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Nanofiltration membranes for drinking water production - retention of nitrate ions

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ABSTRACT

Nowadays, the water resource contamination by nitrates and pesticides is a real problem for drinking water production. Together with conventional methods (active carbon adsorption, ozone oxidation), membrane processes like ultrafiltration, reverse osmosis, and nanofiltration are progressively developing due to their lower cost. This study is focused on the ability of nitrates elimination by two flat sheets of negatively charged nanofiltration membranes: NF and OPMN-K. Experiments were carried out on laboratory equipment in batch circulation at 20°C. Transmembrane pressures were varied between 10 and 25 bars, and the impact on nitrates rejection was characterized. Then, the effects of the nitrate concentration and those of the nitrate salt associated cations (Na^+, K^+, and Ca^{2+}) on nitrate retention were studied. Moreover, the interactions between mono and divalent ions in nitrate rejection in complex solutions and particularly in synthetic water were also studied. At last, the influence of one typical pesticide metabolite, the desethylatrazine, on nitrates retention was also investigated.

Keywords: Nanofiltration; Nitrate rejection; Ions influence; Pesticide effect; Drinking water

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1. Introduction

The developed use of nitrates and pesticides for agriculture intensification leads to water resource contamination. These pollutions are a problem of great importance in many countries, and particularly in Basse Normandie area (France). Their maximum admissible concentrations in drinking water, fixed by European Authorities, are 50 ppm for nitrates and 0.1 $\mu g\ L^{-1}$ for each pesticide or metabolite.

The usual methods for nitrate elimination are ion exchange, biological denitrification, and dialysis or electrodialysis [1–5]. For pesticide elimination, active

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carbon adsorption and oxidation by ozone or ozone coupled to hydrogen peroxide [6–8] are classically employed. These methods are difficult in realization, and in the case of elimination of both nitrates and pesticide, a succession of minimum two processes is to be used. For this purpose, membrane processes, especially nanofiltration, could possibly be used for the treatment of such pollutions. Moreover, nanofiltration allows in the same time to reduce the water hardness and to eliminate micro-organisms without addition of chemical reagents.

Nanofiltration is a membrane process situated between reverse osmosis and ultrafiltration. The high selectivity of nanofiltration membranes is commonly explained in terms of size effect, charge effect (due to electrostatic interactions between ions and membrane charged sites), and at last differences in diffusivity and solubility of solutes [9–12]. Furthermore, nanofiltration apparatus has many other advantages: modular construction, easy to operate, easy to scale-up.

Our previous study [13] allowed characterization of the retention of pesticides and metabolites by two nanofiltration membranes (NF and OPMN-K). The subject of this study was to determine the ability of these two membranes to reject nitrate ions from aqueous solutions. For this purpose, membranes have been tested with simple nitrate ions solutions ($NaNO_3$, KNO_3, $Ca(NO_3)_2$) and ions' mixtures ($NaCl$–$NaNO_3$, $NaNO_3$–$Ca(NO_3)_2$) and at last with a complex aqueous solution close to drinking water. The influence of feed concentration, transmembrane pressure (TMP), and ion nature was studied. The effect of the presence of pesticides (desethylatrazine—DEA, herbicide of the triazine class) on nitrate rejection by both membranes was also characterized.

2. Materials and methods

2.1. Nitrates and pesticide

The nitrate salts used in this study were $NaNO_3$, KNO_3, and $Ca(NO_3)_2$. Chloride salt ($NaCl$) was also used. All solutes were of pure analytical grade. The concentrations studied were in the range of 20–300 ppm. The complex solution (close to local drinking water composition) contained 50 ppm NO_3^-, 70 ppm Cl^-, 50 ppm HCO_3^-, 40 ppm SO_4^{2-}, 20 ppm Na^+, and 90 ppm Ca^{2+}.

Stokes radius and diffusivity of the solutes used are given in Table 1.

Table 1
Stokes radius (r_s) and diffusivity (D_∞) of the different ions [14,15]

Ion	r_s (nm)	$D_\infty \times 10^9$ ($m^2\ s^{-1}$)	Data source
Cl^-	0.181	1.89	[14]
NO_3^-	0.189	1.61	[14]
K^+	0.111	1.957	[15]
Na^+	0.095	1.57	[14]
Ca^{2+}	0.099	1.10	[14]

Atrazine ($C_8H_{14}ClN_5$) is a herbicide of the triazine class. In soil, atrazine is degraded into several products: the principal atrazine metabolite is DEA ($C_6H_{10}ClN_5$). DEA possesses a low solubility in water (27 mg L^{-1}) and is considered to be persistent. For the present experiments, DEA aqueous solution (100 μg L^{-1}) was used.

All solutions were prepared with osmosed water (conductivity less than 2 μS cm^{-1}).

2.2. Analytical methods

For the simple nitrate solutions, the concentrations of the feed solution (C_0) and of the permeate (C_p) were determined by conductivity measurements at 20°C (K611-Consort).

For the complex solutions, the anions concentrations were determined by capillary ion analyzer (CIA-Waters) and the cation concentrations were measured by atomic absorption spectrophotometry (SpectrAA.100-Varian).

The DEA concentration was determined using solid-phase extraction coupled to high-performance liquid chromatography (HPLC 1050-Agilent). The methods used and the analytical conditions are described in details elsewhere [13].

2.3. Membranes

Two negatively charged flat sheet organic membranes, NF (Dow-FilmTec, USA) and OPMN-K (Vladipor, Russia), with different characteristics, were tested (Table 2).

Before use, each membrane was immersed during 48 h in osmosed water and compacted during 12 h at 25 bar in order to avoid swelling and compaction effects during experiments.

2.4. Experimental setup and filtration procedure

The experimental setup, equipped with a flat membrane cell, is shown on Fig. 1. Permeate was collected and weighed before returning to the feed tank. A pressure valve was used to adjust the TMP.

During the experiments, the temperature was maintained constant by means of a flat heat exchanger [16].

Table 2
Specifications of NF (Dow, FilmTec) and OPMN-K (Vladipor) membranes

Membrane	NF	OPMN-K	Data source
Material	Polypiperazine amide	Polyamide	Manufacturer
Operating pressure (bar)	–	16	Manufacturer
Solute rejection NaCl	–	55	Manufacturer
Water flux at 15 bar ($L\ m^{-2}\ h^{-1}$)	–	100	Manufacturer
pH range	3–10	2–12	Manufacturer
Surface charge	Negative	Negative	Manufacturer
Water permeability ($m\ h^{-1}\ bar^{-1}$)	0.0045	0.0079	[13]
Molecular weight cut-off, 95% (Da)	170	330	[13]
Pore radius (nm)	0.35	0.47	[13]

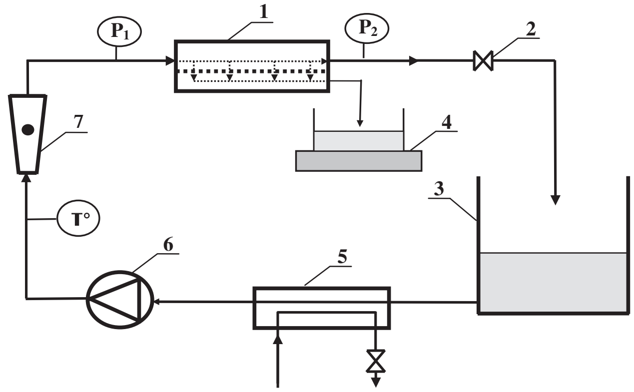

Fig. 1. Experimental setup. (1) nanofiltration cell, (2) pressure valve, (3) feed tank, (4) balance, (5) heat exchanger, (6) pump, and (7) flowmeter, P_1, P_2: pressure gauges, T: temperature gage.

3. Results and discussion

Experiments have been carried out in batch mode at 20°C and the circulation velocity in the membrane cell was fixed to 0.45 m s^{-1} (Re = 3,300). The TMP varied between 10 and 25 bar. The results, at steady state, are presented as observed retention (R_{obs}) defined by:

$$R_{obs} = 1 - \frac{C_p}{C_0} \tag{1}$$

where C_0 is the feed concentration (ppm) and C_p is the concentration of permeate (ppm).

3.1. Simple solutions

Nanofiltration of simple nitrate solutions containing mono or divalent cations ($NaNO_3$, KNO_3, and $Ca(NO_3)_2$) was studied. An NaCl solution was also filtrated. The solute concentration was in the range of 20–300 ppm.

3.1.1. TMP effect

3.1.1.1. NF membrane. The observed rejection of the monovalent ions for the NF membrane vs. the operating TMP for the less concentrated solutions (20 ppm) is presented in Fig. 2.

During the filtration, the observed retention raises slowly with the TMP whatever the salt is. When the pressure increases, the solvent flow through the membrane increases, but the diffusion and solute flux remain constant, therefore the retention observed increases slightly. This phenomenon, reported by many authors, is generally observed during salt rejection by charged nanofiltration membranes.

Concerning the $NaNO_3$ salt at the highest concentration (300 ppm), the observed rejection also increases with pressure as expected (Fig. 3). In addition, one can see that the observed retention for 20 ppm is higher than that for 300 ppm and the difference is up to 10%. This phenomenon is also well known for charged nanofiltration membranes due to screening effect. Indeed, at low concentrations, the co-ions are repulsed outside the membrane due to the electrostatic interactions with charged membrane sites. In order to

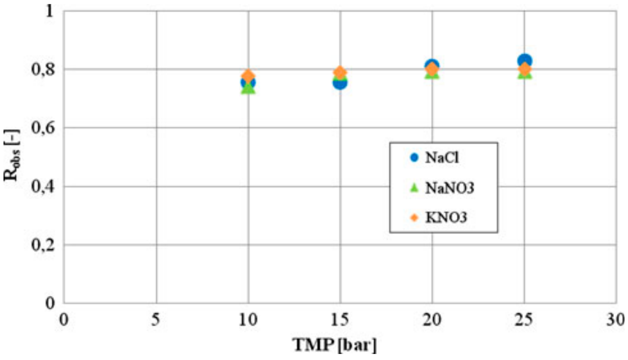

Fig. 2. Monovalent ions observed rejection (R_{obs}) vs. applied TMP (C_0 = 20 ppm). NF membrane.

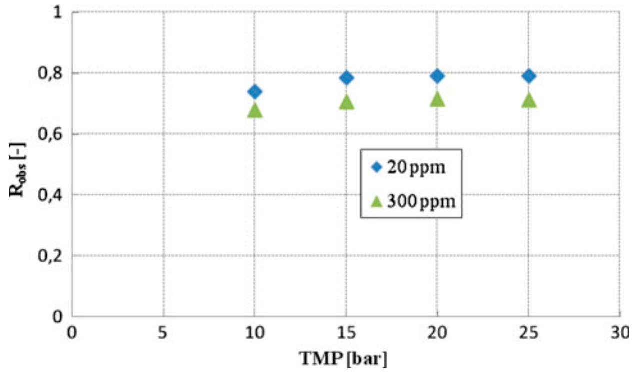

Fig. 3. Observed rejection (R_{obs}) of $NaNO_3$ vs. applied TMP for two concentrations ($C_0 = 20$ and 300 ppm). NF membrane.

assure the permeate electroneutrality, the counter-ions are also retained. Then, when the concentration increases, the counter-ions balance the membrane charges and the co-ions can pass throughout. Consequently, the ion retention decreases.

Furthermore, during the $Ca(NO_3)_2$ filtration, the same phenomenon was observed: the rejection rate first increases with TMP and then tends to stabilize for greater TMP values (Fig. 4).

These results confirm observations of several authors: a strong increase followed by a slower increase or stabilization [10,17–21]. Many authors explain this fact by the concentration polarization in feed-membrane interface [16,19,22]. Indeed, an increase of the TMP promotes the solvent transfer while the solute transfer remains almost constant and therefore, the retention rate rises. When the TMP increases, concentration polarization appears and promotes the solute transport. Therefore, the solute flux increases identically to solvent flux, leading to stabilization of retention rates (Fig. 5).

Whatever the solute, the permeate flux varies linearly with the TMP and its value is close to the water permeability. This linearity indicates that the concentration polarization phenomenon is not marked [23]. In this case, osmotic pressure difference between feed bulk and boundary layer is negligible [24]. However, the values of the permeate are lower in the case of $Ca(NO_3)_2$ due to lower mobility compared to $NaNO_3$.

3.1.1.2. *OPMN-K membrane.* The observed retentions of the different salts concerning the OMPN-K membrane are illustrated on Figs. 6 and 7 for two concentrations.

For low concentrations (20 ppm), the retention decreases with pressure: the increase of the permeate flux with pressure leads logically to the decrease of solute retention, which tends to confirm that the pore size is greater compared to the NF membrane. The estimated pore radii (r_p) for both the membranes are, respectively, $r_{p,OPMN\text{-}K} = 0.47$ nm and $r_{p,NF} = 0.35$ nm [13]. For the $Ca(NO_3)_2$ salt, it was not observed any influence of the pressure: the retention remains quasi unchanged in the studied pressure range (Fig. 6). On the other hand, concerning experiments with high concentration (300 ppm), one can observe the retention stabilization with pressure increase (Fig. 7), due probably to the feed charge effect. Kavitskaya et al. [25] also have observed a stabilization of the NaCl rejection with pressure. It should be noted that the concentration studied by these authors was higher (1.37 g L^{-1}) and the applied pressure lower (3–15 bar).

For all solutes, the permeate flux linearly rises with TMP (Fig. 8) and the permeability for the solutes ($L_{\text{Working Solution}} = L_{WS}$) is close to osmosed water permeability (L_P): $L_{WS}/L_P \approx 0.9$. This shows that the polarization concentration is also negligible like for the NF membrane.

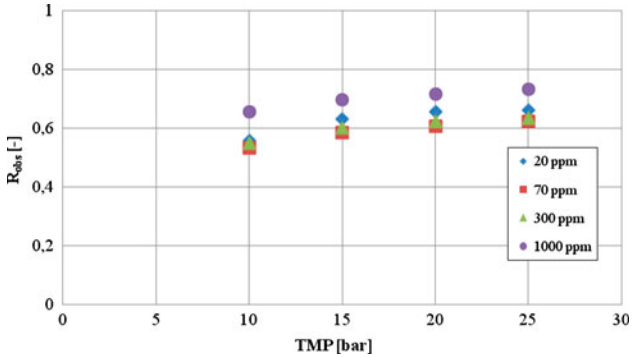

Fig. 4. Observed rejection (R_{obs}) of $Ca(NO_3)_2$ vs. applied TMP for four concentrations ($C_0 = 20$, 70, 300, and 1,000 ppm). NF membrane.

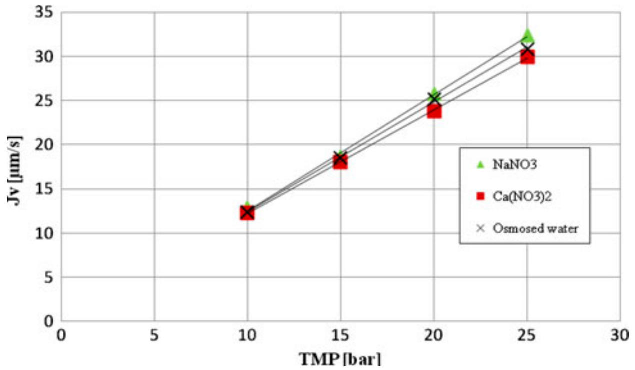

Fig. 5. Permeate flux vs. TMP ($C_0 = 70$ ppm). NF membrane.

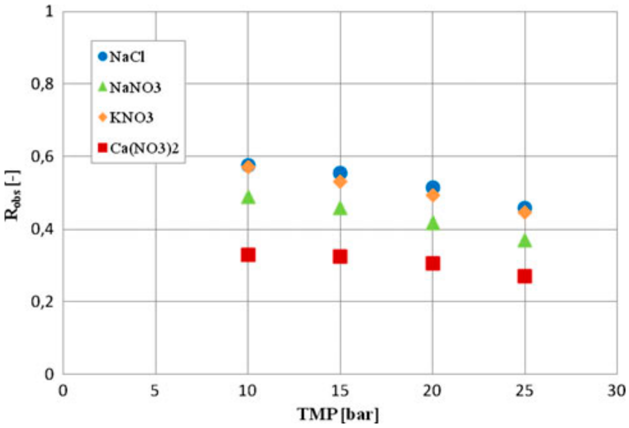

Fig. 6. Observed rejection (R_{obs}) vs. applied TMP (C_0 = 20 ppm). OPMN-K membrane.

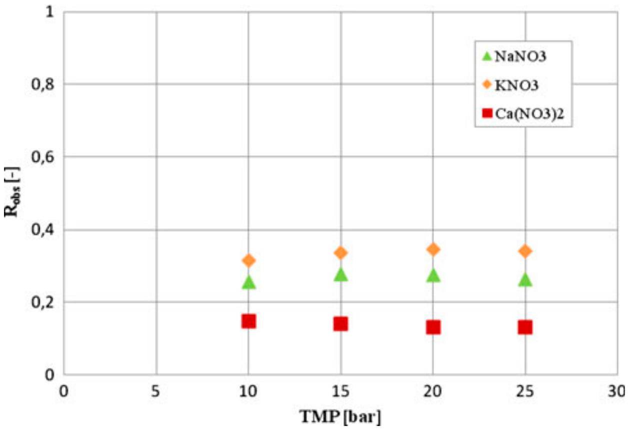

Fig. 7. Observed rejection (R_{obs}) vs. applied TMP (C_0 = 300 ppm). OPMN-K membrane.

3.1.2. *Salt concentration effect*

To investigate the effect of feed concentration on solute retention and on permeate flux, the salt concentration was adjusted between 20 and 300 ppm. Experiments for both membranes were carried out with the lowest applied TMP (10 bar).

3.1.2.1. NF membrane. The nitrate retentions for the different salts are shown in Table 3 for the concentration range of 20–300 ppm.

The results obtained show that the increase of the concentration of KNO_3 and $NaNO_3$ leads to their retention decrease. This phenomenon is generally interpreted by the Donnan exclusion (the counter-ions neutralize progressively the membrane charge) and hence, the repulsion between membrane charged sites and co-ions decreases [26,27]. The Donnan exclusion characterizes the interactions between co-ions (NO_3^- and Cl^-), counter-ions (Na^+, Ca^{2+}, and K^+) and the charge (negative) of the membrane. When the feed concentration increases, solution ion density approaches the membrane one. There is a progressive neutralization of the membrane charges, and therefore, Donnan potential (affinity between the membrane and counter-ions) decreases. When the Donnan potential tends to zero, the influence of membrane charge also tends to zero.

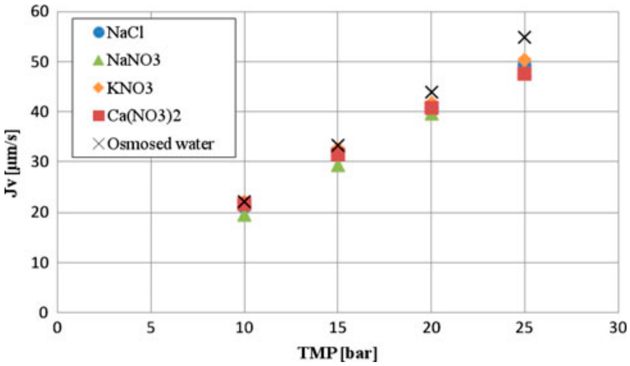

Fig. 8. Permeate flux vs. TMP (C_0 = 300 ppm). OPMN-K membrane.

Comparing the monovalent cations, no marked difference between Na^+ and K^+ retentions was observed. However, sodium retention should be better since the KNO_3 diffusion coefficient is higher than the $NaNO_3$ one. Experimental results do not confirm this hypothesis and show that this difference do not seem to be sufficient to affect the membrane selectivity for these two cations.

Then, the retention of $Ca(NO_3)_2$ remains unchanged despite the concentration. This observation implies that the divalent cations reduce the charge effect of the membrane and the membrane–solute electrostatic interactions remain constant over the whole range of concentrations studied. According to these results, it seems that the part of electrostatic solute–membrane interactions may be considered negligible compared to the screening effect for these concentrations. The same conclusion for divalent counter-ions is cited in the literature [19].

Concerning the counter-ion valency, the observed retention of monovalent counter-ion is higher and varies between 0.65 and 0.78. This result is due to the stronger attraction between the membrane surface charges and divalent counterions. This stronger attraction contributes to the rapid partial neutralization of surface charges, promoting in this way the solute's transport.

Table 3
Observed rejection of the nitrate ions (TMP = 10 bar, NF membrane)

C_0 (ppm)	$R_{\text{obs,NaCl}}$ (–)	$R_{\text{obs,NaNO}_3}$ (–)	$R_{\text{obs,KNO}_3}$ (–)	$R_{\text{obs,Ca(NO}_3)_2}$ (–)
20	0.75	0.74	0.78	0.56
50	–	0.73	0.71	0.52
70	–	0.73	0.70	0.53
100	–	0.73	0.68	0.54
300	–	0.68	0.65	0.55

For all solutes, the permeate flux remains constant vs. solute concentration but one can see that the flux values are higher for monovalent cations (Fig. 9).

3.1.2.2. *OPMN-K membrane.* The observed retentions for the OPMN-K membrane for the different salts are presented in Table 4 in a concentration range from 20 to 300 ppm.

Despite the solute type, the rejection decreases with the feed concentration increase. This retention decrease is due to screening effect modification. For low solute concentrations, membrane potential and Debye length are important, and so, co-ions repulsion and therefore the solute rejection, are also important. When the concentration increases, the screening effect becomes less important, thus leading to lower anion repulsion and lower solute rejection. For $Ca(NO_3)_2$, the retention is clearly lower than for the monovalent ions, despite its lower mobility, which suggests a higher retention.

According to the results shown on Fig. 10, the permeate flux is not dependent on the feed concentration and on the counter-ion nature.

Moreover, due to its higher cut-off, this membrane allows to obtain permeate flows about two times higher than the NF membrane.

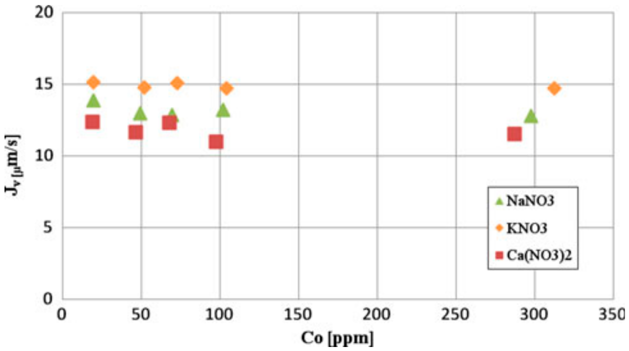

Fig. 9. Permeate flux vs. feed concentration (TMP = 10 bar). NF membrane.

3.2. *Solute mixtures*

In order to study the interactions between the different ions presenting in the treated solution, experiments using salt mixtures have been carried out. First, two feed solutions containing $NaNO_3$, $Ca(NO_3)_2$ and NaCl salts with various concentrations were tested. Finally, a synthetic water containing nitrates ($[NO_3^-]$ = 50 ppm, $[Cl^-]$ = 70 ppm, $[HCO_3^-]$ = 50 ppm, $[SO_4^{2-}]$ = 40 ppm, $[Na^+]$ = 20 ppm, and $[Ca^{2+}]$ = 90 ppm) was nanofiltered.

3.2.1. *Monovalent solutes*

The effect of the counter-ion (Na^+) and of the co-ions (NO_3^- and Cl^-) on their respective rejection was studied using NF membrane and a feed solution containing a mixture of NaCl (20 ppm) and $NaNO_3$ (70 ppm). The same counter-ion was used for the two salts in order to avoid the influence of the counter-ions nature on anions retention.

Fig. 11 shows the results obtained with simple salt solutions and with NaCl–$NaNO_3$ mixture. It clearly appears that observed rejections for all solutions are close with only a difference for NaCl at high TMP.

This minor difference is probably due to the NaCl hydration degree: in fact, the hydration of the molecule increases its size and consequently decelerates solute transport through the membrane. Results obtained for the mixture show a low decrease of Na^+ retention in presence of the two monovalent anions as the pressure increases, due to more important Donnan effect. Nevertheless, the rejection values are similar, confirming the low effect of co-ions on the Na^+ rejection.

The rejections of the two co-ions (NO_3^- and Cl^-) vs. TMP are shown, respectively, on Figs. 12 and 13. The NO_3^- rejection is lower in the complex solution (NaCl + $NaNO_3$) due to the higher hydration energy of the Cl^- ion (Fig. 12).

On the contrary, the Cl^- retention in the complex solution is better (Fig. 13). The addition of NaCl to the $NaNO_3$ accelerates the membrane charge

Table 4
Observed rejection of the nitrate ions (TMP = 10 bar, OPMN-K membrane)

C_0 (ppm)	$R_{\text{obs,NaCl}}$ (–)	$R_{\text{obs,NaNO}_3}$ (–)	$R_{\text{obs,KNO}_3}$ (–)	$R_{\text{obs,Ca(NO}_3)_2}$ (–)
20	0.63	0.49	0.60	0.44
50	0.58	0.41	0.52	0.26
70	0.53	0.38	0.48	0.22
100	0.51	0.35	0.43	0.15
300	0.47	0.26	0.32	0.09

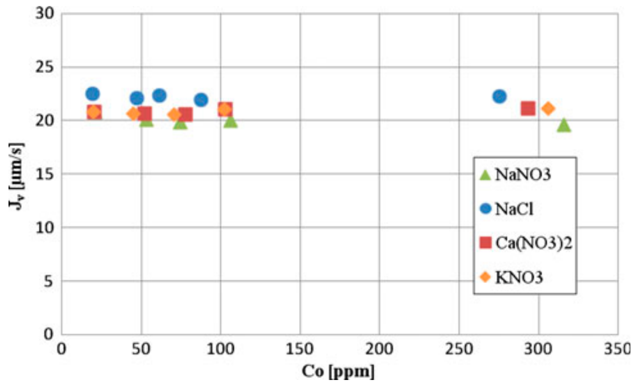

Fig. 10. Permeate flux vs. feed concentration (TMP = 10 bar). OPMN-K membrane.

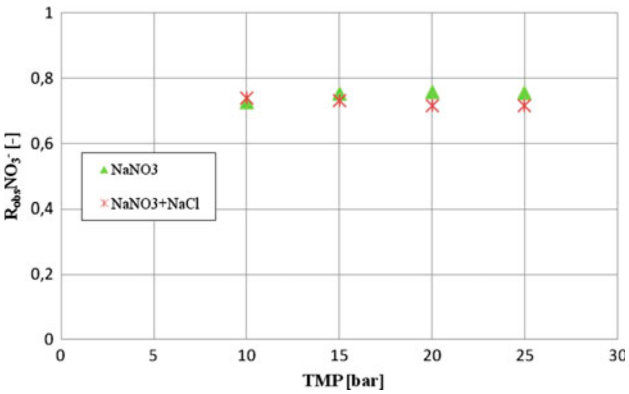

Fig. 12. NO_3^- rejection vs. applied TMP ([$NaNO_3$] = 70 ppm and [NaCl] = 20 ppm). NF membrane.

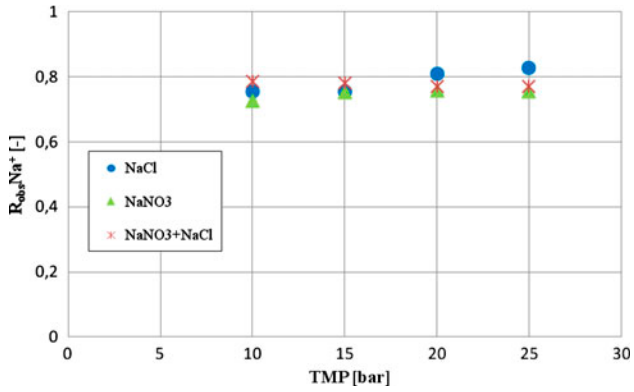

Fig. 11. Na^+ rejection vs. TMP (simple salt solutions concentration: 70 ppm and salts mixture concentration: [$NaNO_3$] = 70 ppm + [NaCl] = 20 ppm). NF membrane.

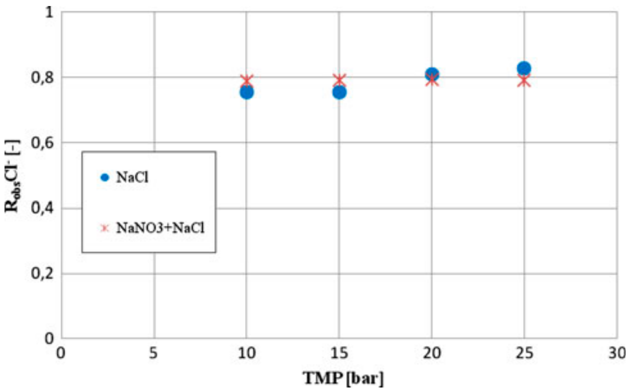

Fig. 13. Cl^- rejection vs. applied TMP ([$NaNO_3$] = 70 ppm and [NaCl] = 20 ppm). NF membrane.

neutralization and hence, decreases the anion repulsion. This phenomenon was also observed by Paugam [19] for TMPs up to 8 bar.

3.2.2. Monovalent and divalent solute mixtures

The evolution of the observed retention for divalent and monovalent ions was studied with a mixture $NaNO_3$–Ca $(NO_3)_2$ vs. TMP (between 10 and 25 bar) for both membranes. The results, presented in Figs. 14 and 15 show that, despite the membrane type and the applied pressure, the Na^+ retention is strongly decreased by the presence of the Ca^{2+} cations.

The influence of the divalent counter-ions (Ca^{2+}) on the monovalent cations (Na^+) rejection by nanofiltration membranes was observed by many authors [17,28,29]. These results can be interpreted by the charge effect: the stronger positive charge of Ca^{2+} causes a balance with the negative charge of the membrane while the lower charged Na^+ cations are weakly repulsed by the membrane and their retention becomes lower (membrane charge inversion).

Nevertheless, the addition of Na^+ (more mobile ion) to the solution of Ca^{2+} (less mobile ion) leads to a very important increase in its retention by the OPMN-K membrane (Fig. 16).

The increase of Ca^{2+} ions rejection rate can be explained by a combination of their electrostatic attraction by negatively charged membrane and their greater molecular weight (and thus their greater size). The neutralization of the membrane leads to the predominance of sieve effect. Otherwise, the $NaNO_3$ addition to $Ca(NO_3)_2$ solution at the same concentration (70 ppm) does not affect the Ca^{2+} retention by the NF membrane: the values of rejection observed remain closed to those of $Ca(NO_3)_2$ solution (Fig. 17).

These results are due to the overlap of two opposite effects. On one hand, the mobility of sodium nitrate ($D_{NaNO_3} = 1.5 \times 10^{-9}$ m^2 s^{-1}; [14]) is higher than that of calcium nitrate ($D_{Ca(NO_3)_2} = 1.2 \times 10^{-9}$ m^2 s^{-1}; [14]). On the other hand, the calcium ion, preferentially attracted by the membrane due to higher positive charge, contributes significantly to the neutralization of the active membrane layer and consequently the sodium ion is subjected only to weak electrostatic interactions with the material. Concerning the results obtained for the NF membrane, one can conclude that the part of the second effect seems dominant.

3.2.3. Synthetic water

A complex solution with a composition close to that of local drinking water (Basse Normandie, France) was nanofiltered by both membranes. Only the results for the higher studied TMP (25 bar) for which the nitrates retention is greatest are presented.

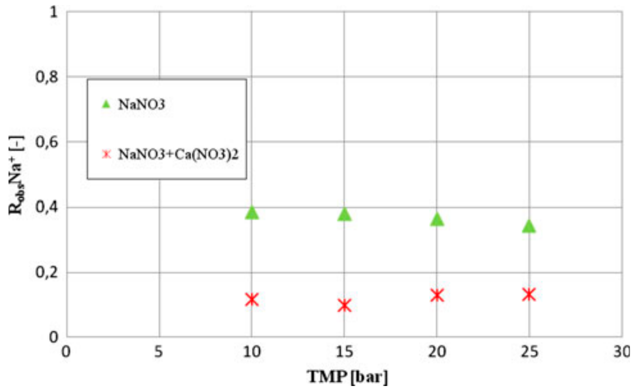

Fig. 14. Na^+ retention vs. TMP ($[NaNO_3]$ = 70 ppm and $[Ca(NO_3)_2]$ = 70 ppm). OPMN-K membrane.

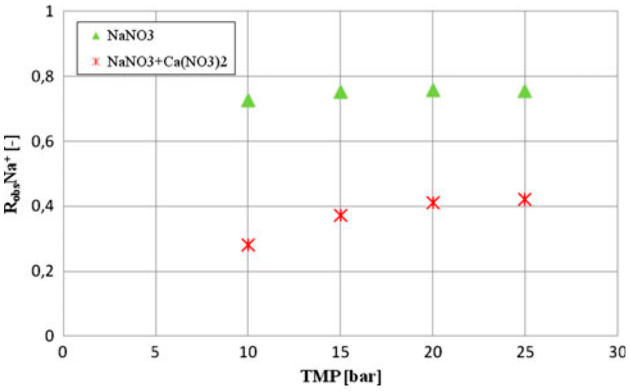

Fig. 15. Na^+ retention vs. TMP ($[NaNO_3]$ = 70 ppm and $[Ca(NO_3)_2]$ = 70 ppm). NF membrane.

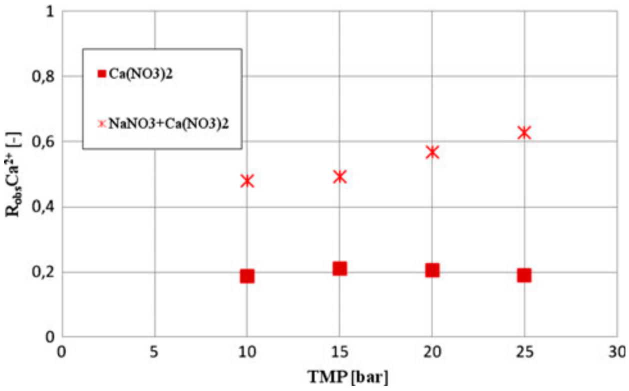

Fig. 16. Ca^{2+} retention vs. TMP ($[NaNO_3]$ = 70 ppm and $[Ca(NO_3)_2]$ = 70 ppm). OPMN-K membrane.

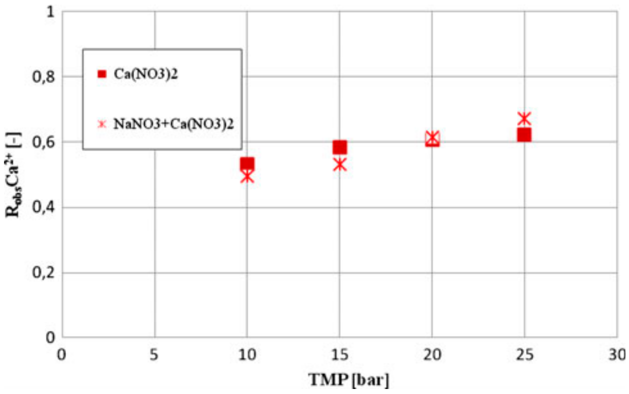

Fig. 17. Ca^{2+} retention vs. TMP ($[NaNO_3]$ = 70 ppm and $[Ca(NO_3)_2]$ = 70 ppm). NF membrane.

Table 5
Feed composition and observed rejection of ions at TMP = 25 bar by NF and OPMN-K membranes

Ion	Feed concentration (ppm)	$R_{\text{obs,NF}}$ (–)	$R_{\text{obs,OPMN-K}}$ (–)	Hydration energy [30] (kJ mol^{-1})
Na^+	20	0.66	0.30	407
Ca^{2+}	90	0.75	0.28	1,584
Cl^-	70	0.70	0.12	376
HCO_3^-	50	0.84	0.32	393
NO_3^-	50	0.44	0.13	329
SO_4^{2-}	40	0.99	0.81	1,138

The retentions for the different ions are presented in Table 5.

One can see that all ions are definitely better retained by the NF membrane because of its pore sizes which are smaller than those of the OPNM-K membrane. Concerning the anions, the retention sequence is: $R_{\text{obs},SO_4^{2-}} > R_{\text{obs},HCO_3^-} > R_{\text{obs},Cl^-} > R_{\text{obs},NO_3^-}$. This result may be explained by the fact that when an ion is strongly hydrated, it becomes more bulky and causes higher retention.

The nitrate ions are the less retained by NF membrane (44%). For the OMPN-K membrane it is found that the retention of Cl^- and NO_3^- are the lowest (12 and 13%). If the nitrate ion retention for this solution is compared to the retention for $NaNO_3$ simple solution, a strong decrease of the retention for the complex solution can be observed.

The best retention of the SO_4^{2-} ions is obtained for both membranes tending toward 99% for the NF membrane. This important retention is due to their hydration energy which is very high (1,138 kJ mol^{-1}), to their large size, but also to the strong electrostatic repulsion with the negatively charged membrane.

The HCO_3^- anions, even if they have properties close to those of Cl^- and NO_3^- (Stokes radius and hydration energy), are more retained. This could be explained by the presence of carbonate ions (CO_3^{2-}) in equilibrium with the bicarbonate ions (HCO_3^-). This equilibrium is depending on the pH of the aqueous solution: carbonic acid/bicarbonate or bicarbonate/carbonate (Fig. 18).

As the carbonate is a divalent ion, the ion-membrane repulsion is higher. However, in this study, pH was maintained constant and the predominantly present ions are HCO_3^- ions, but the solution contains a small amount of CO_3^{2-} ions that can affect HCO_3^- retention [31].

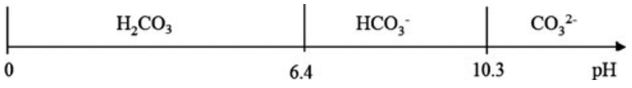

Fig. 18. pH-depended distribution of H_2CO_3, HCO_3^-, and CO_3^{2-} ions at 20°C [31].

Concerning the cations, Na^+ is less rejected that Ca^{2+} by NF membrane. This result confirms that the membrane, negatively charged, attracts preferentially the divalent counter-ions, contributing to a partial neutralization of surface membrane charges responsible for electrostatic exclusion, and therefore monovalent counter-ions pass preferentially. Regarding the OPMN-K membrane, the retention is, in contrast, quasi identical for both cations.

Permeate and pure water fluxes vs. applied TMP are shown on Figs. 19 and 20.

The variation is linear for both membranes and the highest fluxes are obtained for the OPMN-K membrane. For NF membrane, there is a strong difference between the values of the permeate fluxes for complex solution and for osmosed water flux (Fig. 19). The low ratio of permeabilities, $L_{WS}/L_P = 0.67$, shows the presence of a relatively important polarization concentration.

On the other hand, for the OPMN-K membrane, the values of the permeate flux and pure water are very close (Fig. 20), with a permeability ratio of $L_{WS}/L_P = 0.94$, leading to the conclusion that the phenomenon of concentration polarization is negligeable in these conditions.

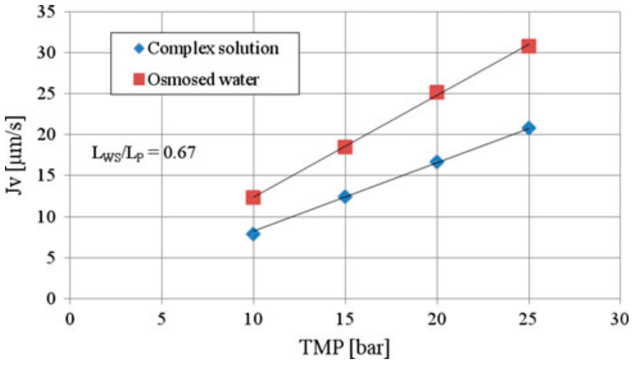

Fig. 19. Permeate and osmosed water fluxes vs. TMP. NF membrane.

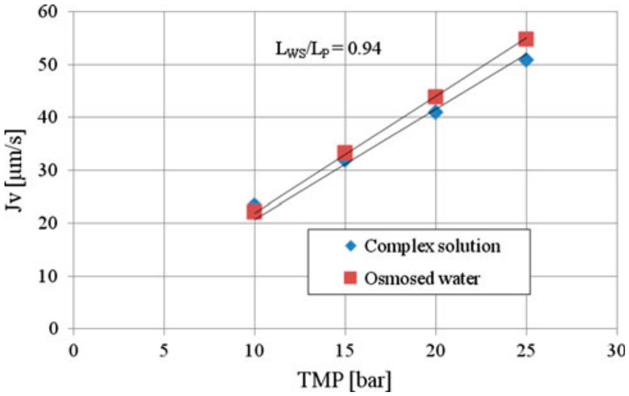

Fig. 20. Permeate and osmosed water fluxes vs. TMP. OPMN-K membrane.

3.3. Influence of pesticide metabolite DEA

Finally, the influence of a pesticide on the selectivity of the membrane with respect to nitrate ions was investigated. The choice of DEA as pesticide is due to its low molecular weight and its size close to that of nitrate ions. The DEA was used in solution with a concentration of 100 µg L^{-1} in mixture with $NaNO_3$ salt (20 and 70 ppm).

Whatever the salt concentration, the same conclusion may be made for both membranes: the nitrate retention decreases, and this decrease is more important for the OPMN-K than for the NF membrane (Figs. 21 and 22).

Indeed, the addition of organic molecules, like pesticides, in the feed solution, increases the solution viscosity in the boundary layer and, therefore, the ion diffusion is blocked and the retention decreases [32].

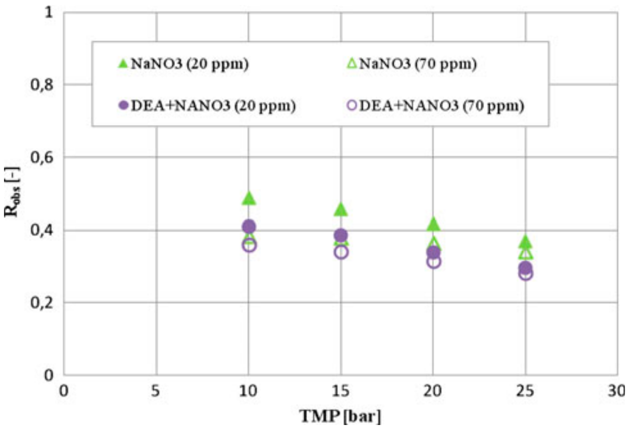

Fig. 21. $NaNO_3$ retention for two concentrations ($C_0 = 20$ and 70 ppm) in simple salt solution and in DEA–$NaNO_3$ solution (DEA concentration = 100 µg L^{-1}) vs. TMP. OPMN-K membrane.

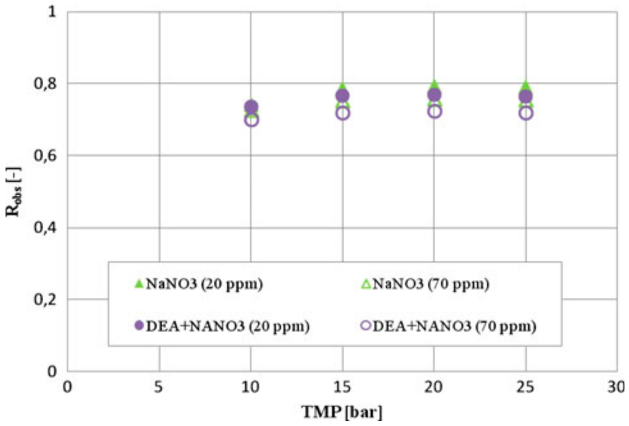

Fig. 22. $NaNO_3$ retention for two concentrations ($C_0 = 20$ and 70 ppm) in simple salt solution and in DEA–$NaNO_3$ solution (DEA concentration = 100 µg L^{-1}) vs. TMP. NF membrane.

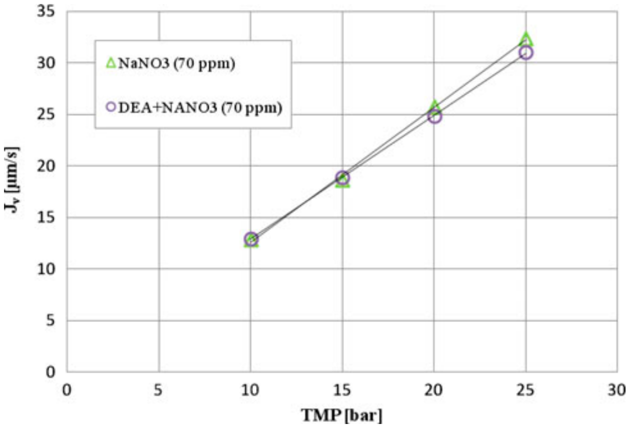

Fig. 23. Permeate flux vs. TMP ($NaNO_3$ and mixture $NaNO_3$ + DEA). NF membrane.

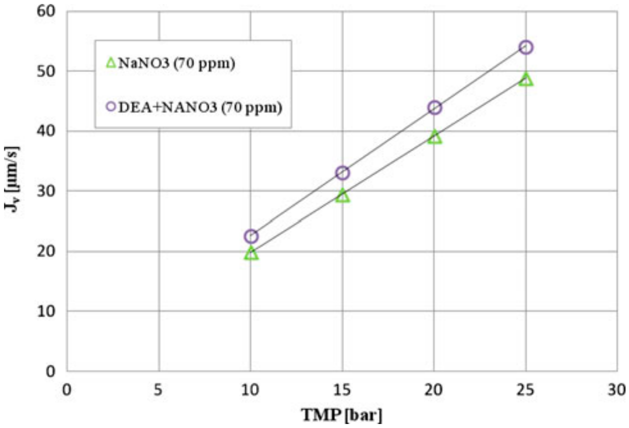

Fig. 24. Permeate flux vs. TMP ($NaNO_3$ and mixture $NaNO_3$ + DEA). OPMN-K membrane.

Finally, the permeate flux remains the same for the NF membrane (Fig. 23), but the DEA seems to enhance the permeate flux through the OPMN-K membrane and it seems to be more marked for high TMP (Fig. 24).

4. Conclusion

The importance of using NF and OPMN-K nanofiltration membranes for nitrate ion reduction in water was demonstrated. With a two times greater permeate flux, OPMN-K membrane presents a lower retention rate compared to NF membrane. The latter ensures three times higher nitrate retention. TMP is an important parameter for permeate flux: for both membranes permeate flux is a linear growing function of the pressure applied. TMP also influences the ion retention: retention increases with pressure for NF membrane but, on the contrary, the ion retention decreases with pressure for OPMN-K membrane. This effect is due to the pore size of NF which is smaller than that of the K-OPNM membrane. The nitrate retention is important but decreases with the concentration increase, due to the screening effect. The addition of a divalent counter-ion (Ca^{2+}) in the solution containing a monovalent counter-ion (Na^+) decreases the retention of this latter for both membranes. On the opposite, the divalent ion retention remains constant for NF membrane and increases significantly for OPMN-K membrane.

Concerning the drinking water nanofiltration, the retention of nitrates is strongly reduced compared to the retention obtained with simple $NaNO_3$ solution. Moreover, divalent sulfate ions are strongly rejected due to the coupled action of the size effect and the electrostatic repulsions, more important than for monovalent ions. Consequently, the monovalent ions are forced to pass through the membrane in order to assure the permeate electroneutrality. In addition, nitrate ions are the less retained anions due to the less important hydrated size and hydration energy compared to other co-ions. At last, the presence of a pesticide (DEA) in a solution containing nitrates leads to a decrease of the nitrate rejection.

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