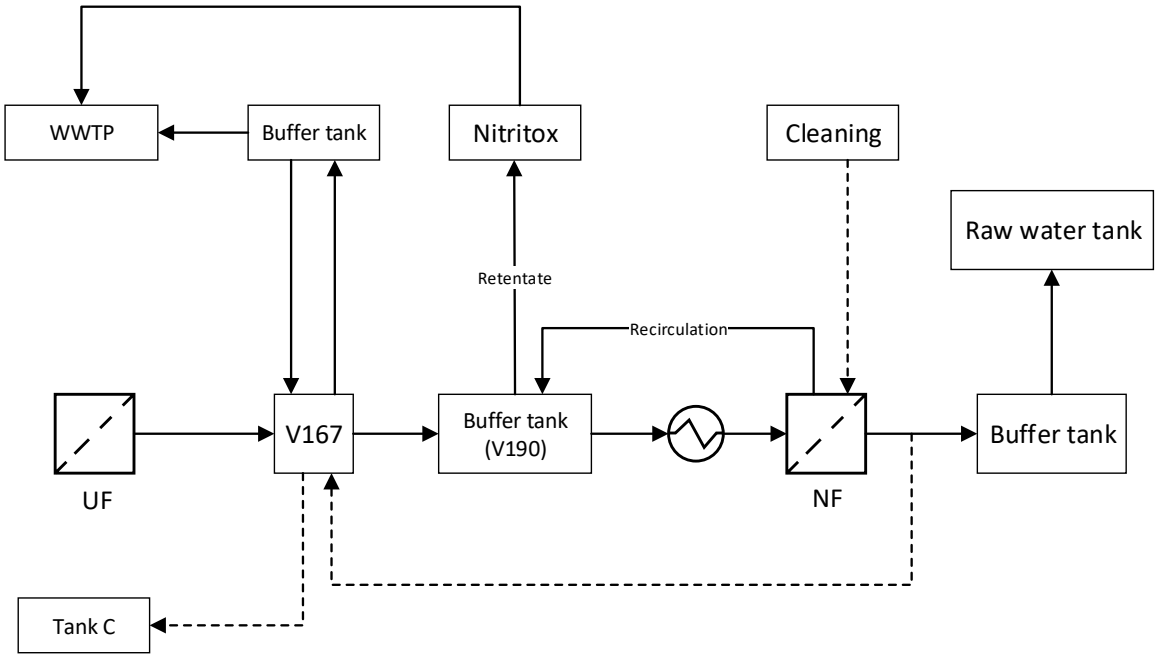
Nanofiltration of ultrafiltration permeate from chemical wastewater



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Master Thesis 2017

Nanofiltration of ultrafiltration permeate from chemical wastewater

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Picture on front page: Process schematic of the planned NF system. Photo by Martin Gunnarsson

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Preface

My crowning achievement of these 5 years at LTH is this Master Thesis report. The end of an era is near but it just marks the next chapter in life.

When I chose Process Design, I did not expect my Master Thesis to be about wastewater filtration. Studying how the wastewater filtration could be improved at Dow has been very interesting and I am very happy that this became the topic of my Master Thesis.

During these 5 years I have never been as motivated as when I was working with this project. The continuous feedback from my supervisors has helped me push my work forward and improve beyond what I thought was possible.

I want to thank Martin Kronvall at Dow for being an excellent supervisor. Our many long discussions about my Master Thesis has been inspiring and helpful. The good connection we have had inspired me to try my hardest with this thesis. I also want to thank my supervisor at LTH, Ann-Sofi Jönsson, for being a great resource and also for the structure you imposed on my report, I learned more about writing a proper report from you than during all my 5 years at LTH.

Extra special thanks to PhD student Johan Thuvander who helped me in all my experiments. I would not have managed to complete this Master Thesis without your help.

Lastly I want to thank my family for always being there for me and supporting me.

Martin Gunnarsson

Abstract

The aim of this report was to investigate the possibility of further cleaning of the wastewater at Dow in Landskrona. Dow produces water based adhesives from acrylic monomers. The wastewater contains different metal ions, surfactants, residual monomers and polymers. The wastewater at Dow is treated with ultrafiltration (UF) which produces a permeate that is sent to the municipal waste water treatment plant (WWTP). The municipal WWTP is heavily burdened and it might not be long until they start refusing to treat the wastewater from Dow. This study is a proactive investigation of nanofiltration (NF) as a method to produce a permeate clean enough to be reused in the process at Dow. Being proactive in wastewater treatment is getting more and more important, especially with the current water shortage in Sweden and many other places in the world.

Five NF and reverse osmosis (RO) membranes were investigated in the initial screening of flat sheet membranes: NF99HF from Alfa Laval, AP from GE, NF270, NF90 and XLE from Dow Filmtec. The UF permeate from Dow was used as feed for the NF. The total organic carbon (TOC) and conductivity was measured in the feed, the UF permeate, and the NF permeates to determine the retention of the membranes. The influence of transmembrane pressure (TMP) and crossflow velocity (CFV) was studied for all membranes to determine the optimal operation conditions.

From the studied membranes, NF90 was chosen for further studying in a spiral wound membrane due to the good retention and common use in industrial wastewater treatment.

The contents of the UF permeate varies a lot due to the varying production schedule at Dow. That means that the NF membranes must be equipped to handle the worst-case scenario at Dow, if all the NF permeate is to be reused in the process. Despite the varying content of the UF permeate a NF permeate with concentrations of TOC and conductivity lower than that of the city water in Landskrona has been produced on several occasions. This is proof that NF membranes are capable of producing a permeate clean enough to be reused in the process. However, on two occasions the UF permeate from Dow contained high concentrations of TOC, conductivity and inorganic carbon (IC). The concentrations of the produced NF permeate were nowhere near the low concentrations of the city water. Further investigations should be made if this can be avoided if Dow wants to proceed with the NF system.

The fouling issue could not be resolved as it seemed that no combinations and concentrations of cleaning detergent could remove the fouling caused by the filtration. The fouling should be of focus in further studies.

NF seems to be a promising method to further clean the wastewater but further studies in a larger scale need to be done before deciding on implementing it at Dow.

Keywords: wastewater; ultrafiltration; nanofiltration; total organic carbon; conductivity

Sammanfattning

Målet med den här rapporten var att undersöka möjligheten att vidare rena spillvattnet på Dows anläggning i Landskrona. Dow tillverkar vattenbaserade bindemedel från akryl monomerer. Spillvattnet innehåller metalliska joner, såpor, restmonomerer och restpolymerer. Idag så renas spillvattnet med ultrafiltrering (UF) där permeatet släpps iväg till det kommunala reningsverket för vidare rening. Eftersom reningsverket är hårt belastat så är Dow intresserade av att undersöka möjligheten att rena sitt processvatten på anläggningen. Den här studien har undersökt om nanofiltrering (NF) kan användas för att producera ett permeat som är rent nog att återanvända i processen. På grund av rådande vattenbrist i Sverige och runtom i världen så är det viktigt att vara proaktiv inom reningen av spillvatten.

Fem olika NF och omvänd osmos (RO) membran undersöktes vid en första screening av plattmembran: NF99HF från Alfa Laval, AP från GE, NF270, NF90 och XLE från Dow Filmtec. UF-permeatet från Dow i Landskrona användes som feed till NF. Innehållet i UF och NF-permeaten undersöktes genom att mäta total organic carbon (TOC) och konduktiviteten. Skillnaden i TOC och konduktivitet bestämde retentionen för de olika membranen. Påverkan av transmembrantryck (TMP) och tvärströmshastigheten (CFV) studerades för att bestämma de optimala driftsförhållandena.

Från de studerade membranen så valdes NF90 för vidare studie med ett spiralmembran på grund av dess goda retention och vanliga förekomst inom industrin för rening av industriellt spillvatten.

På grund av att Dow varierar vilka produkter de producerar så varierar innehållet UF-permeatet väldigt mycket. Därför måste NF membranen klara av att hantera det UF-permeat med högst koncentration av TOC och konduktivitet om allt NF-permeat ska gå att återanvända i processen. Trots det varierande innehållet i UF-permeatet så lyckades NF producera ett permeat med lägre koncentrationer av TOC och konduktivitet än stadsvattnet vid flera tillfällen. Det bevisar att NF-membranen är kapabla att producera ett NF-permeat som kan återanvändas i processen. Vid två tillfällen så innehöll UF-permeatet mycket höga koncentrationer av TOC, konduktivitet och oorganiskt kol (IC). Detta fick till följd att koncentrationerna även var höga i NF-permeatet och inte låg nära de låga koncentrationerna i stadsvattnet. Vidare studier bör göras om detta går att undvika om Dow vill gå vidare med NF.

Problemet med fouling gick inte att lösa under studiens gång då olika koncentrationer och olika tvättmedel inte hade någon påverkan på foulingen som uppstod av filtreringen. Foulingen borde vara i fokus i en framtida studie.

NF verkar vara en lovande metod för att rena Dows processvatten men vidare studier måste göras i en större skala innan Dow bestämmer sig för om de ska investera i NF.

Nyckelord: spillvatten; ultrafiltrering; nanofiltrering; total organic carbon; konduktivitet

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1. Introduction

The Dow plant in Landskrona produces polymer dispersions mainly to the paint industry. The polymers are built from acrylic monomers. City water is used as fresh water at the Dow plant. An ion exchanger is used to reduce the conductivity of the water before it is used in the process. The wastewater is treated in an ultrafiltration (UF) unit. The permeate is discharged into the municipal wastewater network and then treated at the municipal wastewater treatment (WWT) plant. The aim of this work was to investigate if nanofiltration (NF) of the UF permeate will result in an NF permeate pure enough to be reused in the process, thereby closing the process water loop in the plant. The plant would then not have to be reliant on the demands, capacity and ability of the municipal WWT plant. It also has the additional benefit of reducing the risk of polluting the WWT plant as the process water will be kept on the site at the Dow plant. A rough estimate of the investment cost for the NF plant was made to investigate the economic conditions for such an investment.

1.1 Current wastewater treatment

After cleaning the reactor, blend tanks and transfer lines with water, residues of the products end up in the wastewater drainage system (WWDS). As the wastewater collection tank fills up with wastewater it starts pumping the water to a tank system, as shown in Figure 1. The tank system consists of three tanks: tank A, B and C, where tank A acts as feed tank to the UF plant. When the tanks are filled up, pH is adjusted with either a base or an acid depending on the pH of the water. UF can start when the pH is in the appropriate interval of 8 to 9. Permeate is continuously withdrawn while the retentate is recirculated to tank A. The online system, Nitritox, analyzes the permeate continuously to make sure that the permeate meets the stipulated requirements of the municipal WWT plant. The permeate is released to the municipal wastewater network once the analysis has been done and approved. The concentrated solution is transferred to a new tank when the permeate flow falls below a certain level. The retentate is then either sold as a cheap kind of adhesive or incinerated. The UF system is then cleaned before a new batch of wastewater is treated.

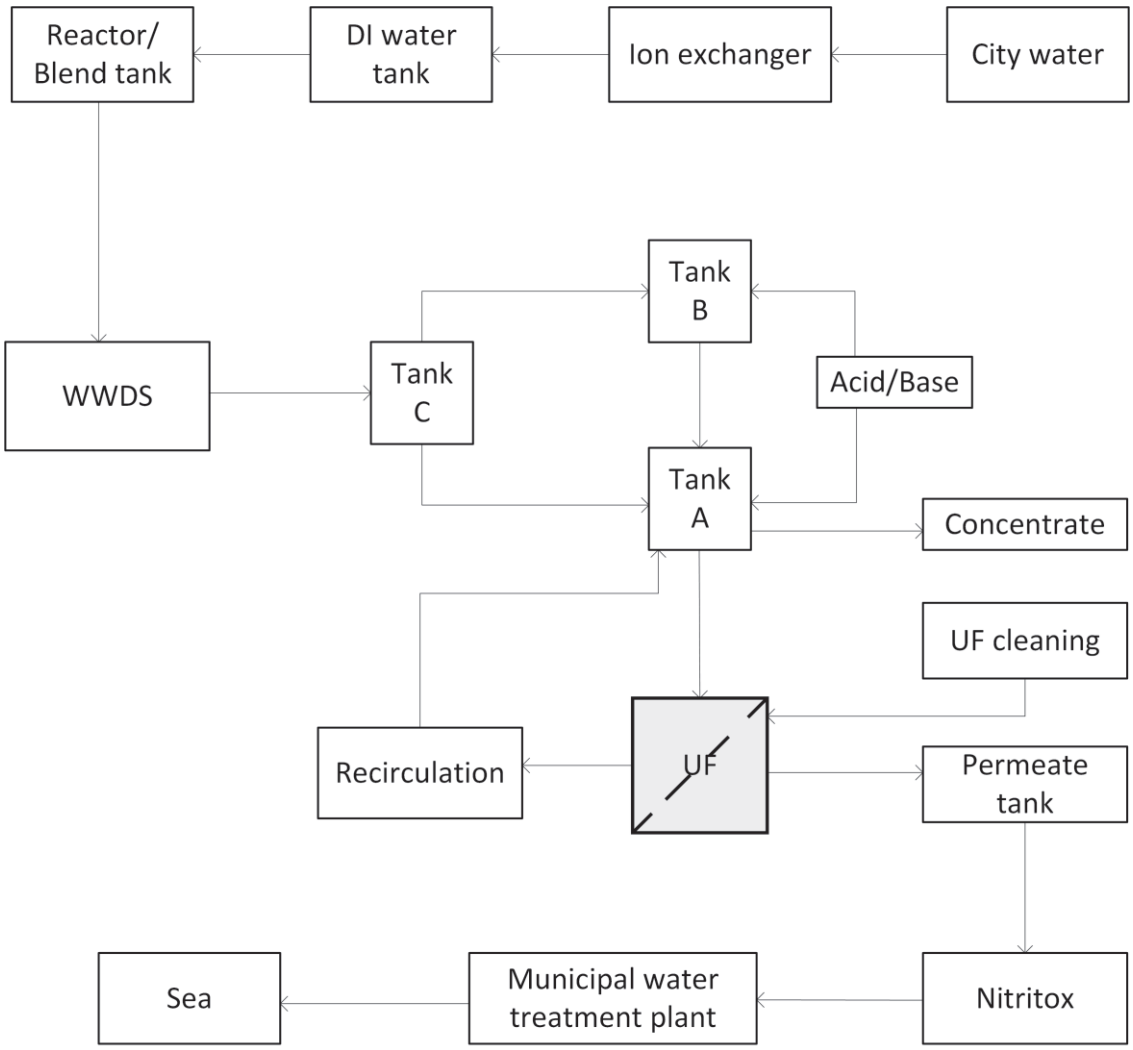


Figure 1. Schematic flowsheet of the wastewater system on site at Dow today

1.2 Wastewater quality

The production process at Dow requires a wide variation of raw materials.

Metals like zinc, iron and tin occur in the products and must be removed when treating the wastewater. Especially zinc is poisonous to aquatic life and shouldn't be released to the environment. The levels of zinc released to the municipal WWT plant today are low and could possibly be reduced to zero with a further treatment of the UF permeate enabling the purified water to be reused in the process. The amount of ions in the water, or the conductivity, is a deciding factor for reusing the process water. If the conductivity is too high, reverse osmosis, or ion exchange could be used to remove the ions. Monovalent ions can be present in the process water but divalent ions must be removed as they might interfere during the emulsion polymerization.

Surfactants are divided into four groups, nonionic, cationic, anionic and amphoteric. Due to the different charges of the surfactants the pH of the wastewater and the surface charge of a membrane need to be chosen with great care to provide optimal filtration. If the membrane and the surfactant have opposite charge they might bind in to each other which could cause fouling or worse, a permanent damage of the membrane. The surfactants cause foaming, which is why the filtration of surfactants is important if the treated water will be reused in the process. Most of the surfactants are anionic and large molecules,

however there are some nonionic surfactants in the size range of 100-150 Da, which is a rather small molecule.

High levels of residue **monomers** might be harmful to membranes, due to their reactivity. Measuring the levels of residue monomers in the UF permeate is important before the subsequent treatment of the wastewater. Previous, preliminary tests at Dow have indicated that the current level of residue monomers is not harmful to NF membranes.

1.3 UF permeate quality

The properties of the UF permeate will vary depending on which products that have been produced. The conductivity and concentration of total organic carbon (TOC) have a large variation which is why the subsequent treatment stage must be designed so that the system can handle even the highest concentration of the UF permeate.

1.4 Quality demands on water to be reused

To be able to reuse the treated wastewater in the process it must be free of bacteria and surfactants, and have a conductivity ≤ 0.02 mS/cm. The most important condition for reusing the process water is a complete absence of surfactants. The surfactants cause foaming which can have a very negative influence on the performance in the reactor. The TOC concentration gives a rough estimate of the content of surfactants. The TOC values should be at the same level as the incoming city water and if possible as low as the values after the ion exchanger. The TOC of the city water is about 3 mg/l (water from 21/2-17) and the conductivity is 0.17 mS/cm and the COD is 1.2 mg O_2/l. [1]. The city water is deionized with an ion exchanger before being used in the process. If the conductivity of the treated wastewater is only slightly higher than 0.02 mS/cm the existing ion exchanger can be used to meet the desired conductivity but it is, of course, beneficial if the treated wastewater can go straight into the process and bypass the ion exchanger.

Even if the quality of the treated wastewater does not meet all the requirements it might still be possible to use in the process, if diluted with clean water. The properties of the retained compounds in the wastewater are very important. The toxicity will decide how the reject needs to be handled and the cost of it.

2. Wastewater treatment methods

Different methods to remove surfactants in wastewater are presented below.

2.1 Coagulation and flocculation

Coagulation and flocculation can be used to remove suspended solids and organic matter in wastewater. Metals and polymers can be used as coagulants to destabilize suspended solids in the water. Naturally, or by adding a flocculant, the destabilized particles form aggregates.

Coagulation and flocculation with iron chloride ($FeCl_3$) have been used for removal of surfactants from wastewater in a dose of 600-1100 mg/l at pH=8 [2]. The analysis shows almost a complete removal of all surfactants, as shown in Figure 2, at a high enough concentration of $FeCl_3$. It was shown that iron had the same effect on removal of COD and surfactant with a R^2 value of 0.99.

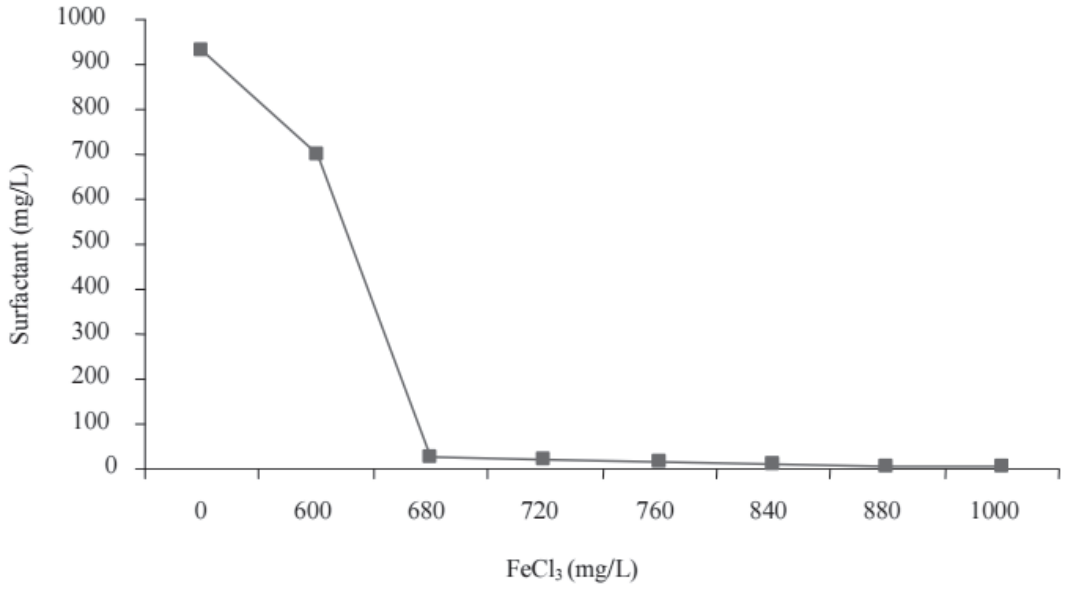


Figure 2. Effect of $FeCl_3$ on surfactant removal [2].

2.2 Fenton oxidation process

Hydrogen peroxide (H_2O_2) and ferrous sulfate ($FeSO_4$) form a strong oxidizing agent which can be used for oxidation of surfactants [3]. Small flocs of dissolved iron are formed which needs to be removed from the water. Coagulation is a proven method for removal of dissolved iron.

As the dissolved iron can be removed by coagulation it can also be incorporated in the treatment process for improvement of turbidity and removal of organic matter.

2.3 Adsorption with alumina

Alumina can be used for adsorption of anionic surfactants. The negatively charged surfactant binds in to the positively charged surface on alumina. When the alumina is saturated the water, treatment is stopped and the alumina is regenerated. Sodium hydroxide works well to regenerate the alumina. A study showed that wastewater containing 8068 mg/l of anionic surfactants had a 94% removal with an adsorbent dose of 120 g/l in a batch [4]. A fixed bed column for anionic surfactant removal was also tested with similar results to the batch study.

2.4 Biological treatment

Pretreatment with coagulation and flocculation, adsorption or Fenton oxidation increases the biodegradability of the organic matter and surfactants so that aerobic bacteria can take care of the substances that are not removed during the pretreatment [5] [6]. The bacteria degrade organic matter and at the same time consume nitrogen and phosphorous. The bacteria grow in floc and must be separated after the treatment. The pretreatment is required since the wastewater otherwise could be toxic and end up killing the bacteria.

2.5 Nanofiltration

NF membranes have two main mechanisms of filtration, size exclusion and electrostatic interactions. The size of the pores decides which compounds that can pass through the membrane. The molecular mass is a good indication of the size of a compound and can be used as reference in most cases. The charge of the membrane and the solute has a

significant influence on the retention. The membrane will repel negative compounds if the zeta potential of the membrane is negative. The zeta potential varies with pH which means that the zeta potential can be set to the point of optimal filtration of the charged compounds by adjusting the pH of the wastewater. For nonionic compounds, a membrane with pores smaller than the size of the compound needs to be used. [7]

Membrane filtration is an already known concept at the Dow plant as UF is used to treat the wastewater. Previous, preliminary tests with NF membranes at the plant have provided promising results, which is why NF is the treatment method that has been studied in this work. Preliminary results indicate that an NF unit can be easily integrated into the existing infrastructure at Dow using already existing equipments such as the cleaning tank and transfer lines. The small footprint of an NF unit also makes it easier to make it fit into the limited space at the Dow facility.

An optimal theoretical process schematic for the combined UF and NF system is shown in Figure 3. Ideally the NF plant will be run at similar operational conditions as the UF plant, with the exception that the NF permeate should have a quality good enough to be reused in the process. If the NF permeate does not fulfill the purity requirements of the water to be used at the Dow plant, additional treatment of the NF permeate with reverse osmosis (RO) or ion exchange might make it possible to fulfill the demands on the quality of the water to be reused. Special handling might be required, depending on the toxic properties of the NF rententate.

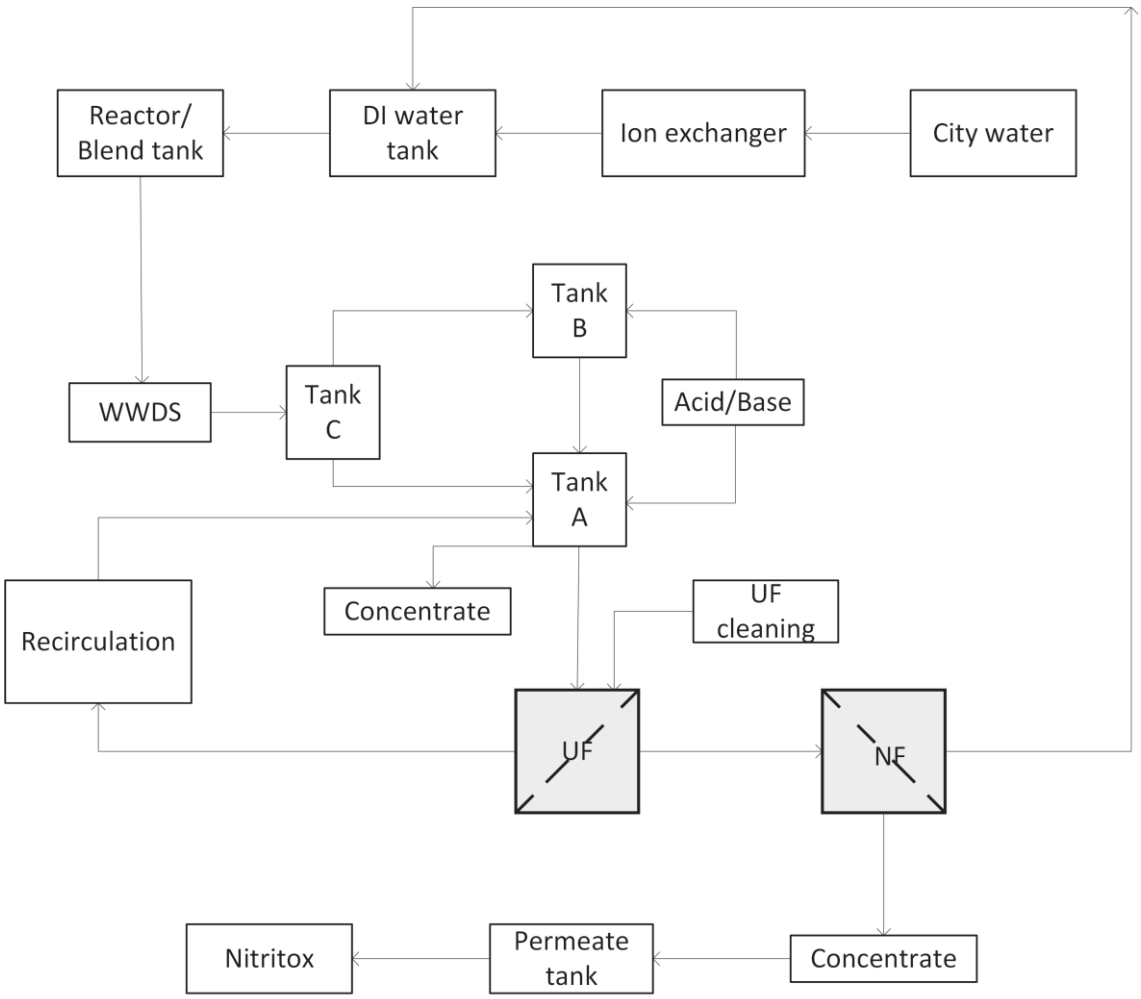


Figure 3. Ideal process flowsheet for a combined UF and NF wastewater treatment system

2.6 Cleaning of membranes

Membranes need to be cleaned. There are five categories of cleaning agents that typically are used: alkaline, acid, metal chelating agents, surfactants and enzymes. A commercial cleaning agent is usually a combination of these cleaning agents [8].

From a study, the cleaning detergent was made up of sodium hydroxide (NaOH), ethylenediaminetetraacetate (EDTA) and sodium dodecyl sulfate (SDS). The NaOH is the alkaline, the EDTA is the metal chelating agent and SDS is the anionic surfactant. The metal chelating agent, in this case EDTA, forms strong complexes with divalent ions and are thereby able to break up the complexes between divalent ions and organic matter. The efficiency of EDTA is heavily influenced by the pH. The pK_a values of EDTAs 4 carboxylic groups are 2.72, 3.24, 6.68 and 11.12. In order to deprotonate almost all of the carboxylic groups a pH of at least 11 is required which is where the alkaline play an important role. The surfactant SDS forms micelles around macromolecules and can thereby solubilize them [8].

3. Materials and method

3.1 Raw material

UF permeate from the Dow plant in Landskrona was used as feed in the experiments. The properties of the UF permeate varies greatly depending on which product Dow has produced. This means that the membrane performance will vary from batch to batch of UF permeate. Since the risk of microbial growth in the UF permeate increases for every day it is stored it was decided that fresh UF permeate should be used in every experiment, despite the varying content and properties of the UF permeate. In the initial screening of different flat sheet membranes, UF permeate in batches of 20 liters were used. The UF permeates were collected at Dow in Landskrona the 6th, 15th, 21st and 28th of February, and the 6th, 7th and 13th of March, and 19th of April. In the experiments with a spiral-wound module, the UF permeate was collected 24th of May.

3.2 Membranes

The performance of four different membranes was studied in a screening test. The selection of membranes was done based on a previous study of NF membranes at Lund University [9] and in consultation with Jochen Henkel at Dow Water and Process solutions [10]. The membranes were chosen based on their TOC retention and flux. Characteristics of the membranes are found in Table 1. The NF90 membrane (NANO 9-2514 made by Oltremare) was used in a concentration experiment with a spiral-wound module.

Table 1. List of the membranes used for initial screening

Model	Manufacturer	Type of membrane	Material	Stabilized rejection
NF99HF	Alfa Laval	Nano	Thinfilm composite on polyester	≥99%[1]
AP	GE Water & Process technologies	RO	Polyamide on polysulfone	95%[2]
NF270	Dow Filmtec	Nano	Polyamide thinfilm composite	>97%[3]
NF90	Dow Filmtec	Nano	Polyamide thinfilm composite	>97%[3]
XLE	Dow Filmtec	RO	Polyamide thinfilm composite	99%[4]

1 Average $MgSO_4$ rejection on 1000 ppm $MgSO_4$, 7.6 bar, 25 °C
2 Average NaCl rejection on 500 ppm NaCl, 5.2 bar, 25 °C
3 2000 ppm $MgSO_4$, 4.8 bar, 25 °C, 15% recovery
4 2000 ppm NaCl, 8.6 bar, 25 °C, pH 8, 15% recovery

3.3 Equipment and experimental procedure

Screening experiments with flat sheet membranes
Flat sheet membranes can be used when screening the membrane performance of a number of membranes, in order to find the optimal membrane to use in further investigations with a spiral-wound module. Samples of the flat sheet membranes are commonly cut from a large sample of the membrane, shown in Figure 4.

Figure 4. A typical flat sheet membrane

Batch versus continuous filtration
The filtration can be operated as a batch process where the concentration of the feed increases during the process or it can operate continuously where fresh feed is supplied constantly.

The filtration was operated as a batch process in these experiments.

Modes of filtration
There are two modes of filtration, crossflow filtration and dead-end filtration. In dead-end filtration, the feed passes through the membrane. A filter cake of retained material is formed on the membrane why regular backwashing is required to remove the filter cake. This mode is very effective if the concentration of foulants is very low in the feed. If the concentration is high, a filter cake would emerge immediately making the filtration highly ineffective. When the concentration of foulants is high it is more appropriate to use crossflow filtration. In this case the feed flows parallel to the membrane and due to the pressure difference between the feed and the permeate side of the membrane, there is a transport of water and solutes to the membrane. By regulating the crossflow velocity, the

thickness of the cake layer can be controlled so that fouling is minimized. The principle of the two modes are shown in Figure 5 [11].

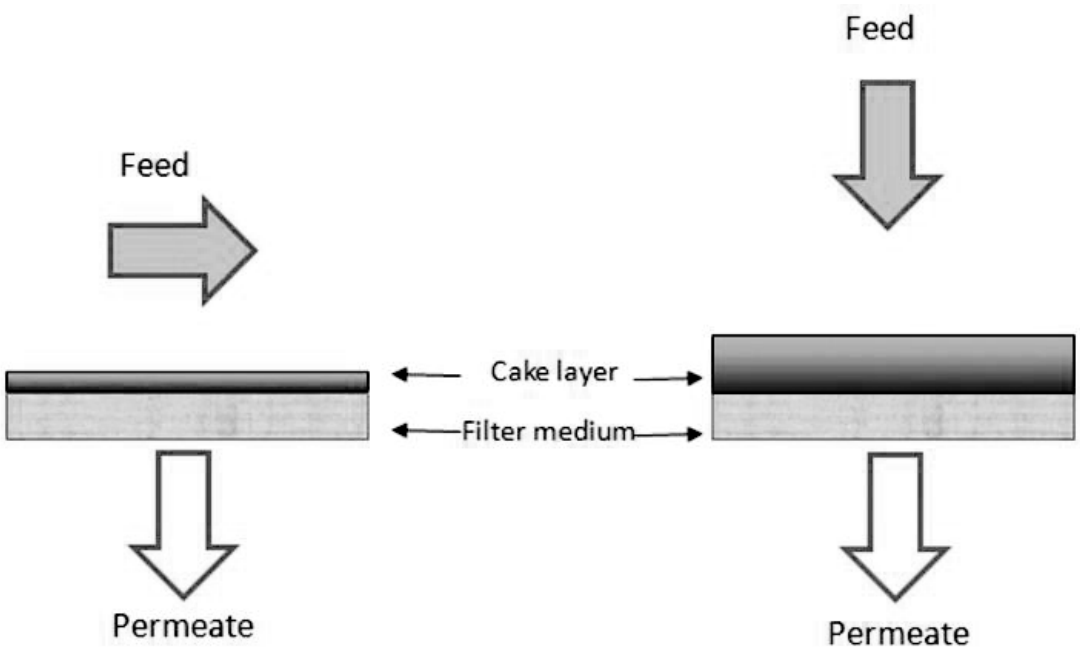


Figure 5. The two modes of filtration, crossflow filtration at the left and dead-end filtration at the right [11].

Based on this information the crossflow filtration was used for the study to minimize fouling and flux reduction.

Spiral-wound membrane

A spiral wound membrane is made up of many flat sheet membranes wound around a central tube as a spiral, hence the name. The center consists of a hollow permeable tube in which the permeate flows to and then exits the membrane. A schematic of an unfolded spiral wound membrane is shown in Figure 6.

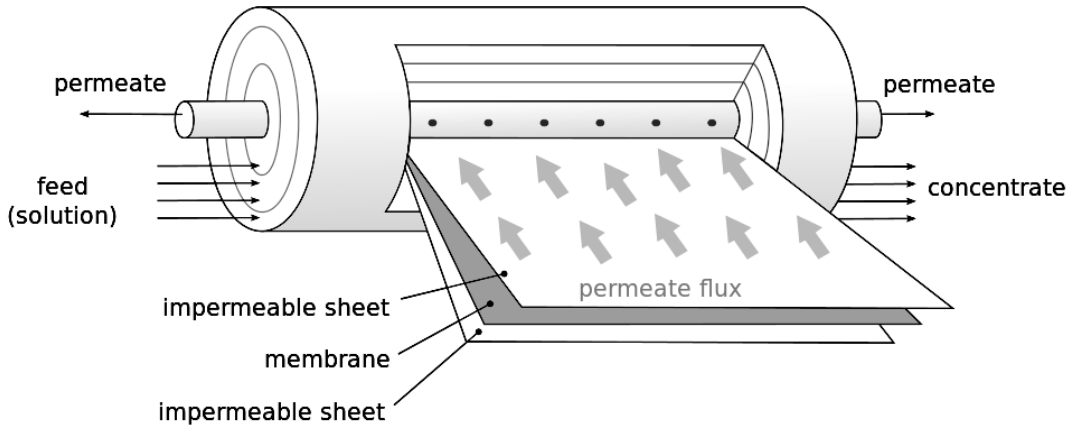


Figure 6. An unfolded spiral wound membrane. Reproduced with permission from Wikipedia Commons (https://commons.wikimedia.org/wiki/File:Spiral_flow_membrane_module-en.svg)

Recovery
The filtration process should strive for as high recovery of permeate as possible. A high recovery has the two benefits that a large amount of the process water can be reused and only a small amount of retentate needs to be disposed of. In batch filtration, the concentration will increase in the feed water until it reaches the point where the flux decline is too high to continue. This is where the filtration is stopped and the recovery is determined.

Equipment
An equipment at the Department of Chemical Engineering, LTH, with three flat sheet modules in parallel was used in the screening test. The fourth module, shown in Figure 9, was not used because of earlier experiences of unreliable results when using this module. The area of each membrane is 19.6 cm^2. The equipment can be changed to use a spiral-wound membrane module instead of the flat sheet membrane modules. The spiral-wound module can fit membranes with the diameter of 2.5 inches and a length of 18 inches.

Pressure, temperature, crossflow velocity (CFV) and permeate flow rate were recorded by a PC equipped with LabView 6.0 software (National Instruments Co., TX, USA). The permeate flow was measured using an electronic balance. The flux ($l/(m^2h)$) was calculated from the weight difference with time and the membrane area. The temperature was measured by a temperature probe in the feed tank. The temperature could be increased using an immersion heater and decreased using an immersion cooler placed in the feed tank. The (CFV) was measured by a flow meter after the retentate valve. The CFV was regulated using a frequency converter connected to the pump. The transmembrane pressure (TMP) is the mean value of the two pressure gauges placed before and after the membrane modules. The TMP was regulated by adjusting the retentate valve and the frequency of the pump.

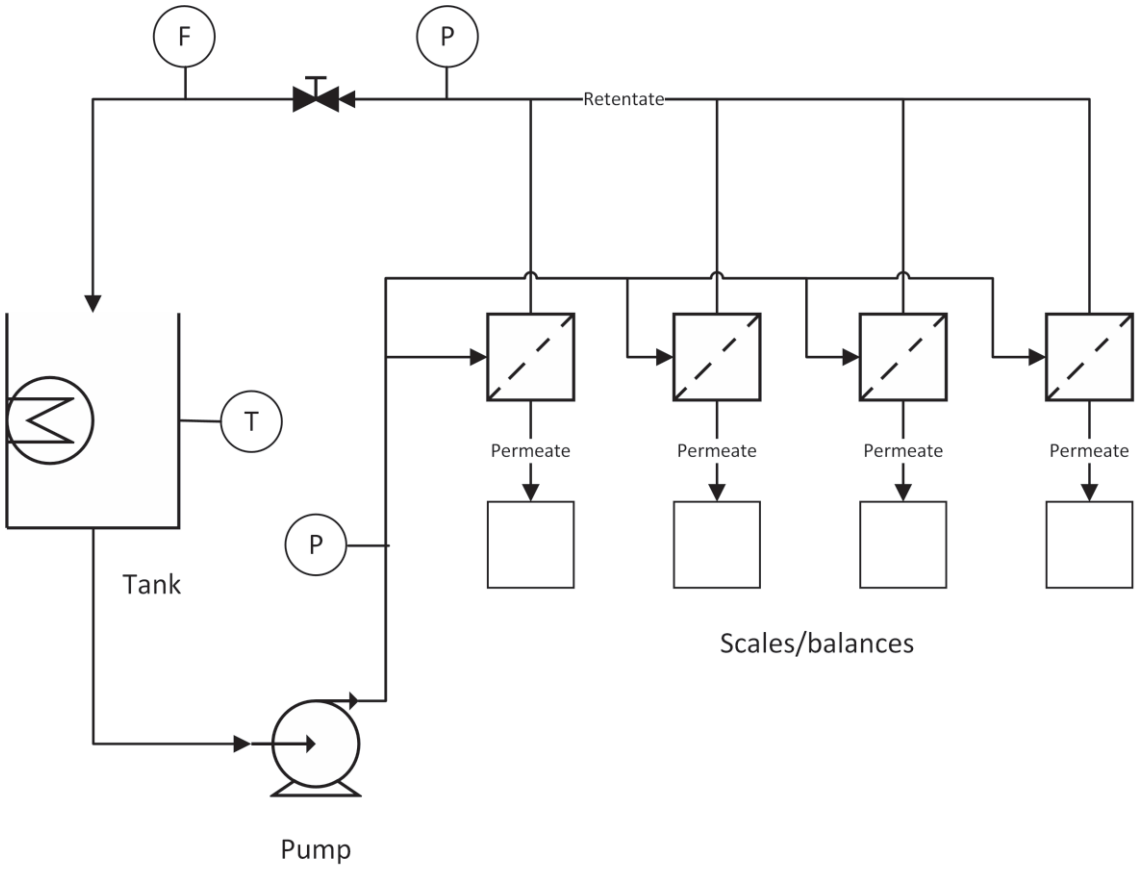


Figure 7. Flow scheme of the flat sheet membrane system. T indicates measurement of temperature, P pressure and F crossflow.

A photo of the experimental setup is shown in Figure 8.

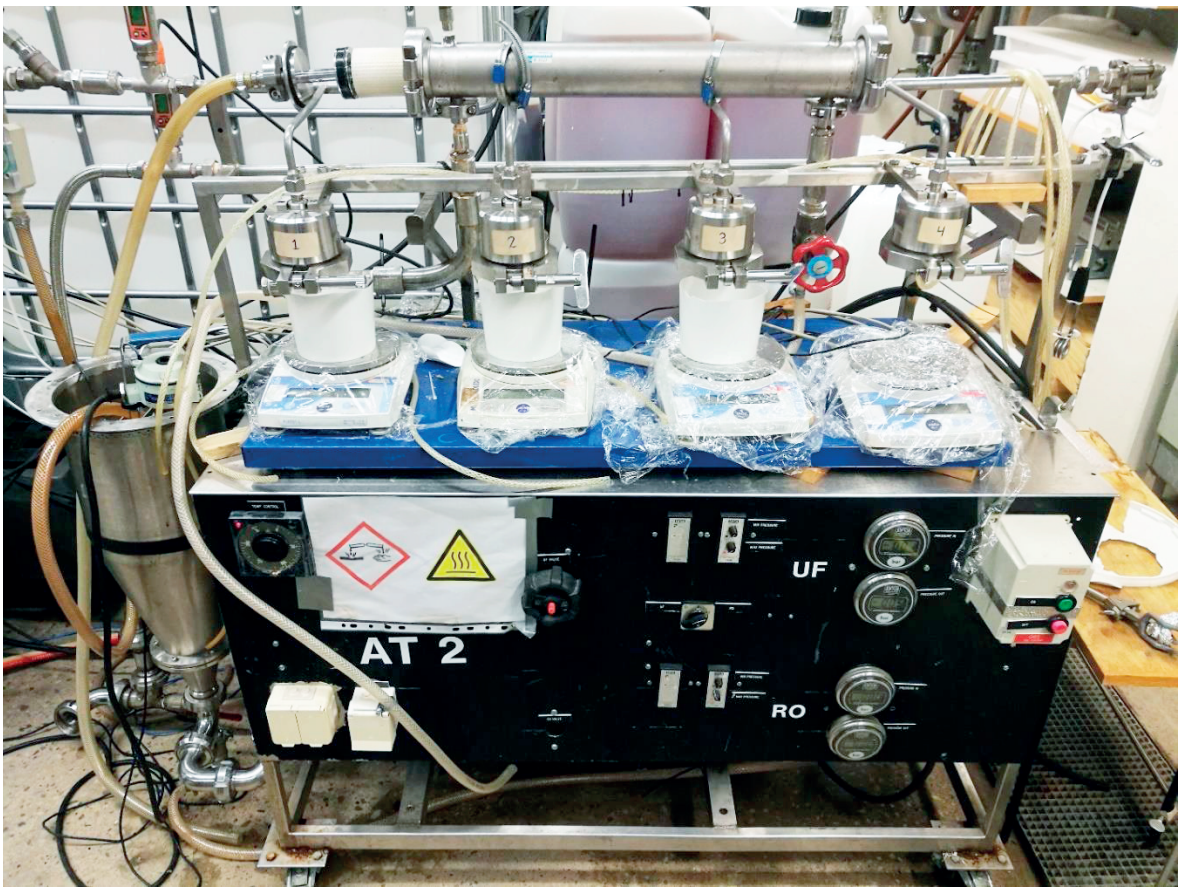


Figure 8. Photo of the experimental setup

For the spiral wound module, a larger feed tank was used and the permeate was collected in a larger bucket. The feed tank volume was about 200 l and the bucket volume around 10 l. When the bucket was full the permeate was emptied into an intermediate bulk container (IBC). The equipment with the spiral wound module connected can be seen in Figure 9.

Figure 9. Photo of the experimental setup when the spiral wound module was used

The experiments began by filling the feed tank with deionized water and the temperature was raised to the preset cleaning temperature. The cleaning detergent was added slowly to make sure that there are no pulses of highly concentrated cleaning detergent which might damage the membranes. When all cleaning detergent had been added and thoroughly mixed with the water, the cleaning procedure started. The cleaning solution was initially circulated at 45 °C during one hour. After measuring the pH of the cleaning solution in experiment 7 and onwards the temperature was lowered to 25 °C according to the given maximum temperature in the specific pH interval for the membranes.

When the cleaning procedure was done, the system was flushed with deionized water in order to remove all cleaning detergent and the pure water flux (PWF) was measured at 30 °C and a crossflow velocity of 0.5 m/s. The PWF increases linearly with TMP according to Darcy's law which is shown in equation 1.

$$PWF = \frac{TMP}{\mu R_m} \quad (1)$$

μ is the viscosity and R_m the filtration resistance of the membrane. The pressure was increased stepwise giving a linear flux.

The deionized water in the system was discharged and the remaining water was displaced by UF permeate. The feed tank was filled up with approximately 12 liters of UF permeate. No adjustment of pH was done during the experiments with UF permeate. The temperature was 45 °C and the crossflow velocity was 0.5 m/s. Both retentate and permeate were recirculated to the feed tank during the experiments. The TMP was increased stepwise from 2 to 10 bar in the experiments with the NF99HF, AP and NS270

membranes and from 5 to 20 bar in the experiments with the NF90 and XLE membranes. Samples to be analyzed were withdrawn when the system was stabilized after altering TMP.

When the filtration of the UF permeate was completed the membrane was cleaned and PWF was measured, the same way as before filtration of the UF permeate. The PWF before and after treating the UF permeate was used to investigate fouling of the membrane.

The following screening experiments were done:

Exp.	Date of experiment	Membrane(s)	Temp (°C)	CFV (m/s)	TMP (bar)	Cleaning
1	8/2	NF99HF, AP, NF270	45	0.5	2, 4, 6, 8, 10	0.1 wt% (U10)
2	16/2	NF99HF, AP, NF270	45	0.5	2, 4, 6, 8, 10	0.1 wt% U10
3	23/2	AP, NF90, XLE	45	0.5	5, 10, 15, 20	0.1 wt% U10
4	1/3	AP, NF90, XLE	45	0.3, 0.4, 0.5	5, 10, 15, 20	0.1 wt% U10
5	7/3	AP, NF90, XLE	45	0.5	5, 10, 15, 20	0.4 wt% U10
6	9/3	AP, NF90, XLE	45	0.5	5, 10, 15, 20	1 wt% U10, 2 wt% U73, 1 wt% U10
7	10/4	AP, NF90, XLE	45	0.5	5, 10, 15, 20	2 wt% U10, 25 °C
8	20/4	AP, NF90, XLE	45	0.5	2.5, 5, 7.5, 10	1 wt% U10, 25 °C, 2 wt% Dow detergent

Concentration experiments with a spiral-wound membrane

The concentration experiment was done to study how high the UF permeate could be concentrated. 180 l of feed solution was added to the feed tank and kept at a constant level by adding feed solution continuously from an IBC with UF permeate from Dow in Landskrona. By measuring the permeate flux the permeate volume (PV) can be calculated using the membrane area. The volume reduction (VR) in percentage could then be calculated from the feed volume (FV) and permeate volume, which can be seen in equation 2.

$$VR = \frac{PV}{FV+PV} * 100 \quad (2)$$

A high VR is desirable since it leaves a lower volume of retentate which is a waste product that needs to be disposed of.

The following concentration experiment was done:

Exp.	Date of experiment	Membrane(s)	Temp (°C)	Flow (l/min)	TMP (bar)	Cleaning
9	29/5-2/6	NF90 (NANO 9-2514)	45	16.5	10	1 wt% U10

3.4 Analysis

Conductivity and TOC were analyzed at the Department of Chemical Engineering, LTH, and the ionic content and biological oxygen demand (BOD) were analyzed at ALcontrol [12].

Conductivity
A HANNA HI 99301 was used to measure the conductivity of the NF and UF permeates. It measures the conductivity in the range of 0.00 to 20.00 mS/cm.

TOC
TOC was measured using the total organic carbon analyzer TOC-5050A made by Shimadzu. A set amount of the sample is injected. The sample is heated until all water has evaporated and the total carbon (TC) is measured by a sensor. The carbon in the sample is mixed with phosphoric acid which reacts with the inorganic carbon (IC). The IC is then measured and subtracted from the TC which gives the TOC. Analysis of each sample is made in triplicates and a mean value as well as the values of each measurement are printed on a paper roll.

Molecular mass
The molecular mass can be measured with size exclusion chromatography (SEC) [13]. The different compounds in the sample are separated by their difference in molecular size. SEC usually consists of a hollow tube packed with small porous polymer beads of different sizes. The smaller molecules are entangled in the polymer beads while the larger molecules slide down along the surface of the beads. Due to this phenomenon, the molecules are eluted in decreasing molecular size.

Bacterial growth
Dip slides were used to measure bacterial growth in the solutions. The dip slide from Merck [14] contains an agar gel with non-selective nutrients [15]. A dip slide was dipped in the sample and then left in a 30 °C water bath for 7 days for the bacterial growth to occur. The bacterial growth can then be observed visually on the surface of the agar gel.

3.5 Cost estimate

The capital and operating costs for the integrated NF system were estimated with the program Reverse Osmosis System Analysis (ROSA) version 9.1 made by Dow Water & Process Solutions [16]. ROSA is a simulation program specifically made for Dow Filmtec membranes. Cost information for the equipment was given by BWT Vattenteknik and Dow.

4. Results and discussion

Average molecular mass of the UF permeate
The cut-off of the UF membrane at Dow is 40 nm. The average molecular mass of dissolved substances was measured in the UF permeate used in experiment 1. This UF permeate was transparent with relatively low conductivity and TOC content (see Table 3). The average molecular mass was measured by SEC and was found to be 400 Da. The SEC chromatogram is shown in Figure 10.

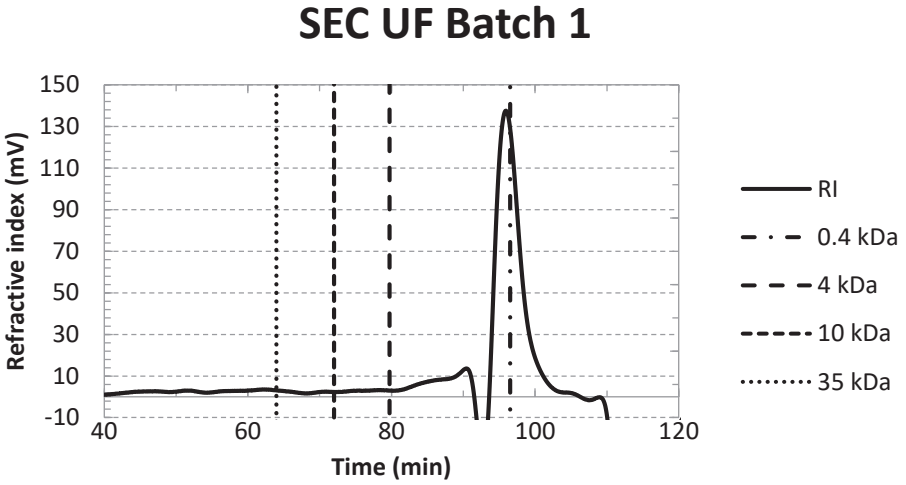
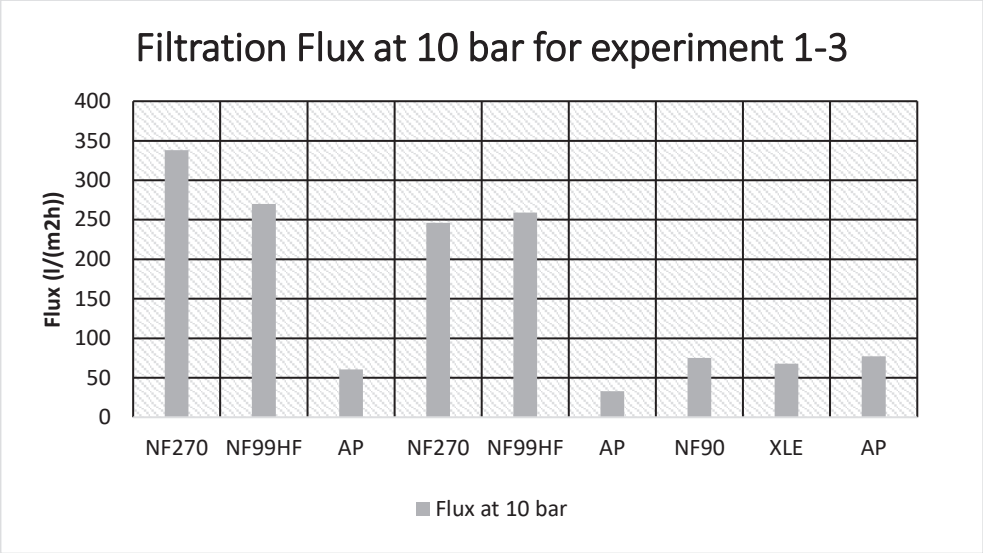


Figure 10. Molecular mass distribution in the UF permeate sampled February 6, 2017.

4.1 Influence of transmembrane pressure

The influence of TMP on membrane performance was studied in experiment 1 - 2 (2-10 bar) and 3 (5-20 bar).

Influence of transmembrane pressure on flux
A linear correlation between flux and TMP was experienced for all membranes. The flux at 10 bar is shown in Figure 11. The flux was correlated to the TOC and conductivity levels of the UF permeate, as shown in the figure. The AP membrane was used in all 3 experiments and the flux was highest for the UF permeate with the lowest level of TOC and conductivity (exp. 3) and lowest for the UF permeate with the highest levels of TOC and conductivity (exp. 2). The large differences in the content of the UF permeate makes it impossible to determine a constant flux for the membranes, which means that the NF system must be designed to handle the worst-case scenario for the UF permeate, which was experiment 2 in this investigation.



Exp. 1 (477 mg/l) Exp. 2 (717 mg/l) Exp. 3 (400 mg/l)

Figure 11. Comparison of the flux at 10 bar for the membranes in experiment 1-3. The TOC of the UF permeate used as feed in the parentheses

Influence of transmembrane pressure on retention

The aim of the project was to find a NF membrane that produces a permeate with a conductivity ≤ 0.02 mS/cm and a concentration of TOC comparable with the concentration in the deionized water used as process water at Dow. The concentration of TOC in the city water in Landskrona, the deionized (DI) water after treatment of the city water by ion exchange, and the DI water used in the experiments at Kemicentrum, Lund, is shown in Table 2.

Table 2. TOC concentration in the city water in Landskrona, after ion exchange of the water and the deionized water at Kemicentrum.

	Conductivity (mS/cm)	TC (mg/l)	IC (mg/l)	TOC (mg/l)
City water Landskrona	0.17[1]	9.073	6.121	2.952
DI water Dow	≤ 0.02	0.369	0.125	0.244
DI water LTH		1.206	0.152	1.054

[1] the conductivity was measured by NSVA [1]

The TOC concentration and the conductivity was markedly different in UF permeates obtained from the Dow facility in Landskrona at different times. TOC and conductivity varied between 64 mg/l and 0.45 mS/cm (experiment 4) and 717 mg/l and 3.55 mS/cm (experiment 2). There was also a big visual difference where the more concentrated UF permeate in experiment 2 was yellow in contrast to the other UF permeates which were almost completely transparent. This big difference might be explained by the release of scrubber lye in the UF permeate used in experiment 2. The roughly 8 times higher IC concentration in this UF permeate strengthen this assumption since the scrubber lye absorb inorganic compounds from the exhaust gas of the process. A discussion arose if the scrubber lye should be treated by UF or handled separately. The large concentration differences in the UF permeate from time to time, makes it difficult to compare the retention between different NF experiments.

The TMP, the CFV, the temperature and the pH of the solution, all influences the membrane performance. The temperature affects the viscosity of the water which has an

impact on the flux according to Darcy's law. The viscosity increases with a decreasing temperature which means that the flux can be improved by increasing the temperature of the feed. The pH of the feed is important for the retention and flux. Most membranes have a negative zeta potential which means that the membrane repel negatively charged substances. By increasing the pH of the feed, the repelling effect is enhanced which improves the filtration. Influence of temperature and pH was not studied as all experiments were performed at the maximum acceptable temperature for the membranes,45 °C, and pH 8-9 which is the pH of the UF permeate.

NF permeate was collected at 6 and 10 bar in experiment 1, at 4 and 6 bar in experiment 2 and at 10 and 20 bar in experiment 3. Concentration of TOC and conductivity are shown in Table 3-5.

Table 3. Concentration of TOC and conductivity of feed (UF permeate) and NF permeate in experiment 1. UF permeate was withdrawn at Dow February 6, 2017.

	TC (mg/l)	IC (mg/l)	TOC (mg/l)	TOC retention (%)	Conductivity (mS/cm)	Conductivity retention (%)
UF-permeate	512	34.94	477.06		1.52	
NF270 (6 bar)	119.5	10.73	108.77	77.2	0.38	75.0
NF270 (10 bar)	142.1	12.23	129.87	72.8	0.4	73.7
NF99HF (6 bar)	56.43	5.488	50.942	89.3	0.15	90.1
NF99HF (10 bar)	57.53	5.808	51.722	89.2	0.16	89.5
AP (6 bar)	24.98	3.54	21.44	95.5	0.06	96.1
AP (10 bar)	20.32	2.924	17.396	96.4	0.06	96.1

Table 4. Concentration of TOC and conductivity of feed (UF permeate) and NF permeate in experiment 2. UF permeate was withdrawn at Dow February 15, 2017.

	TC (mg/l)	IC (mg/l)	TOC (mg/l)	TOC retention (%)	Conductivity (mS/cm)	Conductivity retention (%)
UF permeate	993.9	277.35	716.55		3.55	
NF270 (4 bar)	303.1	75.43	227.67	68.2	1.27	64.2
NF270 (6 bar)	276.8	64.16	212.64	70.3	1.14	67.9
NF99HF (4 bar)	207.7	94.28	113.42	84.2	0.95	73.2
NF99HF (6 bar)	171.4	48.93	122.47	82.9	0.76	78.6
AP (4 bar)	103.1	27.78	75.32	89.5	0.47	86.8
AP (6 bar)	75.07	19.23	55.84	92.2	0.34	90.4

Table 5. Concentration of TOC and conductivity of feed (UF permeate) and NF permeate in experiment 3. UF permeate was withdrawn at Dow February 21, 2017.

	TC (mg/l)	IC (mg/l)	TOC (mg/l)	TOC retention (%)	Conductivity (mS/m)	Conductivity retention (%)
UF permeate	467.4	67.2	400.2		1.72	
NF90 (10 bar)	11.66	1.881	9.779	97.6	0.03	98.3
NF90 (20 bar)	10.24	1.819	8.421	97.9	0.02	98.8
XLE (10 bar)	10.67	2.065	8.605	97.8	0.03	98.3
XLE (20 bar)	9.766	1.904	7.862	98.0	0.03	98.3
AP (10 bar)	14.81	2.513	12.297	96.9	0.04	97.7
AP (20 bar)	17.39	5.852	11.538	97.1	0.03	98.3

Measurements of total organic carbon (TOC), biochemical oxygen demand (BOD), chemical oxygen demand (COD), conductivity, metal ion levels and concentration of surfactants are of interest when determining the retention. The measurements of TOC and conductivity could be done at Lund University while the others had to be done at ALcontrol.

How much that is retained during the filtration is presented as the retention of the membrane. The retention is defined as $R = 100\times(1 - C_P/C_F)$, where C_P and C_F are the concentrations of the permeate and the feed (here the UF permeate), respectively. The NF90, XLE and AP membranes had by far the highest retention of both TOC (97-98%) and conductivity (98-99%), as shown in Table 3-5. As can be seen in the tables the tighter membranes (NF90, XLE and AP) show a slight increase in retention with increasing TMP. Although a very small and possibly insignificant increase it's still an indication that there is a correlation between TMP and retention. The increase is most noticeable for the AP membrane in experiment 2 where the retention increases several percent when TMP is increased from 4 to 6 bar.

4.2 Influence of crossflow velocity

The CFV determines the thickness of the filter cake and the degree of concentration polarization. A high CFV reduces the thickness of the filter cake and the concentration polarization due to shear forces on the boundary layer at the membrane surface.

Influence of crossflow velocity on flux

The influence of the CFV on the flux of NF90 when filtrating the UF permeate is shown in Figure 12. When the CFV is increased the filter cake thickness and concentration polarization are reduced which results in a higher flux. This is apparent from Figure 12 and shows that the CFV has a greater influence at a higher TMP. The influence of the CFV for the XLE and AP membranes were similar to the influence for NF90 and can be found in Appendix A.

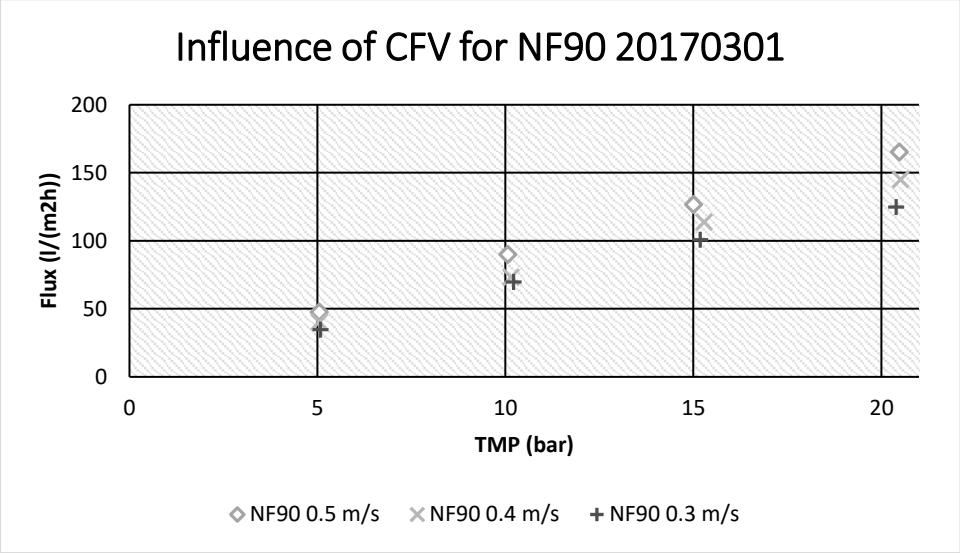


Figure 12. Influence of CFV for NF90 when filtrating UF permeate in experiment 4

Influence of crossflow velocity on retention

The influence of CFV on retention is shown in Table 6. As can be seen the retention is almost identical for every CFV for all the membranes. Theoretically CFV should have no impact on the retention so this result was expected.

Table 6. Concentration of TOC and conductivity of feed (UF permeate) and NF permeate in experiment 4. UF permeate was withdrawn at Dow February 28, 2017.

	TC (mg/l)	IC (mg/l)	TOC (mg/l)	Retention (%)	Conductivity (mS/m)	Retention (%)
UF permeate	74.25	10.35	63.9		0.45	
NF90 (0.3 m/s)	8.413	1.005	7.408	88.4	0.02	95.6
NF90 (0.4 m/s)	6.053	1.021	5.032	92.1	0.02	95.6
NF90 (0.5 m/s)	6.147	0.95	5.197	91.9	0.02	95.6
XLE (0.3 m/s)	7.01	1.389	5.621	91.2	0.02	95.6
XLE (0.4 m/s)	6.341	1.013	5.328	91.7	0.02	95.6
XLE (0.5 m/s)	5.922	1.005	4.917	92.3	0.02	95.6
AP (0.3 m/s)	6.07	0.972	5.098	92.0	0.02	95.6
AP (0.4 m/s)	6.41	0.998	5.412	91.5	0.02	95.6
AP (0.5 m/s)	6.48	0.971	5.509	91.4	0.02	95.6

4.3 Reproducibility

The membrane performance at similar operation conditions but with UF permeates sampled at different occasions was studied in experiment 5, 6 and 8. By accident the NF permeate from experiment 7 was not analyzed. In these experiments both TOC and conductivity was below or just above the values of the city water in Landskrona, and the conductivity almost fulfilled the demands on the conductivity of the DI water at Dow, as shown in Table 7-9.

This shows that the NF membranes NF90, XLE and AP, that were used in these experiments, can deliver permeate that can replace a significant part of the city water.

Table 7. Concentration of TOC and conductivity of feed (UF permeate) and NF permeate in experiment 5. UF permeate was withdrawn at Dow March 6, 2017.

	TC (mg/l)	IC (mg/l)	TOC (mg/l)	TOC retention (%)	Conductivity (mS/m)	Conductivity retention (%)
UF permeate	411.2	19.35	391.85		0.87	
NF90 (0.5 m/s 20 bar)	4.804	1.075	3.729	99.0	0.02	97.7
XLE (0.5 m/s 20 bar)	4.619	1.49	3.129	99.2	0.02	97.7
AP (0.5 m/s 20 bar)	4.172	1.065	3.107	99.2	0.02	97.7

Table 8. Concentration of TOC and conductivity of feed (UF permeate) and NF permeate in experiment 6. UF permeate was withdrawn at Dow March 7, 2017.

	TC (mg/l)	IC (mg/l)	TOC (mg/l)	TOC retention (%)	Conductivity (mS/m)	Conductivity retention (%)
UF permeate	214	40.28	173.72		0.67	
NF90 (0.5 m/s 20 bar)	3.507	1.248	2.259	98.7	0.02	97.0
XLE (0.5 m/s 20 bar)	2.674	1.227	1.447	99.2	0.01	98.5
AP (0.5 m/s 20 bar)	3.196	1.427	1.769	99.0	0.01	98.5

Table 9. Concentration of TOC and conductivity of feed (UF permeate) and NF permeate in experiment 8. UF permeate was withdrawn at Dow April 19, 2017.

	TC (mg/l)	IC (mg/l)	TOC (mg/l)	TOC retention (%)	Conductivity (mS/m)	Conductivity retention (%)
UF permeate	135.06	24.74	110.32		0.5	
NF90 (0,5 m/s 10 bar)	3.468	1.053	2.415	97.8	0.03	94.0
XLE (0,5 m/s 10 bar)	2.24	0.795	1.445	98.7	0.03	94.0
AP (0,5 m/s 10 bar)	2.212	0.813	1.399	98.7	0.03	94.0

4.4 Fouling

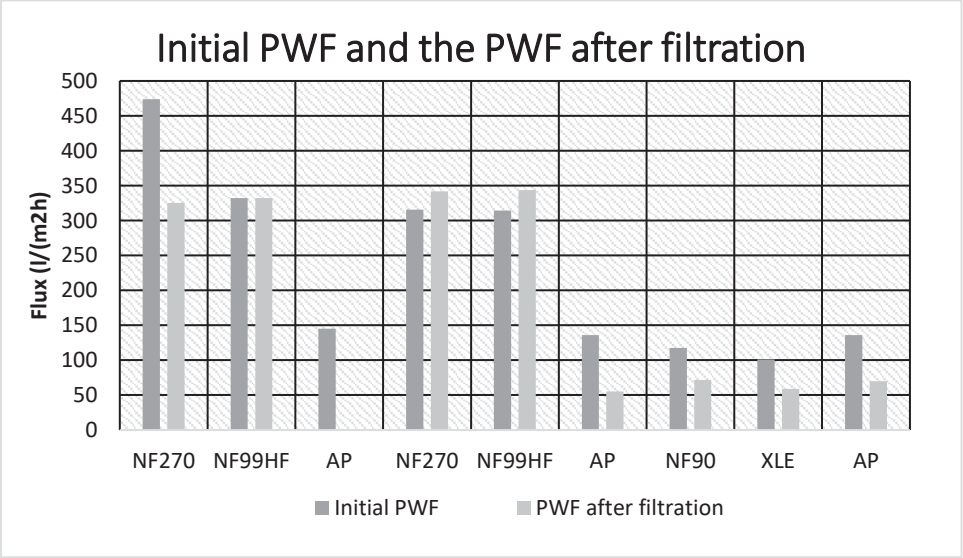
The fouling of the membrane can be of two types: irreversible and reversible fouling. The irreversible fouling can be established by measuring the pure water flux (PWF) before filtration and comparing it to the PWF after filtration and after the membranes have been cleaned with a cleaning agent.

Divalent cations like Ca^{2+} can form complexes together with organic foulants. These complexes can form compact fouling layers causing severe flux declines [8].

The comparison between the initial PWF and the PWF after filtration in experiment 1-3 is show in Figure 13. For the NF270 and NF99HF membranes there appears to be no

fouling. It is most likely that the membrane pores for these membranes are too big for any foulants to plug the pores. This assumption is supported by the poor retention of these membranes in comparison to the other membranes. In experiment 2, the PWF of NF270 and NF99HF is higher after filtration than before, which was unexpected, especially since the PWF of NF270 was markedly lower after filtration in experiment 1. The reason may be that the properties of the membrane changes a lot from piece to piece.

For the NF90, XLE and AP membranes the fouling is very apparent as the PWF is markedly reduced after filtration. The tighter pores of these membranes most likely cause the foulants to block the pores. The high retention indicates that the foulants are retained by these membranes which supports the assumption.



Exp. 1 (477 g/l) Exp. 2 (717 g/l) Exp. 3 (400 g/l)

Figure 13. Comparison of the initial PWF and the PWF after filtration for the membranes used in experiment 1-3. The missing staple for AP in experiment 1 is due to a malfunction of the balance which meant that the flux was not recorded.

4.5 Cleaning

Different cleaning agents and concentrations were evaluated in experiment 3-8. An alkaline cleaning agent, Ultrasil 10 (U10), and an acidic one, Ultrasil 73 (U73), both from Henkel, Diversey, were used in the experiments. It would be advantageous to be able to use the same cleaning agent as is used to clean the UF membranes at Dow and therefore this cleaning agent was also included in the experiments. As can be seen in Figure 14, the PWF after cleaning only increased in one of the experiments (5) and when the cleaning was replicated in experiment 6, but at higher concentrations, the PWF after cleaning was not higher than the filtration flux. In order to be able to decide whether it is possible to recover the initial PWF after cleaning further, repeated experiments are needed.

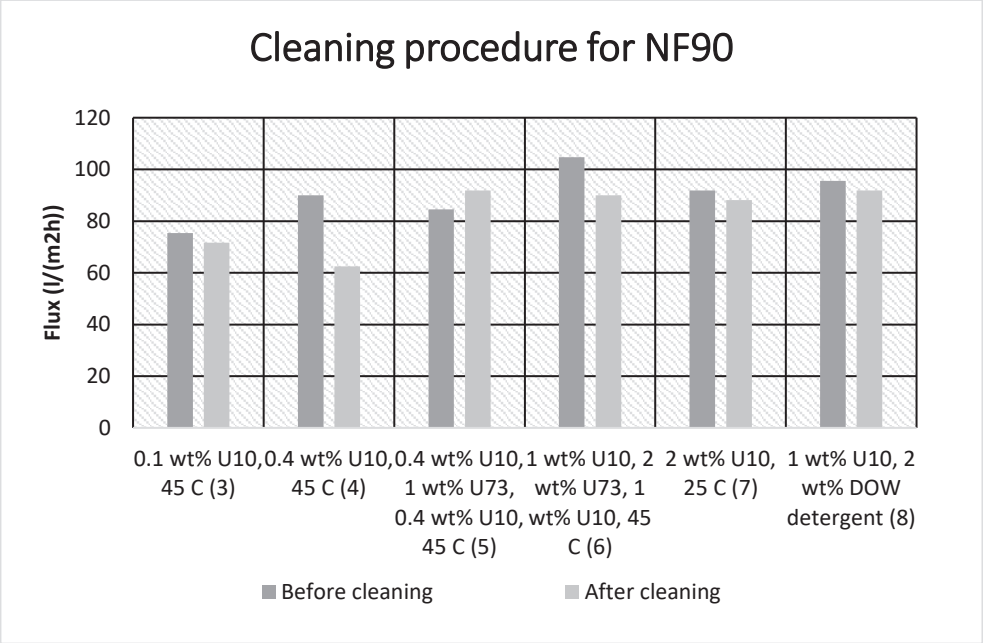


Figure 14. Comparison between filtration flux and PWF after cleaning for different cleaning procedures

The ideal case would be to clean the NF membranes at the same time as the UF membranes are cleaned. This might not be possible if the NF membranes foul more than the UF membranes and require cleaning more often. Further experiments where a cleaning procedure based on the cleaning agent already used at Dow is optimized are recommended.

4.6 Concentration with spiral wound module

The concentration of UF permeate with the NF90 spiral wound membrane was done over 3 days. The experiment was stopped when the flux dropped to 1 l/(m^2h) which resulted in an 85 % VR.

Influence of concentration on retention

Samples of permeate and retentate were withdrawn continuously during the filtration plus an additional sample with a mix of all the permeate. The concentration of TOC and conductivity in the feed (UF permeate) and NF permeates and retentates can be found in Table 10. As expected, the TOC and conductivity increases as the VR increases since the concentration of the retentate is also increasing. The concentration increases exponentially as the VR reaches 85 % which is also logical since the same is true for the retentate. The UF permeate withdrawn at Dow was the second dirtiest of all 9 batches. The concentrations were very close to the UF permeate used in experiment 2. The retentions are very similar to that of AP in experiment 2 (see Table 4), they were even slightly better. This means that the retentions of the spiral wound membrane are very similar to the retentions of the flat sheet membrane and can be expected to behave similarly when filtrating cleaner UF permeates.

The high concentration of IC seems to cause the largest issues. Methods to prevent this should be investigated if NF is to be an option for the Dow plant in Landskrona.

Table 10. Concentration of TOC and conductivity of feed (UF permeate) and NF permeate and retentate in experiment 9. UF permeate was withdrawn at Dow May 23, 2017.

	TC (mg/l)	IC (mg/l)	TOC (mg/l)	TOC retention (%)	Conductivity (mS/m)	Conductivity retention (%)
UF permeate	697.8	196.4	501.4		2.45	
NF permeate VR 5 %	42.05	10.42	31.63	93.7	0.18	92.7
NF permeate VR 35 %	48.99	14.33	34.66	93.1	0.24	90.2
NF permeate VR 50 %	42.09	15.92	26.17	94.8	0.25	89.8
NF permeate VR 60 %	47.25	18.9	28.35	94.3	0.27	89.0
NF permeate VR 75 %	72.25	29.62	42.63	91.5	0.47	80.8
NF permeate VR 80 %	189.4	61.68	127.72	74.5	0.98	60.0
NF permeate VR 85 %	310.1	99.96	210.14	58.1	1.59	35.1
NF permeate Mix	55.79	28.33	27.46	94.5	0.33	86.5
NF retentate VR 40 %	1109	302.4	806.6		3.87	
NF retentate VR 50 %	1364	360.6	1003.4		4.51	
NF retentate VR 75 %	2607.2	646.4	1960.8		8.1	
NF retentate VR 85 %	3922.4	978.4	2944		12.37	

Influence of concentration on flux

The flux during filtration declined as the VR increased, which is expected as the concentration increased in the feed tank. This increases the osmotic pressure which decreases the driving force. The filtration flux during volume reduction is shown in Figure 15. The logging software crashed when the volume reduction reached 75 % at which point the flux and VR had to be manually measured and calculated. This is the reason for the fewer data points after 75 % VR. The filtration was done for three days. No filtration was done overnight but the flow was reduced to 8.5 l/min and the TMP was lowered to 1 bar to keep the membrane soaked. The permeate was recycled to the feed tank as well. The sharp increase in flux around 45 % and 65 % VR is due to the start up on day 2 and 3. The most likely explanation is that the crossflow over-night reduced the thickness of the filter cake. The reduced thickness of the filter cake leads to an increased flux when filtration was resumed. As can be seen in the figure, the flux dropped rapidly as it approached the final VR.

The flux decreased linearly which seems reasonable given that the concentration increases in the feed tank.

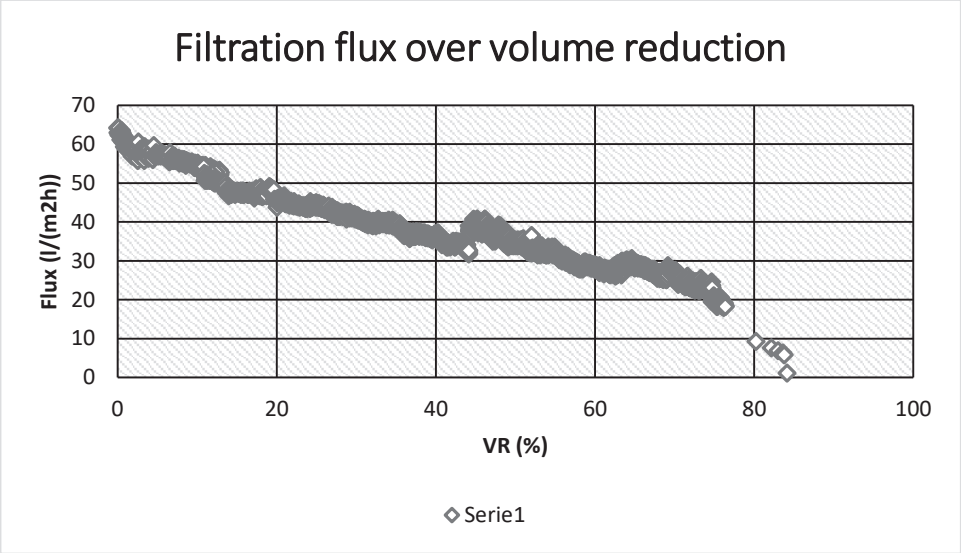


Figure 15. The filtration flux over the volume reduction for the NF90 spiral wound membrane

The PWF was measured at 2.5, 5, 7.5 and 10 bar. The flux increased linearly, both before and after filtration of the UF permeate, as in previous experiment. The comparison of the initial PWF and the PWF after filtration is shown in Figure 16. The difference in PWF before and after is bigger for the spiral wound membrane than for the flat sheets. The UF permeate was among the dirtiest that were filtered in this study having the second highest conductivity, TOC and IC. This means that a higher concentration of foulants were present in the feed which caused a lower PWF after filtration. Another explanation might be that dirt plugged the entrance to the membrane sheets and resulted in a lower PWF after the filtration. The fouling is a big issue in the spiral wound membrane as well and further studies must be made on the cleaning of the membranes.

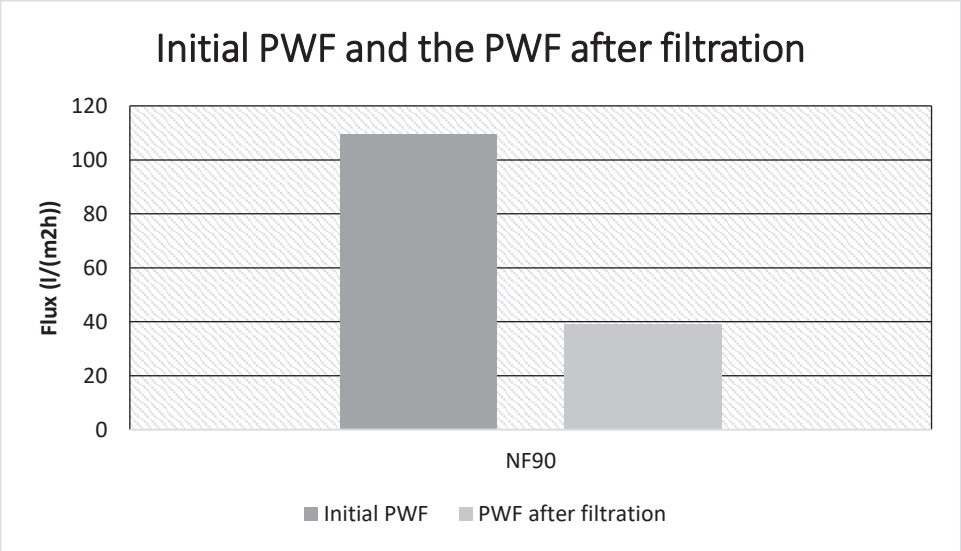


Figure 16. Comparison of the initial PWF and the PWF after filtration for the NF90 spiral wound membrane

Recovery

A high recovery is beneficial as a low amount of retentate is easier to dispose of. A high recovery comes at the cost of high concentrations of TOC and conductivity in the retentate and permeate. It might be wiser to have a lower recovery if the retentate can be sent to the municipal WWT plant. A large portion of the wastewater could still be reused and the remaining retentate could be sent to the municipal WWT plant using the existing system

for the UF permeate. An initial analyze using the Nitritox system at Dow showed that the retentate from experiment 9 did not harm the municipal WWT plants bacteria. Future studies should take this in consideration.

4.7 Analysis of the permeate and retentate content

Samples were taken of the mixed NF permeate and the NF retentate from the experiment with the spiral wound membrane. Results from ALcontrol were yet not received at the time of this report.

4.8 Bacterial growth

Two dip slides were used to determine the bacterial content in the UF permeate from the 13th of March and in the NF permeate of NF90 from the 9th of March. The growth of bacteria in the UF permeate and NF permeate is shown in Figure 17 where the left sample is the UF permeate and the right one the NF permeate. As can be seen in the figure there is a lot of bacterial growth in the UF permeate sample, represented by the red dots on the surface, and none in the NF sample. This indicates that the retention is good and that there are not enough substances in the NF permeate for the bacteria to grow. Most likely there will be no issues with bacterial growth in the NF system on the permeate side.

Figure 17. Two dip slide samples where the left one is the UF permeate from the 13th of March and the right one is the NF90 permeate from 9th of March

4.9 Cost estimate for full-scale system

A cost estimate was done for a model of a full-scale system to see if the investment cost is reasonable for Dow. A cost estimate was given by BWT Vattenteknik for the NF system

with accompanying cleaning system and UV lights [17]. The estimated cost for the remaining equipment such as pipes, valves and heat exchanger was given by Dow.

A process schematic was made for the existing and planned equipment to combine the existing UF with the planned NF system. This is shown in Figure 18. Boxes and text in black indicate existing equipment while red boxes and text indicate equipment that needs to be purchased. The dotted connectors indicate transfer lines for the cleaning system while the regular connectors indicate transfer lines for the UF-NF permeate and retentate.

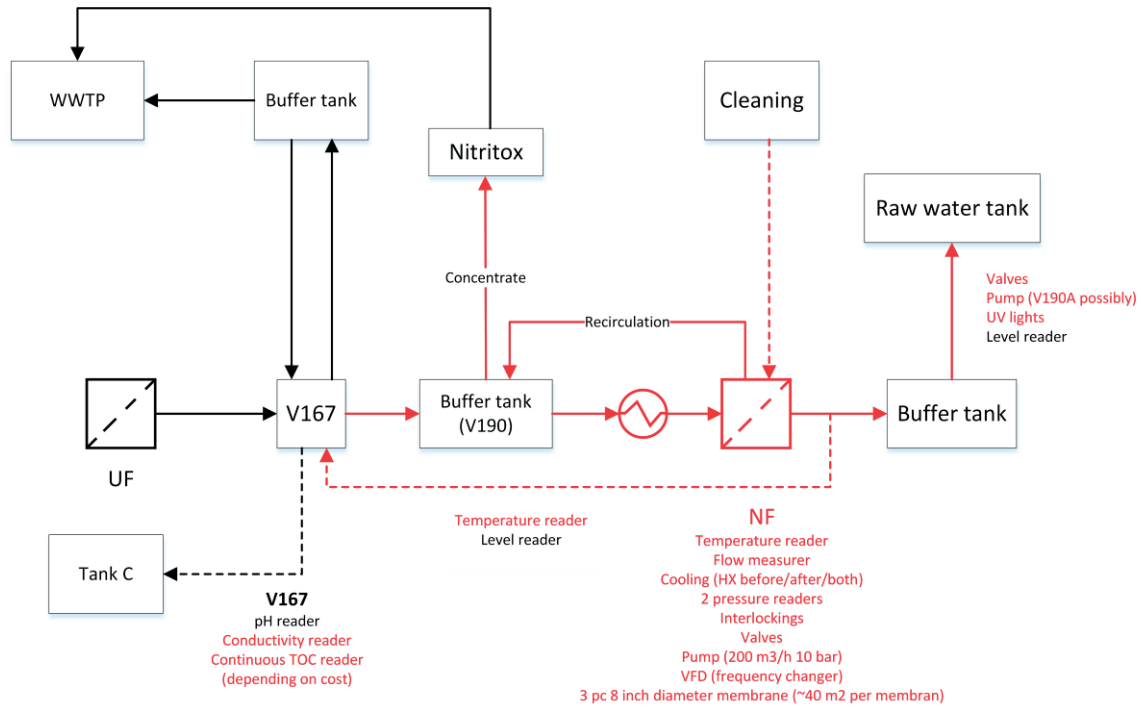


Figure 18. Process schematic over the existing equipment and the planned combined UF and NF system

The operating cost was calculated with the cost analysis function in ROSA using Dow specific data as input. The calculations and their results are shown in Table 11. The permeate recovery was set to 95 % and the permeate flow was set to the amount of wastewater Dow produces, 50 m^3/day. The recirculation flow was set to 200 m^3/h due to the large amount of recirculation required in NF. The average flux 18 l/(m^2h) was given from the simulation. BWT Vattenteknik considered this recovery too high and warned that the result might be that the NF membrane must be replaced as often as twice a year. In the concentration experiment 85 % recovery was reached but the UF permeate feed in that experiment was very dirty, similar to the feed used in experiment 2. With a lower concentration in the UF permeate a higher recovery should be achievable. The operating costs can be subtracted by the costs of the incoming city water, fee to the municipal WWTP and fee for exceeding the BOD threshold. These costs were taken from the latest invoices from Dow. Additional unknown costs are the cost of cleaning the NF membranes and the cost of treatment of the retentate. The retentate cost will depend on the retentates properties and what kind of handling is required for the removal of the retentate.

Table 11. The cost estimate analysis made in ROSA

Operating Expense	
Power	
Pass 1 pumping power (kW)	2,21
Pass 1 pump specific energy (kWh/m³)	1,12
Brine energy recovery (kWh/m³)	-36,00
Pass 1 net energy consumption (KWh/m³)	37,12
Pass 1 net energy cost ($/year)	$1931,03
Energy expense NPV ($)	10478,25
Pass 1 energy expense ($/m³)	$1,86
Membrane replacement cost	
Pass 1 replacement rate (%/year)	200
Replacement price ($/element)	$1100,00
Pass 1 replacement cost for elements ($/year)	$6600,00
Pass 1 replacement membrane NPV ($)	$35813,21
Pass 1 membrane replacement expense ($/m³)	$0,38
Operating expense subtotal	
Pass 1 operating expense NPV ($)	$46291,45
Pass 1 operating expense per m³	$2,24
Pass 1 Total	
Pass 1 cost NPV ($)	$0,00
Life Cycle Cost ($/m³)	$0,00
Total System	
Capital	$114000,00
Operating expense NPV ($)	$46291,45
Cost of water NPV ($/m³)	$0,92

The costs for implementing the NF system, the reduction in costs that Dow would have if the NF system was implemented and the total costs for the NF system can be found in

Table 12 -Table 14. The depreciationtime of the NF plant was set to 10 years with a 13 % interest rate. Implementing the NF system would increase the cost of the permeate with 11.16 SEK/ m^3, an increase by 68 % from what Dow pay today for the UF permeate and the city water. A large part of the operating expense is the cost of replacing NF membranes which was assumed to be twice a year. This is in the absolute worst-case scenario and most likely they will not require replacement that often. If the system can be used for more than 10 years without new investments the cost per m^3 NF permeate would drop after 10 years. It is a large increase in cost per m^3, due to the high assumed replacement rate of membranes, but with the municipal WWTP being at max capacity and the current water shortage in Sweden it might be a necessary investment to ensure the future of the Dow plant in Landskrona.

Table 12. Costs for implementing the NF system

Investment cost (SEK)	Energy expense NPV (SEK)	Cost of replacing membranes NPV (SEK)	Cost of water NPV (SEK/m^3)	Operating expense (SEK/m^3)
986 700	91 000	310 000	7.99	19.54

Table 13. Costs that would be removed if the NF system was implemented

City water (SEK/m^3)	Cost of UF permeate handling (SEK/m^3)	BOD fee (SEK/m^3)
5.63	5.19	5.55

Table 14. Total costs for the duration of the project lifetime with consider to the eliminated costs

Total cost during project life time (SEK)	Total cost during project life time per m^3 (SEK/m^3)	Reduction of operation cost during project life time (SEK/m^3)	Cost increase per m^3 during project lifetime (SEK/m^3)
1 389 300	27.53	16.37	11.16

5. Conclusions

The NF membranes NF90, XLE and AP are capable of producing a permeate that can be reused in the process. As the VR reaches 85 % the concentration of TOC and conductivity increases greatly in the permeate. However, the volume of this permeate is very low and does not have a great impact of the overall concentration of the mixed permeate, as can be seen in Table 10.

The TMP and CFV did not have a significant impact on the retentions of the membranes and should be set at optimal economic conditions. The cost of membranes and cost of energy have to be balanced against each other to decide if a larger membrane area or higher pressure should be used.

The PWF after cleaning the spiral wound membrane was significantly lower than the initial flux during filtration which shows that the cleaning detergent used in the experiment was not capable of removing the fouling caused by the filtration. This is true for the earlier experiments as well.

The cost estimate is designed after the worst-case scenario of reaching a VR of 95 % with very high concentrations of TOC, IC and conductivity UF permeate. This would shorten the membranes lifetime and increase the replacement rate, which is why the replacement rate is set at twice a year. The cost of replacing the membranes was the dominant part and the reason why the cost estimate was high. If the filtration is interrupted before reaching a VR of 95 % the lifetime of the membranes increases and the cost decreases.

6. Future studies

Future studies should focus on solving the fouling issue. Longer repeated runs with the same membranes should be done to determine if the fouling increases with every run or if it finds an equilibrium. NF might not be possible in Landskrona if the membranes foul irreversibly.

Larger membranes of NF90 should be tested to see if the same results are achieved in a larger scale.

The impact of RO or ion exchange on the NF permeate should be studied to guarantee that the permeate can be reused in the process.

Studies on the retentate needs to be done to decide the required handling of it.

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Appendix A. Flux during the screening experiments

The pure water flux was measured before the filtration of UF permeate and after cleaning the membrane after the experiment. PWF and flux during the screening experiments are shown below.

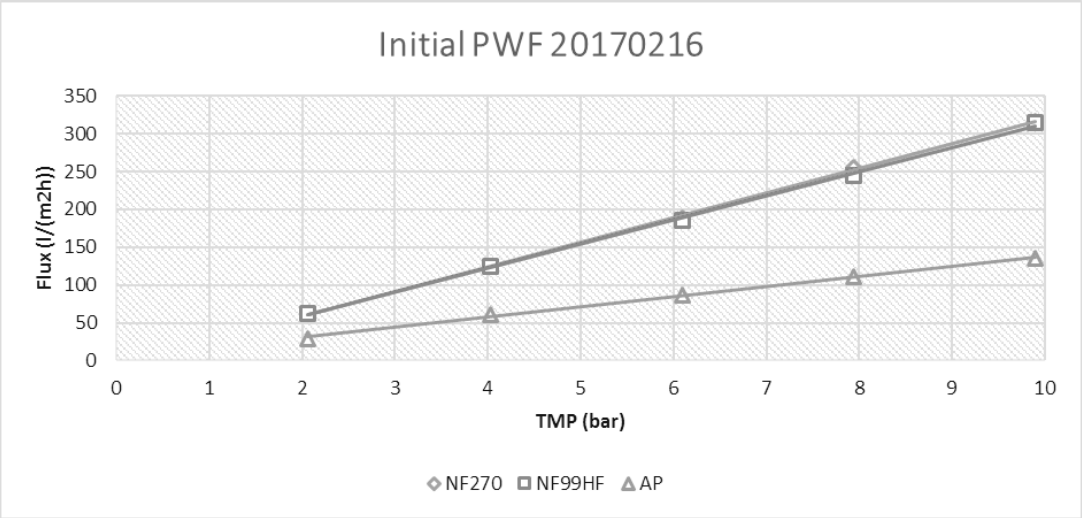

Figure 19. Initial pure water flux for NF270, NF99HF and AP. Experiment 2

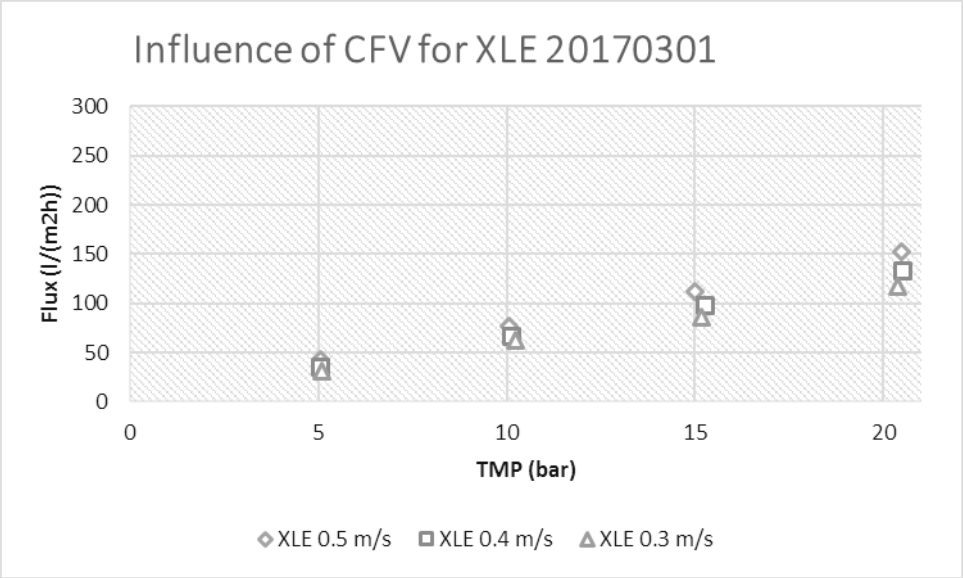

Figure 20. Influence of CFV for XLE when filtrating UF permeate. Experiment 4

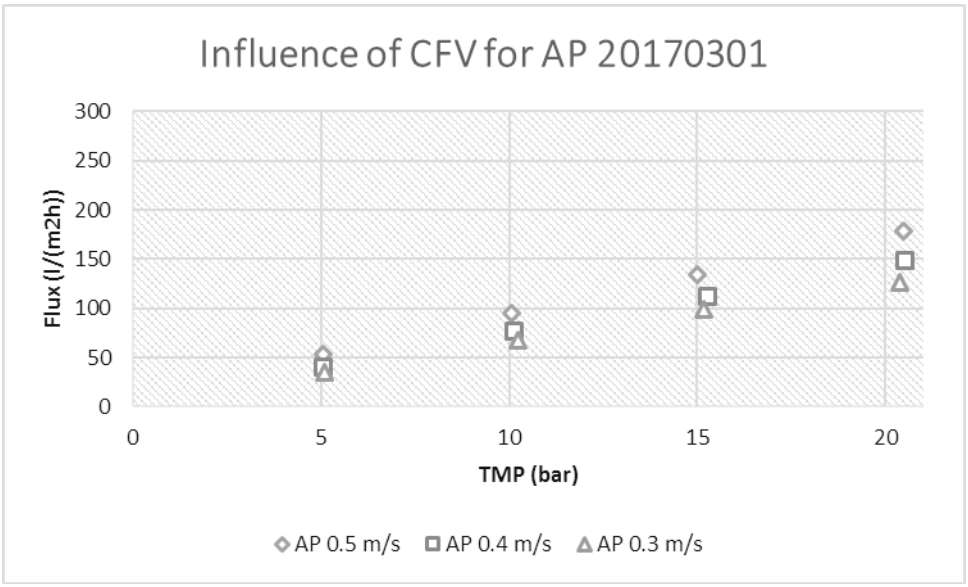

Figure 21. Influence of CFV for AP when filtrating UF permeate. Experiment 4

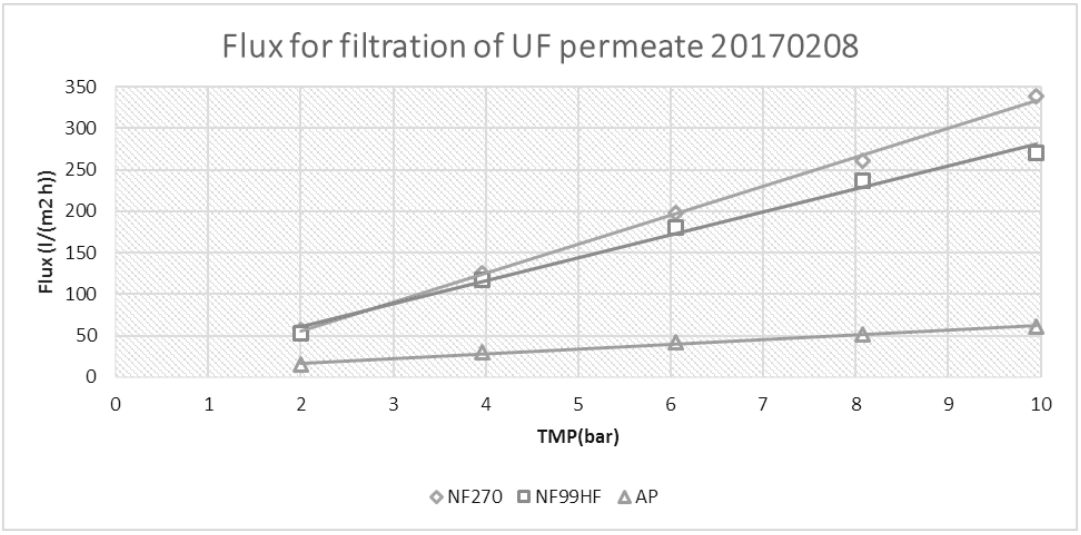

Figure 22. The flux for filtration of UF permeate for NF270, NF99HF and AP. Experiment 1

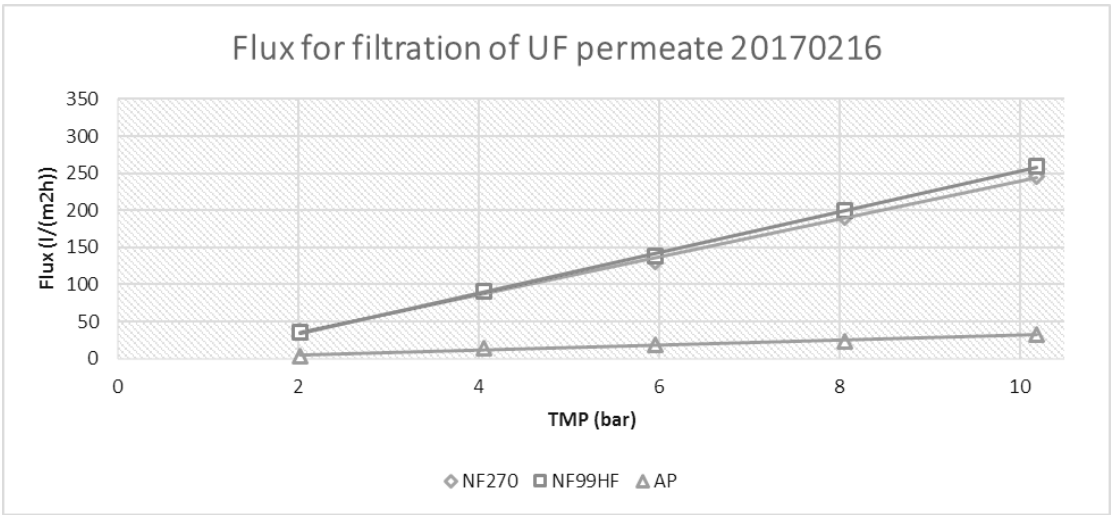

Figure 23. The flux for the filtration of UF permeate for NF270, NF99HF and AP. Experiment 2

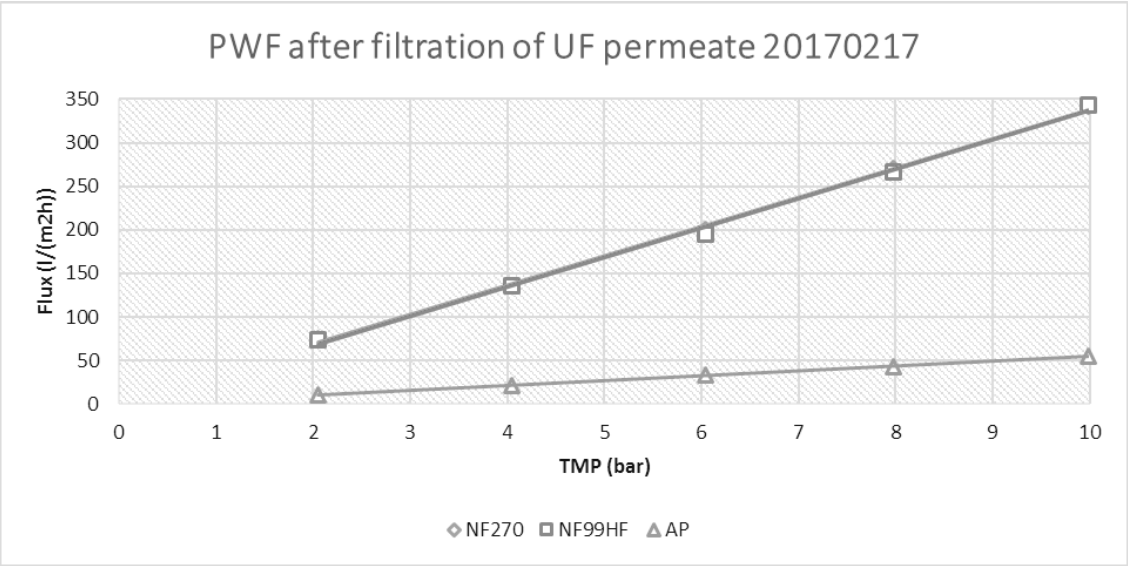

Figure 24. PWF after filtration of UF permeate for NF270, NF99HF and AP. Experiment 2

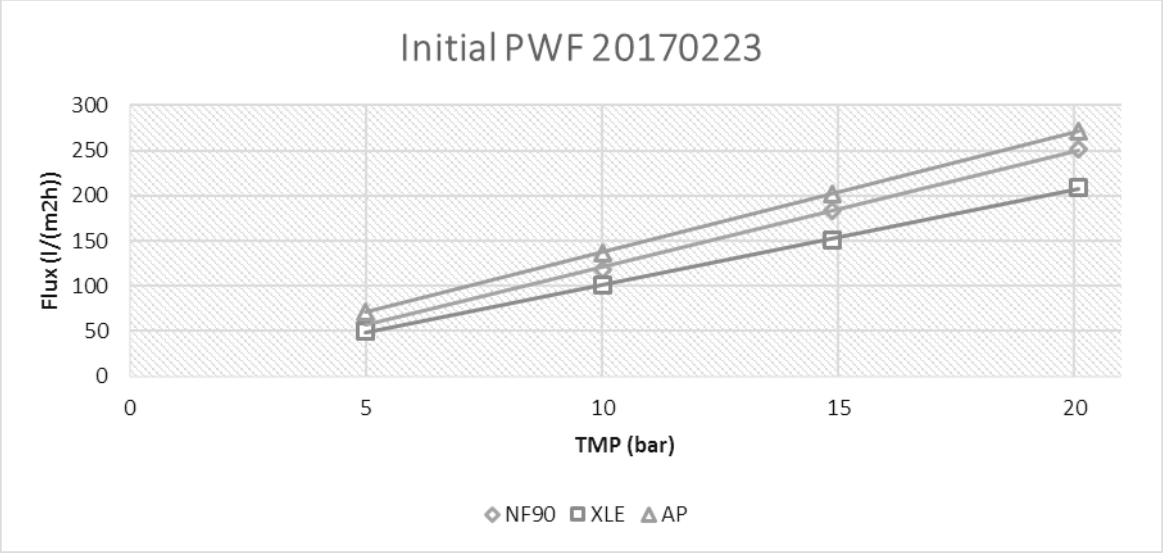

Figure 25. Initial PWF for NF90, XLE and AP. Experiment 3

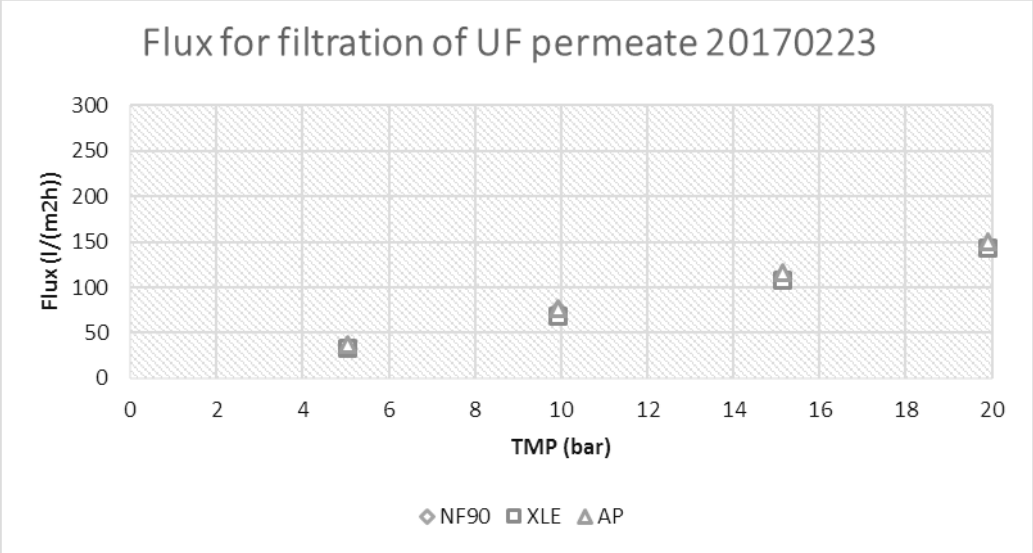

Figure 26. Flux for filtration of UF permeate for NF90, XLE and AP. Experiment 3

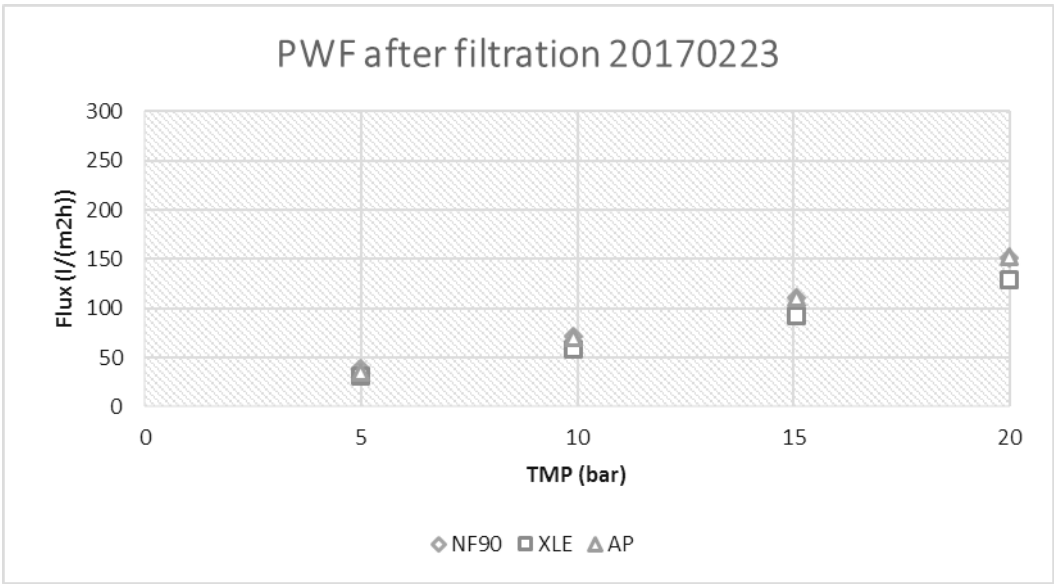

Figure 27. PWF after filtration of UF permeate for NF90, XLE and AP. Experiment 3

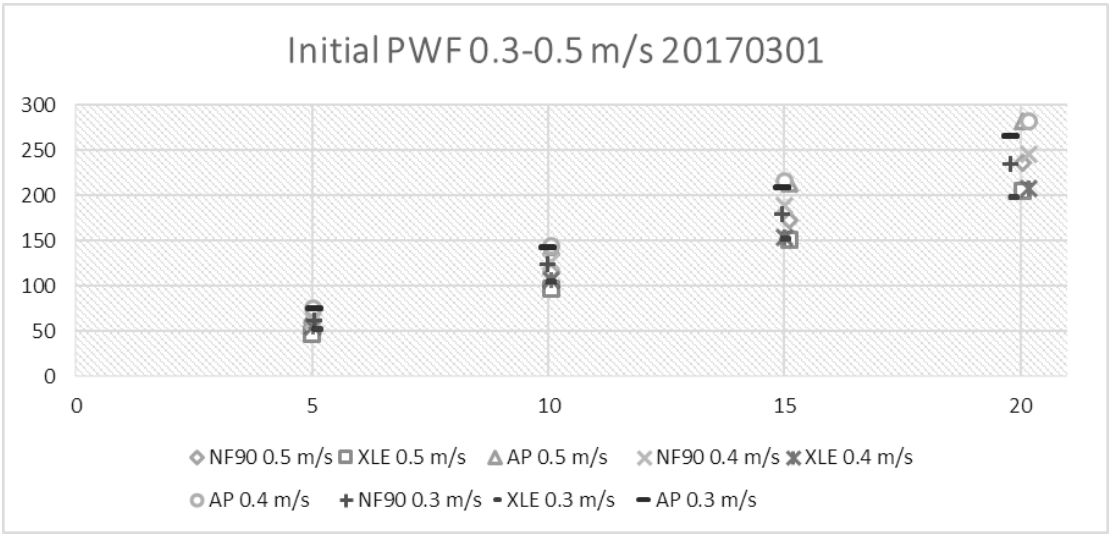

Figure 28. Initial PWF for NF90, XLE and AP at different CFV. Experiment 4

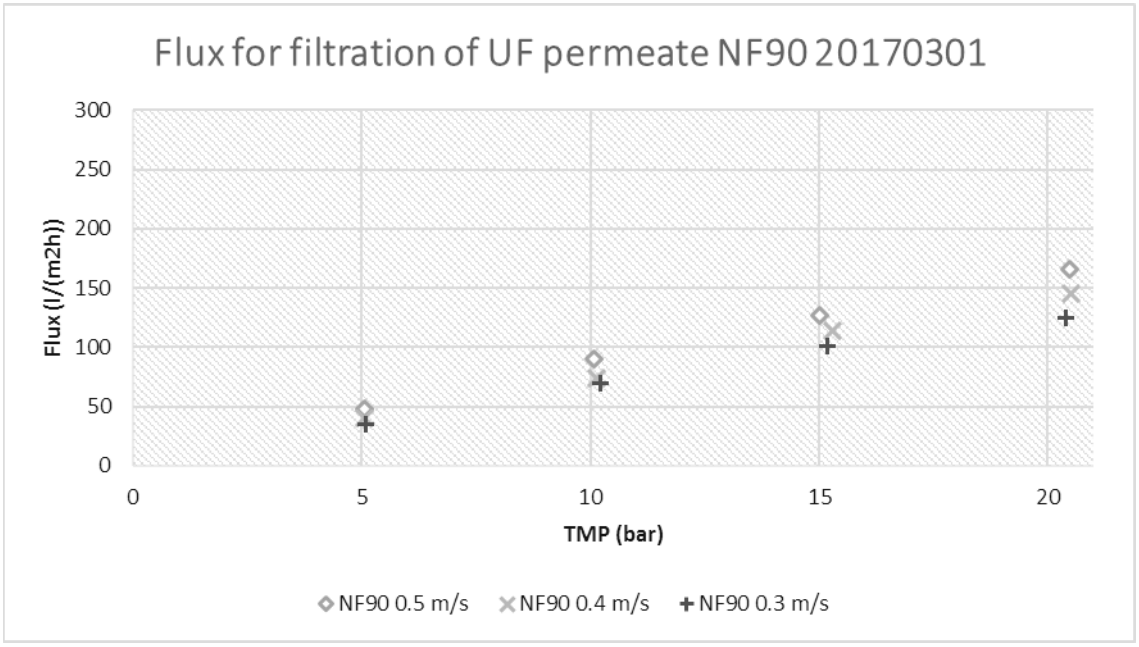

Figure 29. Flux for filtration of UF permeate for NF90 at different CFV. Experiment 4

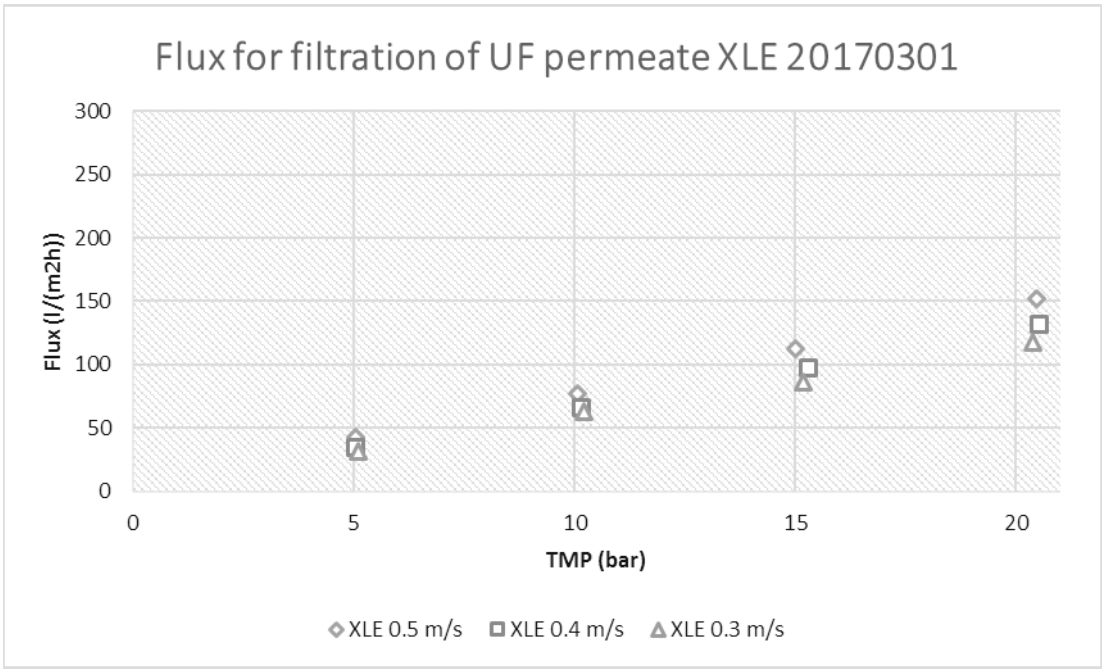

Figure 30. Flux for filtration of UF permeate for XLE at different CFV. Experiment 4

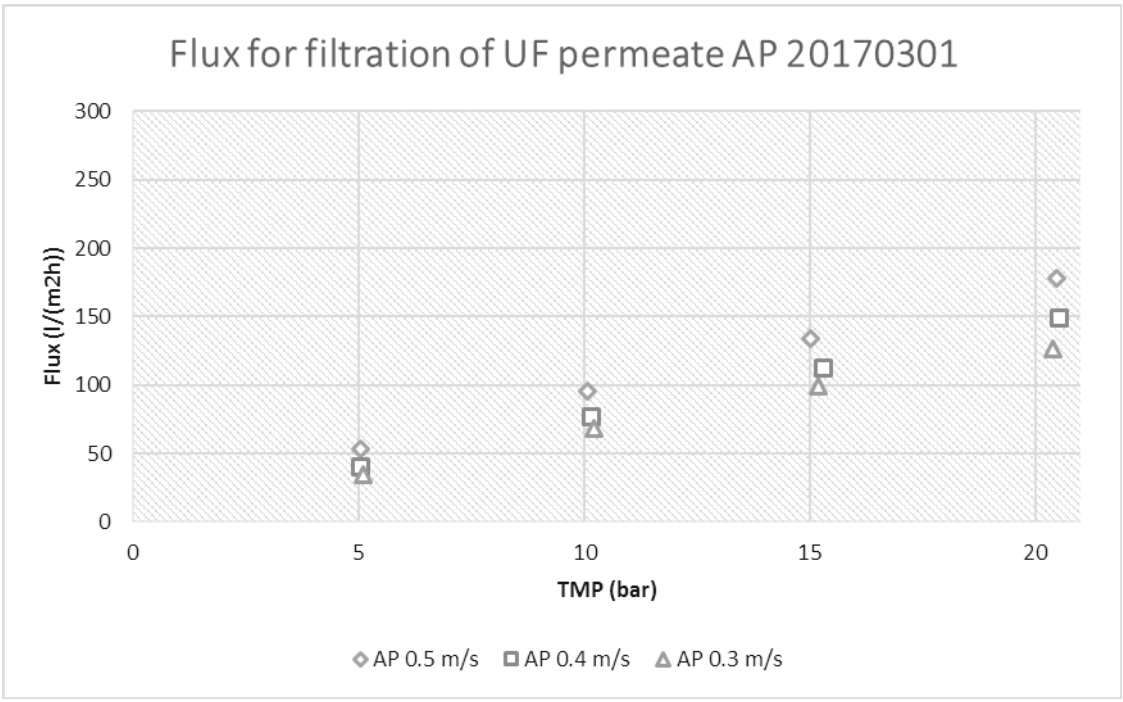

Figure 31. Flux for filtration of UF permeate for AP at different CFV. Experiment 4

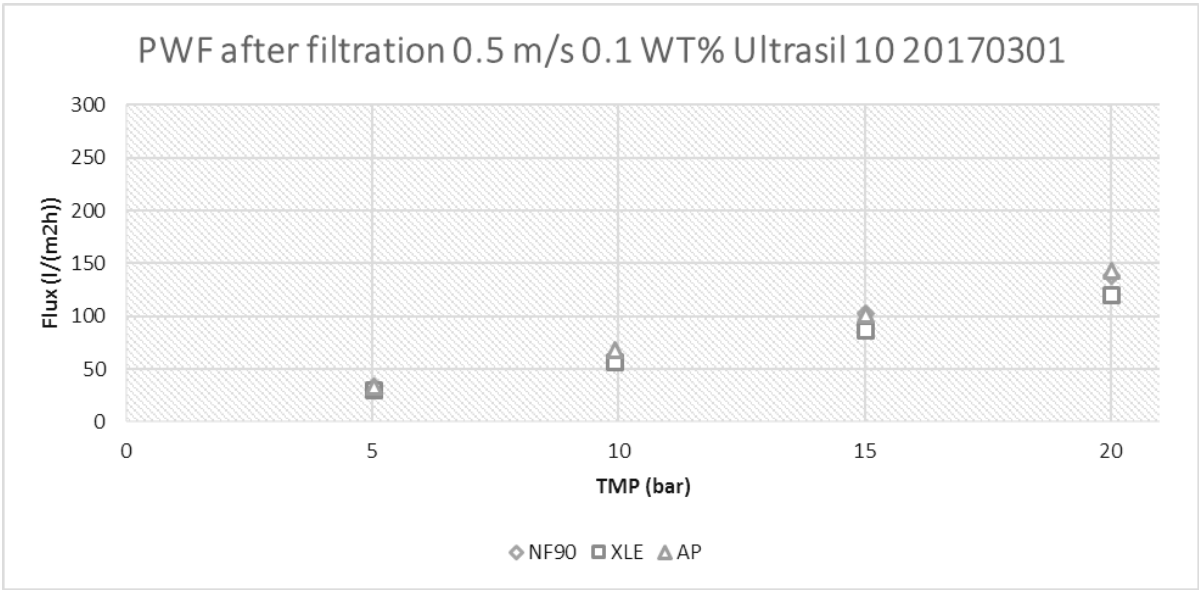

Figure 32. PWF at CFV 0.5 m/s after filtration of UF permeate after cleaning with 0.1 WT% Ultrasil 10. Experiment 4

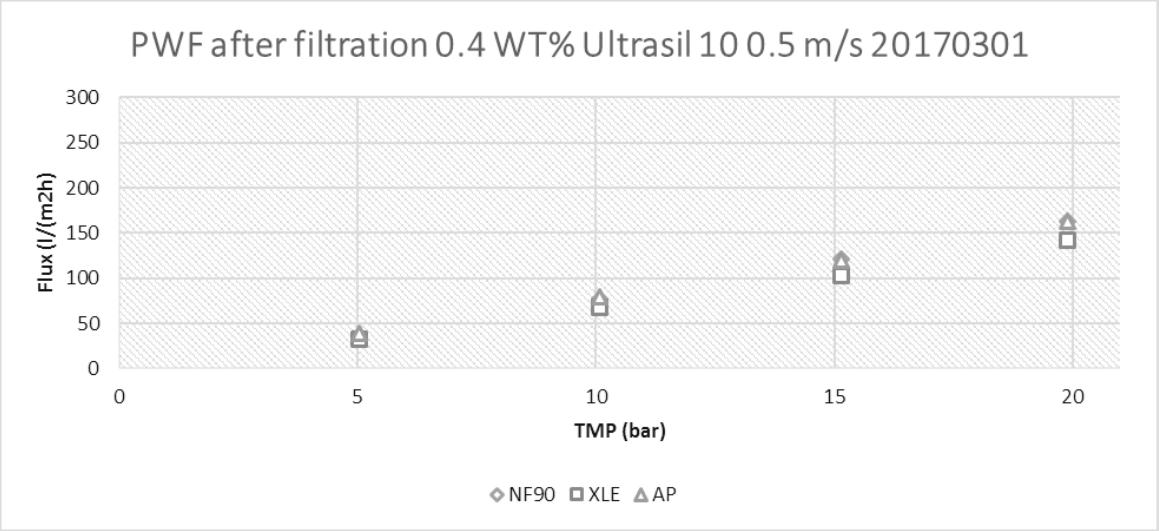

Figure 33. The PWF after the second cleaning with 0.4 WT% Ultrasil 10. Experiment 4

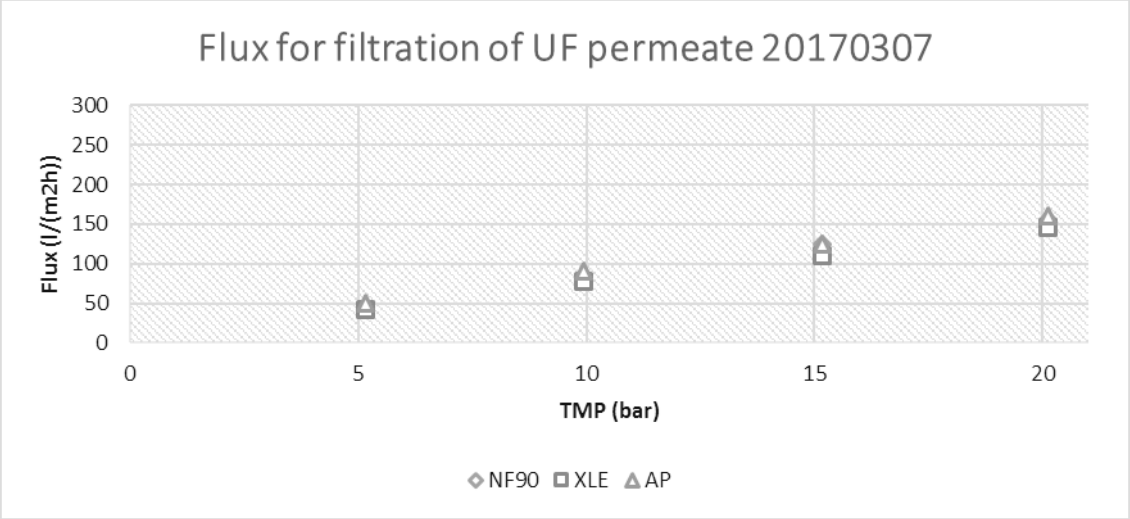

Figure 34. The flux for filtration of UF permeate for NF90, XLE and AP. Experiment 5

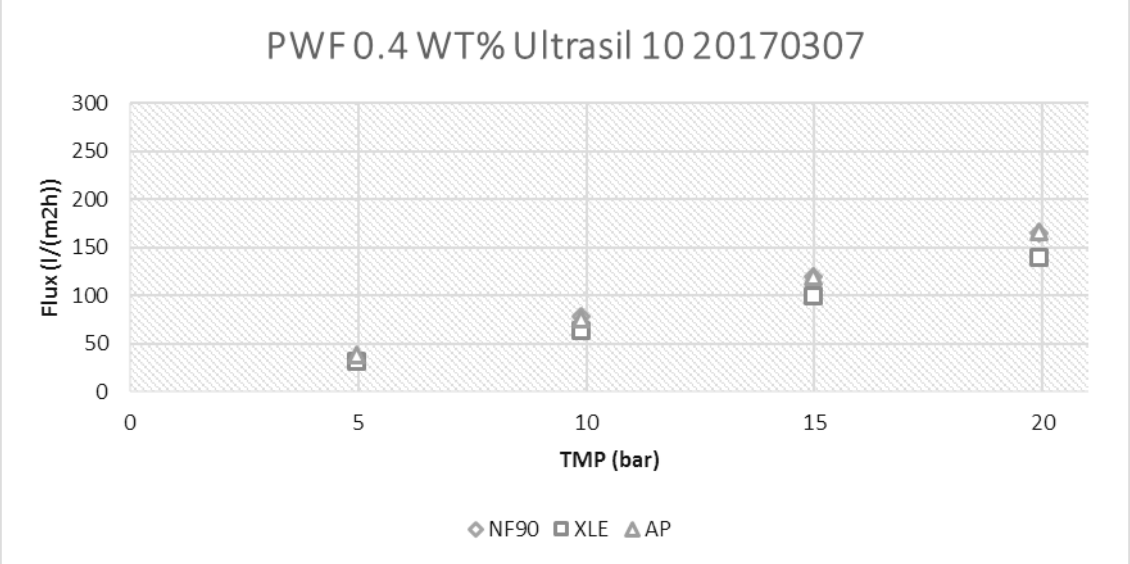

Figure 35. PWF after cleaning with 0.4 WT% Ultrasil 10. Experiment 5

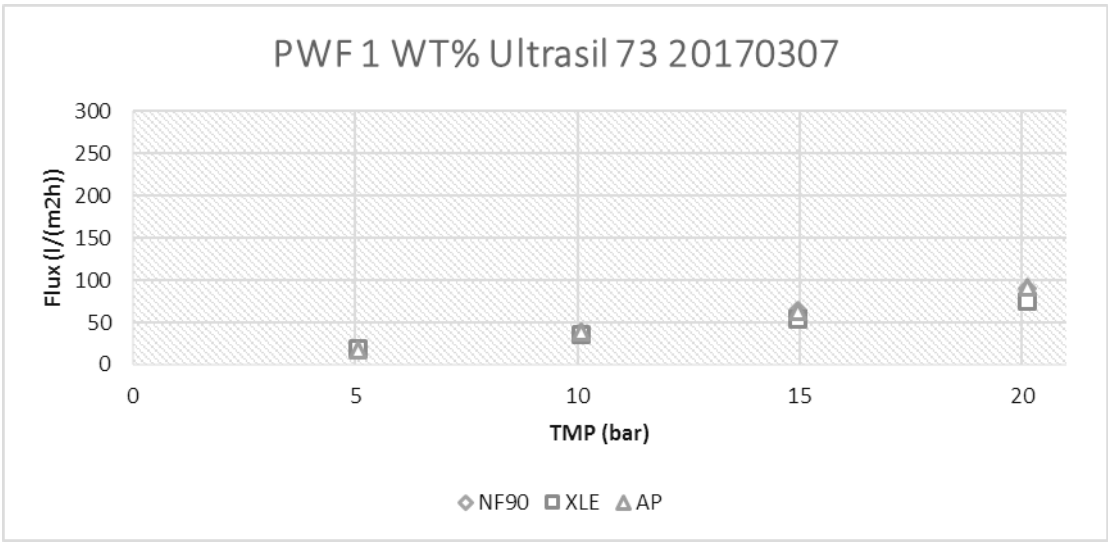

Figure 36. PWF after cleaning with 1 WT% Ultrasil 73. Experiment 5

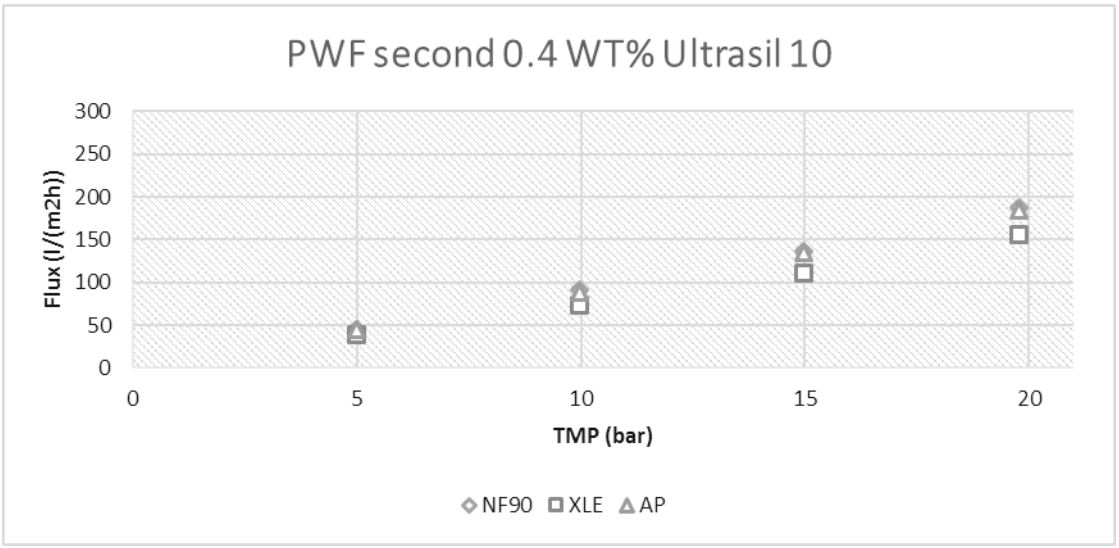

Figure 37. PWF after cleaning a second time with 0.4 WT% Ultrasil 10. Experiment 5

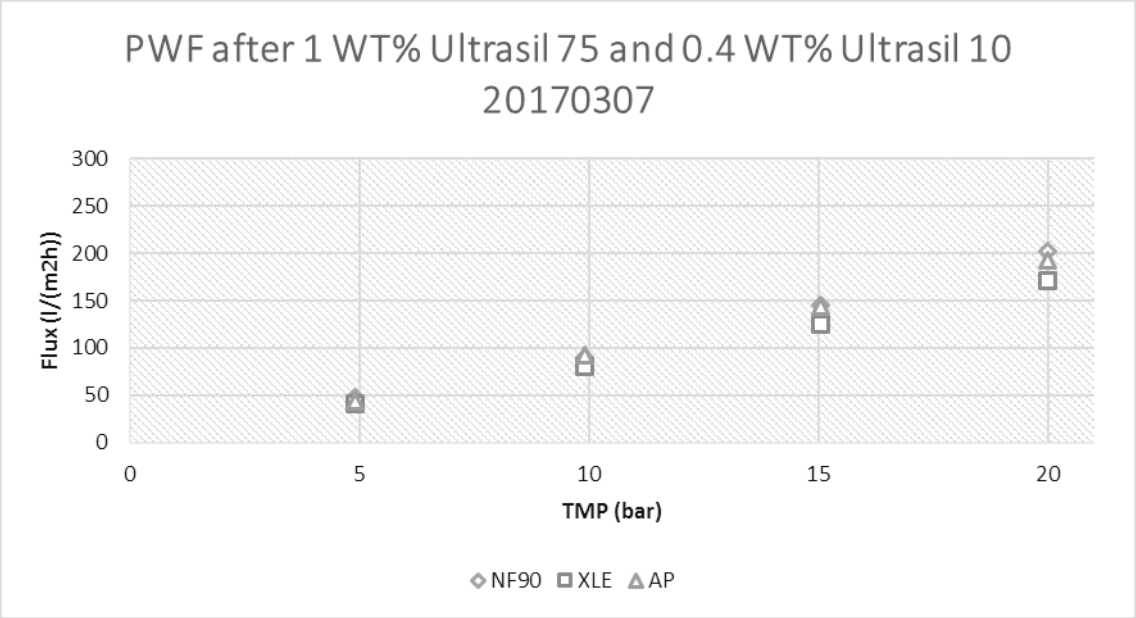

Figure 38. PWF after cleaning with 1 WT% Ultrasil 75 and 0.4 WT% Ultrasil 10. Experiment 5

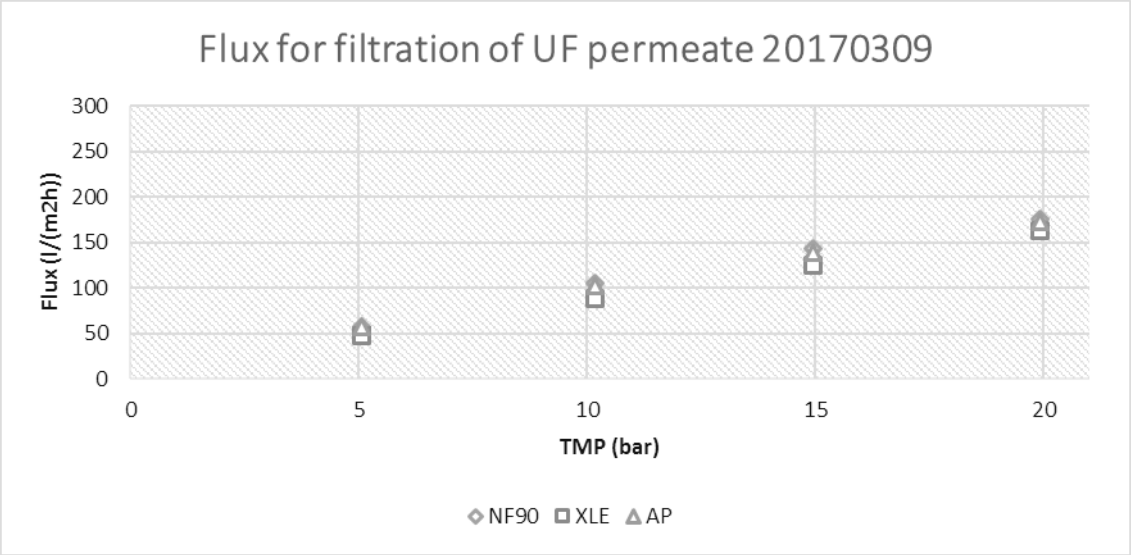

Figure 39. The flux for filtration of UF permeate for NF90, XLE and AP. Experiment 6

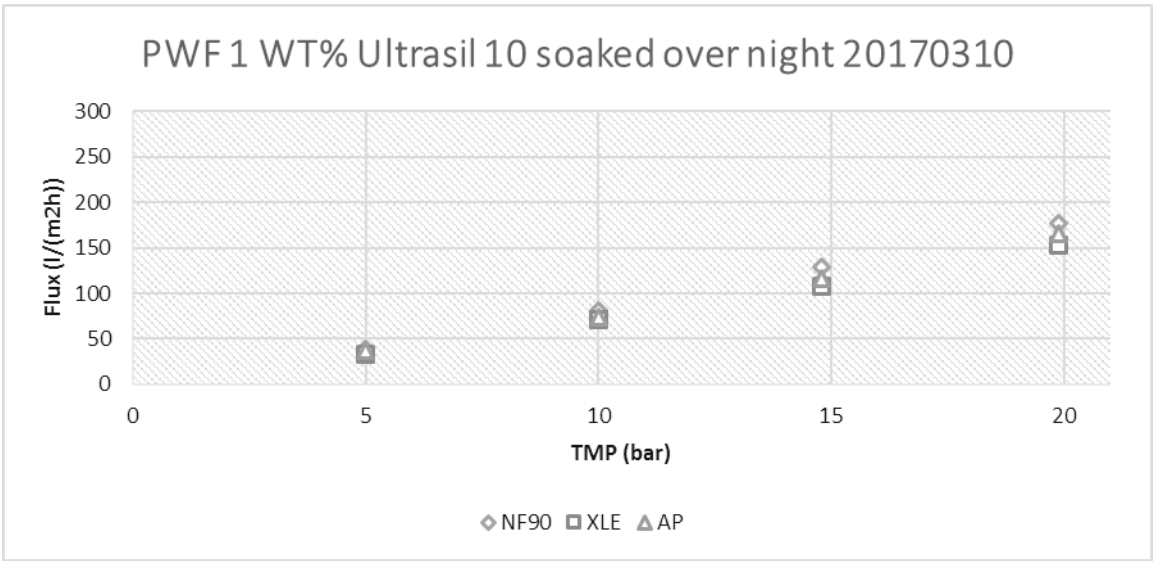

Figure 40. PWF after cleaning with 1 WT% Ultrasil 10 and soaked over night. Experiment 6

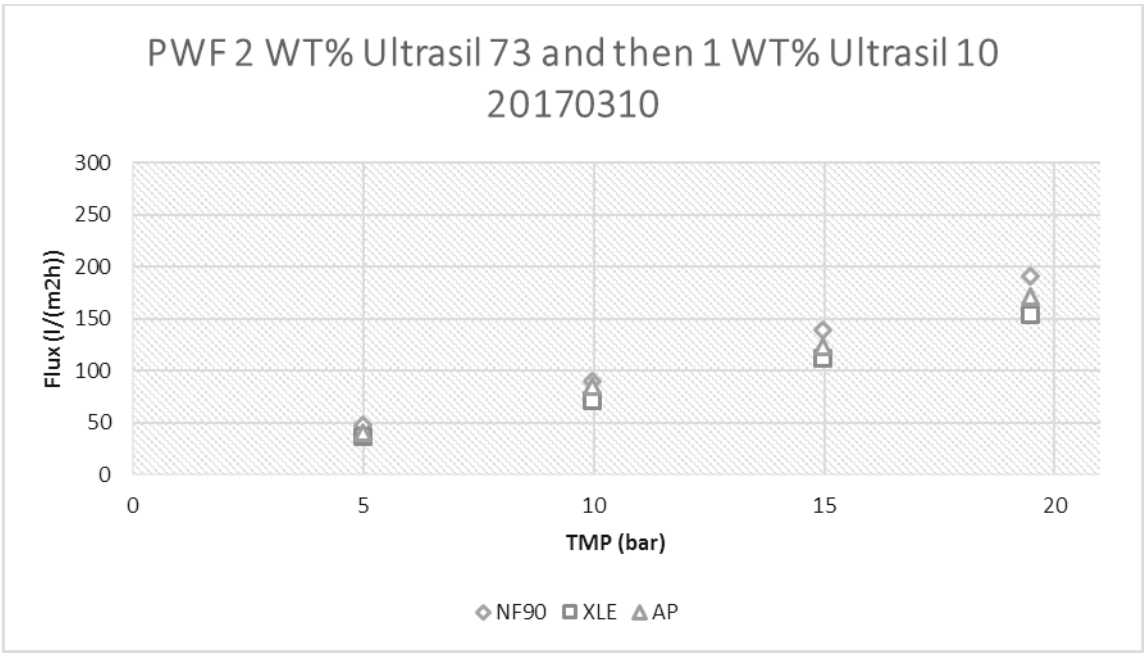

Figure 41. PWF after cleaning with 2 WT% Ultrasil 73 and then 1 WT% Ultrasil 10. Experiment 6

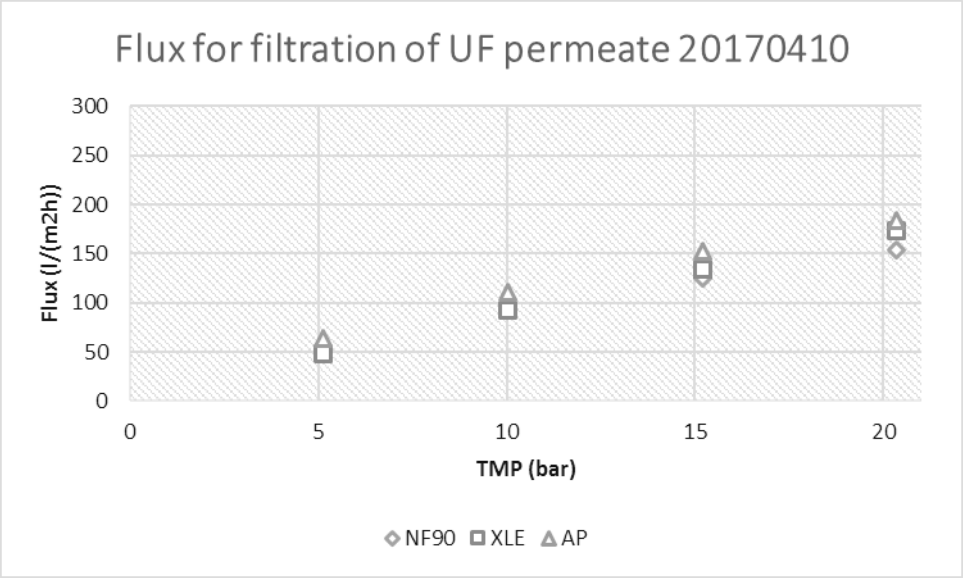

Figure 42. The flux for filtration of UF permeate for NF90, XLE and AP. Experiment 7

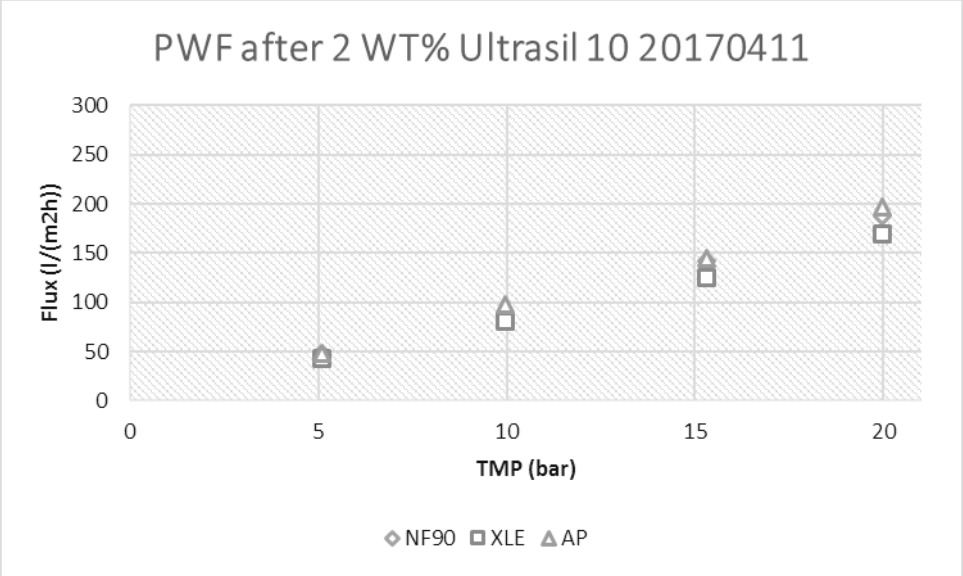

Figure 43. PWF after cleaning with 2 WT% Ultrasil 10. Experiment 7

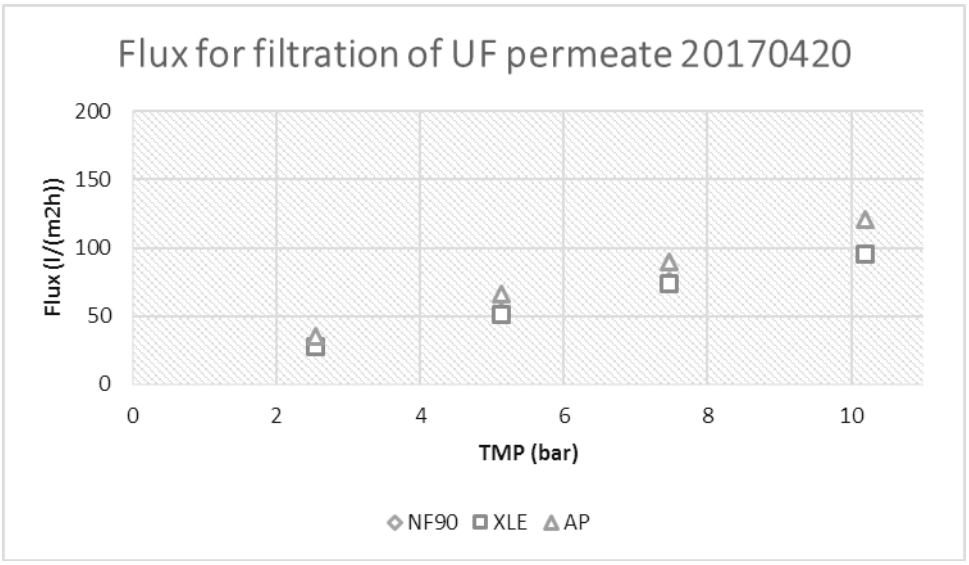

Figure 44. The flux for filtration of UF permeate for NF90, XLE and AP. Experiment 8

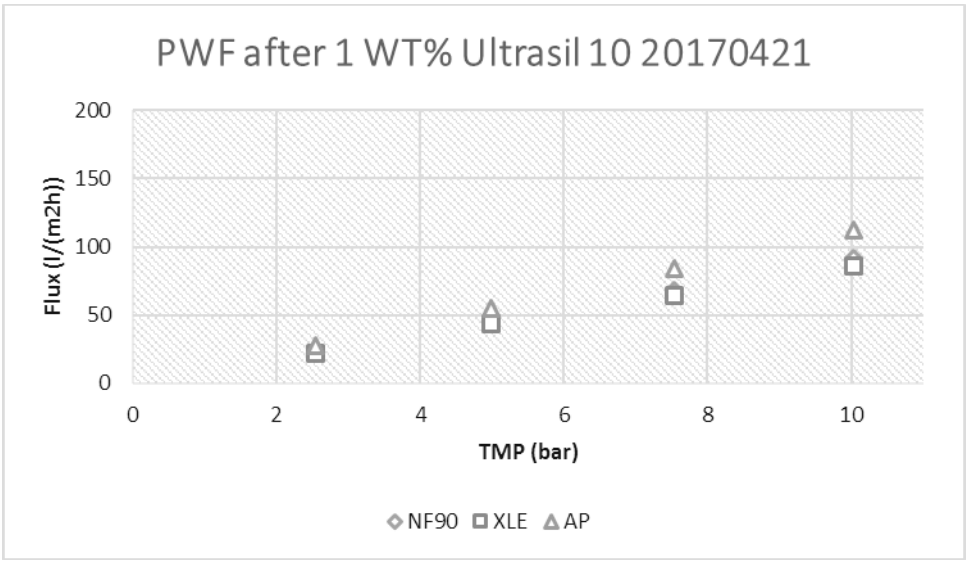

Figure 45. PWF after cleaning with 1 WT% Ultrasil 10. Experiment 8

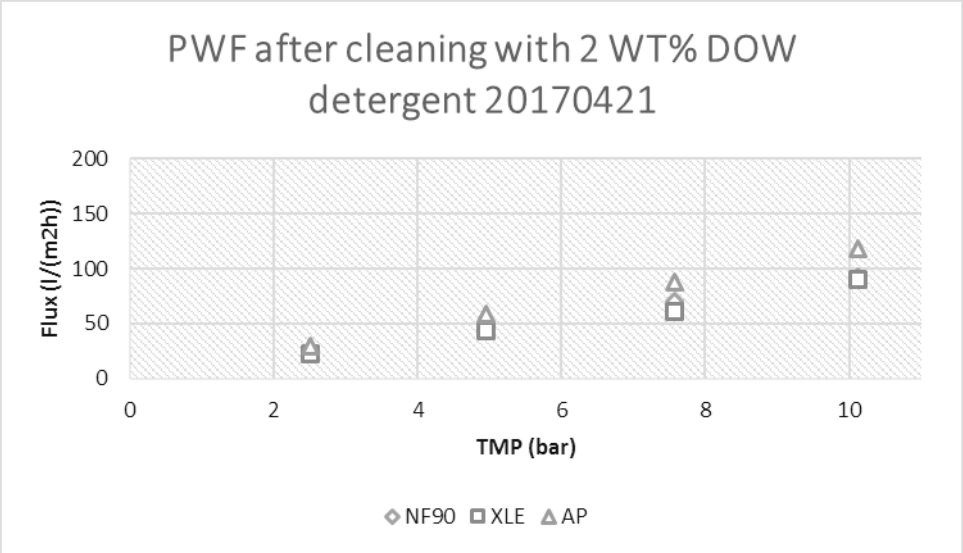

Figure 46. PWF after cleaning with 2 WT% Dow cleaning detergent. Experiment 8

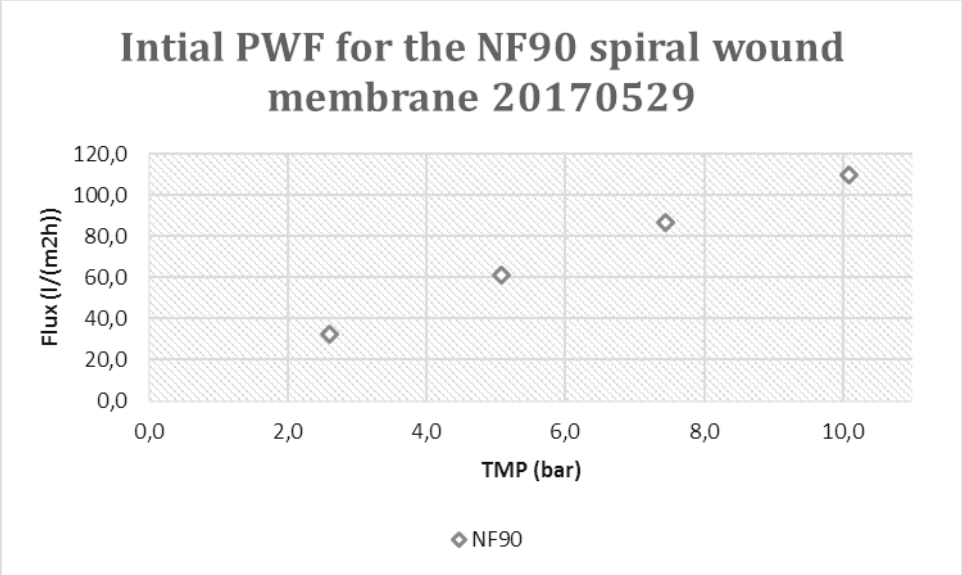

Figure 47. Initial PWF for the NF90 spiral wound membrane. Experiment 9

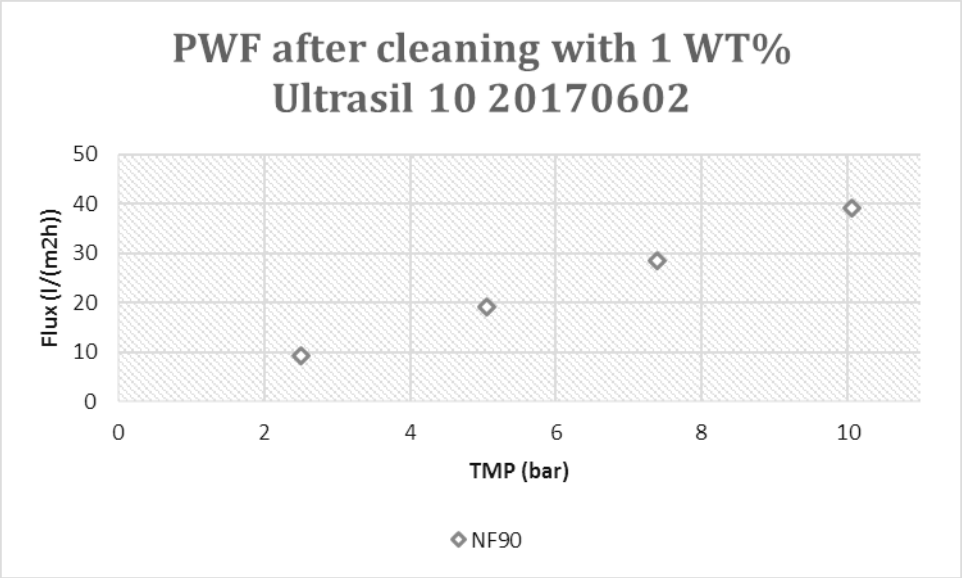

Figure 48. PWF for the NF90 spiral wound membrane after cleaning with 1 WT % Ultrasil 10. Experiment 9

Table 15. The more detailed initial PWF for NF270, NF99HF and AP. Experiment 1

TMP (bar)	NF270 (l/(m2h))	NF99HF (l/(m2h))	AP (l/(m2h))
2.0	91.8	73.5	27.6
4.0	180.0	128.6	62.4
6.0	270.0	192.9	84.5
8.0	367.3	260.8	115.7
9.9	473.9	332.4	145.1

Table 16. The more detailed initial PWF for NF270, NF99HF and AP. Experiment 2

TMP (bar)	NF270 (l/(m2h))	NF99HF (l/(m2h))	AP (l/(m2h))
2.1	62.4	62.4	29.4
4.0	124.9	124.9	60.6
6.1	189.2	185.5	86.3
7.9	255.3	244.3	110.2
9.9	315.9	314.1	135.9

Table 17. The more detailed flux for the filtration of UF permeate for NF270, NF99HF and AP. Experiment 1

TMP (bar)	NF270 (l/(m2h))	NF99HF (l/(m2h))	AP (l/(m2h))
2.0	56.9	53.3	14.7
4.0	124.9	117.6	29.4
6.0	198.4	180.0	42.2
8.1	260.8	236.9	51.4
9.9	338.0	270.0	60.6

Table 18. The more detailed flux for the filtration of UF permeate for NF270, NF99HF and AP. Experiment 2

TMP (bar)	NF270 (l/(m2h))	NF99HF (l/(m2h))	AP (l/(m2h))
2.0	36.7	34.9	3.7
4.1	90.0	90.0	14.7
6.0	130.4	137.8	18.4
8.1	191.0	200.2	23.9
10.2	246.1	259.0	33.1

Table 19. The more detailed PWF after filtration of UF permeate for NF270, NF99HF and AP. Experiment 2

TMP (bar)	NF270 (l/(m2h))	NF99HF (l/(m2h))	AP (l/(m2h))
2.0	75.3	73.5	11.0
4.0	135.9	135.9	22.0
6.0	200.2	194.7	33.1
8.0	270.0	266.3	42.2
10.0	341.6	343.5	55.1

Table 20. More detailed values for the initial PWF for NF90, XLE and AP. Experiment 3

TMP (bar)	NF90 (l/(m2h))	XLE (l/(m2h))	AP (l/(m2h))
5.0	58.8	49.6	71.6
10.0	117.6	101.0	135.9
14.9	183.7	150.6	202.0
20.1	251.6	209.4	271.8

Table 21. More detailed values for the flux for filtration of UF permeate for NF90, XLE and AP. Experiment 3

TMP (bar)	NF90 (l/(m2h))	XLE (l/(m2h))	AP (l/(m2h))
5.0	33.1	33.1	36.7
9.9	75.3	68.0	77.1
15.1	112.0	108.4	115.7
19.9	145.1	143.3	150.6

Table 22. More detailed values for the PWF after filtration of UF permeate for NF90, XLE and AP. Experiment 3

TMP (bar)	NF90 (l/(m2h))	XLE (l/(m2h))	AP (l/(m2h))
5.0	38.6	31.2	34.9
9.9	71.6	58.8	69.8
15.1	110.2	91.8	110.2
20.0	150.6	128.6	152.4

Table 23. More detailed values for the initial PWF for NF90, XLE and AP at CFV 0.5 m/s. Experiment 4

TMP	NF90 (l/(m2h))	XLE (l/(m2h))	AP (l/(m2h))
5.0	53.3	47.8	68.0

10.1	115.7	97.3	143.3
15.1	172.7	150.6	213.1
20.1	236.9	205.7	282.9

Table 24. More detailed values for the flux for filtration of UF permeate at CFV 0.5 m/S. Experiment 4

TMP	NF90 (l/(m2h))	XLE (l/(m2h))	AP (l/(m2h))
5.0	47.8	42.2	53.3
10.1	90.0	77.1	95.5
15.0	126.7	112.0	134.1
20.5	165.3	152.4	178.2

Table 25. More detailed values for the flux for filtration of UF permeate at CFV 0.4 m/S. Experiment 4

TMP	NF90 (l/(m2h))	XLE (l/(m2h))	AP (l/(m2h))
5.1	40.4	34.9	40.4
10.1	73.5	66.1	77.1
15.3	113.9	97.3	112.0
20.5	145.1	132.2	148.8

Table 26. More detailed values for the flux for filtration of UF permeate at CFV 0.3 m/S. Experiment 4

TMP (bar)	NF90 (l/(m2h))	XLE (l/(m2h))	AP (l/(m2h))
5.1	34.9	31.2	34.9
10.2	69.8	62.4	68.0
15.2	101.0	86.3	99.2
20.4	124.9	117.6	126.7

Table 27. The more detailed values of PWF at CFV 0.5 m/s after filtration of UF permeate after cleaning with 0.1 WT% Ultrasil 10

TMP (bar)	NF90 (l/(m2h))	XLE (l/(m2h))	AP (l/(m2h))
5.0	33.1	29.4	33.0
9.9	62.4	56.9	68.0
15.0	102.9	86.3	101.0
20.0	137.8	119.4	143.3

Table 28. The more detailed values of PWF at CFV 0.5 m/s after second cleaning with 0.4 WT% Ultrasil 10

TMP (bar)	NF90 (l/(m2h))	XLE (l/(m2h))	AP (l/(m2h))
5.0	36.7	33.1	38.6
10.1	77.1	68.0	79.0
15.2	121.2	102.9	119.4
19.9	163.5	141.4	163.5

Table 29. The more detailed values of flux for filtration of UF permeate for NF90, XLE and AP. Experiment 5

TMP (bar)	NF90 (l/(m2h))	XLE (l/(m2h))	AP (l/(m2h))

5.2	45.9	42.2	49.6
10	84.5	77.1	90.0
15.2	124.9	110.2	124.9
20.1	156.1	145.1	159.8

Table 30. The more detailed PWF after cleaning with 0.4 WT% Ultrasil 10. Experiment 5

TMP (bar)	NF90 (l/(m2h))	XLE (l/(m2h))	AP (l/(m2h))
5.0	34.9	31.2	38.6
10.0	79.0	64.3	75.3
15.0	119.4	99.2	119.4
20.0	165.3	139.6	167.1

Table 31. The more detailed PWF after cleaning with 1 WT% Ultrasil 73. Experiment 5

TMP (bar)	NF90 (l/(m2h))	XLE (l/(m2h))	AP (l/(m2h))
5.1	16.5	18.4	16.5
10.0	38.6	34.9	38.6
15.0	64.3	53.3	62.4
20.1	90.0	75.3	91.8

Table 32. The more detailed PWF after cleaning a second time with 0.4 WT% Ultrasil 10. Experiment 5

TMP (bar)	NF90 (l/(m2h))	XLE (l/(m2h))	AP (l/(m2h))
5.0	44.1	38.6	44.1
10.0	91.8	73.5	88.2
15.0	135.9	110.2	134.1
19.8	187.3	156.1	183.7

Table 33. The more detailed PWF after cleaning with 1 WT% Ultrasil 75 and 0.4 WT% Ultrasil 10. Experiment 5

TMP (bar)	NF90 (l/(m2h))	XLE (l/(m2h))	AP (l/(m2h))
4.9	47.7	40.4	44.0
9.9	90.0	80.8	91.8
15.0	145.1	124.8	143.2
19.9	202.0	170.8	192.8

Table 34. The more detailed values of flux for filtration of UF permeate for NF90, XLE and AP. Experiment 6

TMP (bar)	NF90 (l/(m2h))	XLE (l/(m2h))	AP (l/(m2h))
5.0	56.9	47.7	56.9
10.1	104.6	88.1	102.8
14.9	143.2	124.8	139.5
19.9	176.3	163.4	172.6

Table 35. The more detailed PWF after cleaning with 1 WT% Ultrasil 10 and soaked over night. Experiment 6

TMP (bar)	NF90 (l/(m2h))	XLE (l/(m2h))	AP (l/(m2h))
5.0	38.5	33.0	36.7
10.0	80.8	71.6	73.5
14.8	128.5	108.3	115.7
19.9	176.3	152.4	165.3

Table 36. The more detailed PWF after cleaning with 2 WT% Ultrasil 73 and then 1 WT% Ultrasil 10. Experiment 6

TMP (bar)	NF90 (l/(m2h))	XLE (l/(m2h))	AP (l/(m2h))
5.0	47.7	36.7	40.4
10.04	89.9	71.6	84.4
15.0	139.5	112.0	123.0
19.4845	191.0	154.2	170.8

Table 37. The more detailed values of flux for filtration of UF permeate for NF90, XLE and AP. Experiment 7

TMP (bar)	NF90 (l/(m2h))	XLE (l/(m2h))	AP(l/(m2h))
5.1	51.4	47.8	64.3
10.0	91.8	91.8	110.2
15.2	124.9	134.1	152.5
20.3	154.3	172.7	183.7

Table 38. The more detailed PWF after cleaning with 1 WT% Ultrasil 10. Experiment 7

TMP (bar)	NF90 (l/(m2h))	XLE (l/(m2h))	AP (l/(m2h))
5.1	47.8	42.2	47.8
10.0	88.2	80.8	97.3
15.3	141.4	124.9	145.1
20.0	187.3	169.0	196.5

Table 39. The more detailed values of flux for filtration of UF permeate for NF90, XLE and AP. Experiment 8

TMP (bar)	NF90 (l/(m2h))	XLE (l/(m2h))	AP (l/(m2h))
2.5	27.6	27.6	34.9
5.1	53.3	51.4	66.1
7.5	75.3	73.5	90.0
10.2	95.5	95.5	121.2

Table 40. The more detailed PWF after cleaning with 1 WT% Ultrasil 10. Experiment 8

TMP (bar)	NF90 (l/(m2h))	XLE (l/(m2h))	AP (l/(m2h))
2.5	23.9	22.0	27.6
5.0	44.1	44.1	55.1
7.5	68.0	64.3	84.5
10.0	91.8	86.3	112.0

Table 41. The more detailed PWF after cleaning with 2 WT% Dow cleaning detergent. Experiment 8

TMP (bar)	NF90 (l/(m2h))	XLE (l/(m2h))	AP (l/(m2h))
2.5	23.9	22.0	29.4
4.9	45.9	44.1	58.8
7.6	69.8	60.6	88.2
10.1	91.8	90.0	117.6

Table 42. The more detailed initial PWF. Experiment 9

TMP (bar)	NF90 (l/(m2h))
2.6	32.6
5.1	61.3
7.4	86.6
10.1	109.6

Table 43. The more detailed PWF after cleaning with 1 WT% Ultrasil 10. Experiment 9

TMP (bar)	NF90 (l/(m2h))
2.5	9.4
5.0	19.1
7.4	28.4
10.1	39.1