

Application of nanofiltration in fluoride separation from aqueous solutions containing nitrate

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ABSTRACT

Fluorine is a chemical element which could be hazardous for human health. The World Health Organization (WHO) estimated the safe fluoride level in drinking water to be 1.5 mg F/dm³. Contamination of water environment by fluoride is observed all over the world, thus there is a need to develop an efficient fluoride removal method from natural waters. The objective of the study was to evaluate the fluoride removal efficiency from aqueous solutions by nanofiltration (NF) in the presence of monovalent salt (nitrate). The research was performed with the use of Amicon UF/NF stirred cell at the transmembrane pressure of 0.3 MPa. The NF membranes made of polyethersulfone (NP010P and NP030P, Microdyn-Nadir®) varied in divalent salt rejection, were applied in the process. The treated solutions contained fluoride ions (5, 15, and 100 mg F/dm³) as well as nitrate ions (30, 60, and 90 mg NO₃/dm³). The performed NF experiments revealed that it was possible to decrease the fluoride content in the permeate below the permissible limit of 1.5 mg F/dm³ only for the lowest fluoride/nitrate content in the feed. The adverse effect of the nitrate presence on the fluoride removal efficiency was also detected. The relative permeability for both applied membranes varied from 0.37 to 1.0 depending on the salt concentration in the feed.

Keywords: Fluoride; Nanofiltration; Nitrate; Monovalent anions; Permeate flux

1. Introduction

Fluorine is a chemical element commonly present in the environment characterized by the highest electronegativity [1]. Due to the harmful influence on human health, the permissible limit of F⁻ ion in drinking water was estimated to 1.5 mg F/dm³ according to the WHO guidelines [2], however the recent recommendation of US Public Health Service (USPHS) for optimal fluoride concentration in municipal water systems is 0.7 mg F/dm³ [3]. About 90% of fluoride detected in drinking water and approximately 30%–60% of fluoride present in food are absorbed by the digestive tract [4]. Fluoride in excess may result in dental and skeleton fluorosis. Besides, other health issues like

Alzheimer's, problems with the liver, lungs, and osteosclerosis may occur [5,6]. Fluoride has also negative effect on plant growth and can lead to the ecological imbalance [7]. Problems with an elevated fluoride content were noticed all over the World (e.g., Ethiopia, Tanzania, Germany, USA, Mexico, India) [1,8]. The content of fluoride in sea water is around 1 mg F/dm³, whereas in lakes and rivers the concentration of F⁻ ion reaches also rather low levels (0.5 mg F/dm³). However, the excessive content of fluoride (1–35 mg F/dm³) can be found in groundwater [9], as well as in some specific places on the Earth. For example, in local soda lakes in the East African Rift Valley, the content of fluoride can reach up to 2,800 mg F/dm³ [10]. Fluoride is released to the environment due to the weathering

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and dissolution of minerals containing fluorine (e.g., fluoroapatite, vermiculite, topaz, or micas) [11]. The mean content of fluoride in the Earth's crust is 585 mg/kg [11]. A significant anthropogenic source of fluorine is electroplating, pesticide production, toothpaste production, copper and aluminum smelting [9,12]. In wastewater from phosphate production, the content of fluoride can reach up to 3,000 mg F/dm³ [8,13].

Nitrate is found naturally in the water environment, also in groundwater simultaneously with fluoride ion. It is a non-reactive, the most oxidized form of nitrogen. The content of nitrate in groundwater is affected mainly by biogeochemical processes. However, a significant nitrate pollution could be caused by fertilization, industrial discharges, defective sewage systems, and leaking septic tanks [14]. Due to the harmful impact on living organisms, the WHO estimated the permissible content of nitrate in drinking water to 50 mg NO₃/dm³ [2]. The excess levels of nitrate in the water environment can enhance the growth of algae and suppress the microorganism activity. Too high content of nitrate in water bodies may lead to eutrophication resulting in dissolved oxygen deprivation [15,16]. Nitrate compounds can migrate to the environment due to agriculture, industrial or urban activity. Contamination of water by nitrate is a very serious problem in rural areas [17]. The excess of nitrate may lead to DNA damage, cancer, and birth defects [18].

Several techniques enable removal of fluoride from water solutions, among others, conventional processes such as ion exchange, precipitation, or adsorption [19–22]. Due to their advantages, membrane techniques, that is, reverse osmosis (RO), electrodialysis (ED), Donnan dialysis (DD), and nanofiltration (NF) recently became promising and competitive methods of F⁻ ion removal [5,8,23,24]. Although there is a recent trend towards preparation and application of advanced nanocomposite materials (for example, containing Ag nanowires, TiO₂ nanosheets and graphene [25]) as well as nature-inspired nanocomposite membranes [26,27], the synthetic polymeric nanofiltration membranes are still in use. Nanofiltration allows obtaining high rejection coefficients due to the combination of various separation mechanisms (charge repulsion, diffusion, adsorption, and size exclusion). The NF membranes are generally characterized by a high charge density (usually negative), which has significant effect on the selective mass transport through these membranes. Thus, the NF membranes have recently gained importance in a selective and partial demineralization of water, which made NF competitive process to RO [1,8,28]. Some of the latest research developments in separation of fluoride and coexisting ions from water by nanofiltration are given below.

Tahaikt et al. [29] used nanofiltration for fluoride removal from groundwater. The experiments were conducted with the use of a NF/RO pilot plant. Two commercial polyamide NF membranes (NF90 and NF400) placed in spiral wound modules were applied. The fluoride content in water samples was equal to 1.8, 5, 10, and 20 mg F/dm³. The applied transmembrane pressure amounted to 1 MPa. Application of the NF400 membrane produced permeate containing 0.9–2.78 mg F/dm³, whereas the NF90 membrane showed much better separation efficiency – the final

fluoride concentration in permeate varied between 0.07 and 0.09 mg F/dm³. However, it was found that after treatment by NF90 membrane, remineralization of produced water was needed due to the very low content of total dissolved solids (TDS).

Hoinkis et al. [30] performed experiments on nanofiltration to remove fluoride from model and tap water contaminated with nitrate. The laboratory Installation Lab-20 (DDS Division, Denmark) and NF membranes (NF90, NF270) were used in the experiments. The tested solutions were spiked with nitrate and fluoride ions at 100–400 mg NO₃/dm³ and 5–20 mg F/dm³, respectively. The content of fluoride was reduced below 1.5 mg F/dm³ when the NF270 membrane was used, providing that the initial fluoride concentration was rather low (up to 10 mg F/dm³). The experiments with NF90 membrane exhibited better results – the fluoride content in permeate did not exceed 0.5 mg F/dm³, even when the concentration of fluoride in the feed amounted to 20 mg F/dm³. The effect of pH on fluoride separation efficiency was rather minor. The deterioration of the permeate quality was observed at the pH equal to 5 only. The commercial thin-film composite NF membranes (NF90 and NF270) were also used by Valentukeviciene et al. [1] to remove fluoride from RO retentate generated in groundwater treatment system. The initial fluoride content was equal to 5 and 10 mg F/dm³. Similarly to the results obtained by Hoinkis et al. [30], the NF90 membrane was characterized by better fluoride removal efficiency (up to 92%) in comparison to NF270 membrane, which exhibited only 67% reduction of F⁻ ion. The authors deduced that the membrane pore size is crucial for separation efficiency in NF.

Ayala et al. [31] verified the suitability of NF process for concentration of fluoride solution. They applied a flat polyester NF membranes (Alfa Laval, Sweden) placed in a cross-flow filtration set-up (Alfa Laval LabStak[®] M20, Sweden). A model water system simulating fluoride-contaminated water was prepared and subjected to concentration at a transmembrane pressure of 0.9 MPa. It was found that the concentration of fluoride was reduced from 15 to 1.7 mg F/dm³ at the beginning of the process. However, the quality of the permeate significantly deteriorated with the increasing concentration factor. The content of fluoride in the permeate increased to 2.4 and 3 mg F/dm³ for feed concentration factor equal to 2 and 3, respectively. The authors concluded that the obtained permeate was not suitable for human consumption.

Natural water contaminated with fluoride ions, usually contains various mineral salts as well as organic matter. Thus, it can be anticipated that the co-existing ions will influence the fluoride rejection by NF membranes. Ben Nasr et al. [32] evaluated the effect of chloride, sulfate and calcium ions on the fluoride separation from model solutions and real groundwater with the use of commercial NF5 and NF9 membranes. The initial content of fluoride in the treated solutions varied from 5 to 50 mg F/dm³. In the course of NF process (operated in a concentration mode) the F⁻ ion content was lowered to 1.26–21.7 and 0.39–3.10 mg F/dm³ when NF5 and NF9 membranes were used, respectively. When multicomponent solutions were treated by NF, the fluoride removal efficiency decreased to 59.4%–66.8%

(in comparison to 74.8% rejection noted when only fluoride ions were present in the solution). This negative effect of chloride, sulfate and calcium ions on fluoride separation was explained by shielding effect or Donnan equilibrium. On the other hand, the authors found that F^- ions were better retained than Cl^- ions, because fluoride ions were more solvated than chloride ions. Richards et al. [33] arrived at similar conclusions during their study on fluoride, boron, and nitrate removal from model solutions contaminated with single ions and mixture of ions. The authors proved that the ion retention varied according to the hydrated ionic radius – the more hydrated was the ion, the more difficult was transported through the NF membrane. In addition, the decreased anion retention was observed during NF of salt mixtures due to the screening effect induced by cations (mainly sodium cations). In this study the fluoride separation (from solutions containing 3 mg F^-/dm^3) varied with pH and exceeded 87% for pH higher than 7.

Although the NF membranes can be recognized as selective in nature, their selectivity can be enhanced significantly by deposition of polyelectrolyte multilayers (PEMs) as a skin on the NF composite membranes. Hong et al. [34] used PEM-NF membranes for separation of fluoride from other monovalent ions. The applied membranes enabled fluoride rejection by 73.1%, whereas chloride was retained by 9.5% only. It was concluded that separation among the monovalent ions was based on the Stokes radius. It is worth noting that due to minimal thickness of PEMs, these NF membranes have good permeability (typically from 62.5 to 125 $dm^3/m^2 h$ at 0.48 MPa).

Nanofiltration has been applied to water defluoridation with promising results on a pilot scale by Pontie et al. [35]. Brackish groundwater from Tan Tan city (Morocco) containing 1.1 mg F^-/dm^3 was treated by NF90 membranes. Moreover, the fluoride content was artificially increased to 5, 10, and 15 mg F^-/dm^3 . Regardless of the treated water composition, the final concentration of fluoride was lowered below the WHO permissible limit of 1.5 mg F^-/dm^3 . The strict Moroccan standards for drinking water (0.7–1.5 mg F^-/dm^3) were also fulfilled. The study demonstrated that NF exhibited specific advantages for fluoride

removal as compared to RO (i.e., partial reduction of total salinity, low operating pressure, and high water flux).

The importance of cost estimation, especially for advanced technologies such as membrane processes, is indisputable. Elazhar et al. [36] carried out an economical evaluation of fluoride removal by NF process. The calculation was made for a plant having a capacity of 100 m^3/h . It was pre-assumed that the water recovery rate was equal to 84%, whereas the fluoride retention reached 97.8% at the initial F^- ion concentration of 2.32 mg F^-/dm^3 and operating pressure equal to 1 MPa. The water pre-treatment stage comprised of two sand filters. After filtration water was directed to the NF unit consisted of 10 pressure tubes containing 70 Film-Tec spiral wound membranes. The post-treatment stage involved remineralization. The capital cost was calculated as 748 003 €, whereas the operating cost was established at 0.212 €/m³.

Data given above are summarized in Table 1.

On the grounds of the above literature review, it can be stated that nanofiltration offers good prospects for fluoride removal, especially from water of low salt content. However, there are still some problems that need to be solved (for example, poor retention rates of fluoride as well as flux decline when solutions containing high amounts of fluoride and coexisting ions are treated). The precipitation of divalent salts causing membrane blockage seems to be one of the important NF shortcoming. Thus, it is worth investigating the NF membrane behavior when only monovalent salts are present in the feed. The possible beneficial results in view of the NF efficiency could be a recommendation for divalent salt removal prior to the fluoride separation. Therefore, the presented study aimed at the evaluation of fluoride removal by nanofiltration for drinking water purpose, that is, to reach the F^- ion concentration in the permeate below 1.5 mg F^-/dm^3 (according to the WHO guidelines [2]). Model solutions containing monovalent sodium salts (NaF and $NaNO_3$) at both low and high fluoride concentrations in the feed were used in the study. Considering the possible energy savings, the loose NF membranes of rather high cut-off values (500–1,400 Da) were examined. The applied NF membranes can operate

Table 1
Nanofiltration performances in fluoride removal from water

Membrane type	Initial fluoride concentration	Fluoride content in permeate	Reference
NF400, NF90	1.8, 5, 10, and 20 mg F^-/dm^3	0.9–2.78 mg F^-/dm^3 with the NF400 membrane usage, and 0.07–0.09 mg F^-/dm^3 with the NF90 membrane usage	Tahaikt et al. [29]
NF90, NF270	5–20 mg F^-/dm^3 + 100–400 mg NO_3^-/dm^3	Fluoride content in the permeate did not exceed 1.5 mg F^-/dm^3 with NF270 usage and 0.5 mg F^-/dm^3 with NF90 usage	Hoinkis et al. [30]
Flat polyester NF membranes (Alfa Naval)	15 mg F^-/dm^3	1.7 mg F^-/dm^3	Ayala et al. [31]
NF5 and NF9	5–50 mg F^-/dm^3	1.26–21.7 and 0.39–3.10 mg F^-/dm^3 for NF5 and NF9 membrane, respectively	Ben Nasr et al. [32]
NF90	5, 10 and 15 mg F^-/dm^3	For each concentration permeate concentration did not exceed 1.5 mg F^-/dm^3	Pontie et al. [35]

under a low transmembrane pressure (0.3 MPa) unlike the commonly used tight NF membranes, which need a pressure of 1 MPa at least. Most of already published papers deal with tight NF membranes for water defluoridation experiments (Table 1). The effect of monovalent salt presence in the feed solutions on the membrane flux and the relative permeability was also verified.

2. Methodology and equipment

2.1. Installation

In the nanofiltration process of fluoride removal the Amicon 8400 UF/NF cell was used. The filtration device operated in a dead-end mode. The overall volume of the cell amounted to 350 cm³. During the experiments the volume of treated solution was also equal to 350 cm³. The membranes being tested had a diameter of 76 mm. The NF process was performed under the transmembrane pressure of 0.3 MPa, which was generated by nitrogen coming out from a gas cylinder. The fluoride model solutions were continuously mixed with a magnetic stirrer. In order to maintain a constant concentration of the feed solution, the permeate was recirculated periodically. The used installation is presented in Fig. 1.

2.2. Membranes

Commercially available NF membranes made of polyethersulfone, NP010P and NP030P (Microdyn-Nadir[®]) were used in the experiments. These membranes are characterised by a rather high molecular weight cut-off (>500 Da) and can be recognized as a “loose” NF membranes. The Microdyn-Nadir[®] membranes are cast on a porous polypropylene/polyethylene support and the membrane thickness varies from 210 to 250 μm. The used membranes differed in the rejection of divalent salt as well as in pore size. The membrane active surface area was equal to 0.0045 m². The characteristics of the investigated membranes is given in Table 2.

2.3. Reagents

The experiments were performed with the use of model solutions prepared by dissolving appropriate amounts of sodium fluoride (NaF, molar mass 41.99 g/mol) and/or sodium nitrate (NaNO₃, molar mass 84.99 g/mol) in distilled water. Both reagents were obtained from Chempur (Poland). The concentration of fluoride in the treated solutions was equal to 5, 15, and 100 mg F⁻/dm³, whereas the nitrate concentration in the model solutions amounted to

30, 60, and 90 mg NO₃⁻/dm³. The pH of the treated solutions was close to the pH of natural water, that is, 6–7. Due to common occurrence in the environment, nitrate was chosen as the coexisting ion in fluoride solutions. The applied concentration range of fluoride and nitrate ions was characteristic for some specific natural waters [8,40].

2.4. Methodology

All NF experiments were performed at the transmembrane pressure of 0.3 MPa and at a room temperature. Before experiments the examined membranes were pre-treated with distilled water until the constant permeate volume flux was established. Generally, a steady water flux for a fresh/cleaned membrane was established after 2–3 h of transmembrane pressure operation. In the course of the NF process with model solutions the membrane permeability was monitored every 10 min. The permeate volume fluxes and the quality of permeate were determined after the steady conditions of flow were settled (approximately, after 1 h of operation). All measurements were made in triplicate and the average values of fluxes and ion concentrations were considered in the discussion of the obtained results.

During the experiments the fluoride and nitrate concentration in the feed and permeate were monitored. The content of fluoride ions was determined by the colorimetric method with the SPADNS reagent (method no. 8029, the program no. 190). A wavelength of 580 nm was applied. The SPADNS reagent contains zirconium dye

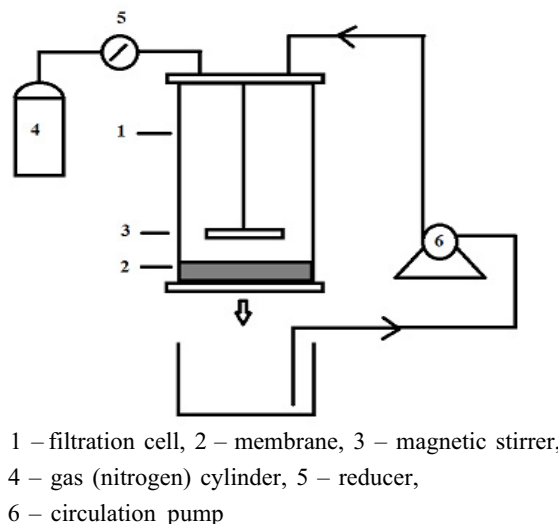


Fig. 1. Scheme of the dead-end stirred filtration cell.

Table 2
Characteristics of Microdyn-Nadir[®] membranes [37,38]

Symbol	Membrane material	Cut-off, Da	pH range	Max. temp., °C	Surface charge	Mean pore width ^a , nm	Water flux ^b , dm ³ /m ² h	Na ₂ SO ₄ rejection ^b , %
NP010P	Polyethersulfone	1,040–1,400	0–14	95	Negative	25.6	>200	35–75
NP030P		520–700			Negative	11.7	>40	80–95

^aDerived from isothermal N₂ physisorption and calculated using the Barrett–Joyner–Halenda pore model [39];

^bTest conditions: 4 MPa, 20°C, stirred cell (700 rpm).

which generates colorless complexes with fluoride. As the result, the less color of the sample, the more fluoride ions are present in the examined aqueous solution. The measurements were performed with the use of the spectrophotometer Hach DR3900 (Hach, USA). The accuracy of the method was established as $\pm 9\%$.

The nitrate concentration was analysed by a colorimetric method with NitraVer 5 reagent. A spectrophotometer Hach DR2900 was used for nitrate analyses at a wavelength of 500 nm (method no. 8039, the program no. 355). The method accuracy amounted to $\pm 5\%$.

After each series of the NF experiments the membranes were cleaned with NaOH solution (0.1 mol/dm^3) for 10 min to restore the original properties of the membrane.

The permeate volume flux was calculated according to the equation:

$$J = \frac{V}{A \cdot t}, \text{ dm}^3/\text{m}^2\text{h} \quad (1)$$

where J – permeate volume flux ($\text{dm}^3/\text{m}^2 \text{ h}$), V – volume of permeate (dm^3), t – time (h), A – surface area of the membrane (m^2).

The relative permeability, which is a measure of membrane sensibility to fouling, was calculated as the ratio J/J_0 , where: J – permeate volume flux ($\text{dm}^3/\text{m}^2 \text{ h}$) and J_0 – distilled water volume flux ($\text{dm}^3/\text{m}^2 \text{ h}$).

3. Results

3.1. Fluoride separation

The main aim of the reported study was the evaluation of fluoride separation by NF polyethersulfone membranes from model solutions, especially containing the

elevated fluoride amounts. Nitrate was chosen as the coexisting ion in the fluoride solutions. The variation of fluoride concentration in the permeate after NF treatment of solutions containing only fluoride (5, 15, and $100 \text{ mg F}^-/\text{dm}^3$) and both fluoride and nitrate ions ($30, 60,$ and $90 \text{ mg NO}_3^-/\text{dm}^3$) is presented in Fig. 2.

When the treated solutions contained $5 \text{ mg F}^-/\text{dm}^3$ and $5 \text{ mg F}^-/\text{dm}^3 + 30 \text{ mg NO}_3^-/\text{dm}^3$, it was possible to decrease the fluoride content in the permeate below the permissible limit of $1.5 \text{ mg F}^-/\text{dm}^3$, however merely for the NP030P membrane (Fig. 2a). In these cases the content of F^- ion in the permeate reached 1.15 and $1.35 \text{ mg F}^-/\text{dm}^3$, respectively. In the NF experiments with solutions of the increased fluoride concentration ($15 \text{ mg F}^-/\text{dm}^3$) the F^- content in the permeate significantly exceeded the recommended level, irrespectively of the nitrate concentration in the feed. The F^- ion concentration in the permeate amounted to 7.8 – 13.5 and 5.3 – $10.2 \text{ mg F}^-/\text{dm}^3$ for NP010P and NP030P membrane, respectively (Fig. 2b). The NF series performed with the model solutions of the highest fluoride concentration ($100 \text{ mg F}^-/\text{dm}^3$) arrived at rather poor rejection – the fluoride content was lowered merely to 49 and $66 \text{ mg F}^-/\text{dm}^3$ with the use of NP030P and NP010P membrane, respectively (Fig. 2c). Generally, the increase in the initial fluoride concentration brought about the worsening of fluoride separation efficiency. Clarifying this relationship, it should be noted that the increase in fluoride amount in the feed was accompanied by the augmented sodium concentration. These sodium cations neutralize the negative sites of the NF membrane and the repulsive forces between the membrane and the fluoride anions are therefore diminished. This brings about a facilitated transport of fluoride ions to the permeate.

The influence of nitrate presence in the treated solutions on the efficiency of fluoride rejection was quite

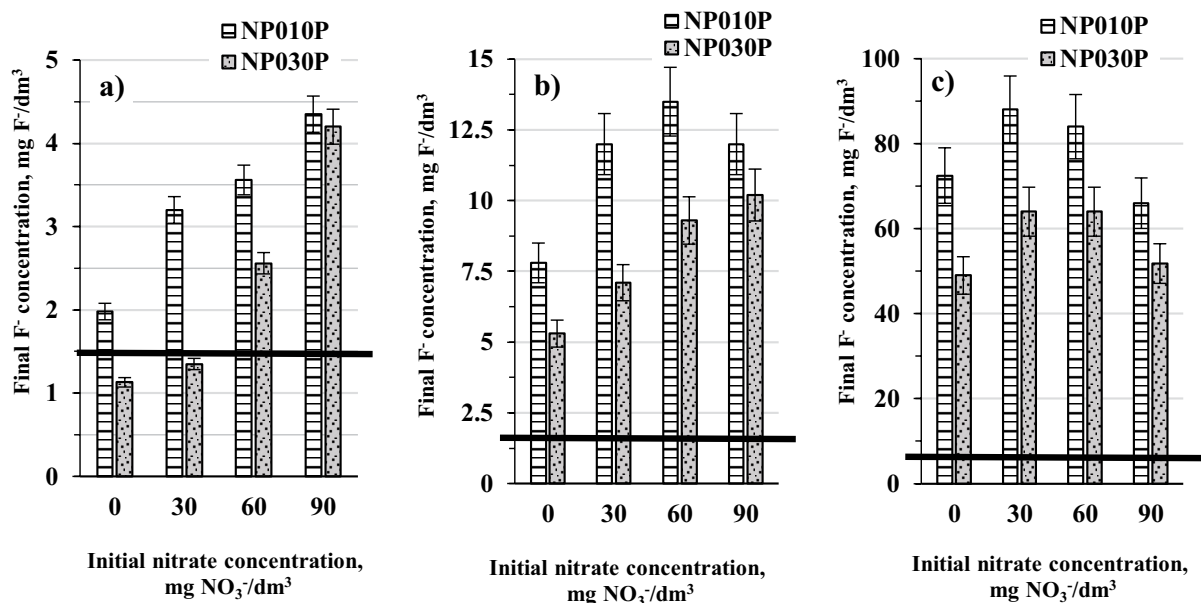


Fig. 2. Fluoride concentration in the permeate after NF process performed with NP010P and NP030P membranes vs. nitrate concentration in the feed; (a) $C_0 = 5 \text{ mg F}^-/\text{dm}^3 + \text{NO}_3^-$, (b) $C_0 = 15 \text{ mg F}^-/\text{dm}^3 + \text{NO}_3^-$, and (c) $C_0 = 100 \text{ mg F}^-/\text{dm}^3 + \text{NO}_3^-$; $\Delta p = 0.3 \text{ MPa}$, error bars $\pm 9\%$, with marked permissible concentration $1.5 \text{ mg F}^-/\text{dm}^3$.

evident. The addition of nitrate ions to model solutions led to the deterioration of the permeate quality in view of the fluoride concentration (compared to the permeate quality for NF series with solutions containing only fluoride). What is more, the increase of nitrate concentration up to 60 mg $\text{NO}_3^-/\text{dm}^3$ caused the increase of the fluoride content in the permeate for the NF series performed with solutions containing low and moderate fluoride amounts (i.e., 5 and 15 mg F^-/dm^3) (Fig. 2a and b). In the presence of nitrate ions, it was possible to decrease the F^- ion content below the permissible concentration in drinking water (i.e., below 1.5 mg F^-/dm^3) only for the solution containing 5 mg F^-/dm^3 and 30 mg $\text{NO}_3^-/\text{dm}^3$. In this case the fluoride concentration in the permeate amounted to 1.35 mg F^-/dm^3 on condition that the NP030P membrane was applied. Hence, the “loose-tight” membrane can be recommended for drinking water treatment only at feed concentration below 5 mg F^-/dm^3 and below 30 mg $\text{NO}_3^-/\text{dm}^3$. The negative effect of nitrate on fluoride separation can be explained by the shielding effect – by increasing the nitrate content in the feed, the number of associated cations (Na^+) is also increased. The sodium ions (as the counter-ions) neutralize the negative membrane charges. The repulsive forces between the membrane and the anions present in the solution are, therefore, diminished, leading finally to the deterioration of fluoride rejection [41].

It is worth noting that in the course of the NF series performed with solutions of the highest initial fluoride concentration and the elevated concentrations of NO_3^- ions (60 and 90 mg $\text{NO}_3^-/\text{dm}^3$) (Fig. 2c), the tested membranes behaved differently from the NF series conducted with low and moderate fluoride concentration in the feed – the fluoride content in the permeate slightly decreased when the nitrate concentration increased to 60 and 90 mg $\text{NO}_3^-/\text{dm}^3$. This relationship was especially noticeable for the NP010P membrane. In this case the initial amount of sodium cations in the feed was extremely high (due to high concentration of NaF salt), which was augmented by the consecutive addition of NaNO_3 salt. As it was already mentioned, the Na^+ cations interact with the membrane and reduce the negative charge of the membrane. Possible, this will also result in the suppression of the electrostatic repulsion between the negatively charged sites within the membrane structure. Therefore, the pores of the membrane can be compressed in a narrower size, which can improve the rejection of fluoride ions [42].

Comparison of the membrane properties indicated that the NP030P membrane exhibited better rejection of fluoride ions than the rejection obtained by the NP010P membrane. This finding can be explained by the membrane pore size – the NP030P membrane is characterized by a smaller pore width than the pore size determined for the NP010P membrane (Table 2).

Generally, the electrostatic repulsion forces between charged membrane sites and ions is the main mechanism of separation by nanofiltration membranes. However, when the concentration of counter-ions in the feed is increased, the shielding effect occurs and the convective transport could be dominant. Hence, the pore size of membrane can play a significant role in ion separation. This is supported by the comparison of nitrate and fluoride separation efficiency

(Figs. 2 and 3) and the ion hydration energy. Due to lower hydration enthalpy (329 kJ/mol) of nitrate than the hydration enthalpy of fluoride (519 kJ/mol), the NO_3^- ions can migrate more easily than fluoride ions [30] (Chapter 3.2).

3.2. Nitrate separation

Similarly to the drinking water standards established for fluoride ion, the nitrate presence in drinking water is also limited to a certain concentration level (50 mg $\text{NO}_3^-/\text{dm}^3$). Therefore, the separation efficiency of nitrate by the NF membranes was certainly worth investigating. The variability of nitrate concentration in the permeate after NF treatment of solutions containing only nitrate (30, 60, and 90 mg $\text{NO}_3^-/\text{dm}^3$) and both nitrate and fluoride ions (5, 15, and 100 mg F^-/dm^3) is presented in Fig. 3.

At the lowest nitrate concentration in the tested solutions nanofiltration allowed to decrease nitrate content from 30 to 22.5–27.7 mg $\text{NO}_3^-/\text{dm}^3$ depending on the membrane type and fluoride concentration (Fig. 3a). During the NF series performed with solutions containing moderate nitrate amounts (60 mg $\text{NO}_3^-/\text{dm}^3$), the nitrate content in the permeate reached 46.2–58.1 mg $\text{NO}_3^-/\text{dm}^3$ (Fig. 3b). The NF tests with the highest nitrate concentration (90 mg $\text{NO}_3^-/\text{dm}^3$) resulted in the permeates containing 66.9–87.3 mg $\text{NO}_3^-/\text{dm}^3$ (Fig. 3c). Overall, the nitrate rejection by the applied NF membranes was quite poor (below 30%), what should not be a surprise, as the NO_3^- ion is a monovalent ion of a rather low hydrated radius (0.335 nm) [33]. Besides, the unsatisfactory results of nitrate separation can be attributed to the shielding effect of membrane charge by sodium cations (as it was explained in the Chapter 3.1 for fluoride separation). Abidi et al. [43], while investigating the rejection of phosphate ions by NF membranes, arrived at the similar conclusion – a high concentration of salt in the treated solutions was associated with a high number of counter ions (Na^+), which neutralized the negative membrane charges, and therefore the repulsion forces between the nitrate anions and the charged membrane sites were inhibited. However, the impact of fluoride on nitrate removal was rather insignificant – merely, for the NF tests performed with the lowest nitrate concentration in the feed (30 mg $\text{NO}_3^-/\text{dm}^3$), a slight deterioration of permeate quality in view of the nitrate content in the presence of fluoride ion was observed (compared to the permeate quality for NF series with solutions containing only nitrate) (Fig. 3a).

Analyzing the results given in Fig. 3, it can be stated that among the two membranes tested, the NP030P membrane exhibits better separation properties, irrespectively of the nitrate and fluoride concentration in the feed. This statement is in agreement with the results reported for fluoride separation (Fig. 2) and is correlated with the pore size of the tested membranes (Table 2).

Comparing the results given in Figs. 2 and 3, it is evident that fluoride ions are retained significantly better than the nitrate ions – in the case of fluoride ions the maximal percentage of rejection reaches even 77.4% (for solutions containing 5 mg F^-/dm^3), whereas for nitrate ions the highest degree of separation is only 31%. This difference in retention between F^- and NO_3^- ions can be attributed to the disparity in the molecular size of the analyzed ions. The F^- ion is

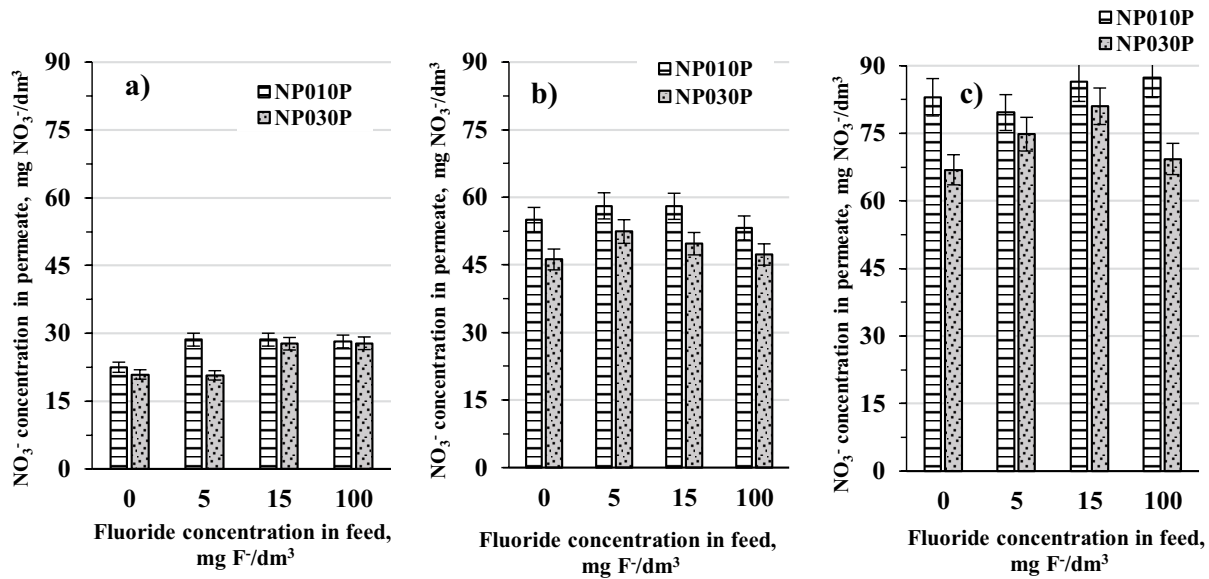


Fig. 3. Nitrate concentration in the permeate after NF process performed with NP010P and NP030P membranes vs. fluoride concentration in the feed; (a) 30 mg NO₃⁻/dm³ + F⁻, (b) 60 mg NO₃⁻/dm³ + F⁻, and (c) 90 mg NO₃⁻/dm³ + F⁻; $\Delta p = 0.3$ MPa; error bars $\pm 5\%$.

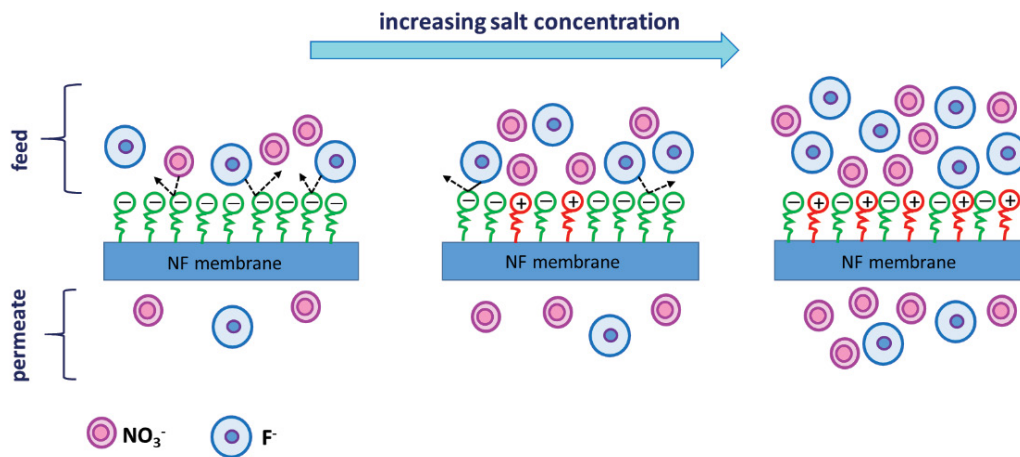


Fig. 4. Salt concentration effect on fluoride and nitrate separation by NF membrane.

a very small ion (with crystal radius of 0.135 nm), however it is characterized by a high charge density. Therefore, the fluoride ion is strongly hydrated and has a larger hydrated radius (0.352 nm) compared to the hydrated radius of the nitrate ion (0.335 nm) [33]. As a consequence, due to steric exclusion, fluoride is more strongly retained by the NF membranes than nitrate. This approach is consistent with the observations made by other researchers. Richards et al. [33] as well as Ma et al. [44] proved that the ion retention varied according to the hydrated ionic radius – the more hydrated was the ion, the more difficult was transported through the NF membrane. Similarly, Ben Nasr et al. [32] found that F⁻ ions were better retained than Cl⁻ ions, because fluoride ions were more solvated than chloride ions.

Generally, when sodium nitrate and sodium fluoride were added together, nitrate ions rather than fluoride ions permeated through the membranes to match the sodium

ions in the permeate, regardless of the fluoride concentration in the feed (Fig. 3).

The concept of fluoride and nitrate ions rejection by NF membrane is presented in Fig. 4. This concept involves the already discussed phenomena, that is, shielding effect due to increasing concentration of cations in the feed as well as the difference in the ion hydration.

3.3. Permeate flux

The membrane permeability, besides the rejection rate, is of key significance for practical application of nanofiltration. Thus, simultaneously with the evaluation of the membrane separation properties, the permeate flux (J) was determined (according to Eq. (1)). The mean values of permeate volume fluxes for the tested membranes are given in Fig. 5. The NF tests were performed with solutions containing only

fluoride ions (5, 15, and 100 mg F/dm³) as well as fluoride and nitrate (30, 60, and 90 mg NO₃⁻/dm³) mixtures. The mean water flux for each membrane was also placed in Fig. 5 for comparison purpose.

Prior to the NF tests aiming on the evaluation of the fluoride and nitrate separation rates, the pure water volume flux was determined for each membrane. The calculated water flux was equal to 2.96×10^{-5} and 0.79×10^{-5} dm³/m² h for the NP010P and NP030P membrane, respectively. The revealed membrane permeability was in accordance with the determined membrane pore size (Table 2). Generally, the NP010P membrane can be recognized as a “loose” membrane, whereas the NP030P membrane has a feature of a “tight” membrane (to be precise, “loose tight” membrane, as its cut-off is higher than the cut-off of commonly known “tight” NF membranes).

The NF experiments conducted with the contaminated solutions showed more or less permeate flux decline in comparison to the water flux. For both membranes it was found that with the increasing salt concentration in the feed, the drop in permeability was more pronounced. However, the differences between the pure water flux and the F/NO₃⁻ solution flux were comparable for both applied membranes, especially for the NF series performed with solutions containing (besides nitrate) 15 and 100 mg F/dm³ in the feed (Figs. 5b, c, and 6b, c). The permeability of the NP030P membrane declined from 0.79×10^{-5} dm³/m² h (water) to $0.38\text{--}0.75 \times 10^{-5}$ dm³/m² h (nitrate and 15 mg F/dm³) and to 0.29×10^{-5} dm³/m² h (nitrate and 100 mg F/dm³). For the NP010P membrane the decrease in the permeate flux was as follows: from 2.96×10^{-5} dm³/m² h (water) to $1.33\text{--}2.83 \times 10^{-5}$ dm³/m² h (nitrate and 15 mg F/dm³) and to 1.42×10^{-5} dm³/m² h (nitrate and 100 mg F/dm³). Merely in the case of the NF process performed with solutions of the lowest salt content (Figs. 5a and 6a), it seemed that the NP030P membrane was less vulnerable to block by ions present in the feed, than the NP010P membrane. It is worth

noting that both tested membranes exhibited rather low permeate flux decline (in comparison to the water flux) when only fluoride were present in the feed.

The problem of flux decline in pressure membrane processes has been intensively researched and described in literature. In general, this problem (also in nanofiltration) is correlated with such adverse phenomena as membrane fouling and concentration polarization. The nature of fouling and its intensity depends on the membrane characteristics, as well as solute-solute and membrane-solute interactions. Some other process parameters (flow, pressure, temperature) can also contribute to membrane fouling. The course of concentration polarization and its side effects depends mainly on the feed concentration, applied transmembrane pressure, and flow velocity. The concentration polarization, which is considered as a reversible and time independent process, occurs in any selective mass transport, also in nanofiltration.

According to a study made by Silva [25], the variation of flux with time in the nanofiltration process can be described by three various stages. In the first stage a significant and sudden drop in flux occurs. This phenomenon is caused by a concentration polarization of solutes on the membrane surface and is reversible. In the next stage the flux decline is rather gentle and the accumulated solutes begin to precipitate. Consequently, the membrane pores are blocked and some solution components are adsorbed inside the membrane. Finally, the polarization layer and membrane incrustation appears, as irreversible processes. In the last stage the membrane flux, due to consolidation of incrustation, decreases slowly and continuously.

Considering the composition of the feed solutions (only monovalent salts) involved in this study, it is rather difficult to adopt the above description as an explanation of the observed permeate flux decline. It is more likely that the increase in osmotic pressure contributed to the diminishing of membrane permeability with the increase in feed salinity. What more, the osmotic pressure of the retentate may raise

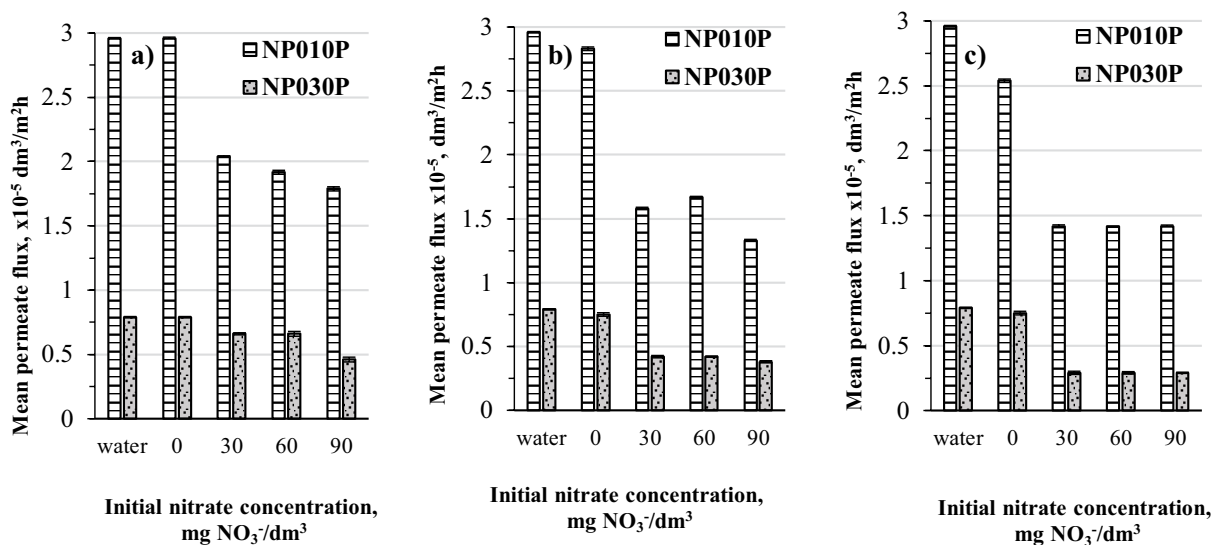


Fig. 5. Permeate flux for NP010P and NP030P membranes during the NF process performed with fluoride and nitrate containing solutions; (a) 5 mg F/dm³ + NO₃⁻, (b) 15 mg F/dm³ + NO₃⁻, and (c) 100 mg F/dm³ + NO₃⁻; $\Delta p = 0.3$ MPa (with marked standard deviation).

with process time due to the concentration polarization phenomenon. The osmotic pressure evaluated for the applied binary feed solutions was in the range of 0.005–0.03 MPa, thus it seems reasonable that the decrease in driving force (the transmembrane pressure difference) was the reason of the observed flux decline. On the other hand, the interactions between the solutes and membranes, as well as changes in solution viscosity cannot be neglected. As it was already mentioned, sodium cations, due to shielding effect, can influence the membrane pore size, thus increasing the membrane resistance to permeate flow. Nyström et al. [45] during their study on nanofiltration membrane fouling, arrived at similar conclusions. However, the authors emphasized that the adsorption of solutes in the NF membrane pores may not necessarily cause the flux decrease – some solutes can interact with membrane material creating additional free volumes in membrane matrix, and thus increasing the permeate flux. On the other hand, Park et al. [46] showed that the reduction of pore size in the NF membranes was induced by the polymer matrix compaction at a high ionic strength of the tested solutions.

It was also proved by Nyström et al. [45] that most of the mineral salts did not foul the examined NF membranes, with the exception of some salts, which precipitated at the specific solution pH. The formation of a gel layer was also detected by the study of Nyström et al. [45], however this was a symbiotic effect of salt and organic substance, which were present in salt solution. Therefore, the results reported in this paper clearly indicate that the observed permeate flux decline is the effect of the osmotic pressure increase, concentration polarization as well as pore size variation, due to the shielding effect of membrane charge by sodium cations.

3.4. Relative permeability

The relative permeability is a parameter, which enables evaluation of the intensity of flux decrease (in comparison to water flux for a fresh membrane) due to the membrane

fouling, concentration polarization and/or some other phenomena that can occur during the pressure membrane processes. The relative permeability was estimated for the NP010P and NP030P membranes when solutions containing only fluoride ions (5, 15, and 100 mg F/dm³) as well as fluoride and nitrate (30, 60, and 90 mg NO₃⁻/dm³) mixtures were subjected to the NF tests. The calculated values of the relative permeability are given in Fig. 6 and they are simply the reflection of the permeate flux shown in Fig. 5.

As it was already mentioned, the permeate flux decrease (in comparison to the water flux) was rather insignificant when only fluoride ions were present in the tested solutions and, therefore, the relative permeability was in the range of 0.85–1.0 for both tested membranes. In the course of the NF tests performed for solutions containing nitrate and the lowest fluoride amount (Fig. 6a) the flux decline was rather low for the NP030P membrane and the relative permeability amounted to 0.58–0.84, whereas the NP010P membrane exhibited greater flux decrease and the relative permeability was lower (0.61–0.69). The increase in salt content caused a significant worsening of solution permeability for both membranes resulting in the relative permeability values as follows: 0.45–0.56 (nitrate + 15 mg F/dm³), and 0.37–0.48 (nitrate + 100 mg F/dm³) (Fig. 6b and c).

Although the tested membranes varied in the pore size significantly (Table 2), their behavior in the NF of fluoride/nitrate solutions is ambiguous. When the tested solutions contained low salt amount, the greater flux decrease was observed for the “loose” NP010P membrane than for the NP030P membrane, indicating that changes of pore size, due to the facilitate solute-membrane interactions, were dominant for the NP010P membrane. On the contrary, when the tested solutions contained high salt amount, a slightly greater flux decrease was observed for the “tight” NP030P membrane than for the NP010P membrane, indicating that in this case the osmotic pressure effect (induced by the concentration polarization) was dominant for the NP030P membrane.

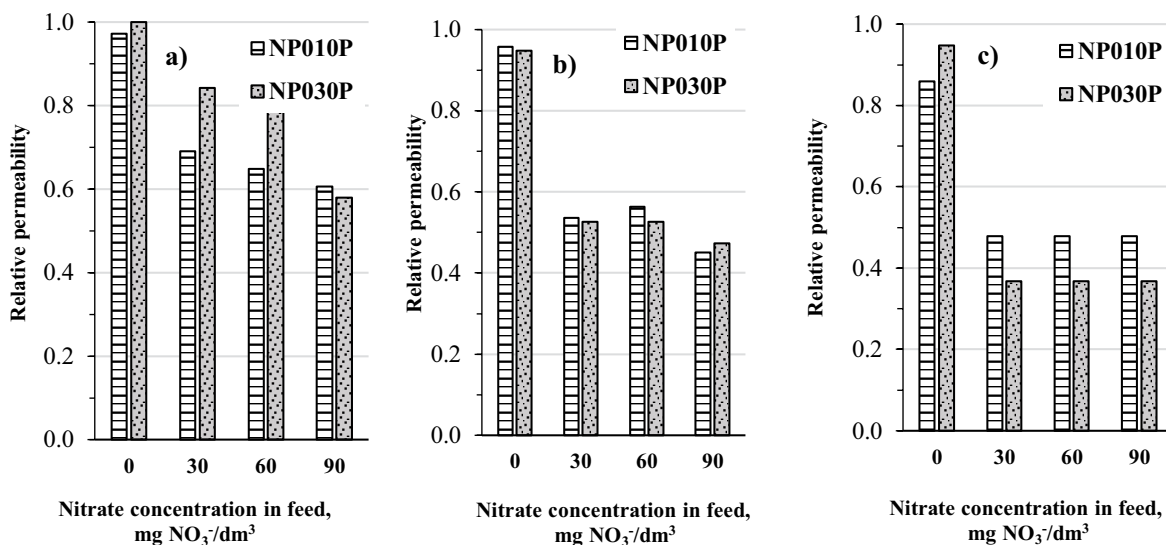


Fig. 6. Relative permeability for NP010P and NP030P membranes during the NF process performed with fluoride and nitrate containing solutions; (a) 5 mg F⁻/dm³ + NO₃⁻, (b) 15 mg F⁻/dm³ + NO₃⁻, and (c) 100 mg F⁻/dm³ + NO₃⁻; $\Delta p = 0.3$ MPa.

The observed differences between the water flux through a fresh membrane and the permeate flux for contaminated feed solutions can be recognized as a rather significant disparities. Similar values of the relative permeability (0.33–0.76) were obtained by Koyuncu et al. [47] during the NF tests of single model solutions, however the salt (NaCl) concentration was much higher than the fluoride and nitrate salt concentrations applied in this study and varied from 1 to even 80 g/dm³. Park et al. [46] found that the relative permeability is correlated with membrane separation properties. They performed the nanofiltration experiments using the NF membranes of high and low salt retention, which exhibited the relative permeability in the range of 0.45–0.95 and 0.75–0.95, respectively. The authors confirmed that the permeate flux decreased dramatically with increasing salt (NaCl) concentration from 0.5 to 5 g/dm³. In the both mentioned research [46,47] the decrease in the transmembrane pressure difference, as a consequence of the increase in osmotic pressure of the feed/retentate was the explanation of the noted flux decline. It is clear that the values of the relative permeability obtained in this study are in fact much adverse than those reported by Koyuncu et al. [47] and Park et al. [46], when the salt concentration in the tested solutions is considered. This can be simply explained by the different NF process mode – the dead-end mode was applied in this study, whereas cross-flow mode was used in the cited papers. It is well known that the cross-flow mode in the pressure membrane processes is more beneficial for the overall process efficiency than the dead-end system.

It should be also emphasized that in a real membrane system a serious fouling is caused, for example, by organic dyes or humic substances and the values of the relative permeability can be as low as 0.1–0.2 [47,48].

4. Conclusions

Nanofiltration process can be potentially applied for the removal of fluoride from aqueous solutions containing monovalent salts. However, the NF performance notably depends on the salt concentration in the feed, and therefore the permissible limit of 1.5 mg F⁻/dm³ (according to the WHO guidelines for drinking water) can be achieved when the fluoride and nitrate concentrations are below 5 mg F⁻/dm³ and 30 mg NO₃⁻/dm³, respectively.

The fluoride ion was significantly better retained by the NF membranes than the nitrate ion – the maximal rejection of the F⁻ ion reached 77.4%, whereas for the NO₃⁻ ion the highest degree of separation was only 31%. This finding can be explained by a larger hydrated radius of the F⁻ ion compared to the hydrated radius of the NO₃⁻ ion. As a consequence, due to the steric exclusion, fluoride is more strongly retained by the NF membranes than nitrate. Consistently, the tight NF membranes should be recommended for water defluoridation by nanofiltration.

The fluoride and nitrate rejection in the NF process is enhanced by the electrostatic repulsion between the anions and the negatively charged sites within the membrane. However, with the increasing ionic strength of the feed, this repulsion force is weakened due to shielding of the negative membrane charge by the sodium cations. Therefore,

the worsening of the permeate quality is observed for the elevated salt concentration in the feed.

Although the NF defluoridation was performed for solutions containing only monovalent salts, the observed relative permeability was in the range of 0.37–1.0. With the increasing salt concentration in the feed, the permeate flux was decreasing. The flux decline (in comparison to pure water flux) is the effect of the osmotic pressure increase, concentration polarization phenomenon as well as pore size variation, due to shielding effect of membrane charge by sodium cations.

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