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Abstract: Nanofiltration membranes (NF) are being employed in pretreatment unit operations in both thermal and membrane seawater desalination processes and as partial demineralization to seawater. In order to predict NF membrane performance, a systematic study on the filtration performance of selected commercial NF membranes against seawater is presented in this paper. Two commercial nanofiltration membranes (NF90 and NF270) have been investigated in details to study their performance in filtering the salt mixture, synthetic and real seawater in a cross-flow NF membrane process at a pressure range from 4 to 9 bars. The Spiegler-Kedem model was used to fit the experimental data of rejection with the permeate flux in order to determine the fitting parameters of the reflection coefficient (σ) and the solute permeability (P_s). The results showed that the rejection increases with pressure for NF90 and slightly increases with pressure for NF270. Also, the NF90 membrane has

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shown to be able to reject both monovalent and divalent of all investigated mixtures and seawater with very reasonable values but at a relatively low flux. Moreover, it reduced the salinity of investigated seawater from 38 to 25.5 g/L using one stage of the NF membrane at 9 bars. This makes NF90 more suitable for the application in the pretreatment of desalination processes. On the other hand, NF270 can reject monovalent ions at relatively low values and divalent ions at reasonable values. It has also reduced the seawater salinity to 33.6 g/L, but at a very high permeate flux. The SKM model fitted the experimental data of divalent ions in salt mixture and seawater.

Keywords: Nanofiltration, salt mixture, synthetic seawater, real seawater, salt rejection, pretreatment, partial demineralization, Spiegler-Kedem model

INTRODUCTION

A nanofiltration membrane is a type of pressure driven membrane that has properties in between those of ultrafiltration (UF) and reverse osmosis (RO) membranes. NF membranes extend the applications of membrane processes and are considered a promising technique for many future applications including water treatment. Moreover, NF membrane processes have many desirable features such as low operation pressure, high flux, high retention of multivalent anion salts, and organic molecular compounds with relatively low molecular weight (200–1000 g/mol), relatively low investment, operation, and low maintenance costs. A recent comprehensive review on the use of NF membranes in water treatment has been presented elsewhere (1).

Nanofiltration (NF) membranes have recently been used in pre-treatment units in both reverse osmosis (RO) and thermal processes (2, 3). This will treat most of the desalination problems such as scaling, fouling, high-energy requirements, and the requirement of high quality construction materials. Furthermore, the combination of NF with thermal processes will make them work at a high distillation temperature in the range of 120 to 160°C with high distillate recovery, while NF-RO will produce a high quality of water without the need for a second desalination stage. This will enhance the production of desalted water and reduces its production cost; yet it is an environmentally friendly process. On the other hand, NF membranes have also been used to filtrate seawater directly for partial demineralization applications where the RO process cannot be used to carry out this operation (4, 5). Two successive NF stages using NF90 membrane were conducted by Pontie et al. (4) to obtain partial demineralization of Biarritz's seawater (south-west France). The results showed that the salinity of the seawater was reduced from 35 to 9 g/L at a pressure of 10 bar. In another study (5), two different NF membranes (NF70 and NF200) were also employed to partially demineralize the same seawater by measuring the permeate salinity and the rejection of three cations of Na^{+1}, Ca^{+2}, and Mg^{+2}. In comparison between NF70 and

NF200, it was seen that the latter membrane is able to reject calcium ion more than the magnesium ion. Moreover, the salinity was reduced from 35 to 9 g/L with one stage using NF70 at pressure of 25 bars, while for the NF200 membrane four stages at 10 bars were employed to reach the latter salinity. This ability of novel NF membranes for a more selective demineralization of salty solutions using low costs materials makes it an interesting technique in many respects.

In a previous work (6–8), the filtration of the single seawater salts at different concentration levels was investigated using three NF90, NF270, and N30F membranes. It was seen that the rejection of all investigated salts was increased with increasing pressure and decreasing concentration. The Spiegler-Kedem model (SKM) was used to fit the experimental results of rejection *versus* permeate flux and to find the fitting parameters of reflection coefficient (σ) and solute permeability (P_s) for each salt and the corresponding membrane. The results showed that there was a good agreement between the theoretical and the experimental data of all investigated salts for all membranes except one case. This case was for the membranes that have low rejection and low flux.

In this work, the filtration of different salt mixtures at high salinity and the synthesis and real seawater using only NF90 and NF270 membranes will be investigated. Two different mixtures will be used in order to prepare ions at high salinity similar to the ions found in the real seawater. Furthermore, the effects of pressure on permeate flux and rejection for each ion in the investigated salt mixtures will also be discussed. SKM model will be applied to the experimental data of rejection *versus* permeate flux for each ion in all salt mixture including the seawater sample in order to check its validity to the experimental data of each ion in the investigated mixtures, including real seawater and to find the fitting parameters of reflection coefficient (σ) and solute permeability (P_s) for each ions. Finally, the seawater sample collected from the coast of Oman will be analyzed and rejected at different pressure using both investigated membranes.

THEORY

The transport of the solute through ultrafiltration, nanofiltration, and reverse osmosis membranes can be described by irreversible thermodynamics where the membrane is considered as a black box. Kedem and Katchalsky (10) introduced the relation of the volumetric flux J_v and the solute flux J_s through a membrane in the following equations:

$$J_v = L_P(\Delta P - \sigma\Delta\Pi) \qquad (1)$$

$$J_s = P_s\Delta C + (1 - \sigma)CJ_v \qquad (2)$$

where σ, P_s, and L_p are the reflection coefficient, solute permeability and pure water permeability respectively. Equation (2) shows that the solute flux is the sum of diffusive and convective terms. Solute transport by convection takes place because of an applied pressure gradient across the membrane. A concentration difference on both sides of the membrane causes diffusive transport. When high concentration differences between the reject and the permeate exist, Speigler-Kedem (11) used the above equations and obtained the following expression of the rejection rate of the solute related to the permeation flux:

$$\mathrm{R} = \sigma \frac{(1 - \mathrm{F})}{(1 - \sigma\mathrm{F})} \tag{3}$$

$$\mathrm{F} = \exp\left(-\frac{(1 - \sigma)}{\mathrm{P_S}} \mathrm{J_v} \right) \tag{4}$$

where R is the rejection. According to equation (3), the rejection increases with increasing the water flux. The parameters σ and $\mathrm{P_s}$ can be determined from the experimental data of rejection (R) as a function of volume flux ($\mathrm{J_v}$) using the best-fit method. The reflection coefficient (σ) is a parameter that measures the degree of semi-permeability of the membrane, reflecting its ability to pass the solvent in preference to the solute. When an osmotic difference ($\Delta\pi$) across an imperfectly semi-permeable membrane is compensated by an applied pressure (ΔP) so that the volumetric flow is zero (ΔP is smaller than $\Delta\pi$), the ratio between the two is defined as σ, as shown in equation (5).

$$\sigma = \left(\frac{\Delta P}{\Delta \pi} \right)_{Jv=0} \tag{5}$$

A value of $\sigma = 1$ means that the convection solute transport does not take place at all. This is the case for ideal RO membranes where the membranes have no pores available for the convective transport. In an entirely unselective membrane in which a concentration gradient does not cause volumetric flow at all, $\sigma = 0$. While for the UF and NF membranes which have pores, the reflection coefficient will be $\sigma < 1$ especially if the solutes are small enough to the entire membrane pores under the convective transport effect (12).

Since the concentration polarization was neglected according the experimental conditions, the rejection, R, was calculated using the following equation:

$$R = 1 - \left(\frac{C_p}{C_f} \right) \tag{6}$$

where $\mathrm{C_p}$ and $\mathrm{C_f}$ are permeate and feed concentrations (ppm) respectively.

The pure water permeability, PWP ($L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$), was calculated as:

$$PWP = \frac{V_p}{t \cdot A \cdot P} \tag{7}$$

where V_P is the Volume of permeate (L), t is time (h), A is effective membrane area (m^2) and P is the applied pressure (bar).

EXPERIMENTAL

Set-Up and Chemicals

The filtration experiments were carried out in a laboratory scale test cell using a cross-flow module. The experimental rig used in the filtration of single salts is described in detail elsewhere (6–8). The permeation experiments were carried out in a laboratory scale test cell. Three liters of the feed were pumped using a stainless steel gear pump into the filtration cell. A circular disc membrane with an effective membrane area of 12.6 cm^2 was employed. The trans-membrane pressure and volumetric flow rate were adjusted using the concentrate (reject) outlet valve. The pressure was varied between 2 bars and 9 bars. The experiments were carried out at ambient temperature in a total re-circulation mode, i.e. both the concentrate and the permeate streams are re-circulated into the feed tank, so that the feed concentration is kept approximately constant. Two polyamide NF membranes (NF90 and NF270), manufactured by the Dow company, were used to carry out the filtration experiments for all investigated salt mixture solutions. The manufacturer claims NaCl Rejection % (Product Water flux (L/m^2h)) of $85–95^{++}(28.4)^{+}$ and $40–60^{++}(55.6)^{+}$ for NF90 and NF270 respectively. The deionized water used for preparation of the salt solutions was obtained through demineralization using ion exchange followed by reverse osmosis. The conductivity of the water was lower that 1 $\mu S/cm$. All salts used to prepare salt mixtures were obtained from Fisher scientific-UK with the purity higher than 99.5%. In this study, two different salt mixtures have been prepared and filtered at concentration similar to seawater. Table 1 shows the concentration of anions and cations of the salt mixtures. Mixture *I* contains the main ions and cations in seawater which have the highest concentration in the seawater, while mixture *II* is the synthetic seawater as its concentration of anions and cations are similar to that in the real seawater (9), they are shown in the last column in Table 1. The remaining ions such as (Br^-, HCO_3^-, Mn^{-2}, and I^-) have been neglected for the reason that their concentrations are relatively very low (108 ppm). The last column in Table 1 shows that the most salinity (around 86%) of the seawater comes from two ions (Na^{+1} and Cl^{-2}). Therefore, all investigated mixtures contain NaCl salt at relatively high concentration as a basic

Table 1. The ions concentration for the investigated salt mixture (ions concentration (ppm))

Ion	Mixture *I* ($NaCl + MgCl_2 + Na_2SO_4$) (ppm)	Mixture *II* (Mixture *I* + $KCl + CaSO_4$) (ppm)	Real seawater (Dusogi, 2003) (ppm)
Na^+	11910	11267	11019.6
Cl^-	18129	20014	19810.8
SO_4^{-2}	2704	1084	2764.8
Mg^{+2}	595	442	1328.4
Ca^{+2}	–	524	417.6
K^{+1}	–	241	417.6
Total (ppm)	33338	35742	35759

compound. Mixture *I* ($NaCl$, $MgCl_2$, and Na_2SO_4) contain four main ions (Na^{+1}, Cl^{-1}, Mg^{+2}, and SO_4^{-2}) found in the seawater at high concentrations nearly similar to their concentrations in the seawater. Both salts (KCl and $CaSO_4$) were added to mixture *I* to prepare mixture *II* to study their effect on the rejection and the permeate flux of each investigated ion in this mixture. Mixture *II* contains, in this case, six ions (Na^{+1}, Cl^{-1}, SO_4^{-2}, Mg^{+2}, K^{+1}, and Ca^{+2}) at high concentration similar to their concentration in the seawater as shown in the last column of Table 1. So, mixture II is called synthetic seawater for the reason that its ions are similar to the main ions found in the real seawater. Finally, the real seawater sample has been collected from the Indian Ocean in the Sultanate of Oman. One of the advantages of using real seawater in this study is that it contains biological and organic matters which are not found in laboratory prepared seawater. The main characteristics of the studied seawater were presented elsewhere (13) and shown in Table 2. These parameters have been measured for the Indian Ocean during a test period of 18 months. More details about these parameters

Table 2. Main seawater characteristics for the Indian Ocean at the coast of Oman (12)

Parameters	High	Low	Average
Temperature (°C)	26.7	21.6	33.2
pH	8.13	7.86	8
Conductivity (mS/cm)	55.3	54.2	56.5
SDI, %/min.	6.2	3.6	20
Turbidity, NTU	0.22	0.12	0.56
Fe, mg/L	<0.01	–	–
TOC, mg/L C	<5	<2	–
Particles >1 μm part/mL	2469	1633	3296
Hydrocarbons, μm/L	2.06	0.46	4.36

were found in a later reference (13). On the other hand, parameters such as the ion concentration, conductivity meter, and pH value will be measured again for the typical collected seawater sample.

Filtration Procedure

In all filtration experiments, the membranes were immersed overnight in water before being used in any experimental work and each membrane was pressurized to 9 bars for at least 2 hours using pure water to avoid any compression effects and to establish leak tightness. The filtration experiment was carried out by circulating five liters of the feed solution using a stainless steel gear pump into the filtration cell. The trans-membrane pressure and volumetric flow rate were adjusted using the concentrate (reject) outlet valve and the variable speed key of the pump. The pressure was varied between 9 and 4 bars. The experiments were carried out in a total re-circulation mode, i.e. both the concentrate and the permeate streams were re-circulated into the feed tank, so that the feed concentration was kept approximately constant. Full details about sample collection is shown elsewhere (1–8).

The permeate flux and rejection were determined by varying the applied feed pressure. On the other hand, salt mixture and synthesis have the same procedure with a little difference. The feed pressure for both salt mixture and seawater filtration experiments was changed from high pressure at 9 bars down to 4 bars at the specific pressure of (9, 8, 7, 6, 5, 4 bars). Before carrying out the filtration experiments for the real seawater, a vacuum filtration using Buchner filtration with 8 μm size filter paper was used to remove the sand and large particles from the seawater sample (Table 3).

Table 3. Analysis of the investigated seawater before and after filtration experiments with NF90 and NF270 membranes at 9 bar

Parameter	Investigated seawater	Permeate after 1 stage NF90 (at 9 bar)	Permeate after 1 stage NF270 (at 9 bar)
Salinity (g/l)	38.0	25.5	33.6
PH	8.29	7.96	7.98
Conductivity (mS/cm)	51.4	36.2	46.6
Na^{+1}	12720.1	8531.9 (31.5%[a])	11110.2 (9.7%)
K^{+1}	420.5	281.2 (32.7%)	350.2 (12.8%)
Cl^{-1}	23255.8	14504.2 (37.5%)	20000.6 (12.7%)
Ca^{+2}	448.6	165.8 (62.1%)	297.0 (35.3%)
Mg^{+2}	1515.4	555.4 (62.9%)	763.0 (52.7%)
SO_4^{-2}	3143.1	1076.4 (66.5%)	460.2 (86.5%)

[a] Rejection value.

Analytical Methods

Several analytical methods were used to determine the solute concentration salt mixture and seawater samples in feed and permeate solutions in order to calculate the solute rejection. Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) was used to measure the investigated ions (Na^{+1}, K^{+1}, Mg^{+2}, Ca^{+2}, CO_3^{-2} and SO_4^{-2}) in salt mixtures and seawater. It is a highly sensitive method for multi-elemental detection. The basis of the technique is that when an atom is excited, and then returns to its ground state, it emits radiation of intensity that is directly proportional to the number of emitting atoms and hence concentration. More details about the analytical method are found elsewhare (14). The chloride ion concentration was measured using a chloride ion selective electrode. A Russel chloride ion selective electrode Model 662–0632 with a double junction reference electrode Russel Model S8168 was used to measure the electrode potential of chloride ion in the feed solution and the permeate line. These electrodes were used specifically in the filtration experiments mixtures and synthesis and real seawater in order to determine the concentration of chloride ion present in the solution. They allowed the measurement of the electrode potential quickly, simply, and accurately. A digital pH/mV meter Russel Model CD660 was used to measure the electrode potential given in mV up to one decimal place.

An ionic strength adjustor (ISA) was used to provide a constant background ionic strength for both standard and sample solutions; the activity coefficient of the chloride ion in solutions will be similarly constant. It was made up from 5.0 M $NaNO_3$ solution. For the chloride ion solution, the 1000 ppm chloride solution was used as a standard, as well as a 5 M ISA solution. A calibration curve between the electrode potential reading and concentration of a standard chloride solution on a log axis was prepared which will be linear over a range of analytical concentrations as shown in Fig. 1. This curve was used to calculate the concentration of chloride ion in the investigated salt mixtures and seawater.

Once the chloride potential is taken, the concentration of chloride is calculated using the line or the linear regression equation shown in Fig. 1. More details about the analytical method are found elsewhere (15).

RESULTS AND DISCUSSION

Filtration results for the investigated salt mixtures, synthetic seawater, and real seawater will be presented separately. The effect pressure on rejection will be shown for both investigated membranes (NF90 and NF270) and a comparison between both membranes in their treatment of the seawater sample will also be discussed.

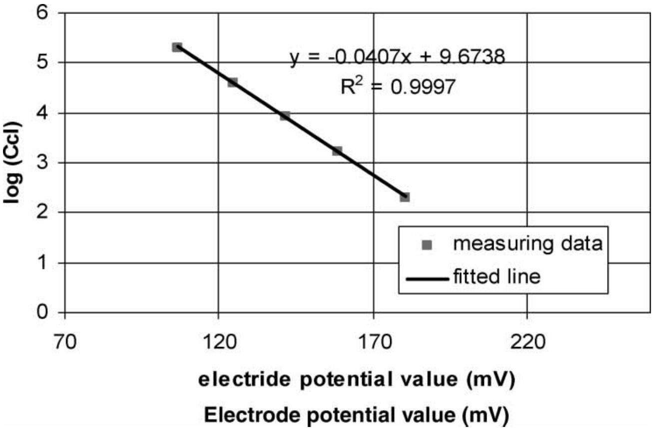

Figure 1. The calibration curve for chloride concentration.

Mixture *I* (NaCl, Na_2SO_4, and $MgCl_2$)

The ions of this mixture (Na^{+1}, Cl^{-1}, SO_4^{-2}, and Mg^{+2}) represent the main ions found in the seawater, Table 1 shows their concentrations. Figure 2 shows the rejection of these ions with pressure for both membranes. It is clear that the rejection of all ions increases with increasing pressure for NF90 while for NF270 it slightly increases with pressure. Also, the rejection of divalent ions is higher than that of monovalent ions for both membranes due to the ion size of the former ions. The rejection of Mg^{+2} for NF90 (82% at 9 bars) is higher than that of NF270 (58% at 9 bar), while both membranes are able to reject sulphate anions at the same efficiency (85%). However, NF270 is better than NF90 in rejecting the latter anion at pressures lower than 8 bars. On the other hand, NF90 is more efficient than NF270 in rejecting monovalent ions. This could be explained on the basis of the steric hindrance mechanism due to the fact that NF90 has a relatively smaller pore size than NF270 which was measured using an Atomic Force Microscope as shown in previous work (16). It can be seen from the filtration results that both investigated membranes are capable of preventing the scaling over the desalination equipments with the same efficiency. For the reason that the NF90 membrane is able to reject the monovalent ions more than NF270 membrane, the NF90 membrane is preferred to be used for partially desalination processes. However, in order to have a complete rejection of the later ions it is recommended to carry out the filtration experiment at pressures higher than 9 bar or use more than one NF stage in filtration of the seawater to find out if the linearity still exist. On the other hand, the permeate flux of mixture *I* with pressure for both membranes under study is shown in Fig. 3 where the permeate flux increases with increasing pressure due to the increase of the solvent flux. In addition, the permeate flux for NF270

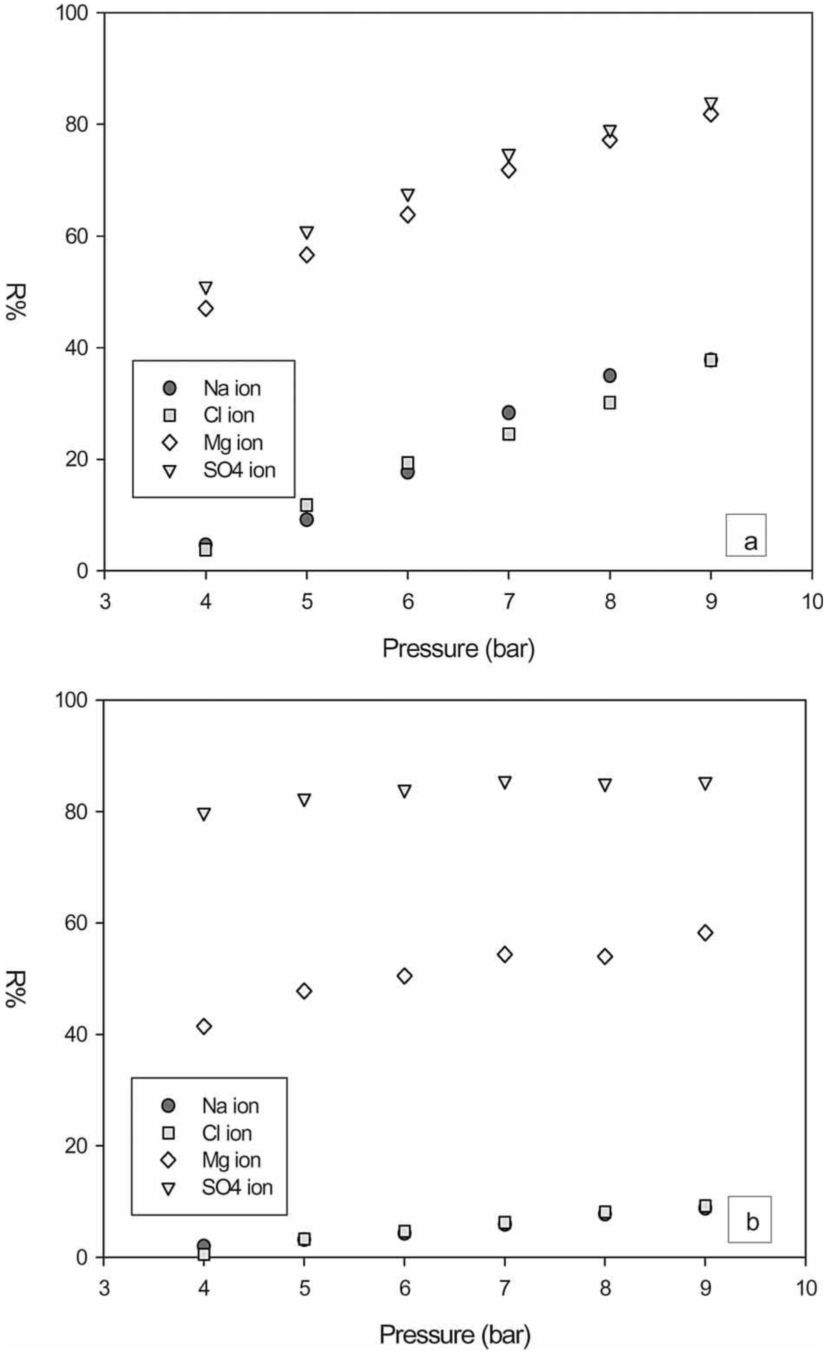

Figure 2. Rejections of Na^{+1}, Cl^{-1}, SO_4^{-2}, and Mg^{+2} ions *versus* pressure for both membranes (a) NF90 and (b) NF70.

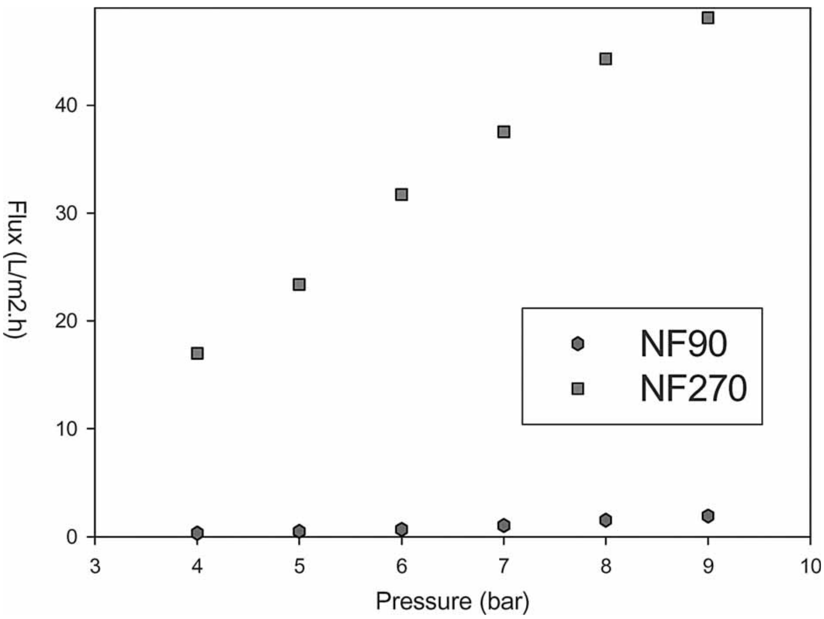

Figure 3. The permeate flux of mixture *I* *versus* pressure for NF90 and NF270 membranes.

($51.6\ L/m^2 \cdot h$) is very much higher than that of NF90 ($1.91\ L/m^2 \cdot h$). As a result, NF270 membrane is better than NF90 membrane in preventing sulphate scaling. The higher rejection obtained for SO_4 when NF270 was used may be due to a higher negative charge for this membrane.

The rejection of all investigated ions found in mixture *I* with permeate flux for both membranes is shown in Fig. 4. This figure shows that the rejection for all ions increases with pressure for NF90 while for NF270 the rejection slightly increases with pressure (almost constant). This means that the NF270 membrane is potentially able to reject the investigated ions even at low permeate flux (pressure). Furthermore, this membrane has a high rejection of SO_4^{-2} with higher flux than that of NF90 as shown in Fig. 4 while the rejection of Mg^{+2} and monovalent ions for the latter membrane is higher than that of NF270 but at a relatively low flux. The SKM model was used to fit the experimental data of rejection with flux, which is shown as a dashed line in Fig. 4. The model fitted the data of divalent ions (Mg^{+2} and SO_4^{-2}) well for both membranes while the model is weak for monovalent ions and not valid especially for NF270, which has relatively low rejection for the later ions. For this reason, it was not possible to have real values for the fitting parameters of σ for both membranes and P_s for NF270 as shown in Table 4. On the contrary, there are real values of the later fitting parameters for the divalent ions for both membranes. These values are dependent on the type of ion and on membrane as shown in Table 4. For divalent ions, NF90 has

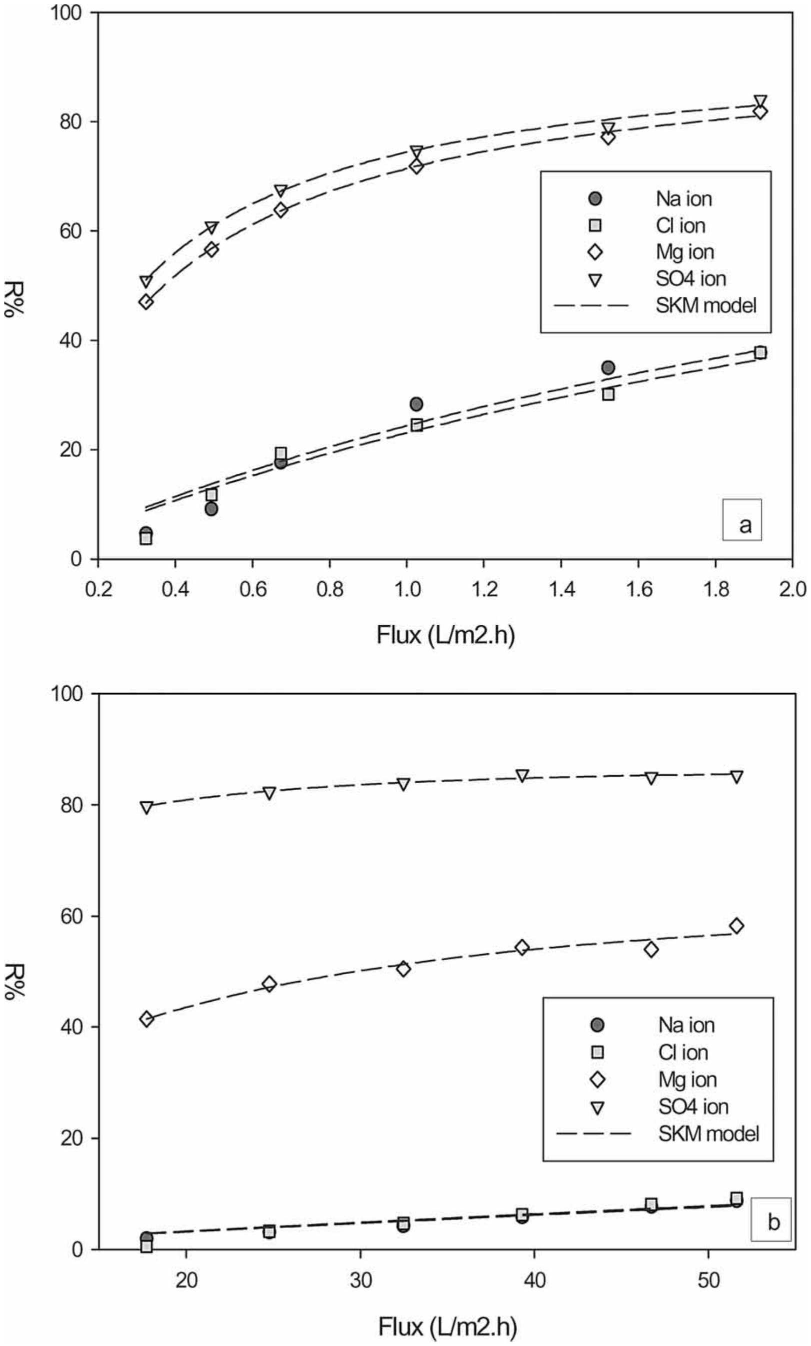

Figure 4. Rejections of Na^{+1}, Cl^{-1}, SO_4^{-2} and Mg^{+2} ions with the flux for both membranes (a) NF90 and (b) NF270.

Table 4. Reflection coefficient (σ) and solute permeability (P_s) for investigated ions of mixture *I* for NF90 and NF270 membranes

Ions with feed concentration (ppm)	Membranes			
	NF90		NF270	
	σ	P_s $(L/m^2 \cdot h)$	σ	P_s $(L/m^2 \cdot h)$
Na^{+1} (11910)	[a]	3.10	[a]	[a]
Cl^{-1} (181129)	[a]	3.33	[a]	[a]
Mg^{+2} (595)	0.917	0.323	0.618	11.77
SO_4^{-2}(2704)	0.915	0.270	0.862	2.44

[a] No obtained data

a relatively high value of σ with low value of P_s while NF270 has a high value for the later paramter with a medium value for the former one.

Mixture *II* (Synthetic Seawater)

The filtration of synthetic seawater is presented in this section. The composition of synthetic seawater is shown in Table 1, it contains both monovalent ions (Na^{+1}, K^{+1}, Cl^{-1}) and divalent ions (Ca^{+2}, Mg^{+2}, and SO_4^{-2}) at salinity similar to that of the seawater. These ions represent the main ions found in the real seawater as shown in the last column in the Table 1. Figure 5 shows the rejection of each ion in the synthetic seawater with pressure in the range of 4 to 9 bars for both investigated membranes. As found in the rejection of all ions in the above mixture, the rejection increases with pressure for NF90 and slightly increases with pressure for NF270 as shown in Fig. 5. In addition, the rejection of divalent ions is higher than that of the monovalent ion for both membranes. For NF90 the rejection of divalent ions are around to be $\sim$75% at 9 bars and higher than that of NF270 especially the rejection of Ca^{+2}, and Mg^{+2} cations (41% and 56% at 9 bars). This means that the former membrane is better than the latter membrane in preventing the magnesium and calcium scaling. A possible reason for that may be because of the higher concentration of mixture *II* (35000 ppm compared to 33000 ppm for mixture *I*). However, both membranes have the same efficiency in the rejection of sulphate ions. On the other hand, the rejection of all monovalents for NF90 is again higher than that of NF270 especially at pressures higher than 6 bars. It is worth mentioning that the addition of the new ions (Ca^{+2} and K^{+1}) to the ions in mixture *I* has decreased their rejections of both membranes. This could be explained for the reason that there is a competition between the latter cations and other previous cations (Na^{+1} and Mg^{+2}) in passing through the pores during the filtration processes. From the filtration of the

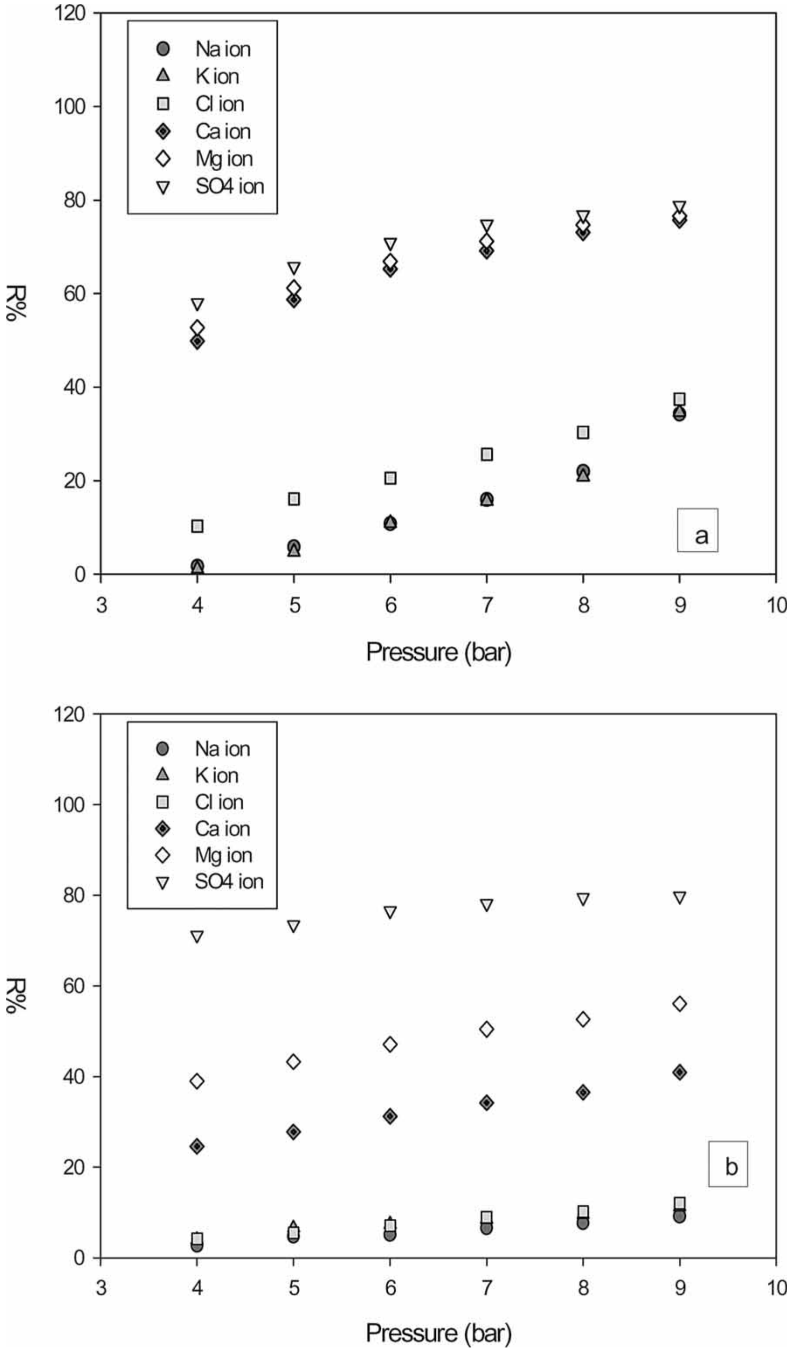

Figure 5. Rejections of all ions found in synthesis seawater *versus* pressure for both membranes (a) NF90 and (b) NF270.

synthetic seawater, it can be concluded that NF90 can potentially reject all main ions found in the seawater with reasonable values. This confirms its suitability to be employed for pretreatment in the desalination processes but with a relatively low permeate flux. However, NF270 shows less rejection for most ions of seawater but with high permeate flux as shown in Fig. 6. This figure shows that the flux of synthetic seawater increases with pressure. Again, NF270 has a flux ($47\,\mathrm{l/m^2 \cdot h}$ at 9 bar) higher than that of NF90 ($4.1\,\mathrm{l/m^2 \cdot h}$ at 9 bar). The ion rejections of synthetic seawater *versus* permeate flux for both membranes are shown in Fig. 7. It is obvious that the rejection for all ions expect SO_4^{-2} increases with pressure for both membranes. The rejection of all ions for NF90 at low flux is shown to be higher than that of NF270 at high flux.

The dashed lines shown in Fig. 7 represent the fitting of SKM model to the experimental rejection data of all ions of synthetic seawater with flux for both membranes. It is clear that the model is fitted well to the experimental data of divalent ions for both membranes and in one case for monovalent ion. This case is for the data of Cl^{-1} anion for NF90 as shown in Fig. 7a, and this is due to its large rejection among the investigated monovalent ions. Although the dashed lines fitted the experimental data of monovalent for NF270 as shown in Fig. 7b, but according their fitting parameters (σ and P_s) which are shown in Table 5, the model is not valid to the data of the later ions.

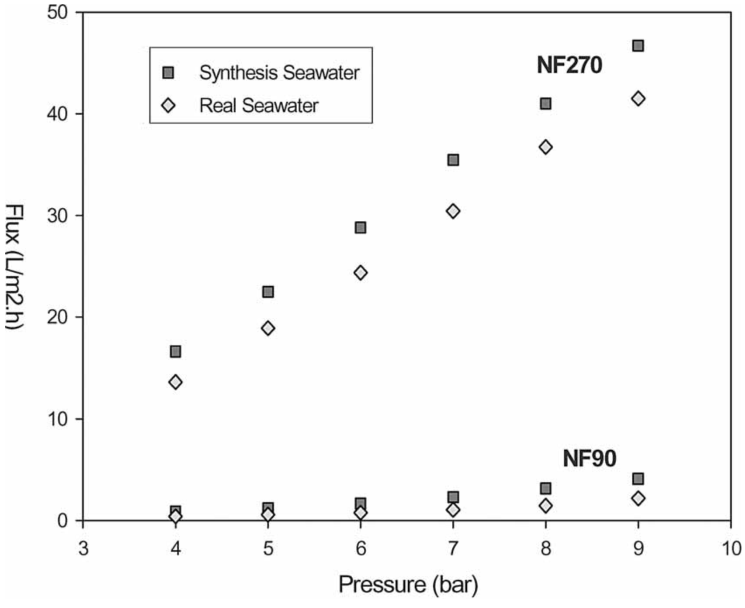

Figure 6. The permeate flux of synthetic and real seawater *versus* pressure for NF90 and NF270 membranes.

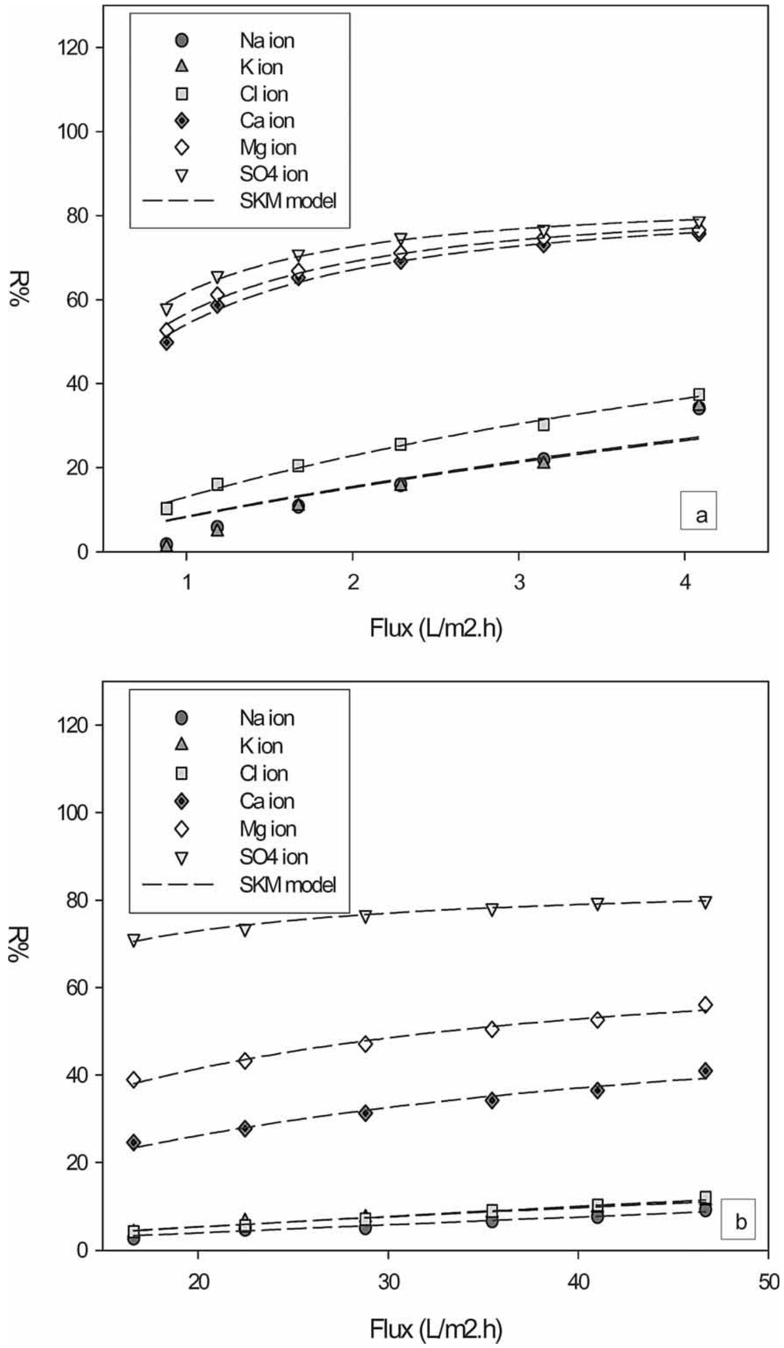

Figure 7. Rejections of all ions found in synthetic seawater with the flux for both membranes (a) NF90 and (b) NF270.

Table 5. Reflection coefficient (σ) and solute permeability (P_s) for each ions of filtered synthetic and real seawater for NF90 and NF270 membranes

Investigated ions	Membranes							
	NF90-Synthesis		NF270-Synthesis		NF90-Real		NF270-Real	
	σ	P_s ($L/m^2 \cdot h$)	σ	P_s ($L/m^2 \cdot h$)	σ	P_s ($L/m^2 \cdot h$)	σ	P_s ($L/m^2 \cdot h$)
Na^{+1}	[a]	10.9	[a]	[a]	[a]	6.77	[a]	[a]
K^{+1}	[a]	11.1	[a]	[a]	[a]	6.93	0.619	[a]
Cl^{-1}	0.830	5.42	[a]	[a]	[a]	4.87	[a]	[a]
Ca^{+2}	0.815	0.594	0.511	23.6	0.813	0.838	0.397	15.9
Mg^{+2}	0.815	0.524	0.629	13.7	0.786	0.735	0.586	12.7
SO_4^{-2}	0.830	0.411	0.817	3.93	0.739	0.451	0.868	2.17

[a] No obtained values.

According to this table, there are no obtained real values for σ for all monovalent ions except for Cl^{-1} anion using NF90 ($\sigma = 0.83$ and $P_s = 5.4\ L/m^2 \cdot h$). In addition, the values of the parameter of P_s for the latter ions are very high and not logical. This finding again confirms that the SKM model is not valid to most of the data of monovalent ions for both membranes. However, for the divalent ions there are real values to the fitting parameters (σ and P_s) as shown in Table 5. For NF90, The values of σ seemed to be relatively high ~0.82 for all divalent ions and Cl^{-1} anion while for NF270 the value of σ was in the range of 0.51 to 0.82 depending on the rejection values of the typical ion. The membranes with high rejection usually have a high value of σ. On the other hand, Ps depends on the type of used membrane in the filtration processes as shown in Table 5.

Real Seawater (Indian Ocean-Coast of Oman)

The filtration study of real seawater from the Indian Ocean, collected from the coast of Oman, is discussed in this section to study the potential of both NF90 and NF270 membranes in the Gulf region. The seawater sample was analyzed in terms of salinity, pH, and conductivity. The main ions found in the seawater are shown in Table 3. It is clear from the analysis that the seawater sample is basic with relatively high salinity compared to the salinity of seawater shown in Table 1. In particular, the measured salinity (38 g/I) to the investigated seawater sample is slightly higher than the salinity (~35 g/I) and the concentration of all measured ions is higher than measurements quoted elsewhere (4–5). This could be explained due to the high temperature and humidity of the Indian Ocean in the Sultanate of Oman in comparison to Biarritz's seawater which was studied by Pontie et al. (4–5). On the other hand, the second and third columns in Table 3 show the filtration results of the investigated seawater at 9 bars for NF90 and NF270 respectively. It was seen that NF90 is able to reduce the salinity (25.5 g/I) much better than that of NF270 (33.6 g/I) using one stage of NF membrane at 9 bars. For partial demineralization applications, it is recommended to either carry out the experiment at high pressure or use more than one NF stage. This is what Pontie et al. (2004) found in their work where the salinity was reduced from 35 to 9 g/I by either using of one stage of NF200 under pressure of 25 bars or four stages of NF70 at pressure of 10 bar. Moreover, the rejection of all monovalent and divalent ions for NF90 is higher than that of NF270 expect SO_4^{-2} anion. This leads to a conclusion that NF90 is better in preventing the scaling caused by Ca^{+2} and Mg^{+2} cations than NF270 which is preferred in preventing the sulphate scaling. However, the rejection of all investigated divalent ions at a typical pressure (9 bars) is much lower than 100% where the divalent ions are removed completely.

Figure 8 shows the rejection versus the pressure data of all investigated ions found in the Indian Ocean with a pressure in the range of 4 to 9 bars

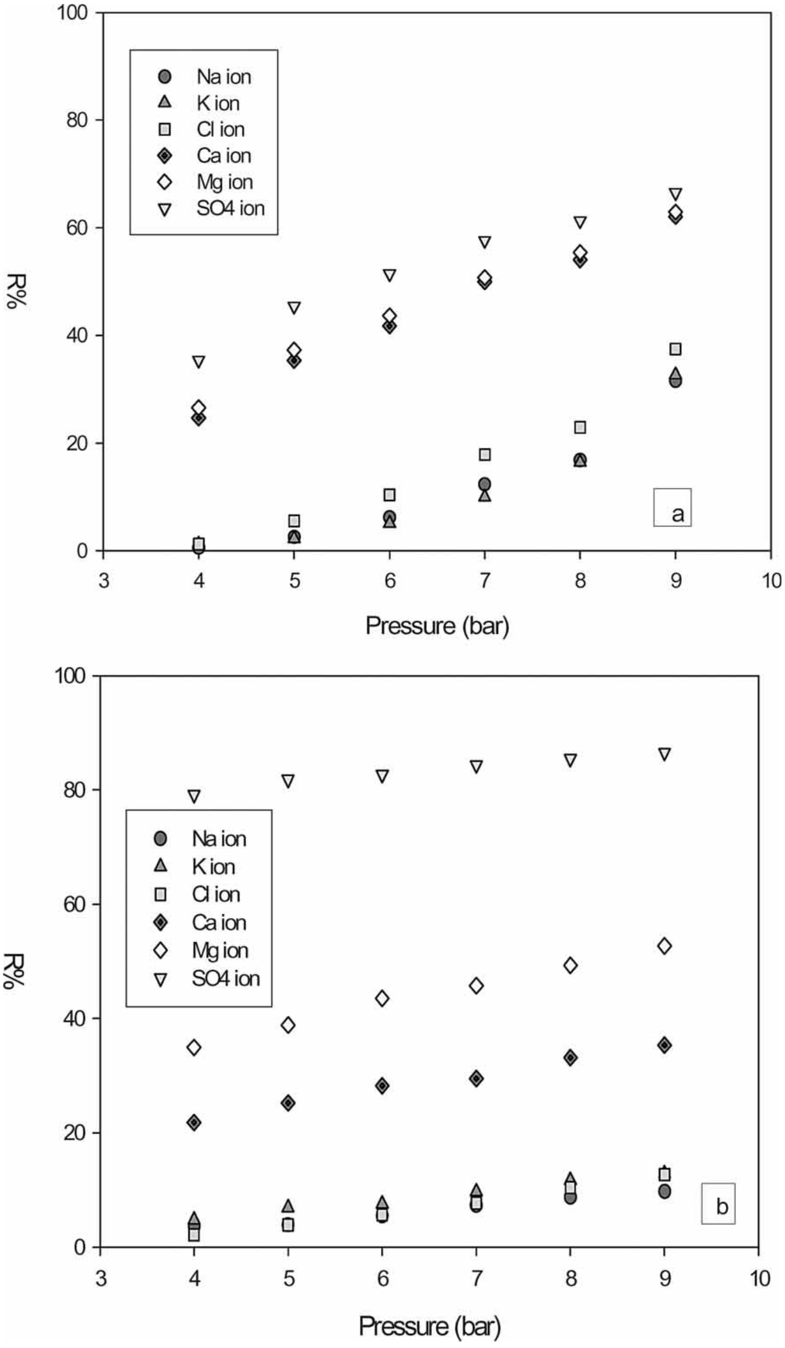

Figure 8. Rejections of all ions found in real seawater *versus* pressure for both membranes (a) NF90 and (b) NF270.

for both NF90 and NF270 membranes. It is obvious that the rejection of all ions increases with increasing pressure for both NF90 and NF270. As a comparison to the rejection of ions of synthetic seawater for both membranes, the rejection of ions of real seawater is lower than that of the ions of the synthetic seawater. The reason for that is the real seawater usually contains some secondary ions such as Br^-, $HCO_3{}^-$, Mn^{-2}, and I^- at low concentrations and some impurities such as bacteria and viruses. Furthermore, the relation of rejection of all ions in real seawater with pressure is almost similar to the relation found for synthetic seawater as shown in Fig. 5 and Fig. 8. In particular, the rejection of divalent ions of the investigated real seawater is higher than monovalent ions for both membranes; while for NF90 the rejection of all ions at pressure higher than 6 bars is more than that of NF270 expect SO_4^{-2} anion which its rejection using NF270 is higher than the rejection using NF90 over the range of studied pressure. However, at pressure lower than 6 bars, both membranes are shown to give similar rejection expect for the SO_4^{-2} anion (Fig. 8). This data clearly show that NF90 is better than NF270 in treating the investigated seawater sample. However, if the permeate flux is included as a new parameter to compare the efficiency of both membranes, NF270 is preferred to NF90 as the former membrane has a much higher flux ($41.5\ L/m^2 \cdot h$ at 9 bars) than the flux ($2.2\ L/m^2 \cdot h$ at 9 bars) of NF270 as shown in Fig. 6. This figure also shows that the permeate flux of real seawater increases with pressure for NF270 and slightly increases with pressure for NF90. Furthermore, the flux of real seawater seems to be lower than the flux of synthetic seawater, as shown in Fig. 8, due to the secondary ions and impurities, which are normally found in the real seawater. The ion rejections of real seawater versus the permeate flux for both membranes are shown in Fig. 9. It is clear that the rejection of all ions increases with pressure for NF90 while it slightly increases with pressure for NF270. Moreover, the rejection for the NF90 membrane is high at a relatively very low permeate flux while the NF270 membrane has a medium rejection with a high flux expect SO_4^{-2} anion where its rejection and flux are higher for NF270. The SKM model was also applied to fit the rejection of ions of seawater with flux for both membranes and shown as dashed lines in Fig. 9. The model is fitted well to the experimental data of divalent ions for both membranes. However, for monovalent ions the model was not good for both membranes even though the dashed lines fitted the experimental data of monovalent for NF270 as shown in Figure 9b. This is for the reason that the fitting parameters (σ and P_s) of all monovalent ions of real seawater for both membranes shown in Table 5 are not real and logical, confirming the invalidity of the SKM model to the data of later ions for both membranes. On the contrary, the model is applicable to the data of divalent ions for both membranes as their parameters are real and logical. Table 5 shows that the values of σ and P_s depend on the type of membrane and ions. The values of fitting parameters for real seawater are different than that for synthetic seawater, and this can be explained for the reason

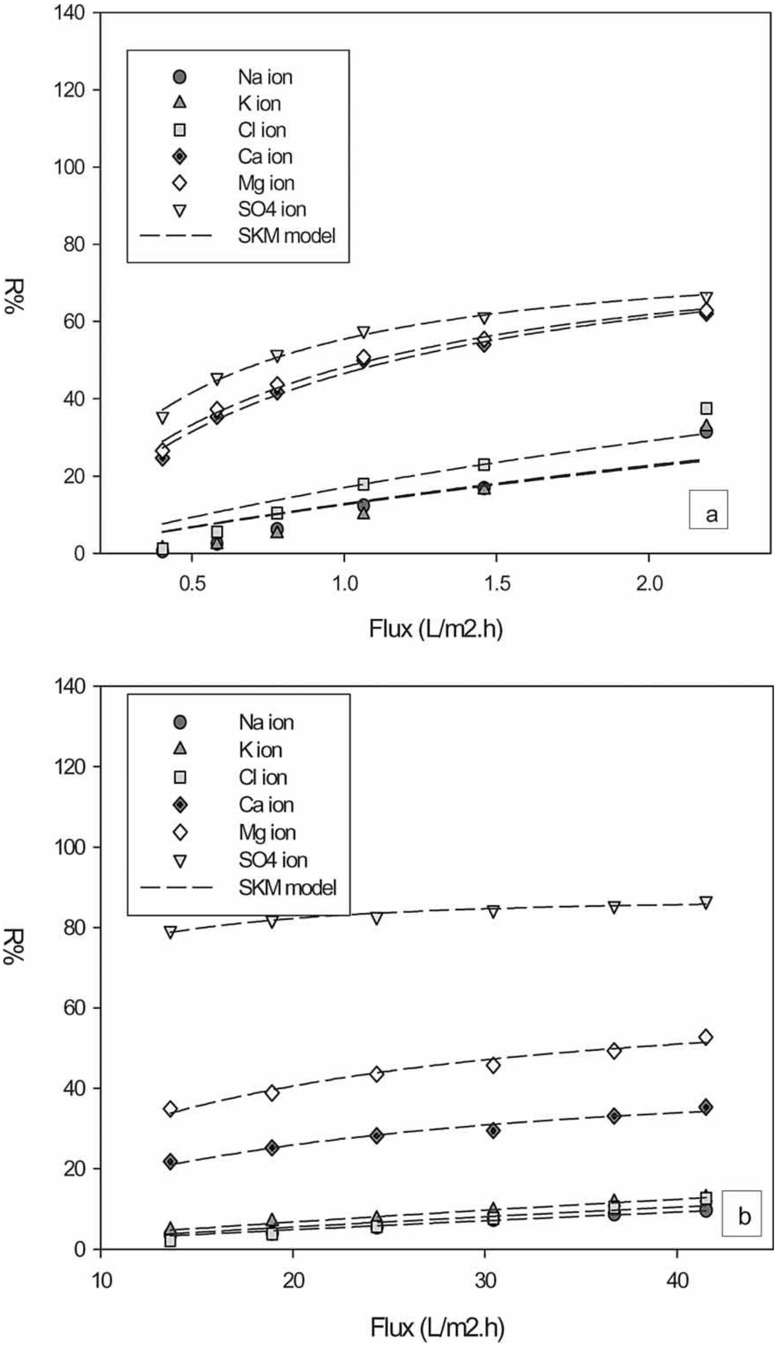

Figure 9. Rejections of all ions found in real seawater with the flux for both membranes (a) NF90 and (b) NF270.

that the feed concentration of all ions for both types of seawater is not the same as shown in Table 3.

CONCLUSIONS

NF90 and NF270 membranes have been used to filter different mixtures including synthetic seawater at salinity levels representative of seawater and pressure in the range of 4 to 9 bars. The results showed that the rejection increases with pressure for NF90 and slightly increases with pressure for NF270. The former membrane was found to be able to reject both monovalent and divalent of all investigated mixtures and seawater with reasonable values but with relatively low flux. Moreover, it reduced the salinity of investigated seawater from 38 to 25.5 g/I using one stage of NF membrane at 9 bar. This makes NF90 suitable for the application in the pretreatment of desalination processes and in partial demineralization applications. On the other hand, NF270 can reject monovalent ions at relatively low values and divalent ions at reasonable values and reduced the seawater salinity to 33.6 g/I, but at very high permeate flux. SKM model was used to fit the experimental data of rejection of each of the ions in salt mixtures and real seawater with the permeate flux in order to determine the fitting parameters of the reflection coefficient (σ) and the solute permeability (P_s). The model was not able to represent most experimental data of monovalent ions in salts mixture and seawater sample for both NF90 and NF270 due to their low rejection values. However, for divalent ions the results showed that there was a good agreement between the SKM fitting and the experimental data for both membranes.

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