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Influence of operating conditions on the retention of fluoride from water by nanofiltration

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ABSTRACT

As any oligoelement, fluoride is necessary and beneficial for human health to low concentrations, but an excess amount of fluoride ions in drinking water has been known to cause undesirable effects, especially tooth and bones fluorosis. Many methods have been used to remove fluoride from water such as precipitation, adsorption, electrocoagulation and membrane processes. In the present study, removal of fluoride ions from aqueous solution was investigated using a polyamide thin film composite nanofiltration membrane denoted HL from Osmonics. This study deals with the characterisation of the HL membrane used in permeation experiments with aqueous solutions of charged inorganic solutes. The effect of feed pressure, concentration, ionic strength, type of cation associated to fluoride and pH on the retention of fluoride ions were studied. The retention of fluoride anions was in the order of 60%. It relatively depends on feed concentration, ionic strength, pH and applied pressure. Spiegler–Kedem model was applied to experimental results in the aim to determine phenomenological parameters σ and P_s respectively, the reflection coefficient of the membrane and the solute permeability coefficient of ions. The convective and diffusive parts of the mass transfer were quantified with predominance of the diffusive contribution.

Keywords: Defluorination; Nanofiltration; Spiegler–Kedem model; Mass transfer

1. Introduction

Fluoride in drinking water can be either beneficial or detrimental to health depending upon its concentration. The World Health Organization (WHO) accepted the maximum fluoride concentration in drinking water as 1.5 mg/L [1]. In excess of 1.5–2.0 mg.L^{-1} fluoride is known to cause permanent gray or black mottling of teeth enamel and the long-term intake of 3–10 mg.L^{-1} may result in abnormal bone growth in both humans and animals [2]. Invertebrates and fish in fresh water are also very sensitive to fluoride toxicity [3]. Over 0.5 mg.L^{-1} fluoride in fresh water can detrimentally influence the upstream migration of salmon [4]. Fluorine compounds are industrially important and are extensively used in semiconductors, fertilizers, aluminium industries, glass manufacturing and nuclear applications [5,6]. The effluent of those industries thus contains high levels of fluoride.

Various treatment technologies were studied for removing fluoride from water in which the concentration exceeds the permitted levels [7] such as precipitation [8], adsorption onto activated alumina [9], ions exchange [10] and membrane processes like electrodialysis [11], reverse osmosis [12,13] and nanofiltration [14].

Fluoride can be removed by adsorption onto many adsorbent materials. Some of the most frequently en-

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countered sorbents are: activated alumina, clays and soils, spent bleaching earth, spent catalyst, rare earth oxides, bone charcoal and activated carbon. Ion exchange resins are effective in removing F^- from water. Castel et al. [10] studied the removal of F^- by a two way ion exchange cyclic process, using two anion exchange columns. The results show that this process can effectively remove fluoride from water. The use of anion exchange resins for F^- removal is impractical because of their relatively high costs.

Membrane processes such as reverse osmosis, nanofiltration, dialysis and electrodialysis have been recently developed methods for F^- removal from drinking waters [15–17] and brackish waters [11,18–20].

Some applications of reverse osmosis to purification of water are discussed by Arora et al. [21]. Ndiaye et al. [13] observed that the rejection of fluoride ion was typically higher than 98%, considering that the RO membrane was fully regenerated after each set of experiments.

Nanofiltration makes use of the same overall phenomenon as reverse osmosis. For nanofiltration, the membranes have slightly larger pores than those used for reverse osmosis and offer less resistance to passage both of solvent and of solutes. As a consequence, pressures required are much lower, energy requirements are less, removal of solutes is much less exhaustive, and flows are faster. The selectivity of nanofiltration relative to reverse osmosis is a particular advantage, and much experimental and theoretical research is being devoted to obtaining a clearer idea of the mechanism of solute retention to facilitate production and selection of targeted membranes as well as optimisation of conditions [22–25]. Retention of solutes is attributed mainly to steric and charge effects [22] and although fluoride is a very small ion it is more strongly hydrated than other monovalent anions because of its high charge density, and the consequent steric effect leads to fluoride being more strongly retained on nanofiltration membranes than competing monovalent anions such as chloride or nitrate, a particular advantage in defluoridation of brackish waters.

Kettunen and Keskitalo [26] studied the removal of fluoride from groundwater sources in Finland (380–600 m^3/d membrane filtration plant). The fluoride rejection was 76% with NF 255 (Filmtec).

Lhassani et al. [15] studied the selective demineralization of water by nanofiltration especially with respect to its application to the defluoridation of brackish water.

Tahaikt et al. [20] carried out fluoride removal operations on underground water using a nanofiltration pilot plant with two modules. The performances of two commercial spiral membranes were proved.

The aim of the present work is to study the effectiveness of a given nanofiltration membrane for fluoride removal, in view of understanding the underlying mechanisms that may lead to changes in observed retentions. The retention was studied according to operational factors such as feed concentration, nature of the associated cation, ionic strength, feed pressure and pH. The membrane permeability to ultrapure water, the charge of membrane surface, and the molecular weight cut-off were determined. The model of Spiegler–Kedem was applied in order to determine the phenomenological parameters σ and P_s in a respective way, the reflection coefficient of the membrane and the solute permeability coefficient of the membrane to the aqueous solution. The convective and diffusive values of the parameters of the mass transfer were measured.

2. Experimental

The experiments were performed on a pilot plant, which was carried out in our laboratory and equipped with a nanofiltration module in order to investigate fluoride removal. The NF tests were carried out with the use of Osmonics spiral module equipped with HL membrane. As we are interested by the use of HL membrane, we sought to apply it to fluoride removal. This membrane is of type “thin film composite”, which is a composite membrane since it is manufactured with two layers of different polymers. Its active layer is made out of polyamide and has an asymmetrical structure. The membrane has a molecular weight cut-off for the organic compounds of about 150–300 Da. The module HL used for this study is a module of the spiral type. It is approximately 2.5 inch in diameter and 14 inch in length.

The nominal active surface of membrane rolled up in the Osmonics module is of 0.6 m^2. This module is characterised by a flow of production of maximum of 0.83 m^3/d. All experiments were carried out at constant temperature of 25°C. The set-up has been presented in a previous work [27]. Ion analyses were performed by ionic chromatography, coupled to a conductimetric detector.

3. Results and discussion

3.1. Membrane characterisation

3.1.1. Membrane permeability and charge

In order to interpret the performance results, studying the characteristics of the membrane is considered necessary. In the case of dilute solutions the pure water permeability coefficient L_p was estimated using the Darcy’s law given by Eq. (1).

$$J_v = \frac{\Delta P}{\mu \cdot R_m} = L_P \cdot \Delta \mathrm{P} \tag{1}$$

The mean value of pure water permeability coefficient L_p was obtained by statistical linear regression of permeate flux J_v vs. applied pressure ΔP and is found to be 9.015 $L.h^{-1}.m^{-2}.bar^{-1}$.

The charge of the membrane is generally quantified either by the measurement of the potential zeta (ζ) [28],

Table 1
Titration results

Negatively charged groups, eq/m^2	1.9×10^{-6}
Positively charged groups, eq/m^2	5.09×10^{-7}

or by the study of retentions of salts [29], or by the titration method [30]. In this study, we were limited to the two latest techniques.

Salt retention measurements with $CaCl_2$, NaCl and Na_2SO_4 at 10^{-3} mol.L^{-1} as a function of permeate flux gives the following retention sequence: $R_{Na_2SO_4} > R_{CaCl_2} > R_{NaCl}$, which is caused by differences in diffusion coefficients between the different salts.

This order of diffusion coefficients is inversely reflected in the retention sequence [31].

Although the membrane show this retention sequence, the surface charge was not neglected. The presence of the charged groups at the membrane surface was confirmed by titration experiments [29,30]. The results are summarized in Table 1, they show that the membrane carry a surplus of negatively charged groups. Consequently, the charge effect contributes to the retention phenomenon in addition to the diffusion effect.

It is also shown that among the nanofiltration membranes studied by Schaep et al. [32], which are negatively charged according to the manufacturer, the salt retention measurements are inversely proportional to diffusion coefficients of solutes in water.

3.1.2. Separation mechanisms

The transport of the solute through NF membranes can be described by irreversible thermodynamics where the membrane is considered as a black box. Kedem and Katchalsky [33] proposed the relation of the solvent flux J_v and the solute flux J_s through a membrane in the following equations:

$$J_v = L_p(\Delta P - \sigma\Delta\pi) \tag{2}$$

$$J_s = P_s(C_0 - C_p) + (1-\sigma)J_v C_m \tag{3}$$

where ΔP: transmembrane pressure, C_0: concentrations in the bulk side, σ: reflection coefficient, C_m: solute concentration in the membrane, C_p: concentrations in the permeate and $\Delta\pi$: osmotic pressure difference across the membrane.

Integration of Eq. (3) on the membrane thickness yields, in term of the real salt rejection; give the following rejection expression [34]:

$$R = \sigma.\frac{1-F}{1-\sigma F} \tag{4}$$

with

$$F = e^{\left(-\frac{1-\sigma}{P_s}J_v\right)} \tag{5}$$

To quantify both convective and diffusive parts of the solute mass transfer in NF the following approximate expression was used:

$$J_{\text{diff}} + J_v.C_{\text{conv}} = C_p.J_v \tag{6}$$

where J_{diff} is the solute flux due to diffusion [with $J_{\text{diff}} = P_s(C_0 - C_p)$], and C_{conv} is the solute concentration due to convection [with $C_{\text{conv}} = (1-\sigma)C_m$]. Eq. (8) can be expressed as follows:

$$C_p = \frac{J_{\text{diff}}}{J_v} + C_{\text{conv}} \tag{7}$$

As illustrated in Fig. 1, analysis of sodium halide ions concentration (C_p) in the permeate as a function of the reverse permeate flux ($1/J_v$) revealed a linear relation in conformity with Eq. (7).

From the experimental data of rejection and flux, the values of the parameter σ and P_s were calculated starting from the relation of Pusch [35] and:

$$\frac{1}{R} = \frac{1}{\sigma} + \left(\frac{L_D}{L_p} - \sigma^2\right)\frac{L_p.\pi_1}{\sigma.J_v} = A_1 + A_2.\frac{1}{J_v} \tag{8}$$

where L_D represents the osmotic permeability coefficient.

Plotting the experimental values (Fig. 2) of ($1/R$) vs. ($1/J_v$) permits to calculate σ which corresponds to the reverse of original ordinate. The curves obtained are also of linear lines and are checking well Eq. (8).

All the experimental results are reported in Table 2.

The HL membrane implies two different mechanisms of transfer of aqueous solution, both acting separately, but

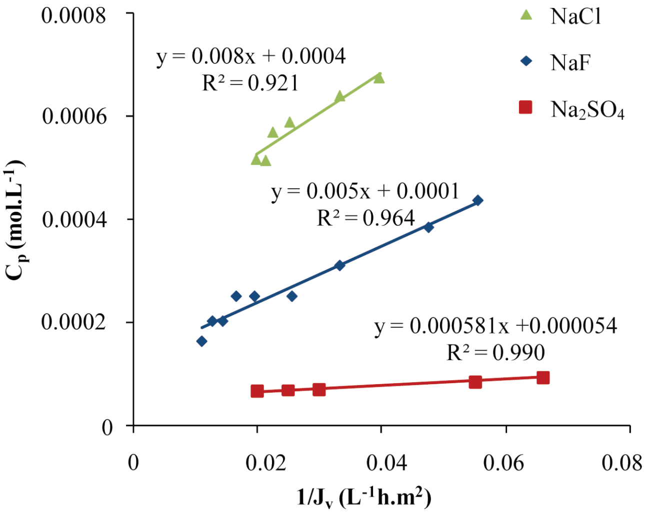

Fig. 1. Variation of the permeate concentration in function of $1/J_v$ for different salts, $C = 10^{-3}$ mol.L^{-1}, pH = 6.5.

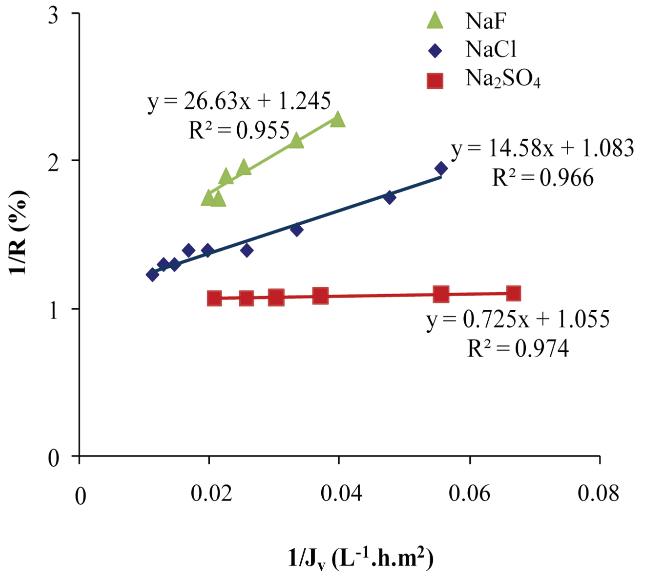

Fig. 2. Variation of $1/R$ in function of $1/J_v$ for different salts, $C = 10^{-3}$ mol L^{-1}, pH = 6.5.

Table 2
Transport coefficients and single salt flux distribution, $C_{\text{feed}} = 10^{-3}$ mol.L^{-1}

Salt (10^3 mol.L^{-1})	σ	P_s	J_{diff} (L.h^{-1}.m^{-2})	C_{conv} (mol.L^{-1})
NaCl	0.803	26.02	0.008	0.0004
NaF	0.923	15.18	0.005	0.0001
Na_2SO_4	0.947	1.29	0.00058	0.000054

Table 3
Hydrations energies [36], hydrated radii [37] and diffusion coefficients [38] of some electrolytes

Ions	Hydrations energies (kJ.mol^{-1})	Hydrated radii (nm)	D (10^9 m^2.s^{-1})
Na^+	454	0.358	1.333
K^+	363	0.331	1.957
Ca^{2+}	1615	0.412	0.718
Cl^-	325	0.332	2.032
F^-	449	0.352	1.48*
SO_4^{2-}	1047	0.379	1.065

* [39] Diffusion coefficient of fluoride ion

in an additive way on the transfer. The slopes obtained confirm that this membrane has high diffusionnal transport compared to the convective one. It was also observed that the value of slope obtained with sulfate salt is lower than for other halide ions form and in reverse to the hydration energy order. So, the more the hydrated ion is small, the more it diffuses through the membrane. P_s values depend on the type of anion associated to sodium. Strongly solvated sulfate anions lead to lower values of P_s in comparison with the less solvated monovalent anions (F^-) and (Cl^-). The σ values obtained are dependent to the hydration energy order; it is higher for sulfate than fluoride and chloride anions (Table 3).

From the C_{conv} values obtained before, it is possible to calculate the molecular weight cut-off (MWCO) of the NF membrane from Eq. (9), as reported recently by Lhassani et al. [40].

$$C_{\text{conv}} = C_0\left[1-\left(\frac{M}{\text{Sc}}\right)^{\frac{1}{3}}\right]^2 \tag{9}$$

where M the molecular weight of a solute, Sc the molecular weight cut off (MWCO) of the membrane and C_0 the initial concentration of the solute in the feed.

The results obtained for the determination of the MWCO is under diluted solution (10^{-3} M) using a divalent salt such as Na_2SO_4 because the definition of the MWCO determination is based on rejections higher than 90%. The value obtained of MWCO is of 314 Da.

3.2. Fluoride retention

3.2.1. Effect of permeate flux and feed concentration on fluoride retention

Fig. 3 shows an increase of the retention rate of fluoride ions with permeate flux, consequently with the applied pressure, for all concentrations in fluoride ions studied until a value about 60 L.h^{-1}.m^{-2}. In this field the mass transfer is due to convection. Beyond this value, a slightly stability of fluoride retention rate was observed, where the mass transfer became diffusive and the retention is not affected any more by the permeate flux, therefore by pressure.

The effect of the concentration on fluoride retention was observed for values included between 10^{-4} mol.L^{-1} to 10^{-2} mol.L^{-1}. The salt concentration increase leads to the rejection increase. This can be explained by the effect of dielectric exclusion which is caused by the interactions of ions with the bound electric charges induced by ions at the interfaces between media of different dielectric constants, in particular, a membrane matrix and a solvent [41,42]. It has been shown that the dielectric exclusion is equivalent to a decrease of the electrolytes concentration in solution which is known to provoke an increase of electrostatic exclusion, and that its effect is stronger in the presence of multivalent ions. For the different initial fluoride content of the feed water $[F^-]_0$, the fluoride was partially rejected. The standard is obtained for low concentration 10^{-4} mol.L^{-1}, but the fluoride leakage increases

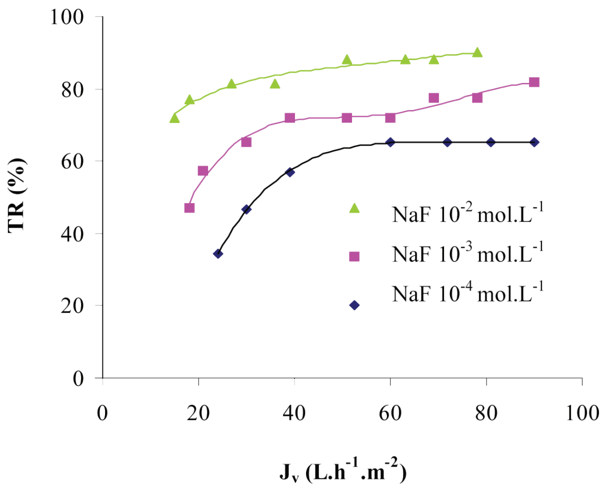

Fig. 3. Variation of retention rate of fluoride anions vs. permeate flux, pH = 6.5.

Table 4
Fluoride rejection values from literature

$[F^-]_0$ (mg/L)	$[F^-]_p$ (mg/L)	R (%)	References
230	0.7	99.69	[43]
190	1.9	99	[44]
380	19	95	[45]
13.5	0.7	95	[15]
380	19	95	[18]
22.32	3.78	83	[19]
2.32	0.4	82.75	[19]

with its initial concentration in the feed water as illustrated in Table 4, with $[F^-]_p$ is the permeate concentration of fluoride.

It can be observed that fluoride removal in some cases can attain the required limits, but for others, the standards are not obtained, so additional treatment is necessary to bring back the contents of fluorides to the standards.

3.2.2. *Effect of ionic strength*

In order to investigate the ionic strength influence on the retention of fluoride ions, the retention rates of fluoride ions were performed for several NaCl concentrations between 0 and 2.10^{-2} mol.L^{-1} as a function of permeate flux. Fig. 4 shows that the retention rate decreased with the increase of NaCl concentration from 60% to 18%.

This can be explained by the screening phenomenon where sodium ions neutralize partially the negative charges of the membrane when the NaCl concentration increases, which involves the decrease of the retention of charged ions, consequently, facilitates the passage of the fluoride ions [44].

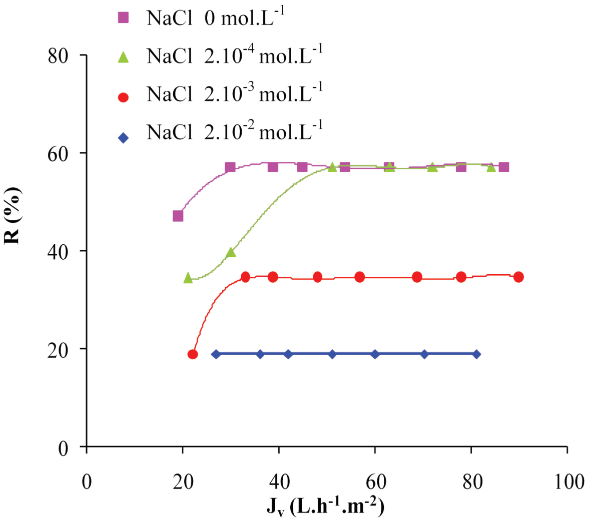

Fig. 4. Effect of the ionic strength on the retention of fluoride ions, θ = 25°C, pH = 6.5.

3.2.3. *Effect of the type of associated cation to fluoride*

Fig. 6 shows that the retention rate of fluoride for the three cations Ca^{2+}, Na^+ and K^+ follows this retention sequence:

$$R_{CaF_2} > R_{NaF} > R_{KF}$$

Consequently

$$R_{Ca^{2+}} > R_{Na^+} > R_{K^+}$$

This retention sequence is inversely proportional to the diffusion coefficients of associated cation to fluoride as shown in Table 3. We note also that the difference in retention between the fluoride ions associated with calcium, sodium and potassium could be related to the difference in hydration energies indicating the existence of the steric effect on the retention.

The transfer parameters σ and P_s, C_{conv} and J_{diff} for the three salts were investigated (Figs. 5 and 6). As illustrated in Table 5, the different results show that the convective contribution was the higher for monovalent cations and lower for the calcium [46]. The P_s value depends on the nature of associated cations to fluoride, it is the lower for more solvated cation (Ca^{2+}) in comparison with the less solvated Na^+ and K^+. The reflection coefficient σ is higher for calcium than monovalent cations, as we can note proportionality with hydration energies.

3.2.4. *Effect of pH*

In order to investigate the pH effect and to estimate the membrane isoelectric point, the pH was set by add-

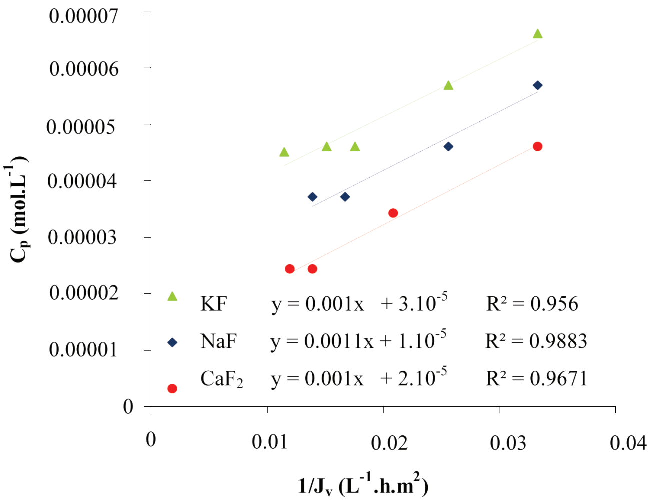

Fig. 5. Variation of the permeate concentration as a function of $1/J_v$ for different salts, $C = 10^{-4}$ mol.L^{-1}, θ = 25°C, pH = 6.5.

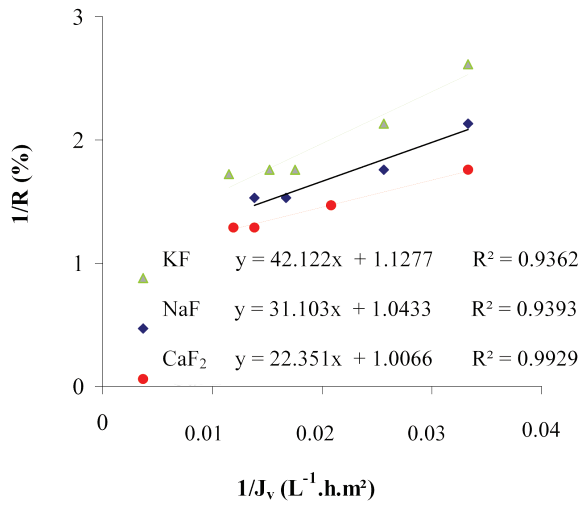

Fig. 6. Variation of $1/R$ in function of $1/J_v$ for different salts, $C = 10^{-4}$ mol L^{-1}, θ = 25°C, pH = 6.5.

Table 5
Transport parameters (σ and P_s), diffusive flux J_{diff} and C_{conv} of fluoride salts at $C_o = 10^{-4}$ mol.L^{-1}, θ = 25°C and pH = 6

Salts	σ	P_s	J_{diff} (L. h^{-1}.m^{-2})	C_{conv} (mol.L^{-1})
CaF_2	0.99	22.26	0.001	1×10^{-5}
NaF	0.95	35.72	0.001	2×10^{-5}
KF	0.88	40.73	0.001	3×10^{-5}

ing HCl or NaOH to the solution and was varied in the range from 4 to 11.

The variation of retention rate as a function of permeates flux at various pH values for the membrane is plotted in Fig. 8. These results show that the removal of fluoride ions depends on the pH. Indeed, for acidic pH, the retention rate does not exceed 60%. On the other hand, for basic pH, the retention rate varies between 77.3% and 93.6%. In general, fluoride is primarily present as F^- above pH 3 and there are no major species changes between pH 3 and 11 (Fig. 7, [47]. Since this is practically the range that was studied experimentally (4–11), it is expected that there is no apparent pH dependence of retention observed experimentally, but membrane type, due to its characteristics was observed to impact fluoride retention

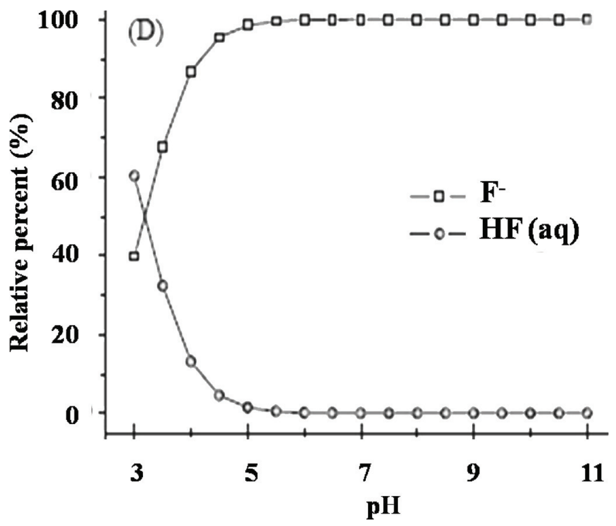

Fig. 7. The variation of retention rate as a function of permeates flux at various pH values, [F$^-$] = 2×10^{-4} mol.L^{-1}, θ = 25°C.

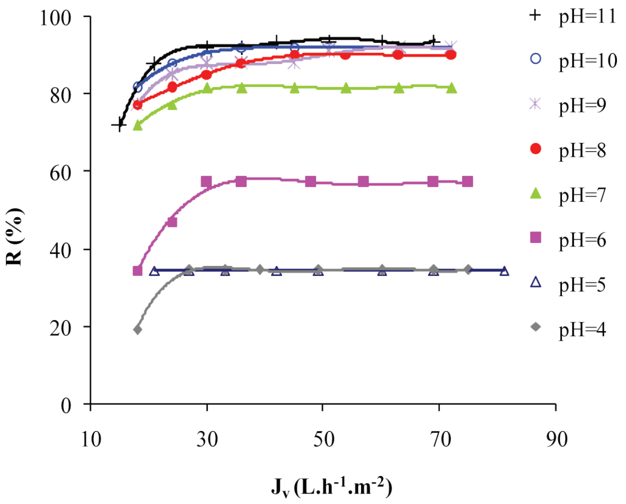

Fig. 8. The variation of retention rate as a function of permeates flux at various pH values, $C = 2\times10^{-4}$ mol.L^{-1}, θ = 25°C.

[47]. In fact, pH affects the membrane surface which in turn, affects fluoride retention.

The retention rate of fluoride ions at various pH values for a fixed J_v of 40 L.h^{-1}.m^{-2} shows that the HL membrane is slightly positively charged at low pH values and become increasingly negatively charged at higher pH values.

As it is found by many authors, this result is expected due to the presence of carboxyl and amine functional groups in HL membranes, the surface charge of the membrane could affect the flux at both high and low pH, particularly around the isoelectric pH which is near 5. The positive charge below the isoelectric point is attributed to the protonation of amine functional groups ($NH_2 \rightarrow NH_3^+$). Beyond this value, the membrane acquires a more negative charge from the deprotonation of carboxyl functional groups ($COOH \rightarrow COO^-$).The isoelectric point value was found by other researchers [48]. In both cases, the electrostatic repulsion between the charged groups could have an effect on the surface charge of the membrane and thereby causes a decrease in flux [49,50].

Rejection obtained for pH = 7 and pH = 8, (pH of natural waters), are respectively about 81% and 90% which correspond to a permeate concentration of respectively 0.7 mg/L and 0.37 mg/L. For higher concentration and in this range of pH, standards could not be attained. Tahaikt et al. [19] tested many configurations: simple pass, double pass with one type of membranes and combination of two types of membranes and supplied batch configuration. The water parameters were followed as a function of the running conditions (time, pressure, fluoride content, etc.) in order to follow the behaviour of the membranes tested and to improve the rejection.

4. Conclusion

The pure water permeability of the HL membrane checks well Darcy's law and was L_p = 9 L.h^{-1}.m^{-2}.bar^{-1}. The retention order for the salts tested was:

$$R_{Na_2SO_4} > R_{CaCl_2} > R_{NaCl}$$

showing a retention sequence inversely proportional to the diffusion coefficients between the different salts. The titration method has confirmed the presence of charged groups on the membrane surface. It presents also an MWCO of 314 Da. The application of the phenomenological model of Spiegler and Kedem shows that these results confirm well that the HL membrane involves two different mechanisms of transfer (diffusion and convection), both acting independently but in an additive way to the transfer. The study of fluoride ions removal by the HL membrane was performed and the results obtained show that retention may exceed 60% for fluxes exceeding 60 L.h^{-1}.m^{-2}. The increase in flow rate results in higher flux and higher rejection, thus better permeate quality. Increasing feed concentration causes an increase in retention rate, which is due to the dielectric exclusion between the feed solution and the matrix of the membrane. These retention rates are sensitive to increased ionic strength which causes a progressive neutralization of the negative charge of the membrane. Retention of fluoride ions depends also on the feed pH and differs from both sides of an isoelectric point which is close to 5. Thus, for acidic pH the retention rate does not exceed 60%, while it may exceed 80% in alkaline solutions.

References

[1] World Health Organization, Fluoride in Drinking Water, WHO Guidelines for Drinking Water Quality, 2004, accessed on 3 April 2005.

[2] Kirk Othmer Encyclopedia of Chemical Technology, 3rd ed., vol. 10. Wiley-Interscience, New York, 1980.

[3] J.A. Camargo, Fluoride toxicity to aquatic organisms: A review, Chemosphere, 50 (2003) 251–264.

[4] D.M. Damkaer and D.B. Dey, Evidence for fluoride effects on salmon passage at John Day dam, Columbia River, 1982–1986, North Amer. J. Fisheries Manage., 9 (1989) 154–162.

[5] C.J. Huang and J.C. Liu, Precipitate flotation of fluoride-containing wastewater from a semiconductor manufacturer, Wat. Res., 33 (1999) 3403–3412.

[6] T.C. Chuang, C.J. Huang and J.C. Liu, Treatment of semiconductor wastewater by dissolved air flotation, J. Environ. Eng., 128 (2002) 974–980.

[7] P. Mazounie and P. Mouchet, Available processes for fluoride removal from drinking waters, Rev. franç. Sci. l'eau, 3(1) (1984) 29–51.

[8] G. Singh, B. Kumar, P.K. Sen and J. Majumdar, Removal of fluoride from spent pot linear leachate using ion exchange, Wat. Environ. Res., 71(1) (1999) 36–42.

[9] K.R. Bulusu and W.G. Nawlakhe, Defluoridation of water with activated alumina continuous contacfing system, Indian J. Environ. Health, 32(3) (1990) 197–218.

[10] C. Castel, M. Schweizer, M.O. Simonnot and M. Sardin, Selective removal of fluoride ions by a two-way ion-exchange cyclic process, Chem. Eng. Sci., 55 (2000) 3341–3352.

[11] Z. Amor, B. Bariou, N. Mameri, M. Toky, S. Nicolas and A. Elmidaoui, Fluoride removal from brackish water by electrodialysis, Desalination, 133 (2001) 215–223.

[12] S. Bouguecha and M. Dhahbi, The role of membrane technologies in supplying drinking and industrial water in Tunisia: conventional process and new trends, Desalination, 151 (2002) 75–86.

[13] P.I. Ndiaye, P. Moulln, L. Dominguez, J.C. Millet and F. Charbit, Removal of fluoride from electronic industrial effluent by RO membrane separation, Desalination, 173 (2005)25–32.

[14] K. Hu and J.M. Dickson, Nanofiltration membrane performance on fluoride removal from water, J. Membr. Sci., 279 (2006) 529–538.

[15] A. Lhassani, M. Rumeau, D. Benjelloun and M. Pontié, Selective demineralization of water by nanofiltraton application to the defluorination of brackish water, Wat. Res., 35 (2001) 3260–3264.

[16] H. Garmes, F. Persin, J. Sadeaur, G. Pourcelly and M. Mountadar, Defluoridation of groundwater by a hybrid process combining adsorption and Donnan dialysis, Desalination, 145 (2002) 287–291.

[17] M. Hichour, F. Persin, J. Sandeaux and C. Gavach, Fluoride removal from waters by Donnan dialysis, Separ. Purif. Technol., 18 (2000) 1–11.

[18] C.K. Diawara, M. Sidy Lô, M. Rumeau, M. Pontié and O. Sarr, A phenomenological mass transfer approach in nanofiltration of halide ions for a selective defluorination of brackish drinking water, J. Membr. Sci., 219 (2003) 103–112.

[19] M. Tahaikt, A. Ait Haddou, R. El Habbani, Z. Amor, F. Elhannouni, M. Taky, M. Kharif, A. Boughriba, M. Hafsi and A. Elmidaoui, Comparison of the performances of three commercial membranes in fluoride removal by nanofiltration continuous operations, Desalination, 225 (2008) 209–219.

[20] M. Tahaikt, R. El Habbani, A. Ait Haddou, I. Achary, Z. Amor, M. Taky, A. Alami, A. Boughriba, M. Hafsi and A. Elmidaoui, Fluoride removal from groundwater by nanofiltration, Desalination, 212 (2007) 46–53.

[21] M. Arora, R.C. Maheshwari, S.K. Jain and A. Gupta, Use of membrane technology for potable water production, Desalination, 170 (2004) 105–112.

[22] C.K. Diawara, Nanofiltration process efficiency in water desalination, Separ. Purif. Rev., 37 (2008) 303–325.

[23] E. Drioli, F. Lagana, A. Criscuoli and G. Barbieri, Integrated membrane operations in desalination processes, Desalination, 122 (1999) 141–145.

[24] A. Szymczyk and P. Fievet, Investigating transport properties of nanofiltration membranes by means of a steric, electric and dielectric exclusion model, J. Membr. Sci., 252 (2005) 77–88.

[25] X. Lefebvre, J. Palmeri and P. David, Nanofiltration theory: an analytical approach for single salts, J. Phys. Chem., B108 (2004) 16811–16824.

[26] R. Kettunen and P. Keskitalo, Combination of membrane technology and limestone filtration to control drinking water quality, Desalination, 131 (2000) 271–283.

[27] A. Mnif, S. Bouguecha, B. Hamrouni and M. Dhahbi, Coupling of membrane processes for brackish water, Desalination, 203 (2007) 331–336.

[28] A.I. Schäfer, A. Pihlajamäki, A.G. Fane, T.D. Waite and M. Nyström, Natural organic matter removal by nanofiltration: effects of solution chemistry on retention of low molar mass acids versus bulk organic matter, J. Membr. Sci., 242 (2004) 73–85.

[29] J.M.M. Peeters, J.P. Boom, M.H.V. Mulder and H. Strathmann, Retention measurements of nanofiltration membranes with electrolyte solutions, J. Membr. Sci., 145 (1998) 199–209.

[30] J. Schaep and C. Vandecasteele, Evaluating the charge of nanofiltration membranes, J. Membr. Sci., 188 (2001) 129–136.

[31] J. Schaep, C. Vandecasteele, A.W. Mohammad and W.R. Bowen, Modelling the retention of ionic components for different nanofiltration membranes, Separ. Purif. Technol., 22–23 (2001) 169–179.

[32] J. Schaep, B. Van der Bruggen, C. Vandecasteele and D. Wilms, Influence of ion size and charge in nanofiltration, Separ. Purif. Technol., 14 (1998) 155–162.

[33] O. Kedem and A. Katchalsky, Permeability of composite membranes, Part I: Electric current, volume flow and flow of solute through membranes, Trans. Faraday Soc., 59 (1963) 1918–1930.

[34] S. Jain and S.K. Gupta, Analysis of modified surface force pore flow model with concentration polarization and comparison with Spiegler–Kedem model in reverse osmosis systems, J. Membr. Sci., 232 (2004) 45–62.

[35] W. Push, Determination of transport parameters of synthetic membranes by hyperfiltration experiments, part I: derivation of transport relationship from linear relations of thermodynamics of irreversible process, J. Chem. Phys., 81(3) (1977) 269–276.

[36] R. Audinos, Membranes semi-perméables, Membranes d'osmose inverse, Techniques l'ingénieur, K 362 (2000) 2.

[37] E.R. Nightingale, Phenomenological theory of ion salvation. Effective radii of hydrated ions, J. Phys. Chem., 63 (1959) 1381–1387.

[38] D.X. Wang, M. Su, Z.Y. Yu, X.L. Wang, M. Ando and T. Shintani, Separation performance of a nanofiltration membrane influenced by species and concentration of ions, Desalination, 175 (2005) 219–225.

[39] J.E. Enderby, Ion solvation via neutron-scattering, Chem. Soc. Rev., 24(3) (1995) 159–168.

[40] A. Lhassani, M. Rumeau and D. Benjelloun, Solute transfer through membranes and selectivity in nanofiltration, Tribune de l'eau, 603–605/1–3 (2000) 100–107.

[41] A.E. Yaroshchuk, Dielectric exclusion of ions from membranes, Adv. Colloid Interf. Sci., 85 (2000) 193–230.

[42] A. Szymczyk and P. Fievet, Ion transport through nanofiltration membranes: the steric, electric and dielectric exclusion model, Desalination, 200 (2006) 122–124.

[43] M. Pontié, J.-C. Schrotter, A. Lhassani and C.K. Diawara, Traitement des eaux destinées à la consommation humaine. Élimination domestique et industrielle du fluor en excès, L'actualité chimique, Oct.–Nov. (2006) 301–302.

[44] A. Mnif, M. Ben Sik Ali and B. Hamrouni, Effect of some physical and chemical parameters on fluoride removal by nanofiltration, Ionics, 15 (2009).

[45] A. Abouzaid, A. Mouzdahir and M.L. Rumeau, Étude de la rétention des sels monovalents et bivalents par nanofiltration, Comptes Rendus Chimie, 6 (2003) 431–436.

[46] G.T. Ballet, L. Gzara, A. Hafiane and M. Dhahbi, Transport coefficients and cadmium salt rejection in nanofiltration membrane, Desalination, 167 (2004) 369–376.

[47] L.A. Richards, B.S. Richards, H.M.A. Rossiter and A.I. Schäfer, Impact of speciation on fluoride, arsenic and magnesium retention by nanofiltration/reverse osmosis in remote Australian communities, Desalination, 248 (2009) 177–183.

[48] V. Freger, T.C. Amot and J.A. Howell, Separation of concentrated organic/inorganic salt mixtures by nanofiltration, J. Membr. Sci., 178 (2000) 185–193.

[49] M.J. Hurndall, E.P. Jacobs and R.D. Sanderson, The performance of novel reverse osmosis membranes made from poly-2-vinylimidazoline, Desalination, 86 (1992) 135–154.

[50] A. Al-Amoudi, P. Williams, A.S. Al-Hobaib and R.W. Lovitt, Cleaning results of new and fouled nanofiltration membrane characterized by contact angle, updated DSPM, flux and salts rejection, Appl. Surf. Sci., 254 (2008) 3983–3992.