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# Selection of NF membrane to improve quality of chemically treated surface water

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## Abstract

The requirement for higher quality drinking water necessitates the application of more efficient water treatment techniques. Nanofiltration is one promising option for enhanced water treatment, for example, in enhanced organic matter removal. The characteristics of different nanofiltration membranes vary remarkably, and the selection of a membrane has to be made according to the requirements of an application. In this study six nanofiltration membranes (NF70, NF255, NTR-7450, NTR-7410, Desal-5 and TFC-S) were evaluated in improving the quality of chemically pre-treated surface water in a pilot-scale process. The results indicate that the membrane with high organics removal and slightly reduced ion removal characteristics (NF255) performed best in terms of product water quality as well as membrane productivity and fouling. The most permeable membrane (NTR-7410) suffered intensive fouling and insufficient product water quality. An interesting finding was that the permeates of all the tested membranes possessed a significant potential for microbial growth, despite the low nutrient contents.

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**Keywords:** Nanofiltration; Membranes; Organics removal; Drinking water

## 1. Introduction

As our knowledge of harmful compounds in drinking water increases, the demand for more efficient water treatment processes also intensifies. Often, water quality problems require the enhanced removal of organic compounds. Generally, organic matter levels of chemically treated surface water complies with current

drinking water quality standards, but is still enough for remarkable formation of mutagenic disinfection by-products (DBP) at disinfection with chlorine. In addition, organic matter is a substrate for the bacteria present in distribution networks, and consequently bacterial regrowth can be expected. One promising option for enhanced organic matter removal from traditionally treated surface water is the introduction of nanofiltration (NF) [1,2].

NF membranes typically retain substances with molar masses higher than 200–300 g/mol and multivalent ions. As a consequence, NF membranes are able to remove a high degree of organic matter and hardness-causing compounds, and virtually all microbes from the feed water [2–5]. In applications for treating soft waters, the NF membrane's ability to remove hardness-causing compounds is undesirable. To overcome this shortcoming, specifically designed membranes with a lower

*Abbreviations:* AOC, assimilable organic carbon; DBP, disinfection by-product; C, concentration; ECW, Espoo City Waterworks; HPC, heterotrophic plate count; HGR, heterotrophic growth response; MAP, microbially available phosphorous; NDP, net driving pressure; NF, nanofiltration; PWF, pure water flux; TOC, total organic carbon; UVA, ultraviolet absorbance at 254 nm.

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divalent ion retention coupled with high organics removals and permeabilities have been manufactured [6,7].

The molar mass value of an NF membrane allows a rough estimation of membrane organic matter removal efficiency. However, in NF the rejection of organics not only depends on the sieving effect, but also on the charge and hydrophobicity effects between the membrane and the organic compound. Ionic species retention by NF membranes is due to sieving, electrostatic interactions between the ions and the membrane and differences in diffusivity or a combination of these [8].

In addition to the membranes' ability to remove the required components, their productivity and fouling tendency are of importance in evaluating the membrane performance. In an optimal case, a membrane is capable of retaining stable and high productivity for long periods. Membrane fouling will first require the application of increased feed pressure to maintain a constant permeate flow rate through the membrane, and finally the membranes have to be cleaned to maintain the production capacity of the plant. Both procedures increase the operational costs of the membrane process.

As the characteristics of the different NF membranes vary remarkably, the selection of an optimal membrane for each application is essential in order to achieve the required product water quality and optimise the operation of the process. In this study, the performance of six NF membranes (Table 1) was investigated in treating chemically treated surface water. The first objective was to find a membrane with high organics removal and low alkalinity removal characteristics. Secondly, the required permeate quality should be coupled with high membrane productivity and low fouling.

The study was conducted at a water treatment plant with a pilot-scale NF process. The permeate quality and the rejection characteristics of the membranes were examined with respect to organic and inorganic constituents. In addition, the microbial stability of the permeates was evaluated. The operational performances

of the membranes were evaluated through membrane flux and fouling.

## 2. Materials and methods

### 2.1. Pilot process and membranes

The NF pilot process used in the experiments is illustrated in Fig. 1. The feed water was filtered by a 5- $\mu\text{m}$  cartridge filter before it entered the pressure vessels housing the membrane elements. Two spiral-wound membrane elements with nominal dimensions of 6.1 cm in diameter and 101 cm in length (corresponding to the membrane surface area of 2.6 m<sup>2</sup>) were run parallel in the one-stage process. The operating pressures and flows were measured at the locations indicated in Fig. 1.

The membranes used in the experiments are summarised in Table 1 with their respective properties. The NF70, NF255, NTR-7450 and NTR-7410 membranes had been used for approximately 100 h under normal operating conditions before the tests, and they had been stored in a 1% sodium bisulphite solution. Desal-5 and TFC-S were new, unused membranes delivered directly from the manufacturers.

### 2.2. Experimental

The experiments were conducted at Espoo City Waterworks (ECW), which draws its raw water from a small humus-rich lake (average total organic carbon (TOC) 6.9 mg/l). The process at ECW consists of ozonation, chemical coagulation with ferric chloride, dissolved air flotation, rapid sand filtration and post-treatment with chloramine and lime. Feed water for the NF pilot was drawn from the ECW process before the post-treatment. The feed water quality during the experiment is presented in Table 2. Most of the feed water characteristics remained stable during the test period. The only notably variable parameters were the

Table 1  
Tested membranes and their characteristics. Information provided by manufacturers if not indicated otherwise

Membrane	Manufacturer	Material	Cut-off	MgSO <sub>4</sub> rejection (%)
NF70	Filmtec	PA	200–300	95
NF255	Filmtec	PPZ	300	97
NTR-7450	Nitto Denko	SPS	600–800 <sup>a</sup>	32 <sup>b</sup>
NTR-7410	Nitto Denko	SPS	n.a.	9 <sup>b</sup>
Desal-5 DL	Osmonics	PPZ	150–300	96
TFC-S	Fluidsystems	PA	200–300	99

PA = polyamide; PPZ = polypiperazine amide; SPS = sulphonated polyethersulphon; n.a. = not available.

<sup>a</sup>Estimated by Van der Bruggen et al. [26].

<sup>b</sup>Ikeda et al. [6].

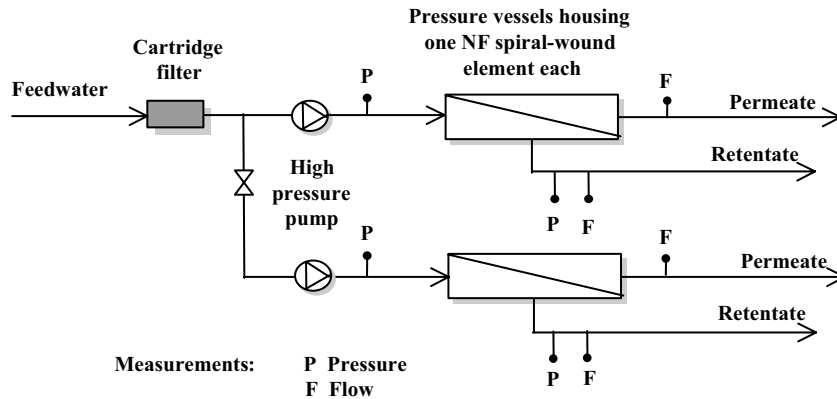


Fig. 1. Schematic view of the pilot process.

Table 2

Feed water quality as average values  $\pm$  standard deviation during the experiment

Temperature, °C <sup>a</sup>	18.1 $\pm$ 0.4
pH <sup>b</sup>	5.9 $\pm$ 0.1
Conductivity, mS/m <sup>b</sup>	14.3 $\pm$ 0.7
Turbidity, FTU <sup>b</sup>	0.14 $\pm$ 0.07
Alkalinity, mmol/l <sup>b</sup>	0.09 $\pm$ 0.01
Hardness, mmol/l <sup>b</sup>	0.10 $\pm$ 0.01
TOC, mg/l <sup>b</sup>	2.17 $\pm$ 0.11
UVA, cm <sup>-1b</sup>	0.024 $\pm$ 0.002
HPC, CFU/ml <sup>c</sup>	4200 $\pm$ 2400
Al <sup>3+</sup> , µg/l <sup>c</sup>	17.5 $\pm$ 14.3
Ca <sup>2+</sup> , mg/l <sup>c</sup>	13.1 $\pm$ 1.1
Mg <sup>2+</sup> , mg/l <sup>c</sup>	1.39 $\pm$ 0.00
Na <sup>+</sup> , mg/l <sup>c</sup>	7.28 $\pm$ 0.16
Cl <sup>-</sup> , mg/l <sup>c</sup>	12.3 $\pm$ 0.3
SO <sub>4</sub> <sup>2-</sup> , mg/l <sup>c</sup>	33.5 $\pm$ 2.7

<sup>a</sup> Continuous measurement.

<sup>b</sup>  $n = 9$ .

<sup>c</sup>  $n = 3$ .

heterotrophic plate count (HPC) and the aluminium content.

The tested membranes were operated for 136–142 h with two membranes being run in parallel. During the experiments, the feed pressure and recovery were kept constant at 4 bar (corresponding to approximately 3.5 bar net driving pressure (NDP)) and 15%, respectively. With NTR-7410 it was not possible to maintain the standard running conditions because of the technical limitations of the NF pilot. Thus, the operational conditions were 3.5 bar and 25% during the NTR-7410 test.

After installation, the stored membranes were rinsed with NF permeate for 2 h. The new membranes were rinsed with permeate and stabilised for 20 h by running them at 7 bar driving pressure with permeate. After

these procedures, the membranes were pre-cleaned with an alkaline solution to give them all the same initial reference conditions despite different histories. After this, the run with feed water was started. During the run, the process was re-adjusted to the standard pressure and recovery daily, excluding weekends. After the run, the membranes were cleaned with a three-step process with alkaline, acidic and alkaline cleaning solutions.

The alkaline cleaning was performed with a solution of 0.2% Na<sub>4</sub>EDTA and 0.1% Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub>, and the acidic cleaning with a solution of 1.5% citric acid. The cleaning time with each solution was 30 min. The cleaning scheme was recommended for all the tested membranes according to manufacturers' manuals.

### 2.3. Evaluation of the performance of the membranes

The effect of NF on the water quality was assessed by taking feed water and permeate samples for different analyses after a run of 1 h, 1 day and at the end of the run. The retention of the examined components were determined to assess the performance of the membrane. Removals were calculated as percentage by comparing the concentrations of the substance in the permeate ( $C_p$ ) and in the feed water ( $C_f$ ) as follows:

$$\text{Removal} = (1 - C_p/C_f)100\%.$$

The productivities and fouling of the membranes were evaluated by examining the changes in the normalised fluxes (4 bar and 20°C) during the run under standard operating conditions. Normalised fluxes were used instead of operational fluxes in order to obtain comparable figures despite the slightly varying operation pressures and temperatures.

The changes in the membrane permeation characteristics due to fouling and cleaning were calculated by comparing the membrane pure water flux (PWF) in

different phases of operation with the PWF of the pre-cleaned membrane according to the following formula:

$$\text{PWF}_{\text{change}} = [(\text{PWF}_p - \text{PWF}_{\text{pc}})/\text{PWF}_{\text{pc}}]100\%,$$

where  $\text{PWF}_{\text{change}}$  is the PWF change in a certain phase of the test,  $\text{PWF}_{\text{pc}}$  refers to the pre-cleaned membrane, and  $\text{PWF}_p$  to the certain phase of the test. The PWFs were measured after storage or delivery ( $\text{PWF}_i$ ), after run ( $\text{PWF}_r$ ) and after final cleaning ( $\text{PWF}_c$ ). The PWF measurements were performed using heated (25°C) distilled water, which was passed through the system at a steady 5 bar pressure and 15% recovery, or as close to these figures as each situation would allow. Since the pilot apparatus did not allow the use of standard conditions for all tested membranes, the PWFs were normalised to 5 bar NDP.

#### 2.4. Analyses

The following tests were conducted, according to national standards, on all the feed water and permeate samples: pH, conductivity, turbidity, alkalinity, hardness and TOC. These samples were also analysed for UV absorption at 254 nm (UVA) according to the APHA [9] with the exception that filtering was replaced by a 10-min centrifugation at 4000 rpm. In addition to this, the final set of samples was also tested for assimilable organic carbon (AOC), microbially available phosphorus (MAP), HPC, heterotrophic growth response (HGR), anions and cations.

The AOC was analysed by a modification [10] of the standard AOC method [11]. AOC results were determined by standardising the growth of test bacteria using acetate. AOC content is expressed as micrograms of acetate eq-C per litre ( $\mu\text{g Ac-C/l}$ ). The MAP analyses were done according to Lehtola et al.'s [12] method. The HPC was analysed using spread plate counting with the sensitive R2A agars at  $20 \pm 1^\circ\text{C}$  [13]. In the HGR assay, the growth of indigenous heterotrophic bacteria in the water sample was followed according to Noble et al. [14]. Anions were analysed by ion chromatography and cations by inductively coupled plasma atomic emission spectrometry, or by mass spectrometry.

### 3. Results

#### 3.1. Effect of the different membrane histories on the results

By comparing the initial membrane retentions and the retentions in this study the histories of the membranes did not affect the membrane retention characteristics. According to the PWF values of new pre-cleaned membranes and stored membrane PWFs after pre-cleaning, the histories of the membrane did not affect

the permeability of NF70, NF255 and NTR-7450. This indicates that the results of the NF70, NF255 and NTR-7450 membranes are representative, and comparable to the results of the unused Desal-5 and TFC-S membranes.

On the other hand, the storage and cleanings affected the behaviour of the NTR-7410 membrane remarkably. Similar, inconsistent behaviour was noticed with the NTR-7410 membrane in our study conducted with a flat-sheet membrane pilot. This suggests that the chemical composition of the membrane is unstable. Thus the results can be considered representative for that membrane too.

#### 3.2. Permeate water quality

No remarkable differences could be seen in the permeate samples taken at different points during the run; therefore only average permeate qualities are presented here.

The average permeate pH, conductivity and alkalinity, and related removal efficiencies of different membranes are presented in Table 3. The feed water and permeate alkalinities are presented, despite the fact that they were notably below the directive detection limit (0.4 mmol/l) of the analysis method. All the membranes totally removed the minor hardness present in the feed water. NF did not affect the turbidity of the water.

The organic matter content and HPC of the permeates with the membrane removal efficiencies are summarised in Table 4. When evaluating the TOC results it should be borne in mind that the TOC content of the NF70, NF255, Desal-5 and TFC-S permeates is presented as the analyser's detection limit of 0.3 mg/l. Thus, the real organic matter removal efficiency of the tight NF membranes is between 96% and 100%. On the whole, the AOC removals were lower than the TOC or UVA removals by all the other membranes than NTR-7410. NF did not affect the MAP content of the water: MAP contents of the permeates and feedwater were at the lower detection limit of the analysis ( $0.08 \mu\text{g PO}_4\text{-P/l}$ ), and are considered to be the same.

Table 3

Average permeate quality  $\pm$  standard deviation ( $n = 3$ ) and removal efficiency of the tested membranes

Membrane	pH	Conductivity (mS/m) (%)	Alkalinity (mmol/l) (%)
NF70	5.6	$0.82 \pm 0.05$ (95)	0.04 (60)
NF255	5.8	$5.16 \pm 0.05$ (66)	0.06 (36)
NTR-7450	5.9	$6.95 \pm 0.59$ (50)	0.08 (16)
NTR-7410	5.9	$11.44 \pm 0.05$ (18)	0.09 (8)
Desal-5	5.7	$3.48 \pm 0.05$ (75)	0.05 (37)
TFC-S	5.6	$0.55 \pm 0.04$ (96)	0.03 (61)

Table 4

Average permeate quality  $\pm$  standard deviation ( $n_{\text{TOC,UVA}} = 3$ ,  $n_{\text{AOC,HPC}} = 1$ ) and removals of organic matter and bacteria with the tested membranes

Membrane	TOC (mg/l) (%)	UVA ( $\text{cm}^{-1}$ ) (%)	AOC ( $\mu\text{g eq-C/l}$ ) (%)	HPC (CFU/ml) (%)
NF70	<0.30 (> 86)	0.000 (99)	5 (90)	3 (99.9)
NF255	<0.30 (> 86)	0.001 (96)	29 (42)	15 (99.7)
NTR-7450	$0.50 \pm 0.05$ (78)	0.006 (77)	27 (41)	93 (98.6)
NTR-7410	$1.33 \pm 0.02$ (41)	0.015 (41)	27 (41)	3 (100.0)
Desal-5	<0.30 (> 86)	0.001 (98)	13 (86)	1 (100.0)
TFC-S	<0.30 (> 86)	0.001 (99)	7 (93)	17 (99.5)

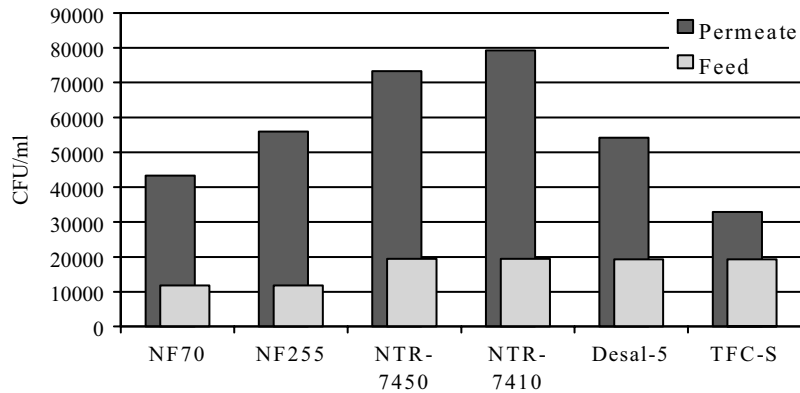


Fig. 2. Maximal number of heterotrophic bacteria in permeates ( $n = 1$ ) and feed waters ( $n = 1$ ) of the tested NF membranes during the 20-day incubation.

Table 5

Permeate ion content ( $n = 1$ ) and removals with different membranes

Membrane	$\text{Al}^{3+}$ ( $\mu\text{g/l}$ ) (%)	$\text{Ca}^{2+}$ (mg/l) (%)	$\text{Mg}^{2+}$ (mg/l) (%)	$\text{Na}^+$ (mg/l) (%)	$\text{Cl}^-$ (mg/l) (%)	$\text{SO}_4^{2-}$ (mg/l) (%)
NF70	<b>1.0 (97)</b>	<b>0.07 (99)</b>	<b>0.05 (96)</b>	0.79 (89)	0.86 (93)	<b>0.10 (100)</b>
NF255	4.3 (87)	3.29 (77)	0.29 (79)	3.67 (51)	11.3 (12)	0.23 (99)
NTR-7450	9.8 (34)	4.74 (64)	0.55 (60)	4.67 (35)	9.3 (24)	8.69 (73)
NTR-7410	15.1 (–1)	9.74 (25)	1.11 (20)	6.22 (13)	12.3 (0)	23.3 (28)
Desal-5	1.0 (79)	0.74 (94)	<b>0.05 (96)</b>	4.62 (36)	7.78 (39)	<b>0.10 (100)</b>
TFC-S	1.9 (60)	0.11 (99)	<b>0.05 (96)</b>	0.52 (93)	0.29 (98)	0.11 (100)

The bold removals indicate situations where the real removals might have been even higher than presented, since the ion contents in the permeates were below the detection limit of the analysis method.

All the membranes performed high bacteria removal. Nevertheless, low numbers of heterotrophic bacteria were found in all the permeates. The NTR-7450 presented surprisingly high HPC in its permeate. Despite the low number of bacteria and low nutrient contents in the permeates, all the permeates showed remarkable potential for microbial growth according to the maximal HGR value during the 20-day incubation (Fig. 2).

The removals of selected ions are presented in Table 5. The removal of divalent ions was generally higher than the removal of monovalent ions, even though the tighter membranes removed monovalent ions efficiently as well. The lowest ion removals were obtained with NTR-7450 and NTR-7410, and the NF255 and Desal-5 membranes also seemed to be modified to allow through more ions than the traditional NF membranes. The low calculated removals of aluminium by the NTR-7450, NTR-7410,

Desal-5 and TFC-S membranes are probably due to inaccuracy in determining the feed water aluminium content, which varied significantly.

3.3. Membrane flux and fouling

Very similar average normalised fluxes of 29.7, 27.1, 31.4 and 31.0 l/m<sup>2</sup> h were achieved using the NF70, NTR-7450, Desal-5 and TFC-S membranes, respectively. The normalised fluxes of the NF255 and NTR-7410 membranes were higher, in the average 39.1 and 77.0 l/m<sup>2</sup> h, respectively.

The flux declines of the membranes are presented in Fig. 3. The NTR-7450 and NTR-7410 membranes experienced remarkable decrease of flux during the first 4 days of the experiment. With the NF70, NF255 and TFC-S membranes the flux decline was pronounced during the first day of operation, after which it remained fairly stable. Since the flux decline stabilised after the beginning, the real operational parameters can be evaluated after the operation of the first 10–20 h. No fouling could be observed with the Desal-5 membrane. If the membrane flux decline is evaluated against the amount of water passed through the membrane, the performance and rating of the membranes does not change from the run-time-based evaluation.

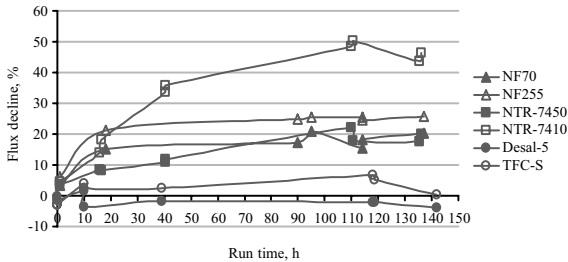


Fig. 3. Flux declines of tested membranes in the experiment.

According to the general guidelines, the fouled membranes should be cleaned when the normalised flux has dropped by 10–15% [15, p. 128]. For the NF70, NF255, NTR-7450 and NTR-7410 membranes, 15% flux decline corresponds to 5, 15, 15 and 55 h cleaning intervals, respectively. With Desal-5 and TFC-S the cleaning interval exceeds the tested run period, 140 h. If the initial fouling is excluded from the cleaning interval calculations, the resulting cleaning intervals for NF70 and NF255 exceed the tested run period as well.

3.4. Effect of chemical cleaning

The effects of cleaning and fouling on the membrane PWF are presented in Fig. 4. The pre-cleaning improved the flux of the NF70, NF255 and Desal-5 membranes from the initial situation, with the most remarkable effect seen in NF255 and a minor effect in Desal-5. By contrast, the pre-cleaning decreased the fluxes of NTR-7450, NTR-7410 and TFC-S.

The PWF of all the membranes apart from NTR-7450 and NTR-7410 decreased from the pre-cleaned situation during the run due to fouling. The final cleaning increased the flux from the fouled situation of all the membranes apart from NF70. With respect to the pre-cleaned situation the final cleaning recovered or improved the PWF of the NF255, NTR-7450, NTR-7410 and Desal-5 membranes.

4. Discussion

4.1. Permeate water quality

One main objective in applying the NF process as a refining step in surface water treatment is the removal of residual organic matter and bacteria to levels, which restrict the need for post-chlorination and limits

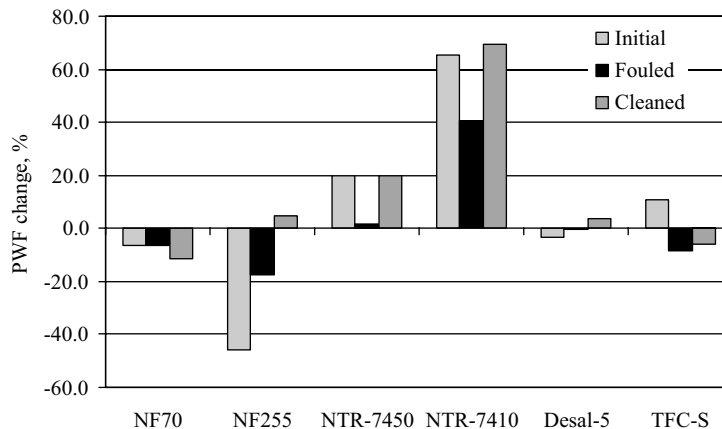


Fig. 4. Change of the membrane PWF in different phases of the test run with respect to the of a pre-cleaned membrane.

consequent DBP formation and bacteria growth in distribution network. According to the TOC and UVA reductions in this study, it can be assumed that the deprivation of organic matter in the NF70, NF255, Desal-5 and TFC-S permeates limits the DBP formation and restricts the bacterial growth in the distribution network. However, according to the AOC threshold (10 µg Ac-C/l) proposed by van der Kooij [16], only in the NF70 and TFC-S permeates was the AOC content low enough to restrict microbial regrowth in distribution network.

Other NF studies support the finding of lower AOC removal in comparison to TOC or UVA removal [4,5]. This is due to the fact that AOC consists mainly of the low molar mass organics, which pass through the NF membranes more easily than higher molar mass organics, which is the main fraction of TOC and UVA [17].

Surprisingly some heterotrophic bacteria were found in all the permeates, in spite of the fact that the bacteria cannot theoretically pass through the pores of the membranes. We assume that the microbes originate from non-sterile pipes or joints or the permeates were contaminated at sample collection.

Judged by the criterion of bacterial growth, none of the tested NF membranes produced a biologically stable permeate. Consequently, post-chlorination is required to suppress microbial growth in distribution systems. Still, the small numbers of culturable bacteria found in the permeates suggests that only a minor chlorine dosage is needed for inactivation of the microbes. In addition, Laurent et al.'s [18] observations indicate that even low chlorine residuals are retained in distribution system, if the organic matter content is low enough so as not to consume the chlorine residual. Minimal TOC levels and lower chlorine dosages, in turn, decrease the formation of DBPs. The removal of DBP precursors by NF was not studied here, but several studies have indicated that these compounds are removed by up to 80–97% in NF [2,3,5].

An interesting finding in the HGR analysis was that the microbial growth in the permeates was stronger than in the feed water. This in conjunction with poor AOC and MAP reductions results indicate that particularly the smallest and most easily biodegradable nutrient compounds are able to pass through a NF membrane. It has been shown that phosphorus is the limiting nutrient in most Finnish drinking waters, and that extremely low levels are sufficient for bacterial growth [19]. Thus all permeates contained enough nutrients for significant bacterial growth. Furthermore, an inhibition phenomenon caused by components in the water, e.g. metals like aluminium, may be responsible for the weakened microbial growth in NF feed water in comparison to purer NF permeate. Consequently, the few microbes which contaminated the permeates had a favourable

environment for intensive microbial growth in permeate waters. A similar phenomenon was found in a study comparing HGRs of several treated surface waters and groundwaters: The microbial growth potential was higher in the chemically and microbially purer drinking waters produced from groundwater [20].

The chemical stability of the permeate also affects the suitability of the water for distribution. Chemically treated feed water in the study had low pH, alkalinity and hardness, and consequently so did all the permeates. However, the looser NF membranes reduced permeate pH and alkalinity significantly less than the traditional NF membranes. The use of a membrane with lower inorganic removal capacity can considerably reduce the need for post-treatment for alkalinity recovery and stability control.

Refining treatment with NF can also be used to secure the inorganic quality of the water by removing harmful compounds. Here the concentrations of the studied inorganic components in chemically pre-treated feed water were well below the current water quality standards, but especially aluminium content of the pre-treated water occasionally exceeds the limit of the quality standard. Then NF would cut the concentration to acceptable levels.

The membranes used in this study can be divided into three groups according to their removal characteristics. Traditional softening-type membranes, NF70 and TFC-S, have high rejection of both organic and inorganic compounds. NF255 and Desal-5 are specifically modified for high organics and slightly reduced inorganics removal. NTR-7450 and NTR-7410 have the lowest rejection of inorganic species, but unfortunately the organics removal is quite low as well.

#### 4.2. Membrane productivity and fouling

The fluxes and the fouling rates of the tested membranes varied remarkably. In the majority of the tests, the membrane fouling that developed during the run caused a noticeable loss of flux. The membrane with the highest assumed cut-off value (NTR-7410) displayed the highest flux, the lowest contaminant removal, and fouled most. This observation is in line with Nyström et al.'s [21] finding that more open NF membranes foul more easily. In addition to cut-off value, membrane charge and hydrophobicity affect the membrane–feed water interaction, and consequently membrane flux and fouling. However, no conclusions could be drawn with insufficient information on membrane characteristics.

The fluxes of the membranes tested here have been studied in different applications by other authors as well. When comparing the fluxes achieved in this study to the results of other studies, the rating of the membrane productivity seems to remain of the same



order [3]. However, the fluxes of certain membranes varied significantly between the studies, depending on the feed water characteristics [3,22,23].

Regarding the flux decline patterns, the applied pressures resulted in stable fluxes for the NF70, NF255, Desal-5 and TFC-S membranes, after the initial flux decline. This indicates that the membranes were operated at pressures favouring sustainable membrane use. Even higher NDPs could have been applicable according to manufacturers' guidelines and other studies [24]. The NTR-7450 and NTR-7410 membranes exhibited a continuous flux decline, and it may be concluded that the operational pressures and fluxes were too high for these membranes. In other studies, NTR-7410 has been successfully operated at a NDP below 2 bar [3,25]. In conclusion, the optimised operation of the tested membranes would differ from the experimental situation in many cases, and the productivity of the tighter membranes would possibly increase, while the productivity of NTR-7450 and NTR-7410 would decrease.

#### 4.3. *Effect of chemical cleaning*

The cleaning tests indicated that there were vast differences in the way the membranes reacted to the cleaning, as well as the way the same membrane responded to the pre-cleaning and the final cleaning. The performed cleaning was efficient in recovering the initial and pre-cleaned PWF after the membrane fouling of all the membranes other than NF70 and TFC-S. The NF70 and TFC-S membranes were made of polyamide, and their incompatibility with the cleaning may be related to the membrane material. On the other hand, the alkaline pre-cleaning improved the flux of NF70 by 7%, which may indicate that acidic cleaning was not compatible with NF70.

The pre-cleaning decreased the flux of the membranes made of sulphonated polyethersulphone (NTR-7450, NTR-7410). The decreased flux was, however, recovered during the test run and in the final cleaning. This unpredictable behaviour may be a result of the changes in the membrane characteristics due to storage, or the reactions between the storage solution rests and the alkaline cleaning chemical.

These cleaning results emphasise the importance of choosing a suitable cleaning chemical to optimise the performance of the membrane process. Cleaning chemicals have to be employed with consideration given to the specific application and taking into account both the foulants and membrane material.

#### 4.4. *Ranking of membranes*

The product water quality requirement is the main factor that determines the possible membrane choices.

Of the tested membranes, NF255 and Desal-5 balance the permeate requirements of low organic content and little need for post-chlorination and alkalinity recovery in the most acceptable way. After determining the membranes with agreeable permeate quality, the operational performance and economy of the membranes have to be analysed. Desal-5 did not foul at all during the experimental run, but with NF255, higher flux coupled with relatively low membrane fouling can be obtained.

When investigating and analysing the results of the study, it has to be borne in mind that the ranking of the membranes may change from application to application. The criteria for permeate quality vary, and different feed water characteristics also significantly affect the performance of the membrane.

## 5. Conclusions

The following conclusions can be drawn from the results of the study:

- The NF membrane with high organics removal and slightly reduced ion removal characteristics (NF255) performed best both in respect of product water quality and process economy in filtering chemically treated surface water. The most permeable membrane (NTR-7410) did not perform well due to insufficient product water quality and intensive fouling.
- Different NF membranes showed remarkably different removals of organic and inorganic matter. With tight membranes higher than 95% removal of TOC content was achieved. However, the membranes with the highest organics removals resulted in a considerable reduction in permeate alkalinity, and the permeate water requires intensive post-treatment for alkalinity recovery.
- Despite low nutrient and microbe contents, microbial growth occurred in all NF permeates. This indicates that significant microbial growth can occur even in NF water and post-chlorination is required to suppress microbial growth in distribution systems. However, the low HPC values suggests that only a minor chlorine dosage is needed for inactivation of the microbes.
- Different membranes reacted in different ways to chemical cleaning. The performed cleaning improved the flux of the NF255 membrane approximately by 20% from the fouled situation, while the flux of NF70 decreased in cleaning by 5%. Thus, the choice of cleaning chemical is an important factor that affects the overall performance of the process.

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## References

- [1] Jacangelo JG, Laine JM, Cummings EW, Coté P, Mallevalle J. Influence of feedwater characteristics on ultrafiltration and nanofiltration permeate water quality. Proceedings American Water Works Association Membrane Technology Conference, Baltimore, MD, August 1–4, 1993. p. 293–321.
- [2] Siddiqui M, Amy G, Ryam J, Odem W. Membranes for the control of natural organic matter from surface waters. *Water Res* 2000;34(13):3355–70.
- [3] Fu P, Ruiz H, Lozier J, Thompson K, Spangenberg C. A pilot study on groundwater natural organics removal by low-pressure membranes. *Desalination* 1995;102:47–56.
- [4] Escobar IC, Randall AA. Influence of NF on distribution system biostability. *J Am Water Works Assoc* 1999;91(6):76–89.
- [5] Härmä V. Nanofiltration for water quality improvement in Finnish surface waterworks (Finnish). Licentiate thesis, Helsinki University of Technology, Espoo, Finland, 1999.
- [6] Ikeda K, Nakano K, Ito H, Kubota T, Yamamoto S. New composite charged reverse osmosis membrane. *Desalination* 1988;68:109–19.
- [7] Ventresque C, Turner G, Bablon G. Nanofiltration: from prototype to full scale. *J Am Water Works Assoc* 1997;89:65–76.
- [8] Wiesner MR, Buckley CA. Principles of rejection in pressure-driven membrane processes. In: Mallevalle J, Odendaal PE, Wiesner MR, editors. *Water treatment membrane processes*. New York: McGraw-Hill, 1996. p. 1–16.
- [9] APHA (American Public Health Association). In: Greenberg AE, Clesceri LS, Eaton ED, editors. *Standard methods for the examination of water and wastewater*, 19th ed. Baltimore, USA: Victor Graphics, Inc., 1995.
- [10] Miettinen I, Vartiainen T, Martikainen PJ. Determination of assimilable organic carbon in humus-rich drinking waters. *Appl Environ Microbiol* 1999;33(10):2277–82.
- [11] APHA (American Public Health Association). Greenberg AE, Clesceri LS, Eaton ED, editors. *Standard methods for the examination of water and wastewater*, 18th ed. Baltimore, USA: Victor Graphics, Inc., 1992.
- [12] Lehtola MJ, Miettinen IT, Vartiainen T, Martikainen PJ. A new sensitive bioassay for determination of microbially available phosphorus in water. *Appl Environ Microbiol* 1999;65(5):2032–4.
- [13] Reasoner DJ, Geldreich EE. A new medium for the enumeration and subculture of bacteria from potable water. *Appl Environ Microbiol* 1985;49:1–7.
- [14] Noble PA, Clark DL, Olson BH. Biological stability of groundwater. *J Am Water Works Assoc* 1996;88(5):87–96.
- [15] AWWA M46 (American Water Works Association). *Manual of water supply practices, reverse osmosis and nanofiltration*, 1st ed. Denver, CO, USA: AWWA, 1999.
- [16] Van der Kooij D. Assimilable organic carbon as an indicator of bacterial regrowth. *J Am Water Works Assoc* 1992;84(2):57–65.
- [17] Hem LJ, Efraimsson H. Assimilable organic carbon in molecular weight fractions of natural organic matter. *Water Res* 2001;35(4):1106–10.
- [18] Laurent P, Servais P, Gatel D, Randon G, Bonne P, Cavard J. Microbial quality before and after nanofiltration. *J Am Water Works Assoc* 1999;91(10):62–72.
- [19] Miettinen I, Martikainen PJ, Vartiainen TK. Contamination in drinking water. *Nature* 1996;381:654–5.
- [20] Lehtola MJ, Miettinen IT, Vartiainen T, Martikainen PJ. Microbially available phosphorus, assimilable organic carbon and microbial growth in Finnish drinking waters. Proceedings IWA Paris 2000, 3–7 July 2000.
- [21] Nyström M, Kaipia L, Luque S. Fouling and retention of nanofiltration membranes. *J Membr Sci* 1995;98:249–62.
- [22] Mänttari M, Nuortila-Jokinen J, Nyström M. Evaluation of nanofiltration membranes for filtration of paper mill total effluent. *Filtr Sep* 1997a;34:275–80.
- [23] Schäfer AI, Fane AG, Waite TD. Nanofiltration of natural organic matter: removal, fouling and the influence of multivalent ions. *Desalination* 1998;118:109–22.
- [24] Mänttari M, Nuortila-Jokinen J, Nyström M. Influence of filtration conditions on the performance of NF membranes in the filtration of paper mill total effluent. *J Membr Sci* 1997b;137:187–99.
- [25] Amy G, Cho J. Interactions between natural organic matter (NOM) and membranes: rejection and fouling. *Water Sci Technol* 1999;40(9):131–9.
- [26] Van der Bruggen B, Schaep J, Wilms D, Vandecasteele C. Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration. *J Membr Sci* 1999;156:29–41.