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Fluoride removal from aqueous solutions with the use of electrodialysis with monovalent permselective anion-exchange membranes

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ABSTRACT

Water contamination by fluoride has become a significant problem in many regions of the world. Due to its harmful influence on living organisms, the World Health Organization has estimated the permissible fluoride content in drinking water to 1.5 mg F^-/dm^3. Various methods can be used for water defluoridation. Due to many advantages, when compared with conventional techniques, membrane processes have become more popular. In this paper, tests with the use of electrodialysis (ED) were described. The ED experiments were performed for synthetic multicomponent solutions containing fluoride (5,10,100 and 200 mg F^-/dm^3), humic acids (5, 10 and 15 mg/dm^3) and sodium chloride (0.5 g/dm^3). Standard cation-exchange membranes (PC-SK) and monoanion permselective membranes (PC-MVA) were employed. The volumes of the diluate and the concentrate were 2 dm^3 (each). As a result of the ED process, the fluoride concentration was lowered below the permissible level at a low initial fluoride content (5 and 10 mg F^-/dm^3). For the elevated initial fluoride concentrations, the removal efficiency was also very satisfying (80%–91%). The energy demand varied from 0.226 to 0.549 kWh/m^3 and was mostly influenced by the fluoride content. The presence of organic matter had a moderate influence on the fluoride removal efficiency, the process duration, as well as on the energy demand.

Keywords: Fluoride; Organic matter; Electrodialysis; Monovalent permselective anion-exchange membrane

1. Introduction

Fluorine is a chemical element commonly present in the environment. A large amount of fluorine migrates to the environment from industry. Industrial wastewater discharge leads to water pollution. Wastewater from fertilizers, semiconductors, pharmaceuticals, as well as food or glass production especially characterizes with a high fluoride content. Moreover, pesticides containing fluoride have become more common. As a result, large amounts of fluorinated wastes are produced. Fluorine is also used in the nuclear applications and the metallurgical industry [1–4]. In wastewater from phosphoric acid production, the F^- ion content can reach even 3,000 mg/dm^3 [4]. Some fluoride migrates to the environment from natural sources. Fluoride is mostly dissolved from rocks and minerals that contain fluoride (e.g., topaz, biotite, fluorite, villiaumite, fluorapatite and hydroxyapatite) [5–7]. The fluoride content in the earth's crust usually varies from 0.065 to 0.09 wt.% [8]. The World Health Organization (WHO) has stated that fluoride and arsenic are the most significant inorganic pollutants in drinking water [6–7]. Many factors influence on the fluoride content in natural waters, and they are listed as pH, contact time, solubility of minerals and the anion exchange capacity of minerals [5].

A low amount of fluoride is beneficial for human health. It helps to mineralize bones and protects teeth. This element is especially essential for the health of children below 8 [4–7]. The excess of fluoride is harmful and can cause some health

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problems. The most common health issue is fluorosis – dental and skeleton one [9]. Cancer and problems with the brain are also possible [10]. Moreover, gastrointestinal and neurological issues have been noticed. Lesions of the thyroid, urinary tract problems and muscular manifestation may also occur [4]. Due to the harmful impact on human health, the WHO established the permissible content of F^- ions in drinking water as 1.5 mg F^-/dm^3 [11]. Fishes, algae, aquatic plants and invertebrates are also very vulnerable to the excess of fluoride [3].

Water contamination by fluoride has become a global problem. It has been observed in many regions of the world. In Tanzania, the fluoride content has even reached 330 mg F^-/dm^3. In Kenya, the fluoride concentration in groundwater has reached 180 mg F^-/dm^3 [12,13]. Problems with an elevated fluoride concentration have also been noticed in India, Argentina, Pakistan, Mexico, Canada, USA, Brazil, Sri Lanka and China [10,12,14]. More than 200 millions of people probably consume water that does not fulfil standards regarding the F^- content [15,16]. In Tanzania, it has been necessary to lift the permissible fluoride content to 4 mg F^-/dm^3 [15], where it is also observed that fluoride is often present in water, which also contains natural organic matter (NOM) [15].

The presence of NOM in water results in odour, changes in taste and colour deterioration. It reacts with the disinfectants, which are used during water treatment, and as a result, toxic and carcinogenic trihalomethanes are formed [15,17]. Humic acids (HA) represent about 50%–90% of the NOM in lakes, rivers or terrestrial lakes. They constitute in a major part of the dissolved organic carbon in waters. The HA content usually varies from 20 μg/dm^3 (in groundwaters) to 30 mg/dm^3 in surface waters [18,19]. In neutral to acidic conditions, they create micelle-like structures, which are called pseudo-micelles [20]. HA contain many carboxyl (–COOH) and phenolic hydroxyl (–OH) groups, which are attached to aromatic rings. The origin of HA is the main factor that determines their composition and structure [17,21]. The molecular weight of HA usually varies from 2.0 to 1,300 kDa [20]. HAs are soluble in an alkaline aqueous media but insoluble in water under acidic conditions [20]. They are commonly present in nature and their application as soil fertilizers has been examined [21]. The ionic strength and pH of a solution affect the structure of NOM. When pH is high and salt content is low, the NOM molecules have a linear structure (due to charge repulsion). In the opposite situation, that is, at low pH and a high salt content, the NOM structure is curled (the reason is intramolecular bonding) [22].

Fluoride can be removed from the water environment by various methods: ion exchange, adsorption, precipitation and membrane processes (reverse osmosis, nanofiltration, Donnan dialysis or electrodialysis (ED)) [12,23–26]. Many of the conventional techniques have disadvantages, such as low capacity and selectivity, expensive and complicated regeneration of the materials used or high investment costs. For this reason, membrane processes have become more popular – additional chemicals are not needed and they are characterized by simplicity in use [27]. They also allow a high removal efficiency to be obtained and no undesirable by-products are formed [18]. Due to the low chemical demand and the high selectivity, ED can be recognized as a suitable technique for both, defluoridation and desalination [24]. ED reversal (EDR) allows inorganic scaling and fouling to be minimalized by periodical reversal of electrodes polarity, and thus the reveal of accumulated ions on the membrane surface. Moreover, it is easy to fit ED to varying qualities of water. EDR can operate at a relatively high water recovery rate, which is an important economic advantage in applications, which have high productivity as a priority. ED with the use of monovalent selective ion-exchange membranes enables preferential separation of monovalent ions from a multivalent ion mixture. This type of ED has widely been used in environmental applications (e.g., the removal of arsenic or nitrate from drinking water). ED with monovalent selective ion-exchange membranes has also been applied to treat municipal or industrial wastewater (e.g., the textile industry). An integration of pressure membrane processes and ED has enabled water recovery and the reuse of valuable substances such as hydroxides, acids, salts, dyes, as well as complexing or dispersing agents [28]. The most recent application of monovalent selective ion-exchange membranes involves the upgrading of groundwater for irrigation purposes [28].

The application of electromembrane processes for the treatment of natural water seems to be a challenge due to the variety of components present in treated solutions, as well as the risk of salts precipitation. Geothermal water obtained from Balcova (Turkey) was subjected to defluoridation by ED [27]. The process was run with AMX and CMX membranes (Tokuyama Co., Japan) under two modes of operation. In the first mode, the water pH was adjusted to 7.0–7.5 with the use of an HCl solution. The adjusting of pH allowed the risk of salt precipitation to be minimized. In the second method, chemical water pretreatment with the use of Na_2CO_3 and NaOH was employed. In the next step, and after 1 d of sedimentation, the water was filtered and the water pH was adjusted to 7.0–7.5. The initial fluoride concentration amounted to 7.72 mg F^-/dm^3 and it was lowered to 0.06 mg F^-/dm^3 in the first operation mode. A comparable result was obtained for the second method – with the final F^- content reaching 0.07 mg F^-/dm^3.

The possibility of fluoride removal from brackish water by conventional ED was investigated in Tunisia [26]. Tests were made on real groundwater samples taken from Borj-Cédria with the use of the laboratory PCCell ED 64 002 installation equipped with standard PC-SA and PC-SK ion-exchange membranes. The ED experiments were performed at a constant current (1.57 A) and a flow rate of 25 dm^3/h. The initial fluoride content amounted to 2.9 mg F^-/dm^3 and it was lowered to 0.4 mg F^-/dm^3. A similar study on fluoride removal from underground brackish water (Pine Hill, Australia) by ED was conducted by Banasiak et al. [29]. Conventional anion-exchange and cation-exchange membranes (Tokuyama Soda Co.) were applied in a laboratory BEL-500 ED unit (Berghof, Germany). The initial fluoride content was equal to 2.8 mg F^-/dm^3, and thus only 50% of F^- ion removal was required to meet the WHO standards for drinking water regarding the contaminant concentration. It was demonstrated that ED was suitable for defluoridation and drinking water production, however, scaling and fouling were the major disadvantages in the course of bore water treatment.

The applicability of ED with monoanion permselective membranes in fluoride removal was verified by

Amor et al. [30]. Standard cation-exchange membranes (CMX, Neosepta) and monovalent permselective anion-exchange membranes (ACS, Neosepta) were applied. The experiments were carried out with synthetic fluoride solutions reflecting the composition of the Algerian water. The initial fluoride content was equal to 3 mg F^-/dm^3. The influence of voltage variation on defluoridation efficiency was verified. The beneficial effect of a voltage increase on fluoride ion removal was proved. The final fluoride concentration was lowered to 2.87, 0.67 and 0.21 mg F^-/dm^3 when the voltage amounted to 5, 10 and 15 V, respectively. It was also found that the enhanced fluoride ion removal occurred with an increase of liquid flow rate in the ED stack – the rise of flow rate from 50 to 180 dm^3/h brought about the final fluoride content decrease from 1.79 to 0.67 mg F^-/dm^3. Finally, the impact of temperature on the process efficiency was also confirmed. Three temperature values were considered – 16, 25 and 40°C. It became evident that better results were obtained with a higher temperature. When the temperature was equal to 16°C, the final fluoride content decreased to only 1.95 mg F^-/dm^3, however, it was lowered to 0.67 and 0.60 mg F^-/dm^3 when the temperature was risen to 25°C and 40°C, respectively.

The impact of NOM on ion-exchange membranes and ED efficiency is the most significant concern in the operation of electromembrane processes. The research regarding fluoride removal by ED under the presence of organic substances was conducted by Banasiak et al. [24]. Neosepta CMX-SB and AMX-SB ion-exchange membranes were applied during the experiments. The influence of organic matter (OM) on fluoride removal from synthetic aqueous solutions was examined. Three different types of organic acids were chosen for the study –HA, tannic acids (TA) and alginic acids (AA). The initial fluoride concentration amounted to 5 mg F^-/dm^3. In the course of ED experiments with no OM addition, the fluoride removal was independent of pH and was equal to 65.6% ± 12.0%. It was found that the presence of OM enhanced the fluoride separation efficiency. The average percentage of F^- ion removal in the presence of TA, HA and AA amounted to 74.8% ± 6%, 72.5% ± 4.5% and 72.9% ± 5.9%, respectively. However, a decrease of fluoride ion flux was observed, when organic acids were present in the tested solutions. The beneficial effect of OM on defluoridation efficiency combined with deteriorated F^- ion flux clearly indicated the deposition of fluoride and organic acids on/in ion-exchange membranes.

New viable technologies designed to improve water quality must take into account the production costs, the impact on the environment, as well as the final water composition. The research on the cost evaluation of defluoridation by ED was carried out by Lahnid et al. [31]. Water production in the ED installation was equal to 100 m^3/h. The system was designed to provide 50,000 people with drinking water (50 dm^3/d per capita). It was assumed that the membrane lifetime was equal to 8,000 h and the electrodes were supposed to be replaced after 5,000 h of continuous operation. The total cost of the metal frames and the building construction was calculated to be 429,000 €. The total investment cost of the ED installation involving 1,000 cell pairs reached 833,207 €. The operating costs, including maintenance and energy consumption, were estimated to be 0.154 €/m^3. The pumping energy was assessed at a level of 0.4 kWh/m^3, whereas the energy needed for water desalination was much lower (0.064 kWh/m^3). The ED system enabled the fluoride content to be decreased from 2.32 to 1.2 mg F^-/dm^3.

The literature review confirmed the huge capability of electromembrane processes to remove fluoride from drinking water, however, a variety of problems for water treatment by ED (e.g., fouling, scaling, leakage of pollutants, electrical resistance increase and membrane adsorption) were also reported. It therefore seemed reasonable to examine the usability of ED with monovalent selective ion-exchange membranes in fluoride removal. In the study, monovalent permselective anion-exchange and classic cation-exchange membranes were used and the defluoridation of multicomponent solutions by ED was performed. The main aim of the experiments was focussed on the efficiency of fluoride removal in the presence of OM (HA), and also the recognition of the deposition of fluoride and HA in the electrodialytic membrane system.

2. Methods and installation

2.1. Installation and membranes

The experiments were conducted with the use of the PCCell BED-1 System installation (PCCell GmbH, Germany). The membrane stack consisted of 10 pairs of diluate and concentrate cells. Eleven classic cation-exchange membranes (PC-SK) and 10 monovalent permselective anion-exchange membranes (PC-MVA) were involved. All the membranes were produced by PCCell GmbH (Germany). Each membrane had an effective area equal to 64 cm^2. The thickness of the electrodialytic cell was equal to 0.5 mm.

The volume of concentrate and diluate chambers amounted to 2 dm^3 (each). 0.05 mol/dm^3 NaCl solution was used as the electrode rinsing bath. The electrode solution tank had the volume of 9 dm^3. The flow rate of the diluate, concentrate and electrode solution was equal to 90 dm^3/h, which corresponded to the linear liquid velocity of 6.25 cm/s.

The membrane characteristics are presented in Table 1.

2.2. Reagents

Synthetic aqueous solutions were used in the ED tests. The treated solutions consisted of fluoride, HA (Aldrich) and the mineral salt (sodium chloride). The fluoride solutions were made of sodium fluoride (NaF) and the concentration of fluoride ions amounted to 5, 10, 100 and 200 mg F^-/dm^3. All the tested solutions contained sodium chloride in an amount of 0.5 g NaCl/dm^3. The presence of OM was simulated by adding HA at concentrations of 5, 10 and 15 mg HA/dm^3, which corresponded to the solution colour of ca. 25, 50 and 75 mg Pt/dm^3.

2.3. Methodology

The process was run in a batch mode, that is, both the diluate and concentrate streams circulated in the ED stack until the end of defluoridation. At the beginning of the process, the concentrate cells were only filled with sodium chloride, whereas in the diluate cells the NaCl solution was supplemented with fluoride and OM.

Table 1
Membrane characteristics

Parameter	Membrane type	
	Cation-exchange (PC-SK)	Monovalent permselective anion-exchange (PC-MVA)
Size, mm	110 × 110	110 × 110
Thickness, μm	90–130	110
Exchange capacity, meq/g	~1.2	1
Electrical resistance, Ω·cm^2	1–3	20
Chemical resistance, pH range	0–9	0–12
Mechanical resistance, MPa	0.4–0.5	0.2
Permselectivity, transfer number	>0.95	>0.97
Ionic form	Na$^+$	Cl$^-$
Functional group	Sulfonic acid	Ammonium

The ED defluoridation experiments were performed at a constant electrical current (0.11 A) and the applied current density was equal to 1.72 mA/cm^2. The process was terminated when the voltage reached 24 V.

During the ED process, the diluate and the concentrate samples were collected at the same time intervals for chemical analysis. The fluoride concentration was measured using a colorimetric method with SPADNS reagent. This reagent contains zirconium which reacts with the fluoride present in the analysed solution. As a result, colourless complexes are created. The higher the fluoride concentration, the less coloured the sample is. The fluoride ion concentration was analysed with the use of Hach 2000 spectrophotometer at a wavelength of 580 nm (method no. 8029, program no. 190). The measurement error amounted to ± 9%.

The sample colour was measured with the use of the spectrophotometer Hitachi-U 1900 at a wavelength of 350 nm. The calibrated curve allowed the sample absorbance to be expressed as colour intensity in mg Pt/dm^3. The HA content was also detected spectrophotometrically at a UV wavelength of 254 nm. The measurement error reached ± 0.2%.

The electrical conductivity of the diluate and concentrate was measured with the use of the multimeter HQ40D. The method sensitivity was equal to 0.5%.

The specific electrical energy demand (EC) was calculated on the basis of the voltage variation during the ED process according to Eq. (1) [32] as follows:

$$\mathrm{EC} = \frac{I\int_0^t U dt}{V_d} \tag{1}$$

where EC – specific electrical energy demand (kWh/m^3), I – current intensity (A), U – voltage (V), V_d – the volume of the diluate (m^3) and t – process duration (h).

The ion transport was calculated according to Eq. (2) as follows [33]:

$$J = \frac{V_t C_t - V_i C_i}{A_m t} \tag{2}$$

where J – ion transport (mol/m^{2}h), A_m – total surface area of the anion-exchange membranes (m^2), V_i and V_t – volume of the concentrate at the beginning of the process and at a time t, respectively (m^3), C_i and C_t – fluoride concentration at the beginning of the process and at a time t in the concentrate cells, respectively (mol/m^3) and t – process duration (h).

The mass of fluoride or HA deposited on/in the membranes, as well as in the ED system, was calculated according to Eq. (3) as follows [34]:

$$M = \left(V_{\mathrm{id}}C_{\mathrm{id}} + V_{\mathrm{ic}}C_{\mathrm{ic}}\right) - \left(V_{\mathrm{fd}}C_{\mathrm{fd}} + V_{\mathrm{fc}}C_{\mathrm{fc}}\right) \tag{3}$$

where M – mass of fluoride or HA accumulated in the ion-exchange membranes (mg), V_{id} and V_{fd} – initial and final volume of the diluate (dm^3), V_{ic} and V_{fc} – initial and final volume of the concentrate (dm^3), C_{id} and C_{fd} – initial and final concentration of fluoride or HA in the diluate (mg/dm^3) and C_{ic} and C_{fc} – initial and final concentration of fluoride or HA in the concentrate (mg/dm^3).

3. Results and discussion

3.1. Variations of fluoride concentration in the course of the ED process

The study was basically focused on the usability of the batch ED with monovalent selective anion-exchange membranes for fluoride removal. It was very important to evaluate the membrane behaviour towards OM present in the treated solutions. The ED tests were performed for synthetic solutions containing fluoride in an amount of 5–200 mg F$^-$/dm^3 at varied HA contents (5–15 mg HA/dm^3). All the experimental solutions also contained 0.5 g of NaCl/dm^3. The variations of fluoride concentration in the diluate and the concentrate streams in the course of the ED study are given in Fig. 1.

Taking into account the results given in Figs. 1(a) and (b), it can be concluded that for a low fluoride content (5 and 10 mg F$^-$/dm^3) the final fluoride concentration fulfilled the WHO guidelines for drinking water. It means that the final fluoride content in the diluate was not higher than 1.5 mg F$^-$/dm^3. For tests with the 5 mg F$^-$/dm^3 solutions containing HA in amounts of 5, 10 and 15 mg HA/dm^3, the final fluoride content was lowered to 1.04, 1.45 and 1.45 mg F$^-$/dm^3, respectively. The fluoride removal efficiency was quite satisfactory (71%–79.2%) and comparable with the result obtained

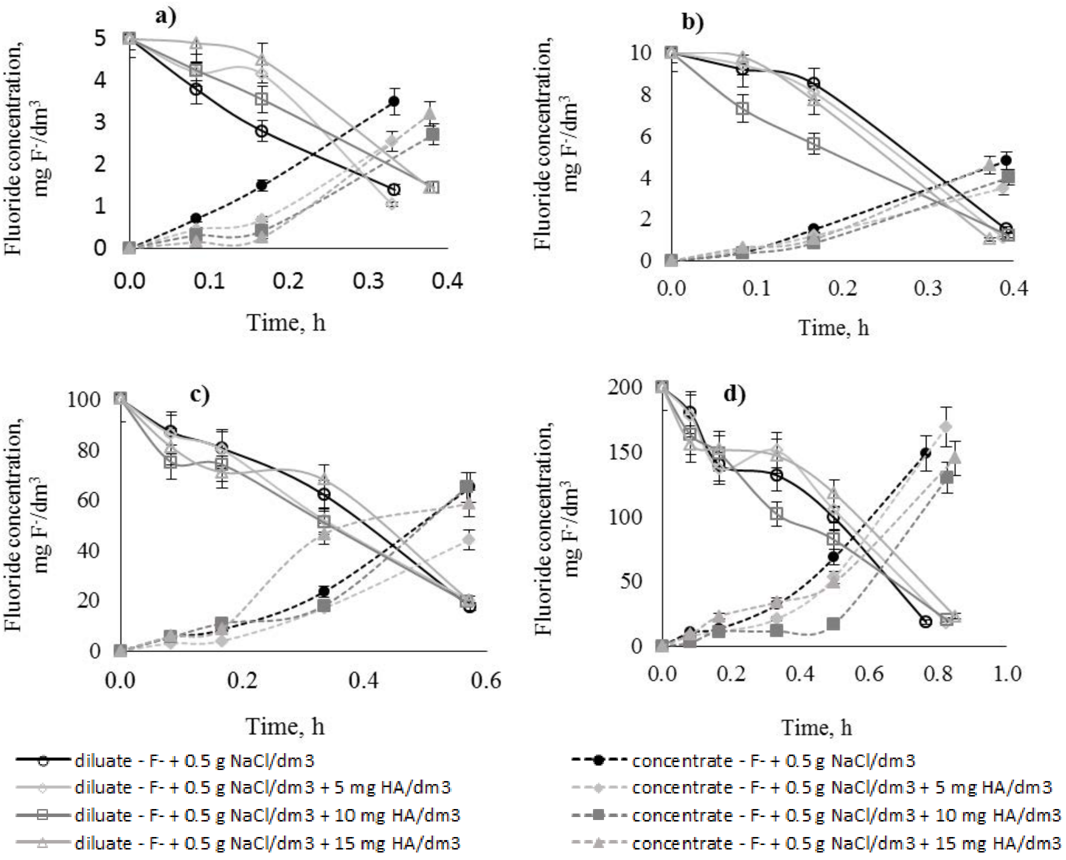

Fig. 1. The variation of fluoride concentration in the diluate and the concentrate versus ED operational time at various HA and initial F^- ion contents: (a) 5 mg F^-/dm^3; (b) 10 mg F^-/dm^3; (c) 100 mg F^-/dm^3; (d) 200 mg F^-/dm^3; current density: 1.72 mA/cm^2, error bars ± 9%.

for the fluoride solution without the addition of HA (72% removal efficiency). In this case, the final fluoride content was reduced to 1.4 mg F^-/dm^3. When the solution containing 10 mg F^-/dm^3 (no OM) was treated, the final fluoride concentration in the diluate was 1.5 mg F^-/dm^3. The presence of HA in amounts of 5, 10 and 15 mg HA/dm^3 caused a slight improvement in the diluate quality – the final fluoride concentrations were 1.1, 1.2 and 1.03, respectively. In this case, 84.6%–89.9% of fluoride was removed.

The analysis of the results given in Figs. 1(c) and (d) gave different conclusions. Although the percentage of fluoride removal was still high (above 80%) due to the elevated initial fluoride concentration (100 and 200 mg F^-/dm^3), the final diluate quality in the view of the fluoride content was rather low. The lowest F^- ion concentration in the diluate (17.5 mg F^-/dm^3) was observed for the test with the 100 mg F^-/dm^3 solution and in the absence of OM. When the OM content was equal to 5 and 15 mg HA/dm^3, the final fluoride concentration amounted to 20 mg F^-/dm^3 (80% removal efficiency). In the course of ED with solutions containing the highest fluoride content (200 mg F^-/dm^3), the F^- ion removal efficiency reached 88.5%–91%, which corresponded to the final fluoride concentration in the diluate in the range of 18–23 mg F^-/dm^3. The impact of the OM on the diluate quality (in the view of fluoride content) for the ED experiments with 200 mg F^-/dm^3 solutions was ambiguous – the lowest fluoride concentration was obtained when the HA content amounted to 5 mg HA/dm^3, and the worst quality of the diluate (in the view of fluoride content) was monitored when the OM concentration was equal to 15 mg HA/dm^3.

The duration of the process in electromembrane techniques is of a great importance due to its influence on the energy demand. The operational time in ED depends on many factors (e.g., the number of cell pairs and membrane surface area, current density, initial salt concentration, solution composition and capacity). For ED of solutions of a low fluoride content (5 and 10 mg F^-/dm^3), the average time of the process was comparable and amounted to 21 and 23 min, respectively. The ED experiments with solutions of elevated fluoride ion concentrations (100 and 200 mg F^-/dm^3) were run significantly longer, that is, 34 and 49 min. Based on the earlier observations, it can be inferred that the fluoride concentration was the main factor affecting the duration of the ED process. The increase in the process duration with the rise in the salt concentration complies with Faraday's law. According to this law, at a constant current density, the time of the process is directly proportional to the amount of ions to be removed. It was found that the presence of OM in the diluate stream had a slight impact on the duration of the process. HA might have been deposited on the ion-exchange membrane surface and in turn increased the membrane and the ED stack resistance. As a consequence, more time and energy were needed to perform the defluoridation process. The problem of the deposition of organics on/in ion-exchange membranes is discussed in more detailed in Section 3.5.

It was found that the fluoride removal efficiency, depending on the initial fluoride concentration, was not influenced to a great extent by OM. A slight improvement in the diluate quality (in the view of fluoride content) was observed for a low initial fluoride concentration, whereas in the case of an elevated initial fluoride content, the opposite trend, that is, worsening of the diluate quality (in the view of fluoride content) was monitored under the presence of HA (especially when the HA concentration amounted to 15 mg/dm^3). It is possible that fluoride ions are trapped inside the large structure of HA (the 'open-cage' concept) [35]. Another possible explanation is that positively charged sodium ions are bounded to the negatively charged particles of HA, which may allow fluoride ions to be bounded to sodium cations. As a result, a minor enhancement of the defluoridation efficiency could be observed. Moreover, Hayes et al. [36] investigated the bonding of fluoride to HA macroparticles. Their observations were similar – the fluoride ions were trapped into the large structure of HA (without bonding to functional group) under the solution pH range of 5.0–6.6. On the other hand, it should be kept in mind that the migration of 'free' (unbounded) fluoride ions can be inhibited by the deposition of HA on the ion-exchange membrane surface (predominantly on the anion-exchange membrane surface).

3.2. Desalination efficiency

The possibility of brackish or even seawater desalination by electromembrane processes has been well recognized for several decades. Thus, the overall desalination efficiency was not the primary aim of the reported study. However, the effect of OM on the salinity removal seemed to be worth of the consideration. The desalination efficiency was calculated based on the electrical conductivity measurements. The obtained results are presented in Fig. 2.

The electrodialytic desalination of fluoride solutions was performed with no obstacles. Generally, the desalination efficiency attained in the ED experiments was very high and amounted to 82.5%–95.4%. It was observed that the desalination time increased with the increasing solution conductivity by the increase in fluoride concentration (sodium chloride concentration was constant for all the treated solutions). The presence of HA in the treated solutions resulted in a slight deterioration of mineral salt removal and also extended the duration of the process. These phenomena were especially pronounced for the solutions containing fluoride in the amount of 5 mg F^-/dm^3 (Fig. 2(a)) and 200 mg F^-/dm^3 (Fig. 2(d)) – the operational time was prolonged due to the presence of HA by 15% and 10%, respectively, with a simultaneous decrease of the desalination rate from 88.6% to 82.5% and from 95.4% to 92.5%, respectively. The worsening

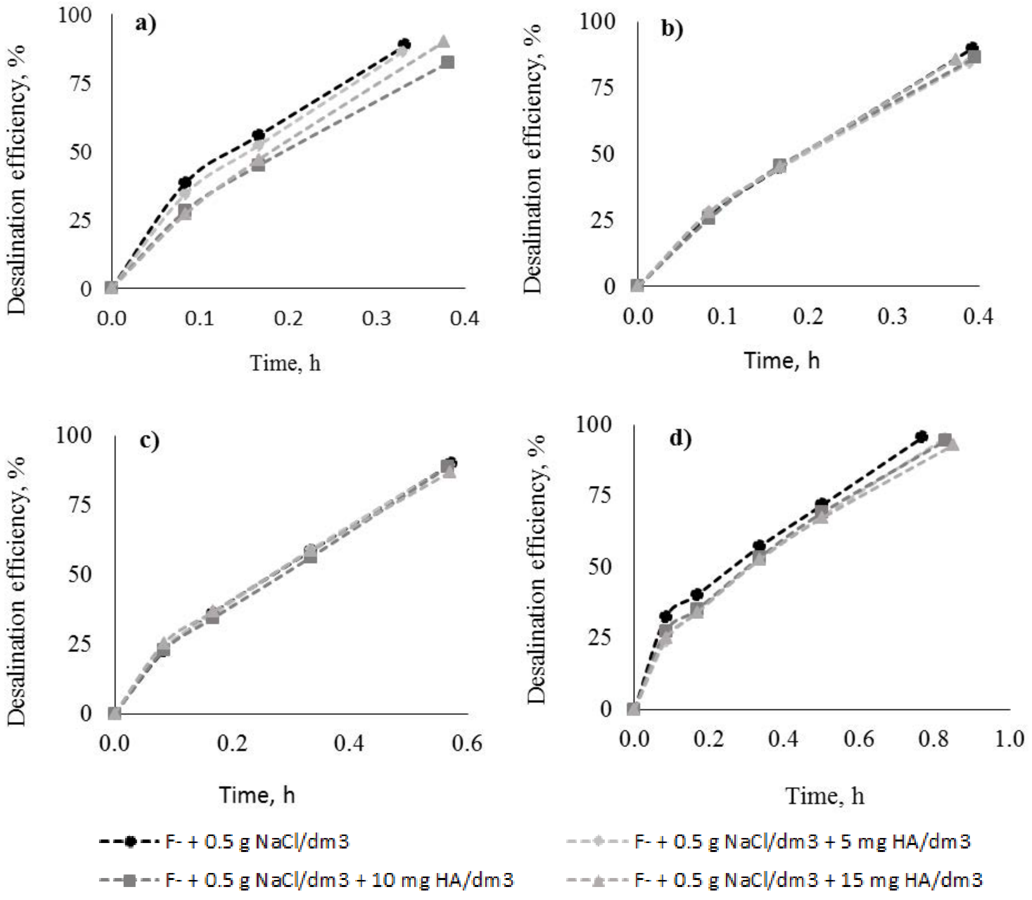

Fig. 2. The desalination efficiency versus ED operational time for various HA and initial F^- ions contents: (a) 5 mg F^-/dm^3; (b) 10 mg F^-/dm^3; (c) 100 mg F^-/dm^3; (d) 200 mg F^-/dm^3; current density: 1.72 mA/cm^2.

of the ED performance under the presence of OM confirmed the presumed deposition of HA on the ion-exchange membrane surface, thus inhibiting the migration of fluoride and chloride ions from the diluate cells to the concentrate cells.

It was found that the calculated desalination efficiency based on electrical conductivity was higher than the defluoridation efficiency – the conductivity was diminished by 82.5%–90.2%, 85.7%–89.9%, 87.1%–90% and 92.9%–95.4%, whereas the fluoride concentration was reduced by 71%–79.2%, 84.6%–89.9%, 80%–82.5% and 88.5%–91.0% for solutions containing 5, 10, 100 and 200 mg F^-/dm^3 (with 0, 5, 10 and 15 mg HA/dm^3), respectively. It can be assumed that the differences between the total desalination rate and the fluoride removal were caused by the variation in the ion mobility and the size of the hydrated radius of the F^- and Cl^- ions. Chlorides have a smaller radius (0.332 nm) and are more mobile (7.91 m^2/s V) when compared with the F^- ion radius (0.352 nm) and its mobility (5.70 m^2/s V) [24]. Consequently, chloride ions, which are also responsible for the salinity of the solution, are transported through the anion-exchange membranes more easily.

3.3. Fluoride deposition

As it was mentioned in Section 3.1, the incidental beneficial effect of the OM on the fluoride removal could be caused by the trapping of fluoride ions into the large macromolecules of HA, which in turn could be deposited on the ion-exchange membrane surface. It was anticipated that analysis of the fluoride mass balance in the ED system would be helpful in solving this issue. The amount of fluoride adsorbed by membranes and/or by HA was calculated according to Eq. (3). The obtained results are given in Fig. 3.

Generally, the considerable fluoride adsorption was observed during ED, irrespective of the solution's composition. As expected, the amount of deposited fluoride increased with the increasing initial fluoride content, with the exception of the solution with 5 mg HA/dm^3 (see comments later). For the solutions containing 5, 10, 100 and 200 mg F^-/dm^3, the following amounts of fluoride were deposited in the ED system: 0.2–2.82, 7.4–10.8, 31–72 and 26–100 mg, respectively. The given fluoride ion masses accounted for 25%–50% of the total amount of fluoride present in the system at the beginning of the process. Even, for the ED tests with no addition of HA, a significant adsorption of fluoride in the membranes was observed.

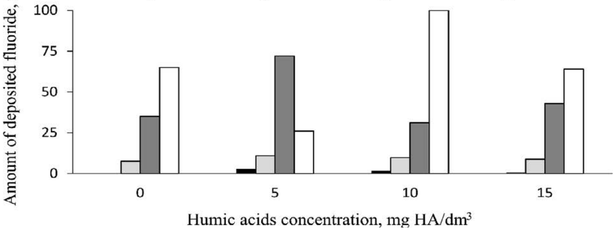

Fig. 3. The amount of fluoride deposited in the ED system versus HA concentration for various initial fluoride concentrations (5, 10, 100 and 200 mg F^-/dm^3); current density: 1.72 mA/cm^2.

The impact of NOM on the fluoride removal by membrane processes is not understood to date [15,35]. Generally, it seems that the following mechanisms govern the fluoride behaviour (including adsorption) in the ED system under the presence of HA: (1) the fluoride ion trapping in macroparticles of HA (territorial binding of fluoride to the structure of NOM) [36]; (2) the decrease of the fluoride hydrated radius due to the presence of excessive amounts of HA in the treated solution and, as a consequence, the facilitating transport of fluoride ions through the anion-exchange membranes and (3) the hindering of the rate of fluoride ions transport in the ED cells by an excessive amount of HA (membrane fouling).

The obtained results seemed to be ambiguous and indicate that, depending on the ratio between the fluoride and HA content, one of the earlier mechanism could be dominant. Moderate amounts of HA (5 and 10 mg HA/dm^3) intensified fluoride adsorption, indicating fluoride ion trapping in organic particles, with the exception of the solution containing 5 mg HA/dm^3 and 200 mg F^-/dm^3. The higher final fluoride concentration in the concentrate for the solution containing 200 mg F^-/dm^3 and 5 mg HA/dm^3 (in comparison with the final fluoride concentration for the solution containing 200 mg F^-/dm^3 and 0 mg HA/dm^3) (Fig. 1(d)) indicated on the facilitated transport of fluoride ions under the presence of HA. In this case, the mechanism no. 2 (decreased fluoride radius) could be an explanation of the variable trend in the quantitative fluoride adsorption.

However, at the highest HA concentration (15 mg HA/dm^3) the fluoride adsorption was weakened, especially when the concentration of fluoride ions amounted to 200 mg F^-/dm^3. This finding can support the premise related to the decrease of the fluoride ion hydrated radius due to an increased amount of OM in the treated solution. Due to the higher final fluoride concentration in the concentrate for the solution containing 200 mg F^-/dm^3 and 15 mg HA/dm^3 (in comparison with the final fluoride concentration for solution containing 200 mg F^-/dm^3 and 10 mg HA/dm^3) (Figs. 1(c) and (d)), the mechanism no. 2 could again be an explanation of the variable trend in the quantitative fluoride adsorption. The fluoride ions with a small energy of hydration [37] have soft hydration shells, and for that reason is able to rearrange or lose water molecules during membrane transport. According to the dehydration hypothesis, this rearrangement of water molecules around ions can be induced by the increased pressure, as well as by variations in ionic strength, temperature, pH and solution viscosity [38]. The result was that more fluoride ions (in comparison with the solution with 10 mg HA/dm^3) could migrate through the anion-exchange membranes.

Further analysis of the results showed in Fig. 3 give the conclusion that, for solutions containing high fluoride amounts and moderate amounts of HA, the fouling mechanism with fluoride ion trapping in HA particles (mechanism nos. 1 and 3) is dominant.

3.4. Mean fluoride transport

The mean fluoride transport was calculated according to Eq. (2) on the basis of fluoride ion enrichment in the concentrate cell. The obtained results are presented in Fig. 4.

Obviously, the mean fluoride transport was proportional to the initial concentration of the fluoride ions in the treated solutions, irrespective of the OM content. The calculated

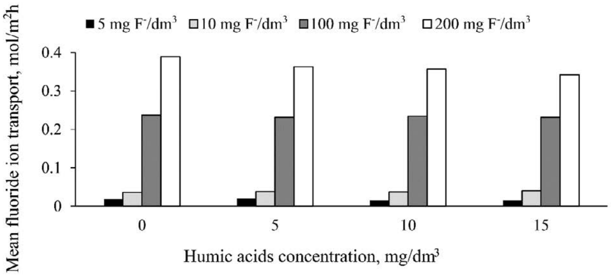

Fig. 4. The mean fluoride ion transport in the ED course versus organic matter content for various initial fluoride concentrations (5, 10, 100 and 200 mg F^-/dm^3); current density: 1.72 mA/cm^2.

transports varied from 0.015 to 0.04 mol/m^{2}h, when the initial fluoride ion concentration was equal to 5 and 10 mg F^-/dm^3. For the ED trials with the elevated fluoride concentrations (100 and 200 mg F^-/dm^3), the ionic transport was in the range of 0.231–0.389 mol/m^{2}h.

A slight, but systematic impact of HA on the mean fluoride transport was observed. A general tendency of the decreasing fluoride transport with the increasing concentration of OM was observed. This relationship was especially pronounced for the highest initial fluoride ion concentration – approximately a 12% drop of transport occurred when the HA concentration in the treated solutions increased from 0 to 15 mg HA/dm^3. For the other tested solutions, the disparities in the fluoride transport were observed to a lesser extent, but they should not however be disregarded.

The deterioration of the fluoride ions transport under the presence of OM could be clarified by either membrane blocking due to HA particles, and thus hindered ion migration through the ion-exchange membranes, or by fluoride trapping inside the HA aggregates. Both behaviours seem to be reasonable and compatible with the results described in previous chapters. This phenomenon was also observed by Banasiak et al. [24], however, the initial fluoride concentration in their investigation did not exceed 2 mg F^-/dm^3.

3.5. The deposition of humic acids

The presence of OM in solutions treated using electromembrane processes can cause serious exploitation problems that influence on the process efficiency and energy demand (see Section 3.6). It is well known that humic substances (especially HA) are a severe foulant that can block ion-exchange membranes. Humic substances are the common constituents of surface water, and it is therefore reasonable to evaluate their behaviour in the course of ED with regards to membrane fouling.

The variation in colour intensity, as well as in the HA concentration in the diluate and the concentrate cells during ED can be a measure of fouling intensity. The initial HA concentration in the diluate compartments amounted to 5, 15 and 15 mg HA/dm^3, which corresponded to a colour intensity of ca. 25, 50 and 75 mg Pt/dm^3.

The colour intensity of the diluate and the concentrate streams was systematically monitored in the course of the ED. It was found that the colour of the diluate solutions decreased at the end of process, whereas the concentrates remained colourless, irrespective of the solution composition. These observations indicated that colour depletion (Fig. 5) was only brought on by the deposition of OM in the ED system.

The colour depletion varied from 7.7% to 28%, however, it was hard to detect a regular relationship. For each of the tested fluoride and HA concentrations, various trends in colour diminishing were observed. At the lowest fluoride concentration (5 mg F^-/dm^3), the highest colour depletion occurred at the highest HA concentration (15 mg HA/dm^3). When the fluoride concentration amounted to 100 mg F^-/dm^3, a higher OM content in the diluate corresponded to a lower colour depletion. In turn, at the highest fluoride concentration (200 mg F^-/dm^3), an increasing trend in colour reduction was observed with an increasing HA content. The most regular dependence of the final diluate colour on the fluoride concentration was detected for the ED series with solutions containing 10 mg HA/dm^3. In this case, it was obvious that the increase in fluoride concentration resulted in the enhancement of colour depletion, that is, in the increase of fouling intensity. Nevertheless, a slight tendency of a rise in colour depletion with the increase of HA and fluoride concentrations in the treated solutions could be seen.

It should be emphasized that the current experiments were performed with the use of monovalent permselective anion-exchange membranes. It was assumed that the monoanion selective membranes would allow the deposition of OM in the ED system to be reduced. This supposition was confirmed by comparing the colour diminishing in the course of the ED with conventional and monovalent selective anion-exchange membranes (Fig. 5). In our previous investigation [39], a considerable deposition of OM in the course of ED with classic anion-exchange membranes (PC-SA) was stated. As it can be seen in Fig. 5, the colour depletion amounted to 20%–34.5% and it was in average twofold higher than for monoanion selective membranes (with the exception of the ED trials with solutions containing 200 mg F^-/dm^3 and 10, as well as 15 mg HA/dm^3 – in these cases the depositions of OM were comparable for both membranes). The monovalent selective anion-exchange membrane is characterized by a denser structure than the structure of the conventional anion-exchange membrane. What is more, it has an additional layer of a negative charge, which makes migration of macroanions difficult, while the movement of small monovalent anions across the membrane is still possible.

The quantitative evaluation of the fouling phenomenon due to the deposition of organics can be performed by calculating the mass balance of the HA in the ED stack. The HA concentration was determined on the basis of the absorbance analysis (at a wavelength of 254 nm). Similarly to colour intensity determinations, no HA was detected in the concentrate cells during the ED process. The amounts of HA adsorbed in the ED/membrane system are given in Fig. 6 and they generally reflect the results of colour depletion. Nonetheless, the tendency of the rise in HA adsorption intensity with an increasing OM and fluoride content was more noticeable than for colour diminishing. The masses of HA deposited on the membranes varied from 0.5 to almost 10 mg, which corresponded to 10%–40%, 10%–30% and 10%–30% of the total amount of HA present in the diluate compartments at

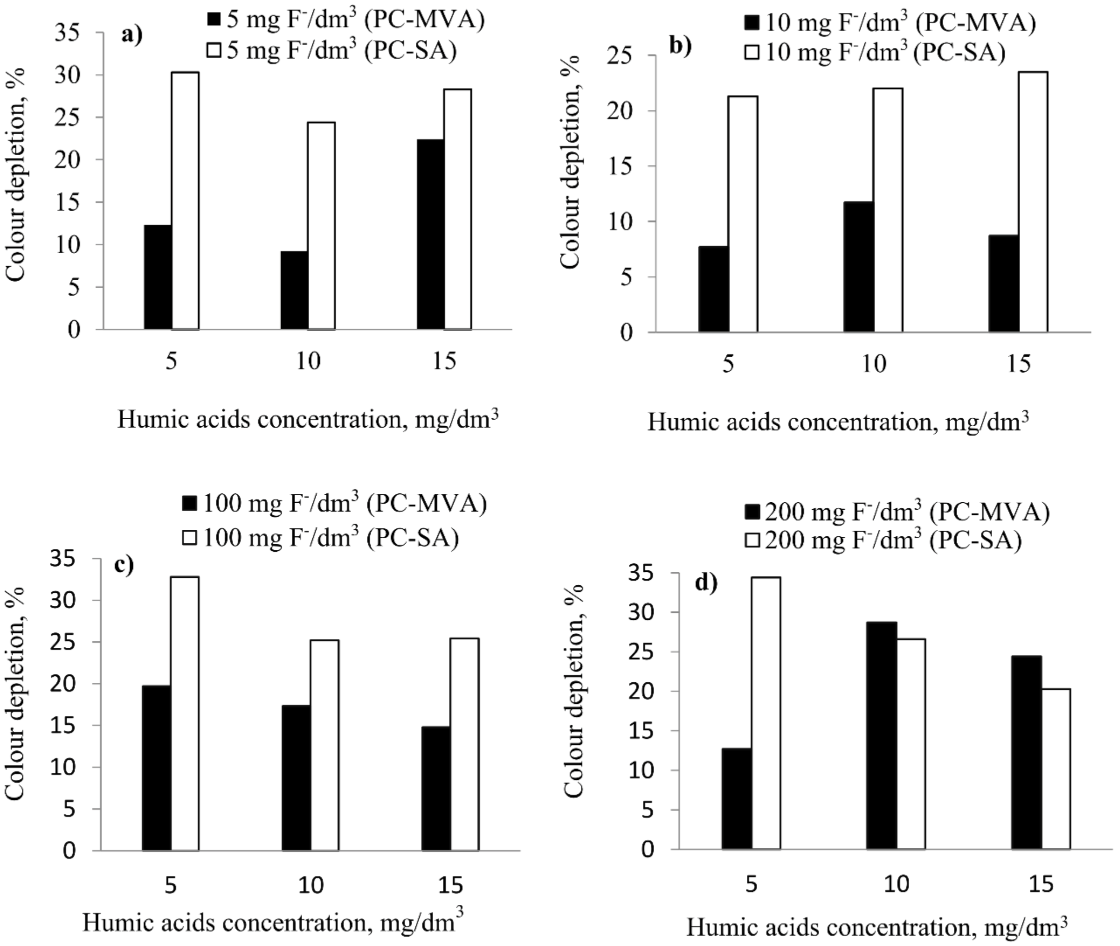

Fig. 5. Colour depletion at the end of the ED process versus HA and fluoride concentrations for classic (PC-SA) and monovalent selective (PC-MVA) anion-exchange membranes: (a) 5 mg F^-/dm^3; (b) 10 mg F^-/dm^3; (c) 100 mg F^-/dm^3; (d) 200 mg F^-/dm^3; current density: 1.72 mA/cm^2. Data for ED with conventional anion-exchange membranes adopted from [39].

the beginning of the process, that is, 5, 10 and 15 mg HA/dm^3, respectively. Although the monovalent selective anion-exchange membranes were applied, the magnitude of the deposition of HA in the ED system was still high. It was interesting to note that the high fluoride concentration evidently favoured adsorption of HA particles at the membrane surface.

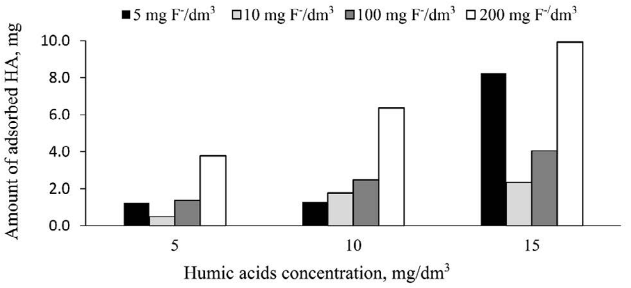

Fig. 6. The amount of HA deposited in the ED system versus the HA concentration for various initial fluoride concentrations (5, 10, 100 and 200 mg F^-/dm^3); current density: 1.72 mA/cm^2.

In line with expectations, a higher OM concentration corresponded to the higher amount of the OM deposited on the surface of the membranes. Another observation, related to the intensified deposition of HA under elevated fluoride concentrations, was unexpected. This phenomenon was more likely to be caused by the variation in the ionic strength of the fluoride solutions. Under the increased ionic strength, the repulsive force between the HA macroparticles was weakened. In turn, large structures of HA aggregates could be formed, or the precipitation of single particles could even be possible. As a result, an intensive membrane fouling occurred. It is also known that dissociated HA particles and fluoride ions can compete for specific sorption sides in the ion-exchange membrane matrix. For the ED test with the solution containing 5 mg F^-/dm^3 and 15 mg HA/dm^3, the fluoride sorption intensity was the lowest among all the performed tests (Fig. 3), thus the high deposition of HA could be expected.

3.6. Energy consumption

For desalination systems involving electromembrane processes, the energy efficiency typically is measured in terms of specific energy consumption (EC), which quantifies how much energy the system uses to produce a given volume of water. Low ECs indicate on high efficiency. It is clear that the energy demand in ED directly depends (among others) on the feed salinity. In the case of low initial salinity (1.2 g/dm^3) and moderate desalination efficiency (60%) the value of EC (needed for ion transport) is rather low (0.064 kWh/m^3), as it was reported by Lahnid et al. [31]. Taking into account the pumping energy, the EC value increased to 0.646 kWh/m^3, which corresponded to the unit energy cost of 0.046 €/m^3, whereas the total unit operating cost was estimated at 0.154 €/m^3. It is evident from the results reported by Lahnid et al. [31] that power consumption constitutes 30% of operating cost and cannot be ignored in economical evaluation of the ED desalination installation. Nevertheless, the capital expenditure (833,207.5 €) of ED plant (for detailed plant description see Section 1) comprises of the crucial plant cost, although it is difficult to compare both costs (capital and operating) in a direct way.

When brackish water is treated by ED and 90% of total salt is removed, the EC increases to about 1.1 kWh/m^3 [40]. The desalination of brine (salt concentration of 80 g/dm^3) by ED seems to be economically unjustified due to the high EC value (12.5 kWh/m^3) [40]. The desalination costs can constitute even 60%–70% of total operating costs for ED treatment of brackish water [41], thus estimation of a specific energy consumption for a given ED process is significant for the process evaluation.

Membrane fouling can be one of the major obstacles for ensuring an economically efficient operation of membrane systems. It has been proven that anion-exchange membranes are especially susceptible to fouling by negatively charged organics, including HA. As an adverse result of this phenomenon, the electrical resistance of the ED stack and the power demand can increase.

The specific electrical energy demand (EC) was calculated according to Eq. (1). The obtained results are given in Fig. 7 and compared with the EC values estimated in the ED experiments with classic anion-exchange membranes (PC-SA) [39]. It should be noted that the calculations of energy consumption did not involve the energy demand for pumping of circulated solutions in the ED installation.

The calculated energy demand varied in a small range (from 0.226 to 0.27 kWh/m^3) for the solutions containing low amounts of fluoride (5 and 10 mg F^-/dm^3) (Figs. 7(a) and (b)). The impact of HA on the EC value was almost negligible.

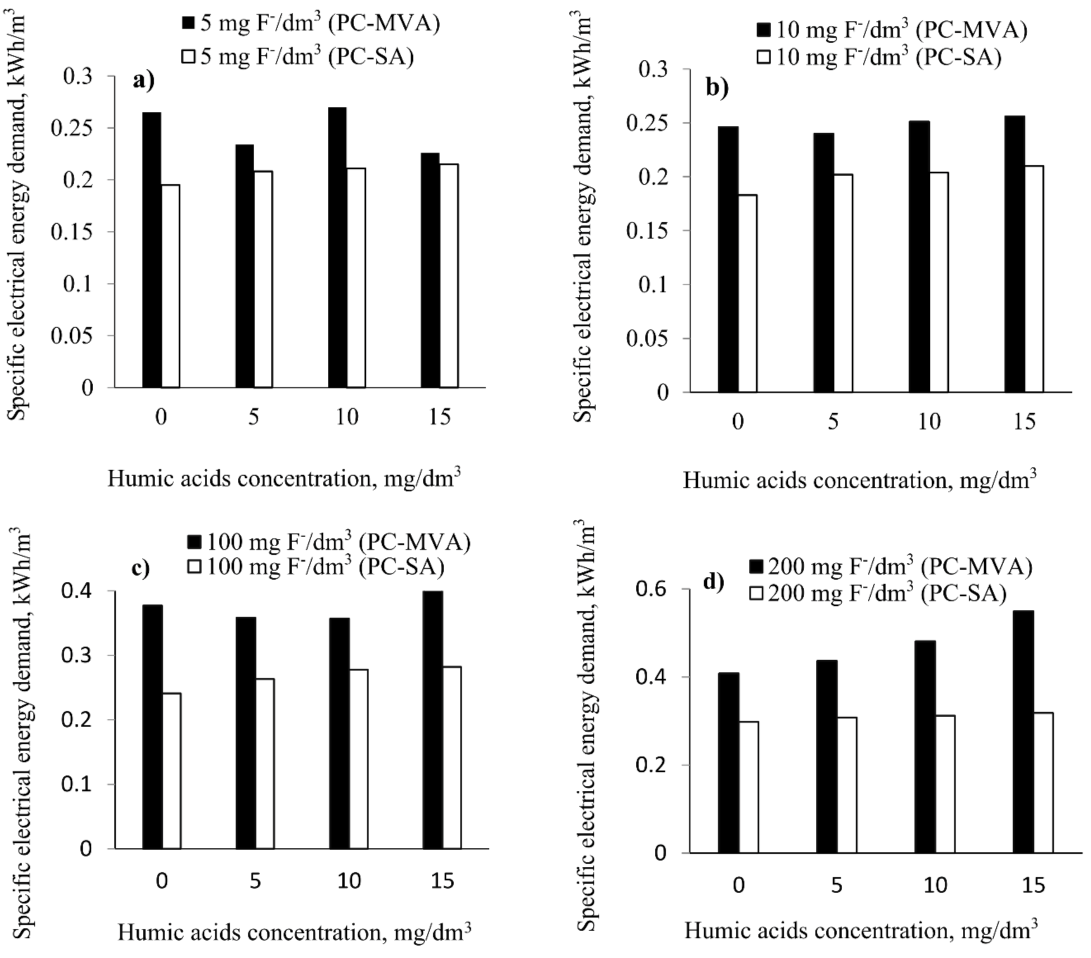

Fig. 7. The specific electrical energy demand versus HA and fluoride concentrations for conventional (PC-SA) and monovalent selective (PC-MVA) anion-exchange membranes: (a) 5 mg F^-/dm^3; (b) 10 mg F^-/dm^3; (c) 100 mg F^-/dm^3; (d) 200 mg F^-/dm^3; current density: 1.72 mA/cm^2. Data for ED with conventional anion-exchange membranes adopted from [39].

For the ED trials with an elevated fluoride concentration, a different situation occurred (Figs. 7(c) and (d)). The specific electrical energy demand increased to 0.357–0.407 kWh/m^3 (for solutions with 100 mg F$^-$/dm^3) and to 0.408–0.549 kWh/m^3 (for solutions with 200 mg F$^-$/dm^3). It should be noted that the calculated EC values were one order of magnitude higher than the energy consumption reported by Lahnid et al. [31], although the salt content in the feed was similar. However, this should not be a surprise, because the estimated energy demand for small laboratory installations might be much higher in comparison with the ECs for real industrial plants.

It was evident that fluoride concentration was the main factor influencing the power consumption in the course of ED. This finding seemed to be quite obvious in view of Faraday's law. Another demonstrable relationship was related to the influence of the presence of HA in the fluoride solutions on the power demand. The rise in the concentration of HA resulted in the increase of EC, which was especially pronounced for the ED experiments with the highest fluoride concentration (Fig. 7(d)). This phenomenon could be attributed to a hampered fluoride ion transport in the presence of large HA aggregates, which in turn could be easily accumulated at the membrane surface. Consequently, the ED stack resistance and the power consumption increased. Lee et al. [42] arrived at a similar conclusion during their study on anion-exchange membrane fouling. The presence of various organic foulants (humate, anionic surfactant and albumin) in synthetic brackish solutions led to a meaningful rise in power consumption (by 10%–25% in comparison with power consumption during ED of brackish water free of foulants). At the same time, membrane electrical resistance increased from 2.15 (fresh membrane) to 2.6 Ω cm^2 (fouled membrane), whereas current efficiency dropped from 98.1% to even 70%, respectively.

It was interesting to note that the ED process with monovalent selective anion-exchange membranes (PC-MVA) exhibited higher energy consumption than the ED with standard anion-exchange membranes (PC-SA). The energy demand for the ED defluoridation of solutions containing only fluoride and chloride (no HA addition) was by 35%–55% higher when PC-MVA membranes were used (in comparison with the ED with PC-SA membranes). These differences in EC values between PC-MVA and PC-SA membranes were bigger (even to 73%) for the ED trials with solutions supplemented with OM. This could be attributed to the diverse electrical resistance of both membranes (20 and 1–3 Ω cm^2 for PC-MVA and PC-SA, respectively) and the denser structure of the PC-MVA membrane when compared with the PC-SA membrane. The unquestionable advantage of the monovalent selective anion-exchange membrane over the classic anion-exchange membrane was the total lack of OM in the concentrate streams in the course of ED process. The undesirable phenomenon relating to HA leakage (in trace amounts) to the concentrate cells was occasionally monitored for the ED experiments with classic anion-exchange membranes [39].

4. Conclusions

- The ED with monovalent selective anion-exchange membranes and classic cation-exchange membranes was suitable for fluoride removal from aqueous solutions. The final fluoride concentration in the diluate fulfilled the WHO standards for drinking water (<1.5 mg F$^-$/dm^3), provided that the initial F$^-$ ion content was rather low (5–10 mg F$^-$/dm^3).
- The presence of OM (HA) in fluoride solutions treated by ED with monoanion selective membranes had a moderate impact on fluoride removal efficiency, depending on the initial F$^-$ ion concentration. In the view of the fluoride content, a slight improvement of the diluate quality was observed for a low initial fluoride concentration, whereas in the case of an elevated initial fluoride content, a minor worsening of the diluate quality was monitored (especially when HA concentration amounted to 15 mg/dm^3). The observed phenomena could be explained by the trapping of F$^-$ ions inside the large structures of HA, or also by the hampered migration of F$^-$ ions due to the deposition of HA on the surface of anion-exchange membranes.
- The desalination efficiency attained in the ED with monoanion selective membranes was very high (82.5%–95.4%), however, a slight deterioration of mineral salt removal was detected due to the presence of OM in the treated solutions.
- A considerable fluoride adsorption (25%–50% of the total amount of fluoride present in the system) in/on membranes during ED was observed, irrespective of the composition of the solution. The amount of the deposited fluoride increased with the increasing initial fluoride concentration. The moderate amounts of OM intensified fluoride adsorption, whereas at the highest concentration of HA, the fluoride deposition was weakened.
- A slight impact of HA on the mean fluoride flux in the ED course was seen. For ED trials with the highest fluoride concentration (200 mg F$^-$/dm^3), an approximate 12% drop of fluoride ion flux occurred when the concentration of HA increased from 0 to 15 mg HA/dm^3.
- The colour depletion in diluate cells during the ED with monoanion selective membranes varied in the range of 7.7%–28% and was approximately 50% lower than colour depletion for the ED with conventional anion-exchange membranes. Although the monovalent selective anion-exchange membranes were applied, the magnitude of the deposition of HA was still high (10%–40% of the total amount of OM present in the diluate compartments at the beginning of the process) and increased with the rise in fluoride concentration. This phenomenon was more likely to be caused by the increasing ionic strength of the fluoride solutions and the diminishing of the repulsive force between the particles of the HA. As a result, large structures of HA aggregates were formed and intensive membrane fouling occurred.
- The specific electrical energy demand calculated for defluoridation by ED varied from 0.226 to 0.549 kWh/m^3 and it increased with the increasing fluoride concentration. The rise in HA concentration also resulted in the power demand increase. The ED with monovalent selective anion-exchange membranes exhibited the higher energy demand (by 35%–73%) than the ED with standard anion-exchange membranes. This finding could be attributed to the higher electrical resistance of monoanion selective membranes when compared with the resistance of standard anion-exchange membranes.

Symbols

A_m — Total surface area of anion-exchange membranes, m^2
EC — Specific electrical energy demand, kWh/m^3
C_i — Initial fluoride concentration in the concentrate cells, mol/m^3
C_t — Fluoride concentration in the concentrate cells at a time t, mol/m^3
F — Faraday constant, 96,500 As/eq
I — Current intensity, A
J — Ion transport, mol/m^{2}h
t — Duration of the process, s or h
U — Voltage, V
V_{fd} — Final volume of the diluate, m^3
V_{id} — Initial volume of the diluate, m^3
V_{ic} — Initial volume of the concentrate, m^3
V_{fc} — Final volume of the concentrate, m^3
M — Mass of fluoride or HA accumulated in the ion-exchange membranes, mg
C_{id} — Initial concentration of HA or fluoride in the diluate, mg/dm^3
C_{fd} — Final concentration of HA or fluoride in the diluate, mg/dm^3
C_{ic} — Initial concentration of HA or fluoride in the concentrate, mg/dm^3
C_{fc} — Final concentration of HA or fluoride in the concentrate, mg/dm^3

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