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Nanofiltration flux, fouling and retention in filtering dilute model waters

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Abstract

Fouling of membranes decreases the applicability of the nanofiltration (NF) process, and thus a deeper understanding of membrane fouling is needed. Fouling and retention of different NF membranes by model feed waters was investigated in a laboratory-scale filtration unit. The model waters were composed so as to imitate the characteristics of chemically pre-treated surface water. No differences were seen in membrane flux declines when filtering feed waters containing the studied organic compounds of different characteristics. However, organic matter containing feed waters resulted in remarkably lower flux than the metal ions containing feed waters. An additional decrease in flux was seen when both organic matter and metal ions, especially silica, were present in the feed water. An increased feed water organics concentration increased the retention of organic matter, but the addition of metal ions to organics containing feed water caused a decrease in the retention of both organic matter and conductivity. The different behaviour is most probably caused by the differences in the fouling layers and foulant characteristics as well as by the electroneutrality effect. Generally, it is difficult to change feed water composition to non-fouling, but the operating pH can be used to some extent in optimising membrane performance.

Keywords: Nanofiltration; Model waters; Organic matter; Metal ions; pH

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1. Introduction

Nanofiltration (NF) is one of the most efficient techniques for drinking water quality improvement. However, fouling of the membranes decreases the applicability of NF in water treatment, and a deeper understanding and a better control of membrane fouling are needed for more widespread use of NF.

Fouling of the NF membranes depends on the foulant–membrane and foulant–foulant interactions. These interactions are controlled by the chemical characteristics of foulants and membranes, solution chemistry, operational environment and permeation drag force.

A wide spectrum of feed water components, e.g., dissolved macromolecular organic compounds, weakly soluble inorganic compounds, colloidal and suspended particles and microorganisms contribute to membrane fouling. Several studies have demonstrated that natural organic matter (NOM) plays an important role in membrane fouling in water treatment applications [1–4]. The high molar mass hydrophobic fraction of NOM has generally been found to be responsible for membrane fouling [1–3].

Humic substances, at the most, account for as much as 90% of the aquatic NOM, or more precisely, of the dissolved organic matter (DOM), which is a term used later in this paper. Aquatic humic substances are most commonly further partitioned into humic and fulvic acid fractions. The heterogeneous mixture of aquatic humic substances contains, in addition to various aromatic and aliphatic components, also carboxylic and phenolic functional groups that determine the intensity of the charge of these macromolecules.

The operational environment during NF remarkably affects the charge and other characteristics of the membrane and the fouling material, and thus membrane fouling. Several studies indicate that fouling of polymer membranes decreases with high pH and low salt content of the feed water due to an increased negative

charge of both membranes and DOM, and the consequent increase in mutual electrostatic repulsion [1,2,5,6]. The increased charge also increases the repulsive forces between the functional groups of the DOM molecules, making their conformation more stretched and linear, and consequently the fouling layer becomes more permeable [1,2,5]. Increasing pH also makes humic substances more hydrophilic and thus less prone to attach to the membranes.

Permeation drag through the membrane also affects the rate and extent of membrane fouling, and the optimisation of the process parameters is a crucial factor in fouling mitigation. The higher the flux, the more fouling material is in contact with the membrane surface, and the more extensive is the membrane fouling.

The retention efficiency of NF membranes depends on the size, charge and morphology of the feed water components and the cut-off value and charge of the membrane. High molar mass compounds with the same charge sign as the membranes are retained better than small non-charged or oppositely charged compounds. It should be borne in mind that membrane fouling changes the membrane properties as well as the characteristics of the components in the fouling layer, and thus also affects membrane retention [1,7,8].

Since membrane fouling can deteriorate the performance of the NF process, it is valuable to find out the role of different feed water components in membrane performance. In an existing surface water treatment plant the present chemical water treatment process is a presumable option for pre-treatment in the NF process. Most studies have concentrated on NF fouling by untreated surface water where the feed water characteristics are different from pre-treated surface water. In this study, the fouling of different NF membranes by model feed waters, which imitated chemically pre-treated surface water to some extent, was investigated on a laboratory-scale filtration unit.

The main objective was to find the feed water components or characteristics that are critical to membrane flux decline. In addition, the effects of feed water characteristics on membrane flux and retention were evaluated.

2. Experimental

2.1. Filtration unit and membranes

The laboratory-scale membrane filtration unit used in the study is presented in Fig. 1. Three cross-flow flat-sheet membrane modules were run in parallel with the same feed water. The membrane area and the channel height in each module were 53.0 cm² and 2 mm, respectively. The simultaneously compared membranes in parallel modules were Desal-5 DL, Desal-51 HL, and NF270. The surface layer of all the membranes is made of polypiperazine amide, and the cut-off values are around 300 g/mol (Table 1). Membranes with very similar characteristics were chosen to the study as these membranes were

well-suited for filtration of pre-treated surface waters in a previous study [9].

The membrane sheets were cut into suitable pieces for the modules, and the pieces were pre-treated by soaking them for an hour in 0.1% Ultrasil 10 cleaning solution. The pre-treated membranes were rinsed with and let to soak in distilled water for another hour. Finally, the membranes were rinsed with ultra pure deionised distilled water and stored wet in a refrigerator until use.

2.2. Feed waters

Different model waters were used as NF feed waters in the study. The feed water components and concentrations were chosen to resemble those of chemically pre-treated surface waters. Distilled water with 1.5 mmol/L of NaCl was used as base water for all the feed waters to achieve an appropriate ion content.

A “run” refers to the operation of the NF unit with each tested feed water. The runs consisted of

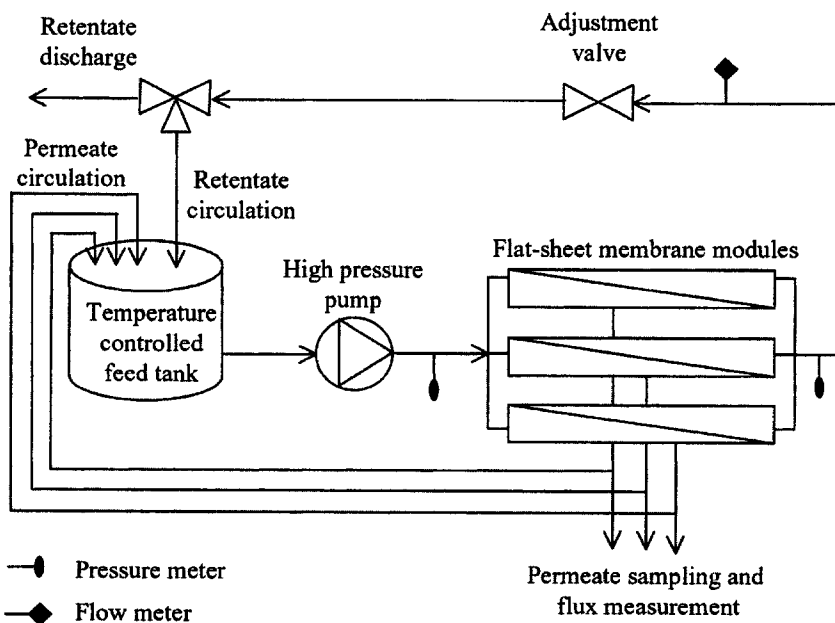


Fig. 1. Schematic picture of the laboratory-scale membrane filtration unit.

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

	Desal- 5 DL	Desal- 51 HL	NF270
Manufacturer	Osmonics	Osmonics	Filmtec
Material	PPZ ^a	PPZ ^a	PPZ
Cut-off, g/mol	150–300	150–300	300
Operating pH range	2–11	2–11	3–10
CaCl ₂ rejection, %	96		
MgSO ₄ rejection, %	96	98	>97
Isoelectric point	3 ^b	3 ^c	<3 ^b
Contact angle, °	30 ^b	52 ^c	29 ^b

^aPolypiperazine amide.

^bMeasured at Lappeenranta University of Technology.

^cHobbs et al. [10].

sequential 1-h stages during which feed water characteristics remained stable. The feed water components were added as base water dilutions to the base water/feed water circulating in the filtration unit in the beginning of each stage. The feed water pH was adjusted after chemical addition either with NaOH or HCl. In the runs with varying pH, the feed water composition remained the same in the different run stages but the pH was readjusted.

NF of organic matter containing feed waters was studied with small organic acids, polystyrene sulphonates and natural fulvic acid. The information of the used organic chemicals is summarised in Table 2 and the TOC concentrations of the feed waters in Table 3. The pH of these feed waters was adjusted to 7.5.

The behaviour of small organic acids in NF was studied with the feed waters containing benzoic acid (BA), butanedioic acid (BDA) and glycyrrhizic acid (GA). These organic components have molar masses close to the membrane cut-off values and similar carboxylic and phenolic functional groups as in natural DOM. These

Table 2
Organic chemicals used

Chemical	Formula	M, g/mol
Benzoic acid (BA)	C ₇ H ₆ O ₂	122
Butanedioic acid (BDA)	C ₁₈ H ₁₄ O ₈	358
Glycyrrhizic acid (GA)	C ₄₂ H ₆₂ O ₁₆	823
Polystyrene sulphonate 1.4 (PSS1.4) ^a	(C ₈ H ₈ O ₃ S) _x .xNa	1,290
Polystyrene sulphonate 17 (PSS17) ^b	(C ₈ H ₈ O ₃ S) _x .xNa	15,200
Mekkojärvi fulvic acid (FA)		5,400

^aPoly(styrenesulphonic acid) sodium salt standard 1400 g/mol.

^bPoly(styrenesulphonic acid) sodium salt standard 17,000 g/mol.

Table 3
Calculated and measured feed water TOC concentrations at the different stages of the runs with organic matter

Feed water	Calculated/measured TOC, mg/L		
	Stage 1	Stage 2	Stage 3
Benzoic acid	1.1/0.9	3.2/2.2	6.3/4.4
Butanedioic acid	1.4/0.9	4.3/1.9	8.6/3.2
Glycyrrhizic acid	0.8/1.1	2.3/2.2	4.7/4.3
Polystyrene sulphonate 1.4 (PSS1.4)	1.0/1.0	3.1/2.6	6.2/4.9
Polystyrene sulphonate 17 (PSS17)	1.0/1.0	3.1/2.4	6.2/4.5
Mekkojärvi fulvic acid	1.0/1.2	3.1/2.6	6.1/4.7

kinds of small organic molecules are most probably left in surface waters after pre-treatment.

The feed waters with polystyrene sulphonates of 1,400 g/mol (PSS1.4) and 17,000 g/mol (PSS17) were used to compare the effect of molar mass on NF of organic matter. The polystyrene sulphonates are reported to correspond somewhat

Table 4

Calculated feed water component additions at the different stages of the runs with Lake Mekkojärvi fulvic acid (FA) and metal ions

	Calculated addition, mg/L				
	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5
FA + Al + Si + Fe	3.8 TOC	+ 0.085 Al	+ 2.4 Si	+ 0.090 Fe	
FA + Si + Fe + Ca	3.8 TOC	+ 2.4 Si	+ 0.090 Fe	+ 26 Ca	
FA + Fe + Al + Ca + Si	3.8 TOC	+ 0.090 Fe	+ 0.085 Al	+ 26 Ca	+ 2.4 Si
FA + Ca + Al + Fe	3.8 TOC	+ 26 Ca	+ 0.085 Al	+ 0.090 Fe	

to natural DOM in high performance size exclusion chromatography analysis [11,12], and thus are assumed to behave similarly in NF too.

The natural DOM containing feed water was made using Lake Mekkojärvi fulvic acid (FA) [11]. FA constitute the fraction of DOM that carries the highest charges and is thus more difficult to remove by traditional surface water treatment than, for example, the humic acid fraction [13, 14]. Accordingly, FA was chosen to represent natural DOM in pre-treated surface water. One should bear in mind that the characteristics of FA in chemically treated surface water would differ from the characteristics of the extracted natural FA used. For example, the main fraction of DOM in pre-treated surface waters has been noticed to have a molar mass of 1000–4000 g/mol, which is slightly smaller than the molar mass of FA [15].

The effect of different metal ions on NF of organic matter containing feed water was studied by adding different inorganic salts, aluminium hydroxide $[Al(OH)_3]$, calcium hydroxide $[Ca(OH)_2]$, ferric sulphate $[Fe_2(SO_4)_3]$ and silica $[SiO_2]$, in different combinations to FA solution (Table 4). These metal ions are generally found in chemically treated surface waters. The pH of these feed waters was adjusted to 7.5.

The performance of NF at different pH was studied using feed waters containing metal ions (M_{pH}), FA (FA_{pH}) and FA and metal ions (FA +

M_{pH}) (Table 5). In the runs M_{pH} and FA+ M_{pH} the operating pH was decreased from 10 to 3 in the sequential stages and in the FA_{pH} run the pH was increased from 3 to 10.

2.3. Operation

New, pre-treated membranes were used in each test run. When installed in the filtration unit, the membranes were rinsed with distilled water for 10 min and then pressurised at 15 bar for 30 min to assure membrane wetting. Fresh base water was added and the initial pure water flux (PWF) was measured at a constant cross flow velocity (CFV) of 1.0 m/s using a net driving pressure (NDP) of 7 bar at 25°C. The NF unit operation with the feed waters was carried out at the same operating conditions as for the PWF measurements, and both retentate and permeate flows were circulated back to the feed water container. The volume of the circulating feed water was kept constant at 20 L.

NDP, feed water temperature and retentate flow were monitored continuously by a data logger. Permeate flow was measured volumetrically three times at the end of each 1-h test stage. Feed water pH was monitored continuously, and the readings were taken after permeate flow measurements.

At the end of the run the membranes were

Table 5
Calculated and measured feed water compositions in the runs at varying pH

Feed water	Conductivity, mS/m	TOC, mg/L	Al, mg/L	Ca, mg/L	Fe, mg/L	Si, mg/L
M_{pH}, feed containing metal ions:						
Calculated composition			0.085	26	0.090	2.35
Measured composition at:						
pH 3	76.9		0.028	20.2	0.04	<0.050
pH 4	32.4		0.020	20.1	0.022	<0.050
pH 5	29.2		0.011	20.0	0.014	<0.050
pH 6	28.5		0.008	19.9	0.014	<0.050
pH 7	28.0		0.016	20.2	0.014	<0.050
pH 8	26.9		0.02	19.9	0.021	<0.050
pH 9	24.4		0.02	19.4	0.025	<0.050
pH 10	25.5		0.020	17.3	0.055	<0.050
FA_{pH}, feed containing Mekkojärvi fulvic acid:						
Calculated composition		3.8				
Measured composition at:						
pH 3	82.8	2.6				
pH 4	31.7	3.0				
pH 5	27.7	3.2				
pH 6	27.2	3.4				
pH 7	26.7	3.4				
pH 8	26.1	3.5				
pH 9	25.6	3.7				
pH 10	26.5	3.9				
FA+M_{pH}, feed containing Mekkojärvi fulvic acid and metal ions:						
Calculated composition		3.8	0.085	26	0.090	2.35
Measured composition at:						
pH 3	43.4	3.5	0.032	21.6	0.144	0.058
pH 4	23.9	3.4	0.026	20.5	0.089	0.056
pH 5	23.2	3.3	0.025	20.2	0.077	0.051
pH 6	23.0	3.2	0.023	20.2	0.072	0.050
pH 7	23.2	3.1	0.023	19.8	0.071	<0.050
pH 8	24.4	3.0	0.024	19.0	0.072	<0.050
pH 9	24.7	2.9	0.023	18.8	0.074	<0.050
pH 10	31.6	2.6	0.025	18.1	0.086	<0.050

membranes was measured with fresh base water. The resulting difference in PWF compared to the initial state was assumed to depend on fouling.

The cleanliness of the membrane filtration unit was inspected by conductivity and UV absorption at 254 nm (UV_{254}) of rinsing waters between each run. The pilot unit was chemically cleaned whenever needed.

2.4. Evaluation of the NF performance

The fluxes of the membranes were evaluated using base water values as PWF and the feed water values as operational flux. Fluxes were normalised to a standard temperature ($T = 25^\circ\text{C}$) by following the instructions of the manufacturers to overcome the problem of slightly varying operation temperatures (base water: $T = 24.3 \pm 1.5^\circ\text{C}$; feed water: $T = 24.7 \pm 0.3^\circ\text{C}$). The osmotic pressure was considered negligible in the calculations due to the dilute feed water solutions.

Retention of the membranes and the effect of feed water characteristics on retention were evaluated by taking both feed water and permeate samples at the end of each stage. The retention was calculated as percentage removals (R) by comparing the concentrations of the component in permeate (C_p) and feed water (C_f) as follows:

$$R = (1 - C_p/C_f) * 100\%$$

2.5. Water analysis

All the feed water and permeate samples were characterised by pH, conductivity and UV_{254} . In addition, feed waters and permeates containing organic matter were tested for total organic carbon (TOC) and feed waters containing inorganic salts were tested for specific cations.

The following tests were performed according to national standards: pH, conductivity, and TOC. TOC was measured by a Shimadzu TOC-5000A analyser by the combustion–nondispersive infra-

red gas analysis method. UV absorption was measured according to the APHA method [16]. The iron content was analysed by an atomic absorption spectrophotometer (Varian 400P) and the aluminium, calcium and silica concentrations were measured by an inductively coupled plasma atomic emission spectrometer (Varian Liberty).

3. Results and discussion

3.1. NF membrane fouling and retention of organic matter

The comparability of the runs with pure organic matter containing feed waters was acceptable with respect to feed water pH, conductivity and TOC (Table 3), which should remain stable in parallel runs. Also, the quality of the base water used in the PWF measurement was stable.

The measured feed water TOC concentrations were generally lower than the calculated concentrations (Table 3), especially at the third stage of the run. This indicates that some organic matter was removed from the circulating feed water stream due to accumulation on the membranes or on the membrane filtration unit.

The PWF decline caused by the filtration of the studied solutions of organic compounds was on an average $3 \pm 3\%$, $7 \pm 3\%$ and $3 \pm 3\%$ with the Desal-5 DL, Desal-51 HL and NF270 membranes, respectively. None of the organic compounds used resulted in any remarkable membrane flux decline at low concentrations in the short-term test runs. A negligible effect was seen in the fluxes between the different stages of the individual runs (average change in flux $\sim 0 \pm 3\%$). Childress and Elimelech [17] also noticed that humic acid had very little effect on the flux in short-term NF despite the fact that humic substances adsorbed easily on the membrane surface and made them more negatively charged.

The TOC retention of the small organic acids at the highest studied feed water TOC con-

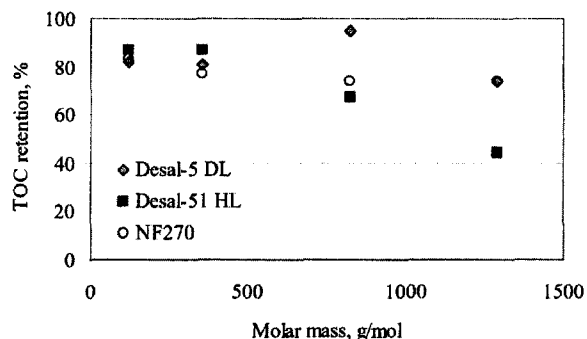


Fig. 2. TOC retention of the low molar mass organic compounds by the tested NF membranes (NDP = 7 bar, CFV = 1.0 m/s, pH = 7.5, $T = 25^{\circ}\text{C}$).

centration (third stage) varied between 67–95%. Surprisingly, no correlation was found between the molar mass of the small organic acids and the retention efficiency (Fig. 2). The retention of benzoic acid was high (79–90%), even though its molar mass is smaller than the membrane cut-off. The retention of the organic molecules with molar masses close to the membrane cut-off can be affected remarkably by charge and hydrophobicity effects, and this could explain the higher removals than expected according to molar masses. Small molecules may also aggregate with each other forming bigger, less permeable molecules.

The TOC retention of the polystyrene sulphonates (PSS) containing feed waters at the highest tested feed water TOC concentration (third stage) varied between 44–74% for PSS 1.4 and between 92–95% for PSS 17. The TOC retention of natural Lake Mekkajärvi FA was 93–94% at the highest used feed water TOC concentration (third stage). High retention was expected as the molar masses of these compounds are remarkably higher than the membrane cut-offs. On the basis of this assumption, the retention was surprisingly low, especially for the lower molar mass compound (PSS 1.4). The incomplete retention of high molar mass compounds was most probably due to the presence of low molar mass organics in these feed waters.

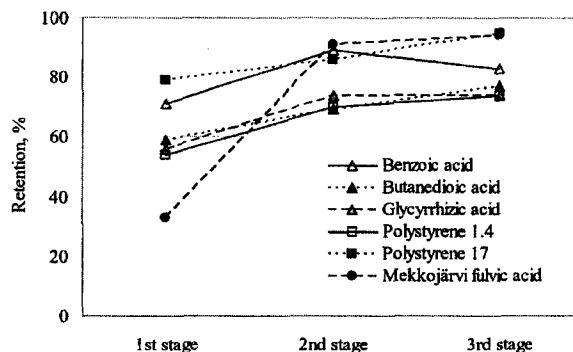


Fig. 3. TOC retention of the NF270 membrane at different stages of the runs with organic matter containing feed waters (NDP = 7 bar, CFV = 1.0 m/s, pH = 7.5, $T = 25^{\circ}\text{C}$).

The TOC retention of all the tested organic components by the NF membranes tested increased by 10–68% as the concentration of the feed water was increased approximately from 1 to 4.5 mg TOC/L. This phenomenon is illustrated in Fig. 3 with the NF270 membrane. It is possible that at high concentration small molecules form bigger, less permeable complexes due to more contact with other molecules and decreased intermolecular charge repulsion. On the other hand, the accumulation of a foulant layer on the membrane during the course of the run hinders DOM transport through the membrane. The adsorption of organic foulants on the membrane surface may also increase the negative charge of the membrane surface, and thus increase the repulsion forces and consequently retention. Water molecules are small and almost without charge, and they pass through the fouled membrane more easily than DOM molecules, and thus practically no flux decline was experienced. A similar small effect on membrane flux but a remarkable retention increase with increasing TOC concentration was reported by Visvanathan et al. [18]. Schäfer et al. [3] noticed that the organic matter retention increased as the run proceeded and the membranes became fouled.

3.2. NF membrane fouling and retention of organic matter and metal ions

The comparability of the runs using organic matter and metal ions containing feed waters is acceptable with respect to feed water pH and TOC and metal ion concentrations. However, the calcium dose was so much higher than the other metal ion additions that it increased the feed water conductivity almost to double (approximately from 16 mS/m to 28 mS/m). Thus, the membrane flux reduction and the conductivity retention decline in these stages of the test partially resulted from the high ion content. The feed water pH and TOC concentrations were also in accordance with the second stage of the run with Lake Mekkojärvi FA, where FA was used at a comparable concentration without metal ions. The quality of the base water used in the PWF analysis was stable.

The measured feed water TOC concentrations were 19–38% lower than the calculated TOC concentrations. The measured aluminium, calcium, iron and silica concentrations in the feed waters were on an average 92%, 27%, 16% and ~100% lower than the calculated additions. This feed constituent disappearance indicates that material was removed from the circulating feed water stream by accumulation on the membranes and membrane filtration unit either by fouling or precipitation. The TOC disappearance was the highest (31–38%) after the addition of calcium to the feed water, indicating calcium–DOM complexation. All the tested metal ions were in the feed waters at concentrations high enough for precipitation.

The runs with FA and metal ions containing feed waters resulted on average in a PWF decline of 20±14%, 9±3% and 9±4% with the Desal-5 DL, Desal-51 HL and NF270 membranes, respectively. These PWF declines are higher than seen with pure FA containing feed water (0%, 5% and 4% with the Desal-5 DL, Desal-51 HL and NF270 membranes, respectively). The average

changes in the operational fluxes after the addition of aluminium, calcium, ferric and silica components to FA solutions were -2%, -3%, -2% and -8%, respectively. Accordingly, the addition of silica to feed water seemed to be the most harmful to membrane flux.

The phenomenon of organic and inorganic compounds fouling more when together than alone has been noticed by several authors [2,3,6,7]. The cation acts as a bridge between the membrane surface and the free negatively charged functional groups of the humic substance or with intermolecular bridging [2,7]. As a consequence, the total charge of membrane and humic macromolecules decreases. The mutual electrostatic repulsions decrease and the foulant layer thicknesses and densities increase [1,2,5]. A dense fouling layer has been noticed to cause a higher flux decline than a high deposition of loose foulant material [3].

The feed waters containing a mixture of FA and metal ions resulted in most cases in a lower retention of TOC and conductivity than when using a pure FA solution (Table 6). Visvanathan et al. [18], Yoon et al. [7] and Schäfer et al. [8] also noticed a decreased DOM retention at increased divalent cation concentration.

Table 6
TOC and conductivity retention of the tested membranes with Lake Mekkojärvi fulvic acid (FA) and metal ions and pure FA containing feed waters

Feed water	Desal-5 DL	Desal-51 HL	NF270
TOC retention, %			
FA+ metal ions, averages	70 ± 14	82 ± 9	84 ± 3
FA, second stage	89	91	91
Conductivity retention, %			
FA + metal ions, averages	42 ± 14	66 ± 20	60 ± 16
FA, second stage	84	87	92

The reason for a lowered retention in the presence of metal ions in organic matter containing feed water is probably due to charge neutralisation. A lower charge repulsion between the membrane and the organic molecules enables organic molecules to pass the membrane easier. In addition, the lower charge of organic molecules makes their conformation denser and smaller and thus they pass more easily through the membrane.

3.3. Effect of pH on NF membrane fouling and retention

The comparability of the pH runs is good with respect to the feed water conductivity and TOC at the pHs other than 3 where the conductivity was remarkably high due to the high concentration of H^+ ions (Table 5). Also the quality of the base water used in the PWF measurements was stable.

In the runs with Lake Mekkojärvi FA containing feed waters (FA_{pH} and $FA+M_{pH}$), the measured feed water TOC concentration was 68% of the calculated TOC concentrations in the beginning of the runs and the concentration increased to the calculated concentration as the run proceeded. The phenomenon was most probably due to the soaking of the accumulated TOC from the membrane filtration unit by pH changes. However, the TOC increase was so small that it did not disturb the comparability of the runs. The measured aluminium, calcium, iron and silica concentrations in the feed waters containing metal ions (M_{pH} and $FA+M_{pH}$) were lower than calculated (Table 5). This feed constituent disappearance indicates that material was removed from the circulating feed water stream by accumulation or precipitation on the membranes and the membrane filtration unit. The effect of pH on the metal salt solubility was seen from the variable detected metal ion contents.

The run conducted with metal ions containing feed water (M_{pH}) showed a higher operational flux than the organic matter (FA_{pH}) or organics

and metal ions ($FA+M_{pH}$) containing feed waters with all the tested membranes. This trend is shown in Fig. 4 with the NF270 membrane. The average operational flux decline from the M_{pH} run was 23%, 29% and 9% in the FA_{pH} run and 52%, 35% and 21% in the $FA+M_{pH}$ run for the Desal-5 DL, Desal-51 HL and NF270 membranes, respectively. Thus, the presence of organic matter in feed water caused a decreased membrane flux and the metal complexation with DOM further decreased the flux.

The $FA+M_{pH}$ feed water, the best simulation of real pre-treated surface water, showed the highest flux at pH 5 with the tested membranes. Fluxes decreased gradually when the pH decreased or increased, the maximum decrease being 15% at pH 10. With the M_{pH} feed water, the operational fluxes decreased gradually as feed pH was increased from pH 3, the maximum flux decrease being 13% at pH 10. With the FA_{pH} feed water the fluxes of the tested membranes showed a quite different pH behaviour than the other feed waters. The Desal-51 HL and NF270 membranes showed the highest fluxes at pH 5, from where the flux decreased gradually as the pH was decreased, and showed the lowest fluxes at pH 6, from where the fluxes increased as the pH was increased. The behaviour of the Desal-5 DL membrane with the FA_{pH} feed water could not be analysed due to membrane failure during the tests. The pH dependence of the flux is shown in Fig. 4 with the NF270 membrane.

The effect of pH on TOC retention was small with the $FA+M_{pH}$ feed water on all the membranes (average retention $93\pm 2\%$), but a slightly higher retention was seen around pH 6–7. The TOC retention with the FA_{pH} feed water was stable at 91–92% over the tested pH range with the Desal-51 HL, and with the NF270 the retention decreased from 90–92% to 85–87% at pH 5–6.

In the retention comparisons the low retention at pH 3 was not comparable due to the remarkably higher feed water conductivity. The

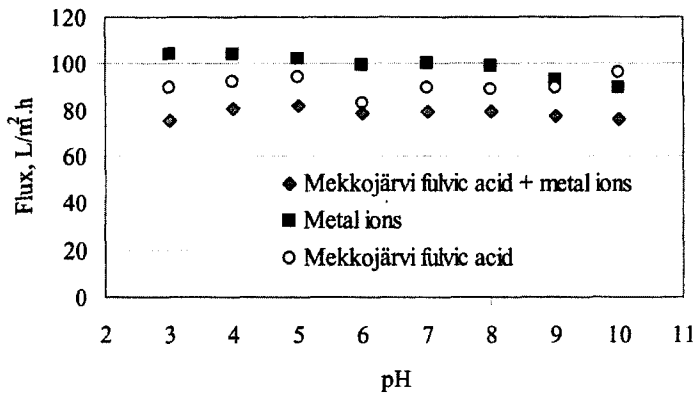


Fig. 4. Fluxes of the NF270 membrane with the different feed waters at varying pH (NDP = 7 bar, CFV = 1.0 m/s, $T = 25^{\circ}\text{C}$).

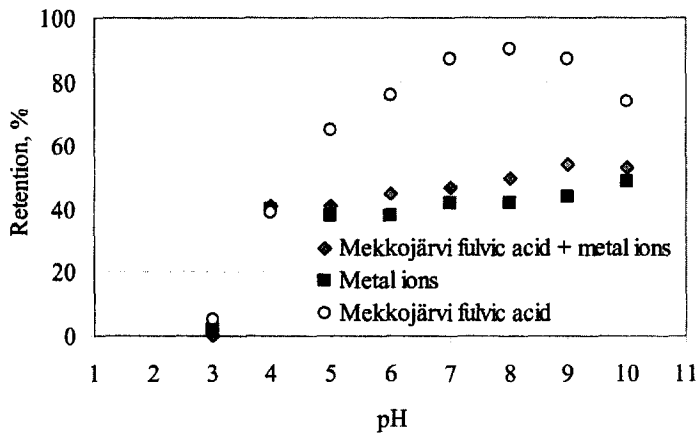


Fig. 5. Retention of conductivity with different feed waters at varying pH using the NF270 membrane (NDP = 7 bar, CFV = 1.0 m/s, $T = 25^{\circ}\text{C}$).

conductivity retention of the M_{pH} and $\text{FA}+M_{\text{pH}}$ feed waters was the lowest at pH 5–6, and it increased as the pH decreased or increased with all the tested membranes. The retention increase at high pH may be explained by the precipitation of metal ions. The aggregation of metal salts or metal–DOM complexes on the membrane surface at high pH also explains the flux decline at high pH with the M_{pH} and $\text{FA}+M_{\text{pH}}$ feed waters. The conductivity retention of the FA_{pH} feed water did not show such smooth changes with pH as the metal ions containing feed waters. The conductivity retention of the FA solution decreased from a maximum retention of 94% by 22% with the Desal-51 HL membrane as the pH increased from 5 to 6. Conductivity retention was stable and high at pH below 5 and increased from pH 6

up to 8 and decreased again above that. With the NF270 membrane the conductivity retention increased steadily up to pH 8 (90% retention) and then decreased at a pH above that. The pH dependence of the conductivity retention with the tested feed waters is shown in Fig. 5 with the NF270 membrane.

3.4. Rating of the tested membranes

The fluxes of the membranes differ remarkably despite their very similar characteristics. The PWFs of the membranes increase in the following order — Desal-5 DL, Desal-51 HL and NF270. The rating of the membranes remains the same if the average operational fluxes are used in the evaluation.

With the organic matter containing feed waters, the Desal-51 HL membranes, and with organic matter and metal ions containing feed waters, the Desal-5 DL membranes experienced the most fouling. The NF270 membrane generally showed low fouling tendency with the tested feed waters.

No remarkable and consistent differences were seen in the organic matter and conductivity removal characteristics when comparing the tested membranes.

In summary, the NF270 membrane performed the best with the tested model waters when evaluating productivity, fouling and retention characteristics.

4. Conclusions

All the tested NF feed water components caused some membrane fouling. As these components are commonly found both in natural and treated waters, it seems impossible to totally remove the fouling components from the NF feed water.

None of the tested organic molecules with different characteristics caused any remarkable flux decline at dilute concentrations in these short-term tests when alone in the feed water. However, organic matter seems to have a crucial influence on flux, since the organic matter containing feed water resulted in remarkably lower flux than only inorganic salts containing feed water. An additional decrease in flux was seen as both organic matter and metal salts, especially silica, were present in the feed water.

An increased feed water organics concentration caused an increased retention of organic matter, most probably due to the formation of a denser DOM foulant layer on the membrane surface and DOM molecule aggregation to bigger, less permeable particles. No change in the membrane flux was noticed as the feed DOM concentration increased. The addition of metal

ions to Mekkojärvi FA containing feed water caused, in most cases, a decrease in the retention of organic matter and conductivity, even when the flux declines indicated membrane fouling.

TOC retention of polystyrene sulphonates increased by 29% when the molar mass increased from 1,300 g/mol to 15,000 g/mol. The difference in retention is surprising, as both molecules should have been totally removed since the NF membrane cut-offs were much smaller than the size of the lower molar mass polystyrene sulphonate. On the other hand, the retention of small organic acids was higher than expected according to their molar mass compared to membrane cut-offs. This was explained by the effects of the membrane/organic matter charge and hydrophobicity.

The feed water and membrane characteristics were noticed to affect the pH dependency of the NF process remarkably. Generally, it is difficult to change the composition of the feed water to less fouling, but if the composition is known, the effect of operating pH can be used to some extent in optimising the NF productivity and retention.

The behaviour of the tested membranes indicates that, despite their similar characteristics, the membranes are different, and the best alternative for each application should be found through test runs.

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