BIOECONOMY

Process integration by using membranes in a tissue plant

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Summary

In this project, financed by Åforsk, ÅF and Sofidel, the possibilities to use membranes for reuse of water via process integration in a tissue mill was investigated. Water saving is an increasing interest even in the Norden European countries due to the climate change resulting in higher temperatures and longer periods of draught. In 2016 the river supplying the water to the Sofidel mill in Kisa had very low levels of water which could be a threat to the production of paper at the mill.

Several process streams from the mill were collected and evaluated with membranes for recirculation in the mill. One possible process integration identified in the project was to purify the outgoing water with membranes and replace some of the fresh water intake. To reach the COD and conductivity numbers required reverse osmosis membranes were used, in combination with pre-treatment of the process water. Pre-treatment utilizing centrifugation or chemicals in combination with a membrane process using reverse osmosis gave promising results. A cost estimation for the size of the required membrane equipment needed was made.

In addition to the waste water sample some other process streams were also evaluated, and the results show that membranes could function as kidneys in the process, removing some organic components from the process. The integration and use in the mill of the tested process streams could not be identified.

The experimental work in the project was carried out as a master thesis study and the thesis report is included as an appendix to this report (Appendix 2).

1 Sofidel Sweden AB Mill in Kisa

Sofidel Sweden AB (Sofidel) develops and produces tissue. The company is owned by Sofidel Group, headquarters in Italy. White and colored tissue of surface weights in the range of 14-37 g/m² is produced on two paper machines, PM3 and PM4. About 55 different product qualities are currently produced. Both paper machines use Crescent forming technique and have yankee cylinders in the drying position.

The mill is situated at Kisa river, about 3.5 km outside Kisa community in Östergötland. The river water is used as process water and the effluent streams are after treatment discharged to the same river.

In appendix 1 a block diagram of the water process flow in the mill is presented.

1.1 Raw water treatment

Raw water from the Kisa river is used as process water. The Kisa river flows from Lake Nedre Föllingen to Kisasjön, a distance of about 3 km. The main receiving water for the effluent is Motala Ström. The normal flow in the Kisa river is about 1.4 m³/s, but the last two years the summer period has been dry and the river flow has been reduced to about 0.4 m³/s.

Water from the raw water intake is treated in two pressurized sand filters. Polyaluminium chloride and sodium hypochlorite are dosed to the filters. The sand filters are rinsed after approximately 300-500 m³ flow with ca 10 m³ rinsing water. The rinsing water is discharged to the effluent sewer. The total amount of rinsing water used per day is approximately 20 m³. Via a fresh water tank the water is distributed to PM3 and PM4.

The average raw water intake to the mill is 1100 m³/d (based on data January 2017 to March 2018). Monthly average flows are shown in Figure 1.

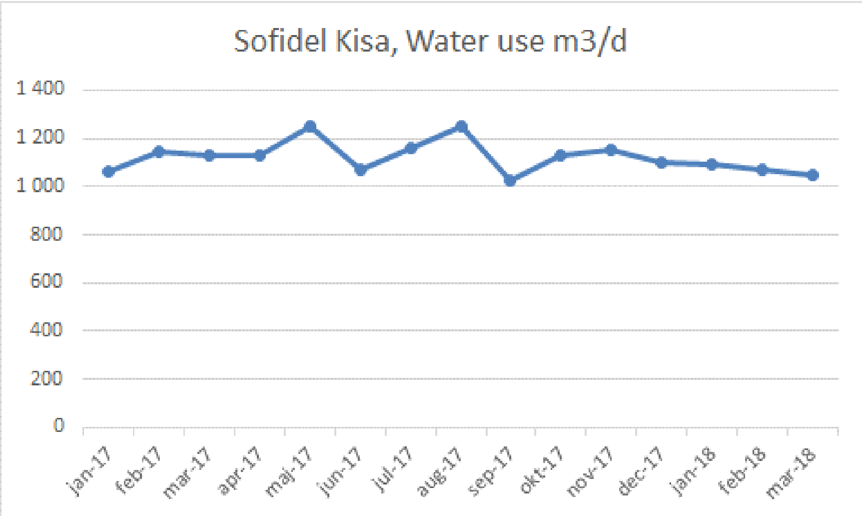

Figure 1 Raw water intake to the Sofidel mill.

1.2 Raw water quality

Table 1 the average of a few grab sample data on river water and sand filtered water from September - November 2016 are presented. For suspended solids there is also some data from January 2018.

Table 1. River water data, Sofidel, average of three grab samples, September 2016

		Inlet sand filters[1)]	Outlet sand filters[2)]
COD	mg/l	28	34
SS	mg/l	0.9	1.6[3)]
Total Nitrogen	mg/l	0.8	0.9
Total Phosphorus	mg/l	0.01	0.01
Conductivity	µS/cm	130	168
pH		7.1	7.0

1) Average of three grab samples from September 2016.
2) Average of 19 grab samples from September - November 2016.
3) In two samples from January 2018 the SS values were 18 mg/l and 38 mg/l. These values are not included in the average value.

When comparing the measured parameters in these positions, the sand filters do not seem to improve the water quality. All parameters are of the same level or even somewhat higher after the sand filters than before, but no certain conclusions can be drawn out of so few data.

1.3 Cooling water system

Cooling water is taken from PM 3:s main water distribution pipe for use in different positions in the mill.

The cooling water amount is approximately 25 m^3/d. It is distributed to different positions including lubrication systems and the press sections of the paper machines.

Return flow from the cooling water system is led to the Warm water tank in PM3 water system and to the Mill water tank in PM4 water system.

1.4 Paper process, PM 3

PM 3 is a tissue machine with Crescent former technique and a Yankee cylinder for paper drying. The heat in the drying cylinders is from biofuel-produced steam.

From the fresh water tank, the water is led to a warm water tank, a clear filtrate tank, a flat filter, a spray water tank, and thereafter to PM3. From PM3 one water stream is treated in a flotation unit and led back to the clear filtrate tank. There are effluent streams from the clear filtrate tank and from PM3 to the effluent treatment.

Fibre containing white water is treated in a flotation unit.

On the roof there is a scrubber for treatment of evaporated steam. There have been frequent problems with scaling in this scrubber and it is not always in operation. During the fall of 2018 it was decided that the scrubber will be taken out of operation permanently.

The main fresh water consuming processes/positions are:

- Warm water tank for further distribution to
  * High pressure spray water (25 bar) to paper machine
  * HD Cleaner
  * Spray water tank
- Clear filtrate tank
- Flat filter
- Buffer tank 1

1.5 Paper process, PM 4

PM 4 is also a tissue machine with Crescent former technique and a Yankee cylinder for paper drying.

From the fresh water tank, water is led to a mill water tank, from which it is distributed to PM4 via pulper 1 and 2, and to a spray water tank. From PM4 and from the spray water tank, water is led to a white water tank, from which water to nozzles and concentration regulation is taken. Fiber containing water from the white water tank is treated in a flotation unit and then led back to the spray water tank. An effluent stream origin from the white water tank is led to the effluent treatment.

For PM 4 there is no scrubber system.

The main fresh water consuming processes/positions are:

- Mill water tank for further distribution to
  * Pulper 2
  * White water Flume 1
  * Spray water tank
- Warm water tank for further distribution to HP spray water
- Direct to spray water
- Vacuum pumps 1, 2 and 3

1.6 Evaporated water in the paper process

The average pulp dryness is 88 %. The average dryness of produced paper is 94 %. Based on the production of 2016, this causes an extra volume of approximately 10.4 m^3 water/day to the system, since the volume of water that is entering the mill in the pulp is greater than the water leaving the mill in the paper.

According to the yearly environmental report from 2016 the evaporation from the paper machines is approximately 2 m^3/ton produced tissue, corresponding to approximately 300 m^3/d based on the production of 2016.

1.7 Effluent treatment plant

Effluent streams from different parts of the plant are gathered in an equalization basin (R1). Ferric sulphate and polymer are dosed to the water and there is a flocculation chamber and a primary clarifier (R3) for withdrawal of primary sludge.

Primary clarified water is pumped to biological treatment in two MBBR reactors. Nitrogen, phosphorus and defoaming agent is dosed before the first reactor. Additional defoaming agent can be dosed to the second MBBR unit.

To the biologically treated water Ferric sulphate and polymer are dosed. Formed flocs are separated in a flotation unit with a flocculation chamber. Treated water is discharged to the Kisa river.

Biological and chemical sludge from the flotation unit is mixed with primary sludge in a sludge tank and dewatered. Reject water from the sludge dewatering is returned to the effluent treatment process ahead of the equalization basin R1.

1.8 Effluent treatment data

The yearly average flow from the effluent treatment plant 2015-2017 is shown in Table 2 and monthly average flow values in Figure 2. Effluent flow measurements from Sofidel 2015-2017.

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Table *2*. Sofidel Kisa, Average flow from effluent treatment plant

		2015	2016	2017
Average flow	m^3/d	653	584	741

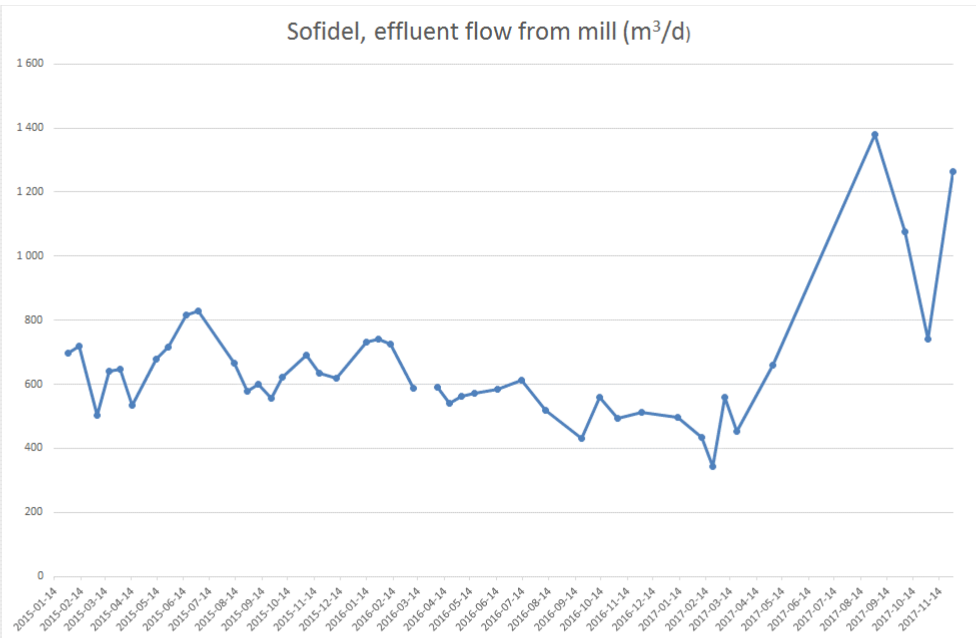

Figure 2. Effluent flow measurements from Sofidel 2015-2017.

The yearly average COD in to and out from the effluent treatment plant 2015-2017 and COD reduction is shown in Table 3 and monthly average data in Figure 2 and Figure 3.

The COD reduction level is 35-37 % as yearly average value.

The effluent discharge limit has until September been 300 kg/d. From October 2018 the BAT-AEL limits, 0.3-5 kg COD/ton produced tissue will also be applicable. The yearly mean value for 2016 was 1.3 kg COD/ton produced tissue.

Table 3 Sofidel Kisa, Average COD in to and out from effluent treatment plant

		2015	**2016**	**2017**
COD inlet	mg/l	390	590	560
COD inlet	kg/d	250	350	420
COD outlet	mg/l	250	370	350
COD outlet	kg/d	160	220	260
COD limit	kg/d	400	400	400
COD reduction	%	35	37	36

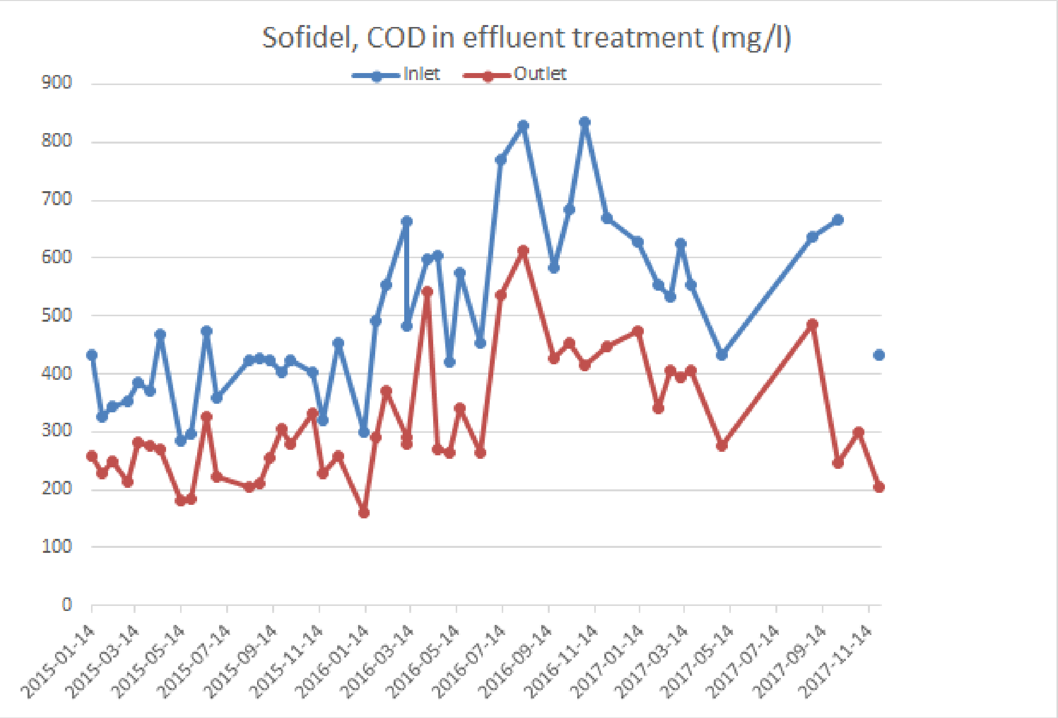

Figure 2 COD inlet to and outlet from effluent treatment plant, 2015-2017

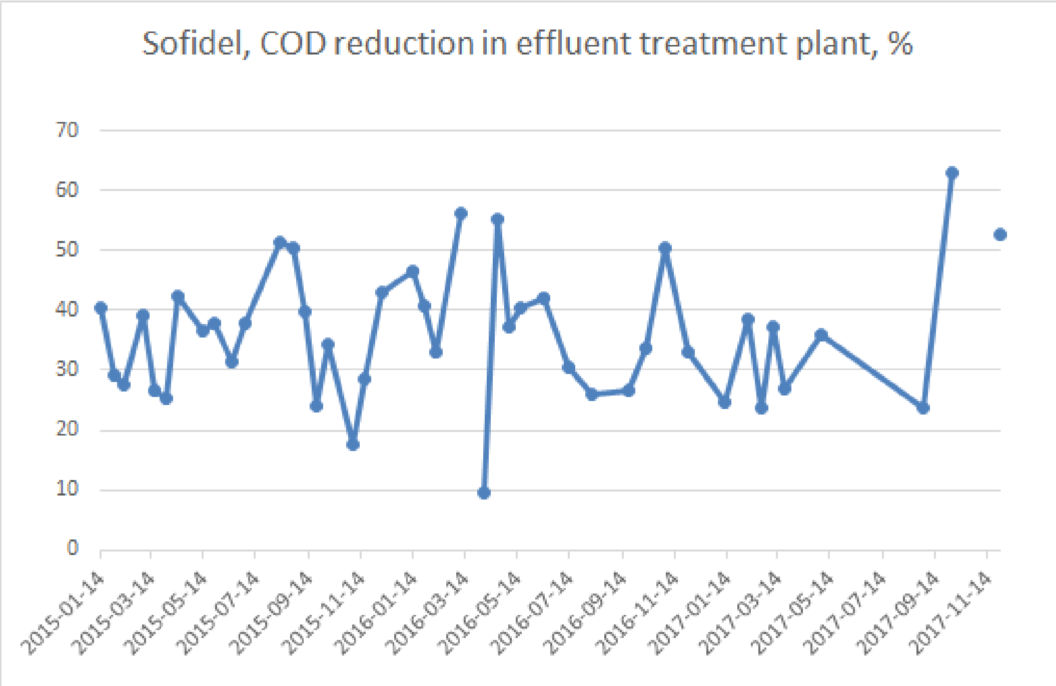

Figure 3 COD reduction in the effluent treatment plant, 2015-2017

1.9 Raw water quality demand

To examine raw water and treated process water quality several parameters could be measured. Among these parameters are color, total hardness, iron content, manganese content, and residual aluminum. Some normal data for good raw water quality and standard values for fine paper are shown in Table . It must be noted that the quality according to this specification is much better than the fresh water intake used today in the mill. Most of the parameters in the table have not been measured at Sofidel for many years.

Table *4* Normal fresh water data according to Würtzell, 2001, and standard Fresh Water Specification, according to Sofidel and to TAPPI demand for Fine paper

Parameter	Unit	Fresh Water specification, Sofidel	TAPPI process water demand Fine paper	Normal data for good raw water quality[1)]
Color	mg Pt/l	clear	5	<10
Total hardness[2)]	°dH (German)[3)]	<8[3)]		
Total hardness as $CaCO_3$	mg/l	<143[4)]	100	
Total dissolved solids	mg/l	<150	200	
Free carbonic acid	mg/l	<10		
Free carbon dioxide	mg/l		10	
Free chloride content (Cl_2)	mg/l	<20		
Iron content (Fe)	mg/l	<0.2	0.1	0.05-0.2
Manganese content (Mn)	mg/l	<0.1	0.05	
Copper content (Cu)	mg/l	<0.1		
$KMnO_4$	mg/l	<12		<12[5)]
COD_{Cr}[5)]	mg/l	< 7.5[6)]		< 7.5[6)]
SÄ GF/A	mg/l	<2[7)]		
Nitrates (NO_3^-)	mg/l	<20		
Conductivity	µS/cm	<600		
pH		6.5-7.5		6-8
Turbidity	NTU	<5	1.3[8)]	
Sulphates ($SO4_2^-$)	mg/l	<30		

1) Würtzell, 2001
2) Very soft water 0-2 °dH, Soft water 2-5 °dH, Average hardness 5-10°dH, Hard water 10-21 °dH and Very hard water >21 °dH
3) 1 °dH (German) corresponds to 7.2 mg/l Ca or 17.85 mg/l $CaCO_3$
4) ÅF calculation
5) $KMnO_4$: Very low concentration ≤4 mg/l, Low conc. 4-8 mg/l, Average conc. 8-12 mg/l, High conc. 12-16 mg/l and Very high conc. >16 mg/l
6) Calculated from $KMnO_4$ (Dow, 2018), COD_{Cr} [mg/l] = 1/1.6 $KMnO_4$ [mg/l] Varies for different waters
7) Normally the minimum possible analyzing value is said to be 5 mg/l
8) Based on transformation, 1 mg/l SiO2 units = 0.13 NTU

2 Membrane filtration experiments

In this section a summary of the conducted membrane filtration experiments in the project is presented. In the master thesis report from this project all details regarding the membrane filtration trials are given. The full version of the master thesis report can be found in Appendix 2.

2.1 Sampling positions for membrane filtration tests

Water samples for membrane filtration tests were taken in four positions:

- After raw water sand filters
- After spray water tank in PM 3 system, before scrubber
- After flotation in PM 4 system
- At the outlet of the waste water treatment (two different sampling days)

2.2 Membrane filtration tests

In this study a laboratory scale filtration unit from Alfa Laval called M20 was used. It is a suitable filtration unit for screening and very easy to operate. In the unit several membranes can be tested simultaneously in order to determine which membrane is the most suitable.

The pores in the membrane allow penetration of smaller particles and water from one side of the membrane to the other side, whereas most particles are retained. The clean water produced is called permeate and is characterized by a drastically lower concentration of contaminants in comparison to the reject stream (retentate)

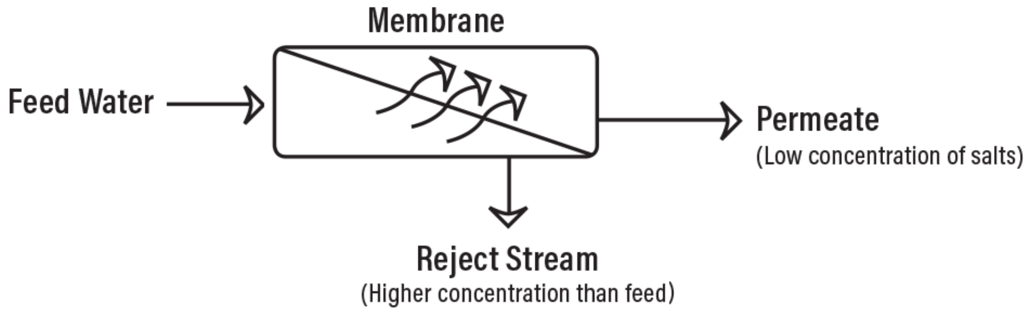

Figure 5. Principle for mebrane filtration. (figure from R. Singh, 2015)

The main focus in the project was to test ultrafiltration and reverse osmosis membranes. The ultrafiltration membranes reject large dissolved organic molecules but will not reject ions and inorganic molecules. Reverse osmosis membranes reject much smaller molecules but has higher operating pressure making them costlier to operate.

The flow through the membrane, called the flux, is determined as filtrated amount of permeate per m^2 of filtration area and hour. This is an important design parameter to estimate the size of a membrane installation. Another important parameter is the level of fouling in the membrane. The level of fouling is measured by testing the flux of pure water before and after a test run. If components in the treated water clog the membranes during filtration and the clogging components can not be removed with a cleaning step the application of membranes is not feasible. Different cleaning agents can be used for regeneration of the membranes but there are limitations of the properties of the cleaning solution (pH, temperature, concentration) depending on what type of membrane is used. When testing the osmosis membrane before the actual trials, the flux recovery was low and it was discovered that even after filtrating a dilute saline solution (2000 ppm NaCl) only 60% flux recovery was measured. The saline solution is specified in the membrane filtration data sheet for testing the membrane performance. It is possible that the osmosis membrane requires more conditioning before use-

2.2.1 After spray water tank in PM3 system before the scrubber

A water sample was taken from the PM3 system on the 21 of March for membrane testing. The sample was taken before the scrubber, and the purpose to try membrane filtration was problems with clogging in the scrubber equipment which is therefore not always in operation. The sampling position is shown in Figure 4. If this water stream was treated further it could have enabled a decrease in fresh water usage, even though the volume of potentially saved water probably would be small. In October 2018, however, it was decided to take the scrubber out of service. Therefore, this alternative will not be further evaluated.

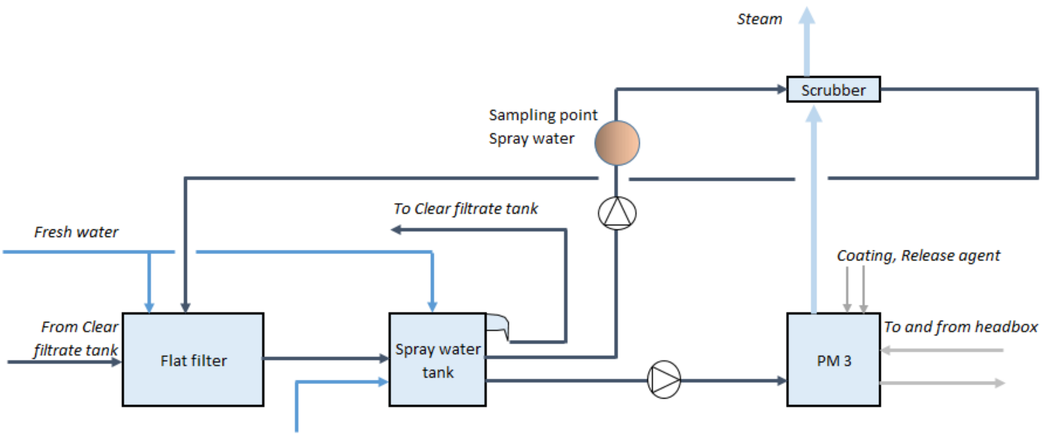

Figure 4. Sampling point, PM3 system - spray water before scrubber

The purpose of the scrubber was to heat water in the spray water tank, and in that way save energy. The function was as follows:

The produced paper, from PM3, is dried with steam in a dryer hood. The hot air, with a temperature around 110 ⁰C, from the dryer hood was led to the roof to the scrubber. Water from the spray water tank was led to the roof and sprayed on the hot air from the dryer hood. The water was then, after passing the scrubber, led to a flat filter, and then to the scrubber again, and was thus circulating.

Both ultrafiltration (UFX 10) and reverse osmosis membranes (RO 90+RO 98) were evaluated for this process stream.

Table 2 Membrane test on spray water to scrubber, PM3 Water system

Membrane used		UFX10	RO90	RO98
Flux recovery*	%	89	65	60
Permeate flux 120 min	$l/m^2,h$	90	70	70
COD reduction	%	38	74	70
COD in permeate	mg/l	348	132	153

*Flux recovery of a dilute saline solution (used for membrane specification datasheet) was 60% for the RO90 membrane

The COD levels in the permeate are rather high and the permeate stream should not be suitable for the purpose to replace the water in positions where sand filtered water (raw water intake) is used. The raw water has a reported COD levels of around 40 mg/l.

A cleaner spray water could theoretically reduce the needed fresh water supply to the flat filter and to the spray water tank, but these fresh water flows are already low, so there is not an important water saving measure. On the other hand, clogging problems in spray water nozzles and other runnability problems might be reduced by employing membranes in this position. If the membranes remove the compounds that caused problems with the scrubber substantial energy savings could be gained by being able to operate the scrubber again.

2.2.2 After flotation in PM4 water system

A water sample was taken from the PM4 water system on the 21st of March for membrane testing. See sampling position in Figure 5.

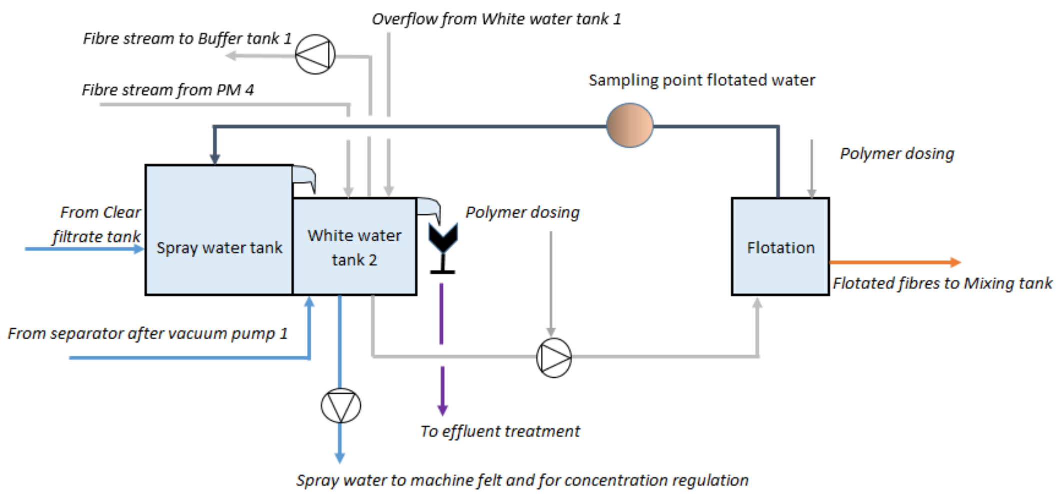

Figure 5 Sampling point, PM4 system, after flotation

Fibre containing white water from the wet end of PM 4 is led to White water tank 2. All water from a spray water tank ahead of this tank is also led to White water tank 2. A third flow to the white water tank 2 is outlet water from vacuum pump 1 after separation and sound silence equipment. One stream from White water tank 2 is pumped to Buffer tank 1. One stream is pumped to lubrication spray equipment to moister the machine felt and for concentration regulation. Overflow from the white water tank is led to a sewer and to effluent treatment. One stream is pumped to a flotation unit. Separated fibres is used in a mixing tank. Water from the flotation process is led back to the spray water tank ahead of the white water tank 2.

One purpose to try membrane filtration in this position was to minimize the needed fresh water addition to the spray water basin ahead of the white water tank 2. This fresh water flow is very low, so the water saving potential in this position is fairly low. Further treatment after the flotation unit will, however, give a clearer white water which might improve the paper quality and possibly reduce the fresh water consumption.

On the PM4 process stream two membrane types were tested: one ultrafiltration membrane (UFX 10) and one reverse osmosis membrane. The results are shown in table 9 below.

Table 3 Membrane test on spray water to scrubber, PM4 Water system

Membrane used		UFX10	RO90
Flux recovery *	%	88	60
Permeate flux 120 min	$l/m^2,h$	85	70
COD reduction	%	30	73
COD after membrane filtration[1)]	mg/l	455	160

*Flux recovery of a dilute saline solution (used for membrane specification datasheet) was 60% for the RO90 membrane

As for the PM3 process water the COD levels remain too high to replace the raw water intake. However, the decreased COD concentration could still possibly improve paper quality and runnability in PM4.

2.2.3 After effluent treatment

Water samples were collected after the effluent treatment for membrane testing on the 25th of January and the 14th of February. The sampling position can be seen in Figure 8.

The purpose of this sampling position was to investigate possibilities to return the water to the raw water intake and thus close the system and use less water from the Kisa river. Depending on the reached water quality from the membrane filtration, the water could also be returned to other positions in the process.

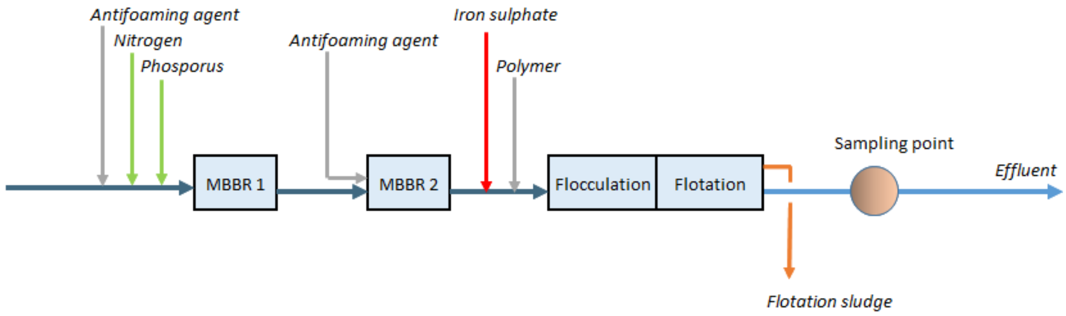

Figure 6 Sampling point after the effluent treatment

Water from this position was tested in two steps. Several different membranes were tested on this process stream; both microfiltration (MF), ultrafiltration (UF) and reverse osmosis (RO) membranes. The membranes were also tested using cascade filtration where first a coarser membrane was used as a pre-filtration step when producing pure water in the reverse osmosis filtration. The microfiltration membrane was FS40PP, the ultrafiltration membrane was a UFX10 membrane and the reverse osmosis membranes were RO90, RO 98 and RO 99.

The different combinations of pre-treatment and RO are listed below. The reduction rates presented in Table 4 are for combined process water treatment including the pre-treatment.

Table 4 Membrane test on effluent sampled after the effluent treatment. Several different pre-treatments were tested. MF= microfiltration, UF = ultrafiltration, Screen = filtration through a 70µm mesh, centrifuge = centrifugation at 5000g.

Experiment		1	2	3	4	5	6	7
Pre-treatment		MF	MF	Screen + UF	Screen + UF	Centrifuge	Centrifuge	Chemical
Membrane used		RO90	RO98	RO90	RO98	RO90	RO98	RO90
Flux recovery*	%	74	54	65	47	72	73	72
Permeate flux 120 min	$l/m^2,h$	58	75	75	90	75	110	63
COD reduction	%	75	50	60	54	74	45	75
COD after membrane filtration	mg/l	60	120	69	80	42	80	40

*Flux recovery of a dilute saline solution (used for membrane specification datasheet) was 60% for the RO90 membrane

For some treatment combinations the COD levels in the RO permeate are relatively close to the normal levels of the raw water intake at Sofidel. It could be possible to recirculate the membrane filtrated water to replace the fresh water intake. A more detailed analysis of the composition of the water is required, including metal ion determination, in order to know if this is possible.

A possible way to improve the water quality of the effluent might be to optimize the biological and chemical effluent treatment process. This might also be needed in the future to meet new EU BAT discharge levels.

2.3 Economic calculations – installation of membrane unit

The main components of the cost of membrane treatment are capital cost, membrane replacement, energy usage, labour, cleaning, and maintenance. The capital cost is the sum of membrane units cost and the non-membrane units. The non-membrane cost includes all mechanical and electrical items, control equipment, piping and associated civil engineering costs. The non-membrane costs are not covered in the following calculation.

The economic calculations will include the fixed capital cost (FCI) and total capital investment (TCI) for the membrane filtration of the incoming wastewater. To determine the FCI and TCI, the purchase cost for all equipment needs to be calculated. All other costs that add to the needed investment are estimated by standard factors on the purchase cost.

The cost for membrane investment and operating energy required are based on inquiries from AlfaLaval Nakskov A/S in Denmark.

To determine the cost of the membrane, the most important defining factor is the surface area required. Based on all the fulfilled experiments an average flux was considered for both UF and RO membranes as 138 and 92 L/m^2.h respectively. As previously mentioned, the aim of the project was to reduce freshwater consumption by 100 m^3. The surface area required for the filtration can then be calculated as:

$$UF : 100\ \frac{m^3}{day} * \frac{1\ day}{24\ h} * \frac{m^2.h}{138\ L} * \frac{1000\ L}{1\ m^3} = 30\ m^2$$

$$RO: 100\ \frac{m^3}{day} * \frac{1\ day}{24\ h} * \frac{m^2.h}{92\ L} * \frac{1000\ L}{1\ m^3} = 45\ m^2$$

Due to the technical uncertainties and the fact that the feed will not fully pass the membrane, 30% is added to the required surface area, making it 40 and 60 m^2 for ultrafiltration and reverse osmosis respectively.

Based on contact with AlfaLaval, prices and energy consumptions for 8.0" spiral wound plug flow plants were estimated, which are summarized in **Table 5**. It should be noted that the cost refers to DAP (Delivery at point) at AlfaLaval Nakskov and does not include shipping and freight costs.

Table 5- Cost estimations for membranes.

Membrane Type	**Surface Area (m^2)**	**Price (kEur)**	**Energy Consumption (kW/m^3 permeate)**
Ultrafiltration	40	195	1-4
Reverse Osmosis	60	500	8-12

3 Further studies

In order to further evaluate the possibilities to use membrane filtration and reduce fresh water consumption at the mill pilot plant scale tests are recommended.

Based on this study the most promising position for testing is after the effluent treatment plant. Some pre-treatment will be needed ahead of the membranes. For evaluation of the test results a more detailed chemical characterisation as compared with this study, for inlet and outlet water to the test unit and also on inlet water to the mill would be valuable.

4 Conclusion

The aim of this study was to discuss the technical feasibility when using membranes to reduce the water consumption within a tissue mill in Kisa. The main focus of the experiment was on filtering and recirculating the wastewater effluent to replace part of the freshwater intake. Additional experiments were also performed on process waters in the tissue production process.

The experiments showed that a pre-treatment step coupled with reverse osmosis could be used for the tertiary water circuit, i.e. the water from the effluent treatment. The high water flux and shear rates require a membrane module that can embody high surface areas; therefore a spiral wound module should be utilized. Spiral wound modules are more prone to fouling, though, which means the pre-treatment technique has to work efficiently in reducing contaminants which may cause fouling.

Several different pre-treatment steps and different reverse osmosis membranes were tested in lab-scale. It was concluded that centrifugation, flocculation, and membrane filtration are all feasible pre-treatment techniques; each with their own merits and faults. Flocculation can be assumed as the most appropriate method, given the better performance.

The RO90 membrane proved far more efficient than other membranes, both in terms of separation and flux recovery, but experienced a lower average flux. This can be attributed to the polyester support on TFC, and its corresponding properties such as low wettability. UFX10 and RO98 did not provide sufficient separation and RO98 also exhibited high fouling levels. The cleaning procedure was typically comprised of both alkaline and acidic cleaning. The flux recoveries were used to compare the fouling levels. The alkaline cleaning step was far more effective, indicating the wastewater contaminants are biological in nature.

The experiments also showed that ultrafiltration and reverse osmosis can be used as kidneys for the paper machine, depending on what water quality is needed for a specific application.

A cost estimation was made for the membrane equipment required to produce 100m^3 of purified water. The cost is reasonable for the installation of membranes, but it has to be stressed that no cost was taken into account for the pre-treatment of the water before the membrane filtration purification and no installation cost for the process integration at the mill was made.

5 References

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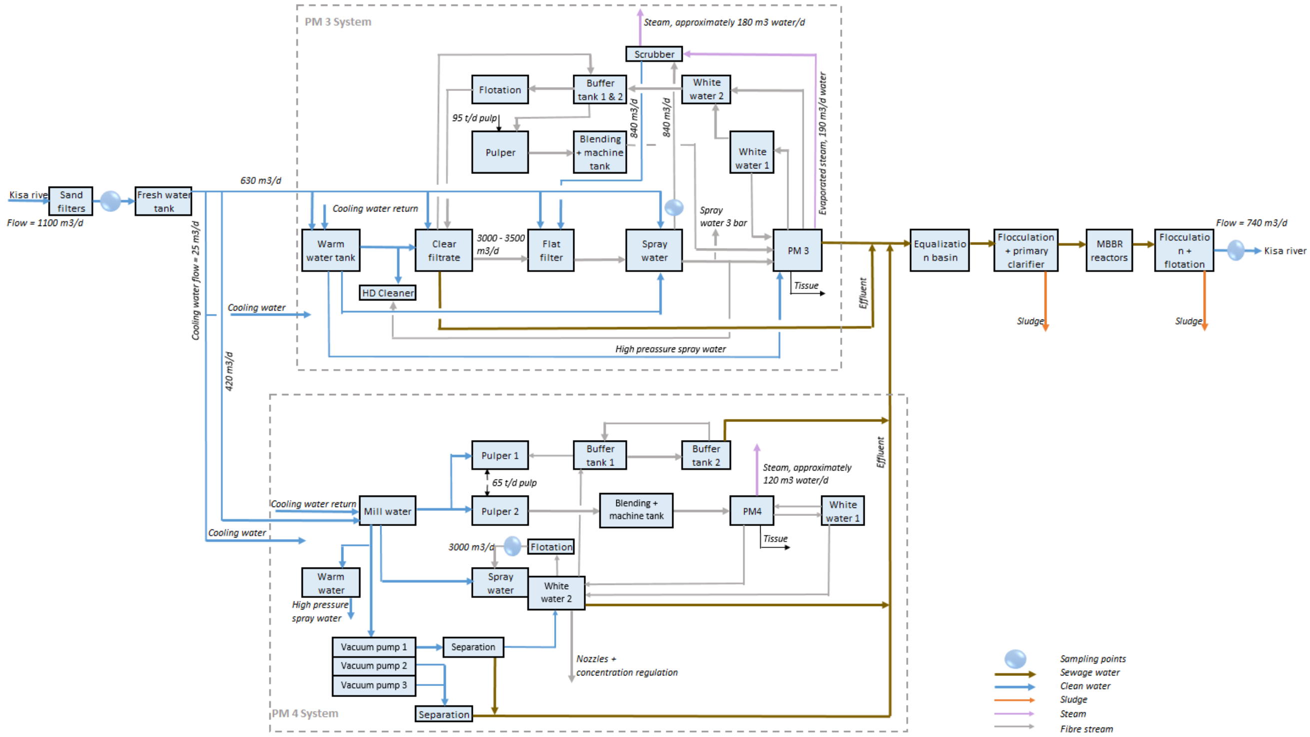
APPENDIX 1

Process flow diagram Sofidel



APPENDIX 2.

Master thesis - Ehsan Moslehi

EXAMENSARBETE INOM KEMITEKNIK,
AVANCERAD NIVÅ, 30 HP
STOCKHOLM, SVERIGE 2018

Integrating membrane filtration for water reuse in tissue mill

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Abstract

Water is an essential and indispensable component is the pulp- and paper production industry. The increase in energy costs, stricter environmental regulations and water resource shortages have caused a reduction of the water footprint in the industry as well as an increase in water recycling and water circuit closure. Reducing water usage requires an understanding of where contaminants originate, as well as which streams are critical to the process and how they impact mill operation. The recirculation of water can cause contaminant accumulation; therefore mills employ technologies for water treatment in the internal water cycles, the so-called 'kidneys'. Application of membrane technology is one such option which can improve the recycled water quality and reduce contaminant buildup.

The present study was carried out on a lab-scale for the treatment of a tissue mill effluent using membrane separation. A combination of pretreatment methods and various membranes were compared with regards to separation, flux and fouling. The AlfaLaval M20 device was to treat wastewater samples sent from the mill, where the permeate was recirculated to the feed tank. COD and TOC levels are compared with regards to determining the separation efficiency. The permeate flux was measured over the two-hour filtration period, as well as flux recovery to determine fouling levels. Additionally, some economic aspects of the process are discussed.

This study suggests the potential application of a combination of flocculation or centrifugation pretreatment, with reverse osmosis membranes for recycling water to replace freshwater intake. The results also indicate the possibility of using ultrafiltration as kidneys to decrease contamination buildup for further water loop closure.

Keywords: Membrane separation; Paper industry; Paper mill effluent; Water reuse ; Reverse Osmosis

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Ehsan Moslehi

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Introduction

Water is a critical component in the pulp and paper production due to its role in transporting raw materials and removing contaminants, as well as providing the necessary environment for the formation of the hydrogen-bonding network between fibres and fillers, which is the essence of the paper production mechanism [1]. Water scarcity and stricter environmental regulations, as well as economic reasons, have led to the need for decreasing the water consumption in paper mills as well as limiting the wastewater discharge to the environment.

Paper production typically requires an immense amount of freshwater intake, due to the high quality of water required for some applications, in addition to the high evaporation levels within the process. However, varying qualities of water are needed based on their application, meaning water with relatively low purity can be used in less demanding applications. This has led to a high amount of water recirculation within the mill. This can be extremely problematic as it can lead to the accumulation of contaminants; which may decrease the quality of the finished product. Therefore, additional treatment technologies may be required to enhance the process water quality. Biological treatments, as well as physicochemical treatment techniques such as sedimentation, coagulation and precipitation, chemical oxidation and membrane filtration, are commonly applied for this purpose.

Membrane technology plays a vital role in water and energy sustainability and is applied in several industries today. Examples include brackish and seawater desalination via reverse osmosis, water, and wastewater treatment via membrane bioreactors (MBR) as well as membrane-based fuel cells and lithium-ion batteries. Membrane technology is considered a sustainable solution due to lower environmental impacts, fewer space requirements, ease of operation, flexibility and adaptability. However, the process is still deemed expensive. In recent years, advancements in membrane material selection have led to more opportunities for membrane technologies to be utilized water and energy sustainability [2].

Membrane filtration can be utilized at various points within the pulp and paper water treatment systems to decrease contamination levels. The most widely applied technologies include nano-filtration, reverse osmosis or membrane bioreactors. However, the limitation connected with the application of the membrane technologies is the flux decline due to the membrane fouling, which also decreases the membrane lifespan. Another disadvantage is the very high cost of this treatment caused by the high energy input required [3].

Aim and Goals

The purpose of the project is to evaluate the possibilities for using membrane technology to reduce freshwater intake in a tissue use in the Sofidel mill in Kisa. The Kisa River has been experiencing drought and a lack of year-round water supply, which has caused many problems for the Sofidel AB tissue mill.

The work includes an evaluation of possible installation points as well as laboratory scale membrane filtration of the more interesting streams. The goal has been defined to reduce freshwater intake by 10%, which is equivalent to approximately 100 m^3 per day. Preliminary studies from the mill have found the incoming freshwater has a COD of approximately 30 mg/l.

Theory

Membranes

Membranes are defined as perm-selective barriers between two homogeneous phases, where the semi-permeable barrier selectively passes desired components and prevents the passage of contaminants. The separation occurs due to the differences in chemical properties, namely size and shape of the substances. Membrane separation is a continuous steady-state operation and is composed of three main streams: feed, product (permeate) and reject (retentate) [3].

Membranes are typically produced from polymer or inorganic materials which embody numerous microscopic pores. The small pores in the membrane allow penetration of smaller particles and water from one side of a membrane to the other side, whereas most particles are retained. The clean water produced is then called permeate, which is characterized by a drastically lower concentration of contaminants in comparison to the reject stream (retentate) [4].

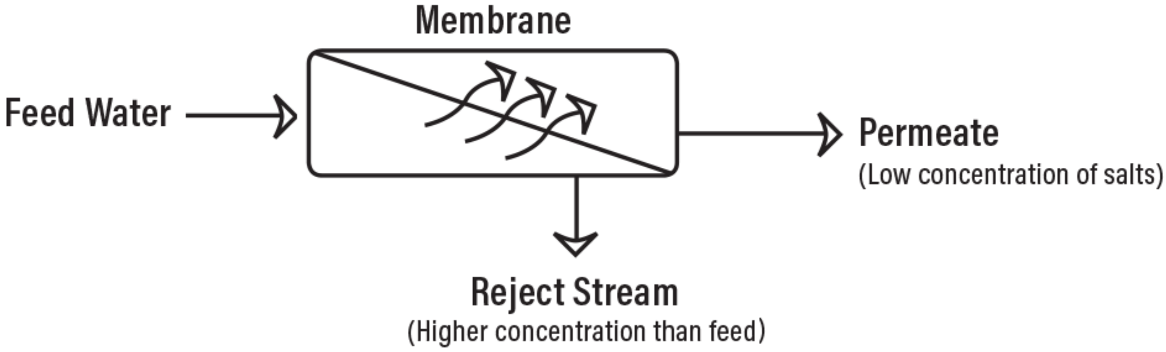

Figure 1- Schematic of a basic membrane process [3]

The efficiency of the separation process depends on the membrane's selectivity and flux; mechanical, chemical and thermal stability of membrane materials, fouling during operation, and the operating conditions [3]. The membrane's performance is a trade-off between membrane selectivity and membrane productivity. Membrane selectivity, (α =A/B), is defined as the ratio of permeability of components through the membrane, where A is the water permeability coefficient and B is the solute permeability coefficient [3].

An important advantage of membrane separation is that selectivity can be modified based on the application of the purified water. Membrane processes used today for wastewater recycling can be classified into pressure-driven processes and electrically-driven processes. Pressure-driven processes include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Electrically-driven processes include electrodialysis and electro deionization.

MF and UF are commonly applied to remove suspended or colloidal particles via sieving mechanisms based on the size of the membrane pores [3]. NF and RO membrane processes are mostly used in applications which require the removal of dissolved contaminants, as in the case of softening or desalination [3]. Basic characteristics of these processes are summarized in Table 1.

Table 1- Classification of typical membrane separation processes for water purification [3]

Process	**Nominal pore size**	**Driving force**	**Average Permeability ($L/m^2.h\ bar$)**
Micro-filtration	0.05-10 µm	1-3 bar	500
Ultra-filtration	0.001-0.05 µm	2-5 bar	150
Nano-filtration	<2.0 nm	5-15 bar	<20
Reverse Osmosis	~ 0.5 nm	15-75 bar	<5

Micro-filtration (MF) refers to membranes with pore sizes ranging from 0.05-10 µm and is the membrane with the largest pores. The molecular weight cut-off (MWCO) is greater than 1000,000 Daltons and the feed water operating pressure is approximately 1-3 bars. The major separation mechanism in MF is physical sieving. MF is applied to filter suspended particles, large colloids, bacteria, and organics. The separation can also be used as a pretreatment step for NF and RO processes to reduce fouling potential. MF is also commonly applied to reduce chemical addition in wastewater treatment steps, such as chlorination [5, 6].

UF removes all microbiological species removed by MF, as well as humic materials such as lignin and xylan. Ultrafiltration has a pore size of approximately 0.001 to 0.05 microns, an MWCO of approximately 10,000 to 100,000 Daltons and operates at a pressure of approximately 2-5 bars [1, 3].

Nano-filtration membranes have a nominal pore size of less than 2 nm and an MWCO of 1,000 to 100,000 Daltons. The smaller pore sizes lead to higher operating pressures, ranging from 5-15 bars, and thus require higher energy input [6]. Applying nano-filtration (NF) allows for the removal of metal ions such as barium, iron, and manganese, which lead to a high consumption of bleaching chemicals. NF is also an efficient means for removing sulphate ions [1, 3]. NF membranes remove alkalinity and hardness as well, therefore the permeate stream may be corrosive [6]. Sodium chloride rejection when applying NF varies from 0-50 % depending on the feed concentration. NF is desirable for applications where moderate salt removal is acceptable, with the advantage of lower power consumption and costs [7].

Reverse osmosis utilizes membranes with a nominal pore size of less than 0.5 nm, which effectively removes nearly all inorganic contaminants and most dissolved non-ions from the water. The units operate at pressures as high as 75 bars. Reverse osmosis is used for desalination to produce fresh water from seawater and brackish water [8].

‘Figure 2 summarizes the extent of particle removal of the aforementioned pressure-driven membranes.

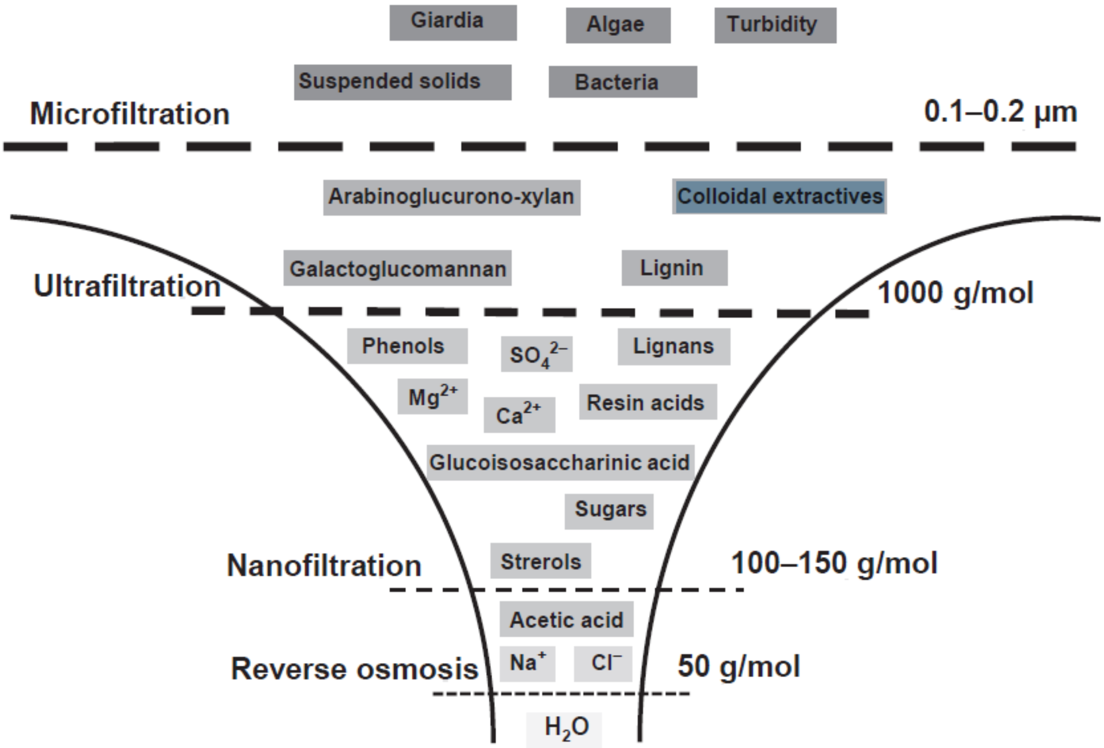

Figure 2- Separated particles in for pressure-driven membrane processes [1]

Membrane Materials

Membranes can be composed of a large number of materials, based on processing requirements, thermal and chemical stability and fouling tendency. Membrane surface chemistry and other properties such as roughness, charge, and hydrophilicity effect performance and fouling. Interfacial tension and adsorption rates are also crucial parameters since the solid membrane phase is in contact with a fluid phase. Synthetic organic polymers are the most widely used material for membranes [3].

Membrane fouling, insufficient separation, low lifetimes and resistance to certain chemicals are the most well-known problems related to polymeric membranes [9]. Fouling is the most major issue in membrane configurations as it can adversely affect efficiency, permeability and membrane lifetime. A solution to this problem is to make membranes more hydrophilic. This can be achieved by

1- Modification of polymers before fabrication to enhance hydrophilicity
2- Blending with hydrophilic agents
3- Coating of hydrophilic polymers on the membrane surface

These resolutions will decrease fouling but may have negative effects such as narrowing or even blocking of the pores and even reduced lifespans due to additional coating layers [2].

Polymer and ceramic compounds are both be applied to fabricate MF and UF membranes. Ceramics provide higher chemical stability and mechanical strength, ease of cleaning as well as longer and reliable lifespans. However, higher prices, lower mechanical strength, and difficulties for large-scale production have prevented widespread application of ceramic membranes; Therefore, polymeric membranes dominate the market[8]. Common commercial polymers used for MF and UF membranes are poly-ether sulfone (PES), polyvinylidene fluoride (PVDF), polyethylene (PE), polypropylene (PP) and polytetrafluoroethylene (PTFE) [2].

Polymeric membranes are commercially used for reverse osmosis desalination, due to low-cost production, ease of handling, and high performance in terms of selectivity and permeability[8]. Thin Film Composite (TFC) membranes now dominate the RO/NF market. They are stable over a greater pH range as well as operating with higher intrinsic water permeability due to their extremely thin (~100 nm) PA-selective layers[2].

Thin film composite polyamide membranes

Dense membranes provide higher selectivity but lower flux, whereas porous membranes have low selectivity but a higher flux. Increasing the flux in a dense membrane can be achieved by reducing the thickness to the extent where it is still defect-free and possesses adequate mechanical strength. This can be achieved by the implementation of Thin Film Composites (TFCs)[9]. These membranes consist of a selective thin skin layer which is supported by a porous substrate. The active outer layer is deposited as a thin film on a porous layer and consists of a cross-linked polyamide layer. The layer is extremely thin (0.1 mm or less) which leads to higher membrane permeability and selectivity, also due to the high cross-linking of polymers

[10]. These membranes have high temperature and pH resistance but are not able to tolerate oxidizing environments [7].

Polysulfone

Polysulfone membranes have been widely used for UF and MF operations due to their enhanced temperature and pH resistance. These membranes are commonly used in food and dairy applications [7].

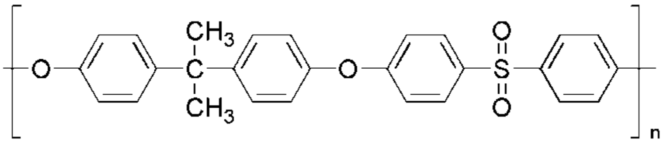

Figure 3-Polysulfone repeating unit [11]

Polypropylene

Polypropylene is also used in particular for support layers in membranes for waterproofing the top layer. Polypropylene is a good candidate for industrial applications such due to its outstanding properties such as high melting temperature, chemical resistance and good mechanical properties [7].

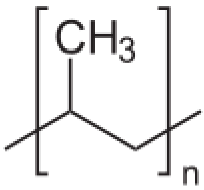

Figure 4- Polypropylene repeating unit [11]

Fluoropolymer

A fluoropolymer is a fluorocarbon-based polymer with multiple carbon-fluorine bonds. The polymers are best characterized with their high resistance to solvents, acids, and bases, owing their stability to the multiple carbon-fluorine bonds within the chemical composition. The high electronegativity difference between carbon and fluorine (4.0 for F vs. 2.5 for carbon) makes the bond significant polar [7].

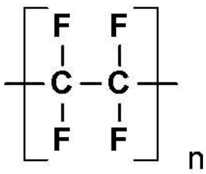

Figure 5- Fluoropolymer repeating unit [11]

Membrane Modules

The membranes are installed in a proper device, referred to as modules. The core objective of a module is to provide maximum membrane surface area in a relatively smaller volume, as to facilitate the highest feasible permeate flux [12]. Membrane modules must also meet requirements regarding production cost, packing density, energy consumption and fouling control. Membrane surface areas typically range from hundreds to thousands of square meters to meet the flux and separation requirements set by the industry. Efficient economic modules with high surface areas are designed based on the membrane application [13].

Spiral wound

Spiral-wound membrane modules were originally developed for industrial reverse osmosis applications, namely water desalination. The design consists of a feed flow channel spacer, the membrane and a porous membrane support, which forms an envelope, which is wound around a perforated central collection tube and inserted into an outer tubular pressure shell [12] [13].

The feed flows axially down the module across the membrane envelope. The permeate spirals toward the centre and exits through the collection tube. The module operates in cross-current flow[12]. Small spiral wound modules include only one envelope, which limits the total membrane surface area to about 1-2 m^2. Higher surface areas would result in pressure drop in the permeate channel. Industrial spiral wound modules are 1 meters long and have a diameter of 10-60 cm, providing 3-60 m^2 of surface area [13]. The spiral-wound module provides a high surface area per unit volume, which means the module is cost-effective. However, the module is prone to fouling and feed channels may be easily clogged. A pretreatment step to remove particles and fibres must be implemented for longer lifetimes and better separation.

Due to the demanding setting in the pulp and paper industry, specific module configurations with high shear forces are utilized to prevent flux decline. The high shear results in higher levels of fouling and lower membrane lifespan. Spiral wound modules, coupled with physical and chemical pretreatment, have also been used in the paper industry [1].

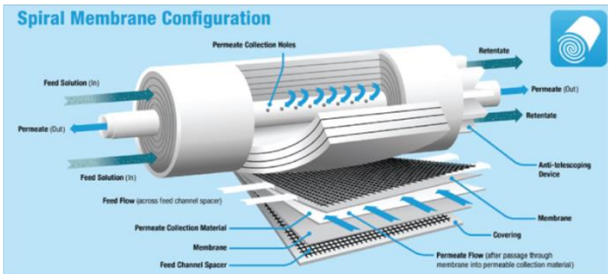

Figure 6- Spiral Membrane Configuration [13]

Fouling

Fouling is defined as the deposition and accumulation of rejected contaminants from the feed stream on the membrane surface, which inevitably leads to water flux reduction. Fouling can also be viewed as the reduction of the active membrane surface area, which then leads to a reduction in flux to below the membrane capacity before operation [14, 15].

In MF and UF processes, fouling can be high enough to reduce the process flux to less than 5% of the original water flux. Several parameters affect the fouling rate such as the concentration and composition of the water and its foulants, membrane type, module and material, pore-size distribution, surface characteristics [14].

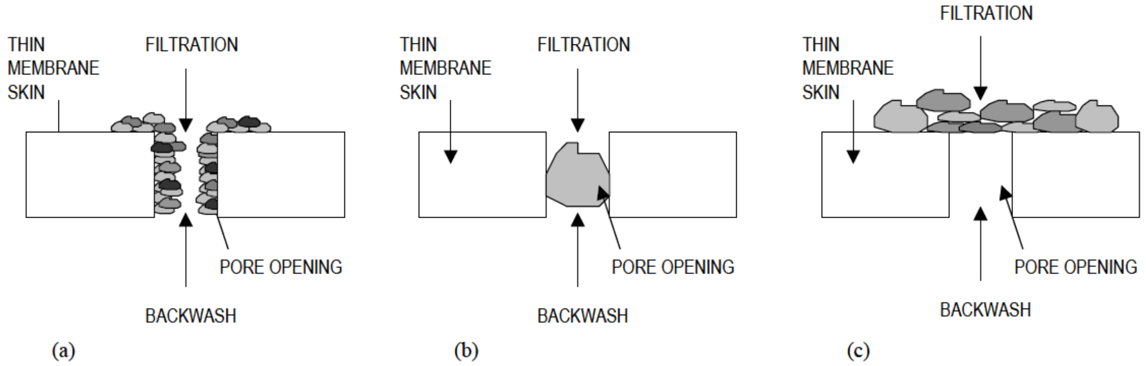

Figure 7- Fouling mechanisms (a) Pore Narrowing, (b) Pore Plugging, and (c) gel/cake formation [15]

Foulants have been categorized into four groups: organic precipitates (macromolecules, biological substances, etc.); colloids; inorganic precipitates (metal hydroxides, calcium salts, etc.) and particulates [14]. Organic fouling occurs when the feed wastewater contains natural organic matter, which causes a gel/cake formation on the membrane surface.[15]

Particles present in the feed cause blockage of the module channels and form a cake layer on the membrane surface. Colloidal particles can create fouling layers and macromolecules cause gel or cake formation on the membrane. Biological fouling can also cause bacteria growth on the membrane surface and excretion of the extracellular polymers. Chemical reactions may also take place on the membrane surface which leads to scaling, concentration increase and pH changes, which lead to precipitation of salts and hydroxides. The major ions that lead to scaling are calcium, magnesium, barium, bicarbonate, and sulphate. [14].

Fouling types and causes vary from location to location and so does the energy and maintenance costs. This means that process optimization for plants should be performed on a plant by plant basis. The only constant is that membrane fouling is the most common reason for process and operation problems, such as reduced flux and salt rejection and increased trans-membrane pressure .Membrane fouling is still the principal limitation of membrane performance. In addition to process optimization, techniques such as pretreatment, chemical cleaning, hydraulic cleaning have been used to reduce or prevent fouling [15].

Membrane Cleaning

The purpose of membrane cleaning is to restore the flux which has decreased due to fouling. The four possible membrane cleaning procedures are chemical, electrical, mechanical and hydraulic cleaning. The main focus of this thesis is chemical cleaning.

Chemical cleaning involves the mass transfer of chemicals to the fouling layer and the reaction products back to the bulk liquid phase, which removes the fouling layer into the solution. Chemical cleaning is conducted in conjunction with maintenance washes while the membrane is online. Clean-in-place (CIP) washes are conducted by adding the chemicals to the feed tank while the membrane is offline.

The cleaning agent should be able to dissolve the foulants, avoid and prevent new fouling as well as not cause any damage to the membrane. The cleaning agent must also be chemically stable during cleaning and easy to rinse away after the cleaning procedure. Safety concerns and costs are also important factors when choosing cleaning agents [16].

There are a variety of different chemicals that may be used for membrane cleaning, and each is targeted to remove a specific form of fouling. Selection of the appropriate cleaning agent is highly dependent on the fouling composition. Inorganic foulants are typically removed by acidic cleaning agents, while organic foulants are removed by surfactants, alkaline cleaning agents, and oxidizing cleaning agents. Chemical cleaning may also use a strong chlorine solution to control biofouling. There are a number of formulated cleaning agents available, such as Ultrasil 10, a mixture of alkalis, phosphates, sequestering agents and wetting agents, which are used in this projects experiment section. Sodium hydroxide can also be used for cleaning of membranes with organic and microbial fouling. The effectiveness of sodium hydroxide as a cleaning agent can be increased by adding sodium hypochlorite, which enlarges the pores of the membrane [17]. Due to the various kinds of foulants present in wastewaters, a combination of different chemicals is added in series to address the multiple types of fouling. Chemical cleaning options are limited for membranes which cannot tolerate oxidants or extreme pH levels [18].

Pretreatments for Membrane Treatment

In cases of industrial water reuse, generally, reverse osmosis (RO) processes are utilized to remove the dissolved ions. The most important goal in RO process design is to minimize membrane fouling, as RO membranes are very sensitive to foulants. As well as selecting a suitable low-fouling membrane, designing a state of the art pretreatment plant considerably reduces fouling [19].

The selection and design of the pretreatment process depend heavily on the feed water characteristics. Different water compositions require different types and extents of pretreatment as to ensure higher membrane efficiency and lifetime[20]. Reverse osmosis membranes are quite sensitive to fouling which typically necessitates an extensive pretreatment process, which may include coagulation, sedimentation, flotation or low-pressure membrane systems such as microfiltration and ultrafiltration[19].

Literature review

Water in pulp and paper industry

Water is a vital component in the pulp and paper industry as it is utilized to transport raw materials, wash and clean process equipment, remove contaminants, and generate the necessary environment for the formation of the hydrogen-bonding network between fibres and fillers, which is the paper formation mechanism [1]. Water is also used in the wire and press sections, pumps as well as cooling and heating purposes [21]. In theory, paper production may require several hundred cubic meters of water per kg of water produced. This number is much lower in practice due to the recirculation and reuse of water [22]. Modern paper machines consume between 5 to 100 m^3 of water for producing each ton of paper, depending on characteristics of the substrate, type of produced paper and the extent of water reuse [23]. High volumes of water are lost in the evaporation step during production, between 0.5 and 2 m^3/ton, which results in an immense freshwater demand [23].

Water consumption is higher in tissue production compared to many other grades like newsprint or fine paper and typically ranges from 8 to 100 m^3/ton [24]. Tissue products have higher standards regarding brightness, texture, and odour, which lead to a higher intake of freshwater. Recycled water can still be used to replace freshwater and be applied for specific purposes, such as dilution waters in pulping and stock preparation, and shower and washing waters in the machine area [23].

As water is a finite environmental resource, conservation and sustainable water resource management are of utmost importance. The current trend in the papermaking industry is toward closed-loop water circuits and reducing the discharge of liquid effluents into the environment. Regulations have been implemented to control the extent of suspended solids, oxygen-consuming wastes, and chemicals toxins released into marine life [15,24]. Harder regulations concerning the acceptable amounts of wastewater and the toxicity of pulp and paper mill effluents have also been imposed in recent years [23]. Water scarcity and extreme weather conditions are other major driving forces for reducing the water footprint, as the decline of water resources is becoming a growing concern in different parts of the world. Economic reasons may also play a role and encourage mills to invest in technologies which reduce water consumption [1]. A high level of water consumption will result in more energy consumption and will also generate more wastewater, requiring more expensive treatment plants [23].

The aforementioned trends have led to a reduction in the freshwater use of in the paper industry and an increase in water reuse recycling. The industry has reduced the water footprint by almost tenfold in the past decades[24]. According to an analysis from Frost & Sullivan, the global market for water and wastewater treatment within the pulp and paper industry will grow from $983.9 million in 2012 to $1.569 billion in 2020 [23]. Several solutions, such as process modification and integration, water recirculation and water recycling have been implemented to decrease freshwater use in the mills [24].

Paper Production

The paper production process follows four prominent process steps. These process steps include pulp production, stock preparation, paper machine, and coating and finishing.

Primary fibres, obtained from wood and annual plants, and secondary fibres, produced from recovered paper are introduced to the pulping process, which may be mechanical or chemical pulping or a combination of the two. Mechanically produced pulps are essentially wood where the bark has been removed. Chemical pulps are composed primarily of cellulose and the less desirable constituents of the wood have been removed by the chemical treatment processes.

Mechanical pulping is the de-fiberisation of timber via mechanical equipment such as grinding stones or rotating disks. The wood and fiber are pretreated with water during the screening operation. Water is also lost in the process in rejects as well as through evaporation. Chemical pulping is commonly performed via the Kraft process due to higher pulp strengths in the product as well as higher chemical recoveries and reduced water pollutions.

The next step is named stock preparation, where various chemicals and pulps are added to the pulp based on the desired characteristics and grade of the finished paper. Sizing agents are introduced to increase the paper resistance to water and fillers, such as calcium carbonate, are added to increase the paper density. The stock is diluted from 4% to 0.5% then cleaned and screened as to eliminate dirt particles [21].

The mixed stock is then pumped by the fan pump to the paper machine, where the slurry of highly diluted fibre suspension is distributed evenly across a moving screen, the wire. The formed sheet is then dewatered mainly under gravitational forces. The formed sheet is then mechanically pressed which further decreases the water content. The paper web then passes a rotating heated iron cylinder where the remaining water content is evaporated. The head-box in the paper machine assures uniform distribution of flow across the paper machine. The fibrous mat is then wound into a reel of paper on the paper machine [26].

For the production of paper requiring high quality and high brightness, as well as a longer shelf life and a superior surface on which to print, a coating layer can be added to the base paper produced on the paper machine [26].

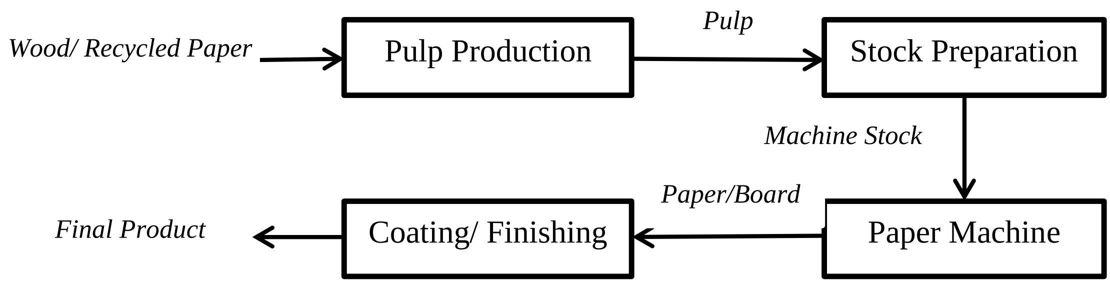

Figure 8- Paper production process steps

Water types used in pulp and paper production

Freshwater

Surface water or groundwater is the prominent source of freshwater, depending on local conditions and availability. The majority of the freshwater is consumed in high- and low-pressure showers, trim squirts, vacuum pumps and additive preparation and dilution. To reduce the freshwater intake, water is reused and recirculated several times. For instance, the freshwater used for cooling in condensers is collected and can be reused as fresh warm water for the paper machine [21].

Approximately 40% of the entire freshwater intake, amounting to 1.0-2.5 m^3 per ton of paper produced, dependent on the degree of water circuit closure, is consumed in the high- and low-pressure showers in the wire and press section. The consumed sealing water in the liquid-ring vacuum pumps is as low as 0.5 m^3 per ton of paper produced, provided the sealing water circuit is installed with a cooling tower. Without a sealing water circuit, the consumption may be as high as 4-5 m^3 per ton of paper produced. Pumps also consume around 0.15 m^3/h of freshwater and 0.2 m^3/h is used in refiners [21].

Generally freshwater does not possess the required water quality composition to be used directly in the paper production process and hence requires treatment. The treatment should effectively remove solids, colour, dissolved solids and organic substances as well as decrease hardness and disinfect the water. The choice of water treatment method depends on the inlet water quality, water volume, and space available. Predominantly mechanical or chemical-mechanical treatment technologies are applied for freshwater treatment. Filtration is by far the most commonly utilized method and is often coupled with other treatment methods such as chemical coagulation, flocculation, and subsequent sedimentation [21].

Process Water

The installation and optimum design of water circuits are of the utmost importance in pulp and paper mills as it directly influences freshwater intake as well as product quality. Using freshwater for every water stream would raise water consumption to 100 m^3 per ton of paper produced. The designed water circuit should provide the required amount and quality of water for every stream. Therefore the water can be recycled and reused several times through different loops. There are various possibilities for water recirculation based on the raw material and the grade of paper produced [21].

Process water is produced in the thickening and dewatering stages of the paper production process by the separation of the liquid phase from solid phase via disk filters, screw and double wire presses and drum thickeners. Membranes and ozone treatment can also be utilized to provide further treatment to achieve better water qualities [21].

Process water has replaced freshwater in some process steps and is now mainly used for pulping, consistency control, showers, foam destruction, sealing water of liquid-ring vacuum pumps, or additive preparation [21].

Wastewater

Wastewater in the pulp and paper industry primarily consists of the excess process water, which can be discharged due to the input of freshwater. The wastewater mainly consists of organics that have been added to the process as additives or raw materials, which are commonly non-toxic and biologically degradable [21].

The wastewater may also consist of inorganics, for instance, salts such as calcium and sulphate, which may cause deposit formation when calcium carbonate is precipitated. The deposits tend to accumulate in the sludge and reduce the active biomass share and will also cause problems if they are recirculated back into production [21].

Sulphate levels in wastewater are another major concern in paper mills, which originate from recovered papers or the aluminium sulphate used for resin sizing. Process waters become increasingly concentrated when attempting to close water loops and sulphate concentrations as high as 600 ppm are to be expected. Moreover, high sulphate concentrations under anoxic conditions, may cause sulphate reduction and lead to sulphide formation. The hydrogen sulphide produced causes corrosion as well as odour problems [21].

Water recirculation

The increasing closure of water circuits has led to a demand for increased waters qualities within the process. The clarified water must be of high quality and free of all suspended solids, especially in cases such as the showers in the high-pressure range and sealing water, where it is to replace freshwater. A wide variety of methods are employed, including biological treatment, softening, membrane technology, and ozonisation. These so-called kidney technologies aim at obtaining effluent-free paper production [21].

Closing the loop and water recirculation leads to the accumulation of unwanted substances known as “detrimental substances”. Detrimental substances are dissolved or colloid-soluble anionic oligomers or polymers and non-ionic hydrocolloids, which can have a negative effect on paper production and on product properties. These substances can have negative effects on the paper drying, drainage, sizing, etc. processes as well as on the products optical and strength properties. The quantity of these contaminants is commonly regulated using a sum parameter named chemical oxygen demand (COD), which measures the volume of oxidizable substances in a water sample. A list of common detrimental substances is presented in Table 2 [21].

Table 2- Composition and origin of detrimental substances[21]

Chemical compound	Origin
Sodium Silicate	Bleaching, de-inking, recovered paper
Polysolphate	Filer dispersing agent
Polyacrylate	Filer dispersing agent
Starch	Coated broke, recovered paper
Humic Acids	Freshwater
Lignin	Pulp
Volatile Fatty Acids	Anaerobic processes
Chloride	Chemical additives
Calcium	Recovered paper, fillers
Sulphides	Anaerobic processes, Sulphate
Exopolymer Saccharides	High C/N ratio

The water quality required for every stream depends on the application. Lower water purities can be applied to less demanding situations. Therefore, water effluents can be purified and recirculated for use in pulp and paper mills [1]. Reducing water usage requires an understanding of where damaging chemicals originate, as well as which streams are critical to the process and how they impact mill operation [24]. Control of microorganisms, appropriate piping and storage, and material selection are needed to keep the surfaces clean and reduce the fouling potential and washing requirements [25].

There are three categories of water circuits within the paper production process: primary, secondary and tertiary water circuits. The primary circuit is by far the largest of the three and consists of white water, which originates from the wire section. The objective is to dilute the main stock flow after the machine chest in the approach flow system to a consistency of approximately 0.7–1.5%. The circulating flow rate depends on the retention of the wire section and the consistency in the head-box [21].

The secondary circuit originates from the forming section or the press section. The stream is then filtered, where the recovered fibres are recirculated to stock preparation. The permeate is then sent to a buffer tank and it can then be used for pulping, consistency control, foam destruction, and showers. The water can be further purified with membrane filtration and be used for more sensitive applications such as sealing waters and high-pressure showers [21].

The tertiary circuit is only installed when a part of the treated wastewater is recirculated. The recirculated wastewater can be applied for miscellaneous applications depending on the water quality attained. Biological and calcium scaling are common operational problems faced when adding a tertiary circuit [21].

The circuit water treatment needs to provide clarified water and reduce the contaminants, such as insoluble and colloidal components as well as dissolved substances, from the water stream. Sedimentation, flotation, and filtration, or a combination of these methods, are typically employed in circuit water treatment [21].

Sedimentation is the simplest most conventional method for fibre recovery; however, the technology has experienced a decrease in market share due to high hydraulic retention times and low density of the sediment. Flotation units use air bubbles to float undissolved substances to the surface of a suspension, where they are scooped off by a skimming device. The flotation devices may experience a sharp variation in inflow loadings which lead to inadequate performance [21].

Biological processes are the state of the art technology in wastewater treatment plants and are suitable for the treatment of biologically degradable substances and sulphates as well as a pretreatment step for nanofiltration and reverse osmosis. Aerobic and anaerobic designs have both proven effective. Thermophilic water treatment has the benefit of eliminating the need for process water cooling and reheating for water recycling [21].

Filtration technologies are currently widely applied in circuit water treatment due to their ability in effectively separating solid particles and producing high-quality clarified water. However, high investment and maintenance costs are limiting factors in the implementation of this technology [21]. Membrane technologies can also be implemented for water reuse and circulation due to its ability to remove suspended solids, microorganisms, colloidal COD and even salts. [21].

Pulp and Paper Wastewater Treatment

Pulp and Paper wastewater characteristics depend significantly on the process stage from which they originate [1]. The chemical composition will also differ in every mill and every day, however, the effluents are usually highly concentrated. Wastewater effluent from Kraft pulp process contains high organic matter concentrations as well as phenolic compounds with high molecular weights and other toxic substances which cause significant damages to aquatic environments, such as a reduction in phytoplankton and fish populations and eutrophication. Typical values for the chemical composition of the paper manufacturing process wastewater are exhibited in Table 3 [23].

Table 3-Typical chemical composition of paper mill wastewater [23]

Chemical	Concentration (mg/l)
COD	480-4450
Chlorides	80-980
Sulphates	240
Phosphates	155-470
Volatile fatty acids	950
Acetic acid	200
Propionic acid	98
Butyric acid	36
Polyphenols	48
Total dissolved solids	395-2500
Cellulose	1200

Wastewater treatment in pulp and paper mills typically involves a pretreatment mechanical treatment for solid removal, followed by a biological treatment step. The treatment plants consist mainly of activated sludge processes or aerated lagoons, which reduce the biochemical oxygen demand (BOD) levels by 90 to 95% and the chemical oxygen demand (COD) by 40 to 60% [27]. Despite the relatively high removal rates, more advanced treatments may be required to enable the water effluent to be reused in the process as the biologically treated water may still contain significant amounts of fibres, micro-organisms, organics, suspended solids and colour [17]. Furthermore, inorganic compounds cannot be effectively removed via biological treatment[28]. Therefore, the water discharge from this process is not sufficiently clean for reuse in the production of higher grade papers but can be used in packaging paper production [17].

Mechanical Pretreatment

The principal methods used for solid separation in wastewater treatment plants in the pulp and paper mills include screening, settling, clarification, and flotation. Screens can be installed to remove coarse, bulky, and fibrous components from the effluents. The choice of method depends on the characteristics of the solid matter and quality requirements on the treated water[21].

Biological Treatment

Biological wastewater treatment utilizes microorganisms to degrade the contaminants dissolved in the wastewater effluent. The treatment is most effective when the contaminants are soluble in water and nontoxic. Both anaerobic and aerobic treatments can be used and multistage processes which operate as aerobic–aerobic or anaerobic-aerobic are far more reliable. Cascade systems, which allow a graduation of the loading conditions, can also be used [21]. The activated sludge formed in the biological reactors undergoes secondary clarification to separation and thickening of the biomass.

Anaerobic treatment uses microorganisms which metabolize only in the absence of oxygen for the treatment of effluents from recovered paper production mills. Anaerobic processes are characterized by their small amount of sludge produced as well as low energy requirements and concurrent biogas production. The biogas can be used as an energy source in the generation process steam, heat, and electricity. Fully biological degradation of the effluents is not yet feasible and water discharges commonly undergo a pretreatment and posttreatment step [21].

Aerobic treatment uses microorganisms which require oxygen for their metabolic activities. Oxygen is introduced to the effluent in the form of air by aeration equipment. The bacteria then use dissolved oxygen to convert organic components into carbon dioxide and biomass. The process efficiency depends on whether there is an adequate amount of nutrients in relation to the amount of biomass, a certain temperature and pH regime, and the absence of toxic substances. Aerobic treatment is characterized by their high sludge production, high energy demands, and larger space requirements. Effluent aeration also increases the plant operating cost. On the other hand, the treatment is stable and effective in degrading biological contaminants and removes 90-98% of BOD [21].

Membrane technology implementation on water circuits

Full circuit closure is not necessarily the optimum choice and the degree of closure relies heavily on both economic and ecological parameters [21]. Despite the aforementioned advantages, closed-loop water circuits may lead to pollutant accumulation in the process water. There exists a breakpoint in the accumulation of contaminants, which limits the closure of the water circuits. Therefore, contaminants must be removed to reduce the adverse complications such as corrosion, clogging of the equipment, scaling and slime formation in the process or the final product [24]. The closed water system also causes risks such as operational problems, reduced product quality, and increased complexity of the papermaking process[29]. These effects can be managed by treatment of a side flow of water via evaporation or membrane filtration [4]. Membrane technology offers the flexibility to remove a wide range of interfering substances from effluent or circulation waters, which enables paper mills to reduce water consumption [22].

Another issue for pressure-driven membrane processes is the concentrate stream. The reject stream often contains an unwanted by-product of water treatment and requires further treatment. The stream may be reused, decontaminated or directly discharged into a water source [9]. Furthermore, streams in pulp and paper mills have large volumetric flows, as high as cubic meters per second. Therefore, the membranes are required to exhibit high permeability and a stable flux[1]. The high capacity of filtration present challenges as to whether membranes are economically feasible [24].

Currently, membrane technology can be implemented in several stages of the papermaking process including fresh water treatment, internal circulation water treatment; coating color treatment and downstream treatment of biological treatment system [22]. Membrane processes can be applied to ensure a high freshwater quality for certain papermaking systems. An ultrafiltration step can be implemented to prevent the intake of solids and colloids from surface waters, and reverse osmosis may be installed when deionized water is required [22]. Ultrafiltration can also be utilized for internal water circulation, and the soil-free permeates can replace freshwater for applications such as spray nozzles and utilities. The internal circulation would reduce the water consumption and maintenance costs substantially since the water would otherwise have to go through an extensive treatment process to be disposed of [22].

Figure 9 exhibits the current most common installation positions of membrane technology in the paper-making process: Fresh water treatment; internal circulation water treatment; treatment of coating colour effluents; wastewater treatment by means of a membrane bioreactor MBR; tertiary wastewater treatment downstream of a biological effluent treatment system (NF or RO) [24].

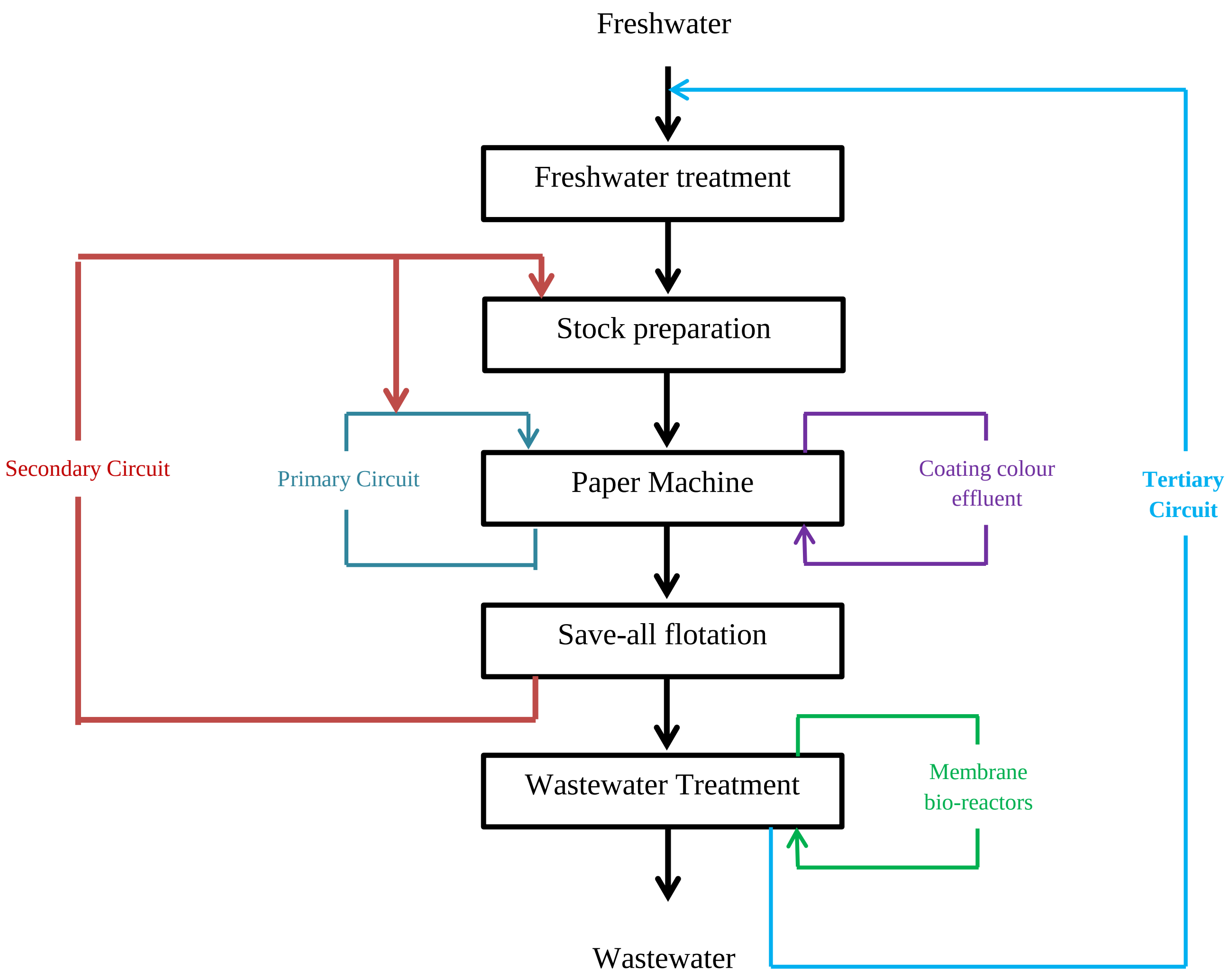

Figure 9- Simplified schematic of water circuits and possible membrane implementation sites

Treatment of membrane retentate

The treatment of the retentate from a membrane process depends on the composition and application. A retentate which contains valuable products, such as colour coatings, can be recirculated back to the production process, and a retentate which is a waste stream needs to be treated before it is discharged to the environment [30]. When the produced concentrate is a waste stream, it can be incinerated or circulated to the wastewater treatment plant. Waste streams can be evaporated to lower the retentate water content, and then incinerated in the boiler. In most cases, where the retentate cannot be reused it is sent to the wastewater treatment plant to be biologically degraded to be discharged to the waterway [30].

Industrial case studies

Membrane technologies with high shear modules, such as tubular modules and conventional spiral-wound modules, have been implemented in several mills to purify and recirculate paper mill water [1]. The first recorded experiments with membranes in the pulp and paper industry involved filtration of white water from the paper machine for reuse purposes and bleach plant effluents for colour removal [30].

The membrane process was first commercialized in 1972 in Wisconsin (USA) where a reverse osmosis system was installed to treat the paper mill circulation water. Mills in Canada and Norway installed plate and frame RO systems in the 1980's, to concentrate sulphite liquor.

LINPAC paper recycling plant is composed of a two-stage tubular UF system and VSEP (Vibratory Shear Enhanced Processing) to annihilate impurities for water reuse. The process was used to treat the overflow for dissolved air flotation (DAF) at an operating pressure of 10.2 atm. A recovery rate of 72% and a concentrated reject with total solids of over 20% was reported [15].

Membrane filtration can also be used to enhance the efficiency of a wastewater treatment plant. For example, the Eltmann newsprint mill in Papierfabrik Palm uses spiral wound NF to improve the quality of activated sludge process effluent. This technology is coupled with a pretreatment step of sand filtration was able to reduce COD levels by 89%[15]. The NF plant permeate is 190 m^3 per hour at a recovery rate of 84% and a flux of 10-30 $L/m^2.h$ [17].

A pulp mill in New Brunswick, Canada implemented a membrane process in lieu of a conventional wastewater treatment plant due to limited space available. A reverse osmosis (RO) plant was installed to purify wastewater streams which would then be recirculated into the beaching process. The process was successful in reducing concentrations of phenols and guaiacols, as well as the compounds responsible for endocrine disruption in fish. A moving bed reactor (MBR) was added in conjunction with the RO plant, as to reduce the BOD levels. The process led to a 40% reduction in water consumption [15].

Four German mills are currently operating with integrated closed circuit water treatment, producing no effluents. This has been achieved via the installation of different process water treatment plants as 'kidneys'. One of these mills is located in Cologne and produces 410,000 tons per year brown packing paper made from recovered paper. An anaerobic water treatment unit is installed followed by two aerobic units in the second stage. COD levels have been decreased by 80% and organic substances (in terms of fatty acids) are reduced in an effective manner [29].

Another recent utilization of the zero-effluent process was implemented in a mill outside Dusseldorf. The decision to close the mill's water system was stimulated by the high effluent fee of 1.50 Euro/m^3 for the use of the town's treatment plant. The limited mill area also limited the addition of an in-house wastewater treatment plant. Membrane technologies were not as advanced at the time and were not implemented. Instead, a process called IC (internal circulation) reactor was developed. The process water is first clarified by micro-flotation and then is fed into a pre-acidification tank after cooling in order to reduce the temperature to 38 ^{o}C. The anaerobic degradation takes place in the IC tower reactor. The biogas generated is then desulphurised in an alkali washer to avoid corrosion and odor problems [29].

Nano-filtration membrane plants have been added to mills to purify the discharge effluent of the biological processes. The wastewater treatment process consisted of settling tanks, a sand filter, a back-washable screen-filter and a 5µm bag filter. The membranes were installed to remove color, organic carbon and dissolved solids. The high efficiency of the treatment plant meant spiral wounds membranes could be utilized despite common challenges with fouling [22].

The Papeterie du Rhin's paper mill in France utilizes a membrane bioreactor with UF membranes to treat their wastewater effluents. The discharge is pretreated with drum screens and then sent to an equalization basin. The process removes 95% of COD and above 99% of BOD levels, and the permeate is partly recycled as process water [30].

The Artic Paper Munkedals uses UF tubular membranes to treat their white water. The water is pretreated with sedimentation to remove the suspended solids. The ultra-filtered water is used in the showers in the wire section [30].

Methodology and Apparatus

The following section will cover how the AlfaLaval M20 device works and the experimental procedure which was designed to test the efficiency of the membrane treatment. Characteristics of the used membranes and water samples are also discussed, as well as the chemical analyses used to determine the water quality.

Device

The Alfa Laval Labstak M20 is a crossflow membrane filtration unit. The device is designed to provide rapid and precise evaluations on a laboratory scale, which are ideal for gathering data for scaling up and process development. This wheeled unit is comprised of a membrane module, high-pressure pump, tank, heat exchanger, valves, gauges, and hydraulic hand pump. A selection of various flat-sheet membranes, ranging from reverse osmosis, nanofiltration, ultrafiltration, and microfiltration can be used within the module. As an option, the unit can be fitted with a spiral element for testing in continuation of preceding flat sheet membrane screening [31].

Figure 10- Alfa Laval M20 Device[32]

The machine encompasses a number of membrane filter sheets, and support and spacer frames, which are compressed into a vertical frame. The plates are circular and are designed to establish a serial connection between the membrane sheets contained in the membrane/plate stack.

The membrane sheets developed by AlfaLaval are polymeric membranes reinforced by a non-woven support material. The membrane sheets are mounted to both sides of a support plate so that the smooth polymeric layer is in contact with the inflowing liquid. The membrane support plate is composed of two perforated halves forming an inside cavity, which allows for the collection of the permeate flow passing through the membrane. The permeate flow is directed towards a tubular outlet pipe located at the plate periphery and can be collected via attachment of a silicone rubber hose.

The spacer plates have a set of radial crossflow channel beads, starting at the centre and ending at a number of holes located adjacent to the plate periphery. When stacked together, the membranes and plates form a series connected crossflow pattern over the membranes through the channel beads and periphery holes.

The device is also attached to a multi-tube heat exchanger fitted with a 0-100 bar pressure gauge, which indicates the inlet crossflow pressure. An adjustable spring-loaded pressure regulator is also attached with a 0-100 bar pressure gauge, which is used for control and measurement of the outlet crossflow pressure. A separate hand-lever operated hydraulic unit with incorporated oil reservoir is also connected to the M20 device which is attached to a pressure gauge.

The device can be fitted with a range of flat sheet membranes for microfiltration, ultrafiltration, nano-filtration and reverse osmosis. The external steel body of the device is composed of AISI Type 304 Stainless Steel and the interior is made of Stainless Steel 316L. The support and spacer plates are made of polysulphone [31].

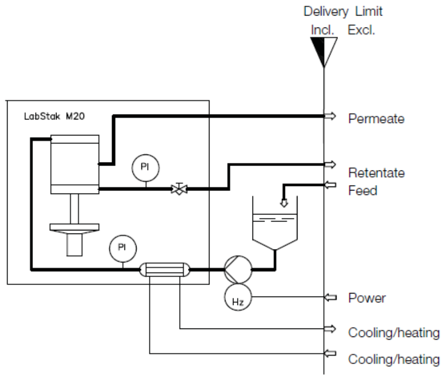

Figure 11- Flowchart of Alfa Laval M20 Device[32]

Membrane Assembly

The membrane sheet has a paper support size on the back and a membrane layer side, which can be identified via light, with the membrane layer side appearing glossy and the paper side as dull. Two membrane sheets are mounted on a support plate with two lock rings. The support plates should be stacked carefully to avoid scratching the membrane layer of the sheet.

Mounting the membranes starts by first putting the spacer plate on the flange. The side with an indentation in centre should always face upwards, and the side with the flat centre should face downwards. Afterwards, the support plate with membrane sheets is placed in the module. The permeate outlet connection should face towards the tank. The next spacer plate is then pressed in the module above the support plate. All the plates should be in parallel and pushed up against the thin metal piece. In theory, up to 20 different membranes can be tested at the same time with the M20 device[31].

Membranes

The membranes used in this project were polymeric flat-sheet membranes from Alfa Laval with various molecular-weights cut-offs (MWCOs) and flux properties. The FS40PP membrane is made of fluoropolymers and has an MWCO value of 100,000. The ETNA01 and ETNA10 membrane are made of composite fluoro-polymer with 1,000 and 10,000 MWCO values, respectively.

The UFX10pHt membrane is characterized by being resistant to high pH values and temperatures and is made of polysulphone. The membrane is also permanently hydrophilic and has an MWCO value of 10,000. A summary of the used micro-filtration and ultra-filtration membranes and their respective properties are exhibited below in Table 4- MF and UF membrane properties:

Table 4- MF and UF membrane properties[32]

Membrane Type	Support Material	Characteristics	MWCO value
FS40PP	Polypropylene	Fluoro Polymer	100,000
UFX10pHt	Polypropylene	Polysulphone Permanently Hydrophilic	10,000
ETNA10PP	Polypropylene	Composite Fluoro Polymer	10,000
ETNA01PP	Polypropylene	Composite Fluoro Polymer	1,000

The flat sheet membranes for reverse osmosis are made of thin-film composite based on a unique construction on either polypropylene (PP) or polyester (PE) support material which provides optimum cleaning conditions. The RO membranes are categorized based on their sodium chloride rejections. The RO90 membrane is cast on a polyester support, with sodium chloride rejections of above 90%. The RO98pHt membrane, which has a sodium chloride rejection of above 98%, is cast on polypropylene support and is tolerant to high pH and temperature [32].

Table 5-Reverse Osmosis membrane properties[32]

Membrane Type	Support Material	Characteristics	Rejection
RO90	Polyester	Thin Film Composite	≥ 90%*
RO98pHt	Polypropylene	Polysophune- Permanently Hydrophilic	≥ 98%*

**Measured on 2000 ppm NaCl at 16 bars and 25 °C*

The recommended operation limits and cleaning procedure of the membranes are summarized in the tables below:

Table 6- Recommended Operation limits for membranes [32]

Membrane Type	**pH Range**	**Operating Pressure (bar)**	**Operating Temperature (ºC)**
FS40PP	1-11	1-10	5-60
UFX10pHt	1-13	1-10	5-75
ETNA10PP	1-11	1-10	5-60
ETNA01PP	1-11	1-10	5-60
RO90	3-10	15-42	5-50
RO98pHt	2-11	15-42	5-60

Table 7- Recommended cleaning parameters for membranes [32]

Membrane Type	**pH Range**	**Operating Pressure (bar)**	**Operating Temperature (ºC)**
FS40PP	1-11.5	1-5	5-65
UFX10pHt	1-13	1-5	5-75
ETNA10PP	1-11.5	1-5	5-65
ETNA01PP	1-11.5	1-5	5-65
RO90	1.5-11.5	1-5	30-50
RO98pHt	1.5-12.5	1-5	30-60

Water Samples

Three points for membrane installation within the process were identified based on meetings and discussions with the Sofidel plant employees. The first sample point is the wastewater effluent discharge. This stream is an accumulation of the process waters recirculated in the process, which has undergone a treatment mechanism, comprised of pre-flocculation, biological treatment, post-flocculation, and flotation. Based on the data from the plant's environmental report, the wastewater flow was an average of 741 m^3/day with an average COD of 359 mg/l in the previous year.

The second sample point is the spray water for the paper machine referred to as "PM3". The stream is the effluent from the spray-water tank which is sent to the scrubber. The water consumption for this paper machine is approximately 600 m^3/day.

The third sample point is the flotation discharge within the paper machine called "PM4". The fibre-rich water stream has undergone a flotation process and is intended to be circulated back to the spray-water tank. Polymers are also introduced to the flotation tank and sludge is discharged. The water consumption for this paper machine is approximately 400 m^3/day.

The water samples were refrigerated at a temperature of 4 ^oC as to limit the biological and chemical reactions which could occur within the wastewater over time. Furthermore, the wastewater never went below freezing temperature. The itinerary of the received wastewater and process water is summarized in Table 8:

Table 8- Water and Process water characteristics (Average)

	Date Arrived	Volume (L)	COD (mg/l)	TOC (mg/l)	SS (mg/l)
Wastewater Effluent Sample 1	25-Jan	50	323	92	16
Wastewater Effluent Sample 2	14-Feb	100	213	65	18
Spray water PM3	21-Mar	50	631	214	6
Spray water PM4	21-Mar	50	739	268	14

Experimental Procedure

Pre-cleaning

The first step after assembling a new membrane is pre-cleaning. The goal of the pre-cleaning procedure is to remove preservatives and chemicals which are left from the membrane preparation, as well as any other contaminants added during assembly. The pre-cleaning usually increases the flux and changes the pore surfaces due to adsorption of the cleaning chemicals, which opens the membrane pores.

The cleaning agent is poured into the feed tank and cleaning takes place under recirculating conditions, meaning that the permeate is circulated back to the feed tank. The cleaning agent, Ultrasil 10, contains sodium hydroxide (NaOH) and Ethylene-di-amine-tetra-acetic acid (EDTA) with a 2:3 ratio. A volume of 25 ml Ultrasil 10 solution was used in every batch, increasing pH levels to almost 11.5

Operating parameters influence the membrane performance during membrane filtration and cleaning. The temperature used for cleaning should be at least moderately high since the solubility of the cleaning agent as well as the organic foulants increases at higher temperatures. The transmembrane pressure during pre-cleaning should be kept as low as possible. Cleaning with high concentrations shortens the membrane lifetime and is also disadvantageous from an economic perspective as it leads to higher costs. All of the aforementioned parameters should be implemented while considering the limitations of the membrane and the cleaning agent.

When the pre-cleaning is finished, the distilled water flux is measured after 30 minutes of recirculation. The distilled water flux measured after pre-cleaning is used as a reference to determine the degree of the membrane fouling and the efficiency of the membrane cleaning.

Membrane Filtration

The wastewater discharge and process waters are filtrated in the Alfa Laval M20 device. The filtration is conducted in recirculation mode, meaning the permeates are circulated back to the feed tank for the two-hour period. Since the feed solution is not altered, the feed quality remains constant. A water sample of approximately 100 ml is taken at the start of the experiment from the feed tank and another sample is taken from the permeate at the end of the filtration period. Since there is a volume of dead water within the system, the wastewater contamination levels may differ slightly from the feed, due to dilution.

The filtration tests were carried out under turbulent conditions with a polymeric MF, UF and RO flat-sheet modules, with a membrane area of 1960 mm^2. Since two membranes were assembled in every experiment, the total surface area is 3920 mm^2. It should be noted that in every experiment four spacer plates were placed below the support plate, as well as four above it.

All MF and UF experiments were conducted at a pressure of approximately 2 bars whilst reverse osmosis experiments were performed under 35 bars of pressure, based on prior experiments conducted with the device at RISE. Flux measurement was conducted every 15 minutes at the same temperature, 15 ºC for MF and UF and 25 ºC for reverse osmosis respectively. This was done to eliminate the effect which pressure and temperature have on flux and so fouling calculations would be reasonable.

Post Cleaning

The final step of the membrane filtration is the post-cleaning process, which is carried out in the same manner as the pre-cleaning. However, in this case, two different cleaning agents, one alkaline and one acidic were used. The alkaline cleaning agent was Ultrasil 10 and the acidic was Nitric Acid. A volume of 25 ml Ultrasil 10 solution and 7g of 35% solution of nitric acid was used in every batch, changing pH levels to almost 11.5 and 2.0, respectively.

Cleaning efficiency

The standard method to calculate the cleaning efficiency is by comparing the pure water flux of a new membrane and that of the same membrane when it has been fouled and then cleaned. The efficiency can be determined via flux recovery, defined as the flux ratio after cleaning and before wastewater treatment. The decline in the distilled water flux after filtration of wastewater and membrane cleaning is an indication of irreversible fouling.

Measurements of the pure water flux can be used to determine the cleaning efficiency, denoted as fouling ratio and flux recovery, defined below.

$$Fouling\ ratio = 1 - \frac{J_f}{J_0}$$

$$Flux\ recovery = \frac{J_c}{J_0}$$

Where J is the measured flux and the subscript *0* is for initial, f for final and c is for after cleaning procedure. A drawback of the method is that the flux measurements are heavily dependent on pressure and temperature. Furthermore, a decrease in flux only suggests that fouling occurs, but does not give any information about the fouling type and how to eliminate it. To avoid the first problem, flux measurements were carried out at the same temperature and pressure so the comparison would be more logical.

A better method to measure fouling would be to measure flux over several filtration and cleaning steps, and then compare the average permeate flux. This measurement was only conducted once, due to the limitation of the amount of the available wastewater [18].

Chemical Analysis

During the experiments, samples of the feed and permeate were withdrawn. The permeate sample was collected at the end of a two-hour filtration process. All the samples were checked for their chemical oxygen demand (COD), total organic carbon (TOC), conductivity and several other relevant parameters. In several experiments, permeate samples were collected during the experiment as well. The wastewater samples were analysed without any pre-filtration. The samples were diluted, when necessary, with distilled water.

COD measurement

Chemical oxygen demand (COD) is an indirect measurement of organic compounds in a wastewater sample. The value is critical in wastewater for determining the amount of waste in the water and is an indicator of how much oxygen will be required to treat the incoming waste streams. COD contrasts with biochemical oxygen demand (BOD), which relies on the use of microorganisms to break down the organic material in the sample by aerobic respiration over the course of a set incubation period (typically five days). In a COD analysis, hazardous wastes of mercury, hexavalent chromium, sulfuric acid, silver, and acids are generated, which require special disposal.

COD measures organic matter with a chemical oxidant which should be strong enough to react with virtually all organic material in the sample. Currently, most COD tests use potassium dichromate as the oxidant, a hexavalent chromium salt which can oxidize 95-100% of the organic material. During the oxidation, the sample is heated with an excess amount of dichromate, which converts organic matter to carbon dioxide and water while dichromate is reduced to Cr^{3+}. The amount of oxygen that is chemically equivalent to the dichromate consumed is defined as the sample COD. A spectrophotometer is used to determine this value. Colorimetric analysis principle states that the two chromium ions absorb in the visible range but at different wavelengths. The dichromate ion is visible at 420nm, and the Cr^{3+} ion around 600 – 620nm. A spectrophotometer sends the correct wavelength through the sample cell to a detector which measures transmittance [33].

TOC measurement

Total organic carbon (TOC) is the organic carbon content in a compound and is often used as an indicator of water quality. The measurement of TOC is a quick online method which is recognized as a suitable alternative method compared to BOD and COD.

The principal behind TOC measurement is that a water sample is acidified to pH= 2-3, to remove the inorganic carbon (as well as CO_2 and ions of carbonic acid). The organic carbon components are then oxidized to form carbon dioxide. The oxidation is typically performed by high-temperature digestion, where all organic matter is incinerated at 650 ^{o}C, supported by a catalyst. The total carbon concentration value is then measured in mg/L via non-dispersive infrared detector (NDIR), where the CO_2 is detected at a specific wavelength. The NDIR generates a non-linear signal, proportional to the CO_2 concentration, which is plotted against the sample analysis time. The peak area is then compared to calibration data of samples with various concentrations. TOC value obtained as the difference between Total Carbon and Total Inorganic Carbon [34].

Conductivity

Conductivity is a measurement of the total concentration of ions in a solution, which determines the capacity the solution has for conducting an electric current. This parameter is a general indicator of water quality and is widely used in various industries, such as process control in food and pharmaceutical industries as well as wastewater treatment.

Conductivity is generally expressed in S/cm (or mS/ cm). The scale for aqueous solutions starts at a conductivity of 0.05 µS/cm at 25 °C for ultrapure water. Tap water or surface water typically has conductivity within the range of 100 - 1000 µS/cm. The conductivity of a solution increases with temperature as temperature affects dissolution and ion mobility. Conductivity is measured using a device called conductivity meter, which applies an electrical field between two electrodes and measures the electrical resistance of the solution.

Turbidity

Turbidity is an optical property of a water sample, which measures the scattering effect that suspended solids have on light. Primary contributors to turbidity include clay, silt, organic and inorganic substances, soluble coloured organic compounds and biological organisms. The measurement is qualitative and cannot be expressed as micrograms per litre of suspended solids. Turbidity is measured in nephelometric turbidity units (NTU) which depend on passing specific light of a specific wavelength through the sample. Visible turbidity is found at levels higher than 5 NTU.

To measure turbidity, a clear index-marked cell with the turbidity standard is rinsed, cleaned, dried. The water sample is then shaken and poured into the sample cell whilst the cell exterior is dried with a lint-free cloth. The turbidity can then be read via the turbid-meter. The instrument is calibrated beforehand within the appropriate measurement range [35].

Pretreatment Methods

Membrane Filtration

The same experimental procedure as the one in the previous section was performed when conducting membrane pretreatment experiments.

Centrifugation

Centrifugation is an energy-intensive process which sediments all suspended solids. The centrifugal acceleration causes the heavier particles to move outward in the radial direction, causing them to settle in the bottom of the tube. The centrifugation is performed at 5000 rpm for a duration of 5 minutes on a lab scale of 200ml at a time. The device used was the CR15 Centrifuge by Braun Biotech International. The water was then decanted and used for membrane filtration.

Flocculation

Flocculation is a widely applied treatment technique in water and wastewater purification. A one-litre sample of the wastewater is placed into a beaker and the flocculant chemical is added during rapid stirring of the sample. After one minute the stirring rate is slowed down to approximate 90 rpm and the sample is flocculated during slow stirring. The flocculation is stopped after 10 minutes and the formed flocs are allowed to settle for one hour. After the sedimentation of the sample, the upper water layer is decanted off and analysed. Two different flocculants, AVR and PAC, were used at different dosing levels to find the optimum scenario, which both decreases contamination levels and produces the least sludge. The results for the preliminary round of the study are in Appendix B.

Results

In this section, the results obtained from the membrane filtration are presented. First, the results for the mill wastewater and then the process water are presented. The results will then be discussed further in the discussion part.

Wastewater

The first round of experiments was carried out on the wastewater effluent of the plant. Various membranes and pretreatment methods were tested to determine the feasibility and up-scalability the process. The ideal scenario would provide sufficient separation; high permeate flux and low or reversible fouling. As previously mentioned, the goal presented for the project would be to achieve water quality sufficient to be re-used as the freshwater intake or be used as process water within the paper production chain.

The experiment was carried out in two steps. In the first step, different UF membranes were compared to determine the most suitable membrane. The optimum conditions were defined with respect to average operating flux, separation efficiency and fouling rate. It should be noted that if the membranes exhibited a high fouling tendency in small-scale flat sheet membranes, the fouling rate would be more severe in large-scale spiral wound modules.

The second round focused on reverse osmosis membranes. Reverse osmosis membranes are extremely prone to fouling; therefore various pretreatment steps were combined with reverse osmosis membranes were utilized to determine the appropriate method. Microfiltration, ultrafiltration, centrifugation, and flocculation were compared as pretreatment steps, prior to the reverse osmosis membrane filtration.

As previously mentioned an ideal scenario would provide efficient separation, high average flux, and low fouling levels. For every round of experiments, three graphs will be presented. The first one, titled fouling and cleaning, will be a column chart which will show permeate flux at four different stages. The first column shows the flux of distilled water after the membrane has gone through the pre-cleaning process, the second column shows the average permeate flux during the two-hour filtration period. The third and fourth columns indicate the flux of distilled water after alkaline and acidic cleaning has been performed. This can be a measure of how irreversible the fouling is on the membrane surface. The second graph will show the permeate flux over the two-hour filtration period and the third graph will be a general scheme of the process and the COD and TOC separation. Removal rates of conductivity, turbidity, and total nitrogen can be found in the Appendix E. In the graphs, technologies used as pretreatment steps are written in parentheses.

UF Experiments

AlfaLaval produces several UF membranes which can be applied in the process. Among the available ones, three different membranes were chosen for this study. The membranes differ based on their molecular weight cut-offs (MWCO), materials and support layers. Table 4 provided a summary of the characteristics of the ultrafiltration membranes.

The pressure difference in all ultrafiltration experiments was measured at 0.6 bars, with a 1.6 bar pressure in the feed and 2.2 bars at the permeate. It can be observed that the ETNA10 membrane displayed the highest measured flux recovery after filtration and chemical cleaning, with a 95% flux recovery, followed by UFX10 and ETNA01 membrane, each with 86 and 43% respectively. Furthermore, the ETNA10 had the highest average wastewater flux during filtration with 86 L/m^2.h, followed by UFX10 and ETNA01, each with 68 and 55 L/m^2.h respectively.

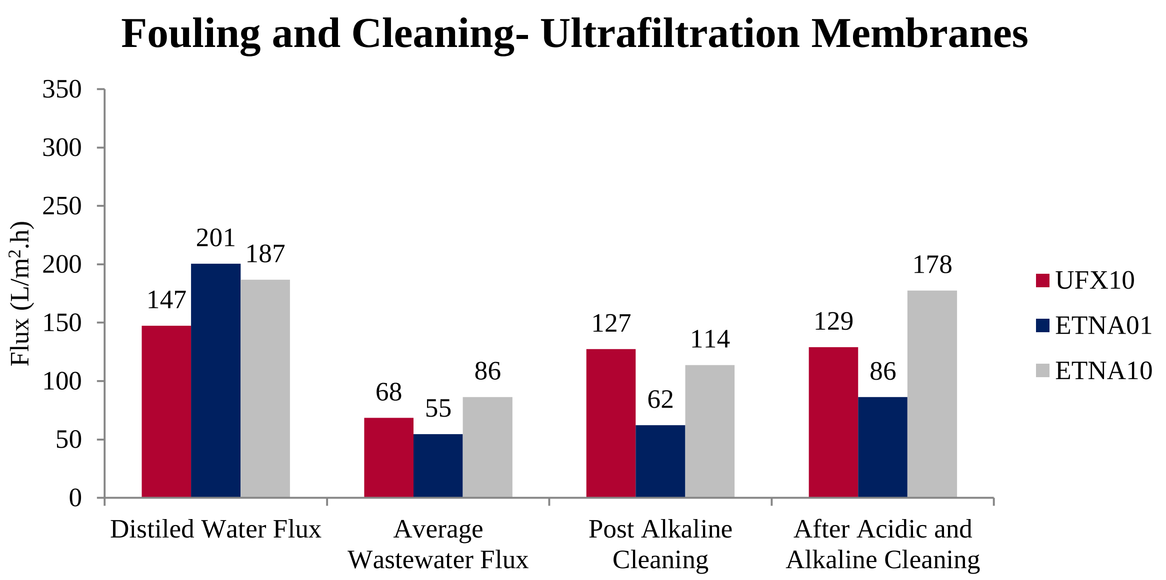

Figure 12- UF membrane Fouling and Cleaning Flux

As expected, all membranes exhibited a decreasing trend within their permeate flux over the filtration period. The UFX10pHt membrane flux stayed practically constant throughout the second hour of wastewater filtration, after a 20% decrease within the first hour. Other membranes had higher flux reduction rates, which is an indication of higher levels of fouling during the filtration.

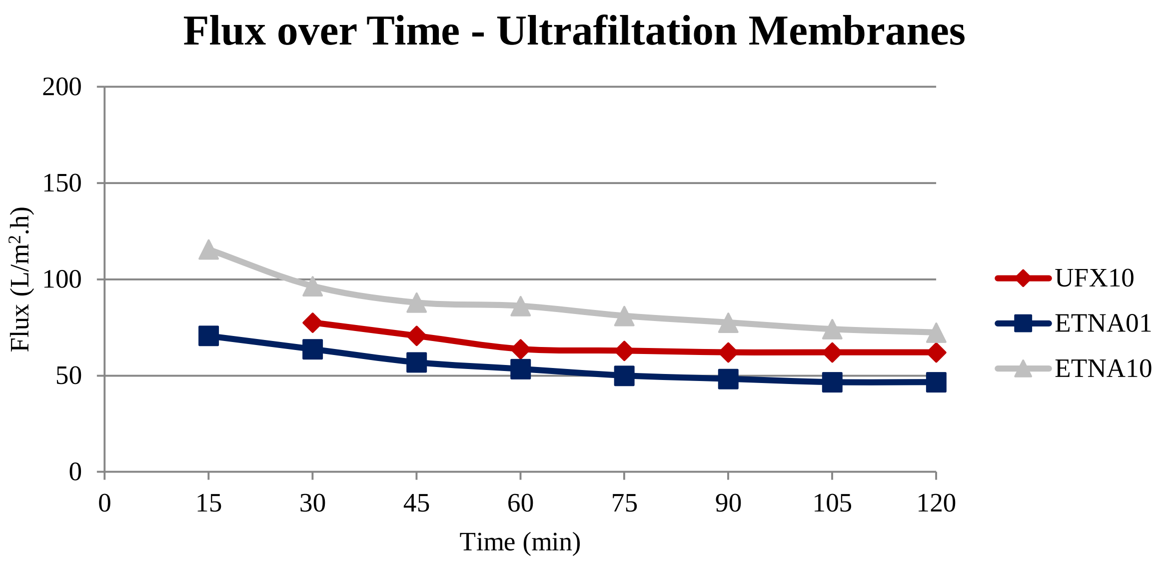

Figure 13- UF permeate flux during filtration

The ETNA01 membrane exhibited the best results in terms of separation, reducing the COD and TOC value by 22 and 26% respectively. This result was expected due to the ETNA01 membranes having the lowest MWCO and therefore smaller pore size, which allow for less contaminant to pass through. Figure 14 summarizes the TOC and COD removal rates of the studied membranes.

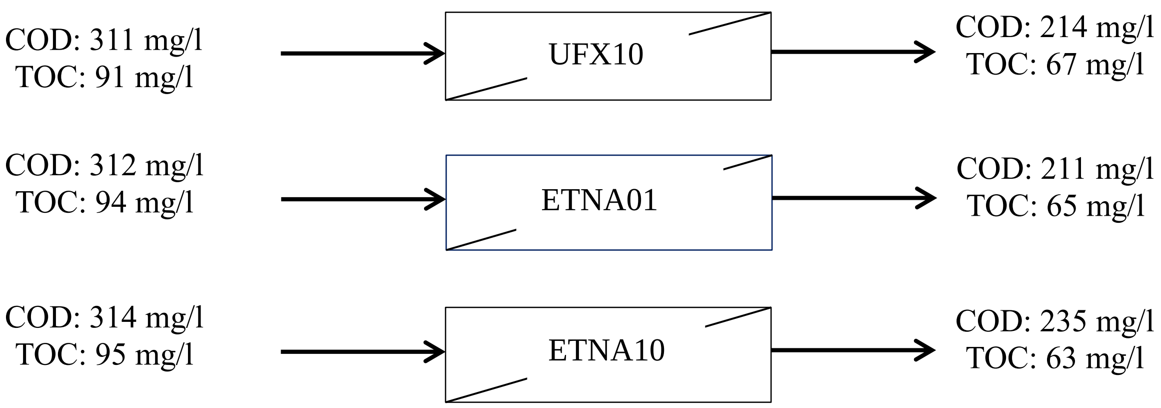

Figure 14- Separation Efficiency for UF membranes

To sum up, the UFX10pHt membrane provided the overall best results with respect to average operating flux, separation efficiency and fouling rate. The low removal rates observed with ETNA10 and high fouling rates of ETNA01 made them inappropriate choices for this wastewater. The data used for comparison of the UF membrane experiments are summarized in Table 9. Therefore, the UFX10pHt membrane was used in the follow-up experiments performed as the most appropriate ultrafiltration membrane.

Table 9- Summary of UF membranes results on wastewater effluent

Characteristic	UFX10pHt	ETNA01	ETNA10
Average Permeate Flux(L/m^2.h)	68	54	86
Flux recovery after cleaning (%)	86	43	95
COD removal (%)	31	32	25
TOC removal (%)	26	30	34

The experiments also concluded that ultrafiltration by itself is not an appropriate separation method, as it does not provide the permeate COD levels required to replace the freshwater intake. Membranes with lower MWCOs such as nano-filtration or reverse osmosis are therefore required to achieve the water quality required.

Pretreatment Methods for Wastewater Effluent

Due to the high fouling tendencies of reverse osmosis membranes, a pretreatment method is required to reduce the fouling rate to keep the membrane lifetime at an acceptable rate. Several methods, including membranes, screens, centrifuges, and flocculation were investigated. The pre-treated water was then filtered via different reverse osmosis membranes under the same operating conditions. An optimum scenario would be one where the pretreatment method is upscaleable whilst simultaneously decreasing fouling rates in the RO membrane. Investment and operating costs, energy usage and separation efficiency are also important factors which need to be taken into consideration.

It should also be noted that the wastewater used for the MF pretreatment was collected at the plant on a different date than the wastewater used in the other experiments. The first batch of wastewater had higher contamination levels, the data has been shown in Table 8. The removal rates have hence been reported as percentages as well as mg/l for better comparison.

Microfiltration pretreatment and reverse osmosis

Microfiltration membranes were applied as a pretreatment step to investigate their performance. The FS40PP membrane was utilized for this purpose due to previous experience and experiments conducted at RISE with the M20 device. The characteristics of the FS40PP membrane were presented in Table 4. A pressure difference of 0.8 bars was observed, with 1.4 bar at the feed and 2.2 bars at the permeate outlet. The water flux reduced from 122 to 69 L/m^2.h after filtration and chemical cleaning was performed on the membrane. This indicates a high fouling rate and also demonstrates that the fouling is irreversible. Furthermore, the acidic cleaning did not have any effect on recovering the flux. Figure 15 displays the flux measurements during the experimental procedure.

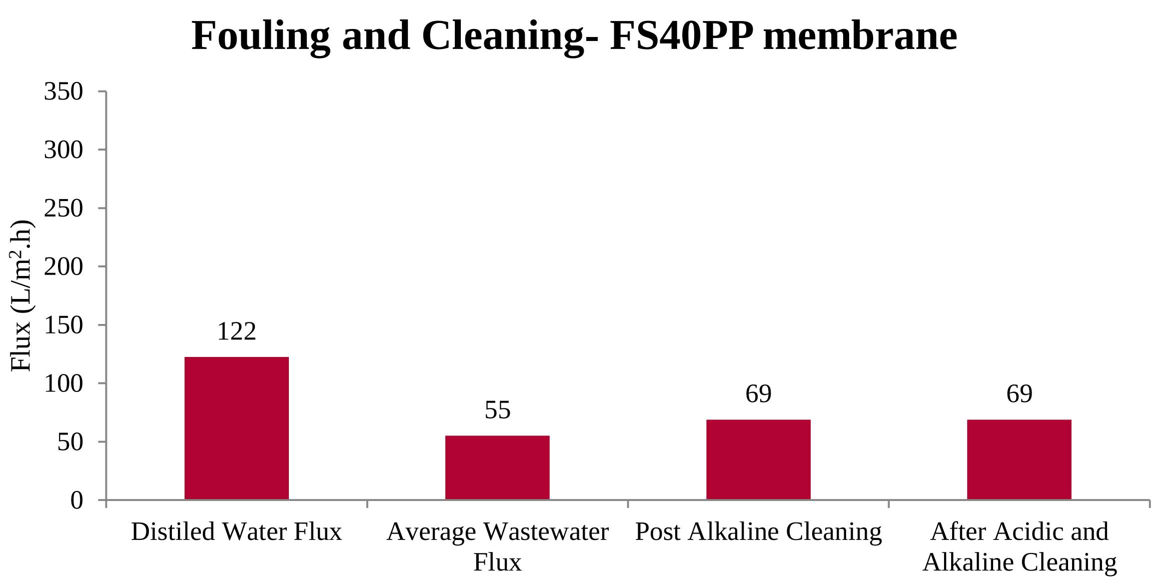

Figure 15- FS40PP membrane Fouling and Cleaning Flux- Wastewater effluent with no pretreatment

To further investigate the fouling conditions in the FS40PP membranes, the used and dried membrane was put under a microscope to examine the pores. As can be seen in the photos, the membrane has experienced irreversible fouling and pore closures.

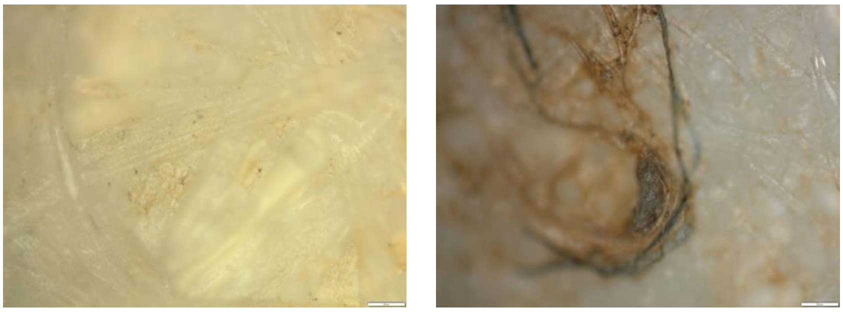

Figure 16- FS40PP membrane after filtration and cleaning

The flux measurement over time exhibits a steadily decreasing trend as expected, however, the flux remains almost constant in the last hour of the experiment. The average permeate flux is 55 L/m^2.h, decreasing from 70 to 50 L/m^2.h during the two-hour filtration period.

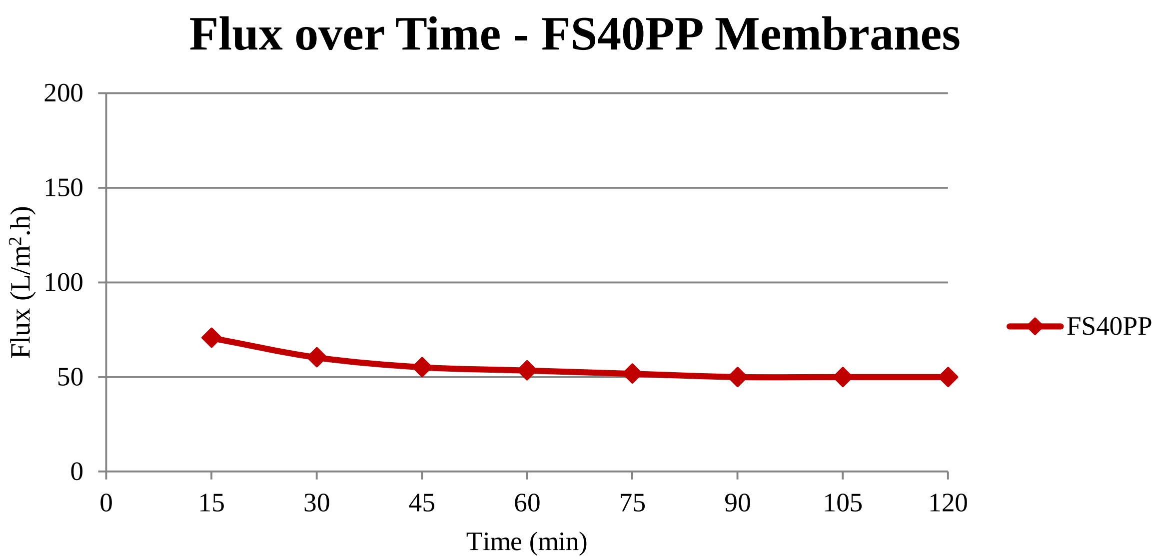

Figure 17- FS40PP membrane - Flux over time - Wastewater effluent with no pretreatment

The membrane is used as a pretreatment step for a reverse osmosis membrane and the separation efficiency is not regarded as the most important factor. Regardless, the membrane decreases COD and TOC levels by 15 and 12% respectively. The most important thing, however, is the decrease of suspended solids to almost zero, which subsequently will reduce fouling in the reverse osmosis membranes in the next step.

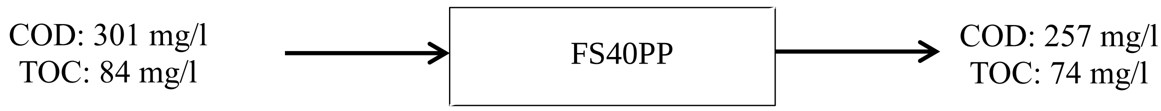

Figure 18- Separation Efficiency for MF pretreatment- Wastewater effluent with no pretreatment

The MF membrane permeate was collected and filtered through the reverse osmosis membrane afterward. Two different RO membranes were studied and their characteristics were exhibited in Table 2. The operating pressure was kept at approximately 35 bars and 25 ^{o}C and all flux measurements were conducted under the same exact conditions.

The RO90 membrane demonstrated more reversible fouling than the RO98 and the original flux was recovered by 77% by the RO90 membrane, compared to 54% in the RO98. Furthermore, acidic cleaning did not have a noteworthy effect on recovering the flux.

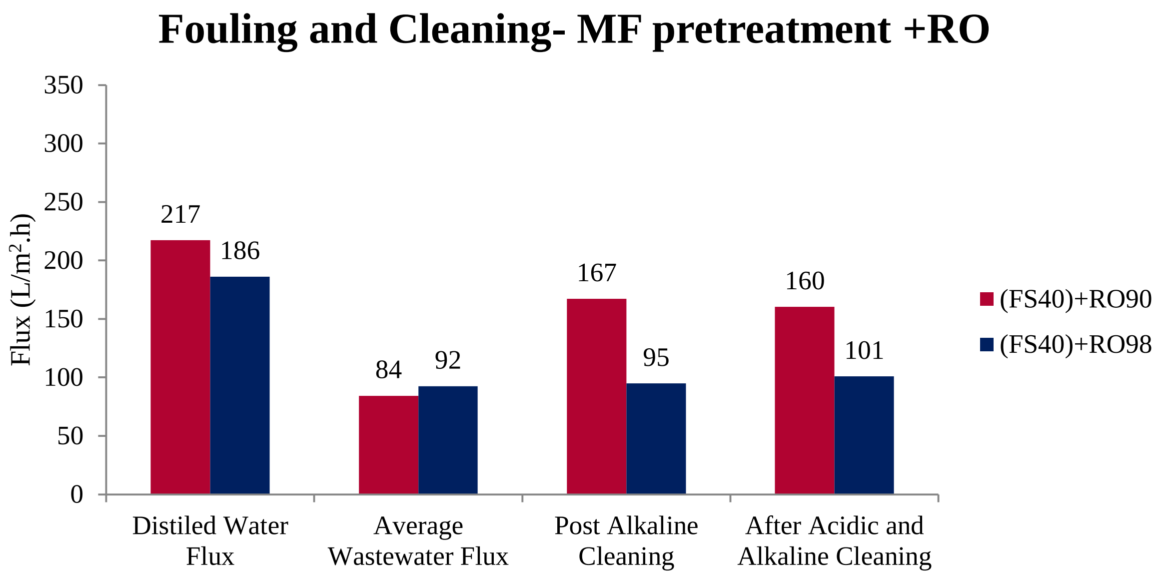

Figure 19- MF pretreatment + RO - Fouling and Cleaning- Wastewater effluent

The RO90 membrane exhibited a decreasing flux over the course of the experiments, decreasing from 129 to 58 L/m^2.h. The RO98 experiences an unexplained sudden flux increase after the first hour but experiences a decreasing trend at all other times. The RO98 had a higher average wastewater flux than the RO90. The permeate flux over time is exhibited in Figure 20.

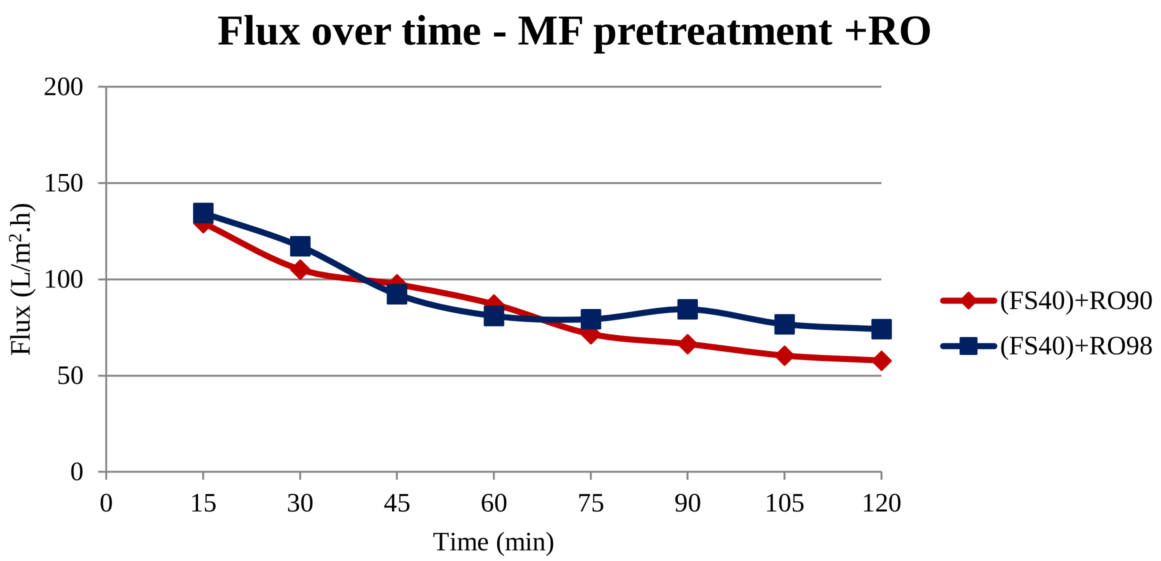

Figure 20-Flux over time - MF pretreatment +RO - Wastewater effluent

The RO90 membrane was far more effective in reducing contamination levels, decreasing both COD and TOC levels by 75%. Whereas the RO98 membrane proved far less effective, decreasing COD and TOC values by 50 and 39 % respectively. Despite the information provided by the manufacturers manual that the RO98 should provide a more efficient separation, this was not the case with this wastewater. The reason for this could be the membrane active-layer polymers, namely the polysulphone, or the hydrophilic nature of the RO98 membrane, which will be explained more in detail in the discussion section.

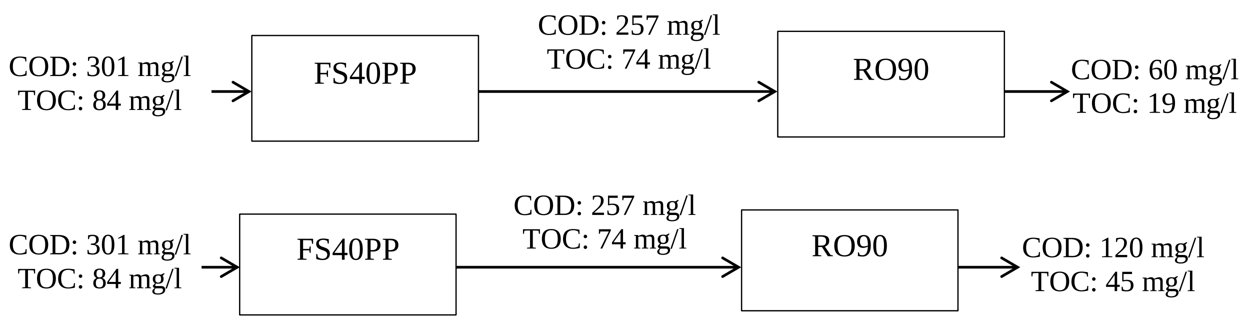

Figure 21- Separation Efficiency for RO membranes with MF pretreatment - Wastewater effluent

Screen and ultrafiltration pretreatment in combination with reverse osmosis

The next pretreatment method used was a combination of a screen and an ultrafiltration membrane. The nylon mesh screen had a pore size of 70 µm and was designed to remove suspended solids. However, when filtering the wastewater through the screen, it was observed that the screen clogged up extremely fast, which would be problematic at higher scales. Further analysis also showed that suspended solid levels had only dropped by half, being reduced from 16 to 8 mg/l. Figure 22 shows the suspended solids clogging up the screen. However, the screen clogging was reversible and the screen could be used for filtration again after physical cleaning using water. Therefore, an additional pretreatment step, ultrafiltration with UFX10, was utilized to further reduce contaminants.

Figure 22- Screen clogging on the Wastewater effluent

Applying the screen before the UFX10 did not seem to have much effect, compared to when the screen was not used, as the same flux recovery was observed as previous experiments. The average wastewater flux did increase, however, which may be an indication of lower fouling levels. Furthermore, the membrane experienced a much lower flux decline during filtration. The screen decreased the COD levels from 229 to 219 mg/l and the UFX10 membrane further decreased them to 169 mg/l. The graphs for the fouling and cleaning, permeate flux over time and separation can be found in Appendix A.

The results demonstrated a similar trend to the previous experiments. As can be seen in Figure 23, the RO90 membrane exhibited higher flux recoveries as opposed to the RO98, with 64 and 47 % respectively. Furthermore, acidic cleaning did not have a noteworthy effect on recovering the flux in neither scenario.

The RO98 membrane displayed higher permeate flux levels than the RO90 but was unable to perform separation efficiently. The RO90 also experienced a lower flux drop within the two-hour filtration period. The results of these experiments are shown in Figure 23 and Figure 24.

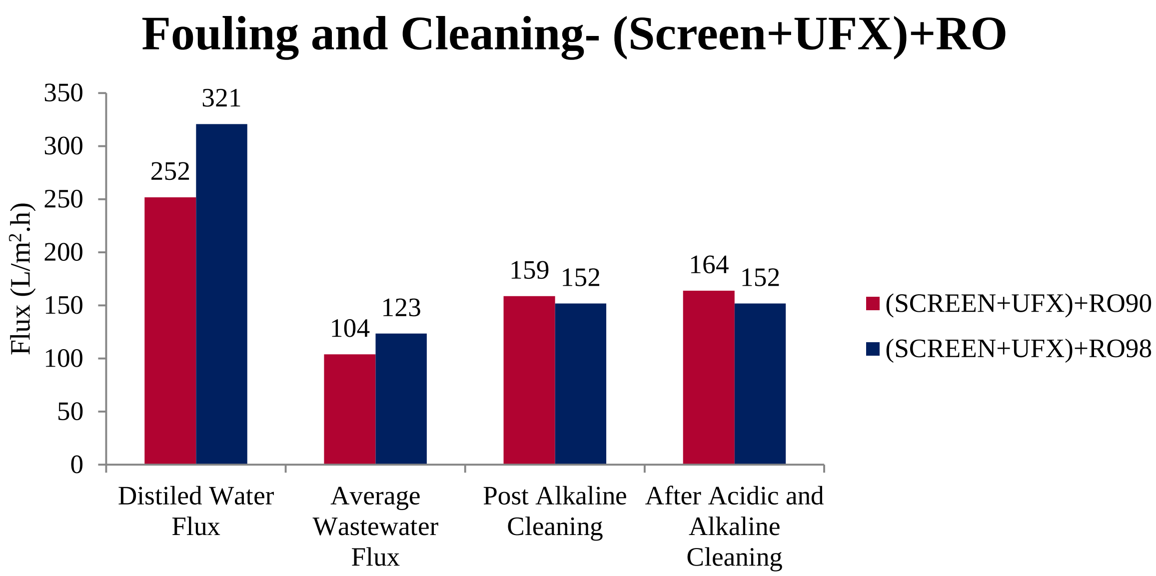

Figure 23- Fouling and Cleaning- (Screen + UFX) +RO90- Wastewater effluent

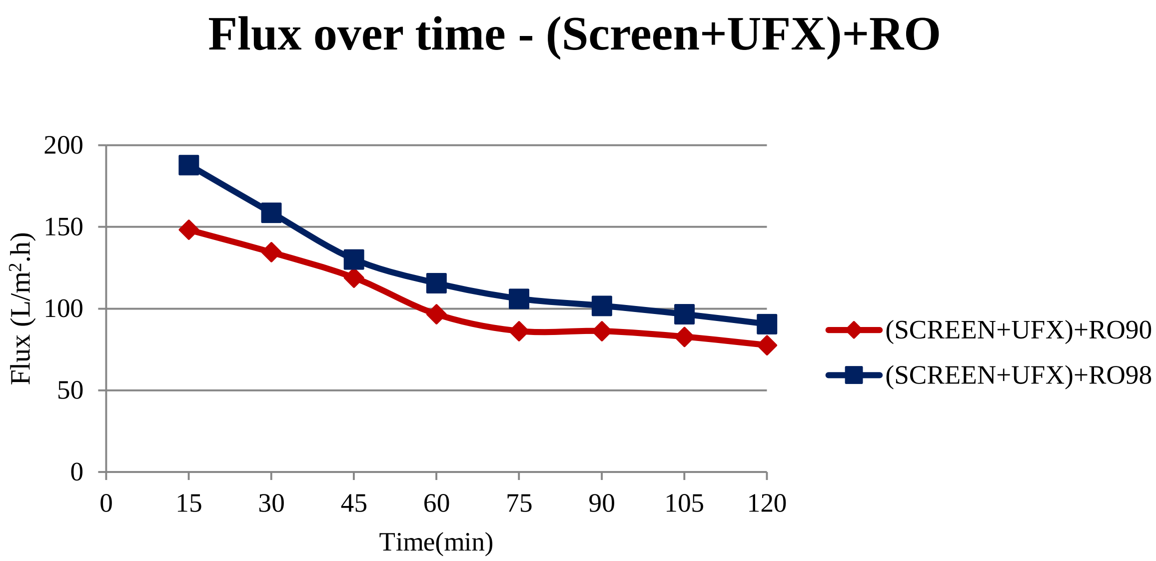

Figure 24- Flux over time Screen and UFX10 pretreatment + Reverse Osmosis membranes- Wastewater effluent

In concurrent with previous results, the RO90 proved to be more efficient in reducing the contamination levels than the RO98. The RO90 membranes decreased COD and TOC levels by 60 and 48 %, whereas the RO98 decreased them by 54 and 46 % respectively.

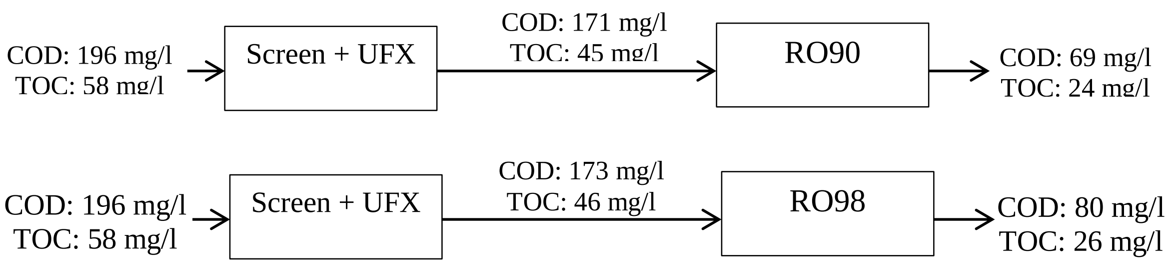

Figure 25-Separation Efficiency for RO membranes with Screen and UF pretreatment- Wastewater effluent

Centrifugation pretreatment and reverse osmosis

Centrifugation was the next pretreatment step that was applied to examine its effects to counter fouling and increase flux recoveries. The contaminants settled as a brown and black sluggish compound. The water was then decanted and the suspended solids appeared to have plummeted down from 16 mg/l to less than 1 mg/l. Figure 26 illustrates the water settling after the centrifugation has taken place. The pretreatment step did not significantly reduce COD and TOC levels, by only 5 and 2 % respectively but removed all suspended solids.

Figure 26- Centrifuged sample

The centrifuged and decanted wastewater was then filtered through both RO membranes to compare flux, fouling, and separation. As previously seen in earlier experiments, the RO90 membrane exhibited better results in terms of separation and flux recovery. Both membranes had a flux recovery of approximately 73 %. The results are summarized in Figure 27.

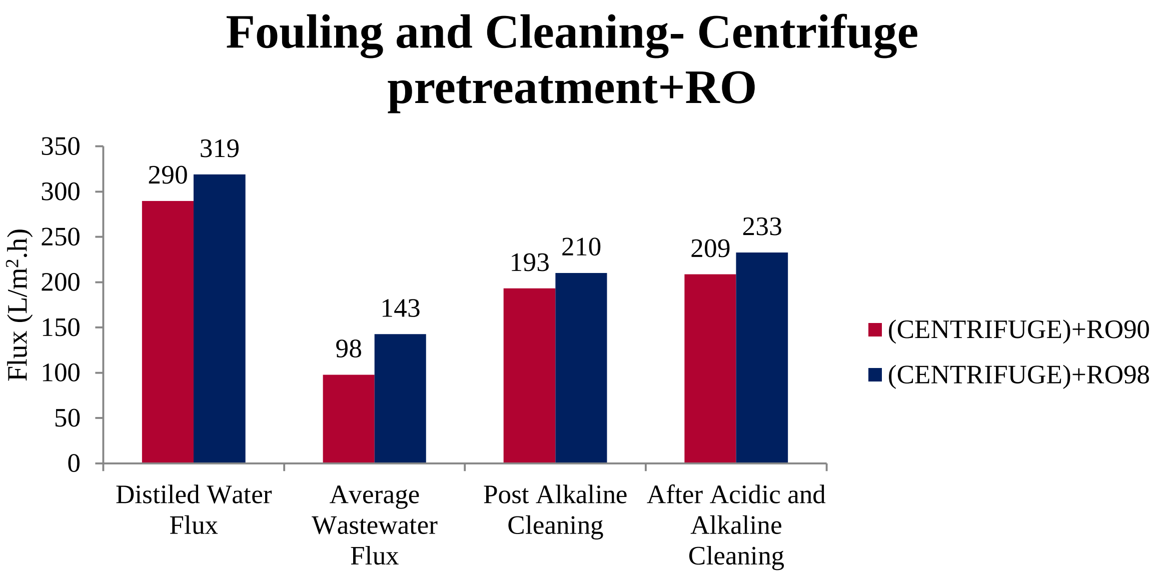

Figure 27- Fouling and Cleaning- Centrifuge pretreatment +RO- Wastewater effluent

Both membranes exhibited a decreasing flux during their experiments, with the RO98 having a much higher average permeate flux than the RO90. The permeate flow versus time is illustrated in Figure 28.

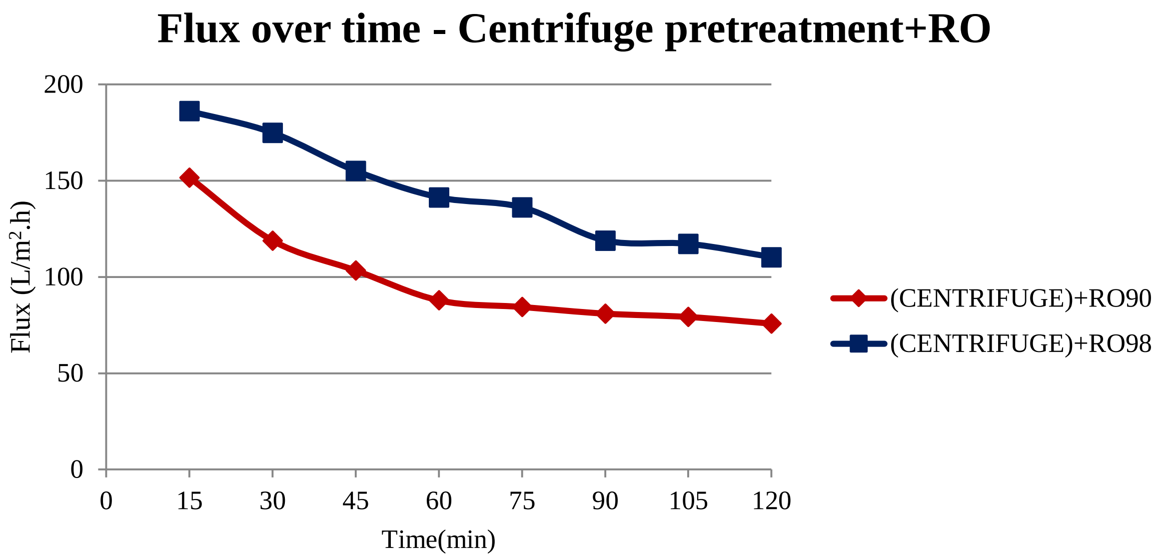

Figure 28-Flux over time - Centrifuge pretreatment + RO- Wastewater effluent

The RO90 exhibits the best results, reducing COD and TOC levels by 74 and 63 % respectively, while the RO98 removes less contamination, reducing the levels only by 45 and 17 %, respectively.

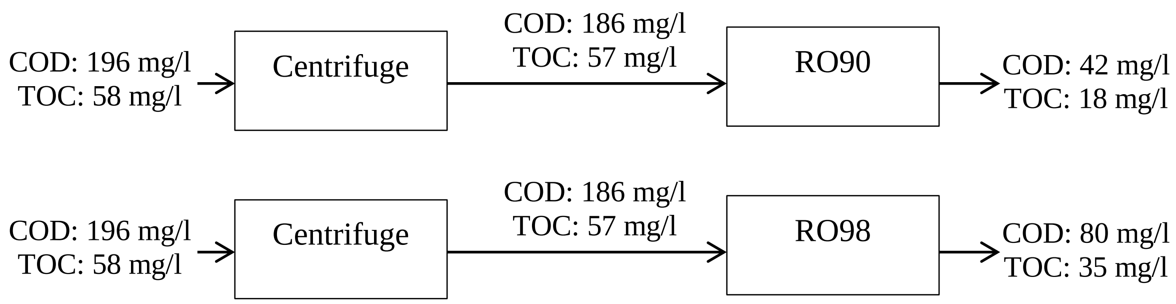

Figure 29-Separation Efficiency for RO membranes with centrifuge pretreatment- Wastewater effluent

Flocculation pretreatment and reverse osmosis

The optimum flocculation for the wastewater was identified was the addition of 0.2 grams AVR per litre of wastewater. The AVR was added in the form of 4 ml of a 50g/l AVR in water solution. The top 75 % of the water content was then decanted and filtrated through the membrane. The pretreatment step reduced the COD and TOC levels to 177 mg/l and 49 mg/l.

The permeate was then filtrated through the RO90 membrane for a two-hour period. A flux recovery rate of 72% after filtration and cleaning was measured, indicating an average fouling ratio. The RO98 membrane was not used for the flocculation experiments, due to the lack of wastewater available as well as its poor performance in previous experiments.

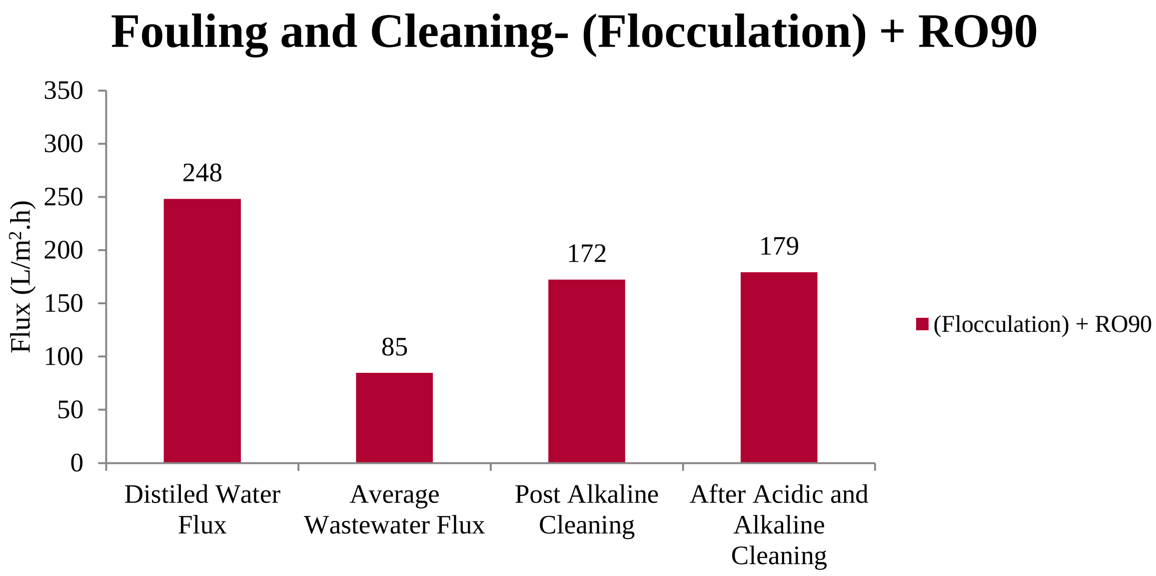

Figure 30-Fouling and Cleaning- (Flocculation) + RO90- Wastewater effluent

During the filtration period, membrane fouling caused the flux to be reduced to approximately half of its starting value, dropping to 63 from 125 $L/m^2.h$. The average permeate flux was measured as 85 $L/m^2.h$.

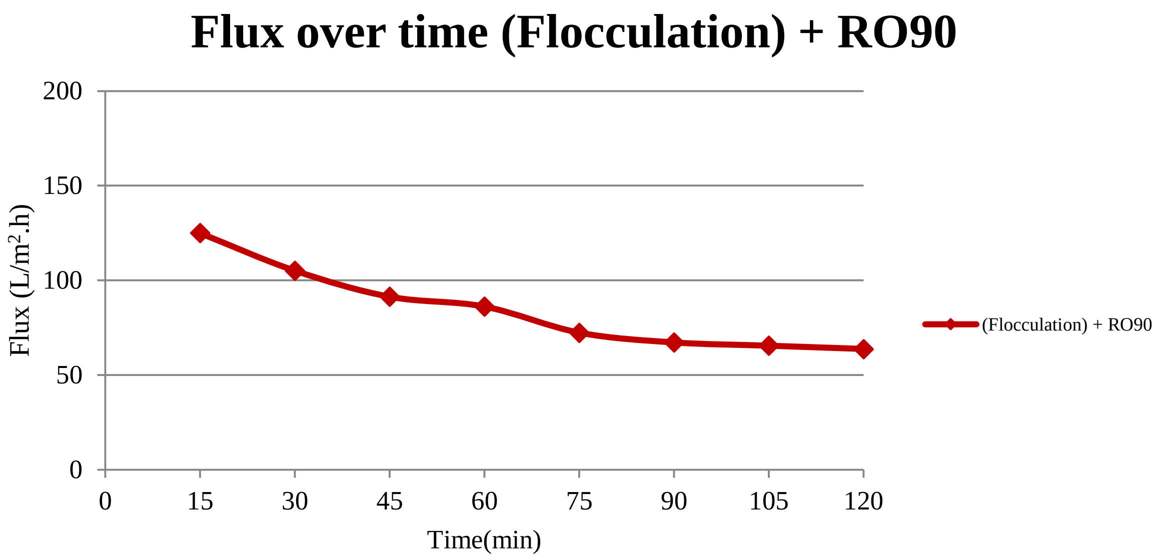

Figure 31- Flux over time (Flocculation) + RO90- Wastewater effluent

The RO90 membrane further decreased the COD and TOC levels by 75 and 64 % respectively.

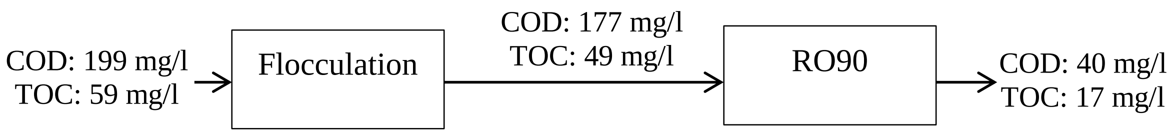

Figure 32-Separation Efficiency for RO membranes with flocculation pretreatment on Wastewater effluent

Spray water PM-3

The process water used as spray-water in the paper machine, called PM-3, was also examined as a possible point for membrane installation in the tissue mill. The stream used is the spray-water tank effluent which is fed to the scrubber, which has had problems in recent years causing the scrubber to be shut down. The water was analysed and filtrated through four different UF and RO membranes with the same experimental procedure as before, except acidic cleaning was not performed. Due to the inefficient results attained from the ETNA01, only the results for UFX, RO90, and RO98 will be reported in this section.

The PM-3 process water contained fibres of various sizes, which may have caused pore clogging and fouling during the filtration. Microscopic pictures of the membrane are provided in Figure 33

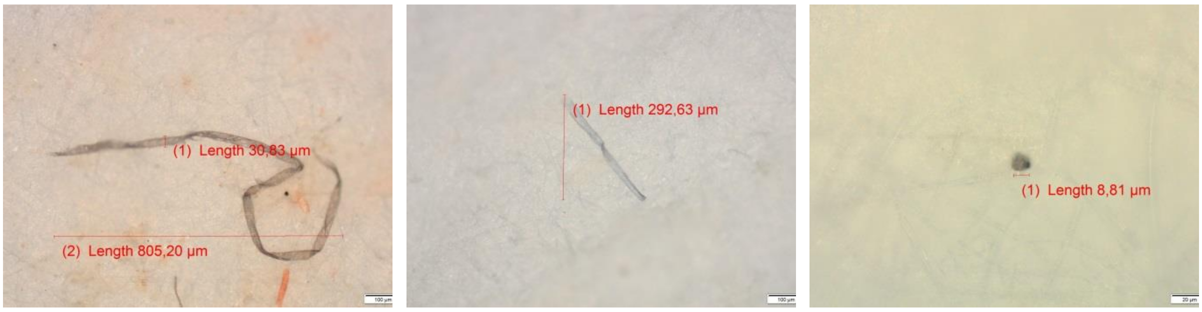

Figure 33- Microscopic pictures of RO90 membranes with Process water PM-3

The UFX10 membrane had the highest flux recovery rate with 89%, followed by RO90 and RO98 with 65 and 60 % respectively, which is concurrent with the results obtained in other experiments. The results for flux measurements are summarized in Figure 34.

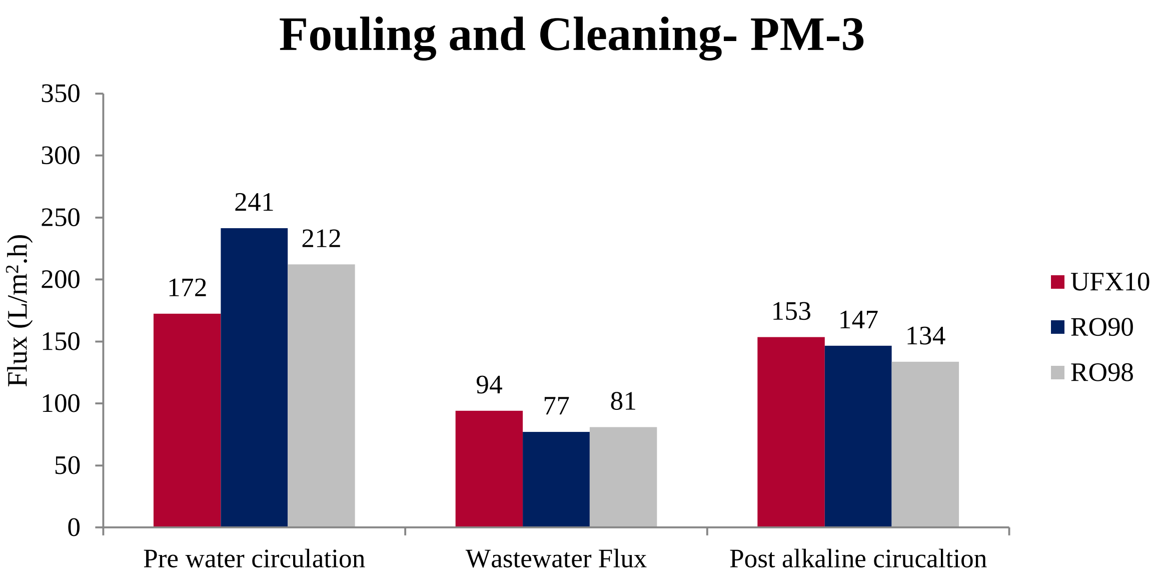

Figure 34- Fouling and Cleaning- PM-3 Process water-

Figure 35 shows the permeate flux over the course of the filtration period. The UFX10 has the highest average flux and the least flux decline over the course of the experiment. The RO98 has a higher average flux than the RO90 but have similar flux declines during the filtration process. It should be noted that flux measurement for the UFX membranes was done at different operating conditions than the reverse osmosis membranes.

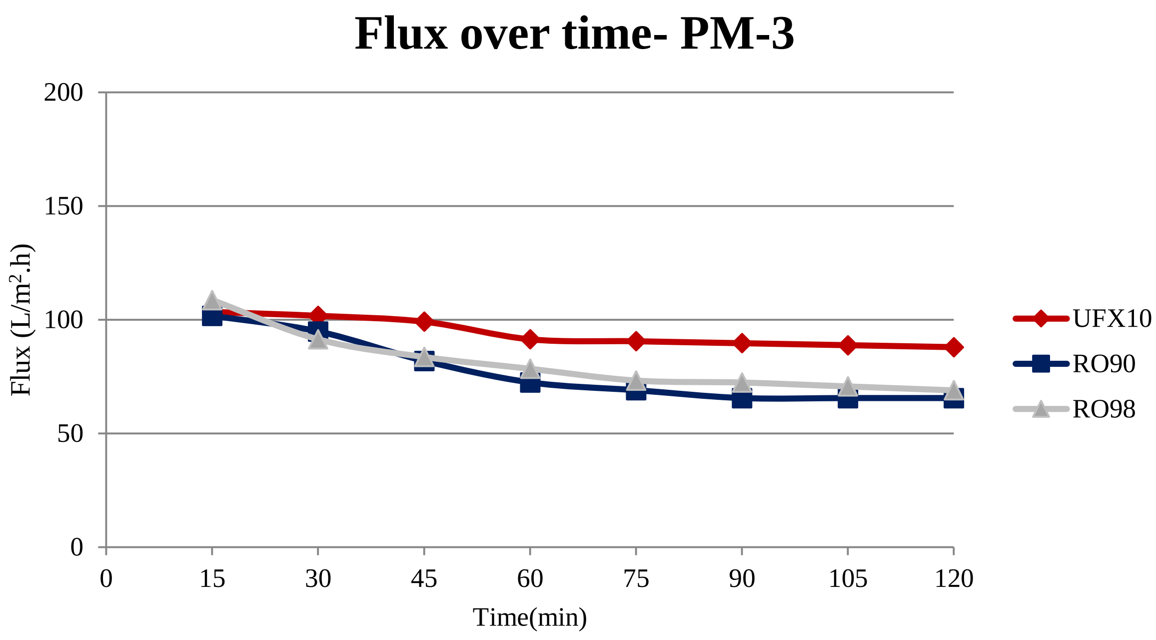

Figure 35- Flux over time- PM-3 Process water

In terms of separation, the RO90 was the most effective membrane with reducing COD and TOC levels by 77 and 75 %, while the RO98 removed 74 and 70 %. As expected, the UFX membrane was not as effective as the osmosis membrane, decreasing the levels by 38 and 41 %, respectively.

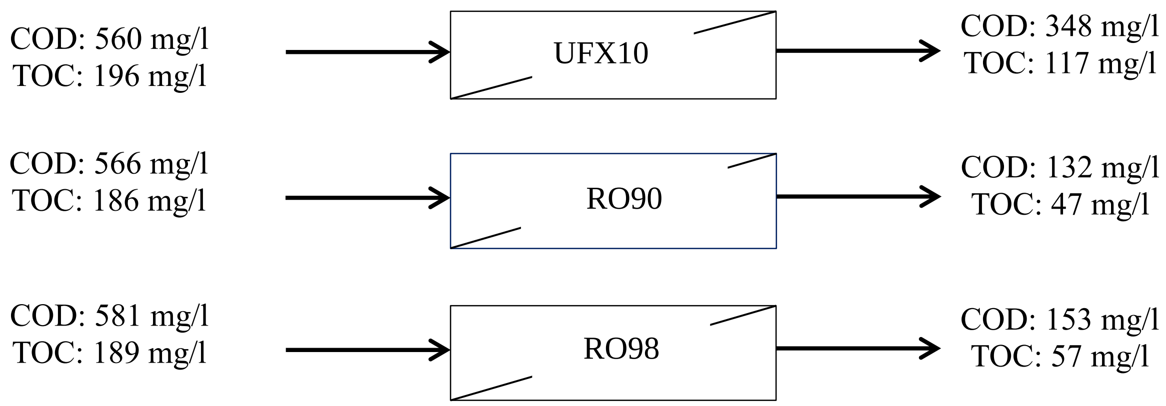

Figure 36- Separation efficiency for membranes with PM-3 process water

Process water PM-4

The next process water stream investigated is related to the paper-machine PM-4. The stream has passed a flotation tank and it will then be fed to the spray-water tank. Polymers are also introduced to the flotation tank and sludge is discharged. The sample water was chemically analysed and filtrated through UF and RO membranes under the same experimental procedure described as before, except acidic cleaning was not performed.

The UFX10 membrane exhibited superior results in terms of flux recovery, with almost 88% while the RO90 showed 60% flux recovery. The values for flux measurements are presented in Figure 37Figure 37- Fouling and Cleaning- PM-4.

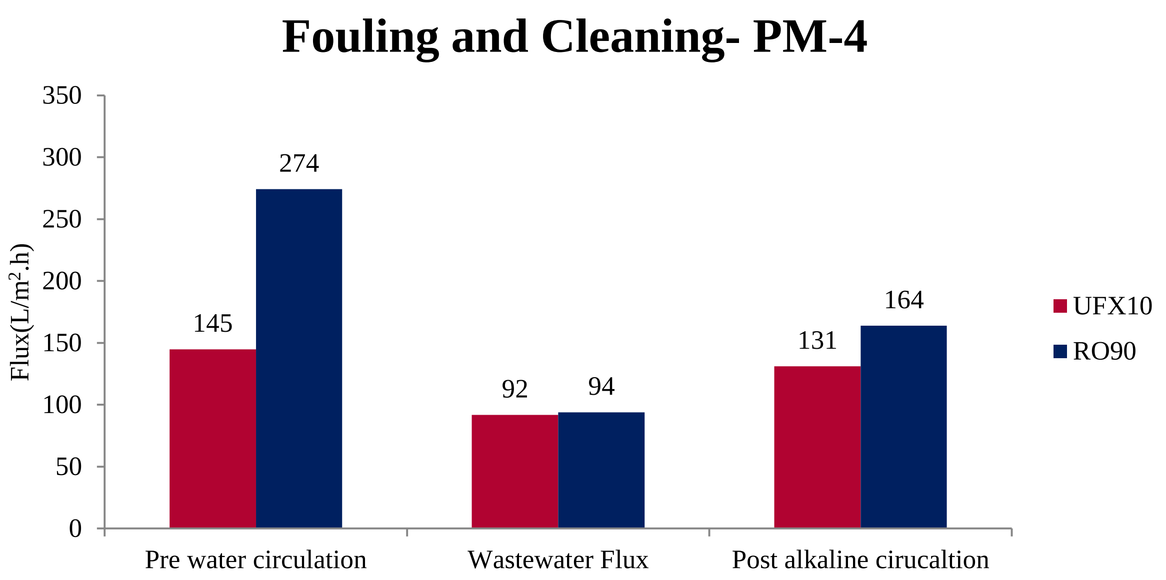

Figure 37- Fouling and Cleaning- PM-4

Figure 38 shows the permeate flux during the two-hour filtration period. Both membranes have a similar average flux over the course of the experiment. The RO90 has a higher flux decline than the UFX10. It should be noted that flux measurement for the UFX membranes was done at different operating conditions than the reverse osmosis membranes.

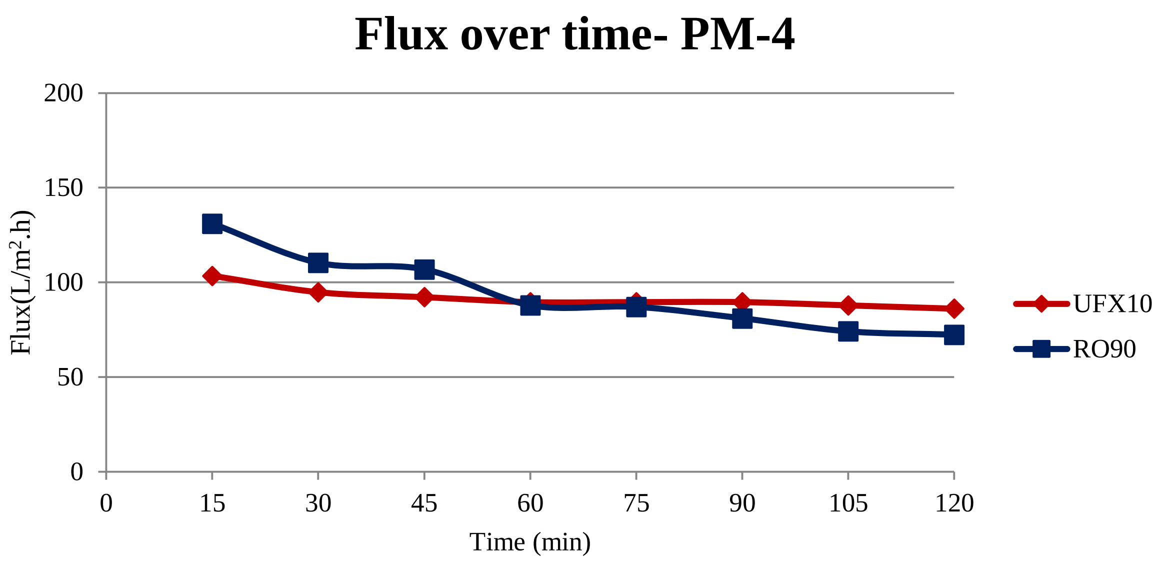

Figure 38- Flux over time- PM-4

The RO90 membrane was able to remove 73 % of the COD, while the UFX could only remove 30 %, respectively.

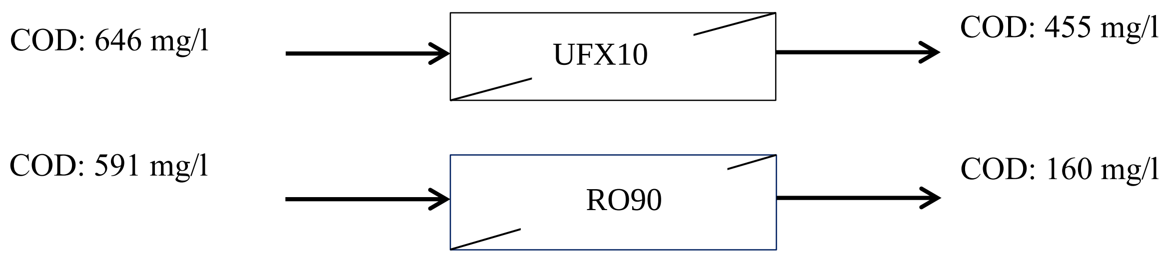

Figure 39- Separation efficiency for membranes with PM-4 process water

Discussion

Tertiary Circuit

In the result section, the data gathered from various pretreatment methods coupled with reverse osmosis filtration data was presented. The goal of the project is to replace a portion of the freshwater intake from the Kisa River with the membrane permeate. According to Sofidel AB, the freshwater intake from the Kisa River has an average COD of 30 mg/l, which was defined as the goal of the project.

Microfiltration, screen, and ultrafiltration, centrifuge and flocculation were performed and compared with each other as pretreatment steps. The pre-treated samples were then filtrated using two different reverse osmosis membranes, RO90 and RO98. A discussion and comparison of the aforementioned technologies are presented below.

Membrane Comparison

Among the reverse osmosis membranes, the RO90 membrane provided much better results in terms of separation than the RO98. This can be attributed to the RO98 membrane's chemical composition, given that the RO98 membrane has a polypropylene support, compared with the polyester support in the RO90. The polypropylene support is by far more durable and resistant towards chemical, pH and a wide range of solvents, but faces problems due to it's the hydrophilic characteristics. The wettability of the propylene surface is low and adhesion does not occur efficiently between the selective and supporting layer. These explanations are based on the fact that the experimental procedure was consistent throughout and all other parameters, such as surface area, temperature, operating pressure and transmembrane pressure were kept constant throughout the process, and no other characteristic dissimilarity was observed [7].

The RO90 membrane exhibited lower fluxes during filtration in all experiments. The results from various other experiments performed in the literature [10, 27, 36, 37] indicate that the polyester supports typically present in thin-film composite (TFC) reverse osmosis membranes do not fully wet when exposed to water, causing a decrease in permeate flux.

The time-interval flux measurements indicated varying degrees of decline in flux levels over the course of the experiment. This can be attributed to the level of fouling within the membrane. The nature of the fouling and whether or not it is irreversible can be determined via comparing the flux of distilled water before the filtration and after the filtration and chemical cleaning step has taken place.

The more precise method to determine fouling levels and their nature would be to compare the average permeate flux during several filtration steps. This was performed once with the RO90 membranes and it was observed that the decline in distilled water flux was much less severe when wastewater samples were filtered (see Appendix C). This was not performed in all cases, however, due to time limitations and cost of transporting wastewater to the laboratory.

Chemical cleaning was performed to decrease the fouling levels and recover the flux as close to the original flux as possible. As previously discussed in the literature review section, mixtures of alkaline substances and surfactants are commonly used to remove biological contaminants, whereas acidic substances are utilized to remove the organic pollutants. The nature of the contaminants in the studied wastewater was identified as biological, which is also apparent in the higher efficiency of the alkaline cleaning step on the membrane flux recovery compared to the acidic cleaning step. A numerical comparison between the membranes based on results from the experiments is presented in Table 10.

Table 10- Comparison of the reverse osmosis membranes for wastewater effluent treatment

	Pretreatment Method	**RO90**	**RO98**
Average Flux (L/m^2.h)	*Microfiltration*	84	92
	Screen and UF	104	123
	Centrifuge	98	143
	Flocculation	85	NA
Flux Recovery (%)	*Microfiltration*	74	54
	Screen and UF	65	47
	Centrifuge	73	73
	Flocculation	72	NA
COD Separation (%)	*Microfiltration*	75	50
	Screen and UF	46	36
	Centrifuge	74	45
	Flocculation	75	NA

Pretreatment Method Comparison

Due to the nature of the reverse osmosis process and the fouling tendencies observed in membranes, a pretreatment step was required to reduce contamination levels, specifically to annihilate the suspended solids. Given that the wastewater effluent had already passed an extensive biological treatment process, the remaining contaminants are troublesome to remove. Various methods were found in literature studies and tested in the laboratory, including membrane filtrations, centrifugation, and flocculation.

The microfiltration membranes proved to exhibit high fouling tendencies when used as a pretreatment step. The fouling can be categorized as irreversible since chemical cleaning was not sufficient in removing contaminants, and a very low flux recovery rate was observed. The high fouling levels observed at laboratory scale question the process's up-scalability. Furthermore, the low average permeate flux in the membrane meant that the process would require a higher investment cost. Despite the disadvantages, the pretreatment provided superior separation compared to other pretreatments. The permeate of the microfiltration membrane also displayed lower fouling and contamination levels when used in the reverse osmosis process.

The screen was also not suitable for removing the suspended solids. As well as the problems mentioned before when upscaling that process, the filtered water was still contaminated. This shows that there are suspended solids within the wastewater which are smaller than 70 µm since that was the mesh pore size. The high variations in the size of the suspended solids may be a reason for the complications. After contact with the mill, it was revealed to us that a company had previously opted to utilize several types of screens to treat the same wastewater at a pilot scale, and had largely been unsuccessful as well.

The ultrafiltration membranes performed better in terms of fouling levels and exhibited much higher flux recoveries. Chemical cleaning steps showed that fouling seemed to be more reversible in nature, increasing the processability of the technology. The average permeate flux was also higher in ultrafiltration compared to microfiltration, as was the contamination separation rate. However, the permeate exhibited lower flux recovery ratios in the reverse osmosis step. These issues can lead to concerns regarding fouling and low membrane lifetime higher scales.

Centrifuges were also applied as a pretreatment step due to their ability in removing suspended solids. The technology is energy intensive in nature and may seem excessive. However, since the designed technology would only be required only at certain points of the year, the solution may be reasonable. The process was performed at lab scale and attaining similar results at higher scales may be in question. The effluent of the centrifuge performed better than other technologies in the reverse osmosis membrane in terms of flux recoveries and separations, also displaying a higher average permeate flux.

Flocculation was another pretreatment step that was utilized due to its availability within the mill as well as its ability to remove suspended solids. The technology is adaptable to various conditions and requires far less operating costs and is easily up-scalable. The effluent performed well, almost as good as the centrifuge, in terms of flux recoveries and contaminant separation.

Table 11- Comparison of various pretreatment methods (Average value for RO90 and RO98 membranes)

		Microfiltration	*Screen and UF*	*Centrifuge*	*Flocculation*
RO90	**Average Flux ($L/m^2.h$)**	88	114	**121**	85
	Flux Recovery (%)	64	56	**73**	72
	COD Separation (%)	63	41	60	**75**
RO98	**Average Flux ($L/m^2.h$)**	92	123	**143**	**-**
	Flux Recovery (%)	54	47	**73**	**-**
	COD Separation (%)	**50**	36	45	**NA**

Primary Circuit

Ultrafiltration and reverse osmosis membranes were used on process waters in the paper machine, without any pretreatment. The goal in this round of experiments was to use membrane filtration as a kidney, to purify water to avoid contamination buildup within the process. The water permeate can then circulated for various applications, such as the scrubber. The retentate from the membrane can also be directed towards the wastewater treatment plant. Given that the mill did not provide any information on what quality requirements are expected, no further discussion can be made on the results. Table 12 summarizes the results from the process water membrane filtration

Table 12- Comparison of the reverse osmosis membranes for wastewater effluent treatment

	Pretreatment Method	UFX10	RO90	RO98
Average Flux (L/m^2.h)	*PM-3*	**94**	77	81
	PM-4	92	**94**	-
Flux Recovery (%)	*PM-3*	**89**	64	63
	PM-4	**90**	60	-
COD Separation (%)	*PM-3*	38	**77**	74
	PM-4	28	**77**	-

Other Experiments

Several follow-up experiments were performed to examine other aspects of the membrane filtration process. An experiment was performed to determine the effect of several rounds of cleaning and wastewater filtration. The experiment showed that despite the high decline in distilled water flux, the average permeate flux did not decrease as drastically. A similar experiment was performed using saltwater, which provided similar results. This proves that the methodology of calculating flux recovery for determining fouling levels may not be entirely valid in reverse osmosis membranes.

Another experiment was performed to see the trend of contaminants in the permeate evolve over time. COD and TOC levels had a decreasing trend over the course of the filtration period. This can be due to the fact that the feed sample has been diluted since a permeate sample has been taken, or can indicate the accumulation of fouling on the membrane surface.

Economic Calculations

Membrane technology offers several advantages over conventional water and wastewater treatment processes including better standards, reduced environmental impact of effluents, reduced land requirements and the potential for mobile treatment units. Despite the merits, the use of membranes is currently limited by the high capital and operating costs with which they are associated. The main components of the cost of membrane treatment are capital cost, membrane replacement, energy usage, labour, cleaning, and maintenance. The capital cost is the sum of membrane units cost and the non-membrane units. The non-membrane cost includes all mechanical and electrical items, control equipment, piping and associated civil engineering costs[38]. This thesis will not cover the non-membrane cost.

The economic calculations will include the fixed capital cost (FCI) and total capital investment (TCI) for the membrane filtration of the incoming wastewater. To determine the FCI and TCI, the purchase cost for all equipment needs to be calculated. All other costs that add to the needed investment are determined by using factors of the purchase cost.

The economic calculations in this section will only cover the cost of membrane purchase and installation and will not cover the pretreatment method. The cost for pumps and %ages applied for different equipment are based on guidelines provided by ÅF. The cost for membrane investment and operating energy required are also based on inquiries made from AlfaLaval Nakskov A/S in Denmark.

To determine the cost of the membrane, the most important defining factor is the surface area required. Based on all the experiments conducted, an average flux was considered for both UF and RO membranes as 138 and 92 L/m^2.h respectively. As previously mentioned, the aim of the project was to reduce freshwater consumption by 100 m^3. The surface area required for the filtration can then be calculated as:

$$UF : 100\ \frac{m^3}{day} * \frac{1\ day}{24\ h} * \frac{m^2.h}{138\ L} * \frac{1000\ L}{1\ m^3} = 30\ m^2$$

$$RO: 100\ \frac{m^3}{day} * \frac{1\ day}{24\ h} * \frac{m^2.h}{92\ L} * \frac{1000\ L}{1\ m^3} = 45\ m^2$$

Due to the technical uncertainties and the fact that the feed will not fully pass the membrane, 30% is added to the required surface area, making it 40 and 60 m^2 for ultrafiltration and reverse osmosis respectively.

Based on contacts and emails with AlfaLaval, prices and energy consumptions for 8.0” spiral wound plug flow plants were estimated, which are summarized in Table 13. It should be noted that the cost refers to DAP (Delivery at point) at AlfaLaval Nakskov and does not include shipping and freight costs.

Table 13- Cost estimations for membranes

Membrane Type	Surface Area (m^2)	Price (kEur)	Energy Consumption (kW/m^3 permeate)
Ultrafiltration	40	195	1-4
Reverse Osmosis	30	250	8-12

Conclusion

The aim of this study was to discuss the technical feasibility when using membranes to reduce the water consumption within a tissue mill in Kisa. The main focus of the experiment was on filtering and recirculating the wastewater effluent to replace part of the freshwater intake. Additional experiments were also performed on process waters in the tissue-production process.

The experiments showed that a pretreatment step coupled with reverse osmosis could be used for the tertiary water circuit. The high water flux and shear rates require a membrane module that can embody high surface areas, therefore a spiral wound module should be utilized. Spiral wound modules are more prone to fouling, which means the pretreatment technique has to work efficiently in reducing contaminants which may cause fouling.

Several different pretreatment steps and different reverse osmosis membranes were tested on a lab-scale. It was concluded that centrifugation, flocculation, and membrane pretreatment are all feasible scenarios, each with their own merits and faults, which have examined in the discussion section. Flocculation can be assumed as the most appropriate method, given the better performance.

The RO90 membrane proved far more efficient than other membranes, both in terms of separation and flux recovery, but experienced a lower average flux. This can be attributed to the polyester support on TFC, and its respective properties such as low wettability. UFX10 and RO98 did not provide sufficient separation and RO98 also exhibited high fouling levels The cleaning procedure was typically comprised of both alkaline and acidic cleaning. The flux recoveries were used to compare the fouling levels. The alkaline cleaning step was also far more effective, indicating the wastewater contaminants are biological in nature.

The experiments also showed that ultrafiltration and reverse osmosis can be used as kidneys for the paper machine, depending on what quality of water is needed for which specific application.

Future Work

- Further experiments are required to determine the optimum operating conditions of the membranes used in the project.
- The author would recommend using more variety of different process waters, namely the effluent of the flocculation tank.
- Additional experiments need to be conducted to determine the optimum cleaning process and operation.
- To determine long-term effects of fouling, longer trials with cleaning steps in between are required.
- The use of the system as a continuous device, as opposed to the batch recirculation mode in these experiments.

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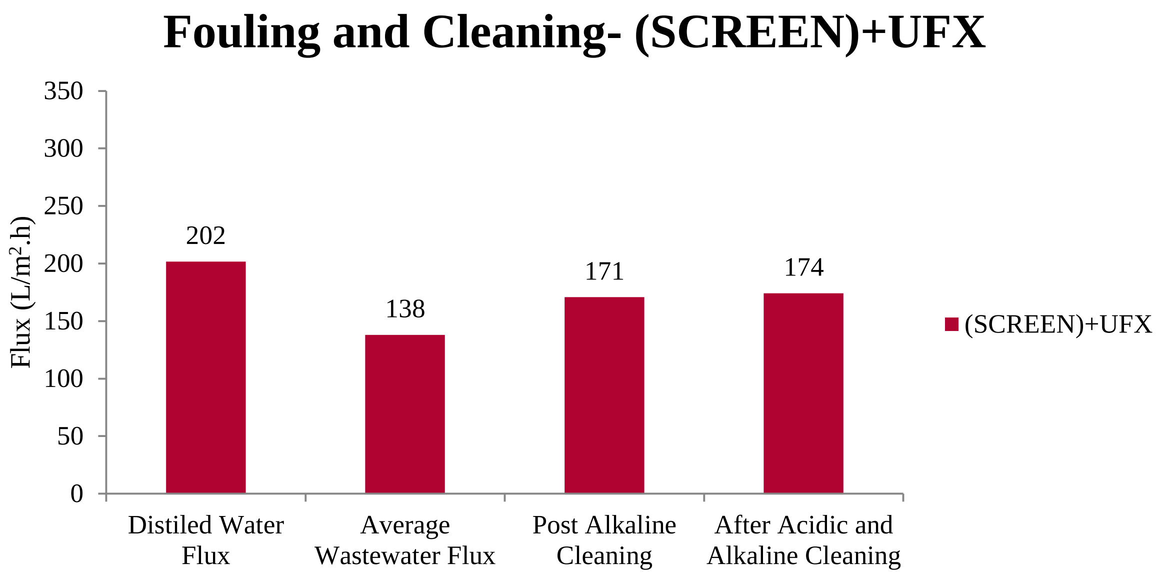
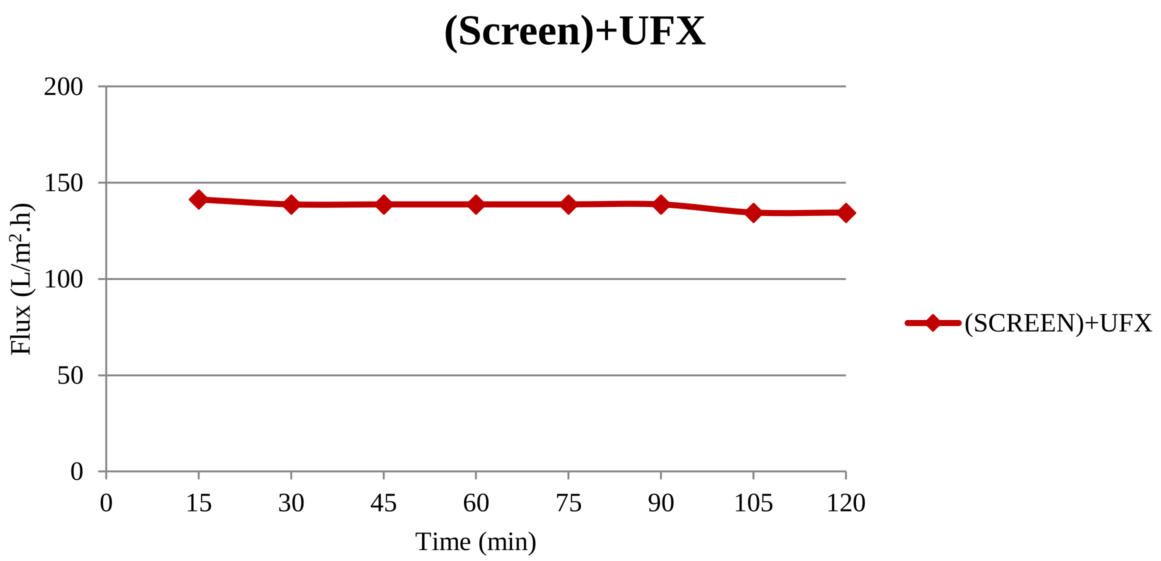
Appendix A - Screen and UFX Pretreatment

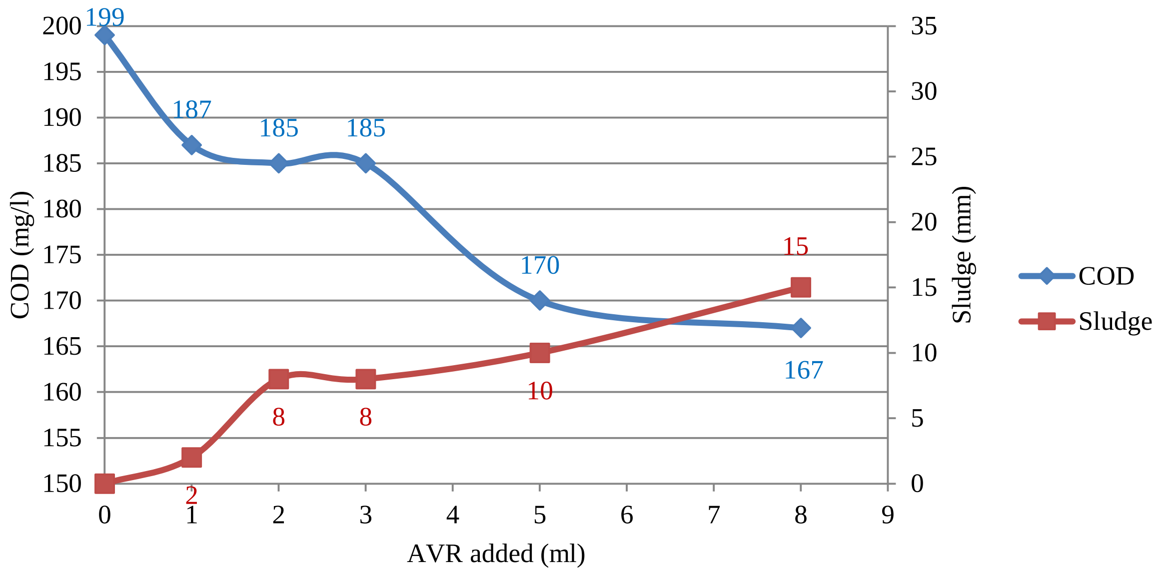
The graphs for the fouling, cleaning and permeate flux over time for the screen and UFX pretreatment method are exhibited below. It should be noted that the screen decreased the COD levels from 229 to 219 mg/l

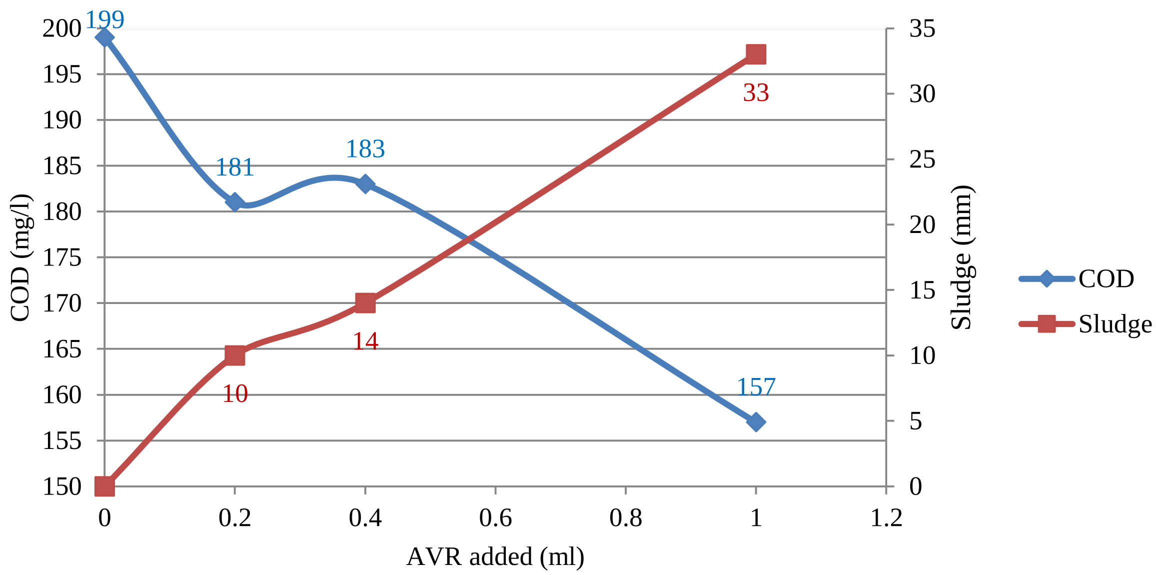




Appendix B- Flocculation experiments

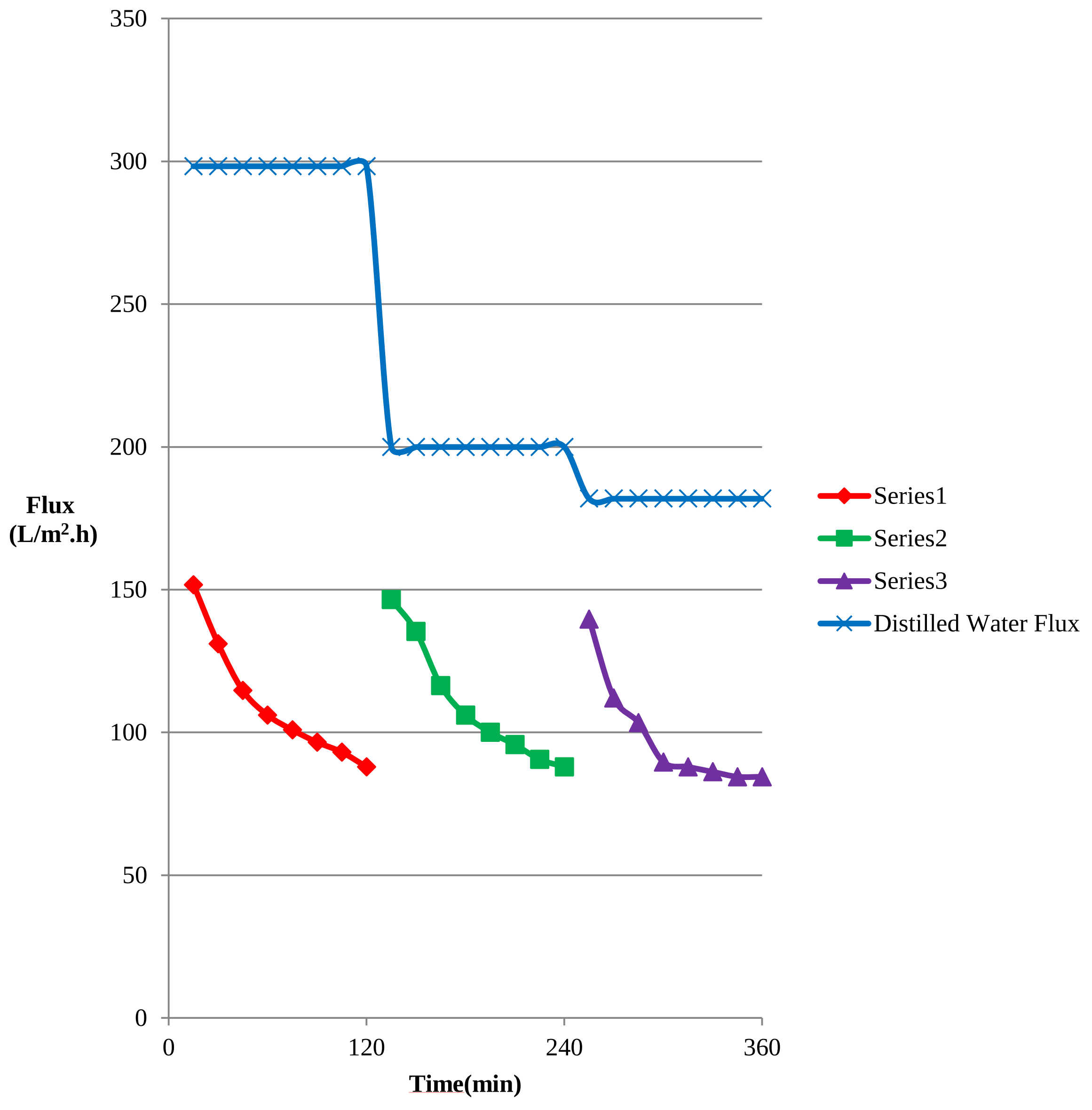
Below is the of the top 3/4th of the flocculated water decanted, when varying amounts of AVR and PAC addition, as well as the amount of sludge produced in the beaker. It should be noted that an optimum scenario would provide sufficient COD removal as well as low sludge production. The optimum scenario was picked as adding 4 ml of AVR for every litre of the process water.





Appendix C - Repeated Experiments

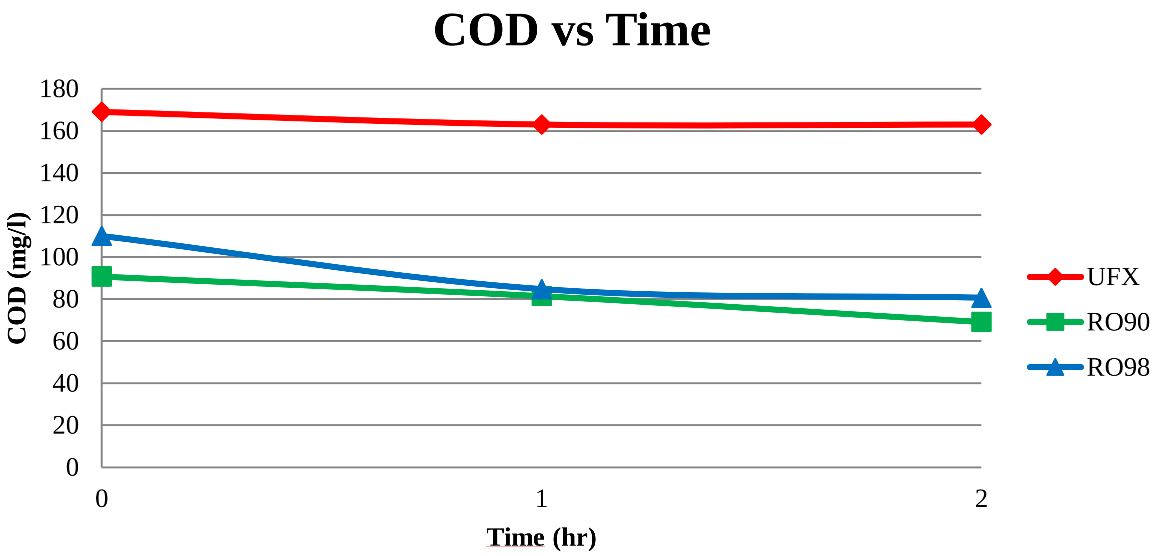
On one occasion, three rounds of filtration were performed as to determine the flux recovery and the average permeate flux decline. It was revealed that despite the high decline in distilled water flux, the average permeate flux did not decrease as drastically. The average flux was 128, 127 and 124 L/m^2.h in the three sets of experiments, while the water flux decreased from 348 to 211 and 183 L/m^2.h. This experiment was only performed once due to limitations in both time and available samples. The permeate flux is plotted during the three rounds of filtration in the below figure, as well as the distilled water flux. The sample used was already filtrated via a microfiltration membrane beforehand.



Appendix D- COD over time

On some experiments, the COD of the permeate was measured three times during the filtration as to see the effect of fouling. One sample was taken at the beginning of the experiment, one after an hour had passed and one at the end of the two-hour filtration period. In all membranes, the COD had a decreasing trend over the course of the experiments. As it can be observed the UFX membrane experienced the least decline, and it also experienced the least fouling and highest flux recovery.

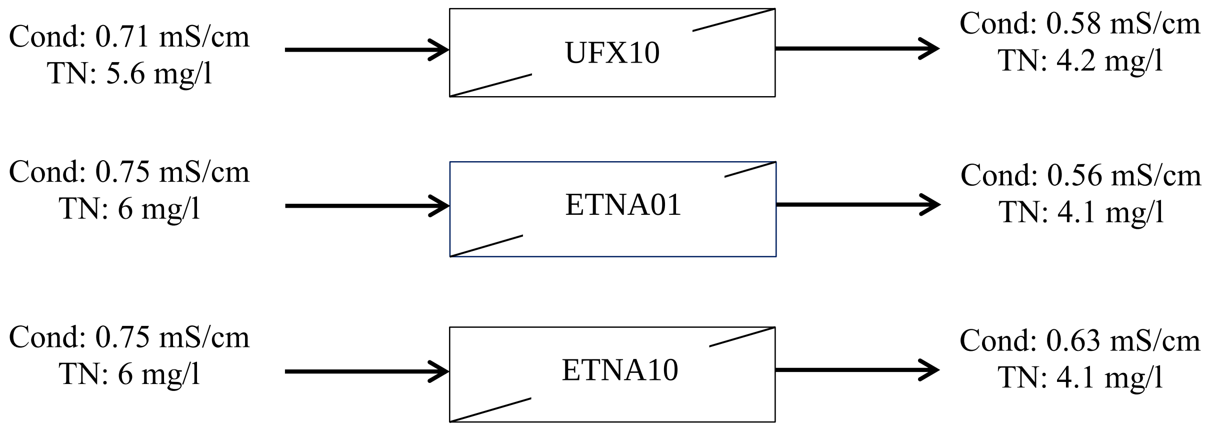
The samples used were during the Screen and Ultrafiltration pretreatment step.



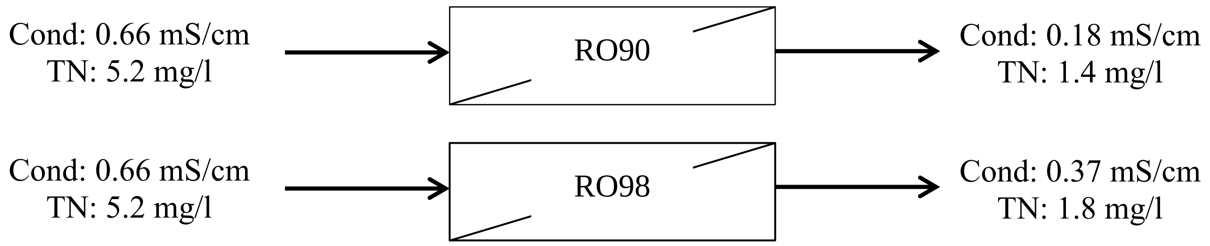
Appendix E- Conductivity and Total Nitrogen measurements

The conductivity and TN measurements for some experiments are presented below:

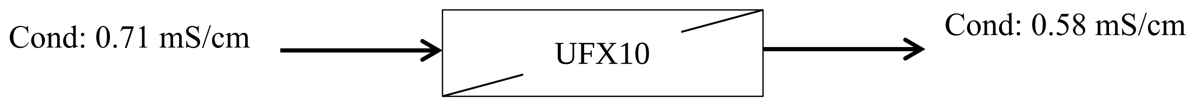
UF Experiments



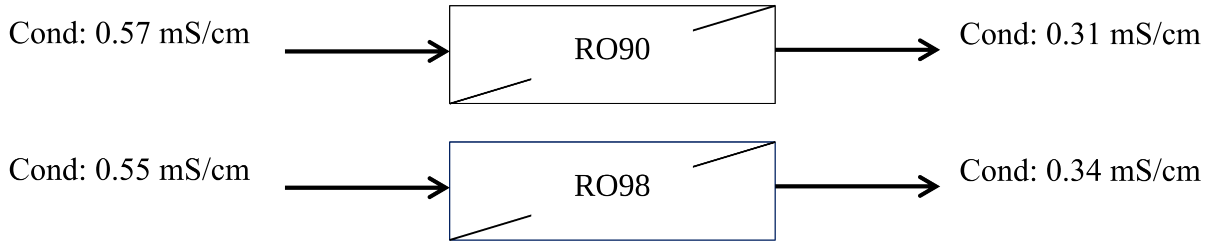
(MF)+ RO Experiments



(Screen) + UF

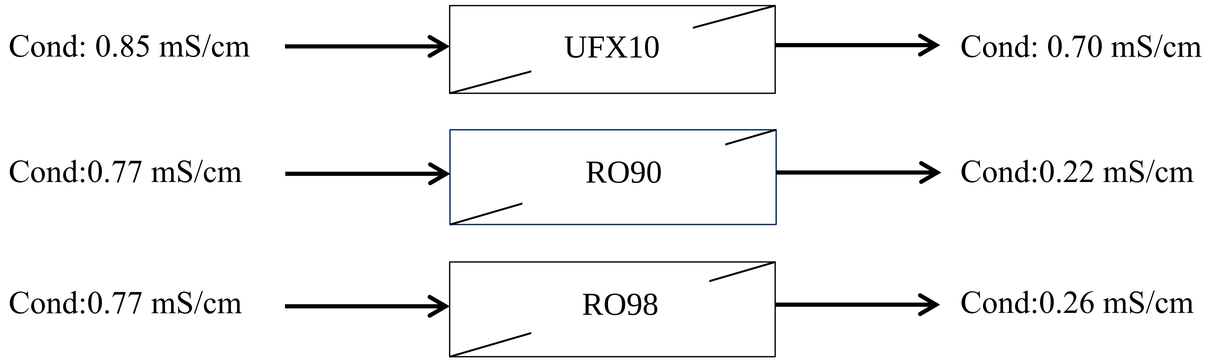


(Screen + UF) + RO



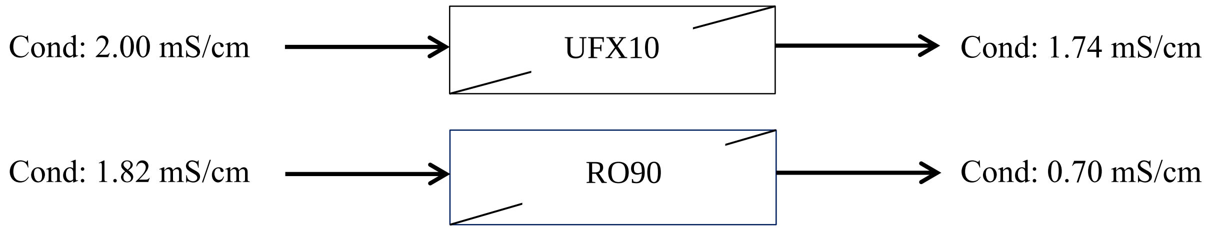
Process water PM-3, no pretreatment

Total Nitrogen for all process waters was zero.



Process water PM-3, no pretreatment

Total Nitrogen for all process waters was zero.



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