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Graduated in Chemical Engineering

Development of a novel drinking water treatment for colored surface waters: Ultrafiltration - Nanofiltration

Dissertation for obtaining the Master degree in Membrane Engineering

Erasmus Mundus Master in Membrane Engineering

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FACULDADE DE CIÊNCIAS E TECNOLOGIA
UNIVERSIDADE NOVA DE LISBOA

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The EM3E Master is an Education Programme supported by the European Commission, the European Membrane Society (EMS), the European Membrane House (EMH), and a large international network of industrial companies, research centres and universities (http://www.em3e.eu).

Projecto financiado com o apoio da Comissão Europeia. A informação contida nesta publicação vincula exclusivamente o autor, não sendo a Comissão responsável pela utilização que dela possa ser feita.

ACKNOWLEDGMENTS

Firstly, I would like to thank the EM3E-4SW Consortium for accepting me in their Master programme and allow me to continue my studies through outstanding European universities. I am also grateful to my professors during my studies in the Université de Montpellier, the University of Chemistry and Technology of Prague and the Universidade Nova de Lisboa, for sharing their knowledge and experience with me.

I wish to express my sincerely gratitude to my thesis supervisor Philippe Sauvignet for guide me through this project which has allowed me to put into practice the knowledge gathered during my Master studies. I also sincerely appreciate Mr. Sauvignet for opening the doors of Gahard drinking water treatment plant, a fantastic place where I not only obtained a better understanding of a drinking water plant and the role membrane systems can perform but also found lifetime friends.

I am particularly grateful for the assistance given by Remi Percier, who patiently explained the operation of the membrane pilots and shared his experience in membranes plants. More important, I appreciate his support during the pilot daily operation and the membranes cleanings in place.

I would also like to thank Beatrice Houssais for her assistance in selecting the analytical methods and Xavier Bedez, for his help in the electrical field.

Special thanks to Justine Goirand for her partnership in operating the membrane pilots and her always joyful company during the membrane pilots cleaning in place. Similarly, Fernanda Colella for making my new live in Rennes a pleasant experience.

I would like to express my appreciation to the members of the thesis evaluation panel for their insightful questions; especially to Vanessa Pereira whose comments improved the thesis writing.

Last but not least, I would like to express my gratitude towards my family, for their unconditional support and continuous motivation; without them, the present thesis would not have been possible.

ABSTRACT

The increase of natural organic matter and hence color in Swedish surface waters during the last decades has hindered the treatment of drinking water. Conventional treatment plants have increased their coagulant dosage to overcome this situation. Consequently, their production of sludge has risen.

To reduce the use of chemicals and the production of sludge, the viability of a coupled ultrafiltration (UF) with low pressure nanofiltration (NF) is studied. Negatively charged NF membrane with a molecular weight cut-off (MWCO) of 1 kDa was tested in a 2 stages membrane pilot. Since the trials took place in France, the NF feed was spiked with natural ingredients to resemble Swedish surface waters. The NF membrane was capable to remove 85% and 65% of the color and dissolved organic carbon found in the NF feed, regardless of whether the system operates with or without the recirculation of concentrate. Furthermore, the NF membrane worked during long trials (9 months) without any cleaning procedure and with a permeability decrease of 7% in each membrane stage. Additionally, the NF average permeability was 6.5 $l/m^2/h/bar$ and the fluxes ranged between 22.5 and 18 $l/m^2/h$.

The NF process presented a poor salt removal and thus the remineralization of the permeate was not needed. Besides, the UF-NF coupled system operated with water losses under 18%. In general, the obtained results confirm the effectiveness of NF for color removal and the UF as a pretreatment

Keywords: Surface water; Ultrafiltration; Nanofiltration; Color removal; Natural organic matter

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ABREVIATIONS

BBs	Building blocks
BPs	Biopolymers
CEB	Chemical enhanced backwash
CDOC	Chromatographic dissolved organic carbon
DBPs	Disinfection by-products
DOC	Dissolved organic carbon
DWTP	Drinking water treatment plant
HSs	Humic substances
LC-OCD	Liquid chromatography – organic carbon detection
LMWA	Low molecular weight acids
LMWN	Low molecular weight neutrals
MWCO	Molecular weight cut-off
NB	Normal backwash
NF	Nanofiltration
NOM	Natural organic matter
PES	Polyethersulfone
PLC	Programmable logic controller
PVP	Polyvinylpyrrolidone
RC	Recirculation of NF concentrate
SP	Sample point
UF	Ultrafiltration
UV_{254}	Ultra-violet absorbance at 254 nm

1 INTRODUCTION

1.1Background and motivation

Surface waters, like lakes and rivers, are frequently used as sources for drinking water production. In Sweden, half of the water supply comes from surface waters. However, in the last decades Swedish surface waters have experienced a browning effect or an increase in the water color (Lindén 2016). The increase in water color has also been recorded in other north hemisphere countries (Evans et al., 2005). Tang et al. (2013) suggest that this increase is due to climate change and its effect in the rain-fall period.

The color in surface waters is the outcome of natural organic matter (NOM) (Ericsson and Tragardh, 1996; Grose et al., 1998; Evans et al., 2005). Usually described as a complex matrix of organic materials (Sillanpää, 2014), NOM results from animal and vegetation decay (Guo et al., 2019) and as the by-products of bacteria, algae and aquatic plants (Sillanpää, 2014). Terrestrial NOM is introduced into the surface waters by surface runoff from rain, among other sources.

Most Swedish drinking water treatment plants (DWTP) operate using conventional treatments, coagulation and flocculation followed by sedimentation. However, high colored waters hinder the operation of DWTP and thus affect their efficiency. Lake Bolmen, the main source of water for Ringsjö DWTP, have triplicate its color since 1997. Therefore, in order to remove the color Ringsjö DWTP have increased their coagulant dose; at present, the coagulant dose has double the quantity that was used back in 1997 (Lindén 2016). Actually, it is expected that the coagulant dose will soon reach its maximum treatment capability, whereby further increasing the dose is ineffective (Lindén 2016).

Inefficient water treatment leads to the presence of high residual organic matter in the treated water. This will cause aesthetic problems (odor and color) and the formation of disinfection by-products (DBPs). The concern for DBPs has increased considerable in recent years due to research that investigated their adverse effect in human health (Hamidin et al., 2008).

In order to avoid the presented situation, special interest has been placed in membranes technology; more specifically in low-pressure nanofiltration (NF), due to the following advantages: (1) the independence of chemicals, since NF is a physical treatment. Hence, less chemical consumption and sludge production. (2) NF membranes are less sensitive to raw water quality (Ericsson and Tragardh 1996; Grose et al. 1998). (3) Negligible salt removal in Low-pressure NF, meaning the process does not require a remineralization post-treatment. On the other hand, a commonly discussed disadvantage of NF is the energy consumption, mainly due to crossflow and pressure. Nonetheless, Lidén and Persson (2016) through an economical study between conventional treatment and NF pointed out that with the NF the energy consumption is in fact moving from chemical production to hydraulic requirements.

Veolia Water Technologies VA-Ingenjörerna evaluated between 2016 and 2017 the performance of a low pressure NF pilot on Swedish surface waters. The NF pilot was feed directly with surface water without any pretreatment, only a strainer of 20µm was placed before the NF membrane for its protection. The NF pilot was tested under an operational temperature of 0-3 °C, since at lower temperatures the pump requirements are higher. These trials showed a good reduction of organic matter and color (80% and 90% respectively). But, fouling issues principally due to suspended solids were observed. Fortunately, research has demonstrated that the addition of an ultrafiltration step as a pretreatment can help to avoid membrane fouling (Ericsson and Tragardh 1996; Hoslett et al. 2018).

Ericson et al. (1996) evaluated the feasibility to treat high colored surface water from Lake Muskan (Sweden) with a UF-NF coupled system. The tested system was capable to remove color and organic matter to undetectable levels. Nonetheless, the recovery of the UF was about 75-80% and the recovery of the NF was 85%, providing an overall recovery of 63-68%.

1.2 Objectives

The present project aims to:

1. Evaluate the performance of an NF system with UF pretreatment for color removal in Swedish surface waters.
   1.1. Since the evaluation takes place in France, replicate Swedish surface waters conditions (organic carbon profile) by spiking UF permeate.
   1.2. Evaluate the NF system under different operational conditions.
   1.3. Validate the low removal of dissolved salts by the NF membranes.
   1.4. Demonstrate the NF pilot with UF pretreatment delivers a recovery rate above 90% with minimal water losses.

2 Literature Review

2.1 Colored surface water - Brownification

Surface waters can be defined as those waters that are collected on the earth's surface, such as lakes, rivers, wetlands, oceans, among others. In recent years, surface waters more specifically rivers and lakes found in north hemispheric countries like Sweden, Norway, United Kingdom and Finland have experienced a steady increase of their water color.

In 2017, E. Kritzberg, studied the color evolution since 1935 of 50 Swedish lakes, he concluded that there is a strong increase in the water color, which in some case even triplicated the values in 1935. Similar results were found in Norwegian forest lakes by Hongve *et al.* (2004), were the water color has doubled its values from 1990 to 2000.

The color in the water is the result of the interactions between the sunlight and all the compounds found in the water. The blue color of the water frequently found in deep lakes and rivers is the results of the blue wave length not been completely absorbed by the water molecules. On the other hand, the brown-color is due to the presence of natural organic matter (NOM) or more specifically Humic substance (HSs). The NOM found in surface waters has two main sources: internal production due to plankton, and aquatic plants; and external production due to terrestrial plants and animals which is introduced by surface runoff from rains (Graneli, 2012).

This increase in the yellow-brown color of lakes and streams has been named Brownification for several researchers in order to facilitate its discussion (Graneli, 2012; Lindén, 2016). Among the possible causes for this phenomenon can be mentioned: (1) The reduction of sulphur deposition and therefore the acidification of lakes, which has enhanced the mobility of NOM (Evans *et al.*, 2005; Vuorenmaa *et al.*, 2006; Kritzberg, 2017) (2) climate variations such as the increase in the amount of precipitations, resulting in an increase of the surface runoff of the NOM from upper forest floor (Hongve *et al.*, 2004; Ritson *et al.*, 2014); and (3) land-use/management of catchment areas, which could have influenced the physical and chemical properties of the NOM (Ritson *et al.*, 2014; Kritzberg, 2017).

In accordance to Graneli (2012) Brownification has affected aquatic ecosystem by reducing the penetration of solar light into the lakes and the increase of NOM has improved the availability of organic carbon for bacteria growth which results in oxygen consumption and carbon dioxide production. In resume, this has caused the reduction of fish production and thus biodiversity, the loss of water sport value due to aesthetic problems, and finally the hindered of drinking water treatment.

2.2Natural organic matter

Usually described as a complex matrix of organic materials (Sillanpää, 2014) the NOM can be split into hydrophilic and hydrophobic compounds, with the latter representing the majority of the dissolved organic matter content (Karlsson, 2018). Hydrophobic compounds, also known as humic substances (HSs) are the result of animal and vegetation decay (Guo *et. al* 2019). HSs comprise according to Sillanpää (2014): Humic acids, fulvic acids and humins. Moreover, hydrophobic compounds are rich in aromatics and conjugated double bond (Sillanpää, 2014). The double bond in the structure of these compounds absorbs visible light and results in the coloring of water.

On the other hand, hydrophilic NOM compounds contain more aliphatic and nitrogenous compounds (carbohydrates, sugars and amino acids) (Sillanpää, 2014).

2.2.1 Natural organic matter removal

NOM is conventional removed from surface waters by using coagulation followed by clarification and filtration stages (Ritson *et al.*, 2014). However, NOM can also be removed by absorption, advanced oxidation process, biological processes and more. Adsorption treatment methods like Granular Activated Carbon (GAC) can be easily implemented and provide high NOM removal; nevertheless, these methods require frequent regeneration and partial replacement of the adsorbent. In this perspective, Advanced Oxidation Processes like ozonation provide a complete pollutant mineralization and DBPs oxidation yet employ toxic reagents and accomplish a low NOM removal.

2.3 Nanofiltration

Introduced into the market in the late 1980´s, NF has proven to be an effective technology in color and organic matter removal. In 1996, Ericsson and Tragardh (1996) concluded that conventional treatment needs to be coupled with Granular Activated Carbon (GAC) in order to accomplish NF efficiency. Even GAC followed by UF is not as effective as NF. Following studies have reinforced that membranes with a MWCO ranging 3-5kDa are capable to accomplish a humic acid removal of 90% (Lowe and Hossain, 2008).

NF has a pore size of the order of 1nm, which translates to a MWCO ranging between 100 and 5000 Da (Oatley-Radcliffe et al. 2017). However, some researches consider a membrane with 1 kDa MWCO as a tight UF. NF is a pressure driven process usually operating at 5-20 bar. Nevertheless, low pressure (<5 bar) operation is also possible, in this case chemical selectivity of the membranes is predominant (Abouzaid et al., 2003).

3 MATERIALS AND METHODS

3.1 Gahard drinking water treatment plant

The test of a Nanofiltration (NF) system with a Ultrafiltration (UF) pre-treatment took place in Gahard Drinking Water Treatment (DWTP), located in Bretagne France, the DWTP is managed by Veolia Water. Gahard DWTP provides 510 000 m^3 of drinking water to 10 000 habitants distributed in 10 communes north-east Rennes. Gahard raw water comes from three boreholes capable to deliver approximately 80 m^3/h, its characteristics are presented in Table 1. Gahard raw water possesses a low color content (3 mg/l Pt/Co) but a medium high dissolved organic carbon (DOC) of 5 mg/l. In addition, the raw water has a high alkalinity and can be considered as hard water.

Table 1 Gahard raw water characteristic

		Gahard raw water	Gahard treated water
True Color	mg/l Pt/Co	7-8	~ 3
UV_{254}	UA	11.0 (13.5 – 9.0)	4.5 (7.8 – 3.1)
DOC	ppm-C	4.7 (7.0 – 3.3)	2.6 (4.0 – 1.0)
Conductivity	µS/cm	550 – 600	~350
Alkalinity	mg/l $CaCO_3$	190 (250 – 140)	54 (100 – 26)
Hardness	mg/l $CaCO_3$	270 (332 – 220)	168 (220 – 120)

Gahard drinking water treatment process is shown in Figure 1. As it was expected the hardness of the raw water implies the need of a softening treatment, the same is performed by using an Actiflo® Softening unit. A water polishing treatment is also employed by using Filtraflo Carb®; the treatments continues with sand filters and activated carbon filters. Finally, in order to ensure the elimination or control of pathogens in the treated water, a disinfection step is performed by the addition of Chlorine.

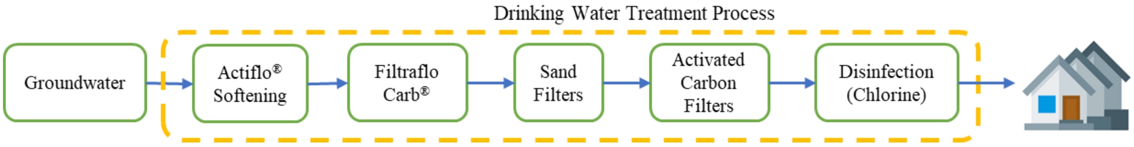

Figure 1 Gahard Drinking Water Treatment Plant flow diagram

Within the Gahard DWTP facilities several water treatment prototypes are tested, most of them use as inlet flow the water treated by the different units of the drinking water treatment process. Nevertheless, all the water that is treated by the prototypes units is returned to the main drinking water treatment process in order to ensure the water quality.

The NF project was developed in two parts; the part I from September 2018 to June 2019 was dedicated to test the NF pilot color removal capacity and its performance overtime. Part II started in July 2019 was focused on evaluate the UF-NF system performance. Due to the low color content in Gahard raw water (*see* Table 1), the same was spiked to resemble the conditions of Swedish colored surface water. However, during part I the NF inlet flow was spiked after the UF pilot while part II the water will be spiked before the UF system.

3.2 Project part I: UF1-NF

The NF pilot was connected to an already existed UF pilot (UF1) which combines macro-coagulation with UF for the organic matter removal. The inlet flow to the UF1-NF system is a mixture of Gahard raw water and water treated by the Actiflo® Softening and the Filtraflo Carb® units. Figure 2 shows the flow diagram of the project part I, as it can be seen the flow produced by the UF1 not only feed the NF pilot but also the Gahard DWTP process, since the flow capacity of the UF1 fourfold the NF feed requirement.

The spiking of Gahard raw water was done on the UF1 permeate and not before to avoid the introduction of undesired organic matter into the Gahard DWTP process. In addition, the NF pilot operated in a close loop to retain control of the color.

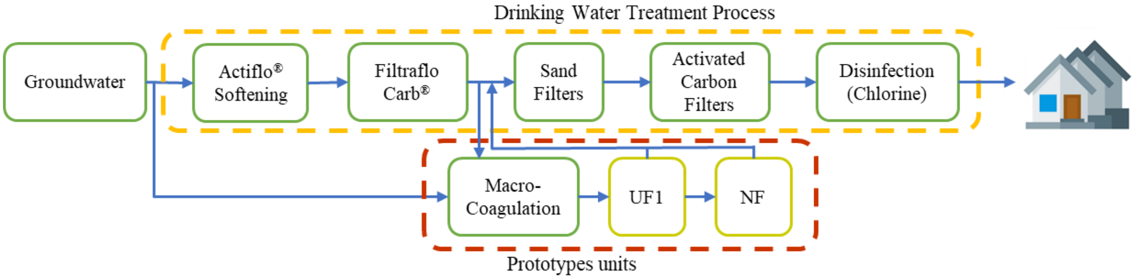

Figure 2 Flow diagram of UF1-NF project part I

3.2.1 Actiflo® Softening

The aim of the Actiflo® Softening is the clarification and softening (decarbonation) of Gahard raw water. The unit operation can be divided in three phases: (1) Decarbonation, (2) Clarification and (3) Decantation. During the first phase calcium hydroxide ($Ca(OH)_2$) is added to the raw water. The lime addition increases the concentration of calcium ion and the pH of the mixture. A basic mixture favors the formation of carbonates (CO_3^{2-}) from bicarbonates (HCO_3^-). The excess of calcium ions and carbonates lead to the precipitation of calcium carbonates ($CaCO_3$) and hence the reduction of the water alkalinity and hardness.

During the Clarification phase the water turbidity is reduced by the addition of coagulant ferric chloride ($FeCl_3$) and an ionic polymer. In addition, microsand (µsand) is added to the mixture to reduce the sedimentation time of the flocs. A Turbomix™ improve the mixture and also the recovery of the µsand. In the last phase of the process, the calcium carbonates and the hydroxyl/colloid sludge are removed by a lamellar decantation.

3.2.2 Filtraflo Carb®

This water treatment process aims to reduce the organic matter, micropollutants and the turbidity in the water. Filtraflo® Carb employs granular activated carbon which forms a filtration bed inside the unit. The organic matter is reduced by the activated carbon while the filter bed reduced the turbidity in the water. The activated carbon is regenerated by a thermal process.

3.2.3 Macro-Coagulation

The macro-coagulation treatment of water takes place in 5 m^3 Tank, where Gahard raw water and Filtraflo Carb® outlet are mix in a ratio of 2:1. Like in the Actiflo® Softening process, the coagulant employed is ferric chloride, the same is added until reach a concentration of 120 ppm of coagulant. The residence time of the water and the coagulant is approximately 10 minutes. the scheme of the macro-coagulation tank and its photo can be seen in Figure 3.

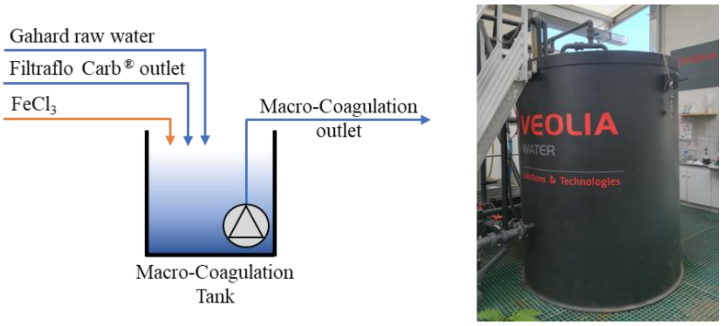

Figure 3 Macro-Coagulation scheme and photo

3.2.4 Ultrafiltration pilot UF1

The aim of the unit is the reduction of fouling possibilities in the NF system. UF1 removes the flocs formed during the macro-coagulation step; together UF1 and macro-coagulation reduce the turbidity and remove colloids and suspended matter in the water. The scheme of the process can be seen in Figure 4.

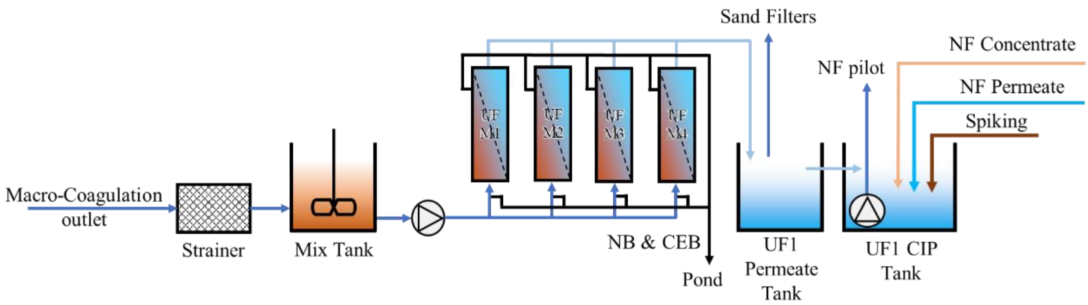

Figure 4 UF1 scheme

An Amiad SAF1500 prefilter is placed before the membranes modules to protect the membranes from larger colloids. The prefilter possess a pore size of 30 µm and a self-cleaning mechanism. The Mix Tank with an agitator inside is not a required step by the current process; but something from previous trials performed in the UF1 pilot.

The membrane section of the UF1 consists of 4 membrane modules with a total membrane area of 220 m^2. The X-Flow Aquaflex 55 membranes are fabricated by Pentair and possess a Molecular Weight Cut-Off (MWCO) of 150 kDa. Made of Polyvinylpyrrolidone (PVP) and Polyethersulfone (PES), the membranes are hollow fiber that operate inside-out. The system at normal conditions operates dead-end with a feed flow of 14-16 m^3/h. The feed pressure variates from 1.35 to 1.55 bar in order to compensate the permeability losses due to membrane fouling.

The UF1 membrane cleaning procedure comprise normal backwash (NB) and chemical enhanced backwash (CEB). The NB is performed every 55 minutes and has a duration of 140 s. The feed flow decreases to 10 m^3/h and the pressure increase to 2.2 bar.

The CEB is performed after 20 normal backwash and combines a bleach and a sulfuric acid cleaning. The bleach prevents the development of bacteria and oxidizes certain organic molecules. Similarly, the sulfuric acid solubilizes the deposit of metal hydroxides or mineral salts. The cleaning procedure consist in a chemical injection during 70 s followed by a membrane soaking which last 120 s for the bleach and 300 s for the sulfuric acid, finally the membrane is rinsed during 120 s. During the soaking step the remaining 3 membranes modules are operative, in order to reduce the water losses, which at present are approximately 13% due to NB and CEB.

After the NB and CEB the used permeate is discarded into a pond, where later the water will be treated and reintroduce into the Gahard DWTP process.

The permeate of the UF1 membranes is collected in the UF1 permeate tank, and when required also in the UF1 CIP tank. The latter is normally used to collect the UF1 permeate, NF permeate, NF concentrate and the spiking solution. Nevertheless, when a cleaning in place (CIP) is required in the UF1 membranes, the CIP tank is drained and fill solely with UF1 permeate. The CIP is done when the membrane permeability is less than 180 l/m^2/bar/h. The permeability losses highly depend on the Gahard raw water conditions; a CIP is usually performed every 3-4 months or after 2500 operational hours.

3.3 Project part II: UF3-NF

Started at the beginning of July 2019, a new UF unit (UF3) was acquired and connected to the NF pilot. During the second part, Gahard raw water is the main source of inlet water to the system UF-NF, without any previous softening (Actiflo® Softening), polishing (Filtraflo Carb®) and coagulation process. The UF3 allows the spiking of the raw water before the UF system. Figure 5 shows the diagram flow of the project part II.

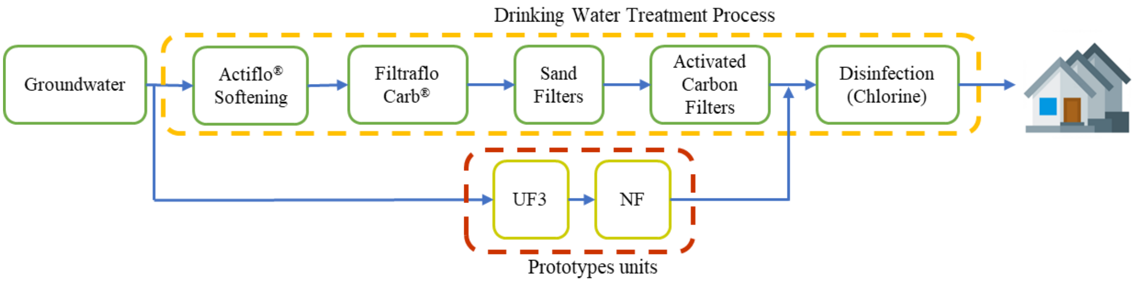

Figure 5 Flow diagram of the UF-NF project part II

3.3.1 Ultrafiltration pilot UF3

The UF3 system comprise one capillary membrane module and one strainer of 30 µm. The membranes are made of Polyethersulfone (PES) with a pore size of 0.02 µm or 150-200 kDa MWCO. The system operates dead-end with a feed flow of 4.5 m^3/h and a TMP of approximately 0.3 bar. NBs are performed on the membrane to reduce the fouling every two hour, similarly CEB are done after 10 NBs. The chemical used for the CEB and so its duration is the same used in the unit UF1. Figure 6 shows the flow diagram of the UF3.

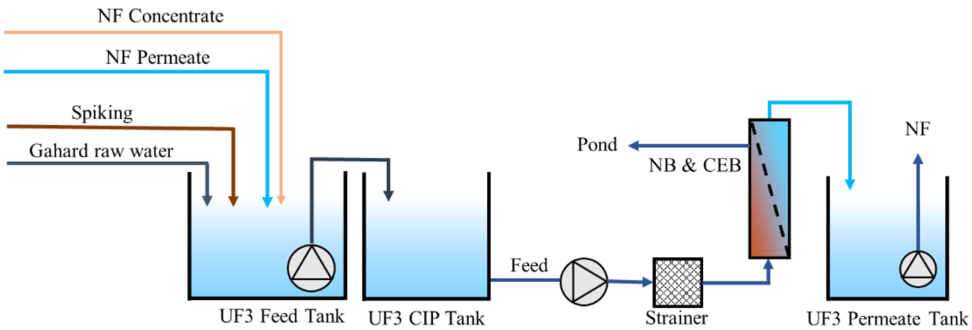

Figure 6 UF3 flow diagram

3.4 Nanofiltration pilot

The NF pilot aims to remove color and organic matter from water, its scheme is presented in Figure 7. The NF system operated in a close loop to retain control of the color. The NF permeate and concentrate flow were recirculate to the UF1 CIP Tank (Part I) or to the UF3 Feed Tank (Part II). Nevertheless, spiking solution and UF1 permeate or Gahard raw water were added periodically to overcome the water losses due maintenance of the equipment.

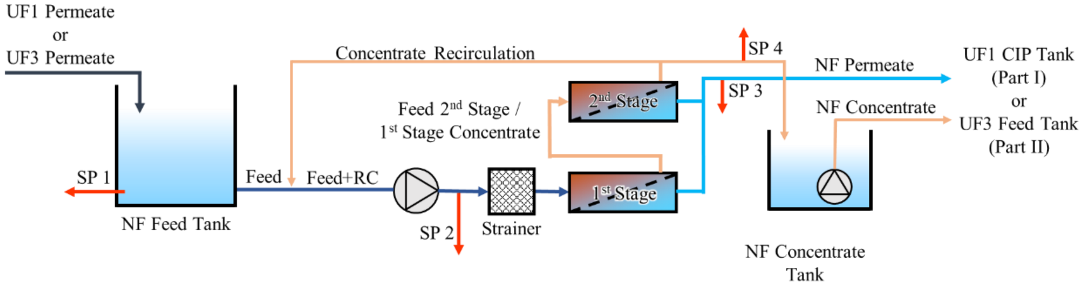

Figure 7 NF Scheme (SP: Sample point)

The NF Feed is collected in the NF Feed tank where a centrifugal pump feed a fixed flow to the NF system, the fixed flow does not consider the concentrate recirculation flow. After the pump there is a 5 µm strainer for the membrane protection.

The NF system operates in cross-flow mode with part of the concentrate flow being recirculate into the Feed stream to increase the cross-flow velocity and thus decrease the membrane fouling possibilities. The NF pilot comprises two membrane stages in series, each stage has inside three spiral wound membranes with a membrane area of 37 m^2, therefore the total membrane area is 222 m^2. The HydraCoRe 50-LD membranes (fabricated by Hydranautics Nitto Group Company) are negatively charged and made of Sulfonated PES (SPES) with a MWCO of 1000 Da.

There are 4 samples points in the NF pilot, the same are shown in Figure 7. Sample point 1, refers to the Feed stream of the NF system; sample point 2 placed before the strainer represents the feed combined with the concentrate recirculation flow and will be named Feed+RC stream, sample point 3 is the total permeate from the 1st and 2nd stage. Finally, sample point 4 is the concentrate of the system.

The NF pilot instrumentation covers the measure of flow, pressure, temperature, turbidity and conductivity of the different streams. Table 2 shows a resume of the NF pilot instrumentation, the parameters were continuously controlled and recorded. Nevertheless, a technical problem prevented the record of data for 13 days in October 2018.

Table 2 NF pilot instrumentations

	Flow	Pressure	Temperature	Turbidity	Conductivity
Feed	•	•	•		•
Feed+RC		•		•	
Concentrate 1st stage / Feed 2nd Stage		•			
Permeate 1st stage	•	•			
Total permeate		•	•	•	•
Rejected concentrate	•				
Concentrate recirculation	•				

3.4.1 NF Operational Conditions

During the approximately nine months of operation, the NF operational conditions were varied to study the NF pilot performance. The parameter that were varied are the flows in the streams feed, concentrate and concentrate recirculation (feed+RC). These variations were classified into seven phases and are explained in Table 3; the temperature showed is the average during that phase. The temperature of the water could not be fixed and due to the close loop operation the same was above 10 ºC even during winter. Nevertheless, during the phase VI part of the UF1 permeate which is normally at 10ºC was circulate through a hose inside the UF1 CIP Tank as an intent to reduce the water temperature.

Each phase had a duration of approximately 30 days with phase IV being the longest due to Christmas break in Gahard DWTP. In addition, the conditions tested during phase IV are the same as phase II, as a result of the pilot stability during phase II. Phase V operated without spiking the UF1 permeate and in an open loop, the NF permeate was fed to the sand Filters in the DWTP process and the concentrate to the waste. However, problems in the Gahard DWTP process affected the quality of the UF1 feed and thus its treatment capability by fouling UF1 membranes. The UF1 inefficient treatment of the water resulted in the NF strainer being clogged, therefore to ensure the NF membranes were not damaged the NF pilot operated in a close loop with Gahard treated water as feed for approximately 10 days. After this period, the NF pilot returned to operate with spiked UF1 permeate.

Table 3 NF Phases description (RC: Recirculation of concentrate)

Phase	Period		Description	Feed Flow	Recirculate Flow	Rejected Concentrate Flow	Recovery	Temp.
	Dates	Nº Days		m^3/h	m^3/h	m^3/h	%	ºC
I	20/09/2018 – 05/10/2018	23	Colored water without RC	5.2	-	0.3	94	22.0
II	06/10/2018 – 05/11/2018	30	Colored water with RC	4.2	2.9	0.2	95	21.7
III	06/11/2018 – 04/12/2018	28	Colored water with RC	5.3	1.8	0.3	95	19.6
IV	05/12/2018 – 07/02/2019	64	Phase II	4.2	2.9	0.2	95	15.6
V	14/02/2019 – 26/03/2019	40	Colorless UF1 permeate	4.2	2.8	0.2	95	16.7
VI	08/04/2019 – 20/05/2019	42	Colored water with RC	4.2	3	0.2	95	18.8
VII	21/05/2019 – 17/06/2019	27	Colored water without RC	4.4 4.3*	-	0.1 0.213*	98 95*	20.7

* Values calculated by rotameters.

The concentrate and concentrate recirculation flow were adjusted manually through a valve in the exit of the concentrate, while the feed was fixed by the NF pump. The NF operated with a recovery of approximately 95%, as it can be seen in Table 3; the recovery was accomplished by daily adjustments of the concentrate valve.

During phase VII was found that the concentrate flow reported in the programmable logic controller (PLC) was not accurate, hence the real recovery of the NF system from September 2018 to May 2019 was approximately 93% and not 95%. Therefore, a rotameter in the concentrate stream was added, and the recovery from May 2019 was manually reported.

3.4.2 Spiking

Colored surface water conditions were simulated by “spiking” UF1 permeate in the UF1 CIP tank with a cocktail of leaf tea, beetroot juice, black tea and natural dyes. The spiking ingredients, except the natural dyes, were produced by “steamer”. The effect of different concentrations of the spiking ingredients on the color and DOC content of the raw water was tested and the result can be seen in Figure 8. Among the spiking ingredients natural dyes are the most effective, capable to increase the color of the water two orders of magnitude higher than black tea which was the next in colored ability.

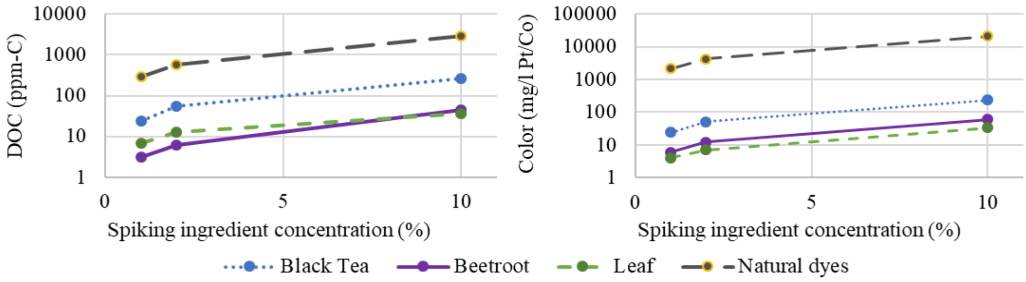

Figure 8 Spiking ingredients effect on color and DOC

In accordance to the color and DOC results of the spiking ingredients, the same were poured in the UF1 CIP Tank as a first approach. The raw water color was tuned by trial and error of different cocktails concentrations.

UF1 Cleaning in Place (CIP) required the UF1 CIP tank, hence the tank was drainage and the NF concentrate was collected in barrels to save the color. Since September 2018 two CIP have been performed in the UF1 (12-13/12/2018 and 11-13/02/2019), therefore the NF concentrate has been collected and then re-introduced into the NF system two times. After the second UF1 CIP the concentrate was not immediately re-introduced to let the NF system run without color (phase V). Despite the efforts during tank drainage, color losses were experienced. Thus, the spiking cocktail was periodically added to the UF1 CIP Tank to overcome the color losses. The schedule of the spiking cocktail addition and its result in the NF Feed is presented in Table 4.

Table 4 Spiking Schedule and water losses.

Phase	Date	Description	Feed Color mg/l Pt/Co	Feed DOC mg/l	Feed+RC Color mg/l Pt/Co	Feed+RC DOC mg/l
II	08/10/2018	Spiking	-	-	55	14.4
III	16/11/2018	Spiking	11	4.6	47	15.4
	22/11/2018	Water losses	4	2.5	18	8.0
	27/11/2018	Spiking	5	3.2	21	10.8
	30/11/2018	Spiking	7	4.6	24	11.4
	03/12/2018	Spiking	11	4.7	46	15.3
IV	11/12/2018	Concentrate collection	10	4.2	56	18.3
	13/12/2019	Re-introduction collected concentrate	7	3.3	36	15.7
	11/02/2019	Concentrate collection	-	-	-	-
VI	10/04/2019	Re-introduction collected concentrate	3	5.1	-	-
	15/04/2019	Spiking	15	5.7	89	25

In November 2018 (Phase III) technical problems in the UF1 occasioned considerable water losses that negatively impacted the water color, therefore several spiking additions were done to recover the color. In Table 4 the values of color and DOC showed for the Feed and Feed+RC were taken the day after the spiking was performed.

3.4.3 Swedish lakes

Two Swedish lakes that are the main water source for two DWTPs were used as reference to evaluate the quality of the spiking cocktail and the performance of the NF pilot. The samples came from lake Bolmen and Lake Malaren, also the samples were analysed in Gahard DWTP in July 2018 (Kridene, Sauvignet and Assadi, 2018).

Lake Bolmen

Located in the province of Småland, lake Bolmen has a surface of 184 km^2 and a maximum depth of 37 m. The lake catchment area is made up of 47% forest, marsh lands (22%) and lakes (20%), with a fraction of 9% from cultivation land. Bolmen lake is the main source of water for Ringsjöverket DWTP managed by SYDVATTEN, with a production of 1645 l/s (SYDVATTEN, 2019), Ringsjöverket is the main source of fresh water to Skåne. The characteristics of the lake are presented in Table 5.

Lake Mälaren

Third largest lake in Sweden with an area of 1140 km^2 and a maximum depth of 64 m. Lake Mälaren catchment area is formed mainly by forest (60%), cultivated land (20%) and lakes (11%). The lake supplies water to Görväln DWTP owned by Norrvatten company. The lake main features can be seen in Table 5.

Table 5 Swedish lakes characteristics (taken from (Kridene, Sauvignet and Assadi, 2018))

Parameters		Lake Bolmen	Lake Malären
True Color	mg/l Pt/Co	60	25
UV_{254}	m^{-1}	43.4	33.8
DOC	mg/l	10.0	9.4
SUVA	l/mg.m	4.3	3.6
Turbidity	NTU	1.2	2.7
Conductivity	µS/cm	117	268

3.5 Analytical Methods

3.5.1 True Color

Measurements of true color were performed at 410 nm with a spectrophotometer fabricated by HACH model DR6000. All the samples except the NF permeate, were filtrated with a 0.45 µm filter before the analysis.

Color in freshwater is commonly measured by visual comparison of chloroplatinate standards. Nevertheless, this method has several errors due to visual measures, hence measuring the absorbance on a spectrophotometer is more accurate. Despite not existing a standard wavelength for such measurement. (Brezonik and Arnold, 2011) recommend its measure at 410 nm since the absorptivity of colored dissolved organic carbon is higher and thus its sensitivity.

3.5.2 UV_{254}

The Ultraviolet absorbance is an indirect measure of the amount of organic matter. Different chromophores in the NOM structure can absorb UV-light in the wavelength range of 220-280nm; aromatic groups are detected at 254nm (Sillanpää, 2014). Since the project aim is to evaluate NOM linked to water color, and the previous is a consequence of Humic Substances (aromatics), the UV absorbance analysis were performed at 254nm. The equipment used was a UV VIS spectrophotometer from HACH model DR6000.

3.5.3 Electrical Conductivity

The conductivity of a liquid refers to its capability to conduct an electrical current. This phenomenon is due to the presence of ions in the liquid, the higher the ion concentration the higher the conductivity of the liquid. Ions are the results of dissolved salts and inorganic materials like sulfides and carbonates in the water. There is a correlation between conductivity and the dissolved salt content (Rodier, 2009), the same is presented in Equation 1. However, the mineral content obtained through the conductivity is not strictly identical to that obtained by drying the sample and weighting the remains, since there are inherent error in the determination of both measures (Rodier, 2009).

$$M = 0.715920 \times C \times 1.116 \qquad \text{Equation 1}$$

Where M is the salt content (mg/l) and C is the electrical conductivity at 25ºC (µS/cm)

The conductivity was employed as an estimation of the dissolved salt removal in the NF pilot. It was measured with multimeter MU 6100H from VWR.

3.5.4 Total Alkalinity

A reference to the capability of the sample to resist changes in pH, the alkalinity is due to the presence of weak acids and their conjugated bases (Rodier, 2009). In natural waters the alkalinity is the result of hydroxides and carbonates. The total alkalinity of the samples was calculated by using a Titrimetric method, bases on the neutralization of the sample by a diluted mineral acids and using a color indicator (Rodier, 2009).

3.5.5 Hardness

The water hardness represents the sum of the metal cations concentrations; most of the time it refers to calcium and magnesium ions. The samples hardness was calculated by a titrimetric method using EDTA (Rodier, 2009).

3.5.6 DOC and Theoretical DOC

Dissolved organic carbon refers to the quantity of organic carbon contain in the sample after the same has been previously filter by a 0.45 µm filter. The DOC in the samples was measured using a laboratory total carbon Content Analyzer from HACH model QbD1200. However, this equipment was replaced in May 2019. The new equipment which was the same model as the previous presented problem when measuring samples with a DOC value below 2 mg/l.

The theoretical DOC of the NF concentrate was calculated through a mass balance in the two modules stages and the recovery reported by the PLC and later by the rotameters. Equation 2 shows the calculus and Figure 9 the general membrane scheme. The difference between the NF concentrate and the theoretical concentrate DOC was considered as the organic matter absorbed or retained in the membrane surface.

$$DOC_{Theoretical\ Concetrate} = \frac{DOC_{Feed} - Recovery \cdot DOC_{Permeate}}{(1 - Recovery)} \quad \text{Equation 2}$$

Where DOC is dissolved organic carbon (mg/l) and Recovery is the NF pilot recovery (-).

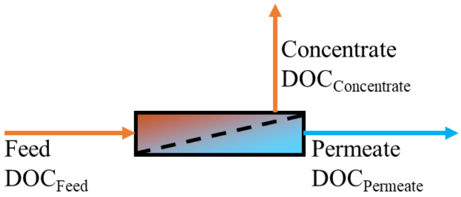

Figure 9 Membrane scheme for theoretical DOC calculus

3.5.7 LC-OCD

Liquid chromatography with organic carbon detection (LC-OCD) analysis were performed by DOC-Labor in Germany, using a SEC HW-50S column with an exclusion limit of $1.8x10^4$ Da and an analysis time of 150 minutes. Swedish lakes analyses were performed the 19/07/2018, NF feed and NF feed+RC streams after the spiking were evaluated the 09/10/2018 and the 04/12/2018. In addition, the NF permeate and concentrate were analyzed the 04/12/2018. The main organic matter fractions detected by the LC-OCD analysis are:

1. Bio-polymers (BPs): Comprise polysaccharides (like starch), proteins and colloids. BPs have an approximately molecular weight >>20 000 g/mol. They are detected between 25 and 35 minutes of analysis. In relation to natural waters, BPs are only present in surface waters and usually represent 5-10% of the DOC (Bernier-Gherman, 2018).
2. Humic Substances (HSs) and Building Blocks (BBs): Detected during the 35 and 50 minutes of started the sample analysis, they represent ~60% of DOC. HSs are organic molecules with a molecular weight of ~1000 g/mol. On the other side, BBs usually 15-25% of DOC are the intermediate products of the HSs degradation with a molecular weight of ~300-500 g/mol.
3. Low molecular weight acids (LMWA): with a molecular weight inferior of 350 g/mol, LMWA can be associated to volatile fatty acids or low molecular weight humic compounds; in addition they can also represent bacterial and algal products (Bernier-Gherman, 2018). They are detected during a peak at 52 minutes.
4. Low molecular weight neutrals (LMWN): representing 10-30% of the DOC, LMMN are weakly charged molecules considered as non-biodegradable and with a low hydrophobicity such as mono-oligosaccharides, alcohols (Bernier-Gherman, 2018)…

The chromatographic dissolved organic carbon (CDOC) is the sum of the organic matter fractions previously mentioned. The difference between the CDOC and the DOC represents hydrophobic compounds that are retained on the chromatographic column (They are usually between 0-25% of the total organic matter in surface natural waters) (Bernier-Gherman, 2018).

4 Results and discussions

4.1 Spiking

The LC-OCD analyses of the Swedish lakes and the NF feed and feed+RC streams are presented in Table 6. On the 09/10/2018 (Phase II) the NF feed sample was not included due to limitations in the number of samples. Nevertheless, the missing NF feed sample can be related to the NF feed analyzed the 04/12/2018 (Phase III), since both phases operated under similar conditions and their feed+RC analysis do not differ greatly.

Table 6 Organic matter composition of Swedish lakes and NF streams

			Lake Mälaren 19/07/2018	Lake Bolmen 19/07/2018	UF1 permeate 09/10/2018	NF feed+RC 09/10/2018	NF feed 04/12/2018	NF feed+RC 04/12/2018
DOC		mg/l	9.423	10.078	1.509	14.174	3.783	12.931
		% DOC	100%	100%	100%	100%	100%	100%
CDOC		mg/l	8.982	9.933	1.445	14.05	3.303	11.978
		% DOC	95.3%	98.6%	95.8%	99.1%	87.3%	92.6%
CDOC	BPs	mg/l	0.349	0.259	0.009	0.001	<0.001	<0.003
		% DOC	3.7%	2.6%	0.6%	0.0%	-	-
	HSs	mg/l	6.308	7.649	0.638	9.901	1.999	8.552
		% DOC	66.9%	75.9%	42.3%	69.9%	52.8%	66.1%
	BBs	mg/l	1.581	1.216	0.494	2.685	0.663	1.971
		% DOC	16.8%	12.1%	32.7%	18.9%	17.5%	15.2%
	LMWA	mg/l	0.068	0.027	0.013	0.01	<0.001	<0.003
		% DOC	0.7%	0.3%	0.9%	0.1%	-	-
	LMWN	mg/l	0.677	0.782	0.291	1.46	0.64	1.454
		% DOC	7.2%	7.8%	19.3%	10.3%	16.9%	11.2%
UV_{254}		m^{-1}	27.2	42.3	3.1	68.9	19.4	75.6

The comparison between the UF1 permeate and NF feed DOC shows that the spiking of the UF1 permeate was capable to double the DOC while roughly keeping the same organic carbon composition. The values obtained in the feed+RC streams for DOC and UV_{254} are higher than those in the NF feed since the feed+RC stream is the combination of the NF feed with the concentrate recirculation.

The major contributor to DOC content in the six streams samples is HSs, they comprise more than 50% of the total DOC (except in UF1 permeate where is 42%). The second contributor to DOC is BBs with values higher than 10%.

BPs are present in Swedish lakes (~0.3 mg/l) but not in the NF feed or NF feed+RC streams. BPs fraction include polysaccharides, proteins and colloids. Polysaccharides can be produced by sugar fermentation and bacteria synthesis, through the later extracellular polymeric substances (EPS) are formed (Bernier-Gherman, 2018). BPs are one of the most important DOC fractions in membrane processes due to their impact in membrane fouling. Biofouling represents between 5-56% of the total membrane fouling, the same is mainly caused by BPs and EPS (Shao *et al.*, 2018). Hence, the absence of BPs in the NF feed and feed+RC streams suggest a low fouling possibility in the NF membrane.

Swedish lakes presented a DOC of around 9.6 mg/l while the NF feed value was below 4 mg/l; however, NF feed+RC DOC exceed the values in Swedish lakes with an average of 12.6 mg/l. By analyzing the DOC percentages of the different organic matter fractions, can be seen that lake Malären and lake Bolmen have similar organic carbon composition, with the first resembling more the NF streams feed and feed+RC in terms of HSs and BBs percentages of DOC.

The organic carbon profiles of the Swedish lakes and the NF feed and feed+RC streams analyzed the 04/12/2018 are presented in Figure 10. The shape of the curve represents the organic matter composition while the height represents the organic matter content. The higher the curve the higher the content of organic matter.

In Figure 10 can be seen that the NF feed and the Swedish lakes present similar curve shapes with the difference that the NF feed curve is shorter than those of the Swedish lakes. The previous correspond to the DOC values presented in Table 6 Organic matter composition of Swedish lakes and NF streamsTable 6. Moreover, the NF feed+RC stream presents a taller curve that is more in the range of the Swedish lakes.

In addition to the difference in heights, Figure 10 illustrates another difference between the Swedish lakes and the NF feed, being this the presence of BPs; this can be seen in the small peak between 25 and 35 minutes, Swedish lakes has it while NF feed does not.

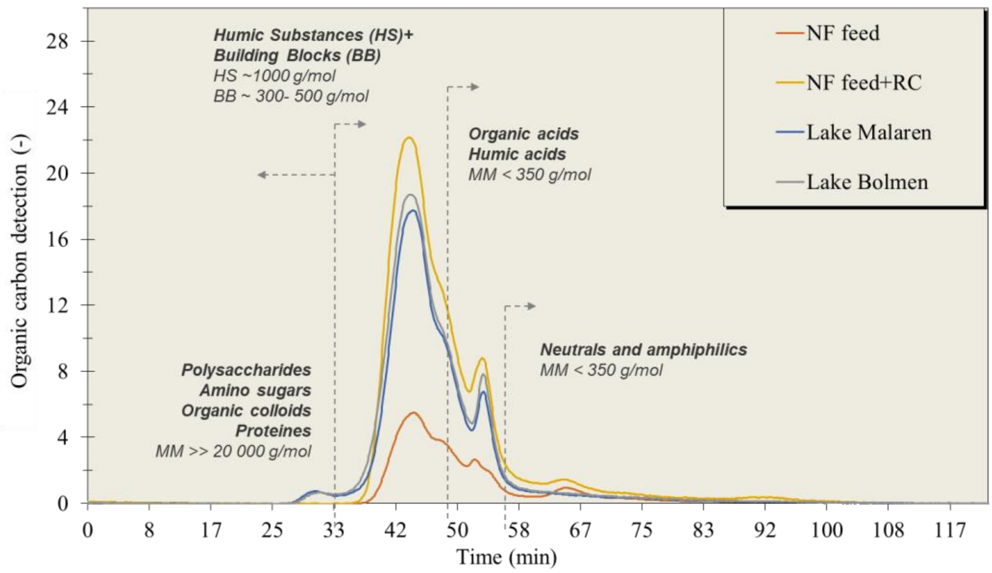

Figure 10 Organic carbon profile of Swedish lakes and the NF feed and feed+RC streams.

The average color and DOC accomplished after the spiking procedure in every phase is presented in Table 7. The Phase I was not included because during that period the samples were not analyzed. As mentioned before, the NF feed+RC stream possess a higher color and DOC due to its mix with part of the concentrate. In phase VII the NF feed and NF feed+RC present similar values due to the absence of concentrate recirculation.

Figure 11 shows the correlation between DOC and color on the NF feed and feed+RC streams. The correlation was calculated by considering the values obtained during those phases that operated with spiked water (Phase V was omitted). The color in the phases VI and VII is higher than the color in phases III and IV; but still, none of the phases color and DOC met the Swedish lakes conditions (*see* Table 5). Using the DOC-Color correlation (*see* Figure 9) to generate roughly estimations, the features presented by lake Malären (color: 25 mg/l Pt/Co, DOC: 9.4 mg/l) can be accomplished by the NF system by increasing the addition of spiking cocktail. But, lake Bolmen features cannot be accomplished and would require another spiking cocktail.

Table 7 NF phases DOC, color and UV_{254}

		Color mg/l Pt/Co	DOC mg/l	UV_{254} m-1
II	Feed	-	-	-
	Feed+RC	51.1	14.5	62.4
III	Feed	9.0	4.0	12.3
	Feed+RC	37.4	12.1	46.8
IV	Feed	7.1	3.5	12.6
	Feed+RC	40.3	16.1	46.8
V	Feed	1.5	2.2	3.82
	Feed+RC	2.5	8.6	14.8
VI	Feed	13.7	4.8	14.7
	Feed+RC	81.9	22.8	74.6
VII	Feed	14.5	5	16
	Feed+RC	14.6	5.3	16

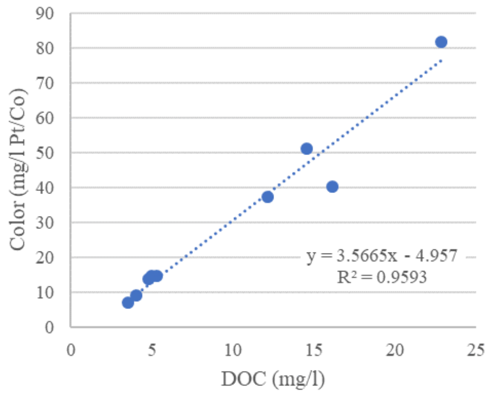

Figure 11 Correlation DOC-Color

In resume, the spiking procedure performed on UF1 permeate to resemble Swedish surface waters was not effective. Swedish lakes composition differed from the NF feed stream, since BPs fraction was absence and the DOC-color content was not the same. Nevertheless, NF feed can be used as a first approach in the treatment of surface waters similar to lake Malären.

The high content of DOC in phase V Feed+RC, could be due to organic matter remains in the pipes from previous phases. The UV_{254} presents a relation with the DOC and color in the samples, the higher the color the higher the UV_{254}, as expected due to their high sensibility to aromatics.

4.2 Organic Matter Removal

The organic matter removal accomplished by the NF membranes was measured through the removal of color, UV_{254} and DOC in relation to the feed and feed+RC streams, Table 8 shows the obtained results. The removal of organic matter is higher when the same is calculated in relation to the Feed+RC stream due to its higher organic content. Phase VII color and UV_{254} removal in relation to the Feed stream is similar to the removal calculated in relation to the feed+RC, since the NF pilot operated without concentrate recirculation and thus the NF feed and NF feed+RC are the same stream.

Table 8 Organic Matter removal in relation to the NF feed and the NF feed+RC streams.

	Color		UV_{254}		DOC	
	Feed	Feed+RC	Feed	Feed+RC	Feed	Feed+RC
II	-	96.1%	-	93.3%	-	86.2%
III	77.8%	95.1%	69.8%	92.0%	52.7%	83.2%
IV	82.0%	96.9%	72.8%	95.0%	60.4%	91.4%
V	100.0%	100.0%	58.1%	88.8%	49.8%	86.5%
VI	85.3%	97.6%	69.9%	94.1%	65.9%	92.6%
VII	85.5%	84.3%	70.8%	71.2%	65.0%	81.2%

In general, omitting the values reported during phase V (operation without color content) the removal of UV_{254} and color in relation to the feed stream were roughly stable despite the operational phase, being those 70% and 83% respectively. Similarly, the removal of UV_{254} and color in relation to the feed+RC also remained constant and higher than 90%.

Phase IV have the same operational conditions as phase VI in terms of flows, being the only difference the feed color and DOC which is lower in phase IV. Nevertheless, regardless of this difference, NF system was capable to provide similar results with a higher effectiveness in phase VI. On the other hand, phase VI and VII operated with the same spiked solution and so the feed conditions were similar. The removal of color, UV_{254} and DOC were roughly equal despite one phase operated with concentrate recirculation and the other did not. These results suggest that the concentrate recirculation has a minimum impact in the membrane removal of organic matter.

The removal of organic matter was also evaluated in relation to the organic matter composition of the NF permeate and concentrate. Table 9 shows the LC-OCD results obtained for the NF inlet and outlet streams. It can be seen in Table 9 that the general compositions of the NF feed, feed+RC and concentrate are similar, with HSs being the main contributor of DOC (~60%), followed by BBs (~16%) and last LMWN (~13%). On the other hand, NF permeate, presents an organic matter composition slightly different, in this case HSs are still the major contributor to DOC but BBs and LMWN have similar values, with the latter being in a higher concentration.

By comparing the DOC values of the NF feed and permeate, can be seen that NF membrane was capable to remove 63% of the NF feed DOC (the difference between this value and the one presented in Table 8 is that the first represents just one day while the latter represents the average of phase III period).

The organic matter composition of the NF permeate shows the NF system removed 73% of the HSs and 55% of the BBs found in the NF feed. Similarly, NF membrane removed approximately 40% of the LMWN.

Table 9 Organic matter composition of NF streams

			NF feed	NF feed+RC	NF permeate	NF concentrate
			04/12/2018	04/12/2018	04/12/2018	04/12/2018
DOC		mg/l	3.783	12.931	1.415	39.874
		% DOC	100%	100%	100%	100%
CDOC		mg/l	3.303	11.978	1.201	37.453
		% DOC	87.3%	92.6%	84.9%	93.9%
CDOC	BPs	mg/l	<0.001	<0.003	<0.001	<0.01
		% DOC	-	-	-	-
	HSs	mg/l	1.999	8.552	0.537	27.326
		% DOC	52.8%	66.1%	37.9%	68.5%
	BBs	mg/l	0.663	1.971	0.292	6.164
		% DOC	17.5%	15.2%	20.6%	15.5%
	LMWA	mg/l	<0.001	<0.003	<0.001	<0.01
		% DOC	-	-	-	-
	LMWN	mg/l	0.640	1.454	0.372	3.957
		% DOC	16.9%	11.2%	26.3%	9.9%
UV_{254}		m^{-1}	19.4	75.6	4.6	245.2

The organic carbon profile can be seen in Figure 12, the difference in height between the NF streams curves shows the removal of organic matter by the membrane and that the organic matter is retained in the NF concentrate, which possess the highest peak. In addition, the almost flat NF permeate curve shows the removal of the organic matter and that the remaining compounds like HSs, BBs and LMWN keep a similar concentration.

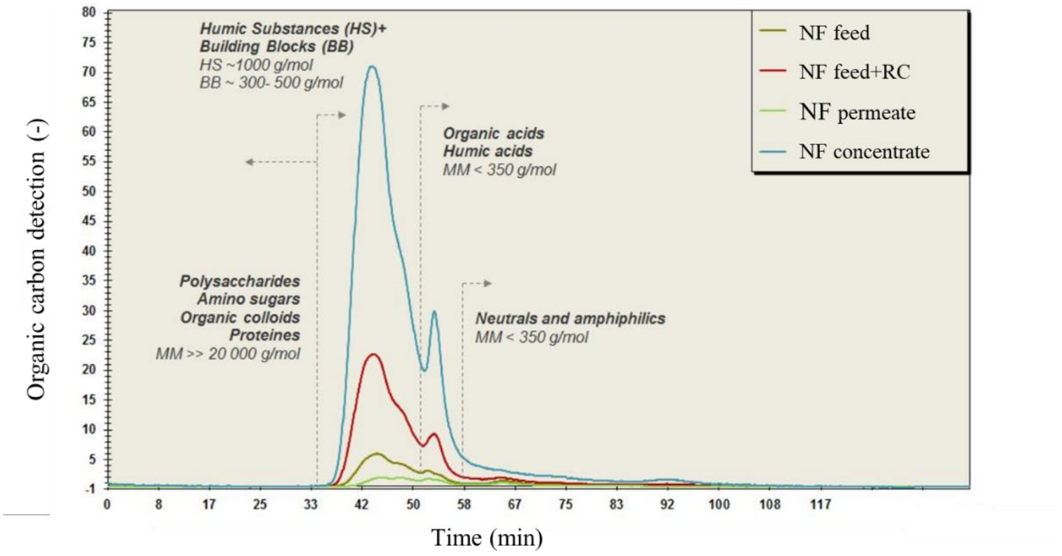

Figure 12 Organic carbon profile of the NF inlet and outlet streams taken 04/12/2018.

4.3 Membrane performance

4.3.1 Pressure

The evolution of the pressure in the different parts of the NF pilot over time is presented in Figure 13. In the Figure can be seen that the feed pressure of the system was not fixed but at the contrary it varied as a result of the 1st Stage feed flow (feed+RC stream) and the feed temperature. The higher the 1st stage feed flow the higher the pressure, since more energy is required to pump the total flow. Similarly, high water temperatures imply lower feed pressures, due to the water viscosity decrease at high temperatures.

The pressure drops after the strainer and the membranes 1st and 2nd stage remained almost constant during the seven phases. These pressure drops were smaller when the pilot operated without concentrate recirculation (phase I and VII). The increase in the pressure drop of the strainer (feed pressure – 1st Stage Feed pressure) during phase V, shows the clogging of the strainer cartridges. The strainer clogging was the result of problems upstream in Gahard DWTP, which affected the UF1 performance and reduce the UF1 permeate quality and so the NF feed. The cartridges were changed, and the strainer pressure drop recover its usual value in the following phase (phase VI).

The 1st and 2nd stage permeate pressure remained constant over time, the pressure drop between both streams was the result of a perforate valve that controls the flow of permeate in the 1st stage. Hence, it avoids the overburden of the 1st stage membranes.

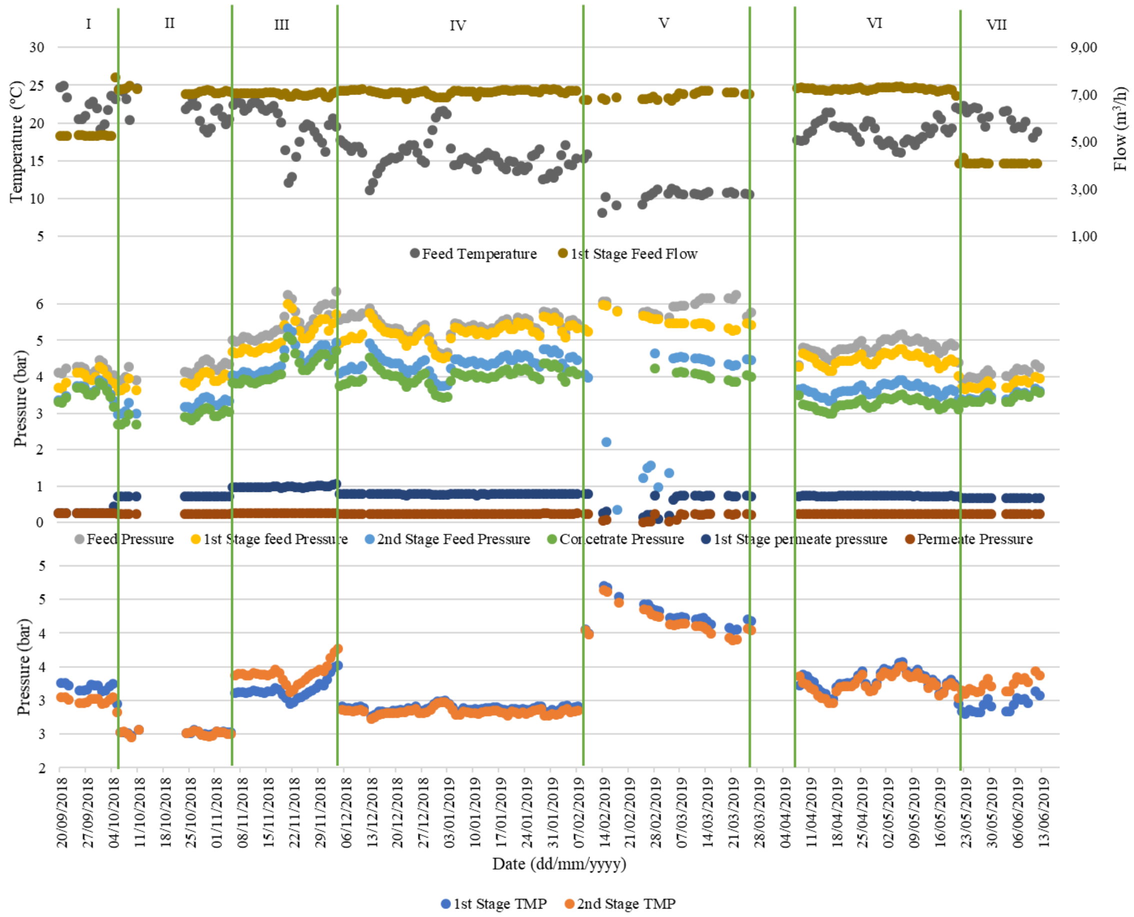

Figure 13 Pressure evolution in time.

The TMP in the 1st and 2nd stage was influenced by the feed temperature and flow. Figure 13, shows that the TMP for both stages varied between the phases. The TMP average values for each phase are shown in Table 10. During the phases II, IV, V and VI, the TMP values in both stages were similar, as a result that in these phases were studied the same operational conditions (Feed and RC flow). Additionally, the difference between the average TMP in the phases II, IV, V and VI is a result of the temperature. In accordance to the previous, the TMPs in phase V should have been lower than those in phase IV, however, difference in the viscosity of colored and colorless water could have influenced this value.

Table 10 TMP values for each phase

	TMP		
	1st Stage bar	2nd Stage bar	Average bar
I	3.15	3.0	3.1
II	2.54	2.53	2.5
III	3.15	3.38	3.3
IV	2.88	2.83	2.9
V	4.28	4.18	4.2
VI	3.3	3.24	3.3
VII	2.93	3.22	3.1

4.3.2 Membrane permeability and flux

The general performance of the NF membrane in terms of permeability and flux is presented in Figure 14. The permeability trends were similar for the 1st and 2nd stage, with the latter being approximately 15% lower than the 1st stage permeability. The permeability difference between the stages could be the result of 2nd stage operating with a lower cross-flow velocity (less feed flow) and therefore being more prone to membrane fouling.

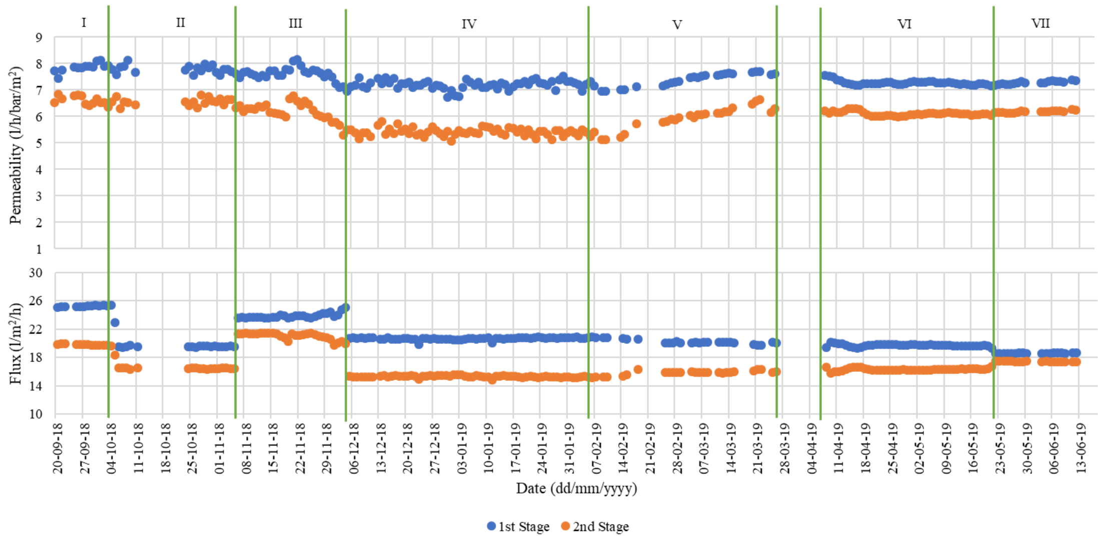

Figure 14 NF membranes performance

The membrane permeability experienced a considerable decrease during phase III due to the water and color losses. A series of spiking processes were performed to recover the color; however, it is suspected that during the spiking, the natural ingredients were not properly filtrated and thus some suspended solids fouled the membrane. The permeability losses in the 2nd stage were slightly recover in phase V by operating the system without spiked water. Therefore, the membrane only experienced an external fouling.

In Figure 14 can be seen, that the membrane permeability in both stages remained roughly stable during the phases I, II, IV, VI and VII; the phases III and V were not considered since phase III presented water losses and V operated without color. This stability in the permeability trends suggests the absence of fouling in the NF membranes. Moreover, the absence of fouling considering the NF membranes operated during nine months without any cleaning procedure, demonstrates the efficiency of the UF as a pre-treatment. However, it is important to consider that the absence of fouling could also be the result of the BPs absence in the NF feed and therefore no possibility for biofouling.

Similar to the membrane permeability, the flux also kept stable during the trials with the exception of phase III and V. In addition, in phase VII it was possible to accomplish similar flux in each stage. Table 11 shows the average values of permeability and flux accomplished in each phase.

During the last nine months of operation the total membrane permeability losses were about 7% in each stage. Phase III caused permeability losses of 7% and 17% in stages 1st and 2nd respectively. 2nd stage was the most affected by the problems in phase III; nevertheless, phase V considerably helped in the permeability recover. The difference in the permeability of each stages remined approximately constant and of 15%.

On the other hand, the NF system was capable to provide average fluxes between 22.5 and 18 $l/m^2/h$, phases I and III have higher fluxes due to the feed flow being 5.2 and 5.3 m^3/h respectively. Phase VII operates with both stages at similar fluxes (~7%).

Table 11 Permeability and Flux values for each phase

	Permeability			Flux		
	1^{st} stage l/m²/h/bar	2^{nd} Stage l/m²/h/bar	Average l/m²/h/bar	1^{st} Stage l/m²/h	2^{nd} Stage l/m²/h	Average l/m²/h
I	7.86	6.61	7.2	25.2	19.8	22.5
II	7.78	6.55	7.2	19.73	16.57	18.2
III	7.64	6.22	6.9	23.85	21.04	22.4
IV	7.2	5.41	6.3	20.68	15.32	18.0
V	7.44	6.04	6.7	20.15	15.94	18.0
VI	7.28	6.11	6.7	19.73	16.31	18.0
VII	7.27	6.18	6.7	18.63	17.4	18.0

Furthermore, the increase of the cross-flow velocity by recirculating part of the concentrate stream, does not seem to affect the membrane fouling process. Despite the fact, the concentrate recirculation should decrease the membrane fouling possibilities, the same cannot be clearly seen in the permeability trends. Longer trial should be performed to confirm the membrane operation regardless the concentrate recirculation.

4.4 Treatment of non-spiked water

Since the 14/02/2019 until the 26/03/2019 (40 days) the NF pilot operated in an open loop with non-spiked UF1 permeate. The organic matter removal accomplished by the NF system is shown in Table 12, there can be seen that the macro-coagulation UF-NF system is more efficient than the last part of Gahard DWTP process.

Table 12 Comparison organic matter removal between UF-NF system and Gahard DWTP

	UV_{254}		DOC	
	m^{-1}	Removal %	mg/l	Removal %
Filtraflo Carb®	5.2	-	3.3	-
Macro-coagulation UF1 permeate	4.0	23%	2.2	33%
NF permeate	1.5	63%	1.1	50%
Gahard treated water	4.7	10%	3.0	9%

The NF system was capable to remove 63% of the DOC and 50% of the UV_{254} present in the macro-coagulation UF1 outlet. Altogether, the macro-coagulation UF1-NF couple system removed 67% and 71% of the Filtraflo Carb® outlet UV_{254} and DOC respectively. On the contrary, Gahard DWTP remaining processes (GAC and sand filters) could only remove 10% of the UV_{254} and 9% of DOC. As a result, the outlet quality of the macro-coagulation UF1-NF exceeds the quality of Gahard treated water.

4.5 Removal of dissolved salts

The removal of salts was evaluated through electrical conductivity measures in the NF feed and permeate streams. The NF pilot possess a conductivity sensor capable to measure the conductivity every minute; in addition, periodical measures of the conductivity were performed in the Gahard

DWTP Laboratory to confirm the values reported by the NF sensor. Figure 15 presents the conductivity values reported by the NF sensor and those measured in the Laboratory.

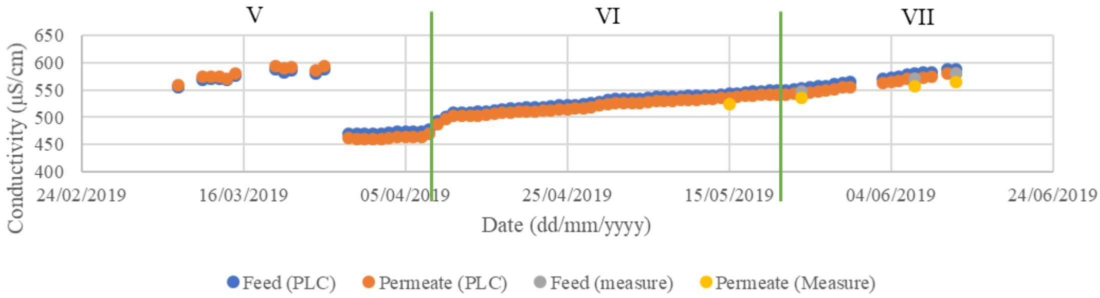

Figure 15 Conductivity measurements

The values reported by the PLC and those measured in the Laboratory are approximately the same; hence the values reported by the NF sensor are reliable. The variation between the feed and the permeate conductivity is less than 2%, which in accordance to Equation 1 represent a retention of 7.2 mg/l salt content. Therefore, the NF dissolved salt removal is negligible.

The increase of the conductivity from phase VI to VII, represents an increase of almost 100mg/l of salt, the same can be the result of water losses due to evaporation in the UF1 CIP Tank or leaks in the system.

The alkalinity and hardness in the NF feed, feed+RC and permeate streams were sporadically measured, the values are presented in Table 13. The reduction of alkalinity and hardness in the permeate is less than 5% in most of the cases. Consequently, it can confirm the almost inexistence removal of dissolved salts by the NF membranes.

Table 13 Alkalinity and hardness removal

	Alkalinity			Hardness		
	Feed mg/l $CaCO_3$	Feed+RC mg/l $CaCO_3$	Permeate mg/l $CaCO_3$	Feed mg/l $CaCO_3$	Feed+RC mg/l $CaCO_3$	Permeate mg/l $CaCO_3$
22/11/2018	41	44	40	203	243	196
14/12/2018	44	49	43	206	255	198
17/01/2019	45	48	43	210	258	202
24/04/2019	44	59	44	188	226	178
24/05/2019	37		34	206		194
13/06/2019	46	-	46	242	-	198

4.6Water losses

The UF1 water losses are calculated through the difference between the total volumes recorded by the flowmeters situated in the permeate and feed streams; the total volume is recorded daily. During the NF trials the UF1 reported a constant recovery of 87% or water losses of 13%. UF1 high water loses are the result of rejecting the water used during the normal and chemical enhanced backwash. The water used for the NB is rejected as a waste due to the presence of flocks in it.

On the other hand, the water losses reported by the NF are calculated by the NF PLC through the feed and rejected concentrate flows. Theoretical DOC of the concentrate stream was calculated as a method to confirm the recovery reported by the PLC. Table 14, shows the measured DOC and the theoretical DOC calculated through the PLC recovery for each phase. As it can be seen in Table 14, the error between the measured and the theoretical DOC (calculated with the PLC recovery) is until phase V approximately 20%. This difference between the measured and theoretical DOC, can be used as a reference in relation to the amount of organic matter that remains in the membrane or in the pilot (strainer and pipes).

Table 14 Theoretical and measured NF concentrate DOC

	DOC	NF recovery		Theoretical DOC			
	Measured	PLC	Rotameters	PLC recovery		Rotameter recovery	
	mg/l	%	%	mg/l	Error (%)	mg/l	Error (%)
III	32.1	94.8	-	40.7	27	-	-
IV	34.8	94.8	-	42.1	21	-	-
V	19.0	94.8	-	22.6	19	-	-
VI	45.3	95.1	-	67.1	48	-	-
VII	55.4	97.6	95	126.1	128	61.5	11%

During phase VI the DOC difference between the theoretical and the measured tripled previous values, suggesting some problems in the recovery calculation method. Manual measures of the NF streams (permeate and concentrate) were performed to confirm the recovery values in the PLC. These results showed that the concentrate flow reported by the PLC was lower than the real, and therefore the real recovery of the NF pilot was roughly 93% and not 95%. Consequently, one rotameter was added to the rejected concentrate stream, in order to perform manual reports of the recovery. The theoretical DOC calculated by taken into account the NF recovery from the rotameter, suggested a difference of 11%. In other words, 11% of the DOC remains in the membrane surface; nonetheless, this value still presents some errors due to the equipment sensibility and losses in the permeate flow due to turbidity analysis.

The combined system UF1-NF was capable to operate with a global recovery of approximately 83% or with water losses below 18%. Despite the fact, the global recovery in the UF1-NF is below the desired 90% recovery, the same is higher than the recovery reported by Ericson et al. (1997), which is roughly 65%.

Moreover, it is expected that during the second part of the project the coupled system UF3-NF will accomplish a global recovery above 90% or water losses below 10%. The previous will be the result of increasing the water recovery in the UF3 to 95%. This will be done by recirculating the normal backwash outlet into the UF3 feed tank, this was not possible in the UF1 due to the macro-coagulation and the flocs presence.

5 Conclusions and future perspectives

5.1 Conclusions

The combination of a low pressure NF with a UF pretreatment was tested during approximately 9 months for the treatment of underground water which was spiked in order to resemble Swedish surface waters conditions. The project results provided the following conclusions:

- The spiking of UF1 permeate was not effective, since BPs were absence and the DOC and color did not reach those found in Swedish lakes. Nevertheless, the employed spiking recipe accomplishes a DOC-Color relation similar to that found in lake Malären. The spiked NF feed stream can be used as a first approach in the treatment of surface waters similar to lake Malären.
- The NF membranes are capable to remove 85% and 65% of the NF feed color and DOC respectively, regardless of whether the system operates with or without the recirculation of the concentrate.
- The NF membranes are capable to operate during long trials (9 months) with a permeability decrease of 7% in each membrane stage. The average permeabilities are 7.4 and 6.1 $l/m^2/h/bar$ for the 1st and 2nd stage respectively.
- UF is a robust pretreatment, which allows the stability of NF membranes permeability during long trials and in absence of cleaning procedures.
- The combination of macro-coagulation, UF and NF provides an organic matter removal almost 6 times higher than that accomplished by GAC and sand filters.
- Negatively charged NF membranes with a MWCO of 1000 Da at low pressure operation do not remove dissolved salts significantly, this means no remineralization step is required.
- The UF1-NF coupled system has a global recovery of approximately 83%.

The obtained results show the UF-NF system has the potential to be considered as a feasible drinking water treatment for colored surface waters, with the main advantage that it has a low chemical consumption, low sludge production and a global recovery above 80%.

5.2 Future perspectives

The good results accomplished by the UF1-NF system have allow the project to continue and start at the end of July 2019 the project second part. During this new part it will be studied the performance of the UF3-NF system under the following conditions:

- Addition of starch in the spiked Gahard raw water to evaluate the performance of the NF membrane in the presence of BPs.
- Improve spiking quality by increasing the feed color to values above 30 mg/l Pt/Co.
- Increase the global recovery above 90% by testing the UF3 at 95% recovery.
- Increase the membrane flux by increasing the feed flow.
- Operate at temperatures below 5 °C.
- Compare the capital and operational expenses of the coupled system UF3-NF with a conventional treatment.
- Test the UF3-NF system with real surface water, move the pilots to a closer river.

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