

# Modeling of fluoride retention in nanofiltration and reverse osmosis membranes for single and binary salt mixtures

Youssef Amine Boussouga\*, Abdelhadi Lhassani

Laboratory of Applied Chemistry, Faculty of Science and Technology of Fez, Sidi Mohamed Ben Abdellah University, P.O. Box 2202 Fez, Morocco, Tel. +212 671 89 73 13; emails: boussouga.youssef@gmail.com (Y.A. Boussouga), a\_lhassani@yahoo.fr (A. Lhassani)

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#### ABSTRACT

High levels of fluoride in groundwater cause a major problem for drinking water quality in many countries around the world. In addition to reverse osmosis (RO), recent publications indicate that nanofiltration (NF) is a promising technology to deal with fluoride removal from aqueous solutions. First of all, a characterization of commercial NF and RO membranes was performed in terms of hydraulic permeability ( $L_p$  and  $L_p'$ ) and contact angle ( $\theta$ ). Then, performances of the selected membranes on Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> as well as F<sup>-</sup> rejection were determined within a laboratory study in simple salt. At 10 mg/L of concentration, pH = 6.7 and 10 bar, the rejections of fluoride with NF270, NF90 and BW30 were 63%, 91% and 97%, respectively. The influence of sulfate, chloride, nitrate and bicarbonate on fluoride rejection was also studied in binary mixtures with different concentrations of monovalent anions affect positively fluoride rejection. Experimental data of fluoride rejection were modeled by using Spiegler–Kedem–Katchalsky model, first to confirm the experiment by calculating the non-linear parameter ( $\chi^2$ ), and second to evaluate transfer mechanisms (convection and diffusion) of fluoride ions by estimating the phenomenological parameters of mass transfer ( $\sigma$  and  $P_s$ ) for the selected NF and RO membranes in simple and binary mixture. For NF membranes, a duality between both transfer mechanisms was recorded which was strongly affected by the feed composition.

Keywords: Nanofiltration; Reverse osmosis; Fluoride retention; Modeling; Mass transfer

## 1. Introduction

Fluoride ion exists in all natural waters and it is an essential micronutrient for humans. At a range of concentrations between 0.5 and 1 mg/L recommended by World Health Organization (WHO) [1], fluoride can prevent dental caries and stabilize the skeletal system [2]. Fluorine levels above 1.5 and 4 mg/L, respectively, cause dental fluorosis and skeletal fluorosis [3]. Recently, fluoride has been known as one of the responsible elements of developmental neurotoxicity in human [4].

High level of fluoride in groundwater is a global issue, which is found in many countries and depends on the geographical location and climate of the contaminated area [5]. Groundwater resources from Africa, Asia and USA are most exposed to the fluoride contamination [6,7]. Excess fluoride as high as 8.95 mg/L has been reported in drinking water resources in Morocco [8].

High fluoride in groundwater may occur naturally when conditions favor the dissolution of some fluorine-bearing minerals in rocks [9]. Human activities like the use of phosphatic fertilizers in agriculture and industrial activities such as brick kilning and burning coal may also contribute to the fluoride content [10].

<sup>\*</sup> Corresponding author.

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Defluoridation techniques can be classified into four main categories: precipitation, ion-exchange, adsorption and membrane processes [11]. Regarding membrane techniques, reverse osmosis (RO) and nanofiltration (NF) are recently developed by many authors for the removal of F<sup>-</sup> in drinking water [12–15]. NF due to its characteristics ion rejection and permeate flux can be an effective technology for the treatment of groundwater with high contents of fluoride. Furthermore, NF allows to have partial and selective demineralization with low operational pressure compared with RO.

In general, NF membranes have a pore size near to 1 nm and cover an intermediate separation area between ultrafiltration (UF) and RO [16]. Mass transfer mechanisms in RO and UF are made, respectively, by diffusion and convection, whereas in NF, both mechanisms can be observed with a duality which strongly depends on the membrane material (surface charge and molecular weight cut-off [MWCO]) and operational conditions (pH, ionic strength, flow rate, conversion rate and transmembrane pressure) [17]. Therefore, this complexity of mass transfer mechanisms in NF can affect the optimal development of this separation technique, especially on the industrial scale.

In a previous study, Pontie et al. [18] have investigated the selective defluoridation of brackish water using NF membrane and the authors have reported that high fluoride retention was made by diffusion mode. However, groundwater resources contain other anions such as chloride, sulfate, nitrate and bicarbonate which can be as competitive elements to fluoride anion during the separation process with NF. In this case, the diffusion mode of the high fluoride retention with NF membranes can be affected by the presence of such anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and HCO<sub>3</sub><sup>-</sup>). To the best of our knowledge, studies regarding the influence of these elements on Fremoval using NF and RO processes have not been reported. For that, an investigation seems necessary on the efficiency of NF and RO membranes for the retention of F<sup>-</sup> in binary mixture with those anions that coexist in the groundwater and their influence on fluoride ions transfer mechanisms.

The main objective of this work was to highlight the application of NF membranes on fluoride retention and comparing their performances with RO. This study should also provide a clearer understanding of fluoride ions transfer mechanisms in NF as well as RO. Mechanisms of fluoride ions transfer through pores of the studied NF and RO membranes have been investigated by using the simplified phenomenological Spiegler–Kedem–Katchalsky model for simple and binary mixtures. This approach would lead to a better prediction of the possibilities of NF application on defluoridation with its optimal operating conditions.

## 2. Materials and methods

## 2.1. NF/RO membranes

The three selected membranes for this study were two NF membranes, denoted as NF270 and NF90, and an RO membrane denoted as BW30. All membranes were provided from the company FilmTec (DOW, USA). These polymeric membranes are of asymmetric and thin-film composite type, the active layer is deposited with polyamide on microporous polysulfone support, through a binding layer of polysulfone.

According to the manufacturer, the characteristics of these membranes are summarized as follows: NF270 and NF90 have maximum temperature of 45°C, maximum pressure of 41 bar and operating pH range of 3–10; while BW30 has maximum temperature of 45°C, maximum pressure of 41 bar and operating pH range of 2–11. 300, 200 and 100 Da are, respectively, the MWCO of NF270, NF90 and BW30 [19,20]. Before use, these membranes were reconditioned with ultrapure water (conductivity < 1  $\mu$ s/cm) for 24 h at a temperature of 4°C.

## 2.2. Experimental procedure

The laboratory scale cross-flow filtration unit was operated in batch mode with recirculation of permeate and concentrate in the feed tank where the concentration is constant. The unit is equipped with a stainless steel plane module provided by the company GE Osmonics (USA) which can support flat membranes of RO and NF having a surface area of 138 cm<sup>2</sup>. The unit also has a pump HP (Wanner, USA) which features a feeding circulation speed regulator. Two valves were installed at the outlet (concentrate) and the inlet (feed) to adjust the differential pressure applied and two flow meters (Omega, USA) to control the conversion rate. The total volume of the system is 5 L and a thermostat to set the desired temperature. A schematic representation of the equipment is illustrated in Fig. 1.

Individual salt solutions were freshly prepared from mixing bidistilated water with NaF, NaCl, NaNO<sub>3</sub>, NaHCO<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> salts which were supplied by Sigma-Aldrich (France). Salts rejections in the simple system were performed with at fixed concentration of 10 mg/L. Effect of concentration on fluoride retention has been investigated on two different concentrations of F<sup>-</sup> (5 and 10 mg/L). Concerning fluoride retention in binary mixture once with chloride Cl<sup>-</sup>, nitrates NO<sub>3</sub><sup>-</sup>, bicarbonate HCO<sub>3</sub><sup>-</sup> and sulfate SO<sub>4</sub><sup>2-</sup>, F<sup>-</sup> concentration were fixed at 10 mg/L, then tests of filtration were done at different concentration ratios (1/1, 1/2 and 2/1) between fluoride and each element (F<sup>-</sup>/Cl<sup>-</sup>, F<sup>-</sup>/NO<sub>3</sub><sup>-</sup>, F<sup>-</sup>/HCO<sub>3</sub><sup>-</sup> and F<sup>-</sup>/SO<sub>4</sub><sup>2-</sup>). All experiments were performed at 24°C.

## 2.3. Analytical techniques and operational parameters

Samples of permeate, feed as well as concentrate were collected and a mean value was calculated for each determination. Changes in concentration of  $Cl^-$ ,  $F^-$  and  $NO_3^-$  were followed by using ion-selective electrodes connected to a digital



Fig. 1. Schematic representation of NF/RO filtration pilot, Laboratory of Applied Chemistry, Faculty of Science and Technology of Fez, Morocco.

Ionometer (Ecoscan Ion 6). The  $HCO_3^-$  concentrations were calculated through potentiometric titration, whereas,  $SO_4^{2-}$  concentrations were measured through gravimetric titration [21]. The pH has also been measured for different samples by using pH meter (Ecoscan Ion 6).

Salts concentrations in permeate  $C_{p}$ , concentrate  $C_{c}$  and feed  $C_{0}$  were useful parameters to calculate the observed retention  $R_{obs}$  which is described by the following equation:

$$R_{\rm obs} = \left(1 - \frac{C_p}{C_0}\right) \times 100 \tag{1}$$

The conversion rate (Y) was fixed at 5%, low enough to prevent concentration polarization and to better estimate the parameters of mass transfer mechanisms. The permeate flow  $Q_p$  and the feed flow  $Q_0$  were followed using flow meters, then Y can be calculated as follows:

$$Y = \left(\frac{Q_p}{Q_0}\right) \times 100 \tag{2}$$

Membrane permeability characterization was performed based on Darcy's law from Eq. (3), which describes the permeate flow  $(J_v)$  as a function of the differential pressure applied  $(\Delta P)$  and hydraulic permeability with pure water  $(L_v)$ .

$$J_v = L_p \Delta P \tag{3}$$

To better understand membranes permeability, measurements of the contact angle with pure water were performed on each membrane surface through the sessile drop method by using a Goniometer with an environmental chamber. The degree of hydrophobicity is obtained from contact angles values, that is, a hydrophilic surface is obtained when the contact angle  $\theta$  is inferior to 90°, while a hydrophobic surface is recorded when water forms droplets having a  $\theta$  higher than 90°.

## 3. Results and discussion

#### 3.1. Membrane permeability and hydrophilicity

Before the application of the selected NF and RO membranes for fluorine rejection, we were first interested to characterize their permeability and hydrophilicity. Determination of hydraulic permeability with pure water  $(L_p)$  and with saline water  $(L_p')$  was investigated in many previous studies to reflect the porous structure of a membrane as well as the starting pressure of a system membrane/salt [17,22,23]. Contact angle measurements can be useful to confirm permeability tests with NF/RO membranes. The investigation results of hydraulic permeability  $L_p$  and  $L_p'$ , respectively, of pure water and of F<sup>-</sup> (10 mg/L), the critical pressure (Pc) which is the starting pressure of permeate flux as well as contact angle values ( $\theta$ ) of the studied NF/RO membranes, are summarized in Table 1.

Permeability order was proportional to the MCWO order of the studied NF and RO membranes. Hydraulic permeability with NF270 was higher comparing with NF90 and BW30, which indicates that this membrane has the highest pores size. BW30 membrane was less permeable than NF membranes due to its dense structure (very narrow pores) of the active layer. NF90 seems closer to RO process in terms of permeability, which reflects that NF90 is useful to remove some monovalent ions. Results of hydraulic permeability of pure water for the selected NF/RO membranes were very different from those reported in the literature [17,22,24–27]. Those differences are generally dependent on water purity and temperature which directly influence on water velocity.

With the aqueous solution of F<sup>-</sup> (10 mg/L) and under the same operating conditions of temperature and applied pressure, NF270, NF90 and BW30 have followed the same order of permeability, except that,  $L_p'$  was lower than  $L_p$ . The membrane surface became more compact in the presence of the electrolyte in the solution due to contraction of pores, resulting in the decreasing in the permeability through the selected membranes [28]. From critical pressure values, the permeate flow with the investigated NF membranes starts at pressures below 1.5 bar, while in the case of permeate flow; it begins at pressures above 2.5 bar.

The contact angle values of the NF/RO membranes were less than 90° (varies from 33° to 58°), which means that they have a hydrophilic surface. Generally, the lower is the contact angle the more hydrophilic is the material [29], as in the case of NF270. Indeed, the hydrophilicity in case of these polyamide membranes is related to the presence of carboxylic and amine groups capable to interact with water molecules by hydrogen bond [30,31]. Moreover, the values of contact angles followed the same order as the values of the hydraulic permeability, which confirm the permeability tests on all the NF/RO membranes.

#### 3.2. Salts rejection in simple system

Initially, the rejection of fluoride was compared with three other monovalent anions and one divalent anion that are important in drinking water. Figs. 2 and 3 show the observed retention of F<sup>-</sup> as well as HCO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> as a function of the applied pressure with a fixed concentration of 10 mg/L in a simple system with the selected membranes.

Table 1

Hydraulic permeability of pure water ( $L_p$ ), hydraulic permeability at 10 mg/L of F<sup>-</sup> ( $L_p$ ), critical pressures (Pc) and contact angles ( $\theta$ ) for NF270, NF90 and BW30

Membrane	$L_p$ (±0.7) (L/h m <sup>2</sup> bar)	$L_p$ [Ref.] (L/h bar m <sup>2</sup> )	$L_{p}'$ (±0.3) (L/h m <sup>2</sup> bar)	Pc (±0.1) (bar)	θ (±1) (°)
NF270	5.48	5.1-14.86 [32,34]	4.47	0.30	33.2
NF90	4.44	6.05–11.2 [30,33]	4.06	1.12	45.2
BW30	2.45	1.97–3.50 [32,33]	2.37	2.55	58.0

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Fig. 2. Retention of fluoride, chloride, nitrates, bicarbonate and sulfates as a function of transmembrane pressure with BW30 membrane ([anion] = 10 mg/L, Y = 5%,  $T = 24^{\circ}$ C, pH = 6.5-7.4).



Fig. 3. Retention of fluoride, chloride, nitrates, bicarbonate and sulfates as a function of transmembrane pressure with (a) NF270 and (b) NF90 membranes ([anion] = 10 mg/L, Y = 5%,  $T = 24^{\circ}\text{C}$ , pH = 6.5–7.4).

For all membranes, the retention order of the  $SO_4^{2-}$  divalent and monovalent anions (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and HCO<sub>3</sub><sup>-</sup>) is strongly related to their hydration enthalpy (Table 2) [19,32,33]. In another way, a divalent ion takes more energy to be extracted through a membrane's pore than a monovalent ion [34]. Fig. 2 shows that for the dense BW30 membrane there is only a small difference in rejection for all anions, whereas in NF membranes (Figs. 3(a) and (b)), the divalent ion  $(SO_4^{2-})$  was much better retained by NF membranes than monovalent ions (F<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>), because of its higher hydration enthalpy [35]. In NF, The membranes MWCO reported by the supplier explain the better rejection of all anions with NF90 than NF270, which means that the more open pores NF membrane (NF270) shows the lower retention. In Fig. 3(b) (case of NF90), the inversion in  $R_{obs}$  order for nitrate and chloride ions reflects that the hydration enthalpy order (or hydration radii) was affected due to a convective mass transfer driving process which occurs predominantly for chloride before 4 bar, as reported previously for Br- and Cl- [36]. At higher pressure, NF90 seems close to the RO side of the NF region, and for such membranes, the retention of the salts depends on diffusional mass transfer.

#### 3.3. Effect of fluoride concentration on observed retention

In order to highlight the effect of fluoride concentration on the observed retention, NF270 and NF90 membranes were investigated using a synthetic solution of F- with two different concentrations (5 and 10 mg/L) as shown in Fig. 4. For NF270 membrane, it was possible to observe a discrepancy in the level of observed retention, which was manifested by a large gap between the two concentrations 5 and 10 mg/L of F- in the high-pressure zone (between 10 and 14 bar) with observed retention varying from 61% to 67%. This difference can be explained by the phenomenon of concentration polarization as reported previously [22]. In case of NF90 membrane, the discrepancy gap in the level of observed retention (varying from 75% to 86%) between the two concentrations was noticed at low pressure (between 2 and 4 bar), which reflects that concentration polarization might be affected by the conventional mass transfer the reason for which the membrane becomes more selective for higher pressure.

## 3.4. Fluoride rejection in binary mixture

Groundwater resources contain other competitive anions to fluoride such as nitrate, chloride, bicarbonate and sulfate. For that, it seemed necessary to highlight the influence of

Table 2

Ionic radius and hydration enthalpy of the studied ions as well as their rejection with the selected membranes [19,32,33]

Ion	r <sub>i</sub>	$-\Delta H_{hyd}$	The highest $R_{obs}$ value reached (%)			
	(nm)	(kJ/mol)	NF270	NF90	BW30	
NO <sub>3</sub> -	0.189	329	27	56	93	
Cl-	0.181	365	32	65	94	
HCO3-	0.163	380	46	72	95	
F-	0.136	515	63	91	97	
SO <sub>4</sub> <sup>2-</sup>	0.240	561	95	98	99	

these anions on fluoride removal with the studied NF (NF270 and NF90) and RO (BW30) membranes. The results of fluoride rejection of the NF/RO membranes with concentrations of each anion are shown in Fig. 5. The operational conditions of all experiments were carried out with a pressure of 10 bar, a conversion rate of 5% and a fixed fluoride concentration of 10 mg/L.

From the separation results with the selected membranes, it was observed that the augmentation of  $SO_4^{2-}$  concentration shows a negative effect on F<sup>-</sup> retention. A similar effect has been observed in a similar study where the presence of  $SO_4^{2-}$  divalent ion results in the decreases of Cl<sup>-</sup> monovalent rejection [37]. In case of monovalent ions effect, the elements which have the same valence as fluoride, the increase in the concentration of  $NO_3^{-}$ , Cl<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> has a positive effect



Fig. 4. Fluoride retention as a function of transmembrane pressure for two different concentrations (5 and 10 mg/L) with NF270 and NF90 membrane (Y = 5%, T = 24°C, pH = 6.7).



Fig. 5. Fluoride retention in binary mixture as a function of the anion concentration ( $\Delta P = 10$  bar, Y = 5%, [F<sup>-</sup>] = 10 mg/L, T = 24°C, pH = 6.5–7.9).

on  $F^-$  retention with all membranes making  $F^-$  the dominant species. In another point, the order of the positive effect is proportional to hydration enthalpy order (Table 2). From results, it seems that chloride and bicarbonate have the greatest positive effect on fluoride removal with the NF90 membrane, which explains its efficiency on some previous studies on brackish water defluoridation [13,38].

## 3.5. Modeling of fluoride retention in simple and binary mixture

To obtain more information about the separation mechanism of fluoride ions with the studied NF and RO membranes and to highlight the influence of the studied anions on fluoride retention, the experimental data were fitted with the simplified Spiegler–Kedem–Katchalsky (SKK) model which is expressed as a function of mass transfer phenomenological parameters ( $\sigma$  and  $P_s$ ). The derivation of the SKK model and its application on some salt/membrane systems are described in previous studies [22,23,39–41]. The SKK model is defined as follows:

$$R_{\rm obs} = \frac{1}{\frac{(1-\sigma)\exp\left(\frac{J_v}{k}\right)}{\sigma\left(1-\exp\left(-\frac{(1-\sigma)}{P_s}J_v\right)\right)} + 1}$$
(4)

where  $\sigma$ ,  $P_s$  and k represent the coefficient of reflection, the solute permeability and the coefficient of mass transfer, respectively.  $R_{obs}$  vs.  $J_v$  was plotted by imposing different pressures for each set of experiment (Fig. 6). Thereafter, the non-linear curve for each experiment was fitted using least squares method between the observed retention ( $R_{obs}$ ) and the calculated retention ( $R_{cal}$ ) (Fig. 6) the parameters  $\sigma$  and  $P_s$  which allowed us to estimate the phenomenological parameters ( $\sigma$  and  $P_s$ ) of fluoride ions transfer through the studied



Fig. 6. Evolution of  $F^-$  retention as a function of permeate flux with NF (NF270 and NF90) and RO (BW30) membranes. The theoretical curve was fitted by Spiegler–Kedem–Katchalsky model ([ $F^-$ ] = 10 mg/L).

NF and RO membranes in each system (Table 3). The validity of the models used in this work was verified by calculating the parameter ( $\chi^2$ ) through the application of the following equation [42]:

$$\chi^{2} = \sum \frac{(R_{\rm obs} - R_{\rm cal})^{2}}{R_{\rm cal}}$$
(5)

where  $R_{exp}$  and  $R_{cal}$  are the real rejections experimentally determined and calculated in accordance with the SKK model, respectively.

The small numbers of the non-linear parameter  $\chi^2$ (Table 3) show that the SKK models describe with high accuracy the experimental F- rejection results for all studied systems. Likewise, the SKK approach was useful as well to study the transfer parameters of F<sup>-</sup> in mixture with other anions. Also, the values obtained for the phenomenological parameters ( $\sigma$  and  $P_s$ ) of the SKK model give a good description of the experimental results. Thereby, high reflection coefficients ( $\sigma$ ) and very low values of fluoride ions permeability  $(P_{a})$  stand in agreement with the good retention of fluoride with a selected membrane, and vice versa. Phenomenological parameters of mass transfer ( $\sigma$  and  $P_{a}$ ) can reveal the behavior of each studied NF and RO in terms of mass transfer mechanisms during a filtration process. A  $\sigma$  value close to 1 means that the convective solute transport is totally hindered and the transport by diffusion takes place [22,43].

For BW30, the values of the reflection coefficient presented in Table 3 are very close to  $\sigma = 1$ , which indicates that the convective transport of fluoride is almost hindered for the BW30 membrane even in the presence of other anions. In the case of NF270,  $\sigma$  values were low and close to each other with a mean value of 0.65. Moreover, low values of  $\sigma$  reflect that the low rejection of fluoride recorded with NF270 membrane in different systems was due to a significant amount of fluoride ions which was transferred by the convective flux through the membrane pores. In addition, the solute permeability (P) was more important with NF270 membrane due to its largest pores, which facilitates the passage of fluoride ions to permeate through membrane pores (convective mode). In the case of defluoridation with the NF90 membrane in simple and binary mixtures, a duality between both mass transfer mechanisms (convection and diffusion) is recorded, given that  $\sigma$  values were within a range from 0.58 to 0.92. Otherwise, the high rejection of fluoride recorded in the simple system and in the presence of monovalent ions, was due to the transfer of fluoride ions by diffusive flux, whereas the low rejection of fluoride in the presence of sulfate was caused by the convective. Moreover, the  $\sigma$  and  $P_s$  values confirm that NF90 membrane is close to RO domain in terms of the selective fluoride rejection.

## 4. Conclusion

It has been shown that the three studied membranes (NF270, NF90 and BW30) can retain fluoride ions, and the retention amount was highly dependent on several parameters, such as pressure, feed composition, fluoride concentration and the MCWO of each membrane.

Permeability tests showed that NF70 is the most productive membrane ( $L_{p.NF270} = 5.48$  L/h m<sup>2</sup> bar) comparing with NF90 and BW30 ( $L_{p.NF90} = 4.44$  L/h m<sup>2</sup> bar,  $L_{p.BW30} =$ 2.45 L/h m<sup>2</sup> bar). The permeability order, which depends on the membrane MWCO, was confirmed by contact angle measurements.

For the studied NF and RO membranes, the retention order of  $SO_4^{2-}$ , F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and HCO<sub>3</sub><sup>-</sup> anions is strongly related to their hydration enthalpy. Assays performed at 5% of conversion rate and pH 6.7 showed that fluoride was rejected to a greater extent with BW30 (97%) and NF90 (91%) than NF270 (63%) other ions. In NF, the superior rejection of fluoride over other divalent anions could be linked to its higher hydrated enthalpy. Moreover, the increasing of monovalent concentration, such as chloride and bicarbonate, promotes fluoride rejection in the binary mixture, unlike the presence of divalent anions (SO<sub>4</sub><sup>2-</sup>). This phenomenon could be related as well to the hydration enthalpy.

These results on fluoride retention were in accordance with the phenomenological SKK models calculated. The low values of the non-linear parameter ( $\chi^2$ ) confirm that SKK model is applicable for simple salt retention as well as for salt retention in a binary mixture. The values of the reflection coefficient ( $\sigma$ ) and solute permeability ( $P_s$ ) give a good description of the experimental results in different system feed/membrane. The values of  $\sigma$ , which were close to 1, indicate that the convective transport of fluoride is almost hindered (BW30) which leads to a high retention of fluoride, and vice versa (NF270). With NF90 membrane, the values of  $\sigma$ , which were within a range from 0.58 to 0.92 depending on the feed composition, reflect that a duality between both mass transfer mechanisms (convection and diffusion) is recorded.

Table 3

Reflection coefficients ( $\sigma$ ) and fluoride ions permeability ( $P_s$ ) obtained by fitting the experimental data with the SKK model

Feed	NF270			NF90			BW30		
	σ (±0.02)	P <sub>s</sub> (±0.01) (L/h m <sup>2</sup> )	$\chi^2$	σ (±0.02)	P <sub>s</sub> (±0.01) (L/h m <sup>2</sup> )	$\chi^2$	σ (±0.02)	P <sub>s</sub> (±0.01) (L/h m <sup>2</sup> )	$\chi^2$
F-alone	0.67	5.83	$4.23 \times 10^{-5}$	0.92	2.83	$6.10 \times 10^{-6}$	0.99	0.89	$4.09\times10^{-5}$
*F-/NO <sub>3</sub> -	0.64	7.17	$2.78 \times 10^{-6}$	0.72	4.11	$5.2 \times 10^{-4}$	0.92	1.23	$4.72 \times 10^{-4}$
*F-/Cl-	0.65	6.23	$6.25 \times 10^{-5}$	0.80	3.26	$3.8 \times 10^{-5}$	0.92	1.07	$6.53 \times 10^{-5}$
*F-/HCO3	0.67	6.03	$1.93 \times 10^{-5}$	0.87	2.96	$8.1 \times 10^{-5}$	0.95	0.93	$1.12 \times 10^{-6}$
*F-/SO42	0.64	11.2	$2.77 \times 10^{-5}$	0.58	6.14	$1.3 \times 10^{-5}$	0.85	2.83	$1.50\times10^{-5}$

 $*[F^{-}] = 10 \text{ mg/L} + [anion] = 20 \text{ mg/L}.$ 

In summary, results of permeability, salts rejection and mass transfer evaluation in this study showed that the NF90 membrane is close to RO domain (comparing its performances to BW30), which means that this membrane can be effective for a selective treatment of fluoride with significant workflow.

#### Symbols

$C_{\text{conv}}$	_	Solute concentration due to convection, $m \alpha^{/1}$					
~							
C <sub>int</sub>	_	Solute concentration in the membrane					
		mol/L					
$C_m$	_	Solute concentration at the surface mem-					
		brane, mol/L					
$C_{v}$	—	Solute concentration in permeate, mg/L					
$C_0$	_	Solute concentration in feed, mg/L					
$J_{v}$	_	Solvent flux, L/h m <sup>2</sup>					
J.	_	Solute flux, L/h m <sup>2</sup>					
Κ <sup>̈́</sup>	_	Coefficient of mass transfer, h <sup>-1</sup>					
$L_{n}$	_	Pure water permeability, L/h m <sup>2</sup> bar					
$L_n^{\nu}$	_	Saline solution permeability, L/h m <sup>2</sup> bar					
ŃWCO	_	Molecular weight cut–off, Da					
Pc	_	Critical pressure, bar					
P	_	Solute permeability, L/h m <sup>2</sup>					
$\check{Q_0}$	_	Feed flow, L/h					
$Q_n^{\circ}$	_	Permeate flow, L/h					
$Q_c^r$	_	Concentrate flow, L/h					
R	_	Observed retention, %					
R	_	Calculated retention, %					
$r_i$	_	Ionic radius, nm					
Ý	_	Conversion rate, %					
$\Delta H_{\rm hud}$	_	Hydration enthalpy, kJ/mol					
$\Delta P$	_	Transmembrane pressure, bar					
σ	_	Coefficient of reflection					
θ	_	Contact angle, °					
$\Delta \pi$	_	Osmotic pressure, bar					
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