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Efficiency of various chemical cleanings for nanofiltration membrane fouled by conventionally-treated surface water

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Abstract

Nanofiltration systems are generally cleaned chemically. The optimal choice of the cleaning agent is a function of membrane material and foulant in a complex manner. This study evaluated the cleaning efficiency and effects of several cleaning agents on NF255 nanofiltration membrane. The nanofiltration pilot plant was fed with conventionally-treated surface water from a water treatment plant in southern Finland. Fouled membranes were cleaned weekly with different chemicals and procedures, and the cleaning efficiencies were compared in terms of flux recoveries and foulant removals. On the basis of the cleaning chemical analysis, the fouling material consisted of biofouling, organic deposits and metal complexes. In these circumstances, alkaline cleaners with chelatants resulted in the most efficient cleaning both in terms of flux recovery and foulant removal. Alkaline cleaning modified the membrane and improved the flux substantially in comparison to the virgin state. The results demonstrate that the choice of chemical cleaning agent is critical to cleaning efficiency, both technically and economically. The same flux recovery could be reached either by a single cleaning phase or by three sequential cleaning phases. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Chemical cleaning; Nanofiltration; Membrane; Surface water treatment; Cleaning agents

1. Introduction

The operation of pressure-driven membrane processes is often limited by fouling. Adequate pre-treatment and membrane selection may slow fouling, but the membranes become fouled eventually. Therefore, membrane cleaning is an essential step in maintaining the performance of the membrane process.

Chemical cleaning is the most common method to clean nanofiltration (NF) membranes. The cleaning should not only be effective against several foulants,

but gentle in repairing the membranes to maintain and restore their characteristics. The optimal choice of the cleaning agent is a function of membrane material and foulant in a complex manner. Other aspects of chemical cleaning concern mainly temperature, chemical concentration, pH, pressure and flow, and time.

The selection of the appropriate agent for a particular cleaning situation is critical. Fu et al. [1] noticed that two NF membranes with different properties required different cleaning processes even when fed by the same feedwater. Thus, the characteristics of the membranes affected the characteristics of the foulant layer. Some cleaning agent–membrane combinations are incompatible and will result in irreversible loss of flux or solute rejection properties. In addition, the use of non-optimal cleaning agents and conditions incurs

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unnecessary costs through chemical over-use or by reducing the membrane lifetime. Several authors have studied the applicability of different cleaning chemicals in specific membrane filtration applications. Reviews of different cleaning methods can be found in Deqian [2], Trägårdh [3] and Ebrahim [4].

The findings of Bartlett et al. [5] suggest that there is a certain cleaning agent concentration and temperature for optimal cleaning. Generally, increased temperatures increase the cleaning efficiency as well; however, the sensitivity of membrane materials usually prohibits the use of high temperatures. An increased cross-flow velocity of the cleaning agent in turn seems to have no effect on cleaning performance, and increasing the *trans*-membrane pressure may even decrease the cleaning efficiency [5]. The time required for efficient cleaning varies owing to the foulant deposited and the employed cleaning process. In some applications, a cleaning time of 15 min is enough [6], while in other cases membranes need cleaning for 1 h [7] or even longer [8] to reach their maximal cleaning effect.

Some cleaning agents significantly increase the membrane flux in comparison to the virgin state. Nyström and Zhu [9] suggest that cleaning may increase the membrane flux partly by ridding the pores of the material that is left from the membrane preparation process, and partly by making the pore surfaces more hydrophilic and charged by the adsorption of the agent. Increased hydrophilicity makes the chemical bonds between the water molecules and surface groups of the membrane stronger, thus, reducing the foulants' possibilities to displace water molecules and adhere on the membrane [10]. An increased charge of the membrane increases the electrostatic repulsion between the active sites of the membrane, and thus, makes the membrane more open [11].

An increased charge of the membrane also increases the repulsive forces between the membrane and similarly charged foulants. Most organic foulants are negatively charged in aqueous solutions, and thus, the introduction of negative charges by anionic surfactants reduces fouling efficiently [12]. In addition, a high pH makes the natural organic matter (NOM) fouling layer more susceptible to cleaning agents by making the conformation of NOM more linear and the foulant layer looser and sparser [13].

A lack of fundamental knowledge of membrane cleaning as well as the variety of membrane and

foulant characteristics in applications reduces the applicability of published studies in different situations. In addition, most papers concerning membrane cleaning deal with ultra- and micro-filtration or reverse osmosis (RO) membranes, and little is published about the cleaning of NF membranes. As a consequence, further research is usually needed to find an ideal cleaning procedure for each application.

This study was conducted to compare the cleaning efficiency of several cleaning agents on one NF membrane fouled by conventionally-treated surface water. The cleaning efficiency of certain agents as well as total cleaning procedures containing several phases were evaluated. The deposits removed by different cleaning agents were also analysed and the effects of cleanings on membrane permeability, fouling and retention characteristics were evaluated.

The results demonstrate that the choice of cleaning agent is critical to cleaning efficiency: the same cleaning result could be reached either by a single phase cleaning or by three sequential cleaning phases. In the studied cases, alkaline cleaners with chelatants resulted in the most efficient cleaning both in terms of flux recovery and foulant removal. Alkaline cleaning modified the membrane, and improved the flux substantially in comparison to the virgin state.

2. Experimental

2.1. Nanofiltration pilot process

Two similar NF pilot processes were run in parallel in the Espoo City Waterworks (ECW) in southern Finland. The pilot processes were fed with the product water of the ECW. The process in the ECW consists of chemical coagulation with polyaluminium chloride, dissolved air flotation, and rapid sand filtration. Raw water is drawn from a small lake. The temperature of the NF feedwater fell from 18.6 to 1.7°C during the test period (Fig. 4), but the other feedwater characteristics did not change to such a degree. The average values of conductivity and organic content (total organic carbon, TOC) with their standard deviation were 14.8 ± 3.22 mS/m and 2.7 ± 0.32 mg/l, respectively.

A schematic view of the nanofiltration pilot plant is presented in Fig. 1. The array of the plant is two-staged, and part of the retentate from the final

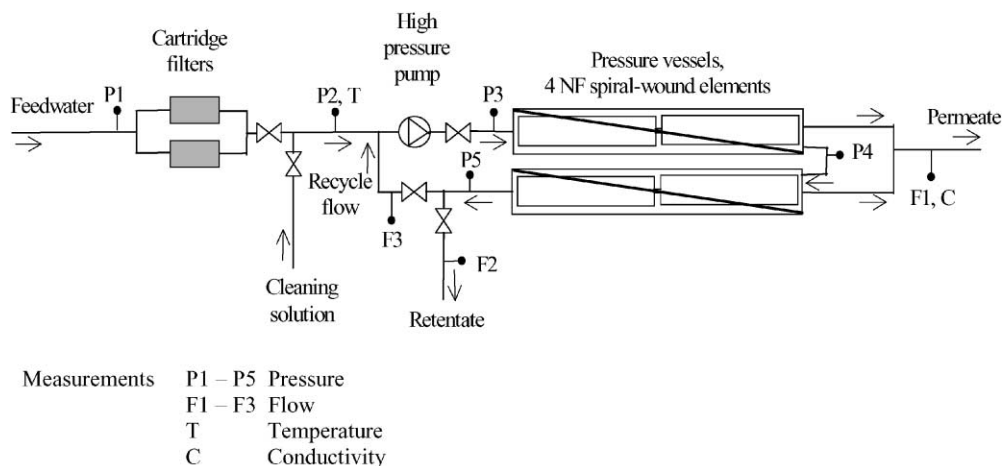


Fig. 1. Schematic diagram of nanofiltration pilot process.

stage can be circulated back to the feedstream of the pilot to enhance the recovery of the plant. Operation pressures and flows as well as the feedwater temperature and conductivity of the permeate are measured from the locations indicated in Fig. 1. The readings were collected by a data logger every 15 min.

The pressure vessels in both stages house two spiral-wound membrane elements with nominal dimensions of 9.9 cm in diameter and 101 cm in length. The same membranes, Filmtec NF255-400 by DOW Liquids Corporation, were used during the whole experiment. The active surface of the membranes is made of polypiperazineamide and the molecular weight cut-off of the membrane is approximately 200–300 Da. The total membrane area of each NF pilot plant was $4 \times 7.7 \text{ m}^2$.

The pilot process was run 1 week between cleanings. During the test period feed pressure, recovery and feed channel flow were kept constant at 8 bar (corresponding to 7.3 bar net driving pressure), 80% and 1300 l/h, respectively. Partial concentrate circulation back to the feed stream was needed to achieve the operation parameters. The filtration process was heavily loaded during the test run, to ensure sufficient fouling between the cleanings.

2.2. Cleaning procedure

Cleaning with each cleaning agent was performed twice, once with both parallel nanofiltration pilots.

The parallel cleanings were conducted either on the same day or on sequential days to ensure similar fouling conditions. A preliminary study with six parallel cleanings indicated that the cleaning efficiencies are so stable (average total flux recovery = 1.46, S.D. = 0.04), that two parallel tests give a reliable picture of each cleaning.

The cleaning scheme of the study is presented in Table 1. The table lists the tested cleanings with chemical concentrations and pHs in the applied solutions. The chemicals were chosen according to the membrane manufacturer's recommendations, and they were either of technical or laboratory grade. The chemical concentrations in the solution were determined so that the applicable pH range of the membrane (2–11) was not exceeded.

In cleanings 2–7, acidic cleaning chemicals were compared, and acidic cleaning was performed first. To ensure the standard membrane condition in the beginning of each test run, acidic cleaning was followed by a standard alkaline cleaning. In cleanings 1 and 10–13, alkaline cleanings were compared, and alkaline cleaning was performed first. During cleanings 8–10, different cleaning procedures were tested. In all cleaning tests, care was taken to ensure similar flux conditions before each test run.

The cleaning solutions were made in 100 l of permeate water, and heated to 25°C. The cleaning solutions were introduced to the membranes at almost zero pressure and low flow rate (600–800 l/h), and

Table 1
Cleaning scheme and cleaning solutions' characteristics

Cleaning no.	Phase	Solution	pH
1	1st	0.06% NaOH	12.2
	2nd	1.5% Citric acid	2.5
2	1st	1.6% Citric acid	2.2
	2nd	0.2% Na ₄ EDTA	10.8
3	1st	0.8% Citric acid and 0.1% oxalic acid	2.1
	2nd	0.2% Na ₄ EDTA	10.9
4	1st	0.2% Oxalic acid	1.9
	2nd	0.2% Na ₄ EDTA	10.9
5	1st	0.3% HCl	2.0
	2nd	0.2% Na ₄ EDTA	10.8
6	1st	1.0% Na ₂ S ₂ O ₄	N.D. ^a
	2nd	0.2% Na ₄ EDTA	10.8
7	1st	1% Ultrasil 73 ^b	2.4
	2nd	0.2% Na ₄ EDTA	10.8
8	1st	0.3% HCl	2.0
	2nd	0.003% NaOH and 0.05% Na ₄ EDTA	10.8
9	1st	0.3% HCl	2.0
	2nd	0.1% Na ₅ P ₃ O ₁₀ and 0.2% Na ₄ EDTA	10.9
10	1st	0.1% Na ₅ P ₃ O ₁₀ and 0.2% Na ₄ EDTA	10.9
11	1st	0.003% NaOH and 0.05% Na ₄ EDTA	10.9
	2nd	0.3% HCl	2.1
	3rd	0.003% NaOH and 0.05% Na ₄ EDTA	10.9
12	1st	0.2% Na ₄ EDTA	11.0
	2nd	0.2% Na ₄ EDTA	11.0
13	1st	0.1% Ultrasil 141 ^c	11.0

^a N.D.: not determined.

^b Contains citric acid, lactic acid and alkyl benzosulphone acid.

^c Contains bases, tensides and organic and inorganic chelatants.

the first 40 l (first-flush) of solution was run through the membrane system to the sewerage. The rest of the solution was circulated in the membrane system for 10 min at low flow rate (800–1000 l/h) and for 15 min at high flow rate (1800–2000 l/h). The feed pressure was kept so low during the cleaning procedure that minimal permeate was produced. The recycling valve was totally closed during the cleaning procedure. After chemical cleaning, the membranes were rinsed with permeate water at low flow rate until the conductivity of the permeate was returned almost to its normal value, and then for 5 min at high flow rate. The procedure was repeated with the next cleaning agent(s).

2.3. Evaluation of cleaning efficiency

The criterion to assess the cleaning efficiency of each cleaning solution and total cleaning procedure was the flux recovery of the NF process. Total cleaning refers to the total cleaning procedure applied in a certain cleaning test. Flux recovery is defined according to Eq. (1):

$$\text{flux recovery} = \frac{J_{wc}}{J_{wi}} \quad (1)$$

where J_{wc} is the flux after the application of a certain cleaning solution or total cleaning procedure and J_{wi} the flux of the virgin, unfouled membrane. The flux

used in the recovery calculations was measured with heated permeate water (+20°C) at 5 bar feed pressure and 50% recovery (which corresponds to an average recovery of approximately 15% in one membrane element). No circulation was applied during these measurements. The standardised permeate fluxes were determined from the virgin membranes (J_{wi}), after each week's run (J_{wf}), and after each cleaning phase (J_{wc}).

The fouling of the membranes after 1-week run was evaluated by the fouling ratio, which is calculated according to Eq. (2):

$$\text{fouling ratio} = \frac{J_{wf}}{J_{wi}} \quad (2)$$

The cleaning chemical characteristics and foulant removal efficiency of the cleanings were assessed by analysing the cleaning solutions. The virgin, first-flush and circulated cleaning solutions were analysed for pH, turbidity, colour, total solids (TS) and cations.

The organic matter content (TOC and absorption of UV₂₅₄ light), pH, alkalinity, hardness, and ion content of the permeate water were analysed before and after cleaning to evaluate the effect of the cleaning on the selectivity properties of the membranes. Permeate conductivity was monitored continuously by conductivity meters (Bürkert 8225). The disinfection capability of the total cleaning was analysed by a heterotrophic plate count (HPC) of the permeate and retentate samples before and after cleaning. After cleaning, the process was run for 1 h before samples were taken. The NF feedwater was analysed regularly for the same parameters as permeate during the study period.

The TOC, pH, conductivity, alkalinity, hardness, TS and HPC analyses were conducted according to national standards. The UV₂₅₄ absorption was conducted according to the American Standard Methods, with the exception that a 10-min centrifugation at 4000 rpm was used instead of filtering as sample pre-treatment. Ions were analysed according to accredited techniques, anions by ion chromatography and cations by inductively coupled plasma atomic emission spectrometry, or by mass spectrometry. The water samples for the cation analyses were filtered (0.45 mm) and acidified by ultra-pure nitric acid in the field.

3. Results and discussion

3.1. Comparability of the cleaning tests

The variation in feedwater organic and inorganic content was so slight that the characteristics of the fouling material can be assumed to have remained stable during the test period. However, the amount of fouling varied during the study. A preliminary study suggested that the experienced variation in fouling does not significantly affect the cleaning performance (flux recovery standard deviation 2.8% corresponding to a fouling ratio standard deviation of 10.9%).

As the flux recoveries and fouling ratios are determined from the measurements made with heated permeate water, the variability of the permeate quality may have affected the results. The conductivity, pH and alkalinity of the permeate water increased from 5.8 to ~16.0 mS/m (Fig. 3), from 5.8 to 6.4 and from 0.07 to 0.19 mmol/l, respectively during the test period. The organic content of the permeate remained below the detection limit of both the TOC analyser (0.3 mg/l) and spectrophotometer (absorbance 0.005) throughout the whole test period. As the ion content of the permeate increased, the measured flux recoveries may be lower than they would have been with permeate water of the same quality as in the beginning of the study. However, the flux recoveries remained stable throughout the experiment.

3.2. Flux recoveries in total cleanings

The performances of total cleaning procedures are presented as flux recoveries in Fig. 2. Cleaning 1 was performed on a virgin membrane after normal running, and it increased the flux by approximately 50%. The second cleaning increased the flux even more, by 100%, in comparison to the virgin state. In cleanings 2–12, fluxes recovered uniformly to twice the flux of a virgin membrane. The studies of Mänttari [14] with a membrane similar to the one used in this study (NF200) support our findings: cleaning improved the pure water flux of the membrane by 26%.

The membrane permeability reached a stable state, and it was not improved in the cleanings after cleaning 2. Nonetheless, in subsequent cleanings 3–12, the increased flux was recovered. Since the cleanings modified the membranes and made them more permeable,

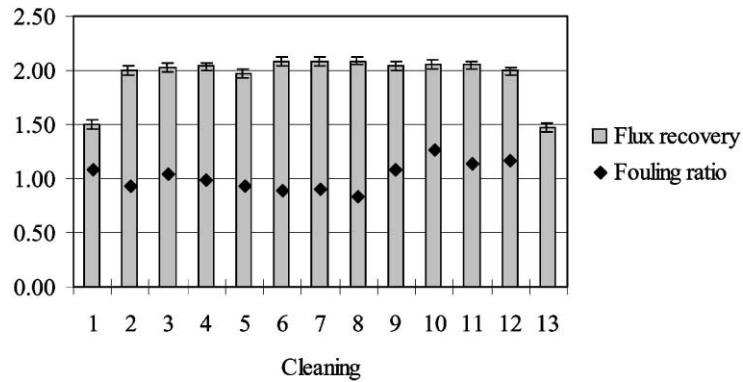


Fig. 2. Flux recoveries in different cleaning procedures and subsequent fouled membrane flux in comparison to the virgin membrane flux (fouling ratio).

the state of the virgin membrane before run and cleaning number 1 is not equal to the other cleanings. Thus, the poor cleaning efficiency in cleaning 1 is not totally comparable to other cleanings. However, cleaning 13, after membrane modification by cleaning agents, recovered the flux only to a level similar to cleaning 1.

One interesting question is whether the differences in the membrane fouling in sequential runs are more related to changing feedwater quality or to the effects of different cleaning chemicals. According to statistical analysis examined by linear regression, the changes in feedwater quality did not explain the variability of membrane fouling very well ($r^2 = 0.03\text{--}0.51$ for correlations between fouling ratios and feedwater quality

parameters both individually and in combinations). Thus, it may be assumed that the variability in membrane fouling is at least partly due to the previous cleaning. The fouling ratio values after each 1-week run are presented in Fig. 2. Cleanings 1, 9–12 appeared to reduce membrane fouling since the fouling ratios, i.e. fluxes of a fouled membrane, after 1-week run were higher than after the other cleanings, and even higher than the flux of a virgin membrane.

3.3. Membrane retention changes in total cleanings

In addition to significant flux improvements, the total cleanings changed the membrane ion retention

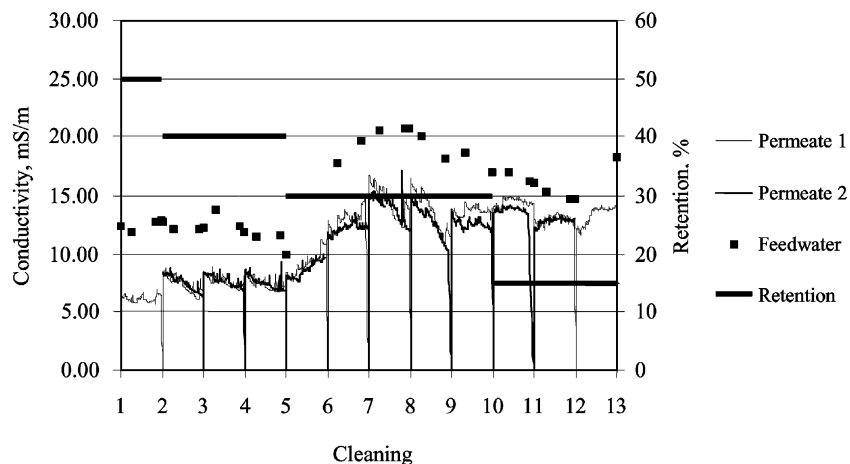


Fig. 3. Conductivities of feedwater and permeate waters, and average conductivity retentions during the study period.

during the runs as indicated in Fig. 3. The permeate conductivity generally increased after cleaning, but the membrane conductivity retention was at least partially recovered as the run proceeded. The average conductivity retention during the run was decreased from 50 to 40% in the first cleaning. When observing the conductivity retentions, it should be borne in mind that the membrane ion retention tends to decrease as the feedwater conductivity increase. This is indicated in the retention decrease to 30% after cleaning 5. The conductivity retention was further decreased to 15% in cleanings 10–12, where acidic cleaning was omitted or it was performed in the middle of alkaline cleanings. This suggests that acidic cleaning had a role in preserving the membrane ion retention capability, probably by making the membranes tighter by charge neutralisation.

The organic content of the permeate was stable and below the detection limit of the analysis throughout

the test period, and no changes in the membrane organics retention was observed. When the objective of nanofiltration is enhanced organics removal after the conventional surface water treatment, high ion passage is often preferred to reduce the need for permeate alkalinity recovery and stabilisation. In that respect, the deterioration of the ion removal capability of the membrane did not compromise the applicability of the tested cleanings. However, in the applications requiring high ion retention, cleaning's effect on membrane ion retention should be considered more carefully.

3.4. Foulant removal efficiencies of total cleanings

The total aluminium, calcium, iron and TS removals in total cleaning procedures are listed in Table 2. Out of 13 samples, three were unavailable for ion analysis and as such the ion removals of those cleanings are not presented. Removals of ions other than those listed in

Table 2
Membrane foulant removals in different cleaning procedures, and in each phase of the procedure

Cleaning no.	Al removal (g)	1st phase (%)	2nd phase (%)	3rd phase (%)	Ca removal (g)	1st phase (%)	2nd phase (%)	3rd phase (%)
3	3.3	100	0		0.2	81	19	
4	5.2	100	0		0.2	56	44	
5	4.3	19	81		0.2	62	38	
7	4.7	71	29		0.2	0	100	
8	3.7	30	70		0.2	57	43	
9	3.8	32	68		0.2	54	46	
10	7.1	100			0.2	100		
11	10	41	39	20	0.5	47	37	16
12	13.6	90	10		0.3	87	13	
13	1.1	100			–			
	Fe removal (g)	1st phase (%)	2nd phase (%)	3rd phase (%)	TS removal (g)	1st phase (%)	2nd phase (%)	3rd phase (%)
1	–				430	100	0	
2	–				285	100	0	
3	0.1	51	49		230	100	0	
4	0.2	54	46		95	100	0	
5	0	27	73		10	15	85	
6	–				35	0	100	
7	0.2	71	29		20	0	100	
8	0.2	45	55		15	10	90	
9	0.2	40	60		15	100	0	
10	0.4	100			20	100		
11	0.7	4	80	16	65	40	40	20
12	0.7	66	34		50	100	0	
13	0	100			10	100		

the table were <10 mg in each cleaning, and they are expected to be minor foulants with little importance.

Ion removals in cleanings depend on the efficiency of the cleaning agent, feedwater quality, and ion tendency to attach on the membrane. The correlation of aluminium concentrations in the feedwater and removals in the total cleanings was moderate ($r^2 \leq 0.55$, $P = 97\%$), while the correlation of calcium concentrations in the feedwater and removals in the total cleanings was poor ($r^2 \leq 0.05$, $P = 22\%$). Correlation could not be calculated for iron, since the feedwater iron content was always below the detection limit of the analysis method (30 mg/l). Considering the feedwater concentrations and the amount of removed material cleanings number 5, 10–12 are most efficient in removing aluminium precipitates, and cleanings 11 and 12 in calcium precipitate removal. According to the amount of removed material cleanings number 10–12 are most efficient in removing iron precipitates.

Since the correlation of ion concentrations in the feedwater and removals in the total cleanings were moderate or poor, some of the fouling material probably remained on the membrane after some of the cleanings. On the other hand, some cleanings may have modified the membrane surface in such a way that ion deposition on it was inhibited. Thus, the membrane characteristics may have differed slightly from one test run to another even though the cleaned membrane fluxes were equally recovered before each run.

The total removal of TS decreased remarkably after the third cleaning. Changes in the feedwater quality

could not be the reason for this, but the correlation of TS removals and HPC of the retentate is good ($r^2 = 0.86$, $P > 99\%$). As a consequence, TS removals appeared to consist mainly of micro-organisms. The decline in TS removals was due to the decline in the accumulation of micro-organism on the membrane, as the feedwater temperature fell to values that are unfavourable for biogrowth. Since the membrane attached micro-organisms and subsequent TS removals decreased remarkably as the feedwater temperature fell, it is difficult to compare the TS removal efficiencies in the cleaning procedure. Nonetheless, cleanings 11 and 12 seem to be effective in TS removal as well.

Fig. 4 presents the HPC of retentate before and after each cleaning. It is impossible to compare the disinfecting ability of different cleanings, since the temperature fall inhibited bacterial growth after cleaning 4. Temperatures below 13°C seemed to inhibit bacterial growth on the membrane in the long-term. However, it can be noted that, when NF operating temperatures favoured bacterial growth, all cleanings reduced the HPC of the retentate. As a conclusion, the cleanings were able to remove possible accumulated micro-organisms from the membrane surface.

3.5. Flux recoveries by different cleaning chemicals

The flux recoveries in acidic cleanings are presented in Fig. 5(a). Cleaning with combined citric acid and oxalic acid solution (cleaning 3) resulted in the best flux recovery. Sodium hydrosulfite (cleaning 6) with

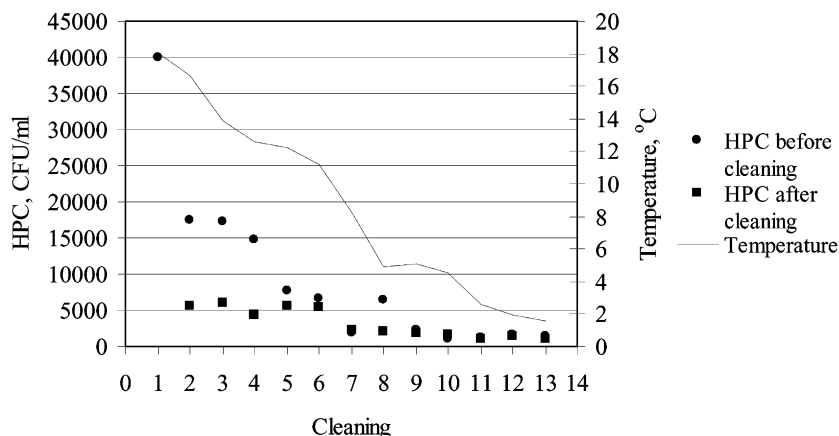


Fig. 4. Heterotrophic plate count in retentate before and after different cleaning procedures, and feedwater temperature over the study period.

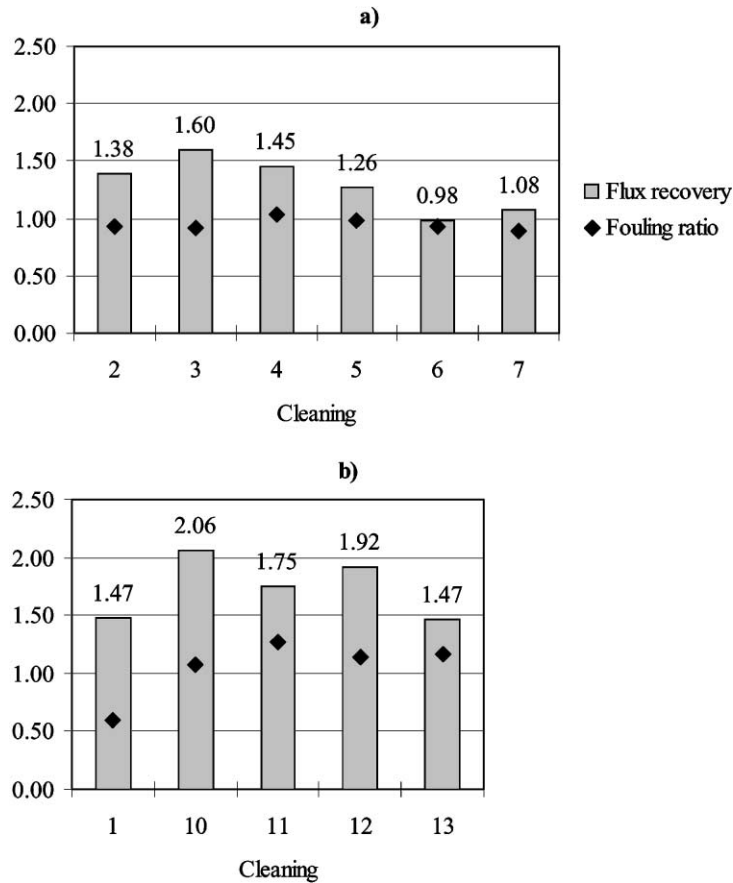


Fig. 5. Flux recoveries in cleanings applying (a) acidic, (b) alkaline cleaning chemicals, and fouled membrane flux before cleanings in comparison to the virgin membrane flux (fouling ratio).

only 5% flux recovery in the cleaning appeared to be rather ineffective as a cleaning agent. The flux recovery efficiency of the commercial cleaning agent Ultrasil 73 (cleaning 7) was quite poor as well. After each acidic cleaning, the cleaning was complemented by alkaline cleaning. From Fig. 2, it can be seen that, despite the differences in the cleaning efficiencies in the acidic cleaning phase, the alkaline cleaning returned the flux of totally cleaned membranes to a stable level.

Fig. 5(b) illustrates the cleaning efficiencies of alkaline cleanings. The solution of $\text{Na}_5\text{P}_3\text{O}_{10}$ – Na_4EDTA (cleaning 10) was the most efficient alkaline cleaning agent, leading to maximal flux recovery on its own. The commercial alkaline cleaning agent, Ultrasil 141 (cleaning 13), demonstrated the poorest flux recovery.

In NaOH (cleaning 1) cleaning, flux recovery from the virgin state was the same as in Ultrasil 141 cleaning, but the recovery of the fouled membrane was more efficient. In addition, the NaOH cleaning was not totally comparable to other cleanings, since the cleaning was performed as a first cleaning on a virgin membrane, before any membrane modification by cleanings.

The flux recovery efficiencies of the cleaning chemicals are summarised in Table 3. Alkaline cleanings were generally better in recovering membrane flux than acidic cleanings. This is probably due to the fact that the membrane charge increase in alkaline environment. Increased charge makes the membrane more open [11] and increases the repulsive charges between the membrane and similarly charged foulants

Table 3
Summary of flux recovery and foulant removal efficiencies of different cleaning chemicals

Chemical	Flux recovery ^a	Al removal ^b	Ca removal ^c	Fe removal ^c	TS removal ^d
Citric acid	++	N.D. ^e	N.D.	N.D.	+
Citric and oxalic acid	+++	+	+	–	+
Oxalic acid	++	+	–	–	+
HCl	+	–	–	–	–
Na ₂ S ₂ O ₄	–	N.D.	N.D.	N.D.	–
Ultrasil 73	–	+	–	+	–
Noah	++	N.D.	N.D.	N.D.	+
Na ₅ P ₃ O ₁₀ and Na ₄ EDTA	+++++	+	+	+	–
NaOH and Na ₄ EDTA	++++	–	–	–	–
Na ₄ EDTA	+++++	+	+	+	+
Ultrasil 141	++	–	–	–	–

^a –: Flux recovery 0.9–1.1; +: flux recovery 1.1–1.3; ++: flux recovery 1.3–1.5; +++: flux recovery 1.5–1.7; ++++: flux recovery 1.7–1.9; +++++: flux recovery 1.9–2.1.

^b +: Deposit removal >60% of total cleaning removal and >3 g.

^c +: Deposit removal >60% of total cleaning removal and >1.4 g.

^d +: Deposit removal >60% of total cleaning removal and >30 g.

^e N.D.: not determined.

[12]. Both phenomena can increase the membrane flux, even though the permanence of the effects is questionable. The introduction of alkaline chelating agent (Na₄EDTA) increased the membrane permeability more than plain alkaline cleaning (NaOH), probably by complexing some constituents from the membrane structure, and thus, making the membrane more open and permeable.

3.6. Flux recoveries in different cleaning procedures

The efficiencies of different cleaning combinations can be seen in Fig. 6. Differences in the cleaning effi-

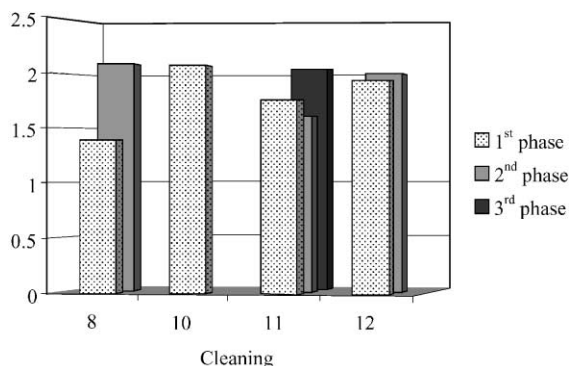


Fig. 6. Flux recoveries in different phases of different cleaning procedures.

ciencies of total procedures were not significant, and thus, with all procedures, the same flux recovery was attained. However, the same flux recovery required the application of only one or even three sequential cleaning chemicals. Therefore, the choice of cleaning chemicals is an important parameter in reducing cleaning costs.

In cleaning 11, when cleaning was performed in three steps, acidic cleaning following alkaline cleaning decreased the flux recovery. However, the subsequent alkaline cleaning increased the flux even more. According to this finding, NaOH–Na₄EDTA solution modifies the membrane by making it more permeable, while HCl solution, despite removing material from the membrane, makes the membrane less permeable.

3.7. Foulant removal efficiencies of chemicals in different cleaning procedures

Table 2 lists the percentage removals of selected ions and TS in different cleaning phases. Since the feedwater quality varied during the study period, it is difficult to evaluate the cleaning chemicals definitively according to their ion or TS removal efficiencies. The ability of each cleaning chemical to remove the aluminium, calcium, iron or TS deposits from the membrane surface as a single-stage cleaning is rated in Table 3. Some cleaning chemicals required another

cleaning phase to reach good foulant removal efficiency. In cleaning 11, after NaOH–Na₄EDTA cleaning, another cleaning phase was required for efficient deposit removal, and in cleaning 12 two Na₄EDTA cleaning phases were required to reach good cleaning efficiency in terms of iron removal. HCl, in turn, was not very efficient in removing aluminium, calcium, iron or TS as a 1st phase cleaning agent, but turned out to be more efficient when applied after NaOH–Na₄EDTA in cleaning 11. NaOH–Na₄EDTA cleaning probably modified the foulant layer making it more readily available for HCl solution.

On the basis of proportions of total TS and ion removals, it can be expected that the main foulants are micro-organisms and organic material. This conclusion is supported by the fact that alkaline cleaners, which are the most effective against biofilms, colloidal silts and organic foulants [15] were in general more efficient cleaners than acidic agents. Nevertheless, inorganic precipitates and NOM metal complexes contribute to the fouling as well, since alkaline cleanings containing chelating agent (Na₄EDTA) were most efficient cleaners. Chelators are effective against inorganic scale, organic fouling and biofilms [15], and they disrupt the fouling layer structure through a ligand exchange reaction between chelant and metal complexes [13].

4. Conclusions

Micro-organisms and organic deposits with metal NOM complexes were the principal foulants of the membranes fed by conventionally-treated surface water. Thus, alkaline chelating cleaning agents were most efficient in cleaning the membranes. However, alkaline chelant cleaning may not remove all inorganic foulants, and acidic cleaning may be periodically required to ensure the removal of inorganic precipitants.

Alkaline cleaning modified the NF255 membrane by improving its flux by 50%. The introduction of alkaline chelant further increased the flux to double the virgin membrane flux. The flux improvements are suggested to be due to membrane charge modifications in alkaline environments and their ability to remove some constituents from the membrane structure, both of which make the membrane more open. The membrane modifications seemed to be permanent, as

the flux improvement was recovered in the subsequent cleanings.

In addition to increased flux, membrane modification resulted in lower membrane ion retention. Ion retention loss was most profound in the cleanings containing only alkaline chelant cleaning phases. Acidic cleanings, in turn, made the membranes less permeable and seemed to repair the membrane ion retention characteristics, even if they removed fouling material from the membrane. On the basis of the findings of this study, alkaline and chelant cleanings improve membrane flux, but result in a decrease in ion retention, while acidic cleanings may be used for membrane ion retention recovery.

The organics retention remained high and stable during the experiment. Consequently, the cleanings did not deteriorate the applicability of the membrane for use in processes aimed at high organics and only low inorganics removal. However, in the applications requiring high ion retention, the effect of cleaning membrane ion retention should be considered more carefully.

Substantial savings can be gained with the proper choice of cleaning agent in terms of membrane productivity and retention, cleaning chemical use and the time required for cleanings. Cleaning with Na₅P₃O₁₀–Na₄EDTA solution recovered the flux efficiently in one cleaning phase, while other agents and agent combinations required two or three phases to reach similar recoveries. Nonetheless, it should be borne in mind that high flux recovery does not automatically mean total foulant removal, and multiphase cleanings may be occasionally needed to intensify foulant removal.

The long-term effects of certain cleanings were not evaluated, but generally the frequent cleanings that were tested did not deteriorate the membrane characteristics in a 13-week study. In addition, frequent cleanings seemed to effectively prevent the accumulation of micro-organisms on the membrane.

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