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The influence of organic matter on fluoride removal efficiency during the electrodialysis process

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ABSTRACT

Fluorine is a common chemical element that is freely soluble in water. An excess of fluorine leads to many health problems and for that reason the fluoride content in drinking water cannot be higher than 1.5 mg/dm^3. The purpose of this paper was to evaluate the influence of natural organic matter (NOM) on fluoride transport through anion-exchange membranes in the course of conventional electrodialysis (ED). The ED installation operated in a batch mode with no concentration gradient between the diluate and concentrate cells at the start-up of the process. Model solutions with a variable content of fluoride (5–200 mg F$^-$/dm^3) and humic acids (5–15 mg/dm^3) were used in the ED treatment. Each tested solution also contained mineral salt (0.5 g NaCl/dm^3). During experiments the commercial PC-Cell BED-1-System, equipped with classic ion-exchange membranes PC-SA and PC-SK, was used. The constant current density (1.72 mA/cm^2) was applied for all ED trials. The fluoride concentration, conductivity, colour intensity, and voltage variation were monitored in the course of the ED process. The obtained results showed that the solution composition could have an influence on fluoride removal efficiency and batch electrodialysis performance. In the event of a high initial fluoride content, the presence of humic acids in model solutions led to an improvement of the fluoride transport rate across the ED stack. It was also revealed that the mechanism of fluoride removal by electrodialysis under the presence of humic acids has a manifold nature, resulting from mutual interactions between mineral salts, organic matter and ion-exchange membranes.

Keywords: Electrodialysis; Fluoride; Water treatment; Humic acids; Organic matter

1. Introduction

Fluorine is a common and highly reactive chemical element [1]. It naturally exists in the form of F$^-$ ions, which are very reactive. In a natural environment fluoride mainly occurs as fluorspar (CaF_2), sellaite (MgF_2), cryolite (Na_3AlF_6) or fluoroapatite [$3Ca_3(PO_4)_2Ca(F,Cl_2)$] [2–4]. Anthropogenic sources of fluoride occur in semiconductor manufacturing, coal power plants, glass manufacturing, fertilizer manufacturing, the metallurgical industry, ceramic production or electroplating [1,5]. According to WHO guidelines the content of fluoride in drinking water cannot be higher than 1.5 mg F$^-$/dm^3 [6,7]. A small amount of fluorine has a positive influence on our health. Fluorine prevents dental caries. Fluorine content above the permissible level leads to skeleton and dental fluorosis, cancer, osteosclerosis or neurological problems. Lung, liver and muscle diseases can also occur. Some researchers suggest that chronic exposure to fluoride can decrease birth rates or lower child intelligence. Fish and aquatic plants are also very vulnerable to fluoride toxicity [8–16].

In many parts of the world excessive concentrations of fluoride have been observed [2, 6–8,11]. For example, in Morocco the concentration of F$^-$ ions in natural water can be higher than 20 mg/dm^3 [13]. In South Africa the content of F$^-$

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ions in some cases is higher than 40 mg/dm^3 [9]. In Australia a concentration of around 13 mg F$^-$/dm^3 was detected [17]. In Tanzania the content of fluoride in some cases exceeds 330 mg/dm^3 [9]. It has been found that in tropical water in Tanzania fluoride commonly occurs simultaneously with natural organic matter (NOM) and can compete with NOM during adsorption processes. It has been estimated that probably 200 million people (more than 20 nations) suffer from fluorosis [18,19]. It has also been calculated that in China and India 35 and 26 million people, respectively are exposed to fluorine intoxication [20,21]. This data proves that the problem of an excessive concentration of F$^-$ ions exists in the world and that there is an urgent need to improve the methods of fluoride removal from water.

Adsorption, ion exchange or precipitation are techniques that can be used for fluoride removal from aqueous solutions. Most of these methods have drawbacks such as low capacity, lack of selectivity, complicated regeneration or high initial costs. Besides, adsorption efficacy is highly dependent on pH. The high costs of chemicals used for adsorbent regeneration are also one of the drawbacks and for that reason membrane processes like reverse osmosis (RO), nanofiltration (NF), electrodialysis (ED) or Donnan dialysis (DD) are perceived as the best option for water treatment. Electromembrane technologies are characterized by high energy consumption, but also by high effectiveness. There are many factors that could have an influence on fluoride removal efficiency – pH, the initial concentration of F$^-$ ions, membrane properties or coexisting ions [21–25].

Electrodialysis is a technique in which ions migrate through ion-exchange membranes under the influence of an electric field. The anion-exchange membranes are able to transfer anions, and cations cannot migrate through these membranes. The opposite situation occurs in the case of cation-exchange membranes. Cations are transported to the cathode, and anions migrate to the anode. Consequently, two streams are formed – diluate and concentrate. Additionally, it was observed that ED technology is more economically efficient than pressure driven processes in the case of a low salt content (< 0.5%) [26].

The National Office of Drinking Water (ONEP Co.) conducted research on fluoride removal from underground water using the electrodialysis process to evaluate the costs of the ED technique [27]. The capacity of the plant was equal to 2200 m^3/day and the initial fluoride and TDS concentration amounted to 2.32 mg F$^-$/dm^3 and 1.2 g/dm^3, respectively. The final content of F$^-$ ions attained 1 mg F$^-$/dm^3, whereas TDS decreased to 0.7 g/dm^3. The total costs involved expenditure on treatment, pretreatment, building construction and auxiliary equipment. The installation maintenance and energy consumption comprised the operating costs. They were assessed to 0.154 €/m^3, while the capital costs were equal to 833,207 €. It was noticed that the estimated costs depended mainly on the quality of feed and product water, the membrane area, membrane price and plant capacity.

Ben Sik Ali et al. [22] used the ED process for fluoride removal from brackish underground water from Borj-Cèdria (Tunisia). They applied the PCCell ED 64 002 installation. Experiments were conducted with PC-SK and PC-SA ion-exchange membranes. Due to the high TDS content in brackish water (approximately 15 g/dm^3), the experimental sample was diluted by raw water, which made TDS decline to 5 g/dm^3. The initial fluoride content of 2.9 mg F$^-$/dm^3 was reduced to 0.4 mg F$^-$/dm^3 and the specific energy consumption was calculated as 15.5 Wh/dm^3. Moreover, the final concentrations of the various ions that were present in the treated sample fulfilled the permissible limits for drinking water.

Ergun et al. [10] applied ED technology for defluoridation of real water containing 20.6 ± 0.8 mg/dm^3 of fluoride ions. The researchers used the strong-basic anion-exchange membranes SB-6407. The fluoride removal efficiency reached 96% and the final F$^-$ ion content was below WHO guidelines. Experiments involving model solutions with varied F$^-$ concentrations (from 0.1 to 100 mM) revealed a 5–78% removal efficiency of fluorides. In this study it has also been reported that the presence of other ions in the treated solution markedly deteriorated the transport rate of fluoride ions.

Arda et al. [28] performed investigations on fluoride removal from Balcova geothermal water with the use of the electrodialysis process. The concentration of TDS was equal to 1026 mg/dm^3 and F$^-$ concentration amounted to 7.72 mg F$^-$/dm^3. During the research the TS-1-10 batch type ED unit and Neosepta CMX and AMX membranes were used. The diluate, concentrate and electrode rinse tank volume was equal to 1 dm^3 (each). The authors employed two methods of fluoride removal. In the first technique, HCl acid was added to geothermal water to adjust the pH to 7.0–7.5. In the next method, experimental water was pretreated by precipitation of calcium ions. The precipitation was carried out with the use of Na_2CO_3 and NaOH. After settling, water was filtered through the paper filter and the pH was then corrected to 7.0–7.5 by HCl. In the first method the TDS content decreased to 33 mg/dm^3 and F$^-$ ion concentration was lowered to 0.06 mg F$^-$/dm^3. In the second method the TDS content after the ED process was 32 mg/dm^3, whereas the final fluoride content achieved 0.07 mg F$^-$/dm^3.

Banasiak et al. [29] performed ED experiments aimed at investigating the influence of feed composition on the removal of chosen ions (boron, fluoride, and nitrate). The volume of feed solutions (diluate and concentrate) was 4 dm^3 (each). Model solutions were prepared by mixing ultrapure water with the following chemicals: NaCl (5 g/dm^3), $NaHCO_3$ (84 mg/dm^3), NaF (5 mg/dm^3), $NaNO_3$ (100 mg/dm^3) and H_3BO_3 (10 mg/dm^3). The content of NO_3^-, H_3BO_3 and F$^-$ in experimental solutions was characteristic for brackish waters. In the course of the ED process the F$^-$ ion concentration decreased by 65.6 ± 12.0%. With regards to fluoride removal, the efficiency of the process was independent of pH (pH does not have an influence on fluoride speciation).

The above reported results confirm a great potential of electromembrane processes for fluoride ion removal from drinking water. However, it should be noted that extensive studies are mainly focused on F$^-$ ion removal in the presence of mono- and bi-valence ions, whereas the impact of natural organic matter (NOM) is only considered to a minor extent. NOM, including humic substances (HS), is a common constituent of surface water and can cause a variety of problems during water treatment (e.g. perturbation of coagulation, reduction of adsorption efficiency, membrane fouling and the formation of complexes with water constituents).

The purpose of this paper was to evaluate the influence of humic acids (HA) on fluoride migration through anion-exchange membranes in the course of batch electrodialysis. The ED experiments were conducted with no concentration gradient between the diluate and concentrate cells at the beginning of the process. Model solutions with a variable fluoride and HA concentration were treated by ED, and both F^- ion removal and energy consumption were analyzed.

2. Materials and methodology

2.1. Installation

During the experiments a commercial ED installation (PCCell BED-1 System, PCCell GmbH, Germany) was used. Classic ion-exchange membranes (PC-SA and PC-SK, produced by PCA GmbH, Germany) were applied. The membrane stack was made of 11 cation-exchange membranes and 10 anion-exchange membranes. The effective surface area of each membrane was equal to 64 cm^2. Table 1 shows the membrane characteristics.

The electrodialytic cell had a thickness of 0.5 mm. The volume of the diluate and concentrate tank was equal to 2 dm^3 (each). The electrode solution tank had a volume of 9 dm^3 and was fed by 0.05 M NaCl solution. The ED stack was connected to a DC power supply (output voltage – max 24 V, output amperage – max 5 A). Both the diluate and concentrate streams, as well as the electrode solution, circulated in the ED stack at a flow rate of 90 dm^3/h, which corresponded to a linear liquid velocity of 6.25 cm/s.

2.2. Reagents

The fluoride concentration in aqueous solutions amounted to 5, 10, 100, and 200 mg F^-/dm^3. Model solutions were made of sodium fluoride (NaF) and distilled water. They also contained NOM in the form of humic acids (HA, Aldrich) at concentrations of 5, 10, and 15 mg HA/dm^3. The humic acids were used to simulate humic substances in surface water. HS are the main constituents of natural organic matter, which is typically present in surface water in an amount of 0.1–20 mg/dm^3 [30]. Mineral salt (NaCl) was also added to the fluoride solutions in an amount of 0.5 g NaCl/dm^3, which is characteristic of freshwater. All ED experiments were performed at a natural pH of the model solutions, which was in the range of 6–7.

Table 1
Membrane characteristics

Parameter	Membrane type	
	PC-SK (cation-exchange)	PC-SA (anion-exchange)
Size, mm	110 × 110	
Electrical resistance, Ω cm^2	1–3	1–3
Thickness, μm	90–130	90–130
Functional group	$-SO_3^-$	$-NR_3^+$
Chemical resistance (pH range)	0–9	0–9
Mechanical resistance, MPa	0.4–0.5	0.4–0.5
Ionic form	Na^+	Cl^-
Ion exchange capacity, meq/g	Approx. 1.2	Approx. 1.1
Permselectivity (transfer number)	>0.95 (t-K^+)	>0.93 (t-Cl^-)

2.3. Methodology

The ED installation operated in a batch mode with no concentration gradient between diluate and concentrate cells at the process start-up, i.e. the same model solution filled up both the diluate and concentrate cells at the beginning of the process. The diluate and concentrate streams were circulated in the stack until the end of the treatment process. The process was stopped when the maximum voltage was achieved (24 V). The ED 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 applied current density was chosen in such a way as to not exceed the limiting current density. The limiting current density was evaluated theoretically on the basis of the Rauntenbach et al. [31] approach. The calculated limiting current density (for the initial salt concentration of 0.5 g/dm^3) was equal to 2.46 mA/cm^2 at 85% desalination efficiency for the ED process with standard PC-SA and PC-SK membranes.

During the process the concentration of F^- ions, colour and conductivity were determined in both the diluate and concentrate samples at the same time intervals. The voltage value was monitored every 5 min.

Fluoride ion flux through the membranes was calculated according to the following equation:

$$J = \frac{V_t C_t - V_i C_i}{A_m \cdot t} \tag{1}$$

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

The specific electrical energy demand (EC) was evaluated from the following equation:

$$EC = \frac{I \int_0^t U dt}{V_d} \tag{2}$$

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

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

The concentration of fluoride ions was determined by the colorimetric method with SPADNS reagent. This method involves the reaction of fluoride with a red zirconium-dye solution. Fluorides form a colourless complex with zirconium, thus bleaching the red colour in an amount proportional to the fluoride concentration. The F^- ion content was monitored with the use of a spectrophotometer DR 2000 (HACH) – method 8029, program no. 190, wavelength 580 nm. The measurement error was estimated to ±9%.

The colour intensity of the tested solutions was determined by an absorbance measurement at a wavelength of 350 nm with the use of a spectrophotometer Hitachi U-1900. The calibration curve allowed colour intensity as mg Pt/dm^3 to be expressed. The measurement error amounted to ±0.2%.

The diluate and concentrate salinity in the ED runs was monitored indirectly by electrical conductivity measurements. A conductometer Elmetron CC-411 was used for this purpose (the measurement error was equal to ± 0.25%).

3. Results and discussion

3.1. Efficiency of fluoride removal

Primarily, the study aimed to evaluate the application of conventional batch electrodialysis to fluoride removal in the presence of humic substances. The most important was to receive diluates containing fluoride ions in amounts permissible for drinking water (i.e. 1.5 mg F^-/dm^3). The total desalination result was only considered to a minor extent.

The experiments were performed for model solutions containing differentiated amounts of fluoride and humic acids. The initial concentration of NaCl for all experiments was equal to 0.5 g/dm^3. The variation of fluoride concentration in the diluate and concentrate streams in the course of the ED process is presented in Fig. 1.

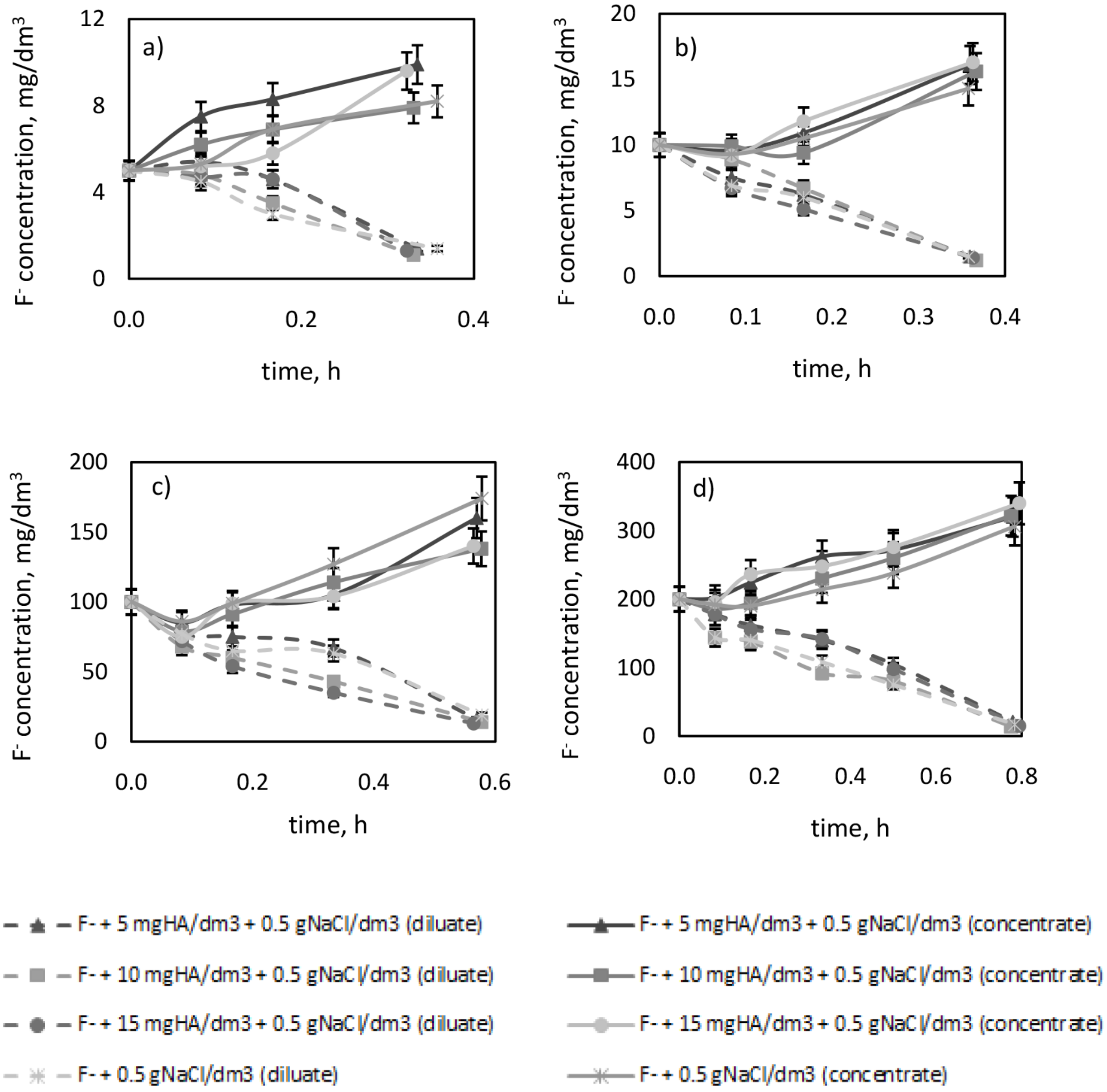

Fig. 1. Concentration of F^- ions in diluate and concentrate versus ED operational time a) 5 mg F^-/dm^3 + 0.5 g NaCl/dm^3 + HA; b) 10 mg F^-/dm^3 + 0.5 g NaCl/dm^3 + HA; c) 100 mg F^-/dm^3 + 0.5 g NaCl/dm^3 + HA; d) 200 mg F^-/dm^3 + 0.5 g NaCl/dm^3 + HA (error bars ±9%).

It was shown that the initial fluoride concentration affected the efficiency of treatment. In the case of solutions containing 5 and 10 mg F^-/dm^3, the final fluoride concentration did not exceed WHO guidelines (1.5 mg/dm^3) regardless of the humic acid concentration (Fig. 1a and Fig. 1b). The F^- ions content in the diluate varied from 1.1 to 1.4 mg F^-/dm^3 when the initial concentration was equal to 5 mg F^-/dm^3. The lowest concentration (1.1 mg F^-/dm^3) was obtained for the solution containing 10 mg HA/dm^3. When the fluoride content was equal to 10 mg F^-/dm^3, the final concentration was diminished to 1.2–1.5 mg F^-/dm^3 (the best results were also observed for an HA concentration of 10 mg HA/dm^3). In the event of no organic matter dosage, the F^- ion content decreased from 5 to 1.4 mg F^-/dm^3 and from 10 to 1.5 mg F^-/dm^3. The increase of the initial fluoride concentration to 100 and 200 mg F^-/dm^3 resulted in a significant worsening of the diluate quality. Fluoride concentration was lowered from 100 to 13–19 mg F^-/dm^3 and from 200 to 14–21 mg F^-/dm^3. For solutions containing only fluoride ions and sodium chloride (a lack of humic acids), F^- concentration was lowered from 100 and 200 mg F^-/dm^3 to 19 and 17 mg F^-/dm^3, respectively. The final F^- ion concentration exceeded the permissible level for drinking water, however the removal efficiency was high.

The above results indicate that a slight improvement of fluoride removal can be caused by the presence of humic acids in a moderate concentration. A possible explanation for this phenomenon is that fluoride ions attach to the dissociated macroparticles of humic acids, which can subsequently be deposited on the surface of ion-exchange membranes (predominantly on the anion-exchange membranes). The binding phenomenon of fluoride ions to HA macroparticles under a pH range of 5.0–6.6 was confirmed by Hayes et al. [32]. Shen et. al [33] also performed research on fluoride and HS interaction in an aquatic system. They presented a new "open cage" concept, which allowed the spatial interaction between humic substances and fluoride to be described. Ions are not bound to functional groups, but they are able to migrate inside the HS structure. The idea assumes that an internal electric field is negligible and the HS aggregation has a cage-like framework. Free ions are able to migrate inside and outside the framework. Moreover, restrictions like territorial binding, site binding or electrostatic attraction do not exist. The researchers also have another conception of interaction between the fluoride and HS. The alternative idea assumes that molecules of organic matter firstly bind cations, and in the second step fluoride anions are attracted by the bound cations (via cation-anion interaction).

It was demonstrated that the duration of the ED process strongly depended on the initial fluoride concentration (Fig. 1). For a fluoride content equal to 5, 10, 100 and 200 mg F^-/dm^3, the process was terminated after 20, 22, 34, and 47 min, respectively. This finding was evident because a constant current density was applied for all experimental solutions. Due to the increased salt (NaF) concentration, more time was needed to attain the comparable desalination effects. According to Faraday's law, the amount of ionic equivalents to be removed is directly proportional to the current intensity and time of the process.

Quantitative evaluation of fluoride adsorption can throw some light on F^- ion behaviour in the course of the ED process. The amount of fluoride deposited in the ED system was calculated by using a mass balance. The obtained results are given in Fig. 2.

It has been calculated that the amount of adsorbed fluoride anions in the presence of organic matter was equal to 0–2 mg and 4.6–6.4 mg when the initial fluoride content was equal to 5 and 10 mg/dm^3, respectively. After increasing the F^- content to 100 mg/dm^3 and 200 mg/dm^3, the amount of adsorbed fluoride ions increased to 48–96 mg and 118–190 mg, respectively. This data allows it to be stated that about 10–24% of F^- ions present in the system were adsorbed by membranes and/or HA. Without the addition of organic matter to the tested solutions, the amount of adsorbed fluoride anions was equal to 0.8; 8.4; 14 and 154 mg when the fluoride content amounted to 5, 10, 100 and 200 mg/dm^3, respectively. During the experiments with solutions containing only mineral salts (NaF and NaCl), 3.5–21% of fluoride ions were adsorbed. It has been observed that even in the case of a lack of organic matter, the amount of adsorbed fluoride ions was high. This phenomenon is caused by the sorption of fluoride ions into the structure of the membrane. It has also been noticed that in some cases the amount of adsorbed F^- ions decreased when HA concentration increased. It can be assumed that the fluoride hydrated radius decreases in the presence of organic matter. As a consequence, the fluoride migration through the membranes is enhanced and a less amount of F^- ions is deposited in the system.

The obtained removal efficiencies, as well as the final fluoride concentrations in the diluate, are shown in Fig. 3. It was found that the F^- ion removal varied from 72 to 78% for solutions containing 5 mg F^-/dm^3. The highest degree of fluoride removal occurred when HA concentration was equal to 10 mg/dm^3. With no organic matter in the treated solution, the fluoride concentration was lowered by around 72%, and when increasing the fluoride concentration to 10 mg F^-/dm^3, the removal efficiency was equal to 85–88%. In this case the best results were also obtained when the HA content was equal to 10 mg/dm^3. When the fluoride content was further elevated to 100 mg F^-/dm^3, the removal efficiency was comparable and it varied from 81 to 87%. The best results were obtained for the organic matter content equal to 15 mg/dm^3. After increasing fluoride concentration to 200 mg F^-/dm^3, the removal degree reached the highest values, i.e. 89.5–93%. The highest treatment efficiency (93%) was obtained for the solution with an organic matter content of 10 mg/dm^3. When there was no organic

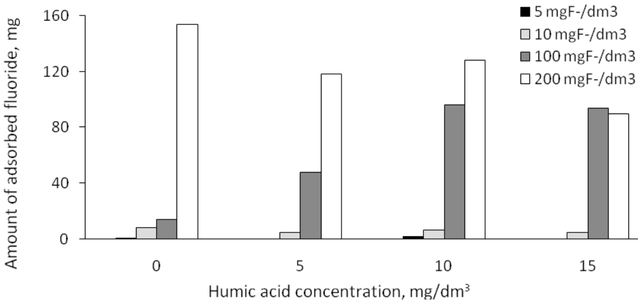

Fig. 2. Amount of adsorbed fluoride versus humic acid concentration and fluoride concentration.

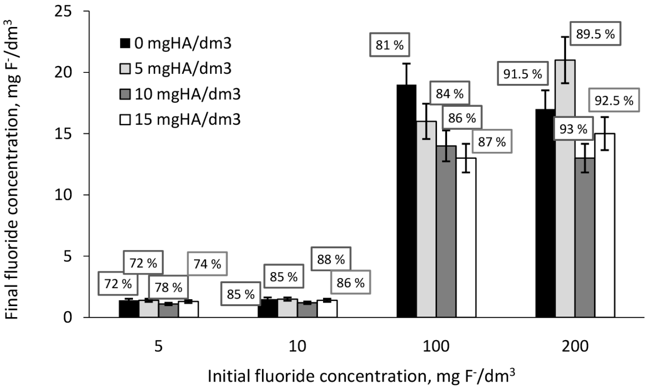

Fig. 3. Final fluoride concentration and removal efficiency versus initial fluoride concentration and humic acid concentration (error bars ±9%).

matter addition the removal efficiency reached 91.5% (for 200 mg F^-/dm^3). It should be pointed out that a seemingly high fluoride separation (for initial concentrations of 100 and 200 mg F^-/dm^3) did not ensure a satisfying quality of the diluate (in view of the fluoride limit concentration for drinking water).

Rather astonishing findings were obtained by analyzing the fluoride flux through the anion-exchange membranes (Fig. 4). The flux was calculated on the basis of the F^- ion concentration increase in the concentrate cells at a given time. The mean flux for each ED course was given in Fig. 4.

Basically, the ion flux is proportional to the initial fluoride concentration, although for a low F^- ion content (5 and 10 mg F^-/dm^3) the flux differential is not meaningful. The calculated mean fluoride flux varied from 0.012–0.029 mol/m^2h (for ED trials with solutions containing a low fluoride amount) to 0.134–0.264 mol/m^2h (in the ED courses with the highest fluoride concentration). The greatest impact of humic acids on the F^- ion flux was detected for solutions containing 200 mg F^-/dm^3. Unexpectedly, in this case the HA presence in the treated solutions markedly enhanced the F^- ion migration through the ion-exchange membranes. Furthermore, for other tested solutions a general trend of a diminishing fluoride flux with an increasing HA concentration can be observed. The obtained relationships seem to confirm the "open cage" concept. In the case of a high F^- ion content (200 mg F^-/dm^3), more fluoride ions remain unbounded to the HA cage-like framework than for solutions with a lower F^- concentration (100 mg F^-/dm^3). As a result, the increased flux is observed for the 200 mg F^-/dm^3 solution.

The noted fluoride ion behaviour appears to be dependent on the adsorption vulnerability of both fluoride and humic acids on the membranes, as well as on the ability of HA to trap free F^- ions. It was a rule that fluoride concentration in the concentrate cells decreased at the initial stage of the ED process, which confirmed the sorption phenomenon. The possible diminishing of the fluoride hydrated radius, due to the presence of humic acids, should not be disregarded.

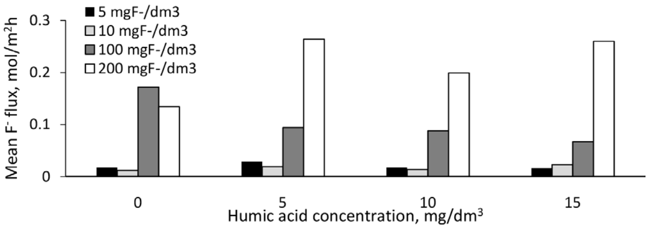

Fig. 4. Mean fluoride ion flux versus concentration of humic acids and initial fluoride content (5, 10, 100 and 200 mg F^-/dm^3).

Likewise, the deposition of humic acid macroparticles on the membrane surface can be anticipated due to colour reduction in both the diluate and concentrate cells (Fig. 5). The colour reduction of the diluate, irrespective of the HA concentration, varied from about 16.7 to even 28.8%, indicating the membrane sorption phenomenon. The HA deposition in the concentrate cell was observed to a lesser extent (the colour was reduced by 12.5% on average). In general, organic particles of high molecular weight cannot enter the membrane matrix with micropores. Thus, HA deposition on a membrane surface is more probable than the ionic transport of the dissociated macroparticles of humic acids.

The impact of HA on the fluoride flux can be explained by competition between HA particles and F^- ions for specific sorption sides in the membrane matrix. In the case of an excessive fluoride content (200 mg F^-/dm^3), the F^- ion sorption is relatively small (HA deposition is dominant) and a high fluoride flux is possible. It is also quite likely that the presence of organic matter in the treated solution leads to the reduction of the size of the F^- hydrated radius, thus facilitating fluoride ion transport. On the other hand, the humic acid deposition on the ion-exchange membrane surface can inhibit migration of ions through the membranes, or ions can even be trapped by HA macroparticles. The latter case was especially observed in the ED process with solutions containing 100 mg F^-/dm^3 (Fig. 4). Banasiak et al. [29] arrived at a similar conclusion that humic acids lowered the ion flux (including F^- ions) and at the same time improved ion removal. However, this observation was found for solutions containing a very low amount of fluoride (approximately 2 mg F^-/dm^3).

Due to a common view that humic substances can cause a serious fouling of ion-exchange membranes, the behaviour of humic acids under electrodialytic transport was verified. During the tests the concentrate tank was filled with a solution containing only sodium chloride (0.5 g/dm^3), while the diluate compartment was supplemented by sodium chloride (0.5 g/dm^3) and humic acids. The initial colour of the diluate containing 5, 10, 15 mg HA/dm^3 was approximately equal to 25, 50 and 75 mg Pt/dm^3. The concentrate solution (without HA addition) did not exhibit any colour at the beginning of the process (Fig. 6).

It was found that the colour of the diluate decreased by about 15.9–36.1% after termination of the ED process. The lowest colour drop occurred in the case of the solution containing 5 mg HA/dm^3 and the highest colour decrease was noted when the HA concentration was equal to 15 mg HA/dm^3. However, the most meaningful observation was devoted to the colour of the concentrate after the ED process – it still remained close to 0 mg Pt/dm^3. The lack of a significant change of the concentrate colour with a simul-

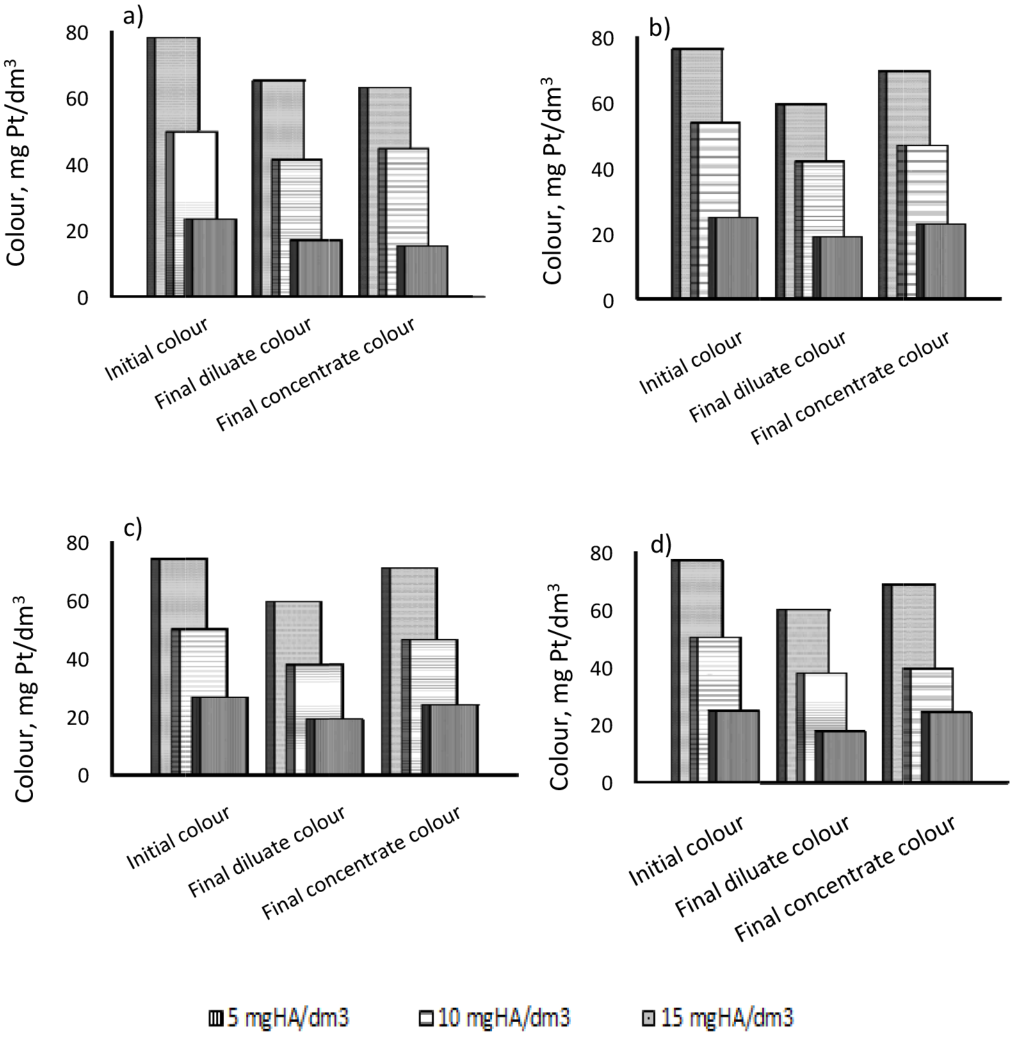

Fig. 5. Colour at the beginning and end of the process versus various concentrations of humic acids and fluoride ions a) 5 mg F⁻/dm³ b) 10 mg F⁻/dm³ c) 100 mg F⁻/dm³ d) 200 mg F⁻/dm³.

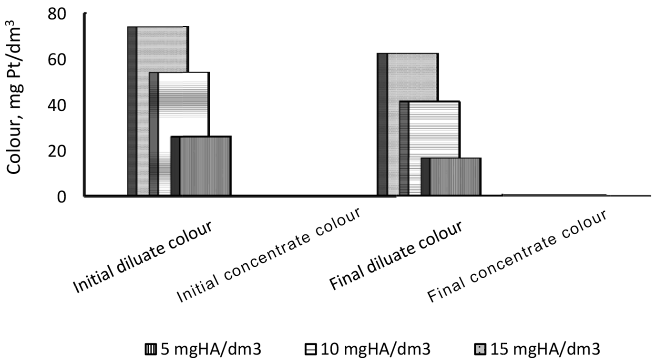

Fig. 6. Colour at the beginning and end of the process versus various concentrations of humic acids, C_0= 0.5 g NaCl/dm³.

taneous decrease of the diluate colour at the end of the process allows the claim that HAs do not migrate between the diluate and concentrate compartments. The colour depletion in the diluate cells was caused by the deposition of HA particles at the membrane surface (predominantly at the anion-exchange membrane surface).

3.2. Desalination efficiency

In the course of the ED process the total desalination effect, as well as the fluoride ion separation, was also determined by electrical conductivity measurements. The obtained results are given in Fig. 7.

The desalination process was run with no disturbances for all tested solutions. As was already mentioned, the increase of the ED operational time was caused by an increasing salinity (i.e. the fluoride content at a constant NaCl concentration). The initial conductivity for solutions containing 5 and 10 mg F⁻/dm³ decreased from 1029–1106 µS/cm and 1126–1163 µS/cm to 106–150 µS/cm and 95–108 µS/cm, respectively. In the case of a high fluoride content (100 and 200 mg F⁻/dm³), despite the initial conductivity being significantly elevated (1560–1644 µS/cm and 2060–2090 µS/cm, respectively), the final quality of the diluate was comparable with the diluate quality obtained for a low F⁻ content and amounted to 92.7–114 µS/cm and 84.6–114.4 µS/cm, respectively.

Generally, the impact of HA on diluate conductivity was negligible. On the other hand, it is worth noting that conductivity reduction was always higher than the

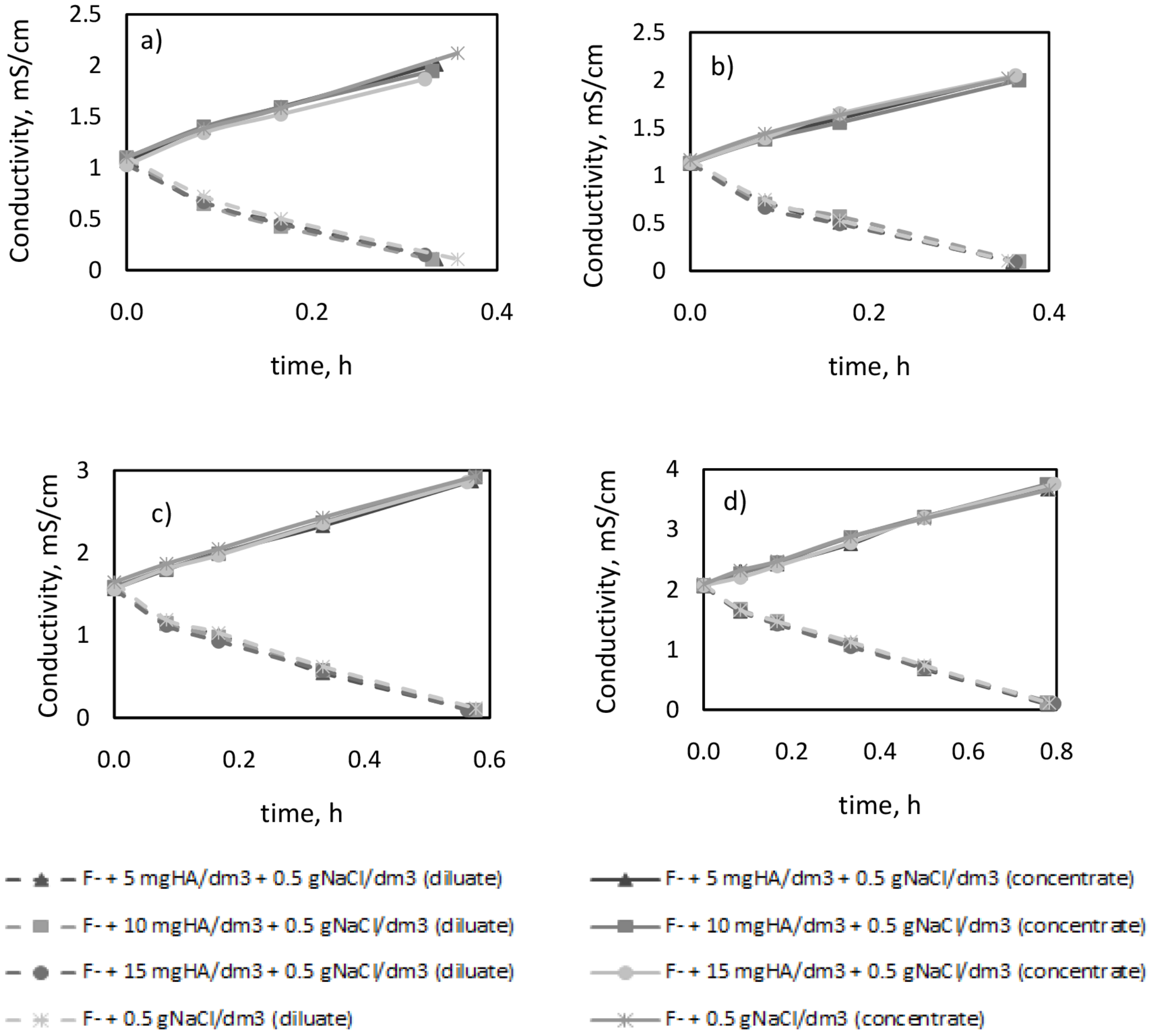

Fig. 7. Variation of diluate and concentrate conductivity versus ED operational time a) 5 mg F^-/dm^3 + 0.5 g NaCl/dm^3 + HA; b) 10 mg F^-/dm^3 + 0.5 g NaCl/dm^3 + HA; c) 100 mg F^-/dm^3 + 0.5 g NaCl/dm^3 + HA; d) 200 mg F^-/dm^3 + 0.5 g NaCl/dm^3 + HA.

fluoride removal rate – the conductivity was reduced by 85.5–90.5%, 90.7–91.6%, 93.1–94.5 and 94.5–96%, while the F^- ion removal amounted to 72–78%, 85–88%, 81–87%, and 89.5–93% for solutions containing 5, 10, 100, and 200 mg F^-/dm^3, respectively. It can be anticipated that the coexisting ions can influence the fluoride migration in the ED stack. In the case of the NaCl and NaF mixture, this can be explained by taking into account the ion mobility and ionic radius of Cl^- and F^- ions. The ionic mobility of chloride and fluoride ions is equal to 7.91 and 5.70 m^2/s·V [34], respectively, whereas the radius of hydrated Cl^- ion is 0.332 nm compared to 0.352 nm for the F^- ion [35]. For that reason, the more mobile and less hydrated Cl^- ion can migrate through the anion-exchange membrane more easily than the F^- ion. This adverse effect of coexisting ions (including Cl^- ions) on fluoride transport has been reported in literature [10,29,36].

3.3. Energy consumption

Energy demand is of crucial importance for practical applications of membrane processes. Thus, a specific electrical energy demand (EC) was calculated. The obtained results are presented in Fig. 8.

Firstly, it was demonstrated that the energy demand increased with an increasing fluoride content. The EC values varied slightly from 0.19 to 0.22 kWh/m^3 (when the F^- content amounted to 5 mg F^-/dm^3), regardless of the humic acid concentration. After increasing the fluoride content to 10 mg F^-/dm^3, the EC value was equal to 0.20–0.22 kWh/m^3 and similarly, the HA content did not significantly influence the energy consumption. For solutions containing 100 mg F^-/dm^3, energy demand rose to 0.28–0.31 kWh/m^3. The greatest fluctuation in energy demand was detected when the fluoride concentration was elevated to 200 mg F^-/dm^3. The value of energy demand was in a range of 0.32 to 0.42 kWh/m^3 and a visible increasing tendency of EC with a raising HA content was observed. This latter finding provides evidence that HA deposition on the membranes could increase the ED stack resistance and EC value. However, the impact of OM on the final ED performance strongly depends on the solution composition subjected to ED treatment.

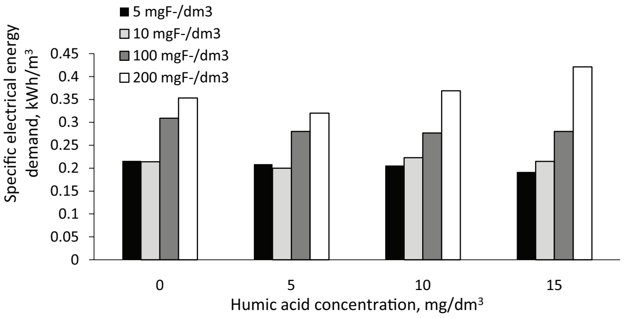

Fig. 8. Specific electrical energy demand versus concentration of humic acids and initial fluoride content (5, 10, 100 and 200 mg F^-/dm^3).

4. Conclusions

The obtained results revealed that the composition of water could have an influence on fluoride removal efficiency and batch electrodialysis performance. The degree of this impact depends on the concentration of fluoride and organic matter. While an increased fluoride concentration brings about appreciable worsening of the diluate quality in view of the fluoride content, the effect of organic matter is less evident. Unexpectedly, the presence of humic acids in the treated solution leads to an improvement of the fluoride transport rate (ion flux) as well as the fluoride removal rate, but only in the case of an elevated fluoride concentration (200 mg F^-/dm^3). A beneficial effect of humic acids on fluoride removal is also observed for solutions containing 100 mg F^-/dm^3, but this effect is accompanied by the hampered ion flux. The electrodialysis of aqueous mixtures containing a low amount of fluoride (5–10 mg F^-/dm^3) was not influenced (or influenced to a minor extent) by a variable concentration of humic acid (5, 10, 15 mg HA/dm^3).

The mechanism of fluoride removal by electrodialysis under the presence of humic acids has a manifold nature, resulting from mutual interactions between mineral salts, organic matter and ion-exchange membranes. The following phenomena can be distinguished: 1) the binding of fluoride ions to humic acid macroparticles, 2) the sorption of both fluoride ions and humic acid macroparticles on/in the ion-exchange membranes 3) the hindering of the rate of F^- ion transport in the ED cells by an excessive amount of HA.

The obtained results demonstrated that the electrodialysis process can be used as an effective method for fluoride removal from moderately contaminated water solutions. When the initial fluoride content amounts to 5–10 mg F^-/dm^3, the final ED product fulfills standards for drinking water regarding F^- ion content (1.5 mg F^-/dm^3). The elevated fluoride content (100–200 mg F^-/dm^3) in treated water brings about a significant deterioration of the ED process efficiency, and the final F^- concentration exceeds the permissible standard for drinking water.

It has been found that the presence of humic acids in treated solutions has an insignificant influence on the conductivity reduction and process duration. It was observed that both the operational time and energy consumption are primarily affected by the initial fluoride content. Besides, it was stated that organic matter has a minor or even no influence on energy demand.

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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 (96500 As/eq)
I — Current intensity (A)
J — Ion flux (mol/m^2h)
t — Duration of the process (s or h)
U — Voltage (V)
V_d — Volume of the diluate (m^3)
V_i — Initial volume of the concentrate (m^3)
V_t — Volume of the concentrate at a time t (m^3)

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