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A novel anionic electrodialysis membrane can be used to remove nitrate and nitrite from wastewater

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ABSTRACT

A recently developed anionic membrane has been found to be highly efficient for electrodialysis, a process commonly used to remove ions from aqueous solution. Nitrate ions are often present in too a high concentration in wastewater, therefore we investigated this electrodialysis system for their removal from aqueous solution. The good selectivity of the membrane for nitrate anions is shown by acid–base and spectrophotometric measurements, and also by comparison with the removal of acetate anions. This membrane itself is easy to prepare, shows good characteristics and could find applications in large electrodialysis units.

Keywords: Anionic exchange membrane; Electrodialysis; Nitrate; Nitrite; Acetate; COD

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1. Introduction

Over the last 50 years a large number of studies concerning the application of ion-exchange membranes in various industrial processes have been published. Anion-exchange membranes are always associated with their cation-exchange counterparts in electrodialysis, a water-treatment process that is widely applied in different industries [1], especially for the removal of heavy metals [2] or undesirable ions, such as nitrate ions, from wastewater [3–5]. This process is also used to produce highly pure deionized water and drinking water [6,7]. Electrodialysis requires the use of permselective membranes [8]. Cation-exchange membranes are widely used in many applications, such as the extraction of metallic cations [9,10], and their selectivity is usually satisfactory, whereas both the selectivity of anion-exchange membranes and their thermal stability are often rather poor [11].

Alkaline solid electrolytes have been developed for many years in the Industrial Electrochemistry Laboratory of CNAM [12–14] in order to produce membranes for use in fuel cells. Herein, we describe a procedure involving treatment of the pendant CH_2Cl groups of commercially available poly(epichlorhydrine) with a tertiary amine, in this case 1, 4-diazabicyclo[2.2.2]octane (DABCO), in a polar aprotic solvent, to yield a soluble polymer containing quaternary ammonium groups. Only one nitrogen of DABCO reacts at the moderate temperatures used. A solution of this polymer is then cast over a flat surface, the solvent evaporated, and the resulting membrane heated to activate the second nitrogen of DABCO and obtain an insoluble polymeric anion-exchange membrane (PAEM). The use of DABCO as the tertiary amine results in a heat-resistant membrane, even in concentrated alkaline media. The resulting

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PAEM was found to be quite selective for anion transportation [14]. A similar kind of membrane can be obtained from ERAS-Labo, a small chemical company located in Sait-Nazaire-Lès-Eymes (France).

Cooling water is often the main corrosive agent acting on the metallic lining of water circuits in industrial equipment, therefore nitrite corrosion inhibitors are frequently added to the water. However, the addition of these inhibitors increases the nitrate concentration above the maximum permitted level for wastewaster (>50 mg·l^{-1}), thereby creating a problem when the cooling water needs to be discharged. The elimination of nitrite and nitrate ions from wastewater therefore requires an efficient anionic membrane for use in electrodialysis-type processes.

In this study, we have prepared and used the above-mentioned PAEM in order to measure its efficiency for the electrodialysis of nitrite and nitrate solutions prepared in the laboratory. Furthermore, we have tested the selectivity of our PAEM membranes towards these ions versus proton back-migration. In order to determine whether nitrate could be selectively removed from different salt-loaded water samples, we performed an electrodialysis of a solution containing both nitrate and acetate ions.

2. Materials and methods

2.1. Membranes studied

The membranes used (thickness: approx. 80 µm) were prepared by quaternization of commercial poly (epichlorhydine) (H55, Zéon Chemicals) with 1,4-diazabicyclo[2.2.2]octane (Dabco, Aldrich), as described in the literature [14].

The PAEM was characterized by measuring its ionic conductivity (potentiometric method and electrochemical impedance), and transport numbers were measured using the Henderson and Hittorf methods. Ion-exchange capacity (IEC) and water content were also determined. The IEC was found to be about 0.56 meq·g^{-1} [15], and ionic conductivities were generally superior to 10^{-2} S in aqueous KOH solutions with concentrations of between 0.5 and 6 M at 25°C. The Henderson transport numbers were about 0.95, whereas the Hittorf method gave values in the range 0.99–1.00. The water content was found to be between 13% and 18%.

2.2. Electrodialysis

Electrodialysis was conducted in a small Hittorf cell with two platinized titanium electrodes in galvanostatic mode. The electric current was generated using a P. Fontaine MC 2030 C current generator. The cell had three compartments: an anodic compartment, which was separated from the central compartment by our PAEM, and a cathodic compartment, which was separated from the central compartment by a commercially available cationic-exchange membrane (CEM). This membrane (Nafion®, purchased from Aldrich) has been made by Dupont de Nemours since 1960 [16]. The area of each membrane sample was 4.15×10^{-4} m^2, and all membranes were stored in deionized water.

2.2.1. Analyses

The electrical conductivity of sample solutions was measured both before and after electrodialysis with a conductivity meter (Kipp & Zonen) equipped with platinum electrodes (cell constant: 1.06 cm^{-1}). The pH values were determined using a pH glass electrode (model 290 A from Orion) calibrated with standard buffers at pH values of 4 and 7.

2.2.2. Nitrate ion analysis

Nitric acid was titrated with sodium hydroxide solution using a titralab TIM 865 Titration manager from Radiometer Analytical. Nitrate ions were determined using a UV–Visible Beckman UV 640B spectrophotometer at 300 nm.

2.2.3. Nitrite ion analysis

Nitrite ion concentrations were measured by oxidative voltamperometric titration using a Universal Pulse Dynamic EIS Voltammetry Voltalab 40 from Radiometer Analytical using a saturated Calomel electrode (SCE) as the reference electrode, a platinum electrode as the auxiliary electrode and a rotating platinum disc (diameter: 1 mm; rotation speed: 29.66 s^{-1}) as the working electrode.

2.2.4. Chemical oxygen demand (COD)

Acetate ion concentration was determined by the COD method following a procedure described in the literature [17].

2.2.5. Reagents and solution

All reagents used were of analytical reagent grade. Nitrate, nitrite and acetate solutions were prepared by dissolving $NaNO_3$, $NaNO_2$ (Riedel-de-Haën, Germany) and sodium acetate (Prolabo-Rhône-Poulenc) in pure water obtained using a VWR system.

3. Results and discussion

3.1. Electrodialysis of nitrate solutions

The electrodialysis cell (see Fig. 1) was filled with 0.05 M nitrate solution (55, 30 and 40 ml in the central,

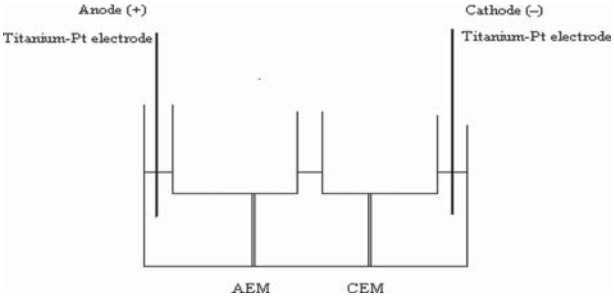

Fig. 1. Electrodialysis cell.

cathodic and anodic compartments, respectively). The ion content of the central compartment was 2.75 mmol and the initial pH of the solution was 6.45.

As it has been shown previously [5] that the percent removal of nitrate from the solution increases with nitrate concentration in the feed solution, and that the running time is reduced when a high current is applied, we applied a current intensity of 100 mA for a running time of 44 min (2.74 mF).

When an electrical field is applied to the electrolytic cell, sodium ions move into the cathodic compartment and nitrate ions move into the anodic compartment. Subsequent electrolytic reduction of water in the cathodic compartment produces hydrogen gas (Eq. (1)), and the resulting hydroxide ions combine with the incoming sodium ions to form sodium hydroxide.

In the anodic compartment, water is oxidized to oxygen and protons (Eq. (2)), which go on to form nitric acid with the nitrate ions removed from the middle compartment through the anionic exchange membrane.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (1)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (2)$$

The level of the solution in the central compartment was found to drop slightly, whereas it increased in the other two. Hydration of the ions that migrate through the membranes would explain this phenomenon [18].

3.1.1. Conductivity

The conductivity of the solution measured before electrodialysis was 5.50 $mS\cdot cm^{-1}$, whereas at the end of the experiment it had increased to 29 and 21.5 $mS\cdot cm^{-1}$ in the anodic and cathodic compartments, respectively, but had dropped to only 24.8 $\mu S\cdot cm^{-1}$ in the central compartment. The final conductivity of the solution in the central compartment is therefore some 200 times lower than before electrodialysis, thus showing that the solution is largely depleted of ions. Conversely, the conductivity of the solutions in the anodic and cathodic compartments increases as a result of ionic migration from the central compartment.

3.1.2. pH measurement and solution properties

At the end of the experiment, the quantity of solution in each compartment, and its pH, was determined (Table 1). The anodic solution was found to be more acidic due to the formation of H^+ ion, which combined with the incoming NO_3^- ions to produce nitric acid. The solution in the central compartment also became slightly acidic, possibly due to the passage of a small quantity of H^+ ions through the cationic membrane. The solution in the cathodic compartment had a basic pH due to the formation of sodium hydroxide in this compartment.

After the electrodialysis, the solution in the anodic compartment was titrated with 0.1 M sodium hydroxide and the nitric acid concentration found to be 5.93×10^{-2} M, which is equivalent to 242×10^{-5} mol of H^+ ions. We can therefore deduce that at least 242×10^{-5} mol of NO_3^- migrated into the anodic compartment from the central compartment.

3.1.3. Spectrophotometric analysis of nitrate

The nitrate concentration in the central compartment was measured spectrophotometrically and found to be 7.22×10^{-5} mol (83 $mg\cdot l^{-1}$). As the initial concentration was 275×10^{-5} mol, 268×10^{-5} mol had migrated out of this compartment and the solution was therefore depleted of NO_3^- (the maximum limit recommended by the WHO for drinking water is 50 $mg\cdot l^{-1}$). Continued electrodialysis depleted the central compartment completely to below measurable nitrate content values, although the potential difference between the electrodes rose considerably.

The amount of H^+ ions which appeared in the anodic compartment was 242×10^{-5} mol, which is less than the value of 268×10^{-5} mol for nitrate ions. This discrepancy is not related to proton migration through the membrane, since the amount of H^+ which appeared in the central compartment was very low (around 2×10^{-7} mol, as calculated from the pH of 4.47), but may be related to

Table 1
pH(at 25°C) and volume measurement before and after electrodialysis of nitrate solution

Compartment	Initial volume (ml)	Final volume (ml)	Volume variation ΔV (ml)	Initial pH	Final pH
Anodic	40	40.816	0.816	6.45	1.51
Middle	55	53.806	–1.194	6.45	4.47
Cathodic	30	30.383	0.383	6.45	11.92

Table 2
Ionic H^+ and NO_3^- composition of solutions in anodic and central compartments before and after electrodialysis

Compartment	$[H^+]_f$ (mol·l^{-1})	$(nH^+)_f$ (10^{-5} mol)	$(nNO_3^-)_i$ (10^{-5} mol)	$(nNO_3^-)_f$ (10^{-5} mol)	$\Delta(nNO_3^-)$ (10^{-5} mol)
Anodic	5.93×10^{-2}	242	200	442	+ 242
Central	1.22×10^{-5}	0.066	275	7.22	–267 (Spectrophotometry) –242 (pH–metry)

some evaporation caused by oxygen evolution. The very small amount of H^+ detected in the central compartment confirms that our PAEM is very selective against proton back-migration, and compares well with the selectivity of the Nafion membrane against hydroxyl back-migration, which is claimed to be negligible. Calculation of the faradic yield (1 mol requires 1 Farad) gave a value of 97% for nitrate (by spectrophotometry), a very satisfying result. A slightly lower value (88%) was obtained from the results of the acid–base titration in the anodic compartment. These results are summarized in Table 2.

3.1.4. Energy consumption

The energy consumed by larger-scale electrodialysis processes cannot be predicted on the basis of our laboratory cell. The energy consumption of industrial processes is related to the ionic conductivity, the amount of salt and the geometry of the cells. We assume here that a pilot system would contain 10 concentration cells and 10 depletion cells in series, each cell being 1 cm wide. The energy consumption in this case is largely dominated by the ohmic drop. The initial nitrate concentration in both cells is 0.05 M, with a conductivity of 5 mS/cm. At a current density of 25 mA/cm^2, the ohmic drop across a set of two cells is 10 V. During electrodialysis, the conductivity decrease in the depletion cell is compensated by the conductivity increase in the concentration cell, which means that the voltage remains almost constant, except at the very end of the process. Since the process has a faradic yield of close to 1, the amount of electricity needed to remove 0.05 mol of nitrate from 1 l is 0.05 F (5000 C). The energy consumption is therefore 5000 C × 10 V = 50,000 J (14 W·h). Under these conditions, treatment of one cubic meter of effluent will consume 7 kW h and yield 500 l of depleted solution and 500 l of concentrated solution with a concentration of 0.1 M. The 500 l of concentrated solution can be treated again to yield 250 l of concentrated solution at 0.2 M and 250 l of depleted solution, although both the conductivity and the running time will double. This process can be repeated until a concentrated nitrate solution, which can easily be destroyed, is obtained.

A decrease in the current density by a factor of two will decrease the energy consumption by a factor of two but increase the running time by a factor of two. Reducing the cell width will also reduce the energy consumption proportionally, although the system will need larger membrane surfaces or longer running times.

3.2. Nitrite electrodialysis

Electrodialysis was conducted under the same conditions as for nitrates (concentration: 0.05 M; current intensity: 100 mA; same initial solution volumes). The initial pH of the solution was 7.22 (at 25°C). The results of these studies are shown in Table 3.

3.2.1. Nitrite voltamperometric dosage

For nitrite ions, we carried out a voltamperometric titration that involved oxidizing the nitrite ions to nitrate in an acidic medium. The experimental conditions for this titration are as follows:

- Initial potential: 0.1 V
- Final potential: 1.3 V
- Supporting electrolyte: 0.25 M Na_2SO_4
- Potential sweep rate: 5 mV·s^{-1}

The following curves (Figs. 2 and 3) were observed for the diffusion-limited currents ($I = f(E)$). The results of these titrations are shown in Table 4, where it can be seen that nitrite ion concentration decreases in the central

Table 3
Volumes and pH(at 25°C) of each compartment before and after electrodialysis of nitrite solution

Compartment	Initial volume (ml)	Final volume (ml)	ΔV (ml)	Initial pH	Final pH
Anodic	40	40.69	0.69	7.22	1.64
Middle	55	53.23	–1.77	7.22	3.62
Cathodic	30	31.06	1.06	7.22	12.19

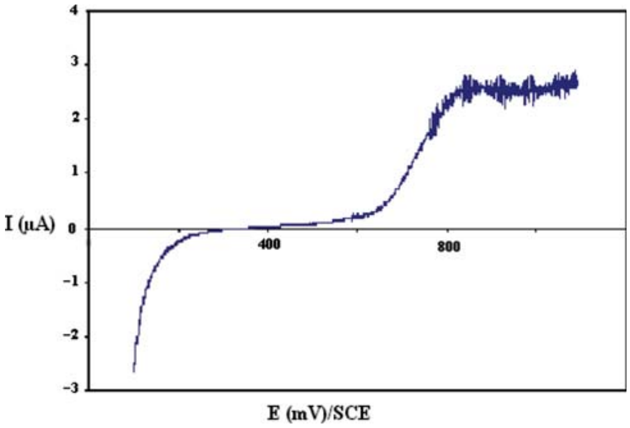

Fig. 2. Curve $I = f(E)$ concerning the dosage of the nitrite ions present in the solution of the central compartment after electrodialysis.

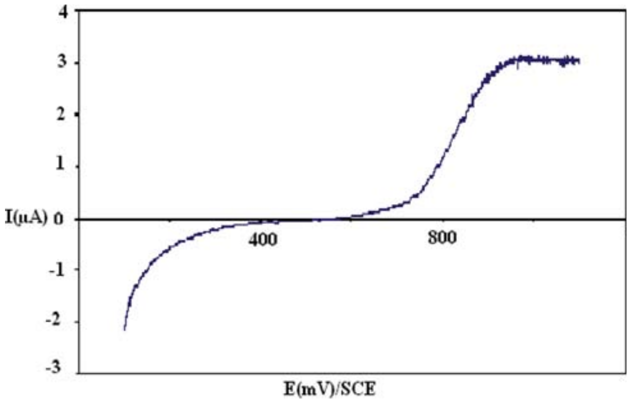

Fig. 3. Curve $I = f(E)$ concerning the dosage of the nitrites presents in the solution of anodic compartment after electrodialysis.

Table 4
Diffusion limited currents and nitrite concentrations in the anodic and central compartments

	Initial solution	Medium compartment	Anodic compartment
I_∞ (µA)	246.7	2.56	3
Concentration of nitrite (mol·l^{-1})	5×10^{-2}	5.2×10^{-4}	6.1×10^{-4}

compartment due to migration into the anodic compartment. The absence of nitrite in the anodic compartment is due to chemical or electrochemical oxidation into nitrate.

3.2.2. Faradic yield

Measurement of the amount of nitrite in the central compartment gave an initial value of 275×10^{-5} mol and a final value of 2.84×10^{-5} mol, thus indicating that 272×10^{-5} mol of nitrite had migrated into the anodic compartment. This value gives a faradic yield for the electrodialysis of nitrite through the PAEM of 99%.

3.3. Electrodialysis of nitrate in the presence of acetate ions

In order to determine the ability of our membrane to selectively remove nitrate from different salt-loaded solutions, we studied the electrodialysis of a solution containing a mixture of nitrate and acetate ions. Thus, we initially electrodialysed solutions containing either nitrate or acetate ion and then a mixture of both ions at the same concentration (0.05 M). The current intensity was set at 50 mA for 44 min. The membrane was found to behave in a similar way towards both nitrate and acetate (Fig. 4), with the migration rate being linked to the value of the current. However, once the anions were mixed, we found that the migration of nitrate ion from the central compartment into the anodic compartment was much faster than that of acetate ion, with NO_3^- migrating continually easily but CH_3COO^- migration stopping after about 10 min (Fig. 5), thus demonstrating the selectivity of this membrane towards nitrate anion. Ionic characteristics such as crystal ionic radii, hydrated ionic radii, number of water molecules, ion mobility and

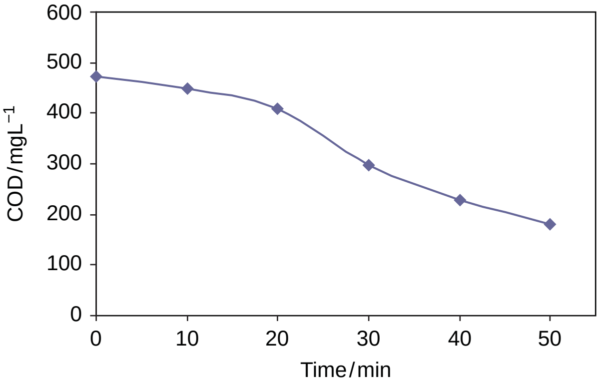

Fig. 4. Variation with time of the COD of the central compartment solution's containing initially acetate ions ($[CH_3COO^-]$ = 0.05 mol·l^{-1}).

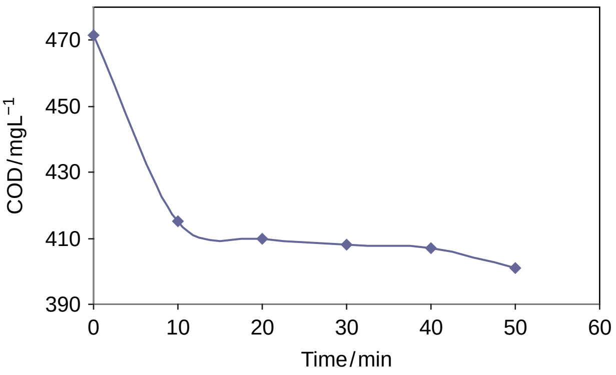

Fig. 5. Variation with time of the COD of the central compartment solution's containing initially nitrate and acetate ions ($[CH_3COO^-] = [NO_3^-] = 0.05$ mol·l^{-1}).

ion equivalent conductivity cannot be used to explain the transport differences (removal and flux) between CH_3COO^- and NO_3^-.

It has been reported previously [19] that the ionic mobility of NO_3^- through a membrane can be greater than that of CH_3COO^-. Similarly, Tansel et al. [20] have shown that ions with a smaller intrinsic crystal radius have higher hydration numbers, larger hydrated radii and bind their hydration shells more strongly. It can therefore be assumed that NO_3^- ions are less hydrated than CH_3COO^- and that they lose their hydration layer more readily, thus meaning that they are transported through the ion-exchange membrane more easily. It can also be assumed that a small diffusion layer in the central compartment close to the membrane is slightly acidic (due to some water splitting at the membrane surface and subsequent migration of hydroxyl anion through the membrane), which results in protonation of acetate ion at the interface to form non-migrating acetic acid. In any case, the final acidity of the solution in the central compartment is very small.

4. Conclusion

Electrodialysis with our PAEM membrane gives good results, with both nitrate and nitrite test solutions becoming depleted in the central compartment. Indeed, the nitrate concentration drops to below the recommended limit in some cases (between 50 and 100 mg·l^{-1}). The pH-metric results show that both NO_2^- and NO_3^- ions migrate selectively and that only a very limited number of H^+ ions back-migrate.

Spectrophotometric analysis of NO_3^- ions during electrodialysis confirmed the migration of these ions from the central compartment, with a faradic yield of about 97% at an applied intensity of 22.5 mA/cm^2. Likewise, voltamperometric measurements showed that nitrite ions migrate towards the anode with a faradic yield of 99% at the same applied intensity.

Nitrate ions migrate easily and continually from a mixed nitrate/acetate-containing solution, whereas acetate ions essentially stop migrating after 10 min, thus confirming the selectivity of this membrane towards nitrate anion.

Our electrodialysis study of the removal of nitrate, nitrite and acetate ions from aqueous solutions has shown the good performance of a new anionic organic membrane developed at CNAM by simple polymer modification. This membrane presents a high selectivity for the transfer of nitrate ions, is easy to prepare and shows good mechanical characteristics, thus making it suitable for use in large electrodialysis plants. We now intend to use larger cells with continuous solution flows in order to confirm its suitability for large industrial applications.

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