



Nanofiltration usage for fluoride removal in the sodium chloride presence

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Abstract: Fluorine and sodium chloride are common elements present in the water environment. According to WHO guidelines fluoride content in water cannot be not higher than $1.5 \text{ mgF}^{\text{-}}/\text{dm}^3$. Elevated fluoride content was observed all over the world and it leads to many health issues. It can be removed with the usage of various methods (ion exchange, membrane processes, adsorption, precipitation). In this paper fluoride removal with nanofiltration usage was described. Tests were performed with the application of Amicon 86400 filtration cells. Two types of commercial nanofiltration membranes NP010P and NP030P (Microdyn Nadir) were used. Transmembrane pressure was established as 0.3 MPa. For lower fluoride concentrations ($5 \text{ mgF}^{\text{-}}/\text{dm}^3$) NF process allowed to decrease fluoride content under level $1.5 \text{ mgF}^{\text{-}}/\text{dm}^3$. Removal efficiency decreased with increasing fluoride content. Membrane NP030P showed better separation properties. Sodium chloride influenced removal efficiency as well as fluoride adsorption on/in membranes during the process. According to obtained data, better hydraulic properties exhibited membrane NP010P. For both membranes decrease in permeate flux in comparison to pure water was noticed what was observed. Relative permeability was lowered even to 0.32.

Introduction

Fluorine is a natural element that commonly occurs all over the World. It states about 0.08% of Earth's crust. It can be easily soluble in water. It is known as the most reactive element (Akuno et al. 2019). According to World Health Organization standards fluoride content in water cannot be higher than $1.5 \text{ mgF}^{\text{-}}/\text{dm}^3$ (WHO 2017). Elevated fluoride content in water is a common problem. It was noticed in China, Ethiopia, Tanzania, Germany, Vietnam, Mexico, Brazil, Pakistan, Germany, Sri Lanka, or USA (Shen and Schäfer 2014, Ali et al. 2015). In Tanzania fluoride content in water reached up to $350 \text{ mgF}^{\text{-}}/\text{dm}^3$ (Shen and Schäfer 2014). It was estimated that about 200 million people consume water with excessive fluoride content (Shen and Schäfer 2015). Fluoride can be weathered from minerals like fluoroapatite or vermiculite. Especially, groundwaters contain high amounts of fluoride (which is determined by geological conditions) (Akuno et al. 2019). Wastewater from electroplating, pesticides, glass, or toothpaste productions releases fluoride into the environment (Ali et al. 2015, Vinati et al. 2015). In effluent from phosphate production fluoride content amounted to $3000 \text{ mgF}^{\text{-}}/\text{dm}^3$ (Shen and Schäfer 2014). Fluoride is known as a toxic element that negatively impacts our health. Contaminated water is one of the main sources of human exposure (Vinati et al. 2015). In small concentrations, it protects against dental caries and is used in osteoporosis treatment (Szmagara and Krzyszczak 2019).

Excess of fluoride leads to problems with kidneys, endocrine gland, reproductive system, cancer, or liver (He et al. 2020). Common issue linked to excessive fluoride consumption is fluorosis – dental and skeleton and teeth mottling (brown stains) (Chatterjee 2014).

Various methods can be applied for fluoride removal – ion exchange, adsorption, electrocoagulation, or precipitation (Damtie et al. 2019, Bhatnagar et al. 2011). Membrane processes (nanofiltration, reverse osmosis, electrodialysis) became more popular. They allow obtaining high removal efficiency. Simultaneously, they reducing the problem with process residues. Also, additive chemicals are not required (Nasr et al. 2013, Shen and Schäfer 2014).

Sodium chloride is a common salt that is characterized by high solubility, 39% of this salt states sodium. It can be found in salt beds, seawater, and brines all over the World. In nature, it is rarely found in free form. Sodium chloride in a concentration higher than $180 \text{ mg}/\text{dm}^3$ gives water a salty taste (Steele 1966).

Shu et al. (2005) examined the possibility of reusing the salts and water from dyebaths. TFCCSR NF membrane was applied in the process. Solutions contained Reactive Black 5 (from 50 to $700 \text{ mg}/\text{dm}^3$) and NaCl ($10\text{--}80 \text{ g}/\text{dm}^3$). Prepared solutions were concentrated in the process course. 99.7% of dye and about 66.3% of NaCl were removed. Besides, increase in sodium chloride content (from 10 to $80 \text{ g}/\text{dm}^3$) led to NaCl retention efficiency deterioration (from 64.3 to 58%).

Kambarani et al. (2016) applied thin polymeric NF membranes (NE4040-90, CSM) for filtration of sodium chloride solution. Different NaCl content was examined – 0.1, 0.3, and 1% wt. The higher initial NaCl content the lower removal efficiency was obtained.

NaCl removal with the NF usage was also investigated by Krieg et al. (2004) NF90 and TFC-SR. Three membranes were examined – NF90, NF270, and TFC-SR. The working pressure was estimated as 2 MPa. Within a concentration range of 0–200 mgNaCl/dm³ salt content had a minor influence on membrane permeability. At higher concentrations (20–80 gNaCl/dm³) permeate flux decrease was noticed. NaCl removal reached 44–92%.

Mnif et al. (2010) performed experiments into fluoride removal in salt presence. Obtained results showed that fluoride removal was significantly affected by the recovery rate. 94.3 and 98.3% fluoride was separated when the recovery rate was equal to 70 and 10%, respectively. This dependence could be caused by polarization concentration. In the next step influence of ionic strength on fluoride separation was investigated. Various concentration of sodium chloride (between 0.01 and 0.02 M) was added to treated solutions. The higher NaCl content, the lower F⁻ separation was obtained. Also, fluoride separation efficiency in the terms of different concentrations was investigated. An increase in fluoride content was linked to fluoride removal deterioration – 90% and 99% for 10⁻¹ and 3·10⁻³ molF/dm³, respectively.

Tahaikt et al. (2007) for fluoride removal applied polyamide NF90 and NF400 membranes. Fluoride content in treated solution amounted to 1.8, 5, 10, and 20 mgF/dm³. Better separation efficiency exhibited membrane NF90. Retention efficiency decreased with increasing initial fluoride content. Fluoride content in permeate varied from 0.07 to 0.9 mgF/dm³ (membrane NF90) and from 0.9 to 2.788 mgF/dm³ (membrane NF400).

Hoinkis et al. (2011) conducted experiments into fluoride removal in the nitrate presence with the use of nanofiltration. Two commercial membranes NF90 and NF270 were examined. Membrane NF270 allowed to decrease fluoride content under desirable level 1.5 mgF/dm³ when initial content was not higher than 10 mgF/dm³. Membrane NF90 usage allowed to maintain F⁻ content under 0.5 mgF/dm³ when initial fluoride concentration was not higher than 20 mgF/dm³.

Ayala et al. (2018) also performed experiments into fluoride removal with nanofiltration application. Initial F⁻ content was established to 15 mgF/dm³. At the beginning of the process fluoride content decreased to 1.7 mgF/dm³ (removal efficiency equal to 89%). Fluoride separation was dependent on concentration factor (CF). Fluoride content in permeate amounted to 2.4 mgF/dm³ when the concentration factor reached 2. When CF was higher than 3, fluoride content in treated water exceeded 3 mgF/dm³. This observation can be attributed to concentration polarization phenomena, which is better seen in higher concentrations.

Thin-film composite polyamide nanofiltration membrane (HL1812T) was used by Ma et al. (2009). For fluoride content higher than 6 mgF/dm³ its content in permeate dropped to 1.2 mgF/dm³. The higher initial fluoride content the lower separation efficiency was observed. Temperature influence investigations showed that the fluoride rejection coefficient

was lower in higher temperatures. It was caused due to solution viscosity decrease in higher temperatures whereas simultaneously the diffusion coefficient increase.

Xi et al. (2014) performed research that examined fluoride removal with the NF usage. In the process, spiral wound membrane elements were applied (GE Inc, USA). The concentration of F⁻ was established as 4.01±0.02 mg/dm³. Treated water also contained arsenic in the amount of 156.4±0.23 µg/dm³. pH was close to natural (7.2). The calculated fluoride removal efficiency was in the range of 70–73%.

Richards et al. (2010) were removing fluoride from solutions containing nitrate and boron. Fluoride removal from single and mixed solutions was affected by pH value. At pH 3, for single feed F⁻ removal efficiency amounted to 5–65%. When pH increased to 12.5 removal efficiency was equal to 95–98%. For solutions containing a mixture of ions similar tendency was observed. Obtained results suggest that the steric effect influenced removal efficiency.

Diawara et al. (2015) used the nanofiltration process for fluoride removal from aqueous solutions. Fluoride content was established to 5 mgF/dm³. Treated solutions contained also sodium sulfate, sodium nitrate, and sodium chloride. The sulfate and chloride content amounted to 50–200 mg/dm³ and 450 mgCl/dm³, respectively. The pH varied between 6–8. During experiments membranes DESAL5 DL and MT08 were applied. Fluoride content was lowered about 83–90% whereas chloride rejection amounted to 69–85%. It was noticed that Cl⁻ ions presence decreased the defluoridation efficiency.

Epsztein et al. (2018) removed fluoride in the sodium chloride, sodium bromide and sodium nitrate presence from water solutions with the NF usage. Membrane NF270 was applied. The concentration of each compound amounted to 2 mM. Transmembrane pressure was equal to 5.5 bar. Obtained results showed that fluoride separation was pH dependent. In pH range within 5.5–6.5 fluoride rejection was higher than obtained for Cl⁻ and Br⁻ and it reached about 50%. Whereas in the pH lower than 3.5 fluoride was always removed less efficient than other ions.

Hong et al. (2007) applied multilayer polyelectrolyte NF membranes for fluoride removal in the anions presence. Membranes coated by polyelectrolyte films were used: poly(styrene sulfonate) (PSS), poly-(allylamine hydrochloride) (PAH), and poly(diallyldimethylammonium chloride) (PDADMAC). The support was made of porous alumina. Treated solutions contained NaF, NaCl, or NaBr. The concentration of each component amounted to 1mM. Applied pressure was equal to 4.8 bar. Fluoride rejection varied between 73.1–79.5%. Chloride separation was much lower and it reached 9.5–40.9%. Separation efficiency was highly dependent on film architecture and the number of layers in the film. Solution flux was in the range 3.5–3.4 m³/m²day. Results were compared to NF270 and NF90 commercial membranes. They allowed obtaining higher removal efficiencies (till 81.6% for Cl⁻ ions and 80.6% for fluoride). Simultaneously they have much lower permeability – 0.3 and 1.11 m³/m²day for NF90 and NF270 membrane, respectively.

Chibani et al. (2019) applied electrocoagulation for fluoride removal in the NaCl presence. Initial fluoride content amounted to 10 mgF/dm³. Various sodium chloride concentrations was

examined – from 0.1 to 0.7 gNaCl/dm³. The highest fluoride removal efficiency was observed when treated solutions contained 0.5 gNaCl/dm³. F⁻ removal efficiency varied from 54.68 to 88.65%. Energy consumption was calculated to 0.0360–0.0468 kWh/m³.

This paper aims to evaluate the separation mechanism of fluoride in the electrolyte (sodium chloride) presence. According to the literature overview fluoride contamination became a global problem and it was noticed all over the World. Exposure to excessive fluoride concentration results in many health problems and in every year more people are at risk of fluoride intoxication. During performed experiments, one of the main points of interest was fluoride removal under the permissible limit of 1.5 mgF⁻/dm³. In natural water F⁻ ions commonly occur with Na⁺ and Cl⁻ ions what was the reason for choosing NaCl as accompanying salt. From among many methods, nanofiltration has a high potential in fluoride removal due to its high removal efficiencies, simplicity, and low usage of additional chemicals. Basing on the literature research it may be a competitive defluoridation technique in comparison to other processes. There is limited literature describing F⁻ removal only in NaCl or monovalent ions presence. Divalent ions are likely to precipitate what finally may lead to membranes blockage, their hydraulic properties deterioration, and life cycle shortage. Due to that, it is worth investigating membranes behavior in the presence of only univalent ions. In this study, the effect of fluoride and NaCl concentration and membrane type on the nanofiltration performance was investigated. The assessment of separation efficiency, fluoride adsorption phenomena, and membrane hydraulic properties were implemented in the paper scope.

Methodology

Reagents

Treated solutions contained fluoride 5, 15, and 100 mgF⁻/dm³ and mineral salt (sodium chloride) in amount of 0.5 or 1 gNaCl/dm³. Model solutions based on distilled water. Fluoride came from NaF, molar mass 41.9 g/mol (Chempur). Whereas sodium chloride was added in a NaCl form (molar mass 58.44 g/mol) (Chempur). The pH of tested solutions was close to neutral and the experiments were performed at room temperature.

Chosen fluoride and sodium chloride content was characteristic for some natural waters.

Membranes and installation

Nanofiltration membranes NPO10P and NPO30P (Microdyn Nadir) were applied during experiments. Each membrane had an active surface area equal to 0.0045 m² what corresponded to 76 mm diameter.

A detailed description of the membranes is presented in Table 1.

Chosen membranes were differentiated by pore size

All experiments were performed with the use of ultrafiltration cell Amicon 8400. The initial volume of treated solutions was equal to 350 cm³. Transmembrane pressure was created by a nitrogen gas cylinder and it amounted to 0.3 MPa. Magnetic stirrer mixed continuously treated solutions.

Procedures

Before experiments, pure water flux was established for both membranes. Prior flux analysis membrane worked during 1–2 hours under pressure equal to 0.3 MPa. After that time permeate flux was stated as stable. In the process course permeate flux was measured every 10 minutes. Nanofiltration was conducted within 1 hour – after that final permeate quality and its flux were measured.

During experiments, fluoride and chloride content were monitored. Fluoride concentration was checked with the use of a colorimetric method with SPADNS reagent. Fluoride ions from solutions create colorless compounds with zirconium present in the reagent. So, the less sample color the higher fluoride content. The analysis were performed with the spectrophotometer Hach DR3900. Method no. 8029 and program no. 190 were applied. Method accuracy was calculated to ±9%.

Chloride content was monitored with the use of Mohr method. It means the sample was titrated by silver nitrate in the presence of potassium chromate as an indicator. Method selectivity was established as ±8%.

Permeate flux was calculated according to Equation 1:

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

where:

J – permeate volume flux (m³/m²day),

V – a volume of permeate (m³),

t – time (day),

A – surface area of the membrane (m²).

The relative permeability was calculated as the ratio J/J_0 , where: J – permeate volume flux (m³/m²day) and J₀ – distilled water flux (m³/m²day).

Within the process course amount of fluoride adsorbed into the membrane structure was examined. Due to that after the process termination (1 hour) volume of obtained permeate and retentate was monitored. Besides, the final fluoride content in permeate and retentate was examined. According to these values the amount of adsorbed fluoride was calculated with the use of Equation 2:

Table 1. Membrane characteristic

Symbol	Membrane material	Cut-off, Da	pH range	Max. temp. (°C)	Surface charge	Pore radius, nm
NP010P	Hydrophilic polyethersulfone	1040–1400	0–14	95	Negative	25.6
NP030P		520–700			Negative	11.7

$$M = V_0 C_0 - V_p C_p - V_r C_r \quad (2)$$

where:

- M – a mass of adsorbed fluoride, mg
- V_0 – an initial volume (dm³),
- V_p – a volume of permeate (dm³),
- V_r – a volume of retentate (equal to $V_0 - V_p$) (dm³),
- C_0 – an initial fluoride concentration (mgF⁻/dm³),
- C_p – a fluoride concentration in permeate (mgF⁻/dm³),
- C_r – a fluoride concentration in retentate (mgF⁻/dm³).

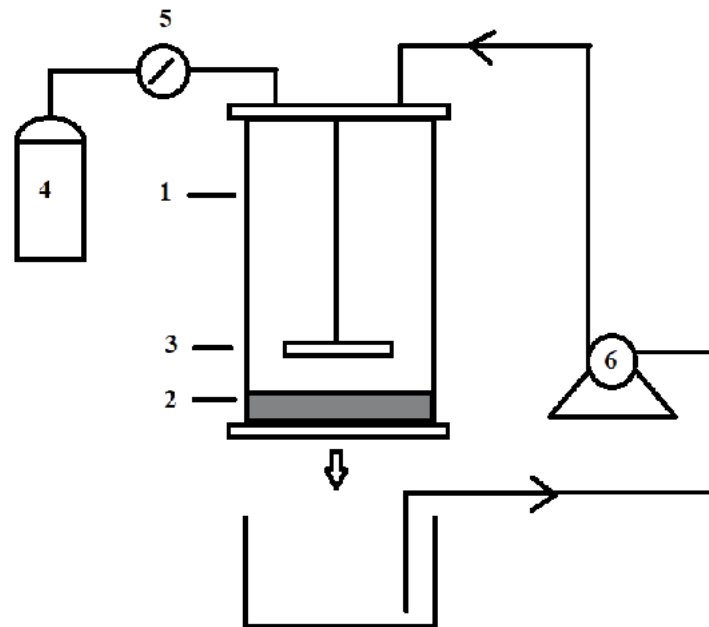
Results and discussion

Fluoride separation

Fluoride content in permeate for solutions containing fluoride (5–100 mgF⁻/dm³) and NaCl (0.5 or 1 gNaCl/dm³) are given in Fig. 2.

NPO30P membrane allowed to decrease fluoride content under demanded guideline 1.5 mgF⁻/dm³ during the process with 5 mgF⁻/dm³ (without sodium chloride addition) (Fig. 2a,b). In other cases F⁻ concentration was above this level. During experiments with 15 mgF⁻/dm³ fluoride content was maximally lowered to 5.3 and 7.8 mgF⁻/dm³ with membrane NPO30P and NPO10P, respectively (Fig. 2a). Minimal fluoride content in permeate for initial concentration amounted to 100 mgF⁻/dm³ was 49 mgF⁻/dm³ (for membrane NPO30P) (Fig. 2b).

According to the obtained results, it is seen that sodium chloride content deteriorates fluoride removal. Similar observations were made by Ma et al. (2009). From the two chosen membranes, the NPO30P exhibited better removal efficiency. Mainly it was caused due to its smaller pore size. Cassano et al. (2019) also showed that NP030P membrane allowed obtaining higher removal efficiencies. The next



1 – ultrafiltration chamber, 2 – membrane, 3 – magnetic stirrer, 4 – bottle with the gas, 5 – reducer, 6 – circulation pump

Fig. 1. Scheme of the nanofiltration installation

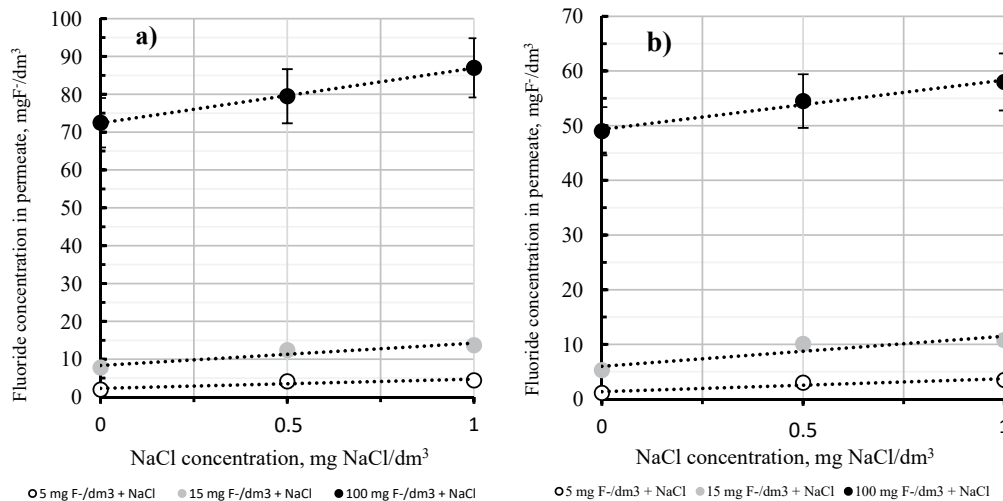


Fig. 2. Fluoride content in permeate for membrane a) NPO10P b) NPO30P, $C = F^- + NaCl$, $\Delta p = 0.3$ MPa, error bars $\pm 9\%$

observation is that an increase in fluoride ion content lowered fluoride removal efficiency. An increase in fluoride ions content is unambiguous to an increase in counterions (Na^+) concentration from NaF. It leads to a membrane charge screening. Finally, electrostatic repulsion between membrane and solution compounds is diminished and it is easier to transport ions through the membranes to establish Donnan equilibrium. As a consequence, compounds are easier transported through membranes, and removal efficiency decreased (Diawara et al. 2005). Also, fluoride separation was higher than chloride (Fig. 2). Cl^- ions have bigger ionic radius (0.164 nm) in comparison to fluoride (0.133–0.135 nm). The smaller radius the higher hydration energy and the size of the hydrated radius also increases – 0.332 and 0.352 for Cl^- and F^- , respectively. It explains fact that smaller ions can hold water molecules stronger. For dissolved ions (like fluoride) the effective ionic size also supposed to include hydration layers. (Banasiak and Schäfer 2009, Shen and Schäfer 2014). The bigger hydrated radius it is harder to transport ions through the membrane and separation efficiency increases (Ma et al. 2009, Labarca and Bórquez 2020). Shen and Schäfer (2014) stated that are four main mechanisms responsible for separation within NF process – size exclusion, charge interaction, solution-diffusion, and adsorption. Size exclusion and charge interaction are typical for F^- ions but also solution-diffusion takes part in fluoride removal. Solution diffusion is rather characteristic for nonporous membrane and is based on 3 steps: solute leaves the solvent and then it is dissolved in the membrane. Next, solute migrates through a membrane as a result of a concentration gradient. Size exclusion separation is a complicated phenomenon due to that the pore size is not constant. Membranes can be rather described in terms of pore size distribution than specific pore diameter (what complicates pores size estimation). Also, an important factor during the NF process is Donnan equilibrium (Teixeira et al. 2005). Negatively charged functional groups inhibit F^- ions entering into the membrane phase. At the same time counterions (Na^+) are attracted. Due to that some amount of low-charge ions is retained what allows to maintain the electroneutral conditions.

Results given in section 3.3.–3.5. proves the fouling phenomena during the performed process. According to Cassano et al. (2019) fouling phenomena may increase

retention efficiency. Besides, it has been reported that during nanofiltration of salt solutions „pore swelling” may occur. It is known as an increase in the average pore size (as the result of bigger repulsive forces between the counterions inside the membrane pores). Also, it is supposed to be noted that the higher salt concentration the higher surface charge densities inside the membranes. An increase in salt content is unambiguous to counterions amount increase. Due to counterions presence, repulsive interactions are stronger and finally pore swelling phenomena may occur (Klimonda and Kowalska 2019). Some studies (Bannoud and Darwich 2007) showed that retention decrease can be also the result of the solution osmotic pressure increase. As the consequence of osmotic pressure increase, effective pressure on the membrane decreases and the flux of solvent declines.

Chloride separation

During experiments also chloride separation efficiency was calculated. It allowed estimating interaction between F^- and Cl^- and determined each other influence on separation efficiency. Results for solutions containing sodium chloride (0.5 or 1 gNaCl/dm³) and 5–100 mgF⁻/dm³ are given in Fig. 3.

Initial chloride content amounted to 303 and 606 mgCl⁻/dm³ for solutions containing 0.5 and 1 gNaCl/dm³, respectively. The lowest obtained chloride content with solutions containing 0.5 gNaCl/dm³ amounted to 274.4 and 258.7 mgCl⁻/dm³ for membrane NPO10P and NPO30P, respectively (Fig. 3a). According to expectations much higher Cl^- concentration in permeate was noticed for solutions containing 1 gNaCl/dm³. Its content was maximally decreased to 563 and 504.7 mgCl⁻/dm³ for membrane NPO10P and NPO30P, respectively (Fig. 3b).

Similarly, like for fluoride (Fig. 2), better separation efficiency was noticed for NPO30P membrane. Which mainly, was caused due to its smaller pore size. Given data allowed to state that fluoride content in treated solutions influences chloride removal. Cl^- separation deteriorated with F^- content increase. It may be caused due to their competition during transport through the membrane. Similar observations were made by Krieg et. al (Krieg et al. 2004). Mnif et al. (Mnif et al. 2010) also showed that fluoride ions were removed more efficiently than Cl^- ions. They also noticed that chloride

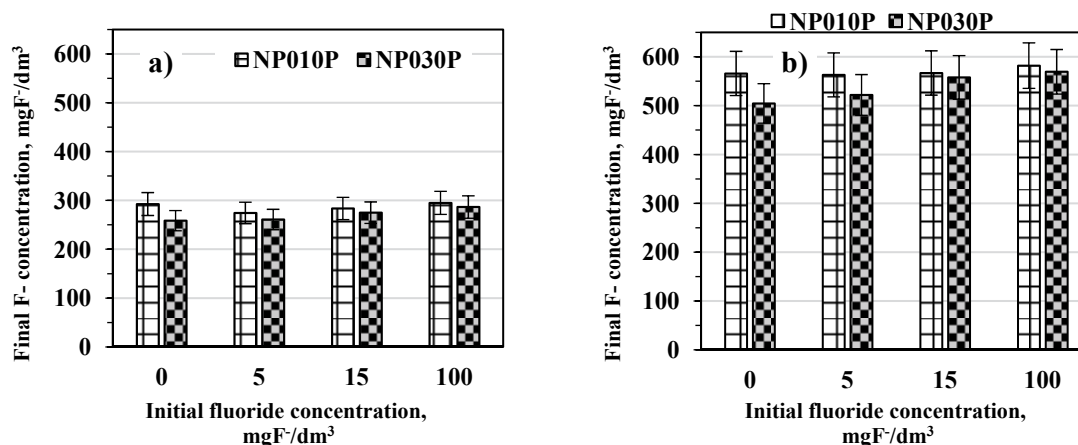


Fig. 3. Chloride content in permeate for membrane NPO10P and NPO30P a) 1 gNaCl/dm³ + F⁻ b) 0.5 gNaCl/dm³ + F⁻, $\Delta p = 0.3$ MPa, error bars $\pm 8\%$

separation was more efficient for single salt solutions than for mixtures. Klimczak et al. (2016) have shown that the increase in Cl^- content in the initial solution led to increasing chloride content in permeate as well as in membrane pores. This phenomenon was the result of a sodium ion presence. Na^+ transport through membrane involved chloride ions. More precisely, NaCl addition caused the driving force for chloride ions permeation what finally results in a large difference of Na^+ ions on both membrane sides. So, chloride and fluoride ions are supposed to be transported through membranes to maintain electroneutrality (Madaeni and Salehi 2009). Also, it is seen that chloride ions were removed less efficiently in comparison to fluoride ions (due to the difference in hydrated radius size). Similar results were obtained by Diawara et al. (Diawara et al. 2005). According Madaeni and Salehi (2009) the main separation mechanism of Cl^- during nanofiltration was its internal pore closure.

Fluoride adsorption in/on membranes

Adsorption of separated compounds in/on membrane structure is a common issue linked to membrane techniques. Due to that amount of fluoride adsorbed during the process course was calculated (according to Eq. 2). Values of these calculations for solutions containing sodium chloride (0.5 or 1 gNaCl/dm^3) and fluoride (5 – $100 \text{ mgF}^-/\text{dm}^3$) are presented in Fig. 4.

Unsurprisingly, the amount of adsorbed fluoride ions in the system increased with initial fluoride content. For C_0 equal to $5 \text{ mgF}^-/\text{dm}^3$ this value reached up to 0.54 mg for membrane NPO10P. Whereas for membrane NPO30P it was almost two times smaller (0.26 mg) (Fig. 3a). After increasing the initial concentration to $15 \text{ mgF}^-/\text{dm}^3$ amount of adsorbed fluoride varied between 1.72 – 2.59 mg and 0.0 – 0.32 mg , for membrane NPO10P and NPO30P, respectively (Fig.4b). The highest value occurred during tests with $100 \text{ mgF}^-/\text{dm}^3$. It reached even 17.4 mg (membrane NPO10P) and 8.86 mg (membrane NPO30P) (Fig. 4c).

The main factor that influenced the amount of adsorbed fluoride in/on membrane structure was initial F^- concentration. Hu and Dickson (2006) also confirmed fluoride ions adsorption inside/on the membrane structure. Some research (Bowen et al.

1997, Tsuru et al. 1991) also points to the dependence between feed concentration and the number of adsorbed ions. The ions concentration in the membrane decreased with the decrease of feed concentration. According to mass balance, the amount of the particles adsorbed on the membrane structure will be dependent on the permeate volume, foulants concentration, and particle adsorption factor (Salgado et al. 2016). Wang et al. (2010) examined ionic strength influence (expressed as NaCl content) on diuron adsorption. Similarly, it was observed that the higher ionic strength, the lower amount of adsorbed diuron. It can be explained by the fact that electrostatic interaction between negatively charged membrane and electrolyte increased. Due to that interaction between solution compounds and membrane was reduced. It can be explained shortly that NaCl addition screened electrostatic interaction.

Some studies also show that the membrane zeta potential decreases in the electrolyte presence. An increase in ionic strength diminishes the effective thickness of the diffused layer what finally influences the adsorption phenomena (Nechifor et al. 2013). Some reports showed that ionic strength exceeding 0.01 M led to critical coagulation concentration. This kind of particles aggregation may lead to a greater back diffusion effect. As the result, it prevents the particles from adsorbing onto the membrane surface (Vigneswaran et al. 2015). Besides, the higher NaCl concentration the stronger electrostatic interaction between the membrane and the electrolyte. Due to that, an increase in sodium chloride content may decrease the adsorption phenomena of some compounds during NF process (Shurvell et al. 2014).

The affinity between the permeant and the membrane matrix plays an important role in the process course. The affinity may result in pore swelling and influence the movement capacity of the permeant inside the membrane. It also affects membrane behavior. The transport through nanofiltration membranes (which are stated as dense membranes) can be described by the solution-diffusion model (diffusion is a dominant salt transport mechanism in many NF). It consists of three steps: absorption on the feed side, diffusion through the membrane, and desorption on the permeate side (Fierro et al. 2012). In fact the diffusive transport across the membrane influences the

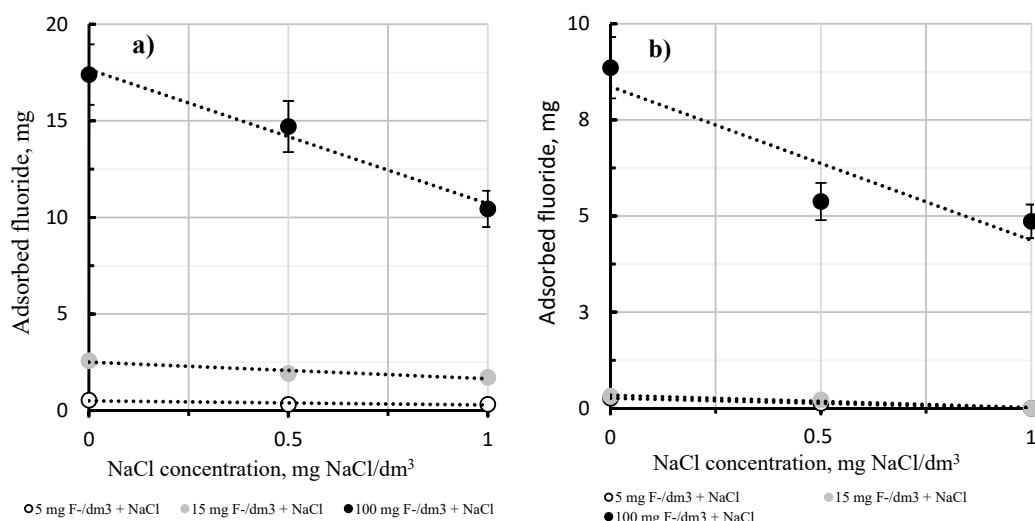


Fig. 4. Amount of adsorbed fluoride for membrane a) NPO10P and b) NPO30P, $C = \text{F}^- + \text{NaCl}$, $\Delta p = 0.3 \text{ MPa}$, error bars $\pm 9\%$

adsorption phenomena and impacts the number of compounds that will be adsorbed inside the membrane matrix.

Accumulation of solute which is retained in/on the membrane surface leads to concentration polarization. This concentrated layer is less permeable to the solvent due to higher osmotic pressure at the membrane interface what results in decreasing the effective driving force. The layer formed by compounds present in treated solutions hinders the back diffusive ions transport from the membrane surface and finally ion concentration on the membrane surface increases. This phenomenon is called “cake-enhanced osmotic pressure” (Park et al. 2010, Gomes et al. 2005).

Van der Bruggen and Vandecasteele (2001) also stated that molecules adsorption on the membrane surface may be the result of various physicochemical interactions like hydrophobic interactions (dispersion forces), polar interactions (dipole-dipole and dipole-induced-dipole forces), and charge transfer (hydrogen bonding). The solute concentration, the membrane material, the solute type or pH are parameters that can determine the extent of adsorption. Molecules can also be attached to the membrane surface or pores due to the chemisorption process what finally leads to a net pore opening decrease.

During membrane processes adsorption is caused due to interactions between the solute and membrane. Physisorption and chemisorption are included in non-electrostatic adsorption. Physisorption is mainly the effect of van der Waals interactions. Chemisorption is caused by chemical bond formation. Those reactions can be so strong that they can affect the membrane properties (Shen and Schäfer 2014). Electrostatic repulsion between membrane and fluoride ions inhibits adsorption potential. Also due to the high hydration of fluoride ions probability of hydrophobic adsorption is diminished. On the other hand F^- can be trapped by the positively charged groups of the negatively charged membrane. Sodium ions present in treated solutions can modify membrane charge what affects adsorption phenomena indirectly. F^- ions can be also adsorbed together with other ions as a complex (Shen and Schäfer 2014). Molecules can only migrate into pores only when they are smaller than pores. Adsorption takes place when molecules and pore size is comparable. Finally, adsorption phenomena lead to a pore size decrease. Also, NF membranes contain dense structure and pores can be rather defined as the free volume between polymeric chains (Van Der Bruggen et al.,

2002). Some models describe the transport of small molecules into the dense membrane structure. Chen et al. (2001) stated that transport behavior can be classified into three categories: Fickian diffusion (the rate of diffusion is lower than the rate of sorption), sorption control process (sorption is slower than diffusion rate), and non-Fickian (anomalous) diffusion – sorption and diffusion rate are comparable. In the case of Fickian diffusion increase in adsorption is unambiguous to retention increase. But simultaneously, it was stated that there is no simple correlation between retention and adsorption. Due that adsorption may be the effect of different mechanism or ion-exchange and supposed to be examined individually for different membrane types.

It was observed that a higher amount of fluoride was adsorbed with membrane NPO10P usage. Carvalho et al. (2011) examined the roughness of the NP010P and NPO30P membrane. In the case of the unused membrane, higher roughness characterized membrane NPO10P. It can explain fact that it adsorbed more fluoride ions in comparison to membrane NPO30P. It was confirmed (Elimelech et al. 1997, Wong et al. 2009) that the higher surface roughness the bigger adsorption area is and more ions can be adsorbed on the membrane. The rough surface creates “valleys” in which compounds are preferentially adsorbed. Finally, it leads to “valleys” clogging. Cassano et al. (2019) showed that NP010P membrane exhibits higher hydrophilicity in comparison to NP030P membrane. The adsorption potential is influenced by membrane hydrophilicity. An increase in hydrophilicity enhances vulnerability to fouling potential. It may explain the fact that more fluoride ions were adsorbed by the more hydrophilic NP010P membrane (it has a contact angle equal to 72° in comparison to 88.4° obtained for NP030P) (Cassano et al. 2019). Some experiments exhibited that membrane NP030P has a higher pore volume ($0.008 \text{ cm}^3/\text{g}$) in comparison to NP010P ($0.005 \text{ cm}^3/\text{g}$). The bigger pore volume is univocal with a bigger surface for ions adsorption (Vieira et al. 2018).

Permeate flux

One of the main important factors describing pressure-driven membrane processes is permeate flux. This parameter was calculated according to Eq. 1. Permeate flux values for solutions containing $5\text{--}100 \text{ mgF}^-/\text{dm}^3$ and $0.5, 1 \text{ gNaCl}/\text{dm}^3$ are seen in Fig. 5.

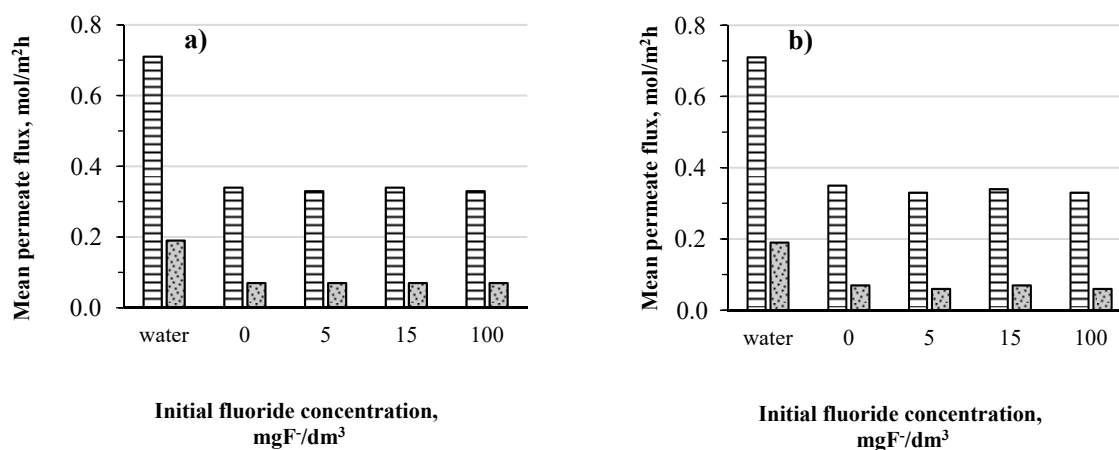


Fig. 5. Mean permeate flux values in time for a) $0.5 \text{ gNaCl}/\text{dm}^3 + F^-$ and b) $1 \text{ gNaCl}/\text{dm}^3 + F^-$, $\Delta p = 0.3 \text{ MPa}$

At the beginning of the experiments permeate flux for pure water was established. For membrane NPO30P it amounted to $0.19 \text{ m}^3/\text{m}^2\text{day}$, whereas for NPO10P membrane this value was almost four times higher – $0.71 \text{ m}^3/\text{m}^2\text{day}$. A significant decrease in permeate flux was observed during experiments involving solutions with fluoride and sodium chloride. Permeate flux varied between $0.32\text{--}0.38 \text{ m}^3/\text{m}^2\text{day}$ for membrane NPO10P (Fig. 5). Much lower range of J value occurred during experiments with membrane NPO30P. It fluctuated between $0.06\text{--}0.8 \text{ m}^3/\text{m}^2\text{day}$ (Fig. 5).

Cassano et al. (2019) during experiments also have shown that higher permeability was obtained for NPO10P membrane. Both membranes have similar composition, but NPO10P membrane has greater MWCO. It can be stated that NPO10P membrane has “looser” structure in comparison to membrane NPO30P. Besides, NPO10P membrane exhibited higher hydrophilicity (contact angle equal to 72°) in comparison to NPO30P membrane (88.4°) (Cassano et al. 2019). The fouling phenomenon which is caused by blocking membrane pores by contaminants present in water may lead to flux decrease. Adsorption of those compounds decreases available pores size. Finally, permeability is reduced and the decrease is proportional to occupied sites. Flux decrease is the highest when pores and compounds size are comparable. When the molecule’s diameter is smaller than the pore size, permeate flux will be decreased gradually because pores blockage also will be progressively (Van Der Bruggen et al. 2002). Similar conclusions and observations were given by Cassano et al. (2019) which examined permeate flux change in time with the use of membrane NPO30P. Within experiments under the pressure 0.2 MPa about 25% flux decrease within 3 hours was noticed. They linked this behavior to membrane fouling and concentration polarization. Hirose et al. (1996) discovered a relationship between membrane roughness and its permeability. Due to higher roughness effective membrane area become larger and permeate flux increase. Membrane NPO10P was characterized by higher roughness as well by higher permeability – it complies with obtained results.

Also the higher feed salinity the higher osmotic pressure of treated solutions will be noticed what finally may result in diminishing the membrane hydraulic properties. According to Park et al. (2010) the high ionic strength of the treated solutions

resulted in the reduction of membrane pore size due to polymer matrix compaction.

Relative permeability

Relative permeability is a factor that allows estimating membrane blockage (understand as flux decrease) due to fouling concentration polarization, fouling phenomena and other factors which may take place during the separation process. Relative permeability values for different solution compositions ($5\text{--}15 \text{ mgF}/\text{dm}^3$ and $0.5\text{--}1 \text{ gNaCl}/\text{dm}^3$) are given in Fig. 6.

Relative permeability for solutions containing in composition $5 \text{ mgF}/\text{dm}^3$ was lowered to $0.98\text{--}0.34$ (Fig. 6). The highest value was obtained during experiments without sodium chloride content. After increasing fluoride ions content to $15 \text{ mgF}/\text{dm}^3$ relative permeability was in the range $0.38\text{--}0.96$ (Fig. 6). Values within a range $0.32\text{--}0.95$ were observed for solutions containing $100 \text{ mgF}/\text{dm}^3$ (Fig. 5a–c). The highest values occurred when purified solutions did not contain mineral salt. In most cases, higher relative permeability was obtained for the NPO10P membrane.

A significant decrease in relative permeability was observed for both membranes (mostly higher value of this parameter was exhibited by membrane NPO10P). It may confirm fouling phenomena that resulted in decreasing hydraulic properties. It is stated that one of the most important factors decreasing permeate flux is the adsorption of compounds from solution on membrane surface (Lee et al. 2011). The fouling phenomenon may be linked to the formation of a gel layer on the membrane surface, suspended solids adsorption in membrane pores, or precipitation of dissolved solids on the membrane surface (Silva 2018). Xu et al. (2020) we propose a semi-empirical multiple linear regression model to describe flux decline, incorporating the five fouling mechanisms (the first and second kinds of standard blocking, complete blocking, intermediate blocking, and cake filtration researched fouling stages). The fouling mechanism’s first stage is cake formation. Part 2 and 3 involves adsorption inside the membrane pores. Next stage (stage 4–5) slowly adsorption inside the membrane pores occurs. In the last stages (6 and 7) gradual growth of a cake layer on the membrane surface is noticed. Carvalho et al. (Carvalho et al. 2011) examined permeate flux for membranes NPO10P and NPO30P. They stated that initial permeability was high but on

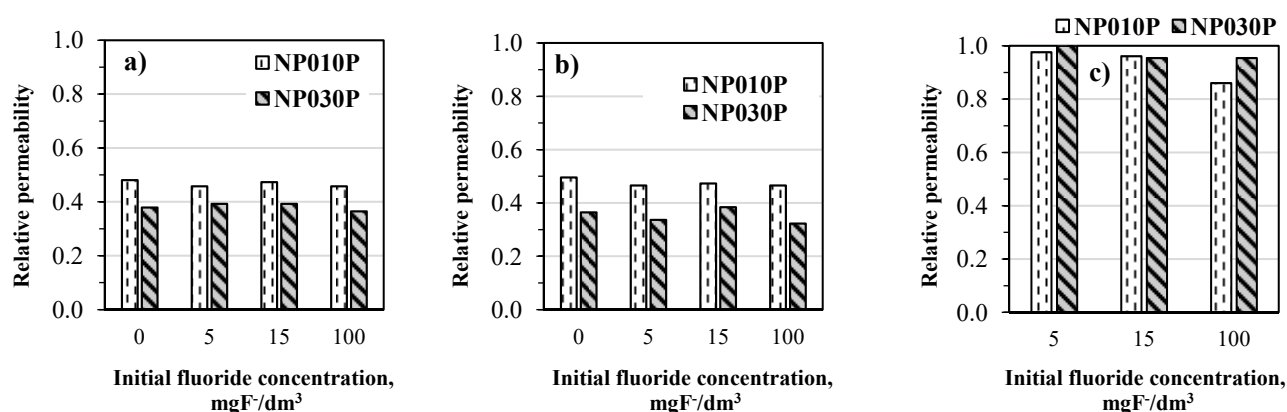


Fig. 6. Relative permeability from membrane NPO10P and NPO30P
a) $0.5 \text{ gNaCl}/\text{dm}^3 + \text{F}^-$ b) $1 \text{ gNaCl}/\text{dm}^3 + \text{F}^-$ c) F^- , $\Delta p = 0.3 \text{ MPa}$

the other hand significant flux decrease for those membranes was one of the main disadvantages. It could be caused by the chemical nature of the membrane, pore size, roughness, porosity, operation conditions, or membrane electrical charge. Park et al. (Park et al. 2010) during research confirmed that the permeate flux was significantly lowered when salt sodium chloride concentration rose from 0.5 to 5 g/dm³. The relative permeability decline (which is directly linked to permeate flux) was explained by the increase in osmotic pressure of the feed/retentate what led to lowering the transmembrane pressure.

Conclusions

Only for solutions containing 5 mgF/dm³ nanofiltration allowed to decrease fluoride content under permissible level – 1.5 mgF/dm³. An increase in fluoride content resulted in process efficiency deterioration. Better separation efficiency was exhibited by membrane NP030P. It was mainly caused by a lower cut-off value in comparison to the NP010P membrane.

Chloride ions were removed less efficiently. Their content was lowered maximally to 258.7 and 504.7 mgCl/dm³ when NaCl content amounted to 0.5 and 1 gNaCl/dm³, respectively. Cl⁻ ions are characterized by a higher ionic radius, in comparison to fluoride, but simultaneously it corresponds to lower hydration energy. As the result, Cl⁻ ions can be transported more easily through the membrane. Those ions also were separated more efficiently with the use of membrane NP030P (mainly due to lower cut-off value).

Fluoride ions were adsorbed on/inside the membrane structure. The amount of adsorbed fluoride increased with an increase in fluoride content. Even 17.4 mg of F⁻ were adsorbed in the system. Also, it was observed that an increase in NaCl content led to a decrease in the amount of adsorbed fluoride. It may be caused due to change in electrostatic interactions between membrane and solution components as the result of electrolyte presence. Membrane NP010P was more vulnerable to fouling phenomena among others due to its higher roughness.

Higher permeate flux was obtained for membrane NP010P. It was caused by a larger pore size and higher roughness (which resulted in a bigger filtration area). Distilled water flux amounted to 0.19 and 0.71 m³/m²day for membrane NP030P and NPO10P, respectively. About twofold decrease in relative permeability was observed. Hydraulic properties deterioration was the result of various factors like fouling phenomena (caused by ions adsorption in the system) and difference in osmotic pressures what influenced the pore size variation.

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