Membrane screening to identify optimal properties when separating organic matter from Bolmen water

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Picture on front page: Different TOC-concentrations. Photo by Olivia Söderman.

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Preface

This Master Thesis report within water resource management marks the end of five enjoyable, exhausting and fun years of studying Environmental Engineering at LTH. When I used to explain what I was hoping to achieve with my education, my standard answer would be "saving the world". In hindsight, this may seem as a bit of an overstatement. However, given the fact that over half of the 17 sustainable development goals stated by the UN does concern water, I'd say I wasn't too off the mark. Thankfully, I now possess a bit more knowledge which can help me to at least try to make reality of the statement, something I didn't have when I first started to boast out my ambitions.

The past autumn has been spent writing this thesis which has been a collaboration between Sydvatten and the Department of Chemical Engineering at LTH. The combination of academic work within the department and the opportunity to work for a company was in my opinion the best of two worlds. I've thoroughly enjoyed the process of writing and working with this study and I would like to thank some people who made it into such a pleasant journey. First and foremost, I'm incredibly grateful to have been given the chance to work with Tobias Persson, my supervisor at Sydvatten, who was always very easy going and supportive no matter if I did something really well or really bad.

I would also like to say a special thanks to Ann-Sofi Jönsson and Michael Cimbritz, my supervisor and examiner at the department, for helpful advice and comments as well as always taking the time to steer me in the right direction.

Apart from my supervisors, there has been a lot of people who have helped me within the department. I'm very appreciative that you've welcomed me in the best way possible even though it meant sacrificing your own time in order to help me out with various tasks. I would above all like to send out a very, and I mean a very, special thanks to Johan Thuvander for everything you've helped me with during the course of this study. I highly doubt anything would have worked without you. Gertrud and Maja, thank you for all the lab assistance as well as general advice in life, much appreciated. Mirjam and Linnea, I couldn't have asked for better office roomies, I sincerely hope our recorded Christmas Choir CD will be a best seller.

If this were the Oscars I think the music would have started to play ages ago but finally I think my family and friends are worth some recognition as well so thank you, thank you.

Olivia Söderman

Populärvetenskaplig sammanfattning

Vilket membran lämpar sig bäst när det kommer till avskiljning av organiskt material från Bolmenvatten?

Med vattendrag som blir brunare och brunare – hur ska våra dricksvattenverk klara av att säkra vårt vatten i framtiden? Svaret heter membranteknik! Vilket membran som passar bäst är däremot en svårare fråga att besvara och således också det som har undersökts i denna studie.

Att den globala uppvärmningen påverkar vår planet och vår vardag är det förhoppningsvis ingen som har missat vid det här laget. Men att växthuseffekten också är en av bovarna bakom att våra sjöar blir rikare på organiskt material och därmed blir alltmer bruna är kanske inte något som man har noterat i någon större utsträckning. Att vattendragen blir lite mörkare till färgen är inget direkt hot för oss som badgäster men eftersom en stor del av Sveriges dricksvattenproduktion använder dessa sjöar som vattentäkter innebär brunifieringen ett växande problem för våra reningsverk och därmed oss som konsumenter.

Vid många dricksvattenverk, till exempel Ringsjöverket som ägs av Sydvatten, avskiljer man i dagsläget oönskade molekyler från vattnet med bland annat kemisk fällning. Med hjälp av olika metallsalter klumpar lösta ämnen i vattnet ihop sig, sjunker till botten och kan därmed tas bort. Då det organiska materialet i våra vattentäkter stadigt ökar krävs det mer och mer kemikalier för att kunna se till att vattnet vi dricker inte påverkas. Då man doserar mer kemikalier innebär det att det produceras mer slam från vattenverken som naturligtvis måste tas om hand på ett bra sätt. Den samlade effekten blir alltså en större kostnad samt en större miljöpåverkan då man fortsätter använda konventionell rening om brunifieringen fortgår. För att förhindra detta samt säkerställa en bra kvalité på dricksvattenproduktionen har Sydvatten initierat en undersökning där alternativa lösningar utreds med syftet att komplettera reningsprocessen som redan används. Det finns flera möjligheter men en som utmärker sig och som har varit fokus i denna studie, är membranfiltrering.

Membran består av porösa material som separerar olika typer av vattenburna molekyler genom filtrering. Dess avskiljningsförmåga beror alltså till stor del av membranets porstorlek och vad för slags lösning man filtrerar. En av de av tätaste membrankategorierna kallas för nanofiltrering och kan fjärma det mesta, inklusive organiskt material som består av små, komplexa och varierande molekyler. Olika membran är lämpade mer eller mindre bra för varje specifikt tilllämpning och måste således testas under verklighetstrogna omständigheter. Olika typer av nanofiltreringsmembran samt ett fåtal ultrafiltreringsmembran, som är något öppnare, har därför undersökts med vatten från den tilltänkta vattentäkten. Koncentrationen av organiskt material och färg på vattnet är några av de parametrar som har analyserats med syftet att försöka hitta vilket membran som är bäst lämpat.

Studien lyckades särskilja flera membran som producerade ett väldigt rent filtrerat vatten det vill säga att det innehöll väldigt lite organiskt material. Då vattenverken dagligen omsätter stora mängder vatten ställs dock även krav på att membranet skall ha en hög kapacitet. Efter flera olika slags testfiltreringar så ansågs ett av membranen vara lämpligt för den tilltänkta processen. Membranet kunde snabbt filtrera mycket vatten samtidigt som avskiljningen av organiskt material var väldigt hög, men även om kvalitén samt produktiviteten ansågs vara bra finns andra aspekter som man behöver ta ställning till då man bedömer lämpligheten av ett särskilt membran. I detta fall handlar det bland annat om möjligheten att behandla membranet med bakteriedödande kemikalier så som klorbaserade lösningar samt huruvida man kan backspola membranmodulerna vilket gynnar membranets kapacitet. Det identifierade membranet uppfyllde inte något av dessa kriterier och dess lämplighet måste därför utredas ytterligare. Frågetecken kring membranets flux i en fullskaleanläggning, samt graden av nedsmutsning (fouling) av membranet behöver studeras vidare där detta arbete förhoppningsvis kan utgöra en grund för vidare studier.

Summary

In many places across the northern hemisphere, drinking water treatment plants (WTPs) need to avert the effects of deteriorating quality in surface water sources caused by increasing levels of natural organic matter (NOM). The two major factors responsible for this phenomenon, also called brownification, are the greenhouse effect and changes in soil acidification. Additional treatment steps needs to be investigated and implemented in order to ensure safe drinking water in the future. Membrane technology is a candidate that has proven to be effective in terms of organic matter removal as well as functioning as a microbiological barrier. The company responsible for producing drinking water in southern Sweden, Sydvatten, has experienced a change in raw water quality and as a consequence, an increasing demand for dosing coagulant chemicals in order to treat the incoming water. They want to investigate the possibility of introducing membrane filtration units as part of the treatment process.

The efficiency of membranes are very site specific. This thesis is therefore executed with water from Lake Bolmen, which is the raw water source for the largest WTP owned by Sydvatten; Ringsjöverket. A comparative study of 12 different membranes was performed with the purpose of identifying a suitable membrane, or membranes, for removing organic matter. The membranes, ranging between tight nanofiltration to ultrafiltration, were all flat sheet membranes with the exception of one hollow fibre membrane. Screening tests with cross flow filtration were executed using a batch unit with the capacity of testing three membranes at once. An additional bench scale batch unit was used for the hollow fibre membrane. The test procedures were designed to accommodate the studying of flux, fouling and the effect of changing different operational parameters. Samples of the surface water and permeate were collected and analysed in terms of UVA_{254}, total organic carbon (TOC) and colour to estimate the retention capabilities of the membranes.

Initial screenings identified two promising membranes, Alfa Laval NF99HF and [1]DOW FILMTEC(TM) NF270 (hereinafter "NF270"), both displayed a prominent flux trend combined with efficient removal of NOM with a TOC retention of approximately 94% and 95% respectively. However, the two membranes also showed signs of irreversible fouling which would affect the efficiency and lifetime of the membrane. Changing the transmembrane pressure (TMP) affected the membranes with larger pore sizes where the permeate quality decreased at higher pressures. For the tighter membranes, NF99HF and NF270 included, this effect was negligible and the TOC retention remained at the same level. After the initial screenings, spiral wound module tests were performed with the NF99HF membrane which achieved the same level of NOM separation. However, the fouling behaviour and the flux capacity somewhat contradicted previous results where the flux was halved and the cleaning managed to restore the permeate flux completely.

The combined results from the different experiments showed that Alfa Laval NF99HF could potentially be suitable in terms of achieving a high flux without compromising the permeate quality. However, there are certain contingencies concerning flux and fouling behaviour as well as drawbacks such as the inability to treat the membrane with disinfectant chemicals containing chlorine which is an advantage from a hygienic perspective.

Keywords: drinking water; membrane technology; nanofiltration; ultrafiltration; natural organic matter

[1] ™Trademark of The Dow Chemical Company

Sammanfattning

Dricksvattenverk över hela den norra hemisfären behöver vidta åtgärder för att motverka den alltmer försämrade ytvattenkvalitén som orsakas av ökande halter av naturligt organiskt material (NOM). De två främsta orsakerna bakom detta fenomen, som också går under begreppet brunifiering, är växthuseffekten och förändringar av jordförsurningen. Företaget Sydvatten som ansvarar för att producera dricksvatten i södra Sverige har upplevt en sådan förändring av deras råvatten och har då tvingats öka doseringen av koaguleringskemikalier för att behandla inkommande vatten. Alternativa behandlingssteg måste därför undersökas och implementeras för att kunna säkra dricksvattenproduktionen i framtiden. En kandidat som visats sig vara effektiv när det gäller separation av organiskt material samt som en mikrobiologisk barriär är membranteknologin. Sydvatten vill därför undersöka möjligheten att introducera membranfiltreringsenheter som en del av deras reningsprocess.

Effektiviteten av membran är väldigt platsspecifik. Detta examensarbete har därför utförts med vatten från Bolmen som är vattentäkten för det största vattenverket ägt av Sydvatten, Ringsjöverket. En komparativ studie mellan 12 olika membran har genomförts med syftet att identifiera ett eller flera lämpliga membran för avskiljning av organiskt material. De studerade nanofiltrerings- och ultrafiltreringsmembranen, var alla plattmembran förutom ett hålfibermembran. Screeningtester med tvärströmsfltrering utfördes med en batch-enhet med kapacitet att testa tre membran samtidigt. Ytterligare en labbskaleenhet användes för hålfibermembranet. Testerna var designade så att det fanns möjlighet att studera flux, fouling och vad som sker då driftsparametrar ändras. Prover på rå- och permeatvattnet samlades in och analyserades med hänsyn på UV_{254}, total organisk kolhalt (TOC *från engelskans total organic carbon*) och färg för att kunna bedöma membranens retentionsförmåga.

Första delen av försöken identifierade två lovande membran, Alfa Laval NF99HF och [2]DOW FILMTEC(TM) NF270 (hädanefter "NF270"), som kombinerade ett högt flux med en bra separationsförmåga av NOM med TOC retentioner på cirka 94% respektive 95%. De två membranen visade dock tecken på irreversibel fouling som kan påverka effektiviteten samt livslängden av membranet. Att ändra på transmembrantrycket (TMP *från engelskans transmembrane pressure*) påverkade membranen med lite öppnare porer då permeatvattenproverna försämrades i kvalité. För de tätare membranen, där NF99HF och NF270 ingår, ansågs skillnaden vara försumbar och TOC-koncentrationen förblev oförändrad. När första delen av försöken avslutats utfördes ett experiment med en spiralmodul med membranet NF99HF som uppnådde liknande resultat gällande avskiljningen av organiskt material. Däremot visade det på ett inkonsekvent uppförande gällande fluxkapaciteten samt foulingen där det i detta fall visade att fluxet hade halverats och rengöringen lyckades återställa permeatfluxet fullständigt.

De kombinerade resultaten från de olika screeningförsöken påvisade att Alfa Lavals NF99HF skulle potentiellt sett kunna passa bra då syftet med membranet är att kunna producera ett högt flux utan att göra avkall på kvalitén på permeatet. Det finns dock vissa osäkerheter gällande fluxkapacitet och foulinguppförandet samt nackdelar så som oförmågan att kunna behandla membranet med klorinnehållande desinfektionskemikalier vilket hade varit en fördel ur ett hygieniskt perspektiv.

Nyckelord: dricksvatten; membranteknologi; nanofiltrering; ultrafiltrering; naturligt organiskt material.

[2] ™Trademark of The Dow Chemical Company

Abbreviations

CFV	Cross flow velocity
DI water	Deionized water
DOC	Dissolved organic carbon
DBP	Disinfection by-product
HFNF	Hollow fibre nanofiltration
HFUF	Hollow fibre ultrafiltration
MF	Microfiltration
MWCO	Molecular weight cut off
NF	Nanofiltration
NOM	Natural organic matter
PWF	Pure water flux
RO	Reverse osmosis
TMP	Transmembrane pressure
TOC	Total organic carbon
UF	Ultrafiltration
WTP	Water treatment plant

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1 Introduction

Being able to ensure a reliable source of potable water is a global issue and one that lately has gained more attention due to deteriorating quality of surface water. To secure a future production of drinking water, the water treatment plants need to improve and alter their process to withstand the changes in raw water quality. There are different approaches to solving this issue and one that stands out and has increased in popularity is the use of membranes. In this study, different membranes were investigated in terms of their flux capacity and capability of separating organic material for the purpose of installing a membrane facility at a treatment plant in southern Sweden.

The reason behind the deteriorating raw water quality derives from amplified fluctuations and increasing amounts of natural organic matter causing significant long-term effects in surface water across northern Europe as well as in North America. The NOM that finds its way to surface waters consists of humic and non-humic substances from decaying animals and plants and their waste products. The increased concentrations have several reasons, climate change and changes in soil acidification being two of them (Metsämuuronen, et al., 2014).

NOM can be found in all surface water and is especially common in central and southern Sweden (Köhler & Lavonen, 2015). Since approximately 50% of the national drinking water is produced from surface water according to Svenskt Vatten (2016), it is a problem that needs to be obviated. NOM is in itself not a hazardous matter. However, if the separation is not sufficient the subsequent disinfection is less effective. Furthermore, dangerous by-products (DBPs *from Disinfection by-product*) can form when the organic material reacts with chlorine. Remaining NOM in outgoing drinking water also affects the aesthetic appearance such as colour, taste and odour which is not appealing for the consumers (Metsämuuronen, et al., 2014). Conventional WTPs usually include some kind of chemical coagulation step which bind the organic material in flocs and separate them from the water through precipitation. To be able to manage the increasing levels of organic matter, a larger amount of the coagulant has to be dosed resulting in an augmenting sludge production as well as increasing costs. Hence, alternative methods to substitute or complement existing treatment steps have to be introduced in order to remove NOM.

The study has been done in collaboration with Sydvatten which is one of the largest producers of potable water in Sweden and who has experienced the effect of increasing NOM in their surface waters. The production takes place at two different WTPs, Ringsjöverket and Vombverket, where the feed water is currently taken from Lake Bolmen and Lake Vomb respectively (Sydvatten, 2016). The tunnel, which is delivering water from Bolmen to Ringsjöverket, will in the future be extended with a pipe in order to deliver water to Vombverket as well and will coincide with the construction of a new pre-treatment facility. Using membrane technology has been one of the suggested choices for this pre-treatment step hence the study has therefore focused on Bolmen which is the intended feed water.

By using membrane technology as a pre-treatment step for the raw water in a conventional WTP, a successful separation of organic material can be accomplished as well as provide an extra microbiological barrier which removes bacteria and viruses (Lidén & Persson, 2016b). For the purpose of potable water treatment, an ultrafiltration (UF) step can be combined with coagulation to achieve satisfactory NOM removal results. Same or better results, with reference to water quality, can be accomplished by instead introduce a nanofiltration (NF) step. Previous comparative studies between UF and NF membranes have shown that the latter generally results in a more effective separation which also includes DBP precursors and therefore, NF is preferable for WTPs (Lidén & Persson, 2016a). This report is consequently, a comparative study of 12 membranes ranging from UF to tight NF membranes. The membranes have different properties with different materials and densities and was evaluated by the quality and quantity of the permeate i.e. the filtered water.

1.1 Aim

The objective with this work has been to investigate screening properties for UF and primarily NF membranes, with the overall purpose to prevent the effects from increasing NOM content. The aim was to study the optimal membrane properties when screening for retention of organic matter with water from Lake Bolmen. The specific research questions that was investigated within the project were:

- Which membrane/membranes are most suitable in terms of organic matter removal?
- How will fouling affect the different membranes?
- How will the flux and the ability to separate NOM change with varying operational conditions such as different transmembrane pressures?

1.2 Limitations

This comparison will focus on the efficiency and suitability when it comes to organic removal by membrane filtration, hence no calculations concerning cost or environmental impact will be included in the study. The microbiological barrier qualities of each membrane will not be investigated neither.

The tests will be limited in terms of bench scale analyses where very small samples of the membranes were tested. In addition, due to the heat transfer from the pump, the tests also had to be executed at a higher temperature than what it should be operated at in full scale. Temperature do affect the performance of a membrane as explained in section 5.3.6. However, it was kept at the same level for all tests in order to reduce the source of error.

2 Potable Water Treatment

Potable water treatment has in some sense been in practice from 4000 B.C where the treatment were mostly a remedy for aesthetical issues (EPA, 2000). Since then, the process of treating water has evolved due to the raw water sources as well as the demands and requirements that exists in today's society. In Sweden we have access to good quality drinking water in almost every tap. Raw water is usually plentiful and there are rarely any water shortages.

2.1 General water treatment

Half of the drinking water in Sweden is currently produced from surface water and the rest is a product from groundwater, whether it is natural or artificial. The natural groundwater is extracted from aquifers and pumped up from wells which means that the water is usually of much better quality than surface water due to the natural filtration that takes place. In some places one can create the same effect by letting surface water infiltrate layers of gravel and sand, hence creating an artificial groundwater. (Svenskt Vatten, 2016)

Depending on the source of the water, the treatment can look slightly different when comparing treatment plants. However, it is common for surface water treatment plants to include pH adjustments, some kind of coagulation step, followed by flocculation and sedimentation, filtration and as a last step; disinfection. The process for groundwater treatment usually consists of fewer steps but includes similar treatment. (Svenskt Vatten, 2016)

During the coagulation process, the settled flocs create a sludge which has to be disposed of or treated. Increasing levels of NOM in the surface water require more coagulant chemicals and in turn produces more sludge. The consequence is a higher environmental impact as well as an increased cost for the treatment plant. Hence alternative treatment options, such as membranes which can potentially reduce the sludge production, can also have additional positive effects from an environmental point of view in addition to a greater ability to separate organic matter.

With this in mind, the study looked at two water treatment plants in southern Sweden, Ringsjöverket and Vombverket. Both of them are owned and operated by Sydvatten and are presented below.

2.2 Ringsjöverket

The WTP Ringsjöverket is situated in Stehag which is approximately 45 km northeast of Malmö. It was commissioned in 1963 and is now producing around 1.4 m^3/s as a yearly average. The produced drinking water goes to the municipalities of Eslöv, Helsingborg, Höganäs, Kävlinge, Landskrona, Lomma, Lund, Svalöv, Ängelholm parts of Malmö and Staffanstorp. The feed water was initially taken from Lake Ringsjön. However, deteriorating quality and increasing demand initiated the construction of the Bolmen tunnel in 1975 which transports water from Lake Bolmen in Småland. The construction of the tunnel took 12 years to complete and is the result of prospective planning from five neighbouring municipalities who united and created Sydvatten AB. The tunnel is 80 km long and eventually ends up in a pipe network which carries the water from the tunnel to the WTP. The timespan for the water transport is around one week from Bolmen to Ringsjöverket. Out of the 1.3 m^3/s which is transported in the tunnel, around 92% is water from Lake Bolmen and the rest comes from infiltrating groundwater. Besides Bolmen, Ringsjöverket can also use water from the closely situated Lake Ringsjön. However, this is just a redundant raw water source if something prohibits the water from Lake Bolmen to be used. (Sydvatten, 2016)

2.2.1 Process

The surface water is filtered through a 500 µm drum filter at the inlet of the tunnel hence the first step at the WTP is a pH adjustment as shown in Figure 1. This is done to facilitate and streamline the chemical precipitation step. The chemicals used are sodium hydroxide for pH adjustment and ferrous chloride as a coagulant. The water is mixed in order for even flocs to form before it sediments using lamellas. Prior to the rapid sand filter, the pH is adjusted once more to precipitate any leftover iron which is then removed along with remaining flocs once filtrated. The slow sand filter improves odour and taste as well as degrades any organic material. The water is later dosed with carbon dioxide to increase the alkalinity before finally reaching the last step which is hypochlorite treatment as disinfection. (Lidèn, et al., 2015; Sydvatten, 2016)

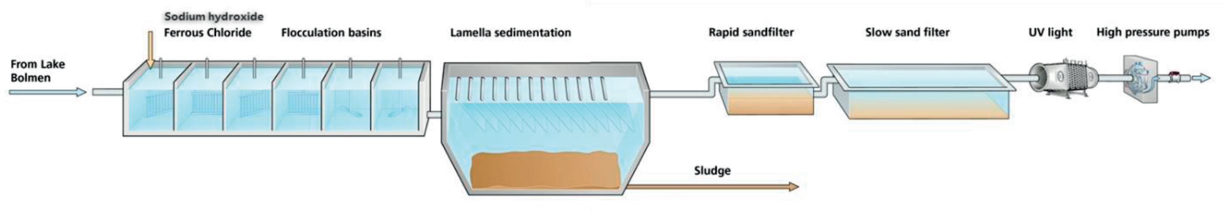


Figure 1. Treatment steps at Ringsjöverket. Published with kind permission from Sydvatten.

Ringsjöverket is currently commissioning another disinfection step which includes one of Sweden's largest UV-light facilities. The UV treatment will complement the hypochlorite step which means that the chlorine dosage can be reduced. (Sydvatten, 2015)

2.3 Vombverket

Vombverket is Sydvattens second WTP and is also situated 45 km from Malmö. It was commissioned in 1948 and located next to the surface water source Lake Vomb where it draws approximately 1 m^3/s from the lake. Vombverket produce drinking water to the municipalities of Burlöv, Malmö, Staffanstorp, Svedala, Vellinge and parts of Lund and Eslöv. (Sydvatten, 2016)

2.3.1 Process

The process at Vombverket is designed to replicate the natural filtration process. It includes 54 infiltration beds where the water seeps through sand and gravel layers to a groundwater reservoir. From the reservoir the water is pumped up from 114 different wells and then aerated to remove iron and manganese. A softening step is required to remove hardness from the water and is accomplished in a reactor where sodium hydroxide is added and lime precipitates. To be able to separate smaller particles and molecules, a mixing step with added ferrous chloride is placed before the rapid sand filters. Finally monochloramine is added to the water for its residual effects before distribution through high pressure pumps. The process is shown in Figure 2. (Sydvatten, 2016)

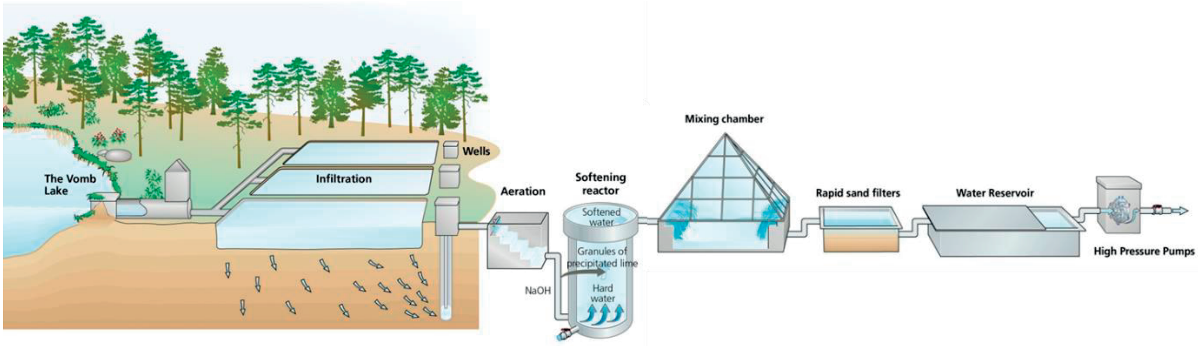


Figure 2. Treatment process at Vombverket. Published with kind permission from Sydvatten.

2.4 Raw water

The surface water sources used by the WTPs Ringsjöverket and Vomberket are presented below. Characteristics of the lakes are found in Table 1.

2.4.1 Lake Bolmen

Lake Bolmen is located in Småland and is the 10^{th} biggest lake in Sweden. The catchment area spreads out on 1650 km^2 and constitutes of mostly forest (48%) but also wetlands (22%), lakes (20%) and pastures (9%). The lake is classified as an oligotrophic with mild humus content (VISS, 2015).

2.4.2 Lake Ringsjön

Unlike Bolmen, Lake Ringsjön is situated in close proximity to the WTP Ringsjöverket as indicated by the name. The lake has a 395 km^2 catchment area whereof the greater part of the land use consists of agriculture. According to VISS (2015) the lake suffers from eutrophication with increased levels of phosphorous as the main reason.

2.4.3 Lake Vomb

Lake Vombsjön is situated in the middle of the agriculture fields of Skåne and has a catchment area of 447 km^2. It has been used as a surface water source for potable water treatment since the commissioning of the WTP in 1948. The surrounding activities and land uses have affected the lake which is suffering from eutrophication where an excess of primarily phosphorus is causing decreasing water quality and recurring algal blooms. (Sydvatten, 2016)

Table 1. Mean annual water quality values for the three lakes used as raw water sources by Sydvatten. (Data was retrieved from the production rapport during 2015 from Sydvatten)

	TOC (mg/l)	Hardness (°dH)	Colour (mg/l Pt)	Turbidity (FNU)
Lake Bolmen	9.8	1.2*	73	2.1
Lake Ringsjön	8.6	6.5	46.7	8.4
Lake Vombsjön	6.9	10.4	25.6	4.2

*Value taken from the Bolmen tunnel water.

2.5 Planned pipe addition to the Bolmen tunnel

The tunnel, which is currently transporting water from Bolmen to Ringsjöverket, will in the future be extended with a pipe in order to deliver water to Vombverket as well. The feed water will then consist of both Bolmen water and water from Lake Vombsjön. The project will coincide with the construction of a new pre-treatment facility at Vombverket which will be placed before the infiltration beds. The purpose of the pre-treatment is to reduce the organic matter and also potentially reduce pharmaceuticals and pesticides. This will most likely be accomplished with membrane filtration units and is the incitement behind the study.

3 Previous studies

Comparative studies between membranes have been performed previously, some with the intent of analysing the organic matter removal. A recent study in Finland investigated the applicability of loose nanofiltration membranes for the removal of NOM. It was found that membranes with a cut-off of approximately 1-5kDa had the potential to satisfactorily reduce NOM concentrations whilst achieve a low hardness reduction. Hence, these membrane properties would be suitable for soft waters. The 5 different membranes which were tested in the Finnish study ranged from tight NF membranes to UF. However it appears that the factor affecting the removal efficiency of NOM was the material more than the actual pore size and distribution. (Laurell, et al., 2015)

The results of membrane screenings are very site specific which means that the performance of a membrane can alter from location to location depending on the feed water and the surrounding conditions. However, there has been studies that have taken place at Ringsjöverket using membrane filtration with water from Lake Bolmen. These studies, performed by Lidén et. al (2016a and 2016b), focused on hollow fibre membranes, HFUF with an added coagulant and HFNF, and compared these to the conventional treatment that is currently installed. The focus of the study was to investigate parameters which could be used to estimate cost and asses environmental impact. The results from the study was that operational costs would increase by 6% and 30% for HFUF and HFNF respectively. Although, from an environmental point of view there are benefits of using the HFNF due to the sludge reduction that the process can achieve. The metal that is used as the coagulant can be hard to recycle and there are also other environmental drawbacks with chemicals as coagulants that ends up in the sludge. Therefore, reducing or eliminating the coagulant chemicals would be ideal from a sustainable perspective.

Lidén also claims that despite the fact that NF is more expensive due to a higher energy demand that derives from a higher pressure and crossflow, it can still be preferable even from an energy requirement perspective. It might not be excessively larger but simply a redistributed demand from production of chemicals to the hydraulic requirements that comes with the membrane plant.

4 Organic Matter

Organic matter are a large variety of chemical compounds all containing carbon. It can be found in terrestrial environments as well as aquatic and derives from the decomposition of animals and plants. Hence, organic matter has an important role in the movement of nutrients in our surroundings.

4.1 What is Natural Organic Matter?

Natural organic matter is present in all surface water and is the reason behind the brownish colour in lakes. The compounds that make up NOM, are mostly humic and is a mixture of inhomogeneous species that derives from decaying animals, plants and their residues (Metsämuuronen, et al., 2014). Beside terrestrial activities, NOM can also be derived from microbiological activities within the waterbody (Lidén, 2016). Humic substances are aromatic rings linked with aliphatic components and can be divided in three different categories based on solubility; humic acids, fulvic acids and humin (Sillanpää, 2014; Hong & Elimelech, 1997). These species come in varying molecular sizes, functional groups and properties. The composition is a result of pH, climate, microbiological degradation processes, ion and sediment content of the water and what kind of plant life that is present in the surroundings. The concentration of NOM present in surface water is therefore mainly dependent on two things; the biogeochemical cycles of the surroundings and the seasonal variations. The latter affects the content in terms of heavy rains, snow melts, algal blooms or drain seasons when more or less of the organic matter makes its way to surface waters (Sillanpää, 2014; Metsämuuronen, et al., 2014).

There are different analytical methods to approximate the aquatic NOM content. The most frequent parameters to measure in order to monitor the water quality at WTPs are TOC, DOC, COD, UV_{254}, turbidity and colour (Sillanpää, 2014). Dissolved organic carbon (DOC) is defined as the organic content left in a water sample after its been filtrated through a 0.45 µm filter. However, it is usually approximated by measuring the TOC instead.

In central and southern Sweden, humic surface water lakes are very common with an average concentration of organic TOC around 7 mg/l but it can reach around 15 mg/l in some cases (Köhler & Lavonen, 2015).

4.2 Increasing concentrations of NOM

Several studies have shown increasing trends over the last 20 years of organic carbon species found in surface waters across Northern America, UK, central Europe and Scandinavia (Ekström, 2013; Sillanpää, 2014). The increase has led to a phenomenon known as brownification which refers to the intensification of colour that is generated by a higher TOC content. Even though brownification is more apparent in lakes which are already high in colour, it has also been discovered in other types of lakes such as eutrophic and oligotrophic clear water lakes (Ekström, 2013). In addition to a general increasing trend of NOM species there are also indications of more drastic and varying fluctuations (Köhler & Lavonen, 2015).

There are several possible reasons behind the increase in NOM. One major reason could be climate change and what it entails, such as vigorous rainfalls and floods as well as more severe droughts (Metsämuuronen, et al., 2014; Sillanpää, 2014). Figure 3 shows the factors that can contributes to an increased concentration of NOM in lakes as a consequence of climate change in Fennoscandia.

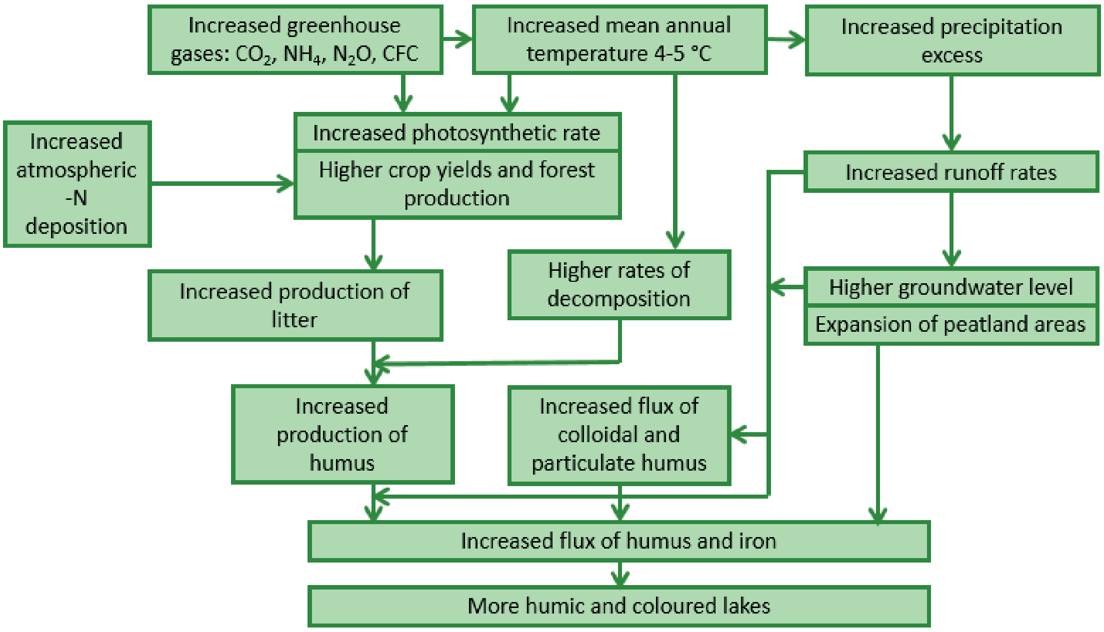


Figure 3. Factors that affect the increased concentrations of NOM in lakes. Modified from (Forsberg, 1992). Published with permission from Springer Copyright Clearance Center.

It has also been claimed that factors such as changes in soil acidification may be an important contributor to the brownification. Over the last 20 years, acid rainfall has decreased as a result from improvements concerning emissions from industrial activities and fossil driven vehicles which consequently affected the pH in the ground. Ekström (2013) claims that less acidic conditions affects the soil horizon in such a way that the organic matter content increases in the surface waters due to a higher solubility and mobility of the NOM species. Other factors that could affect the increase are land use changes, increasing CO_2 concentrations or a combination of several factors (Ekström, 2013).

4.3 Separation of NOM

The current conventional method of removing NOM in Sweden is achieved by coagulation (Svenskt Vatten, 2016). A metal salt, usually aluminium or iron salt, is added to the raw water in order to form aggregates which then can be separated through for example sedimentation (Kemira Kemwater, 2003). The purpose of the chemical precipitation step is to separate different kinds of molecules in the water. Sillanpää (2014) describes that NOM necessitates the major part of the added coagulant. Consequently, any changes in NOM concentrations in the raw water have a significant effect on the subsequent treatment. Several WTPs, including Ringsjöverket, have been forced to increase their coagulant dose over the last 20 years to accommodate the increasing and more fluctuating concentrations of NOM that has been noticed during this time (Lidén, 2016). A graph displaying the changes in NOM-content expressed as UV_{254} absorbance is shown in Figure 4.

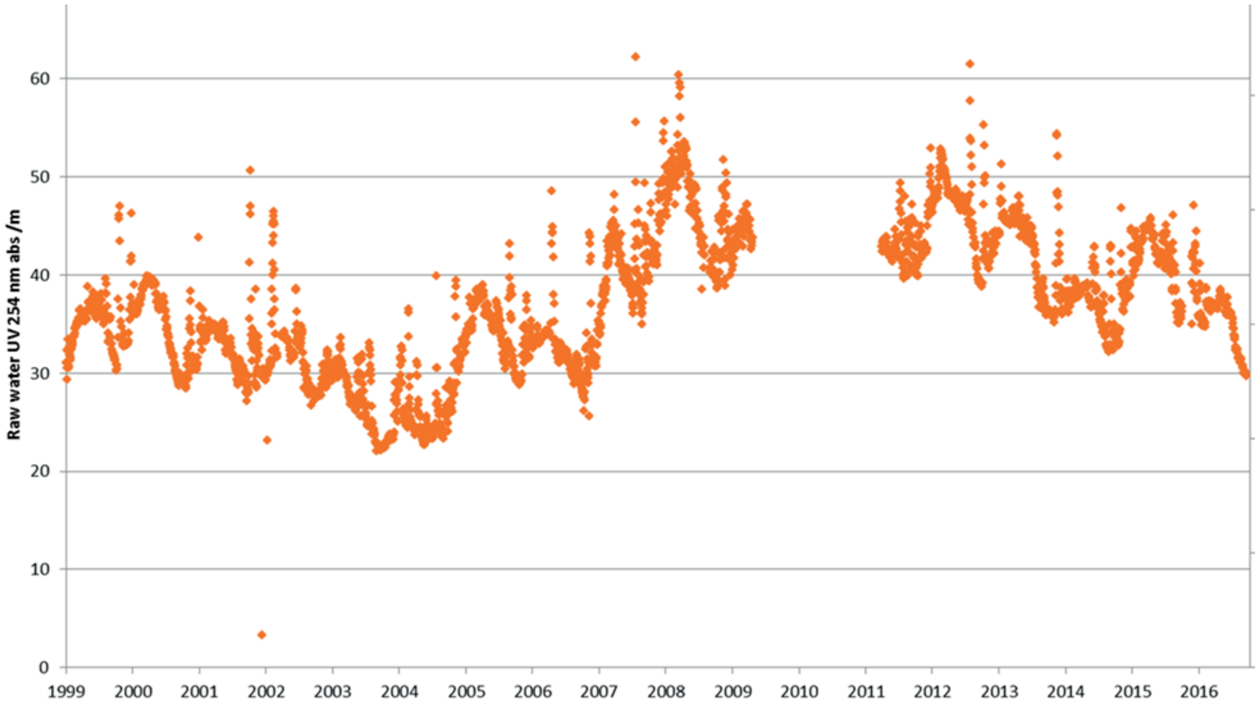


Figure 4. The measured of UV_{254} values from 1999-2016. During 2009-2011 the WTP used Lake Ringsjön as feed water hence the data from this period was excluded from this graph. Published with kind permission from Sydvatten.

Even though an increased dosing can restrain any effects on the finished product, the complexity and variety of the aquatic NOM creates difficulties when separating it at WTPs. Furthermore, increasing levels of NOM in the surface water as well as increasing fluctuations puts more and more stress on the efficiency and stability of the treatment as it is harder to optimize the operation and insure proper process control (Köhler & Lavonen, 2015).

The organic matter is not harmful or toxic in itself. Nevertheless, an inefficient removal during potable water treatment can have serious effects on the water quality since NOM works as a carrier for metals and hydrophobic organic chemicals (Sillanpää, 2014). In addition, it affects aesthetic properties such as colour, taste and odour which is undesirable for the consumers. NOM has also been shown to be the primary source of DBPs. These by-products are generated when residual organic compounds in the water react with chlorine used during the disinfection treatment and form species such as trihalomethanes and haloacetic acids (Metsämuuronen, et al., 2014). These halogenated organics are carcinogens and therefore hazardous for consumers (Zularisam, et al., 2006). A summary of the effect that increasing NOM concentration have for the consumers and WTPs is shown in Figure 5.

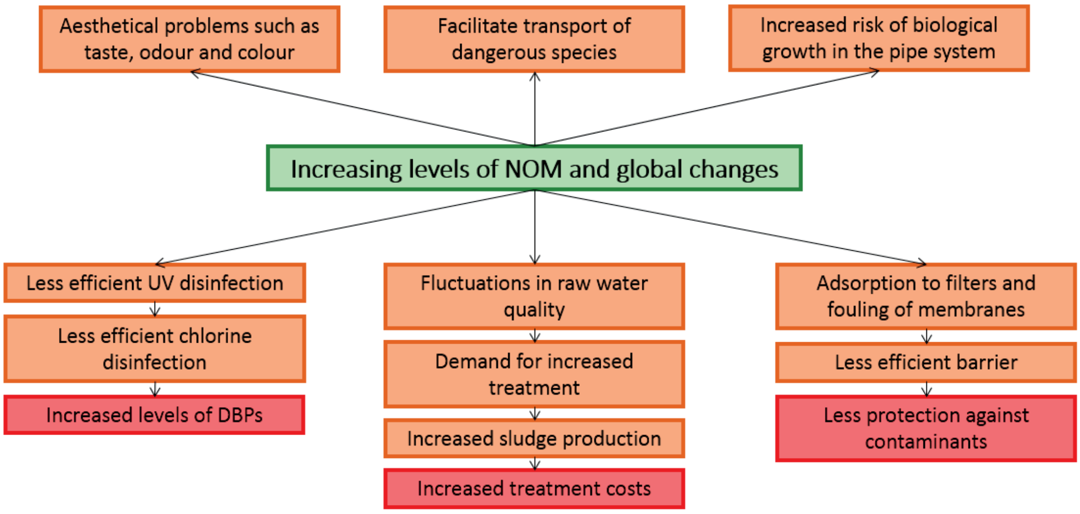


Figure 5. Consequences of increasing levels of NOM and increasing impact from climate change. Modified from (Köhler & Lavonen, 2015). Published with the kind permission from Stephan Köhler.

5 Membrane Technology

The use of membrane filtration is considered as a space-efficient and energy saving alternative to conventional treatment (Jönsson, u.d.). Furthermore, the retention capabilities of membrane processes are very versatile and the fact that it can be used as a microbiological barrier makes it a very good candidate for a lead role in water treatment solutions in the future (Machenbach, 2007).

Low-pressure membranes has been a part of the drinking water treatment technology since the late 1980s (Metsämuuronen, et al., 2014). Factors such as stricter regulations, cost reductions for the technology, more application areas, system design and operation improvements has since then sparked a growing trend for this type of filtration process which has led to the status it has today (American Water Works Association, 2015).

5.1 Filtration process

Membrane filtration is a separation process using a physical barrier to separate different constituents from water. The technique is based on size exclusion where everything from ions to microorganisms can be separated (Jönsson, u.d.). The membrane divides the feed into two streams, the retentate and permeate. The retentate is the part of the feed water that can't pass through the membrane due to rejection caused by the membrane's pore size and pore size distribution (Metsämuuronen, et al., 2014). Permeate is the water that pass through the membrane and can contain various degrees of soluble material, again depending on the character of the membrane pores. A simple sketch of the process can be seen in Figure 6.

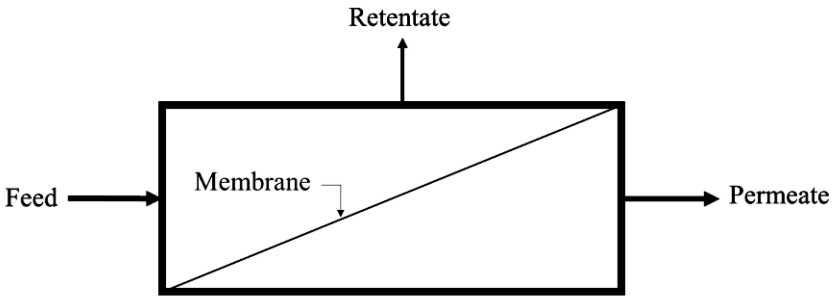


Figure 6. Membrane process.

The application areas within water treatment for membrane technology are many and include production of drinking water, treating waste water and treat or recover valuable constituents from industrial effluents. Membranes are also used within the drug and food industry to concentrate, purify or fractionate macromolecular mixtures, separate gases in petrochemical processes and for medical application such as components in artificial organs (Strathmann, et al., 2006).

When it comes to drinking water treatment, membrane units can either complement other treatment steps or constitute as a stand-alone process (Metsämuuronen, et al., 2014). The applications are diverse and include for example desalination, turbidity reduction, disinfection, removal of NOM, softening and specific ion removal (Hammer Sr. & Hammer Jr., 2014). The choice of membrane significantly depends on the kind and degree of removal the system should achieve, especially when the spectra of removable compounds is so broad.

Membranes are usually categorized according to their pore size which can alter from around 10 µm down to virtually non-existent pores as in the case with reverse osmosis membranes. The categories in decreasing size are; microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). The selectivity and typical operational pressures for the different types of membranes are shown in Figure 7. Although, one should bear in mind that this categorisation is somewhat fluent and the operational pressures and pore sizes do overlap each other to some degree and can also vary depending on intended process. The unit Dalton is often used when pore sizes are concerned as it is used for indicating molecular mass. The relationship between micrometres and molecular mass in Daltons are also shown in Figure 7 as the orange bar.

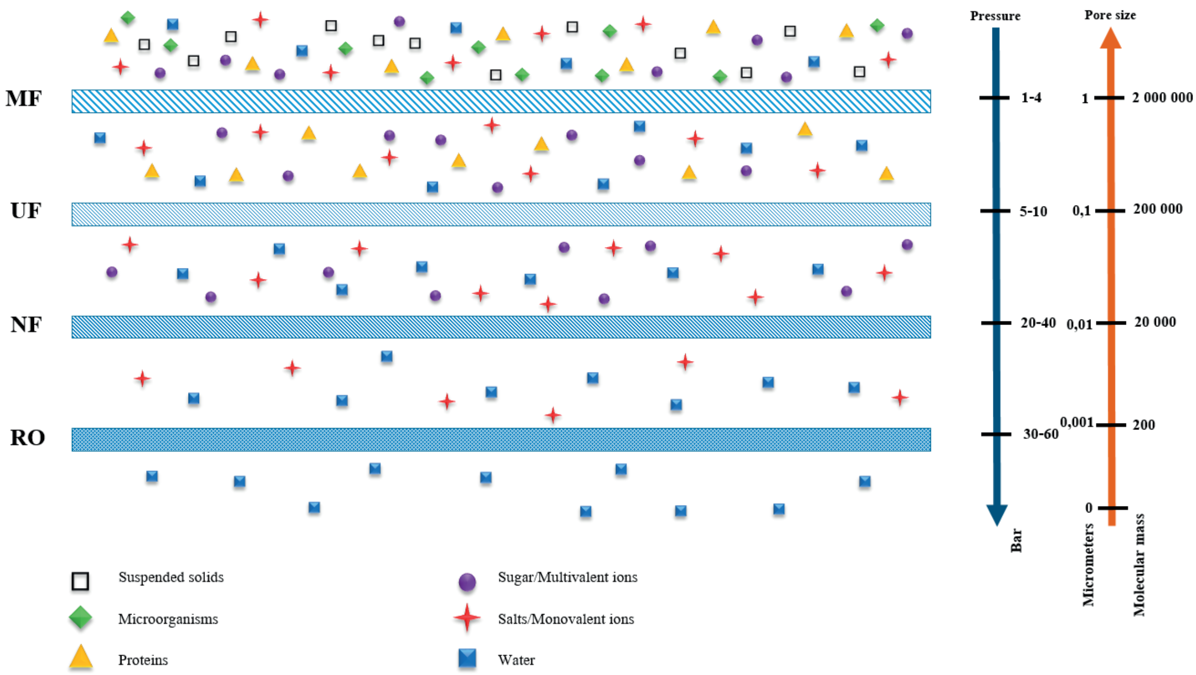


Figure 7. The different types of membrane categories depending on their pore size and size exclusion. Modified from (Nottingham University - Environmental Technology Centre, u.d.). Published with the kind permission from Michele Pattison, Nottingham University.

Another way of describing the retention capabilities of a membrane is in terms of its molecular weight cut off (MWCO). This way of characterizing membranes is not a standardised method. However, it is useful when comparing membranes and is often used amongst membrane manufacturers. MWCO is, according to for example Dow (2016) and Synder filtration (u.d.), defined as the lowest molecular mass (in Daltons) at which greater than 90% of a solute with a known molecular mass is retained by the membrane.

Even though the pore size of a membrane is significant for the outcome, there are also other properties affecting the performance such as pore size distribution, material and sometimes surface charge densities. Hence, two membranes with the same pore size could have a very different removal efficiency depending on the membrane specific properties, the applied feed water and feed water flow.

5.1.1 Ultrafiltration

UF membranes are typically operated between 1-10 bars, and is usually applied when the aim is to retain macromolecules, proteins and colloids due to size exclusion (Jönsson, u.d.). They are porous membranes and therefor usually categorised by their MWCO value. The complexity and diversity of NOM compounds does potentially provide a challenge to successfully achieve an efficient and satisfactory removal of the organic matter solely with UF. An option would be to add a coagulant prior to the filtration process which would cause a conglomeration with a greater retention as a result.

5.1.2 Nanofiltration

NF membranes are operated at higher pressures than the UF membranes, generally around 5-40 bar, but again this is depending on what type of process. Due to the diminutive size of their pores, which are almost unmeasurable, NF membranes are usually categorised according to their ability to retain different species of salt. NF can successfully separate almost all kinds of water held compounds besides small monovalent ions, it is therefore very effective for filtration of NOM. However, a higher removal efficiency comes with a higher cost due to the increased pressure i.e. energy demand.

5.2 Types of membranes

Besides the composition of the membrane itself there are different configurations when assembling membrane units. As when choosing the type of membrane to use, the configuration is also very specific for the intended process and type of solution. In this study, spiral wound and hollow fibre modules are evaluated. However there are many different options on the market. Some of the most widely known within drinking water treatment are:

- Spiral wound
- Hollow fibre
- Tubular
- Plate and frame

A spiral wound unit consists of several flat sheet membranes packed in layers in a spiral fashion around a hollow permeable core where the permeate is collected. If the membrane layers are wound tighter, it increases the membrane area and subsequently produce more permeate due to a higher flux (Alfa Laval, u.d.). The layers are separated by feed spacers with the purpose of evenly distribute the feed solution over the entire membrane area. This spiral wound type of configuration allows a great adaptability of the membrane unit, hence it is easy to customize to the specific process. Although, the flat-sheet nature of the membranes does provide difficulties when it comes to washing or rather, keeping the surface clean and prevent it from fouling. Therefore it is more commonly used for processes that do not require as much backwashing or pressure based integrity tests to maintain sufficient treatment objectives, such as with nanofiltration or reverse osmosis (American Water Works Association, 2015).

As the name indicates, a hollow fibre membrane consists of hundreds, or sometimes even thousands, of semipermeable fibres with a small hollow centre which are all assembled closely together in a module. The sturdiness of the fibres usually allows for backwashing and chemical cleans which is an advantage within drinking water treatment. The membrane units can be designed for two different procedures, for inside-out or outside-in flow. The inside-out configuration enables the flow to distribute more evenly as the feed enters through the core of each fibre and the permeate is pushed through the semipermeable pores of the fibre walls. This is an advantage compared to the outside-in configuration which can provide problems with hydrodynamics within the module such as dead zones or flow channelling. However, a flow from the outside-in does avoid plugging of the fibres by larger particles as well as provide a lower head loss through the module. (American Water Works Association, 2015)

5.3 Operational parameters

The performance of a membrane can be somewhat influenced by changing different operational parameters. The most relevant ones for this study are described below.

5.3.1 Flux

The permeate is measured in terms of flux which is the amount of water that is filtered through the membrane per unit area of the surface per unit time often expressed as l/m^2h or in short lmh. The membrane properties that affect the flux are porosity, pore size and how thin the membrane is. If a thin membrane have a high porosity and large pore sizes, the flux is high. From an economical perspective it is of course preferable to have a high flux since the energy demand will be lower and it will be more space efficient. (Jönsson, u.d.)

An additional factor which has great impact on the performance of the membrane, and subsequently the flux, is the concentration polarization. Rejected molecules accumulate on the surface of the membrane, causing a higher concentration near the membrane surface than in the bulk solution. This concentration gradient enables particles to diffuse back into the solution. This phenomenon is the result of a molecule build-up on the surface of the membrane and is sometimes referred to as a filter cake or gel once the concentration becomes constant. (American Water Works Association, 2015)

5.3.2 Retention

The retention of the membrane is the ability to retain substances, particles and molecules. When mentioning retention it is usually the observed retention which is referred. The observed retention is presented in equation 1, where C_p and C_b is concentration in permeate and bulk respectively. Retention is expressed in percentage for instance, if a membrane achieves a retention of 100 % it means that it rejected everything and only water was able to filter through. The retention of a membrane is dependent on concentration polarization which in turn is affected by different operational parameters. It is therefore important to relate to given retentions as condition specific values. (Jönsson, u.d.)

$$R_{obs} = 1 - \frac{C_p}{C_b} \qquad \text{(Eq 1)}$$

5.3.3 Recovery

How much of the feed water that becomes permeate is called the systems recovery and can range from around 30-98% depending on the process (Hammer Sr. & Hammer Jr., 2014).

5.3.4 Transmembrane pressure

With different TMPs one can affect the flux and the retention, to what extent depends on the membrane process and the feed solution (Jönsson, u.d.). When filtrating pure water through clean porous membranes, the flux (J) increases linearly with an increasing TMP (ΔP) and is inversely proportional to the solution viscosity (μ). This can be described using an altered Darcy's law, equation 2, where R_m denotes the hydraulic resistance of the clean membrane.

$$J = \frac{Q_{total}}{A} = \frac{\Delta P}{\mu R_m} \quad \text{(Eq 2)}$$

A similar pattern can be seen when filtering solutions at low TMPs as well. However, when the concentration gradient increases with a higher TMP, the flux levels out until reaching a limiting flux due to the polarization. Equation 3 shows the modified flux equation where K is the mass transfer coefficient, C_m is the maximum particle concentration at the membrane surface and C_b is the concentration in the bulk. (American Water Works Association, 2015)

$$J_{lim} = Kln\left(\frac{C_m}{C_b}\right) \quad \text{(Eq 3)}$$

5.3.5 Cross flow velocity

Another parameter which is able to affect the performance of a membrane process is the cross flow velocity (CFV) which is the circulation velocity of the water. A higher CFV can significantly reduce concentration polarization and the formation of a cake layer on the membrane surface due to a higher velocity of the water which prevents some molecules from accumulating. This effect is most apparent for membranes with a high permeability i.e. a high pure water flux since the concentration polarization is more prominent with increasing permeability. (Jönsson, u.d.)

5.3.6 Temperature

Temperature has a significant impact on the performance of the membrane which primarily is due to the impact the viscosity has on the flux, see equation 2. The viscosity of water increases with decreasing temperature which provides a challenge when operating a membrane process in Scandinavian countries where the climate is colder most part of the year (Lidén & Persson, 2016a).

5.3.7 Volume reduction

The relation between the extracted permeate volume, V_p, and the initial volume, V_0, is called the volume reduction, VR, and is shown in equation 4 (Jönsson, u.d.). A higher volume reduction means that the concentration of the feed water is increasing and will therefore affect the flux.

$$VR = \frac{V_p}{V_0} \quad \text{(Eq 4)}$$

Volume reduction is usually expressed in percentage. Another way of describing this ratio is to instead relating the initial volume to the remaining volume, that is the retentate V_r (Jönsson, u.d.). The quotient is called volume reduction factor, denoted VRF, and can be seen in equation 5.

$$VRF = \frac{V_0}{V_r} \quad \text{(Eq 5)}$$

The correlation between volume reduction and its factor is presented in equation 6.

$$VRF = \frac{100}{100-VR} \quad \text{(Eq 6)}$$

As an example; a volume reduction of 50% then corresponds to a VRF of 2, and 80% means a VRF of 5.

5.4 Fouling

A well-known negative aspect concerning membrane technology is fouling which is a mechanism that potentially can have distinguishable effect on the performance and lifetime of a membrane. A decreasing flux and yield over time despite a constant pressure is a sure sign of fouling caused by the accumulated matter which is deposited on the surface or adsorbed by the membrane. There are three different types of fouling mechanisms; pore blocking, pore narrowing and cake or gel layer formation, these are shown in Figure 8.

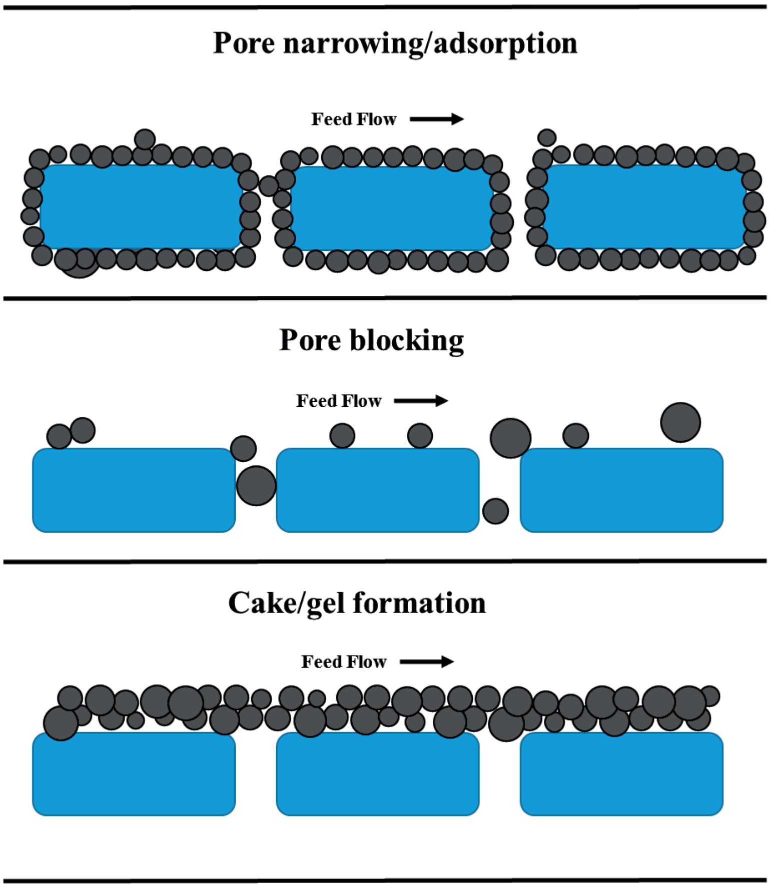


Figure 8. The three different fouling mechanisms.

The pore blocking and narrowing are known as internal mechanisms whilst the cake layer formation takes place on the surface and is referred to as an external mechanism. Pore blocking occurs when the molecules are approximately the same size or slightly bigger than the pores in the membrane. The molecules then tend to block the pores, hence the total number of pores available for filtration decreases and the flux is reduced. Molecules with a smaller diameter than the pores are deposited alongside the pore walls and results in a narrowing mechanism. This reduces the pore volume whilst keeping the number of pores unchanged. Cake formation takes place when the molecules carried in the feed are deposited on the surface of the membrane due to the molecules being too big to pass through the pores. This also results in a decrease of flux due to the number of pores available is limited. (Metsämuuronen, et al., 2014; American Water Works Association, 2015)

As described, fouling causes alterations of the membranes properties which is the reason behind the decrease in productivity and is usually categorized as reversible or irreversible. Reversible fouling is the deposition of particles, usually in a cake, that can be removed by chemical cleaning or backwashing. However, when molecules are absorbed or are plugging the pores, the cleaning can prove unsuccessful and the fouling is therefore permanent thus irreversible.

5.5 Membrane filtration modes

A membrane process can be operated in two different filtration modes; dead-end or crossflow filtration. During a dead-end filtration the flow is perpendicular to the membrane surface and the entire flow is forced through the pores by applying pressure. This configuration implies a build-up of particles on the surface of the membrane and the process would have to be backwashed or cleaned regularly depending of course on the concentration of the solution (Munir, 2006). The dead-end filtration is more suitable for membranes with a larger pore size since the energy demand would be a lot higher when using membranes with smaller pores.

The other filtration mode, the crossflow, use a cross flow that flows parallel with the membrane surface and therefore reduces the amount of molecules that accumulate on the surface compared to dead-end filtration. The feed flow is pressurised which is the driving force for filtration through the membrane whilst a high cross flow velocity insures a turbulent condition at the membrane surface. A crossflow filtration mode is very suitable for solutions with high concentrations (Munir, 2006). Both of the filtration modes are shown in Figure 9.

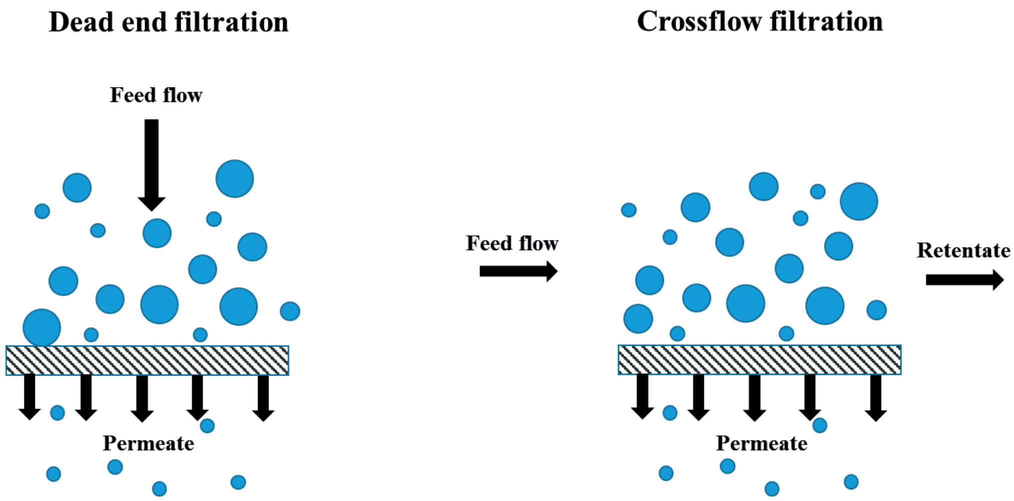


Figure 9. The two different filtration modes within the membrane process.

6 Materials and Method

To investigate the properties of the membranes, different sets of tests were designed all of which are described below along with specifics of the raw water and membranes used. All tests and analysis were performed at the Department of Chemical Engineering from the beginning of October 2016 until the end of January 2017.

6.1 Raw water

Raw water was delivered from the WTP Ringsjöverket to the Department on 6 different occasions; 3rd, 10th and 17th of October, 7th and 14th of November 2016 and 10th of January 2017. 50 litres was delivered each time with the exception of the 10th of January when 200 litres were delivered. The water was used within 5 days of delivery and in the meantime it was stored in a cooling-room at 4 °C.

6.2 Membranes

All of the membranes used in this study are found in Table 2 and are sorted according to specified cut off and selectivity.

Table 2. Compilation of all the membranes used in this study.

Model	Manufac-turer	Type of membrane	MWCO[VII] (Da)	Selectiv-ity	Material	Chlorination possible
			Ultrafiltration			
ETNA10	Alfa Laval	Flat sheet	10 000	-	Composite fluoro polymer	Yes
UFX5	Alfa Laval	Flat sheet	5000	-	Polysulphone permanently hydrophilic	Yes
GH	GE	Flat sheet	2500	-	Polyamide on polysulfone	Yes
ETNA01	Alfa Laval	Flat sheet	1000	-	Composite fluoro polymer	Yes
			Nanofiltration			
HFW1000	Pentair	Hollow fibre	1000	-	PESm/PES [I]	Yes
HL	GE	Flat sheet	150-300	98% [IV]	Polyamide on polyethersulfone	Yes
NF99HF	Alfa Laval	Flat sheet	-	≥ 99% [V]	Thinfilm composite on polyester	No
NF270-400/34i Element	Dow	Flat Sheet		>97%[VI]	Polyamid thinfilm composite	No

			Tight nanofiltration			
AP	GE	Flat sheet	-	95% [III]	Polyamide on poly-sulfone	Yes
AL	GE	Flat sheet	-	Similar to AP	Polyamide on poly-sulfone	Yes
DL	GE	Flat sheet	150-300	96% [IV]	Polypiperazineamide on polysulfone	Yes
DK	GE	Flat sheet	150-300	98% [IV]	Polypiperazineamide on polysulfone	Yes

[I] Polyethersulfone, m stands for modified
[II] Polyvinylpyrrolidone
[III] Average NaCl rejection on 500 ppm NaCl, 520 kPa, 25 °C
[IV] Average $MgSO_4$ rejection on 2000 ppm $MgSO_4$, 760 kPa, 25 °C
[V] Average $MgSO_4$ rejection on 1000ppm $MgSO_4$, 900 kPa, 25 °C
[VI] Average $MgSO_4$ rejection on 2000 ppm $MgSO_4$, 480 kPa, 25 °C
[VII] Specifications from the manufacturers

6.3 Experimental setup

6.3.1 Equipments

There were two different cross flow filtration units used for this study, one of own design at the Department of Chemical Engineering and one provided by Pentair. The membrane filtration unit used for flat sheet membranes and located at the apparatus hall at the department, was a batch unit where 12-13 litres of feed water was added to the tank before every test run. The feed water was then pumped and divided into four different lines where a flat sheet membrane with the approximate diameter of 5 cm and a membrane area of 19.6 cm^2 was placed. The permeate could be collected or recirculated back to the feed tank. When permeate was collected it was done so on electronic balances placed underneath each module. The balances were connected to a computer which logged the flux. The retentate could also be drained through the outlet hose or recirculated back to the feed tank. A flow scheme of this set-up is shown in Figure 10.

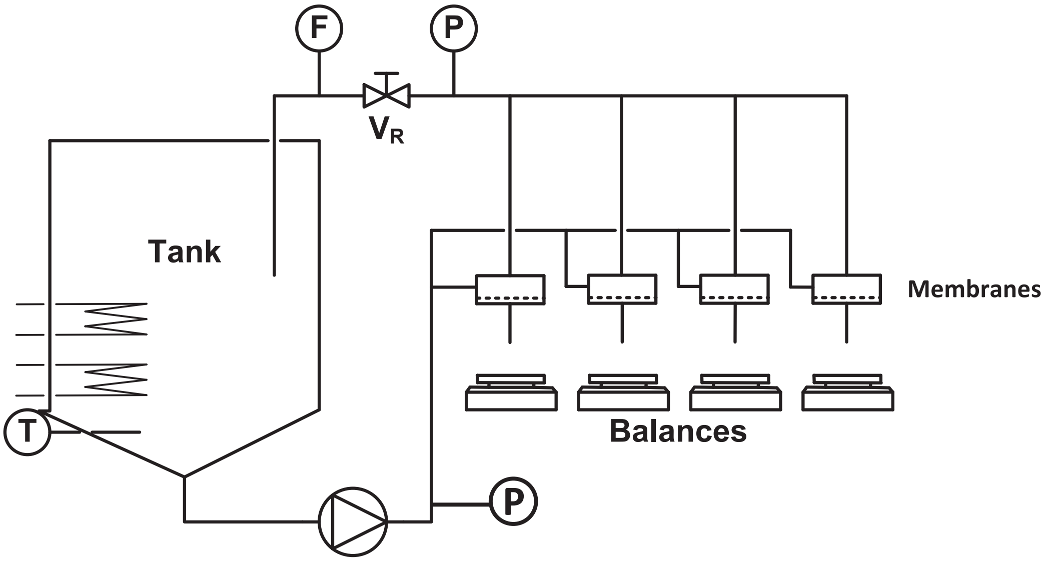


Figure 10. Flow scheme over the crossflow filtration unit for the flat sheet membranes.

The unit is equipped with a flow meter to measure the cross flow velocity of the water. Two pressure gauges are also placed on the inlet and outlet pipe in order to log the TMP. To ensure a stable temperature for the feed water, a heater and a cooler was placed inside the feed tank. A temperature meter to log and control the heater was also installed.

As one of the membranes was a hollow fibre membrane, an additional unit was needed to facilitate filtration with this kind of membrane. The unit, T/RX-300 is shown in Figure 11 and works in a similar fashion to the former described filtration unit. Feed water was poured into the small tank, approximately 5-6 litres, where it was pumped from the bottom of the tank and up through the membrane. The permeate could either exit through a small tube and be collected and measured, also on a balance, or circulate back to the feed tank. The retentate was automatically returned to the feed tank but when the unit needed to be emptied, a hose was attached so that the water could be easily drained.

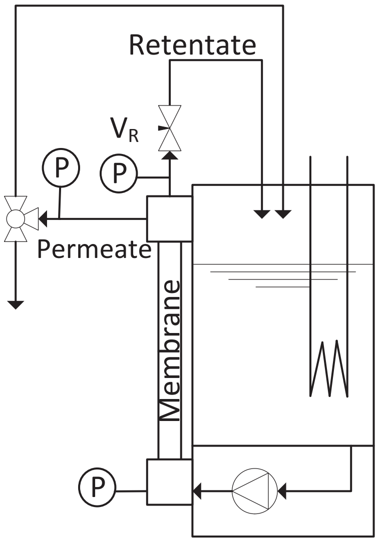


Figure 11. Flow scheme for the hollow fibre filtration unit.

Water that was filtered in this unit was pre-treated with a 250 µm sieve to make sure it wasn't plugging the equipment. The membrane area was 750 cm^2.

6.3.2 Experimental procedure

To be able to study the membrane properties, different types of filtrations was made. A pure water flux (PWF) test is a filtration made with deionised water at 30 °C while measuring fluxes at different TMPs. A PWF allows for conditions to be more or less the same, hence creating a good base for comparing fluxes before and after screenings and cleanings of the membrane. However, the performance of a membrane during a screening with the intended feed water is not always deductible from a PWF. It is therefore important to include both PWFs and screening with water from Lake Bolmen such as described in the procedures below.

The first part of the experimental procedure consisted of performing pure water flux tests with the same kind of membrane to make sure the four modules achieved a similar flux. This was done to ensure that a good comparative study could be accomplished. The initial check showed that the fourth module was unreliable and was excluded from further tests. During the preliminary PWF tests a reference membrane was also chosen to be placed in one of the modules for every screening. The choice to use a reference membrane was partly made due to the fact that the water was delivered at different times which could aggravate the comparison if there were irregularities in water quality. Furthermore, conditions surrounding the equipment could also result in slightly different results and with the help of a reference membrane this could be noticed easier.

6.4 Screenings

6.4.1 Initial screening

The initial part of the membrane screening study consisted of several test sets where different membranes were installed, each set was accompanied by the reference membrane. The standard test procedure and specifics for the different membranes are found in Table 3. The use of cleaning agent was based on what kind of preservatives the membranes were delivered in as well as recommendations from the suppliers. The membrane screening was executed at different TMPs depending on the cut off of the membranes tested. Membranes with a lower cut off value were tested at higher pressures to ensure a sufficient permeate production to collect samples. The temperature for the membrane screenings was set to 25 °C since previous tests had shown that this was the lowest achievable temperature at the highest CFV and pressure when the pump had maximum heat transmission. The CFV was set to 0.2 m/s for all filtrations except during cleaning with Ultrasil when it was 0.5 m/s.

The permeate was collected as an accumulated quantity during the whole TMP interval which means that the collected volume was different for each membrane depending on the flux capacity. The samples were then taken from this volume and preserved in bottles that were frozen until analysis could be made. Samples of the raw water were also collected pre- and post-filtration.

Table 3. Steps and specifics for the initial membrane screenings.

Test step	Membranes	Cleaning agent	Time	Temperature
Cleaning	GE: HL, AL, AP, DL, DK, GH	Deionised water	10 min	-
	Pentair: HFW1000	Deionised water	30 min	-
	Alfa Laval: Etna01, Etna10, UFX5, NF99HF	Ultrasil10 0.5 wt%	60 min	50 °C
	Dow: NF270-400	Deionised water	10 min	-
PWF	All	-	10 min at each TMP	30 °C
Membrane filtration with water from lake Bolmen	All	-	60 min at each TMP	25 °C
PWF	All	-	10 min at each TMP	30 °C
Cleaning	GE: HL, AL, AP, DL, DK, GH	Ultrasil10 0.05 wt%	60 min	50 °C
	Pentair: HFW1000	Sodiumhypochlorite 200 ppm	30 min	-
	Alfa Laval: Etna01, Etna10, UFX5, NF99HF	Ultrasil10 0.05wt%	60 min	50 °C
	Dow: NF270-400	Ultrasil10 0.05wt%	60 min	50 °C
PWF	All	-	10 min at each TMP	30 °C

6.4.2 Secondary screening

After the initial screening a handful of membranes were chosen for the second part of the experimental procedure. The purpose of the second part was to investigate if the TMP had any effect on the performance and quality of the permeate. The procedure was very similar to the one shown in Table 3 with the exception that all membranes were cleaned for 60 minutes at a TMP of 2 bar. This was done in order to pre-compress the membrane so that the flux would be more representative at lower pressures. The steps and the specifics of the tests are found in Table 4.

Table 4. Steps and specifics of the second part of the experimental procedure.

Test step	Membranes	Cleaning agent	Time	Temperature
Cleaning	Pentair: HFW1000	Deionised water	60 min	-
	Alfa Laval: UFX5, NF99HF	Ultrasil10 0.5 wt%	60 min	50 °C
	Dow: NF270-400	Deionised water	60 min	-
PWF	All	-	10 min at each TMP	30 °C
Membrane filtration with water from lake Bolmen	All	-	90-120 min at each TMP	25 °C
PWF	All	-	10 min at each TMP	30 °C
Cleaning	Pentair: HFW1000	Sodiumhypochlorite 200 ppm	30 min	-
	Alfa Laval: Etna01, Etna10, UFX5, NF99HF	Ultrasil10 0.05wt%	60 min	50 °C
	Dow: NF270-400	Ultrasil10 0.05wt%	60 min	50 °C
PWF	All	-	10 min at each TMP	30 °C

Samples of the permeate were collected at the end of each TMP period and were frozen until analysis could be performed.

6.4.3 Third screening with spiral wound module

The last part of the experimental procedure was to scale up the test and try the most promising of the membranes in a spiral wound module configuration. The spiral wound module was attached to the batch unit but the feed tank was replaced with a larger one that could hold approximately 200 litres in order to accommodate the capacity of the membrane module. Since the membrane was preserved in glycerine, the cleaning procedure followed the same as previously described with an alkaline solution, Ultrasil10, circulated at 2 bars TMP for one hour. The cleaning after the screening with Bolmen water was also executed with the same alkaline solution but at 0.5 wt% instead of the lower concentration of 0.05 wt% which was used during the first and second screening tests.

The membrane surface was 1.1 m^2 and the screening was executed at the constant pressure of 2 bars with the recommended cross-flow of 1 m^3/h at approximately 25 °C. The permeate was collected in a container on a balance which was used to log the flux continuously throughout the test. Samples of the raw water, permeate and retentate were taken at different volume reductions.

6.5 Analytical methods

6.5.1 TOC

To measure TOC is the primary surrogate for estimating NOM in drinking water (Najm, et al., 2000). The measuring principle is based on the levels of produced CO_2 which occurs after complete oxidation of the organic carbon in the sample. Depending on the standards used to calibrate the instrument, the CO_2 content is subsequently transformed into a TOC value. The unit used for the TOC analysis in this study was a Total Organic Carbon Analyser model TOC-5050A from Shimadzu.

6.5.2 UV_{254}

By using a spectrophotometer it is possible to approximate the organic matter content by measuring the UV absorbance at 254 nm. The chemical structure of the organic matter contains, as previously mentioned, aromatic rings which absorb UV light at this wavelength (Sillanpää, 2014). Hence, UV_{254} is a relatively quick and good way of quantifying NOM. The unit used in the study was a Hach Lange DR6000 which is a UV-VIS-spectrophotometer with a wavelength range between 190-1100 nm. The permeate samples were transferred into a 5 cm glass cuvette and measured with a set wavelength of 254 nm. The raw water samples were measured at the same wavelength but in a 1 cm cuvette.

6.5.3 Colour

Colour was measured with a spectrophotometer with an absorbance of 436 nm which is the same procedure used at the WTPs owned by Sydvatten. The analysis was made with the unit Hach Lange DR6000 using the same procedure as when measuring UV_{254}.

6.5.4 SEC

Size exclusion chromatography (SEC) is a useful method of determining the molecular mass distribution, in this case of the molecular size of the organic content. The polymer is dissolved in an eluent before it is injected into an analytical column with a porous filled material of a determined pore size. The polymer then elutes through the column and depending on the retention time a molecular mass distribution can be determined. (Mori & Barth, 1999)

The unit used for the analysis was a Waters 600E chromatography system (Waters, USA) which was equipped with a refractive index (RI) detector (model 2414, Waters) and a UV detector (model 486, Waters) where for this study, only the latter detector was used at 254 nm. The analytical column was packed with 30 cm Superdex 30 and 30 cm Superdex 200 (GE Healthcare, Sweden). 500 µL was used as the injection volume. The eluent consisted of a 125 mM NaOH solution with a flow rate of 1 mL/min. Calibration of the system was executed with polyethylene glycol standards with peak molecular masses of 0.4, 4, 10 and 35 kg/mol (Merck Schuchardt OHG, Germany). The wavelength set to detect fractions was 254 nm. Before determining the molecular mass distribution, the samples were filtered through a 0.2 μm filter (Schleicher & Schuell, Germany).

7 Results and Discussion

The results are discussed throughout this part and divided in sections following the chronological testing procedure.

7.1 Raw water

Samples of the water were analysed for TOC and colour. Online measurement values from the WTP for UV_{254} was also retrieved for the specific dates the water was delivered on and are summarized in Table 5. There was very little variation in quality between the different water deliveries hence, the average values presented here are the ones used for further calculations. All raw water values can be found in Appendix 1.

Table 5. Water quality values for Lake Bolmen during the study period.

	TOC (mg/L)	**UV_{254} (cm^{-1})**	**Colour (cm^{-1})**
Lake Bolmen	7.8±0.22	0.29±0.0026	0.019±0.0038

A sample of the raw water was analysed for molecular mass distribution in order to investigate what could be a suitable MWCO for this application. The result from the SEC analysis is shown in Figure 12. From the graph it is deductible that the organic content in the sample has a molecular mass of around 1-2 kDa. This would conform to the results from Laurell et. al (2015) who performed a similar surface water study in Finland with membranes ranging from 0.3-10 kDa. The five membranes included removed organic matter well which indicates that NOM found in Lake Bolmen also would have a molecular mass somewhere in between that interval since the surface water source that was analysed in that study was of similar quality as water from Lake Bolmen.

Lidén et al. (2016a) also experienced very good retention results when filtering water from Lake Bolmen with hollow fibre membranes with the pore size of 1 kDa which further confirm what range the applied membranes should have.

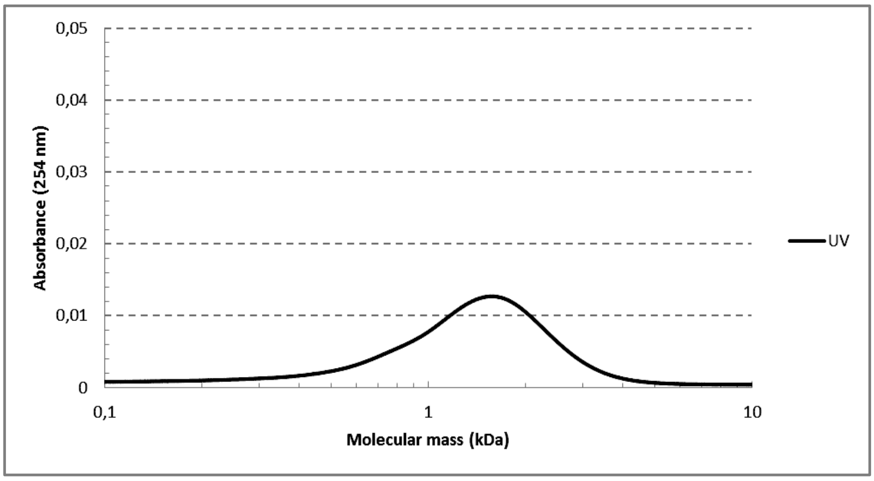


Figure 12. Molecular mass distribution of Bolmen water.

7.2 Initial screenings

During the initial screening, all of the membranes were analysed for flux, TOC, UV_{254} and colour. The different parameters are presented below individually as well as combined.

The permeate fluxes from the initial screenings of all membranes are shown in Figure 13 to Figure 15. Figure 13 shows the UF membranes where UFX5, Etna10, GH and Etna01 are compared. The two membranes that achieved the highest flux are UFX5 and Etna10. Since these two are in the higher range in terms of MWCO, it was expected. However, it is noteworthy that UFX5, which according to specifications should be around half the pore size compared to Etna10, stands out in terms of flux. This relationship is also visible when comparing Etna01 with GH. Even though GH should, solely based on the specified MWCO, have a higher flux than Etna01 the opposite is shown. It is therefore apparent that the performance of the UF membranes does not seem to comply with the specified MWCO. When studying Figure 13 it is also shown that UFX5, Etna10 and Etna01 show trends of subsiding fluxes at higher pressures. This is probably a result of the formation of a concentration gradient substantial enough for a filter cake to be created and the flux to reach a maximum which occur when a sufficient volume of water passes through the membrane.

In Figure 14 the fluxes of the NF membranes are shown. Since NF membranes usually are expressed in selectivity of different salts and under varying circumstances, it's harder to compare them according to specifications. NF99HF achieved the highest flux which, if comparing Figure 13 with Figure 14, are similar to the flux trend Etna10 performed. The NF-membrane hence surpasses both GH and Etna01, which is remarkable for a theoretically much tighter membrane. The flux trend of this membrane also shows a subsiding behaviour probably due to the formation of a filter cake as mentioned for some of the UF membranes. The second best NF membrane, as far as flux is concerned, was NF270. This membrane showed no signs of subsiding flux rate and could therefore be operated at higher pressures before a filter cake forms and limits the filtration through the membrane. The only hollow fibre membrane tested in the study was the HFW1000. The membrane achieved the third best flux amongst the NF membranes. However, it should be noted that the unit used for the hollow fibre membrane only allowed a maximum TMP of 2 bar. Hence, it is difficult to evaluate how the flux would behave at higher pressures and in comparison to the others solely based on this graph.

Figure 15 shows the tighter NF membranes which all displayed a similar permeate flux. These are the very tightest membranes in the study and should therefore also achieve the lowest flux which, in this case, was true. None of the membranes show any significant signs of a filter cake formation which is probably due to the lower flux of these membranes.

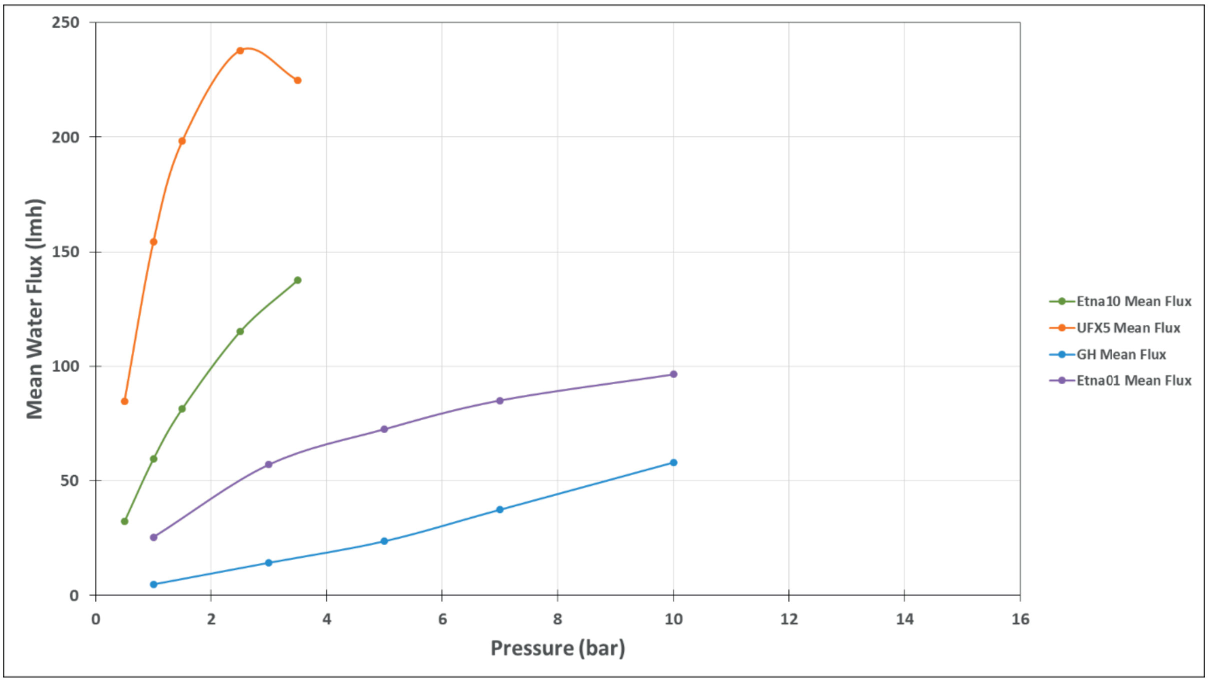


Figure 13. Mean water flux after initial screening with Bolmen water for the UF membranes.

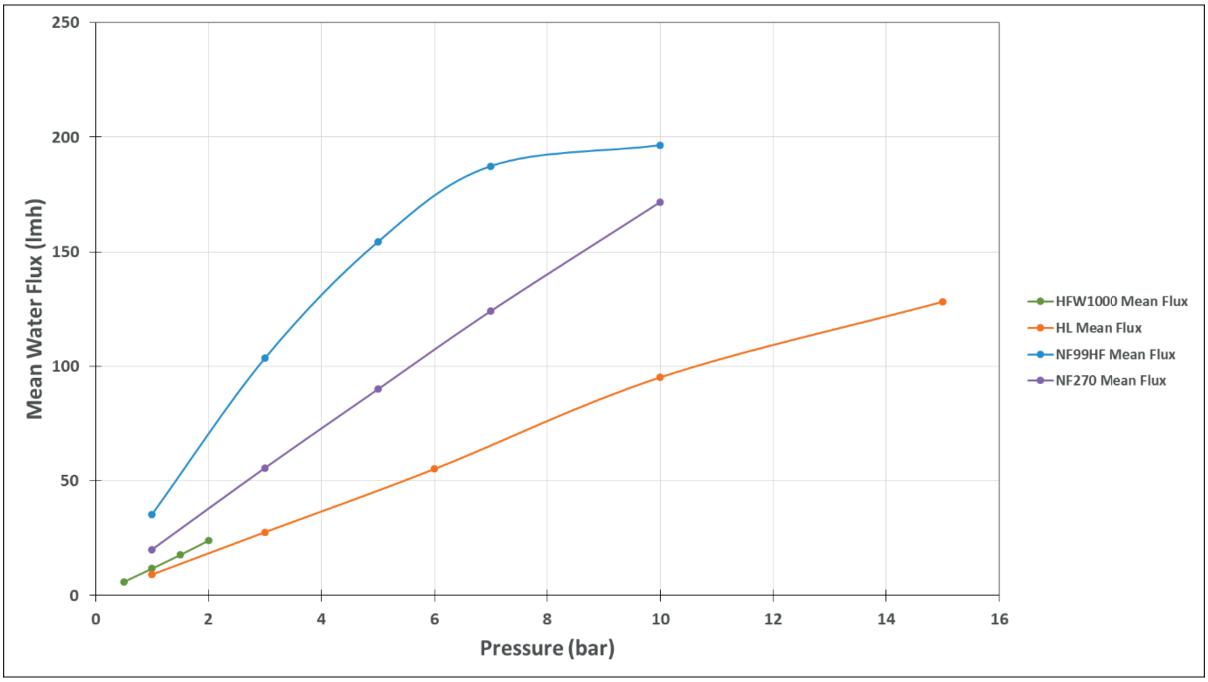


Figure 14. Mean water flux after initial screening with Bolmen water for the NF membranes.

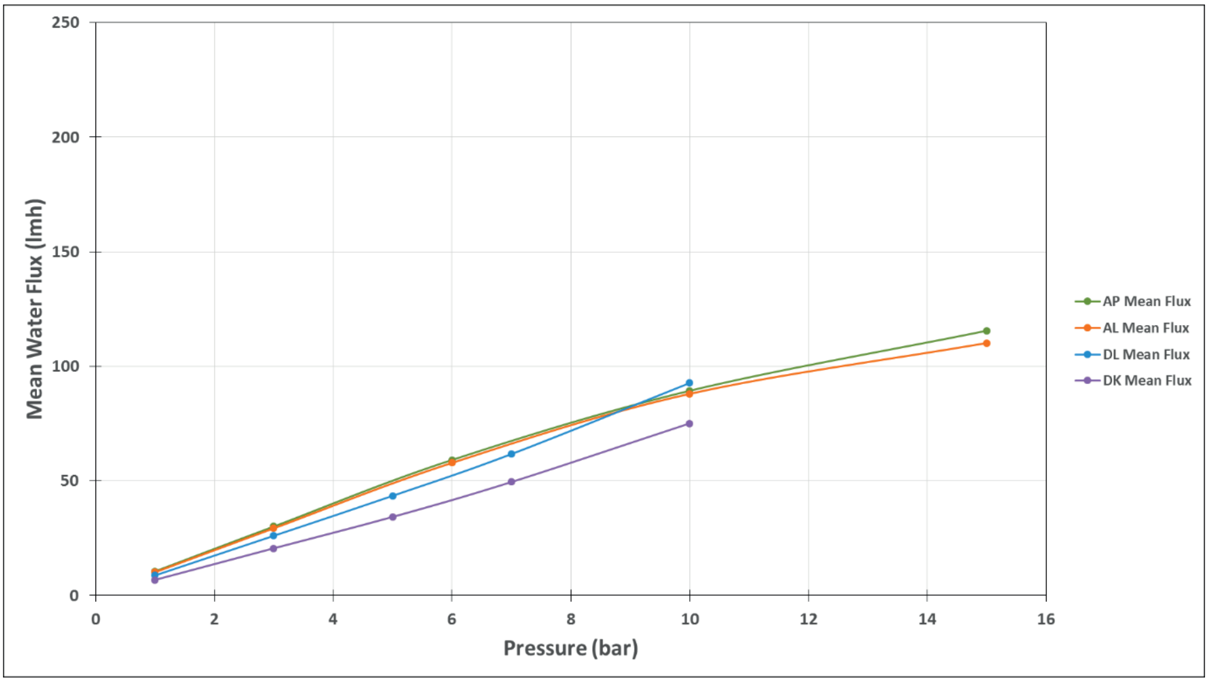


Figure 15. Mean water flux after initial screening with Bolmen water for the tight NF membranes.

Besides flux, the ability to separate organic material was assessed and was done so by comparing the quality of the permeate. TOC measurements of both feed water and filtered water enabled the observed retention to be calculated for all membranes and the result is shown in Figure 16. The graph shows clearly that the achieved retention seems to increase according to the specified pore sizes where the UF membranes doesn't separate as much of the organic matter as the tighter NF membranes. As depicted HL, NF99HF, NF270, AP, AL, DL and DK all achieved a high observed retention which surpassed 90%. These are all tight membranes, hence their ability to separate organic matter conformed to expectations. If a very high separation was the only aim these would have been the best option, especially AP and AL which both had an observed retention around 98%. However, a higher retention usually comes with an increased demand for pressure in order to achieve a sufficient flux which in turn would mean a high cost or a large footprint to accommodate enough water producing units for the WTP. To estimate an efficient removal, in terms of adequate separation without compromising a high flux, the TOC concentration in the permeate along with the flux at 2 bars was compiled and is shown in Figure 17. A TMP of 2 bar was chosen as a comparative point since it was the highest pressure that could be operated in the hollow fibre membrane unit.

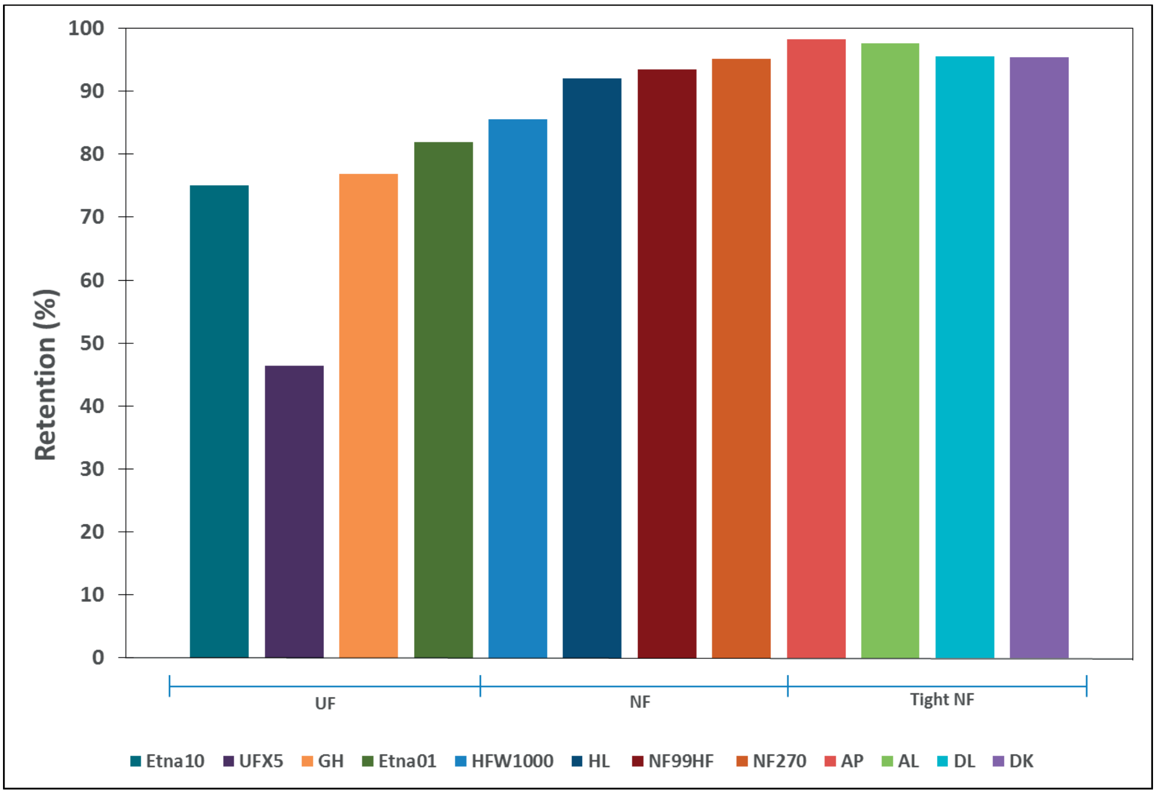


Figure 16. Observed retention of all membranes after the initial screening.

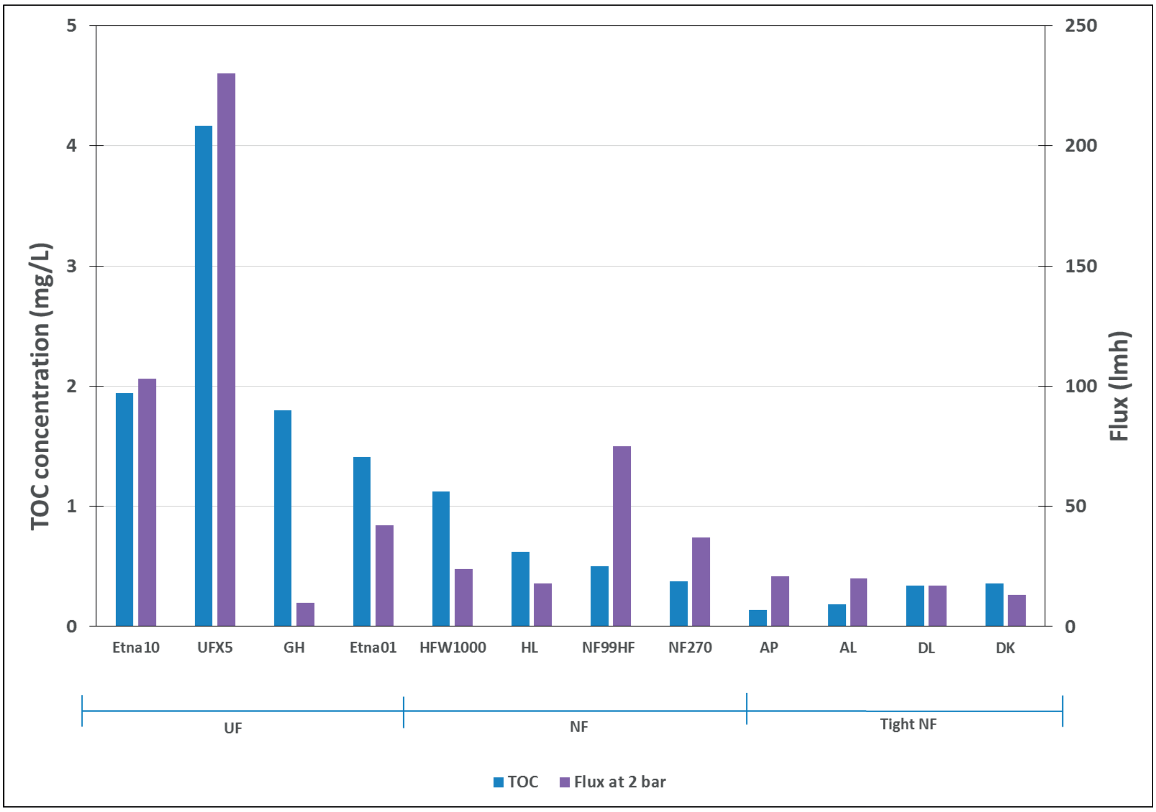


Figure 17. Graph showing the flux and TOC content in the permeate for all membranes.

Looking at Figure 17 it is confirmed that the membranes that achieved the very best retention; AP and AL also achieved, in comparison to other membranes, a low flux at 2 bar. The same could be said for DK and DL which also achieved a very good retention but a lower flux. Hence, a very high removal efficiency would have to be compromised with a higher cost if using the tighter NF membranes.

The opposite would apply for UFX5 and Etna10 which displayed the highest flux but didn't achieve a good TOC retention. In Figure 17 it is further shown that even though these membranes were outstanding in terms of flux they didn't manage to separate organic matter very well in comparison. This conclusion would conform with the results from the SEC analysis of the raw water where it was found that the molecular mass distribution of the organic material was around 1-2 kDa. UFX5 and Etna10 have a MWCO of 5 and 10 kDa respectively, and would therefore not be a good barrier for this specific purpose. However, another factor which could affect the water quality result was the concentration polarization that was shown in Figure 13 for these specific membranes. A higher concentration polarization decreases the flux and also facilitates the diffusive transport of particles and could therefore result in a higher TOC concentration found in the permeate. UFX5 and Etna10, which are both in the higher range of pore size in this study, were tested at high enough pressures to form a concentration gradient unlike some of the tighter membranes. This means that when pressure is low the concentration polarization might not influence the filtrated water to any greater extent. However, since the samples were collected over the entire filtration period and from all TMPs this phenomenon would still affect the analyse result.

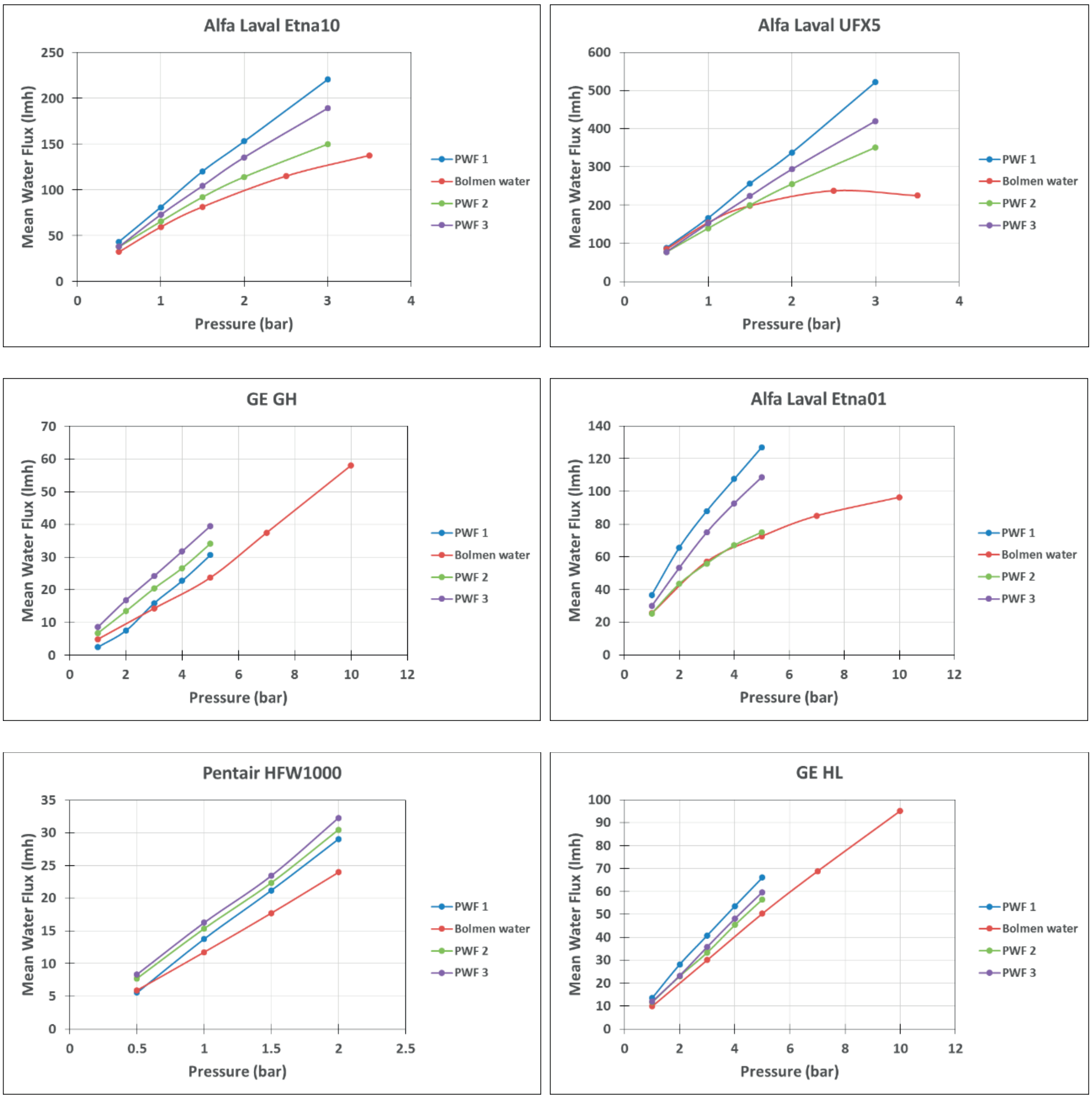
When looking at the NF membranes there are two membranes which stand out in terms of high flux and low concentration of TOC; NF99HF and NF270. Both of these achieved a very high TOC retention with effluent values of 0.5 and 0.4 mg TOC/l respectively, which corresponds to 93.5% and 95.1% in observed retention, but without compromising the flux capacity. NF270 did separate the organic material to a somewhat higher degree but also showed an overall lower flux trend with 37 lmh compared to 75 lmh as for NF99HF at 2 bar. Since the difference in retention is very small, the NF99HF can be considered as the slightly better one based on the fact that it achieves almost double the flux. Furthermore, NF99HF showed signs of a significant concentration polarization from Figure 16 which would also mean that the permeate analysis could be somewhat affected by the added diffusion of molecules and that the membrane could actually achieve a higher separation if analysis had been made at lower TMPs.

The initial screening hence proved that membranes with the highest productivity, in other words permeate flux, weren't tight enough to retain the specific compounds and therefore not suitable for the purpose of separating NOM. With that being said, due to the high productivity and consequential cake formation, the permeate water quality might have been affected and could therefore be less representative compared to the permeate analysis for the other membranes.

The membranes which achieved the very best permeate water quality also requires a high pressure to accomplish an operational flux which would mean a high cost for the WTP and would therefore not be optimal for this specific process. Two membranes proved to be efficient in separating NOM in terms of flux and high retention, NF99HF and NF270 from Alfa Laval and Dow respectively.

7.2.1 Fouling

All of the membranes were also analysed in terms of fouling. The test procedure allowed for fouling to be studied by comparing how the pure water fluxes behaved before and after screening and cleaning. PWF 1 denotes the very first flux that was logged after the initial cleaning (blue line). PWF 2 (green line) is measured directly after the filtration with Bolmen water and PWF 3 (purple line) after the subsequent cleaning. All of the logged flux trends for each membrane are shown in Figure 18. This section focuses on comparison of the fouling behaviour hence, the scaling on the axis is different for each graph.



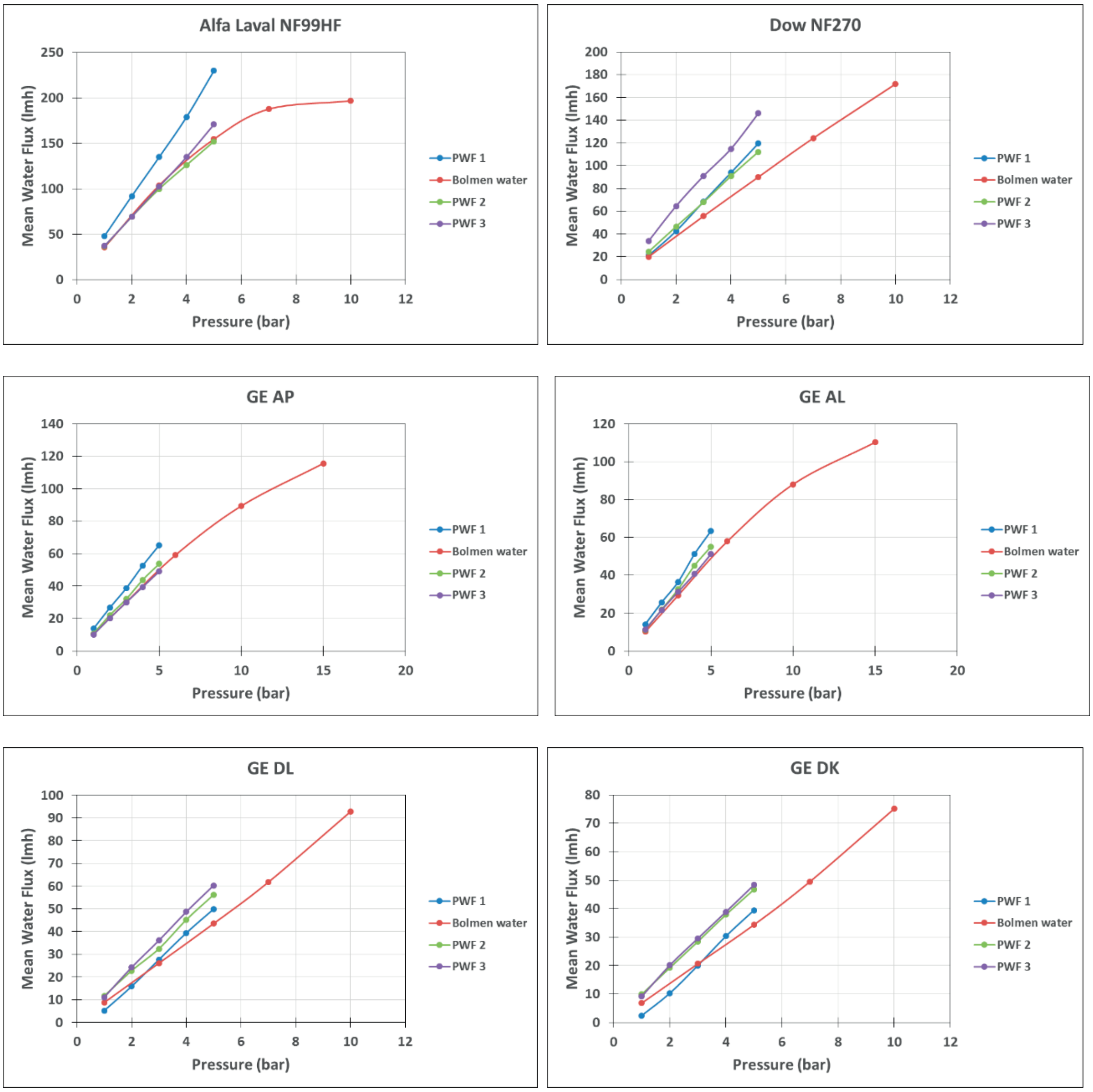


Figure 18. The logged fluxes showing the differences in PWF trends before and after screening and cleaning for all of the tested membranes.

The fouling behaviour differs slightly when comparing the membranes and did so without correlation with the three categories UF, NF and tight NF membranes. This section will therefore not be discussed based on these categories but instead in terms of cleaning performance. By comparing the second pure water flux, which was done immediately after the filtration, with the third one, it's possible to evaluate if the cleaning affected the flux. If that was the case, the restoration of the flux could also be estimated by comparing the third PWF to the initial level, PWF 1.

None of the membranes showed a trend where the flux trend was completely restored to its first value. However, for some of the membranes the cleaning worked well in terms of displaying an increase of flux after cleaning. Studying the graphs of Etna01 and Etna10 there is a significant change after cleaning which can be seen by the difference of PWF 2 and PWF 3. This indicates that the fouling in these cases are predominantly reversible. A good flux efficiency can therefore be achieved since the fouling that do occur, and consequently decreases the flux, can be counteracted with cleaning.

Less significant trends can be seen when studying the graphs of HL, NF99HF and UFX5 where the third PWFs are initially almost identical with the second PWFs and in addition also very similar to the Bolmen water flux trends. Even though higher pressures do cause a slight increase in PWF 3 for these membranes it would mean that the cleaning wasn't efficient enough to reverse the fouling hence the filtration with Bolmen water does cause some irreversible fouling.

Looking at the graphs of AP as well as AL there is a situation where the pure water fluxes after cleaning, PWF 3, is lower than before cleaning, PWF 2. This can be a sign that the cleaning chemicals wasn't rinsed out properly and that the flux after cleaning actually was higher than displayed. When comparing PWF 3 values for the reference membrane, HL, for this particular screening with other screening dates, it does seem somewhat affected but not to any greater extent. This would then mean that although the third PWF trends are low for AP and AL, it might not be quite as low as shown in Figure 18 but according to the unaffected reference membrane the cleaning would still prove to be insufficient in this case.

For the remaining cases, HFW1000, DK, DL, GH and NF270, it seems as though the third PWF was the highest. In theory, the first PWF should always be highest since no filtration has taken place and consequently no molecules can affect the flow. This is therefore an indication that the membranes might need additional initial cleaning/soaking prior to tests than what was specified. In these cases it is hard to determine to what degree the flux was restored after the cleaning i.e. as it was before screening with Bolmen water. To estimate the fouling in this respect, comparison between the second and the third PWF can be made. A significant improvement can be seen for the membranes NF270 and GH which indicates little irreversible fouling. When looking at the graphs for HFW1000 and DL, there are only a slight increase in flux which would mean that these are more prone to fouling but can be somewhat restored with alkaline cleaning. DK seems to be most affected by fouling since the difference between the second and third PWF trend is almost non-existent. However, since the first PWF trend is very irregular and quite low in this case it could also mean that there wasn't any significant fouling to begin with.

7.3 Secondary screening

Some of the membranes were selected to be studied further based on the results from the initial screening. These membranes were UFX5, HFW1000, NF99HF and NF270. As stated in 7.2, the high flux generated at high pressures for membranes such as UFX5 could potentially cause the quality of the permeate to decline, UFX was therefore thought to be a candidate for further tests. HFW1000 was chosen on the basis that the pressure interval could result in a fairer comparison as well as investigating to see if there were any differences between a hollow fibre membrane and a flat sheet one. Since NF99HF and NF270 showed the most promising results from the initial screening these two were also chosen to be part of the second screening.

For comparative reasons the TMP interval was set to 0.5-2 bar and the resulting flux trends are shown in Figure 19. Furthermore the second part of the experimental procedure was also to investigate whether or not the TMP affected the performance and quality of the membranes. The results are shown in Figure 20 where the analysis results from each of the permeate samples at the different TMPs are displayed in terms of UV_{254} and TOC.

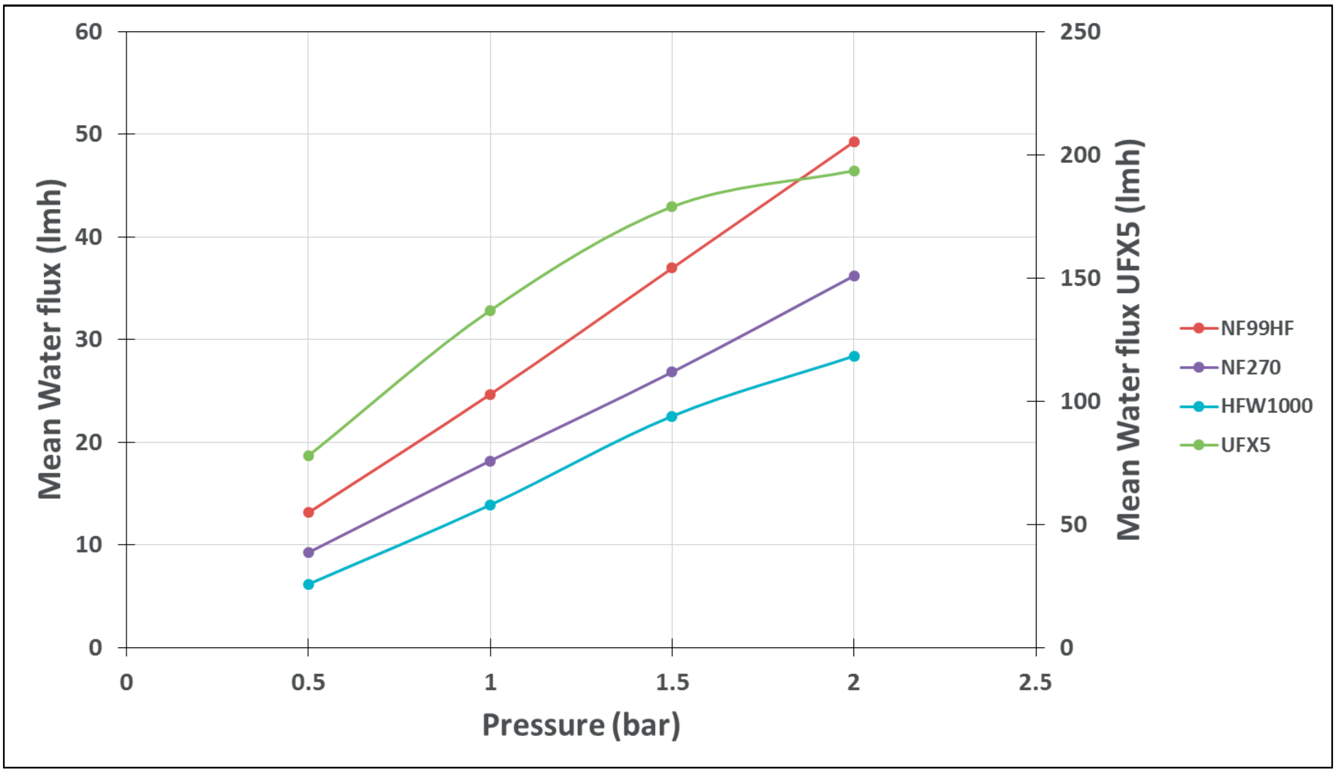


Figure 19. Flux results from the second part of experiments. The secondary axis represents the UFX5 flux values.

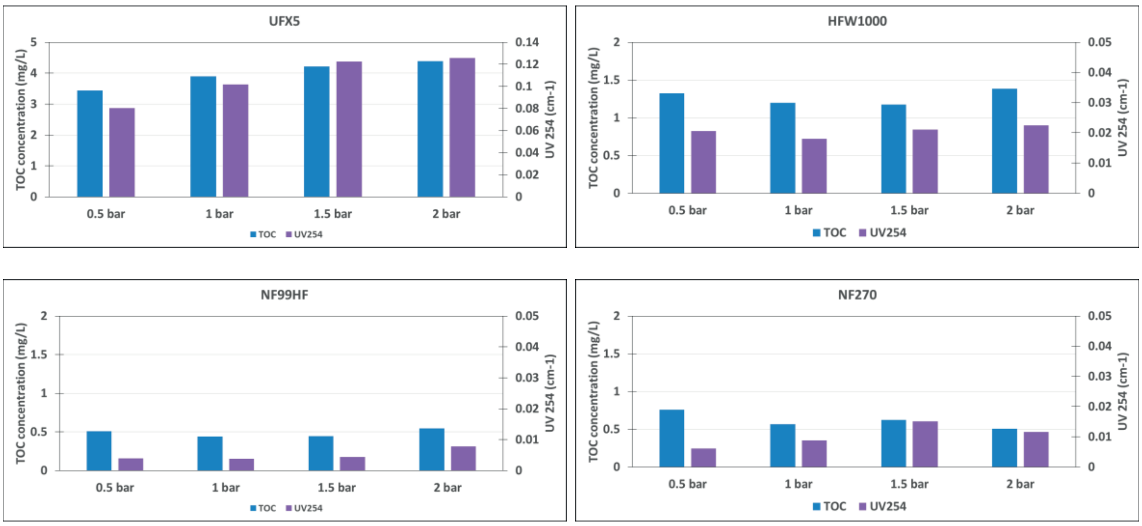


Figure 20. UV_{254} and TOC concentrations in permeate samples collected at the different TMPs. The scale of the axes are all the same with the exception of UFX5.

For UFX, which still produced the highest flux (note the secondary axis for UFX5 in Figure 19), also showed signs of a concentration polarization forming and a flux that levelled off. It is also the permeate quality for UFX5, shown in Figure 20, that shows the most significant increasing trend as a function of increasing pressure which could be a result from the concentration polarization. UFX5 is also, as mentioned in section 7.2, a bit too open in terms of pore size to fully retain the organic matter existent in the water from Lake Bolmen which could also result in a more significant increase of TOC in the permeate when increasing the pressure.

The performance of the HFW1000 appear to be quite unaffected by any changes in TMP as the quality in the permeate is similar throughout the different TMPs. The same applies for NF99HF where there are only slight changes between the different samples.

For NF270 there are changes although not in an increasing trend but appear to be random and also inconsistent when comparing the UV_{254} results with TOC for the different pressures. Since the permeate of the NF270 membrane is very clean and contains little organic matter it is more difficult to get qualitative comparative measurements between the analysed samples which could explain the random result. When focusing solely on the UV_{254} results, a more logical trend is visible where the UV absorbance increases with increasing TMP. Hence, another possibility for the seemingly inconsistent result could be that in this case, when the variations in organic matter content were so small, the TOC measurements weren't as accurate as the UV measurements. This would of course mean that the same applies for the measurements of the permeate from the NF99HF membrane and also for the HFW1000 to some degree.

7.4 Third screening with a spiral wound module

The most promising membrane, NF99HF, was investigated in a larger scale with a spiral wound module. The purpose of the test was to examine whether or not the volume reduction had any effect on the flux and the quality of the permeate. The flux as a function of the volume reduction is shown in Figure 21.

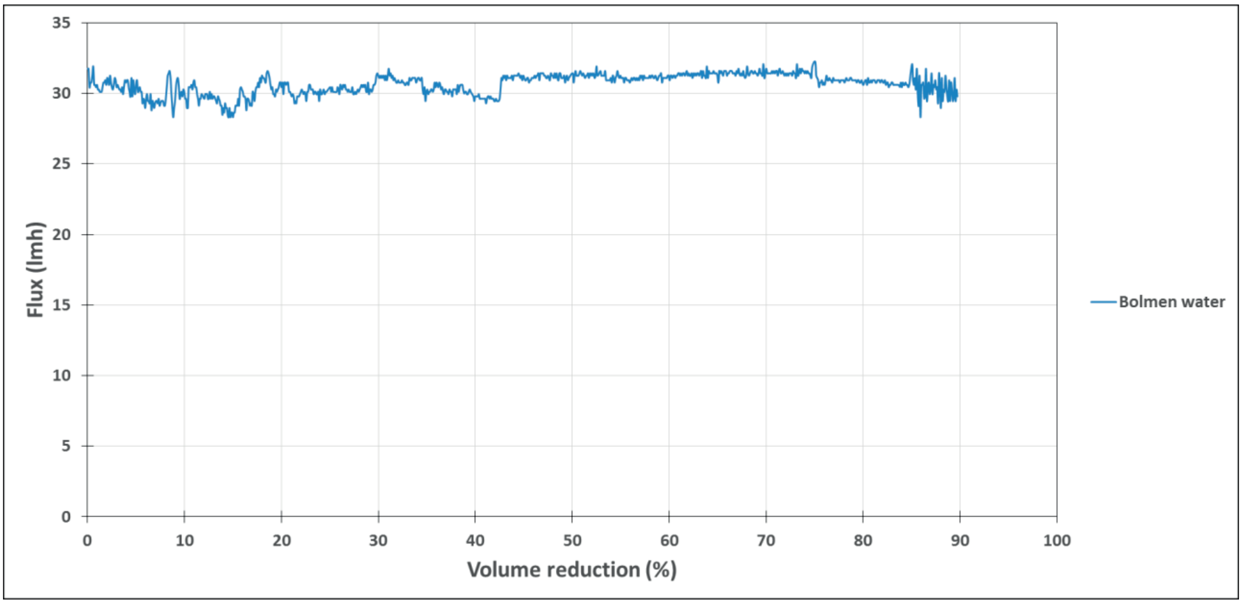


Figure 21. Flux as a function of the volume reduction during the experiment which lasted for about 5 hours. The TMP was 2 bar and the temperature 25 °C.

The flux seemed to be rather steady with little variation during the experiment. However, around a VR of 85% until 90% the flux varies more frequently and there are signs of a slight decline but not significant enough to draw any conclusions from it.

If comparing the flux from the spiral wound module with the flux achieved by the same membrane during the first and second screening at 2 bars, there is a definite reduced flux for the spiral wound membrane configuration. With an average flux of 30.6 lmh, the spiral wound membrane achieved almost half of the flat sheet membrane which had a flux capacity of approximately 62.5 lmh at 2 bars.

The test also examined the fouling behaviour of the module and the PWF trends are shown in Figure 22.

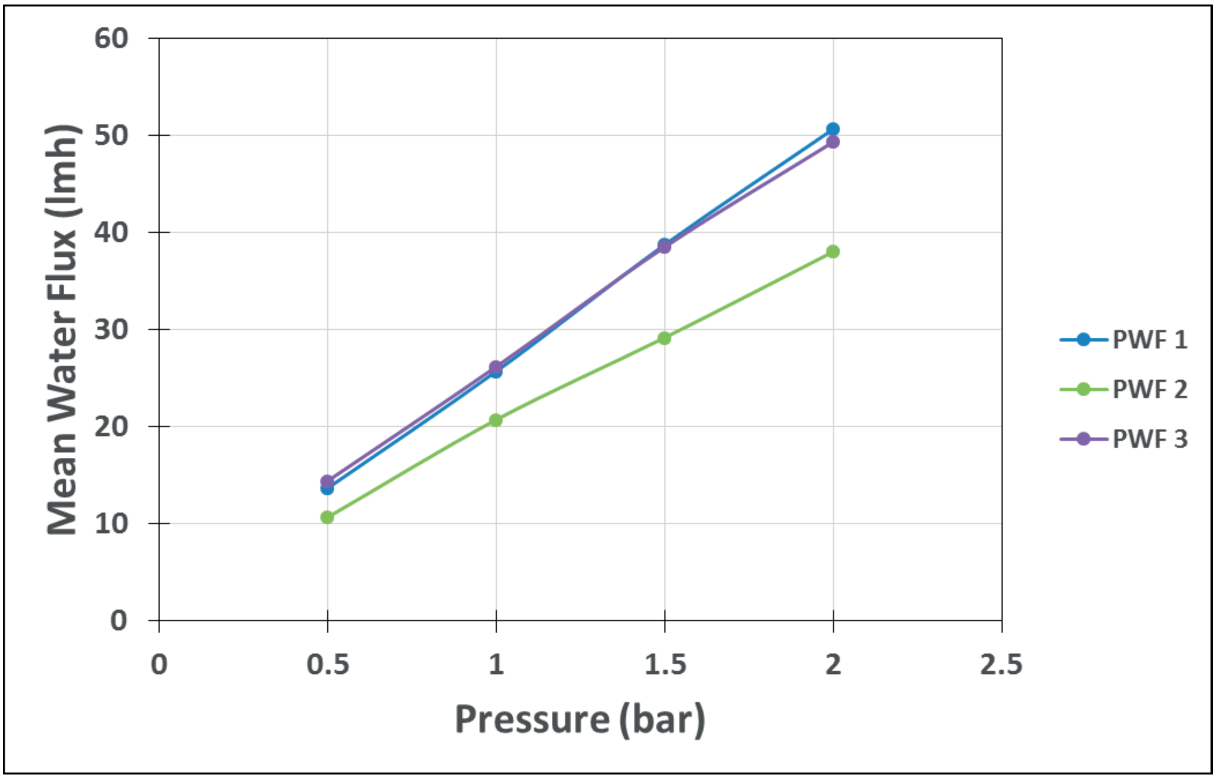


Figure 22. The PWFs of the NF99HF spiral wound module during the third screening process.

The PWF trends show that the cleaning did remove all of the fouling that was caused from the filtration since the first and third PWF are almost overlapping. This contradicts the results found in the first and second screening where the cleaning seemed to have little effect on the attained fouling. Then again, this was cleaned with a higher concentration than was previously used which could explain the results.

The collected samples were analysed for TOC content and UV_{254} and the results are shown in Figure 23.

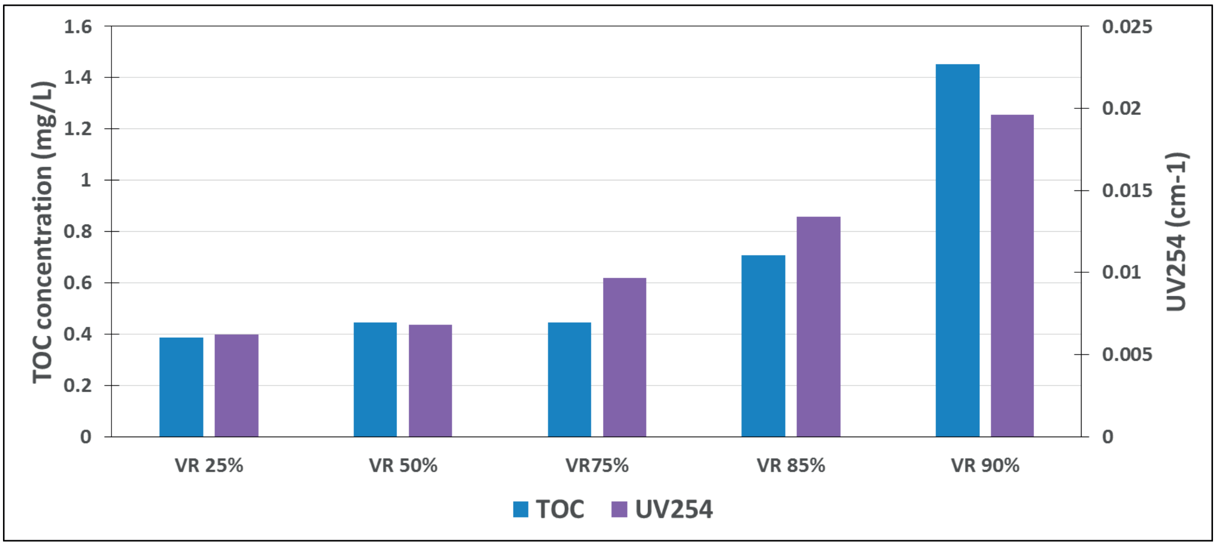


Figure 23. The analysed permeate samples from the third screening. The samples were collected at different volume reductions.

At lower volume reductions the difference in water quality is not very significant. Starting at a VR of 85% there is a slight increase of organic content in the permeate sample and at a VR of 90%, the TOC concentration and the UV_{254} absorption has tripled. However, looking at the observed retentions for the permeate, shown in Figure 24, it is visible that the ability to retain the organic matter is actually increasing until a VR of 85%. This would mean that the membrane can achieve good separation of NOM even if the feed water has a high concentration of organic matter.

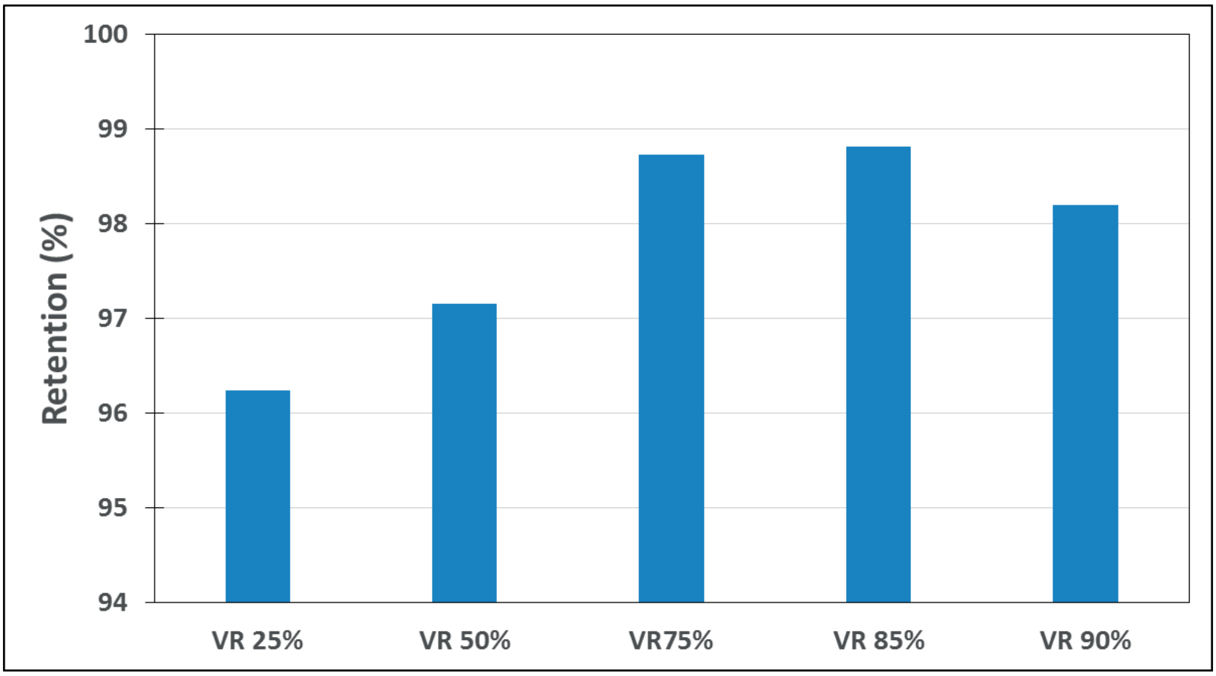


Figure 24. The observed retention for the permeate after the third screening.

8 Reflection

The three screenings showed that membrane technology would be suitable for the intended purpose. Almost all membranes achieved a better removal of TOC than what is currently achieved with the conventional treatment. As anticipated, a few of the more open membranes produced the highest flux but with the consequence that some organic material was still found in the filtered water, hence achieved a low TOC retention. These membranes, especially UFX5 and Etna10, might have been insufficient to function as a stand alone process but could achieve a better result in combination with subsequent treatment steps.

On the other end of the scale, achieving a very high retention, were AP and AL. Even though the removal of organic matter was excellent, these very tight membranes are not well suited for the intended purpose. Both of the WTPs, Ringsjöverket and Vombverket, have a high production rate at 1400 and 1100 l/s respectively and would require a massive energy input as well as numerous modules if these membrane units were to have the capacity to treat the incoming water. So from an economical and environmental perspective the use of tight NF membranes, although achieving the very best retention, would not be feasible. Another aspect worth to consider concerning membranes with a high retention capability, is the hardness reduction. At Ringsjöverket where the source water is from Lake Bolmen, they use lime to increase the hardness before distributing it. Any additional removal of hardness would therefore potentially mean an extra cost for the WTP. At Vombverket they are experiencing the opposite where they have to decrease the hardness by a softening step. If the membrane treatment step were to be implemented at this WTP using water from Lake Vomb, it would instead be an advantage but there would be a risk of problem with scaling of the membranes.

The optimal combination of a high flux at low pressures and a good retention seemed to be accomplished by the NF membranes and especially Alfa Laval NF99HF. Although DOW FILMTEC NF270 achieved a better retention, the NF99HF stands out with a much better flux and would therefore be more interesting for the specific application. Since the membrane filtration step potentially should constitute as a pre-treatment at Vombverket it is important that the permeate doesn't contain a lot of organic material. The coagulation step at this WTP was not designed for the purpose of removing the the organics in the water as is the case at Ringsjöverket, hence the major part of the NOM separation should be done prior to this step.

An issue concerning the NF99HF is the fouling behaviour that it showed during the initial and second screening. It was shown that the flux wasn't improving after the alkaline cleaning and the same result was apparent after the second screening, as shown in Appendix 3. Irreversible fouling can become very cost and energy intensive for the WTPs since the cleaning frequency has to be high to obviate the fouling. However, as only one type of cleaning solution was used for this study there are perhaps alternative ways and solutions to clean the membrane which would result in a better outcome.

The conclusion from the second screening is that the permeate quality does indeed change when increasing the TMP. However it is negligible for the tighter membranes which are of most interest for this application. With that being said, this test was performed with 2 bars as the highest pressure hence, the tighter membranes never showed any declining flux trend due to concentration polarization which the more open membranes did. If higher pressures were to be applied to some of the tighter membranes, a slightly more significant increase of TOC concentration could be expected to be seen in the permeate.

The third screening with the spiral wound module of NF99HF showed that the quality and productivity of the membrane is almost independent of the volume reduction and is not affected significantly before a VR of 85%. Besides suggesting at which volume reduction span the process could be operated at, the result also indicates that the membrane unit is capable of successfully separate organic matter from a feed water with much higher concentration than what is currently found in Bolmen water. Furthermore, the test also showed that the accumulated material on the membrane surface could be completely removed if cleaned with an alkaline solution at a higher concentration than during previous tests. For the first and second screening the alkaline solution was diluted to 0.05wt% so that all membranes could be cleaned with the same type of solution and the same concentration. This was done to comply with the limits that some membranes had which then had to be applied for all membranes in order to achieve a good comparative base. The spiral wound module allowed a higher pH and could therefore be cleaned with the same solution but at 0.5wt% which proved successful in terms of restore the flux to its initial capability. This result is promising since it implies that the membrane can indeed be cleaned but it would require a higher dosage of cleaning chemicals.

A more worrying result after the third screening was the reduction of the flux, shown in Figure 21, which was half of what the same membrane had achieved in prior tests but then as a flat sheet. Since the spiral wound module has a much closer resemblance of the actual configuration i.e. what it would look like at site, this result would indicate that the flux probably is not quite as remarkable as previously found. Even with the reduced flux NF99HF would still be a promising candidate to make further studies on.

Besides the actual performance of the membranes there are other aspects that should be taken into consideration when deciding a suitable membrane for a specific process. Since drinking water is being produced, very high standards have to be maintained concerning hygienic conditions and the prevention of biological growth on the membrane surface. It is therefore beneficial to be able to treat the membranes with strong oxidants, such as chlorine, without degrading the performance of the membrane. There are only a few membrane materials that are resistant to chlorine, the most usual being polysulfone or polysulfone-derivates (American Water Works Association, 2015). In this study, more than half of the membranes can be treated with more or less chlorine however NF99HF is not one of them.

Another aspect concerning cleaning is the module configuration. As explained in section 5.2, all types of membrane configurations have different pros and cons and this is also something to be considered when evaluating the choice of membrane. In this study two different kinds of membranes were analysed, flat sheet and hollow fibre. Even though the flat sheet membranes in many regards did achieve a better performance, they can't be backwashed as opposed to a hollow fibre membrane. To be able to backwash is advantageous since it can remove filter cakes and material accumulated at the membrane surface which in turn could increase the capacity of the membrane.

8.1 Sources of Error

Time limitation meant that for the first part of the study, each membrane could only be screened once which of course meant that there were less room for anticipating the reproducibility of the results. The reference membrane that was placed in the first module for every test run during the initial screening did display some variety in flux, especially at higher pressures, as shown in Appendix 2. Since the raw water was fairly consistent in content and quality throughout the testing period, this would mean that other factors affected the flux such as irregularities either with the equipment or most likely; the membrane surface. The modules of the unit used for filtration allowed flat sheet membranes with a surface of approximately 20 cm^2. With an area that small, little defects, nicks and scratches could affect the flux significantly. This is of course also valid for filtration with all of the membranes and not only the reference membrane.

A few sources of error have already been discussed in previous sections such as the consequences of using accumulated permeate, i.e. filtered water collected from all TMPs. As mentioned, the quality of the permeate might be more or less affected by this way of sampling. It was also shown that it was especially the open pore membranes that were affected the most while the pressure limitation meant that this behaviour rarely appeared for the tighter membranes. During the initial screenings, where all membranes were tested and compared, samples should preferably have been collected at each different TMP to make a fairer evaluation, as was done during the second screening. Due to time limitations this was not possible to do for every membrane during the first screening. However, since the majority of the membranes were NF membranes the quality would probably not have been affected much which was confirmed during the second screening.

Another possible source of error, that was also mentioned previously, was the insufficient initial cleaning. The majority of the membranes were rinsed with deionized water (DI water), as specifications instructed, although it was apparent after the first tests that some of the membranes might have needed additional cleaning. This could be seen especially after the membrane had been cleaned with an alkaline solution which resulted in a PWF that was higher than the initial PWF. Besides affecting the first PWF, an insufficient initial cleaning could also have a possible effect on the flux when Bolmen water was filtrated which would then be lower than what it should be. Since the comparison is based on these filtration flux values it would potentially affect the result of the study. However, the inefficient initial cleaning could only be discovered at the very end of each test run so it was unfortunately not possible to correct afterwards.

A possible problem, but the opposite of the one just mentioned, is the pre-pressurizing of the membranes. Since the membrane surface is a porous layer, it gets somewhat compressed with increasing TMP. The flux trend can therefore display a higher flux if it hasn't been pressurized prior to testing. This means that the membrane should be pre-pressurized to its operational TMP in order to get the most representable flux values. During the initial testing, the membranes preserved in glycerine were pre-pressurized during the cleaning procedure to 2 bar as opposed to the ones rinsed with DI water which weren't pressurized at all. However, for the second screening all membranes were cleaned with a TMP of 2 bar. This was also the highest pressure used during the subsequent filtration and therefore all of the membranes were pre-pressurized.

All collected water samples were frozen immediately after sampling and later defrosted prior to analysing. This was done in order to analyse all samples at once in an efficient way and so that they were tested equally hence, a fairer comparison could be made. Analysis are always preferable to do as quickly after the sampling as possible since conditions can change over time but within this study, this was not possible. To ensure that the freezing of the samples didn't significantly change the quality, a permeate sample was analysed for UV_{254} and colour directly after filtration which was then compared to the same permeate sample which had been frozen. As the difference was considered negligible this was only done for one of the membrane permeates and not for any raw water samples. Hence, some unreliability could be expected.

Another source of error that concerns the analyse of the samples are the problems that occur when measuring very low concentrations of TOC, especially in the permeate. The permeate of most NF and all tight NF membranes were very clean with little traces of NOM left in the samples. Measuring something close to the detection limit always presents a problem since it is less reliable and also due to the fact that a lot of external factors could interfere with the result and therefore affect the comparison. An example within this study was the colour analysis made on the permeate samples from the initial screening. Measuring colour can be a good way of estimating water quality since humic substances in the water, along with metals if there are any, are responsible for the brown-yellowish appearance of drinking water (World Health Organization, 1997). However, the permeate samples contained so little colour that it hardly gave any fluctuation between the different samples hence a difficult base to compare results on but a positive result nevertheless as this shows the removal of humic substances was good.

There are many aspects within this kind of study that can make the results more or less trust-worthy. However, as mentioned, multiple measures have been taken to insure the most plausible results and that the essential conclusions made in this thesis therefore are reliable.

9 Conclusion

The major part the organic material in the raw water from Lake Bolmen has a molecular mass of 1-2 kDa which means that membranes with a cut off higher than 1-2 kDa proved insufficient in terms removal of the organic matter in the Bolmen water. This is under the premise that the membrane filtration process is run with no other complimentary treatment such as a coagulation step.

Two membranes were found most suitable for the intended purpose: DOW FILMTEC NF270 and especially Alfa Laval NF99HF. The latter membrane managed to achieve a high flux but still retain most of the organic matter which would be efficient without compromising the high quality permeate. However, the study also showed that fouling could be an issue with this type of membrane even though the results were ambiguous. Since the operational cost of a membrane filtration unit often is the largest from an investment perspective it's important that excessive fouling is avoided. Fouling would also be of concern since this type of membrane comes in a flat sheet composition wound into a spiral which means that there are no possibilities of backwashing. Nor is this type of membrane compatible with chlorination which is also undesirable within drinking water treatment.

Higher TMPs did deteriorate the quality of the permeate but this was only significant for membranes with a higher MWCO. For NF membranes the difference was considered negligible. It was also found that the volume reduction had to be around 85% before the quality and potentially quantity of the permeate production was affected.

The study managed to identify which membranes that would be interesting with the purpose of filtering water from Lake Bolmen as well as further emphasise the importance of site specific testing since the performance seemed to be independent of specifications. Even though promising results were obtained the performance of the membrane needs to be investigated further in order to evaluate the suitability for a larger scale.

10 Future work

This study has been the initial attempt to try to identify promising membranes which could potentially be used for a large treatment plant. This implies that any results from this kind of investigation are to be considered a base in the decision making about further tests in a larger scale. The third screening which was executed with a spiral wound module, was the first step towards such an analysis still, it was executed off site and was not representative of the operation in reality. The next step would therefore be to scale up the study and try the membrane/membranes in a pilot plant at the specific location with the intended feed water.

At site it would be possible to run the experiments for a longer period of time which was not possible due to the set up with batch sized equipment at the department. Furthermore, if the testing was done during a longer period of time it could also be beneficial to study the fouling behaviour. The flux recovery in this study was only studied after the initial screening with Bolmen water. Once in operation the membranes will be cleaned numerous times and it's important to know how the fouling behaviour will act in a continuous operation mode since, as mentioned before, the maintenance and operational costs are what's generating the biggest cost for the WTP.

The pilot plant could also enable other parameters to be tested, such as temperature. As described, temperature does influence the performance and result of a membrane, and since the lab scale experiments only allowed a much higher temperature than anticipated at the WTP, this would have to be examined at site.

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Appendix 1

Table A. 1. Collected and analysed values of raw water values for Lake Bolmen.

Date for delivered water	Date for collected sample	TOC[I] (mg/l)	Colour[II] (abs/cm)	UV_{254}[III] (abs/cm)
2016-10-03	2016-10-03	7.588	0.0232	0.292
	2016-10-05	7.469	0.0228	
	2016-10-07	7.92	0.0184	
2016-10-10	2016-10-11	7.931	0.0174	0.286
	2016-10-13	7.984	0.0182	
2016-10-17	2016-10-17	7.747	0.0156	0.288
	2016-10-19	7.881	0.0202	
2016-11-07	2016-11-08	7.4845	-	0.29
	2016-11-10	7.6865	-	
2016-11-14	2016-11-14	7.992	-	0.297
2017-01-10	2017-01-10	8.032	-	0.322

[I] An average value after two measurements
[II] An average value after 5 measurements
[III] Measured online at the WTP Ringsjöverket.

Appendix 2

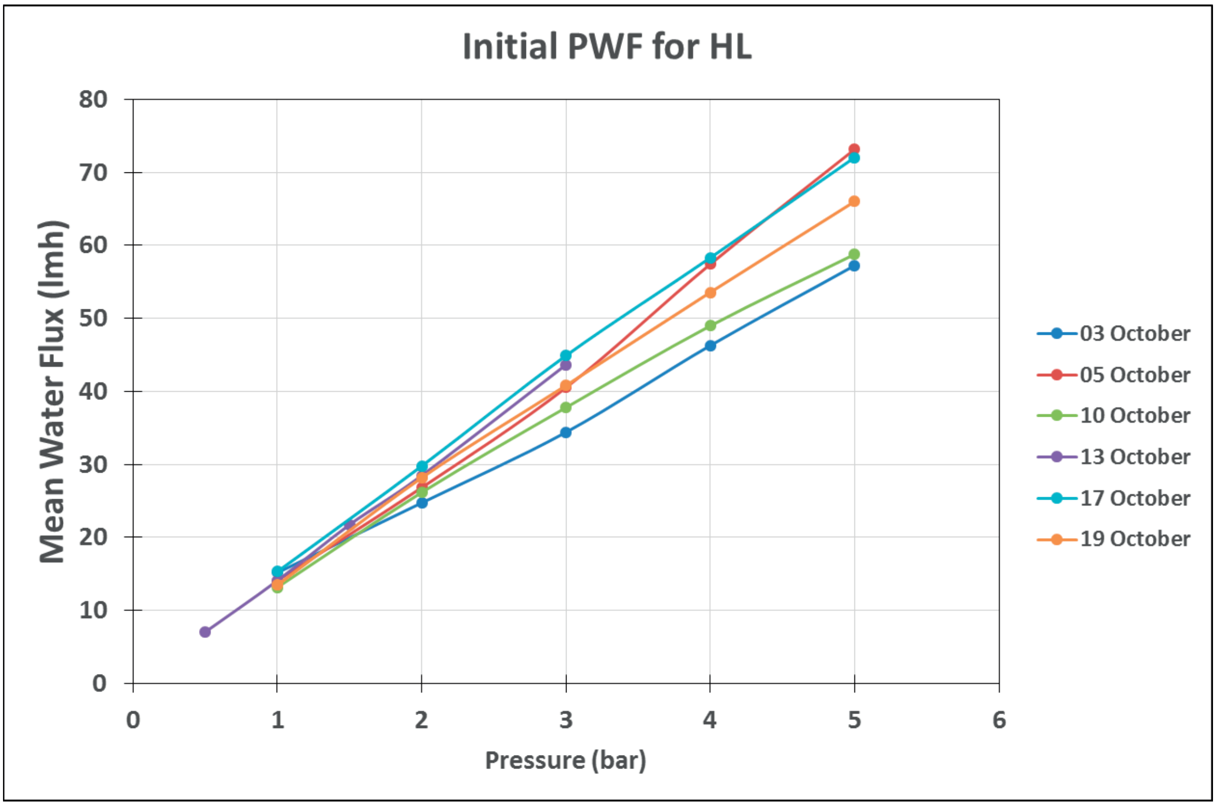

Figure A. 1. Graph which shows the variation in PWF for the reference membrane HL.

Appendix 3

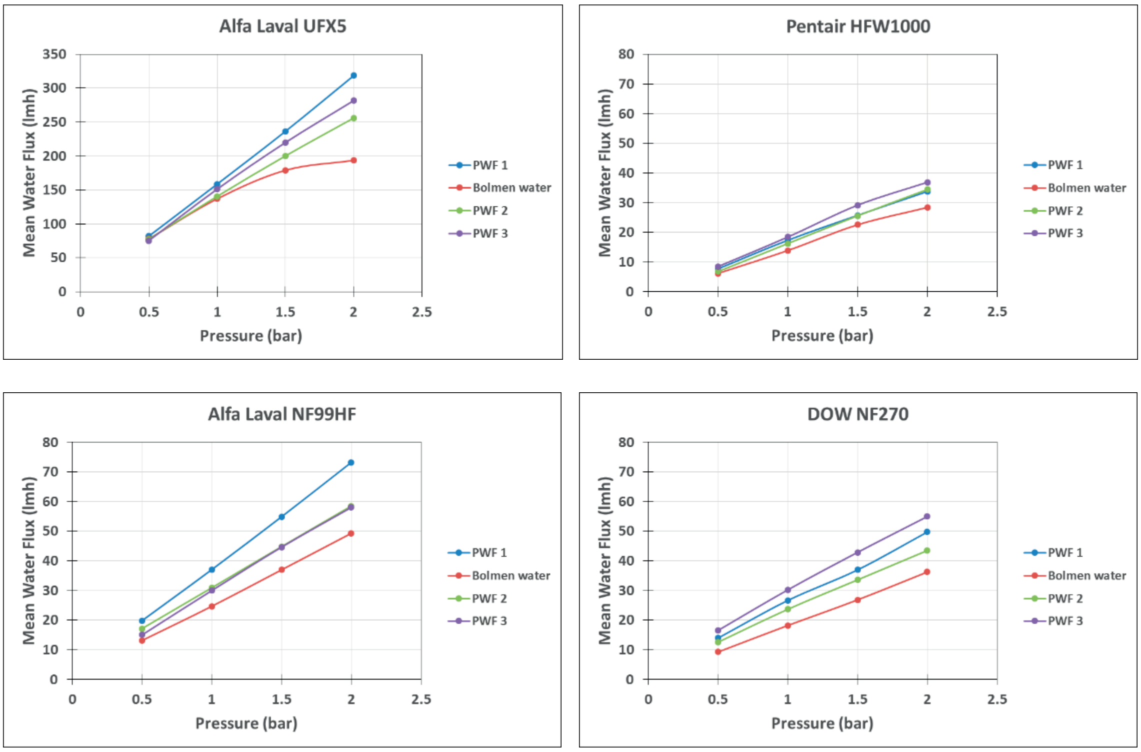

Figure A. 2. Screening graphs from the second screening for the four tested membranes. Note that all graphs have the same y-axis with the exception of UFX5.