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Influence of Chloride, Nitrate, and Sulphate on the Removal of Fluoride Ions by Using Nanofiltration Membranes

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Abstract: This study investigates the removal of fluoride from various solutions(NaF, NaCl, $NaNO_3$, and Na_2SO_4) by using three commercial nanofiltration membranes denoted NF70(Filmtec), DESAL5 DL(Osmonics), and MT08(PCI) under 8 bars, 293 K in batch recirculation mode. The membranes were tested for their rejection potential of fluorides in the presence of chlorides, nitrates and sulphates. To identify the mechanisms of selectivity, we successively analyzed the rejections in turn of different combinations of NaF, NaCl, $NaNO_3$, and Na_2SO_4 in order to simulate the behavior of a real brackish water from Senegal. Fluorides rejection efficiency ranges from 78% to 95%. The efficiency of nanofiltration membranes improved is closely linked to the nature of the solution. The high rejection level(above 98%) of the divalent sulphate ions(50 or 200 mg/L) induces a Donnan effect establishment.

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In brackish water conditions, for all the membranes, there was a noticeable influence of anion size and hydration energy on fluoride rejection.

Keywords: Fluoride, nanofiltration, anions effects, brackish water

INTRODUCTION

The presence of fluorides drinking water may be beneficial or harmful to human health depending on their concentration level (1). In the physiological system, fluoride ions represent a trace element required by humans. Certain countries have practiced for many years a supplement of fluoride for children and even for expectant mothers. In low concentrations, fluoride is useful in the fight against tooth decay by strengthening the tooth enamel. At high concentrations, it weakens bones and causes articulate osteoarthritis (2). The recommendation of the World Health Organization (WHO) for drinking water is 1.5 mg/L, while the "Institut Senegalais de Normalisation" gives a concentration limit of 2 mg/L. Regular consumption of water by a child less than six years of age with a concentration between 2–4 mg/L results in dental fluorosis, which is seen as a coloration of the teeth. If the concentration of fluoride is above 4 mg/L, with at least two years of exposure, there is an increase in the number of diseases such as osseous fluorosis, as reported in Senegal. It has been established since July 2000 by Physicians from the University Cheikh Anta DIOP of Dakar, that dental fluorosis is an indication of fluoride concentration level and exposure duration. On the other hand, no correlation has yet been found between fluoride concentration level and the severity of cases of osseous fluorosis.

In reality, the excess of fluoride in drinking water is not the only salt which exists in the medium and the other salts present in the water will have an impact on the rejection of fluoride. This paper covers the rejection of fluoride ions at very high concentration level in brackish drinking water conditions by nanofiltration methods with different kinds of membranes. For this study, demineralized water was used, with a conductivity of less than 1 μS/cm, to which different anions in different concentrations were added.

MATERIALS AND METHODS

The experiments were operated in batch recirculation mode, i.e. both permeate and concentrate were pumped back into the vessel. Three nanofiltration membranes; NF70(Filmtec), DESAL5 DL(Osmonics) and MT08(PCI) with characteristic shown in Table 2, were each tested in the pilots. All the membranes are composite spiral wounds of a standard size(2540). The experiments were all performed using sodium salts(NaF, NaCl, $NaNO_3$, Na_2SO_4)

dissolved in demineralized water(less than 1 μS/cm). Fluoride concentration was fixed at 5 mg/L; chloride concentration at 450 mg/L and nitrates concentration at 50 mg/L. The influence of sulphates was observed at two concentrations: 50 and 200 mg/L. These values were chosen to model concentrations previously found in brackish water, in natural Senegal waters (3) (Table 1). The pH for all solutions was between 6 and 8. All these experiments were performed at 293 K, with a recirculation flux of 600 $L \cdot h^{-1}$ and a pressure of 8 bars. Each analyzed sample of the permeate in this study was collected after one hour of filtration and the permeate volumetric flux is comparable to the pure water flux for all experiments and membranes. Moreover, in these conditions, preliminary results do not highlight a better rejection rate at higher cross-flow. So, it can be considered that there is no significant effect of concentration polarization. The observed rejection rate(R) is derived from the following relationship:

$$\cdot R(\%) = \left(1 - \frac{Cp}{C_0}\right) \times 100$$

where C_p and C_0 are respectively the concentration in the permeate water and the feed solution.

Anion concentration was measured by Ionic Chromatography(using a DIONEX DX-120) and solutions were prepared with UltraPure milli-Q water(UP).

RESULTS AND DISCUSSIONS

The filtration of a solution containing the fluoride salt NaF alone by the three types of membranes produces a high level of rejection (Table 3). The level is above 80% for solutions containing NaF alone, and highlights the good rejection of fluoride ions when not in the presence of other ions. Regarding the membranes DESAL5 DL and MT08, the fluoride rejection rate (respectively 83% and 90%) is higher than that of chlorides which are 69% and 85%.

Table 1. Example of certains anions composition in Senegalese drinking water

cities	pH	Fluoride ($mg \cdot L^{-1}$)	Chloride ($mg \cdot L^{-1}$)	Sulphate ($mg \cdot L^{-1}$)	Nitrate ($mg \cdot L^{-1}$)
Diourbel	7.7	2.7	494.0	86.0	154.0
Fatick	8.2	3.6	672.0	53.0	1.2
Gossas	8.7	2.5	444.0	60.0	<0.4
Thiadiaye	8.3	4.5	291.0	122.0	<0.4
WHO standard	6.5–8.5	1.5	250	400	50

Table 2. Characteristics of the nanofiltration membranes studied

Membrane	Cut off (dalton)	Surface (m^2)	Water flux at 8 bars ($L \cdot h^{-1} \cdot m^{-2}$)	Membrane material	Membrane purchased from
NF 70	200	2.2	71	Polyamide	FILMTEC (D)
DESAL5 DL	150-300	1.8	50.5	Polyamide	OSMONICS (USA)
MT 08	200	1.6	8	Polyamide + PES	PCI (UK)

Both fluoride and chloride give results below that of sulphate which also has a high retention level, as already seen in nanofiltration of divalent solutions (4, 5) (Table 3). This is due to the double negative charge and the size of the ion. The hydration energy of the sulphate ion(561 kJ·mol^{-1}) is stronger than that of fluoride(515 kJ·mol^{-1}) and chloride(381 kJ·mol^{-1}). This difference in rejection can be attributed to the strong hydration energy, steric hindrance, and the strong associated electrostatic repulsion. Indeed, the more hydrated the ion is, the more difficult its transfer across the membrane will be (6). This explanation is not sufficient to explain the comparable values observed between fluoride and chloride in the case of the NF70 membrane. Electrolyte rejection of membranes in the current investigation allows us to think that the charge of the membrane pore may have an additional significant effect on membrane rejection (7). Because the zeta potential measurements were not conducted in the current investigation, this could not be verified. However, pore streaming potential measurements would be expected to be as important as hydration energy is for salt

Table 3. Observed rejection rate(%) at 8 bars and pH = 6 of fluoride, chloride, nitrate respectively in single salt and a global mixture seems as brackish water conditions.

Membrane	Fluoride ($5\,mg \cdot L^{-1}$)		Chloride ($450\,mg \cdot L^{-1}$)		Nitrate ($50\,mg \cdot L^{-1}$)		Sulphate ($200\,mg \cdot L^{-1}$)
	Single[a] (%)	Mixture[b] (%)	Single (%)	Mixture (%)	Single (%)	Mixture (%)	Single (%)
NF 70	91	92	92	97	90	85	98
DESAL5 DL	83	67	69	67	59	33	99
MT 08	90	92	85	88	63	70	99

[a]Observed rejections of each anion in single solution.

[b]Observed rejections of each anions in the mixture solution with fluoride, chloride, and nitrate.

rejection. By replacing NaF with NaCl and then Na_2SO_4, we find the same order of performance regardless of the salt used:

NF70 > MT08 > DESAL5 DL

The positive ion Na^+ is characterized by its small diameter(0.095 nm) and weak hydration energy(407 kJ·mol^{-1}); that reason justifies the possibilty for Na^+ to pass through the pores of the membranes, which have a diameter of the order of a nanometer; but this possibilty is not completely satisfied by the fact that Na^+ is partially retained by the membrane surface forces, as described by Pontalier and al. (8). These forces include not only the frictional forces of the pore but also electrostatic forces, where membrane may present a mostly negative charge density according to the nature of the membrane material. Indeed, this is the case in particular of membranes which have an active layer consisting of aromatic polyamide such as NF70 and DESAL5. The latter material, partially hydrolyzed, brings about carboxylic and amine groups which can ionize as a function of pH.

The influence of the chloride and sulphate anions on the level of rejection of fluoride was measured in stages. Figure 1 shows the level of rejection of F^- and Cl^- in a fluoride-chloride solution with regard to the different membranes. The bar chart shows that there is a lower fluoride rejection level for the DESAL5 DL than for the other two membranes and the same is found for

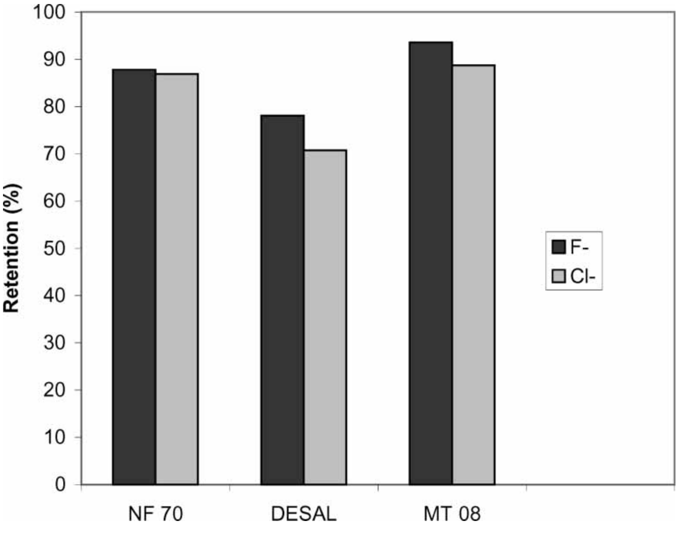

Figure 1. Fluorides (5 mg · L^{-1}) and Chlorides (450 mg · L^{-1}) rejection(%) in a combination of NaF-NaCl solution with fixed pressure at 8 bars as a function of the membrane.

chloride ions. The presence of chloride ions slightly lowers the rejection level of fluoride ions in the case of NF70(90% to 88%) and DESAL5 DL(83% to 78%).

The rejection level of fluoride ions is also significant in other binary mixtures (Fig. 2). The increase in concentration in sulphate from 50 to 200 mg/L also had the effect of reducing the concentration of retained fluoride ions in the case of NF70 and DESAL5 DL. The reduction in fluoride ions rejection is due to the increase in the ionic strength which reduces hydration energy and then increases the partition cœfficient responsible for membrane selectivity. This is further described in literature (9, 10), it is characteristic of heavily loaded membranes and is usually known as a shielding phenomenon. The increase in concentration of sodium sulphate forms a zone of positive ions acting as a screen, thereby neutralizing the negative charge of the membrane. The force of repulsion is reduced between the negatively charged membrane and the co-ions(F^-, SO_4^{2-}). At lower concentrations, the screen effect is less significant than the repulsion of the anions and therefore produces a higher rejection level. When the concentration of sulphate ions is important, the screen effect is increased and the potential of the membrane reduced. The fluoride ion is less affected than the sulphate one, having weaker hydration energy; however, the rejection is lower at higher concentrations. Indeed, the increase of cation(Na^+) concentration involves the increasing formation of a screen which gradually neutralises the negative sites of the membrane. The repulsive forces between the membrane and the anions of the solution are, therefore, decreased. This leads to an easier transfer of fluoride ions for the membranes NF70 and

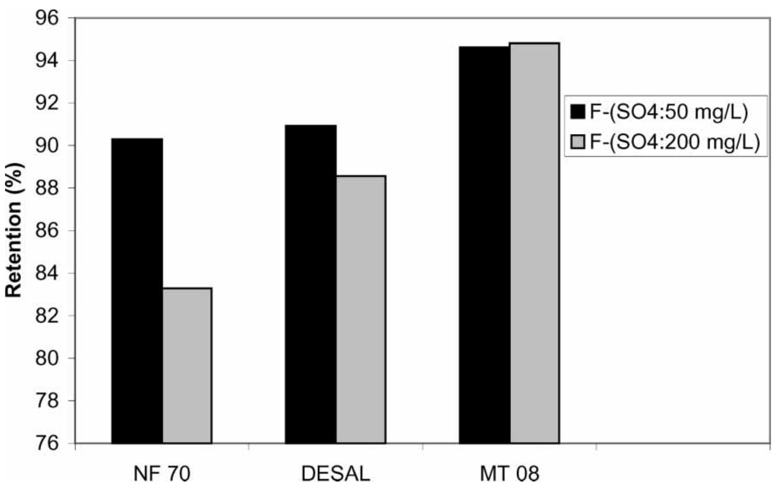

Figure 2. Sulphate(50 and 200 mg $\cdot$ L^{-1}) effect on fluoride rejection with fixed pressure at 8 bars as a function of the membrane.

DESAL5 DL, when the amount of soduim salt rises in solution(from 50 to 200 mg/L of sodium sulphate). This decrease of fluoride ions rejection when the sodium sulphate concentration rises from $50\,mg \cdot L^{-1}$ to $200\,mg \cdot L^{-1}$, is not observed with MT08 membrane, contrary to the NF70 and DESAL5 DL. The MT08 looks less negatively charged, so much so that the screening effect which reduces electrostatic repulsion due to membrane negative charge could not favour more fluoride passage beyong $50\,mg \cdot L^{-1}$ of sodium sulphate.

Table 4 shows the difference in filtration of fluoride in simulated soft water compared to simulated brackish water, with different membranes in nanofiltration taking the presence of divalent ions such as sulphate into account. In a solution containing fluoride($5\,mg \cdot L^{-1}$), chloride($450\,mg \cdot L^{-1}$) and sulphate($50\,mg \cdot L^{-1}$), the rejection of fluoride was the same for the fluoride solution alone. This observed value for each membrane slightly increases when the concentration of sulphate is prepared at $200\,mg \cdot L^{-1}$ instead of $50\,mg \cdot L^{-1}$; 91% to 94% for NF70, 83% to 87% for DESAL5 DL and 90% to 91% for MT08. The absence of chloride in a solution only containing fluoride and sulphate shows that fluoride recjection no longer increases when sulphate is increased up to $200\,mg \cdot L^{-1}$ as seen in Table 4. The slight reduction in fluoride ions rejection, as seen when the concentration in sodium sulphate increases in the absence of chlorides, can only be explained by the screening effect and the Donnan exclusion phenomena (11). The sulphate ions were almost totally rejected by the membrane (Table 3) and the passage of fluoride is increased to balance the electrical charge on each side of the membrane (12, 13). In the case of brackish water, there is competition between fluoride and chloride ions to establish the Donnan equilibrium. Also, by the convection principle and the solution-diffusion effect, chloride ions pass in preference to fluoride ones as previously seen in Fig. 1.

The rejection levels of the different ions(F^-, Cl^-, NO_3^-) from one mixture solution can be seen in Table 3 where a monovalent anion such as nitrate has replaced sulphate. It was found that nitrate ions pass through the membrane

Table 4. Fluorides observed rejection(%) as a function of medium ionic composition

Membrane	NF70	DESAL5 DL	MT08
Fluorides alone	91	83	90
Fluorides + chlorides	88	78	93
Fluorides + chlorides + 50 $mg \cdot L^{-1}$ sulphates	91	83	90
Fluorides + chlorides + 200 $mg \cdot L^{-1}$ sulphates	94	87	91
Fluorides + 50 $mg \cdot L^{-1}$ sulphates	91	91	95
Fluorides + 200 $mg \cdot L^{-1}$ sulphates	83	89	95

more easily than fluoride and chloride ions. For all tested membranes, the nitrate ion gives the lowest rejection rate. The nitrate ion has weaker hydration energy(329 kJ·mol^{-1}) than the fluoride and chloride ones and passes through the membrane more easily than the sulphate ion. This does not interfere with the Donnan equilibrium and generally gives better rejection of fluoride and chloride ions (14). The DESAL5 DL membrane, however, still gives lower fluoride(67%) and chloride(67%) ions rejection, even though these rejections are still higher than that of nitrate(33%) ion. This phenomenon may certainly be better understood by characterizing the membrane polymer and hydrophilicity.

CONCLUSION

A change in rejection levels of fluoride ions was observed when another ion was added to a solution of sodium fluoride; the rejection of fluoride ions was particularly affected by the addition of divalent anions. The mixture of NaF, NaCl, and Na_2SO_4, gave an increase in fluoride ions rejection when the concentration of Na_2SO_4 was increased from 50 to 200 mg/L; that was caused by sulphates size effect which carry a shielding phenomenon along the membranes. This latest increase of fluoride rejection ions disappeared when the concentration of Na_2SO_4 was increased from 50 to 200 mg/L in the absence of chloride ions. However, the increase in Na^+ improves the screening of the membrane, thereby reducing membrane-solute electrostatic repulsion and then making the crossing-over of less hydrated anions easier in order to establish Donnan equilibrium. The replacement of sodium sulphate by a nitrate solution still gives a screening of the membrane, but in this case, it is the nitrate ions with their lowest hydration energy that pass through the membrane rather than chloride ions. The rejection of fluoride ions depends on the salt composition of the solution to be filtered. It is the ionic composition of the solution that is the main influencing factor. The ionic force plays an important role in the selectivity due to the charge of the membrane and the membrane-solute interaction intensity. For the treatment of brackish water containing fluoride, as found in Senegal, we can deduce that the concentration of divalent anions such as sulphate will have an impact on the filterability of the water. These results allow an estimation of the rejection of fluoride to be further tested at pilot scale using real water sources.

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