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REMOVAL OF FLUORIDE IONS BY BATCH ELECTRODIALYSIS

Suitability of conventional batch electrodialysis to fluoride removal from aqueous solutions has been investigated. The experiments were conducted with the use of laboratory installation PCell BED-1 System at a constant current density (1.56 or 2.34 mA/cm²). The influence of initial fluoride and salt (NaCl) concentration, as well as the presence of organic matter on the process performance was studied. It was found that the separation efficiency increased upon decrease of initial fluoride content in model solutions. Permissible final concentration of fluorides in the product water (1.5 mg/dm³) was obtained for experiments with solutions of initial fluoride concentration equal to 5 mg F⁻/dm³ and 10 mg F⁻/dm³. The presence of humic acids in fluoride solutions subjected to electrodialysis treatment has no adverse effect on the defluorization and desalination efficiency. The calculated electrical energy demand depended on composition of fluoride solution and varied from 0.121 to 0.895 kWh/m³.

1. INTRODUCTION

Drinking water pollution by fluorides as a result of natural processes or anthropogenic activities has been considered as one of the important problems worldwide. Due to permanent threat to human health, fluoride removal from water of high fluoride concentration is recognized as urgent necessity.

Fluorine is a yellow gas with strong odour. It has strong oxidative and corrosive properties. Characteristic attribute of fluorine is strong chemical reactivity, e.g. it is able to form hydrogen fluoride with water vapour. Fluorine is present in living systems in bones, teeth and plants. There are two possible sources of fluorine in the environment: natural and anthropogenic. Minerals like fluorite, cryolite or fluoroapatite can be considered as a natural source of fluorine. Such processes as

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weathering and leaching cause migration of fluorine to water [1]. Fluorine is used in cement and brick factories, as well as in glass industry [2]. Excessive concentrations of fluoride ions are common for groundwater. The highest F^- concentrations are characteristics of areas rich with fosforites and apatites. High levels of fluoride ions in surface water are the result of wastewater pollution [3, 4]. In some cases, fluoride ions come from fluoridation of tap water. It is generally assumed that this process prevents dental caries and osteoporosis [5]. According to WHO guidelines [6], the maximum permissible content of F^- ions in drinking water amounts to $1.5 \text{ mg } F^-/\text{dm}^3$. Pursuant to Ordinance of the Ministry of Health [7] concentration of fluorides in drinking water in Poland cannot be higher than $1.5 \text{ mg } F^-/\text{dm}^3$. In wastewater discharging to water bodies, the maximum allowable content of fluoride is equal to $25 \text{ mg } F^-/\text{dm}^3$ [8].

Fluorine has significant impact on human health. High content of fluorine in drinking water leads to fluorosis and bones lesion. Concentration in the range of $1.5\text{--}4 \text{ mg } F^-/\text{dm}^3$ causes cancer, gastrological problems, liver deterioration or Alzheimer disease. Dosage of $3\text{--}5 \text{ g NaF}$ is deadly for adults [1, 5, 9]. On contrary, shortage of fluorine may results in dental caries and osteoporosis [5]. Fluorine compounds are accumulated mainly in bones, hair, teeth and nails [10]. The problem of excessive concentrations of fluoride ions occurs in many countries in North Africa, Thailand, China, Afghanistan, India and Japan. Fluoride content in natural water can come to $67 \text{ mg}/\text{dm}^3$ [9–14]. In Poland high concentration of fluorides was monitored in intake waters in Żuławy and Lower Silesia [15, 16].

Conventional techniques like precipitation, ion exchange, adsorption and coagulation are able to remove F^- ions from aqueous solution to various extents. Common adsorbents used for fluoride removal are: alumina and aluminum based adsorbents, calcium based adsorbents, metal oxides or carbon based sorbents [12]. Expensive or complicated regeneration, high initial cost, lack of selectivity and insufficient F^- ion removal are common disadvantages of these techniques.

Membrane processes (electrodialysis, reverse osmosis, nanofiltration) are very effective technologies which are able to separate many different contaminants. Especially, electrodialysis (ED) becomes more popular. It is a relatively simple technique and has fewer disadvantages compared to conventional methods. During the electrodialysis, ions are selectively transported through alternately aligned anion-exchange and cation-exchange membranes. Transport of ions is caused by direct electric current potential applied between two electrodes. Anions are attracted by the anode and they are passing through the positively charged membranes. Then, they are retained by negatively charged cation-exchange membranes. On the contrary, cations migrate to the cathode through cation-exchange membranes. Next they are retained by anion-exchange membranes. As a result, in some chambers ion concentration increases while in another chambers ion content decreases [17]. The efficiency of electrodialysis depends on many factors such as pH, initial electrolyte concentration, applied current, flow rate, and coexisting ions. The presence of cations like Cl^- , SO_4^{2-} ,

in a treated solution may reduce process efficiency [18]. What is important, the electrodialysis can be periodically disabled from exploitation when fluoride content decreases under permissible limit.

Amor et al. [19] conducted research on fluoride removal by electrodialysis. They studied two variants of electrodialysis:

- two-stage electrodialysis: in the first stage, monoselective membranes ACS-CMX were used, then water was purified with conventional membranes ANF-CMX;
- electrodialysis with preliminary removing of divalent ions (by chemical methods) and a pair of conventional membranes ANF-CMX.

It was observed that the electrodialysis was an effective process for fluoride removal. The first variant (without pretreatment) was preferred. This method was simple and did not require any chemicals. The fluoride content was reduced from 3 mg F⁻/dm³ to 0.63 mg F⁻/dm³ in the former variant, and to 0.81 mg F⁻/dm³ in the latter one. The fluoride concentration was lower than required by WHO and this means that the produced water can be used as drinking water.

Ergun et al. [18] performed research on fluoride removal with commercial, strong-basic, anion-exchange membrane (SB-6407, Gelman Sciences). They found that the current density influenced the removal efficiency. With the increase of current density, the amount of separated fluoride ions increased. For the initial content of fluorides in water equal to 20.6 mg F⁻/dm³, the final F⁻ concentration was lowered to 0.8 mg F⁻/dm³. This concentration is much lower than 1.5 mg F⁻/dm³ required by the WHO. Zeni et al. [20] studied the ED process with anion-exchange membranes AMP[®] (Asahi Glass Co.) and photopolymer membranes MZA. They were removing F⁻ ions from artesian well water. The AMP[®] membranes removed 69% of fluoride ions under the current density of 0.1 A/dm². After increasing the current density to 0.7 A/dm², 97% of F⁻ ions were removed. The latter membrane (MZA) was able to remove only 40% of fluoride ions when the current density had the same values.

Some researchers [21, 22] investigated fluoride removal by a continuous electrodialysis in a pilot scale. Tahaikt et al. [21] applied ED process to treat Moroccan groundwater of varying F⁻ ion concentration. Among two commercial anion-exchange membranes (ACS and AXE 01, Neosepta) used in the experiments, better results were obtained for ACS membranes. Almost total removal of F⁻ ions was achieved at relatively low elimination of sulfate ions. It was also found that to ensure the optimal ED efficiency, the water recovery should be maintained at approximately 40%. Finally, the fluoride content was lowered from 1.8 mg F⁻/dm³ to 0.5 mg F⁻/dm³, whereas TDS decreased from 1127 mg/dm³ to 656 mg/dm³. The favorable effect of antiscalant dosing on fluoride removal was stated.

Keri et al. [22] in order to evaluate the efficiency of ED pilot unit in F⁻ ion removal conducted a series of experiments at varying process parameters (pH, applied potential, initial fluoride concentration, and flow rate). Satisfactory results were obtained for solutions of initial F⁻ concentration lower than 10 mg F⁻/dm³ – the removal efficiency

of F^- ions amounted to 99.6% and the final fluoride content in product water was considerably lower than $1 \text{ mg } F^-/\text{dm}^3$. The experiments performed for F^- concentrations higher than $10 \text{ mg } F^-/\text{dm}^3$, i.e. 20 and $50 \text{ mg } F^-/\text{dm}^3$ resulted in moderate rejection rates of fluorides (95.95 and 79.22%, respectively) and the final diluates did not fulfil the WHO standards.

Economic evaluation of the costs of fluoride removal by ED is very beneficial. Taking into account the industrial data for ED installation of capacity $2200 \text{ m}^3/\text{day}$, the investment costs are estimated to be about 830 000 €, whereas the operating costs amount to 0.154 €/m^3 [23].

The aim of the presented study was to evaluate the efficiency of fluoride ion removal by conventional batch electrodialysis in the presence of mineral and organic constituents in the treated solutions. The current efficiency and energy demand have also been estimated.

2. MATERIALS AND METHODS

Reagents. Model solutions were made of sodium fluoride (NaF) and distilled water. Sodium chloride (mineral salt, $1 \text{ g}/\text{dm}^3$) was added to the tested solutions to increase the salinity. Model solutions containing organic matter (OM) were prepared by dissolving humic acids (HA, Aldrich) in distilled water. The average concentration of HA in model solutions was equal to $6.5 \text{ mg C}/\text{dm}^3$, whereas the color of obtained solutions amounted to approximately $40 \text{ mg Pt}/\text{dm}^3$.

Membranes and experimental installation. In the experiments, the PCA ion-exchange membranes (produced by PCA GmbH, Germany) were applied. Table 1 presents the membrane parameters.

Table 1

Parameters of the experimental membranes

Parameter	Membrane type	
	Cation-exchange (PC-SK)	Anion-exchange (PC-SA)
Size, mm	110×110	
Thickness, μm	90–130	
Thermal resistance, $^\circ\text{C}$	60	60
Chemical resistance (pH range)	0–9	0–9
Mechanical resistance, MPa	0.4–0.5	0.4–0.5
Functional group	$-\text{SO}_3^-$	$-\text{NR}_3^+$

The experiments were conducted in the ED installation PCCell BED-1 System (PCCell GmbH, Germany) with an electrodialyzer PCCell 64002 type. The ED installation consisted of an electrodialytic stack 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.

Thickness of the electrodialytic chamber was 0.5 mm. Concentrate, diluate and electrode solutions circulated in three independent circulations. Each circulation was equipped with a separate pump and a rotameter. Flow rates could be adjusted from 10 to 100 dm³/h. Flow rates of diluate and concentrate were maintained at 90 dm³/h, flow velocity at 6.25 cm/s.

Methods. Low content of fluorine salt resulted in rapid termination of the electrodialysis process. For this reason, during the ED experiments solutions with addition of mineral salt (1 g NaCl/dm³) were applied. Concentration of fluoride ions in the tested solutions amounted to 5, 10, 100, 200 mg F⁻/dm³ (salt solutions) and to 100, 200 mg F⁻/dm³ (without NaCl dosage). At the beginning of the ED experiments, the diluate and concentrate chambers contained the same solution. Concentrate and diluate solutions were circulated in the ED installation. The process was terminated when the voltage applied to the ED stack achieved 24.4 V. For salt solutions, the applied current was equal to 0.15 A, which corresponds to the current density of 2.34 mA/cm². Experiments with solutions containing only fluoride ions were carried out at the current of 0.1 A (1.56 mA/cm²). The experiments on the influence of OM on ED efficiency were conducted for salt solutions containing 5 and 10 mg F⁻/dm³ at the current of 0.15 A (2.34 mA/cm²). The samples of diluate and concentrate were taken at the same time intervals. The ED process was also carried out for salt solution (1 g NaCl/dm³) at current intensity of 0.15 A (2.34 mA/cm²).

During the ED experiments, pH and conductivity were measured with the use of pH-meter Elmetron CPC-551 and conductometer Elmetron CC-411, respectively. Fluoride contents in diluate and concentrate were determined by the colorimetric analysis with SPADNS reagent. This method is based on the reaction of fluorides with red zirconium dye solution. Fluorides form a colorless complex with zirconium, thus reducing the intensity of the red color in proportion to the fluoride concentration. Spectrofotometer DR 2000 (HACH) was used for fluoride ion analysis.

Organic matter content (OM) in the tested solutions was established by dissolved organic carbon (DOC) determination with the use of a Shimadzu Analyzer TOC 5050. Concentration of chloride ions in salt solutions was determined by the Mohr method (PN-ISO 9297:1994).

Changes of voltage were monitored every 5 min. The specific electrical energy demand (*EC*) was calculated according to [20]:

$$EC = \frac{\int_0^t U dt}{V_d} \quad (1)$$

where: EC – electrical energy demand per 1 m³ of treated solution, kWh/m³, I – current, A, U – voltage, V, V_d – volume of the diluate, m³, t – duration of the process, s.

The current efficiency (η_c) was determined with the use of the following equation [20]:

$$\eta_c = \frac{FV_d(C_i - C_f)}{nIt} \times 100 \quad (2)$$

where: η_c – the current efficiency, %, V_d – volume of the diluate (assuming $V_{d, \text{initial}} = V_{d, \text{final}}$), m³, C_i – initial total concentration of cations or anions in the diluate cells, eq/m³, C_f – final total concentration of cations or anions in the diluate cells, eq/m³, F – Faraday constant, 96500 As/eq, n – number of diluate cells.

3. RESULTS AND DISCUSSION

3.1. ELECTRODIALYTIC REMOVAL OF FLUORIDES FROM SOLUTIONS WITH NO SALT ADDITION

The preliminary tests on fluoride removal were carried out for model solutions without the addition of salt. The initial concentration of fluoride anions in diluate and concentrate amounted to 100 and 200 mg F⁻/dm³. Electrodialysis process was performed at a constant current equal to 0.1 A (corresponding to the current density of 1.56 mA/cm²).

The results of electrodialytic separation of fluorides are presented in Fig. 1. Generally, the process efficiency was not very satisfying; fluoride anions were removed in 83.4 and 68.6% for initial concentration of 100 and 200 mg F⁻/dm³, respectively (Fig. 1b). The final fluoride concentration reached only 16.6 and 61 mg F⁻/dm³, respectively (Fig. 1a). These concentrations were significantly higher than the acceptable fluoride level in drinking water (1.5 mg F⁻/dm³) [6, 7].

It is worth mentioning that the time of ED process in the case of fluoride model solutions (with no salt addition) was very short (10–20 min) in comparison to the duration of ED desalination of NaCl solution (Fig. 6), although the applied current density for experiments with fluorides was smaller (1.56 mA/cm²) than for salt solution (2.34 mA/cm²). This observation confirms the well-known opinion that ED

process should be applied for solutions containing dissolved solids at minimal concentration of 500 mg/dm^3 .

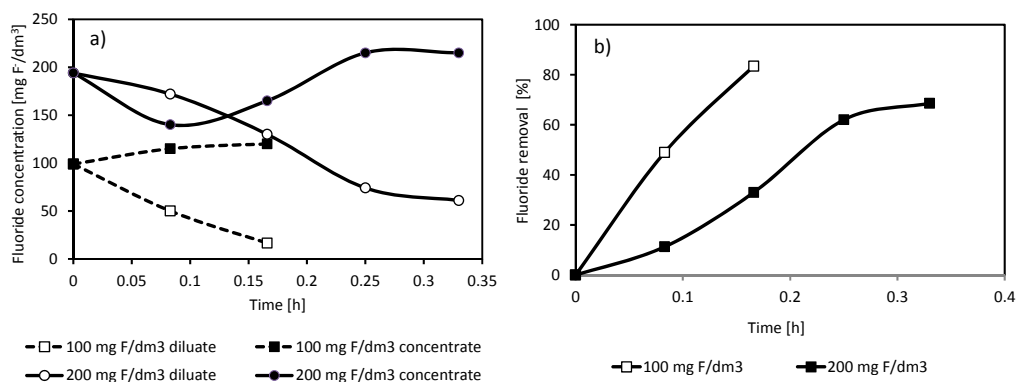


Fig. 1. Removal of fluoride ions by ED process: a) concentration of fluorides in diluate and concentrate during the ED process, b) efficiency of fluoride removal during the ED process; no salt addition, $I = 0.1 \text{ A}$ (1.56 mA/cm^2)

The obtained results indicate also that during the ED process the sorption of fluoride ions in ion-exchange membrane structure occurs (Fig. 1a). A possible method of preventing this sorption phenomenon could be the initial membrane conditioning (saturation) by fluoride anions.

3.2. ELECTRODIALYTIC REMOVAL OF FLUORIDES FROM SALT SOLUTIONS

Due to too low concentration of electrolyte (NaF salt) and rapid increase of applied voltage (and in consequence, also ED stack resistivity) further experiments were conducted for solutions containing 1 g NaCl/dm^3 and 5, 10, 100, and 200 $\text{mg F}^-/\text{dm}^3$. The initial concentration of fluorides and sodium chloride in both diluate and concentrate cells were the same. The ED desalination was carried out at the constant current of 0.15 A (current density of 2.34 mA/cm^2).

The effects of fluoride removal by ED in the presence of sodium chloride are presented in Fig. 2. It can be observed that the ED operation time, i.e. time to reach the limited voltage (24.4 V) was significantly extended – to 30 min for low fluoride concentrations (5 and 10 $\text{mg F}^-/\text{dm}^3$, Fig. 2a) and to more than 1 h for high fluoride concentrations (100 and 200 $\text{mg F}^-/\text{dm}^3$, Fig. 2b). The ED effects for low initial fluoride content were very satisfying – the final fluoride concentration in diluate cells amounted to 0.7–0.85 $\text{mg F}^-/\text{dm}^3$ thus fulfilling the drinking water standards. On the other hand, high initial fluoride concentrations still brought about undesired high level of fluoride ions in the diluate cells (approximately 50 $\text{mg F}^-/\text{dm}^3$). The sorption of fluoride ions in membrane structure during ED desalination of two-component solutions

was also noticeable, especially at high initial fluoride concentrations (Fig. 2b). This finding was confirmed by decreasing fluoride concentration in concentrate cells at the initial stage of the ED process.

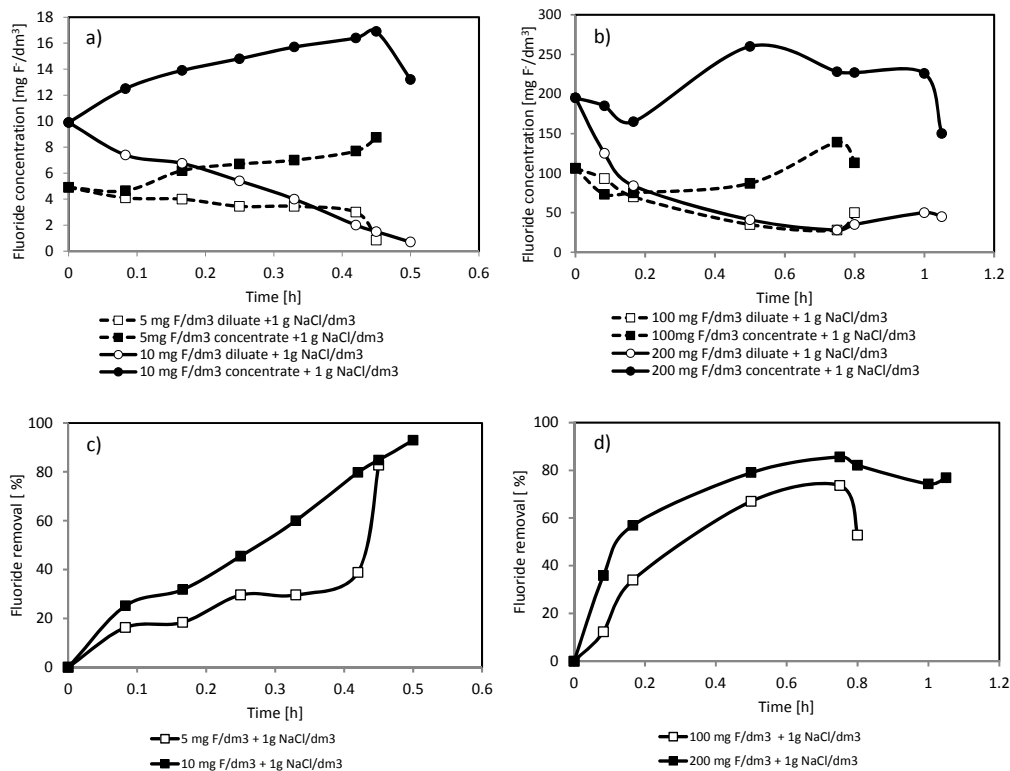


Fig. 2. Removal of fluoride ions from salt solutions by the ED process:
 a) and b) concentrations of fluorides in diluate and concentrate during the ED process,
 c) and d) efficiency of fluoride removal during the ED process;
 salt – 1 g NaCl/dm³, $I = 0.15$ A (2.34 mA/cm²)

According to Banasiak et al. [25], the presence of sodium chloride in solutions treated by ED can affect the transport of other ions and process efficiency. Taking into account the removal rates of F⁻ ions (Figs. 2c and 2d) and desalination rates (Fig. 6), it can be concluded that elimination of TDS is much better (85–97.4% and 97.4–97.7% for solutions of low and high fluoride contents, respectively) than that of fluorides. This can be explained by ion mobility and ionic radius. The ionic mobility of Cl⁻ ions (7.91 m²/(s·V)) is much higher than the ionic mobility of F⁻ ions (5.70 m²/(s·V)) [25]. On the other hand, the radius of hydrated Cl⁻ ion (0.332 nm) is smaller than the radius of hydrated F⁻ ion (0.352 nm) [25]. Therefore, the transport of Cl⁻ ions (less hydrated and more mobile than F⁻ ions) through anion-exchange membranes is facilitated in

comparison to the transport of fluorides. The unfavorable influence of sodium chloride on the F^- ion removal by ED process was also confirmed by Ergun et al. [18].

The obtained results indicate the suitability of conventional electro dialysis for production of drinking water from water containing moderate amount of fluorides at simultaneous presence of electrolyte (e.g. sodium chloride). It was possible to achieve the decrease of concentration of fluoride ions in the range of 83–93% (Fig. 2c). At the increased concentration of fluoride anions (characteristic of industrial wastewater), the complete elimination of these ions seems to be impossible – the degree of F^- ion removal at the end of ED process was unstable and varied from 53 to 76% (Fig. 2d).

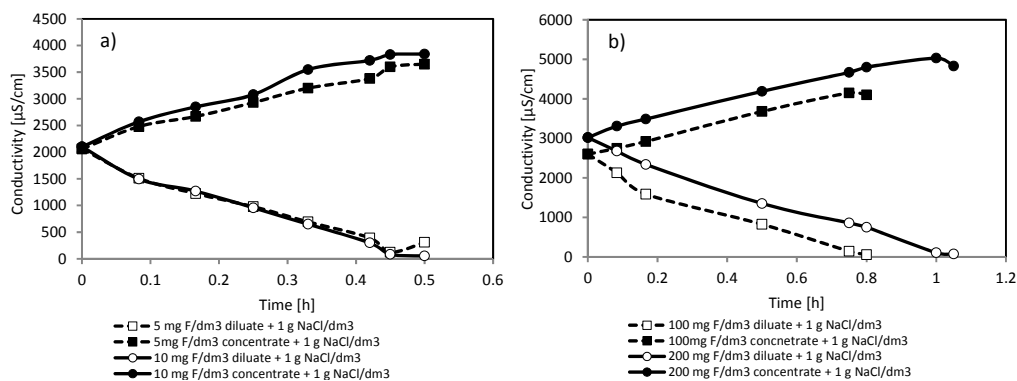


Fig. 3. Conductivities of diluate and concentrate during fluoride removal from salt solutions by the ED process: a) initial fluoride concentration 5 and 10 mg F/dm^3 , b) initial fluoride concentration 100 and 200 mg F/dm^3 ; salt – 1 g NaCl/dm^3 , $I = 0.15 \text{ A}$ (2.34 mA/cm^2)

The run of ED desalination of fluoride solutions containing 1 g NaCl/dm^3 was monitored by conductivity measurements (Fig. 3). The desalination process was stable – for low fluoride content both operation time and the final desalination effect (i.e. final conductivity of diluate and concentrate) were similar (Fig. 3a). The desalination runs for solutions containing high F^- amounts were more differentiated (Fig. 3b). The ED operation time for solution of 200 mg F/dm^3 was extended to more than 1 h, whereas the diluate conductivity was maintained below 100 $\mu\text{S/cm}$.

3.3. ELECTRODIALYTIC REMOVAL OF FLUORIDES FROM SALT SOLUTIONS CONTAINING ORGANIC MATTER

The ED fluoride removal efficiency was also evaluated under the presence of organic matter (i.e. humic acids, HA). This series of experiments was performed for salt solutions of low fluoride concentrations (5 and 10 mg F/dm^3). The initial composition of diluate and concentrate was the same. The ED process was carried out at constant

current of 0.15 A (2.34 mA/cm²). The results of electrodialytic removal of fluoride anions from salt solutions in the presence of humic acids are given in Fig. 4.

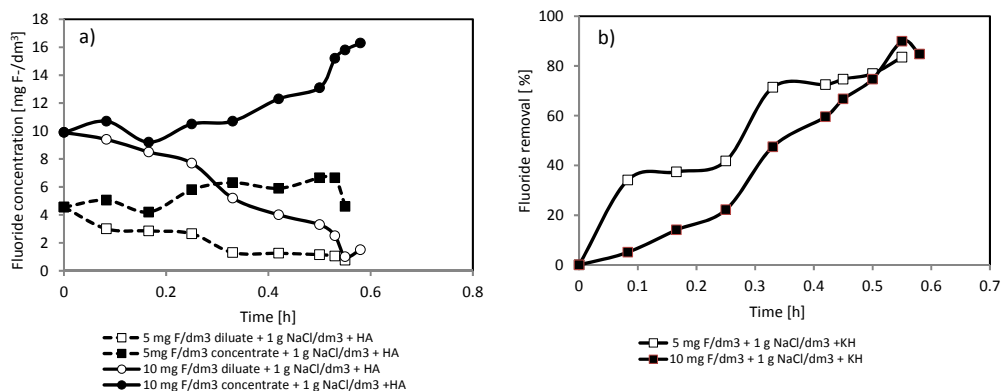


Fig. 4. Removal of fluoride ions from salt solutions containing OM by the ED process:
 a) concentrations of fluorides in diluate and concentrate during the ED process,
 b) efficiency of fluoride removal during the ED process;
 salt – 1 g NaCl/dm³, $I = 0.15$ A (2.34 mA/cm²)

The extension of ED operation time (in comparison to series for salt solutions without humic acids addition) by 20% on average was observed (Fig. 4a). This may suggest a decrease in the rate of ion transport through the membranes at the probably unchanged stack resistivity. In view of a general opinion that humic substances have an ability to create membrane fouling, the increase in ED duration seems to be evident. The final concentration of fluoride ions in diluate cells still meets the drinking water standards, however the quality of product water was significantly better when solution of the lowest fluoride content (5 mg F⁻/dm³) was treated. Sometimes it happens that the fluoride removal is even improved under the presence of humic substances due to attachment of fluoride anions to dissociated macroparticles of humic substances, which in turn adsorb on the surface of ion-exchange membrane [25]. However, the HA adsorption was not significant in the reported study – the initial DOC value decreased from 6.5 to 6.2 and 6.3 mg C/dm³ at the end of ED in diluate and concentrate, respectively. The phenomenon of OM removal from both diluate and concentrate cells indicates deposition of HA on membrane surface rather than ionic penetration into the membrane matrix. This finding can be supported by pH of the treated solutions during the ED process – for all solutions containing OM the monitored pH values in both diluate and concentrate compartments were always below 7. According to literature data [26], humic acids have neutral charge at acidic solutions, thus the electrostatic interactions between HA macroparticles and ion-exchange membranes can be neglected. As a consequence, the impact of OM on the defluorization efficiency was not as significant, as it could be expected.

Similarly to previous experiments (Figs. 1 and 2), a temporary decrease of fluoride concentration in concentrate cells at the initial stage of electrodialysis was noticed. This phenomenon confirms the tendency of fluoride anions to penetrate into the ion-exchange membrane structure. The degree of fluoride removal was increasing systematically in the course of electrodialysis to reach 83–85% at the end of the process (Fig. 4b).

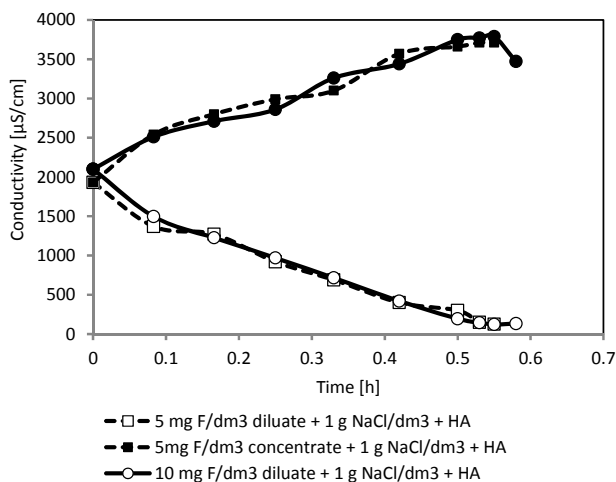


Fig. 5. Conductivities of diluate and concentrate during fluoride removal from salt solutions containing OM by the ED process; salt – 1 g NaCl/dm³, $I = 0.15$ A (2.34 mA/cm²)

The variation in the conductivities of diluate and concentrate during the electrodialysis of salt solutions containing fluorides and humic acids is presented in Fig. 5. The desalination process was performed without any disturbances – for both treated solutions, the final diluate conductivity was similar (approximately 130 µS/cm), however a slightly higher than conductivity of the diluates obtained after electrodialysis of salt solutions without OM dosage.

3.4. ENERGY DEMAND IN ELECTRODIALYSIS OF FLUORIDE SOLUTIONS

Energy demand for electrodialytic treatment and concentration of aqueous solutions is of great importance due to economic aspects and application potential. The calculated values of electrical energy demand for fluoride solutions varying in composition are given in Table 2. The obtained values can be recognized as moderately high, although they are higher than those reported by Kabay et al. [26]. This unfavorable difference in energy demand is caused by the presence of additional electrolyte (NaCl) in fluoride solutions. The values of electrical energy demand determined for solutions

containing only sodium fluoride (with no additional salt) were very low and amounted to 0.121 kWh/m^3 ($100 \text{ mg F}^-/\text{dm}^3$) and 0.235 kWh/m^3 ($200 \text{ mg F}^-/\text{dm}^3$). However, it was proved that the electrodialysis of solutions containing only sodium fluoride (even in high concentration) is not feasible due to rapid voltage increase and short operational time.

Table 2

Initial composition of treated solutions, final concentration of fluoride ions, specific electrical energy demand and current efficiency for conventional ED process

Composition of model solution (at the beginning of ED process)			Fluoride concentration in ED product water [$\text{mg F}^-/\text{dm}^3$]	Specific electrical energy demand [kWh/m^3]	Current efficiency [%]
[$\text{mg F}^-/\text{dm}^3$]	[$\text{g NaCl}/\text{dm}^3$]	[$\text{mg C}/\text{dm}^3$]			
–	1	–	–	0.49	100
5	1	–	0.85	0.37	100
10	1	–	1.5	0.395	100
100	1	–	28	0.725	92.2
100	–	–	16.6	0.121	100
200	1	–	50	0.895	85
200	–	–	61	0.294	100
5	1	6.5	0.75	0.35	100
10	1	6.5	1.5	0.43	98.5

Current efficiency was very high (Table 2) – 100% in the majority of experiments. Only for salt solutions containing 100 and 200 $\text{mg F}^-/\text{dm}^3$, the current efficiency was slightly decreased indicating the improper performance of ED process.

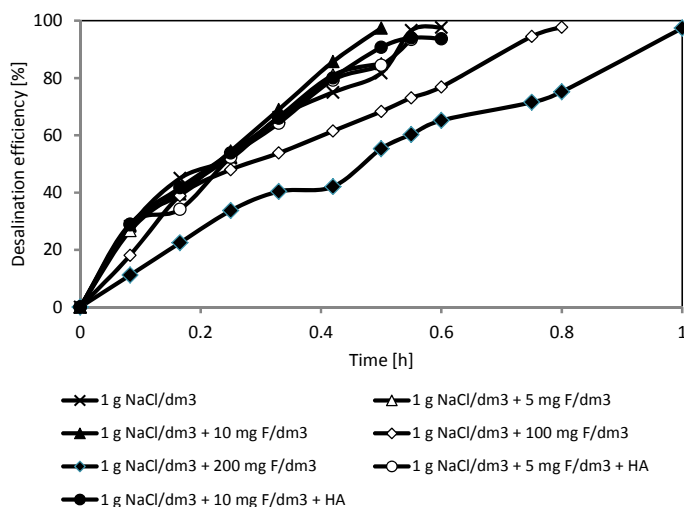


Fig. 6. Desalination efficiency for solutions varying in composition

The desalination efficiency obtained for all salt solutions is given in the Fig. 6. Almost complete desalination was achieved irrespectively of the composition of treated solution. A significant increase in ED operation time was observed for solutions of high fluoride content probably resulting in the highest electrical energy demand. Unexpectedly, the presence of organic matter in the treated solutions did not influence the defluorization and desalination efficiency, as well as the energy demand.

4. CONCLUSIONS

According to WHO standards, the content of fluorides in drinking water cannot be higher than $1.5 \text{ mg F}^-/\text{dm}^3$. Conventional electro dialysis is suitable for treatment of natural waters containing moderate amounts of fluoride ions ($5\text{--}10 \text{ mg F}^-/\text{dm}^3$). The quality of product water fulfils the WHO standards – the final content of fluoride ions in diluate can be maintained in the range of $0.85\text{--}1.5 \text{ mg F}^-/\text{dm}^3$. In solutions with high fluoride contents, the final diluate quality exceeds the permissible level.

The rate of energy consumption increases with increasing total salt (fluorides and chlorides) content in water. It means that the solute concentration influences the electro dialysis operational costs. Electro dialysis of solutions of high salt content needs extended operation time at a constant current in comparison to ED process with solutions of low salinity.

The composition of solutions has only minor effect on the desalination efficiency. Almost complete desalination of fluoride solutions can be reached. Although humic substances are considered serious foulants of ion-exchange membranes, the presence of humic acids in fluoride solutions subjected to electro dialysis treatment has no adverse effect on the defluorization and desalination efficiency. However, fluoride ions show a slight tendency to penetrate into the membrane structure, especially in the presence of organic matter.

Electro dialysis can be recommended for treatment of good quality water or it should be applied after water pretreatment. Otherwise the ED technique is costly and inefficient.

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