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Removal of organic matter from soft water by loose nanofiltration membranes

Thesis submitted in a partial fulfilment of the requirements for the degree of Master of Science in Technology

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Abstract of master's thesis

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Abstract

Organic matter content is observed to rise in the surface waters used as raw water sources of water treatment plants in the Nordic countries. Nanofiltration is considered as a promising technology for the effective removal of organic material. When treating soft raw waters, the downside of traditional nanofiltration membranes has been their effective removal of inorganic compounds. Modern, loose nanofiltration membranes are designed to efficiently remove organic matter but have lower removal of inorganic substances than traditional, tight nanofiltration membranes. The suitability of such membranes to treat soft raw water was investigated. Additionally, the effect of pretreatment to the fouling of membrane and the necessity of pretreatment was in interest. The study was conducted in bench-scale with two feed waters: raw water from Lake Päijänne and conventionally treated water (i.e. coagulated, clarified and sand filtered water).

Both studied membranes, UA60 (molecular weight cut-off ~3500 Da) and NF270 (~300 Da), effectively removed organic matter. Inorganic substance removal was intermediate with both feed waters, however significant with soft water. In particular, the looser UA60 membrane gave promising results for the low removal of inorganic substances but low flux and low removal of microbes were disadvantages. Nevertheless, loose nanofiltration membranes seem promising for the low removal of inorganic substances and further studies with membranes of different material and with even looser membranes are suggested.

Both feed waters caused significant fouling and flux decline with 90% recovery. Lesser flux decline was observed with conventionally treated feed water than with raw water but the difference was of minor importance. Both feed waters with both membranes require an effective membrane cleaning program in larger-scale use. However, raw water can be considered as possible feed water alternative and pretreatment may be unnecessary. In order to further evaluate the suitability of raw water feed for full-scale use, a proper cleaning program is needed and the ability of cleaning program to restore the flux has to be studied.

Keywords nanofiltration, loose membrane, soft water, drinking water treatment

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Tiivistelmä

Orgaanisen aineksen pitoisuuden on havaittu nousevan pohjoismaisissa pintavesissä, joita käytetään raakavesilähteinä talousveden valmistuksessa. Nanosuodatusta pidetään lupaavana vaihtoehtona orgaanisen aineksen tehokkaaseen poistamiseen. Perinteisten tiukkojen nanosuodatuskalvojen haittapuolena on pidetty niiden kykyä poistaa tehokkaasti myös epäorgaanista ainesta, mikä ei ole toivottavaa käsiteltäessä pehmeitä raakavesiä. Markkinoille on tullut löyhempiä nanosuodatuskalvoja, jotka on suunniteltu poistamaan tehokkaasti orgaanista ainesta, mutta joiden epäorgaanisen aineen poistokyky on tavanomaisia nanosuodatuskalvoja matalampi. Tutkimuksessa selvitettiin tällaisten kalvojen soveltuvuutta pehmeiden raakavesien puhdistukseen. Lisätietoja haluttiin myös esikäsittelyn vaikutuksesta kalvon tukkeutumiseen ja erityisesti pyrittiin selvittämään vaatiiko nanosuodatus esikäsittelyn. Tutkimus suoritettiin koelaitteistolla, jossa syöttövetenä käytettiin raakavettä Päijänteestä sekä vettä, joka oli saostettu, selkeytetty ja hiekkasuodatettu.

Molemmat tutkituista kalvoista, UA60 (leikkausluku ~3500 Da) ja NF270 (~300 Da), poistivat tehokkaasti orgaanista ainesta. Epäorgaanisen aineen poisto oli tavanomaisia nanosuodatuskalvoja vähäisempää molemmilla syöttövesillä, mutta kuitenkin merkittävää näin pehmeällä raakavedellä. Erityisesti löyhempi tutkimuksessa käytetty kalvo antoi lupaavia tuloksia epäorgaanisen aineen suhteen, mutta kyseisen kalvon tuotto ja mikrobienpoistokyky olivat toivottua huonommat. Epäorgaanisen aineen poiston kannalta löyhät nanosuodatuskalvot ovat lupaavia ja jatkotutkimuksia tulee tehdä eri materiaaleista valmistetuilla sekä hieman löyhemmillä kalvoilla.

Molemmat syöttövedet aiheuttivat merkittävää kalvojen tukkeutumista ja vuon alenemista 90 % saannolla. Hiekkasuodatuksen jälkeen otetulla syöttövedellä tukkeutuminen oli hieman hitaampaa kuin raakavedellä, mutta eroa ei pidetty ratkaisevana. Kumpikin syöttövesi vaatisi tehokkaan kalvojenpesuohjelman kummallakin kalvolla suuremmassa mittakaavassa käytettynä. Raakavettä voidaan kuitenkin pitää varteenotettavana vaihtoehtona syöttövedeksi, eikä esikäsittelyä välttämättä vaadita. Lopullisen soveltuvuuden arvioimiseksi tulee raakavedelle määrittää sopiva kalvonpesuohjelma ja tarkastella kalvopesun kykyä palauttaa kalvon vedenläpäisykyky.

Avainsanat nanosuodatus, löyhä kalvo, pehmeä vesi, talousveden valmistus

Foreword

This thesis was a part of ADWATECH project funded by Tekes, HSY and Kemira. I want to thank the participants for making it possible to me to work on this subject.

Writing this thesis and conducting the pilot experiment required a lot of nerves from me and other people involved in this study. I am grateful to Heikki Poutanen for his advices in the small and the larger issues and his practical help concerning on the pilot equipment. Thanks to Panu Laurell for his comments, advises and his help with the study. Also, I want to thank Riku Vahala for his supportive words.

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Vantaa, September 5th 2014

Karoliina Sivonen

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Nomenclature

Abbreviations

AOC	Assimilable organic carbon
ATP	Adenosine triphosphate
CFU	Colony forming unit
DAF	Dissolved air flotation
DOC	Dissolved organic carbon
GAC	Granular activated carbon
HMM	High molecular mass
HPSEC	High performance size-exclusion chromatograph
IMM	Intermediate molecular mass
LC-OCD	Liquid chromatograph with organic carbon detector
LMM	Low molecular mass
MF	Microfiltration
MFI	Modified fouling index
MWCO	Molecular weight cut-off
NDIR	Nondispersive infrared sensor
NF	Nanofiltration
NF270	Filmtec™ NF270 membrane
NOM	Natural organic matter
NPOC	Non-purgeable organic carbon
NTMP	Net transmembrane pressure
PAC	Powdered activated carbon
R2A	Reasoner’s 2A agar
RO	Reverse osmosis
SDI	Silt density index
SUVA	Specific UV absorbance
TMP	Transmembrane pressure
TOC	Total organic carbon
UA60	Trisep™ UA60 membrane
UF	Ultrafiltration
UV_{254}	Ultraviolet absorbance at 254 nm

Symbols

A	area
c	concentration
C	resistance coefficient
dt	change in time
dV	change in volume
J	flux

ΔP	transmembrane pressure
Q	flow
r	rejection
T	temperature
μ	dynamic viscosity of water
Π	osmotic pressure
$\Delta\Pi$	osmotic pressure difference

Subscripts

c	critical
f	feed
i	irreversible
k	specific
M	measured temperature
NET	net
p	permeate
r	concentrate
S	standard temperature
s	strong form
sus	sustainable
t	total
w	weak form

1 Introduction

1.1 Background

Majority of drinking water in Helsinki region in Finland is produced from the surface water of Lake Päijänne at Pitkäkoski and Vanhakaupunki water treatment plants. Typically Finnish surface waters are soft and rich in humic substances, containing an abundance of natural organic matter (NOM). During the last two decades, the level of total organic carbon (TOC) at raw water intake in Päijänne has been rising, and for the past few years this has been evident with the rise of TOC from 6.0 mg/l to nearly 8.0 mg/l. Increased run-off and biodegradation due to the climate change has been suggested as a cause for elevating NOM levels (Eikebrokk et al. 2004). NOM causes taste and odor in drinking water, promotes biofilm growth in water distribution system and causes disinfection by-products in water treatment.

Currently, advanced water treatment process, meaning conventional treatment process (coagulation, clarification and sand filtration) enhanced with ozonation and activated carbon filtration, has been sufficient for removing organic matter and producing good quality water from Päijänne water. However, increasing levels of organic matter may result in difficulties if the removal capacities of existing water treatment plants are insufficient.

Previously, possibilities to retrofit low pressure membranes, i.e. microfiltration (MF) membranes, to an existing water treatment plant were studied and use of those as a replacement for some treatment processes was experimented. MF was able to compete in NOM removal with conventional treatment (Laurell 2013). This however, is an inefficient solution for the increasing NOM levels. Nanofiltration (NF), instead, has a high rejection of organic matter compared to the low pressure membranes and is thus a more promising treatment method (Vigneswaran et al. 2012b).

Typically NF is used with challenging feed water containing harmful compounds that are difficult to remove with conventional treatment, for example pesticides. Also calcium and magnesium ions are removed with NF due to its softening effect. In Finland, however, hardness of water is rarely a problem and NF is usually used just for special cases, such as in removal of phosphorus or fluoride (Nurminen 2001). The raw water from Lake Päijänne has low hardness, low turbidity, and low alkalinity, but increased content of organic carbon. Thus, high NOM removal is beneficial but the softening effect is not desired. Improvements in polymer technology have resulted in new, looser NF membranes which are promising in compromising between high NOM removal and low softening effect.

1.2 Research objectives

This research is a part of ADWATECH project which focuses on the removal of NOM in drinking water treatment and on the challenges brought on by increasing NOM levels in surface waters. In particular, the applicability of loose NF membranes in the removal of NOM from soft waters was the object in this research.

This thesis consists of a literature review and an experimental part. The literature part gives an overview on the NF process, introduces the most important design factors of NF and discusses on membrane fouling and its prevention with a pretreatment in the case of NF. The source literature contained a few books in a field of membrane science but consisted mainly of research reports and journal articles, since universally valid research results for different raw waters and membranes are nonexistent. The experimental part is based on bench-scale trial runs performed at Pitkäkoski water treatment plant for this research.

One goal of this experiment was to compare the qualitative and quantitative performance of two loose NF membranes. Another goal was to evaluate the importance of pretreatment in decelerating fouling and to study possible effect of feed water on product quality. Product quality was evaluated based on quantitative and qualitative NOM analysis and on chemical, physical and microbial analysis. Product qualities were reflected to the current Pitkäkoski product water and the prerequisites to distribute NF product water to consumers were evaluated.

1.3 Research outline

The experimental part of this thesis was limited to two pretreatment options and two different membranes. In previous studies of former Helsinki University of Technology, NF has been used with extensive pretreatment as a polishing step in water treatment process (Härmä 1999, Liikanen 1999, Liikanen et al. 2002). In this research, the ability of NF to replace several treatment steps was studied. NF was used with raw water and with conventionally treated (i.e. coagulated, settled and sand filtered) water. Two commercially available loose NF membranes, Filmtec NF270 and Trisep UA60, were selected to be tested. NF270 is developed to diminish softening effect but remain high removal of NOM. UA60 is much looser than NF270, thus, hypothesized to diminish softening effect even more, possibly with an expense of high NOM rejection. Since total removal of NOM is unreasonable and softening effect is undesirable, reduced rejections of UA60 were of interest.

The focus of the thesis is on the NF design factors from the perspective of performance. Thus, investment and operating costs are not considered even if operating costs are occasionally touched upon while discussing on the energy consumption and the frequencies of changing and cleaning membranes.

Even though sometimes the treatment of concentrate is considered problematic, in this case concentrate is supposed to be drained to the wastewater treatment plant since it contains no harmful substances. The effect of membrane cleaning is covered only in the literature part. Even though cartridge prefilters were used in the study, those are covered only briefly in the literature part as an alternative for cartridge filters is easily washable microsieves which can solve the problem of prefilter fouling. The discussion on post-treatment of NF treated water is based on the quality analysis of permeate.

2 Nanofiltration process

This chapter gives an overview on the membrane technology in water treatment, membrane filtration as a process and membrane performance.

2.1 Membrane technology

Though the history of membrane science begins at 18th century, large scale applications of membrane technology have been implemented just in the 1960s and 1970s. The incentive of developing membrane technologies was desalination of water. Later on, the possibilities of membrane technology have been noted and water treatment industry has begun to employ membrane processes to remove a variety of unwanted components from water, such as pathogens, inorganic ions and organic material.

Membrane filtration separates dissolved, colloidal and particulate constituents from fluid using semipermeable materials. Membrane processes are categorized into four groups: reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF). These can be further categorized to high-pressure (RO, NF) membranes and low-pressure (UF, MF) membranes depending on the operational pressure. At its earlier stages, NF was referred as low-pressure RO (Zhang et al. 2012) or loose RO (Yacubowicz and Yacubowicz 2005), and still it may not always be differentiated from RO.

The classification between different membrane technologies is imprecise which is why different authors and manufacturers might categorize same membrane differently. Table 1 presents one possible classification of membrane processes based on the pore size and the molecular weight cut-off (MWCO), which refers to the size of the molecules a membrane is able to reject by 90% (Kumar 2012). However, this is only one suggestion and some may place the limits differently. For example, some may grade a loose NF membrane as a tight UF membrane or a tight NF membrane as a RO membrane.

Table 1. Classification of membrane processes according to Vigneswaran et al. (2012b)

Membrane process	**RO**	**NF**		**UF**		**MF**	
		Tight	**Loose**	**Tight**	**Loose**	**Tight**	**Loose**
MWCO/ pore size	< 200 Da	200 Da to 300 Da	300 Da to 1,000 Da	1,000 Da to 10,000 Da	10,000 Da to 100,000 Da	100,000 Da to 0.01 µm	0.01 µm to 0.05 µm

Instead of categorizing membrane processes based on the MWCO, it is also possible to do the classification based on the characteristics of membranes. The categorization is problematic especially for NF membranes since NF combines some properties of RO and UF but has also some specific characteristics (Van der Bruggen and Geens 2008). For example, NF and RO are believed to have no distinct pores, which differentiate NF and RO from MF and UF (Yacubowicz and Yacubowicz 2005). One common way to categorize membranes is based on their separation potential. The general division of membrane separation potentials is presented in Figure 1. MF and UF are used for particle and microorganism removal while NF removes also dissolved substances such as organics and larger ions. RO aims to remove practically all substances from water. RO can reject both monovalent and polyvalent ions while NF rejects mainly polyvalent ions.

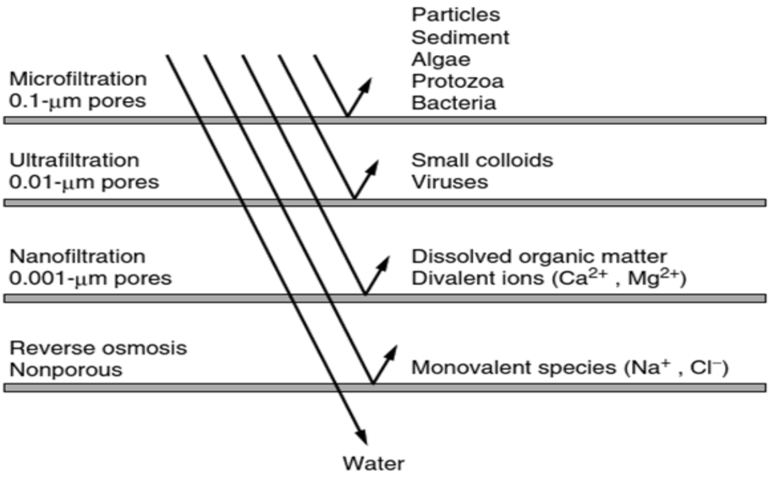

Figure 1. Separation potential of different membranes (Crittenden et al. 2012a)

Table 2 presents more detailed NOM removal abilities of different membranes and summarizes some main characteristics of different membrane processes. The differences between abilities of membrane technologies to remove NOM of different sizes (high molecular mass HMM, intermediate molecular mass IMM and low molecular mass LMM) are presented. While NF and RO both have the capability to remove salts, NF operates at lower pressure. The pressure ranges presented are only approximates and a membrane can be operated also in lower pressure if feed water quality allows (Van der Bruggen and Geens 2008). NF can be operated even at 3 bar (Metsämuuronen et al. 2014).

Table 2. Characteristics of different membrane processes, adapted from Zhang et al. (2012), Vignesvaran et al. (2012a), and Vignesvaran et al. (2012b)

Membrane type	**MF**	**UF**	**NF**	**RO**
Porosity	porous	porous	finely porous	nonporous
Pore size (nm)	50-1,000	5-20	2-5	-
Membrane type	isotropic	asymmetric	asymmetric/ composite	asymmetric/ composite
Transfer mechanism	sieving, adsorption	sieving, preferential adsorption	sieving, electrostatic hydration, diffusion	diffusion
Driving force	pressure	pressure	pressure	pressure
Operating pressure (bar)	0.5-5	1-10	7-30	15-100
Removes				
HMM NOM	no	yes	yes	yes
IMM NOM	no	no	yes	yes
LMM NOM	no	no	yes/no	yes

Compared to conventional treatment processes, membrane process has smaller footprint and it might result in fewer unit processes. However, this advantage is lost if only a part of water is treated with membranes and the rest with conventional treatment. Membrane technology is applicable for broad range of water qualities resulting in stable product water and it can stand well the fluctuations in the feed water quality. Membrane system is easy to modularize, scale-up, control, and integrate (Zhang et al. 2012). In addition to the common membrane advantages, well-designed NF may also improve the water quality compared to conventional treatment by a more efficient removal of unwanted components, such as color, turbidity, pesticides and disinfection by-product precursors. NF may also decrease the chemical consumption of, for example, disinfectants (Van der Bruggen and Geens 2008).

One common application of NF is water softening since NF has good capability to remove divalent ions from water. As a result of recent development, some newer NF membranes have high rejection of organic matter but moderate removal of hardness. This depends on the MWCO of the membrane and this is beneficial when treating soft waters. Development has also decreased the consumption of energy as membranes can be operated at lower pressures. Some disadvantages or problems in membrane processes which yet remain unresolved are the post-treatment of concentrate and lower recoveries compared to conventional treatment processes which must be considered if NF is applied in water treatment plant (Van der Bruggen and Geens 2008).

2.2 Membrane filtration process

In a membrane filtration process, feed water is conveyed to the membrane. Depending on the membrane, certain molecules penetrate the membrane. This penetrating aqueous solution is called permeate. A driving force is required for some of the molecules to permeate the membrane. In water treatment, the driving force is usually pressure, but it can also be for instance concentration, temperature or electric potential. Solution which does not penetrate the membrane is called concentrate (or retentate) and it may be disposed or partially recirculated back to the system as feed water. Recirculation increases the recovery of the process but it will concentrate the feed water. Figure 2 shows the principle of membrane filtration process.

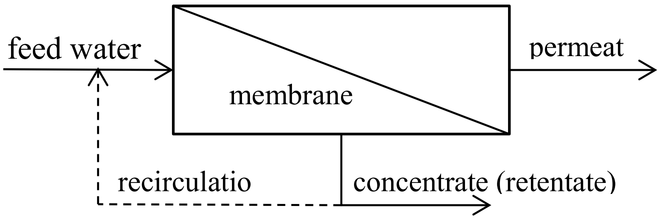

Figure 2. Principle of membrane filtration

Membranes can be operated as dead-end or crossflow operation. In dead-end system the feed water approaches the membrane perpendicularly and this operation is used mostly in MF and UF. Crossflow provides tangential movement of feed water over the membrane surface. The benefit of crossflow operation is the minimization of accumulation of retained species on the membrane surface and thus lower energy consumption, especially with small MWCO membranes. Vigneswaran et al. (2012b) state that NF system will always operate crossflow. In some laboratory-scale tests however, NF membranes are operated dead-end (de la Rubia et al. 2008). In crossflow, the concentrate is usually recirculated since otherwise the recovery would be very low.

Membrane filtration process consists of the membrane itself, modules housing the membranes and supplementary parts including pumps and tanks. The purpose of the module is to support the membrane, improve the hydrodynamics especially for crossflow membranes (Vigneswaran et al. 2012a), and enable easy cleaning (Guo et al. 2012). Modules can be flat-sheet, spiral-wound, tubular or hollow-fiber modules. Flat-sheet module comprises a flat membrane and a porous plate which supports the membrane and allows permeate outlet. Spiral-wound module consists of flat-sheets wound around a central tube and separated by mesh-like channel spacers. Figure 3 illustrates the structure of a spiral-wound membrane. Tubular module is a tube, the inside of which is coated with membranes, usually of ceramic material. Hollow-fiber module consists of semipermeable fibers with central pore which are collected into a tube. Table 3 presents some characteristics of these module types which can affect the choice and the applicability of membrane type. Most NF modules are spiral-wound (Crittenden et al. 2012a, Vigneswaran et al. 2012b) but all types are available (Yacubowicz and Yacubowicz 2005). Modules can be installed in parallel or in series to increase the capacity or to improve the rejection or recovery, respectively.

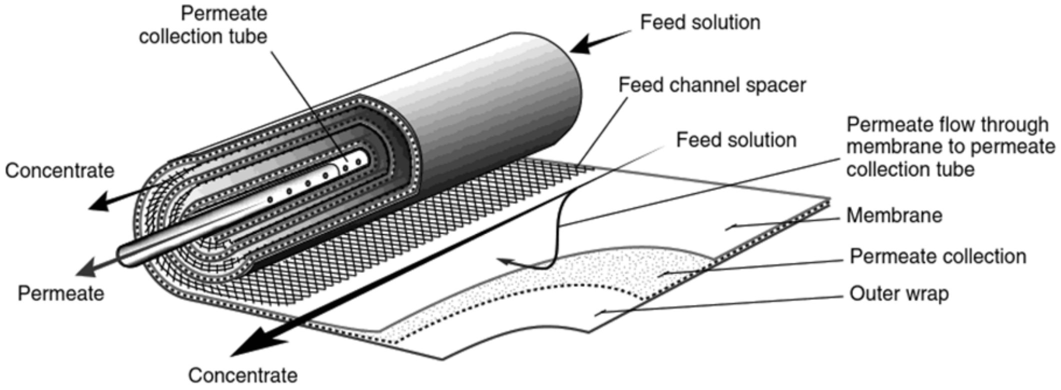

Figure 3. Structure of spiral wound module (Crittenden et al. 2012b)

Table 3. Characteristics of different module types (Vigneswaran et al. 2012b)

	Packing density	**Operation energy**	**Fouling control**	**Cleaning**
Flat-sheet	Moderate	Low – Moderate (laminar flow)	Moderate	Moderate
Spiral-wound	High	Moderate (spacer pressure losses)	Moderate – Good (no suspended solids) Moderate – Poor (suspended solids)	Sometimes difficult (if spacers blocked)
Tubular	Low	High (turbulent)	Good	Good
Hollow-fiber	High	Low (laminar or dead-end)	Moderate – Good (lumen feed) Moderate – Poor (shell-side feed)	Back-flushing is possible

2.3 Membrane performance

Membrane performance is measured with two factors: quantity and quality of water produced. Quantity of water produced by membrane is usually described as flux. Flux is the ratio of permeate flow rate and membrane surface area (Equation 1). Flux is usually expressed as liters of water per membrane area per hour ($l/m^2/h$ or LMH) but gallons per square foot per day ($gal/ft^2/d$, GFD or gfd) is also used, especially in American literature. When converting flux from GFD to LMH, GFD is multiplied by a constant of 1.7.

$$J = \frac{dV}{Adt} = \frac{Q_p}{A} \tag{1}$$

where J = flux [$l/m^2/h$]
dV = change in volume [l]
A = area of membrane surface [m^2]
dt = change in time [h]
Q_p = permeate flow [l/h]

Solution flux can also be expressed by modified Darcy's Law (Equation 2). This equation separates the effect of water viscosity and the membrane resistance from the overall flow resistance (Hwang and Kammermeyer 1975). It also notices the effect of osmotic pressure difference, $\Delta\Pi$, which reduces the efficiency of the transmembrane pressure (TMP).

$$J = \frac{\Delta P - \Delta \Pi}{\mu C_t} \tag{2}$$

where J = flux [$l/m^2/h$]
ΔP = transmembrane pressure [bar]
$\Delta \Pi$ = osmotic pressure difference [bar]
μ = dynamic viscosity of water [kg/m/s]
C_t = total resistance coefficient [m^{-1}]

For dilute solution, osmotic pressure can be calculated with Equation 3. When loose NF membranes and fresh surface water are at issue, the effect of osmotic pressure can be assumed to be minor.

$$\Pi = cRT \tag{3}$$

where Π = osmotic pressure [bar]
c = concentration of all solutes [mol/l]
T = solution temperature [K]
R = gas constant = $8{,}314 * 10^{-2}$ bar·l/mol/K

According to Darcy's Law, the permeate flux increases as the net transmembrane pressure (NTMP), i.e. $\Delta P - \Delta \Pi$, increases while other operating conditions remain constant. The law also states that flux is dependent on viscosity of water which further depends on temperature. This means that the flux is dependent on operating temperature. At lower temperature, viscosity is higher resulting in smaller flux. This must be noted when designing a membrane system that uses surface water with changing temperature as feed water. To be able to compare fluxes at different temperatures, they are converted to fluxes at standard temperature, typically 20°C (Equation 4).

$$J_S = J_M \left(\frac{\mu_M}{\mu_S}\right) \tag{4}$$

where J_S = flux at standard temperature [$l/m^2/h$]
J_M = flux at measured temperature [$l/m^2/h$]
μ_M = dynamic viscosity of water at measured temperature [kg/m/s]
μ_S = dynamic viscosity of water at standard temperature [kg/m/s]

Based on Equation 4, the ratio of flux at standard temperature and measured temperature should be constant. However, Park et al. (2005) found that the ratio is inconstant for different membranes. This can be explained by the fact that Equation 4 only comprises the changes in viscosity of water even though temperature may also affect the membrane, for example, by swelling it in higher temperatures (Crittenden et al. 2012a).

To normalize the flux for pressure, membrane flux at standard temperature is divided by NTMP, or in a simplified case, by TMP (Equation 5). This is called specific flux or permeability if pure water is filtered through an unused membrane. Specific flux is usually expressed in units of l/m^2/h/bar or gal/ft^2/d/atm (Crittenden et al. 2012a).

$$J_k = \frac{J_s}{\Delta P - \Delta \Pi} \tag{5}$$

where J_k = specific flux [l/m^2/h/bar]
J_s = flux at standard temperature [l/m^2/h]
$\Delta P - \Delta \Pi$ = net transmembrane pressure [bar]

The effect of membrane filtration to the other part of membrane performance, water quality, is measured by rejection (Equation 6). Rejection, or retention, describes the membranes ability to reject certain component, such as NOM or calcium ions, from water.

$$r = 100 * (1 - \frac{c_p}{c_f}) \tag{6}$$

where r = rejection [%]
c_p = concentration of substance in permeate [g/mol]
c_f = concentration of substance in feed water [g/mol]

The rejection is affected by the operational conditions, the membrane properties and the characteristics of the feed water, which will be studied in more detail in the chapter 3. In many cases, greater flux results in smaller rejections (Österlund 1999).

2.4 Energy consumption

Since even looser NF membranes are quite tight, feed water requires high operation pressure to permeate. Naturally, producing such high pressure consumes a lot of energy which increases the operational costs of NF. This is a clear disadvantage compared to conventional treatment process which may operate almost completely without additional energy if designed appropriately.

Energy consumption increases even more when membrane fouling occurs since the system requires higher pressure to reach the same flux. However, fouling can be reduced with suitable cleaning program. On the other hand, cleaning requires energy, increases the need of chemicals and reduces total recovery by increasing downtime and the amount of water needed for cleaning. Therefore, the control of fouling has lately been an important focus point in research.

By increasing knowledge, the optimization of membrane processes has already improved, which have decreased the energy demand (Zhang et al. 2012). The key elements to achieve the lowest possible energy consumption are proper plant design, proper membrane selection, well-adjusted pretreatment, and proper plant control (Majamaa et al. 2011).

3 Nanofiltration design factors

This chapter presents the three design factors of nanofiltration; operational conditions, membrane characteristics and feed water characteristics.

3.1 Operational conditions

3.1.1 General

As was previously shown in section 2.3, pressure and temperature affect the membrane flux. Furthermore, these and other operational conditions, such as crossflow velocity and recovery rate of the system, can affect the membrane performance by influencing the rejections.

Proper choice of operational parameters can improve membrane performance and reduce membrane fouling thus extending the cleaning frequencies (Vrijenhoek et al. 2001, Seidel and Elimelech 2002). Under optimal conditions for each NF membrane, different tight membranes can produce water of equal quality (Alborzfar et al. 1998). As a result, operation conditions must be optimized to achieve these benefits.

3.1.2 Pressure

Pressure difference is an important operational condition in NF. The effective driving pressure is the difference of the supplied hydraulic pressure and the osmotic pressure solutes apply on the membrane (Yacubowicz and Yacubowicz 2005). Membrane systems operate in constant NTMP or constant permeate flux. Constant NTMP is commonly used in laboratory studies whereas full-scale plants use constant flux because of production capacity requirements (Crittenden et al. 2012a). In NF systems, NTMP is calculated with the Equation 7:

$$\Delta P_{NET} = \Delta P - \Delta \Pi \tag{7}$$

where ΔP_{NET} = net transmembrane pressure [bar]
ΔP = transmembrane pressure [bar]
$\Delta \Pi$ = osmotic pressure difference [bar]

With the assumption that osmotic pressure is negligible in loose NF membrane system with fresh surface water, NTMP is reduced into TMP. TMP can be calculated from feed, concentrate and permeate pressures (Equation 8):

$$\Delta P = \frac{P_f + P_r}{2} - P_p \tag{8}$$

where ΔP = transmembrane pressure [bar]
P_f = feed pressure [bar]
P_r = concentrate pressure [bar]
P_p = permeate pressure [bar]

Alborzfar et al. (1998) found out that changes in operation pressure had no major influence on permeate quality either for water high in humic acids (pressures of 10 and 12.5 bar) or high in fulvic acids (pressures of 8, 10 and 12 bar). However, the researchers also revealed that a higher pressure resulted in a greater flux decline. Thus, they recommended lower pressures, which would also decrease the energy costs. Findings of Chang et al. (2009) supported this as they showed that a higher pressure resulted in a greater flux decline but had no significant effect on NOM rejection (pressures from 6.9 to 10.35 bar). According to Metsämuuronen et al. (2014), several other studies have also indicated that increase in TMP has no significant effect on the NOM rejection even though flux increases.

3.1.3 Temperature

The second important operational parameter is temperature. As stated in section 2.3, increasing temperature reduces viscosity which enhances NF performance by increasing flux. In NF, the rejections are in dependent on the process temperature (Yacubowicz and Yacubowicz 2005). However, the precipitation of calcium increases with increasing temperature due to its solubility characteristics, which may affect its rejection (Vigneswaran et al. 2012b).

3.1.4 Crossflow velocity

Third important operational condition is crossflow velocity. Crossflow velocity is the velocity of feed water flow across the membrane surface. Crossflow velocity affects concentration polarization, i.e. the concentration of solutes on membrane-solution interface, which causes fouling on the membrane surface. High crossflow velocity hinders the accumulation of molecules on membrane surface. Thus, increasing crossflow velocity in NF reduces accumulation of NOM on the membrane surface and increases the average flux (Vrijenhoek et al. 2001, Seidel and Elimelech 2002). However, the endurance of the membrane and the module limits the applicable velocity (Yacubowicz and Yacubowicz 2005).

Alborzfar et al. (1998) found that high crossflow velocity reduces flux decline of tight NF membranes while the rejection of NOM stayed high, above 94% in terms of non-purgeable organic carbon (NPOC). Chang et al. (2009) in turn showed that rejection of dissolved organic carbon (DOC) was not affected by crossflow velocity but UV reduction was higher at lower crossflow velocity.

3.1.5 Recovery

Fourth important operation condition is recovery. Recovery describes the proportion of water which permeates the membrane in percentages (Equation 9):

$$recovery = 100 * (\frac{Q_p}{Q_f}) \tag{9}$$

where Q_p = permeate flow [m^3/h]
Q_f = feed water flow [m^3/h]

For crossflow NF system, recovery is low if no recirculation is used, usually from 5% to 15% (Crittenden et al. 2012b). Recovery rate can be adjusted by recirculating a proportion of concentrate back to feed water, whereupon the recovery is usually around 85% (Alborzfar et al. 1998). Recirculation increases energy consumption as concentrate is pumped several times to the membrane. On the other hand, low recovery increases the energy of post-treating the concentrate.

Increasing recovery increases the concentration of feed water as larger portion of concentrate is recirculated back to the system as feed water. Gorenflo et al. (2002) found that the rejection of NOM is independent from recovery rate, even though the feed water concentrated up to 20 mg/l DOC. They tested recovery rates from 6% to 85% and achieved rejections of DOC of over 95%. Alborzfar et al. (1998) confirmed that the removal of NOM was high, over 94% in terms of NPOC, despite of the recovery (from 67% to 90%). However, they also found that the permeability of calcium and magnesium increased with increasing recovery. Lopes et al. (2013) noticed the same phenomena, which they argued favorable for soft waters.

Too high recovery may lead to remarkable flux decline which is why the recovery should be optimized by testing (Alborzfar et al. 1998). Ericsson et al. (1996a) state that 5% increase in recovery, from 85% to 90%, decreased the flux recovery after cleaning by almost 20%.

3.2 Membrane characteristics

3.2.1 General

There are several physical and chemical membrane characteristics which influence the selection of membrane. Membrane selection depends on the features wanted to achieve. Table 4 presents some potentially important characteristics which should be considered in membrane selection. In addition to the MWCO, also hydrophobicity, surface charge, and roughness affect the applicability of a membrane.

Table 4. Potentially important membrane properties, adapted from Crittenden et al. (2012a), Vigneswaran et al. (2012a), and Vigneswaran et al. (2012b)

Membrane character	**Influence on:**						
	flux	**separation**	**fouling**	**interactions**	**cleaning**	**operation**	**economics**
Pore size, MWCO	x	x	x				
Hydrophobicity			x	x	x		
Surface charge		x	x				
Chemical compatibility			x		x	x	
Surface roughness			x				
Ease of fabrication							x

3.2.2 Membrane materials

As a result of increased knowledge on material chemistry, artificial membranes have been fabricated from variety of materials such as ceramics (e.g. aluminum oxides, silicon carbide, zirconium oxide), polymers, heterogeneous solids (e.g. polymeric mixes, mixed glasses), and liquids (Zhang et al. 2012). The majority of membranes in water industry are polymeric although the number of applications of ceramic membranes is increasing (Vigneswaran et al. 2012a). Virtually all NF membranes are polymeric (Yacubowicz and Yacubowicz 2005). NF membranes can be manufactured from cellulose acetate, polysulfone, polyethersulfone, (aromatic) polyamides, polyimide and polypiperazine amide (Van der Bruggen and Geens 2008).

Most popular membrane materials for NF are cellulose acetate and polyamide compounds. Cellulose acetate membranes are typically asymmetric and hydrophilic. They are inoperable at temperatures over 30°C, at acidic or alkali conditions (below pH 3 or above 8), or at free chlorine concentration above 1 mg/l. They are also prone to severe biodegradation, which can lead to complete loss of integrity. Polyamide membranes are not biodegradable. They withstand pH variations from 3 to 11 and are chemically and physically more stable than cellulose acetate membranes. Under the same pressure and temperature conditions, polyamide membranes can produce higher flux than cellulose acetate membranes. Polyamide membranes are more hydrophobic, thus more prone to fouling, and free chlorine at any concentration is intolerable. Ideal membrane material is physically durable, chemically stable, non-biodegradable, chemically resistant and inexpensive, and it can produce high flux without fouling or clogging (Crittenden et al. 2012b).

3.2.3 Pore size

For NF, size exclusion and electrostatic repulsion are the major removal mechanisms for humic substances (Schäfer et al. 1998). Molecules larger than the MWCO of membrane will mainly be rejected by the size exclusion. Molecules about the size of MWCO and smaller are rejected by electrostatic repulsion rather than size exclusion (Nilson and DiGiano 1996, de la Rubia et al. 2008, Metsämuuronen et al. 2014). The effect of electrostatic repulsion becomes less important when molecules are larger than the pores of the membrane (Van der Bruggen et al. 1999).

The removal of NOM and divalent cations increases with decreasing pore size. NF membrane with MWCO 1,000 Da can significantly reduce color of water (Vigneswaran et al. 2012a). NF membranes with MWCO 100-400 Da can achieve almost complete NOM rejections (Metsämuuronen et al. 2014). For example, Meylan et al. (2007) found that with the NF270 membrane (MWCO ~300 Da) DOC removals can be over 98%. Lopes et al. (2013) confirmed that NF270 membrane can remove all microorganism and almost all (>99%) TOC and DOC, even with recovery rate of 98%.

3.2.4 Surface charge

Electrostatic repulsion, i.e. charge repulsion, occurs when membrane surface and a molecule in feed water has the same charge. Membrane surface becomes charged when it is in contact with aqueous electrolyte solution, such as surface water or groundwater. The surface charge of membrane is often characterized by zeta potential. The zeta potential is the potential at the plane of shear between the charged surface and the liquid that move in relation to each other. Charging may result from dissociation of functional groups, ion adsorption, adsorption of polyelectrolytes, ionic surfactants, charged macromolecules etc. (Kallioinen and Nyström 2008). At neutral pH most NF membranes are negatively charged and at lower pH positively charged (Vigneswaran et al. 2012b). Over majority of pH range (tested at pH 2…9), the presence of humic substances increases the negative charge of the membrane (Childress and Elimelech 1996).

If a membrane surface is negatively charged and NOM includes negatively charged groups, charge repulsion occurs. Thus, increasing negative charge density on the membrane surface and in the pores increases the removal of NOM. Positive charge of membrane causes attraction between membrane and negatively charged NOM components which may lead to significant fouling (Metsämuuronen et al. 2014). However, the accumulating NOM on the membrane surface changes the charge of the membrane surface. At the beginning of filtration, flux decline is much steeper for positively charged membranes than for negatively charged. As the filtration continues, the positive membrane surface gets covered by negatively charged foulants and the charge effect diminishes. This makes charge effect significant mainly at the initial stage of operation (Lee and Lee 2007).

In contrast to most other studies, Reiss et al. (1999) found that negatively charged membrane has more tendencies to foul. Researchers suggested that this could be explained by other membrane characteristics. Charge effect is argued to be less important for flux behavior than hydrophobicity (Lee and Lee 2007).

3.2.5 Hydrophobicity

Membrane hydrophobicity affects the membrane performance strongly when organic molecules are separated from aqueous solution (Kallioinen and Nyström 2008). The hydrophobicity of a membrane can be determined by a contact angle measurement, which defines the angle between liquid drop and the membrane surface (Figure 4). If the surface is hydrophilic, the drop spreads along the surface and the contact angle is small. If the surface is hydrophobic, the contact angle is high. Contact angle of membrane has found to change due to fouling and different pretreatments result in different contact angles (Shon et al. 2012).

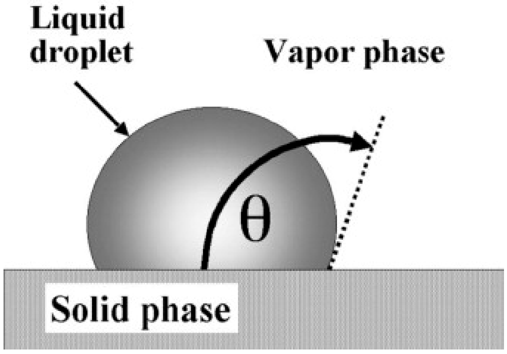

Figure 4. Contact angle (Hubbe 2001)

Despite of the hydrophobicity of the membrane, it can remove both hydrophobic and hydrophilic NOM (Siddiqui et al. 2000). However, usually hydrophobic membrane materials have more tendencies to foul than hydrophilic materials (Mänttäri et al. 2002, Crittenden et al. 2012a). Many bacteria have some hydrophobic character, and it has been found that bacteria attach most readily to hydrophobic surfaces (Vigneswaran et al. 2012a, Vigneswaran et al. 2012b). Similar observations have been made for virus and protein removal (Vigneswaran et al. 2012a). This means that hydrophobic membranes might have an advantage in reducing the quantity of organic particles, such as bacteria, viruses and proteins, in permeate. According to Braeken et al. (2005) hydrophobicity is the most important parameter in rejection of molecules with molecular weight below the MWCO.

3.2.6 Roughness

Uneven surface of the membrane enables the accumulation of matter on the surface in crossflow system. Membrane roughness correlates with the colloidal fouling regardless of the physical or chemical test conditions. More particles deposit on rough membranes than on smooth membranes (Reiss et al. 1999, Vrijenhoek et al. 2001). For example, cellulose acetate membranes have found to have lower tendencies to foul, which has been attributed to the smoother surface of cellulose acetate membranes (Elimelech et al. 1997, Reiss et al. 1999).

3.3 Feed water characteristics

3.3.1 General

The rejection efficiency of membrane is affected by hydrodynamic conditions, which were covered in section 3.1, and solute-solute and solute-membrane interactions. Therefore, both membrane and feed water characteristics affect rejections. Feed water modifies membrane characteristics due to physical and chemical interactions. Thus, for different feed waters there are different optimal membranes and different optimal operation conditions (Boussu et al. 2008, Shon et al. 2012). Important feed water characteristics are pH, ionic strength, and NOM composition.

3.3.2 pH

As stated in section 3.2.4, pH of feed water affects the charge of membrane surface. At pH below the isoelectric point of a membrane, which is usually between 3 and 5, the membrane surface is positively charged. At higher pH, the surface is negatively charged (Metsämuuronen et al. 2014). The overall rejection of NOM increases with pH (Hong and Elimelech 1997, Yacubowicz and Yacubowicz 2005, Metsämuuronen et al. 2014). The removal is expected to be higher at higher pH as the humic molecules have more linear configuration, and thus larger radius, and there is larger charge repulsion between the membrane and the molecules (Metsämuuronen et al. 2014).

pH also changes the characteristics of the feed solution, for example by affecting the solubility and thus rejection of ions (Yacubowicz and Yacubowicz 2005). The precipitation of calcium increases with increasing pH which, together with previously mentioned temperature, affects calcium rejection (Vigneswaran et al. 2012b).

3.3.3 Ionic strength

In addition to pH, the ionic strength may change the surface charge of membrane (Seidel and Elimelech 2002, Van der Bruggen and Geens 2008). Adsorption of divalent cations reduces the negative charge of membrane which increases the adsorption of humic substances (Seidel and Elimelech 2002). Positive calcium ions can also bind to the acidic functional groups of the NOM thus neutralizing charges (Lee et al. 2005). The ion rejection of the membrane tends to decrease as the ion concentration in feed water increases, even though the effect on divalent ion rejection may be smaller than on monovalent ion rejection (Liikanen et al. 2002, Matilainen et al. 2004, Yacubowicz and Yacubowicz 2005). High ionic strength of feed water decreases the flux of NF membranes (de la Rubia et al. 2008).

3.3.4 NOM composition

The nature of organic matter is more complex. Organic matter consists of TOC and other constituents, for example colloids. TOC comprises of dissolved and particulate organic carbon, which are operationally usually separated by 0.45 µm filter. The fractions of DOC can be divided as hydrophobic and hydrophilic and further as acids, bases and neutrals. NOM can also be divided into humic and non-humic fractions. Humic fraction constitutes the major fraction of any NOM sample. Humic fraction, which comprises of humic and fulvic acids, is more hydrophobic than non-humic fraction. Fulvic acids are soluble even in very acidic conditions, but humic acids precipitate. Fulvic acids are smaller in average molecular weight, less aromatic and more charged than humic acids. IMM and LMM NOM consists mostly of fulvic acids and HMM NOM matter mostly of humic acids (Matilainen 2007).

The size distribution of NOM varies from some hundreds of Daltons to over 100,000 Da depending on the determining method (Ericsson and Trägårdh 1996b, Matilainen 2007). The size distribution depends on the water source but generally molecules under 1,000 Da are in majority (Metsämuuronen et al. 2014). Since the molecular masses of the NOM components vary greatly, not all the components will necessarily be removed from the water if the MWCO of the membrane is too high compared to the sizes of NOM substances (Van der Bruggen and Geens 2008).

Meylan et al. (2007) found that with NF270 membrane HMM components were almost completely removed (>99%) and the rejections of charged LMM, LMM neutrals and hydrophobic organics were 97%, 94% and 88%, respectively. They suggested that tight NF membranes reject most of the DOC but about 10…20% of the initial concentration of LMM compounds permeate, especially LMM neutrals. Thus, depending on the fractionation of NOM, a membrane with low MWCO may be needed to remove organics to sufficient level (Metsämuuronen et al. 2014).

In addition to the size distribution of NOM, other NOM characteristics, such as hydrophobicity, affect the interactions between NOM and membrane. Hydrophobic NOM, usually humic substances, is responsible for nearly all permeate flux decline but it is also more effectively rejected than hydrophilic fraction. Hydrophilic NOM has an insignificant effect on flux since it is preferentially transported through membrane (Nilson and DiGiano 1996)**.**

When the organic components are charged, a membrane with high surface charge and a small contact angle is favorable. For dissolved organic components, best results are obtained by membranes with low MWCO (Boussu et al. 2008). Hydrophobic NOM can easily accumulate on hydrophobic membrane surface resulting in a significant flux decline (Chang et al. 2009).

4 Fouling and cleaning of nanofiltration membrane

This chapter discusses on membrane fouling, concepts of critical and sustainable fluxes, and membrane cleaning methods concentrating on chemical cleaning.

4.1 Membrane fouling

4.1.1 General

The major challenge to the membrane performance is fouling. Membrane fouling refers to the accumulation of molecules on the membrane surface and into the membrane pores, which causes flux decline. Other disadvantages of fouling are increasing TMP and possible contamination of permeate due to the biomass sloughing from the membrane surface or the loss of membrane integrity. Fouling increases operational costs by decreasing productivity, increasing TMP and thus pumping costs, increasing the need of membrane cleaning, and decreasing membrane lifetime. Fouling can also affect solute rejection either by increasing or decreasing rejection of certain molecules (Van der Bruggen and Geens 2008). Thus, some small fractions may permeate new or just cleaned membrane even if those are otherwise rejected (Vigneswaran et al. 2012a).

Figure 5 summarizes the factors affecting membrane fouling. Fouling is influenced by characteristics of compounds in feed water (e.g. molecular size, solubility, diffusivity, polarity, hydrophobicity and charge), membrane properties (e.g. pore size, hydrophobicity and charge), membrane operating conditions (e.g. flux, TMP and recovery), and feed water composition (e.g. pH, ionic strength and presence of organic matter). Since all of these factors influence fouling, fouling mechanisms are complicated and hardly understood (Shon et al. 2012).

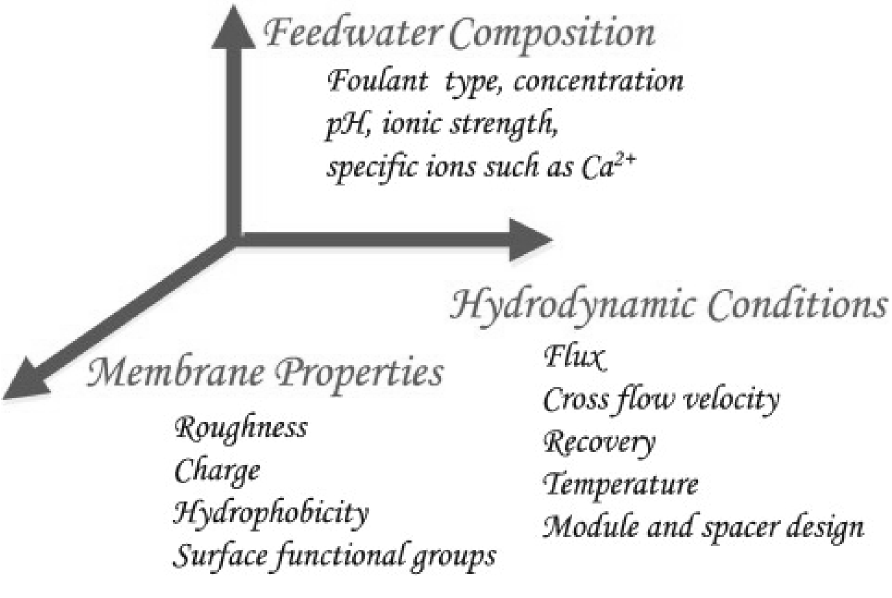

Figure 5. Factors affecting membrane fouling (Tang et al. 2011)

4.1.2 Fouling categories

Fouling can be categorized based on the mechanism, the reversibility or the cause of fouling (Table 5). Four main mechanisms can be defined; cake formation, chemisorption, concentration polarization, and pore blocking. Pore blocking (i.e. substances being physically stuck in the pores) and cake formation (i.e. accumulation of particles on the membrane surface) as mechanisms are much easier to investigate and understand than more complex mechanisms such as concentration polarization (i.e. the concentration of solutes on membrane-solution interface) and chemisorption (i.e. adsorption which includes chemical reactions).

Based on reversibility, fouling can be categorized as reversible and irreversible fouling. Reversible fouling is caused by cake formation and concentration polarization. It can be removed either by physical or chemical cleaning. Irreversible fouling results from chemisorption and pore blocking and it cannot be removed without extensive chemical cleaning (Guo et al. 2012). Based on the cause, fouling can be divided into biological, colloidal, organic and inorganic fouling.

Table 5. Different types of fouling

Mechanism of fouling	Reversibility of fouling	Cause of fouling
• Chemisorption	• Reversible fouling	• Biological fouling
• Pore blocking	• Irreversible fouling	• Colloidal fouling
• Cake formation		• Organic fouling
• Concentration polarization		• Inorganic fouling

4.1.3 Foulants

Considering the characteristics of feed water, the cause of fouling is one of the main interests in membrane processes. Table 6 compiles some of the main membrane foulant types. Inorganic fouling is a result of adsorption and precipitation of mineral deposits, mainly metal salts, such as calcium and iron salts. Organic fouling is due to dissolved organic matter, such as humic and fulvic acids. Biological fouling is caused by microorganism growth on the membrane surface resulting from accumulation of viable microorganisms, such as bacteria and fungi. Colloidal fouling results from a variety of colloidal particulate matter and it can block the membrane pores (Zhang et al. 2012).

Table 6. Membrane foulant types (Shon et al. 2012)

Inorganic foulants	Organic foulants	Biological foulants
• Ca^{2+}, residual Cl^- • Calcium alumino silica • Mg^{2+}/Ca^{2+} phosphonate • $CaCO_3$, $CaSO_4$, $MgCO_3$, silica • Al^{3+} • Fe^{2+}	• Polyacrylic polymers • Protein and polysaccharides • Humic and fulvic acid • Carboxylic acid • Extracellular polymeric substances	• Bacteria • Anaerobic sulfate reducing • Anaerobic heterotrophic • Fungi • Yeast • Algae • Direct attack of membrane surface

Biological fouling occurs most likely after colloidal, organic and inorganic fouling since biological growth requires time. This makes it important especially in long term operation. NF can experience remarkable biofouling since the nutrients are well retained (Shon et al. 2012). Some bacteria can chemically degrade certain polymeric membrane materials damaging the membrane surface, which may result even in complete loss of integrity (Vigneswaran et al. 2012b). Especially cellulose acetate membranes are prone to severe biodegradation (Reiss et al. 1999).

Organic fouling is related to the molecular size, shape, and chemical characteristics of organic matter, such as stericity, polarity, functional groups, and hydrogen bonding. Organic fouling results from precipitation and adsorption of organic matter onto the membrane, and it is affected by interactions with cations in feed water. Finely porous NF membranes are prone to organic and colloidal fouling (Shon et al. 2012). When feed water contains mainly hydrophilic NOM, membrane fouling is colloidal rather than organic (Lee and Lee 2006). Organic and colloidal fouling cause significant flux decline (Vigneswaran et al. 2012b).

4.1.4 Fouling control

The tendency of feed water to cause fouling can be measured by silt density index (SDI) or modified fouling index (MFI). These indexes are determined with laboratory tests where samples are filtered through an MF membrane with constant pressure. In the test, either filtration time of certain volume (in SDI) or volume filtrated in certain time periods (in MFI) is measured. SDI and MFI have been criticized since the tests are quite simplistic small-scale dead-end tests, while NF systems operate crossflow. Also, they measure only particulate matter even if colloidal matter has shown remarkable tendency to cause fouling in NF systems (Crittenden et al. 2012b).

As mentioned in section 3.1.4, crossflow is utilized in NF to reduce fouling. In addition, fouling can be minimized by proper membrane selection, optimized operation conditions and well-planned cleaning strategy. In most cases the use of some pretreatment is necessary (Vigneswaran et al. 2012a). Inorganic fouling can be prevented by adding appropriate chemicals (Zhang et al. 2012). A hydrophilic, smooth and strongly negatively charged membrane seems favorable to reduce fouling (Boussu et al. 2006). The major fouling mechanism for hydrophilic and negatively charged membranes is cake formation while pore blocking is also important for hydrophobic and positively charged membranes (Lee and Lee 2007).

Permeate flux has a critical role in fouling caused by NOM since rapid fouling can occur with high flux even if chemical conditions do not favor fouling. Thus, permeate flux control might be important factor in reducing fouling (Hong and Elimelech 1997). Operation at low flux, low TMP and high crossflow velocity reduces the deposition of insoluble matter at the surface and thus the fouling (Schäfer et al. 1998). These operation factors also prevent NOM from forming complexes with calcium ions, which otherwise may enhance fouling (Seidel and Elimelech 2002). Fouling increases with high NOM concentration and high divalent ion concentration (Reiss et al. 1999, Seidel and Elimelech 2002). Thus, seasonal variations, especially in NOM concentration, can have an effect on fouling resulting in shorter time between cleanings and faster flux decline than in normal conditions. Also low pH and high recovery promotes fouling

(Hong and Elimelech 1997, Reiss et al. 1999). In Norway, fouling is usually caused by too high design flux relative to the characteristics of the feed water, especially with high particle concentration and high NOM content (Ødegaard et al. 2010).

4.1.5 Critical and sustainable fluxes

Critical and sustainable fluxes are concepts related to the flux decline due to fouling. Both of these are determined by comparing the operational flux to the pure water flux of the membrane. Critical flux is an important concept in optimizing filtration productivity. It is widely used term in literature, even though the meaning can vary depending on the authors. The simplest definition of critical flux is the flux at which fouling is first observed for given feed concentration and crossflow velocity (Field and Pearce 2011). In other words, it is the flux below which fouling resistance remains negligible (Guo et al. 2012) or below which no flux decline occurs (Hong and Elimelech 1997). Experimentally this kind of critical flux is defined from the flux–TMP -curve; above critical flux the flux–TMP curve starts to deviate from linearity. Critical flux can also be defined as the flux above which irreversible fouling appears (Bacchin et al. 2006).

To be more precise, three forms of critical flux can be seen; the strong and weak forms of the critical flux and the critical flux for irreversibility, J_{cs}, J_{cw}, and J_{ci}, respectively. These terms have some interrelationships, which may be the reason for incoherent use of terminology (Bacchin et al. 2006). The strong form of critical flux has been developed to determine conditions where no fouling occurs, since below the strong form of critical flux, flux equals that of pure water. This may not be applicable concept for realistic flux levels in NF (Field and Pearce 2011). In weak form of critical flux, flux-TMP gradient is lower than that of clean water but still linear. Above critical flux of irreversibility, irreversible fouling occurs. In flux-TMP curve, critical flux of irreversibility can be seen as hysteresis when flux is increased and decreased (Bacchin et al. 2006). Figure 6 illustrates the concepts of different forms of critical flux.

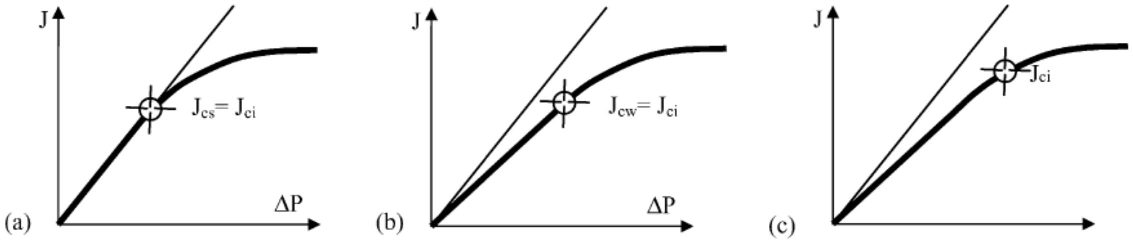

Figure 6. (a) Strong form of critical flux, (b) weak form of critical flux, and (c) critical flux for irreversibility (Bacchin et al. 2006)

Sustainable flux is not considered as a part of critical flux but another concept based on economic factors. For a water treatment plant, sustainable flux can be defined as the flux at which there occurs an acceptable level of fouling that can easily be removed in a cleaning procedure of acceptable frequency. This concept allows modest degree of fouling which compromises between capital costs and operating costs (Field and Pearce 2011). Sustainable flux is determined from the rate of fouling. Acceptable level of fouling must be selected separately for every application, which makes sustainable flux very subjective. However, it is very important practical concept if there is a clear discontinuity in the rate of fouling as a function of flux. Sustainable flux can feature also environmental aspects. For water treatment plant operation, sustainable flux can be seen as more important design factor than critical flux (Bacchin et al. 2006). Table 7 presents an overview on different forms of critical flux and sustainable flux.

Table 7. Definitions of critical and sustainable fluxes (Bacchin et al. 2006)

Definition	**Abbre-viation**	**Discrimination between**		**Determination based on analysis of**
Strong form of critical flux	J_{cs}	No fouling	Any kind of fouling	Linearity of flux-TMP variation
Weak form of critical flux	J_{cw}	Fouling independent of solvent transfer	Fouling driven by solvent transfer	
Critical flux for irreversibility	J_{ci}	Reversible fouling	Irreversible fouling	Irreversibility
Sustainable flux	J_{sus}	Sustainable flux	No sustainable flux	Rate of fouling

4.2 Membrane cleaning

4.2.1 General

Despite the pretreatment methods and system design, all membranes will foul during operation to some extent. When fouling occurs and flux has declined below tolerable limit, foulants must be removed by cleaning, either physically or chemically. Cleaning should remove several foulants efficiently and restore membrane characteristics without damaging the membranes (Liikanen et al. 2002).

Flux recovery after cleaning affects how often membranes have to be rinsed, cleaned, and replaced. Flux recovery after cleaning is calculated as the ratio of specific flux before and after cleaning. Membrane cleaning is costly and time consuming which is why the need of cleaning should be diminished by proper pretreatment. In Norway where minimal pretreatment is used, membranes are chemically cleaned even daily. The duration of cleaning is about an hour and the cleaning is automatized. Membranes are also cleaned extensively once or twice a year with a variety of chemicals, such as wetting agents, sequesters, oxidation chemicals and enzymes (Ødegaard et al. 2000, Ødegaard et al. 2010).

4.2.2 Physical cleaning

Physical cleaning methods are based on mechanical forces that dislodge and remove foulants mainly from the membrane surface. Most employed physical cleaning methods for membranes are forward flushing, backward flushing and backwashing. Also other methods such as vibration, air sparging, and CO_2 back permeation can be used. The effectiveness of physical cleaning depends on the frequency of cleaning and, for example, on the duration of backwash and pressure during forward or backward flushes (Chen et al. 2003).

Backwashing is more effective physical cleaning method than forward flush since it removes contaminants attached to the membrane surface and trapped inside the pores of the membrane while forward flush affects mainly the foulants attached to the membrane surface (Chen et al. 2003). However, backwash is not generally used with NF membranes, since it might damage the spiral-wound module structure for example by separating the active thin-film layer from the support layer (Crittenden et al. 2012b). Backwash can be used with hollow-fiber and flat-sheet modules.

Flushing with permeate is more common physical cleaning method with spiral-wound modules. Ericsson et al. (1996a) found that forward flushing can increase the permeate flow by 5%. They suggested that flushing should be conducted every two days between chemical cleanings.

4.2.3 Chemical cleaning

Physical cleaning is incapable of removing all foulants from membrane surface and pores. Thus, suitable chemical treatment is required to complete the cleaning (Shon et al. 2012). Chemical cleaning can also be used as the only cleaning method. Chemical cleaning methods are based on the chemical reactions which weaken the cohesion forces between the foulants and the adhesion forces between the foulants and membrane surface (Chen et al. 2003). Thus, chemical cleaning removes rejected matter which is physically or chemically sorbed on the membrane (Nilson and DiGiano 1996).

The effectiveness of chemical cleaning depends on the temperature, pH, concentration and composition of the cleaning solution (Liikanen et al. 2002, Chen et al. 2003). It has been noted that chemical cleaning is more efficient at elevated temperature and high pH. Higher temperature facilitates chemical cleaning by doubling the reaction rates with every 10°C. Experiments with UF and RO membranes reveal that backwash after chemical cleaning makes it more efficient since it produces mechanical shear stress that removes deposits weakened by chemical (Chen et al. 2003). In addition to the characteristics of the cleaning agent, also cleaning pressure, flow, and time affect the success of cleaning (Liikanen et al. 2002).

Also membrane characteristics influence the effectiveness of cleaning agent. Fu et al. (1995) noted that same feed water and identical cleaning procedure resulted in different recoveries for different membranes. Furthermore, they discovered that tighter NF membrane (MWCO ~300 Da) required acidic cleaner to remove inorganic fouling in addition to alkaline cleaner while looser NF membrane (MWCO 500-1,000 Da) required only alkali cleaner.

The choice of chemical cleaner is critical to cleaning efficiency, and incorrect choice might even lead to irreversible loss of flux or rejection (Liikanen et al. 2002). Alkaline chemicals remove mainly organic fouling (Ventresque et al. 2000, Bonton et al. 2012) and acidic chemicals inorganic fouling (Liikanen et al. 2002, Vigneswaran et al. 2012b, Lopes et al. 2013). Common acidic cleaners are hydrochloric acid (HCl), sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4) and citric acid ($C_6H_8O_7$), and common alkali cleaners are sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) (Vigneswaran et al. 2012b).

Alkaline cleaners recover membrane flux better than acidic cleaners. Alkaline cleaners with chelatants result in the most efficient cleaning in terms of flux recovery and foulant removal when the fouled material consists of biofouling, organic deposits and metal complexes. Acidic cleaners can restore the ion rejection capability but when treating soft waters, this might be undesirable. Alkaline cleaners, on the other hand, may even decrease the ion rejection (Liikanen et al. 2002).

Detergents, i.e. synthetic surfactants, can be utilized for cleaning purposes since they displace foulants from membrane surface. The most effective detergent is EDTA which reduces calcium and magnesium deposits on membrane surface (Vigneswaran et al. 2012b). EDTA also removes NOM, at least in the presence of calcium (Hong and Elimelech 1997).

It is sometimes unnecessary to combine acidic and alkaline cleaning. After acidic clean, the increase in recovery may be negligible if inorganic fouling is minor. Thus, alkaline cleaning may be sufficient (Ericsson et al. 1996a). When selecting a cleaning procedure, the ability of membrane material to withstand chemical cleaners, maximum temperatures for cleaning, contact time and frequency of cleaning should be considered. Cleaning should be optimized to prevent unnecessary costs caused by over-dosing of non-optimal cleaner and shortening lifetime of membranes (Liikanen et al. 2002). Even chemical cleaning is ineffective in removing irreversible fouling which is why eventually membranes must be changed (Nilson and DiGiano 1996).

5 Nanofiltration in water treatment plant

This chapter revises how nanofiltration should be applied to water treatment plant regarding possible pretreatments and post-treatments.

5.1 Pretreatment

5.1.1 General

In membrane filtration processes, pretreatment has two main objectives: to decrease fouling by improving feed water quality and/or improve product quality. Nanofiltrated water has such a good quality that pretreatment improves feed water quality rather than product quality (Liikanen 1999, Metsämuuronen et al. 2014). When employing NF it may be necessary to pretreat the feed water to prevent remarkable fouling on membrane (Hong and Elimelech 1997, Lee and Lee 2007, Guo et al. 2012, Vigneswaran et al. 2012b) or even blocking of other parts of NF equipment (Lee and Lee 2007). Siddiqui et al. (2000) even suggested that the requirement of pretreatment is the major obstacle why the use of NF has not widened. The extent of pretreatment depends on the quality of source water (Ventresque et al. 2000, Vigneswaran et al. 2012a). Low-turbidity groundwaters have proved to filtrate well even with minimal pretreatment, most of the times only cartridge filter is applied (Siddiqui et al. 2000). Usually pretreatment methods are combined to achieve wanted membrane performance.

Pretreatment strongly affects the need of membrane maintenance (Nurminen 2001). Properly selected pretreatment can significantly enhance the performance of NF and stabilize the permeability (Ahn et al. 2004, Vigneswaran et al. 2012b). These improvements are a result of reduced fouling. Therefore, the objective of pretreatment to a NF system is to remove particles and organics and prevent biofouling (Ventresque et al. 2000, Guo et al. 2012). According to Siddiqui et al. (2000), minimal pretreatment for NF should be scale control and cartridge filtration or MF. Additionally, they suggest pretreatment, such as chemical treatment, MF or UF, for particle and colloid removal.

Since variety of contaminants can cause fouling, it is important to investigate which materials should be removed from feed water by pretreatment (Kim et al. 2007). Table 8 presents some suggested methods for foulant control.

Table 8. Foulants and foulant controls (Vigneswaran et al. 2012a)

Foulant	Control
General	Operation conditions, cleaning, pretreatment
Inorganics	pH adjustment, recovery adjustment (< 90%), chemicals
Organics	Biological treatment, activated carbon, ion exchange, ozonation
Colloids (< 0.5 μm)	Filtration, coagulation
Biological solids	Filtration, coagulation, chlorination/dechlorination

In addition to the composition of source water, membrane characteristics affect the suitability of certain pretreatment. The ability of a certain pretreatment to maintain membrane performance depends on the membrane since fouling mechanisms depend on membrane characteristics (Kim et al. 2007). Since both feed water quality and membrane selection affect the effectiveness of a pretreatment, it is difficult to compare existing research results.

Pretreatments can be divided into physical, chemical, and biological pretreatments. Physical pretreatments, such as sand filtering, affect the contaminant size distributions and can change the type of fouling. Chemical pretreatments, such as coagulation, can change some of the irreversible fouling to reversible by affecting the interactions of foulants. Biological pretreatments, such as biofiltration, reduce biofouling and microbial growth by removing biodegradable contaminants (Guo et al. 2012). Chemicals, such as chelating agents and acids, can also be used to reduce calcium precipitation, i.e. inorganic fouling (Vigneswaran et al. 2012b).

Gorenflo et al. (2002) reported that it is impossible to use NF without pretreatment when hard groundwater with high content of NOM is purified, since microfloc formation clogs the modules. Siddiqui et al. (2000) noticed that pretreatment is required also when feed water is low-turbidity surface water. Generally, research papers content themselves to point out that NF requires pretreatment even though few research results on the subject are published.

As one of the few, Lee and Lee (2006) reported it was possible to operate NF without any pretreatment when the NOM was mostly hydrophilic and the TOC maximum was 3.1 mg/l, yet the flux decline was significant. They observed that this flux decline could be decreased with increasing crossflow velocity. They suggested that the flux decline resulted from particulate and colloidal fouling which could be removed with pretreatment to improve the performance.

Even though pretreatment leads to additional capital or operational costs, or both, it extends the lifetime of the membrane, improves the performance and decreases the energy costs of membrane filtration by reducing fouling. If NF system is to be installed in existing water treatment plant, the existing process can be used as a pretreatment for NF but it might not be the ideal (Korhonen 2000).

5.1.2 Cartridge filters and microsieves

Cartridge filters are usually considered as the minimal pretreatment of NF system. In an ideal case these prefilters have minor effect on water quality and thus prefilters should rather protect sensitive membrane modules than operate as a pretreatment. However, usually either micro-sized cartridge filter or MF is needed prior to NF to achieve stable flux, at least if aluminum coagulation is used (Reiss et al. 1999, Ahn et al. 2004, Park et al. 2005). There are different sizes of pores in cartridge filters, usually larger than 5 µm. The size of cartridge filter may affect the rejection capability of the membrane (Siddiqui et al. 2000).

Lopes et al. (2013) state that cartridge filtration alone is not a sufficient pretreatment, since raw water (turbidity ~4 NTU, TOC ~3,5 mg/l) may block the cartridge filters completely just in a few hours even with low recoveries. Also Siddiqui et al. (2000) had similar results with prefilter clogging in 12…18 h (turbidity 1…5 NTU, DOC 3…5

mg/l). However, Härmä (1999) found that the removal of organic and inorganic matter from surface water is effective even without other pretreatments. Härmä also noted that flux decline rate had little difference between pretreatment with only cartridge filters and with conventionally treated water (chemically treated, clarified, and sand filtered water) though it must be noted that the feed water characteristics were somewhat different.

In full-scale application, replacing cartridge filters with new ones within just a few hours or days is unsustainable and economically unreasonable. An option to prevent cartridge clogging is a more extensive pretreatment. Otherwise, regeneration or effective cleaning program for cartridge filters should be considered. In full-scale application in Méry-sur-Oise, France, where pretreatment consists of extensive ozonation-coagulation-filtration process, 6 µm cartridge filters are automatically backwashed every 24 to 36 hours depending on the particle content of the feed water. In addition to backwashing, cartridge filters are chemically cleaned approximately every 20 days. This procedure prolongs the life expectancy of the cartridge filters to a minimum of five years (Ventresque et al. 2000). However, cartridge filters are quite often regarded as non-washable (Ericsson et al. 1996a).

An alternative for cartridge filters are microsieves. Microsieves are easily cleaned by backwash which may be beneficial in preventing prefilter clogging and decreasing the frequency of prefilter replacement. The backwashing of microsieve can be automated and be as frequent as once every 10 minutes. Sieve sizes of 15 µm and 25 µm were noticed to have no difference in membrane operation (Ericsson et al. 1996a). In Norway, microsieves of 50 µm are typically used before loose NF cellulose acetate membranes (Ødegaard et al. 2010).

5.1.3 Chemical treatment

Chemical treatment as a NF pretreatment refers to coagulation, sometimes combined with flocculation and clarification. When using coagulation as the only pretreatment, it can be referred to also as in-line coagulation. If coagulation is combined with flocculation, it can be called direct filtration (Metsämuuronen et al. 2014). These alternatives are illustrated in Figure 7. Clarification can be either settling or flotation. Siddiqui et al. (2000) state that in-line coagulation cannot be used with NF since it clogs membranes.

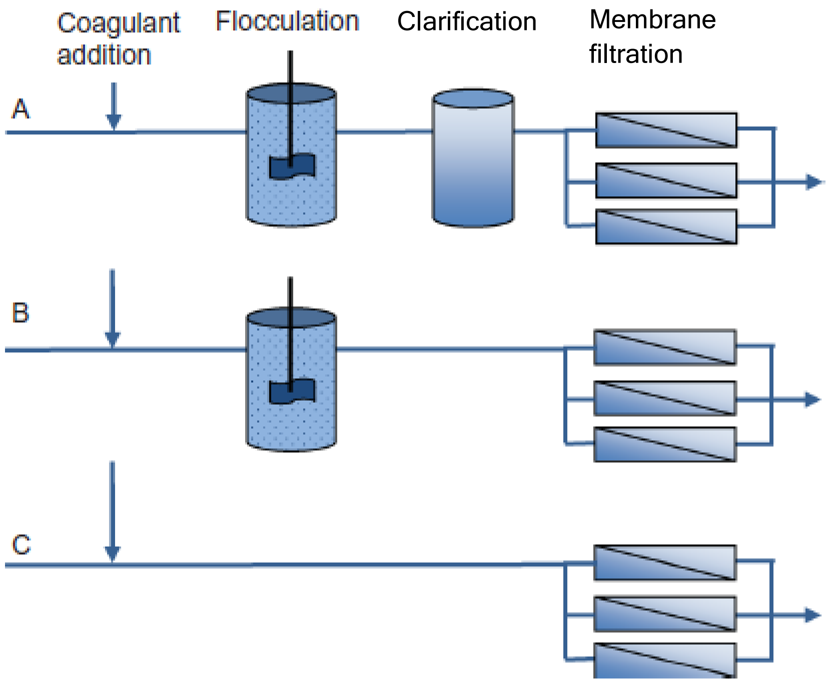

Figure 7. Chemical treatment combined with NF: A. chemical treatment with clarification B. direct filtration C. in-line coagulation (Metsämuuronen et al. 2014)

Chemical treatment can reduce the rate of fouling by enhancing the reformation of dissolved matter into flocs, by increasing particle size which reduces foulant penetration into membrane pores, and by improving cake layer permeability with less dense and more porous flocs. The effectiveness of chemical treatment depends on pH, mixing, dosing, and raw water characteristics (Guo et al. 2012). The residual chemicals in feed water are most likely to react with membranes either decreasing or increasing fouling. Choi et al. (2013) state that residual aluminum combined with humic acid caused remarkable flux decline, especially at low pH. However, the effectiveness of chemical treatment as a NF pretreatment depends also on the selected chemical. Matilainen (2007) states that, in many studies, iron-based coagulants have removed NOM, measured in DOC and UV absorbance at wavelength 254 nm (UV_{254}), more effectively than aluminum-based ones. Aluminum-based coagulants may also increase the removal of hardness which is unwanted in the case of soft feed waters (Härmä 1999). On contrast, Liikanen (1999) examined aluminum- and iron-based coagulants in tank experiments and recommended polyaluminum chloride as a pretreatment chemical based on MFI and SDI measurements.

Generally, the dosing of coagulant is optimized in order to balance between minimal chemical consumption and maximal removal of NOM and other particles. In the case of membrane pretreatment, the optimization of dosing and mixing should be implemented particularly to maximize the overall membrane performance and not only the NOM removal in the pretreatment phase. Several studies show that coagulation removes the hydrophobic fraction of NOM more efficiently. The hydrophobic character of HMM NOM, in contrast to LMM NOM, promotes coagulation (Matilainen 2007). As NF already removes the HMM NOM efficiently, the maximum removal of NOM by chemical treatment may be unable to increase the overall NOM removal. However, properly optimized chemical treatment may improve the NOM removal of membrane system (Guo et al. 2012).

Geraldes et al. (2008) found in bench-scale tests that dissolved air flotation (DAF) alone was unable to reduce the fouling potential of high turbidity surface water based on the determination of MFI and SDI. Further, they found that DAF after chemical treatment with aluminum sulfate and ferric chloride was able to reduce MFI by over two and one order of magnitudes, respectively, but fouling potential was still too high compared to the recommendations. Thus, DAF is not recommended pretreatment for NF either as the only pretreatment or combined with just chemical treatment. However, they suggested to combine DAF with chemical treatment and either media filtration or MF. Härmä (1999) also concluded that chemically treated water should always be filtered after flotation to reduce fouling potential.

5.1.4 Conventional treatment

Conventional treatment refers to the treatment process conventionally utilized in surface water treatment plants; coagulation, flocculation, clarification and filtration, usually through sand filter. Generally, all granular media filters are effective in capturing large particles which in turn reduces membrane fouling. To enhance the efficiency of granular filters pre-coagulation can be used (Metsämuuronen et al. 2014). Especially colloidal fouling can be prevented by combining coagulation and sand filtration (Vigneswaran et al. 2012b). Conventional treatment is an efficient pretreatment for NF if water contains high levels of suspended solids and colloids (Vigneswaran et al. 2012a).

Matilainen et al. (2004) studied NF with five conventionally treated feed waters from different surface water treatment plants in Finland. With all feed waters, NF improved the removal of NOM, based on TOC, UV_{254}, and HPSEC (high performance size exclusion chromatography) measurements. Especially the increased removal of LMM NOM was seen as an important enhancement since it is difficult to be removed with other treatment processes. Also Härmä (1999) examined NF with several conventionally treated waters and reported efficient removals of organic and inorganic matters. Occasionally, rapid flux decline was experienced but the performance was successfully restored with chemical cleaning. Generally, filtering decreases flux decline.

Lopes et al. (2013) discovered that removal of TOC was higher with only chemical treatment and sedimentation as a NF pretreatment than with conventional treatment as a NF pretreatment. However, they state that NF should be placed after the conventional treatment to achieve high performance and to prevent operational problems, such as flux decline and fouling. Mijatovic et al. (2004) investigated that NF with conventional treatment as a pretreatment managed to produce high quality water (TOC rejections >80%) without flux decline in the test period of 3 months

Chang et al. (2009) observed NOM hydrophobicity and flux decline in NF system with conventionally treated feed water. They discovered that conventional treatment removed hydrophobic NOM more efficiently than hydrophilic NOM; by 20% and 11%, respectively. Hydrophobic NOM accumulates more easily to hydrophobic membrane surface. Since the reduction of hydrophobic NOM in conventional treatment was relatively low, flux decline was observed with conventionally treated feed water.

5.1.5 Oxidation

Oxidation as a pretreatment is mainly used to prevent biological growth, biofouling, on the membrane or prefilter surface. Combined with optimal operation conditions the control of biological growth minimizes the need of cleaning. In case of cellulose acetate membrane, the control of biofouling is critical also to prevent membrane biodegradation (Reiss et al. 1999). High level of TOC in feed water is likely to cause severe biofouling. This can be effectively controlled by pre-oxidation, which sterilizes bacteria and microorganisms preventing their growth on the membrane (Vigneswaran et al. 2012b).

In addition to preventing biofouling, oxidation can be used for removing taste, odor, and for enhancing the precipitation of iron and manganese. Oxidation is suggested as NF pretreatment if feed water contains high TOC, color, and plenty of micropollutants (Vigneswaran et al. 2012a). Oxidation can modify physical, chemical and biological characteristics of NOM. It can change functional groups of NOM without breaking the macromolecules; however, it can also break large molecules into micromolecules (Song et al. 2004).

Oxidation can influence fouling and rejections of NF either favorably or unfavorably. Oxidation may enhance flux due to the breakdown of NOM macromolecules (Song et al. 2004). On the other hand, pre-oxidation can form small assimilable compounds which may block membrane pores and actually increase biofouling on the membranes and in distribution system. However, this can be avoided by combining ozonation with biofiltration or activated carbon treatment which either biodegrade or adsorb the compounds (Metsämuuronen et al. 2014).

Pre-oxidation is usually performed by using chlorine compounds, hydrogen peroxide, ozone or UV radiation. It must be noted that residual chlorine can damage membranes by chemical oxidation resulting in the loss of integrity, i.e. loss of rejection and membrane productivity. Therefore, the resistance of membrane for chlorine must be investigated in long term if pre-chlorination is used (Reiss et al. 1999).

Lee & Lee (2007) found that ozonation had insignificant effect on increasing flux. In contrast, the research results of Byun et al. (2011) showed that the ozone dosage had statistically significant effect on flux so that increasing dosage led to increase in permeate flux. Also Speth et al. (2000) found that ozonation pretreatment increased the long-term flux compared to the pretreatment with conventional treatment.

Teixeira et al. (2011) conducted NF experiments with ozonation pretreatment and with a combination of ozonation and chemical treatment with sedimentation as a pretreatment. Researchers found that NF was able to reduce LMM compounds more than conventional treatment. However, they found no significant differences in NF rejections between these two pretreatments. Nevertheless, pretreatment affected the NOM fractionation in the feed water, which was reflected to the fractionation in permeate.

Thus, pretreatment with a combination of ozonation, chemical treatment and sedimentation was more effective in removing smaller NOM compounds. Byun et al. (2011) found that the rejection of DOC remained above 92% despite of the ozone dosage.

Her et al. (2007) discovered that ozonation after conventional treatment decreased the NOM levels in terms of DOC, UVA and specific UV absorbance (SUVA) but at the same time it significantly increased biomass accumulation on the membrane surface compared to employing only conventional treatment as a pretreatment. The amount of accumulated dissolved organic matter on the membranes were similar for pretreatment with conventional treatment and with conventional treatment followed by ozonation, indicating that the quantity of LMM was not significantly affected by ozonation. Researchers also concluded that ozonation can increase bacterial food source which may enhance bacterial cell growth.

Song et al. (2004) found that oxidation by combining hydrogen peroxide and UV radiation reduced organic fouling significantly by changing NOM characteristics into less sorbable form. They also found that oxidation has the potential to mitigate biological fouling. However, the rejection of TOC was found to be inversely proportional to the degree of NOM oxidation. Oxidation decreased the rejection of NOM compared to NF without pretreatment, and the decrease was remarkable, even 35%, with unsuitable dosing. Speth et al. (2000) found that even if chloramine pretreatment prevented biofouling completely, it resulted in lowest overall flux compared to conventionally treated water, conventionally treated water enhanced with ozonation, and conventionally treated water enhanced with ozonation and biofiltration.

5.1.6 Adsorption

In adsorption, a substance in water attaches to a solid by physical or chemical interactions. The most common adsorbent in water treatment is activated carbon. Activated carbon is used either in powdered (PAC), granular (GAC), or in rarer pelletized form. GAC is used as a media filter, typically combined with conventional treatment and/or ozonation. PAC can be dosed either continuously to the membrane system or at the beginning of the filtration cycle. Similar to GAC, it can also be a separate pretreatment step containing settling. Adsorption is effective especially in removing LMM NOM (Guo et al. 2012) but not as effective in removing HMM NOM (Matilainen 2007).

Addition of PAC can enhance membrane performance by reducing the direct load of dissolved organics onto the membrane thus reducing fouling. However, the effectiveness of PAC pretreatment depends on many factors, such as dosing and the characteristics of PAC and water (Guo et al. 2012). Contact time plays an important role as well in effectiveness of activated carbon treatment. Adsorbents usually require long contact time or high concentrations to make the pretreatment effective. Thus, regeneration of activated carbon is required to make the process feasible (Metsämuuronen et al. 2014).

Kim et al. (2007) showed that combining ozonation and activated carbon filtration with conventional treatment resulted in high initial flux but low overall water production. Thus, more advanced pretreatment may be disadvantageous option. Nilson & DiGiano (1996) confirmed that using PAC increased flux decline. They also concluded that NOM was less effectively rejected with PAC than without. Also, PAC did not adsorb those NOM components with a higher tendency to cause fouling. Thus they argued PAC to be an impractical pretreatment at preventing fouling. In contrast, Lee & Lee (2007) found that PAC pretreatment managed to substantially improve flux.

Granular activated filter with biomass attached onto the filter surface as a biofilm is considered as a biofilter. Biofilter acts as a physical filter but it also reacts biologically with the biodegradable dissolved organic carbon in the water. Biomass adsorbs organic matter and biodegrades it. Biofiltration can be used as a NF pretreatment to significantly decrease the amount of organic matter which should assist in preventing membrane fouling (Guo et al. 2012). Nevertheless, Speth et al. (2000) found that combining ozonation with biofiltration had no significant difference to only using ozonation as pretreatment.

5.1.7 Microfiltration and ultrafiltration

Membranes with larger MWCOs, namely MF or UF, can be used as a pretreatment for NF since they remove particles, colloids, microorganisms and even larger NOM substances. Generally, MF and UF produce water suitable for NF feed water (Liikanen 1999).

Lee & Lee (2006) tested MF and UF with different pore sizes to investigate their pretreatment efficiency for NF. They found that NF fouling reduced with decreasing pore size of MF/UF membrane but naturally also operating costs increased. They suggested that when using membrane prefilter, the pore size of MF/UF should be selected so that the specific energy consumption is minimized for efficient pretreatment. The researchers also found that MF decreases the resistance caused by cake layer on NF membrane surface. UF was found to decrease also the external fouling layers on the NF membrane surface. The researchers concluded that the efficiency of MF/UF pretreatment depends on the size distribution of particles in treated water.

Even if pretreatment does not necessarily affect the NF permeate quality, Ahn et al. (2004) discovered that combining conventional treatment and MF in pretreatment step, NOM removal improved by some 10%. Combination of conventional treatment and MF also increased flux by 38% compared to pretreatment with only conventional treatment. However, the applicability of MF depends on the NF membrane. Siddiqui et al. (2000) state that MF is unable to resolve the fouling problem for some NF membranes but even then it prevents rapid cartridge filter clogging. On the other hand, Lee and Lee (2007) claim both MF and UF to be effective as pretreatments although the flux decline in NF is slower with UF pretreatment. UF has smaller MWCO than MF, thus being able to remove particles which can clog NF membrane.

Chang et al. (2009) found that conventional treatment as a pretreatment removed NOM more efficiently than UF pretreatment. UF can remove hydrophilic NOM more readily than hydrophobic NOM, by 54% and 31%, respectively. Nevertheless, hydrophobic NOM removal was higher with UF than with conventional treatment, 31% in contrast to 20%, respectively. Even if UF decreased fouling, the researchers preferred conventional treatment over UF because of lower energy costs. Even though MF and UF can remarkably slow down the fouling of NF membranes, pretreatment membranes also have a tendency to foul (Korhonen 2000). Chellam et al. (1998) state that when existing conventional treatment can be utilized as a pretreatment replacing it with MF or UF in order to improve the NF performance is economically inefficient.

5.2 Post-treatment

Even if well-designed NF system produces high quality water, it still needs post-treatment. The main purpose of post-treatment is to ensure the safety of consumer and the stability of water in distribution system. In the case of NF, this usually means additional disinfection and corrosion control. The need of post-treatment must be evaluated also considering the pretreatment and the vulnerability of treatment process since, for example, a loss of integrity in a single membrane would result in a total absence of treatment for a proportion of water if only minimal pretreatment is used.

Since the MWCO of NF is small, NF may operate even as a disinfecting phase in a water treatment process. Nevertheless, additional disinfection is still needed after NF since biological activity in the distribution system still needs to be prevented (Ventresque and Bablon 1997, Ventresque et al. 2000, Vigneswaran et al. 2012a). LMM NOM can permeate especially loose NF membranes. This fraction of NOM is the preferred carbon source for microorganisms resulting in microbiologically unstable water (Meylan et al. 2007). Thus, the possible microbial growth must be prevented with disinfection. Disinfection also takes into account the possibility for any microbe passage. Since NF is supposed to remove great majority of organic substances, permeate should require lower doses of disinfectants than conventional treated water to maintain desired residual (Kiisto 2000, Vigneswaran et al. 2012a). Low levels of organic matter also form lower levels of harmful disinfectant by-products (Härmä 1999).

All NF membranes remove hardness to some extent which is why, depending on the selected membrane and feed water characteristics, it might be necessary to remineralize the water (Ventresque and Bablon 1997). Treated water may also need pH control in order to reduce corrosion in distributing system (Ventresque and Bablon 1997, Cyna et al. 2002). The need of pH control depends on the applied pretreatment method since NF itself does not remarkably affect the pH. In Norway, an alkaline calcium carbonate filter is included to increase the level of calcium and bicarbonate in soft and corrosive Norwegian water (Ødegaard et al. 2010). Also other chemicals, such as lime water and carbon dioxide, can be used for corrosion control.

Since NF permeate has high quality, it may be unreasonable to treat all the water with NF. It is possible to treat only part of the water with NF and other part with some other treatment, such as conventional treatment. This will require mixing of these two waters after treatment (Cyna et al. 2002). This solution may be convenient if there are no severe contaminants, such as pesticides, that are hardly removed with conventional treatment (Chellam et al. 1998).

5.3 Applicability in water treatment plant

When evaluating the applicability of NF and designing the treatment process, a survey on existing NF treatment plants may be beneficial. Two useful factors to survey are the reason for application of NF and the quality of feed water.

In Finland, few NF applications are in full-scale use. In Kempele water treatment plant, NF is used for the removal of high levels of phosphorus. In Laitila water treatment plant, NF is applied to remove fluoride. In Mustasaari water treatment plant high level of humus is reduced with NF. In all of these water treatment plants only a proportion of conventionally treated water is nanofiltered and then mixed with conventionally treated water (Nurminen 2001). In Kuivala water treatment plant, RO membranes are used for the removal of fluoride.

In Norway, more than 100 water treatment plants are based on NF. Most of these plants are small. Utilized NF membranes are relatively loose (MWCOs 1,000-2,000 Da) cellulose acetate or polyamide membranes in spiral-wound modules. The key points to successful NF operation in Norway are low operating flux (<20 l/m^{2}h), low recovery (<70%), cellulose acetate as membrane material which decreases adsorptive fouling, and daily cleaning combined with more extensive cleaning once or twice a year (Ødegaard et al. 2010).

In France, Mery-sur-Oise plant utilizes NF treatment as parallel to conventional treatment line enhanced with biological treatment. NF pretreatment process is extensive; conventional treatment is enhanced with ozonation and water is conducted to NF through 6 µm cartridge filters. The plant is completely automated, including cleaning and rinsing operations and maintenance alarms. Permeate is mixed with conventionally and biologically treated water in proportion which depends on the feed water quality and then post-treated. With NF, the product quality has improved with lower costs than foreseen (Ventresque et al. 2000, Cyna et al. 2002).

It must be acknowledged that fouling rate and permeate quality depend on membrane selection, raw water quality, operational condition and system design. Thus, existing treatment plants should act as a reference. To ensure optimal process in each case, long-term (over 6 months) tests should be conducted with selected membrane, the raw water should be representative of that of full-scale, seasonal variations should be included in the testing, pilot design should reflect all unit processes in the full-scale, including pretreatment, chemical dosing etc., and operational conditions should be tested to the limits of expected settings (Reiss et al. 1999).

6 Pilot study

This chapter presents the bench-scale nanofiltration experiment. At first, the basis of experiment is presented. This includes raw water characteristics, existing water treatment process, part of which was utilized as a pretreatment in the NF experiment, and the quality of product water from current treatment process in Pitkäkoski treatment plant. Then, the selected membranes, the pilot equipment, and water quality analysis are presented.

6.1 Introduction

Pilot studies were conducted at Pitkäkoski water treatment plant which takes raw water from Lake Päijänne. Raw water from Lake Päijänne is soft, low alkalinity and turbidity but quite high in organic matter. Table 9 presents numerically some main raw water characteristics. In the context of membrane technology and operational performance, the low water temperature is important to take into account.

Table 9. Raw water quality in Pitkäkoski water treatment plant in 2013

	pH (-)	**Temperature (°C)**	**TOC (mg/l)**	**Alkalinity (mmol/l)**	**Turbidity (FTU)**	**Conductivity (mS/m)**
average	7.15	6.07	7.40	0.32	0.29	7.32
min	6.82	2.90	6.90	0.27	0.20	6.81
max	7.39	10.00	8.00	0.34	0.55	7.82

Pitkäkoski water treatment plant utilizes extensive treatment process. Raw water is chemically treated with ferric sulfate, then sedimentated, filtered through sand filter, ozonated and filtered through activated carbon filter. Water is disinfected with ozone, UV radiation and chloramine. Alkalinity and pH are adjusted with carbon dioxide and lime water.

The product water quality from Pitkäkoski treatment process and the Finnish water quality recommendations assigned in the Decree of the Ministry of Social Affairs and Health Relating to the Quality and Monitoring of Water Intended for Human Consumption (461/2000) are presented in Table 10. Pitkäkoski product water fulfills the recommendations even though iron maximum has temporarily exceeded the recommendation.

Table 10. Product water quality from Pitkäkoski water treatment plant in 2013 and related Finnish water quality recommendations

	pH (-)	**TOC (mg/l)**	**Alkalinity (mmol/l)**	**Turbidity (FTU)**	**Conductivity (mS/m)**	**Hardness (°dH)**	**Iron (µg/l)**
average	8.52	1.65	0.70	0.09	14.90	2.94	41.45
min	8.10	1.40	0.60	0.06	13.80	2.60	20.00
max	8.80	1.90	0.75	0.22	15.80	3.10	210.00
recommendation	6.5…9.5			< 1.0	< 250		< 200

6.2 Materials and methods

6.2.1 Experiment setup

Nanofiltration equipment consisted of two parallel, identical operation lines. Both lines had a 5 µm cartridge filter, a feed tank, a pump and a crossflow spiral-wound NF module. Two different membranes were tested; membranes are presented in more detail in the section 6.2.2. Both lines had similar membranes at a time. Lines had recirculation from concentrate to feed tank to increase the recovery of the equipment. The proportion of drained concentrate, i.e. reject, was adjusted by manual valve. Figure 8 shows a schematic diagram of the nanofiltration equipment used. More detailed PI-diagram with valves and gauges is presented in Appendix 1.

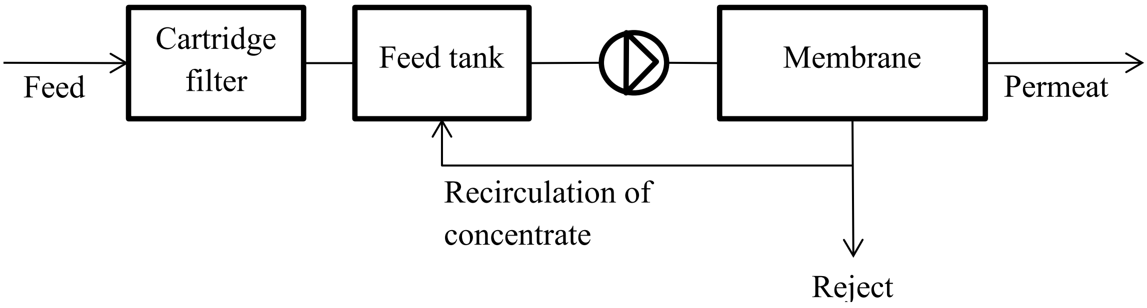

Figure 8. Schematic diagram of nanofiltration equipment

Since previous researches have shown that NF is applicable as a polishing step in water treatment process, the effect of pretreatment to membrane performance was further tested to minimize money- and space-consuming treatment steps. The two parallel treatment lines in NF equipment were fed with different feed waters. One line was fed with untreated raw water and the other line with conventionally treated water.

As noted in sections 5.1.1 and 5.1.2, many researchers state that NF of raw water without pretreatment or just with cartridge filter is not possible. This statement was tested with the stimulus that in Norway only minimal NF pretreatment is used. For the other treatment line, conventionally treated water was selected in order to balance between flux decline and extensiveness of pretreatment.

In this study, the need for post-treatment of nanofiltrated water was evaluated based on the water quality results. It was assumed that there would be need for additional disinfecting phase and for pH and alkalinity control for corrosion prevention.

6.2.2 Membranes in pilot study

Two fairly loose NF membranes, NF270 and UA60, were selected to be tested. Characteristics of these membranes are presented in Table 11. NF270 is designed to remove high percentages of organic matter with decreased removal of polyvalent ions. It is relatively hydrophilic which enhances the removal of uncharged organic compounds. The surface of NF270 is negatively charged which may increase the effect of electrostatic repulsion to negatively charged NOM compounds (Mänttäri et al. 2002, de la Rubia et al. 2008).

Table 11. Characteristics of NF270 and UA60 membranes

	NF270	**UA60**
Manufacturer	Filmtec	Trisep
MWCO (Da)	200-400 [a]	1,000-3,500 [d]
Material	polyamide [d]	polypiperazine amide [d]
Contact angle, hydrophobicity	30° [b], hydrophilic [c]	30-50° [d] (estimated)
Charge	negative [c]	n/a
Active area (m^2)	2.6 [d]	2.4 [d]
Specific flux at 25°C ($l/m^2/h/bar$)	10.7 [d]	5.5 [d]
Salt Rejection (%)	97 [d]	85 [d]
Chlorine tolerance (ppm)	<0.1 [d]	<0.1 [d]

[a](Majamaa et al. 2011), [b](Mänttäri et al. 2002), [c](de la Rubia et al. 2008), [d]Manufacturer

Based on the characteristics, NF270 is hypothesized to remove the majority of organic matter and microbes and decrease the levels of polyvalent cations remarkably. NOM in NF270 permeate is assumed to consist mostly of LMM fraction. The relative hydrophilicity and negative charge of NF270 should slow down the fouling. UA60 is hypothesized to permeate more ions and organic matter, especially LMM and IMM fraction of NOM. The decrease in hardness and alkalinity is assumed to be lower with UA60 than NF270. The contact angle of UA60 is estimated to be the same or larger than NF270, thus, UA60 is as hydrophilic as NF270 or more hydrophobic. Hydrophobic character should result in faster fouling and flux decline.

6.2.3 Pilot operation

Pilot operation consisted of two phases for each membrane; a pressure test phase and a trial phase (Table 12). Pressure tests were conducted to find out the effect of TMP to the product quality and to operational performance. Three different pressures were tested for both membranes, each pressure for one week. TMP for trial phase was selected based on the pressure tests. Trial phases lasted for two weeks. Due to the challenges in reject adjustment, in 2 and 3 bar pressure tests, recoveries were ~80% and in pressure tests with 4 bar, recoveries were ~85%. In trials, recoveries were increased to ~90%.

Before each phase, new cartridge filters were installed and the equipment was emptied from concentrated water. Membrane units were not changed or cleaned in between the pressure tests neither before trials since cleaning procedure suitable for these membranes and feed waters was out of the research object and inappropriate cleaning wanted to be prevented. Thus, membranes were used for three weeks before the trial run.

Table 12. Pilot operation schedule

Week	Membranes	Phase	TMP	Recovery
1	NF270	Pressure test 1.1	~ 2 bar	~80%
2		Pressure test 1.2	~ 3 bar	~80%
3		Pressure test 1.3	~ 4 bar	~85%
4-5		Trial 1		~90%
6	UA60	Pressure test 2.1	~ 2 bar	~80%
7		Pressure test 2.2	~ 3 bar	~80%
8		Pressure test 2.3	~ 4 bar	~85%
9-10		Trial 2		~90%

6.2.4 Operational performance analysis

The operational performance was evaluated based on specific fluxes. For the calculations, operational performance data was collected with an automatic data logger once in every 10 minutes. Flow and pressure values were also collected manually once a day. Manually and automatically collected results were compared in order to notice operation malfunctions of data logger.

Water temperature was not constantly measured since the variations in temperature were assumed to be minor. For the calculation of specific flux, average temperature of 8°C was applied. During 136.5…145 hours of operation and after 160 hours of operation in pressure test 2.3, remarkable drop in room temperature was observed which clearly affected water temperature and flux. For these periods of time, water temperature of 6°C was applied for dynamic viscosity.

6.2.5 Water quality analyses

Product water quality, the rejection ability of the membrane and the equipment, and the need for post-treatment were evaluated based on water quality analyses. Chemical composition and particles were examined with analysis of pH, alkalinity, conductivity, turbidity, iron, hardness, and UV_{254}. Microbial quality was studied with analysis of Reasoner’s 2A agar (R2A), adenosine triphosphate (ATP) and assimilable organic carbon (AOC). The quantity and quality of NOM was investigated with TOC and DOC analysis, and NOM fractionation in more detail with LC-OCD (liquid chromatography with organic carbon detector), and HPSEC analysis. Standards methods for most of the analyses are listed in Table 13.

Table 13. Standardized analyses

Analysis	Based on standard
Alkalinity	SFS-EN ISO 9963-1 (1996)
Conductivity	SFS-EN 27888 (1994)
Hardness	SFS 3003 (1987)
Iron	SFS 3028 (1976)
pH	SFS 3021 (1979)
R2A	Greenberg et al. (1995)
TOC/DOC	SFS-EN 1484 (1997)
Turbidity	SFS-EN 7027 (2000)
UV_{254}	Greenberg et al. (1995)

During the pressure tests, conductivity, pH, turbidity and TOC were analyzed to observe whether remarkable changes in water quality occur. TOC was analyzed from permeates and feed waters three times a week. Conductivity, pH, and turbidity were analyzed from permeates, feed waters, and concentrates five times a week. Frequencies of analyses and samples, from which analyses were made during trials, are presented in Table 14.

Table 14. Analysis frequency and samples during trials

Analysis	Frequency (in 2 weeks)	Samples
Alkalinity	6	permeates, feeds, concentrates*
AOC	3 (trial 2)	permeates
ATP	3	permeates, feeds, concentrates
Conductivity	10	permeates, feeds, concentrates
DOC	6	permeates, feeds, concentrates
Hardness	3 (trial 1), 6 (trial 2)	permeates, feeds, concentrates*
HPSEC	2	permeates, feeds
Iron	4	permeates, feeds, concentrates
LC-OCD	3	permeates, feeds, concentrates
pH	10	permeates, feeds, concentrates
R2A	4	permeates, feeds, concentrates*
TOC	6	permeates, feeds, concentrates
Turbidity	10	permeates, feeds, concentrates
UV_{254}	6	permeates, feeds, concentrates

*Not followed during the whole trial

Table 15 gives an overview of the numerical expression of analysis results and the uncertainty of the analyses.

Table 15. Overview of presenting the results of analysis

Analysis	**Range**	**Unit**	**Numerical expression (at range)**	**Uncertainty (at range)**
Alkalinity	0.01–10	mmol/l	2 decimals (≤1), 1 decimal (>1)	10%
Conductivity	0.10–140	mS/m	2 decimals (<10), 1 decimal (>10)	4%
Hardness	0.2–9.0	°dH	1 decimal	15%
Iron	20–1500	µg/l	2 significant digits	20% (20–200) 10% (200–1500)
pH	0–14	-	1 decimal	5%
R2A	≥10	cfu/ml	2 significant digits	
TOC/DOC	0.4–10.0	mg/l	1 decimal	25% (0.4…4.0) 15% (4…10)
Turbidity	0.03–40	FNU, FTU	2 decimals (<0.99), 1 decimal (1.0…9.9)	20% (0.03…1) 10% (1…40)

The pH of water was analyzed to observe the effects of cartridge filters and recirculating and to evaluate the need of post-treatment. Depart from the standard, pH was measured with electronic pH meter with temperature compensation and with glass electrode by Metrohm with filling solution of potassium chloride (3 mol/l).

Alkalinity represents the ability of water to resist changes in pH. Total alkalinity, including hydrocarbonate, carbonate, and hydroxide concentration, was determined by potentiometric titration of sample to pH 4.5 with hydrochloric acid. Titration was performed with a Metrohm Titrino 794 titrator.

Conductivity represents the concentration of dissolved ionizing molecules. Conductivity was measured with WTW InoLab Cond 720 analyzer from samples tempered to 25.0 ± 0.5 °C.

Turbidity measures scattered or absorbed light indicating the amount of insoluble substances in the water. Analysis was performed with a turbidity meter HACH 2100AN.

In the iron analysis, iron was oxidized with potassium peroxydisulfate at temperature 120 °C and then reduced with hydroxylammonium chloride. Addition of TPTZ formed colored complex compound with the solution which was detected with a PerkinElmer spectrophotometer at wavelength 593 nm.

Hardness analysis determines the total hardness, i.e. the sum of calcium and magnesium in the water. Analysis was conducted manually in trial 1 and automatically in trial 2. In the manual analysis, sample was titrated with Titriplex solution B to green color in the presence of an indicator. In the automatic analysis, Eriochrome Black T indicator was added to the sample. Sample was then titrated with EDTA to pH 10.0, in which metal ions were chelated and solution got blue color. Automatic titration was performed with a Metrohm Titrino 794 titrator. Color change was detected with Spectrosence photoelectrode.

The removal of organic matter was studied with $UV_{254,}$ TOC, and DOC. UV_{254} measures the relative amount of absorbed ultraviolet light at wavelength 254 nm by a water sample compared to ultrapure water. UV_{254} measures mostly presence of conjugated double ponds and aromatics (Metsämuuronen et al. 2014). UV_{254} was measured with a PerkinElmer spectrophotometer at wavelength 254 nm.

TOC analysis was performed with a Schimadzu TOC-V_{CPH} analyzer. Organic carbon was oxidized to carbon dioxide by burning at 680 °C. Inorganic carbon was removed by acidification and non-volatile organic carbon was determined by NPOC method. DOC samples were filtered through a Ø25 mm filter with 0.45 µm pore size to remove particular organic carbon. Otherwise, DOC analysis was performed as TOC analysis.

From UV_{254} and DOC results, SUVA was calculated. SUVA is defined as the ratio of UV_{254} to DOC and it indicates the relative fraction of aromatic NOM components and hydrophobicity of NOM (Equation 10). SUVA > 4 indicates that the majority of NOM is HMM, hydrophobic and aromatic organic compounds, mainly humic substances. SUVA < 2 indicates mainly LMM, hydrophilic material, mostly non-humic substances. SUVA between 2 and 4 indicates a mixture of these characteristics (Edzwald and Tobiason 1999).

$$SUVA = \frac{UV_{254}}{DOC} \tag{10}$$

where SUVA = specific UV absorbance [l/mg/m]
UV_{254} = UV absorbance at wavelength 254 nm [m^{-1}]
DOC = dissolved organic carbon [mg/l]

Reasoner's 2A agar (R2A) and adenosine triphosphate (ATP) were conducted to study the microbiological changes. R2A cultivation was done according to Greenberg et al. (1995). Sample volume of 0.1 ml was cultivated on a Petri dish and incubated for 7 days at 22 ± 2 °C after which the number of colonies (colony forming unit, cfu) was calculated.

ATP is found in and around living cells. It reacts with luciferase and produces light which is directly proportional to the amount of biomass in the sample. ATP analysis was done at Kemira's Research Center in Espoo. Analysis was 2nd generation ATP measurement conducted with a LumiKem water test kit. First, sample was filtered. Then, ATP was extracted from the filter with KemiLyze extraction reagent and reacted with luciferase. Finally, produced light was detected with a luminometer.

AOC was detected from permeates to determine the amount of organic carbon which is easily exploited by microbes. AOC analysis was done by the National Institute for Health and Welfare according to a modification of method description on Greenberg et al. (1992). Samples were sent to Kuopio for the analysis. In the analysis, 100 µl of nutrient solution was added to the samples to maintain nutrient balance. The samples were sterilized at 60 °C for 30 minutes. Bacterial strains of *Pseudomonas fluorescens P17* and *Aquaspirillum NOX* were added to two parallel samples. The bacterial growth was observed with R2A culture. The amount of AOC was determined from the maximal number of colonies produced and expressed as concentrate equivalent to acetate and oxalate carbon which were used as standards for *Pseudomonas fluorescens P17* and *Aquaspirillum NOX,* respectively.

LC-OCD and HPSEC analyses were conducted to analyze the effect of NF to different NOM fractions. LC-OCD samples were analyzed at Kemira's Research Center at Espoo according to method presented by Huber et al. (2011). LC-OCD analysis divides DOC into hydrophobic and hydrophilic fractions. Hydrophilic fraction is further divided to biopolymers (MM ≥10,000 g/mol), humics (MM ~1,000 g/mol), building blocks (300…500 g/mol), and LMM acids and neutrals (MM <350 g/mol). Samples were frozen before analysis. In the analysis, samples are filtered through a 0.45 µm filter and separated in a chromatography column (TSK HW 50S, 250·20 mm). Column is followed by a UV detector at wavelength 254 nm and an organic carbon detector. At organic carbon detector, fractions are acidified with phosphoric acid and oxidized to carbon dioxide. Carbon dioxide is detected with NDIR (nondispersive infrared sensor) detector. Detection limits for different fractions are estimated to range from 0.01 to 0.5 mg/l depending on a compound.

HPSEC implies molecular weight distribution of NOM. It should be noted that for example small aliphatic compounds do not absorb UV light which is often used as a detector (Matilainen 2007). HPSEC samples were analyzed at MetropoliLab. Samples were filtered through a 0.45 µm filter and frozen before analysis. A high performance liquid chromatograph (HPLC-1100) by HP with chromatography columns (BioSep-SEC-s3000, 7.8·300 mm) was used and the distribution was detected with UV detector at wavelength 254 nm.

7 Results & discussion

7.1 Pressure tests

Pressure tests were conducted separately for both membranes to observe if pressure level has remarkable effect on membrane performance and permeate quality. Pressure tests lasted three weeks and TMP's around 2, 3, and 4 bars were tested.

7.1.1 Membrane NF270

Figures 9 and 10 present the specific fluxes of NF270 membrane measured during pressure tests. A malfunction occurred in automated measurement during the first 65 hours of operation with conventionally treated water at 2 bar pressure, as seen in figure 10. Manually observed data was used to indicate the approximate specific flux

For both pretreatments, specific flux was at level 8 l/m^2/h/bar. During the first few hours after starting each pressure test, specific fluxes were lower than after achieving stable state. This phenomenon is not regarded important in long term operation. For the first two weeks of operation, with pressures 2 and 3 bar, specific fluxes remained quite stable. During the third week of operation, i.e. the operation at TMP 4 bar, specific flux decline was observed in both lines. The flux decline was ~11% for conventionally treated water and ~12% for raw water within the one week. The effect of pretreatment was also seen in the specific flux at the end of the pressure tests, which was lower for raw water than for conventionally treated water, 7.0 l/m^2/h/bar and 7.5 l/m^2/h/bar, respectively.

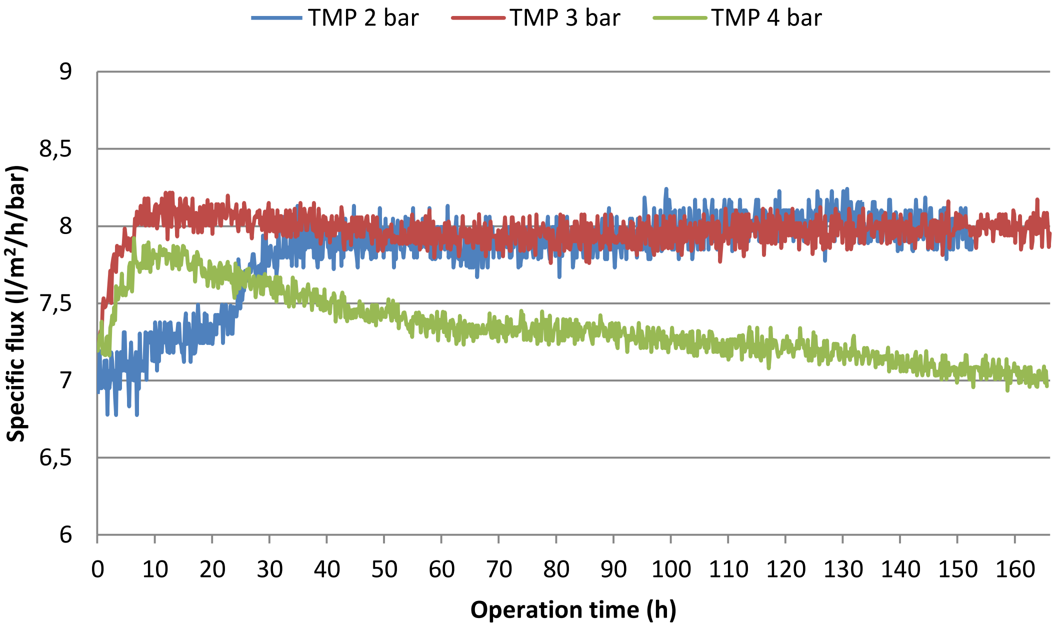

Figure 9. Pressure test: Specific flux of NF270 with raw water

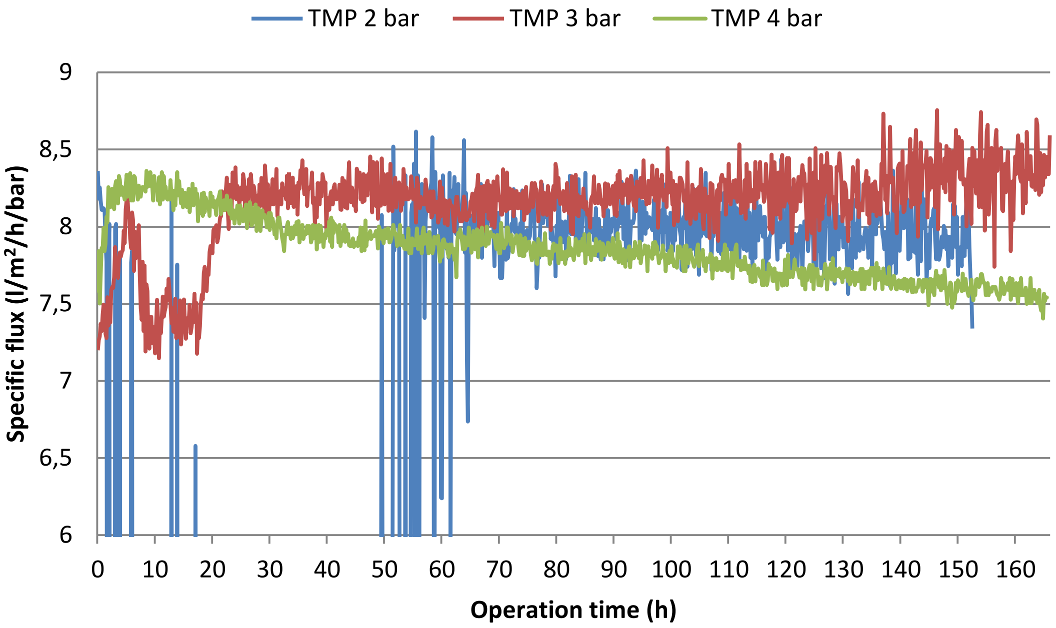

Figure 10. Pressure tests: Specific flux of NF270 with conventionally treated water

Water quality analysis results of pressure test are presented in appendix 2. As hypothesized, neither NF nor recirculation had remarkable effect on pH. 6% elevation in pH was seen in conventionally treated water which results from the rejection of some acidic compounds, for example humic acids and residuals of ferric sulfate. With 3 bar and 4 bar, permeate turbidities were constantly 0.06…0.07 FTU. Thus, turbidity rejection varied depending on feed turbidities. With 2 bar, turbidities were little higher; 0.08 FTU and 0.11 FTU in average for raw water and for conventionally treated water, respectively. Differences between results gained with TMP 2 bar and other TMP's may either result from the novelty membranes or the TMP. No clear dependencies in conductivities could be seen between permeates, feeds, and concentrates. However, interesting observation was that even though conventionally treated feed water had higher conductivities than raw water, permeate conductivities in conventionally treated water line were lower. Permeate TOC's were below determination limit 0.4 mg/l for both lines in all pressure tests.

NF270 produced good quality water with all tested TMP's. Since feed waters were assumed to cause fouling just in few weeks of operation and 4 bar is relatively low TMP for NF, highest pressure were chosen for NF270 trial despite of the flux decline.

7.1.2 Membrane UA60

Available specific flux data is presented in Figures 11 and 12. Data logger was in malfunction during first 16 or 17 h in pressure tests with 2 bar and 3 bar. Thus, no operational performance data is available for these hours. The pilot equipment was in malfunction for two days during the pressure test of TMP 2 bars and no filtration could be performed. Thus, performance results for these days (operation time 83–137 h) are nonexistent. It must be noted that some biological growth may have occurred in the stationary water during the time of equipment malfunction which may have an effect on fouling and/or microbial content on the water.

The data recorded after the equipment malfunction supports the assumption of fouling, since specific fluxes at both lines are lower after than before the malfunction. Thus, the reason for lower specific fluxes at the other two weeks of pressure tests may be the biogrowth occurred at first week of operation but the possible effect of TMP must be taken into account. Specific fluxes at 3 bar remained stable which indicates no fouling occurred during the second operation week. During the third week of operation, with 4 bar, clear flux declines were observed; ~13% for raw water and ~10% for conventionally treated water. The effect of pretreatment was also seen in the specific flux at the end of the pressure tests, which was lower for raw water than for conventionally treated water, 6.5 l/m^2/h/bar and 6.9 l/m^2/h/bar, respectively.

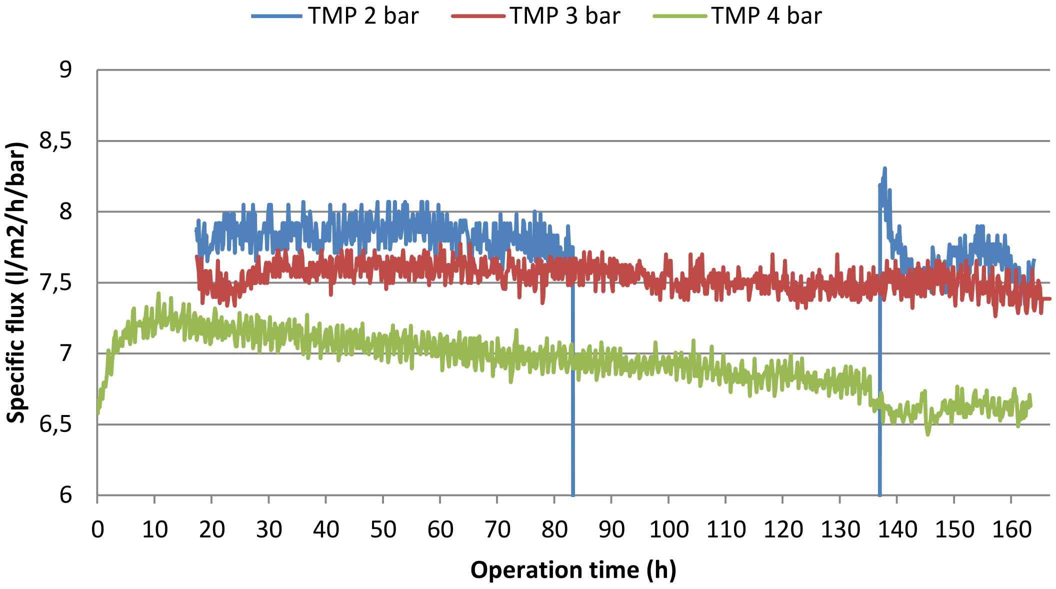

Figure 11. Pressure tests: Specific flux of UA60 with raw water

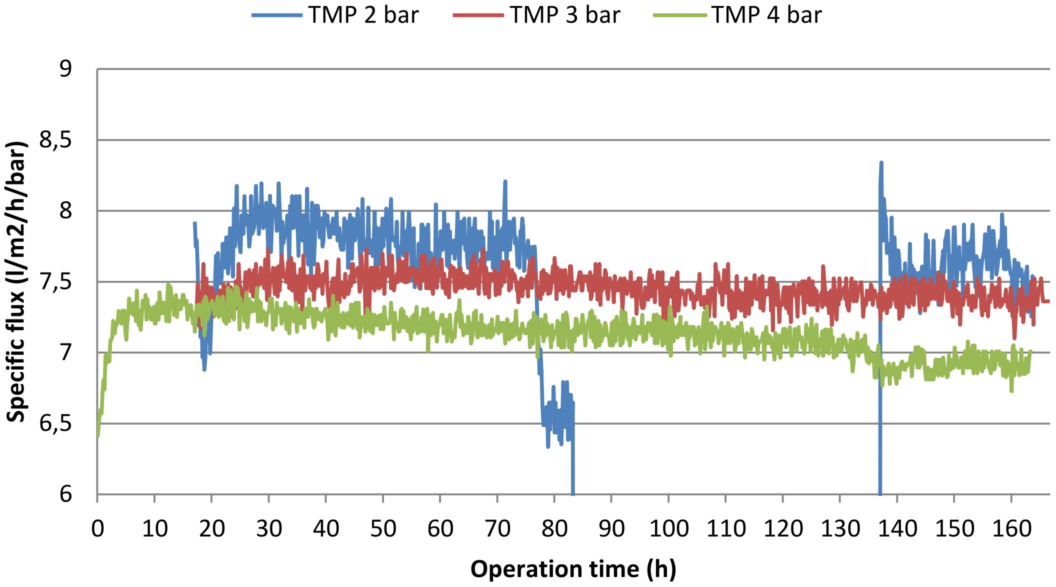

Figure 12. Pressure test: Specific flux of UA60 with conventionally treated water

Water quality analysis results of pressure tests are presented in appendix 3. Similarly to NF270, NF and recirculation had no remarkable effect on pH. However, with UA60, small increases in pH were seen in both lines; 2% and 5% in average for raw water and for conventionally treated water, respectively. For raw water, permeate turbidities were 0.06…0.08 FTU constantly with all TMP's. For conventionally treated water, 3 bar and 4 bar had also turbidities 0.06…0.08 FTU, but 2 bar resulted in little higher turbidities; 0.09…0.11 FTU. Similarly to NF270, turbidity rejections varied depending on feed turbidities. Likewise, no clear dependencies in conductivities could be seen between permeates, feeds, and concentrates. However, in contrast to NF270, permeate conductivity was higher in conventionally treated water line where also the feed conductivity was higher. With raw water, permeate TOC's were below determination limit 0.4 mg/l. With conventionally treated water all TOC's with 2 bar were 0.5 mg/l and the last samples with 3 bar and 4 bar were 0.4 mg/l while the other samples were below determination limit. These differences, however, can result from the uncertainty associated with the analysis, sampling and numerical result. The possibility that greater amount of TOC actually permeates over time was studied more during trials.

Like NF270, UA60 produced good quality water with all tested TMP's. Since feed waters were assumed to cause fouling just in few weeks of operation and 4 bar is relatively low TMP for NF, highest pressure were chosen also for UA60 trial despite of the flux decline.

7.2 Membrane performance in trials

Figures 13 and 14 present specific fluxes during the trial runs with NF270 and UA60, respectively. Comparing the specific fluxes of NF270 and UA60, it can be noticed that the initial specific flux is higher with NF270 than UA60. NF270 had maximum specific fluxes at 7.3 l/m^2/h/bar and at 7.9 l/m^2/h/bar in raw water and conventionally treated water, respectively. UA60 had maximum specific fluxes at 6.8 l/m^2/h/bar and at 7.1 l/m^2/h/bar in raw water and conventionally treated water, respectively. For both membranes, the starting flux is higher for conventionally treated water even though the difference is much more evident with NF270. This results from the flux declines occurred during pressure tests since the same membranes were used in trials and pressure tests without any cleaning in between.

Based on pressure tests, TMP's of 4 bar were chosen for trials. However, since the adjustment options of equipment were limited, starting TMP's of 4.5 bar were applied. TMP's were not adjusted during trials even if those rose as a result of fouling. Figures 15 and 16 show TMP variations during trials which may have affected fouling and flux decline.

During trial with NF270, TMP rose suddenly in raw water line after 5 h and 39 h of operation. Reason for these phenomena was unknown but since these rises were assumed not to result from fouling and they happened at the early stage of trial, TMP was adjusted to restore the initial level after the increases were observed, after 26 h and 49 h of operation. In raw water line, TMP rose constantly during trial 1 indicating remarkable fouling. TMP remained relatively stable in conventionally treated water line.

During trial with UA60, similar sudden changes happened after 236 h of operation in raw water line and after 314 h of operation in conventionally treated water line. These rises occurred at the end part of the trial, thus, no adjustments were made to restore the TMP's.

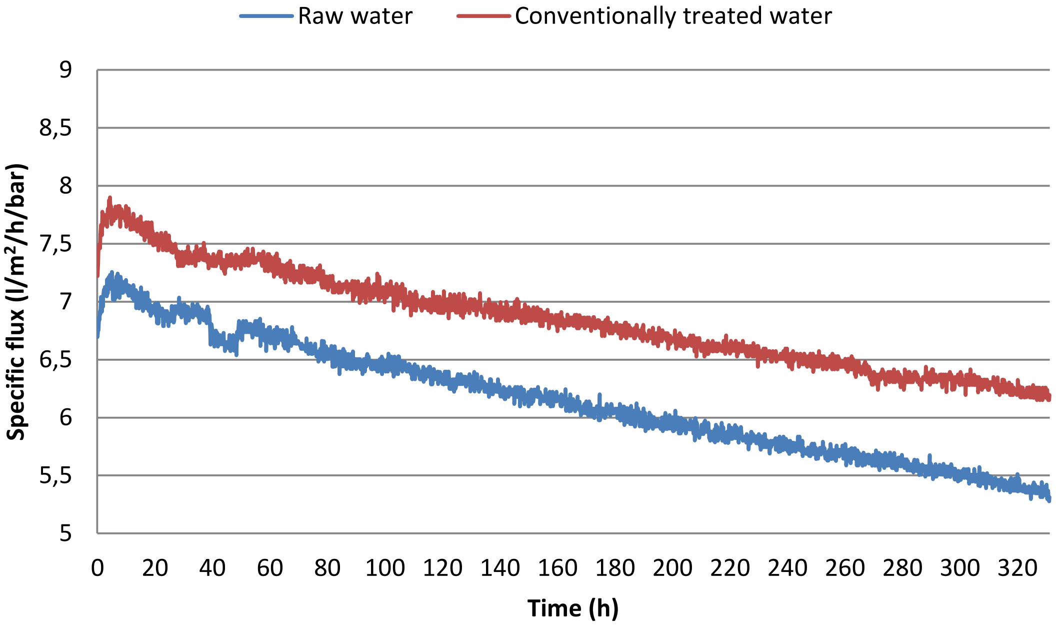

Figure 13. Specific fluxes in trial with membrane NF270

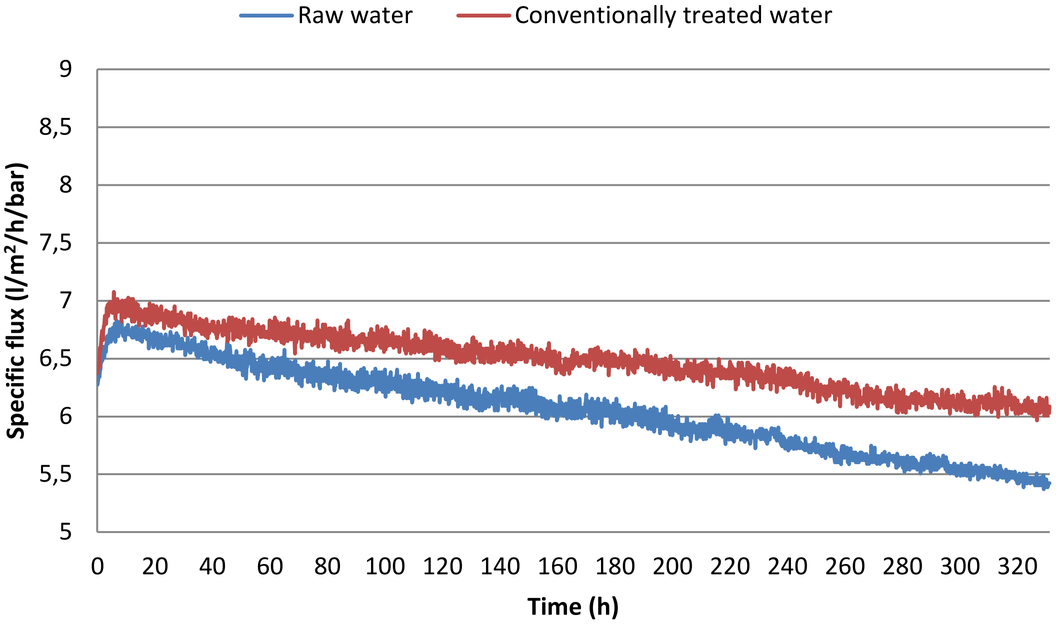

Figure 14. Specific fluxes in trial with membrane UA60

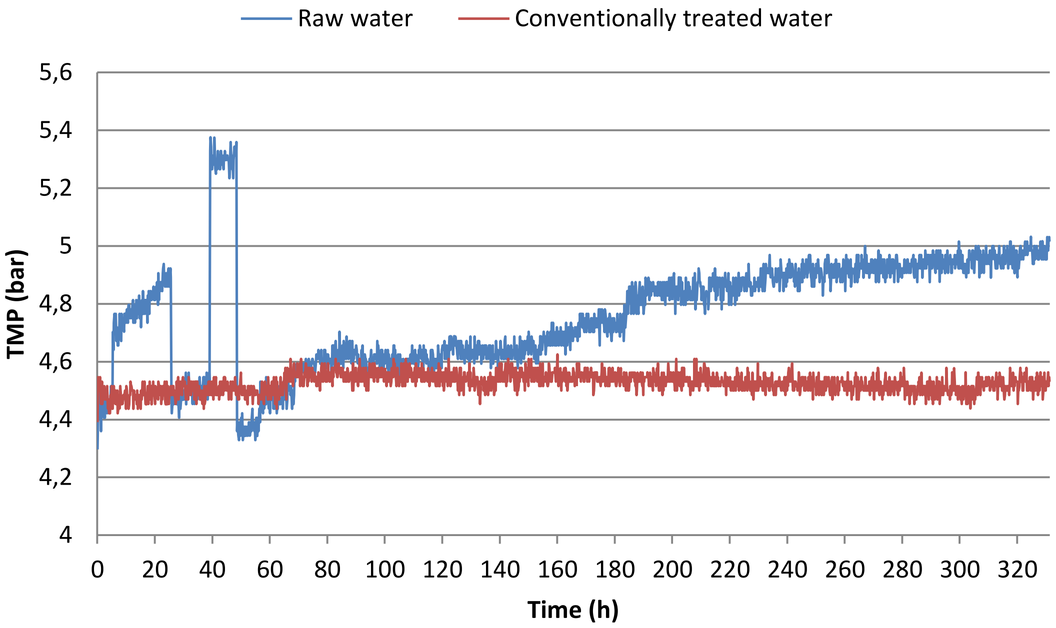

Figure 15. TMP's in trial with NF270

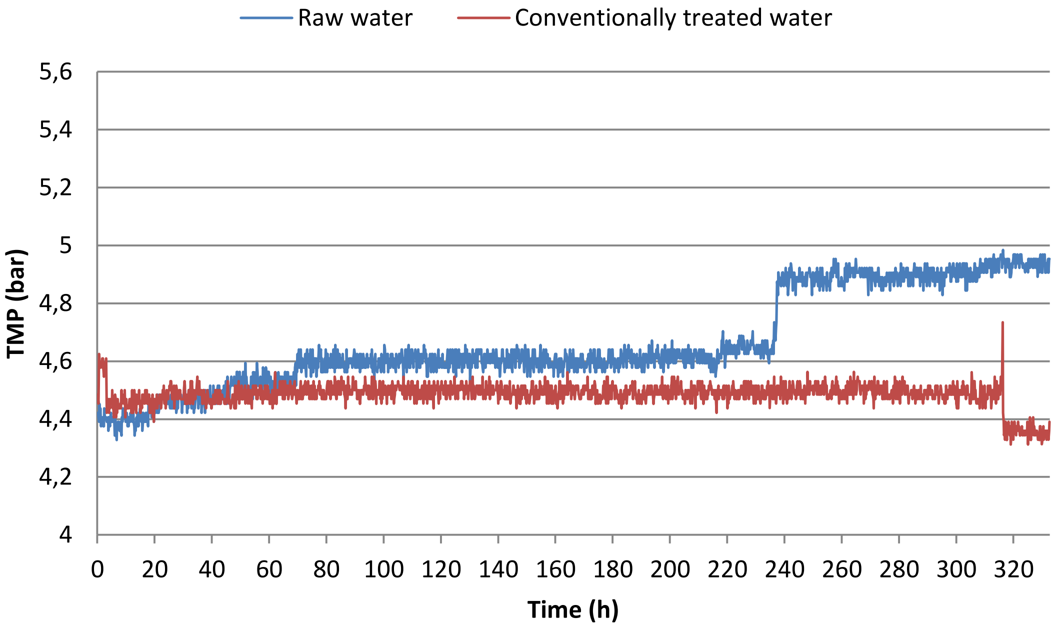

Figure 16. TMP's in trial with UA60

Both trials lasted some 330 hours. Flux declined most with NF270 membrane and with raw water feed (Table 16). Even if UA60 membranes might have been exposed to some biogrowth during pressure tests, UA60 still had lower flux declines than NF270. However, since specific fluxes of UA60 were lower than those of NF270 to begin with, specific fluxes of UA60 after 330 h of trial were at the same level than those of NF270 (Table 17). Thus, performance-wise NF270 seems more effective with both pretreatments even if it experiences remarkable fouling.

Table 16. Flux declines in trials

Flux decline in 330h of operation (%)	NF270	UA60
Raw water	27	21
Conventionally treated water	22	16

Table 17. Specific fluxes at the end of the trials

Specific flux at the end of the trial (l/m^2/h/bar)	NF270	UA60
Raw water	5,3	5,4
Conventionally treated water	6,2	6,0

In contrast to common statement in literature, both membranes were successfully applied with raw water even though the flux declines were significant. In the study of Lopes et al. (2013) NF pilot was operated only 3 hours before complete pre-filter blocking. However, the recirculation flow was conveyed before the cartridge filter, in contrast to this study. Also, relatively low TMP and quite low feed water turbidity in this study may explain the success. Härmä (1999) managed to operate NF70 membrane, similar to NF270, with raw water in similar operation conditions than in this study. He used similar low TMP, the feed water turbidity was relatively low for surface water, <0.7 FTU, as well as the recirculated flow was conveyed after cartridge filter. With suitable raw water and proper operation setup, operation without extensive pretreatment may actually be an option in terms of operational performance. In order to evaluate whether the success with raw water was due to the placement of recirculation inflow after cartridge filter, comparative study should be made.

7.3 Water quality in trials

7.3.1 Inorganic content

Table 18 presents the pH analysis results during the trials. Feed pH's were 7.3 in average for raw water during both trials and 5.1 and 5.2 in average for conventionally treated water. Occasionally feed water pH in conventionally treated line was higher than average as a result of sand filter cleaning. Cartridge filters had no significant effect on pH. For both membranes, permeate pH followed feed pH. Both membranes increased the pH of water by 1…6%. The increase of pH is contrary to the results of Härmä (1999), in which pH decreased with NF70 membrane (precursor of NF270, higher ion rejection ability) with all other than one feed water. Low feed water alkalinity was suggested to be the reason for the one increase which, at some extent, can be seen also in these results (increase of pH was higher with conventionally treated water feed) although both feed waters experienced increase in pH. Lopes et al. (2013) experienced quite insignificant changes in pH (±1%) with NF270 membrane. The change in pH should result from the combined rejection of basic and acidic compounds, in the present case mainly some acidic compounds, such as humic acids or sulfate.

As a post-treatment, permeate may need pH adjustment for corrosion control. The consumption of alkaline or acidic chemical depends on the feed water. If conventionally treated water is used, alkali consumption remains at the same level as at current process in Pitkäkoski treatment plant. If raw water is used, alkali consumption decreases significantly in order to achieve current product water pH.

Table 18. pH results during trials as average ± standard deviation

Feed water	**Membrane**	**Feed (-)**	**Permeate (-)**	**Rejection (%)**
raw water (n=10)	NF270	7.3±0.1	7.4±0.1	-1±1
raw water (n=10)	UA60	7.3±0.0	7.5±0.1	-2±1
conventionally treated water (n=10)	NF270	5.1±0.3	5.4±0.1	-5±5
conventionally treated water (n=10)	UA60	5.2±0.2	5.3±0.1	-2±4

The conductivity results of the trials are presented in Table 19. During NF270 trial, feed water conductivities were 6.93 mS/m and 8.52 mS/m in average for raw water and conventionally treated water, respectively. During UA60 trial, conductivities were a little higher, 7.13 mS/m and 8.78 mS/m in average, respectively. As hypothesized, permeate conductivities were higher with looser UA60 membrane than NF270. With both membranes, rejections were higher in conventionally treated water line than raw water line, probably due to the different, more easily rejected ions such as iron. Still, the actual conductivities were highest in UA60 permeate in conventionally treated water line as the membrane was looser and feed water conductivity was higher. All conductivities were well below the quality recommendation, <250 mS/m.

For UA60, average rejections were 28% and 31% for raw water and conventionally treated water, respectively. For NF270, average rejections were 72% and 48% for conventionally treated water and raw water, respectively. However, with NF270 the conductivity removal in raw water line had decreasing tendency; with a decrease from 51% to 43% in two weeks (Appendix 4). This decrease indicates that the concentration of water resulting from recirculation increases the permeate conductivity. Liikanen (2006) tested NF270 membrane in laboratory scale and documented variety of rejections with several feed waters (41…73%).

Table 19. Conductivity results during trials as average ± standard deviation

Feed water	**Membrane**	**Feed (mS/m)**	**Permeate (mS/m)**	**Rejection (%)**
raw water (n=10)	NF270	6.93±0.06	3.64±0.17	48±2
raw water (n=10)	UA60	7.13±0.12	5.15±0.22	28±2
conventionally treated water (n=10)	NF270	8.52±0.17	2.36±0.03	72±1
conventionally treated water (n=10)	UA60	8.78±0.19	6.08±0.35	31±3

In both trials, feed water turbidities were 0.26 FTU and 0.11 FTU in average in raw water and conventionally treated water, respectively (Table 20). Despite of the feed and concentrate turbidities (Appendix 4), permeate turbidities were 0.05…0.07 FTU with both membranes and both pretreatments. Thus, the reduction of turbidity varied greatly from 13% to 85% depending on the variation on feed turbidity. Lopes et al. (2013) also observed the NF270 permeate turbidity to be independent of the feed turbidity.

Permeate turbidities were below the quality recommendation, <1.0 FTU, and at the same level than turbidities in product water of current treatment process in Pitkäkoski treatment plant.

Table 20. Turbidity results during trials as average ± standard deviation

Feed water	**Membrane**	**Feed (FTU)**	**Permeate (FTU)**	**Rejection (%)**
raw water (n=10)	NF270	0.26±0.07	0.06±0.01	75±6
raw water (n=10)	UA60	0.26±0.05	0.07±0.01	74±6
conventionally treated water (n=10)	NF270	0.11±0.04	0.06±0.01	38±17
conventionally treated water (n=10)	UA60	0.11±0.03	0.06±0.01	42±15

The effect of pretreatment and MWCO of membrane is clearly seen in the alkalinity results (Table 21). In conventionally treated water, alkalinity was very low, ~0.04 mmol/l, and the rejection of alkalinity was namely 0% with both membranes. Statistical variations in rejections can be explained by the uncertainty of alkalinity analysis (10%) and the variations in feed water alkalinity as a result of sand filter cleaning. For raw water, the feed water alkalinity was 0.31 mmol/l in average and the average rejections were 8% and 29% for UA60 and NF270, respectively. Obviously, the rejection was higher with the tighter membrane. Like the retention of conductivity, also the rejection of alkalinity had decreasing tendency with NF270 in raw water line, from 37% to 23% in two weeks (Appendix 4). Liikanen (2006) observed alkalinity rejections of 33…51% with NF270 in laboratory scale study with several conventionally treated feed waters. The difference between feed water alkalinities (higher than in this study) and different operation setup explains the remarkable difference between rejections.

Depending on a pretreatment, the alkalinity of NF permeate was at the same level or higher than alkalinity in the conventionally treated water of current treatment process. Thus, chemical consumption for alkalinity adjustment would remain at the same level as currently or even decrease in order to achieve the alkalinity level of current product water.

Table 21. Alkalinity results during trials as average ± standard deviation

Feed water	**Membrane**	**Feed (mmol/l)**	**Permeate (mmol/l)**	**Rejection (%)**
raw water (n=5)	NF270	0.31±0.01	0.22±0.02	29±5
raw water (n=6)	UA60	0.31±0.01	0.29±0.01	8±2
conventionally treated water (n=5)	NF270	0.05±0.02	0.04±0.01	3±22

conventionally treated water (n=6)	UA60	0.04±0.01	0.04±0.00	-6±19

The effect of MWCO is seen also in hardness results (Table 22). In both trials, both feed waters had hardness of 1.0…1.2°dH. The average rejections of hardness were 67% and over 80% with NF270, and 44% and 47% with UA60, for raw water and conventionally treated water, respectively. With NF270, rejection was significantly higher for conventionally treated water than for raw water; permeate hardness in conventionally treated water line was below determination limit 0.2°dH. No such difference was seen between the UA60 permeates. However, it must be kept in mind that in the case of permeates, hardness is very low and the difference in NF270 permeates hardness is only 0.1…0.4°dH.

In studies of Liikanen (2006) various soft conventionally treated feed waters were treated with NF270. Hardness rejections were significantly lower (47…76%) than in the present study with conventionally treated water. However, rejections of NF270 in raw water line were at the same level in the present study. Partly the difference between conventionally treated waters can be explained by the higher levels of feed hardness (1.9…5.1°dH) compared to this study. Nevertheless, feed hardness is unable to explain the differences of NF270 permeate hardness between different pretreatments in the present study.

A possible reason for the differences in rejections with different pretreatments is that some chemical interactions between magnesium and calcium ions and other substances on the feed side may increase the hardness rejection with NF270 in conventionally treated water line, e.g. the formation of NOM–calcium-complexes (Hong and Elimelech 1997). Also, freezing and storing of the NF270 samples for one month may have affected the permeate hardness, even though this is unlikely since no changes could be seen in feed water hardness measurements.

The argument that increasing pH increases the precipitation of calcium thus affecting rejections (Vigneswaran et al. 2012b) was not observed in these hardness results since both feed waters had similar hardness and the rejections were not higher in the raw water line. The effect of the pH in hardness may be seen only in alkaline, higher pH. If current Pitkäkoski product water hardness is tried to achieve with NF permeates, consumption of lime will increase in post-treatment.

Table 22. Hardness results during trials as average ± standard deviation

Feed water	**Membrane**	**Feed (°dH)**	**Permeate (°dH)**	**Rejection (%)**
raw water (n=3)	NF270	1.0±0.0	0.3±0.1	67±6
raw water (n=6)	UA60	1.0±0.0	0.6±0.1	44±5
conventionally treated water (n=3)	NF270	1.0±0.1	<0.2*	>80*
conventionally treated water(n=6)	UA60	1.1±0.1	0.6±0.1	47±7

* permeate samples below determination limit; minimum rejection based on determination limit

Table 23 presents the iron results from the trials. NF membranes were hypothesized to reject polyvalent ions. Iron results support this hypothesis. Iron rejections were over 57%. Iron was below determination limit 20 µg/l in all permeate samples despite of the iron levels in feed water or in recirculated water (Appendix 4). Quality recommendation of <200 µg/l was fulfilled.

The levels of iron in feed waters remained relatively stable in both trials, but the iron level in UA60 concentrate in conventionally treated water line was remarkably lower, almost half, than with NF270 or with raw water (Appendix 4). Since the difference is larger than uncertainty of the result, either more iron permeated UA60 in conventionally treated water line, even if quantities still remained under determination limit, or some iron precipitated in the system or on the membrane.

Table 23. Iron results during trials as average ± standard deviation

Feed water	**Membrane**	**Feed (µg/l)**	**Permeate (µg/l)**	**Rejection (%)**
raw water (n=4)	NF270	53±7	<20*	>57*
raw water (n=4)	UA60	52±1	<20*	>60*
conventionally treated water (n=4)	NF270	58±4	<20*	>62*
conventionally treated water (n=4)	UA60	53±12	<20*	>57*

* permeate samples below determination limit; minimum rejection based on determination limit

7.3.2 Organic content

Table 24 presents the TOC results from the trials. For NF270, all permeate TOC's were under determination limit of 0.4 mg/l. For UA60, permeate values were 0.5 mg/l at most and for raw water feed below determination limit most of the time. Since raw water had higher TOC values than conventionally treated water, raw water feed enhanced the TOC removal compared to conventional treatment. Rejections with raw water were over 95% for NF270 and over 94% for UA60. For conventionally treated water, rejections were over 82% for NF270 and over 77% for UA60. The statement that increasing pH increases NOM rejection (Hong and Elimelech 1997, Yacubowicz and Yacubowicz 2005, Metsämuuronen et al. 2014) is consistent with these results. However, it must be noted that in addition to pH also quality and quantity of the organic matter differentiate in feed waters.

As a result of recirculation, the TOC levels in concentrates were even nearly 100 mg/l (Appendix 5) and still permeate values were such low, 0.5 mg/l at most. This indicates that these membranes are able to reject TOC efficiently even if the TOC levels in feed water multiply. Thus, membranes seem unsusceptible to changes in feed water NOM quantity. However, the stability of TOC rejection must be studied also with a proper cleaning program since the accumulated deposits may act as an extra filtering layer.

Also Härmä (1999) detected TOC's below determination limit in permeate of two membranes similar to NF270 after various conventionally treated feed waters even with functioning cleaning program within 40 to 60 days of operation with recoveries 50…80%. Lopes et al. (2013) achieved significantly lower TOC rejections and permeate TOC's (59% and 1.26 mg/l) with NF270 membrane in similar experiment setup with recirculation and conventionally treated water with 91% recovery. On the other hand, with recovery of 95%, they received permeate TOC's <1 mg/l and rejections >62%. Reason for this difference is unclear. In laboratory-scale studies of Liikanen (2006) with flat-sheet NF270 membrane and various conventionally treated feed waters, TOC rejections were noticeably lower (46…77%), though some of the feed TOC's were even lower (2.0…4.2 mg/l) and pH's higher (5.7…9.3) than in this study. Liikanen emphasize that the closed circulation lowered the rejection and actual rejection abilities were higher. With similar experimental setup to this study, Liikanen achieved permeate TOC's below determination limit with two membranes similar to NF270.

Table 24. TOC results during trials as average ± standard deviation

Feed water	Membrane	Feed (mg/l)	Permeate (mg/l)	Rejection (%)
raw water (n=6)	NF270	7.7±0.1	<0.4*	>95*
raw water (n=6)	UA60	7.8±0.2	**	>94**
conventionally treated water (n=6)	NF270	2.3±0.1	<0.4*	>82*
conventionally treated water (n=6)	UA60	2.3±0.1	0.5±0.1	80±2

* permeate samples below determination limit; minimum rejection based on determination limit
** permeate samples both below and above determination limit; minimum rejection based on determination limit or lowest rejection

Naturally, permeate DOC results were similar to TOC results since MWCO's of the membranes are lower than the 0.45 µm filter which differentiates DOC from TOC (Table 25). With NF270, permeate DOC's were below determination limit 0.4 mg/l. Thus, rejections of NF270 were over 94% and 82% with raw water and conventionally treated water, respectively. With UA60, conventionally treated feed water resulted in permeate DOC's 0.4…0.7 mg/l and DOC's of raw water permeate were 0.5 mg/l at maximum. With UA60, rejections were over 93% and over 68% for raw water and conventionally treated water, respectively.

Table 25. DOC results during trials as average ± standard deviation

Feed water	Membrane	Feed (mg/l)	Permeate (mg/l)	Rejection (%)
raw water (n=6)	NF270	7.5±0.3	<0.4*	>94*
raw water (n=6)	UA60	7.5±0.3	**	>93**
conventionally treated water (n=6)	NF270	2.3±0.2	<0.4*	>82*
conventionally treated water (n=6)	UA60	2.3±0.1	0.5±0.1	77±6

* permeate samples below determination limit; minimum rejection based on determination limit
** permeate samples both below and above determination limit; minimum rejection based on determination limit or lowest rejection

In addition to actual TOC and DOC analysis, TOC and DOC contents were measured also in the LC-OCD analysis. LC-OCD is more sensitive and also the small amounts of TOC and DOC could be measured. When LC-OCD and TOC analyzer results for feed water were compared, LC-OCD was noticed to provide smaller values in average, especially with higher quantities (Table 26).

Table 26. Feed water TOC and DOC results of TOC analyzer (n=6) and LC-OCD analysis (n=3)

Feed water	**Membrane**	**TOC**		**DOC**	
		Analyzer	**LC-OCD**	**Analyzer**	**LC-OCD**
raw water	NF270	7.7±0.1	6.3±0.6	7.5±0.3	5.8±0.6
raw water	UA60	7.8±0.2	6.7±0.3	7.5±0.3	6.5±0.4
conventionally treated water	NF270	2.3±0.1	1.9±0.1	2.3±0.2	1.8±0.1
conventionally treated water	UA60	2.3±0.1	2.4±0.1	2.3±0.1	2.0±0.1

Based on LC-OCD results, more detailed analysis on TOC and DOC rejections and quantities could be made (Tables 27 and 28). With NF270, permeate TOCs and DOCs were at the same level with both pretreatments, even though the standard deviation was higher in raw water line. The NF270 rejections increased over time by some percentages. With UA60, permeate TOCs and DOCs were lower with raw water feed but no clear tendency of increasing or decreasing rejections was observed in either treatment line. With both membranes, raw water feed resulted in higher rejections. These results indicate that the accumulated deposits may act as an additional filtering layer.

Table 27. Changes in TOC and DOC rejections

Feed water	**Membrane**	**Rejection changes in 11 days (%)**	
		TOC	**DOC**
raw water (n=3)	NF270	94 → 98	95 → 98
raw water (n=3)	UA60	95 → 94	95 → 95
conventionally treated water (n=3)	NF270	90 → 94	91 → 95
conventionally treated water (n=3)	UA60	80 → 80	77 → 80

Table 28. Permeate TOCs and DOCs with LC-OCD analysis presented as averages ± standard deviation

Feed water	**Membrane**	**Permeate values (µg/l)**	
		TOC	**DOC**
raw water (n=3)	NF270	188 ± 126	157 ±106
raw water (n=3)	UA60	352 ±23	295 ±32
conventionally treated water (n=3)	NF270	156 ±40	137 ±41
conventionally treated water (n=3)	UA60	448 ±44	403 ±74

Table 29 presents the UV_{254} results from the trials. UV_{254} measures mostly the presence of conjugated double ponds and aromatic compounds. With NF270, UV_{254} results were 0.000…0.001 cm^{-1} in all permeates. Thus, the decrease in UV_{254} was 100% for raw water and 99% in average for conventionally treated water. With UA60, raw water permeates got values 0.003…0.005 cm^{-1} and permeates from conventionally treated feed water got values 0.006…0.008 cm^{-1}. The decreases were 98% and 81% in average for raw water line and conventionally treated water line, respectively.

Härmä (1999) detected similar low permeate UV_{254}'s (0.000…0.002 cm^{-1}) with two membranes similar to NF270 in the experiments with several conventional treated feed waters and one raw water. Liikanen (2006) detected significantly higher UV_{254}'s (0.007…0.021 cm^{-1}) with several feed waters (0.023…0.068 cm^{-1}) in laboratory-scale studies with NF270, although the results are partly explained with unfavorable experiment conditions. With similar experiment setup to the present study, Liikanen received similar low permeate UV_{254}'s (0.000…0.001 cm^{-1}) with two membranes similar to NF270.

Table 29. UV_{254} results during trials as average ± standard deviation

Feed water	**Membrane**	**Feed (1/cm)**	**Permeate (1/cm)**	**Rejection (%)**
raw water (n=6)	NF270	0.234±0.001	0.001±0.001	100±0
raw water (n=6)	UA60	0.229±0.006	0.004±0.001	98±0
conventionally treated water (n=6)	NF270	0.043±0.003	0.000±0.001	99±1
conventionally treated water (n=6)	UA60	0.039±0.001	0.007±0.001	82±2

SUVA values were determined with DOC and UV_{254} measurements conducted with LC-OCD which had higher resolution for UV_{254}. SUVA indicates the relative fraction of aromatic NOM components and hydrophobicity of NOM. Raw water feed had SUVAs between 3 and 4 indicating a mixture of LMM and HMM, hydrophilic and hydrophobic NOM, and both humic and non-humic substances (Table 30). Conventionally treated water feed had SUVAs below 2 likewise permeate SUVAs with both membranes. SUVA below 2 indicates mostly LMM, hydrophilic NOM and non-humic substances. The effect of membrane is evident; UA60 resulted in permeate SUVAs similar to those of conventionally treated feed water, NF270 resulted in significantly smaller SUVAs. SUVAs were similar with both feed waters for each membrane. Thus, selected membrane affects permeate SUVA more than the feed water.

Table 30. SUVA results presented as averages ± standard deviation

Feed water	Membrane	SUVA (l/mg/m) Feed	SUVA (l/mg/m) Permeate
raw water (n=3)	NF270	3.7 ± 0.1	0.7 ± 0.0
raw water (n=3)	UA60	3.4 ± 0.1	1.7 ± 0.3
conventionally treated water (n=3)	NF270	1.8 ± 0.1	0.6 ± 0.1
conventionally treated water (n=3)	UA60	1.8 ± 0.1	1.8 ± 0.3

7.3.3 Microbial content

Table 31 presents the ATP results from the trials. ATP is directly proportional to the amount of living biomass in the sample. ATP in raw water was over tenfold to conventionally treated water; 26.5…94.8 pg/ml in raw water and 1.5…9.1 pg/ml in conventionally treated water. ATPs of all permeate samples were very low, 0.9…4.4 pg/ml. For NF270, ATP content of permeates seemed to decrease over time; in raw water line from 3.9 to 0.9 pg/ml and in conventionally treated water line from 4.4 to 1.0 pg/ml. For UA60, such apparent behavior was unseen. Since ATP levels in conventionally treated feed water were low, 1.5…9.1 pg/ml, rejections varied a lot, from 0% to 89%. Instead, the rejections in raw water line were quite stable, 96% and 94% in average for NF270 and UA60, respectively. Based on ATP analysis, living biomass seems to be well rejected by the membranes.

Table 31. ATP results during trials as average ± standard deviation

Feed water	Membrane	Feed (pg/ml)	Permeate (pg/ml)	Rejection (%)
raw water (n=3)	NF270	52.7±36.8	2.2±1.5	96±2
raw water (n=3)	UA60	58.7±21.2	3.4±0.1	94±2
conventionally treated water (n=3)	NF270	5.0±3.8	2.3±1.8	30±51
conventionally treated water (n=3)	UA60	3.6±1.1	2.3±0.6	37±5

R2A results (Table 32) also represent the microbial count of water. For NF270, most permeate R2A results were below the determination limit of 10 cfu/ml; only one sample from raw water line was 20 cfu/ml. Thus, the rejection of microbes was excellent. With UA60, however, both permeate lines had R2A values over determination limit. In conventionally treated water line, R2A's were 10…25 cfu/ml. These R2A values correspond to the rejections of 38…83%, but if compared to the R2A levels in recirculated water (260…460 cfu/ml), 88% of microbial content was removed in average (Appendix 6). With raw water, R2A levels in UA60 permeate were very high; 1,200…1,500 cfu/ml which were sometimes even higher than in feed water, indicating 0% rejection. Nevertheless, if permeate R2A's are compared to the R2A levels in recirculated water (33,000…68,000 cfu/ml), 97% of microbial content was removed in average.

Table 32. R2A results during trials as average ± standard deviation

Feed water	Membrane	Feed (cfu/ml)	Permeate (cfu/ml)	Rejection (%)
raw water (n=4)	NF270	1425±750	*	>97**
raw water (n=4)	UA60	1428±528	1375±126	-11±55
conventionally treated water (n=4)	NF270	41±5	<10	>71*
conventionally treated water (n=4)	UA60	55±13	16±6	67±21

* permeate samples below determination limit; minimum rejection based on determination limit

** permeate samples both below and above determination limit; minimum rejection based on determination limit or lowest rejection

Even if R2A results of UA60 permeates in raw water line are much higher than other permeates, no difference can be seen between the ATP results of permeates. Thus, ATP and R2A results are incoherent. In theory, NF membranes should reject all microbes and, with the same conventionally treated feed water, Laurell (2013) achieved rejections of 100% even with much looser MF membrane (pore size 0.1 µm). Instead of actual permeation, there are a few explanations for the high R2A results of UA60 in raw water line. First of all, piping may have been contaminated while changing the membrane from NF270 to UA60, since piping was not disinfected before or after application. Secondly, microbial growth may have occurred in the piping during the equipment malfunction in pressure test phase with UA60 membrane. In either of the case, higher microbial content should also be seen in the ATP results. Lastly, contamination may have occurred in R2A sampling, even though this is improbable since R2A results were similar each sampling time and no similar results are seen in conventionally treated water line. For the same reasons also an error in the analysis is improbable. Loss of membrane integrity can be excluded since the effect should be seen in other analysis, e.g. TOC.

The AOC results of UA60 are presented in Figure 17. In both lines, permeate AOC seemed to have an increasing tendency. In raw water line, the increase was remarkable, from 57 µg AOC-C/l to 438 µg AOC-C/l in one week. If accurate, the result of 438 µg AOC-C/l would mean that most or the entire organic content in permeate would be easily biodegradable. In conventionally treated water line, AOC doubled in one week from 60 to 117 µg AOC-C/l. Changes in TMP can partially explain the rises, since within the one week TMP in raw water line rose by 0.3 bar. However, TMP in conventionally treated water line remained stable. With just three samples, the rising tendency may be misleading and the quantity may rather be fluctuating than rising.

The AOC results in the present study are significantly higher than those of Härmä (1999); permeate AOC were 35 µg AOC-C/l at most with several conventionally treated and one raw feed water. Härmä studied two precursor membranes of NF270 with higher ion rejection which may partly explain the difference. In contrast, Meylan et al. (2007) received NF270 permeate AOC's 50…150 µg/l with two different feed waters, the same level than in the present study. The researchers also notified that since AOC and DOC results in their study were at the same level, the total permeating DOC may be a carbon source for microbial growth. Also Park et al. (2005) received AOC's of same level than in the present study. However, the permeate DOC's were multifold to AOC.

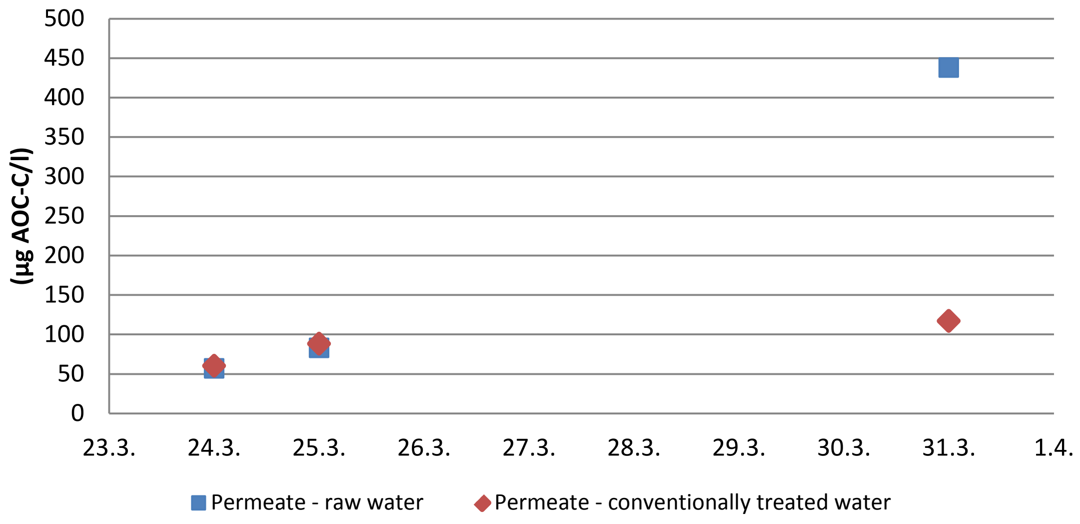

Figure 17. Assimilable organic carbon (AOC) results for UA60

Drinking water is regarded as biologically stable when AOC is 50…100 µg/l with appropriate level of chlorine residual or 10…20 µg/l without chlorine (Van der Kooij 1990). With the assumption of post-chlorination of NF permeates, first two of the three samples were biologically stable. The third samples in both lines were unstable. However, in current Pitkäkoski treatment process, product water AOC is at 100…160 µg/l (Castrén et al. 2014), which is achieved also with the third sample from conventionally treated water line. The amount of AOC in the third sample from raw water permeate was so high that further examinations are needed if UA60 is decided to be used with raw water. For example, stable TMP may prevent the increasing permeation or proper cleaning program may be able to restore the filtering ability of a membrane. More studies of permeate AOC would be needed in order to evaluate the need of biological stabilization as a post-treatment. Since no AOC results of NF270 are available, biological stability of NF270 permeates is unknown.

7.3.4 Quality of NOM

Quality of NOM was measured with LC-OCD analysis and HPSEC analysis which measures the hydrophobicity and the molecular weight distribution of NOM. Since the quantity of NOM in NF270 permeates were very low, quality information achieved from the analyses is limited.

HPSEC results are presented in Figures 18 and 19 as averages of permeate peak height and averages of remaining peak height for different fractions and peak height sum. HMM fractions (>5,000 and 4,000–5,000 g/mol) were absent at detectable levels in all permeates. IMM fractions (3,000–4,000 and 1,000–3,000 g/mol) were present in low levels in UA60 permeates but not in NF270 permeates at detectable quantity. LMM fraction <500 g/mol was detected from all permeates but 500–1,000 g/mol fraction was detected only from UA60 permeates. With NF270, the lowest fraction was the only one detected and it was also very well rejected. UA60, however, rejected only about half of the lowest fraction. These results are coherent with the MWCO's of the membranes.

Even though the permeate peak height sum of UA60 in raw water line was much higher than either of the NF270 permeates, the remaining peak height in UA60 raw water line was only 3%. Thus, the differences in feed water quality must be noticed when examining the values of permeate peak heights. With both membranes and all detected fractions, raw water line resulted in smaller remained peak heights, i.e. all fractions were better rejected in raw water line. These results support the idea that the pretreatment affects the rejection of organic matter.

In the study of Matilainen et al. (2004) with several conventionally treated feed waters, NF270 removed less effectively all fractions of NOM compared to the present study; with only one feed water, the removal of HMM fraction was 100% and one feed water resulted in 86% removal of LMM fraction, all others were well below that (21…60%). However, the samples were collected after only four hours of running and the experiment was laboratory-scale which may partly explain the large differences to the present study.

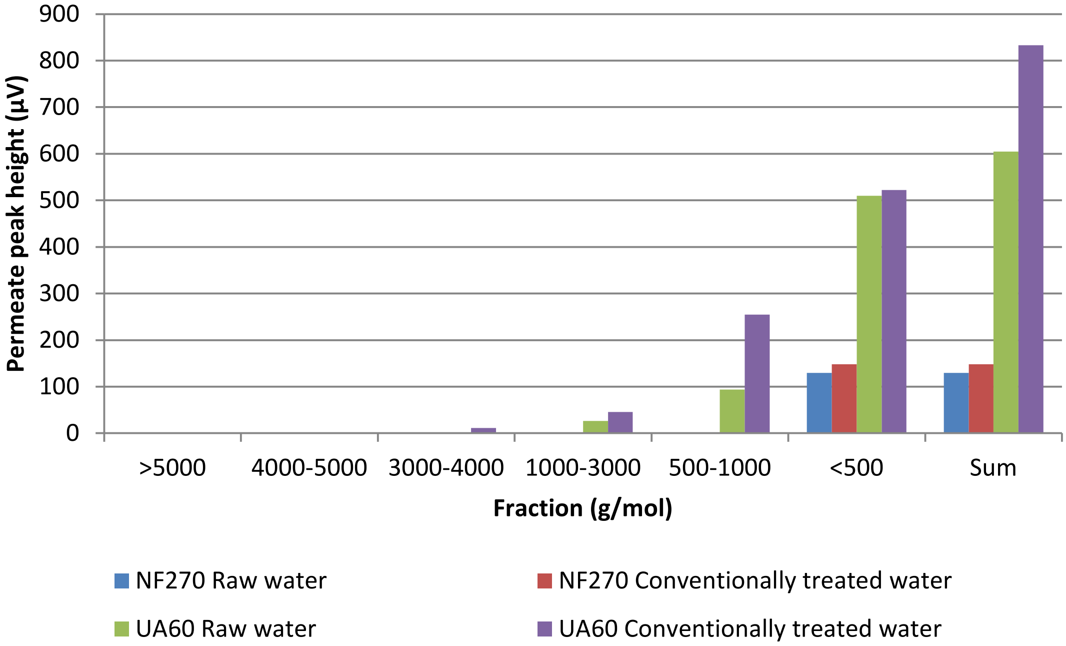

Figure 18. HPSEC results as averages of permeate peak height (n=2)

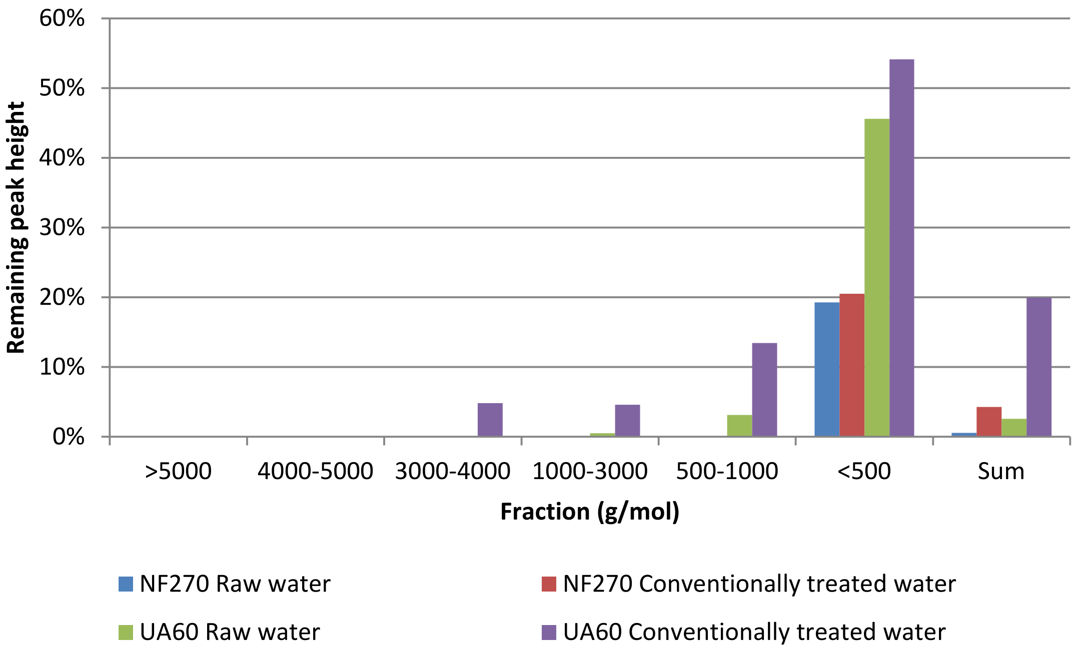

Figure 19. HPSEC results as averages of remaining peak height (n=2)

The low NOM quantities in NF270 permeates resulted in poor-quality LC-OCD chromatograms since the sensitivity of detector was insufficient. Thus, numerical quantities of different fractions were impossible to produce but chromatograms were qualitatively evaluated. Feed water and permeate chromatograms were compared. Detectable quantities of biopolymers were nonexistent in NF270 permeates. Very low quantities of humic substances and degradation products of humic substances existed and the quantities became lower over time. Since the quantities of humic substances and degradation products of humic substances were in the majority in feed waters, the rejection of this fraction was extremely good. The response of LMM acids and humics distinguished well from the chromatogram even though it clearly became smaller over time. Thus, the rejection on LMM acids and humics improved over time and when compared to the response in feed water, the rejection was good. However, presence of humic substances interfere the response of LMM acids for both feed waters and permeates and no detailed analyze can be drawn of the rejection ability of LMM acid fraction. It can be noted that in feed water and concentrate in conventionally treated water line the quantities of LMM acids and humics were minor compared to those in raw water line. The responses of LMM neutral fraction were indistinct. Chromatograms indicate that LMM neutrals existed in permeates but more detailed analysis is difficult. At second sampling time, LMM neutral fraction gave distinct response for conventionally treated water line, which may have resulted from, for example, a residue of a chemical or microbial activity.

These results are in correspondence with the studies of Meylan et al. (2007) which reported that LMM neutrals were the less rejected NOM fraction by NF270 with two pre-filtered surface waters, yet 94% and 95% of LMM neutrals rejected. Also, the researchers detected barely any permeation of biopolymers and humics (<1%).

The NOM quantities in UA60 permeate allowed more detailed analysis than in NF270 permeate. Majority of NOM in UA60 permeates was hydrophilic as supposed; membranes rejects more easily hydrophobic fraction. Rejections of biopolymers and humics increased over time being very good all the time: >91% and >85% with conventionally treated water, respectively, and both >98% with raw water (Table 33). LMM neutrals and LMM acids had lower rejections than larger fractions but still >74% and >88% with raw water and >64% and >15% with conventionally treated water, respectively. The low percentage of LMM acids in conventionally treated line results partly from lower levels in feed water; over half of LMM acids in raw water were removed in the pretreatment with conventional treatment. Degradation products of humic substances, 'building blocks' had rejections of >95% and >82% in raw water line and conventionally treated line, respectively. Majority of hydrophilic NOM in permeates was LMM neutrals, nevertheless, the quantity was very low, <0.2 mg/l. LMM neutrals were at the same level in both treatment lines. Raw water line resulted in lower quantities in all other fractions. The average molecular weight of humic substances was at the same level in both permeates as in conventionally treated feed water (~300 g/mol) even if it was higher in the raw water feed (>500 g/mol) and MWCO of the UA60 membrane is even more higher.

Table 33. UA60 rejections of different fractions based on LC-OCD analysis (n=3)

Rejections (%)	**Biopolymers**	**Humics**	**Building blocks**	**LMM neutrals**	**LMM acids**
Raw water	>98 %	>98%	>95%	>74%	>88%
Conventionally treated water	>91 %	>85%	>82%	>64%	>15%

8 Conclusions & recommendations

In contrast to a common statement that NF is inapplicable without any pretreatment, two loose NF membranes were successfully operated with raw water in bench-scale unit. A pretreatment with conventional treatment process diminished the flux decline less than expected when compared to raw water. In all studied cases, the flux decline was significant, even though flux decline could have been even more remarkable since the recovery was high and no cleaning was applied. Thus, active membrane cleaning program would be essential in larger-scale operation. Flux decline was faster with tighter NF270 membrane than looser UA60 membrane, as expected. However, as reported by manufacturer, the operational performance of UA60 was worse than that of NF270; UA60 produced less water with the same applied pressure. This difference is most likely to result from the differences in the membrane characteristics such as membrane material. However, noteworthy is that UA60 membrane possibly experienced additional biogrowth during the equipment malfunction which may have influenced the flux decline.

In addition to the flux decline, the reversibility of fouling is crucial in membrane selection. The causes, the mechanisms and thus the reversibility of fouling may be divergent with different feed waters since pretreatment affects the quality and quantity of both organic and inorganic matter. Also the MWCO of a membrane may affect the reversibility of fouling as the fouling mechanisms may be different. Depending on the reversibility of fouling and effectiveness of cleaning program, UA60 could be productivity-wise competitive option in long-term use despite of the worse operational performance in this study. In order to compare the long-term effect of pretreatment and membrane selection, the reversibility of fouling and proper cleaning procedure requires further studies.

With both membranes, fouling, i.e. flux decline, was remarkable with both feed waters and steeper with raw water. Generally, high recovery increases fouling but on the other hand low recovery increases loss of water and the quantity of sewage. Thus, a balance must be found between low fouling and high recovery. Recirculation, which is used to increase recovery, concentrates the water and increases the load of substances on membrane. It should be considered whether periodical chemical precipitation of concentrated organic matter would be reasonable in order to reduce the organic load on membrane. Biofouling could be reduced with pre-disinfection, especially in raw water line. However, if chorine compound would be used as disinfectant, THM levels would rise and the monitoring of chlorine residual would be extremely important as most membranes are intolerant to chlorine. UV disinfection, for example, could be more reasonable option.

Quality-wise, NF270 and UA60 removed effectively both organic and inorganic substances. Most organic fractions were rejected well with the membranes. Permeating organic substances were the smallest fractions which are easily consumed by microbes and which increase biogrowth in distribution system. With UA60 membrane, raw water feed resulted in lower concentrations than conventionally treated feed water in all other NOM fractions than LMM neutrals. Also, with UA60 membrane, the majority of NOM was neutral LMM fraction, which is difficult to be removed with any water treatment process. NOM concentrations in NF270 permeates were so low that fractions were impossible to study separately. Overall, both membranes produced water of low organic content (TOC≤0.7 mg/l) with both feed waters even when the TOC of recirculated water increased to nearly 100 mg/l. This indicates that these membranes are able to even out the quality changes in feed water and that rising organic content in raw water source is well withstood.

The rejection of alkalinity and hardness depended on the pretreatment and on the membrane. Alkalinity and hardness levels in permeates were so low that permeate would require remineralization. NF270 and UA60 permeates would need chemical post-treatment before distribution. Alkalinity and pH would require adjustment and some remineralization is necessary to increase hardness. Depending on the pretreatment selection, the consumption of alkaline chemical would remain at current level or decrease. Hardness would require additional calcium dosage. Microbial content was well rejected with tighter NF270 membrane. Looser UA60 membrane resulted in controversial microbial results and no conclusions can be made on the ability of UA60 to reject microbes before confirming the results. Several suggestions of the origin of high R2A results of UA60 permeate from raw water line was provided, even though none were supported by other R2A and ATP results. In order to evaluate the actual rejection of microbes, further studies with disinfection of equipment and control samples of R2A and ATP are required. If the R2A results were a result of biogrowth in the equipment, biostabilization may be needed as a NF post-treatment in order to limit the biogrowth in the distribution system. In the light of these microbial results, the possibility of lower disinfectant consumption is questionable with UA60 membrane. Combination of UV disinfection and chemical disinfection could result in lower disinfectant consumption.

Overall, these loose membranes had high rejection of organic matter and high to low removal of inorganic matter. In contrast to what was desired, the membranes showed insignificant decreases in the removal of hardness. In order to compromise between high removal of organic compounds and low removal of inorganic compounds, the removal of NOM in studied cases can be regarded as unnecessary high. If membrane process is targeted to treat all water, other membrane alternatives should be studied. A membrane with different characteristics can provide better compromise between high removal of organic matter and low removal of inorganic matter without sacrificing the microbial quality and operational performance. Especially, the effect of MWCO and membrane material on the rejection of organic, inorganic and microbial content requires further studies. Performance-wise raw water demonstrated promising results with these two membranes. Thus, raw water should be included also in the further studies.

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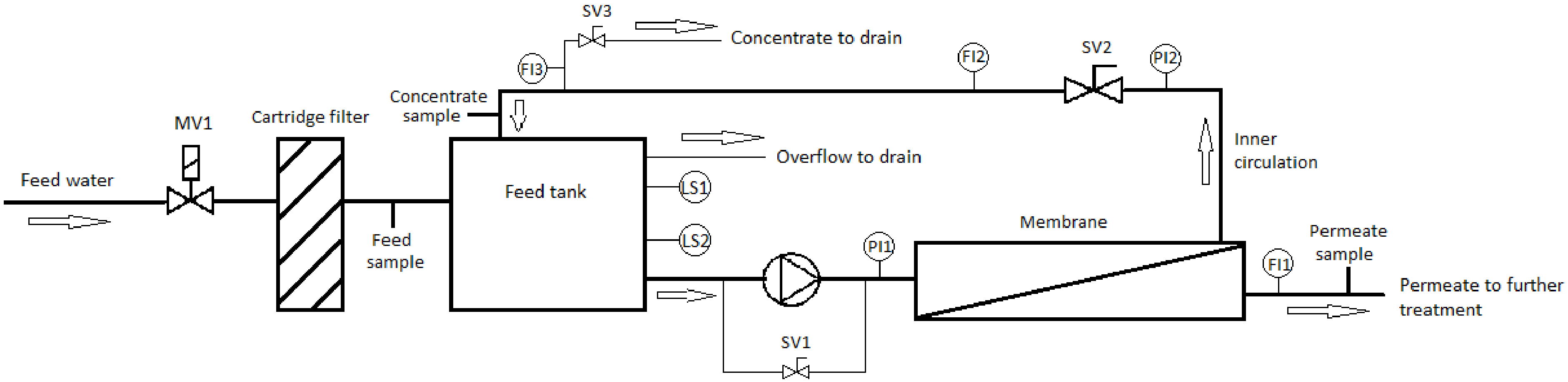
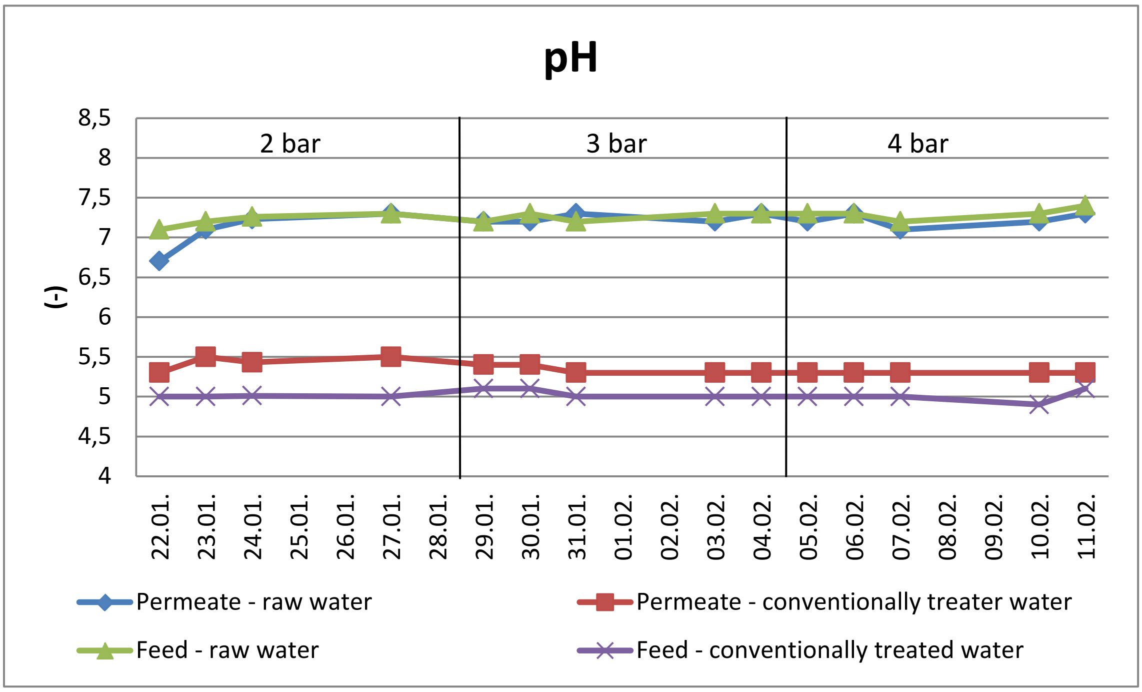
Appendices

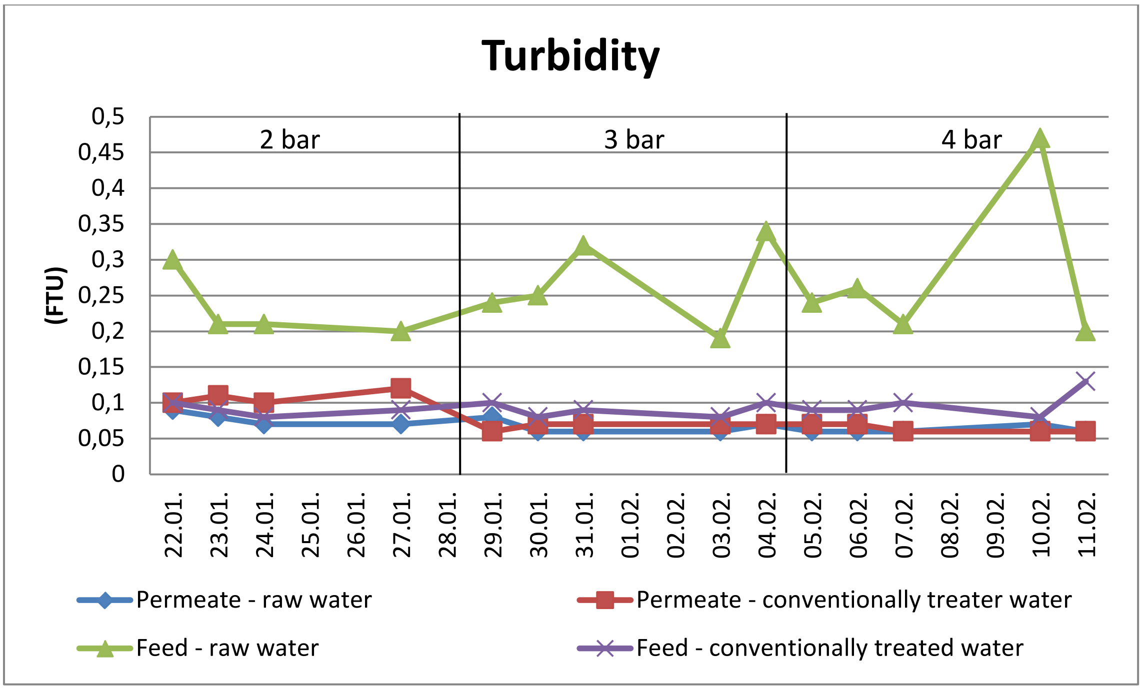
1. PI-diagram of the equipment
2. Pressure tests – water quality results of NF270
3. Pressure tests – water quality results of UA60
4. Inorganic water quality in trials
5. Organic water quality in trials
6. Microbial water quality in trials

Appendix 1. PI-diagram of the equipment

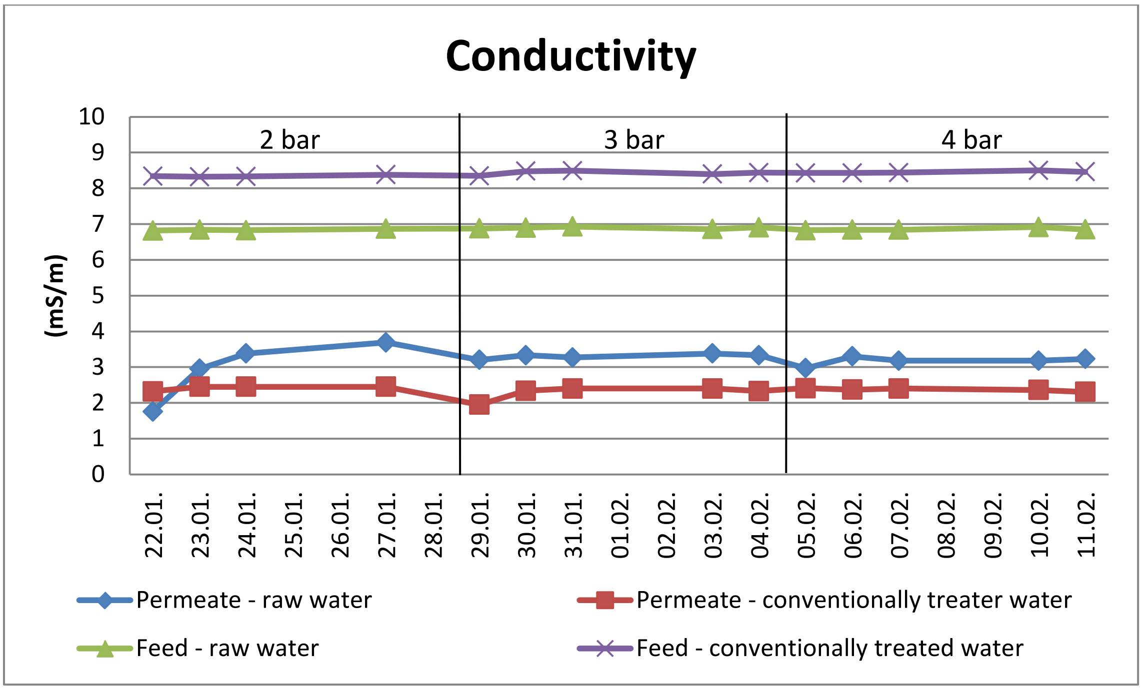


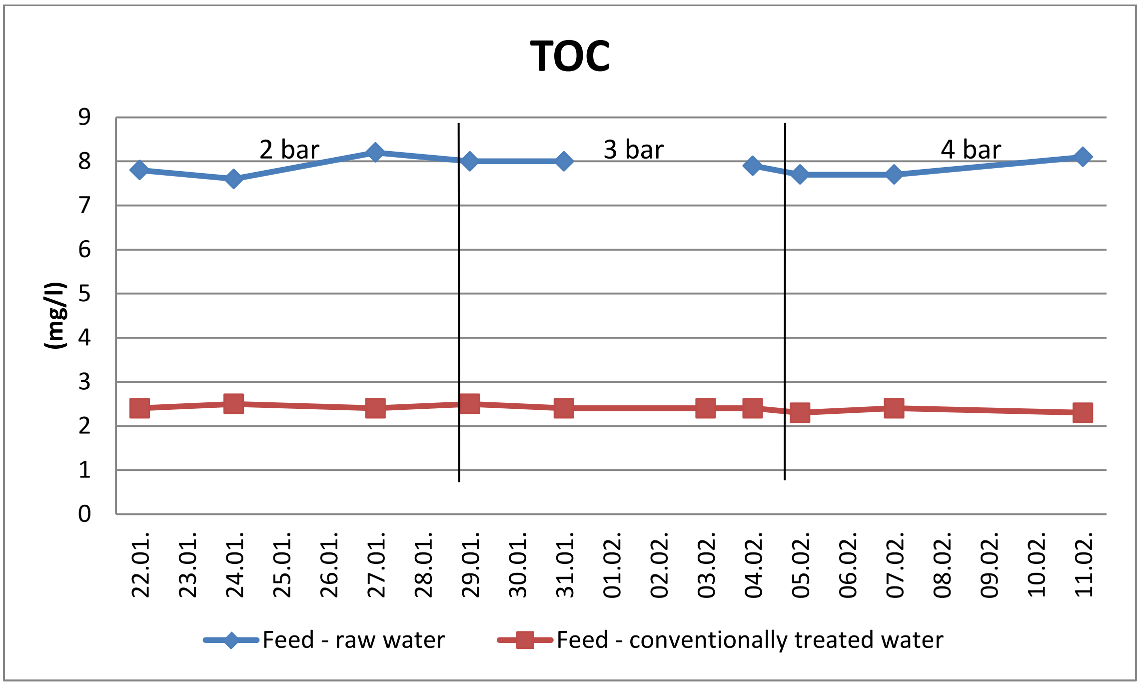
Appendix 2. Pressure tests – water quality results of NF270 (1/2)





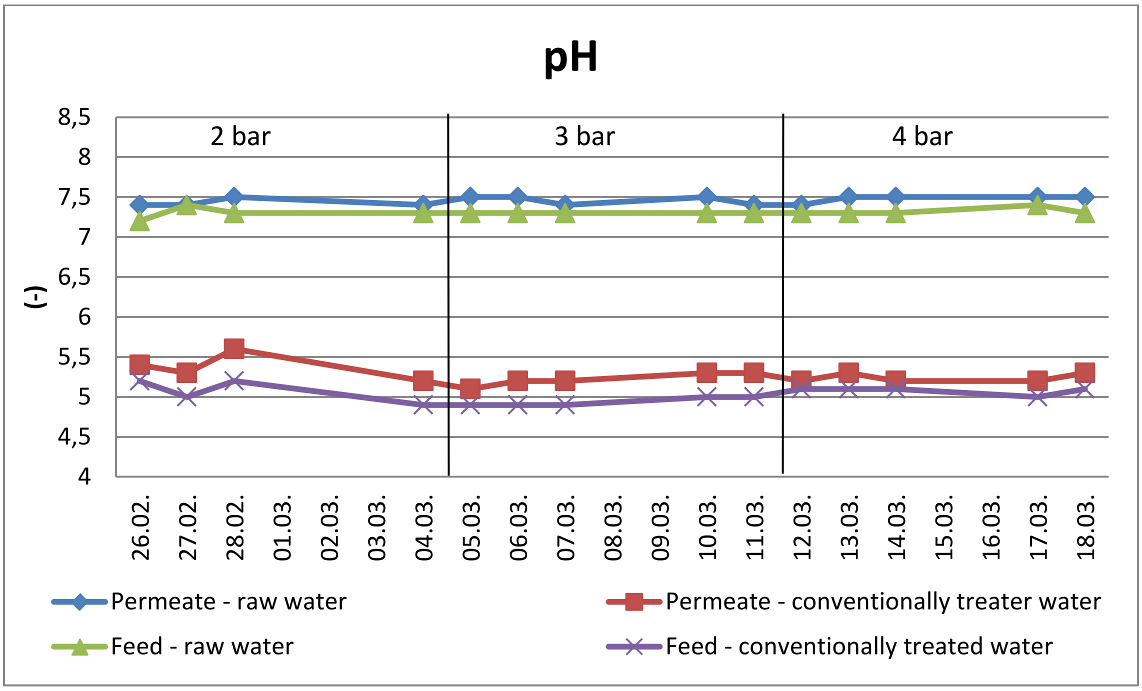
Appendix 2. Pressure tests – water quality results of NF270 (2/2)

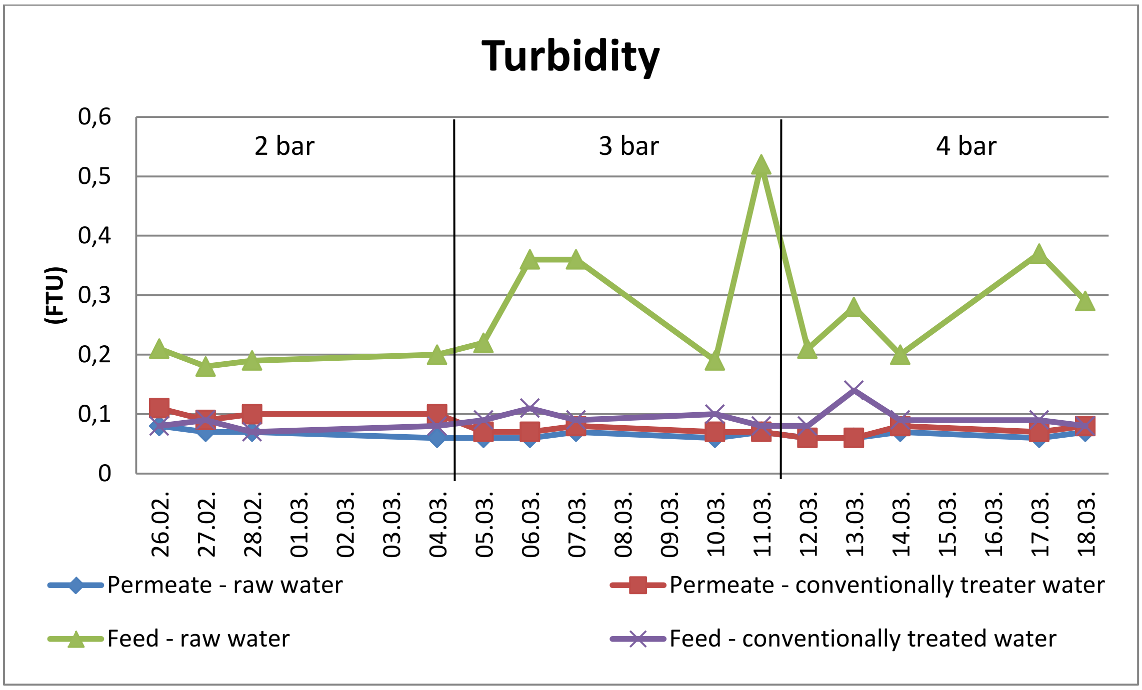




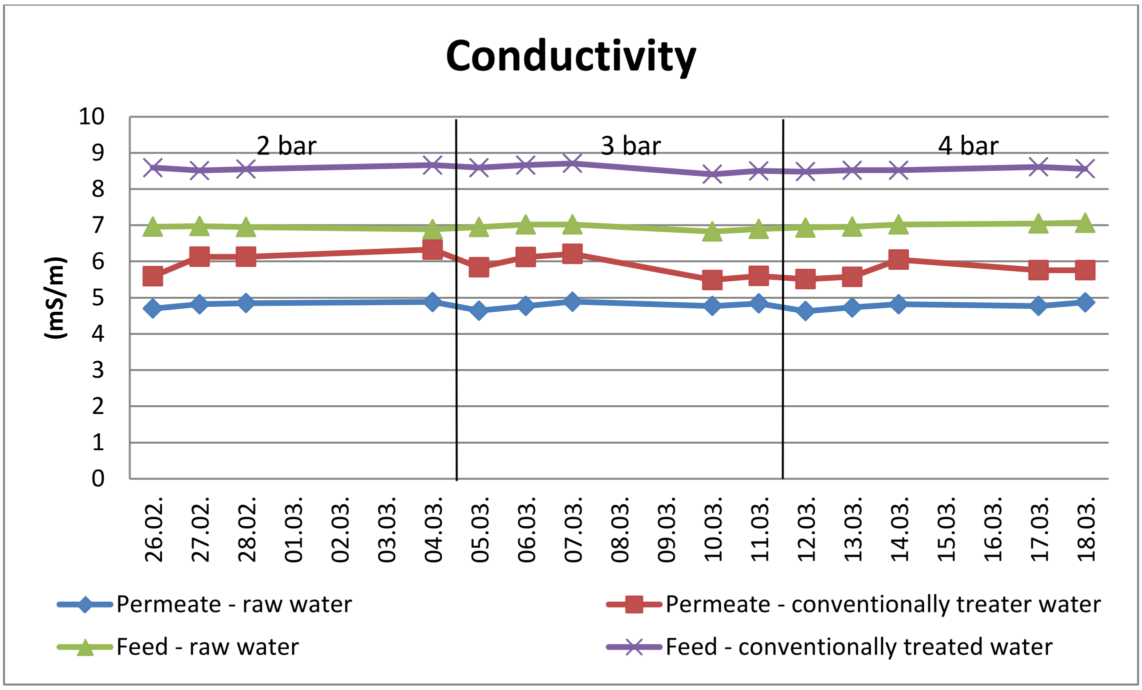
All permeate values under determination limit

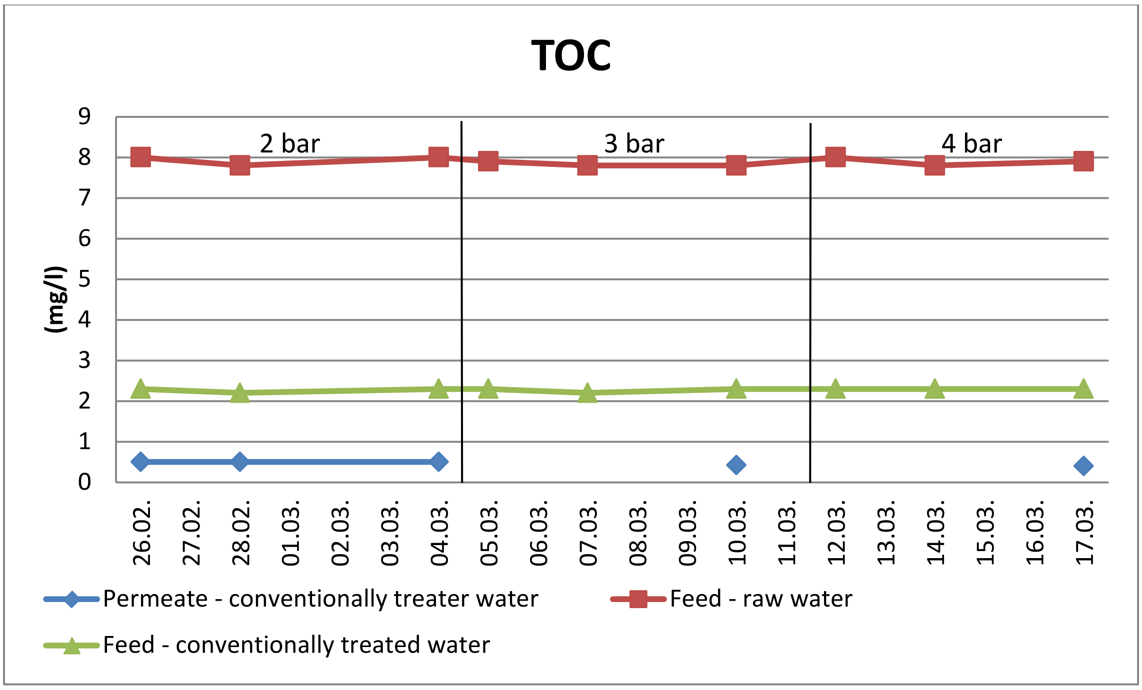
Appendix 3. Pressure tests – water quality results of UA60 (1/2)



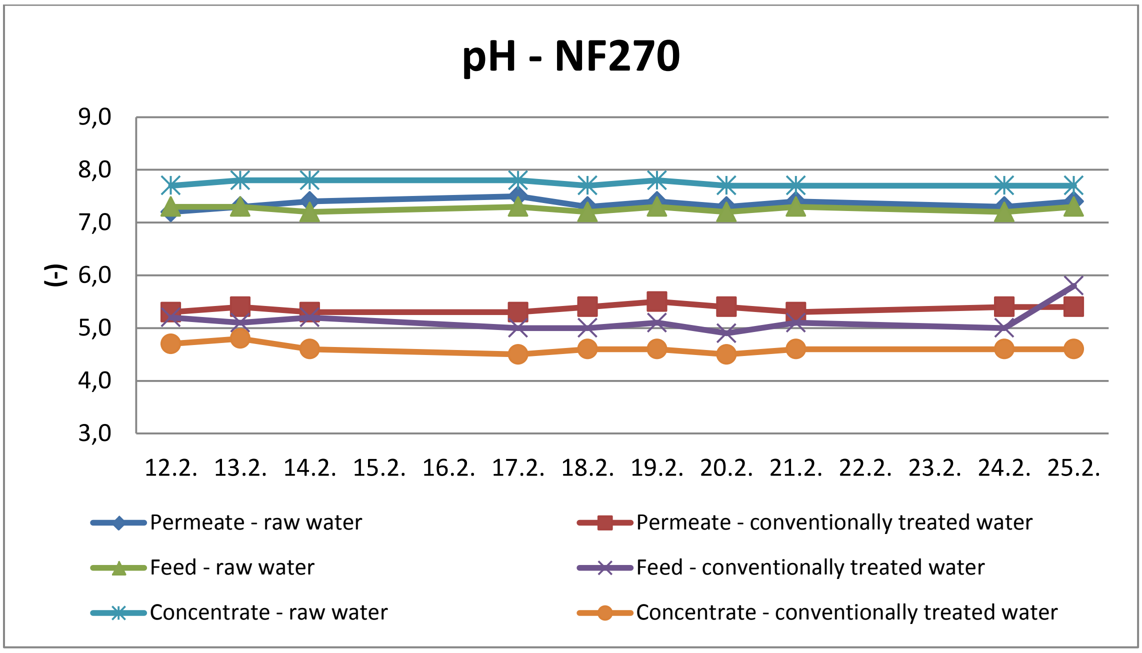


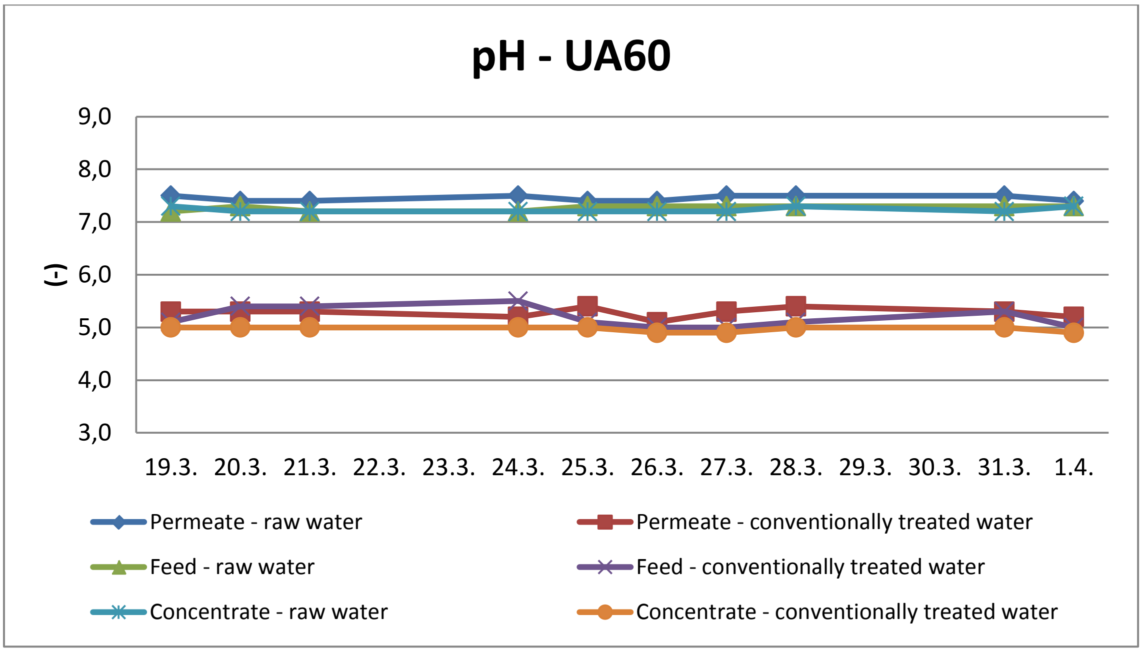
Appendix 3. Pressure tests – water quality results of UA60 (2/2)



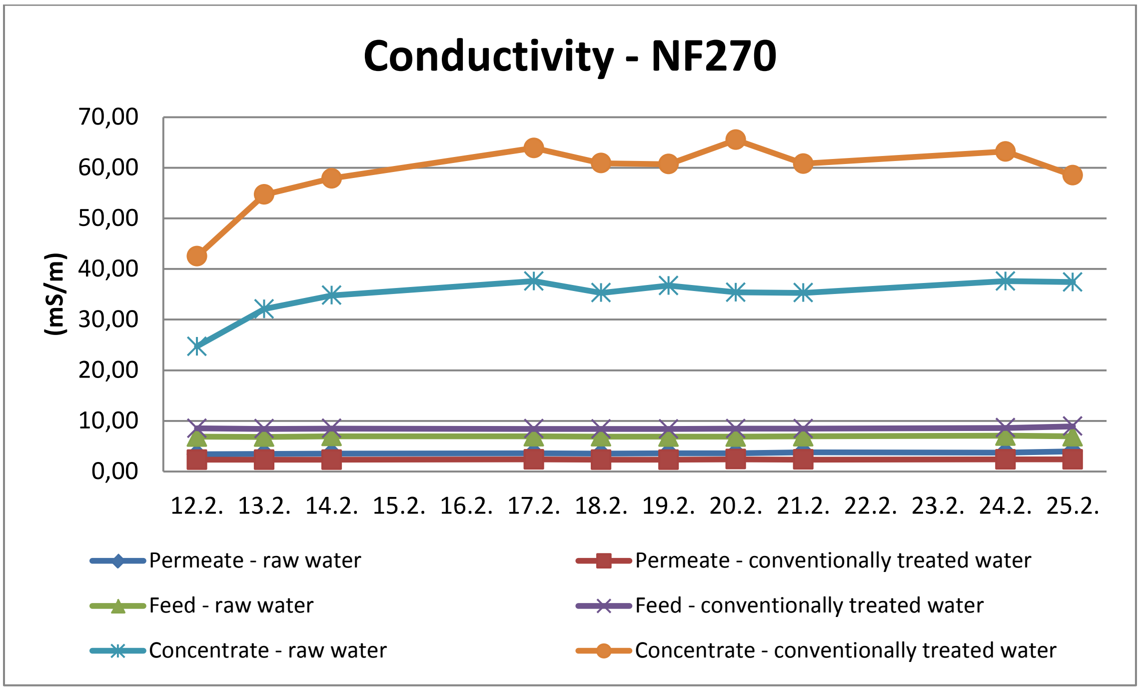


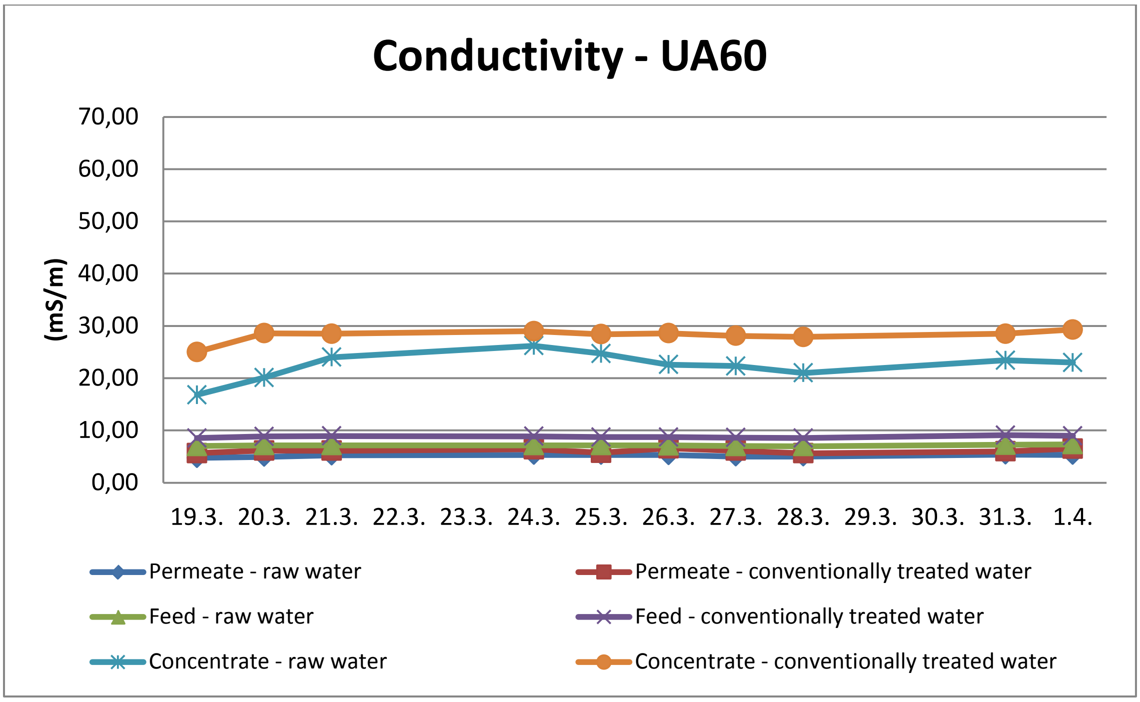
Appendix 4. Inorganic water quality in trials (1/6)



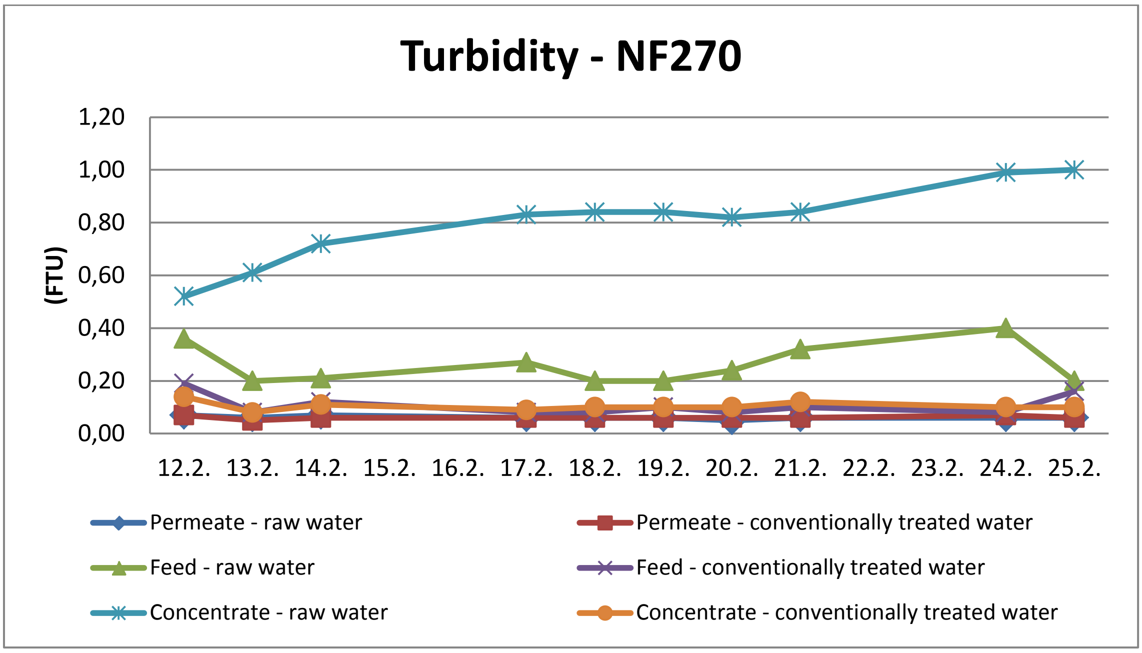


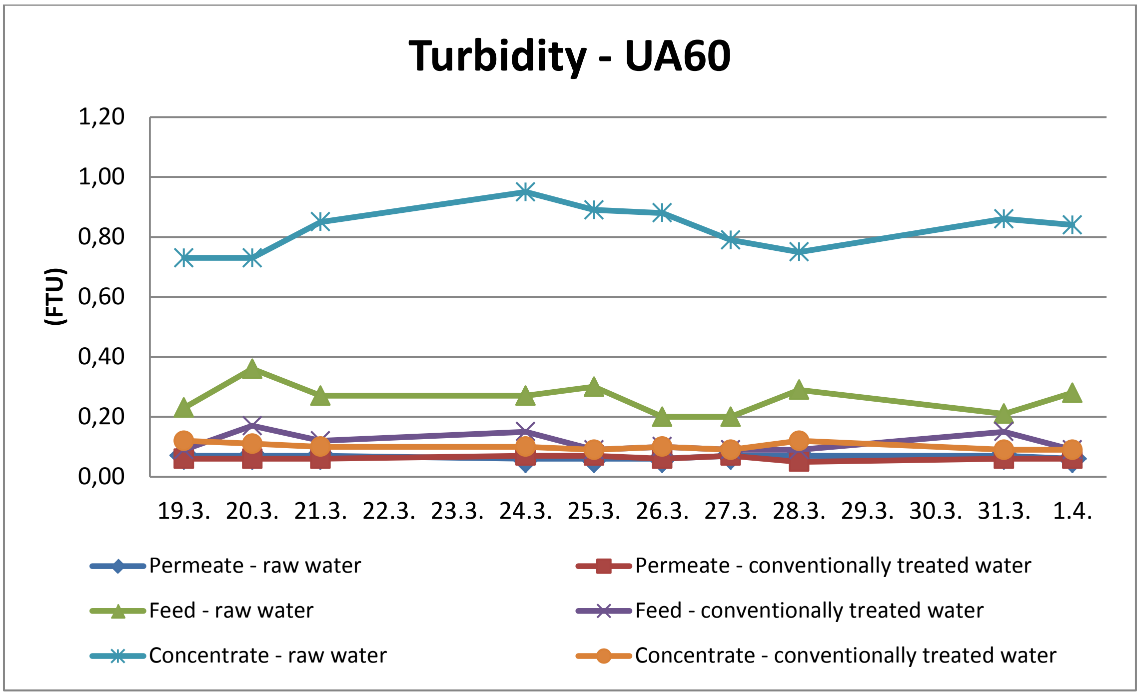
Appendix 4. Inorganic water quality in trials (2/6)



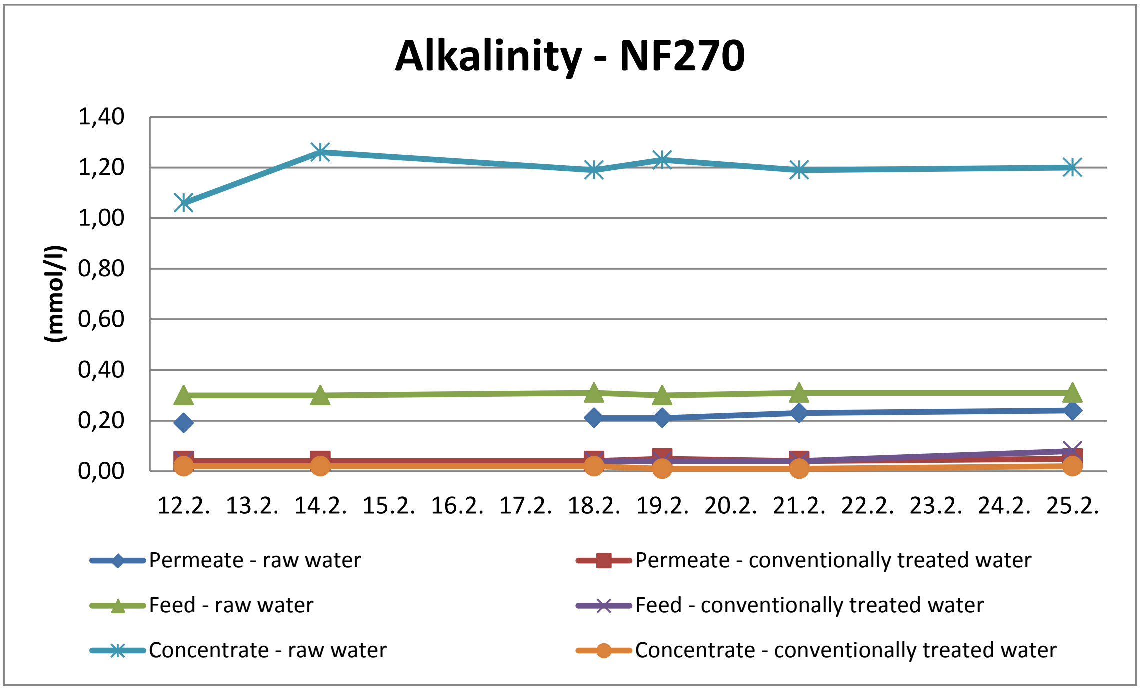


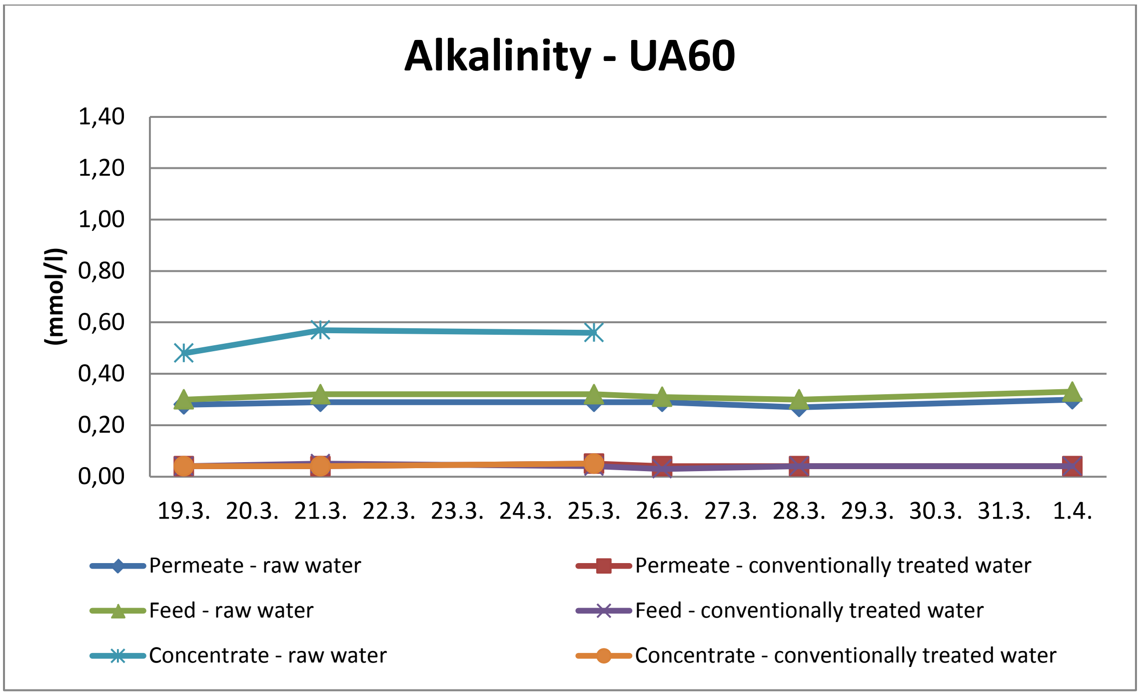
Appendix 4. Inorganic water quality in trials (3/6)



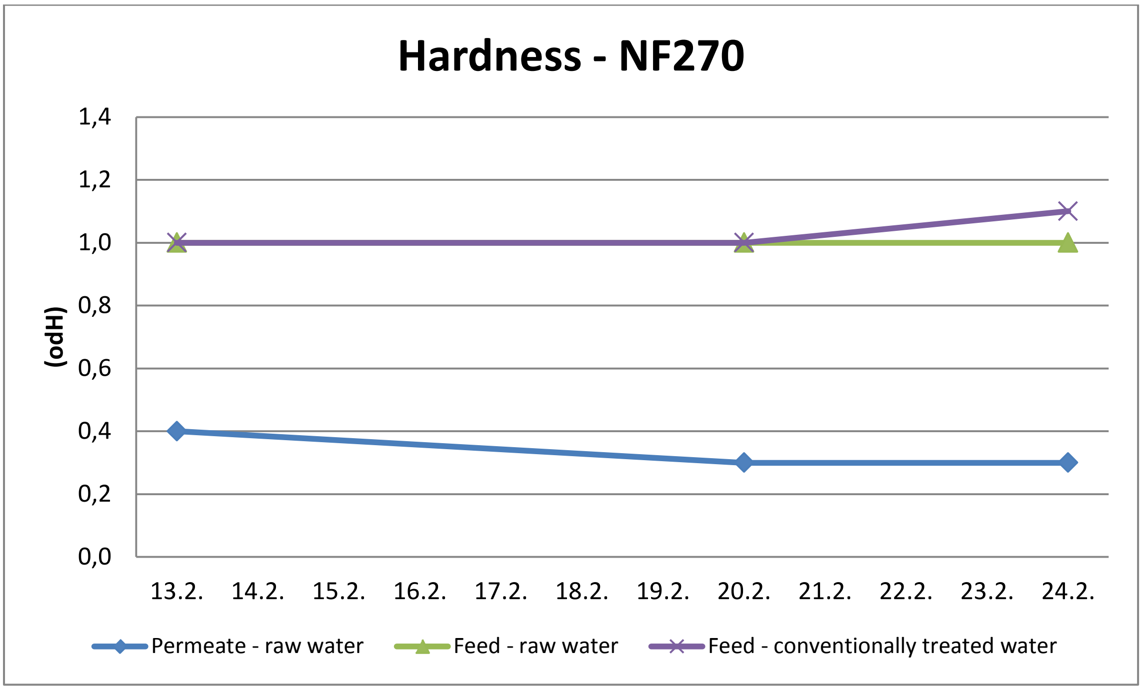


Appendix 4. Inorganic water quality in trials (4/6)

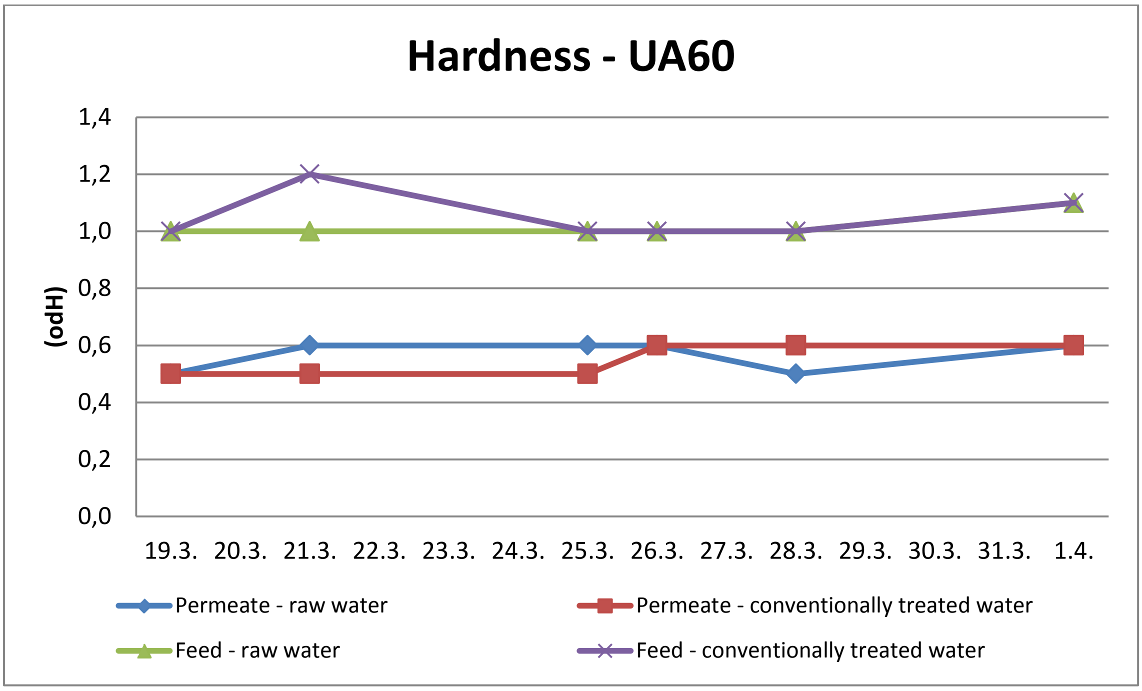




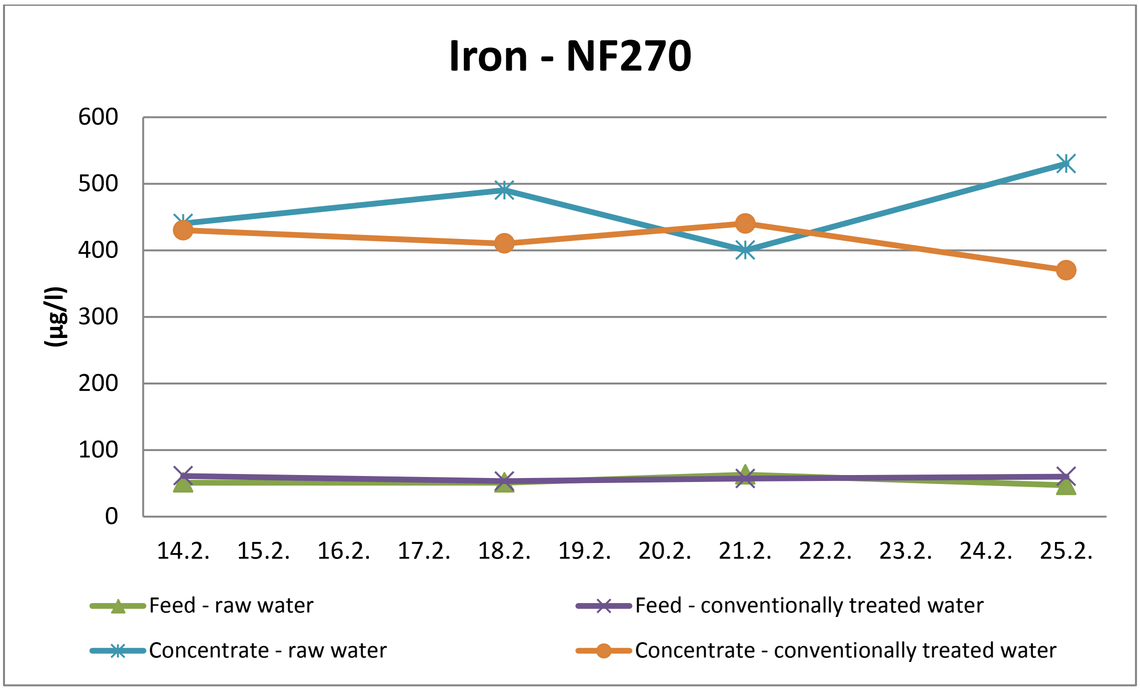
Appendix 4. Inorganic water quality in trials (5/6)



All permeate values in conventionally treated line under determination limit



Appendix 4. Inorganic water quality in trials (6/6)



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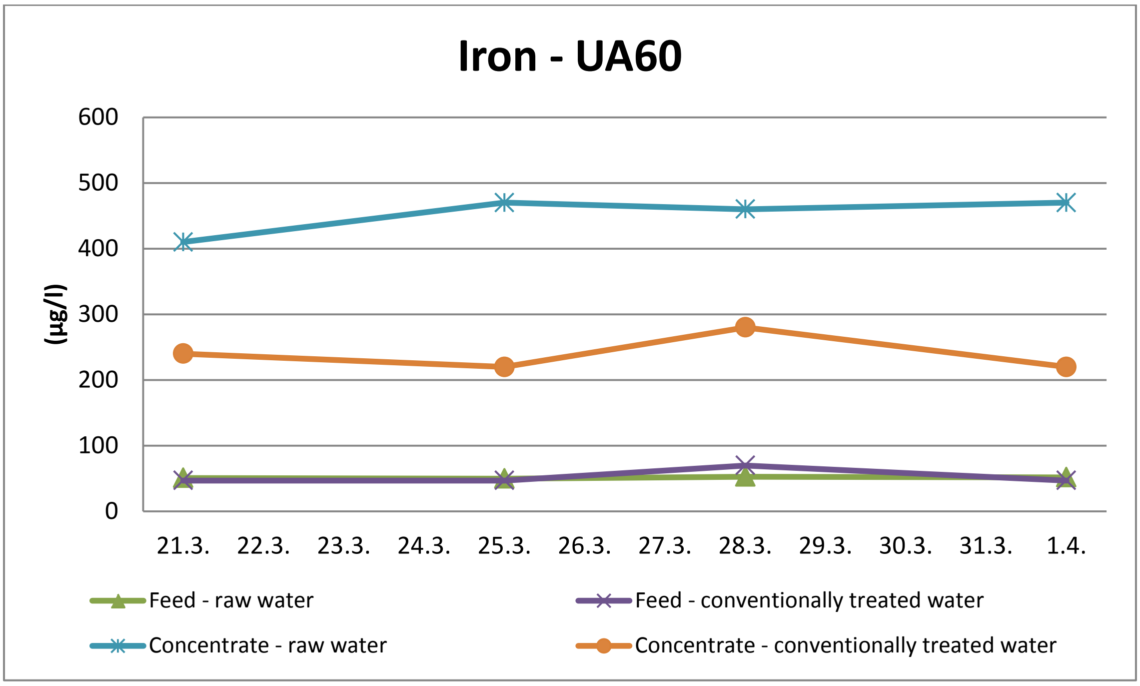
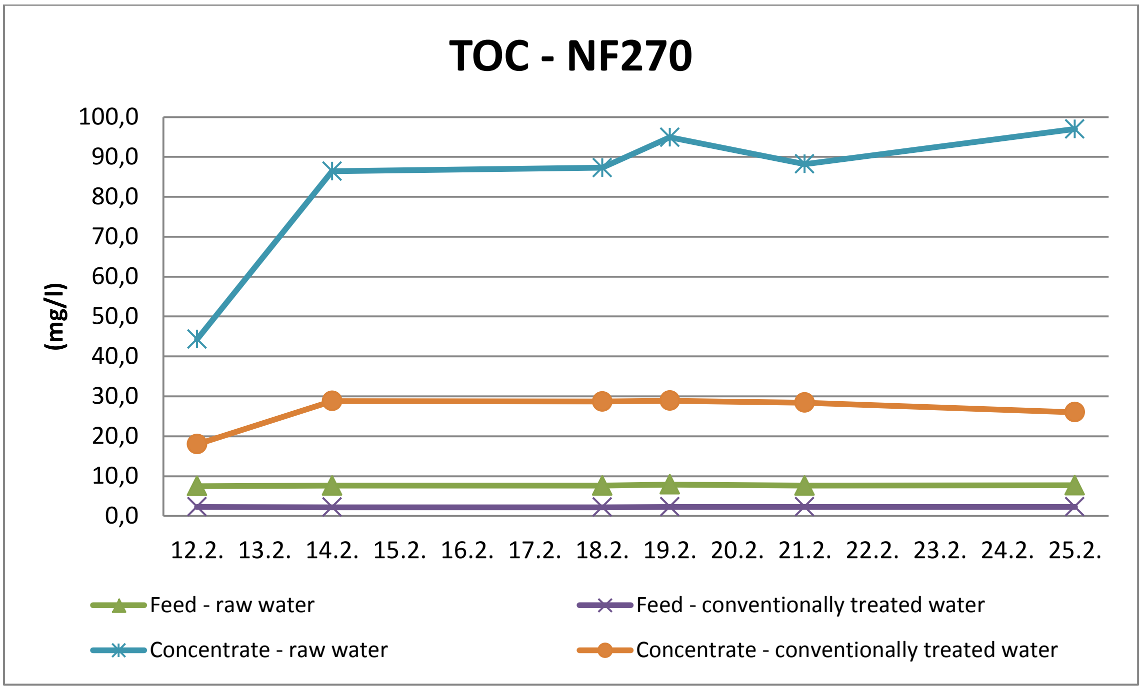


All permeate values under determination limit

Appendix 5. Organic water quality in trials (1/3)



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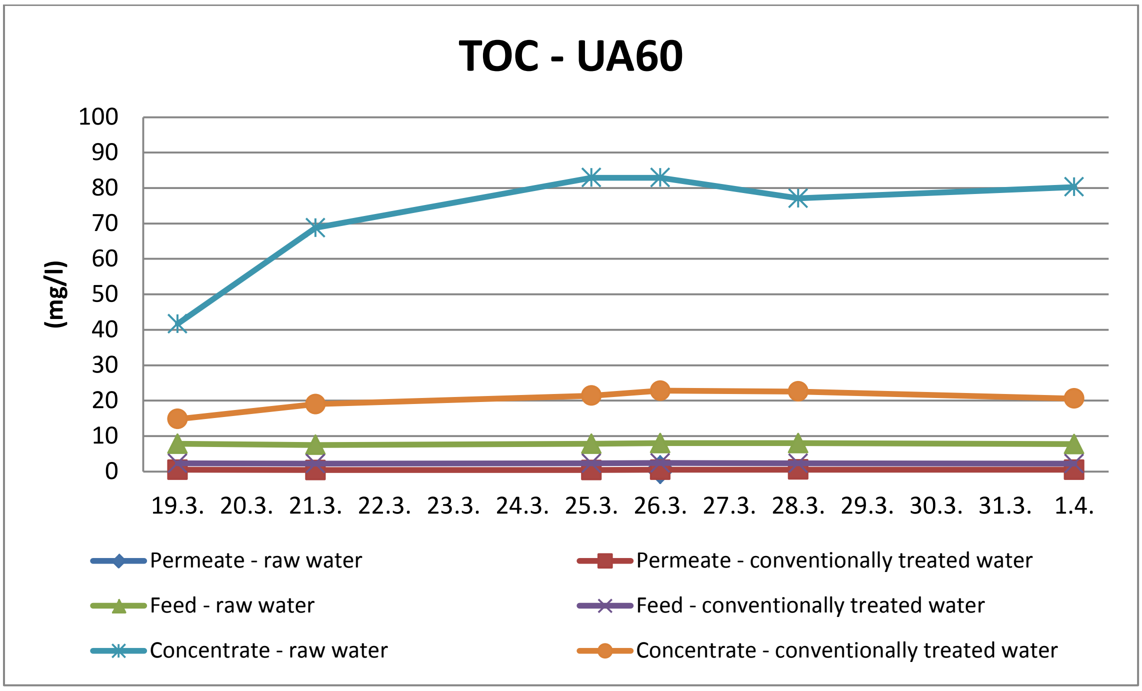
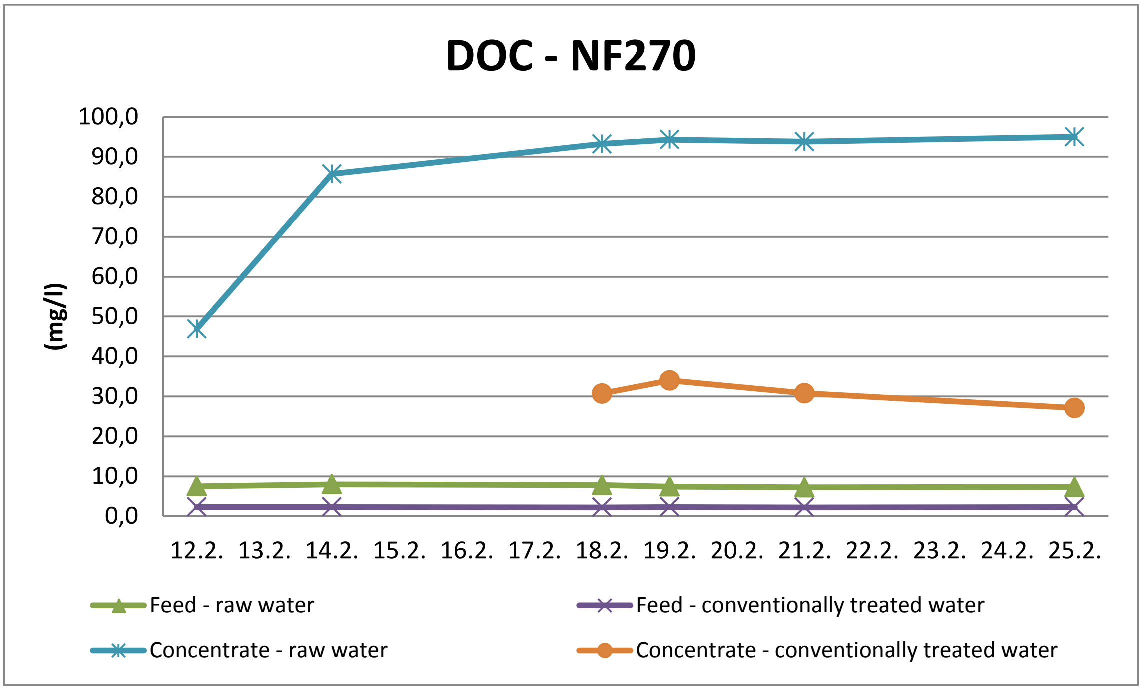


Appendix 5. Organic water quality in trials (2/3)



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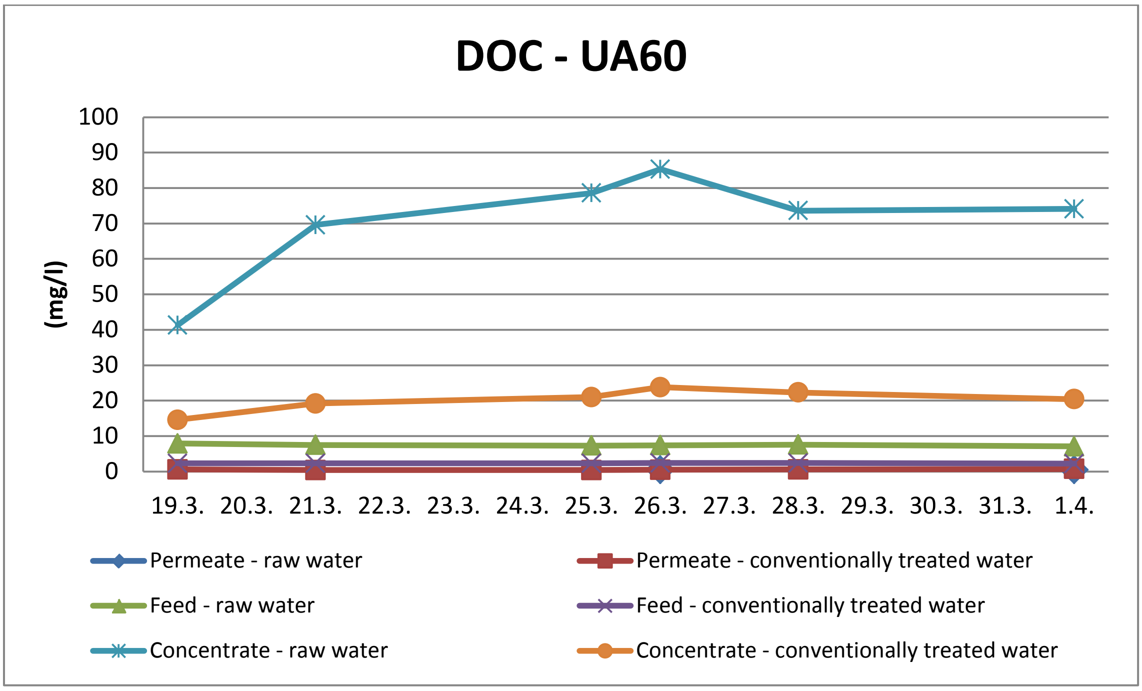
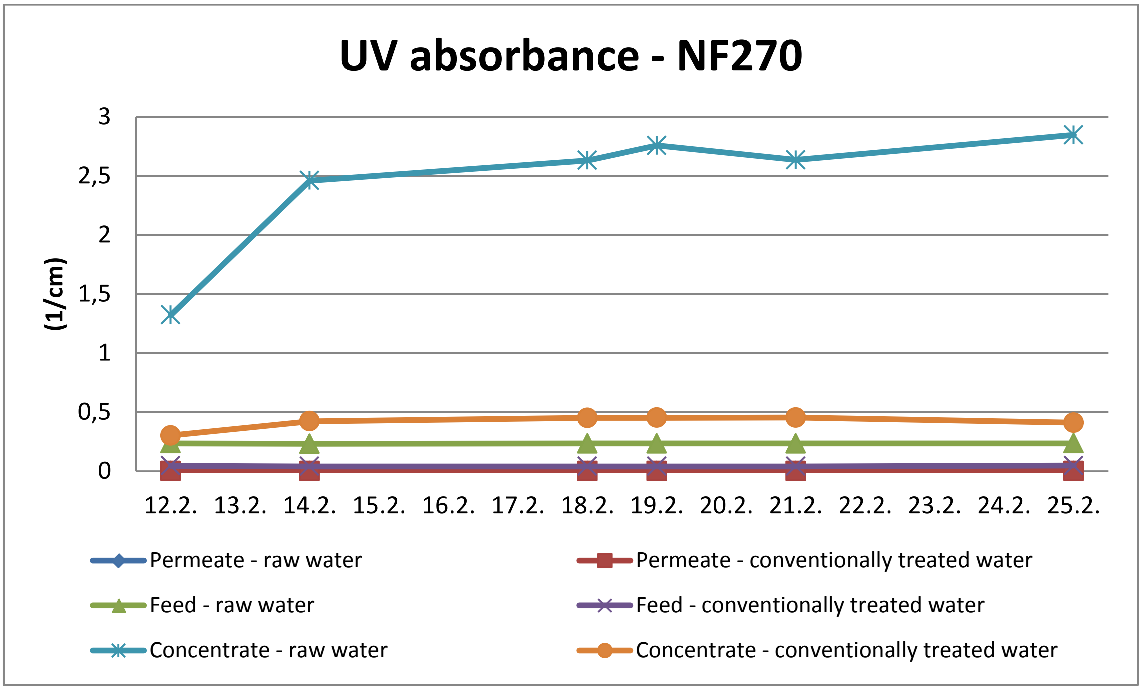
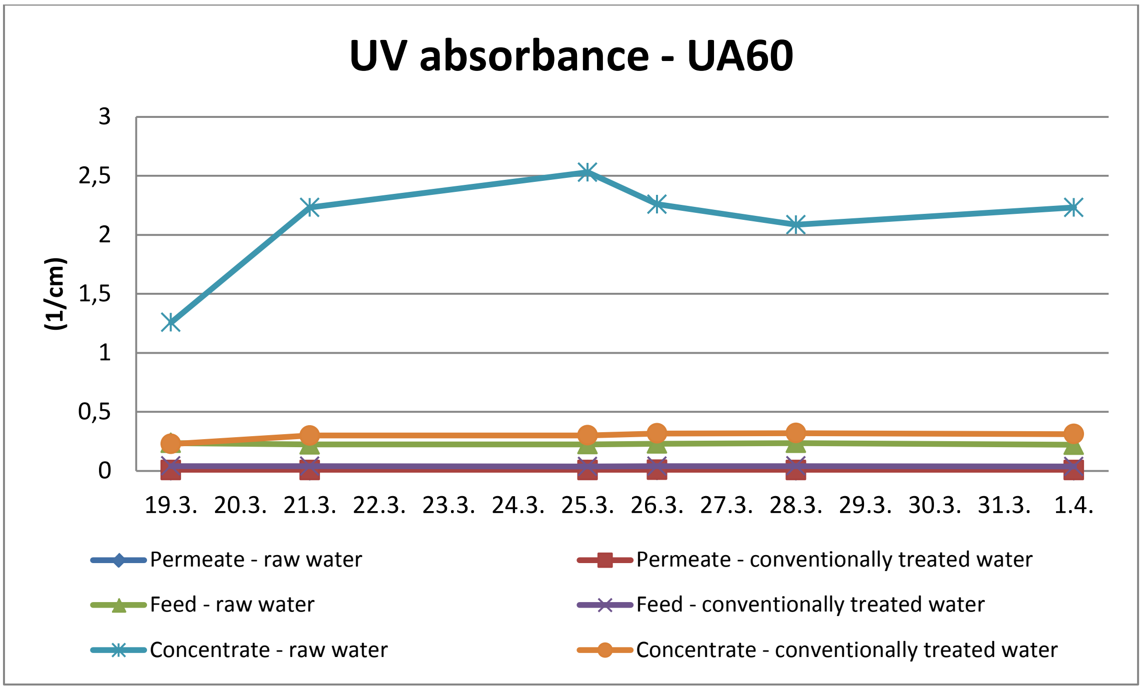
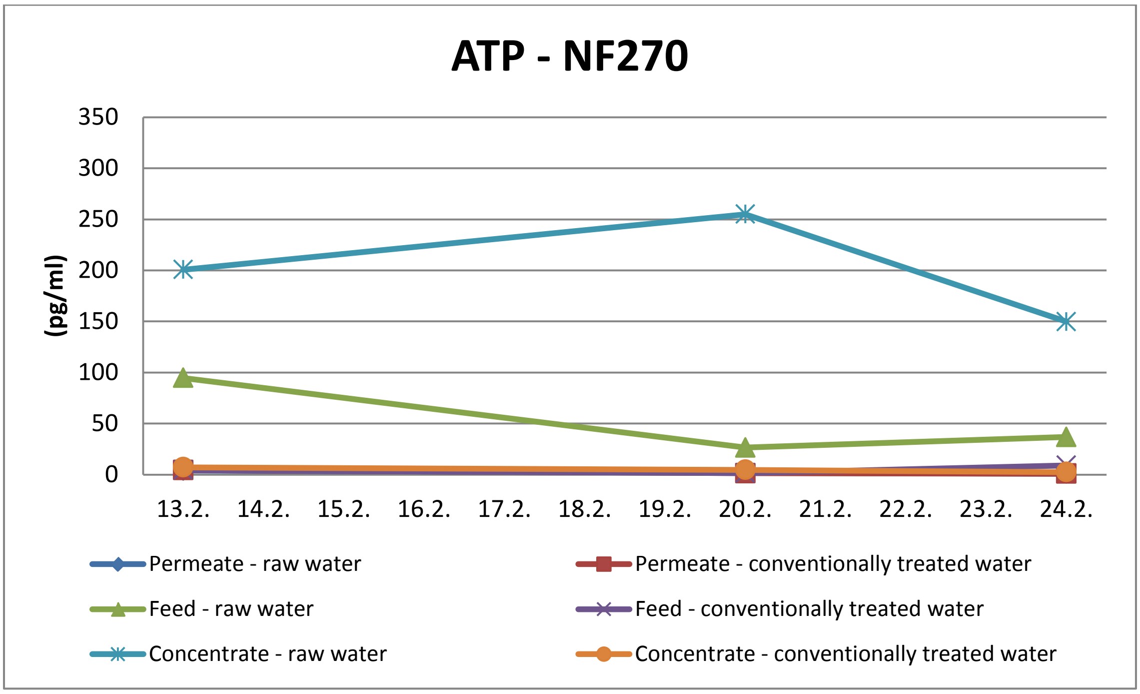


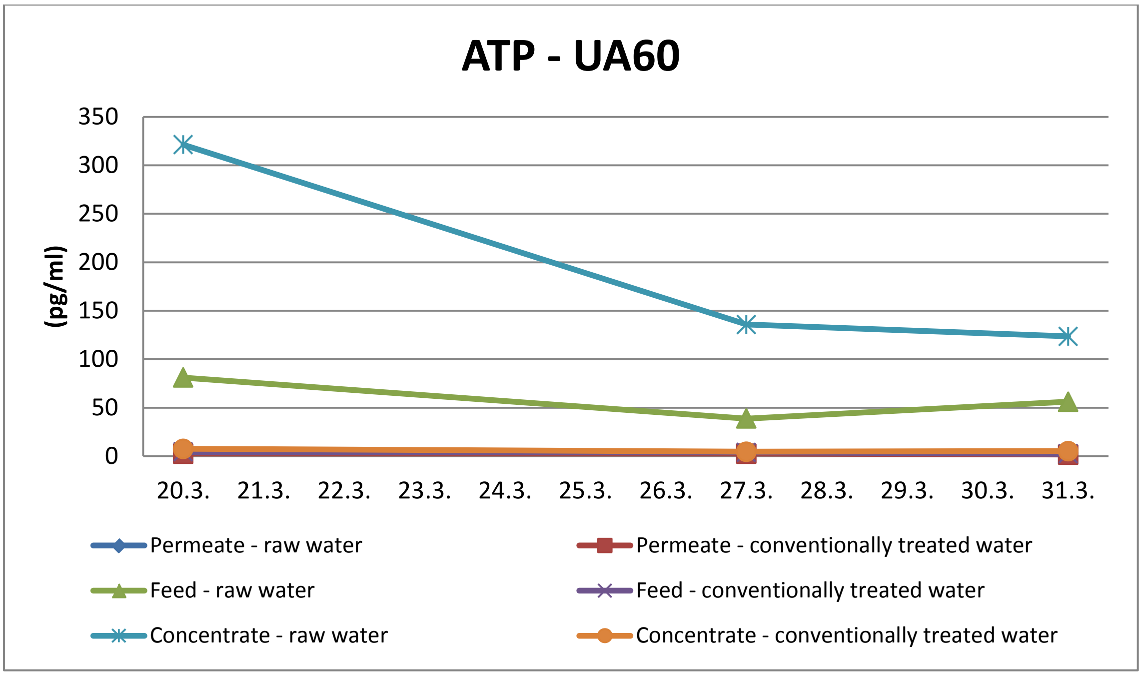
Appendix 5. Organic water quality in trials (3/3)



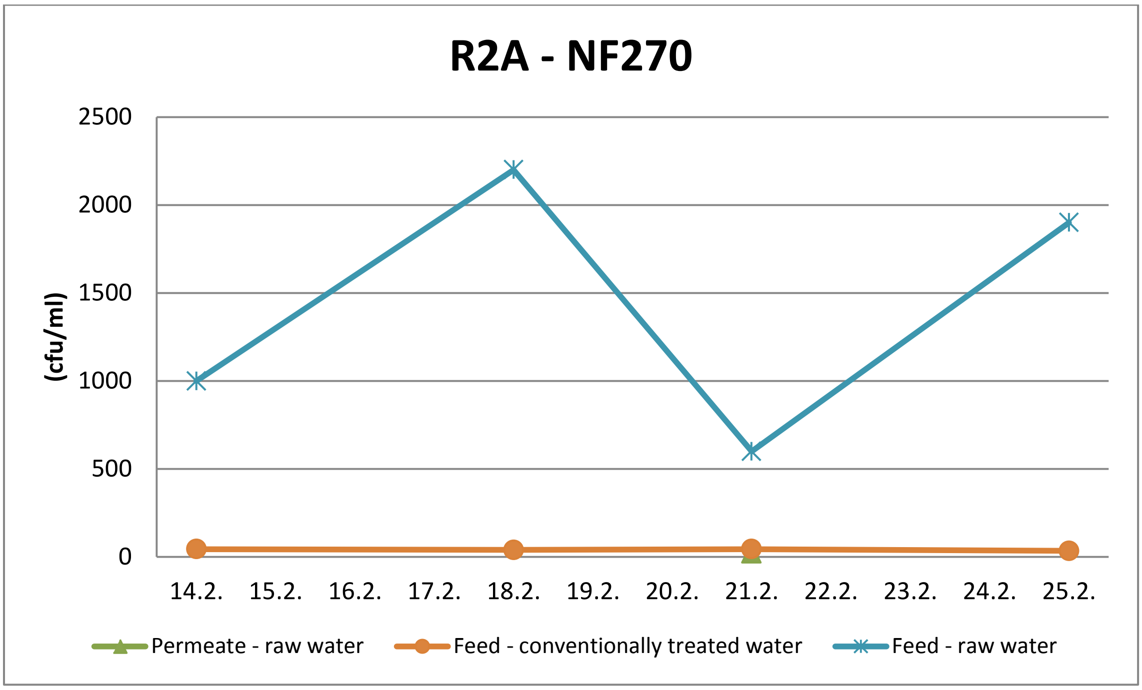


Appendix 6. Microbial water quality in trials (1/2)





Appendix 6. Microbial water quality in trials (2/2)



All permeate values in conventionally treated line under determination limit