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Performance of NF90 and NF270 commercial nanofiltration membranes in the defluoridation of Algerian brackish water

Amina Ramdani[a,b], André Deratani[c], Safia Taleb[b], Nadjib Drouiche[d,*], Hakim Lounici[e]

[a]*Department of Chemistry, Faculty of Sciences, University Dr. Moulay Tahar, Saida 20000, Algeria, email: ramdaniamina010@gmail.com*
[b]*Laboratory of Materials & Catalysis, Faculty of Exact Sciences, Djillali Liabès University, Site I, B.P. 89, Sidi Bel-Abbès 22000, Algeria, email: safiatal@yahoo.fr*
[c]*Institut Européen des Membranes, IEM-UMR 5635, Univ Montpellier, ENSCM, CNRS, Montpellier, France, email: andre.deratani@umontpellier.fr*
[d]*Centre de Recherche en Technologie des Semi-conducteurs pour l'Energétique (CRTSE), 2,Bd Dr. Frantz Fanon P.O. Box: 140, Algiers-7 merveilles, Algiers 16038, Algeria, email: nadjibdrouiche@yahoo.fr*
[e]*MDD lab, University Bouira Pole technologique Bouira, BP10000 Algeria, email: hakim_lounici@yahoo.ca*

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ABSTRACT

Fluoride is one of those ions that cause acute human health problems among the inhabitants of southern Algeria. Naturally occurring high levels of fluoride are closely linked to interactions between groundwater and volcanic rocks. Among the water treatment techniques applied to remove fluoride, nanofiltration (NF) was studied in this work. Fluoride removal operations were carried out on NaF 10^{-3} and 10^{-2} M model solutions and on natural groundwater (Kouinine) in a pilot cross-flow filtration unit at different pressures. The performance of two commercial NF composite thin-film membranes (NF90 and NF270) was evaluated in terms of productivity, desalination efficiency and energy consumption. The results showed that NF90 had the highest retention efficiency while NF270 had the highest permeate flow rate. However, it was observed that the NF90 membrane retained more than 88% of the fluoride ions of a complex natural matrix (Kouinine), while NF270 can retain 79%. The fluoride content of the permeate (0.35 and 0.62 mg L^{-1}) was well below the World Health Organization (WHO) threshold and Algerian standards. The water recovery rate (γ) has a strong impact on salt rejection and energy consumption. The best compromise was obtained by using NF90 with a quality of produced water that complies with the requirements of the WHO and the Algerian standards.

Keywords: Fluoride contamination; Groundwater; Nanofiltration membrane; Performance; Desalination

1. Introduction

The physico-chemical analysis of brackish groundwater samples from southern Algeria revealed that they are characterized by a high level of fluoride ions (F^-), associated with a largely excessive mineralization [1]. A high content of F^- is known to be harmful as it causes serious human health problems leading to endemic fluorosis (dental and skeletal) [2,3].

According to the World Health Organization (WHO) and Algerian guidelines, the optimal value of F^- in drinking water should not exceed 1.5 mg L^{-1} [2,3]. Unfortunately, many people around the world are exposed to fluoride concentrations exceeding the above recommended limit

* Corresponding author.

values. This is the case of the population living in southern Algeria, especially in the city of El Oued. The water tables of this region (Robbah, Kouinine, Tiksebt and Bayada) have F^- concentrations of about 2–5 mg L^{-1} [4]. The treatment of these fluorinated waters has become a major public health concern. This is the subject of our study.

Excess F^- can be reduced by many techniques, including precipitation, adsorption on various materials, ion exchange and membrane processes [5–8]. Membrane technology has attracted increasing attention in recent years due to the improvement of membrane materials [9–11]. It appears to be an appropriate and sustainable alternative for removing F^- from groundwater with a high removal efficiency compared with other methods [12]. Membrane technology is based on physical separation, which includes several techniques using a gradient of pressure, concentration, activity or electrical potential as the driving force [12,13]. Consequently, a wide variety of materials and structures in different process configuration options can be used depending on the technology implemented [13]. This study focuses on F^- removal by nanofiltration (NF), a pressure gradient membrane technique intermediate between ultrafiltration and reverse osmosis (RO). The advantages of this filtration technology operating at a lower pressure than RO include low energy consumption and good selectivity, making it cost-effective in many cases [13]. This is why NF is often proposed as an alternative to RO for water treatment, especially in the case of brackish water [14].

The transfer mechanism through NF membranes mainly involves three modes of transport: diffusion, forced convection and Donnan exclusion. Diffusion, similar to molecular transport by RO, depends on the solvation energy of the solutes and their partition coefficient. The solute concentration gradient is the driving force of diffusion transfer. On the other hand, convection increases with the applied pressure corresponding to a selective transfer of water through the membrane [15]. The charges on the surface of the NF membrane also induce strong electrical interactions with the charged solutes inside the pore due to their nanometric scale [16]. This phenomenon (Donnan exclusion) results in the unique selectivity of these membrane materials with a higher rejection of multicharged solutes.

NF has been shown to be an effective technique for partially removing F^- from hyperfluorinated brackish water [14,17,18]. Unexpectedly, F^-, despite its small size, is better retained than larger halides, so its content in the treated water can meet WHO standards depending on operating conditions, including membrane type, pH and ionic strength of the feed, applied pressure and conversion rate. A lot of work has been done in recent years on this subject, for example, the effect of pressure, solute concentration and conversion rate on salt retention [18], the influence of coexisting ions and the type of NF membrane [19]. Tahaikt et al. [20] have compared the efficiency of three commercial NF membranes to remove F^- at pilot scale. The NF90, a tight NF membrane with a desalination efficiency close to that of an RO membrane [21], showed an F^- removal efficiency from brackish groundwater of more than 98%. The rejection fell to about 85% in the case of the looser NF270 membrane. The influence of pH, humic acid (HA) and inorganic carbon (IC) on F^- removal by NF270 was also studied on model solutions [8]. F^- is more retained when the pH increases due to HF/F^- speciation (pKa = 3.2) and the increase of the negative charge of the membrane surface. The impact of HA and IC on F^- rejection seems more complex because it depends on both pH and concentration. Hoinkis et al. [22] studied the removal of F^- from fluoride spiked model solutions and tap water by NF90 and NF270 membranes. It was shown that NF270 can maintain the F^- level below the WHO recommended value (1.5 mg L^{-1}) as long as the F^- concentration in the feed does not exceed 10 mg/L, whereas this value is 20 mg L^{-1} for the NF90 membrane. Industrial discharges containing fluorides can seriously pollute the water table. In this respect, NF has been studied for the simultaneous removal of F^- and chromium(VI) from synthetic binary solutions using NF300 and PN40 membranes [23]. The highest rejections were observed at applied pressures above 8 bar and pH values of the feed solution above 8. F^- removal decreased from 92% to 68% and 82% to 59% as the concentration of F^- in the feed solution increased from 5 to 100 mg L^{-1} using NF300 and PN40 membranes, respectively.

In this work, the partial defluoridation and demineralization of brackish groundwater in southern Algeria were studied to produce drinking water in compliance with WHO and Algerian standards using NF as an alternative to RO. The objective is to develop a simpler process without remineralization and more energy efficient. The comparison of F^- removal between the two membranes Filmtec™ NF90 and NF270 (DuPont Water Solutions, Edina, MN USA) has been carried out using a laboratory scale pilot plant. Synthetic single salt solutions (NaF) and natural brackish groundwater (Kounine) with a total salinity of about 2.3 g L^{-1} were tested to determine the impact of coexisting ions. The performance efficiency of NaF was estimated in terms of removal ability, permeation flux and energy consumption as a function of operating parameters.

2. Materials and methods

2.1. Experimental apparatus

The polymer membranes Filmtec™ NF90 and NF270 (DuPont Water Solutions, Edina, MN USA), whose characteristics are listed in Table 1, are generally recommended to remove high percentages of salts and organic contaminants from surface and ground water. The NF experiments were performed at 25°C ± 0.5°C with a laboratory filtration pilot comprising a 5-L feed tank and a positive displacement pump delivering a feed rate of 7.9 L min^{-1} (Fig. 1). Flat membrane coupons (19 cm × 14 cm) with an effective membrane surface area of 155 cm^2 were placed inside the cross-flow filtration module with spacers. A valve on the retentate outlet line controlled the applied pressure, which was monitored by two pressure gauges located on the retentate inlet and outlet lines, with the applied pressure varying up to 17 bar.

2.2. Water sampling quality

Groundwater samples were recovered from a well in Kouinine, which is a part of the groundwater Complex Terminal for the water supply of the city of El Oued

Table 1
Characteristics of the membrane used in this study

Characteristics	Membrane NF270	Membrane NF90
MWCO (Da, 30°C)[a]	200–400	200–400
Membrane materials of the filtration layer[a]	Polyamide	Polyamide
Contact angle (°)[c]	53 ± 3	68 ± 2
NaCl rejection (%)[b]	50	90–96
$MgSO_4$ rejection (%)[b]	98+	98+
Average pore size (nm)[c]	0.38	0.31
Pure water permeability (L h^{-1} m^{-2} bar^{-1})[c]	17 ± 1.3	9.0 ± 1.1
Zeta potential at pH 7 (mV)[c]	–66	–25
Maximal temperature (°C)[b]	45	45
Maximal pressure (bar)[b]	40	40

[a]from [24].
[b]Product information from Dow FilmTec (form no. 609-00519-1206 and 609-00378-0811 for NF270 and NF90, respectively).
[c]This study.

(South-eastern Algeria; Fig. 2). The natural water samples were collected in 5-L plastic containers. The water samples were stored at room temperature before being transported by air to the European Membrane Institute in Montpellier, France. Upon arrival in France, the water sample was stored at a temperature of 4°C before being used for analysis. Table 2 lists the physico-chemical characteristics of the brackish water to be treated. This water is characterized by a high hardness, a high content of fluorides, sulfate, bicarbonate and chloride ions. All the parameters exceed the WHO and Algerian drinking water guidelines and must, therefore, be treated. The feed solutions underwent pretreatment by microfiltration on membranes 0.45 or 0.1 μm before NF experiments in order to limit the fouling of NF membranes.

2.3. Analytical methods

Single salt solutions were prepared with NaF (Sigma-Aldrich Chemie, Saint-Quentin Fallavier, France, ACS reagent grade) at concentrations of 10^{-3} and 10^{-2} M (42 and 420 mg L^{-1}, respectively). The pH of feed solutions was adjusted by the addition of acid or base. Ion analyses were performed by two analytical methods: ionic chromatography (DIONEX ICS-1000) and conductivity meter (WTW). Natural groundwater (2.2 mg L^{-1} of F^-) was treated under identical conditions to those of the synthetic solutions.

2.4. NF performance analysis

The performance of the NF membranes for defluoridation was evaluated by the purified water productibility, the membrane selectivity and the specific energy consumption (SEC) [24,25]. The purified water productibility was determined by the slope (L_p) of the permeate flow as a function of transmembrane pressure using the Darcy's law (Eq. (2)) [26].

$$J_P = \frac{Q_P}{A} \quad (1)$$

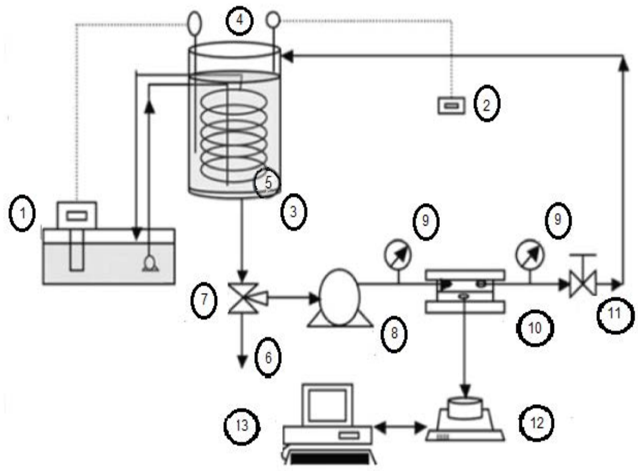

Fig. 1. Schematic experimental setup of the pilot plant with spiral membranes used. (1)-Circulating thermal bath, (2)-preference thermometer, (3)-feed tank, (4)-temperature probe, (5)-coil, (6)-purge, (7)-three-way valve, (8)-high-pressure pump, (9)-manometer, (10)-Sepa CF II Cell, (11)-pressure control valve, (12)-balance, (13)-computer.

$$L_P = \frac{J_P}{P_T} \quad (2)$$

where Q_p is the flow rate of permeate (L/h), A is the effective surface area of the membrane, and P_T is the trans-membrane pressure $((P_a + P_r)/2)$ (bar), where P_a and P_r are, respectively, feed and retentate pressures.

L_p with units corresponding to a membrane permeance (L h^{-1} m^{-2} bar^{-1}) is incorrectly called permeability in most documents related to pressure-driven liquid filtration techniques (MF, UF, NF and RO). This term will, therefore, be used in the rest of the text.

The membrane selectivity was determined by the rejection rate using Eq. (3):

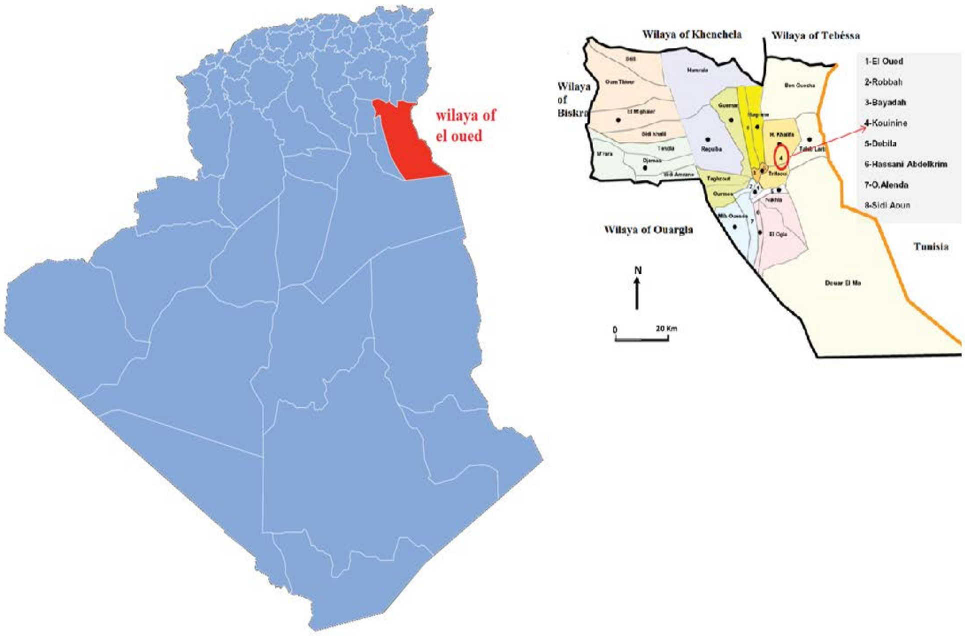

Fig. 2. Geographical location of sampling sites.

Table 2
Physico-chemical characteristics of the raw water from Kouinine

Parameters	Raw water	WHO standard	Algerian standard
TDS (ppm)	2,300	–	–
pH	7.46	≥6.5 and ≤8.5	≥6.5 and ≤9
T (°C)	26	25	25
TH (°F)	107	–	–
Ca^{2+} (ppm)	256	–	250
Mg^{2+} (ppm)	104.49	50	–
Na^{+} (ppm)	294.4	150	200
K^{+} (ppm)	6.6	12	12
Cl^{-} (ppm)	843.75	250	500
F^{-} (ppm)	2.2	1.5	1.5
SO_4^{2-} (ppm)	583.92	250	400
NO_3^{-} (ppm)	12.1	50	50

T: temperature;
TDS: total dissolved solids;
TH: total Hardness;
WHO: World Health Organization.

$$R_i = 1 - \frac{C_p^i}{C_f^i} \tag{3}$$

where R_i is the rejection rate (%), C_p^i and C_f are the permeate and feed concentration (*M*) of solute *i*, respectively.

The osmotic pressure (Π) (bar) of the feed water was calculated using the following equation [11]:

$$\Pi = R \cdot T \cdot \sum C_i \tag{4}$$

where *R* is the universal gas constant (L bar mol^{-1} K^{-1}), *T* is the absolute temperature (K), and ΣC_i is the sum of concentrations of solutes (mol L^{-1}).

The energy operating cost of NF was estimated in this study as the SEC corresponding to the electrical energy (from the pump) needed to produce a cubic meter of permeate, which is proportional to operating pressure and was calculated by Eq. (4) [13]:

$$\text{SEC} = \frac{P_T}{36 \cdot \eta \cdot \gamma} \tag{5}$$

where SEC is the specific energy consumption during the NF operation (kWh m^{-3}), P_T is the transmembrane pressure (bar), η is the efficiency of the pump, 0.5 ≤ η ≥ 0.8, assumed to be 0.8 in this study; 36 is a factor to convert the unit of energy to kWh m^{-3}, and γ is the purified water recovery rate which is given by:

$$\gamma = \frac{V_p}{V_f} \quad (6)$$

where V_f and V_p are the feed and permeate volumes obtained after a batch experiment (L). Optimization of SEC can then be achieved by playing with the purified water recovery rate. SEC is calculated for NF experiments corresponding to the following conditions: P_T = 11 bar, T = 25°C and a treatment time of 15 min.

3. Results and discussion

3.1. Membrane characterization

NF membranes have a macroporous polyester mechanical support, a microporous polysulfone support and a thin polyamide top layer. The top surface filtration layer of NF270 membranes consists of a semi-aromatic polyamide obtained by interfacial polymerization between trimesoyl chloride (TMC) and piperazine [11,27], whereas in the case of NF90, it consists of a fully aromatic polyamide obtained by interfacial polymerization between TMC and *m*-phenylenediamine [27]. The thin-film composite structure of NF membranes allows high permeate flow and good selectivity with a high salt rejection rate. In both cases, the presence of weakly acidic COO^- groups is responsible for the negative surface charge of the membrane at pH above 4 [21].

The zeta potential (charge), roughness, hydrophobicity (contact angle) and molecular weight cut-off (MWCO) are physical properties mainly used for the characterization of the thin filtration layer on the surface of NF membranes. Indeed, the characteristics listed above govern their performance for the desalination of brackish water [28]. Table 1 and Fig. 3 bring together these data for the two membranes studied.

NF270 has a regular nodular surface with very low roughness, whereas, on the contrary, NF90 is very rough with a non-homogeneous surface structure consisting of peaks and valleys (Fig. 3). This observation might confirm the loose membrane character of NF270, while NF90 has a tight membrane structure [14]. In any case, this surface topology is in very good agreement with the contact angle values obtained of 53 ± 3 and 68 ± 2° for NF270 and NF90 membranes, respectively. It can be concluded that NF90 is more hydrophobic than NF270 probably because of its rougher surface topology. Hydrophilicity is an important parameter because it increases permeability for the same pore size and tends to limit membrane fouling due to adsorption of organic matter [27]. The permeability data reported in Table 1 are the average of all experiments performed for each of the two membranes. The pressure range studied for NF90 was 3–20 bar, whereas the maximum pressure was only 15 bar for NF270.

The salt retention performance allows the membrane selectivity to be evaluated [25]. As previously mentioned, the retention of charged solutes is mainly related to the electrical interactions between the membrane charges and those of the solute. Electrokinetic measurement has indicated that the surface of the NF90 and NF270 membranes is strongly negatively charged in the operating pH of the filtration (pH ≈ 7). The negative charge on the membrane surface is due to carboxylic acid groups that are deprotonated at neutral pH [13]. Although the zeta potential value of the NF90 membrane showed a lower negative charge than that of the NF270 membrane, its smaller pore size resulting in more intense electrical interactions can explain the higher salt rejection by this membrane.

3.2. Pure water permeability and osmotic pressure

The initial pure water permeability (PWP) prior to the NF experiments was 9.9 and 16.1 L h^{-1} m^{-2} bar^{-1} for NF90 and NF270, respectively. After each NF filtration, the

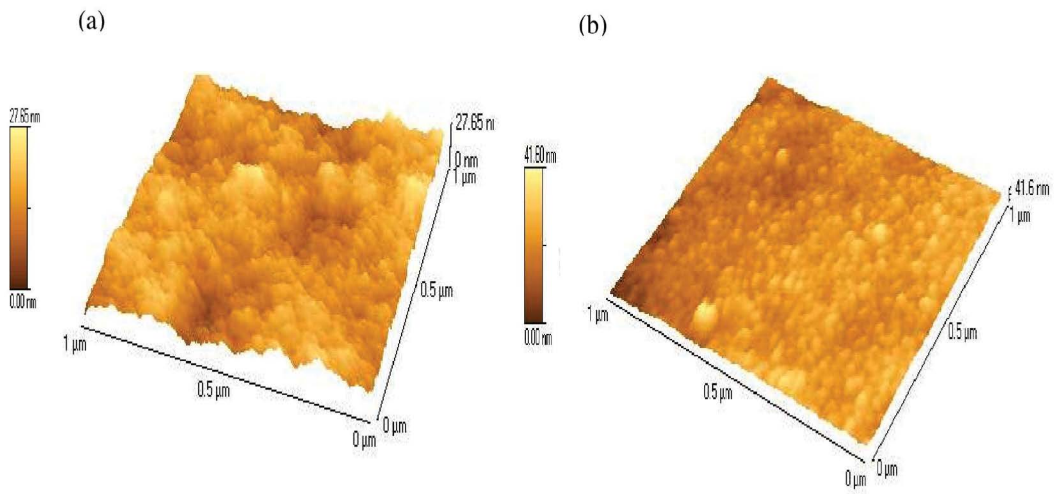

Fig. 3. Three-dimensional AFM images of the surface of (a) NF90, (b) NF270 membranes on a scan area of 1 µm × 1 µm.

membranes were washed with deionized water. The results showed that after rinsing, PWP was practically restored. The PWP data obtained after filtration of the NaF model solutions and raw water were, respectively, 9.9 and 9.1 L h^{-1} m^{-2} bar^{-1} for NF90 membrane and 15.7 and 15.9 L h^{-1} m^{-2} bar^{-1} for NF270. As PWP was maintained in all the NF experiments with different coupons at an average value of 9.0 ± 1.1 and 17.0 ± 1.3 L h^{-1} m^{-2} bar^{-1} for NF90 and NF270, respectively, it was concluded that, under the experimental filtration conditions, the fouling by raw groundwater could be considered as limited and manageable using an appropriate pretreatment by microfiltration or ultrafiltration. This is likely due to the fact that the fouling is mainly composed of inorganic solids in small quantities, as the studied groundwater contains very little organic matter.

The permeability observed during groundwater filtration was lower than that of the NaF model solutions. The theoretical values of osmotic pressure (calculated from (Eq. (4)) are approximately 0.05 and 0.49 bar for solutions with NaF concentrations of 10^{-3} M, 10^{-2} M and 1.29 bar for groundwater (Kouinine). The osmotic pressure must actually be subtracted from the applied pressure to give the effective transmembrane pressure. Moreover, when pure water is replaced by the solution to be treated, the observed flow rate is often much lower depending on the concentration of the solutes. The accumulation of solutes retained on the surface of the membrane resulting in the appearance of a polarization layer that induces a higher osmotic pressure than that of the bulk solution can explain this observation.

3.3. Effect of permeate fluxes and applied pressure on F^- rejection

The F^- rejection by NF90 and NF270 for the two NaF model solutions is plotted as a function of the permeate flow rate in Figs. 4a and b. These tests were carried out at applied operating pressures of 3, 5, 7, 9, 11, 13 and 15 bar. The results show that whatever the concentration studied, F^- rejection initially increases with pressure and then levels off by reaching a limit value when the pressure exceeds 11 bar. This observation is consistent with the transport of F^- across NF membrane through three mechanisms which are diffusion, convection and exclusion of Donnan.

The rejection of monovalent salts (NaF, NaCl, NaBr and NaI) by NF270 was studied by Ramdani et al. [29]. It was found that F^- is better retained than the other halide ions. It has also been reported that F^- retention is higher than that of Cl^{-1} using the two membranes NF90 and NF270 [14]. The most convincing hypothesis proposed in the literature to explain the abnormally high rejection of fluoride ions is to consider the higher dehydration energy of fluoride (515 kJ/mol) compared with other halide ions [17,30,31]. Dehydration would occur during the transport of the ions through the NF membrane. The order of hydration energies provides a satisfactory explanation for the order of retention observed.

As previously seen, NF90 and NF270 are negatively charged at neutral pH. Thus, the combination of steric exclusion and solute/membrane repulsive interactions is responsible for the F^- rejection. Diffusion transport is the dominant mechanism when permeate flow is low. Thus, fluoride ions are moderately retained at low applied transmembrane pressures (3 bar). As the permeate flow rate increases, convective transport becomes more and more important, which strongly affects the passage of fluoride ions and increases their retention. At high applied pressures (13 or 15 bar), the rejection reaches a plateau (limit rejection). These results are in agreement with those of other studies concerning the retention of fluoride ions by NF membranes [14,24].

Most of the time, it is necessary to operate membrane plants including RO and NF at medium pressures (7–10 bar) for technical-economic reasons. This constraint makes it necessary to optimize treatment performance. The results presented in Figs. 4a and b show that NF meets these objectives. The permeate flow has a significant effect on the rejection rate and thereby on the operating cost of the plant. Optimal rejection for F^- by the NF270 and NF90 membranes is observed at a pressure of 11 bar for a permeate flow of about 150 and 65 L h^{-1} m^{-2}, respectively. Above this pressure, energy consumption will increase while fluoride ion retention remains constant.

In addition, the permeate flow rate is higher with NF270, but F^- rejection is lower. This is due to the larger pore diameter [32] and MWCO of this membrane (Table 1). It has also been observed in Figs. 4a and b that diffusive transfer does not seem to have any influence on the F^- rejection below a permeate flow rate of about 60 L h^{-1} m^{-2} for both membranes. It can be concluded that the transfer mechanism involves the pore diameter and the surface charge of each membrane and that the rejection rate is the result of the coupling of diffusion and convection [33].

3.4. Effect of fluoride concentration on fluoride rejection

It was observed that an increase in the NaF concentration in the solution from 10^{-3} to 10^{-2} M resulted in a decrease in the permeate flux. As can be seen in Figs. 4a and b, this decrease is accompanied by a drop in the rejection rate. Thus, for a concentration of 10^{-3} M, the limiting retention rate of F^- is equal to 96% and 89% for NF90 and NF270, respectively, while for the 10^{-2} M concentration, the retention is significantly lower.

The decrease in ion retention with increasing salt concentration is a known phenomenon in NF. There are several causes for this phenomenon. As previously mentioned, the polarization layer that forms on the surface of the membranes by accumulation of retained solutes is more important when the concentration is high. In addition, the interactions of the electric charges of the ions bound to the interface of the NF membrane creates a layer of dielectric constant that can facilitate the passage of the ions [13].

Moreover, it is interesting to note that the selectivity of NF membranes towards F^- depends on the applied pressure. Thus, at low pressure, NF270 retains F^- slightly better than NF90 (Figs. 4a and b). This phenomenon is especially sensitive to the 10^{-3} M concentration. When the pressure is increased, there is an inversion of selectivity between the two membranes. The low permeate flow rate of NF90 at low pressure increases the extent of diffusion transfer compared with that by convection. This probably explains this observation. At higher pressure, the convective flow becomes sufficiently important to counteract

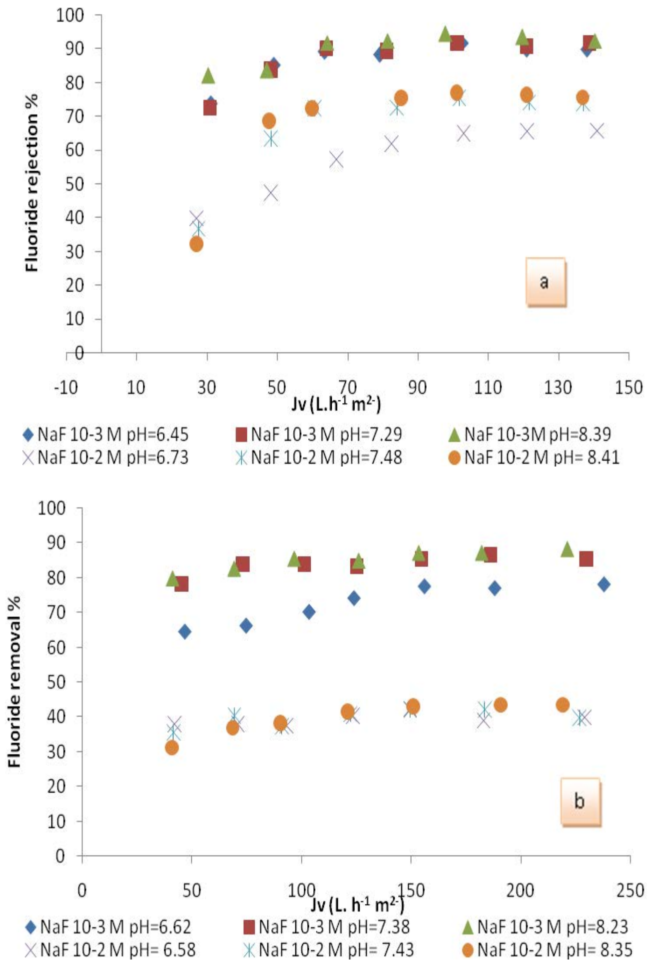

Fig. 4. Variation of fluoride rejection vs. permeate flux for NF90 (a) and NF270 (b).

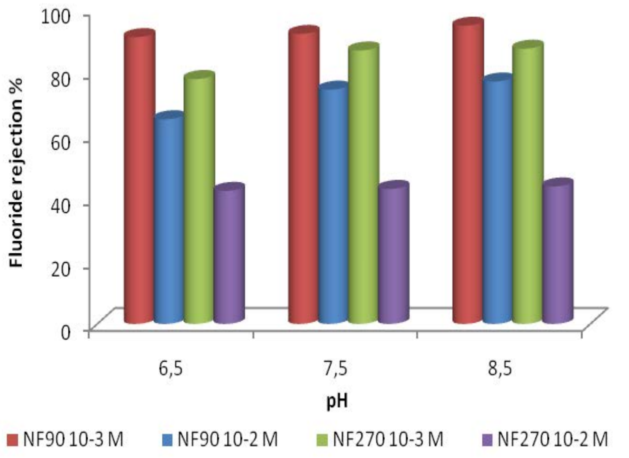

Fig. 5. Evolution of fluoride rejection at different pH and concentration.

this diffusion transfer leading to a clear increase in the rejection of F^-.

3.5. Effect of pH on fluoride rejection

In order to determine the effect of pH, the F^- rejection obtained with the two membranes at an applied pressure of 11 bar for a NaF feed concentration of 10^{-3} and 10^{-2} M is shown in Fig. 5 in the pH range corresponding to that generally observed in natural waters (6.5–8.5). It can be seen that the rejection increases with an increase in pH for both NF90 and NF270 membranes. This effect is especially pronounced in the case of average rejection rates. Thus the rejection rate by NF90 increases from a value of 65% to about 80% between pH 6.5 and 8.5 for the NaF 10^{-2} M concentration. The same trend is observed for the rate of rejection by NF270 for the NaF 10^{-3} M concentration. By contrast, the increase in rejection is modest (about 5%) in case its value is high (NF90 and [NaF] = 10^{-3} M) or low (NF270 and [NaF] = 10^{-2} M).

As pointed out above, the influence of pH on F^- removal is well exemplified in the literature [8,14,33]: the rejection value by NF membranes is lower in acidic media, which is explained by HF/F^- speciation due to a pKa of 3.2. However, in the studied pH range (6.6–8.5), the proportion of HF is negligible. It is, therefore, expected that the pH has a small impact on the release of F^-.

The observed effect must be found elsewhere. Polymer NF membranes can be positively or negatively charged due to the amphoteric nature of their carboxylic and amine surface groups, which can ionize as a function of pH [34,35]. The isoelectric point of the membrane is defined as the pH at which the net charge of the membrane is zero [35]. The isoelectric point of NF90 and NF270 was found to be at about pH 5.8 and pH 3.1, respectively, under the most common analytical conditions (KCl 10^{-3} M), both of which are very close to the median PIE values reported in the literature (Table 3). Thus, the surface charge of NF membranes depends on the pH, which affects anion retention by electrostatic repulsion force (Donnan exclusion) [36].

At a pH value below the isoelectric point, the surface of the membrane is positively charged, resulting from the protonation of the amine groups ($NH_2 \rightarrow NH_3^+$). Above this point, it becomes increasingly negatively charged due to the progressive deprotonation of carboxyl groups ($COOH \rightarrow COO^-$) and levels off at pH about 7 [35]. At a pH higher than the NF90 and NF270 have a negative surface charge and, therefore, repel anions all the more as this surface charge is high. This is consistent with our results, which show that F^- rejection reaches maximum values at pH values above 7 (Fig. 5). Thus, a high fluoride rejection (more than 85%) is obtained for a model solution of NaF 10^{-3} M and a pH close to neutrality (pH = 7–8), which are in fact the usual parameters of most natural groundwaters.

3.6. Kouinine brackish water desalination

Desalination by NF makes it possible to achieve a more or less effective removal of salts from brackish water. The rejection performance of the main divalent and monovalent ions present in Kouinine water (SO_4^{2-}, Ca^{2+}, Mg^{2+}, F^-, Cl^-, Na^+ and NO_3^-) for both membranes is shown in Fig. 6. Experimental data indicate that optimal removal is obtained at medium pressure (11 bar). It should be noted that performance decreases slightly at higher pressure due

Table 3
Reported zeta potential of NF90 and NF270 membranes

Membrane	pH range	Electrolyte solution	IEP	References
NF90	4–8	0.1 mM KCl	5.7	[37]
	2.5–10.5	10 mM KCl	4.8	[38]
	3–9	10 mM NaCl	5.5	[39]
NF270	2–11	5 mM KCl	3.2	[40]
	2.5–10.5	10 mM KCl	2.7	[38]
	3–9	10 mM NaCl	3.1	[39]
	2.5–10	1 mM KCl	2.8	[41]

IEP: isoelectric point.

to the concentration polarization effect related to the combination of high permeate flux and high ion rejection. In fact, the increased concentration in the feed solution and the accumulation of salts at the membrane interface reduce the permeability and thus increase the passage of ions by diffusion [42]. These effects account for the decrease in ion removal performance at high pressures.

NF90 and NF270 can reduce the salinity of brackish water by a more or less complete removal of divalent ions and partial removal of monovalent ions. The treatment leads to the production of softened and partially demineralized water. In the case of Kouinine water, the conductivity of the treated water was less than 400 and 600 µS/cm using NF90 and NF270, respectively, which is in accordance with WHO guidelines and Algerian standards. It can be concluded that the two membranes NF90 and NF270 allow to reach the objective in terms of removal of total dissolved solids (TDS).

The highest rejections were obtained for the NF90 membrane with a removal of more than 88% at an applied pressure of about 11 bar against 68% for NF270 (Fig. 6). This result was expected since NF90 is one of the tight NF membranes that have performances close to RO membranes [21]. In particular, Fig. 6 shows that the most significant difference between the membranes lies in the removal of monovalent ions. The treatment of Kouinine groundwater by NF90 leads to a removal of between 80% and 90% of these ions (except nitrate ions) whereas NF270 only removes 30% to 50%. These findings are in agreement with the results found in the literature [25,26] and have been attributed to the steric exclusion related to the fact that NF90 has a smaller pore size than NF270.

The combination of size exclusion and charge interactions may influence the selectivity of membranes towards ion retention when ions are combined in a complex matrix, depending on the operating conditions and the nature and type of NF membrane [42,43]. This is what we observe in our case. Although the F^- concentration in Kouinine groundwater (0.115×10^{-3} M) is much lower than that of synthetic solutions, it can be seen that their passage through the two membranes NF90 and NF270 is favored. For instance, the rejection rate of F^- in this matrix is 84% compared with the case of the single solution 10^{-3} and 10^{-2} M with respective values of 92% and 75% in the case of the NF90 membrane at the same pH. The same trends can be observed for treatment by NF270. This effect can be explained by the Donnan equilibrium phenomenon and the electroneutrality of the permeate, which must be maintained. Thus, F^- rejection is governed by the rejection of other species. In particular, the high rejection of the divalent ions SO_4^{2-} with values of 95% and 80% for NF90 and NF270, respectively (Fig. 6, Table 4), contributes to the observed decrease in F^- rejection as already observed by other authors in complex matrices [12,22].

Divalent ions are much more retained than monovalent ions because the electrostatic interactions between the membrane and the solutes are more intense. However, the retention values correlate quite well with their hydration energies and hydrated radii. Thus, the most retained anion SO_4^{2-} (Table 4 and Fig. 6) has the highest hydration energy and hydrated radius (1,138 kJ/mol and 0.379 nm) while the Cl^- (376 kJ/mol and 0.332 nm) and NO_3^- (329 kJ/mol and 0.331 nm) anions have the lowest [32,33]. F^- with intermediate values (515 kJ/mol and 0.352 nm) is well retained by NF90 but only moderately retained by NF270. As the surface charge of NF membranes is negative, cations are less retained than anions due to the attractive interactions between the solute and the membrane that facilitate their passage. However, the requirement to ensure the electroneutrality of the retentate and permeate governs their retention. The same trend as for the anions is also observed with respect to hydration energy and hydrated radius: rejection of Mg^{2+} (1,921 kJ/mol and 0.428 nm) > Ca^{2+} (1,584 kJ/mol and 0.412 nm) > Na^+ (407 kJ/mol and 0.358 nm) > K^+ (363 kJ/mol and 0.331 nm) [32,33].

The data in Table 4 show that all parameters meet the water quality requirements (WHO guideline and Algerian standards presented in Table 2) in the case of NF90 and with the exception of Na^+, K^+ and Cl^- for NF270. It can be concluded that NF using NF90 could be an appropriate technology to produce good quality drinking water in the El Oued region in southern Algeria.

3.7. Energy consumption evaluation

In an industrial application, the NF process must operate at high recovery rates (Y) because a higher volume of permeate can then be obtained, which reduces the SEC. For Kouinine brackish water, the impact of increasing the recovery rate on F^- rejection and TDS has been evaluated and the results are shown in Figs. 7a and b. It can be seen

Table 4
Physico-chemical characteristics of the treated water from Kouinine well

Ion	Membrane	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	SO_4^{2-}	F^{-}	Cl^{-}	NO_3^{-}
Content	NF90	30	10.4	96.3	2.5	7	0.35	148.9	16.2
(ppm)	NF270	59.7	20.6	308.6	14.9	88.6	0.62	368	20.8

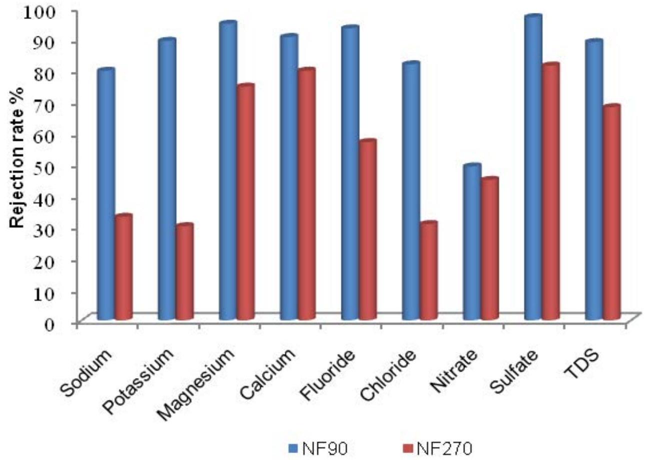

Fig. 6. Average rejection of TDS and common ions in Kouinine feed water by the investigated membranes.

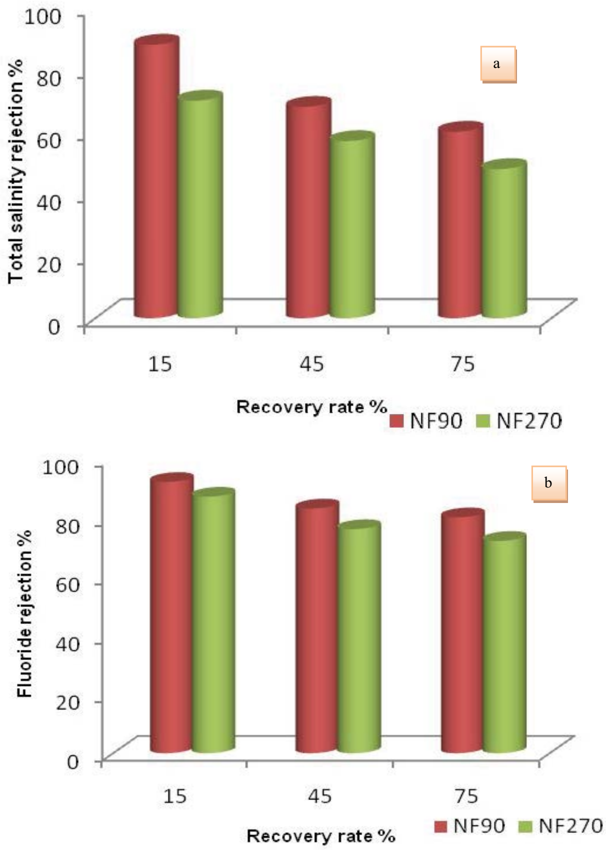

Fig. 7. Total salinity rejection (a) and fluoride rejection (b) during Kouinine water desalination by NF membranes for recovery values of 15%–75%.

that an increase in the recovery rate resulted in a decrease in salt and F^- rejection when working at the same pressure of 11 bar for both membranes. However, although the volume produced with NF270 is much larger than with NF90, the latter membrane gives a better water quality and remains the best candidate for this application.

The SEC for Kouinine water treatment with NF90 is then, respectively, 2.55, 0.85 and 0.51 kWh m^{-3} (calculated using Eq. (5)) for a recovery rate of 15%, 45%, 75% and an applied pressure of 11 bar. On the basis of the WHO guideline and the Algerian standards, the optimal value of recovery for the NF process using NF90 is about 45%.

4. Conclusion

Defluoridation tests were successfully performed by treating a model water solution of single salt NaF and natural groundwater (Kouinine) with the two membranes NF90 and NF270 under different operating conditions on a laboratory scale pilot plant. The study of the different parameters led to the following conclusions:

NF270 and NF90 retain F^- better at a pressure of 11 bar in our working conditions. Above this pressure, the rejection of F^- reaches a plateau. Our data show that F^- rejection slightly increases in alkaline medium (pH = 8.5). Both membranes exhibit high F^- removal: the defluoridation efficiency for single NaF solutions with a concentration value of 10^{-3} M (19 ppm) was approximately 97% and 89% for NF90 and NF270, respectively. It was observed that the rejection decreases at higher concentration levels. NF270 has better purified water productivity than NF90.

The application of both NF90 and NF270 membranes for the production of drinking water from natural groundwater containing 2.2 ppm F^- resulted in treated water containing 0.25 and 0.37 ppm corresponding to a removal rate of 88% and 79%, respectively. At the same time, TDS removal was 88% and 68%, respectively. The data obtained confirmed that more ions are hydrated, the better they are retained. The water produced by treatment with NF90 was of good quality and below the values recommended by the WHO. For NF270, the values of Na^+ and Cl^- exceeded the recommended standard. In conclusion, NF90 proved to be the membrane of choice for the desalination and defluorination of Kouinine groundwater.

The water recovery rate has a strong impact on salt rejection and energy consumption, with the opposite effect. The optimum efficiency of the NF process in terms of SEC and quality of the water produced is obtained for a recovery rate of about 45%.

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