MEMBRANE FILTRATION FOR TERTIARY TREATMENT OF BIOLOGICALLY TREATED EFFLUENTS FROM THE PULP AND PAPER INDUSTRY

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ABSTRACT
Discharge waters from activated sludge processes in the pulp and paper industry and from a municipal wastewater treatment plant were filtered with various nanofiltration (NF) and low pressure reverse osmosis (RO) membranes. The purpose was to study flux, retention, and permeate quality after membrane filtration by using a high shear (CR-250/2) filter. The suitability of the achieved permeates for reuse at the industrial site or for drinking water purposes is also discussed.

The NF permeate was practically free from colour and organic compounds but contained significant amount of inorganic compounds e.g. chloride ions, especially when a high amount of sulphate containing discharge waters were filtered, in which case a low pressure RO membrane is needed to successfully remove monovalent anions. Organic compounds were almost completely retained by NF and RO membranes and organic carbon in the permeate was less than 10 mg/L on an average. However, the average chemical oxygen demand (COD_{Cr}) in permeates was high being from 40-180 mg/L. Probably, a high content of chloride ions and bicarbonates disturbed the COD measurements giving unrealistic values. Therefore, the COD is not a precise method to measure organic compound in NF and RO permeates.

1. Introduction
Membranes are used in the pulp and paper industry in a variety of applications, in particular for the purification and recovery of water and for the recovery of raw materials or energy. The intake of fresh water to the mills has decreased significantly during the last decades and the trend is today towards more and more closed water circulation systems in the mills. However, paper mills cannot operate without sufficiently clean water. To purify effluents for reuse, membrane filtration offers an attractive alternative.

Most of the pulp and paper mills treat their effluents by using an activated sludge process. After this process the effluents are not sufficiently clean for reuse in the production of most paper grades. This kind of water might be reused for production of packaging paper (Bülow et al., 2003) but not for production of high quality printing papers. Biologically treated effluents still contain significant amounts of colour compounds, micro-organisms, recalcitrant organics and a minor amount of biodegradable organics as well as suspended solids. Biological treatment does not significantly reduce the inorganic content in the effluent and desalting is maybe needed before reuse of the effluents in the manufacturing processes. To what amounts these impurities need to be removed before reuse of the water is not well known but the higher the quality (i.e. brightness) of the paper produced, the cleaner the water should be (Möbius and Helble, 2003).

Some mill-scale NF and RO membrane filtration plants have been installed in the pulp and paper industry to purify tertiary effluent from external biological treatment processes. In the middle of the 1990s two spiral wound nanofiltration plants were installed for the treatment of effluent from a paper mill. In both cases, the nanofiltration systems were installed to remove colour, organic carbon and dissolved solids from effluents for reuse or for further processing. Both plants had a very efficient pretreatment prior to the NF spiral wound modules in order to prevent plugging of the filtration elements. For instance, the pretreatment included settling at several stages with chemicals, a sand filter, a back-washable screen filter and a 5 μm bag filter (Lien and Simonis, 1995). Neither plant is in operation today (P. Eriksson, personal communication, 2005).

In 1999 ***Eltmann newsprint mill of Papierfabrik Palm*** has installed spiral wound nanofiltration to reduce COD, AOX and colour in their effluents. Prior to NF, the effluent is biologically treated (activated sludge plant) and prefiltered using sand filters. The NF plant capacity is 190 m^3 permeate per hour (84% recovery for purified water). The flux of the Nadir NF-PES-10 membrane has been around 10-30 L/(m^2h). The reported COD removal is 89%, AOX 61% and colour 93%. Hardness measures divalent cations and is well retained in NF but the retention of conductivity is less than 40%, because of the negative retention of chloride ions. This often measured result in NF depends on the Donnan effect, which is typical for NF membranes. The reuse of NF permeate also decreased the need to heat fresh water to the mill process temperature (Schirm et al., 2001).

These mill-scale examples show that the membranes can be used for recirculation of external effluents. However, public information on these cases is limited. In this paper we have utilised the existent external wastewater treatment plants of paper mills as the biological pre-treatment before nanofiltration and reverse osmosis and have evaluated the possibilities of NF and RO in purification of discharge water so that it could be reused in the paper manufacturing process.

2. Materials and methods

2.1. Nanofiltration unit

A plate and frame type nanofiltration unit, a CR250/2 filter, was operated at very high turbulent conditions. Turbulence is generated on the surface of the membranes by rotating a blade at an average velocity of about 9 m/s near the membrane surface. In this study two different NF or RO membranes, both with the same membrane area, 0.045 m^2, were tested simultaneously.

2.2. Concentration mode filtrations

Prior to experiments the new membranes were flushed with water and dipped in 40% ethanol solution. Then they were put into the modules and the pressure was increased to 10 bar and kept there for 5 minutes. After that pure water was filtered at 6 bar for about 1 h. All filtrations were made in the laboratory in a batch mode (batch volume

110 L) concentrating the feed to end points corresponding to a volume reduction of 15-18. The filtrations were started by circulating both the permeate and the concentrate back to the feed vessel. After three hours of filtration the permeate was lead to an external tank and the concentration filtration was started.

2.3. Membranes

Some properties of the studied membranes are presented in Table 1. The membranes were chosen from the group of NF and low pressure RO membranes based on our earlier experiments with the discharge waters (Mänttäri et al., 2005).

Table 1 Description of membranes used (PA= polyamide, PS=polysulphone, TFC=thin film composite, * proprietary polyamide skin layer on a polysulphone/polyester support, PWP= pure water permeability measured at 25°C in this study).

Membrane	Manufacturer	Material	PWP, L/(m^2h bar)	Temperature (max), °C	pH range
NF270	Dow	Polypiperazine	12	45	3-10
Desal-5 DL	GE Osmonics	Proprietary*	8	70 (90)	1-11
TFC ULP	Koch Membrane Systems	TFC PA on PS base	7	45	4-11
ESPA3	Hydranautics	PA	10	45	2-11

2.4. Analyses

Samples were taken for analysis from the original feed, the accumulated permeate and from the residual concentrate. From these samples pH, conductivity, colour, total dissolved carbon, TDC, dissolved inorganic carbon, DIC, dissolved organic carbon, DOC, and UV absorbance at various wavelengths (e.g. UVA 280 nm measures mostly lignin residuals in paper industry waters, Varian Cary 1C UV-visible spectrophotometer, cuvette diameter 1 cm, unit 1/cm) were measured. The TDC and DOC were analysed using a Shimadzu TOC-5000A analyser (SFS-ISO 8245:1999). The DIC was calculated by subtracting the DOC from the TDC. The total residue (total solids, drying 105 °C) and the total fixed residue (ash content or inorganic matter, 550 °C) in the waters were analyzed according to the standard SFS 3008. The volatile solids content (total organic matter) was calculated as the difference between the total fixed residue and the total residue. Biological oxygen demand (BOD_5) was determined using a DRLange ECM SensorBOD apparatus. Colour was analysed using a Hach spectrophotometer (method 8025, wavelength 455 nm). The Hach spectrophotometer was also used when chemical oxygen demand was analysed (COD_{Cr}, standard SFS 5504). The concentration of anions was determined using an ion chromatography (column Ionpac® AS14) and the metals were analysed by atomic absorption spectrometry (AAS). All concentrations are given in mg/L.

2.5. Studied discharge waters from activated sludge plants

The waters filtered in this study were discharge waters from three aerobic activated sludge plants. Today, these waters are discharged to the waterway from the mill. Two discharge waters were from the pulp and paper industry and one from a municipal waste water treatment plant. In table 2 some measured characteristic values of the discharge waters are compared. The discharge waters from paper industry differed from the municipal discharge water by containing higher amount of impurities with certain exceptions. The municipal discharge water contained 100 times more nitrate ions than the paper industry discharge waters. The specific ultraviolet absorption ($SUVA_{280\ nm}$) values (UVA 280 nm / DOC) showed significantly higher values, over

3 L/(m mg), for the paper industry discharge waters when only 0.3 L/(m mg) for the municipal discharge water. This indicates the existence of hydrophobic aromatic substances in the pulp and paper industry discharge water.

Table 2 Characteristics properties of discharge waters.

		Filtered discharge water		
		Municipal	Pulp and Paper mill	Pulp mill
pH	-	6.6	7.8	7.75
Conductivity	mS/m	69	152	286
Inorg. matter	mg/L	340	940	1930
Chloride	mg/L	50	136	259
Sulphate	mg/L	120	240	780
Calcium	mg/L	51	39	70
Sodium	mg/L	45	280	555
Nitrate	mg/L	139	1	3
DIC	mg/L	26	78	77
TDC	mg/L	80	209	206
Org. matter	mg/L	185	324	306
DOC	mg/L	55	131	128
COD	mg/L	80	465	420
BOD	mg/L	9	17	12
Colour	PtCo units	42	570	435
UVA 254 nm	1/cm	0.17	3.87	4.13
UVA 280 nm	1/cm	0.14	3.12	3.17
UVA 350 nm	1/cm	0.05	0.85	0.84
UVA 450 nm	1/cm	0.02	0.18	0.15
SUVA 254 nm	L/(m mg)	0.3	3.0	3.2

2.6. Calculation

The volume reduction factor (VRF) was calculated using equation 1.

$$VRF = \frac{V_f}{V_c} \tag{1}$$

where VRF volume reduction factor, -
V_f feed volume at the beginning, L
V_c concentrate (feed) volume during a concentration filtration, L

The average retention was calculated using equation 2.

$$\mathrm{R}(average) = (1 - \frac{C_{pa}}{(C_f + C_c)/2}) \cdot 100\% \tag{2}$$

where C_{pa} concentration in accumulated permeate at the end, mg/L
C_f concentration in feed at the beginning, mg/L
C_c concentration in residual concentrate (feed) at the end, mg/L

The fouling was calculated by comparing the pure water permeability before and after the filtration as shown by equation 3.

$$\text{Fouling} = (1 - \frac{PWP_a}{PWP_b}) \cdot 100\% \tag{3}$$

where PWP_a pure water permeability after effluent filtration, L/(m^2h bar)
PWP_b pure water permeability before effluent filtration, L/(m^2h bar)

3. Results and discussion

3.1. Permeate fluxes and fouling

As table II shows the discharge waters from pulp and paper mills contained significantly more impurities than the discharge water from a municipal activated sludge plant. Therefore, also the permeability remained higher level when municipal discharge water was filtered as Fig. 1 a, b and c shows. The lowest permeabilities were measured for the discharge water which originates from the pulp mill. This water contained more inorganic compounds than the other waters and as a result the osmotic pressure difference between the concentrate and the permeate side of the membranes increased to a greater extent during the concentration filtration than when other waters were filtered. In addition, the same water fouled the membranes more than the other waters especially when RO membranes were used (Table 3).

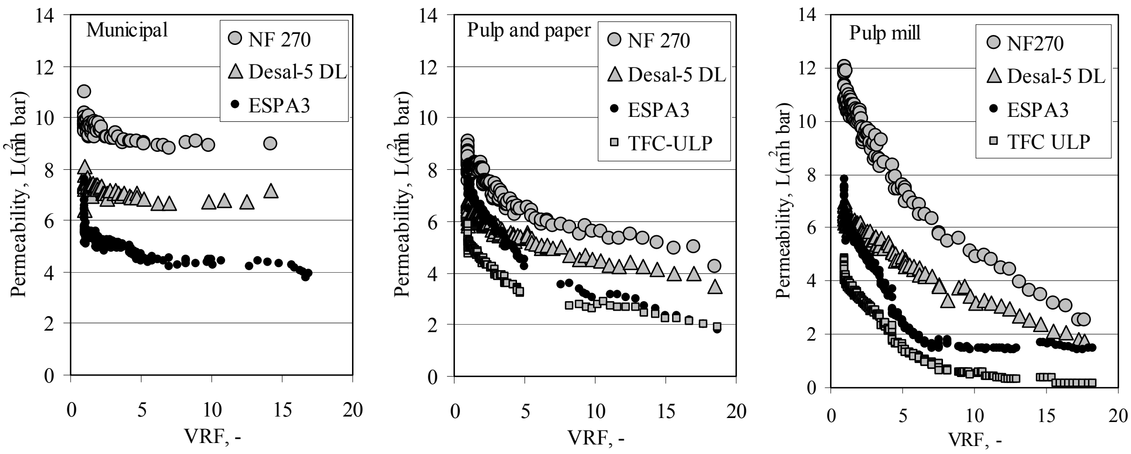

Figure 1 Permeability of various membranes when discharge waters were concentrated by membrane filtration (temperature 25 °C, average pressure in discharge water filtration with NF membranes was 6.8-7.6 bar and with RO membranes 7.6-8.2 bar).

Table 3 presents the fouling values for various membranes when different waters were filtered. The RO membranes fouled more than the NF membranes and the pulp mill discharge water fouled the most.

Table 3 Pure water permeabilities and calculated fouling values for membranes when discharge waters were concentrated by membrane filtration (25 °C, average pressure 6.8-7.6 bar in NF and 7.6-8.2 bar in RO).

Membrane		Discharge water: Municipal		Pulp and paper mill		Pulp mill	
NF 270	PWP_b, L/(m^{2}h bar)	10.3		9.8		14.5	
	PWP_a, L/(m^{2}h bar)	9.7	6 %	8.3	15 %	11.5	21 %
Desal-5 DL	PWP_b, L/(m^{2}h bar)	7.8		7.0		7.6	
	PWP_a, L/(m^{2}h bar)	6.9	12 %	5.5	21 %	6.4	16 %
TFC-ULP	PWP_b, L/(m^{2}h bar)			7.1		7.3	
	PWP_a, L/(m^{2}h bar)			5.5	23 %	2.4	67 %
ESPA3	PWP_b, L/(m^{2}h bar)	9.8		10.0		11.4	
	PWP_a, L/(m^{2}h bar)	5.4	45 %	7.5	25 %	5.8	49 %

3.2. Average retention of inorganic compounds

The pH of the discharge waters was from 6.6 to 7.8. In that pH range the membranes are generally negatively charged as are also many dissolved substances in the effluents. Negatively charged membranes repelled anions and due to the requirement of electroneutrality also counter-ions (cations) were retained by the membrane. The degree of retention increased with increasing valency of the anion due to an increased repulsion by the membrane. As expected, the RO membranes retained monovalent ions but retention of NF membranes varied greatly depending on the feed composition (Table 4). A high concentration and retention of sulphate ions in the filtration of discharge waters forced chloride and nitrate ions through the membrane and even negative retentions were measured for them (Donnan exclusion phenomenon). For instance, the average chloride retention of the Desal-5 DL membrane varied from 72% to –90% corresponding to average sulphate concentration from 735 mg/L (municipal discharge water) to 5890 mg/L (pulp mill discharge water). The RO membranes (TFC ULP and ESPA3) retained over 94% of chloride ions. The hydroxyl ions also preferentially permeated through the NF membranes. The pH was always higher, 0.7 pH units on an average, in the NF permeate than in the feed. High sulphate concentration facilitated the hydroxyl ion permeation similarly as it facilitated the permeation of chloride ions. The decreasing order of permeation for monovalent anions was hydroxyl, nitrate, chloride and bicarbonate (inorganic carbon) ions. The nitrate ions passed the NF membranes almost completely even at a relatively low sulphate concentration in the municipal discharge water.

Table 4 Measured inorganic parameters and their retention in the filtration of municipal discharge water (temperature 25°C, pressure 6.7-7.6 bar in NF and 7.6-8.3 bar in RO).

		pH	Conductivity		Inorg. matter		Cl^-		SO_4^{2-}		Ca^{2+}		Na^+		NO_3^-	
Municipal discharge water	Municipal effluent	-	mS/m		mg/L		mg/L		mg/L		mg/L		mg/L		mg/L	
	Feed	6.7	71		340		49		121		52		45		137	
	Concentrate	7.4	320		2960		130		**1350**		430		160		130	
	Desal-5 DL	7.3	42	79 %	220	87 %	25	**72 %**	9	99 %	20	92 %	43	58 %	120	**10 %**
	NF270	6.9	39	80 %	190	88 %	33	**64 %**	5	99 %	27	89 %	32	69 %	143	**-7 %**
	Feed	6.5	68		340		50		119		50		44		141	
	Concentrate	8	561		4230		569		1410		734		511		1489	
	ESPA3	6.6	4	99 %	35	98 %	5	98 %	6	99 %	2	100 %	5	98 %	12	**99 %**
		pH	Conductivity		Inorg. matter		Cl^-		SO_4^{2-}		Ca^{2+}		Na^+		NO_3^-	
Pulp and paper mill	Pulp and paper mill	-	mS/m		mg/L		mg/L		mg/L		mg/L		mg/L		mg/L	
	Feed	7.8	156		950		134		240		31		279		< detection level	
	Concentrate	8.3	815		10200		180		**4460**		490		2170		< detection level	
	Desal-5 DL	8.4	121	75 %	670	88 %	179	**-14 %**	11	100 %	2	99 %	250	80 %	2	
	NF270	8.6	51	89 %	260	95 %	100	**36 %**	7	100 %	2	99 %	96	92 %	2	
	Feed	7.8	148		930		137		240		48		281		1	
	Concentrate	8.2	2420		13610		1740		4050		700		4400		< detection level	
	ESPA3	7.8	11	99 %	82	99 %	17	98 %	10	100 %	1	100 %	20	99 %	2	
	TFC ULP	7.9	28	98 %	170	98 %	40	96 %	30	99 %	2	99 %	47	98 %	2	
		pH	Conductivity		Inorg. matter		Cl^-		SO_4^{2-}		Ca^{2+}		Na^+		NO_3^-	
Pulp mill discharge water	Pulp mill	-	mS/m		mg/L		mg/L		mg/L		mg/L		mg/L		mg/L	
	Feed	7.7	287		1920		255		760		75		553		3	
	Concentrate	8.3	1660		20650		88		**11020**		420		4850		< detection level	
	Desal-5 DL	8.7	185	81 %	970	91 %	324	**-90 %**	52	99 %	8	97 %	367	86 %	4	
	NF270	8.5	113	88 %	620	94 %	236	**-38 %**	43	99 %	8	97 %	207	92 %	5	
	Feed	7.8	284		1950		263		790		65		556		3	
	Concentrate	8.3	2020		19690		2050		8830		194		5590		< detection level	
	ESPA3	8	48	96 %	320	97 %	69	94 %	74	98 %	2	99 %	86	97 %	2	
	TFC ULP	8.2	52	95 %	280	97 %	63	95 %	70	99 %	5	96 %	95	97 %	3	

3.3. Average retention of organic compounds

The average retention for organic compounds are presented in table 5. The permeate in the filtration of discharge waters contained only a negligible amount of organic carbon. The results showed that biologically treated effluent did not contain low molar mass organic substances (measured by e.g. UVA 254 nm and DOC) because they were degraded during the activated sludge process. Thus, the organic compounds in the discharge water were relatively high molar mass substances (such as lignin and its degradation products), which were well retained by NF. Therefore, both NF and RO membranes had very high and mostly equal retention for organic compounds. Sometimes the RO permeate contained more colour than the NF permeate. The reason could have been the higher charge of the NF membranes which increased the retention of dissociated residual small molar mass compounds in NF. In addition, the RO membranes used in this study were more hydrophobic than the NF membranes and this might have facilitated the permeation of the organic compounds via adsorption/desorption mechanisms.

Table 5 also clearly shows that although permeates did not contain carbon the COD value was still rather high. This might be caused by chloride ions or bicarbonate ions in the permeate. Therefore, the COD was not a proper parameter to evaluate organic compounds in NF or RO permeate.

Table 5 Measured organic parameters and their retention in the filtration of discharge waters (temperature 25°C, pressure 6.7-7.1 bar in NF and 7.6-8.3 bar in RO).

		DOC mg/L		COD_{Cr} mg/L		BOD_5 mg/L		Colour PtCo units		UVA 254 nm 1/cm		UVA 280 nm 1/cm	
Municipal discharge water	Feed	61		73		6		43		0.17		0.13	
	Concentrate	500		380		133		700		2.24		1.80	
	Desal-5 DL	6	98 %	77	66 %	6	91 %	10	97 %	0.04	97 %	0.03	97 %
	NF270	0	100 %	13	94 %	5	94 %	6	98 %	0.02	98 %	0.02	98 %
	Feed	49		87		13		40		0.17		0.14	
	Concentrate	520		390		123		480		2.01		1.61	
	ESPA3	0	100 %	5	98 %	4	94 %	0	100 %	0.02	98 %	0.02	98 %
Pulp and paper mill	**Pulp and paper**	DOC mg/L		COD_{Cr} mg/L		BOD_5 mg/L		Colour PtCo units		UV 254 nm 1/cm		UV 280 nm 1/cm	
	Feed	490		860		19		530		3.90		3.15	
	Concentrate	1 770		6140		98		9600		55.30		50.26	
	Desal-5 DL	1	**100 %**	130	96 %	9	85 %	0	100 %	0.12	100 %	0.08	100 %
	NF270	1	**100 %**	180	95 %	9	85 %	0	100 %	0.03	100 %	0.02	100 %
	Feed	129		465		15		606		3.84		3.08	
	Concentrate	1 670		6190		99		7700		44.69		40.49	
	ESPA3	3	100 %	7	100 %	7	88 %	0	100 %	0.03	100 %	0.02	100 %
	TFC ULP	6	99 %	79	98 %	15	74 %	11	100 %	0.12	100 %	0.09	100 %
Pulp mill discharge water	**Pulp mill**	DOC mg/L		COD_{Cr} mg/L		BOD_5 mg/L		Colour PtCo units		UV 254 nm 1/cm		UV 280 nm 1/cm	
	Feed	130		440		10		380		4.11		3.17	
	Concentrate	1 670		5730		63		7920		56.95		46.09	
	Desal-5 DL	3	100 %	40	99 %	15	59 %	0	100 %	0.08	100 %	0.06	100 %
	NF270	2	100 %	74	98 %	17	53 %	0	100 %	0.04	100 %	0.03	100 %
	Feed	129		410		14		490		4.15		3.17	
	Concentrate	1 380		4090		58		8400		50.51		39.60	
	ESPA3	4	99 %	74	97 %	6	83 %	13	100 %	0.07	100 %	0.05	100 %
	TFC ULP	6	99 %	118	95 %	7	81 %	14	100 %	0.14	99 %	0.11	99 %

4. Conclusion

A direct nanofiltration and reverse osmosis of discharge water from activated sludge processes generated very clean permeate (no colour, about 5 mg/L DOC) even when a very high concentration factor, about 15-18, was used. Both NF and RO membranes retained organic compounds almost completely but differed in their ions retention. Especially when a high concentration of sulphate ions was present in the discharge water the NF membranes lost their retention capability for monovalent anions. Then chloride and nitrate ions detrimentally accumulated in the permeate. The low pressure RO membranes were not so sensitive for the change in composition of the feed solution and they retained over 95% of the monovalent ions. However, the lower flux and the higher fouling, compared to NF, limits the use of RO.

The COD in the permeate was surprisingly high compared to organic carbon or other parameters measuring organic compounds. Therefore, the COD analysis was found to be unsuitable for to measuring organic compounds in the permeate in these types of waters.

The achieved permeate can easily be reused in the paper production. Nanofiltration has a significantly higher flux and also a lower fouling tendency than reverse osmosis but it passes through monovalent ions when there is a high sulphate concentration in the water. Therefore, RO might be needed in such cases to produce excellent process water.

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