fluid Systems	PA	200-300			99	III

PA = Polyamide

PPZ = Polypiperazine amide

SPS = Sulphonated polyethersulphone

1) Yoon *et al.*, 2005

2) Ikeda *et al.*, 1988

## 3.4 Analysis methods

### 3.4.1 Water analyses

The TOC was measured according to national standard SFS-EN 1484 either by an Astro, Total Organic Carbon Analyzer, Model 2001 by the wet digestion method (one-year, I, II, III) or by a Shimadzu TOC-5000A analyser by combustion - non dispersive infrared gas analysis method (IV, V, VI). UV absorbance at a wavelength of 254 nm (UV<sub>254</sub>) was conducted according to the APHA (1995), with the exception that a 10-minute centrifugation at 4000 rpm was used instead of filtering as sample pre-treatment in the studies conducted at Espoo Waterworks (one-year, I, II, III).

The molar mass distributions of organic matter were analysed by a high performance size exclusion chromatography (HPSEC) (Hewlett-Packard HPLC 1100) equipped with a diode array UV detector (254 nm) and a TSK gel G3000SW column (V). Organic matter was categorised to organic matter with apparent molar mass >4000 g/mol, with apparent molar mass 4000-1000 g/mol and with apparent molar mass <1000 g/mol.

In the membrane comparison study (III) the feed water and permeate samples were tested for microbially available nutrients and microbial growth potential by assimilable organic carbon (AOC), microbially available phosphorus and heterotrophic growth response. The AOC was analysed by a modification (Miettinen *et al.*, 1999) of the standard AOC method (APHA, 1992). The AOC results were determined by standardising the growth of test bacteria using acetate and the AOC content is expressed as micrograms of acetate eq-C per litre ( $\mu\text{g Ac-C/L}$ ). Microbially available phosphorus was analysed according to a method of Lehtola *et al.* (1999). In the heterotrophic growth response assay the growth of indigenous heterotrophic bacteria in the water sample was followed according to Noble *et al.* (1996).

Microbial activity in waters was analysed by a heterotrophic plate count (HPC) (one-year, I, III). The HPC was analysed using spread plate counting with the sensitive R2A agars at  $20\pm 1$  °C (Reasoner and Geldreich, 1985).

Ions were analysed according to accredited techniques, anions by ion chromatography and cations by inductively coupled plasma atomic emission spectrometry, or by mass spectrometry (one-year, I, II, III, V, VI).

The membrane fouling tendency of the Espoo feed water was evaluated by SDI and MFI measurements (one-year). The SDI value is calculated from the times that a water sample, generally 500 mL, requires to pass through the sample membrane in the beginning and at the end of the filtration period (ASTM D 4189-95, 1997). In the MFI analysis, in turn, the cumulative volume of the filtered water is measured at every 30 seconds and the MFI value is defined as the slope of an inverse flow versus cumulative volume curve (Schippers and Verdouw, 1980).

All other analyses were conducted according to the Finnish standards.

### **3.4.2 Membrane analyses**

The characteristics of unused, pre-cleaned and fouled membranes were inspected in the study IV. Contact angle measurement by the drop method (Shaw, 1992) was used as an indicator of the membrane hydrophobicity. The contact angle values are calculated as an average of ten measurements. The functional groups on the membrane surface were analysed by Fourier Transform Infrared (FTIR) (Perkin-Elmer 2000) spectroscopy. Scanning electron microscopy equipped with energy dispersive X-ray analysis (SEM-EDS) (JEOL JSM-5800 + Link ISIS 300) was used to analyse the elementary composition and visual appearance of the membrane surfaces. The elementary composition of the NF270 membrane surfaces was also studied by an X-ray photoelectron spectroscopy (XPS) analyser (AXIS 165).





## 4 RESULTS AND DISCUSSION

### 4.1 Retention of organic matter by nanofiltration membranes

#### 4.1.1 Retention of TOC, UV<sub>254</sub> and AOC

One main objective in applying the NF process as a refining phase in surface water treatment is the removal of residual organic matter from feed water to levels, that limit consequent DBP formation and bacterial growth in distribution networks. The measured organic matter content of the permeates and retentions of organic matter from real pre-treated surface waters by different NF membranes are summarised in Tables 3 and 4, respectively. As the TOC and UV<sub>254</sub> contents of the permeates were generally very low it can be assumed that in some cases the deprivation of organic matter in the NF permeate limits the DBP formation and restricts the bacterial growth in the distribution network.

In general, the highest organic matter retentions were measured with UV<sub>254</sub>. This indicates a higher retention of high molar mass compounds as the UV<sub>254</sub> measurement does not detect low molar mass compounds to such a degree as high molar mass compounds. The TOC analysis, in turn, is able to detect both low and high molar mass compounds equally efficiently. The AOC retentions (III) were in most cases lower than the TOC or UV<sub>254</sub> retentions. However, the measured AOC retentions are in accordance with the retentions reported by Park *et al.* (2005b) in NF of conventionally pre-treated surface water and notably higher than the insignificant retentions reported by Escobar and Randall (1999) and Escobar *et al.* (2000) in NF of ground water. As diffusion and electrostatic repulsion are found to be the major factors influencing the AOC retention in NF (Escobar *et al.*, 2001), the quality of feed water strongly affects the retention. The lower retention of AOC in comparison with the retention of TOC or UV<sub>254</sub> is due to the fact that AOC consists mainly of low molar mass organic matter, which pass through the NF membranes more easily than the higher molar mass organic matter, which are the main fractions of TOC and UV<sub>254</sub> (Hem and Efraimsson, 2001).

The higher retention of organic matter from the Espoo feed water in the pilot-scale studies (one-year, II, III) than in the laboratory-scale study (V) were most probably due to the different operational modes of the NF processes and the effect of fouling layer. In the pilot-scale studies spiral-wound modules were used at continuous feed flow, whereas in the laboratory-scale study flat-sheet modules were used at circulating feed flow. The feed water circulation changed the characteristics of the feed water organic matter by cutting the molecules to smaller and more amenable to permeate the NF membranes, and hence lower organic matter retentions were observed. The fouling layer accumulated on the continuously used spiral-wound membranes may have increased their retention characteristics in comparison to almost unused flat-sheet membranes (Xu *et al.*, 2006). The large membrane area of the spiral wound modules also minimised the effect of membrane quality variation.

42 Table 3. Some permeate quality parameters after NF of real pre-treated surface waters. Parameters are presented as averages  $\pm$  standard deviation during one-year study and study II, as averages  $\pm$  standard deviation or as single measurements during study III and after a 4-hour run in study V.

Feed water	Membrane	TOC mg/L	UV <sub>254</sub> l/cm	AOC $\mu\text{g eq-C/L}$	Conductivity mS/m	Alkalinity mmol/L	Hardness mmol/L	HPC CFU/mL	Study
<b>Espoo</b>	NF255	0.08 $\pm$ 0.08	0.001 $\pm$ 0.002		8.8 $\pm$ 3.5	0.10 $\pm$ 0.04	0.08 $\pm$ 0.12	3 $\pm$ 6	one-year
<b>Espoo</b>	NF255	0.08 $\pm$ 0.06	0.001 $\pm$ 0.002		8.0 $\pm$ 2.4	0.08 $\pm$ 0.01	0.18 $\pm$ 0.07		
<b>Espoo</b>	Desal-5 DL	< 0.30	0.001 $\pm$ 0.000	13	3.48 $\pm$ 0.05	0.05 $\pm$ 0.00	0.00 $\pm$ 0.00	1	III
	NF70	< 0.30	0.000 $\pm$ 0.000	5	0.82 $\pm$ 0.05	0.04 $\pm$ 0.00	0.00 $\pm$ 0.00	3	III
	NF255	< 0.30	0.001 $\pm$ 0.000	29	5.16 $\pm$ 0.05	0.06 $\pm$ 0.00	0.00 $\pm$ 0.00	15	III
	NTR-7410	1.33 $\pm$ 0.02	0.015 $\pm$ 0.000	27	11.44 $\pm$ 0.05	0.09 $\pm$ 0.00	0.00 $\pm$ 0.00	3	III
	NTR-7450	0.50 $\pm$ 0.05	0.006 $\pm$ 0.000	27	6.95 $\pm$ 0.59	0.08 $\pm$ 0.00	0.00 $\pm$ 0.00	93	III
	TFC-S	< 0.30	0.001 $\pm$ 0.000	7	0.55 $\pm$ 0.04	0.03 $\pm$ 0.00	0.00 $\pm$ 0.00	17	III
<b>Espoo</b>	Desal-5 DL	0.59	0.003		3.11	0.06	0.13		V
	NF255	0.88	0.008		4.32	0.05	0.15		V
	NF270	0.58	0.009		4.37	0.06	0.12		V
<b>Kotka</b>	Desal-5 DL	0.71	0.003		2.23	0.10	0.03		V
	NF255	0.88	0.022		4.77	0.21	0.15		V
	NF270	1.12	0.013		4.12	0.20	0.14		V
<b>Pietarsaari</b>	Desal-5 DL	0.67	0.000		3.48	0.09	0.16		V
	NF255	1.94	0.022		8.80	0.22	0.33		V
	NF270	1.85	0.016		8.64	0.23	0.31		V
<b>Raisio- Naantali</b>	Desal-5 DL	1.93	0.023		9.95	0.27	0.31		V
	NF255	1.60	0.024		9.60	0.25	0.29		V
	NF270	1.56	0.021		10.8	0.27	0.33		V
<b>Tampere</b>	Desal-5 DL	0.99	0.003		2.79	0.19	0.10		V
	NF255	1.18	0.011		5.07	0.27	0.18		V
	NF270	1.30	0.010		5.97	0.34	0.24		V
<b>Turku</b>	Desal-5 DL	0.85	0.004		6.20	0.17	0.19		V
	NF255	1.23	0.009		11.9	0.33	0.41		V
	NF270	1.29	0.007		12.5	0.33	0.44		V

Table 4. Retention of organic and inorganic matter and bacteria from real pre-treated surface waters by different NF membranes. Retentions are presented as averages  $\pm$  standard deviation during one-year study and study II, as averages  $\pm$  standard deviation or as single measurement during study III and after a 4-hour run in study V.

Feed water	Membrane	TOC	UV <sub>254</sub>	AOC	Conductivity	Alkalinity	Hardness	HPC	Study
<b>Espoo</b>	NF255	97 $\pm$ 3%	96 $\pm$ 4%		42 $\pm$ 15%	35 $\pm$ 15%	79 $\pm$ 28%	99.8 $\pm$ 0.8%	one-year
	NF255	97 $\pm$ 2%	98 $\pm$ 3%		42 $\pm$ 7%	49 $\pm$ 6%	56 $\pm$ 10%		
<b>Espoo</b>	Desal-5 DL	>96%	98 $\pm$ 4%	86%	75 $\pm$ 1%	37 $\pm$ 5%	100%	100.0%	III
	NF70	>96%	99 $\pm$ 2%	90%	95 $\pm$ 0%	60 $\pm$ 1%	100%	99.9%	III
	NF255	>96%	96 $\pm$ 0%	42%	66 $\pm$ 1%	36 $\pm$ 3%	100%	99.7%	III
	NTR-7410	41 $\pm$ 3%	41 $\pm$ 4%	41%	18 $\pm$ 2%	8 $\pm$ 7%	100%	100.0%	III
	NTR-7450	78 $\pm$ 12%	77 $\pm$ 4%	41%	50 $\pm$ 2%	16 $\pm$ 2%	100%	98.6%	III
	TFC-S	>96%	99 $\pm$ 3%	93%	96 $\pm$ 0%	61 $\pm$ 7%	100%	99.5%	III
<b>Espoo</b>	Desal-5 DL	76%	93%		81%	33%	74%		V
	NF255	65%	82%		73%	44%	70%		V
	NF270	77%	80%		73%	33%	76%		V
<b>Kotka</b>	Desal-5 DL	81%	95%		77%	75%	92%		V
	NF255	76%	61%		50%	47%	58%		V
	NF270	70%	77%		57%	50%	61%		V
<b>Pietarsaari</b>	Desal-5 DL	85%	100%		83%	80%	80%		V
	NF255	57%	69%		58%	52%	58%		V
	NF270	59%	77%		59%	50%	62%		V
<b>Raisio-Naantali</b>	Desal-5 DL	47%	60%		45%	46%	50%		V
	NF255	56%	59%		47%	50%	54%		V
	NF270	57%	64%		41%	46%	47%		V
<b>Tampere</b>	Desal-5 DL	71%	93%		83%	73%	83%		V
	NF255	66%	76%		62%	61%	69%		V
	NF270	62%	78%		63%	51%	59%		V
<b>Turku</b>	Desal-5 DL	64%	84%		76%	74%	81%		V
	NF255	48%	64%		54%	50%	59%		V
	NF270	46%	72%		52%	50%	56%		V

#### 4.1.2 Retention of different molar mass fractions of organic matter

According to the HPSEC results (V), the organic matter with molar mass higher than 4000 g/mol (measured as UV<sub>254</sub>) was generally retained very efficiently by the studied NF membranes (Figure 7). The retention of the organic matter with molar mass of 1000-4000 g/mol was not so high, and the lowest retention was seen when the molar mass was lower than 1000 g/mol (Figure 7). Similar retention of organic matter (measured as TOC) of different molar masses was seen with the polystyrene sulphonates containing model feed waters (VI) at a feed water TOC concentration of 4.5 mg/L: Retention of the intermediate molar mass styrene (1400 g/mol) varied between 44 and 74%, and retention of high molar mass styrene (17000 g/mol) between 92 and 95% (VI). On the contrary, the retention of the small organic acids (< 1000 g/mol) from the model feed waters at the feed water TOC concentration of 4.5 mg/L was surprisingly high, varying between 67 and 95% (VI). For example, the retention of benzoic acid was 79-90% even though its molar mass is smaller than the membrane cut-off. No correlation was found between the molar mass of the small organic acids and their retention efficiency.

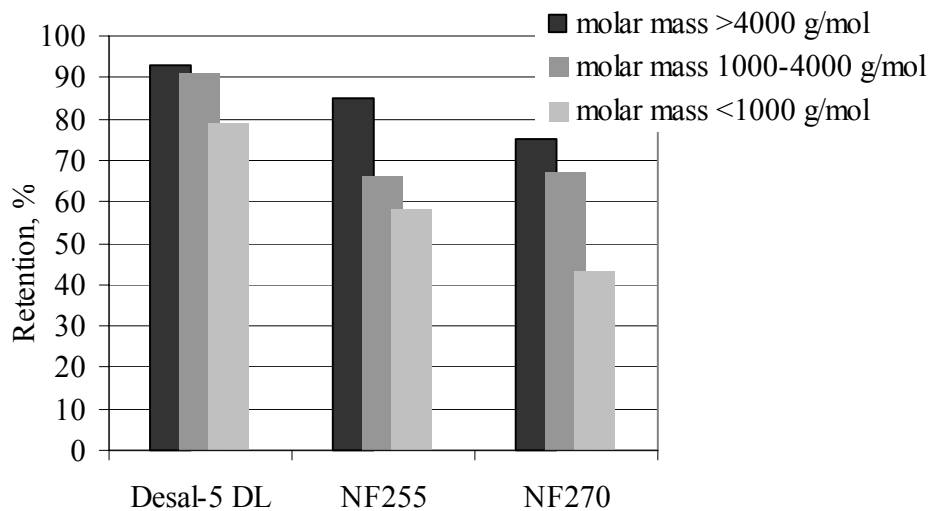


Figure 7. Average retention of different molar mass fractions of organic matter (measured as UV<sub>254</sub>) from different pre-treated feed waters by three different NF membranes (V).

The high retention of high molar mass organic compounds in NF was expected due to size exclusion. On the other hand, the retention of molar mass fractions between 1000-4000 g/mol was lower, and the retention of molar mass fractions below 1000 g/mol higher, than could be expected by the membrane cut-off values. This indicates that the retention of low molar mass organic matter is not only controlled by molar mass, but also molecular charge, hydrophobicity and conformation (Cho *et al.*, 1999; Van der Bruggen *et al.*, 1999; Ozaki and Li, 2002; Braeken *et al.*, 2005) affect the retention. Thus, lower or higher retentions than expected according to molar mass could be seen, especially with the low molar mass compounds. Small molecules may also interact with each other and form bigger, less permeable molecules. Other authors have also reported that NF membranes retain high molar mass fractions of

organic matter efficiently, but low molar mass organic matter is generally retained only slightly (Amy *et al.*, 1990; Van der Bruggen *et al.*, 1999; Chellam, 2000; Siddiqui *et al.*, 2000; Ozaki and Li, 2002).

The low molar mass organic matter, the fraction of organic matter that was retained to the least extent in NF (V, VI) is generally easily used by microbes. Also, the lower retention of AOC in comparison with TOC and UV<sub>254</sub> (III) support the suggestion that the residual organic matter in the NF permeates is easily used as organic substrate for bacterial growth.

#### 4.1.3 Effect of cations on organic matter retention

The model feed waters containing a mixture of natural Lake Mekkojärvi fulvic acid and cations, in most cases, indicated a lower retention of TOC than pure Lake Mekkojärvi fulvic acid containing solution (Table 5) (VI). Visvanathan *et al.* (1998), Yoon *et al.* (1998), Schäfer *et al.* (2000b) and Zander and Curry (2001) also reported a decreased organic matter retention in the presence of increased concentration of divalent cations. The reason for a lowered retention of organic matter in the presence of cations is probably due to charge neutralisation and the electro-neutrality effect. Lower charge repulsion between the membrane and the organic molecules enables organic molecules to pass the membrane more easily. In addition, the lower charge of organic molecules makes their conformation denser and, thus, they pass the membrane more easily.

Table 5. TOC retentions of two types of model feed waters by three different membranes (VI). Single value with Lake Mekkojärvi fulvic acid containing feed water (measured TOC = 2.6 mg/L) and average retentions ± standard deviation with Lake Mekkojärvi fulvic acid and inorganic constituents containing feed waters (measured TOC = 2.7±0.3 mg/L).

Feed water	Desal-5 DL	Desal-51 HL	NF270
Lake Mekkojärvi fulvic acid	89%	91%	91%
Lake Mekkojärvi fulvic acid + inorganic constituents	70±14%	82±9%	84±3%

#### 4.1.4 Stability of organic matter retention

The retention of TOC and UV<sub>254</sub> by the NF membranes remained fairly stable and high throughout the pilot-scale studies (one-year, II, III). The performed cleanings (I) did not seem to affect the organic matter retention of the membranes. In the laboratory-scale studies the TOC retention was almost indifferent to pH (VI), even though other authors have observed the best retention of organic matter at the feed water pH of 7-10 (Braghetta *et al.*, 1997; Mänttari *et al.*, 1997; Visvanathan *et al.*, 1998). Changes in the driving pressure or the recovery of the NF process did not affect the organic matter retention either (II). Since the retention of organic matter was not affected notably by the changes in the quality of the feed water, or by the operation of the process, the retention was mainly controlled by the sieving effect.

In the laboratory-scale studies with feed water recycling (V, VI) the retention of organic matter improved by 10-68% as the run proceeded and the organic matter

concentration of the feed water increased. This may be caused by several factors. It is possible that at high concentration small molecules form bigger, less permeable complexes due to increased contact with other molecules and decreased intermolecular charge repulsion. On the other hand, the accumulation of a foulant layer on the membrane during the run hinders the transport of organic matter through the membrane. The adsorption of organic foulants on the membrane surface may also increase the negative charge of the membrane surface (Xu *et al.*, 2006), and thus increase the repulsion forces and consequently retention. Water molecules are small and pass through the fouled membrane more easily than organic molecules, and thus practically no flux decline was experienced.

A similar phenomenon of little effect on membrane flux, but substantial increase in retention with increasing TOC concentration has been observed by Visvanathan *et al.* (1998) with a laboratory-scale recycle-mode apparatus. Schäfer *et al.* (1998) and Yoon *et al.* (2005), in turn, reported that the retention of organic matter increased as the run proceeded and the membranes got fouled. No increase in the retention of organic matter was seen in the pilot-scale studies because the concentration of feed water organic matter did not increase and the initial foulant accumulation on the NF membranes had happened before the test runs.

## 4.2 Retention of inorganic matter by nanofiltration membranes

### 4.2.1 Permeate pH, alkalinity and hardness

Conductivity, alkalinity and hardness of the permeates and their retentions in the different studies (one-year, II, III, V) with the real pre-treated feed waters are summarised in Table 3 and Table 4, respectively. The tested membranes retained 18-96% of the feed water conductivity, 8-80% of the feed water alkalinity, and 47-100% of the feed water hardness. The effect of NF in alkalinity of the waters is presented, despite the fact that the alkalinity values were notably below the directive detection limit (0.4 mmol/L) of the analysis method. NF did not affect turbidity of the pre-treated feed waters.

All the studied chemically pre-treated feed waters (one-year, II, III, V) had low pH, alkalinity and hardness, and consequently so did all the permeates. However, the looser NF membranes (Desal-5 DL, NF255, NF270, NTR-7410, NTR-7450) decreased permeate hardness and alkalinity significantly less than the traditional NF membranes (NF70, TFC-S). Since these compounds affect the chemical stability of the permeate, and consequently the suitability of the treated water for distribution, the ability of the NF membranes to reduce alkalinity and hardness has to be considered. In applications for organic matter removal the use of membranes with high retention of organic matter and low retention of inorganic matter (Desal-5 DL, Desal-51 HL, NF255 and NF270 of the studied membranes) balance the permeate requirements of low organic content and minor need for alkalinity recovery and post-chlorination in the most acceptable way. Fu *et al.* (1994) also came to the same conclusion. However, in applications treating soft waters the NF permeate requires remineralisation before distribution.

#### 4.2.2 Retention of different ions

The retentions of the selected ions from the real pre-treated feed waters at the pilot-scale NF studies (one-year, III) are presented in Table 6. The retention of the multivalent ions was generally higher than the retention of the monovalent ions, even though the tighter membranes (NF70 and TFC-S) also retained monovalent ions efficiently. The Desal-5 DL and NF255 membranes seemed to be modified to allow more ions to pass than the traditional NF membranes (NF70 and TFC-S) despite equally high organic matter retention. The measured low retentions of aluminium by the NTR-7450, NTR-7410, Desal-5 and TFC-S membranes are probably due to inaccuracy in determining the feed water aluminium content, which varied significantly.

Table 6. Retentions of ions with different NF membranes. Retentions are presented as averages  $\pm$  standard deviation during one-year study and as a single measurement during study III. The highlighted retentions indicate situations where real retentions might have been even higher than presented, since ion contents in permeates were below detection limit of analysis method.

Study Membrane	Al <sup>3+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
One-year						
NF255	92 $\pm$ 6%	50 $\pm$ 19%	69 $\pm$ 20%	15 $\pm$ 14%	19 $\pm$ 19%	98 $\pm$ 1%
III						
Desal-5 DL	79%	94%	96%	36%	39%	100%
NF70	97%	99%	96%	89%	93%	100%
NF255	87%	77%	79%	51%	12%	99%
NTR-7410	-1%	25%	20%	13%	0%	28%
NTR-7450	34%	64%	60%	35%	24%	73%
TFC-S	60%	99%	96%	93%	98%	100%

Refining treatment with NF can also be used to secure the inorganic quality of the water by removing harmful compounds. The fluoride concentration in the Kotka feed water (IV) was slightly above the directive limit of 1.5 mg/L. The retention of fluoride was not studied here, but the earlier studies showed efficient fluoride removal in NF (Härmä, 1999). In the other real pre-treated feed waters the studied inorganic constituents were well below the current water quality standards. However, the aluminium content in the pre-treated Espoo feed water occasionally exceeds the limit of the quality standard (200  $\mu$ g/L). NF would cut the concentration to an acceptable level.

#### 4.2.3 Stability of inorganic quality of permeate

The aluminium and sulphate concentrations in the permeate samples remained stable and retentions high (Table 6) in the one-year pilot-scale study, despite the variation in the quality of feed water and operational parameters of the process. The permeate pH, conductivity, alkalinity, hardness and the contents of most ions, in turn, clearly reflected the feed water concentrations, and retentions varied considerably (Tables 3, 4 and 6). This indicates that the charge and size of aluminium and sulphate ions prevent them from passing the membrane, while the concentration gradient induced

diffusion and the electro-neutrality rule notably affected the retention of the other studied inorganic constituents.

The conductivity retention of the NF membranes was not as indifferent to operational parameters, cleanings and feed water pH changes as retention of organic matter. The higher driving pressure and the lower recovery increased the conductivity retention due to membrane compression and lower concentration gradient (II). The conductivity retention generally decreased in the cleanings performed in the study I, but the retention was often recovered as the membranes were operated.

The pH dependence of the conductivity retention by the studied NF membranes filtering the model feed waters is presented in Figure 8 (VI). The conductivity retention from both pure inorganic constituents and Lake Mekkojärvi fulvic acid and inorganic constituents containing feed waters was lowest at pH 5-6, and increased, as the pH decreased or increased, with all the tested membranes. The increased conductivity retention with increasing pH is in line with the observations of Ribau Teixeira *et al.* (2005) who explained the phenomena by reduced pore size of a charged membrane and electroviscous and osmotic effects.

The retention of conductivity from the pure Lake Mekkojärvi fulvic acid containing feed water did not show as smooth changes with pH as the inorganic constituents containing feed waters: With the Desal-5 DL and Desal-51 HL membranes the conductivity retention decreased from the maximum to the minimum, as the pH increased from 5 to 6. With the NF 270 membrane the conductivity retention increased steadily up to pH 8, and decreased above that. To conclude, the pH dependence of the conductivity retention varies between different NF membranes and feed waters.



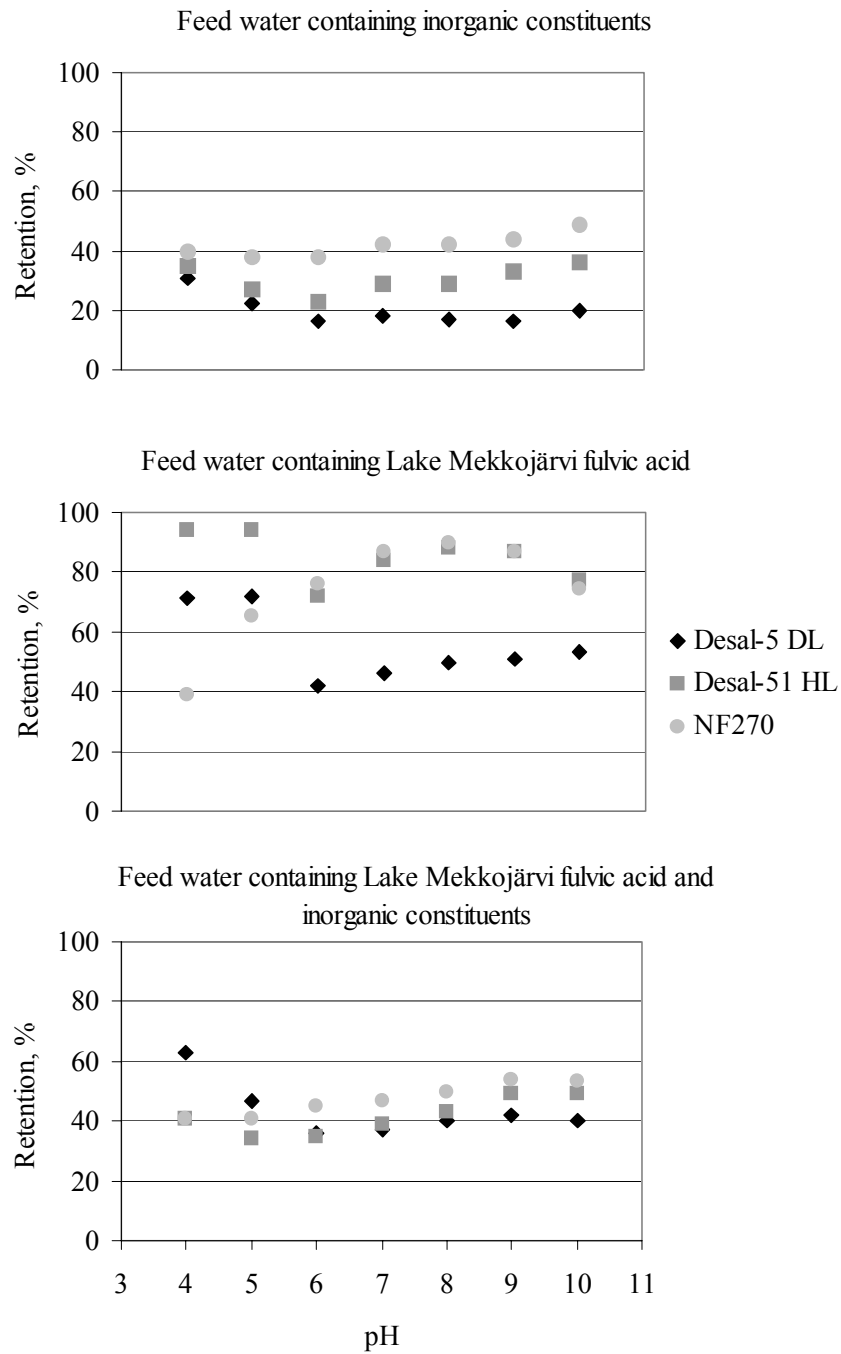


Figure 8. pH dependence of conductivity retention with different feed waters and NF membranes (VI) (retentions at pH 3 are excluded as values are not comparable with others due to higher feed water conductivity).

### 4.3 Microbial quality of nanofiltration permeate

The tested NF membranes showed high, but not complete bacteria retentions in the one-year and the membrane comparison (III) studies (Table 4). Surprisingly, some heterotrophic bacteria (0-93 CFU/mL) were found in the most permeate samples (Table 3), despite the fact that bacteria theoretically cannot pass through the pores of the NF membranes. It was assumed that the microbes originate from non-sterile pipes or joints of the pilot apparatus, from contamination of the membrane permeate side, or from sample contamination at collection. Siddiqui *et al.* (2000) also found some microbes in NF permeate.

As discussed in the previous chapter, NF generally removed organic matter efficiently from the pre-treated surface waters. However, according to the AOC threshold (10 µg Ac-C/L) proposed by Van der Kooij (1992), only in the permeates of the NF70 and TFC-S membranes the AOC content was low enough (III) to restrict microbial growth in the distribution network. On the other hand, it has been shown that phosphorus is the limiting nutrient in most Finnish drinking waters, and that extremely low levels, similar to levels found in the studied NF permeates, are sufficient for bacterial growth (Miettinen *et al.*, 1996; Lehtola *et al.*, 2000). NF did not affect the concentration of microbially available phosphorus in the studied waters: The microbially available phosphorus concentrations of permeates and feed waters were at the lower detection limit of the analysis (0.08 µg PO<sub>4</sub>-P/L), and are considered to be the same (III). Thus, the studied permeates seemed to contain enough carbon and phosphorus for bacterial growth.

All the studied permeate samples in the membrane comparison study (III) showed a remarkable potential for microbial growth according to the maximal heterotrophic growth response value during the 20-day incubation (Figure 9). An interesting finding in the heterotrophic growth response analysis was that the microbial growth was stronger in the permeates than in the feed water. This indicates that particularly the most easily biodegradable nutrient compounds are able to pass through the NF membranes. Furthermore, feed waters may contain material (e.g. aluminium) that does not exist in the purer permeates, and that inhibits microbial growth in water (Lehtola *et al.*, 2002). Consequently, the microbes had a favourable environment for intensive microbial growth in permeates. A similar phenomenon was found in a study comparing the heterotrophic growth responses of several treated surface waters and ground waters: The microbial growth potential was highest in the chemically and microbially purer drinking waters produced from ground water (Lehtola *et al.*, 2000).

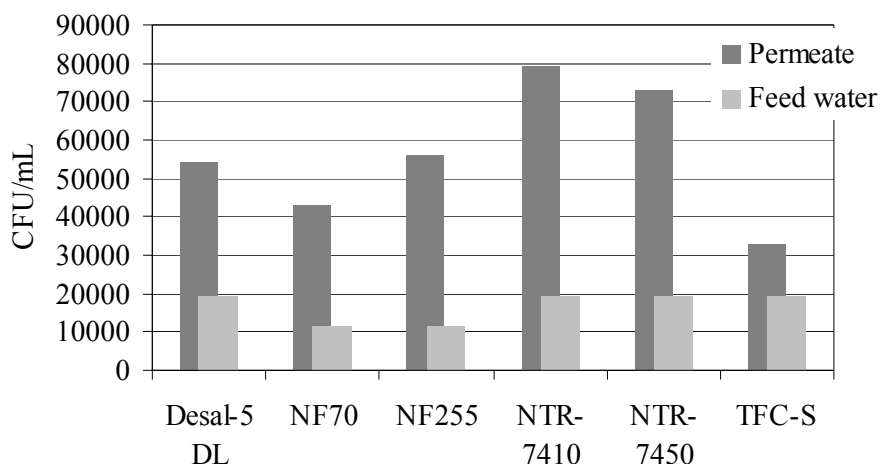


Figure 9. Maximal number of heterotrophic bacteria in feed waters and permeates of studied membranes during 20-day incubation (III).

Judged by the criterion of bacterial growth, none of the tested NF membranes produced a biologically stable permeate (III) and there is a risk for pathogen multiplication. Consequently, post-chlorination is required as an important safety barrier and to suppress microbial growth in distribution systems after NF. Still, the small numbers of culturable bacteria and low levels of organic matter found in the permeates suggest that only a minor chlorine dosage is needed for inactivation of the microbes. In a study conducted in a real distribution network the use of NF allowed post-chlorination to be reduced from about 0.9 mg/L Cl<sub>2</sub> to about 0.2 mg/L Cl<sub>2</sub> (Laurent *et al.*, 1999). In addition, the observations of Laurent *et al.* (1999) and Escobar and Randall (1999) indicate that chlorine residuals are retained well in the distribution systems fed by NF permeate, as the content of organic matter is low enough not to consume the chlorine residual. Laurent *et al.* (1999) also observed that the bacterial activity in the distribution network decreased notably after the installation of NF, and that bacterial counts in distributed NF water remained low even at the far end of the distribution system.

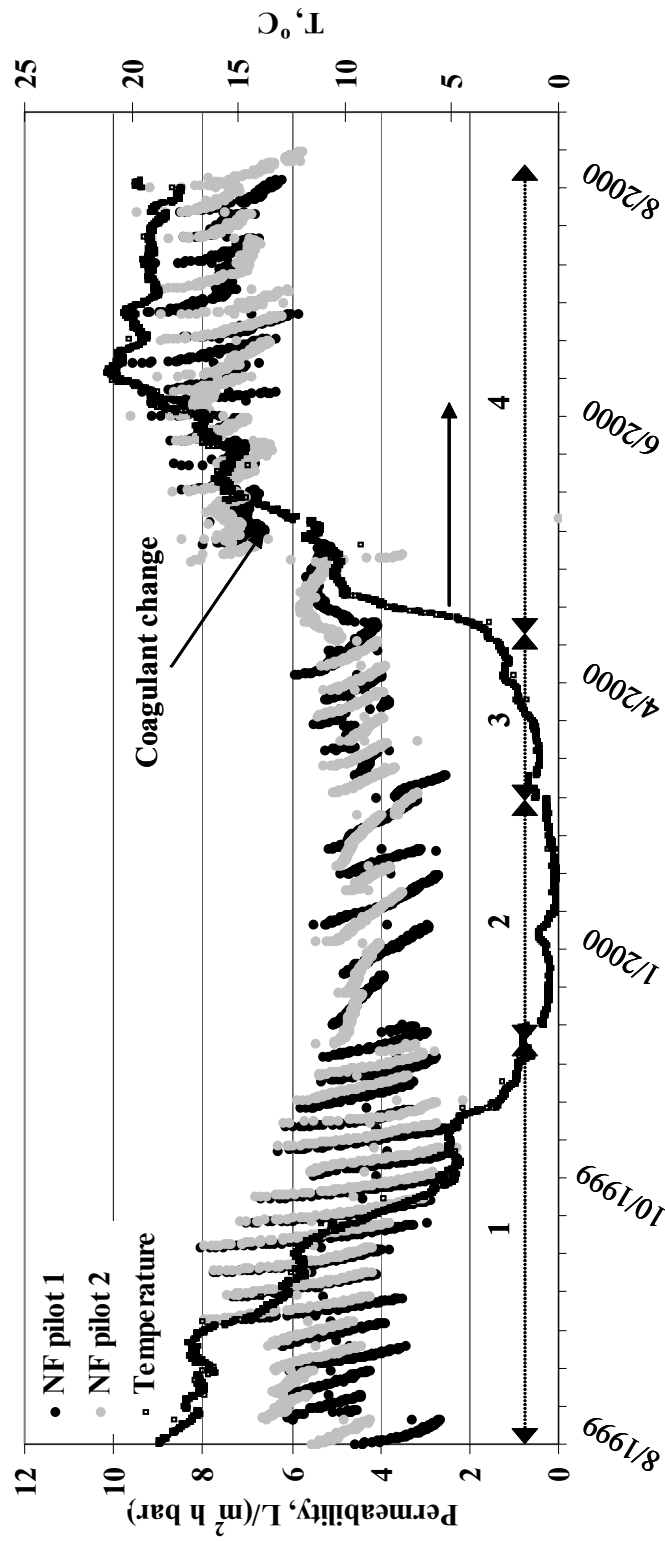
The low concentrations of organic matter and the lower applied chlorine dosages result in low formation of harmful DBPs in NF permeate. The removal of DBP precursors by NF was not studied here, but several studies have indicated that these compounds are retained by up to 97% in NF (Amy *et al.*, 1990; Tan and Amy, 1991; Blau *et al.*, 1992; Visvanathan *et al.*, 1998; Siddiqui *et al.*, 2000).

#### 4.4 Permeabilities, fluxes and flux declines of nanofiltration membranes

##### 4.4.1 Permeabilities and fluxes

The real permeabilities of the NF membranes tested in the pilots, and the feed water temperature during the one-year study, are presented in Figure 10. The specific phases of the one-year study are indicated in the graph. The effect of temperature on membrane permeability can be seen from the graph as well as the improvement in

permeabilities after replacing the polyaluminium chloride coagulant with ferric chloride in May 2000. The NF plant design has to be based on the membrane permeability at low feed water temperature to comply with the plant capacity requirement also during the low temperature season. The effect of pre-treatment on NF performance was not evaluated in this study, but the improved permeability after the change of coagulant suggests that optimisation of the pre-treatment process may result in a notable improvement in the NF process.



- Phase 1 Cleaning comparison study (I) (NDP=7.3 bar, recovery=80%, cross flow=1.3 m<sup>3</sup>/h)
- Phase 2 Operation optimisation study at winter conditions (II) (NDP=4 - 7 bar, recovery=40% or 55%, cross flow=0.6-0.9 m<sup>3</sup>/h)
- Phase 3 Feed water pH adjustment tests (NDP=6.5 bar, recovery=75 %, cross flow=1.3 m<sup>3</sup>/h)
- Phase 4 Operation optimisation study at summer conditions (NDP=4-6 bar, recovery=80 %, cross flow=1.3 or 2.0 m<sup>3</sup>/h)

Figure 10. Real permeability of studied NF membranes, feed water temperature and specific phases of one-year pilot-scale study.

The effect of feed water characteristics on the flux of NF membranes was clearly seen in the runs with varying pH (VI). The run conducted with the inorganic matter containing feed water showed 9-29% higher operational flux than the organic matter (Lake Mekkojärvi fulvic acid), and 21-52% higher operational flux than the organic and inorganic matter (Lake Mekkojärvi fulvic acid and inorganic constituents) containing feed waters (Figure 11). The addition of specific inorganic constituents to organic matter (Lake Mekkojärvi fulvic acid) containing feed water changed the operational fluxes as follows (VI): aluminium -2%, calcium -3%, iron -2% and silica -8%. The observation by Li and Elimelech (2005) of the faster foulant accumulation due to the synergistic effect of the organic and colloidal compounds on the NF membrane similar to used in the study can explain the pronounced decline of flux in the presence of silica.

The pH of the feed water also influenced the flux of the membranes (VI). The pH dependence of the flux with different feed waters is shown in Figure 11 with the Desal-5 DL, Desal-51 HL and NF270 membranes. With the model feed waters containing only inorganic matter the fluxes were the highest at the lowest pH (pH 3). Ribau Teixeira *et al.* (2005), explained the similar flux decrease with increasing pH by membrane charge variation and electroviscous and osmotic effects. The model waters containing organic matter, in turn, showed the highest fluxes around pH 5. The behaviour of the organic matter containing feed waters may be explained by the lowest organic matter absorption on the membranes close to neutral pH (Yoon *et al.*, 1998).

As was assumed, the increasing driving pressure notably increased the operational flux and shortened the cleaning intervals of the NF membranes (II). On the other hand, the higher recovery did not notably increase the operational fluxes, but shortened the cleaning intervals markedly (II). This was partly caused by lower feed water cross flow when operating NF at higher recovery. At the Méry-sur-Oise NF plant, treating polluted and conventionally pre-treated river water of seasonally varying temperature the average operational permeability was very similar to the permeabilities measured during the operation optimisation study (II) with identical NF membrane (Ventresque *et al.*, 2000). However, the permeability of the membranes remained stable for longer periods at the Méry-sur-Oise.

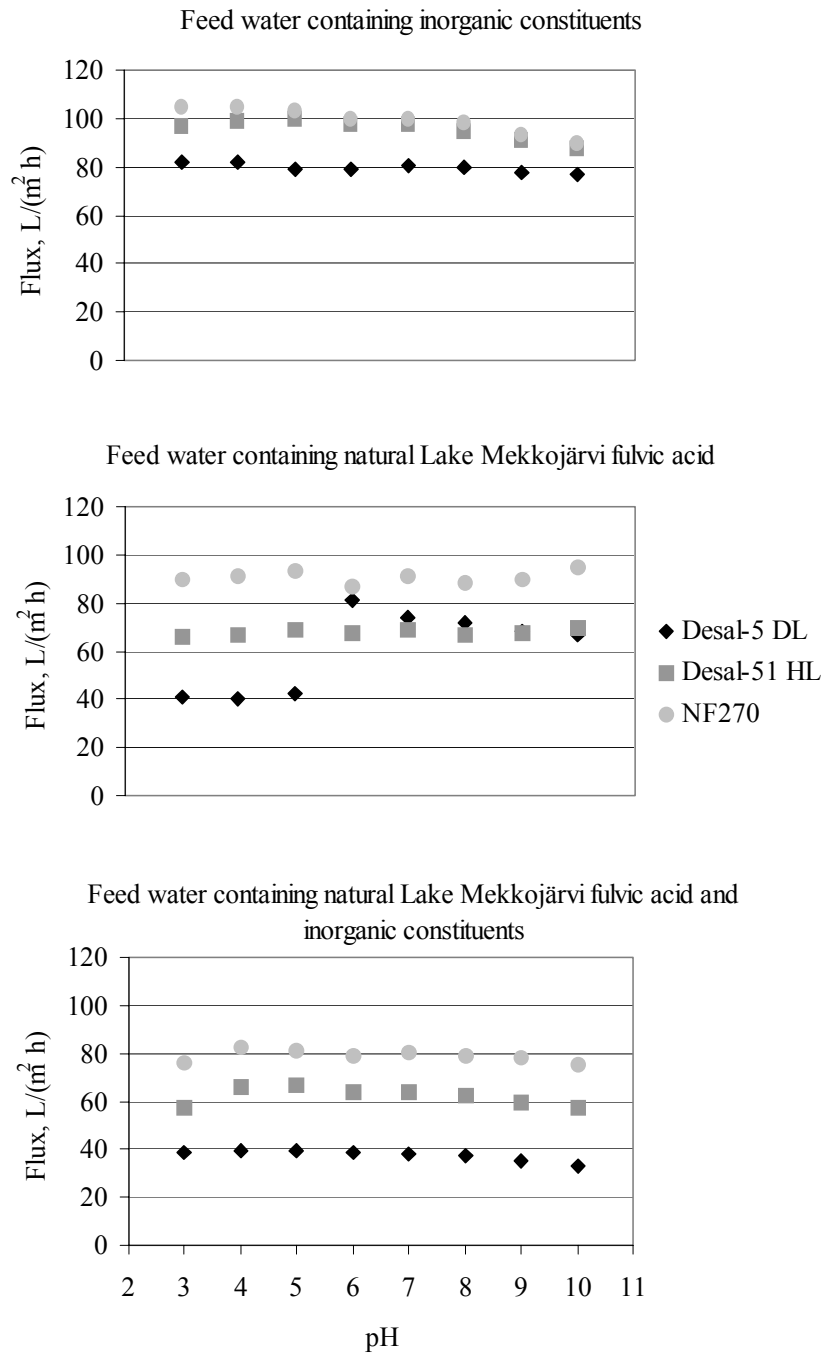


Figure 11. pH dependence of membrane fluxes with different feed waters (NDP=7 bar, cross flow velocity=1.0 m/s, T=25°C) (VI).

The pure water permeabilities of the clean NF membranes in the different studies ranged from 5.8 to 22.5 L/(m<sup>2</sup> h bar) (normalised at T = 20°C) (Table 7). The pure water permeabilities of the membranes that were tested several times (Desal-5 DL, NF255, NF270) showed substantial variability. The variation in the permeabilities of the NF255 membranes in the pilot-scale studies (one-year, I, II) is caused by variability in the membrane quality between the two operated NF pilots, and by the changes in the membrane characteristics due to operation. The variation in permeabilities of the flat-sheet membranes in the laboratory-scale studies (IV, VI) is an indication of the variation in the membrane quality, but can also be caused by improper wetting of the membranes before the studies. Findings of Mänttari *et al.* (2002b) suggest that the applied wetting pressures were not necessarily adequate to wet the tightest NF membranes properly in the laboratory-scale studies.

The operational permeabilities of the membranes varied between the different studies, depending on the feed waters and operational parameters. Thus, the operational permeabilities of the membranes can not be compared between the different studies.

When both the pure water and operational permeabilities are considered the permeabilities of the studied NF membranes seemed to increase approximately in the following order: NTR-7410  $\approx$  Desal-5 DL  $\approx$  NF70  $\approx$  TFC-S < NF255 < NTR-7450 < Desal-51 HL < NF270. Interestingly, the high permeability of the NF membranes did not seem to correlate with lowered retention capabilities. The NF270 membrane, for example, retained efficiently both organic and inorganic matter despite its high permeability and the NTR-7410 membrane, in turn, showed both low retention and low permeability.

When comparing the permeabilities of the Desal-51 HL and NF270 membranes with the older generation membranes, Desal-5 DL and NF255, with similar characteristics substantial improvements can be seen (IV, VI). Charge, hydrophobicity and functional groups of the Desal-5 DL, NF255 and NF270 membranes were observed to be basically the same, and only the visual appearance of the NF270 membrane was not as smooth as that of the others (Figure 14) (IV). It may be concluded that the higher permeability of the NF270 membrane was most probably due to a membrane morphology favouring water permeation. However, the more permeable morphology did not impair retention or fouling tendency of the NF270 membrane.



Table 7. Pure water and operational permeabilities of studied membranes (normalised at  $T = 20\text{ }^{\circ}\text{C}$ ) in different studies. Pure water permeabilities are presented as averages  $\pm$  standard deviation of clean membranes during one-year study and studies I and II, as single measurement of pre-cleaned membranes in study III and as averages of pre-cleaned membranes in studies IV and VI. Operational permeabilities are presented as averages  $\pm$  standard deviation during one-year study and studies I, II, III and IV.

Study	Desal-5 DL	Desal-5I HL	NF70	NF255	NF270	NTR-7410	NTR-7450	TFC-S
Feed water								
<b>one-year</b>					Pure water permeability, L/(m <sup>2</sup> h bar)			
<b>I</b>				9.3 $\pm$ 0.4				
<b>II</b>				10.8 $\pm$ 0.3				
<b>III</b>	7.8		8.9	8.0 $\pm$ 0.2		6.6	16.6	9.6
<b>IV</b>	8.8 $\pm$ 1.5			12.6	22.5 $\pm$ 1.6			
<b>VI</b>	5.8 $\pm$ 1.9	8.5 $\pm$ 1.9		9.2 $\pm$ 2.2	11.5 $\pm$ 1.3			
<b>one-year</b>					Operational permeability, L/(m <sup>2</sup> h bar)			
Espoo				7.7 $\pm$ 1.2				
<b>I</b>								
Espoo				7.3 $\pm$ 0.6				
<b>II</b>								
Espoo				9.8 $\pm$ 1.1				
<b>III</b>								
Espoo	7.4 $\pm$ 0.2		7.2 $\pm$ 0.5	9.4 $\pm$ 0.9		6.8 $\pm$ 1.3	20.2 $\pm$ 3.9	7.4 $\pm$ 0.4
<b>IV</b>								
Espoo	7.3 $\pm$ 0.4			7.2 $\pm$ 0.5				
Kotka	7.0 $\pm$ 0.2			8.1 $\pm$ 0.4				
Pietarsaari	6.5 $\pm$ 0.2			6.1 $\pm$ 0.6				
Raisio- Naantali	8.9 $\pm$ 0.5			8.9 $\pm$ 0.4				
Tampere	6.3 $\pm$ 0.4			6.4 $\pm$ 0.3				
Turku	7.0 $\pm$ 0.1			5.3 $\pm$ 0.4				

#### 4.4.2 Flux declines

Generally, the studied real feed waters resulted in some NF membrane flux decline during the course of the runs (II, III, IV). This indicates that the coagulation pre-treatment of surface water did not remove the feed water fouling tendency. The artificial ground water (Kotka feed water in study IV) was not pure enough to prevent membrane fouling either. The flux declines were seen despite the high quality of the feed waters. On the other hand, the average MFI and SDI values ( $\pm$ standard deviation) of Espoo feed water during the one-year study were  $18 \pm 39$   $s/L^2$  and  $7 \pm 5$ , respectively. These averages exceed the limits proposed for NF feed water. The findings verify the superiority of feed water fouling indices and the importance of pilot testing in predicting the suitability of a feed water for NF. Speth *et al.* (1998) also found that the operation of an NF pilot with coagulation pre-treated river water resulted in significant membrane flux decline.

None of the studied organic substances caused any notable NF membrane flux decline when alone at low concentrations in the model feed waters in the short-term laboratory-scale study (VI). A negligible flux decline was seen when the feed water TOC concentration was increased from 1.0 to 4.5 mg/L (average change in flux  $\sim 0 \pm 3\%$ ) (VI). This is in accordance with the findings of Childress and Elimelech (2000) as humic acid had very little effect on the short-term flux in NF despite the fact that humic substances adsorbed easily on the membrane surface and made them more negatively charged.

The addition of inorganic constituents to the Mekkojärvi fulvic acid containing model feed water (VI) resulted in 2-8% decline in the operational fluxes and in 4-20% higher pure water flux decline after run than the pure Mekkojärvi fulvic acid containing feed water. It has been reported by several authors (Nyström *et al.*, 1995; Hong and Elimelech, 1997; Schäfer *et al.*, 1998; Yoon *et al.*, 1998; Li and Elimelech, 2005) that the flux decreases and the membranes foul more when both organic and inorganic matter present in the feed water. The inorganic cation acts as a bridge between the membrane surface and the free negatively charged functional groups of the humic substance, or by intermolecular bridging (Hong and Elimelech, 1997; Yoon *et al.*, 1998). As a consequence, the charge of both the membrane and humic macromolecules decreases. Further, membrane-foulant and mutual foulant electrostatic repulsion decreases leading to increased foulant layer thickness and density (Childress and Elimelech, 1996; Hong and Elimelech, 1997; Braghetta *et al.*, 1997), and to increased flux decline.

The patterns of flux decline varied between the membranes in the membrane comparison study (III). The membranes made of sulphonated polyethersulphone (NTR-7450 and NTR-7410) showed a remarkable decrease in flux during the first four days of operation. With some polyamide membranes (NF70, NF255 and TFC-S) the flux decline was pronounced during the first day of operation, after which the flux remained fairly stable. No flux decline could be observed with the Desal-5 DL membrane. Regarding these flux decline patterns, the applied NDPs resulted in stable fluxes for the Desal-5 DL, NF70, NF255 and TFC-S membranes, after the initial flux decline. The NTR-7450 and NTR-7410 membranes exhibited a continuous flux decline, and it may be concluded that the NDPs and fluxes were too high for these membranes.

In a statistical analysis the membrane affected the flux and flux decline in NF clearly, but no clear correlation was found between the feed water or feed water constituents and the flux or flux decline (IV). The important role of a membrane for flux decline is supported by the findings of Zander and Curry (2001) showing that the membrane surface chemistry was the most important factor affecting the rate of flux decline. Some studies, in turn, indicate that the membrane surface roughness correlates well with membrane fouling (Zhu and Elimeleh, 1997; Hobbs *et al.*, 2001), but the relationship between membrane charge or hydrophobicity and fouling is questionable (Hobbs *et al.*, 2001). Speth *et al.* (2000), did not find a correlation between the feed water levels of individual inorganic constituents and the differences in the NF membrane flux decline, either.

## **4.5 Foulants on nanofiltration membranes**

### **4.5.1 Visual appearance of fouled nanofiltration membranes**

The SEM images revealed that the NF membranes fed by the pre-treated surface waters were fouled with flocculent dirt and precipitates with sizes up to 50  $\mu\text{m}$  (IV). The appearance of the fouling layer, the ratio of flocculent material and precipitates, precipitate size and precipitate appearance varied from membrane to membrane, and from feed water to feed water. The SEM images of the fouled NF270 membranes are presented in Figure 12. The shape of the precipitates ranged from blocks to star shaped crystals, grape like clusters and doughnuts. Microbes were found on the membranes fed with the activated carbon filtered Tampere feed water. In many cases rinsing had removed part of the fouling layer, and clean and fouled membrane surfaces were seen on the same sample.

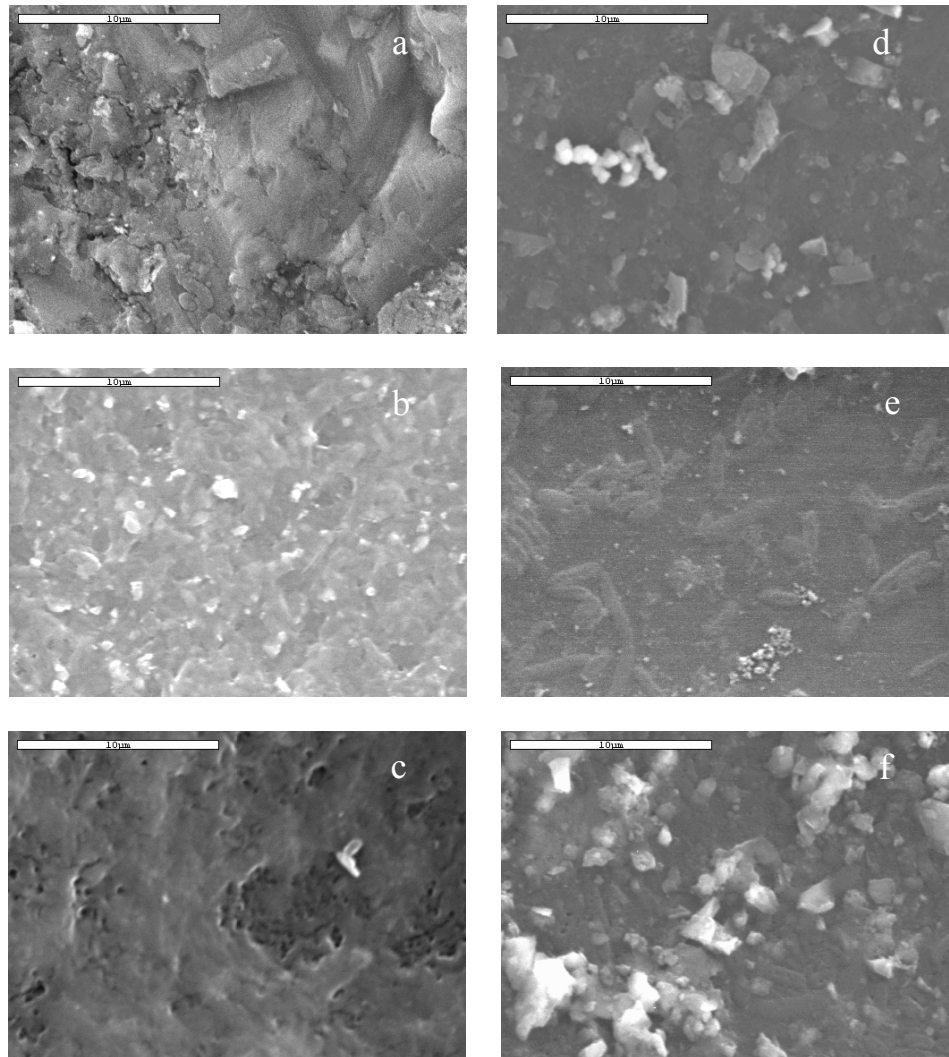


Figure 12. 6000\*SEM images of NF270 membranes fouled by a) Espoo, b) Kotka, c) Pietarsaari, d) Raisio-Naantali, e) Tampere and f) Turku feed waters (IV).

#### 4.5.2 Foulant analysis

The elementary analysis by the SEM-EDS indicated that the NF membranes were fouled with precipitates of aluminium, calcium, iron, sodium, magnesium and silica (IV). The XPS analysis of the NF270 membranes revealed even more foulants and increase in the oxygen and C-O and C-N bonds indicated the presence of organic fouling.

Aluminium was found on nearly all the fouled NF membranes, and also calcium and iron seemed to be present in many fouling layers (IV). The flux declines during the study using the model feed waters (VI), in turn, suggest that silicates play an important role in membrane fouling. This conclusion is supported by the suggestion of Kronmiller (1994) that every reverse osmosis system using natural source waters, even those of very low feed water silicate levels, experience silicate fouling that may result in tightly adsorbed silicate layers on the membranes. The reason for the important role of silicates to membrane fouling may result from the combined effect of silica colloids and organic matter (Li and Elimelech, 2005)

All the above mentioned inorganic constituents are found in natural waters at concentrations of the studied feed waters. In addition, they are integral constituents of conventional water treatment chemicals. Thus, it is difficult, if not impossible, to remove these constituents from the NF feed water to low enough levels in order to prevent membrane fouling completely.

The FTIR spectroscopy analysis revealed that amides and polysaccharides were the predominant organic foulants on the NF membranes (IV). Differences were observed in the fouling layer characteristics with different feed waters, as well as with different membranes. Similar FTIR peaks were seen both on the NF200 membrane fouled by conventionally pre-treated river water (Her *et al.*, 2001) and on the NF270 membrane fouled by conventionally pre-treated lake water (Park *et al.*, 2006). Other authors have also found similar organic foulants on the NOM fouled membranes (Cho *et al.*, 1998; Speth *et al.*, 1998; Amy and Cho, 1999).

The membrane fouling amides and polysaccharides can originate from several different sources. It was assumed that the foulant layers found on the membranes cannot originate from the rather dilute and pure feed waters, but are mainly a consequence of biological growth in the circulating feed waters during the test runs (IV). This assumption is supported by Speth *et al.* (1998) who suggested that the organic foulants on the NF membranes, fed with conventionally treated river water, were dominated by biological growth. Park *et al.* (2005a) reported that the soluble microbial products of micro-organisms provide high membrane fouling potential. These soluble microbial products can be assumed to play a role in the fouling of the studied membranes as well, especially as they compose mainly of protein and polysaccharide materials (Park *et al.*, 2005a).

In the Finnish drinking water applications the bacterial growth on the NF membranes may only be a summer season problem because the feed water temperatures below 13°C seemed to inhibit bacterial growth on the membrane (I).

On the basis of the notably higher proportion of total solids removal compared with total ion removals in the cleanings (I), it can be expected that the fouling material on the NF membranes consisted mainly of organic material and micro-organisms. This conclusion is supported by the fact that alkaline cleaners, which are most effective against biofilms, colloidal silts and organic foulants were in general more efficient cleaners than acidic agents. Nevertheless, both the cleaning chemical (I) and foulant (IV) analysis, and the experienced flux declines (VI), emphasise the role of inorganic precipitates, colloids and NOM-cation complexes in the fouling of the NF membranes by pre-treated surface waters. The efficiency of the alkaline chelating

agent ( $\text{Na}_4\text{EDTA}$ ) in the cleaning of the NF membranes (I) also indicated the removal of inorganic matter from the fouled membranes.

No correlation was found between the feed water characteristics and the foulants seen in the elementary analysis of the flat-sheet NF membranes (IV). The correlation of the constituent concentration in the feed water and the removal in the total cleanings, in turn, was moderate for aluminium in the cleaning comparison study (I). However, the other feed water ions did not correlate highly with the removal in the cleanings. The membrane foulants were not membrane specific either (I).

The fouling increased the hydrophobicity of the NF membranes, and consequently fouling material can be expected to be mainly hydrophobic in nature (IV). This is consistent with the suggestion that the hydrophobic fraction of organic matter in general fouls membranes more than the hydrophilic fraction does (Nilson and DiGiano, 1996; Schäfer *et al.*, 1998; Fan *et al.*, 2001; Violleau *et al.*, 2005).

The Turku feed water resulted in the highest weakening of the FTIR peaks related to the membrane material on all the studied NF membranes (IV). This indicates that the Turku feed water caused most foulant accumulation on the NF membranes. Nevertheless, the Tampere feed water caused most membrane flux decline, emphasising the role of fouling layer morphology on determining membrane flux decline, instead of foulant layer thickness. The suggestion is in line with the findings of Schäfer *et al.* (1998) indicating that dense fouling layers cause more flux decline than a high deposition of loose foulant material.

## **4.6 Cleaning of nanofiltration membranes**

### **4.6.1 Flux recoveries in cleanings**

The flux recovery efficiencies of the tested cleaning chemicals are summarised in Table 8 (I). Alkaline cleanings were generally better in recovering membrane flux than acidic cleanings, and especially an alkaline chelating agent ( $\text{Na}_4\text{EDTA}$ ) increased the membrane flux. Chelating agents are effective against inorganic precipitates, organic fouling and biofilms (AWWA M46, 1999) by disrupting the fouling layer structure and complexing metal foulants (Hong and Elimeleh, 1997).

Table 8. Flux recoveries (pure water flux of a cleaned membrane in comparison with pure water flux of a new membrane) and foulant removal efficiencies with different cleaning chemicals (I)

Chemical	Flux recovery <sup>1)</sup>	Al removal <sup>2)</sup>	Ca removal <sup>3)</sup>	Fe removal <sup>3)</sup>	TS removal <sup>4)</sup>
Citric acid	++	n.d	n.d.	n.d.	+
Citric acid & Oxalic acid	+++	+	+		+
Oxalic acid	++	+			+
HCl	+				
Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub>	-	n.d.	n.d.	n.d.	
Ultrasil 73	-	+		+	
NaOH	++	n.d.	n.d.	n.d.	+
Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub> & Na <sub>4</sub> EDTA	+++++	+	+	+	
NaOH & Na <sub>4</sub> EDTA	++++				
Na <sub>4</sub> EDTA	+++++	+	+	+	+
Ultrasil 141	++				

1) - flux recovery 90-110%, + flux recovery 110-130%, ++ flux recovery 130-150%, +++ flux recovery 150-170%, ++++ flux recovery 170-190%, +++++ flux recovery 190-210%

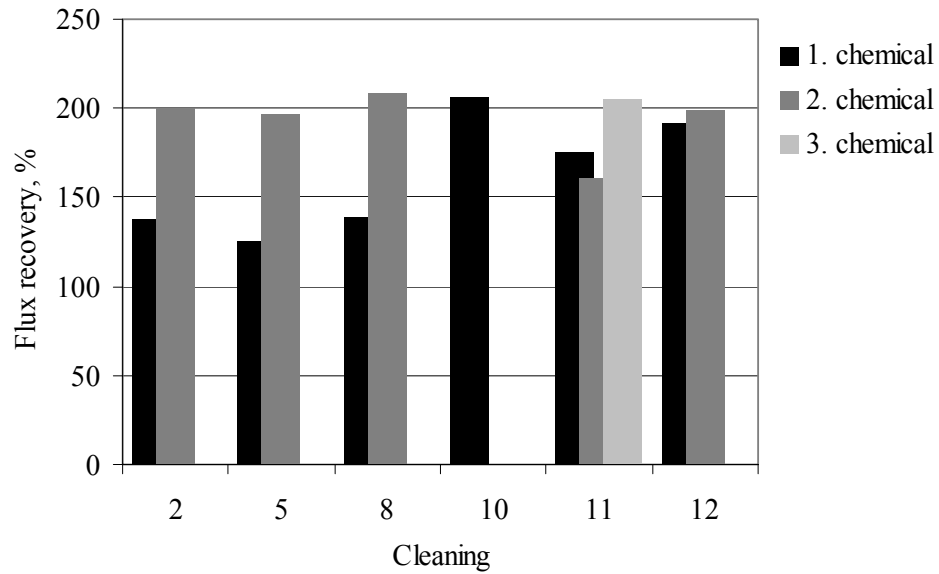
2) + deposit removal > 60% of total cleaning removal and > 3 g

3) + deposit removal > 60% of total cleaning removal and > 1.4 g

4) + deposit removal > 60% of total cleaning removal and > 30 g

n.d.= not determined

The efficiencies of the different cleaning procedures can be seen in Figure 13 (I). All the studied procedures attained nearly the same flux recovery, but required the application of one to three sequential cleaning chemicals. When the acidic cleaning (I, cleanings 2-7) was performed first, the subsequent alkaline cleaning (Na<sub>4</sub>EDTA) returned the flux of the membranes to a stable level despite the differences in the cleaning efficiencies in the acidic cleaning phase. In the cleaning 11, where three phases were performed, the acidic cleaning (HCl) following the alkaline cleaning (NaOH - Na<sub>4</sub>EDTA) decreased the flux recovery, while the subsequent alkaline cleaning (NaOH - Na<sub>4</sub>EDTA) restored the flux again (I).



Cleaning 2 – 1<sup>st</sup> Citric acid, 2<sup>nd</sup> Na<sub>4</sub>EDTA  
 Cleaning 5 – 1<sup>st</sup> HCl, 2<sup>nd</sup> Na<sub>4</sub>EDTA  
 Cleaning 8 – 1<sup>st</sup> HCl, 2<sup>nd</sup> NaOH + Na<sub>4</sub>EDTA  
 Cleaning 10 – 1<sup>st</sup> Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub> + Na<sub>4</sub>EDTA  
 Cleaning 11 – 1<sup>st</sup> NaOH + Na<sub>4</sub>EDTA, 2<sup>nd</sup> HCl, 3<sup>rd</sup> NaOH + Na<sub>4</sub>EDTA  
 Cleaning 12 – 1<sup>st</sup> Na<sub>4</sub>EDTA, 2<sup>nd</sup> Na<sub>4</sub>EDTA

Figure 13. Flux recoveries (pure water flux of a cleaned membrane in comparison with pure water flux of a new membrane) after application of different chemicals in different cleaning procedures (I).

As a conclusion, the use of the alkaline cleaning chemicals generally resulted in higher membrane flux than the use of the acidic cleaning chemicals in the cleaning comparison study (I). This is probably due to the fact that the membrane charge increases in an alkaline environment. Increased charge makes the membrane more open (Braghetta *et al.*, 1997) and can increase the membrane flux, even though the permanence of the effect is questionable. The alkaline chelating agent (Na<sub>4</sub>EDTA) increased the membrane permeability more than plain alkaline cleaning (NaOH) (I), probably by complexing some constituents from the membrane structure, and thus making the membrane more open and permeable. In addition to flux, the modification of the membranes in cleanings may also affect the fouling tendency of the membranes. The increased membrane charge in an alkaline environment increases the repulsive charges between the membrane and similarly charged foulants (Nyström *et al.*, 1995; Childress and Elimeleh, 1996; Braghetta *et al.*, 1997; Hong and Elimelech, 1997), and may retard membrane fouling.

The cleanings performed on the NF membranes during the one-year study recovered the clean membrane pure water fluxes well and steadily. Only once during the nine months of operation an additional cleaning phase with alkaline solution was required to recover the membrane flux to the normal level.



#### 4.6.2 Foulant removals in cleanings

The ability of the studied cleaning chemicals to remove the aluminium, calcium, iron and total solids deposits from the membrane surface as a single-phase cleaning is rated in Table 8 (I). In addition to its excellent ability to recover membrane flux Na<sub>4</sub>EDTA was able to attack all the studied foulants. The disadvantage of the Na<sub>4</sub>EDTA cleaning is the problems it causes with disposal, because it is highly stable and difficult to biodegrade (Sýkora *et al.*, 2001). The shift to EDTA with a lower degree of amino groups would increase the biodegradability of the chemical, while still possessing sufficient complexing ability (Sýkora *et al.*, 2001).

In general, two cleaning phases were required to reach good foulant removal efficiency in the cleaning comparison study (I). The acidic cleaning chemicals did not on the whole restore the membrane flux, even if they were needed to remove foulants from the membrane surface. Thus, the application of an alkaline chemical was needed for flux recovery after the use of an acidic cleaning. On the other hand, the sole alkaline cleaning phase may have been enough to recover the flux of the fouled membranes, although it did not remove all the foulants from the membrane. Thus, a periodic acidic cleaning is recommended to avoid the accumulation of irremovable foulant layer.

The sequence of the cleaning chemical application also seemed important: HCl was not very efficient in removing the studied foulants as a first-phase cleaning agent (I, cleaning 5), but turned out to be more efficient when applied after NaOH - Na<sub>4</sub>EDTA cleaning (I, cleaning 11). This suggests that NaOH - Na<sub>4</sub>EDTA modified the foulant layer to more easily removable by HCl solution.

According to the bacteria counts of the retentate before and after cleanings, all the studied cleaning procedures seemed to be able to remove possible accumulated micro-organisms from the membrane surface (I).

#### 4.6.3 Membrane modification in cleanings

The cleanings improved the fluxes of the new, unused NF membranes by 4-100% (I, III, IV). In the cleaning comparison study (I) the membrane flux doubled from the initial state after two cleanings. Mänttari (1999) also observed a 26% improvement in the pure water flux after cleaning the membrane similar to the one used in this study. The membrane modifications in the first cleanings seemed to be permanent, as the flux improvement was recovered in the subsequent cleanings (one-year, I, II).

Nyström and Zhu (1997) suggested that cleaning may increase the membrane flux partly by ridding the pores of the material that is left from the membrane preparation process, and partly by making the pore surfaces more hydrophilic and charged by the adsorption of the cleaning agent. The increased hydrophilicity makes the chemical bonds between the water molecules and surface groups of the membrane stronger, thus reducing the possibilities of the foulants to displace water molecules and adhere on the membrane (Chapman Wilbert *et al.*, 1998). An increased charge of the membrane increases the electrostatic repulsion between the active sites of the membrane, and thus makes the membrane more open (Braghetta *et al.*, 1997). An increased charge of the membrane also increases the repulsive forces between the

membrane and similarly charged foulants. Most organic foulants are negatively charged in aqueous solutions, and thus the introduction of negative charges by anionic surfactants may also reduce membrane fouling.

In addition to the increased flux, the membrane modification in cleanings resulted in lower ion retention after cleanings, but the retention was often recovered as the membranes were operated (I). The loss of ion retention was most profound in the cleanings using only alkaline chelating agent. Acidic cleanings, in turn, made the membranes less permeable and seemed to repair the membrane ion retention characteristics, even though they removed fouling material from the membrane. The retention of organic matter remained high and stable during the study regardless of the cleanings.

When the objective of NF is enhanced organic matter removal high ion passage is often preferred to reduce the need for alkalinity recovery and stabilisation of permeate. In that respect, the deterioration of the ion retention capability of the NF membrane did not compromise the applicability of the tested cleanings. However, some cleaning agent – membrane combinations may also lead to decrease in organic matter retention, and the effect of cleaning on membrane retention should be considered carefully and site-specifically.

The effect of pre-cleaning with Ultrasil 10 solution on the characteristics of the NF membranes was studied in the laboratory-scale study (IV). The hydrophobicity of the tested NF membranes increased in pre-cleaning according to the contact angle measurements. Based on the increased hydrophobicity, the pre-cleaned NF membranes would be expected to cause more hydrophobic interactions that might lead to flux decline.

The SEM images revealed the accumulation of organic dirt and small precipitates on the surfaces of the NF membranes (Figure 14). The elementary analysis by the SEM-EDS indicated the appearance of inorganic precipitates already on the pre-cleaned membranes (IV). These foulants may be precipitates of EDTA from the cleaning chemical and impurities of rinsing water. The FTIR-spectra of the NF255 and NF270 membranes and the XPS analysis of the NF270 membrane indicated, in turn, the removal of hydroxyl groups, phosphates and sodium from the membrane surface in pre-cleanings. This probably indicates the removal of preservative or bound water from the membranes in pre-cleanings.

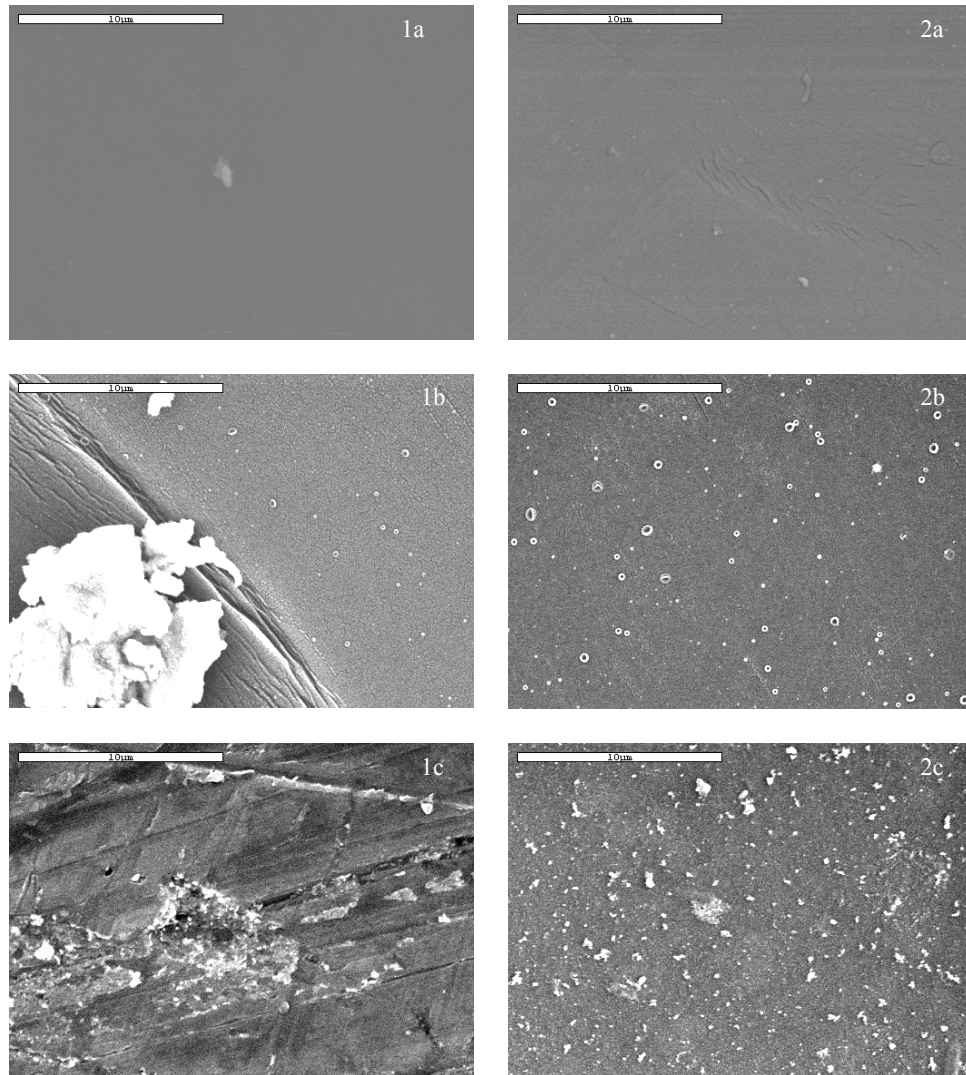


Figure 14. 6000\* SEM images of unused (1) and pre-cleaned (2) membranes: a) Desal-5 DL, b) NF255, c) NF270.

Despite the increased hydrophobicity and the foulant accumulation on the surface of the NF membranes, the pre-cleaned membranes were more permeable than the unused membranes. This indicates the profound effect of pore opening, preservative removal and changes in charge over the permeability decreasing effects of pre-cleaning. Similar phenomena may occur with other cleanings and with other membranes, but the dominance of the different effects may vary and lead to different effects on the membrane permeability.

Vast differences were seen in the way the different membranes reacted to the same cleaning in the membrane comparison study (III). However, the performed cleaning

procedure was recommended for all the membranes by the manufacturers, and resulted in efficient flux recovery of the NF255 membrane in the cleaning chemical comparison study (I). Since differences were also seen in the ways the NF membranes responded to the cleaning before and after the run, the state of the membrane also seems to affect the cleaning result. As a whole, the overall performance of the cleanings should be considered in the design and application of cleaning procedures.

The long-term effects of certain cleanings were not evaluated in the cleaning comparison study (I), but generally the cleanings that were tested did not deteriorate the membrane characteristics in a 13-week study. No change in the membrane permeability or retention was seen due to frequent cleanings during the following phases of the one-year study either. On the contrary, frequent cleanings seemed to effectively prevent the accumulation of micro-organisms on the membrane.

## 4.7 Cost and environmental impact of nanofiltration

### 4.7.1 Cost

The cost calculations of the operation optimisation study (II) suggest that at certain operating parameters the investment and operation and maintenance costs of an NF process are balanced in an optimal way resulting in the lowest total cost of NF. As a whole, the use of higher recovery (83% versus 68%) seemed more economical if NF were to be installed to enhance the conventional surface water treatment at Espoo Waterworks (II).

The calculated investment costs caused by the installation of NF at Espoo Waterworks ranged from 0.024 €/m<sup>3</sup> at a driving pressure of 7 bar to 0.043 €/m<sup>3</sup> at a driving pressure of 4 bar with both 68% and 83% process recoveries (II). Less variance and non-linear relation to driving pressure was seen in the operation and maintenance costs of NF, which ranged from 0.103 to 0.112 €/m<sup>3</sup> at the recovery of 68% and from 0.083 to 0.089 €/m<sup>3</sup> at the recovery of 83% (II). The total estimated cost of installing NF at Espoo Waterworks ranged from 0.110 to 0.151 €/m<sup>3</sup> at the studied operational parameters (II).

The cost of conventional water treatment is approximately 0.17 €/m<sup>3</sup> (excluding capital costs) in Espoo in 2005. In that respect, the addition of NF at Espoo process would increase the price of water treatment notably.

When comparing these treatment costs with the other cost data, it should be borne in mind that the system boundaries, used unit costs and application sites affect the costs and calculations and may make the comparisons impossible. For example, the seasonal variation of the feed water temperature in the Finnish applications requires the NF process to be designed for winter conditions (design flux at feed water temperature of 1°C). This caused up to 20% higher total cost of NF in comparison with the design at the year-average feed water temperature of 10°C (II). However, the calculated cost of installing and operating NF at Espoo Waterworks is very similar to the estimated cost of NF at the Méry-sur-Oise plant (0.12 €/m<sup>3</sup>) treating conventionally pre-treated river water (Ventresque *et al.*, 2000). On the other hand, the calculated costs are somewhat lower than the estimated cost of membrane

softening in Florida: the total cost ranged from 0.15 to 0.27 €/m<sup>3</sup>, and the operation and maintenance cost from 0.11 to 0.18 €/m<sup>3</sup>, at a plant size similar to the NF process designed in Espoo (Bergman, 1996).

The estimated distribution of the operation and maintenance costs at the different driving pressures and recoveries of the NF process treating coagulated surface water of Espoo Waterworks is presented in Figure 15 (II). The results indicate that at the lower driving pressures the operation and maintenance costs are dominated by membrane replacement, and at the higher driving pressures, the shares of energy consumption, membrane replacement and cleaning interval related costs of cleaning and labour become more equal. Other authors have reported the same dominating cost factors of the membrane operation and maintenance, but their shares vary between applications and sites (Pickering and Wiesner, 1993; Wiesner *et al.*, 1994; Owen G. *et al.*, 1995; Bergman, 1996).

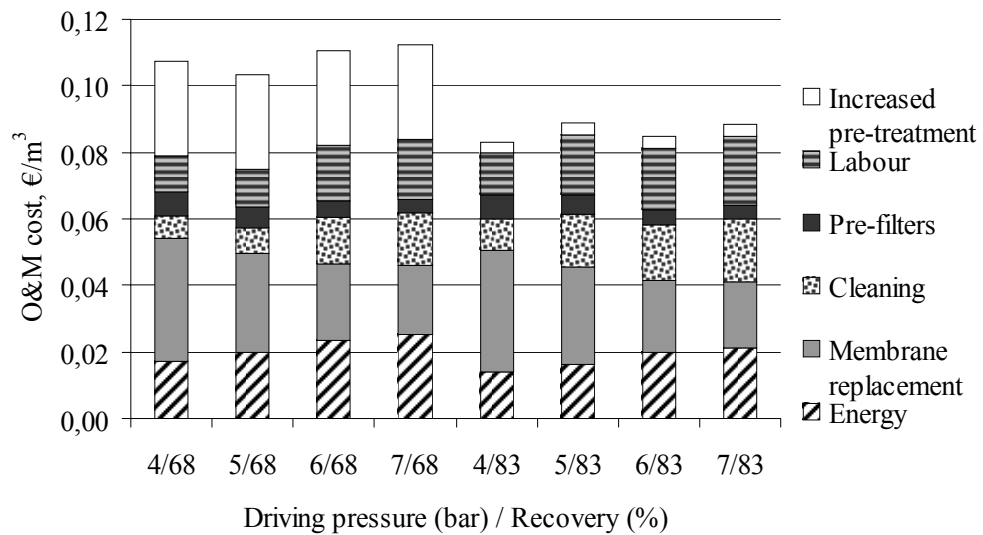


Figure 15. Distribution of operation and maintenance costs of NF process enhancing conventional surface water treatment at different driving pressures and recoveries (II).

Energy consumption and membrane replacement accounted for 42-61% of the operation and maintenance costs at all the studied operational parameters (II). Accordingly, changes in the prices of electricity and membranes, as well as in the energy requirement and the membrane life-time, affect the total cost of NF markedly. For example, a 29% increase to the present price of electricity would increase the total estimated cost of NF by 4-6% (II). On the other hand, more permeable and less energy requiring NF membranes have been developed, with which some savings in energy consumption can be attained.

Since shorter cleaning intervals are needed at the higher driving pressures and recovery, quicker membrane wear out and shorter membrane life-time can be expected. However, the study does not give any basis to predict the effect of a shorter cleaning interval on the real membrane life-time, and even longer than expected membrane life-times are possible. For example, in Norway the same NF

membranes have been operated for more than nine years despite the daily performed disinfection cleaning (Ødegaard *et al.*, 2000). Decreasing the expected membrane life-time of 5 years to 4 years, or increasing it to 6 years, would cause up to 7% change in the total costs of the NF process (II).

The effect of recovery was seen basically in the lower operation and maintenance cost of the increased pre-treatment at the higher recovery (the cost of increased pre-treatment 0.028 €/m<sup>3</sup> at the recovery of 68% and 0.003 €/m<sup>3</sup> at the recovery of 83%) (II). No expected decrease was seen in the investment and membrane replacement costs at the higher recovery, because the average operational fluxes did not increase notably in comparison with the lower recovery (II).

The effect of pre-treatment method on the performance and cost of NF was not studied and no conclusions can be made. However, the increased permeability of the membranes after the change of polyaluminium chloride coagulant to ferric chloride during the one-year study (Figure 10) suggests that better optimisation of the coagulation and sand filtration pre-treatment would most possibly increase fluxes, decrease membrane fouling and increase cleaning intervals, and thus lead to a lower total cost of the NF process. On the other hand, surface water pre-treatment with MF has proved to be both technically and economically feasible with NF (Ebrahim *et al.*, 1997; Chellam *et al.*, 1998), and at least in applications where no pre-treatment is readily available, these total membrane processes should be considered.

In some applications it would be possible and economical to treat just a part of the water by NF and mix less treated water with the NF permeate as drinking water (Bergman, 1996). However, in the studied case the whole water stream needs to be treated by NF, because the goal is to enhance the organic matter removal and odour and/or taste forming compounds are involved.

#### **4.7.2 Environmental impact**

The treatment steps of water treatment including NF, and the related inputs and outputs caused by the installation of NF at Espoo Waterworks, are presented in Figure 16 (II).

The additional inputs caused by the installation of the NF process at Espoo Waterworks include extra raw water due to less than 100% recovery of NF, extra energy for pre-treatment of more raw water, energy for pre-filtration and NF, extra chemicals for pre-treatment of more raw water, pre-filters, NF membranes and chemicals for membrane cleaning (II). The additional outputs from installation of the studied NF process are retentate and used rinsing and cleaning solutions (emissions into water), emissions into atmosphere and waste products (II).

The installation of NF at Espoo Waterworks would decrease some inputs and outputs of water treatment due to no need for ozonation, lower required disinfectant dosage and less need for distribution system maintenance (II). The lower need for disinfection chemical and less distribution network maintenance are related to the lower potential for microbial activity in the drinking water of higher quality.

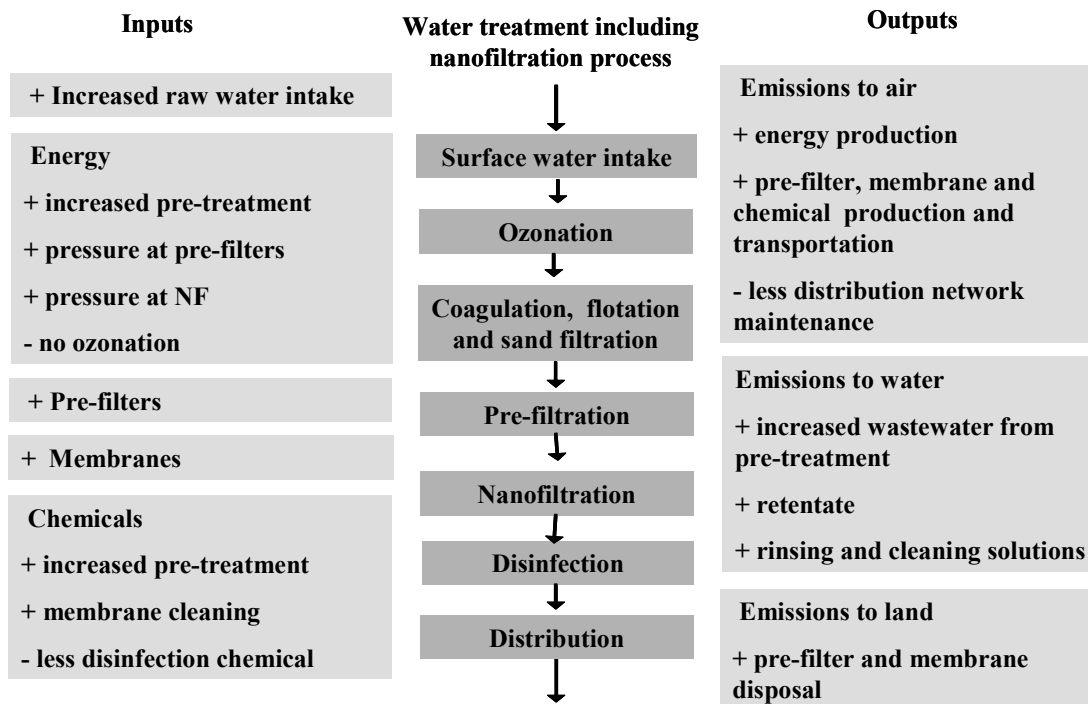


Figure 16. Phases of NF process treating coagulated surface water and related changes in operation and maintenance inputs and outputs of water treatment (II).

The inventory analysis of the environmental impacts caused by the installation of NF at the conventional surface water treatment train at Espoo Waterworks always showed the biggest environmental impact at the lower studied recovery (68%), and either at the lowest (4 bar) or at the highest (7 bar) studied driving pressure (II). From environmental point of view it seemed most efficient to use the higher recovery (83%).

Since the NF process increased the energy consumption of the water treatment by 60-150% (II), efforts should be devoted to decreasing energy consumption, and environmentally friendly energy production systems should be favoured. Sombekke *et al.* (1997) found that the use of green energy was very efficient in improving the environmental impact of NF. At present, the disadvantage of green energy is its high price compared with “conventional” energy.

The pressure increase at NF accounts for 58-75% of the energy consumption caused by the installation of NF process at Espoo Waterworks (II), and thus the most efficient option is to reduce the energy consumption of NF. This can be achieved by development and use of more permeable NF membranes requiring less driving pressure, or by increasing the membrane area and using lower design fluxes and driving pressures. The latter option causes more membrane-related production and transportation effects and bigger waste disposal, and thus optimisation is required to balance the various environmental impacts in an optimal way.

The installation of NF at Espoo Waterworks would increase the use of chemicals remarkably (II). The increased chemical use originates mostly (71-92%) from increased coagulation pre-treatment (II), suggesting that higher recovery of the NF process is the best way to reduce environmental impact of chemical use. However, the environmental impact of the used chemicals varies and small output of some chemical may be more harmful than high loads of another.

The application of higher recovery in the NF process also reduces efficiently the need for raw water intake, retentate discharge and production of wastewater in pre-treatment. The application of 83% recovery instead of 68% reduces the volume of the retentate stream more than 50%, but also increases the concentrations in the retentate notably (II). The effect of the retentate stream on the receiving water should be studied carefully when considering the discharge permission.

Generally, the small footprint is mentioned as an advantage of membrane processes, but in the evaluated case in Espoo (II) the installation of NF would notably increase the footprint of water treatment. However, with proper mitigation measures the adverse environmental impacts of the NF process can be minimised. These measures include optimisation of the pre-treatment process, or even application of an other pre-treatment technique (e.g. MF), operational optimisation of the NF process, use of less energy requiring membranes, use of green energy, use of environmentally friendly cleaning chemicals, cleaning chemical reuse and retentate utilisation.

Despite the lack of previous studies and information on the environmental impact of NF as a water treatment method, it is essential to take environmental aspects into consideration when evaluating NF as a water treatment option. The findings of Sombekke *et al.* (1997) did not indicate any significant difference between treating ground water by NF, or pellet softening and granulated activated carbon filtration from the environmental point of view. This encourages considering NF as a water treatment option also from the environmental point of view at some applications.



## 5 CONCLUSIONS AND RECOMMENDATIONS

The results indicate that **NF provides high and stable removal of organic matter from rather pure conventionally pre-treated surface water**. The low content of organic matter in the treated water suggests further water quality improvement through less formation of DBPs, restricted bacterial growth in distribution networks and less odour and taste related problems.

Contrary to expectations, all the studied **NF permeate samples showed surprisingly high potential for microbial growth and contained enough microbially available carbon and phosphorus for bacterial growth**. Microbes were also generally found in the studied NF permeates. These novel findings indicate an evident risk for pathogen multiplication in the NF permeates. Post-chlorination is recommended as a safety barrier and to suppress microbial growth in distribution systems after NF. Still, the small numbers of culturable bacteria and the low levels of organic matter found in the permeates suggests that only a minor chlorine dosage is needed for inactivation of the microbes and that low chlorine dosages are maintained well in the distribution network fed by NF. More thorough studies of the biological stability of the NF permeate are needed to evaluate the real water quality improvements after installation of NF. Long-term studies of the effects of NF on drinking water quality in real distribution networks in Finnish circumstances are recommended.

**The effect of the changes in the feed water characteristics, as well as the effect of the performed cleanings, or the varying operational parameters on the retention of organic matter in NF, was almost negligible**. These findings indicate that the retention of organic matter was mainly controlled by the sieving effect. However, the higher retention of small organic molecules than expected by their molar mass indicates that their retention was also affected by molecular charge, hydrophobicity and conformation.

The conductivity retention of the NF membranes was not as indifferent to the changes of feed water characteristics, to the operational parameters, or to the cleanings, as the retention of organic matter. However, in the studied application for enhanced organic matter removal, changes in the inorganic quality of the NF permeate do not cause problems. In applications for removal of some problematic inorganic constituents the change in the retention of inorganic matter may be important, and the changes in retention should be considered more carefully.

Despite the differences in the performance of NF between the different feed waters, the performance was found to be more related to the characteristics of the NF membrane than to the feed water. Vast differences were seen in the performance of the different NF membranes. This also emphasises the need of choosing the right membrane for each application.

In applications for enhanced organic matter removal the use of membranes with high organic matter and lowered inorganic matter retention (Desal-5 DL, Desal-51 HL, NF255 and NF270 of the studied membranes) balanced the permeate requirements of low organic content and minor need for post-chlorination and remineralisation in

the most acceptable way. These NF membranes, especially Desal-51 HL and NF270, also showed high permeability and moderate flux decline, when treating chemically pre-treated surface water. The material, charge, hydrophobicity and functional groups of the Desal-5 DL, NF255 and NF270 membranes were found to be basically the same, and only the visual appearance of the NF270 membrane was not as smooth as that of the two other membranes. It was suggested that the higher permeability of the NF270 membrane was most probably due to a membrane morphology favouring water permeation.

As assumed, the increasing driving pressure increased the operational flux and shortened the cleaning intervals of the NF membranes clearly. Surprisingly the higher recovery did not significantly affect the operational fluxes, but just shortened the cleaning intervals.

In Finnish applications, the feed water temperature changes cause seasonal variation in the operation and performance of the NF process. The NF process has to be designed for winter conditions, which increases both investment and operation and maintenance costs of NF notably compared with the average conditions of the year. The extra capacity available at the season of high feed water temperature allows the use of lower driving pressures. On the other hand, bacterial growth on the membranes may cause additional fouling at feed water temperatures above 13°C.

**The studied pre-treated surface waters caused intense flux decline of NF membranes and required short membrane cleaning intervals at the studied operational parameters. This happened despite the fact that the quality of the feed waters was high. Accordingly, it seems impossible to remove the membrane fouling tendency from the surface waters.** However, by optimising the pre-treatment process less flux decline, longer cleaning intervals and a cheaper process can be obtained. Pre-treatment optimisation is site-specific, but also general studies are needed to establish criteria for enhancement of coagulation pre-treatment of NF.

**No unambiguous correlation could be found between the membrane flux decline and single or combined feed water constituents for the tested NF membranes.** The conclusion drawn from this is that natural waters are so complex mixtures of different materials that it is difficult to determine any single constituent responsible for membrane fouling. In turn, it could be assumed that the most feed water constituents interact in membrane fouling. The study with model feed waters indicated that **the interactions of different feed water constituents, especially between organic matter, cations and colloids, affect both membrane flux and flux decline.**

In addition to feed water constituents, the pH of the feed water affected membrane flux and flux decline: with the model waters containing only inorganic matter the fluxes were the highest at low pH (pH 3), whereas with the feed waters containing organic matter the highest fluxes were seen around pH 5. **The effect of pH varied more than expected between the different feed waters and membranes, suggesting that also possible feed water pH adjustment should be optimised site-specifically.**

On the basis of the higher removal of total solids than cations in the cleanings, **the fouling material on the NF membranes fed by pre-treated surface water was**

expected to consist mainly of organic material and micro-organisms. Nevertheless, both the cleaning chemical and foulant analyses and the experienced flux declines, **emphasised the role of inorganic precipitates and organic matter-cation complexes in the fouling of NF membranes** by pre-treated surface waters.

**Amides and polysaccharides, the main organic foulants** identified on the fouled NF membranes, are ubiquitous in natural waters and can originate from several sources. Also **the inorganic foulants, aluminium, calcium, magnesium and silica**, are general constituents in the natural waters, and also integral constituents of conventional water treatment chemicals. Thus, it seems difficult, if not impossible, to remove these constituents from the NF feed water to low enough levels to prevent membrane fouling.

The accumulation of a foulant layer on the NF membranes did not correlate with the experienced membrane flux declines, indicating the role of fouling layer morphology on determining membrane flux decline instead of foulant layer thickness.

**The performed cleanings improved the fluxes of the new, unused NF membranes to the double at most.** These membrane modifications seemed to be permanent, as the flux improvement was recovered in the subsequent cleanings during the one-year study. Generally the studied cleanings did not deteriorate the membrane characteristics during the one-year study. On the contrary, the frequent cleanings seemed to effectively prevent the accumulation of biofouling on the NF membranes.

**The application of one to three sequential cleaning chemicals was required for the same flux recovery.** Alkaline cleanings were generally better than acidic cleanings in recovering the flux of the NF membranes fouled by chemically pre-treated surface water. The most efficient cleaning chemical was an alkaline chelating agent (Na<sub>4</sub>EDTA) both in terms of flux recovery and foulant removal. **Good foulant removal generally required the application of two sequential cleaning chemicals: The sole alkaline cleaning may have recovered the flux of the fouled membranes, but the efficient foulant removal required acidic cleaning as well.**

In the application and design of cleaning procedures the overall performance of the cleaning should be considered. Some cleaning chemicals may not restore the membrane flux, even if they are important in removing foulants from the membrane surface. On the other hand, some cleaning chemicals can be used to modify the foulant layer to more easily removable by the following chemical. The experiences with membrane cleaning emphasise the importance of choosing a suitable cleaning chemical to each application taking into account foulants as well as membrane characteristics. Substantial savings can be gained with the proper choice of cleaning agent in terms of membrane productivity and retention, cleaning chemical use and the time required for cleanings.

**The installation of NF after conventional surface water treatment was calculated to increase the cost of treated water at a minimum by 0.11 €/m<sup>3</sup> in the studied case.** At this cost a very reliable and easy-to-operate treatment process, the substantial increase in treated water quality, a more stable drinking water quality, and hence, better customer acceptance would be gained. **Also, the environmental impact of the water treatment was estimated to increase considerably, and**

**measures should be taken to minimise these effects.** The main ways to minimise the cost of NF were related to recovery of the process, energy consumption, membrane life-time and cleaning, whereas the environmental impact minimisation was mostly related to recovery of the process and energy consumption.

In general, both the lower cost and the least adverse environmental impact were gained at the higher recovery (83%) in the process. The investment and operation and maintenance costs of NF were, in turn, balanced to a minimum total cost at a certain driving pressure, while the environmental impact either increased or decreased linearly with driving pressure. As a conclusion, the operating parameters minimising the cost of NF also seemed to balance the total environmental impact of NF quite well.

Most studies in the field have been carried out in a laboratory-scale apparatus. However, a different membrane module design, small membrane area and feed water circulation limit the correlation between the laboratory-scale studies and the real operation of an NF plant. Thus, we used a pilot-scale NF process that can be expected to estimate the performance of a full-scale operating NF plant rather well. Consequently, the observed quality of NF permeate, as well as the results on the operation, performance and costs of the NF process are reliable estimates of the performance of NF in treating pre-treated surface water at real plant conditions. As both fouling and cleaning change the membrane characteristics, the use of the same membranes during the one-year study gives reliable information about the performance of continually used NF membranes. The laboratory-scale apparatus was used when more in-depth study of the phenomena was required

**The study supports the consideration of NF as a well and reliably performing option to improve the quality of conventionally treated surface water in different circumstances.** In addition, the independence of organic matter and bacteria retention from changes in feed water quality and process parameters, and the easy to operate process, are the advantages of the NF process. On the contrary, the challenges that hamper the use of NF in surface water treatment include problems related to membrane fouling, low process yields in comparison with conventional processes, high energy consumption, need for retentate and cleaning solution disposal, as well as the overall cost and adverse environmental impact of NF.

The quality requirement of treated water is the main factor determining the possible choices of NF membranes in each application. After choosing the NF membranes with agreeable permeate quality, their operational performance has to be evaluated and optimised, and the one with the most economical performance should to be chosen for an application. However, **in applications not requiring notably improved organic matter or ion removals, simpler and less costly process options**, like activated carbon adsorption and ultrafiltration (Baudin *et al.*, 1997; Brasquet *et al.*, 2000) or coagulation and ultrafiltration or microfiltration (Lee *et al.*, 2000; Guigui *et al.*, 2002; Pikkarainen *et al.*, 2004), **may be more suitable process option than NF.** Promising performance has been reported with these relatively new process options, but the application in Finnish circumstances requires further research.

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