

ARIF EFTEKHAR AHMED¹, MARTYNA GRZEGORZEK¹, KATARZYNA MAJEWSKA-NOWAK¹

THE EFFECT OF NITRATE ON FLUORIDE REMOVAL BY BATCH ELECTRODIALYSIS

Fluoride and nitrate are common pollutants in drinking water and their presence deteriorates the quality of drinking water. According to WHO guidelines, the fluoride content in drinking water cannot be higher than 1.5 mg F⁻/dm³. The purpose of this paper was to evaluate the efficiency of fluoride removal from model aqueous solutions under the presence of nitrate. The experiments were conducted with the use of laboratory installation PCCell BED-1 System at a constant current density (0.78, 1.72, and 2.34 mA/cm²) with the use of monovalent selective ion-exchange membranes. The influence of initial nitrate concentration (15, 30, 45 mg NO₃⁻/dm³) and initial fluoride concentration (5, 10, 15 mg F⁻/dm³) on the process performance was studied. The degree of desalination varied from 85 to 91.7% depending on the solution composition and the applied current density, whereas the fluoride removal was in the range of 70–90%. The presence of coexisting NO₃⁻ ions in fluoride solutions improved process efficiency in view of fluoride removal by batch electrodialysis.

1. INTRODUCTION

Ensuring appropriate quality of drinking water is a major task nowadays because of the expansion in pollution of water bodies. Fluoride and nitrate are vital pollutants that undermine living life forms, especially people. According to World Health Organization (WHO) guidelines [1], the F⁻ ion concentration in drinking water cannot be higher than 1.5 mg F⁻/dm³ because the elevated F⁻ content is responsible for various diseases such as Alzheimer's disease, neurological disorders or fluorosis (dental or skeletal) [2, 3]. It is also worth mentioning that nitrate ion concentration in drinking water is limited to 50 mg NO₃⁻/dm³ [4]. Fluoride and nitrate ions can enter into aqueous environment by weathering of fluoride-rich minerals and as through anthropogenic actions, for example, domestic wastewater and industrial drains or agricultural surface run-offs [5, 6]. Nitrate

¹Faculty of Environmental Engineering, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland, corresponding author: K. Majewska-Nowak, e-mail address: katarzyna.majewska-nowak@pwr.edu.pl

can be removed from aqueous solution by various techniques involving biological processes and physicochemical methods. Commonly used methods enabling fluoride removal are adsorption on activated alumina, ion-exchange, reverse osmosis (RO), and electrodialysis (ED).

Adsorption on activated alumina is a good way for environmental cleanup, purification of pharmaceuticals and clean energy applications. Activated alumina is an inorganic substance produced by the dehydration of alumina hydroxide at high temperature. The material is highly porous and exhibits tremendous surface area, resulting in superior adsorbent capabilities [7].

Ion-exchange on natural and synthetic ion-exchangers has been a well known process for many years. Its main advantages for water treatment are simplicity and high effectiveness of ionic compounds removal. However, the necessity of frequent regeneration of exhausted ion-exchange resins and production of troublesome wastewater makes this process less attractive lately. Nevertheless, it is possible to separate 90–95% of fluoride from water with the use of strong base anion-exchange resins [8].

Reverse osmosis is an advanced type of filtration widely used in water desalination, medicine and other industries for water purification or concentration of valuable components. In current years, it has been used increasingly for making pure water for dialysis in hospitals and for producing water for injection [9]. More than 90% of fluoride can be removed, regardless of the initial fluoride concentration in water, using reverse osmosis membranes [10].

The methods discussed above are not always suitable for removal of various kinds of pollutants from water solutions due to their high costs, ineffectiveness and operational problems, thus new technologies have become necessary. Currently, removal of fluoride and nitrate ions from water solutions by electrodialysis with ion-exchange membranes could be a feasible method. Electrodialysis is an electrically driven process that uses a voltage potential to drive charged ions through selective ion-exchange membranes, reducing the concentration of dissolved solids in the source water [11]. In practical applications of ED processes, multiple electrodialysis cells are arranged into configuration called electrodialysis stack, with alternating anion- and cation-exchange membranes. Raw electrolyte solution enters appropriate electrodialysis cells and flows through membranes via flow spacers that are placed between the membranes. The spacers are used to provide a flow path for the water solution, support the membranes, and create turbulent flow. The DC voltage potential induces migration of cations toward the cathode through the cation-exchange membranes and anions toward the anode through the anion-exchange membranes. The cations and anions accumulate in the concentrate cells, whereas water of low salt content is produced in the diluate cells. Newly built ED installations operate mostly on the basis of the electrodialysis reversal (EDR) [12]. In this system, the polarity of the electrical field is periodically reversed, and consequently the diluate and concentrate cells are also reversed, which helps flushing scale-forming ions off the membrane surface and keeps the membranes clean.

As was already mentioned, electromembrane processes have the potential to be a suitable technique for drinking water production, as well as for treatment of industrial effluents. A few examples describing the latest research achievements in fluoride separation by electro dialysis are given below.

Ergun et al. [13] evaluated the effect of feed composition and current density on the efficiency of fluoride removal from natural water with the use of commercial, strong-basic anion-exchange membranes (SB-6407, Gelman Sciences). They found that transport of fluoride ions increased with increasing current density and feed concentration. Despite the presence of chloride and sulfate ions in the real water sample, fluoride concentration was reduced from 20.6 to 0.8 mg F⁻/dm³. The removal of fluoride was better in the absence of coexisting ions, which was explained by decreasing the activity coefficient of fluoride ion in the presence of mono- and divalent ions. Similar results were obtained by Gmar et al. [14] in the course of ED process with tap water containing 15 mg F⁻/dm³. It was shown that fluoride removal was strongly influenced by chloride ions, whereas the presence of sulfates was rather negligible.

The literature review indicates that most problems with excess fluoride removal are related to groundwater resources. The experiments on fluoride removal from groundwater by batch electro dialysis were performed by Arahman et al. [15]. The initial concentration of fluoride ions was extremely high (380 mg F⁻/dm³), nevertheless the obtained removal efficiency of F⁻ ions was surprisingly good (ca. 96%) and the final quality of the diluate met the WHO standards (the final content of F⁻ ions was lower than 1.5 mg F⁻/dm³), irrespectively of the applied current density. The study revealed that process efficiency was not influenced by the type of an anion-exchange membrane; the process duration needed to achieve a maximal reduction of the concentration of fluoride ions was exactly the same for both standard (AMX) and monovalent selective (ACS) anion-exchange membranes. Comparison of fluoride permeation rate for ED series with solutions varying in composition allowed one to state that, due to the presence of other ions in the feed, the removal rate of fluoride decreased.

Treatment of groundwater for drinking water purpose could be a challenge because of the high content of various mineral salts. Ben Sik Ali et al. [16] used the ED process for fluoride removal from brackish groundwater. Due to the high TDS content (ca. 15 g/dm³), the experimental samples were diluted by raw water, which made TDS decrease to 5 g/dm³. The initial fluoride content of 2.9 mg F⁻/dm³ was reduced to 0.4 mg F⁻/dm³ and the specific energy consumption was calculated as 15.5 Wh/dm³. Moreover, the final concentrations of the various ions that were present in the treated samples fulfilled the permissible limits for drinking water.

Besides natural water, the industrial wastewater (e.g., effluent from the photovoltaic industry, spent pickling solutions from the glass industry, wastewater from the fertilizer industry) can also contain fluoride compounds, which should be removed or reused. Belkada et al. [17] investigated the effect of various operational factors on fluoride removal from synthetized PV industry wastewater. The F⁻ ion removal efficiency amounted to

50–60% at the relatively high initial fluoride concentration (100–180 mg F⁻/dm³). The experiments were performed at laboratory conditions and the process duration was extremely short (6–18 min). The study of competition between fluoride and nitrate ions during their elimination showed that the fluoride ions presence did not affect the nitrate removal, while the nitrate ions present in the solution delayed the fluoride removal and made the F⁻ ion removal less effective. The idea of fertilizer wastewater management with the use of electrodialysis was given by Bagastyo et al. [18]. They applied a three-compartment electrodialysis reactor to separate fluoride and calcium ions from phosphate ions for possible further reuse of phosphate in the fertilizer industry. At the initial concentration of PO₄³⁻ and F⁻ ions equal to 4540 and 9720 mg/dm³, respectively, the transfer rate of fluoride ions was five-fold higher than that of phosphate ions. Fluoride ions were preferably transferred faster through the anion-exchange membranes than phosphate ions due to higher ionic mobility.

Promising results of laboratory investigations encouraged the researchers to verify the concept of F⁻ ion removal by ED on a pilot scale. Keri et al. [19] conducted a series of experiments in the pilot ED plant equipped with 11 cell pairs and turbulence promoters to reduce concentration polarization. The quality of product water was satisfied only for ED series with solutions of initial F⁻ ion concentration lower than 10 mg F⁻/dm³. In the case of experiments performed for higher F⁻ ion concentrations, the final diluates did not meet the WHO standards. What more, back diffusion and membrane fouling were monitored at elevated voltage applied to the ED stack.

Application of electrodialysis in fluoride removal from different water sources seems to be perspective, however, there are still some shortcomings of this process: unsuitability for treating water of low salt content, membrane scale and requirement of high-degree pretreatment. To increase recovery rate and minimize rapid precipitation of divalent salts, a special monovalent selective ion-exchange membrane can be used, followed by conventional ion-exchange membranes. Therefore the aim of the presented study was to evaluate the behavior of monovalent selective anion- and cation-exchange membranes in fluoride separation by electrodialysis. The effect of coexisting ion (nitrate) on process efficiency was also verified.

2. MATERIALS AND METHODS

Model solutions. Model solutions were made of sodium fluoride (NaF), sodium nitrate (NaNO₃), sodium chloride (NaCl), and distilled water. The concentrations of fluoride, chloride and nitrate ions in tested solutions amounted to 5, 10, 15 mg F⁻/dm³, 15, 30, 45 mg NO₃⁻/dm³; 303 mg Cl⁻/dm³ (0.5 g NaCl/dm³), respectively. Chloride ions (i.e., sodium chloride salt) were always present in the experimental solutions, whereas fluoride and nitrate ions occurred separately (in two-component solutions) or simultaneously (in three-component solutions).

Membranes and experimental installation. The ED installation (PCCell BED-1 System, PCCell GmbH, Germany) consisted of an electrolysytic stack (PCCell 64002 model) made of 10 anion-exchange membranes and 11 cation-exchange membranes, electrode solution tank (volume of 9 dm³), external tanks for diluate and concentrate (2 dm³ each), and a power supply.

The used ion-exchange membranes (PCA GmbH, Germany) were of a special type monovalent selective ion-exchange membranes (Table 1). These membranes have the capability to separate monovalent ions from a mixture containing both monovalent and multivalent ions. The effective surface area of each membrane was equal to 64 cm².

Table 1

Characteristics of the monovalent selective ion-exchange membranes

Parameter	Anion-exchange membrane (PC-MVA)	Cation-exchange membrane (PC-MVK)
Size, mm	110×110	
Thickness, μm	110	90–130
Thermal resistance, °C	40	
Burst strength, MPa	0.2	0.3
Chemical resistance (pH range)	0–9	0–10
Functional group	ammonium	sulfonic

The ED stack consisted of 10 electrolysytic cells and each cell had a thickness of 0.5 mm. The electrode solution tank was fed with a NaCl solution (0.05 mol/dm³). The ED stack was connected to a DC power supply (output voltage – max. 24 V, output amperage – max. 5 A). Both the diluate and concentrate streams, as well as the electrode solution, were circulated in the ED stack at a flow rate of 90 dm³/h, which corresponded to a linear liquid velocity of 6.25 cm/s. The diluate and concentrate streams were circulated in the stack until the end of the treatment process. The process was stopped when the maximum voltage was achieved. The applied current intensity was 0.05, 0.11, and 0.15 A, which corresponded to the current density of 0.78, 1.72, 2.34 mA/cm², respectively.

Methods. Due to the low initial concentration of fluoride and nitrate, sodium chloride (0.5 g NaCl/dm³) was added to all tested solutions to increase the electrolyte content and improve ionic transport through the ED stack. The preliminary experiments on the desalination of the NaCl solution were carried out at various current densities (0.78, 1.72, 2.34 mA/cm²). At the beginning of the ED process, both diluate and concentrate tanks were filled with sodium chloride solution (0.5 g NaCl/dm³).

The defluoridation process was performed at the current density of 1.72 mA/cm² for solutions containing fluoride and chloride ions at first. Then, NaCl solutions containing variable amounts of nitrate (15, 30, 45 mg NO₃⁻/dm³) and constant fluoride concentration

(10 mg F⁻/dm³) were subjected to electrodialysis. In the last stage of experiments, NaCl solutions containing variable amounts of fluoride (5, 10, 15 mg F⁻/dm³) and constant nitrate concentration (30 mg NO₃⁻/dm³) were subjected to electrodialysis. In the course of the tests on fluoride removal, the concentrate tank contained only NaCl at the beginning of the ED experiments, whereas diluate tank was filled with model solutions contaminated with fluoride, chloride and nitrate ions.

During the experiments, the quality of both diluate and concentrate was monitored by conductivity measurements and the concentration of fluoride was determined. The samples of diluate and concentrate were taken at the same time intervals. The conductivities of the diluate and concentrate were measured with the use of a multimeter HQ40D (method sensitivity 0.5%). The fluoride content was determined by the colorimetric method with SPADNS reagent. A spectrophotometer HACH DR 2000 was used at a wavelength of 580 nm (method No. 8029, program No.190). The measurement error amounted to ±9%. The initial nitrate concentration was analyzed with the use of a HACH DR2800 spectrophotometer at a wavelength of 500 nm (method No. 8039). The NITRAVER-5 reagent was used as nitrate indicator.

Changes in voltage were monitored every 5 min. The specific electrical energy demand (*EC*) was evaluated from the following equation:

$$EC = \frac{I \int_0^t U dt}{V_d}$$

where *EC* – specific electrical energy demand, kWh/m³, *I* – current intensity, A, *U* – voltage, V, *V_d* – volume of the diluate, m³, *t* – process duration, h.

The calculated *EC* value involved only energy used for ion transport across the membranes. The energy needed to pump the diluate and concentrate streams through the ED stack was not considered.

3. RESULTS AND DISCUSSION

3.1. DESALINATION EFFICIENCY

Desalination is the main objective of electrodialysis application. The efficiency of ED desalination depends on many parameters, among them on electrical current density and composition of the treated solution. The desalination efficiency in the course of electrodialysis was calculated on the basis of conductivity monitored in diluate samples. It has been evaluated for ED series with solutions containing only sodium chloride, as well as for ED series with two-component solutions (NaCl + NaF and NaCl + NaNO₃)

and three-component solutions ($\text{NaCl} + \text{NaF} + \text{NaNO}_3$). In all experiments, the concentrate cells were filled with sodium chloride (0.5 g/dm^3) at the beginning of the ED process.

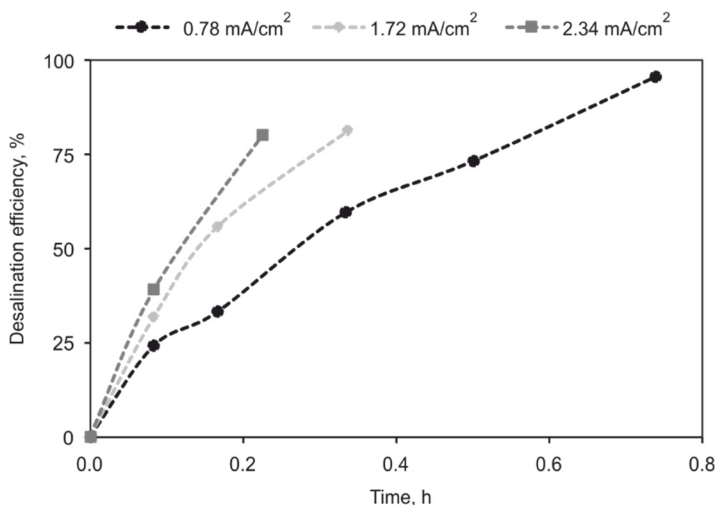


Fig. 1. Desalination efficiency versus ED time, $C_0 = 0.5 \text{ g NaCl/dm}^3$, current densities 0.78, 1.72 and 2.34 mA/cm^2

The effect of the applied electrical current density on the desalination efficiency of sodium chloride solution is presented in Fig. 1. The obtained desalination efficiency at a constant current density was rather high (80–96%). The time needed to reach the maximal desalination degree changed upon the applied current density according to the Faraday's law.

The final diluate conductivity decreased from approximately $1000 \mu\text{S/cm}$ to 42, 168, and $204 \mu\text{S/cm}$ when the current density of 0.78, 1.72 and 2.34 mA/cm^2 was applied, respectively. The worst quality of the diluate obtained for ED process conducted at the highest current density was probably related to the concentration polarization phenomena; the decrease of ion concentration in the membrane boundary layer (at diluate side) occurred faster at a higher current density and this lead to rapid voltage increase and process termination.

In the next step of experiments, the constant current density (1.72 mA/cm^2) was applied. The concentrate contained only sodium chloride (0.5 g NaCl/dm^3) whereas diluate also contained fluoride (5, 10 or $15 \text{ mg F}^-/\text{dm}^3$) or nitrate (15, 30, $45 \text{ mg NO}_3^-/\text{dm}^3$) or both anions F^- and NO_3^- besides Cl^- ($10 \text{ mg F}^-/\text{dm}^3$ and 15, 30 or $45 \text{ mg NO}_3^-/\text{dm}^3$ or 5, 10 and $15 \text{ mg F}^-/\text{dm}^3$ and $30 \text{ mg NO}_3^-/\text{dm}^3$). The results are shown in Figs. 2–5.

Irrespective of the solution composition, the initial conductivities of diluates were quite similar (901–1170 $\mu\text{S/cm}$). Thus, it was concluded that the sodium chloride content had the greatest impact on the initial conductivity of tested solutions.

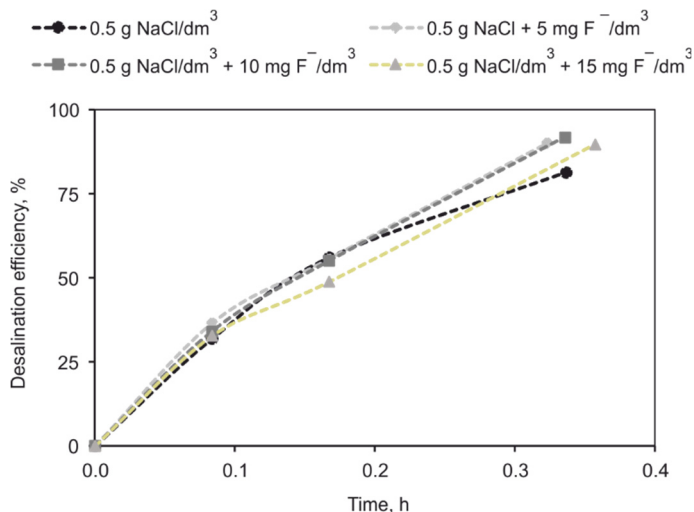


Fig. 2. Desalination efficiency versus ED time, $C_0 = 0.5 \text{ g NaCl/dm}^3 + \text{F}^-$, current density 1.72 mA/cm^2

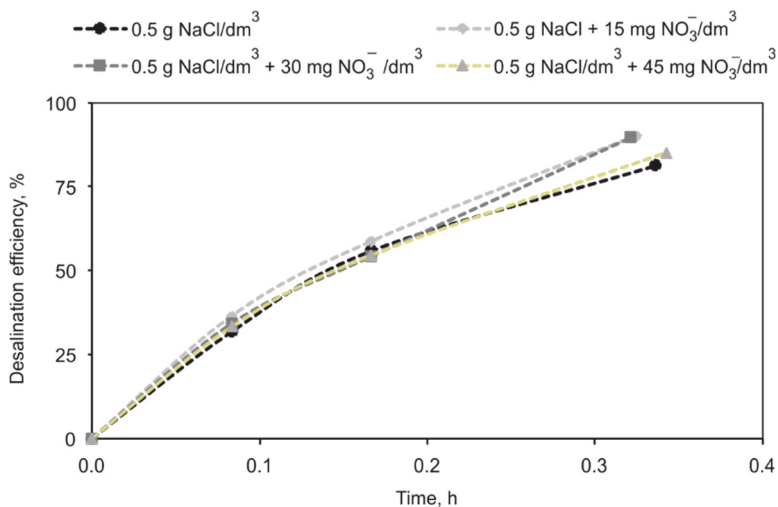


Fig. 3. Desalination efficiency versus ED time, $C_0 = 0.5 \text{ g NaCl/dm}^3 + \text{NO}_3^-$, current density 1.72 mA/cm^2

For ED series with solutions containing fluoride and sodium chloride, the desalination efficiency reached 89.6–91.7% (Fig. 2). The process was terminated after 19.4–21.4 min of ED operation. It was observed that the increase in fluoride content increased the operation time. In the case of ED series with mixtures of nitrate and NaCl, the salinity was lowered by 85–90.1% (Fig. 3). The increase in nitrate content from 15 to 45 $\text{NO}_3^-/\text{dm}^3$

increased the time of electro dialysis from 19.6 to 20.6 min. The increase of the process duration upon increasing salt concentration complies with Faraday’s law.

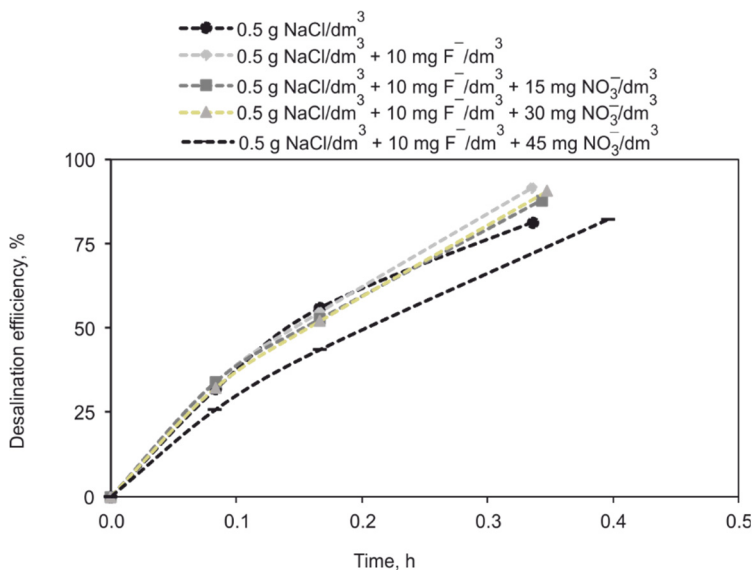


Fig. 4. Desalination efficiency versus ED time, $C_0 = 0.5 \text{ g NaCl/dm}^3 + \text{NO}_3^- + 10 \text{ mg F}^-/\text{dm}^3$, current density 1.72 mA/cm^2

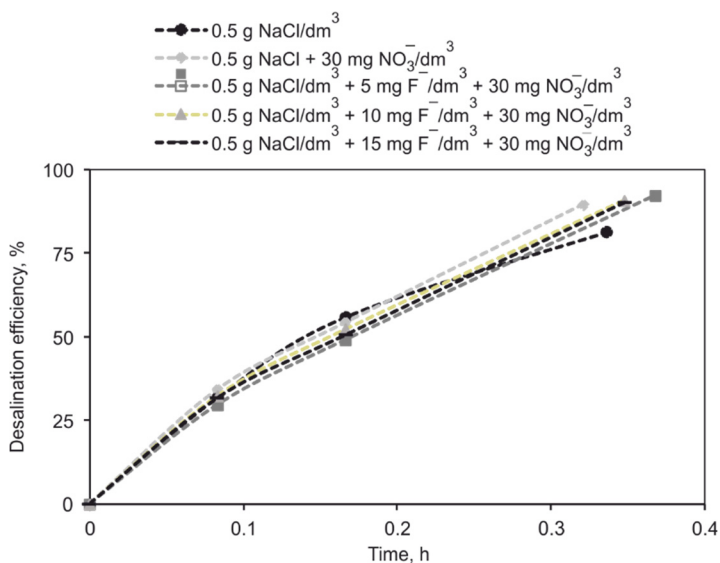


Fig. 5. Desalination efficiency versus ED time, $C_0 = 0.5 \text{ g NaCl/dm}^3 + 30 \text{ mg NO}_3^-/\text{dm}^3 + \text{F}^-$, current density 1.72 mA/cm^2

Similar results were obtained for three-component electrolyte solutions. At a constant F^- ion concentration ($10 \text{ mg } F^-/\text{dm}^3$), independently of the nitrate concentration, the desalination efficiency was still acceptable; it amounted to 82.3–91.7% (Fig. 4). Upon increasing the concentration of NO_3^- ions the process duration was increased from 20.6 to 23.8 min. Finally, the desalination efficiency was calculated for solutions containing sodium chloride, constant nitrate concentration ($30 \text{ mg } NO_3^-/\text{dm}^3$) and variable fluoride content (Fig. 5). The desalination degree remained high (89.6–92.3%) and the process was completed after 20.9–22.1 min depending on the nitrate concentration.

Taking into account the results of the above experiments (Figs. 1–5), some general conclusions can be drawn:

- As results from Faraday's law, the higher the electrolyte content in the treated solution, the longer duration of the process is.
- For binary and ternary electrolyte solutions, the desalination efficiency was somewhat higher than that for sodium chloride solution, probably due to the better ion migration and lower resistivity of electrodialytic cells in ED stack under elevated salt content.
- For ternary electrolyte solutions containing F^- , NO_3^- and Cl^- ions, the increase of nitrate concentration resulted in a slight decrease in the desalination efficiency, what is probably related to the differences in ion hydration energy and ion mobility.

3.2. EFFECT OF NITRATE ON FLUORIDE REMOVAL BY ELECTRODIALYSIS

Figure 6 shows the time dependences of defluoridation for binary ($F^- + Cl^-$) and ternary ($F^- + NO_3^- + Cl^-$) solutions at various nitrate concentration. The final fluoride concentration in diluate was below $1.5 \text{ mg } F^-/\text{dm}^3$, when the initial F^- ion content was not higher than $5 \text{ mg } F^-/\text{dm}^3$ (Fig. 6a). Likewise, the final diluate fulfilled guidelines for drinking water regarding fluoride content when the treated solutions contained $10 \text{ mg } F^-/\text{dm}^3$ and nitrate ($30 \text{ mg } NO_3^-/\text{dm}^3$) (Fig. 6b). For other ED series, the final fluoride content exceeded the permissible level for drinking water. Generally, when fluoride content was higher than $10 \text{ mg } F^-/\text{dm}^3$, electrodialysis did not allow one to obtain the desired fluoride concentration in diluate, however, the fluoride removal efficiency was still high (>84%).

The presence of nitrate ions in fluoride solutions did not influence significantly the defluoridation process in view of operational time and final fluoride concentration. Merely, in the case of the lowest applied fluoride content ($5 \text{ mg } F^-/\text{dm}^3$), the addition of nitrate to the fluoride solution resulted in a slight worsening of F^- removal (Fig. 6a).

The influence of nitrate on fluoride removal can be evaluated in more detail on the basis of the results given in Fig. 7. Figure 7a presents the final fluoride concentration and fluoride removal efficiency for solutions containing F^- , Cl^- and NO_3^- ions and for solutions composed of F^- and Cl^- ions only (for comparison purpose). It is evident that NO_3^- ions have a positive impact on defluoridation efficiency.

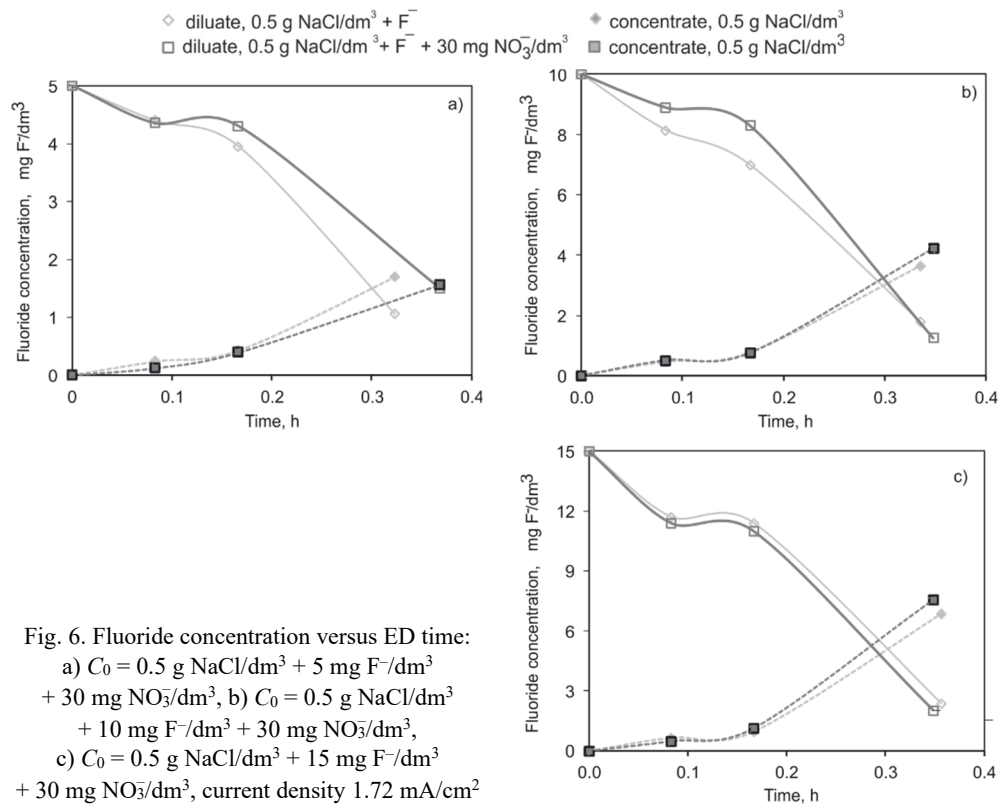


Fig. 6. Fluoride concentration versus ED time: a) C₀ = 0.5 g NaCl/dm³ + 5 mg F⁻/dm³ + 30 mg NO₃⁻/dm³, b) C₀ = 0.5 g NaCl/dm³ + 10 mg F⁻/dm³ + 30 mg NO₃⁻/dm³, c) C₀ = 0.5 g NaCl/dm³ + 15 mg F⁻/dm³ + 30 mg NO₃⁻/dm³, current density 1.72 mA/cm²

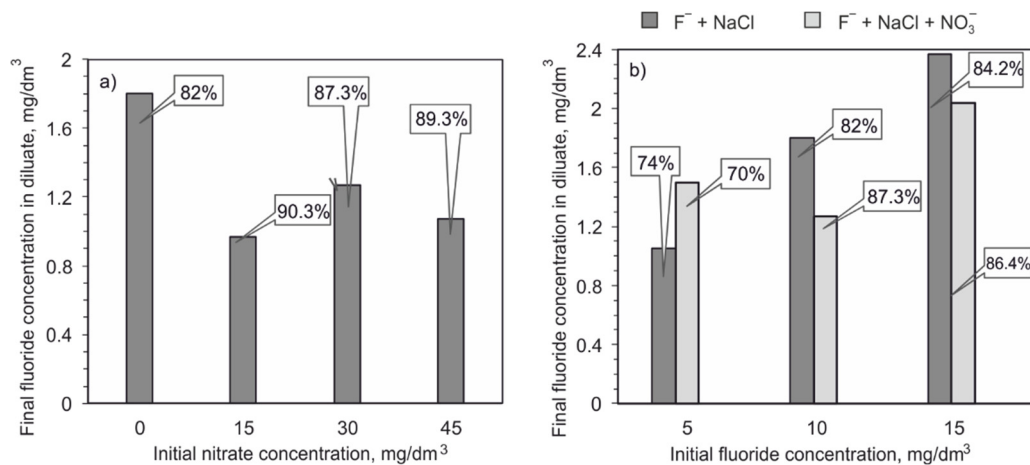


Fig. 7. Final fluoride concentration in diluate and fluoride removal efficiency: a) C₀ = 15, 30 or 45 mg NO₃⁻/dm³ + 10 mg F⁻/dm³ + 0.5 g NaCl/dm³, b) C₀ = 30 mg NO₃⁻/dm³ + 5, 10 or 15 mg F⁻/dm³ + 0.5 g NaCl/dm³

During the experimental series with constant initial fluoride concentration (10 mg F⁻/dm³), the final F⁻ ion concentration in diluate was diminished below the permissible level, irrespectively of the initial nitrate concentration (Fig. 7a). Only when the treated solutions did not contain nitrate, the fluoride content in diluate slightly exceeded 1.5 mg F⁻/dm³. For two-component solutions which contained sodium chloride and fluoride at variable concentrations (Fig. 7b), the desired fluoride concentration was obtained only when the initial F⁻ ion concentration amounted to 5 mg F⁻/dm³. The presence of nitrate seemed to improve fluoride removal efficiency, especially for the elevated initial F⁻ ion content (10 and 15 mg F⁻/dm³).

The presence of coexisting NO₃⁻ ions in fluoride solutions can improve process efficiency in view of fluoride removal by ED. This observation is in a somewhat contradiction to the results reported by other authors. Belkada et al. [17] found that fluoride removal is less effective under the presence of coexisting anions. However, their experiments were performed for solutions containing only fluoride and nitrate (without Cl⁻ ions). The initial concentrations of F⁻ and NO₃⁻ anions in the diluate cells were not comparable (140 and 1000 mg/dm³, respectively). Similarly, Banasiak et al. [20] found that nitrate ions with smaller hydrated ionic radii (0.340 nm) and higher mobility (7.40 m²/(s·V)) were removed more effectively than F⁻ ions with larger hydrated ionic radii (0.352 nm) and lower mobility (5.70 m²/(s·V)). However, in these experiments, the concentrations of both ions were relatively low (10 mg/dm³) and chloride ions were absent. Referring to the results given in Fig. 7, it appears that the total salt concentration (including high predominant sodium chloride content) has the greatest impact on ion transport through the ED stack. The presence of nitrate brings about an increase of ionic strength of electrolyte solutions, thus enhancing the ion transport rate through the ion-exchange membranes.

3.3. ELECTRICAL ENERGY DEMAND IN ELECTRODIALYSIS OF FLUORIDE SOLUTIONS

The amount of electrical energy required to remove given ions from feed solution is an important parameter considered in designing electro dialysis stack. On the other hand, it can be a measure of the correctness of the ED process run. The calculated values of the specific electrical energy demand for fluoride solutions varying in composition are given in Table 2.

The energy demand for solutions containing only sodium chloride varied from 0.20 to 40 kWh/m³ and was directly proportional to the applied current density, which is in accordance with Faraday's law. For ED experiments with solutions containing fluoride and sodium chloride, the EC value was slightly higher than for ED with solution containing only NaCl and amounted to 0.35–0.47 kWh/m³. The presence of nitrate, besides fluoride and chloride ions, in treated solutions had minor effect on the EC increase; the energy consumption was still maintained in the range of 0.36–0.48 kWh/m³.

Table 2

Specific electrical energy demand (*EC*) in relation to solution composition and current density for ED process with monovalent selective ion-exchange membranes

Solution composition	Current density [mA/cm ²]	<i>EC</i> [kWh/m ³]
0.5 g NaCl /dm ³	0.78	0.20
0.5 g NaCl /dm ³	1.72	0.27
0.5 g NaCl/dm ³	2.34	0.40
0.5 g/dm ³ NaCl, 5 mg F ⁻ /dm ³	1.72	0.35
0.5 g/dm ³ NaCl, 10 mg F ⁻ /dm ³		0.47
0.5 g/dm ³ NaCl, 15 mg F ⁻ /dm ³		0.40
0.5 g/dm ³ NaCl, 10 mg F ⁻ /dm ³ , 15 mg NO ₃ ⁻ /dm ³		0.48
0.5 g/dm ³ NaCl, 10 mg F ⁻ /dm ³ , 30 mg NO ₃ ⁻ /dm ³		0.46
0.5 g/dm ³ NaCl, 10 mg F ⁻ /dm ³ , 45 mg NO ₃ ⁻ /dm ³		0.39
0.5 g/dm ³ NaCl, 30 mg NO ₃ ⁻ /dm ³ , 5 mg F ⁻ /dm ³		0.37
0.5 g/dm ³ NaCl, 30 mg NO ₃ ⁻ /dm ³ , 10 mg F ⁻ /dm ³		0.41
0.5 g/dm ³ NaCl, 30 mg NO ₃ ⁻ /dm ³ , 15 mg F ⁻ /dm ³		0.36

The sodium chloride content and the applied current intensity had the primary influence on energy demand in the performed ED process. Nitrate and fluoride, due to their low content in comparison to chloride concentration, had minor impact on energy consumption. Referring to our previous study [21], it is worth noting, that the energy demand determined for ED treatment of fluoride solutions (5 and 10 mg F⁻/dm³ + 0.5 g NaCl/dm³) with use of classical ion-exchange membranes amounted to approximately 0.2 kWh/m³. The difference between *EC* values previously calculated and given in Table 2 (for the same composition of treated solution) arises from higher electrical resistance of monovalent permselective ion-exchange membrane in comparison to the resistance of standard ion-exchange membranes.

4. CONCLUSIONS

Electrodialysis with monovalent selective ion-exchange membranes can be used as an effective method for water desalination and defluoridation. The degree of desalination varied from 85.0 to 91.7% depending on the solution composition and the applied current density, whereas the fluoride removal was in the range of 70–90%. The higher the electrolyte content in the treated solution, the longer time was needed to process termination. For binary and ternary electrolyte solutions, the desalination efficiency was higher than for sodium chloride solution, what could be related to better conditions for ion migration under the elevated salt content. For ternary electrolyte solutions contain-

ing F^- , NO_3^- and Cl^- ions, the increase of nitrate concentration resulted in a slight worsening of desalination efficiency, what was possible related to the differences in ion hydration energy and ion mobility.

The presence of coexisting NO_3^- ions in fluoride solutions improved process efficiency in view of fluoride removal by electrodialysis. This observation was unexpected in view of smaller hydrated ionic radii and higher mobility of NO_3^- ions than ionic radii and mobility of F^- ions. The only possible explanation of the beneficial impact of nitrate on fluoride removal was an increase of the ionic strength of fluoride solutions due to nitrate presence and enhancing the ion transport rate through ion-exchange membranes.

The concentration of sodium chloride and the applied current intensity had the primary influence on the energy demand in the ED defluoridation. Nitrate and fluoride, due to their low content, in comparison to chloride concentration, had minor impact on the energy consumption.

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