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Influence of temperature and cleaning on aromatic and semi-aromatic polyamide thin-film composite NF and RO membranes

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ABSTRACT

Although cleaning removes fouling, it may change the properties of membranes and consequently influence their performance. We have evaluated the combined effect of acidic/alkaline cleaning and temperature on the performance of two aromatic membranes, one a reverse osmosis membrane (HR98PP) and the other a nanofiltration membrane (NF90), two semi-aromatic polypiperazine membranes (NF200, NFT-50) and a Desal-5DK nanofiltration membrane. At the retention minimum of each membrane, the KCl retention and the water permeability were in the order: NFT-50 < NF200 < Desal-5DK < NF90 < HR98PP and HR98PP < NF90 < NF200 < Desal-5DK < NFT-50, respectively. After nanofiltration at elevated temperatures acidic and alkaline cleaning increased the water permeability and decreased the retention of the Desal-5DK membrane. Similar behaviour was observed after acidic cleaning of the aromatic polyamide membranes and with alkaline cleaning of the semi-aromatic polyamide (polypiperazine) membranes. Increased hysteresis was seen in the membrane performance with increasing temperature. The hysteresis behaviour was dependent on the cleaning procedure and could be related to swelling and shrinkage of the active polyamide layer. At 40 °C the reverse osmosis membrane (HR98PP) showed the same performance as the NF90 nanofiltration membrane at 20 °C.

1. Introduction

Employing nanofiltration (NF) directly on warm process streams ($T > 50\,^{\circ}C$) may be beneficial in comparison to lower temperatures. Within the food industry some process solutions are warm and applying NF directly on these solutions is desired to avoid cooling of the feed, while in other cases, elevated temperatures are necessary to reduce the product viscosity and/or to reduce microbiological growth. A high process temperature changes the NF performance due to temperature-dependent changes in the membrane structure as well as temperature effects that may be directly or indirectly related to the decrease in viscosity.

The performance of composite polyamide (PA) NF membranes, which are similar to composite reverse osmosis (RO) membranes in terms of chemical composition, has been found to be dependent on temperature, cleaning procedure and the feed properties such as pH, salt type, salt concentration and valency of the salt. These membranes can withstand elevated temperatures, but they become more sensitive to pH and pressure with increasing temperature and will eventually lose their NF properties. A decrease in membrane permeability after processing at elevated temperatures has been observed in various NF membranes [1]. In an investigation of the influence of alkaline cleaning on a polypiperazine NF membrane Nilsson et al. [2] found that a phosphate buffer solution (∼pH 9) and NaCl had the same effect on NF performance as a commercial alkaline cleaning agent, while NaOH (∼pH 10.5) had no effect. Variations in the water permeability of a polypiperazine membrane with pH and salinity have been observed when the pH was changed in the presence of 9% NaCl [3]. This was correlated to membrane swelling, analysed by atomic force measurements using 15% NaCl [4]. The lack of response to NaOH [2], indicates that the pH must be changed in the presence of an electrolyte in order to be able to observe any effects of pH. Furthermore, Freger [4] found that the swelling of an RO membrane composed of aromatic PA was very low and suggested that completely aromatic networks are more rigid and presumably more regularly packed than the semi-aromatic polypiperazine network of composite NF membranes. Swelling and relaxation have been found to be very time and temperature-dependent, both increasing with increasing temperature [5]. Changes in membrane permeability during NF have been reported in several studies on thin-film PA NF membranes [3,4,6–10], however, only a limited number of articles have been published describing the

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Nomenclature

J_w	water flux ($kg\,m^{-2}\,h^{-1}$)
m	molality (moles of solute per kg of solvent)
M_A	molecular weight of solvent ($kg\,mol^{-1}$)
P	pressure (bar)
P_0	water permeability ($kg\,m^{-2}\,h^{-1}\,bar^{-1}$)
R	gas constant ($J\,K^{-1}\,mol^{-1}$)
T	temperature (K)
v	the number of moles of ions (solute) formed from 1 mole of electrolyte (solute)
V_A	partial molar volume of the solvent ($m^3\,mol^{-1}$)

Greek letters

π	osmotic pressure (Pa in Eq. (2))
$\Delta\pi$	osmotic pressure difference (bar in Eq. (1))
ϕ	molal osmotic coefficient

influence of cleaning procedure on NF performance at elevated temperatures.

In NF, cleaning with commercial acidic and alkaline cleaning agents is generally carried out at ~50 °C [11]. Changes in the membrane performance can be considerable after cleaning due to the influence of temperature on the flexibility of the polymer chain, which increases with increasing temperature [12]. Hysteresis has, for instance, been seen after pretreatment with NaCl, where it was found that the membrane could return to its initial state after rinsing at the pretreatment temperature. While performing NF at ~pH 4 after acidic or alkaline cleaning, it was found that alkaline cleaning increased the flux and decreased the retention relative to acidic cleaning, but when the process was operated at a temperature (55 °C) above the cleaning temperature (50 °C), the flux and the retention were the same for alkaline and acid cleaning [12]. However, when using an industrial feed the best long-term performance was achieved after acidic cleaning, although the initial flux was higher after alkaline cleaning [12]. In this specific case the higher initial flux was due to membrane swelling, but as the swelled structure slowly relaxed this effect disappeared. Thus the only long-term effect was increased fouling caused by a higher initial flux. The strong influence of cleaning on NF performance underlines the need for additional research within this area since the performance of the membranes strongly influences the cost and energy demand.

In this study we evaluated the influence of temperature on membrane performance after acidic and alkaline cleaning of different types of membranes used for NF applications. The aim was to improve current knowledge of the combined effects of membrane swelling and temperature on semi-aromatic and completely aromatic, polyamide thin-film membranes, which are the commonly used in NF and RO applications, and thus simplify the implementation of these types of membranes at elevated temperatures.

2. Theory

2.1. Water permeability

The water permeability, P_0, is defined as:

$$P_0 = \frac{J_w}{(\Delta P - \Delta\pi)} \qquad (1)$$

where J_w is the water flux, ΔP the pressure difference and $\Delta\pi$ is the osmotic pressure difference across the membrane. The osmotic pressure, used for the calculation of the water permeability (Eq. (1)), was determined according to Eq. (2) [13]:

$$\pi = \frac{vRTM_A}{V_A}\phi m \qquad (2)$$

where v is the number of moles of ions formed from 1 mole of electrolyte, R the gas constant, T the temperature, M_A the molecular weight of the solvent, V_A the partial molar volume of the solvent, ϕ the molal osmotic coefficient and m is the molality. Extrapolated tabulated values were used to calculate the molal osmotic coefficient of KCl [13]. Using the polarisation layer thickness estimated by Bargeman et al. [7] to $\sim 2 \times 10^{-5}$ m under similar experimental conditions as in this study, concentration polarisation was found to be negligible.

3. Materials and methods

3.1. Membranes

Five commercial thin-film composite PA membranes were investigated (Table 1), four NF membranes (NFT-50, NF200, NF90 and Desal-5DK) and one RO membrane (HR98PP). The NFT-50 and the NF200 membranes are semi-aromatic and the NF90 and the HR98PP are aromatic. The backbone structure of the PA used for the Desal-5DK membrane is proprietary information.

3.2. Experimental set-up

The NF experiments were performed with a plate-and-frame DSS Labstak® unit M20-0.72-PSO (Alfa Laval Nakskov, Denmark), as illustrated in Fig. 1. The membranes were installed in the following order: HR98PP (0.036 m^2) – NF90 (0.036 m^2) – NF200 (0.036 m^2) – NFT-50 (0.036 m^2) – Desal-5DK (0.072 m^2) – NFT-50 (0.036 m^2) – NF200 (0.036 m^2) – NF90 (0.036 m^2) – HR98PP (0.036 m^2). At the maximum permeate flux, i.e. at 60 °C at 6 bar, the average flux is ~53 l/m^2 h. The total membrane area used in this experiment is 0.36 m^2 which yields a maximum average permeate flux

Table 1
NF and RO membranes used in the experiments

Membrane	Manufacturer	Type	Support	Active layer	pH range	T_{max} (°C)
HR98PP (RO98pHt)	Alfa Laval	RO	PS on PP	Aromatic PA	2–11 at 60 °C	60[a] 60[b]
NF90	Dow FilmTec™	NF	PS on PE	Aromatic PA	2–11 at 35 °C	40[a] 50[b]
NF200	Dow FilmTec™	NF	PS on PE	Semi-aromatic PA (polypiperazine)	2–11 at 35 °C	40[a] 50[b]
NFT-50 (NF99)	Alfa Laval	NF	PS on PE	Semi-aromatic PA (polypiperazine)	2–10 at 50 °C	50[a] 50[b]
Desal-5DK	GE Osmonics	NF	NA	PA	2–11 at 25 °C	70[a] 70[b]

The NFT-50 and the HR98PP membranes from Alfa Laval also correspond to the trade names NF99 and RO98pHt, respectively. NA: not available; PA: polyamide; PE: polyester; PP: polypropylene; PS: polysulphone.
[a] Continuous operation.
[b] Cleaning.

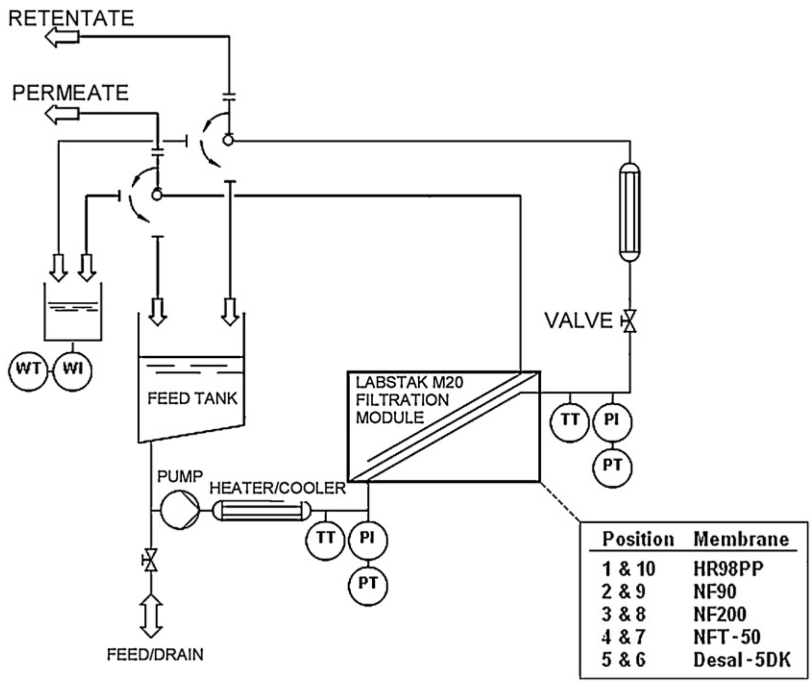

Fig. 1. The M20 single-stage plate-and-frame DSS Labstak® unit and membrane positioning used for the NF experiments. The equipment includes a feed tank (60 l), feed pump, heater/cooler at the inlet and outlet, temperature transmitters (TT) at the inlet and outlet, pressure indicators (PI) and pressure transmitters (PT) at the inlet, and outlet and a weight indicator (WI) and weight transmitter (WT) that measure the permeate flux and retentate flow rate. All transmitters are connected and monitored via a computer.

of 0.32 l/min. In comparison to the re-circulation rate, 8 l/min, the permeate flux is 4% of the re-circulation rate, i.e. the velocity in the entrance of the module is 4% higher than that at the outlet. It is therefore sound to assume that the total hydrodynamic pressure drop scales linearly with the position of the plates in the module. Thus, with this membrane arrangement each of the five membrane set-ups (0.072 m^2) can be assumed to operate at the same average trans membrane pressure. Furthermore, the difference in feed concentration along the module is accounted for by measuring both the inlet and outlet feed concentration, which only varies with maximum 3%.

The feed volume used was 40 l. The feed pump, a 3-piston pump, P21/23–130 (Speck, Germany), was controlled by a frequency converter. The inlet and outlet temperatures were measured with Pt100 class A temperature sensors (Pentronic AB, Sweden) with an accuracy of 0.03 °C and 0.12 °C at 0 °C and 100 °C, respectively.

The inlet and outlet pressure were measured with Gems 2600 series industrial pressure transducers (2600BGB4000G3UB, 4–20 mA, 0–16 bar) with a maximum error of 0.04 bar in the ranges 0–16 bar and 20–50 °C, both connected to Gems temperature isolators (558564-0001) reducing the temperature of the medium by 80% ($T_{transducer} = T_{medium}/5 + T_{ambient}$). The temperature and pressure sensors were connected to a PC logger 2100 and monitored with the program Easy View® (Intab Interface Teknik AB, Sweden). The feed concentration was measured at the inlet and outlet. Mean values were used in the calculations of the water permeability and the retention.

3.3. Feed solutions

Experiments were carried out using a feed solution of KCl (20 mM), dissociated in deionised water. The KCl used was of analytical grade, supplied by Merck. The pH of the feed was adjusted using HCl and KOH.

3.4. Cleaning

During the alkaline cleaning cycles, Divos 108 VM 21® (JohnsonDiversey, Sweden) was used at 0.5 wt% (∼pH 11.5) at 40 °C for 40 min at 6 bar, being the same pressure as used during the experiments in order to eliminate pressure-induced changes in the membrane structure. For acid cleaning, Divos 2 VM 13® (also from JohnsonDiversey, Sweden) was used at 0.5 wt% (∼pH 1.7) for 40 min at 6 bar at 40 °C.

3.4.1. Alkaline–acidic cleaning

Initial alkaline cleaning was performed at 40 °C at 6 bar with final rinse-out at 40 °C (Fig. 2a) or 60 °C (Fig. 3a) using an aqueous 20 mM KCl solution (pH 6). The alkaline cleaning cycle was followed by an acidic cleaning cycle in which the cleaning solution was cooled from 40 °C to 20 °C (5 min cooling time) prior to rinse-out at 20 °C with deionised water, first for 5 min with retentate and permeate dump (no pressure applied) and then at 10 bar and 20 °C for 40 min with retentate recirculation and permeate dump. A recirculation flow rate of 8 l/min was used during cleaning and rinsing.

3.4.2. Acidic–alkaline cleaning

The same procedure as described in Section 3.4.1 was used, but the order of acidic and alkaline cleaning was reversed, see Figs. 2b and 3b.

3.5. Experimental procedure

The membranes were initially pressurised at 25 bar at 40 °C until the flux remained constant for at least 30 min. At 40 °C, the pure water permeability was at this stage: HR98PP = 5.1 kg/m^2 h, NF90 = 7.6 kg/m^2 h, NF200 = 7.2 kg/m^2 h, NFT-50 = 9.7 kg/m^2 h and Desal-5DK = 7.6 kg/m^2 h. The membranes were then cleaned with alkaline and acid cleaning, as described above, in order to stabilise

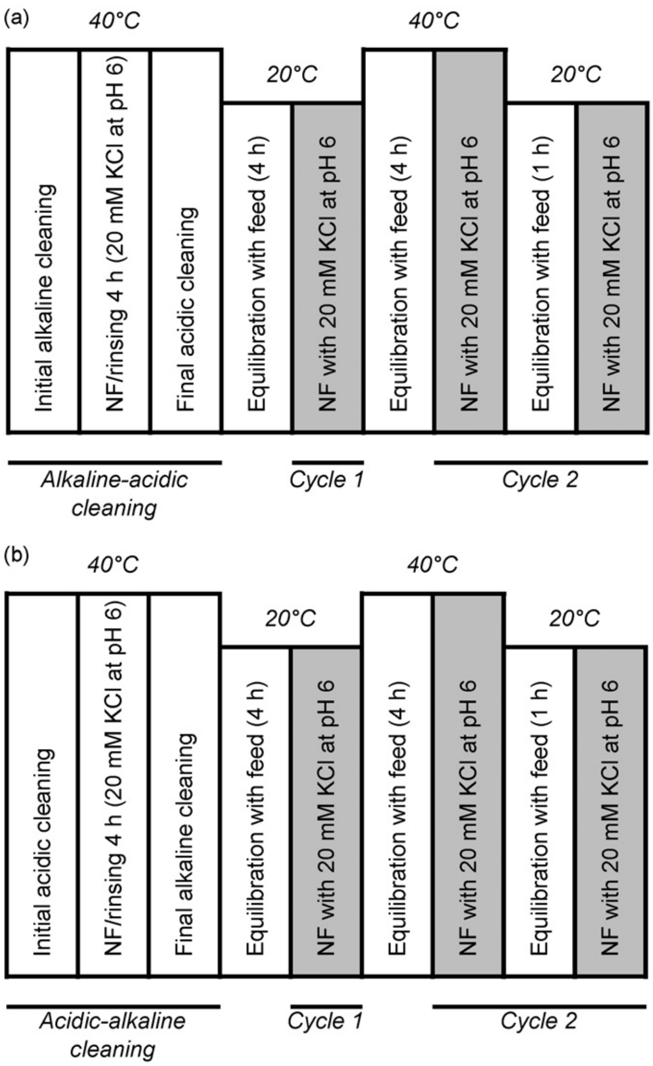

Fig. 2. Schematic showing the experimental procedure during NF at 20–40 °C after: (a) alkaline–acidic cleaning and (b) acidic–alkaline cleaning.

the membrane performance. A recirculation flow rate of 8 l/min was used during all experiments.

3.5.1. Series 1: KCl retention as a function of pH

After performing alkaline–acidic cleaning, the retention minimum was evaluated by performing retention measurements with 20 mM KCl at 20 °C at a constant flux of 20 l/m^2 h ± 0.02 l/m^2 h within the pH range ∼3.5–8, averaged over 4–10 min at each pH level.

3.5.2. Series 2: NF after alkaline–acidic and acidic–alkaline cleaning (20–40 °C)

NF experiments were performed at 20, 40 and again at 20 °C at 6 bar with 20 mM KCl at pH 6 after alkaline–acidic (Fig. 2a) or acidic–alkaline cleaning (Fig. 2b). The experimental order was as follows: 20 °C with 4 h equilibration, 40 °C with 4 h equilibration, and 20 °C with 1 h equilibration. Duplicate NF experiments were performed after both kinds of cleaning. Average flux and retention were calculated, with their standard deviations, based on the results of the duplicate experiments. Flux and retention were measured continuously during the 4 h long equilibration period, to ensure that the membranes were stable when the experimental measurements were made. The drift in flux and retention from hour 3 and to hour 4 during the 4 h long equilibration period was found to be less than 1% and 0.7%, respectively.

3.5.3. Series 3: NF after acidic and alkaline cleaning (20–60 °C)

Prior to the experiments the membranes had not been used at temperatures above 40 °C and they were therefore cleaned with an alkaline–acidic cleaning cycle with rinse-out at 60 °C or an acidic–alkaline cleaning cycle, also with rinse-out at 60 °C in order to stabilise the membrane performance according to the schemes shown in Fig. 3.

NF experiments were then performed at 6 bar with 20 mM KCl at pH 6 after alkaline–acidic (Fig. 3a) or acidic–alkaline cleaning (Fig. 3b). The experimental order was as follows: 20 °C with 4 h equilibration, 40 °C with 4 h equilibration, 20 °C with 1 h equilibration, 60 °C with 4 h equilibration, 40 °C with 1 h equilibration, and finally 20 °C with 1 h equilibration. Duplicate experiments were performed after both alkaline–acidic and acidic–alkaline cleaning. Average flux and retention were calculated, with their corresponding standard deviations, based on the duplicate experiments. During the 4 h long equilibration period, flux and retention were measured to ensure that the membranes were stable when the final experimental measurements were made.

3.6. Analysis

The permeate flux was measured gravimetrically using a Sartorius L610 laboratory scale with a measuring error of 0.01%, which was connected to and monitored via a computer. The concentration of KCl was measured at a temperature of 20 °C with a conductivity meter (Orion Model 150 Conductivity Benchtop Meter® supplied by Tamro Lab, Sweden). H_30^+ and OH^- influence the conductivity, thus the influence of pH on conductivity was taken into account when the KCl concentration was calculated.

4. Results and discussion

4.1. Influence of pH on KCl retention and water permeability

The influence of pH on KCl retention after alkaline-acidic cleaning (3.5.1) can be seen in Fig. 4a and the corresponding water permeability in Fig. 4b. The aromatic NF90 and HR99PP membranes show the same retention behaviour, with a retention minimum at ∼pH 5. The KCl retention of these two membranes was high, and the difference in retention was smaller than normally expected between NF and RO membranes. Similar retention behaviour was seen for the NF200 and NFT-50 NF membranes. These semi-aromatic polypiperazine-based membranes had a retention minimum at ∼pH 4. The retention minimum of the NFT-50 membrane was in accordance with zeta potential measurements, with which the *iso*-electric point was determined to be pH 4.3 with 1 mM KCl at 25 °C [14]. The retention minimum of the Desal-5DK membrane was ∼pH 5.75 (Fig. 4a). In a previous study on the Desal-5DKmembrane, the retention minimum of sodium ions was found to be at ∼pH 5, while the *iso*-electric point, determined with zeta potential measurements, was found to be ∼pH 4 [15]. The *iso*-electric point of the NF200 membrane was determined to be ∼pH 3 [16] or ∼4.5 [9] with zeta potential measurements, while no *iso*-electric point was found for the NF90 membrane [16].

It is difficult to compare retention curves with zeta potential measurements since the *iso*-electric point changes with electrolyte and electrolyte concentration, while in other cases the membrane structure changes with pH, electrolyte and electrolyte concentration. In addition, composite PA membranes are heterogeneous and the surface charge properties of the active layer may not be equivalent to those in the interior of the active layer [17]. This could

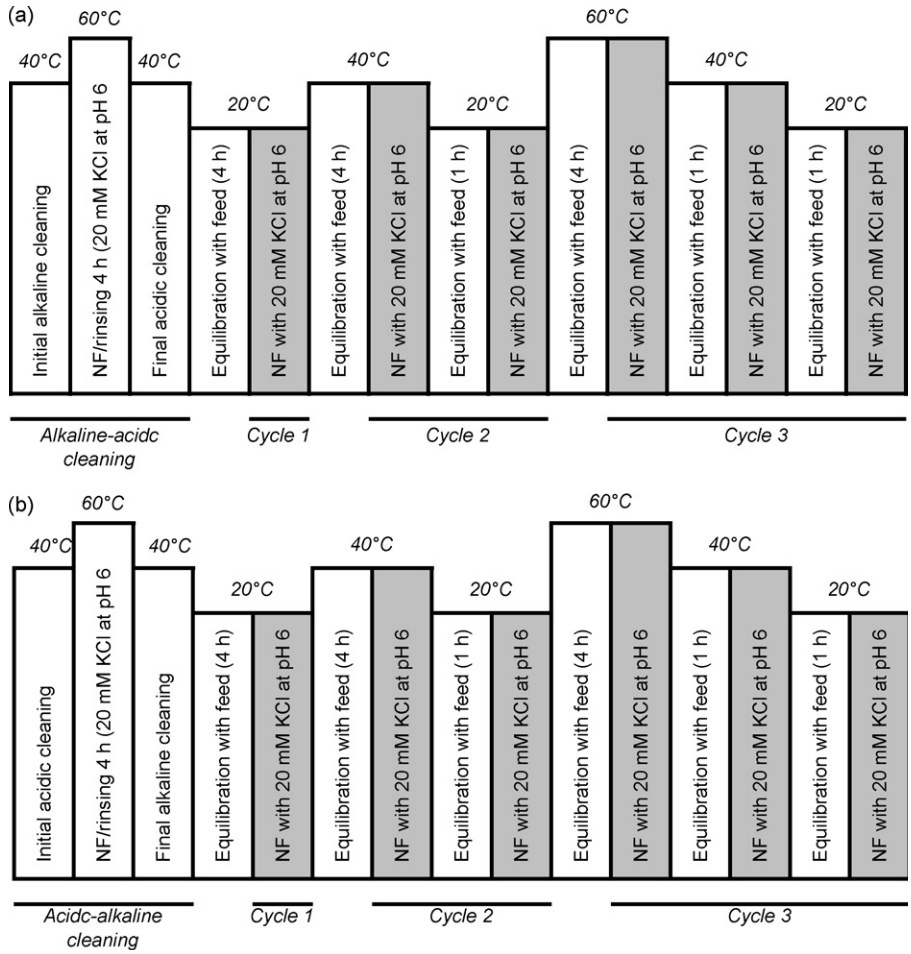

Fig. 3. Schematic showing the experimental procedure during NF at 20–60 °C after: (a) alkaline–acidic cleaning and (b) acidic–alkaline cleaning.

explain the differences observed between zeta potential measurements and retention minima in this study and in the study by Hagmeyer and Gimbel [15].

No increase in retention was seen in the NF200 and NFT-50 membranes when increasing the pH from 7 to 8, and from Fig. 4b it can be seen that increasing the pH increased the water permeability slightly. These changes can be explained by membrane swelling. Regarding the Desal-5DK, NF90 and HR98PP membranes, the retention minimum (Fig. 4a) and maximum in water permeability (Fig. 4b) were seen at approximately the same pH. Assuming that the retention minimum corresponds to the *iso*-electric point, there are two explanations for these findings: membrane swelling and/or electroviscous friction due to a lower charge density.

At the retention minimum of each membrane, the KCl retention and the water permeability were in the order: NFT-50 < NF200 < Desal-5DK < NF90 < HR98PP and HR98PP < NF90 < NF200 < Desal-5DK < NFT-50, respectively.

4.2. Effect of a final acidic or alkaline cleaning step after rinsing at 40 °C

The cleaning procedure (Fig. 2a and b) was found to influence the performance of all the membranes. Variations were seen in the water permeability (Fig. 5) and KCl retention (Fig. 6), which were dependent on the specific cleaning procedure and NF temperature; the changes being different depending on the type of membrane.

The aromatic membranes, NF90 and HR98PP, responded similarly to cleaning and increasing/decreasing NF temperature. Relative to the initial cleaning (40 °C) and rinsing cycles (at 40 °C with 20 mM KCl at pH 6), a small increase in the water permeability (Fig. 5) and a decrease in KCl retention (Fig. 6) were observed after the final acidic cleaning stage at 40 °C (Fig. 2a). A slightly higher water permeability and lower KCl retention were seen after final acidic cleaning than after final alkaline cleaning (Fig. 2b). These differences were probably due to greater swelling of the active layer during acidic cleaning than during alkaline cleaning, where an initially swollen structure could appear “frozen” at lower temperatures [5]. This difference disappeared during/after NF at 40 °C, which can be explained by relaxation of the swelled structure due to an increase in polymer flexibility with increasing temperature. In a previous study by Freger [4], it was found that completely aromatic PA layers had a much lower tendency to swell than semi-aromatic PA layers, and they proposed that completely aromatic PA is more rigid, and presumably more regularly packed, and is therefore less able to swell. The results shown in Figs. 5 and 6 are in accordance with their reported lower degree of swelling.

The results from the polypiperazine-based NF200 and NFT-50 membranes were similar to each other. However, the results for the Desal-5DK membrane differed both from the aromatic membranes and the semi-aromatic polypiperazine membranes (Fig. 4). Relative to the initial cleaning (40 °C) and rinsing (at 40 °C with 20 mM KCl at pH 6) cycle, acidic cleaning decreased the water permeability (Fig. 5) and increased the retention (Fig. 6) of the NF200, NFT-50 and the Desal-5DK membranes, whereas alkaline cleaning had the opposite effect. The changes were pronounced for the NF200 and NFT-50 membranes but almost negligible for the Desal-

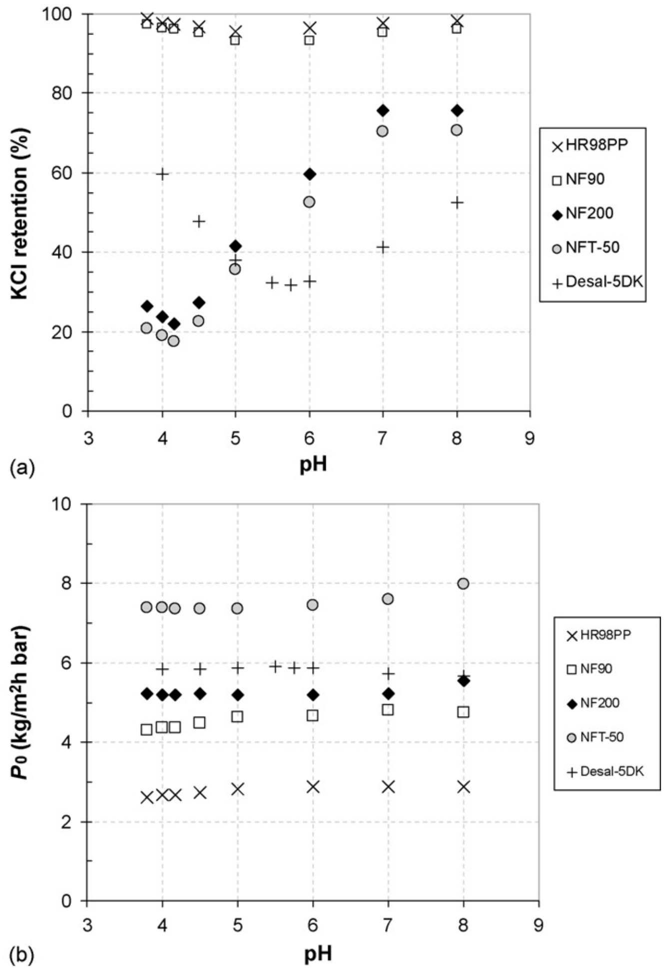

Fig. 4. Results obtained at constant flux (20 l/m^2 h) at 20 °C with 20 mM KCl as a function of pH after alkaline–acidic cleaning: (a) KCl retention and (b) water permeability.

5DK membrane (Fig. 5). The increase in water permeability and decrease in retention, and vice versa, were closely correlated to each other. Similar trends have been reported after NF at 65 °C [1,18], and it was suggested by Mänttäri et al. [18] that membranes that undergo a large change in flux and retention after alkaline cleaning are not resistant to alkaline cleaning, at least not at high temperatures. However, in the experiments reported in Figs. 5 and 6 the membranes had not been exposed to temperatures above the limits given by the manufacturers, although significant changes were seen in the membrane performance. The change was probably due to membrane swelling, which has been reported, for instance, for semi-aromatic polypiperazine membranes [2,4–7,9] when operating below the maximum recommended temperature given by the manufacturers.

Alkaline cleaning followed by NF at 40 °C, with 20 mM KCl at pH 6, changed the membrane performance, as can be seen in Figs. 5 and 6 when comparing the reference points at 20 °C, before and after NF at 40 °C. The change was very small for the Desal-5DK, but large for the NF200 and NFT-50 membranes. In a recent study [5] of the NFT-50 membrane it was found that temperature influenced the degree of polymer flexibility and thus the degree of relaxation after swelling. The change in membrane performance of the NF200 and NFT-50 membranes was thus probably due to a similar mechanism. Bargeman et al. [7] found when employing combined measurements with glucose and salt that the Desal-5DK membrane had a small tendency to swell in the presence of salt in comparison with a polypiperazine-based NF membrane (NF, Dow FilmTec^{TM}). However, since the polymer composition of the Desal5DK membrane is not known it is difficult to compare the behaviour of this membrane with those of the other four membranes. The difference in retention as a function of pH, seen in Fig. 3, is a strong indication of the chemical composition and the rigidity of the polymer structure of the Desal5DK membrane is different compared with the other membranes investigated.

Although there was high reproducibility in the results after both alkaline and acidic cleaning, final acidic cleaning appeared to give more stable process conditions to the NF200 and NFT-50 mem-

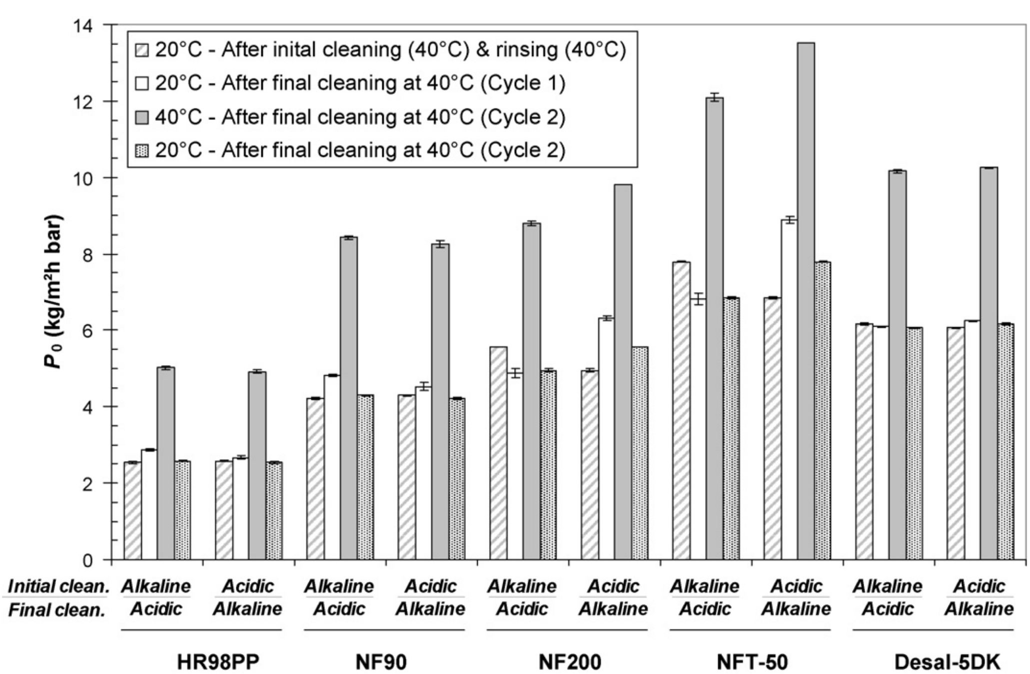

Fig. 5. Water permeability after alkaline–acidic cleaning (Fig. 2a) and acidic–alkaline cleaning (Fig. 2b). The measurements were conduced at 6 bar using a 20 mM KCl solution at pH 6.

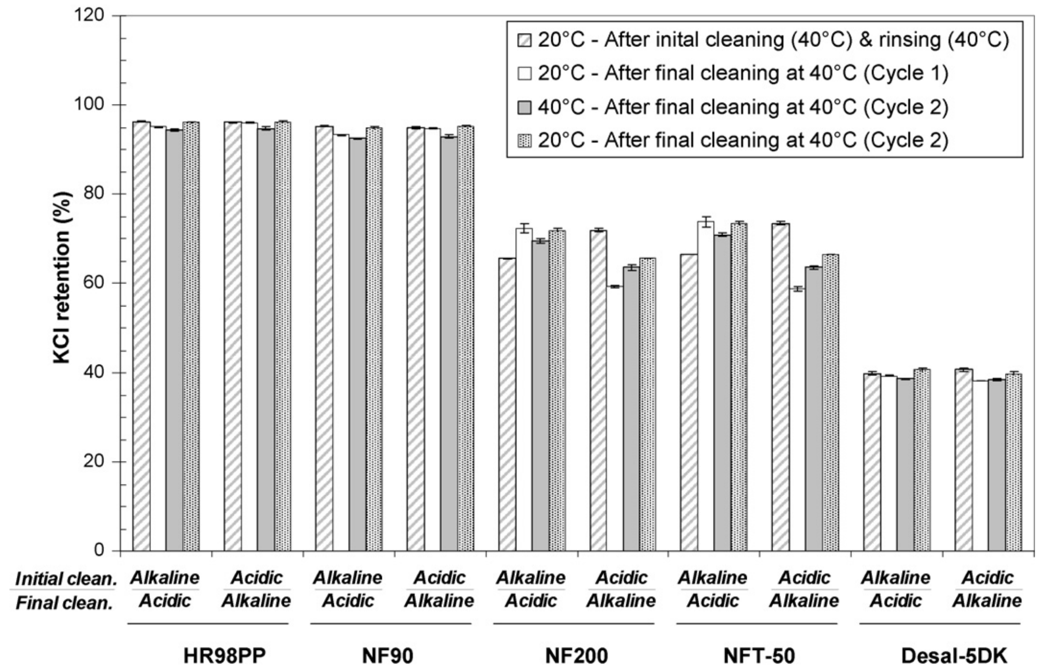

Fig. 6. KCl retention after alkaline–acidic cleaning (Fig. 2a) and acidic–alkaline cleaning (Fig. 2b). The measurements were conduced at 6 bar using a 20 mM KCl solution at pH 6.

branes. A comparison of the permeability and the retention at 20 °C, before and after NF at 40 °C, showed that the performance of these two membranes still depended on whether the final cleaning stage was acidic or alkaline, whereas the Desal-5DK membrane showed no difference. It should be stressed that hysteresis due to cleaning could have a long-term effect on the membrane performance if it is not allowed to return to is original state prior to the next cleaning cycle. This should be considered when cleaning has a strong influence, as in the case of the NF200 and NFT-50 membranes. The effects of acidic/alkaline cleaning on the permeability of the NF200 and Desal-5DK membranes are in accordance with the effects of pH in presence of NaCl reported by Mänttäri et al. [9].

4.3. Effect of a final acidic or alkaline cleaning step after rinsing at 60 °C

Increasing the rinsing/NF temperature to 60 °C after the initial cleaning step changed the response to acidic and alkaline cleaning, compared with 40 °C, as described in Section 4.2. The two aromatic membranes responded similarly, as did the two polypiperazine-

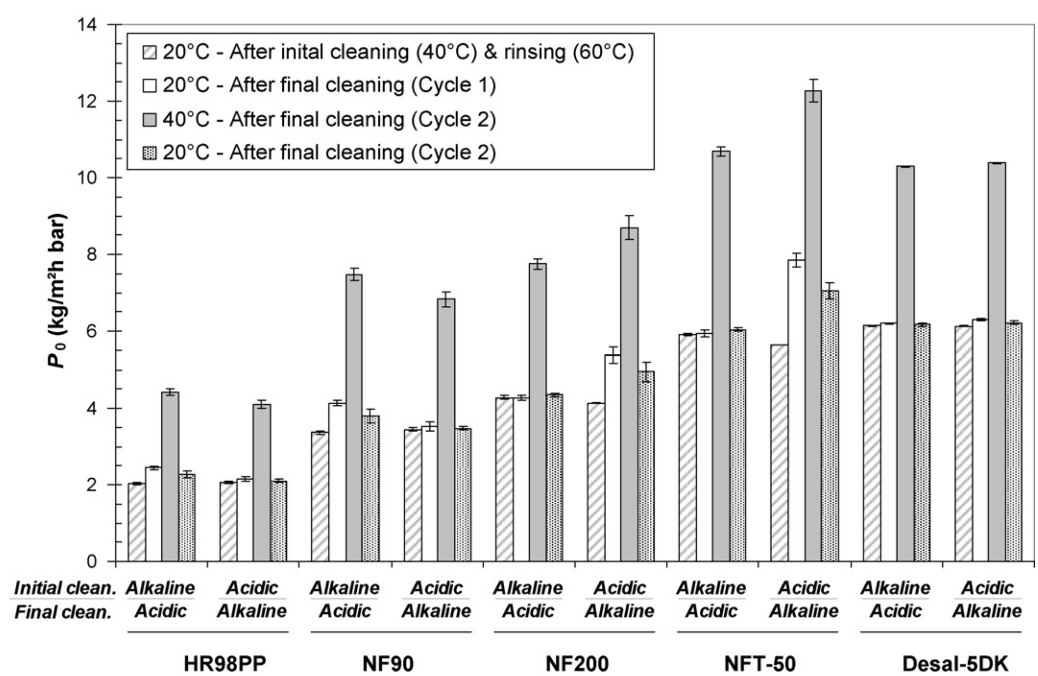

Fig. 7. Water permeability after alkaline–acidic cleaning (Fig. 3a) and acidic–alkaline cleaning (Fig. 3b). The measurements were conduced at 6 bar using a 20 mM KCl solution at pH 6.

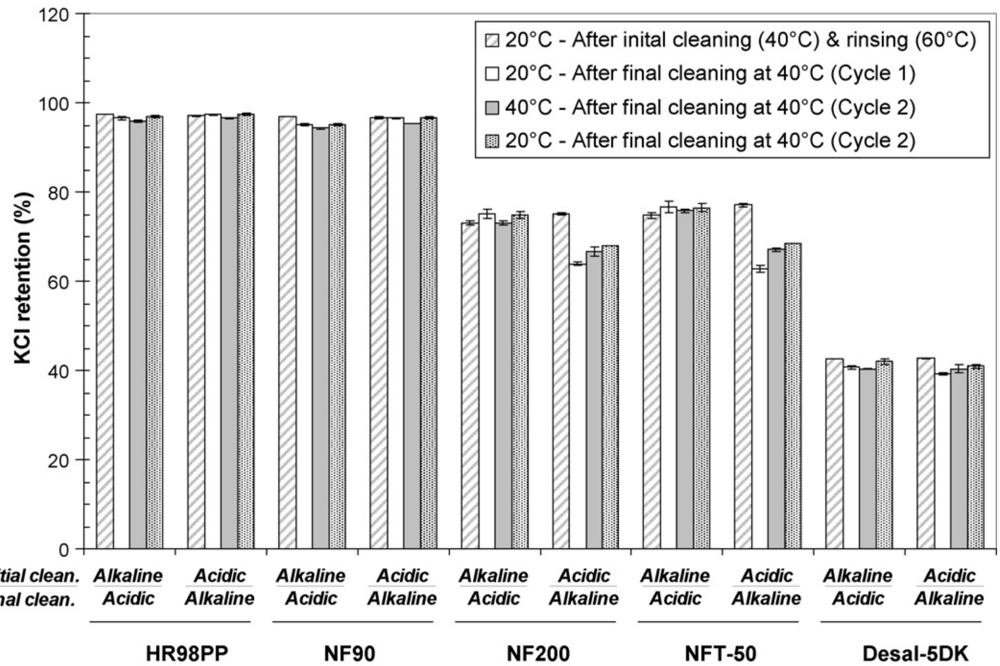

Fig. 8. KCl retention after alkaline–acidic cleaning (Fig. 3a) and acidic–alkaline cleaning (Fig. 3b). The measurements were conduced at 6 bar using a 20 mM KCl solution at pH 6.

based membranes. The influence of cleaning and initial rinsing on the water permeability (Fig. 7) and the KCl retention (Fig. 8) during NF at 20 and 40 °C (cycles 1 and 2 in Fig. 3a and b) is discussed below.

Rinsing/NF at 60 °C changed the water permeability and KCl retention to a larger extent than rinsing/NF at 40 °C, and thus the effect of cleaning on membrane performance became more obvious. As previously discussed above, the aromatic NF membrane seems to have a lower tendency to swell and shrink than the semi-aromatic membrane. The results show that swelling and relaxation become more significant with increasing temperature and that the aromatic membranes can withstand NF at 60 °C under the present conditions.

Alkaline cleaning of the NF200 and NFT-50 membranes increased the water permeability (Fig. 7) and decreased the KCl retention (Fig. 8). Furthermore, the water permeability and the KCl retention were largely unaffected by the final acidic cleaning stage. These results are different from those reported in Section 4.2, where final acidic cleaning-induced additional relaxation of the structure. However, in this case (Figs. 7 and 8), final rinsing at 60 °C had already relaxed the swollen structure and thus no effect of final acidic cleaning was seen. Besides this difference, the water permeability and the KCl retention were similar to those after rinsing at 40 °C, showing that also the semi aromatic membranes can withstand NF at 60 °C under the present conditions.

The Desal-5DK membrane seemed to be less influenced by alkaline cleaning than the NF200 and NFT-50 membranes. Relative to the initial cleaning (40 °C) and rinsing (60 °C), both final acidic and alkaline cleaning slightly increased the water permeability and decreased the KCl retention, whereas only alkaline cleaning had a significant influence on the performance of the NF200 and NFT-50 membranes.

4.4. NF performance at 20–60 °C after alkaline and acidic cleaning

Increasing the temperature stepwise after acidic and alkaline cleaning resulted in different retention behaviour of the membranes (Figs. 9–11). Increased, decreased and constant retention was observed, depending on the cleaning procedure, temperature and the type of membrane. These changes were due to different degrees of membrane relaxation after acidic and alkaline cleaning when initially increasing the temperature from 20 °C to 60 °C. However, all membranes showed a decrease in water permeability and an increase in KCl retention as the temperature was decreased back from 60 °C to 20 °C. The results for each membrane are discussed in more detail below.

The water permeability and the KCl retention of the HR98PP (Fig. 9a) and NF90 membranes (Fig. 9b) showed similar behaviour with temperature and type of cleaning, but different absolute values. When increasing the temperature from 20 °C to 60 °C, the water permeability increased and the retention decreased. These results are contradictory to those obtained in a previous study at constant pressure, where the NaCl retention was found to be independent of increasing temperature [19]. This discrepancy will be discussed below. As a result of increased water permeability and decreased KCl retention with increasing temperature, the performance of the HR98PP RO membrane at 40 °C corresponded to that of the NF90 NF membrane at 20 °C, thus the RO membrane had NF properties at higher temperatures. However, it should be stressed that, as seen in Fig. 4a and b, the HR98PP membrane is quite open for an RO membrane, while the NF90 membrane is rather dense for an NF membrane. Since the aromatic membranes showed very similar behaviour (Figs. 4–9), the major difference between these membranes affecting the water permeability and the retention is probably the thickness of the active layer. When decreasing the temperature back to 20 °C, hysteresis was seen at 20 °C and 40 °C, in terms of a decrease in water permeability and an increase in retention relative to increasing the temperature. The degree of hysteresis was small after alkaline cleaning but greater after acidic cleaning. In a previous study it was found that the best performance during NF of wastewater was achieved when hysteresis due to the combined effect of cleaning and temperature could be avoided [12]. To ensure a stable process when using these membranes at elevated temperatures (e.g.

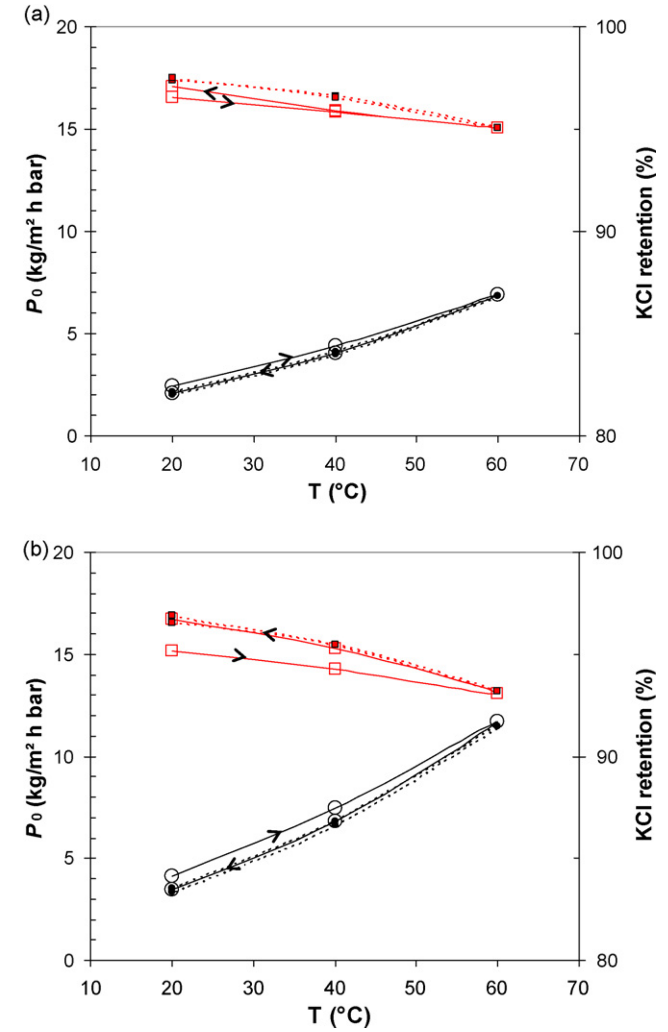

Fig. 9. Water permeability and KCl retention of the two aromatic membranes: (a) HR98PP (RO) and (b) NF90 (NF) when increasing the temperature from 20 °C to 60 °C and returning back to 20 °C. The results are presented after final acidic or alkaline cleaning (rinse-out at 60 °C after the initial cleaning) at 6 bar, at pH 6 using 20 mM KCl. (◯) P_0 final acidic cleaning (●) P_0 final alkaline cleaning, (□) retention final acidic cleaning (■) retention final alkaline cleaning.

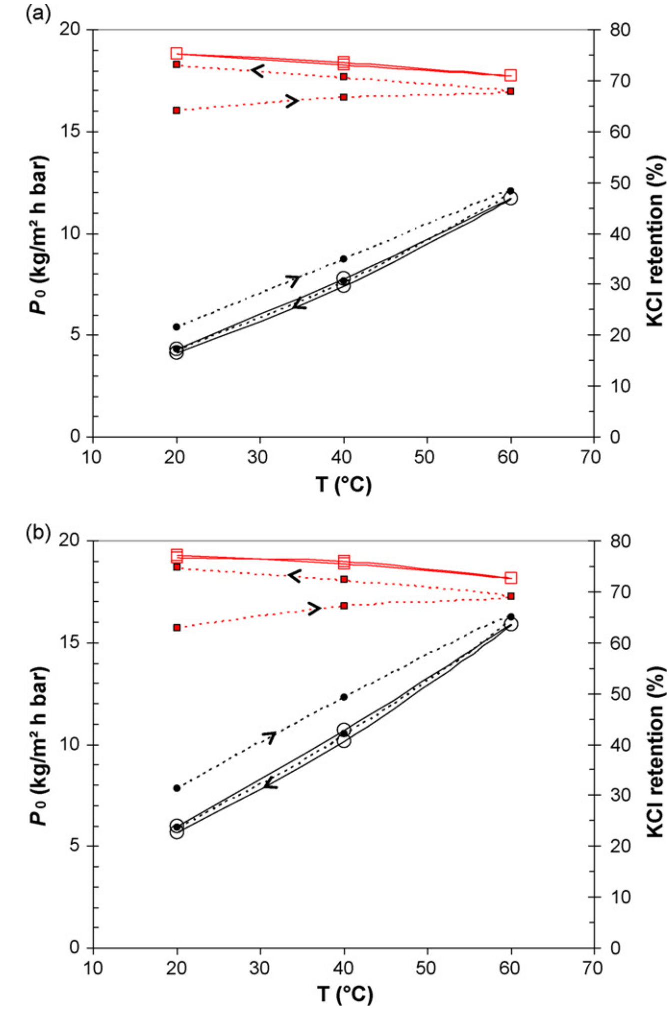

Fig. 10. Water permeability and KCl retention of the two semi-aromatic polypiperazine NF membranes: (a) NF200 and (b) NFT-50 when increasing the temperature from 20 °C to 60 °C and returning back to 20 °C. The results are presented after final acidic or alkaline cleaning (rinse-out at 60 °C after the initial cleaning) at 6 bar, at pH 6 using 20 mM KCl. (◯) P_0 final acidic cleaning (●) P_0 final alkaline cleaning, (□) retention final acidic cleaning (■) retention final alkaline cleaning.

60 °C), a final alkaline cleaning stage with rinsing at 20–60 °C or a final acidic cleaning stage with rinsing at 60 °C is thus recommended.

The water permeability and KCl retention of the NF200 (Fig. 10a) and the NFT-50 membranes (Fig. 10b) showed similar trends as a function of temperature and type of cleaning, but had different absolute values. When increasing the temperature from 20 °C to 60 °C after acidic cleaning, the water permeability increased and the retention decreased. However, after alkaline cleaning both the water permeability and the retention increased with increasing temperature. The increase in retention was probably due to structural changes in the membranes, where the initially swollen structure due to alkaline cleaning relaxed with increasing temperature, as previously discussed above. The change in structure was considerable after alkaline cleaning, which resulted in significant hysteresis in water permeability when decreasing the temperature to 20 °C. The degree of hysteresis was lower after acidic cleaning. Stable performance at elevated temperatures was thus observed after a final acidic cleaning stage with rinsing at 20–60 °C or a final alkaline cleaning stage with rinsing at 60 °C.

The influence of temperature on NF performance after acidic or alkaline cleaning was less for the Desal-5DK (Fig. 11) membrane than for the NF200 and the NFT-50 membranes, which showed no statistically significant change in water permeability with increasing and decreasing temperature. However, a significant but relatively small decrease in selectivity was seen with increasing temperature, after both final acidic and alkaline cleaning stages. When increasing the temperature from 20 °C to 40–60 °C after alkaline cleaning, it appears that the KCl retention reached a maximum at 40 °C. No other changes in performance were observed when increasing the temperature from 40 to 60 and returning back to 40 °C. After final acidic cleaning the KCl retention was found to be constant with temperature when increasing the temperature from 20 °C to 60 °C, whereas hysteresis was seen in the retention when returning back to both 40 °C and 20 °C, showing that the relaxation temperature could be dependent on whether the membrane was initially cleaned with an acidic or an alkaline cleaning agent.

The results reported in this study showed that at constant pressure, the retention decreased with increasing temperature if the membrane was first allowed to equilibrate at a higher temperature

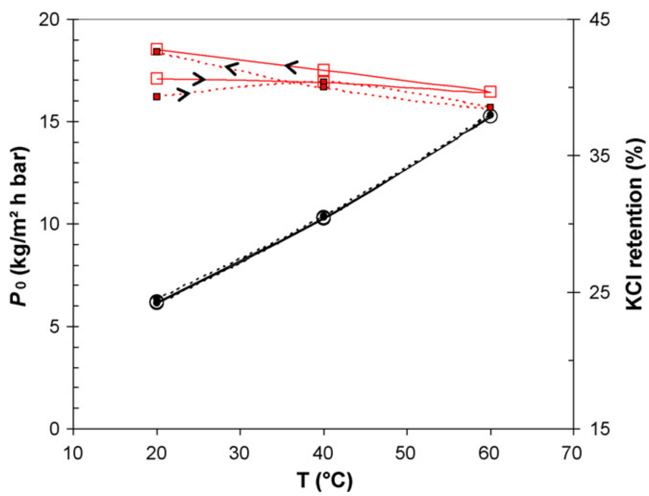

Fig. 11. Water permeability and KCl retention of the Desal-5DK NF membrane when increasing the temperature from 20 °C to 60 °C and returning back to 20 °C. The results are presented after final acidic or alkaline cleaning (rinse-out at 60 °C after the initial cleaning) at 6 bar, at pH 6 using 20 mM KCl. (○) P_0 final acidic cleaning (●) P_0 final alkaline cleaning, (□) retention final acidic cleaning (■) retention final alkaline cleaning.

after acidic or alkaline cleaning. This applied to all membranes in this study, semi- as well as completely aromatic PA ones. These results deviate from others previously reported. Schaep et al. [20] reported an increase in the retention of divalent ions with increasing temperature, while Snow et al. [19] found the retention of monovalent salts to be independent of temperature. The difference in the findings between Snow et al. [19] and Scheap et al. [20] could be due to that the effect of charge exclusion is different for mono- and divalent salts. The charge exclusion is also dependent on membrane type and pH, which might explain the difference in temperature dependency of the retention of monovalent salts reported in this study (Figs. 9–11) and by Snow et al. [19]. However, hysteresis effects due to temperature changes could be a problematic issue when comparing literature data.

5. Conclusions

The NF performance changed depending on the cleaning procedure and rinsing/NF temperature, showing increased, decreased or unchanged KCl retention when increasing the temperature from 20 °C to 60 °C after cleaning depending on the experimental history.

The aromatic PA membranes, NF90 (NF) and HR98PP (RO), showed similar performance when changing the cleaning agent and temperature, and more stable conditions for NF at elevated temperatures were achieved after a final alkaline cleaning stage than after a final acidic cleaning stage for these membranes.

The performance of the HR98PP RO membrane at 40 °C was the same as that of the NF90 NF membrane at 20 °C.

The polypiperazine-based, PA NF membranes, NF200 and NFT-50, showed similar performance when varying the cleaning conditions and operation temperature. A final acidic cleaning stage appears to be more suitable for NF at elevated temperatures for polypiperazine-based PA membranes.

The Desal-5DK membrane showed no changes in water permeability due to the combined effect of cleaning and temperature. However, the retention initially decreased after both acidic an alkaline cleaning, but increased after rinsing at a higher temperature, and resulted in various levels of hysteresis in the retention, depending on the rinsing temperature used. The results indicate that the membrane should be rinsed at the maximum process temperatures prior to NF at elevated temperatures.

These results can be used to optimise the performance of NF at elevated temperatures, and stress the need to separate changes in the membrane itself from those due to fouling.

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