Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Nanofiltration of Magnesium Chloride, Sodium Carbonate, and Calcium Sulphate in Salt Solutions

N. Hilal[a]; H. Al-Zoubi[a]; N. A. Darwish[b]; A. W. Mohammad[c]
[a] Centre for Clean Water Technologies, School of Chemical, Environmental and Mining Engineering, The University of Nottingham, UK [b] Chemical Engineering Program, The Petroleum Institute, Abu Dhabi, United Arab Emirates [c] Department of Chemical and Process Engineering, Universiti Kebangsaan Malaysia, UKM Bangi, Selangor Darul Ehsan, Malaysia

To cite this Article Hilal, N. , Al-Zoubi, H. , Darwish, N. A. and Mohammad, A. W.(2005) 'Nanofiltration of Magnesium Chloride, Sodium Carbonate, and Calcium Sulphate in Salt Solutions', Separation Science and Technology, 40: 16, 3299 — 3321

To link to this Article: DOI: 10.1080/01496390500423680

URL: http://dx.doi.org/10.1080/01496390500423680

Separation Science and Technology, 40: 3299–3321, 2005

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390500423680

Nanofiltration of Magnesium Chloride, Sodium Carbonate, and Calcium Sulphate in Salt Solutions

N. Hilal and H. Al-Zoubi
Centre for Clean Water Technologies, School of Chemical, Environmental and Mining Engineering, The University of Nottingham, UK

N. A. Darwish
Chemical Engineering Program, The Petroleum Institute, Abu Dhabi, United Arab Emirates

A. W. Mohammad
Department of Chemical and Process Engineering, Universiti Kebangsaan Malaysia, UKM Bangi, Selangor Darul Ehsan, Malaysia

Abstract: Nanofiltration (NF) membranes have been employed in pre-treatment unit operations in both thermal and membrane seawater desalination processes. This has resulted in reduction of chemicals used in pretreatment processes as well as lowering the energy consumption and water production cost and, therefore, has led to a more environmentally friendly processes. In order to predict NF membrane performance, a systematic study on the filtration performance of selected commercial NF membranes against brackish water and seawater is required. In this study, three commercial nanofiltration membranes (NF90, NF270, N30F) have been used to treat highly concentrated different salts solutions ($MgCl_2$, Na_2CO_3, and $CaSO_4$) at salinity level similar to that of brackish water and seawater. The main parameters studied in this paper are salt concentration and feed pressure. The experimental data were correlated and analysed using the Spiegler-Kedem model. In particular, the reflection

Received 6 September 2005, Accepted 12 October 2005
Address correspondence to N. Hilal, Centre for Clean Water Technologies, School of Chemical, Environmental and Mining Engineering, The University of Nottingham, NG7 2RD, UK. Tel.: +44(0)115 9514168; Fax: +44 (0)115 9514115; E-mail: nidal.hilal@nottingham.ac.uk

coefficient (σ) of all studied membranes and the solute permeability (P_s) have been determined for all membranes and at different salinity levels of studied salts. All the studied membranes fitted the model well for all investigated salts except the experimental data of $MgCl_2$ using N30F membrane, which did not fit well at low rejection. The results showed that NF90 produced a high rejection around 97% for all salts with medium permeate flux while NF270 gave a high flux with medium rejection and N30F gave low rejection and flux.

Keywords: Membrane, nanofiltration, salt rejections, permeate flux, seawater, pre-treatment, Spiegler-Kedem model

INTRODUCTION

Seawater has become an important source of fresh water (1) because of the changing weather patterns, increased industrialization and the tendency in recent years for the world's swelling population to dwell in areas where local supplies of high quality fresh water are less than adequate. Seawater is characterized by having high degree of hardness, varying turbidity, and bacterial contents and high TDS. These properties give rise to major problems such as scaling, fouling, high-energy requirements and the requirement of high quality construction materials. Conventional seawater thermal and/or membrane desalination processes are complex. To solve seawater desalination problems and to minimize their effects on productivity and water cost of conventional plants, nanofiltration membranes (NF) have recently been employed in pre-treatment facilities in both reverse osmosis (RO) and thermal processes (2–6). This will enhance the production of desalted water, reduce its production cost, and lowers the energy consumption of the desalination processes; yet it is an environmentally friendly process. Furthermore, the combination of NF with thermal processes such as multi-stage flash (MST) makes it possible to operate MSF plants on NF-product at high distillation temperature of 120°C to 160°C with high distillate recovery, and again without chemical additions. Similarly, the NF-RO process makes it feasible to produce high purity permeate from a single-stage RO process without the need for a second desalination stage. This process significantly improves the quality of permeate from otherwise low-performance RO membranes. (2) In addition, the correct choice of NF membrane is of vital importance for the pre-treatment of seawater, which will make or break the economical feasibility of the whole process.

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 have the advantages of providing a high water flux at low operating pressure and maintaining a high salt and organic matter rejection (7). The NF process benefits from ease of operation, reliability, and comparatively low energy consumption as well as high efficiency of pollutant removal (8). This helps in minimizing scale formation on equipment involved in both RO and thermal desalination processes. Therefore, nanofiltration membrane has given rise to worldwide interest. A recent comprehensive review on the use of nanofiltration membranes in water treatment has been presented elsewhere (9).

The separation performance of NF membranes depends mainly on the sieving (steric-hindrance) effect and Donnan (Electrostatic) effect since most of the commercial NF membranes are charged. So, the removal of neutral components (such as organics) results from size exclusion (solute and pore size), or may be a result from differences in diffusion rates in a non-porous structure, which depend also on molecular size (10, 11). The polarity and the charge of organics might influence the separation processes (12), especially when the pore sizes of membranes are large. In addition to the sieving effect, the rejection of ionic components (salt solutions) in NF membranes occurs as a result of charge interactions between the membrane surface and the ions (Donnan exclusion) as well as the difference of diffusivity and solubility of the ionic components or a combination of these. (13) These interactions depend on the characteristics of the electrolyte solution and the membrane itself such as the concentration, PH value, and the composition for the electrolyte solution while the surface charge, pore size, and the roughness for the membrane in addition to the temperature and the pressure of the filtration processes.

Many researchers (13–25) studied the rejection of different salt (e.g., NaCl, $MgCl_2$, $CaCl_2$, Na_2SO_4, $CaSO_4$ and $MgSO_4$) using different types of nanofiltration membranes. Their results showed that the rejection values changed according to the type of the NF membranes used. Schaep et al. (16) found that the rejection of NaCl using NF40 membrane was about 45% and this rejection increased up to 55% using UTC 20 membrane at 10 bars, while the rejection of $MgCl_2$ and Na_2SO_4 was about 95% for the two membranes. Afonso et al. (17) had similar results for the rejection of NaCl and Na_2SO_4, salts using Desal G-10 and Desal G-20 nanofiltration membranes, while the rejection of $MgCl_2$ was about 70% for both membranes at the same pressure. In another work, Hammeyer and Gimbel (19) studied the rejection of the NaCl, Na_2SO_4, and $CaCl_2$ at different concentrations and pressure using Desal 5DK and PVD1 nanofiltration membranes. Their results showed that the rejection of NaCl and Na_2SO_4 was slightly decreased as the concentration increased while the rejection for $CaCl_2$ was increased with increasing salt concentration for Desal 5DK. The reason for that is the higher charge of this membrane surface at higher concentrations. On the other hand, the Spiegler-Kedem model has been used by many investigators (20, 26, 27) in order to correlate their filtration experimental data and to calculate the phenomenological parameters σ (the membrane reflection coefficient) and P_s (the permeability of the salt) using best-fit method.

Koyuncu and Yazgan (26) found that this model was able to fit well with their experimental data (rejection versus permeate flux) for different salt mixtures using TFC-S NF membrane. They concluded that σ is constant for each of the anions and cations in the salt mixture whereas P_s was varied according to the type of the salt ions. Nevertheless, different conclusion has been obtained by other authors (20, 27) for the filtration of single salts showing that both parameters σ and P_s have changed and were dependent on the type of the filtered salt.

The above studies were carried out at relatively low salts concentrations. In this work, therefore, higher salt concentrations, representative of seawater salinity, will be handled using three different commercial NF membranes. This will establish the viability of using NF membranes in the pre-treatment step of desalination process. Towards this end, three different nanofiltration membranes (NF90, NF270, and N30F) are tested using a cross flow filtration cell. The effect of pressure on rejection and permeation flux for different salts ($MgCl_2$, Na_2CO_3, and $CaSO_4$) at high salt concentrations were determined. The salt concentration for each one was determined to cover its salinity in the seawater with the limitation of its solubility in water. The studied concentrations were up to 20000 ppm for $MgCl_2$, 15000 ppm for Na_2CO_3, and 2000 ppm for $CaSO_4$. The concentration of the last salt was chosen to be relatively low for the reason that its solubility in the water is very low (2.0 %). Finally, the experimental data will be fitted using the Spiegler-Kedem model in order to calculate the σ and P_s.

THEORY

The transport of the solute through Ultrafiltration (UF), Nanofiltration (NF), and Reverse Osmosis (RO) membranes can be described by irreversible thermodynamics where the membrane is considered as a black box. Kedem and Katchalsky (28) introduced the relation of the volumetric flux J_v and the solute flux J_s through a membrane in the following equations:

$$J_v = L_P(\Delta P - \sigma\Delta\Pi) \tag{1}$$

$$J_s = P_s\Delta C + (1 - \sigma)CJ_v \tag{2}$$

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, Spiegler and Kedem (29) used the above equations and obtained the following expression of the rejection rate of the solute related to permeation flux:

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

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

where R is the rejection. According to equation (3), the rejection increases with increasing the water flux. The parameters σ and P_s can be determined from the experimental data of rejection (R) as a function of volume flux (J_v) using best-fit method. The reflection coefficient (σ) is a parameter measures the degree of semi-permeability of the membrane. It is a characteristic of convective transport of the solute through the membrane. A value of $\sigma = 1$ means that the convection solute transport dose not take place at all. This is the case for ideal RO membranes where the membranes have no pores available for the convective transport. 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 (16).

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

$$R = 1 - (C_p/C_f) \tag{5}$$

where C_p and 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:

$$PWP = \frac{V_p}{t.A.P} \tag{6}$$

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).

MATERIALS AND METHODS

Membranes

Three commercial NF membranes were used in this study, of which two were supplied by FILMTEC and manufactured by DOW chemical company (USA). These two membranes are NF90 and NF270, which are made from polyamide. The third membrane was NADIR N30F, obtained from MICRODYN-NADIR Gmbh (Germany), which is made of polyethersulfone. 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 to avoid any compression effects and to establish leak tightness. The membranes were characterized in pervious work (30) in terms of surface roughness, pore size, and pore size distribution using Atomic force microscopy technique(AFM).

Permeation Experiments

The permeation experiments were carried out in a laboratory scale test cell. The experimental set-up was the same as shown in our pervious published paper (31). 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 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. The NF experiments consisted of the permeation of single solutions of three different salts ($MgCl_2$, Na_2CO_3, and $CaSO_4$) at varied concentration. The salt concentrations have been chosen to cover their salinity in the seawater with the limitation of their solubility in water (i.e. the concentration of the salt should not exceed its solubility in the water). Particularly, the studied concentrations of $MgCl_2$ were in the range of 5000 to 15000 ppm, Na_2CO_3 in the range of 5000 to 15000, and $CaSO_4$ in the range of 1000 to 2000 ppm. All investigated salts were obtained from Fisher scientific-UK with purity better than 99.5%. The deionized water used was obtained through demineralization using ion-exchange followed by reverse osmosis. The permeate flux and rejection were determined by varying the applied feed pressure at different feed concentrations. In order to determine the concentration of salt in the feed and the permeate solutions, the conductivity of these solutions were measured at 25 °C by a conductivity Hand-Held Meter LF 330/340 (WTW-Germany).

RESULTS AND DISCUSSION

Filtration of sodium chloride (NaCl) at high salinity has been carried out by the authors, using the same membranes and may be seen elsewhere (31). Therefore, this work is addressing the filtration of $MgCl_2$, Na_2CO_3, and $CaSO_4$ salts at different concentrations.

Characterization of the Membranes

Atomic force microscopy (AFM) has been used to characterize the investigated NF membranes. High resolution images and surface characteristic as well as the measuring of water permeability of all investigated membranes have been published elsewhere (30, 31). Table 1 shows the pore size, pore size distribution, surface roughness, the porosity, and pure water permeability. It is clear that NF90 has the lowest pore size, the highest roughness and porosity, and medium pure water permeability among the studied membranes while the N30F has a higher pore size and the lowest roughness, porosity, and pure water flux. Finally, NF270 has the highest pore size with medium roughness and porosity. The last results cause NF270 to have high water permeability.

Filtration Results

Magnesium Chloride Solution

Effect of Pressure on $MgCl_2$ Rejection and Permeate Flux

The rejection of $MgCl_2$ for the studied membranes with different pressures and concentrations are shown in Figs. 1(a–c). The studied concentration was studied over the range of 5000–20000 ppm and pressure in the range of 2 to 9 bar. It is clear that the rejection increases with increasing pressure and decreasing concentration for all membranes investigated. Fig. 1a shows that NF90 can reject $MgCl_2$ up to 96% at a concentration of 5000 ppm and 81% at a concentration of 20000 ppm at 9 bar. These values, which are also promising for use in the desalination process, could be explained on the basis of steric hindrance mechanism due to the fact that NF90 has small pore size (Table 1). Another point may be mentioned here is that the rejection of $MgCl_2$ is slightly effected with pressure at concentration of 5000 ppm while this effect is increased as the concentration increases. On the other hand, Fig. 8b shows that NF270 has a salt rejection in the range of 20 to 78% at different $MgCl_2$ concentration levels from 5000 to 20000 ppm and pressure from 2 to 9 bar. Obviously, these values are better than the rejection values of NaCl solution for the same membrane (31) because of the large ion size of Magnesium (sieving effect). According to Figs. 8(a,b), the membranes NF90 and NF270 nearly gave a constant rejection in the range of pressure 5–9 bar. As an economical point, these membranes could be carried out at medium pressure (5 bar) with the same performance. Figure 8c shows the rejection of $MgCl_2$ using N30F membrane. This membrane gave the lowest

Table 1. AFM surface characteristics of NF90, NF270 and N30F membranes

Membrane	Pore size (nm)	Roughness (nm) RMS	% Porosity	Pure water permeability ($L/h \cdot m^2 \cdot bar$)(31)
NF90 (30)	0.55 ± 0.13	27.75	17	10.16
NF270 (30)	0.71 ± 0.14	3.68	16	27.45
N30F (31)	0.61 ± 0.12	1.45	12	4.45

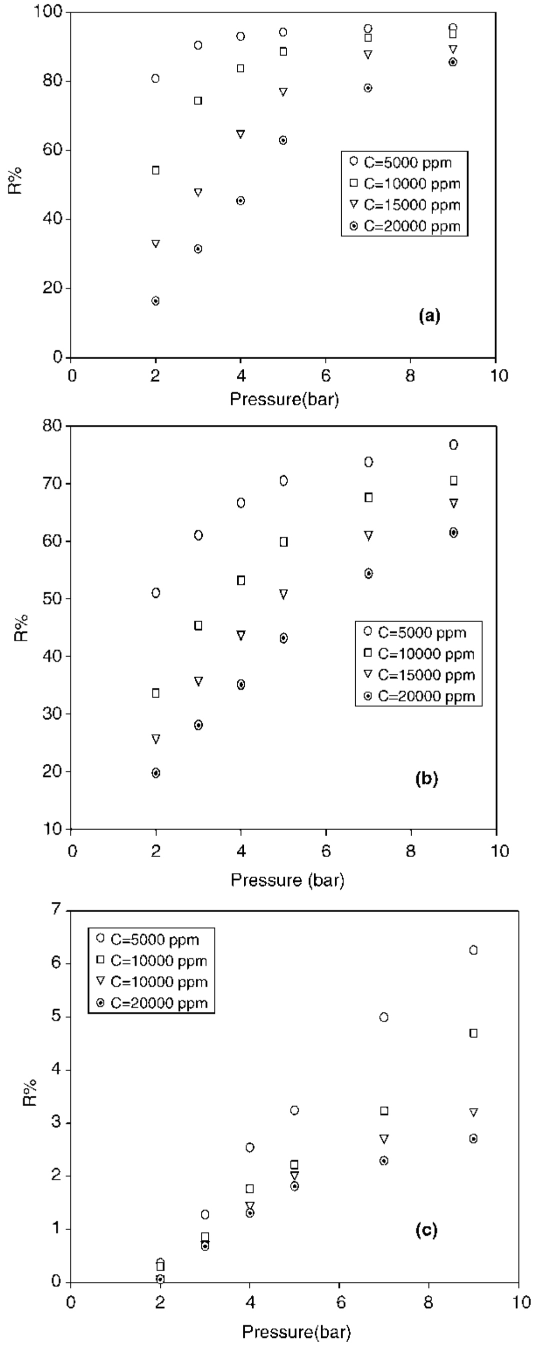

Figure 1. Effects of pressure and $MgCl_2$ concentrations on salt rejection for the investigated NF membranes (a) NF90, (b) NF270, and (c) N30F.

rejection in the range of 6% to 0% for the same range of salt concentration and pressure. This is so not only because N30F has larger pore size and low porosity but also because it is made from a different polymeric polyethersulfone material.

Figures 2(a–c) show the relationships between feed pressure and permeate flux of $MgCl_2$ for all membranes under investigation. The permeate flux increases with pressure for the reason of the increasing of solvent permeate. As shown in Fig. 2b, NF270 has a high permeability in comparison with the other membranes confirmed the obtained data of AFM in which this membrane has relatively large pore size. On the other hand, NF90, which has the highest surface roughness, presented relatively low flux with high rejection. This result is consistent with other investigations (32, 33). However, membranes with high surface roughness are more prone to fouling (34). A conclusion could be drawn based on these results is that if the high quality of water with low flux is required NF90 is used while NF270 is preferred for high permeate flux with lower quality of water. Thus, an optimization study is indispensable for the proper choice of NF membrane in desalination processes. Finally, Fig. 2c shows the permeate flux with the pressure for N30F membrane which gave the lowest flux in the same range of pressure among the investigated membranes.

Effects of Permeate Flux on $MgCl_2$ Rejection Correlation using Spiegler-Kedem Model

Figures 3–5 show the relations between permeate flux and $MgCl_2$ rejection for the three membranes at different concentrations. A high flux with high rejection was obtained for all investigated membranes at low salt concentration while at high concentration the flux and rejection were relatively low. Figures 3(a,b) confirm that NF90 membrane has a high rejection at low flux while NF270 membrane has relatively medium rejection at high flux as shown in Fig. 4(a,b). Similar results have been obtained by other researchers for these membranes (35–37). N30F membrane has the lowest rejection and permeate flux among the investigated membranes as cleared in Fig. 5(a, b). A real fact could be drawn here is that Figures (3–5) give the designer of the nanofiltration membrane cells a good opportunity to choose their preferable rejection at specific permeate flux in which all the designed parameters could be calculated once the rejection and the permeate flux for the membrane are known. The experimental data of rejection and flux were fitted using the Spiegler-Kedem model to determine the refection coefficient (σ) and the solute permeability (P_s). Solid lines in the figures (3–5) represent Spiegler-Kedem model which confirmed that NF90 and NF270 membranes have a good fitting with this model while the fit was not as good for the N30F membrane especially at low flux ($<10\,L/m^2 \cdot h$). This can be explained in terms of the facts that N30F membrane has a very low rejection and that Spiegler-Kedem model is a valid correlative framework for membranes with high rejections. Another main shortcoming

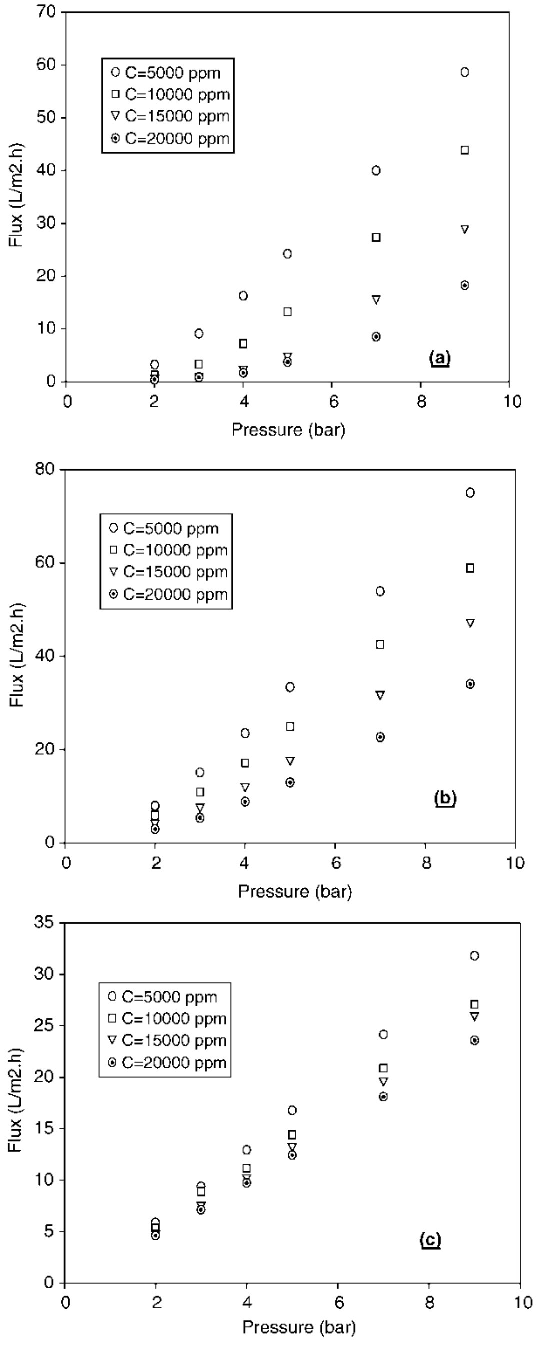

Figure 2. Effects of pressure and $MgCl_2$ concentrations on permeate flux for the investigated NF membranes (a) NF90, (b) NF270, and (c) N30F.

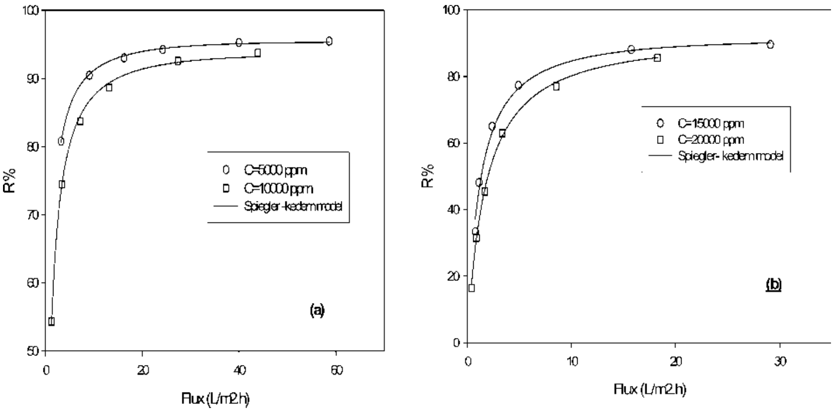

Figure 3. Effects of $MgCl_2$ permeation flux on salt rejection using NF90 at different $MgCl_2$ concentrations (a) for C = 5000,10000 ppm, (b) C = 15000,20000 ppm.

of the Spiegler-Kedem model is that it deals with membranes as a black box neglecting the type of ion charge involved. For this reason we recommend the use of another model taking the charges into account. Donnan steric-pore model (DSPM) (14, 22, 23) may be better since it addresses this point.

The regression parameters σ and P_s, for the three NF membranes under study and for different salinity levels of $MgCl_2$, are presented in Table 2. It is clear that values of P_s and σ are dependent on the salt concentration and the type of the membrane; P_s increases with slat concentration due to the high amount of salt passing through the membrane while σ slightly decreases due to the decreasing of the salt rejection. Table 2 also shows

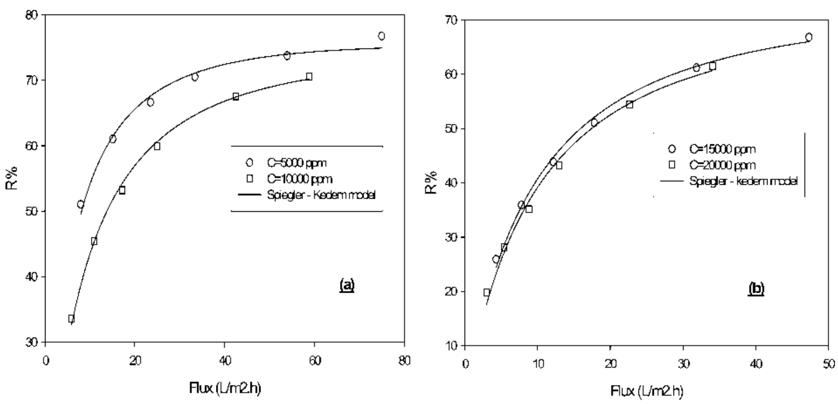

Figure 4. Effects of $MgCl_2$ permeation flux on salt rejection using NF270 at different $MgCl_2$ concentrations (a) for C = 5000, 10000 ppm, (b) C = 15000, 20000 ppm.

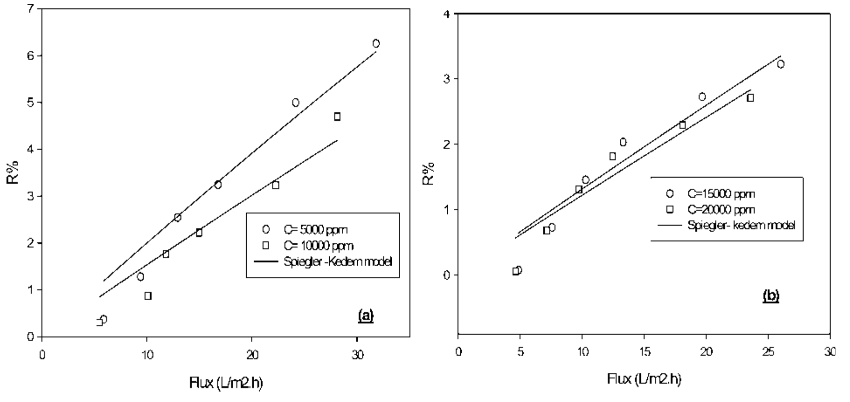

Figure 5. Effects of $MgCl_2$ permeation flux on salt rejection using N30F at different $MgCl_2$ concentrations (a) for C = 5000,10000 ppm, (b) C = 15000, 20000 ppm.

scattered values of σ and P_s for N30F compared to that of other membranes. This due to the invalidity of Spiegler-Kedem model to this membrane since its rejection is very low.

Sodium Carbonate Solution

Effect of Pressure on Na_2CO_3 Rejection and Permeate Flux

The rejection of Na_2CO_3 for the investigated membranes with different pressures and concentrations is shown in Figs. 6(a–c). The studied concentration was investigated over the range of 5000–15000 ppm with the same range of pressure. Although the percentage of the carbonate $(CO3)^{2-}$ is low in most of the seawater in the world, its content is high in the other areas such as the surface and ground water and rivers. As shown in these figures, the rejection increases with increasing pressure and decreasing concentration for all investigated membranes. As the comparison to the $MgCl_2$ filtration case, all studied membranes gave higher rejection values of Na_2CO_3 especially at low concentration and high pressure. Figure 6a shows that at a concentration of 5000 ppm NF90 can reject Na_2CO_3 salt up to 99% at 9 bar and 64% at 2 bar, while at high concentration 15000 ppm the rejection decreased down to 88% at 9 bar and 22% at 2 bar.

Figure 13b shows that NF270 has a salt rejection in the range of 15 to 93% for salinity levels from 5000 to 15000 ppm and pressure from 2 to 9 bars. Finally N30F membrane gave a rejection in the range of 6% to 43% at the same range of concentrations and pressures. These values are higher than the rejection values $MgCl_2$ for the same membrane and conditions. These results confirmed that all studied membranes especially the NF90 and NF270 membranes are very suitable to treat brackish water. The relationships between feed pressure and permeate flux of Na_2CO_3 for all studied membranes are shown in Figs. 7(a–c). Again, the permeate flux increases with pressure for

Table 2. Reflection factor (σ) and solute permeability (P_s) for the studied membranes at different $MgCl_2$ salt concentrations

Membranes →	NF90		NF270		N30F	
$MgCl_2$ concentration (ppm)	σ	P_s $(L/m^2 \cdot h)$	σ	P_s $(L/m^2 \cdot h)$	σ	P_s $(L/m^2 \cdot h)$
5000	0.954	0.666	0.757	5.06	0.999	490
10000	0.936	0.984	0.733	8.15	0.999	642
15000	0.913	1.15	0.711	8.82	0.999	750
20000	0.895	1.68	0.694	9.17	0.999	809

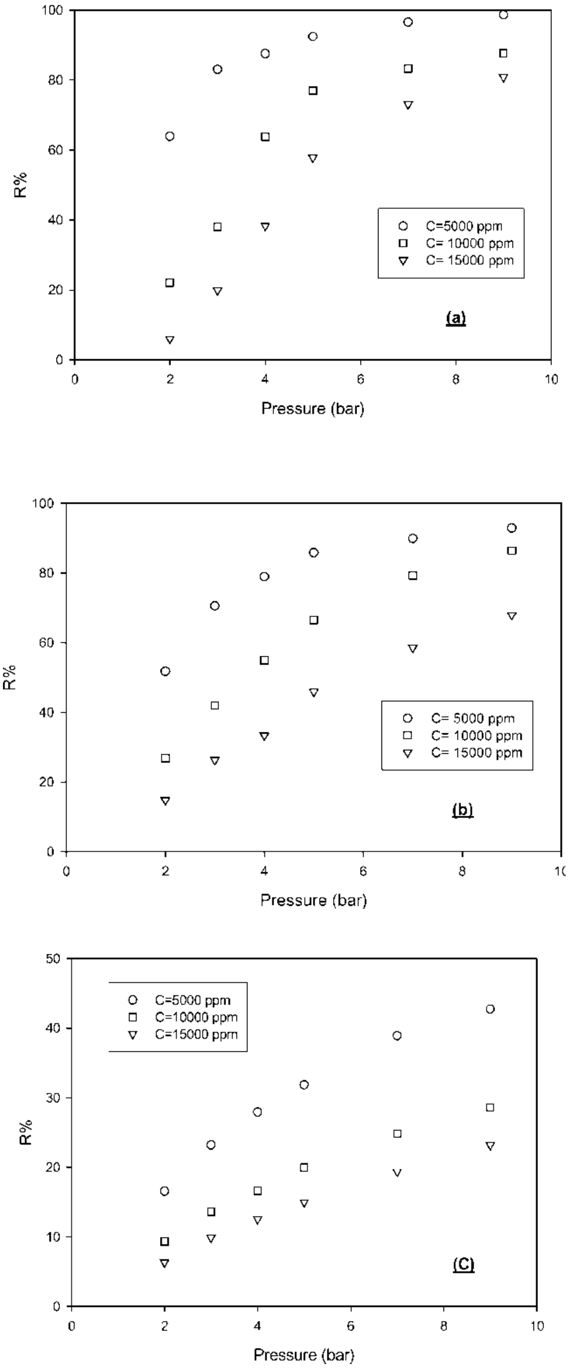

Figure 6. Effects of pressure and Na_2CO_3 concentrations on salt rejection for the investigated NF membranes (a) NF90, (b) NF270, and (c) N30F.

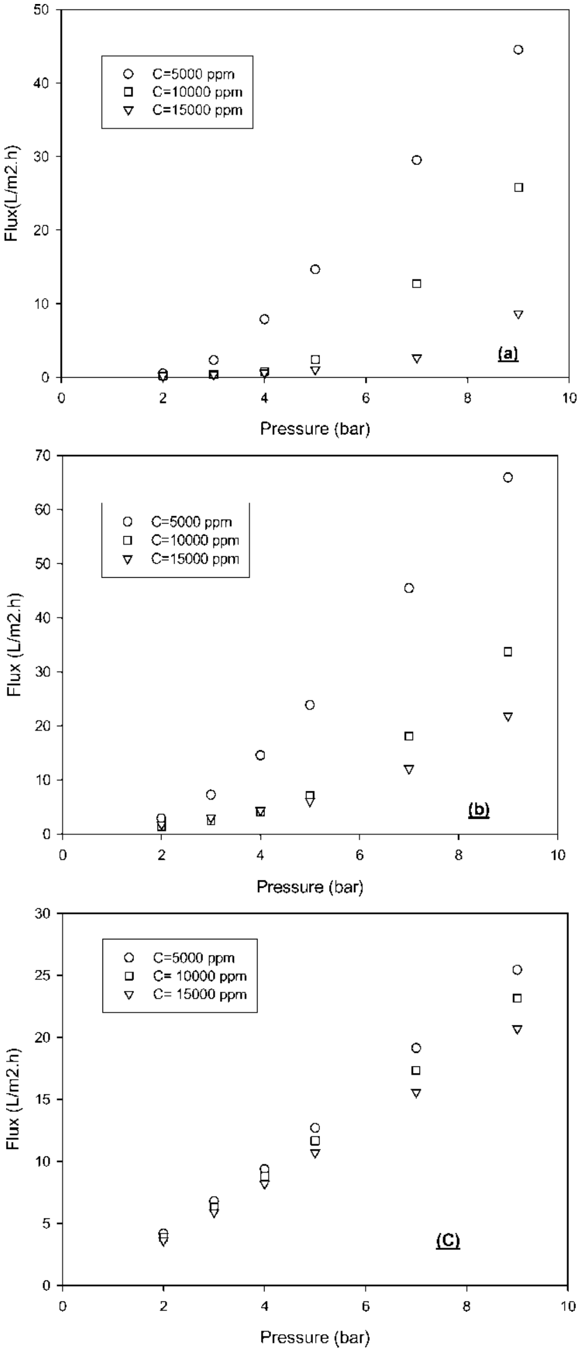

Figure 7. Effects of pressure and Na_2CO_3 concentrations on permeate flux for the investigated NF membranes (a) NF90, (b) NF270, and (c) N30F.

the reason of the increasing of solvent permeate. NF270 membrane still has the highest permeability among the other membranes especially at high pressure confirmed the obtained data of AFM in which this membrane has relatively large pore size. As a comparison to the $MgCl_2$ case, the permeate flux of Na_2CO_3 salt has lower values for all investigated membranes since the ion size of carbonate $(CO3)^{2-}$ is relatively large. Although N30F membrane has the lowest flux as the case of $MgCl_2$ filtration, this membrane has higher flux at low pressure in the range of 2–3 bar but with relatively very low rejection of $MgCl_2$ salt and medium rejection of Na_2CO_3 salt. So again, an optimization study is very crucial for the proper choice of NF membranes in water treatment processes.

Effects of Permeate Flux on Na_2CO_3 Rejection Correlation using Spiegler-Kedem Model

Figures 8(a–c) show the relations between permeate flux and Na_2CO_3 rejection for the three membranes at different concentrations. These relations are similar to the relations in the $MgCl_2$ filtration case. The Spiegler-Kedem model was used to fit the data of rejection and flux in order to determine the refection coefficient (σ) and the solute permeability (P_s). Solid lines in Fig. 15 represent Spiegler-Kedem model which showed a good fitting for the all investigated membranes even for N30F membrane, as shown in Fig. 15c, since its rejection for Na_2CO_3 salt was relatively higher than other studied salts. This confirms the validity of the Spiegler-Kedem model, which is only used for high salt rejection values as mentioned in the theory section. The regression parameters, for the three NF membranes and for different concentration levels of Na_2CO_3, are presented in Table 3. As shown in this table, both values of P_s and σ are dependent on the salt concentration. Again, P_s increases and σ decreases with increasing the slat concentrations. Table 3 also shows higher refection factor σ values for NF90 compared to that of NF270 and NF30. Real values for regression parameters have been obtained this time for N30F membrane due to high rejection values obtained for Na_2CO_3 salt compared to other studied salts.

Calcium Sulphate

Effect of Pressure on $CaSO_4$ Rejection and Permeate Flux

As a comparison to other studied salts, Sodium carbonate ($CaSO_4$) has been studied at low concentrations (1000–2000 ppm) using the same membranes and conditions due to its low solubility in water (2.0%). However, to study the concentration of Sulphate ion (SO_4^{-2}) at salinity similar to its salinity in seawater, another salt like Na_2SO_4 should be studied since its solubility in water is relatively high. Figure 9 shows the relation between the rejection and the pressure of this salt for all studied membranes. It is clear that the order of the rejection is similar to other

Table 3. Reflection factor (σ) and solute permeability (P_s) for the studied membranes at different Na_2CO_3 and $CaSO_4$ concentrations

	NF90		NF270		N30F	
Membranes →	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_2CO_3 concentration (ppm)						
5000	0.948	0.281	0.924	2.50	0.505	9.77
10000	0.896	0.481	0.907	3.053	0.374	13.25
15000	0.898	0.910	0.871	6.92	0.38	19.13
$CaSO_4$ concentration (ppm)						
1000	0.972	0.369	0.915	1.62	0.404	13.7
2000	0.959	0.561	0.912	2.48	0.316	16.0

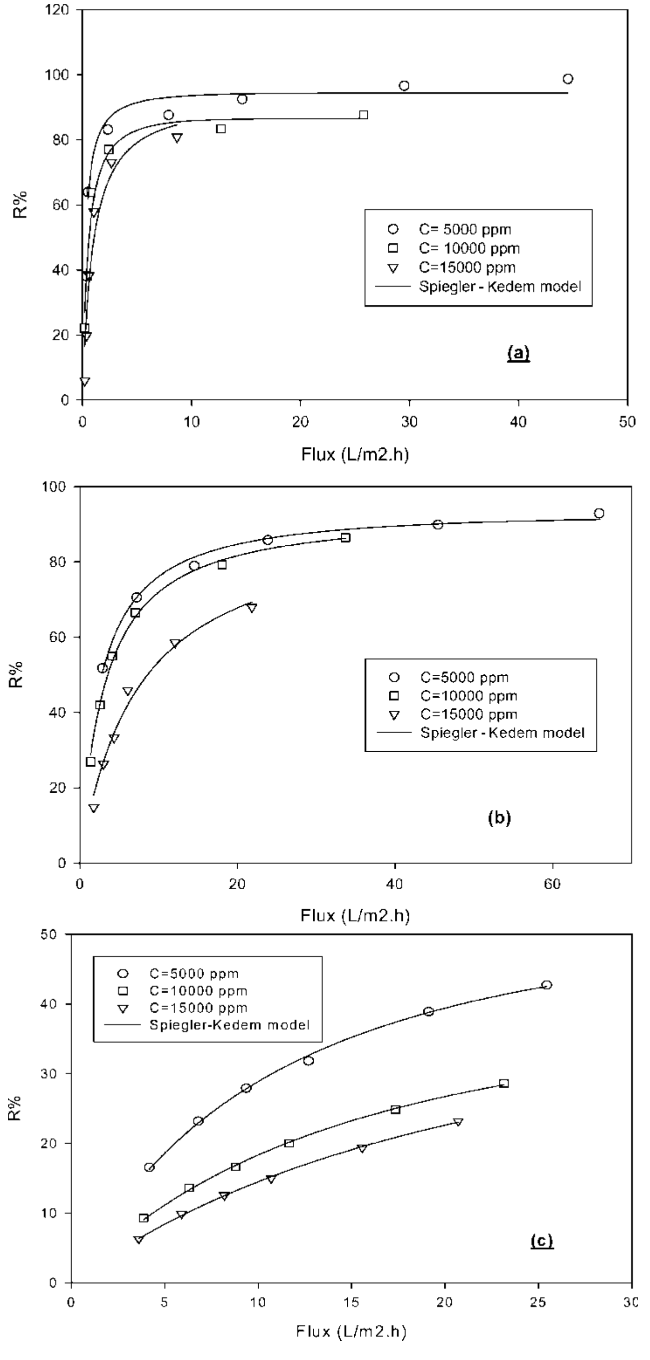

Figure 8. Effects of permeation flux on Na_2CO_3 rejection at different concentration for the investigated membranes (a) NF90, (b)NF270, (C) N30F.

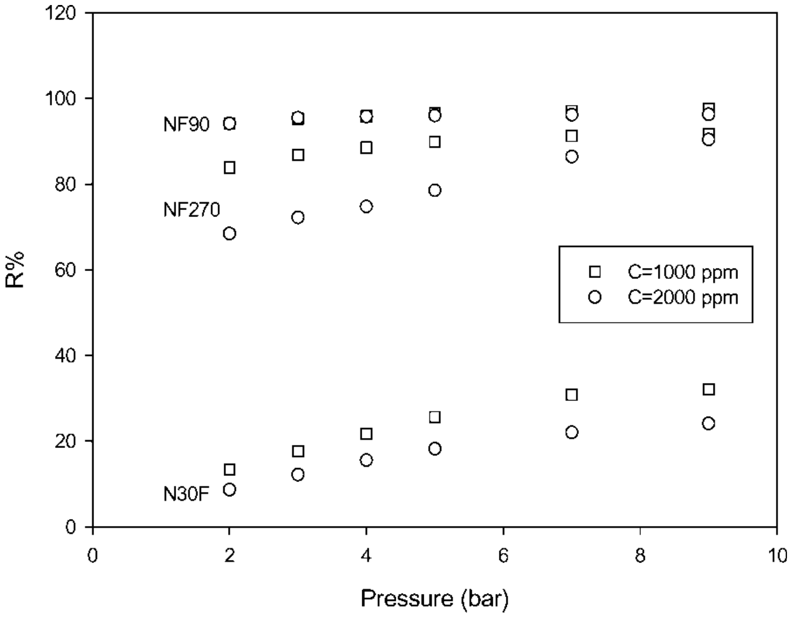

Figure 9. Effects of pressure and $CaSO_4$ concentrations on salt rejection for the investigated NF membranes.

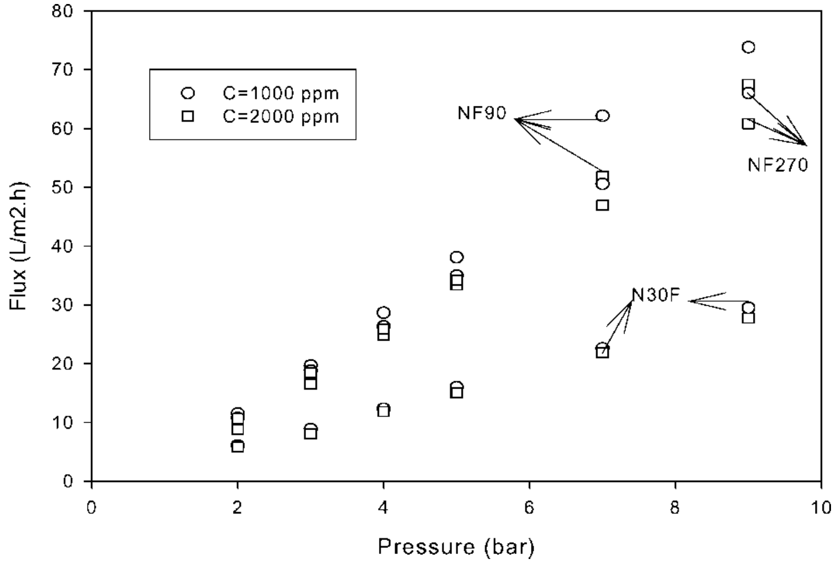

Figure 10. Effects of pressure and $CaSO_4$ concentrations on permeate flux for the investigated NF membranes.

studied salts. NF90 membrane has a high constant rejection with pressure, which means that this membrane could be used to reject $CaSO_4$ even at low pressure. On the other hand, the rejection is slightly increased with pressure for NF70 and N30F membranes. Figure 10 shows the relation between the permeate Flux of the studied salt with pressure for the three membranes. Again, the permeate flux is increased with increasing the pressure. According to Fig. 10, the permeate Flux of NF90 and NF270 membranes are closed due to low concentration while N30F gave relatively low flux.

Effects of Permeate Flux on $CaSO_4$ Rejection Correlation Using Spiegler-Kedem Model

Figure 11 shows the relations between permeate flux and $CaSO_4$ rejection for the three membranes at two low concentrations (1000 and 2000 ppm). It is clear that the rejection is nearly constant with the permeate flux for NF90 membrane while for other membranes (NF270 and N30F), the relation is not right in which their rejections increased with increasing the flux. In addition, Solid lines in Fig. 11 represent Spiegler-Kedem model, which showed a good fitting for the all investigated membranes. Details of fitting procedure are shown elsewhere (31). As the Na_2CO_3 filtration case, the model fit well the rejection and the flux data for N30F membrane. This membrane has relatively high values of rejection for $CaSO_4$ at the same

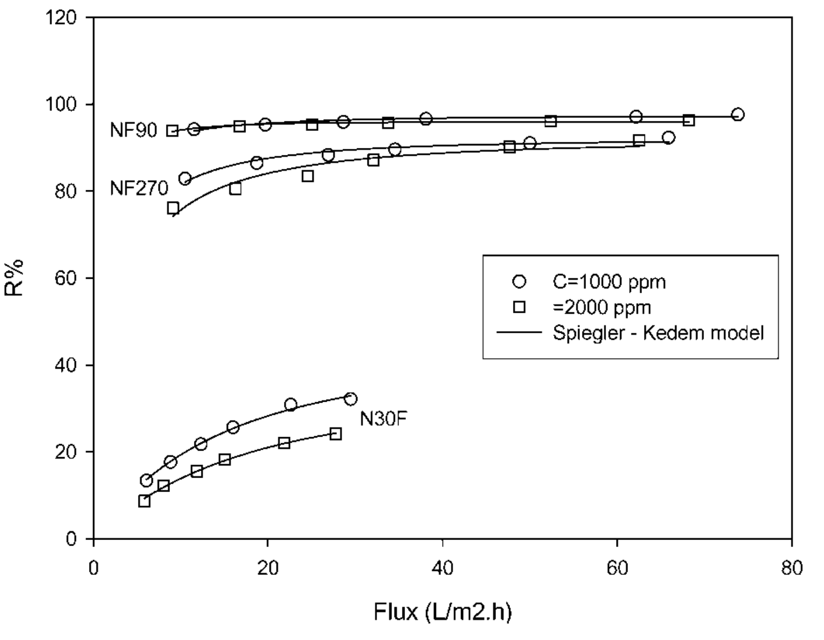

Figure 11. Effects of permeation flux on $CaSO_4$ rejection at different concentrations for the investigated membranes.

range of pressure, which confirms again the validity of the Spiegler-Kedem model at high concentrations. The regression parameters P_s and σ for the three NF membranes and at 1000 and 2000 ppm concentration of $CaSO_4$ are presented in Table 3. Again, both values of P_s and σ are dependent on the salt concentration in which again P_s increases and σ decreases with increasing the salt concentration. The values of σ for NF90 and NF270 membranes are very closed due to their high rejection values for $CaSO_4$ salt.

CONCLUSIONS

To determine their suitability as a pre-treatment alternative in the desalination process, three commercial NF membranes (NF90, NF270, N30F) were employed in a laboratory-scale study to investigate their performance in handling salty water with salinity levels representative of brackish water seawater. The experiments were carried out with trans-membrane pressures ranging from 2 to 9 bars at different salinity of ($MgCl_2$, Na_2CO_3, and $CaSO_4$) salt solutions. Pore size and pore size distribution obtained from AFM measurements were used to analyse both experimental data of pure water permeation and data obtained from salt rejection. The results showed that the rejection of all studied salts and the flux for all membranes increased linearly with the trans-membrane pressure and decreased with the salt concentration. NF90 membrane has high rejection at low flux while the NF270 has lower rejection at high flux. N30F has the lowest rejection and permeate flux. Spiegler-Kedem model was used to fit the experimental data of rejection with the permeate flux. 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 the filtration of $MgCl_2$ using N30F membrane especially at low flux and rejection while the model is just valid for membranes with high rejection. It is thus concluded that NF membranes have the potential to be used as a pre-treatment alternative in desalination processes and to treat perfectly the brackish water.

ACKNOWLEDGMENT

This work has been accomplished as part of a research project sponsored and funded by the Middle East Desalination Research Center (MEDRC).

REFERENCES

1. Bruggen, B.V. and Vandecasteele, C. (2002) Distillation vs. membrane filtration: overview of process evolutions in seawater desalination. *Desalination*, 143: 207–218.

2. Hassan, A. et al. (1998) A new approach to thermal seawater desalination processes using nanofiltration membranes (Part 1). *Desalination*, 118: 35–51.
3. Al-Sofi, M., Hassan, A., Mustafa, G., Dalvi, A., and Kither, M. (1998) Nanofiltration as a means of achieving higher TBT of $\geq$120°C in MSF. *Desalination*, 118: 123–129.
4. Al-Sofi, M. (2001) Seawater desalination—SWCC experience and vision. *Desalination*, 135: 121–139.
5. Hassan, A.M., Farooque, A., and Jamaluddin, A. et al. (2000) A demonstration plant based on the new NF–SWRO process. *Desalination*, 131: 157–171.
6. Criscuoli, A. and Drioli, E. (1999) Energetic and exergetic analysis of an integrated membrane desalination system. *Desalination*, 124: 243–249.
7. Raman, L.P., Cheryan, M., and Rajagopalan, N. (1994) Consider nanofiltration for membrane separation. *Chem. Eng. Prog.*, 90: 68–74.
8. Eriksson, P. (1988) Nanofiltartion extends the range of membrane filtration. *Environmental Progress.*, 7: 58–61.
9. Hilal, N., Al-Zoubi, H., and Darwish, N.A. et al. (2004) A comprehensive review of Nanofiltration membranes: Treatment, Pretreatment, Modelling, and Atomic Force Microscopy. *Desalination*, 170: 281–308.
10. Van der Bruggen, B. and Vandecasteele, C. (2003) Removal of pollutants from surface water and groundwater by nanofiltration: overview of possible applications in the drinking water industry. *Environ. Poll.*, 122: 435–445.
11. Chellam, S. and Taylor, J. (2001) Simplified analysis of contaminant rejection during ground- and surface water nanofiltration under the information collection rule. *Water Res.*, 35: 2460–2474.
12. Van der Bruggen, B., Schaep, J., Wilms, D., and C. Vandecasteele (1999) Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration. *J. Membr. Sci.*, 156: 29–41.
13. Peeters, J.M.M., Boom, J.P., Mulder, M.H.V., and Strathmann, H. (1998) Retention measurements of nanofiltration membranes with electrolyte solutions. *J. Membr. Sci.*, 145: 199–209.
14. Bowen, W. and Mukhtar, H. (1996) Characterisation and prediction of separation performance of nanofiltration membranes. *J. Membr. Sci.*, 112: 263–274.
15. Wang, X., Tsuru, T., Nakao, S., and Kimura, S. (1997) The electrostatic and steric-hindrance model for the transport of charged solutes through nanofiltration membranes. *J. Membr. Sci.*, 135: 19–32.
16. Schaep, J., Van der Bruggen, B., Vandecasteele, C., and Wilms, D. (1998) Influence of ion size and charge in nanofiltration. *Separation and Purification Technology*, 14: 155–162.
17. Afonso, M., Hagmeyer, G., and Gimbel, R. (2001) Streaming potential measurements to assess the variation of nanofiltration membranes surface charge with the concentration of salt solutions. *Separation and Purification Technology*, 22–23: 529–541.
18. Gilron, J., Gara, N., and Kedem, O. (2001) Experimental analysis of negative salt rejection in nanofiltration membranes. *J. Membr. Sci.*, 185: 223–236.
19. Hagmeyer, G. and Gimbel, R. (1998) Modelling the salt rejection of nanofiltration membranes for ternary ion mixtures and for single salts at different pH values. *Desalination*, 117: 247–256.
20. Ballet, G., Gzara, L., Hafina, A., and Dhahbi, M. (2004) Transport coefficients and cadmium salt rejection in nanofiltration membrane. *Desalination*, 167: 369–376.

21. Haddad, R., Ferjani, E., Roudesli, M., and Deratani, A. (2004) Properties of celluose acetate nanofiltration membranes: Application to brackish desalination. *Desalination*, 167: 403–409.
22. Bowen, W.R., Mohammad, A.W., and Hilal, N. (1997) Characterisation of nanofiltration membranes for predictive purposes use of salts, uncharged solutes and atomic force microscopy. *J. Membr. Sci.*, 126: 91–105.
23. Schaep, J., Vandecasteele, C., Mohammad, A.W., and Bowen, W.R. (2001) Modelling the retention of ionic components for different nanofiltration membranes. *Separation and Purification Technology*, 22–23 (1–3): 169–179.
24. Bandini, S. and Vezzani, D. (2003) Nanofiltration modeling: the role of dielectric exclusion in membrane characterization. *Chemical Engineering Science*, 58: 3303–3326.
25. Verissimo, S., Peinemann, K.-V., and Bordado, J. (2005) New composite hollow fiber membrane for nanofiltration. *Desalination*, 184: 981–991.
26. Koyuncu, I. and Yazgan, M. (2000) Application of nanofiltration and reverse osmosis membranes to the salty and polluted surface water. *J. Environ. Sci. Health*, A36 (7): 1321–1333.
27. Diawara, C., Lo, S., and Rumeau, M. et al. (2003) A phenomenological mass transfer approach in nanofiltration of halide ions for a selective defluorination of brackish drinking water. *J. Membr. Sci.*, 219: 103–112.
28. Kedem, O. and Katchalsky, A. (1963) Permeability of composite membranes, Part I: Electric current, volume flow and flow of solute through membranes. *Tans. Faraday Soc.*, 59: 1918–1930.
29. Spiegler, K.S. and Kedem, O. (1966) Thermodynamics of hyperfiltration (reverse osmosis): Criteria for efficient membranes. *Desalination*, 1: 311–326.
30. Hilal, N., Al-Zoubi, H., Darwish, N.A., and Mohammed, A.W. (2005) Characterisation of nanofiltration membranes using atomic force microscopy. *Desalination*, 177: 187–199.
31. Hilal, N., Al-Zoubi, H., Mohammed, A.W., and Darwish, N.A. (2005) Nanofiltration of highly concentrated salt solutions up to seawater salinity. *Desalination*, 184: 1295–1306.
32. Kwak, S.Y., Yeom, M.O., and Roh, I.J. et al. (1997) Correlations of chemical structure, atomic force microscopy (AFM) morphology, and reverse osmosis (RO) characteristics in aromatic polyester high-flux RO membranes. *J. Membr. Sci.*, 132: 183–191.
33. Vrijenhoek, E., Hong, S., and Elimelech, M. (2001) Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes. *J. Membr. Sci.*, 188: 115–128.
34. Bowen, W.R. and Doneva, T.A. (2000) Atomic force microscopy studies of nanofiltration membranes: Surface morphology, pore size distribution and adhesion. *Desalination*, 129: 163–172.
35. Ponti, M., Diawara, C.K., and Rumeau, M. (2002) Streaming effect of single electrolyte mass transfer in nanofiltration: potential application for the selective defluorination of brackish drinking waters. *Desalination*, 15: l267–274.
36. Visser, T.J.K., Modise, S.J., Krieg, H.M., and Keizer, K. (2001) The removal of acid sulphate pollution by nanofiltration. *Desalination*, 140: 79–86.
37. Santafe -Moros, A., Goza lvez-Zafrilla, J.M., and Lora-Garcıa, J. (2005) Performance of commercial nanofiltration membranes in the removal of nitrate ions. *Desalination*, 185: 1707–1713.