



## Influence of current density on fluoride removal using batch electro dialysis

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### ABSTRACT

Fluorine is a common chemical element in the environment. It can have both a beneficial and adverse effect on human health. The World Health Organization estimated the permissible limit of fluoride in drinking water to be 1.5 mg F<sup>-</sup>/dm<sup>3</sup>. Electro dialysis (ED) could be a suitable technique for fluoride ion separation. During ED experiments, model solutions containing 5, 10, 100, or 200 mg F<sup>-</sup>/dm<sup>3</sup>, and 0.5 g NaCl/dm<sup>3</sup> were used. Conventional cation-exchange and monovalent selective anion-exchange membranes were selected for ED defluoridation. The effect of current density (0.78, 1.72, and 2.34 mA/cm<sup>2</sup>) on process efficiency was evaluated. It was observed that with an increasing current density, the fluoride removal efficiency was diminished. In the case of a low initial fluoride content (5, 10, mg F<sup>-</sup>/dm<sup>3</sup>), the ED process allowed the fluoride content to be decreased below the permissible level. For elevated fluoride content, the elimination of fluoride ions was high, but the final fluoride content exceeded the acceptable level of 1.5 mg F<sup>-</sup>/dm<sup>3</sup>. The calculated specific energy demand (0.14–0.42 kWh/m<sup>3</sup>) was dependent on the applied current density, as well as on the salt concentration of the treated solutions. The study also revealed noticeable fluoride deposition on ion-exchange membranes.

*Keywords:* Fluoride; Electro dialysis; Current density; Water treatment

### 1. Introduction

Fluorine (symbol F) is a common element that is characterized by a high reactivity [1]. In an aqueous solution, fluorine commonly occurs as the fluoride ion F<sup>-</sup>. Due to the harmful influence on human health, the World Health Organization (WHO) estimated the fluoride permissible limit in drinking water to be 1.5 mg F<sup>-</sup>/dm<sup>3</sup> [2]. Ingestion of excess fluoride leads to many abnormalities in the human body, such as dental and skeleton fluorosis [3], cancer, Alzheimer's, and neurological problems [4]. The lungs and liver are also susceptible to the toxic influence of fluoride [4]. Elevated fluoride content has been noticed almost all over the world. This problem has occurred in Tanzania, Germany, Kenya, India, Pakistan, Mexico, and Thailand

[5,6]. The concentration of F<sup>-</sup> ions can reach 0.5 mg F<sup>-</sup>/dm<sup>3</sup> in rivers and lakes, 1–35 mg F<sup>-</sup>/dm<sup>3</sup> in groundwater, and up to 1 mg F<sup>-</sup>/dm<sup>3</sup> in seawater [7]. In local soda lakes in the East African Rift Valley, the content of fluoride can even reach 2,800 mg F<sup>-</sup>/dm<sup>3</sup> [6]. Coal-fired power stations, beryllium extraction plants, aluminum smelters, electroplating, coal combustion, as well as ceramic, toothpaste, and glass production also generate high amounts of fluoride [8–10]. In wastewater arising from the etching process, the content of fluoride can reach up to 1,500 mg F<sup>-</sup>/dm<sup>3</sup> [11]. The fertilizer industry discharges wastewater containing fluoride in concentrations up to 9,720 mg F<sup>-</sup>/dm<sup>3</sup> [12].

Fluoride can be removed from water using numerous methods. Adsorption, coagulation, precipitation, ion

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exchange, or the less common electrocoagulation are conventional techniques applicable for diminishing the content of  $F^-$  ions [13–16]. However, due to some drawbacks of these methods, such as low selectivity, low efficiency, and waste formation, advanced membrane technologies have become more favorable. In the field of fluoride removal, membrane processes like nanofiltration (NF), reverse osmosis (RO), and electrodialysis (ED) can potentially be applied [17–20].

When designing electromembrane systems, many parameters should be involved. The efficiency of the ED process on one hand strongly depends on water quality and the initial concentration of pollutants, and on the other hand on process parameters (e.g., membrane type, size of the ED stack, process duration, and current density). Current density is of crucial importance because it should not be higher than the limiting current density that determines the concentration polarization phenomenon.

Arahman et al. [21] used electrodialysis for removing fluoride from groundwater. The membrane stack consisted of standard cation-exchange membranes (CMX), and monovalent selective anion-exchange membranes (ACS) or standard anion-exchange membranes (AMX). The initial  $F^-$  ion content amounted to 380 mg  $F^-/dm^3$ . It was declined to 0 mg  $F^-/dm^3$  after 84 min of operation at a current density of 3.64 A/ $m^2$ , and to 10 mg  $F^-/dm^3$  after 18 min of operation at a current density of 18.18 A/ $m^2$ . Taking into account the membrane surface area (55  $cm^2$ ), the volume of the treated solution (500  $cm^3$ ), and the number of cell pairs (10), the calculated values of the current efficiency amounted to 89.3%–95.5%, which seemed quite reasonable. Arahman et al. [21] arrived at the rather simple conclusion that an increase in current density resulted in a shortening of the duration of the ED process. However, a deterioration of fluoride ion removal efficiency was observed at the increased current density. The membrane type did not have a significant influence on fluoride removal.

In real case applications, the treated water contains both inorganic and organic constituents, which can interact with each other and thus influence the process efficiency. Banasiak and Schäfer [22] conducted research on fluoride removal using ED in the presence of organic matter (OM). Apart from fluoride, the treated solutions also contained nitrate and boron. The initial  $F^-$  ion content was equal to 5 mg  $F^-/dm^3$ . Only 65% of fluoride, and 94% of nitrate was removed. Due to the smaller hydrated radius, nitrate was removed more efficiently than fluoride. The presence of OM in the treated solutions improved the efficiency of fluoride removal by 10%. This phenomenon was explained by the binding of the fluoride ions inside the large structure of OM particles.

The effect of coexisting ions, as well as the current density on the ED efficiency was verified by Belkada et al. [23]. Anion- and cation-exchange membranes (Asahi Glass, Tokyo), each with the effective surface area of 69  $cm^2$ , were applied during the experiments. The membrane stack consisted of 10 cell pairs, whereas the volume of the treated solutions was equal to 1  $dm^3$ . The applied current varied from 0.05 to 0.1 A. The treated solutions contained fluoride and nitrate ions at rather high concentrations (120–180 mg  $F^-/dm^3$ , 750–2,000 mg  $NO_3^-/dm^3$ ). Regardless of the initial fluoride content, about 50%–60% of  $F^-$  ions were removed

during the first 6 min of the process. A significant deterioration of fluoride removal (up to 30%) was detected in a strongly basic pH. This phenomenon can be explained by the possible removal competition between hydroxide and fluoride ions. The current efficiency for fluoride removal using ED performed at the applied current of 0.1 A (calculated based on the available process parameters) was above 100%. The increase in current brought about an improvement in the separation efficiency of both tested ions ( $F^-$  and  $NO_3^-$ ). In the course of the ED experiments with solutions containing fluoride and nitrate ions, it was observed that the presence of  $NO_3^-$  ions caused a decrease in fluoride removal efficiency (as a consequence of ion competition).

Experiments on fluoride removal from real brackish water (Pine Hill, Australia) with the use of ED were performed by Banasiak et al. [20]. The initial concentration of the total dissolved solids (TDS) was equal to 4.7 g/ $dm^3$ , whereas the fluoride concentration amounted to 2.8 mg  $F^-/dm^3$ . Electrodialysis allowed the fluoride concentration to be decreased below the WHO permissible level for drinking water. The preliminary ED tests on the optimization of process parameters performed at variable voltages (9, 12, and 18 V) showed the rather predictable relationship that the ion removal kinetics improved with an increasing voltage. It should be underlined that further research performed by Banasiak and Schäfer [24] resulted in somewhat contradictory findings – the adverse effect of the increased voltage on the treatment efficiency during electrodialysis of real groundwater was confirmed.

It is sometimes the case that even tap water is contaminated by fluoride ions. Research on fluoride removal from tap water with simultaneous desalination was performed by Gmar et al. [25]. Samples of tap water were taken from a mining area in southern Tunisia. The fluoride content varied between 0.8 and 4 mg  $F^-/dm^3$ , whereas water salinity was equal to 0.8–2.2 g/ $dm^3$ . As a result of the ED process, the  $F^-$  ion concentration was lowered by 92% and the produced diluate fulfilled the standards for drinking water. In the course of the ED process, the competition between chloride and fluoride ions was also confirmed. Under the presence of  $Cl^-$  ions in the treated solution, the  $F^-$  ion transport through membranes was inhibited.

Arar et al. [26] performed ED experiments on fluoride removal from multi-component solutions. CMX and AMX membranes were applied. The treated solutions contained fluoride, chloride, and sulfate ions mixed at various equivalent ratios ( $F^-:Cl^- = 1:10$  or  $1:25$ ;  $F^-:Cl^-:SO_4^{2-} = 1:10:10$  or  $1:25:25$ ). The initial fluoride content was equal to 2 mg  $F^-/dm^3$ . With increasing equivalent concentration ratios of chloride to fluoride or sulfate to fluoride, the fluoride removal efficiency was enhanced. The  $F^-$  ion content was decreased by 35% and 48% when the fluoride to chloride ratio and fluoride to sulfate ratio amounted to 1:10, respectively. A significantly better result (93% of fluoride removal) was obtained when the  $F^-:SO_4^{2-}$  ratio increased to 1:25. For ternary solutions, the fluoride concentration in the diluate decreased to 0.7–0.08 mg  $F^-/dm^3$ . It should be noted that when the equivalent amounts of chloride and sulfate in the mixture were increased, apart from the enhancement of fluoride separation, the percent removal of chloride and sulfate also increased. The obtained results were explained

by the elevated ionic strength of solutions containing the increased amounts of ions, and also by the facilitated transport of the ions between the electro-dialytic cells of the ED stack. However, the removal efficiencies of monovalent anions (fluoride and chloride) were higher than the removal efficiency of sulfate ions due to the effect of the hydrated radius of the transported ions [26].

Bagastyo et al. [12] evaluated the usability of electro-dialysis in order to separate fluoride and to recover phosphate from fertilizer wastewater. They used a simple three-compartment ED stack. The volume of treated wastewater was equal to 4 dm<sup>3</sup>. The initial fluoride content was very high and amounted to 9,720 mg F<sup>-</sup>/dm<sup>3</sup>. The fluoride removal attained a mere 2.7% and 4.6% for the ED stack with a membrane surface area of 100 and 200 cm<sup>2</sup>, respectively. Similarly, the increase in current from 0.5 to 1.0 A resulted in a fluoride separation improvement from 2.2% to 4.6%. The current efficiency for fluoride removal using ED (calculated based on the available process parameters) was in the range of 9%–18%. It was emphasized that 99% of phosphate ions remained in the diluate compartments, thus indicating the capability for phosphate recovery from fertilizer wastewater. The fluoride separation efficiency could possibly be enhanced by applying a stacked type reactor.

Lahnid et al. [27] evaluated the cost of electro-dialytic fluoride removal for an ED plant with a capacity of 100 m<sup>3</sup>/h. Sand filters and a microfiltration system (through a cartridge filter) were applied as a pretreatment step. The fluoride content in the treated water amounted to 2.32 mg F<sup>-</sup>/dm<sup>3</sup> and the ED process allowed it to be decreased to 1 mg F<sup>-</sup>/dm<sup>3</sup>. The TDSs content was lowered from 1.2 to 0.7 g/dm<sup>3</sup>. The total investment cost of the ED installation was estimated to be 833,207.5 €. The total operating cost, involving maintenance and power consumption, was calculated as 0.154 €/m<sup>3</sup>.

The above literature review shows that electro-dialysis could be used as an effective method of fluoride removal from aqueous solutions. Nevertheless, there are still many key issues that should be solved, improved, or clarified. The problem of divalent salt precipitation can be overcome by the application of ED with monovalent selective ion-exchange membranes, followed by the conventional ED process. Therefore, the presented study aimed to investigate fluoride removal using electro-dialysis with monovalent selective anion-exchange membranes and conventional cation-exchange membranes. Thanks to such an approach, it was possible to verify the impact of the membrane type on the degree of fluoride removal, as in our previous ED experiments standard anion-exchange membranes were used. Due to the fact that the relationship between the current density and the ED performance is until now ambiguous, the effect of this parameter on the process efficiency was also verified.

## 2. Materials and methods

### 2.1. Reagents

During the ED experiments, model solutions containing 5, 10, 100, and 200 mg F<sup>-</sup>/dm<sup>3</sup> and 0.5 g NaCl/dm<sup>3</sup> were used. The solutions were prepared with the use of distilled

water, sodium fluoride (NaF – molar mass 41.99 g/mol), and sodium chloride (NaCl – molar mass 58.44 g/mol). The range of fluoride concentration in the model solutions was characteristic for water with an elevated fluoride content (due to both natural and anthropogenic activity), whereas the sodium chloride concentration was typical for freshwater. The pH of all the solutions was close to neutral and was in the range of 5–6.

### 2.2. Installation

The ED experiments were performed with the use of the laboratory installation PCCell BED-1-System (PCCell GmbH, Germany). The ED system consisted of an electro-dialytic stack (PCCell 64002 model), electrode solution tank, external tanks for the diluate and concentrate, and a power supply. Both the diluate and concentrate tanks had a volume of 2 dm<sup>3</sup> (each). The volume of the external tank for the electrode rinsing solution (0.05 mol NaCl/dm<sup>3</sup>) was equal to 9 dm<sup>3</sup>. The diluate and concentrate streams, as well as the electrode solution, circulated in three independent circulations at a flow rate of 90 dm<sup>3</sup>/h, which corresponded to a liquid linear velocity (in the stack) of 6.25 cm/s. The ED stack was connected to a DC power supply characterized by a maximum output voltage of 24 V and an amperage of 5 A.

The ED membrane stack consisted of 10 electro-dialytic cells and each cell had a thickness of 0.5 mm. The PCA ion-exchange membranes (PCA GmbH, Germany) were installed in the stack. Their characteristics are shown in Table 1. Eleven classic cation-exchange (PC-SK) and 10 monovalent selective anion-exchange (PC-MVA) membranes were used for water defluoridation. The surface area of each membrane was equal to 64 cm<sup>2</sup>.

### 2.3. Methodology

All ED experiments were conducted with model solutions containing fluoride and chloride ions. The same model solution filled up both the diluate and concentrate tanks at the beginning of each ED series (each solution had a volume of 2 dm<sup>3</sup>). The ED installation operated in a batch mode, that is, the diluate and concentrate streams circulated in the stack until the end of the process. The process was terminated when the maximum voltage was achieved (24 V). The process was conducted under galvanostatic conditions – the electric current during the course of the ED process was constant, whereas the variation in the electrical potential between electrodes was monitored over time.

The applied electric current was 0.05, 0.11, and 0.15 A, which corresponded to the current densities of 0.78, 1.72, and 2.34 mA/cm<sup>2</sup>, respectively. The applied electrical current was chosen in such a way as to not exceed the limiting current density. The theoretical value of the limiting current density was calculated using Rautenbach's equation [28]. Assuming a desalination efficiency of 85% (for the initial salt concentration of 0.5 g/dm<sup>3</sup>), the determined limiting current density was equal to 2.38 mA/cm<sup>2</sup>.

In the course of each ED test, the quality of the diluate and concentrate solutions was monitored by determining the fluoride and chloride concentrations and by measuring the electrical conductivity. The samples of the diluate and

Table 1  
Membrane characteristics

Parameter	Membrane type	
	Cation-exchange (PC-SK)	Monovalent selective anion-exchange (PC-MVA)
Size, mm	110 × 110	
Thickness, μm	90–130	100 (200)
Exchange capacity, meq/g	~1.2	~1.0
Electrical resistance, Ωcm <sup>2</sup>	1–3	20
Chemical resistance (pH range)	0–9	0–7
Mechanical resistance, MPa	0.4–0.5	0.2
Permselectivity (transfer number)	>0.95	>0.97
Ionic form	Na <sup>+</sup>	Cl <sup>-</sup>
Functional group	Sulfonic acid	Quaternary ammonium

concentrate were taken at the same time intervals (after the 5th and 10th minute from the beginning of the process, then – after every 10 min, and finally – when the voltage reached 24 V). The fluoride concentration was analyzed with the use of the spectrophotometer HACH DR 3900 (method 8029, program no. 190, wavelength 580 nm). The determination of the F<sup>-</sup> ion content involved a colorimetric method with the SPADNS reagent. This reagent contains zirconium, which creates colorless complexes with fluoride and thus lightens the sample color in proportion to the fluoride concentration. The measurement error amounted to ±9%. The chloride concentration was measured using the Mohr method (according to PN-ISO 9297). The accuracy of the method amounted to ±8%. The electrical conductivity of the diluate and concentrate was measured with the use of a multimeter HQ40D. The sensitivity of the method was equal to 0.5%. Moreover, the changes in voltage were monitored every 5 min.

The measurements were triplicated in the course of the experiments. On the basis of the obtained values, the standard deviation was calculated.

The ion flux through the membranes was calculated according to Eq. (1):

$$J = \frac{V_i C_i - V_t C_t}{A_m t} \quad (1)$$

where  $J$  is the ion flux (mol/m<sup>2</sup>h),  $A_m$  is the total surface area of the anion-exchange membranes (m<sup>2</sup>),  $V_i$ ,  $V_t$  is the volume of concentrate at the beginning of the ED process and at a time  $t$ , respectively (m<sup>3</sup>),  $C_i$ ,  $C_t$  is the fluoride/chloride concentration at the beginning of the ED process and at a time  $t$  in the concentrate cells, respectively (mol/m<sup>3</sup>), and  $t$  is the process duration (h).

The amount of fluoride ions deposited in the system was calculated according to Eq. (2):

$$M = \frac{(V_{id} C_{id} + V_{ic} C_{ic}) - (V_{fd} C_{fd} + V_{fc} C_{fc})}{A} \quad (2)$$

where  $M$  is the mass of fluoride accumulated in/on the ion-exchange membranes (mg F<sup>-</sup>/m<sup>2</sup> of membrane),

$V_{id}$ ,  $V_{fd}$  are the initial and final volume of the diluate (dm<sup>3</sup>),  $V_{ic}$ ,  $V_{fc}$  are the initial and final volume of the concentrate (dm<sup>3</sup>),  $C_{id}$ ,  $C_{fd}$  are the initial and final concentration of fluoride in the diluate (mg/dm<sup>3</sup>),  $C_{ic}$ ,  $C_{fc}$  are the initial and final concentration of fluoride in the concentrate (mg/dm<sup>3</sup>), and  $A$  is the total membrane surface area (m<sup>2</sup>).

The mass of accumulated fluoride involved F<sup>-</sup> ions deposited in the membrane stack (i.e., on and/or in both the anion-exchange and cation-exchange membranes). Deposition of fluoride ions in other parts of the ED system was not observed.

The specific electrical energy demand was calculated according to Eq. (3):

$$EC = \frac{I \int_0^t U dt}{V_d} \quad (3)$$

where  $EC$  is the specific electrical energy demand (kWh/m<sup>3</sup>),  $I$  is the current (A),  $U$  is the voltage (V),  $V_d$  is the volume of the diluate (m<sup>3</sup>), and  $t$  is the process duration (h).

### 3. Results

#### 3.1. Effect of current density on fluoride removal efficiency

The appropriate adjusting of electrical current is important for the correct running of electromembrane processes. Conducting the ED process at a current density higher than the limiting current density could result in the worsening of the desalination efficiency, and even damage of the ion-exchange membranes [28].

Fluoride removal using the ED process was performed at variable current densities (0.78, 1.72, and 2.34 mA/cm<sup>2</sup>) and the obtained results are presented in Fig. 1. It should be noted that the highest applied current density was lower than the theoretically calculated limiting current density (2.38 mA/cm<sup>2</sup>). The model solutions, varying in fluoride concentration (5, 10, 100, and 200 mg F<sup>-</sup>/dm<sup>3</sup>), were subjected to the ED tests.

The duration of the ED process with regards to the fluoride content and the applied current density is presented in Table 2.

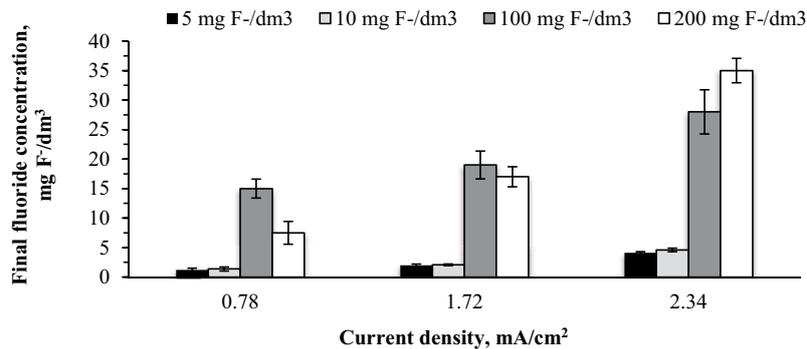


Fig. 1. Final fluoride concentration vs. current density,  $C_0 = 5, 10, 100, \text{ and } 200 \text{ mg F}^-/\text{dm}^3 + 0.5 \text{ g NaCl}/\text{dm}^3$  (with marked standard deviation).

In the case of a low initial fluoride concentration (5 and 10 mg F<sup>-</sup>/dm<sup>3</sup>), the degree of F<sup>-</sup> ion removal varied in a rather moderate range (from 18% to 86%). However, it was possible to decrease the fluoride content below the permissible limit (1.5 mg F<sup>-</sup>/dm<sup>3</sup>) when the current density was not higher than 0.78 mA/cm<sup>2</sup> (Fig. 1). At a current density equal to 1.72 mA/cm<sup>2</sup>, the final fluoride content in the diluate was also very low and close to the WHO guidelines (2 mg F<sup>-</sup>/dm<sup>3</sup>). For an elevated F<sup>-</sup> ion content (100 and 200 mg F<sup>-</sup>/dm<sup>3</sup>), the percentage of fluoride removal was very satisfying (circa 72%–96%), which corresponded to the final fluoride concentration equal to 7.5–35 mg F<sup>-</sup>/dm<sup>3</sup> (Fig. 1). Nevertheless, in this case, the fluoride content in the produced diluate significantly exceeded the permissible level. Taking into consideration the above observations, it can be elucidated that the increase in the initial fluoride concentration brings about an increase in the ionic strength of the electrolyte solution and, as a consequence, the transport of fluoride ions is facilitated [26]. It was clearly seen that the duration of the process was correlated with the applied current density and the solution concentration (Table 2).

Based on the results given in Fig. 1, it can be concluded that both the electrical current density and the initial fluoride concentration influenced the fluoride removal efficiency. The higher the applied current density, the worse the diluate quality with regards to the fluoride concentration. Presumably, this phenomenon was caused by the undesired concentration polarization – the increased current led to a quick depletion of ions in the membrane boundary layer (at the diluate side). Consequently, a rapid voltage increase and termination of the process occurred. However, the fluoride ions could still be present in the bulk solution.

The observed negative impact of increasing the current density on the fluoride removal efficiency was reflected in the desalination efficiency of the sodium chloride solution and the sodium chloride solution containing fluoride ions (Fig. 2). This finding seems to diverge from the results reported by other authors. Based on the literature review, it can be stated that the ion removal efficiency increases with an increasing current density. Ghorbani and Ghassemi [29] proved that the desalination efficiency of NaCl solutions (0.6–2.0 g/dm<sup>3</sup>) increased linearly with electrical current density, however, the limiting current density was not determined. Likewise, Belkada et al. [23] revealed that the treatment efficiency of the photovoltaic industry wastewater

Table 2

Duration of the ED process with regards to the initial fluoride concentration and current density,  $C_0 = 5, 10, 100, \text{ and } 200 \text{ mg F}^-/\text{dm}^3 + 0.5 \text{ g NaCl}/\text{dm}^3$

Fluoride concentration, mg F <sup>-</sup> /dm <sup>3</sup>	Current density, mA/cm <sup>2</sup>	Process duration, h
5	0.78	0.92
5	1.72	0.34
5	2.34	0.21
10	0.78	0.86
10	1.72	0.33
10	2.34	0.22
100	0.78	1.36
100	1.72	0.51
100	2.34	0.38
200	0.78	1.93
200	1.72	0.73
200	2.34	0.58

improved with an increase in the current. However, the removal of pollutants (fluoride and nitrate ions) was evaluated at the same operation time, irrespective of the applied current. Such an experimental procedure could lead to rather misleading conclusions. It is commonly known that the increase in the applied current density brings about the increment of ion flux and the shortening of the operation time necessary for salt removal [21].

It should be underlined that the ED tests reported in this paper were stopped when the voltage reached 24 V (maximum output voltage), which is essential with regards to the final diluate quality. Banasiak and Schäfer [24] performed ED tests on water desalination according to a similar operation mode, and they definitely confirmed the adverse effect of the increased voltage on the treatment efficiency during the electrodesalination of real water (brackish groundwater). The unfavorable effect of concentration polarization, as well as the depletion of electron carriers in the diluate boundary layer, was mentioned when explaining the obtained results.

When comparing the defluoridation performances (at the current density of 1.72 mA/cm<sup>2</sup>) obtained for the ED systems with monovalent selective anion-exchange membranes

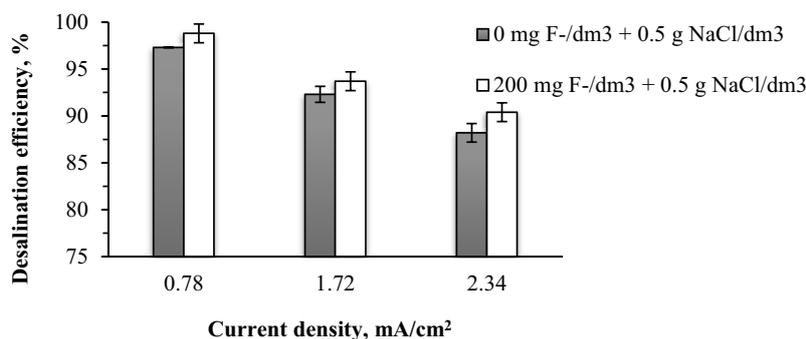


Fig. 2. Desalination efficiency of NaCl solution and NaCl solution containing fluoride ( $C_0 = 200 \text{ mg F}^-/\text{dm}^3$ ) at various current densities (with marked standard deviation).

(PC-MVA) (this study) and standard anion-exchange (PC-SA) membranes [30], it is possible to deduce that fluoride removal is not significantly influenced by the type of anion-exchange membrane. The  $\text{F}^-$  ion removal efficiency was comparable for both membrane types, although the PC-MVA membranes exhibited a slightly worse performance than the PC-SA membranes.

### 3.2. Fluoride and chloride flux

It was predicted that analyzing the ion fluxes (of both  $\text{F}^-$  and  $\text{Cl}^-$  anions) through the anion exchange-membranes should throw some light on the subject of anion transport in the ED system. The fluoride and chloride fluxes were calculated on the basis of the  $\text{F}^-$  and  $\text{Cl}^-$  ion concentration increase in the concentrate cells at a given time (Eq. (1)). The mean  $\text{F}^-$  ion flux at variable current densities (0.78, 1.72, and  $2.34 \text{ mA}/\text{cm}^2$ ) is given in Fig. 3. The treated solution contained 5, 10, 100, and  $200 \text{ mg F}^-/\text{dm}^3$  and  $0.5 \text{ g NaCl}/\text{dm}^3$ .

It can be seen from the data given in Fig. 3 that the fluoride flux varied in a wide range (from  $0.006$  to  $0.147 \text{ mol}/\text{m}^2\text{h}$ ), depending on the current density and initial  $\text{F}^-$  ion concentration. The noticeable improvement of fluoride flux with an increasing driving force (i.e., current density) was detected. This finding is in accordance with Faraday's law – the amount of ions to be removed is directly proportional to the current density. Unsurprisingly, the  $\text{F}^-$  ion flux also increased proportionally to the initial fluoride content, which can be attributed to the increased ionic strength, and thus higher ion flux. At the elevated ionic strength, the conductivity of the solution is higher (as more ions are present in the solution), and at the same time the electrical resistance of the solution is lower and the mobility of ions is improved. However, in the ED course performed at a constant current, the drop of voltage with the increasing ionic strength can be observed and the risk of process failure exists.

When comparing the determined fluoride fluxes with those calculated for the ED tests with the use of standard anion-exchange membranes (PC-SA) [31], it can be stated that the  $\text{F}^-$  ion flux through monovalent selective anion-exchange membranes (PC-MVA) was by circa 50% lower. This phenomenon was caused by the presence of an additional layer of a highly cross-linked polymer on the PC-MVA membrane surface, and thus a higher electrical resistance

of PC-MVA membranes in comparison to the resistance of standard anion-exchange membranes (PC-SA). These factors led to a significant anion flux decrease.

The chloride ion flux was also calculated in the course of the ED defluoridation. The sodium chloride content in the treated solutions ( $0.5 \text{ g NaCl}/\text{dm}^3$ ) corresponded to the initial chloride concentration of  $303 \text{ mg Cl}^-/\text{dm}^3$ . The obtained results are given in Fig. 4.

The chloride ion flux varied between  $0.22$  and  $2.11 \text{ mol}/\text{m}^2\text{h}$ , depending on the current density and fluoride concentration. By analyzing the results given in Fig. 4, two dependencies can be observed. Firstly, it was found that the chloride ion flux increased with the increasing current density, similarly as was observed for the fluoride ion flux (Fig. 3). On the other hand, the noticeable worsening of the chloride ion flux with the increasing fluoride concentration was detected. The chloride ions should be transported more easily than the fluoride ions because they are characterized by lower hydrated ionic radii ( $0.332 \text{ nm}$ ) and higher mobility ( $7.91 \text{ m}^2/(\text{s V})$ ) than the fluoride's ionic radii ( $0.352 \text{ nm}$ ) and mobility ( $5.70 \text{ m}^2/(\text{s V})$ ) [22]. Such behavior appears to be valid for a low fluoride concentration ( $5$  and  $10 \text{ mg F}^-/\text{dm}^3$ ), because in this case, the equivalent fluoride concentration is much lower than the equivalent chloride concentration. Under the increased  $\text{F}^-$  ion content in the treated solutions ( $100$  and  $200 \text{ mg F}^-/\text{dm}^3$ ), the equivalent fluoride concentration is comparable or even higher than the equivalent chloride concentration. In this situation, competition between co-existing ions occurred and the chloride flux is diminished. However, taking into consideration the magnitude of the chloride ion flux, it was still dominant in the total ion flux. The competition between the fluoride and chloride ions during tap water defluoridation with the use of Neosepta and PC cell ion-exchange membranes was also confirmed by Gmar et al. [25].

### 3.3. Fluoride deposition in the ED system

The fluoride mass balance in the ED system could be helpful when clarifying the results of fluoride separation. The amount of fluoride adsorbed on the membrane surface and inside the membrane matrix was calculated according to Eq. (2). The results obtained are given in Fig. 5. The treated solutions contained 5, 10, 100, and  $200 \text{ mg F}^-/\text{dm}^3$  and  $0.5 \text{ g NaCl}/\text{dm}^3$ .

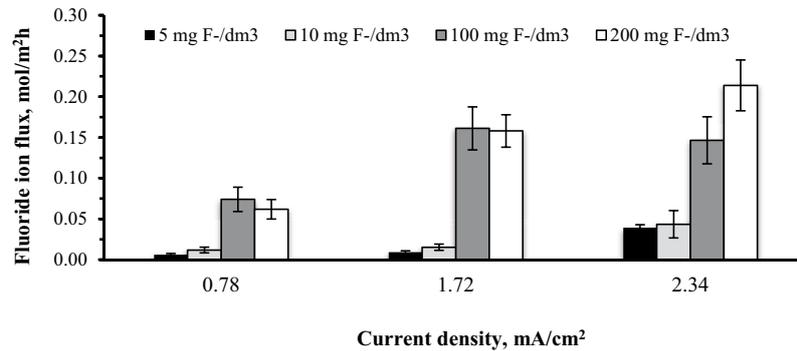


Fig. 3. Fluoride ion flux vs. current density,  $C_0 = 5, 10, 100,$  and  $200 \text{ mg F}^-/\text{dm}^3 + 0.5 \text{ g NaCl}/\text{dm}^3$  (with marked standard deviation).

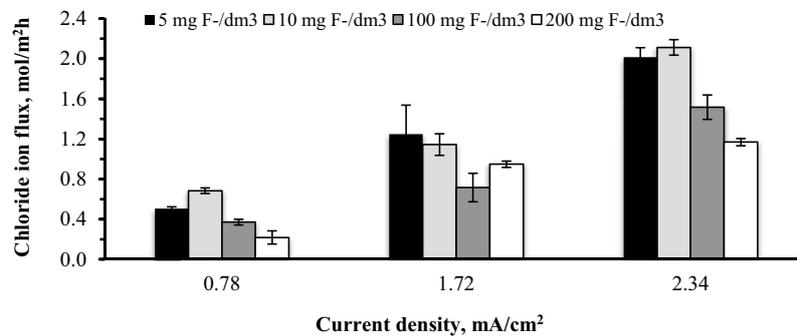


Fig. 4. Chloride flux vs. current density,  $C_0 = 5, 10, 100,$  and  $200 \text{ mg F}^-/\text{dm}^3 + 0.5 \text{ g NaCl}/\text{dm}^3$  (with marked standard deviation).

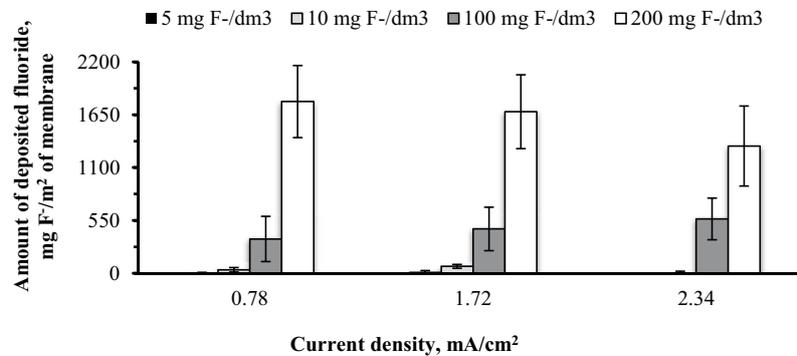


Fig. 5. Amount of deposited fluoride vs. current density,  $C_0 = 5, 10, 100,$  and  $200 \text{ mg F}^-/\text{dm}^3 + 0.5 \text{ g NaCl}/\text{dm}^3$  (with marked error bars,  $\pm 9\%$ ).

As could be expected, the deposition of  $\text{F}^-$  ions on and/or inside the ion-exchange membranes during the ED process occurred. This is a normal phenomenon, especially when new membranes are applied. It seems that due to the extremely low affinity of fluoride ions for quaternary ammonium groups [32], as well as the adverse selectivity order for fluoride by anion-exchangers [13], both ion-exchange and chemisorption cannot be considered as the cause of the deposition of  $\text{F}^-$  ions in the ED system. As the fluoride is soluble in water and the treated solution contained only fluoride, chloride, and sodium ions, the precipitation of salt was also not possible. The most probable mechanism of fluoride deposition is physical adsorption on/in the anion-exchange membranes. This approach is supported by many

studies on fluoride adsorption by anion-exchange membranes [33,34]. It is interesting to note that the amount of fluoride adsorbed by monovalent selective anion-exchange membranes was about 40% higher than the fluoride amount deposited on/in the standard anion-exchange membranes [31], which can be attributed to the highly cross-linked additional polymer layer at the PC-MVA membrane surface.

The amount of adsorbed/absorbed fluoride varied greatly (from 6 to 1,787  $\text{mg F}^-/\text{m}^2$  of membrane), depending on the initial  $\text{F}^-$  ion concentration and the applied current density. The impact of fluoride concentration on the adsorption/absorption intensity was much more pronounced than the effect of the driving force (i.e., the electrical current). The amount of fluoride deposited in the ED

system reached 6–16.4 and 36.2–71.7 mg F<sup>-</sup>/m<sup>2</sup> of membrane when the treated solutions contained 5 and 10 mg F<sup>-</sup>/dm<sup>3</sup>, respectively (Fig. 4). The significant increase in adsorbed fluoride (up to 566–1,787 mg F<sup>-</sup>/m<sup>2</sup>) was detected for the elevated F<sup>-</sup> ion initial concentrations (100, 200 mg F<sup>-</sup>/dm<sup>3</sup>). Surprisingly, the amount of adsorbed fluoride ions increased with the increasing concentration from 0.5% to 12% to even 44.5% to 60% of the total F<sup>-</sup> ions present in the system. The highest adsorption intensity (1,787 mg F<sup>-</sup>/m<sup>2</sup> of membrane) was detected for the highest initial fluoride concentration (200 mg F<sup>-</sup>/dm<sup>3</sup>) at the lowest current density (0.78 mA/cm<sup>2</sup>). On the other hand, a slight weakening of fluoride deposition in the ED system was established at the highest current density. However, it should be kept in mind that this significant fluoride accumulation (up to 60% of the total F<sup>-</sup> ions present in the system) was due to short term experiments in the batch mode.

The observed increase in the fluoride adsorption/absorption intensity with the increasing concentration seems to be reasonable – the higher the total mass of fluoride in the ED system, the more ions that could be trapped on and/or inside the anion-exchange membranes. The effect of the electrical current on fluoride adsorption/absorption was not so univocal. Banasiak and Schäfer [24] found that the mass of all ions present in solution (expressed as TDS) deposited on the membranes increased with an increasing voltage due to the higher initial flux of ions through the ion-exchange membranes. This is partly in agreement with the results presented in Fig. 5. It should be noted that the deposition of fluoride ions was not detected, or was decreased, at the highest current density, indicating that the high current forced the F<sup>-</sup> ions to pass the ion-exchange membranes.

Summing up the above digressions, it could be supposed that two phenomena are important for fluoride removal using ED: (1) electromigration of fluoride ions from the diluate to concentrate cells, (2) adsorption/absorption of fluoride ions on and/or in the anion-exchange membranes. However, it could be anticipated that a certain saturation stage of fluoride accumulation in the system should be attained (e.g., for long ED duration) with no further impact on fluoride transport.

### 3.4. Energy demand

The energy demand in electrodialysis is usually taken into consideration, as it reflects the economics of the process. The power consumption (including pumping energy) constitutes 30% of the operating cost and cannot be ignored in the economical evaluation of the ED desalination installation [27]. However, it should be mentioned that in the analyzed experiments, due to the low current density applied, the power demand represents only a few percent of the maintenance cost. Nevertheless, the magnitude of the energy used could be useful in the evaluation of the ED process.

The specific electrical energy demand (EC) was calculated based on the voltage variation with time (Eq. (3)). The obtained EC values for ED tests conducted at various current densities with solutions varying in composition are given in Table 3. It should be noted that the EC values given in Table 3 do not involve the energy demand for the pumping of circulated solutions in the ED installation.

Table 3  
Specific electrical energy demand (EC) for fluoride removal using ED

Solution composition		Current density	EC
mg F <sup>-</sup> /dm <sup>3</sup>	g NaCl/dm <sup>3</sup>	mA/cm <sup>2</sup>	kWh/m <sup>3</sup>
5	0.5	0.78	0.16
5	0.5	1.72	0.19
5	0.5	2.34	0.25
10	0.5	0.78	0.14
10	0.5	1.72	0.19
10	0.5	2.34	0.23
100	0.5	0.78	0.23
100	0.5	1.72	0.26
100	0.5	2.34	0.41
200	0.5	0.78	0.26
200	0.5	1.72	0.36
200	0.5	2.34	0.42

During the ED experiments with solutions containing 5 and 10 mg F<sup>-</sup>/dm<sup>3</sup>, the specific electrical energy demand varied from 0.14 to 0.25 kWh/m<sup>3</sup>. The calculated EC values increased significantly (0.23–0.42 kWh/m<sup>3</sup>) when solutions containing high fluoride amounts were treated.

According to the data given in Table 3, it can be concluded that the energy demand was directly proportional to the applied current density and the initial concentration of fluoride. These relationships are in accordance with Ohm's law. It should be indicated that the increase in current caused greater changes in power demand than the increase in the concentration of fluoride. This can be simply explained by taking into account the total salt concentration in the treated solutions. The increase in the F<sup>-</sup> ion content from 5 to 10 mg F<sup>-</sup>/dm<sup>3</sup> corresponded to less than a 5% increase in the total salt concentration, whereas for solutions containing 100 mg F<sup>-</sup>/dm<sup>3</sup> the increase in the total salt content (compared to 5 mg F<sup>-</sup>/dm<sup>3</sup>) was approximately 54%.

Comparing the specific electrical energy demand (at the current density of 1.72 mA/cm<sup>2</sup>) with the previous results [30] obtained for the ED system with standard anion-exchange (PC-SA) membranes, it can be deduced that the type of anion-exchange membrane influenced the power demand. The EC values calculated for the ED process with PC-MVA membranes were by circa 7%–20% higher than the EC values obtained for the ED process with standard PC-SA membranes. As was already mentioned, the monovalent selective anion-exchange membranes (PC-MVA) were characterized by a higher electrical resistance (20 Ω cm<sup>2</sup>) than the resistance of the standard anion-exchange membranes (PC-SA) (1–3 Ω cm<sup>2</sup>), which resulted in the increased energy demand for fluoride removal.

## 4. Conclusions

- Electrodialysis with the use of monovalent selective anion-exchange membranes and standard cation-exchange membranes is suitable for water defluoridation. The

fluoride removal efficiency depends primarily on the  $F^-$  ion initial concentration in the treated solution, as well as on the current intensity. Basically, the fluoride ions could be removed to a high degree (up to 96%), however, the permissible limit for drinking water (1.5 mg  $F^-/dm^3$ ) can be obtained when the current density is not higher than 0.78 mA/cm<sup>2</sup> and the initial fluoride concentration does not exceed 10 mg  $F^-/dm^3$ .

- Current (or current density) is of great importance for the correct operation of the electro dialysis process. The higher the applied current density, the worse the diluate quality in view of fluoride concentration. This dependence is caused by undesired concentration polarization. Thus, it must not be forgotten that in practical ED applications the applied current density should be below the limiting current density.
- Fluoride ions are prone to adsorption onto and/or in monovalent selective anion-exchange membranes in the course of electro dialysis. The extent of this undesired phenomenon depends primarily on the initial fluoride concentration. The amount of deposited fluoride ions can be as high as even 60% (up 1,787 mg  $F^-/m^2$  of the membrane) of the total  $F^-$  ions present in the system.
- Competition between  $F^-$  and  $Cl^-$  ions can occur in the course of the ED process, especially when the concentrations of these ions are approximately the same. The effect of fluoride removal in the ED process is the result of fluoride electromigration from the diluate to the concentrate cells, as well as the result of fluoride adsorption in/on the anion-exchange membrane matrix.
- Energy demand for water defluoridation using the ED process is influenced by the current density and total salt content in the treated solutions. The specific electrical energy demand in the course of fluoride removal varied between 0.14 and 0.42 kWh/m<sup>3</sup> (the energy needed for the pumping of the diluate, concentrate, and electrolyte solutions was not involved in the calculations). The magnitude of energy demand for fluoride removal can also be influenced by the type of anion-exchange membranes. Conducting the ED process with monovalent selective anion-exchange membranes could result in an increase in energy consumption by circa 7%–20% (in comparison to the power demand estimated for ED with standard ion-exchange membranes).

## Symbols

$A_m$	— Total surface area of the anion-exchange membranes, m <sup>2</sup>
$A$	— Total surface area of the anion- and cation-exchange membranes, m <sup>2</sup>
$C_{ic}, C_{fc}$	— Initial and final concentration of fluoride in the concentrate, mg/dm <sup>3</sup>
$C_{id}, C_{fd}$	— Initial and final concentration of fluoride in the diluate, mg/dm <sup>3</sup>
$C_p, C_t$	— Fluoride/chloride concentration at the beginning of the process and at a time $t$ in the concentrate cells, respectively, mol/m <sup>3</sup>
EC	— Specific electrical energy demand, kWh/m <sup>3</sup>
$I$	— Current, A

$J$	— Ion flux, mol/m <sup>2</sup> h
$M$	— Mass of fluoride accumulated on and/or in the ion-exchange membranes, mg $F^-/m^2$ of membrane
PC-MVA	— Monovalent selective anion-exchange membrane
PC-SA	— Standard anion-exchange membrane
PC-SK	— Standard cation-exchange membrane
$t$	— Process duration, h
TDS	— Total dissolved solids
$U$	— Voltage, V
$V_d$	— Volume of diluate, m <sup>3</sup>
$V_p, V_t$	— Volume of concentrate at the beginning of the ED process and at a time $t$ , respectively, m <sup>3</sup>
$V_{ic}, V_{fc}$	— Initial and final volume of concentrate, dm <sup>3</sup>
$V_{id}, V_{fd}$	— Initial and final volume of diluate, dm <sup>3</sup>
WHO	— World Health Organization

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