Boron removal from model water by RO and NF membranes characterized using S-K model

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Abstract. Boron is one of the most problematic inorganic pollutants and is difficult to remove in water. Strict standards have been imposed for boron content in water because of their high toxicity at high concentrations. Technologies using membrane processes such as reverse osmosis (RO) and nanofiltration (NF) have increasingly been employed in many industrial sectors. In this work, removal of boron from model water solutions was investigated using polyamide reverse osmosis and nanofiltration membranes. RO-AG, RO-SG, NF-90 and NF-HL membranes were used to reduce the boron from model water at different operational conditions. To understand the boron separation properties a characterization of the four membranes was performed by determining the pure water permeability, surface charge and molecular weight cut-off. Thereafter, the effect of feed pressure, concentration, ionic strength, nature of ions in solution and pH on the rejection of boron were studied. The rejection of boron can reach up to 90% for the three membranes AG, SG and NF-90 at pH = 11. The Spiegler-Kedem model was applied to experimental results to determine the reflection coefficient of the membrane σ and the solute permeability P_s.

Keywords: boron; RO/NF membrane; Spiegler-Kedem model; mass transfer

1. Introduction

Boron is a very abundant element in the environment; it is naturally found in over 80 minerals and is 0.001% of the Earth's crust. It exists in mineral deposits and in natural water in various forms (boric acid, sodium borate, boron hydrides). But the main form in which it is present in water is boric acid. Waters with high boron content are located in areas containing sediments and sedimentary rocks, specifically marine sediments rich in clay. In seawater, the concentration of boron is between 4 and 5 mg/L. The amount of boron in fresh water depends on many factors such as the proximity to coastal areas, the contribution of industrial and municipal effluents as well as the geochemical nature of the hydrographical basin (Loizou *et al*. 2010). In wastewater boron concentrations can reach 100 mg/L.

Boron is an essential element for plants but within fairly narrow concentration limits. A minimum concentration of boron in the irrigation water is necessary for some metabolic activities. Indeed, a concentration greater than the tolerated concentration has a negative effect on plant

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Table 1 Boron standards in drinking water (Sassi and Mujtaba 2013, Tu et al. 2011, WHO Guidelines 2011, USEPA 2006, Drinking-water Standards for New Zealand 2005)

Region	Boron standards (mg/L)	Regulation issued Year
WHO Recommendation	2.4	2011
Australia	4	2004
Canada	0.5	2003
USA California	1.5	2001
Abu Dhabi	1.5	2001
Singapore	1	2001
Japan	1.5	2000
New Zealand	1.4	2000
European Union (EU)	1	1998

growth which translates into signs of toxicity. The toxicity of boron can affect nearly all crops, but there's a range of tolerance among some crops. The lemon plantations are particularly susceptible to excess boron in the irrigation water. The maximum boron concentration should be less than 0.5 mg/L for lemon and mulberry. The corresponding value for the red pepper, peas, carrot, radish, potato and cucumber is 2 mg/L (Kabay *et al*. 2004).

Humans can be exposed to boron by fruits, vegetables, water, air and consumer products. The long-term consumption of water and foodstuff containing high levels of boron is reflected by disturbances of the cardiovascular, nervous, digestive, and sexual systems in humans and animals and can eventually cause death. When man consumes large amounts of food containing boron, the boron concentration of our body can increase to levels of ill health. Exposure to small amounts of boron can cause irritation of nose, throat or eyes. According to investigations medico-biological, boron compounds belong to the second class of toxicological hazard (Mel'nik *et al*. 2008). Therefore, WHO Guidelines for drinking-water quality has fixed a boron concentration of 2.4 mg/L. The boron standards and guidelines of drinking water are summarized in Table 1.

Currently, in many situations, removal of boron in water is necessary and has been the subject of numerous studies. There are several conventional methods for the removal of boron in water based on ion exchange (Dydo and Turek 2013), adsorption (Morisada *et al*. 2011, Demetrioua *et al*. 2013), complexation, precipitation (Irawan *et al*. 2013), coagulation and electro-coagulation (Yilmaz *et al*. 2007, Missaoui *et al*. 2013). These methods are not always able to meet higher and higher environmental standards and they generate sludge often difficult to manage. There are also membrane processes that have been tested for the boron removal. Among the membrane processes that have been tested for boron removal, are reverse osmosis (Sassi and Mujtaba 2013), nanofiltration (Huertas *et al*. 2008), electrodialysis (Nagasawa *et al*. 2011). Reverse osmosis and nanofiltration are generally preferred for their low energy consumption, their simple operating conditions and good selectivity. This paper studies the boron removal by AG, SG, NF-90 and HL membranes. The behavior and the efficiency of reverse osmosis and nanofiltration on the removal of boron under different water quality conditions, such as pH, ionic strength, and the presence of different ions were determined. A mathematical model Spiegle-Kedem was then applied to find the phenomenological and the mass transfer parameters for some operating conditions.

2. Experimental

2.1 Materials

The experimental study was carried out using a pilot designed and constructed in our laboratory. The pilot consists of a self-priming pump (flow range: 40-1100 L/h, pressure range: max 30 bars), feed tank (50 L capacity) equipped with a temperature regulator, two membrane housings for spiral wound membranes (2514 and 2540), valves and pressure sensors. The system was operated in recycle mode of permeate and retentate. Two reverse osmosis membranes (AG and SG) and two nanofiltration membranes (HL and NF-90) were tested in this work. The different characteristics of these membranes were summarized in Table 2.

The flux rate fraction through the membrane, called conversion rate, is expressed by

$$Y(\%) = \frac{Q_A}{Q_P} \tag{1}$$

where Q_A and Q_P are the feed and permeate flux rates, respectively. All experiments were carried out with a rate of 50%.

The membrane selectivity is expressed by a retention rate $R\,(\%)$ as follows

$$R(\%) = \frac{C_A - C_P}{C_A} \times 100 = \left(1 - \frac{C_P}{C_A}\right) \times 100 \tag{2}$$

where C_P and C_A are permeate and feed concentrations, respectively.

The permeate flux J_v is the ratio of the volume flux of the permeate (volume of permeate collected in a given time interval) and the membrane surface area (Eq. (3)).

$$J_v = \frac{\left(\dfrac{V_P}{\Delta T}\right)}{A} = \frac{Q_P}{A} \tag{3}$$

where $Q_p\,(L/h)$ is the permeate flux rate, $V_P\,(L)$ is the volume of permeate collected in a given time interval $\Delta T\,(h)$ and $A\,(m^2)$ is the membrane surface area.

Table 2 Different characteristics of the used membranes (given by the suppliers)

Type of membrane	Membrane area (m^2)	Salt rejection (%)	Max. pressure (bar)	pH range	Max. Temp. °C
AG 2514 (Osmonics)	0.6	*99.4 %	31	2-11.5	50°C
SG 2514 (Osmonics)	0.6	*95.2%	41	2-11.5	50°C
HL 2514 (Osmonics)	0.6	**98 %	31	2-11.5	50°C
NF-90 2540 (Filmtec)	2.6	**> 97.0	41	1-12	45°C

* NaCl, 15.5 bar; **MgSO$_4$ 6.9 bar

2.2 Chemicals and analytical techniques

All chemicals used were of reagent grade or higher. The study of the salts retention and ions effect on boron removal was carried out with solutions of NaCl (99.5%, Sigma Aldrich), KCl (99%, Qualikems), CaCl$_2$ (99.8%, Prolabo), MgCl$_2$ (98%, Dae Jung chemicals), NaNO$_3$ (99%, Akros), NaF(98.5%, Himedia) and Na$_2$SO$_4$ (99%, Acros). The pH change was effected by addition of NaOH solution ($\geq$ 97.0%, Sigma Aldrich). To obtain the desired boron concentration, the boric acid solutions were prepared in distilled water by diluting the stock solutions (1000 mg/L), (H$_3$BO$_3$ > 99.5%, Fluka).

The concentration of boron in the samples was determined by Molecular Absorption Spectrometry in the UV–visible range using Azomethine-H. The validation tests were carried out and showed that the analytical dosing procedure is validated. Other parameters such as pH and salt concentrations were measured by: pH-meter Orion 2 Star and ionic chromatography Metrohm, respectively.

2.3 Separation mechanism

The Spiegler-Kedem model predicts the following mass transfer equations

$$J_v = L_P\left(\Delta P - \sigma\Delta\pi\right) \tag{4}$$

$$J_s = P_s\Delta C_s + \left(1-\sigma\right)J_vC_m \tag{5}$$

where J_v is the flux of solvent, J_s is the flux of solute, L_P is the pure water permeability, σ is the local reflection coefficient, P_s is the solute permeability.

The convective and diffusive transfer parts were expressed as

$$J_{diff} + J_vC_{conv} = C_PJ_v \tag{6}$$

where J_{diff} is the solute flux due to diffusion and C_{conv} is the solute concentration due to convection.

From the values of C_{conv}, it is possible to determine the molecular weight cutoff (MWCO) of the membrane using the following equation

$$C_{conv} = C_0\left[1-\left(M/MWCO\right)^{1/3}\right]^2 \tag{7}$$

where M represents the molecular weight of the solute and C_0 the initial concentration of the solute in the raw water.

Integration of Eq. (5) in terms of the real rejection, give the following rejection expression (Jain and Gupta 2004)

$$R(\%) = \sigma\left(\frac{1-F}{1-\sigma F}\right) \tag{8}$$

With

$$F = e^{-\frac{1-\sigma}{1-\sigma F}J_v} \tag{9}$$

According to the film theory, the relation between the experimental rejection (R_{exp}) rate and the theoretical rejection (R_{th}) may be expressed as

$$Ln\left(\frac{1-R_{exp}}{R_{exp}}\right) = Ln\left(\frac{1-R_{th}}{R_{th}}\right) + \frac{J_v}{K} = Ln\left(\frac{1-\sigma\left(\frac{1-F}{1-\sigma F}\right)}{\sigma\left(\frac{1-F}{1-\sigma F}\right)}\right) + \frac{J_v}{K} \tag{10}$$

Thus

$$R_{exp} = \cfrac{1}{\cfrac{1-\sigma}{\sigma\left(1 - e^{-\left(\frac{1-\sigma}{P_s}\right)J_v}\right)} e^{\frac{Jv}{K}+1}} \tag{11}$$

Were K is the mass transfer coefficient. This model has been applied in the following tests.

3. Results and discussion

3.1 Membranes characterization

The characterization of membrane surface properties is an essential step to describe boron transfer mechanisms. In this section, the permeability to pure water, the surface charge and the molecular weight cut-off of the four studied membranes were determined. The pure water permeability was determined by measuring the permeate flux J_v versus the transmembrane pressure. The linear evolution of flux with transmembrane pressure shows that Darcy's law is valid. This linear behavior is described by a slope corresponding to the pure water permeability. Table 3 summarizes values of the pure water permeability of these membranes.

Most membranes acquire an electric charge when brought into contact with an aqueous solution, by either the dissociation of functional groups of the active layer or by adsorption of ions or molecules in solution to the membrane surface. This surface charge has an influence on the distribution of ions in the adjacent solution: ions bearing a charge opposite to that of the membrane surface are attracted while those who have the same charge are repulsed. This part focuses on the determination of the charges of membranes AG, HL, SG and NF-90 by the salts retention method (Schafer *et al*. 2004). The retention of salts $CaCl_2$, NaCl and Na_2SO_4 at 10^{-3} mol/L as a function of transmembrane pressure were represented in Fig. 1. Experimental data used are marked as solid symbols, where as dash lines represent the Spiegler-Kedem model.

Table 3 Pure water permeability membranes at 25°C

Membrane	NF-90	HL	AG	SG
Permeability (L.h^{-1}.m^{-2}.bar^{-1})	11.450	9.015	3.882	3.457

From this figure, it can be seen two orders of retention:

- The AG and NF-90 membranes show the following salt rejection sequence:
  $R_{Na_2SO_4} \rangle R_{NaCl} \rangle R_{CaCl_2}$.

- While, the other membranes (HL and SG) give the following retention sequence:
  $R_{Na_2SO_4} \rangle R_{CaCl2} \rangle R_{Na_2SO_4}$.

For the two first membranes, sequence retention is $R_{SO_4^{2-}} \rangle R_{Cl^-}$ and $R_{Na^+} \rangle R_{Ca^{2+}}$. In this case, the model of Donnan exclusion plays an important role in retention, and the membrane is negatively charged. For the SG and HL membrane, $R_{SO_4^{2-}} \rangle R_{Cl^-}$ and $R_{Ca^{2+}} \rangle R_{Na^+}$, indicate that the retention is mainly caused by the difference in diffusion coefficients between three salts. This retention sequence is inversely proportional to the order of diffusion coefficients given in Table 4. Although the order of retention of salts gives no indication on the charge of SG and HL membranes, some authors noted that the thin-film composite membranes are characterized by negatively charged surfaces (Norberg *et al.* 2007).

The rejection characteristic of a reverse osmosis and nanofiltration membrane is often quantified by the molecular weight cut-off (MWCO). Usually, the MWCO is defined as the molecular weight of a solute that was rejected at 90 percent (Van der Bruggen *et al.* 1999). The

Table 4 Diffusion coefficients of some electrolytes (Schaep *et al.* 2001)

Electrolytes	NaCl	Na$_2$SO$_4$	CaCl$_2$
D (10^{-9} m^2/s)	1.61	1.45	1.23

(a) AG membrane

(b) SG membrane

(c) NF-90 membrane
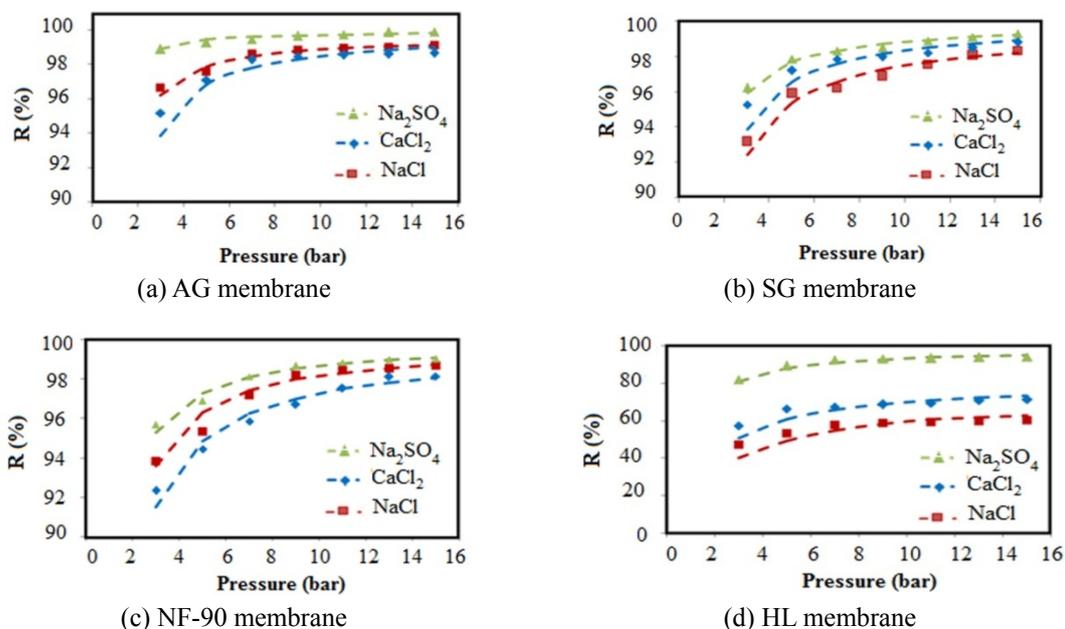
(d) HL membrane

Fig. 1 Experimental evolution of salts rejection with transmembrane pressure for (a) AG; (b) SG; (c) NF-90; and (d) HL membrane, the curves were fitted by the Spiegler-Kedem model

Table 5 Molecular weight cut-off of the studied membranes (Na_2SO_4, 10^{-3} mol/L)

Membrane	AG	SG	HL	NF-90
MWCO (Da)	144	160	247	167

sieving effect described that most of the solutes that having larger molecular weight than the MWCO of the membrane are rejected by the membrane and ones having lower molecular weight than the MWCO of a membrane will permeate easily through the membrane. From the C_{conv} values corresponding to the Na_2SO_4 electrolyte determined by the Spiegler Kedem model (Eq. (7)), it is possible to determine the MWCO of the membranes studied. The results of the MWCO calculated are reported in Table 5. The results obtained show that HL membrane has the highest MWCO, so it presents larger pores compared to the three other membranes. The MWCO of the NF90 membrane is analogous to those of reverse osmosis membranes, showing thus, similar separation properties.

3.2 Boron Removal by RO/NF membranes

3.2.1 The effect of feed concentration and membrane type on the removal of boron

The effect of the boron feed concentration and membrane type on the retention was studied to determine the scope of AG, SG, NF-90 and HL membranes. Boron solutions were prepared at various concentrations, such as 5, 25, 50 and 100 mg/L. Fig. 2 shows the results of the retention of boron by the four membranes versus feed concentration. The highest rejection was obtained by using AG membrane, whereas the lowest rejection was observed for HL membrane. According to the results obtained in Section 3.1, the boron removal by NF-90 membrane is very similar to reverse osmosis membrane due to their molecular weight cut-off which is close to those of reverse osmosis membranes. Concerning the feed concentration effect, the findings show that the boron concentration has no significant effect on the rejection in the range of 5 to 100 mg/L. This result can be explained that an increase of boron concentration in the feed water will cause an increase of the boron concentration in permeate, so the retention rate remains constant. This finding is in agreement with previously reported result by Cengeloglu *et al*. (2008).

The transport parameters σ and P_s were determinated using the Spiegler–Kedem model and results are listed in Table 6. It is clear that values of P_s and σ are independent of the feed concentra-
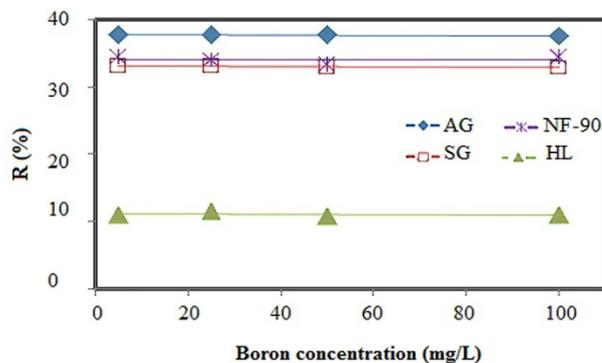
Fig. 2 The effect of initial boron concentration on the boron removal for different NF/RO membranes (pH = 6.8, P = 10 bar, T = 25±2°C)

Table 6 Transport parameters determined for various membrane/feed concentration
  (P = 10 bar, pH = 6.8, T = 25±2°C)

Boron (mg/L)	AG		SG		NF-90		HL	
	P_s	σ	P_s	σ	P_s	σ	P_s	σ
5	7.531	0.420	8.404	0.342	34.157	0.380	46.006	0.135
25	7.589	0.414	8.451	0.344	30.668	0.372	44.186	0.139
50	7.578	0.418	8.845	0.348	30.977	0.371	46.183	0.130
100	7.358	0.419	8.005	0.346	32.301	0.378	46.437	0.132

tion. Indeed, whatever the concentration of feed (within the range of 5 to 100 mg/L), the amount of boron rejected and the amount of boron that crossed the membrane are always the same as compared to the initial amount.

3.2.2 The effect of pH on the removal of boron

Boron is present in water as boric acid. It acts as weak acid and dissociates in function of pH in the solution as follows:

$$H_3BO_3 + H_2O \rightleftharpoons H_2BO_3^- + H_3O^+ \quad pKa_1 = 9.25$$

Based on the above equation, at pH below 9.25, the boric acid predominantly existed in aqueous solution as the neutral form H_3BO_3. In addition, the anionic form of boric acid ($H_2BO_3^-$) went up with an increase in pH value above 9.25. Generally, the rejection of weak acids and bases is highly pH dependent; their retention in RO and NF processes will be high in the ionized form. Consequently, pH is one of the factors that influence the retention rate of boron.

The effect of pH on the retention of boron was studied at fixed concentration 5 mg/L and at transmembrane pressure 10 bar. The pH was adjusted by the adding the NaOH and was varied from 7 to 11. The variation of boron retention as a function of pH values for the four membranes is plotted in Fig. 3.

As can be seen from the Fig. 3, the retention of boron is mainly affected by pH. In neutral pH, the retention of boron by AG, SG, NF-90 and HL membranes were respectively 38, 33, 31 and
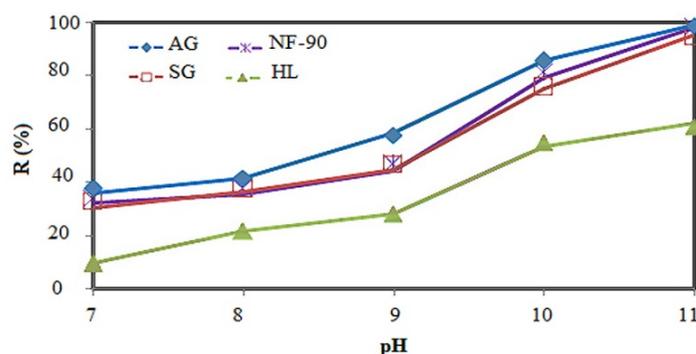
Fig. 3 The effect of pH on the removal of boron by AG, SG, NF-90 and HL membranes
  (C = 5 mg/L, P = 10 bar, T = 25±2°C)

Table 7 Transport parameters determined for various membranes/pH (P = 10 bar, C = 5 mg/L)

pH	AG		SG		NF-90		HL	
	P_s	σ	P_s	σ	P_s	σ	P_s	σ
7	7.423	0.425	8.313	0.346	35.317	0.384	47.356	0.135
8	7.353	0.506	8.062	0.402	23.590	0.421	37.813	0.289
9	4.546	0.699	4.505	0.507	13.514	0.566	25.840	0.339
10	1.625	0.896	2.176	0.775	12.825	0.883	11.925	0.583
11	0.159	0.999	0.456	0.982	1.502	0.998	10.782	0.706

10%. At pH > 9, the retention increases significantly to achieving the 64% for the HL membrane, 96% for the SG membrane and 99% for the both other membrane at pH = 11.

In general, when a compound is partially ionized or charged, electrostatic interactions can occur between the membrane and the solutes (Tabassi *et al*. 2013). Increasing pH leads to an increase of dissociated boric species and to enhancement of the surface membrane negatively charged, subsequently the electrostatic repulsion between charged solutes and the membrane increases. The hydration of the molecular form of boric acid, at neutral pH, is less strong due to the lack of ionic charge. Thus, it cannot improve the charges leading to a smaller size, and therefore, a low rejection accompanied by easy passage of solutes. On the other hand, the ionic form is fully hydrated, resulting in a large radius and an improvement in the negative charge of the ion. This leads to a higher rejection, both by excluding and repelled by the negatively charged membrane (Tomaszewska and Bodzek 2013, Redondo *et al*. 2003). On the other hand, the boric acid in its molecular form creates a hydrogen bridge with the active groups of the membrane and diffuses in a manner similar to that of the carboxylic acid and water (Rodríguez *et al*. 2001).

Spiegler-Kedem model was applied to fit the experimental data and evaluate the transfer parameters of boron (σ and P_s). These parameters are summarized in Table 7.

Table 7 shows that the transport parameters σ and P_s depend on the pH of the feed solution. The reflection coefficient σ increases strongly with the pH, due to the increase in the boron rejection. While the solute permeability P_s decreases with the pH due to the little amount of boron passing through the membrane.

3.2.3 The effect of pressure on the removal of boron

As RO and NF are usually a pressure-driven process, operating pressure is very important factor affecting rejection performance. To investigate the influence of applied pressure on the rejection of boron, the pressure was varied from 3 to 13 bar at a pH of 6.8 and 11 and a feed concentration of 5 mg/L. Fig. 4 represents the influence of applied pressure on the rejection of boron. $R_{exp.}$ is the rate of elimination obtained experimentally, $R_{theo.}$ is the elimination rate calculated by the Spiegler–Kedem model.

As can be seen from Fig. 4, at pH = 6.8, the boron rejection by the four membranes increases with increasing operating pressure and reaches a threshold at a high pressure. Similarly, Wolska and Bryjak (2013), Koseoglu *et al*. (2008) and Prats *et al*. (2000) mentioned that higher boron rejection was observed when increasing the operating pressure. This phenomenon could be attributed to the increase of solvent flux at a higher pressure. At pH = 11, for AG, NF-90 and SG membranes, the rejection of boron does not depend on the pressure. On the other hand, boron retention by HL membrane is little influenced by pressure. Generally, the passage of solutes

through membrane is due to physical and chemical transfers. In the event that the retention is much influenced by pressure, the passage of this solution is more due to physical than chemical forces. In the case of AG, NF 90 and SG membranes, the boron rejection is influenced by the repulsive force between the borate ions and the membrane surface negatively charged. Concerning the HL membrane the sieving phenomenon is introduced into the separation.

3.2.4 The effect of ionic strength on the removal of boron

Really, natural and waste waters contain variable concentrations of salts. In fact, the salts concentration can have an impact on the retention of boron. Recent studies investigating the influence of ionic strength on membrane surface charge have found that the measured surface charge became less negative with increasing ionic strength (Bellona and Drewes 2005, Shim *et al*. 2002). Other studies have found that an increase in the solution ionic strength may also reduce the apparent pKa value of boric acid, leading to a change in the speciation of boric acid particularly at pH in the vicinity of its intrinsic pKa value of 9.25 (Tu *et al*. 2011). The variation of membrane surface charge and the shift in pKa of the boric acid in response to the solution ionic strength is expected to use some influence on the rejection of boron by RO and NF membranes. To investigate the effect of ionic strength on the boron removal for the employed membranes, rejections experiments were performed by the addition of various concentration of NaCl between 0.001 to 0.1 M in solution containing 5 mg/L of boron at pH = 11.

Decrease of pKa with ionic strength theoretically indicates that there will be more boron removal at higher salinity than that at lower salinity (Maung and Lianfa 2009). However, experimental results in this study indicated the opposite trend of boron removal. There was a considerable decrease in boron rejection by the four membranes as the feed solution ionic strength increased from 0 to 0.1 mol/L. The decrease is of the order of 3% for AG, NF-90 and SG membranes and 8% for HL membrane. The results of low boron rejection at high salinity suggest the neutralization of membrane surface charge by Na^+ ions. At this salinity, the membrane surface is less negatively charged, and therefore boron removal by electrostatic repulsion between membrane surface and borate ions becomes less important. Another, as shown in recent studies (Maung and Lianfa 2009, Yoon *et al*. 2005), the membrane charge density was altered and provoked the diffusion of ions faster through the membrane at higher ionic strength.

The transport parameters σ and P_s were calculated and summarized in Table 8. The results fit

(a) pH = 6.8   (b) pH =11
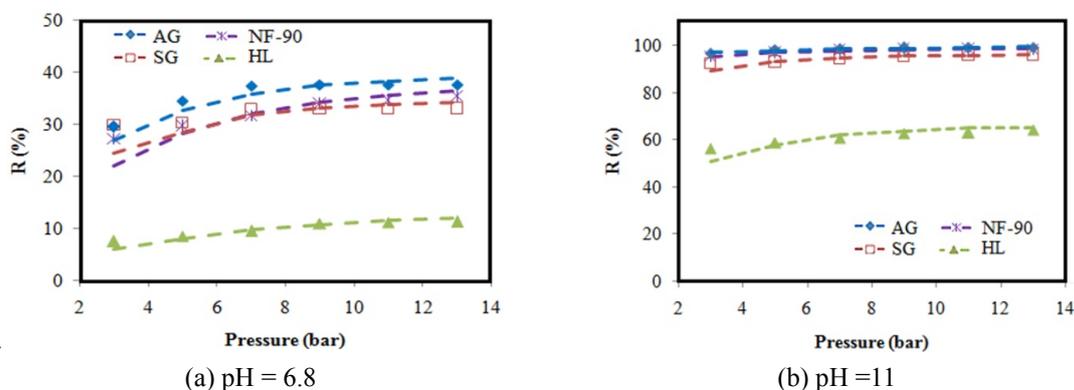
Fig. 4 Experimental evolution of boron rejection with pressure for NF/RO membranes, the curves were fitted by the Spiegler-Kedem model (C = 5 mg/L, pH = 6.8 and 11, T = 25±2°C)
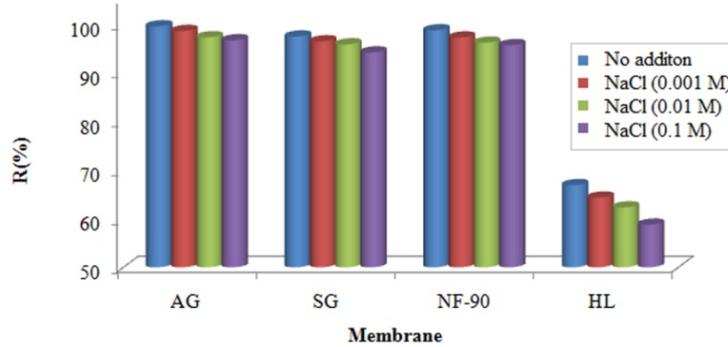
Fig. 5 Effect of NaCl concentrations on boron removal for respective membranes
(C = 5 mg/L, pH = 11, P = 10 bar, T = 25±2°C)

Table 8 The membrane transport parameters determined for various membrane/NaCl concentrations
(C = 5 mg/L, pH = 11, P = 10 bar, T = 25±2°C).

NaCl	AG		SG		NF-90		HL	
(mol/L)	P_s	σ	P_s	σ	P_s	σ	P_s	σ
0	0.159	0.999	0.456	0.982	1.502	0.998	10.782	0.706
0.001	0.206	0.990	0.520	0.974	1.576	0.983	11.010	0.675
0.01	0.273	0.980	0.534	0.971	1.619	0.974	11.249	0.667
0.1	0.286	0.979	0,608	0.968	1.770	0.972	11.742	0.650

well with the experimental curves. It is clear that values of σ and P_s depend on the NaCl concentration; P_s increases while σ decreases and with salt concentration.

3.2.5 Boron removal in the presence of chloride, fluoride, nitrate and sulfate ions

The effect of Cl^-, F^-, NO_3^- and SO_4^{2-} ions on the rejection of boron was investigated using AG, SG, NF-90 and HL membranes at fixed boron concentration of 5 mg/L, pH of 11 and pressure of 10 bar. Fig. 6 shows the effect of these ions on the observed boron retention. As can be seen from this figure, the presence of salts reduced the rejection of boron in a meaningful way. The retention of boron is lower in presence of sulfate salt than for the chloride, fluoride and nitrate salt experiments. It seems that the presence of the high valence anion (SO_4^{2-}) drives more borate ($H_2BO_3^-$) into the membrane, thus decreasing its retention. Krieg *et al*. (2004) found the same results in the retention of mineral salts.

The retention of boron (R_B) for the HL membrane in the presence of anions follows the retention sequence: $R_B(SO_4^{2-}) < R_B(F^-) < R_B(Cl^-) < R_B(NO_3^-)$. This order is related to hydration energy (Table 9). When the hydration energy of anions were compared, it was noticed that the order of hydration energy $NO_3^- < Cl^- < F^- < SO_4^{2-}$. Some retention studies of these four anions by HL membrane have been carried and showed the following order: $R(SO_4^{2-}) > R(F^-) > R(Cl^-) > R(NO_3^-)$ (Mnif *et al*. 2010). Sulphate is the most hydrated anion and the most rejected. In the presence of this anion, the passage of boron through the membrane is easier. However, Chloride is the less hydrated anion and the less rejected. In the presence of this anion, the passage of boron through the membrane is hard.
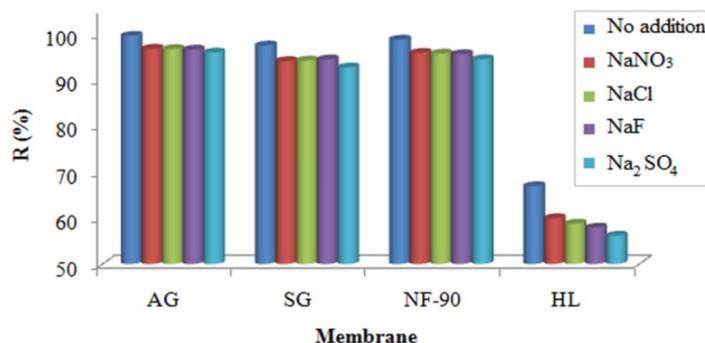
Fig. 6 Effect of anions on the retention of boron for the AG, SG, NF-90 and HL membranes
(C = 5 mg/L; pH = 11, Salts concentration = 0.1 mol/L, T = 25±2°C, P = 10 bar)

Table 9 Hydration energy of some anions (Essington 2004)

Anions	NO_3^-	Cl^-	F^-	SO_4^{2-}
Hydratation energy (KJ/mol)	310	325	449	1047

Table 10 The membrane transport parameters determined for various membrane/anions
(C = 5 mg/L, pH = 11, Salts concentration = 0.1 mol/L, T = 25±2°C, P = 10 bar)

Ions	AG		SG		NF-90		HL	
	P_s	σ	P_s	σ	P_s	σ	P_s	σ
No ion	0.159	0.999	0.456	0.982	1.502	0.998	10.782	0.706
NaNO$_3$	0.282	0.984	0,597	0.969	1.690	0.975	11.561	0.652
NaCl	0.286	0.979	0,608	0.968	1.770	0.972	11.742	0.650
NaF	0.291	0.978	0,631	0.968	1.775	0.971	11.755	0.647
Na$_2$SO$_4$	0.310	0.973	0,639	0.964	1.785	0.969	11.870	0.643

The membrane parameters σ and P_s of boron are summarized in Table 10. According to this table, we can find that the transport parameters σ and P_s depend on the anion type: the reflection coefficient values are lower for sulfate ions compared to the monovalent anion, while the solute permeability P_s values are higher for sulfates ions.

3.2.6 Boron removal in the presence of sodium, potassium, calcium and magnesium ions

The effect of the cation type in the feed solution on the boron removal by AG, SG, NF-90 and HL membrane was determined by measuring boron retentions in the presence of different chloride salts. Fig. 7 gives the percentages of the boron rejection in the presence of K^+, Na^+, Ca^{2+} and Mg^{2+} cations at pH equal to 9.5. It appears that in the presence of bivalent cations, the percentage of the boron removal is lower than in the presence of monovalent cations. Moreover, in the presence of two cations of the same charge, the boron rejection is almost identical for all membranes. This may be explained by the fact that the presence of cations in the solution partly neutralizes the negative membrane surface charge and causes a decrease in the retention of boric species in the solution.
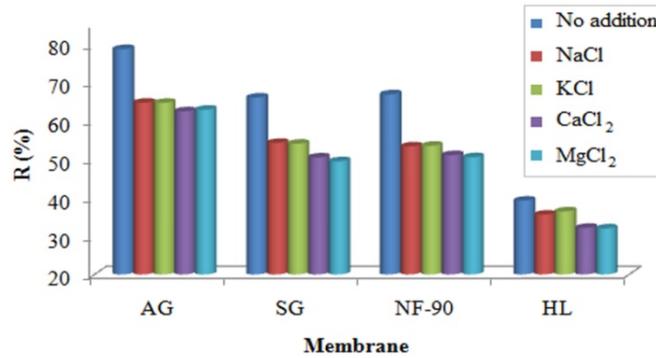
Fig. 7 Effect of cations on the retention of boron for the (a) AG; (b) SG; (c) NF-90; and
(d) HL membranes (C = 5 mg/L; Temperature = 25±2°C; P = 10 bar; pH = 9.5)

Table 11 The membrane transport parameters determined for various membrane/cations
(C = 5 mg/L, pH = 9.5, P = 10 bar, Salts concentration = 0.1 mol/L)

Ion	AG		SG		NF-90		HL	
	P_s	σ	P_s	σ	P_s	σ	P_s	σ
No addition	3.577	0.812	3.919	0.687	13.363	0.692	20.337	0.433
KCl	6.331	0.652	7.220	0.555	19.432	0.572	27.198	0.335
NaCl	6.296	0.654	7.225	0.557	20.441	0.573	27.202	0.337
CaCl$_2$	6.528	0.623	7.657	0.542	25.743	0.558	29.453	0.301
MgCl$_2$	6.545	0.628	7.701	0.541	25.812	0.561	28.927	0.298

The divalent ions are more effective in neutralization of the membrane surface because of their binding capacity to the membrane surface functional groups.

As illustrated in Table 11, the different results show that the σ and P_s values depend on the nature of cations in solution. The P_s values are lower for monovalent cations (Na$^+$ and K$^+$) compared to the bivalent ion (Ca^{2+} and Mg^{2+}), inversely to the reflection coefficient σ which is higher for monovalent ions than bivalent ions.

4. Conclusions

Boron removal from model water was studied using four commercial membranes (SG, AG, HL, and NF-90). For these membranes, the removal efficiency for boron was influenced by operating conditions such as membrane type, pH, transmembrane pressure, ionic strength and the nature of ions present in the solution. It was observed that the rejection of boron is better for the AG membrane. The boron removal by NF-90 membrane is very similar to AG and SG membranes due to their molecular weight cut-off which is close to those of reverse osmosis membranes. This rejection decreases with the increase of the ionic strength and increases with increase of pH of feed solution (a better elimination obtained at pH = 11). Boron retention increases with pH due to electrostatic repulsion between membrane and borate ion formed at basic pH. At pH = 11, the percentages of boron removal by AG, SG and NF-90 membranes exceed 90%. The observed

rejection does not depend of the feed concentration. In fact, by increasing the concentration of 5 to 100 mg/L, the boron retention remains constant. Moreover, when salts concentration increases, boron rejection decreases due to the shielding phenomenon. In the presence of divalent ions, boron removal is lower in the presence of monovalent ions. Whereas in the presence of anions, the boron removal ratio by HL membrane is related to the hydration of these anions, the rejection rate is lowest in the presence of the most hydrated anions. The Spiegler–Kedem model was used to determine the parameters σ and P_s which fit well with experimental results. NF-90, AG and SG membranes show a good efficiency in retention of boron for model water. The NF90 membrane was shown to behave in a similar way to that of the reverse osmosis membrane.

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