

## Physicochemical characterization of a polymeric conductor: application to defluoridation of industrial effluent by electro dialysis

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**Abstract:** In many places around the world, the fluoride concentration in ground water as raw water is higher than the threshold standard for healthy drinking water. The aim of this work is to study the characteristics of an anionic membrane that will be the subject of an application for defluoridation by electro dialysis. The first objective of this work is to evaluate the physicochemical characteristics of the membrane used in experiments by determination of the exchange capacity, water uptake, ionic conductivity, and transport number (Hittorf method). The second part consists of studying the effect of different parameters such as electro dialysis time, supporting electrolyte concentration, coexisting ions (such as  $SO_4^{2-}$ ,  $NO_3^-$  and  $Cl^-$ ), current density, and the pH of the solution to evaluate the effectiveness of the electro dialysis defluoridation process. The high percentage of defluoridation obtained after treatment of industrial effluent (80.3%) reflects the good efficiency of the electro dialysis process.

**Key words:** Anionic membrane, defluoridation, electro dialysis, physicochemical characteristic, industrial effluent

### 1. Introduction

Water is crucial for life and is also used in many industrial processes. The rapid development of industries has led to a high water demand, including the generation of large amounts of wastewaters. This has become a serious issue throughout the world and can trigger environmental risks.

The discharge, directly or indirectly, of wastewater loaded with polluting substances without any prior treatment is a cause for growing concern given the possible undesirable effects on the environment and on health. Fluoride is one such contaminant that threatens living organisms, in particular humans. It is an essential element for the human body at levels between 0.5 and 1.5 mg L<sup>-1</sup>. Bones and teeth contain most of the body's fluoride, and fluoride affects various human life activities as well as teeth and bone tissue metabolism.<sup>1,2</sup> However, it constitutes a considerable health risk if its content exceeds the limiting fluorine concentration set by the World Health Organization at 1.5 mg L<sup>-1</sup>.<sup>3</sup> Endemic dental hypoplasia (tooth discoloration), enamel hypoplasia, and linear enamel hypoplasia are some of the diseases that are categorized under dental fluorosis. Skeletal fluorosis, a crippling disorder, is permanent and irreversible in nature and its effects are detrimental in nature to the health of an individual.<sup>4</sup>

In Tunisia, the legislation on wastewater discharges has become increasingly strict. Most industrial discharges exceeding the thresholds must therefore be treated before being discharged into the public dump.

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According to the Tunisian NT106.002 standard, the limit concentration of fluoride to be released into sewer systems is fixed at 3 mg L<sup>-1</sup>.

So far, several methods have been investigated for defluoridation, such as adsorption processes,<sup>5</sup> precipitation-coagulation,<sup>6</sup> ion exchange,<sup>7-9</sup> membrane-based processes,<sup>10</sup> and electrocoagulation.<sup>11</sup> Among these, electro-dialysis is an attractive option and widely used in real applications. Electrodialysis (ED) involves the preferential transport of ions through ion exchange membranes under the influence of an electrical field. However, satisfactory yield in a membrane process is based, above all, on a judicious choice of the membrane. The development of new ion-exchange membranes with better selectivity, lower electrical resistance, and improved thermal, chemical, and mechanical properties has also created further interest in electrodialysis.<sup>12</sup>

In this context, our research aims to study the physicochemical properties of an anion exchange membrane and its subsequent use in electrodialysis for the defluoridation of industrial effluents.

## 2. Results and discussion

### 2.1. Physicochemical characteristics of membrane

#### 2.1.1. Water uptake and ion exchange capacity

Water uptake and ion-exchange capacity values for the anionic membrane in  $OH^-$ ,  $Cl^-$ ,  $NO_3^-$ , and  $SO_4^{2-}$  form are given in Table 1.

**Table 1.** Water uptake and ion exchange capacity of membrane.

Ionic form	$\sigma$ (%)	$C_E$ (meq g <sup>-1</sup> )	Ionic radius $r_i$ (Å)
$OH^-$	24.90	1.36	1.33
$Cl^-$	18.19	1.37	1.81
$NO_3^-$	15.54	1.36	1.89
$SO_4^{2-}$	12.10	1.38	2.40

Water uptake varies with the ionic form of the membrane. This variation can be explained by the fact that the water uptake of the ion-exchange membrane depends on a number of different parameters such as the membrane matrix, the nature of the counter-ions, their charge, and their size.<sup>12,13</sup> Ion-exchange membranes are insoluble materials, but since their macromolecular network is deficient and contains hydrophilic functions (ion-exchange sites), mobile ions and solvents can penetrate inside and cause swelling. For the solutions (NaCl, NaOH,  $Na_2SO_4$ ,  $NaNO_3$ ), the membrane swells more for the  $OH^-$  ions due to the hydrophilic behavior of the counter-ion. Indeed, the ion  $OH^-$  has the smallest ionic radius (Table 1), so it will be the most hydrated. It can be shown that the water uptake increases with the decreasing of the ionic radius of the counter-ion as given in Table 1. The results shown in Table 1 confirm that ion-exchange capacity is independent of the nature of the counter-ion.<sup>14</sup>

#### 2.1.2. Membrane thickness and electrical conductivity

The current passing through an ionic solution in ED and the resultant transport of ions is related to the conductivity of the ionic solutions. According to the study done by Lteif et al.<sup>15</sup>, it is the counter-ion that intervenes to fix the value of membrane conductivity as a function of its mobility and size. The mobility of an ion varies with the hydrated radius. The more hydrated it is, the more difficult its passage through the

ion-exchange membranes will be and thus conductivity of the membrane decreases. Table 2 shows that the values of membrane conductivity are in reverse to the hydrated radius. The order of conductivity values of different ions is as follows:

$$SO_4^{2-} < F^- < NO_3^- < Cl^- < OH^-.$$

**Table 2.** Membrane thickness and electrical conductivity.

Electrolyte solution	Thickness of membrane (cm)	$\kappa$ (ms cm <sup>-1</sup> )	Hydrated radius (nm)
NaOH	0.0198	8.97	0.300
NaCl	0.0152	0.94	0.332
NaNO <sub>3</sub>	0.0175	0.42	0.340
NaF	0.0185	0.36	0.352
Na <sub>2</sub> SO <sub>4</sub>	0.0155	0.14	0.379

### 2.1.3. Transport numbers of counter-ions (Hittorf method)

Anionic transport numbers were measured for the membrane as a function of the current intensity and the time of ED. The transport numbers of different counter-ions using the Hittorf method are reported in Table 3. Since the values obtained are close to unity, it can be considered that the membrane is selective toward ions  $SO_4^{2-}$ ,  $F^-$ ,  $NO_3^-$ ,  $Cl^-$  and  $OH^-$ .

**Table 3.** Transport numbers obtained for the membrane studied with the Hittorf method.

Ions	Initial concentration (mol L <sup>-1</sup> )	Final concentration (mol L <sup>-1</sup> )	Current intensity (mA)	Time (min)	$t_{\text{anodic}}$	$t_{\text{cathodic}}$	Average value
		Anodic Cathodic					
$SO_4^{2-}$		1.26 1.44	125	192	0.98	1.04	1.01
	1	1.53 1.02	100	240	1	0.97	0.98
		1.5 1.33	75	320	0.97	1.05	1.01
$NO_3^-$		1.81 0.53	125	192	0.98	1.01	0.99
	1	1.78 0.58	100	240	0.99	1.05	1.02
		1.88 0.48	75	320	1.03	1	1.01
$OH^-$		0.99 1.01	125	192	1.04	0.96	1
	1	0.98 1.02	100	240	1.05	0.97	1.01
		0.99 1.28	75	320	1.02	0.99	1
$F^-$		0.93 1.22	125	192	0.97	0.99	0.98
	1	0.97 1.09	100	240	0.98	0.98	0.98
		0.99 1.3	75	320	0.99	1.01	1

#### 2.1.4. Scanning electron microscopy (SEM)

SEM (Figure 1) of the membrane revealed a planar veined surface without any cracks or visible pores. Some grains are visible on its surface. However, it seems that these were probably formed during the synthesis process (crystallized “residues” of cross-linker).

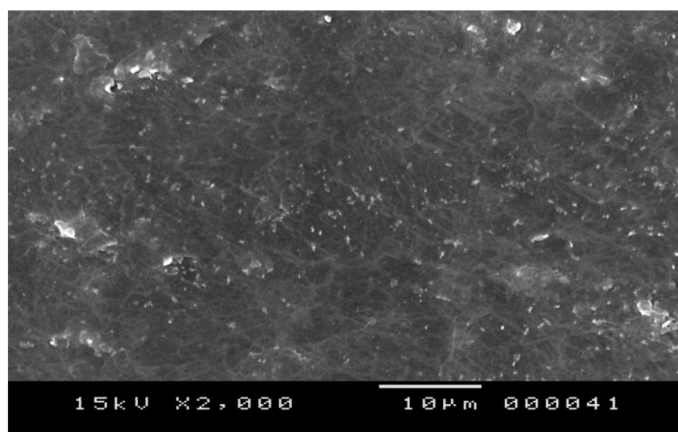


Figure 1. SEM image of the anionic membrane.

#### 2.1.5. FTIR analysis

FTIR analysis is a very useful tool for studying the molecular structure of polymers. The FTIR spectrum of the anionic membrane is represented in Figure 2. The broad band in the  $3500\text{--}3300\text{ cm}^{-1}$  region is attributed to the  $\nu_{OH}$  vibration in the water molecule. There are four characteristic peaks including  $\text{CH}_2$  stretching and bending bonds at  $2920\text{ cm}^{-1}$  and  $1465\text{ cm}^{-1}$ , respectively. The pure DABCO shows a characteristic broad absorbance at  $1000\text{--}1100\text{ cm}^{-1}$  ( $\text{C-N}$  stretching). The band observed at  $1636\text{ cm}^{-1}$  was due to  $\text{C-N}^+$  stretching of the quaternary ammonium group.

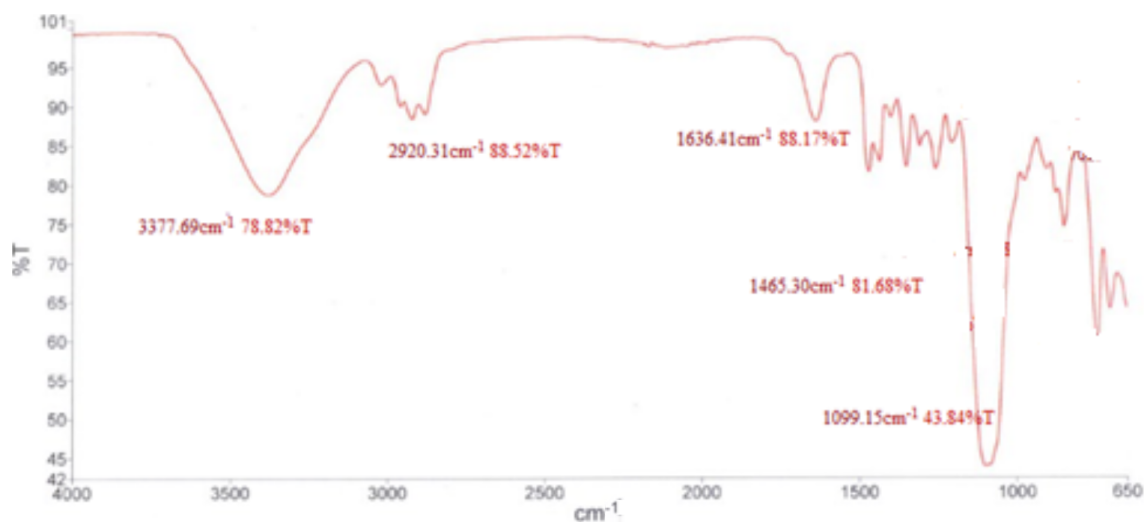


Figure 2. FTIR spectrum of AEM.

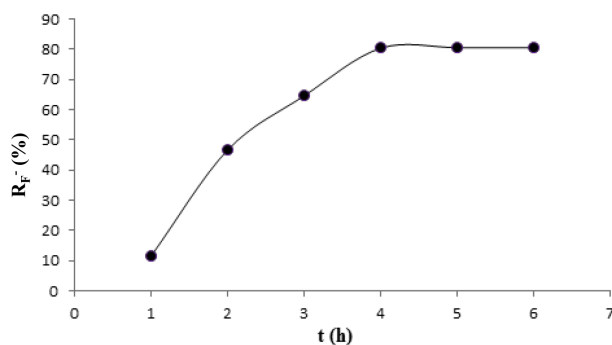
## 2.2. Electrodialysis parameters

The studied anionic membrane shows satisfactory physicochemical characteristics, which would enable its use for electro dialysis application. This application is interesting in the removal of fluoride ions.

In this section, ED performance is evaluated by analyzing several parameters such as electro dialysis time, supporting electrolyte concentration, coexisting ions, current density, and pH of the solution. In order to study the influence of these parameters, we chose to treat synthetic solutions of fluoride ( $10 \text{ mg L}^{-1}$ ) before the application of defluoridation of real water.

### 2.2.1. Effect of electro dialysis time

First the optimum time of electro dialysis was determined. Figure 3 shows the effect of electro dialysis time on the removal of fluoride by electro dialysis.



**Figure 3.** Effect of electro dialysis time on the removal of fluoride ( $[F^-] = 10 \text{ mg L}^{-1}$ ,  $10 \text{ mA}$  current intensity,  $3 \text{ g L}^{-1}$  NaCl).

The percent removal of fluoride was defined as follows:

$$R_{F^-} (\%) = \frac{[F^-]_0 V_0 - [F^-]_t V_t}{[F^-]_0 V_0} \times 100 \quad (1)$$

Here  $[F^-]_0$  is initial fluoride concentration ( $\text{mol L}^{-1}$ ) in the central compartment,  $[F^-]_t$  is the final concentration of fluoride in the central compartment ( $\text{mol L}^{-1}$ ), and  $V_0$  and  $V_t$  are the initial and the final volume (mL) in the central compartment, respectively.

The obtained results from these experiments show that the removal increases with time and attains high defluoridation in 4 h.

### 2.2.2. Effect of supporting electrolyte concentration

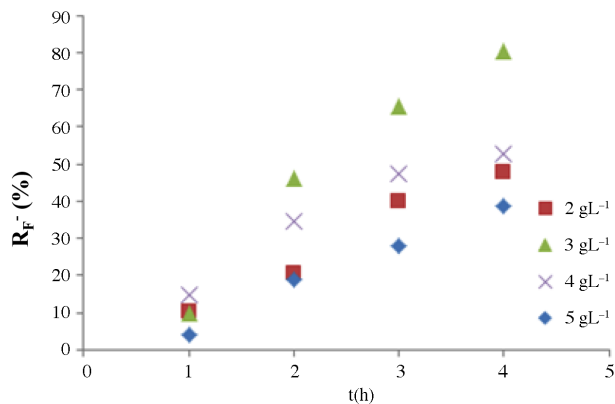
In order to optimize the concentration of the supporting electrolyte for the removal of fluoride, the study was carried out with different concentrations of  $2 \text{ g L}^{-1}$ ,  $3 \text{ g L}^{-1}$ ,  $4 \text{ g L}^{-1}$ , and  $5 \text{ g L}^{-1}$  NaCl. As seen in Figure 4, the concentration of the supporting electrolyte has a significant effect on the fluoride removal. The most important observation is that high removal of fluoride was obtained for  $3 \text{ g L}^{-1}$  NaCl. The decrease in the percentage of defluoridation can be explained by the increase in the number of ions in the solution when the concentration of the salts increases. Consequently, competitive transfer may occur between fluoride ions and other ions (chloride ions in our case).

### 2.2.3. Effect of applied current density

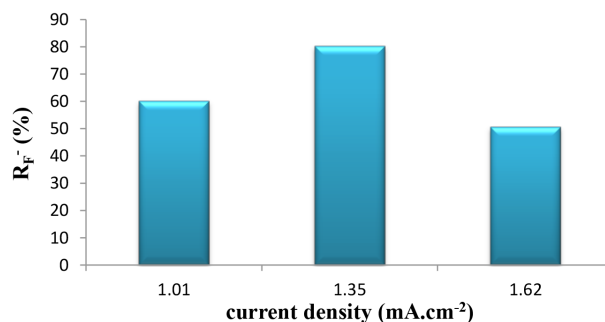
As electro dialysis is an electrochemical separation process, the driving force in this process is the gradient of the electric potential, which causes an electric current and consequently the separation of ionic species.

The operation was carried out using different current densities ( $1.01 \text{ mA cm}^{-2}$ ,  $1.35 \text{ mA cm}^{-2}$ , and  $1.62 \text{ mA cm}^{-2}$ ) and  $3 \text{ g L}^{-1} \text{ NaCl}$ .

The results in Figure 5 show important fluoride removal efficiency (of the order of 80%) by migration at a current density of  $1.35 \text{ mA cm}^{-2}$ .



**Figure 4.** The effect of supporting electrolyte concentration on the removal of fluoride ( $10 \text{ mA}$  current intensity,  $10 \text{ mg L}^{-1} \text{ NaF}$ ).



**Figure 5.** Effect of applied current density on removal of fluoride.

### 2.2.4. Coexistent ions

In the literature, the existence of other ions in ground water will influence the migration process of fluoride in an electro dialysis system. Ions usually found with fluoride in ground water are chloride, nitrate, and sulfate. In this study, the electro dialysis process was carried out with solutions containing  $10 \text{ mg L}^{-1}$  fluorides in the presence of  $3 \text{ g L}^{-1} \text{ NaCl}$ ,  $\text{NaNO}_3$ , and  $\text{Na}_2\text{SO}_4$ , respectively, and under current density of  $1.35 \text{ mA cm}^{-2}$ .

The obtained results are presented in Figure 6. As shown, the nature of the coexisting ion has a significant effect on the removal of fluoride by electro dialysis. The most remarkable observation is that an important percentage removal of fluoride was found in the presence of chloride ion (use of  $\text{NaCl}$  as a support electrolyte).

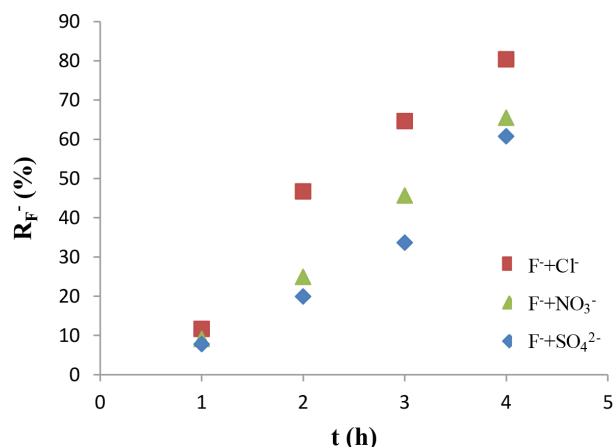
It is also noted that the fluoride removal rate in the presence of monovalent anions (chloride or nitrate) is higher than that determined in the presence of bivalent anions (sulfate). This can be confirmed by the movement of monovalent and bivalent ions in an ion-exchange membrane, which was discussed in detail by Miyoshi et al.<sup>16</sup> They pointed out that the monovalent ion can be transferred with a fixed ion of the membrane. Thus, it can move more easily from one functional group to another. On the other hand, the presence of a bivalent ion will disrupt the movement of the monovalent ions. Under these circumstances, the movement of fluoride ions is prevented by the coexistence of the bivalent ion (the case of use of  $\text{Na}_2\text{SO}_4$  as a support electrolyte). These results are in agreement with those obtained by Ergun et al.<sup>17</sup>

Moreover, the observed difference in defluoridation levels in the presence of chloride ions (80.34%) and nitrate ions (65.47%) is probably due to ion mobility, which is related to membrane conductivity. According to the results presented in Section 2.1.2, the conductivity of the membrane in the presence of the chlorides

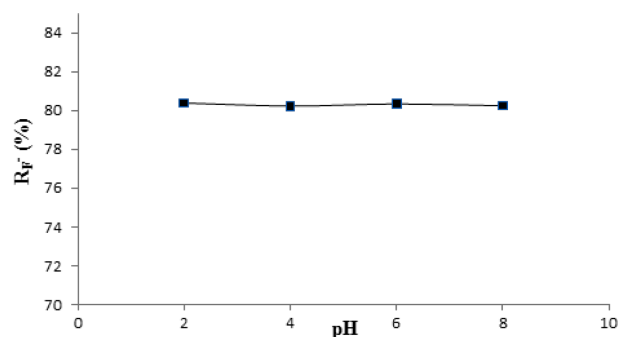
is greater than that in the presence of the nitrates. We can then estimate that the chloride ions conduct the current better and subsequently promote the migration of fluoride ions better than the nitrate ions.

### 2.2.5. Effect of pH

The removal of fluoride was studied at four different pH values ranging from 2 to 8 and a fixed concentration of NaCl of  $3 \text{ g L}^{-1}$ , while maintaining the current density at  $1.35 \text{ mA cm}^{-2}$ . It can be clearly seen in Figure 7 that the removal of fluoride was independent of pH. This is mainly due to the pH independence of fluoride speciation.<sup>18,19</sup> Fluoride is primarily present as  $F^-$  above pH 3 and there are no major species changes between pH 3 and 11. A similar result was found by Ben Sik Ali et al.<sup>20</sup>



**Figure 6.** The effect of coexistent ion on the removal of fluoride (10 mA current intensity,  $10 \text{ mg L}^{-1}$  of NaF).



**Figure 7.** Effect of pH on the removal of fluoride.

### 2.3. Application of electro dialysis to the real water

Our study of optimization of the most influential parameters on the electro dialysis process allows the application of the process to the treatment of wastewater (the fluorine industry). Table 4 illustrates the physicochemical characteristics of a studied sample before and after electro dialysis treatment.

**Table 4.** Composition of the waste water before and after treatment.

Physicochemical parameter	Before treatment	After treatment
pH	3.5	2.79
Conductivity ( $\mu\text{S cm}^{-2}$ )	160.7	1503
Salinity ( $\text{mg L}^{-1}$ )	152.29	1140.09
[F <sup>-</sup> ] ( $\text{mg L}^{-1}$ )	10.3	2.07
[SO <sub>4</sub> <sup>2-</sup> ] ( $\text{mg L}^{-1}$ )	21.736	15.12
[NO <sub>3</sub> <sup>-</sup> ] ( $\text{mg L}^{-1}$ )	13.637	10.36
[Cl <sup>-</sup> ] ( $\text{mg L}^{-1}$ )	24.855	8.03

As seen in Table 4, defluoridation of wastewater was achieved with a fluoride concentration ( $2.07 \text{ mg L}^{-1}$ ) lower than the maximum recommended by the sewer network of the Tunisian National Sanitation Office

(ONAS) ( $3 \text{ mg L}^{-1}$ ). In other words, the high percentage of defluoridation obtained after treatment (80.3%) reflects the good efficiency of the electrodialysis process for the treatment of fluoridated water.

In conclusion, the physicochemical characterization of an anionic membrane was studied by determining the water uptake, exchange capacity, transport number with the Hittorf cell, and membrane conductivity. The results of this study show that the membrane has a sufficiently high exchange capacity. Water uptake varied between 12% and 27% depending on the valence and the hydrophilicity of the counter-ions studied. The membrane is selective toward the ions  $SO_4^{2-}$ ,  $F^-$ ,  $NO_3^-$ ,  $Cl^-$ , and  $OH^-$  and the order of membrane conductivity values of different ions is as follows:  $SO_4^{2-} < F^- < NO_3^- < Cl^- < OH^-$ . The molecular structure and surface of the membrane was investigated by FTIR and MEB. These interesting results allowed us to apply this membrane in electrodialysis. ED performance was evaluated by analyzing several parameters. The obtained results from these experiments show firstly that a large removal of fluorides is obtained after an electrolysis time of 4 h and secondly that the optimal concentration of supporting electrolyte NaCl is  $3 \text{ g L}^{-1}$ . The removal of fluoride was independent of pH. Defluoridation efficiency decreased in the presence of nitrate, chloride, and sulfate ions. Electrodialysis is an effective method for removal of excess fluoride from wastewater. The treatment by ED process of industrial effluent charged in fluoride at  $10 \text{ mg L}^{-1}$  allows us to reach the Tunisian standard for fluoride in the ONAS network.

### 3. Experimental

#### 3.1. Material

The ED stack consisted of pairs of cation exchange membrane (CEM) and anion exchange membrane (AEM). Nafion 117 (commercialized by DuPont) was used as the CEM. An anionic membrane developed in the Industrial Electrochemistry Laboratory of CNAM was used as the AEM. The ion exchange capacity of Nafion 117 was  $0.94 \text{ mEq g}^{-1}$ .

NaF, NaCl,  $Na_2SO_4$ , and  $NaNO_3$  were obtained from Sigma-Aldrich (France).

#### 3.2. Analytical methods

Physicochemical characteristics of the membrane and concentrations of chloride, fluoride, nitrate, and sulfate ions were determined by ion chromatography using a Metrohm 761. An ion meter (Orlab India, model OR930) coupled with a compatible fluoride ion-selective electrode was used for analyses of fluoride.

#### 3.3. Electrodialysis cell

The electrodialysis cell consists of three glass compartments: an anodic compartment, separated from the central compartment by the AEM, and a cathodic compartment, separated from the central compartment by the CEM. These three compartments are connected by means of a joint system. The joints ensure the sealing of the cell and the positioning of the two membranes.

Both electrodes are made of platinized titanium. They are placed at the end of the electrolyzer parallel to the plane of the membranes. The space between the anode and the anionic membrane is 8 cm, that between the cathode and the cationic membrane is 8 cm, and that between two membranes is 9 cm. The active surface area of the membrane is  $0.785 \text{ cm}^2$ . Initial composition and concentration of anodic, central, and cathodic compartments are the same. The electrodialysis cell (Figure 8) was filled with  $10 \text{ mg L}^{-1}$  fluoride solution. The volume of each compartment was 25 mL. Additionally, all experiments were performed in a batch



process at current intensities of 10 mA corresponding to current density of  $1.35 \text{ mA cm}^{-2}$  using an adjustable power/current supply (DC Power Supply AL 924 A). ED operation was continued until the applied voltage reached 30 V, which is the maximum available voltage of the equipment.

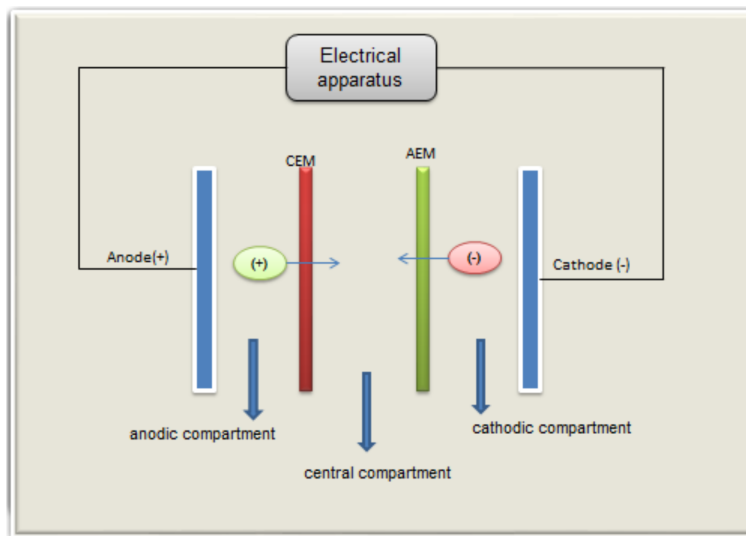


Figure 8. Schematic setup of ED system.

### 3.4. Membranes studied

The membranes used were prepared by quaternization of commercial poly(epichlorohydrin) (H55, Zéon Chemicals) with 1,4-diazabicyclo[2.2.2]octane (Dabco, Aldrich), which serves both for introduction of the quaternary ammonium groups and for thermal crosslinking of the membranes, as described in the literature.<sup>21</sup>

### 3.5. Membrane thickness

The membrane thickness was measured with a Mitutoyo micrometer. The Digimatic indicator was equipped with a 10-mm-diameter flat contact point. The membrane thickness values were averaged from six measurements at different locations on the effective surface of each membrane.

### 3.6. Ion exchange capacity

The ion exchange capacity of a membrane (CE) is the quantity of ionic sites per unit of dry mass ( $\text{mEq g}^{-1}$ ).

To determine this exchange capacity, our anionic membrane ( $5 \times 5 \text{ cm}$ ) was immersed for 24 h in different solutions ( $\text{NaOH}$ ,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ ), each of concentration  $5.10^{-3} \text{ mol L}^{-1}$ , under stirring in a thermostatically controlled bath at  $25^\circ$ . Finally, the membrane was dried at  $60^\circ \text{C}$  for 4 h and weighed. The CE value of AEM was calculated using the following equation:

$$C_E = \frac{C_i \times V_i - C_f \times V_f}{m_s} \quad (2)$$

Here  $C_i$  is the initial concentration,  $V_i$  is the initial volume,  $C_f$  is the concentration after exchange,  $V_f$  is the volume after exchange, and  $m_s$  is the mass of the dry membrane.

### 3.7. Water uptake

Water uptake was determined in aqueous solutions in the presence of four types of anions:  $Cl^-$ ,  $OH^-$ ,  $NO_3^-$  and  $SO_4^{2-}$ . The membranes were equilibrated with deionized water for 24 h and then in a 1 M solution of the anion studied for 1 day to affect the anionic exchange with the membrane. Their surface moisture was mopped with filter papers and the wet membranes were weighed ( $W_w$ ). Wet membranes were then dried at a fixed temperature of 60 °C for 24 h and weighed ( $W_d$ ). Water uptake was calculated using the following equation:

$$\text{Water uptake } \sigma \text{ (\%)} = \frac{W_w - W_d}{W_d} \times 100 \quad (3)$$

### 3.8. Membrane electrical conductivity

Membrane electrical conductivity is one of the most important dynamic characteristics of a membrane. The measurements were performed at 25 °C using the cell (conductivity clip) described elsewhere.<sup>15</sup> The variation of membrane electrical conductance  $G$  requires measuring the conductance  $G_m$  of the membrane and its thickness when it is impregnated with 1 M electrolyte concentration for 24 h. Electrical resistance  $R$  was deduced from the  $G$  measurements ( $R = 1/G$ ). Transversal electric resistance of the membrane  $R_m$  was determined from

$$\mathbf{R}_m = \mathbf{R}_1 - \mathbf{R}_0 \quad (4)$$

Here  $R_1$  is the overall resistance of the membrane and of the electrolyte solution between the electrodes and  $R_0$  is the resistance of the electrolyte solution.

The membrane electrical conductivity  $\kappa$  ( $\text{ms cm}^{-1}$ ) was calculated from

$$\kappa = \frac{l}{\mathbf{R}_m \mathbf{A}} \quad (5)$$

Here  $l$  is the membrane thickness (cm) and  $A$  the electrode area ( $1 \text{ cm}^2$ ).

### 3.9. Transport numbers of counter-ions (Hittorf method)

The transport number of the counter-ions  $t_c$  in a membrane highlights the permselectivity of the IEMs. The Hittorf cell is a glass cell composed of two symmetrical compartments separated by a membrane. The anodic and cathodic compartments have a capacity of 50 mL and the used electrodes are made of platinized titanium. In this study we decided to apply current intensity between the electrolyzer and electrodes of 125, 100, and 75 mA for 192, 240, and 320 min respectively while keeping the quantity of electricity constant.

The principle of the measurement consists in passing a quantity of electricity through a cell containing the membrane separating two compartments filled with the same electrolyte (NaOH, NaF,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ ) at the same initial concentration (1 M). The anodic and cathodic compartments have the same volume,  $V = 25$  mL.

The calculated transport numbers obtained in the cathodic and anodic compartments were deduced from the following equations:<sup>22</sup>

$$t^+ = \frac{ZF}{it} (C^0 V^0 - C^+ V^+) \quad \text{and} \quad t^- = \frac{ZF}{it} (C^- V^- - C^0 V^0) \quad (6)$$

Here  $Z$  is the charge of ions,  $F$  is the Faraday numbers,  $I$  is the applied current during electrodialysis,  $t$  is the electrodialysis time,  $C^0C^+C^-$  are the concentrations of ions at the beginning and the end of electrodialysis in the anodic and cathodic compartment,  $V^0$  is the initial volume in each compartment, and  $V^+V^-$  are the final volume in the anodic and cathodic compartment, respectively.

### 3.10. Scanning electron microscopy

SEM is considered a valuable tool that is used for characterizing the surface morphology of a membrane. The samples were coated with a thin layer of gold/palladium in order to make them electrically conductive and to improve the quality of the microscopy photographs. Images of the membrane were taken with a scanning electron microscope (JEOL, model JSM 5400A, Peabody, MA, USA).

### 3.11. FTIR analysis

The chemical structure of the anionic membrane was characterized by FTIR analysis (PerkinElmer Spectrograph). The solid samples were analyzed in transmission mode within scanning wavelength of 4000–650  $\text{cm}^{-1}$ .

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