Journal of Membrane Science 451 (2014) 276–284

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Nitrate reduction of brines from water desalination plants by membrane electrolysis

M.L. Bosko [a], M.A.S. Rodrigues [b], Jane Z. Ferreira [c], E.E. Miró [a], A.M. Bernardes [c,*]

[a] Instituto de Investigaciones en Catálisis y Petroquímica (FIQ, UNL-CONICET), Santiago del Estero 2829, 3000 Santa Fe, Argentina
[b] Universidade FEEVALE (Federação de Estabelecimentos de Ensino Superior em Novo Hamburgo), BR-239, 2755, CEP 93352-000, Novo Hamburgo, RS, Brazil
[c] UFRGS (Universidade Federal do Rio Grande do Sul), Av. Bento Gonçalves, 9500, CEP 91501-970, Porto Alegre, RS, Brazil

ARTICLE INFO

Article history:
Received 27 April 2013
Received in revised form
30 September 2013
Accepted 1 October 2013
Available online 11 October 2013

Keywords:
Membrane electrolysis
Nitrate reduction
Electrodialysis

ABSTRACT

The disposal of the saline effluent generated during membrane water desalination by electrodialysis (ED) or reverse osmosis (RO) is an increasing problem worldwide, especially for the desalination of inland brackish water. Electrolysis can be an alternative to the denitrification of brines by the reduction of nitrates to the desired product (N_2). Nevertheless, in a paired electrolysis cell the reduced products could be re-oxidized in the anode by the reverse reactions; for example, nitrite could be again converted to nitrate. Membrane electrolysis can avoid these reactions. The aim of this study was to assess the efficacy of the membrane electrolysis technique in the reduction of nitrate in water. The experiments were performed in an electrochemical cell with two compartments separated by a cation-exchange membrane, the cathode being made of copper and the anode of titanium oxide and ruthenium oxide ($70TiO_2/30RuO_2$). Nitrite, ammonium and nitrogen containing gases (most of them N_2) were the reaction products. The best value was achieved with a cell voltage of 9 V and an initial concentration of 526 mg/L of NO_3^-. Under these conditions, high conversion to nitrite and gaseous compounds was registered with the formation of just 7.8 mg/L of ammonium.

1. Introduction

Health and environmental protection is a major concern in the world today and avoiding air, soil and water pollution becomes a significant challenge. Nitrogen compounds are some of the major pollutants; they are essentially originated by human activity, including agriculture, animal processing industries, vehicles and waste treatment. Alternative processes should be studied to meet the new environmental and technological requirements.

Different technologies are available to reduce the concentration of nitrates in drinking water, such as Biological Denitrification, Ion Exchange, Reverse Osmosis and Electrodialysis [1,2].

The conventional treatment for removing nitrogen compounds in industrial wastewater is the biological treatment. This process, however, is greatly influenced by temperature and organic load. In order to remove nitrogen compounds from the groundwater using the biological treatment, the addition of carbon-containing compounds is required because of the low concentration of organic material in these waters [2]. Thus, for natural waters the biological denitrification must be carried out with the addition of methanol or ethanol.

Other technologies have been evaluated for reducing nitrate concentration in water such as ion exchange with a strong anionic resin and regeneration with NaCl. Unfortunately, this process not only adds chloride to the water but also fails to remove other dissolved solids under the form of cations [1].

Among the alternatives for nitrate and nitrite abatement in drinking water, catalytic hydrogenation has been the focus of numerous research studies in the last decade. However, this method must be improved because besides the desired reaction that converts the contaminants into nitrogen, undesired ammonia is produced [3,4].

In this context, the processes that apply membranes as separating agents, namely reverse osmosis (RO) and electrodialysis (ED), appear to be valid alternatives. These processes remove other ions in addition to nitrate, which results in decreased levels of sodium, chloride, hardness, etc. For waters with high salinity, this represents a large increase in the quality of the treated water [5].

Representative examples of large membrane reverse osmosis seawater desalination plants are the 330,000 m^3/day plant in Ashkelon, Israel; the 136,000 m^3/day Tuas Seawater Desalination Plant in Singapore; the 64,000 m^3/day Larnaka Desalination Facility in Cyprus, and the majority of the large desalination plants in Spain, Australia and the Middle East [6]. For the desalination of brackish water, ED has recently proved to be feasible and highly successful [7].

---

* Corresponding author. Tel.: +55 51 33089428.
E-mail address: amb@ufrgs.br (A.M. Bernardes).

0376-7388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.memsci.2013.10.004

Table 1
Some worldwide Electrodialysis Reversal (EDR) systems [10].

Location	Country	Application		Production (m^3/day)	Year
Eurodia					
Montefano	Italy	Groundwater	Nitrate removal	1000	1991
Munchenbuschsee	Switzerland	Groundwater	Nitrate removal	1200	1996
Kleylehof	Austria	Groundwater	Nitrate removal	3500	1997
General electric water & process (fomerly ionics Inc)					
Abrera, BCN	Spain	Surface water	Bromide reduction	200,000	2008
Magna, Utah	USA	Groundwater	Arsenic reduction	22,728	2008
Sherman, Texas	USA	Surface water	Salinity reduction	27,700	1993–1996–1998
Suffolk, Virginia	USA	Groundwater	Fluoride reduction	56,000	1990
Sarasota, Or	USA	Groundwater	Hardness & salts reduction	45,420	1995
Maspalomas	Spain	Groundwater	Salinity reduction	37,000	1986
Barranco Seco, Canary Islands	Spain	Waste water	Reuse	26,000	2002
Bermuda waterworks	Bermudas	Groundwater	Hardness & nitrate reduction	2300	1989
Falconera, Valencia	Spain	Groundwater	Nitrate reduction	16,000	2007

Electrodialysis is less sensitive to membrane fouling and scaling than reverse osmosis. Therefore, higher recovery rates can be achieved and brine disposal problems can be minimized. Brackish waters obtained from deep wells often have a high concentration of divalent ions. These raw waters are difficult to desalt by reverse osmosis without significant pre-treatment. For electrodialysis, however, they pose no problem and can be processed with minimal or no pre-treatment. Even if in some cases electrodialysis requires higher investments and operating costs than low pressure reverse osmosis, it is often the preferred process in brackish water desalination because of the clear technical advantages [8]. In addition, ED is generally the most economical process for water with relatively low salt concentrations (less than 5000 mg/L). Furthermore, when ED is applied to brackish water desalination, a large fraction—typically 80–95%—of the brackish feed is recovered as product water. The degree of water recovery is limited by the precipitation of insoluble salts in the brine [9]. Table 1 shows a list of some of the water treatment installations around the world [10].

Electrodialysis has recently achieved a great development for water denitrification. This process is useful in both water purification and the concentration of ionic species in solution. The GE (General Electric) company has currently installed a treated water capacity of ca. 950,000 m^3/day by electrodialysis. Currently, some regions in the U.S. such as Oklahoma, Arizona, Suffolk (Virginia), Texas and San Diego, as well as cities and regions in Europe such as Barcelona and the Canary Islands in Spain, and Donnington in the UK use the ED technique for the treatment of brackish water and groundwater destined for drinking supply [11–13]. Spain is one of the most arid countries in Europe and has implemented strategies to brackish water desalination. In 2009, this effort resulted in the installation of a reverse electrodialysis plant (EDR) near Barcelona, operated by the Aigües Ter-Llobregat Company (ATLL). ATLL has a drinking water treatment plant, located in Abrera, which draws water directly from the Llobregat river. The installed plant of electrodialysis treats 220,000 m^3/day of water. It works together with a conventional treatment plant. The desalted product of the EDR plant is mixed with the product of the conventional treatment plant to produce an appropriate combined stream for the drinking water needs of the region. The process operates with a flow rate of 2.4 m^3/s, a water recovery yield of 85–90% and a 60–80% conductivity reduction of water [12,13].

Many electrodialysis plants have recently been installed specifically for the removal of nitrates from drinking water. In Israel a plant of GE [14] was installed to reduce the levels of nitrate from water, 100 mg/L to 45 mg/L, with 94% of water recovery. In Kazusa, Japan, the technique has been implemented to reduce nitrate levels from 80 mg/L to 27 mg/L. In Bermuda, a plant removes 86% of nitrate concentration [14,1]. In Nagasaki, Japan, the Astom Corporation has installed an electrodialysis plant to remove nitrates and produce drinking water [15].

Several authors have evaluated the electrodialysis processes and reverse osmosis for nitrate removal from drinking water in terms of process parameters and application conditions [16–23]. Banasiak demonstrated the ability of the process to remove nitrate from brackish waters. However, these authors have highlighted that the main disadvantage of these methods is the uncertain destination of the nitrate concentrated brine.

Managing the high salinity concentrate that is generated during membrane water desalination by ED or RO is a primary issue in desalination of inland brackish water. The saline effluent has been usually considered as waste brine and traditional approaches to its disposal have included evaporation ponds, deep wells, and coastal discharge [24]. Traditional management of RO concentrates from desalination plants is mainly conditioned by the location of the plant. In coastal desalination plants, RO concentrates are directly discharged to seawater, while in inland plants the traditional option consists in reducing the concentrate volume prior to disposal [25]. Applying electrodialysis to brine effluents is an emerging technology that is being studied by different authors [25–27]. Nevertheless, in this latter case there will always remain an ED brine to be dealt with.

Several authors have recently evaluated different options to the treatment of the ED and RO brines. Zhang et al. [28] carried out a systematic investigation to study a pilot scale ED installation to treat the reverse osmosis (RO) concentrate with high scaling potential from a wastewater treatment plant (WWTP), in order to improve the overall water recovery of the system. A high overall recovery (95%) of the WWTP system can be achieved from the integrated RO-ED system; however, the problem of the fate of the residual concentrated solution still remains. Other authors have analyzed the use of bipolar membranes of electrodialysis (BMED) to produce acid and base from RO seawater concentrate [29]. In these cases, mixed acids (HCl; H_2SO_4) and bases (NaOH, KOH, etc.) are produced; therefore, an after treatment is necessary for their separation. Another option, the biological denitrification of brines was studied by different authors [30]. However, in order to be sent into a biological treatment unit, some basic requirements have to be fulfilled, the ED effluent quality should be similar to that of the influent of the biological treatment unit, i.e., concentration of different cations and anions, pH, biodegradability of organic compounds [28].

The past few decades have seen the emergence of electrochemical technology for wastewater treatment. The particular advantages of the electrochemical treatment include high efficiency, ambient operating conditions, small equipment size, minimal sludge generation and rapid start-up [31].

When electrolysis is used in the nitrate removal from ED concentrated solutions, the desired product (nitrogen) and others such as nitrite and ammonium are generated. The associated reduction reactions are shown below:

Reactions (Standard potential (V) [32])		
$NO_3^-{}_{(aq)} + H_2O_{(l)} + 2e^- \rightarrow NO_2^-{}_{(aq)} + 2OH^-{}_{(aq)}$	0.1	(1)
$2NO_3^-{}_{(aq)} + 6H_2O_{(l)} + 10e^- \rightarrow N_{2\,(g)} + 12OH^-{}_{(aq)}$	0.25	(2)
$2NO_2^-{}_{(aq)} + 4H_2O_{(l)} + 6e^- \rightarrow N_{2\,(g)} + 8OH^-{}_{(aq)}$	0.42	(3)
However, more mechanisms may occur and compete with the desired ones (Eqs. (2) and (3))		
$2NO_3^-{}_{(aq)} + 2H_2O_{(l)} + 2e^- \rightarrow N_2O_{4\,(g)} + 4OH^-{}_{(aq)}$	−0.85	(4)
$NO_3^-{}_{(aq)} + 2H_2O_{(l)} + 2e^- \rightarrow HNO_{2\,(aq)} + 3OH^-{}_{(aq)}$	−0.31	(5)
$NO_3^-{}_{(aq)} + 2H_2O_{(l)} + 3e^- \rightarrow NO_{(g)} + 4OH^-{}_{(aq)}$	−0.15	(6)
$NO_2^-{}_{(aq)} + H_2O_{(l)} + e^- \rightarrow NO_{(g)} + 2OH^-{}_{(aq)}$	−0.45	(7)
$2NO_2^-{}_{(aq)} + 3H_2O_{(l)} + 4e^- \rightarrow N_2O_{(g)} + 6OH^-{}_{(aq)}$	+0.15	(8)
$NO_2^-{}_{(aq)} + 6H_2O_{(l)} + 6e^- \rightarrow NH_4OH_{(aq)} + 7OH^-{}_{(aq)}$	−0.16	(9)
$NO_2^-{}_{(aq)} + 6H_2O_{(l)} + 6e^- \rightarrow NH_4^+{}_{(aq)} + 8OH^-{}_{(aq)}$	−0.21	(10)
$NO_2^-{}_{(aq)} + 5H_2O_{(l)} + 6e^- \rightarrow NH_{3\,(g)} + 7OH^-{}_{(aq)}$	−0.18	(11)

It is important to point out that the reduced products could be re-oxidized in the anode by the reverse reactions; for example the nitrite could be again converted to nitrate [33]. A viable option to decrease these processes could be the membrane electrolysis technique. In these systems, the reactions occur in the presence of an electric field and the exchange membrane is employed to separate the electrode compartments, thus impeding the migration of products, and avoiding reoxidation reactions (reversible reactions) (Fig. 1).

Finally, the stability and formation of the nitrogen compounds will depend on the thermodynamics of the system. The conditions under which these reactions (from Eqs. (1) to (11)) are thermodynamically possible or impossible can be predicted by the Pourbaix atlas [32], where the equilibrium diagrams (potential-pH) in dilute aqueous solutions for several compounds are shown. The method employed to calculate these ones was based on the ideas of "chemical potential" and "affinity" and conveniently summarized the majority of the chemical and electrochemical equilibrium laws. The usual notions of equilibrium potential were generalized and provide a useful criterion regarding the direction of all types of electrochemical reactions [34].

The aim of this study was to assess the efficacy of the membrane electrolysis technique in the reduction of nitrate in water. We focused our work on the treatment of concentrate waste streams which can be applied to the treatment of effluents from electrodialysis (ED) and reverse osmosis (RO). For this purpose, a cation-exchange membrane and a copper cathode were used. The cell voltage and initial concentration were varied in order to study their influence on the process, which in turn will contribute to a better understanding of the process and to select appropriate reaction conditions. Ion chromatography was the technique selected to determine the salt content.

2. Experimental

2.1. Electrochemical cell

All experiments were conducted in an electrochemical cell with two compartments separated by a cation-exchange membrane IONAC MC – 3470 (provided by the manufacturer) with a surface area of 16 cm^2. The cell was assembled as described in Fig. 2. The cation membrane used has a thickness of 0.4 mm, with a chemical stability within the pH range of 0–11. For NaCl solutions, the percentage permselectivity registered was equal to 96 (0.5 and 1 N) and the electrical resistances were 15 and 6 W/cm^2 for 0.1 and 1 N, respectively.

The cathode was made of copper and the anode was obtained from titanium coated with titanium oxide and ruthenium oxide ($70TiO_2/30RuO_2$). Platinum (Pt) wires were placed at each side of the membrane to measure the potential difference of the cation-exchange membrane. Luggin's capillary with saturated calomel electrode was placed next to the cathode electrode allowing the register of its potential difference (Fig. 2). In all experiments, 1 L of nitrate solution was placed in the cathode compartment, while the anode compartment was filled with 1 L of sodium sulfate solution to maintain the system conductivity. Each container was connected to a pump that recirculated the solutions.

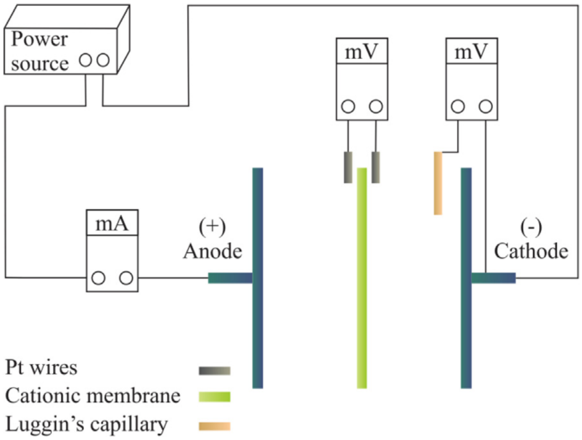

Fig. 2. Schema of cell used in the experiments.

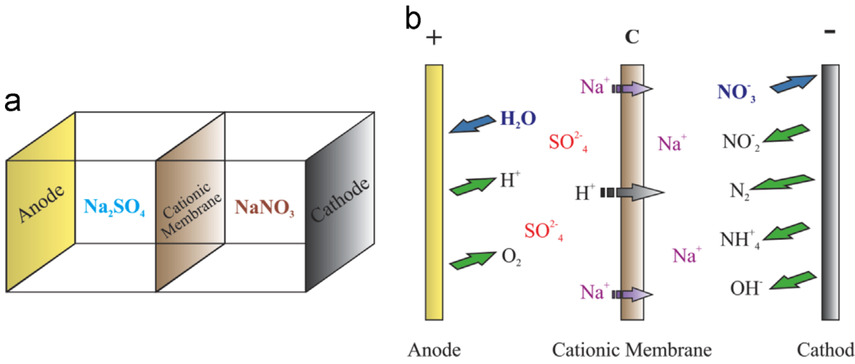

Fig. 1. The cell designed for electrodialysis experiments (a). Schema diagram of the expected ionic transport through the membrane and of the reactions that could occur on the electrodes (b).

The parameters of nitrate concentration were based on literature data of concentrations in groundwater. In Safaria, Israel, water has 100 mg/L of NO_3^- [14]. The municipality of Kazusa, Japan, registered nitrate levels as high as 80 mg/L in their water supply [12]. In Pine Hill Farm, 140 km from Alice Springs, Australia, the nitrate content in water is of 31 mg/L [35].

After the ED treatment, ca. 90% of the treated water has permissible levels for human consumption, but in the remaining 10% high nitrate concentrations are obtained, well above the original ones. These levels depend on factors such as water recovery percentage, recirculation factor, initial concentrations and percentage extraction. When the Kleylehof plant (Austria) of ED began operating, the stack voltage was adjusted to a nitrate removal down to 40 mg/L of NO_3^-, according to the requirements of the client. For this condition, 889 mg/L of NO_3^- were reached in the brine stream [36]. The ED-treatment of two natural waters in the south of France contaminated by nitrates evidenced extraction ratios of 70% and 90% for water 1 and 2, respectively. But their concentrate discharges exhibited enrichment factors as high as 15 and 16 times [37]. Wisniewski et al. [30] studied the treatment of solutions with nitrate concentrations varying from 470 to 2365 mg NO_3^-/L and considered that these concentrations are close to concentrates obtained in ED plants for nitrate removal. Jingjing et al. [38] studied the technical capabilities of electrodialysis and electrodeionization for nitrate removing. Through electrodialysis experiments, they reduced the nitrate concentration from 443 mg/L to 9 mg/L, while the concentration of the waste brine solution was enriched to 2037 mg/L. Based on the concentrations mentioned above, we decided to evaluate high nitrate concentrations to assess the efficiency of the membrane electrolysis technique. Table 2 shows a summary of the solutions employed in this study.

2.2. *Polarization curves*

The current–voltage curves (CVCS) were obtained in galvanostatic mode with a classical two-compartment cell. Electrical current was applied using a DC power source for 120 s with an interval of 180 s without electrical current. The curves were acquired by potential measurements corresponding to the applied current. Besides, the pH and the conductivity of the solutions in the compartments were monitored. These tests were made in duplicate or triplicate and the results were reproducible.

2.3. *Membrane electrolysis experiments*

The experiments were conducted with the application of a constant cell potential which was selected between 7 and 13 V. The tests were conducted at room temperature for 24 h in a batch recirculation mode. The study was carried out in a two-compartment membrane electrolysis cell (Fig. 2). For the chemical analysis, several samples were collected periodically and the pH and conductivity were recorded for each one.

Nitrate, nitrite and ammonium ions were determined by ion chromatography with a DIONEX ICS 3000 instrument, with conductivity detector employing columns IonPac CS12A and AS22 for cations and anions, respectively. The reproducibility of the analytical method was evaluated from a representative sample. Its mean value was equal to 184.607 mg/L of NO_3^- with a standard deviation of ±3.35 mg/L and the 95% confidence interval of 181.78–187.44 mg/L.

Table 2
Concentrations of prepared solutions.

Compartment	Cathode	Anode		
	$NaNO_3$ (M)	NO_3^- (mg/L)	Na_2SO_4 (M)	Na_2SO_4 (mg/L)
Solution A	0.0071	438	0.0039	550
Solution B	0.0100	620	0.0056	800
Solution C	0.0153	802	0.0084	1200

Nitrate total reduction was calculated as the amount of nitrate consumed at different reaction times divided by the initial nitrate concentration. The conversions toward nitrite and ammonium were defined as the amount of nitrite or ammonium produced, respectively, divided by the initial concentration of nitrates. The conversion to gaseous compounds was theoretically estimated from the nitrate total reduction and conversions toward nitrites and ammonium, considering these species as the main products.

Results are expressed as total reduction of nitrate ($R_{NO_3^-}^{reduction}$, %) and nitrate conversions toward nitrite ($X_{NO_3^-/NO_2^-}$, %), ammonium, ($X_{NO_3^-/NH_4^+}$, %), and gaseous compounds ($X_{compounds}^{NO_3^-/gaseous}$, %) and these parameters are defined as follows:

$$R_{NO_3^-}^{reduction}\,(\%) = [1 - C_{N-NO_3^-}/C_0] \times 100$$

$$X_{NO_3^-/NO_2^-}\,(\%) = [C_{N-NO_2^-}/C_0] \times 100$$

$$X_{NO_3^-/NH_4^+}\,(\%) = [C_{N-NH_4^+}/C_0] \times 100$$

$$X_{compounds}^{NO_3^-/gaseous}\,(\%) = [R_{NO_3^-}^{reduction} - (X_{NO_3^-/NO_2^-} + X_{NO_3^-/NH_4^+})] \times 100$$

where C_0 is the initial concentration of nitrates, and $C_{N-NO_3^-}$, $C_{N-NO_2^-}$, $C_{N-NH_4^+}$ are the concentrations of nitrates, nitrites and ammonium, respectively, at time *t*. These calculations were performed using N-based concentrations.

3. Results and discussion

3.1. *Polarization curves*

The polarization curves data together with the electrochemical diagrams [32] allowed us to define the appropriate range of potential to begin this study on membrane electrolysis.

The equilibrium Pourbaix nitrogen plots are shown in Fig. 3. These diagrams are made considering the normal hydrogen potential; standard pressure and temperature and an initial gaseous nitrogen concentration of 10^{-6} M. These graphics show the main dissolved species and gaseous compounds as well as their domain boundaries. Other unstable compounds such as N_2O and NO are not shown. For our purposes, the desired reduction product is the nitrogen gas (Fig. 3b), which could be formed at low cathode potentials.

The evolution of the density current with the cathode potential for the system studied in this paper is presented in Fig. 4a. To begin the study, considering the previous discussion, potentials ranging from 0.3 to 0.7 V_H were selected, which correspond to a current density region on the cell between 1.25 and 2.54 mA/m^2 (Fig. 4b).

Finally, it was evaluated if polarization phenomena occurred in the membrane, which could affect the efficiency of the process. When this happens, the applied current exceeds the limit value producing a drop to zero of the ion concentration in the membrane boundary layer. Similarly, there is an accumulation of ions on the other side of the membrane due to the fact that they arrive at a higher speed than that at which they can diffuse into the solution [39]. Therefore, the polarization phenomena produce an increase of the solution electrical resistance and of the dissociation of water causing a rise in energy consumption [39,40].

The typical current potential curves (CVCs) have three defined regions (Fig. 5a). In the first region (I), a linear relationship is obtained between the current density and voltage due to the

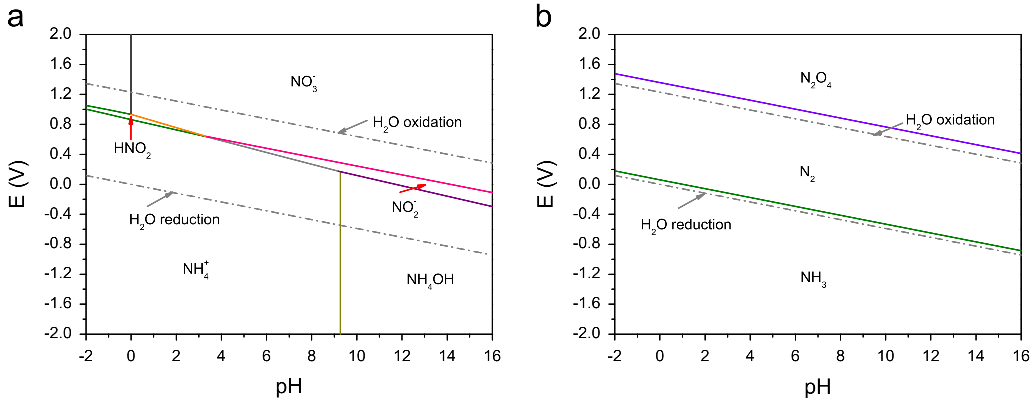

Fig. 3. Pourbaix diagrams for nitrogen. (a) Dissolved species and (b) gaseous compounds.

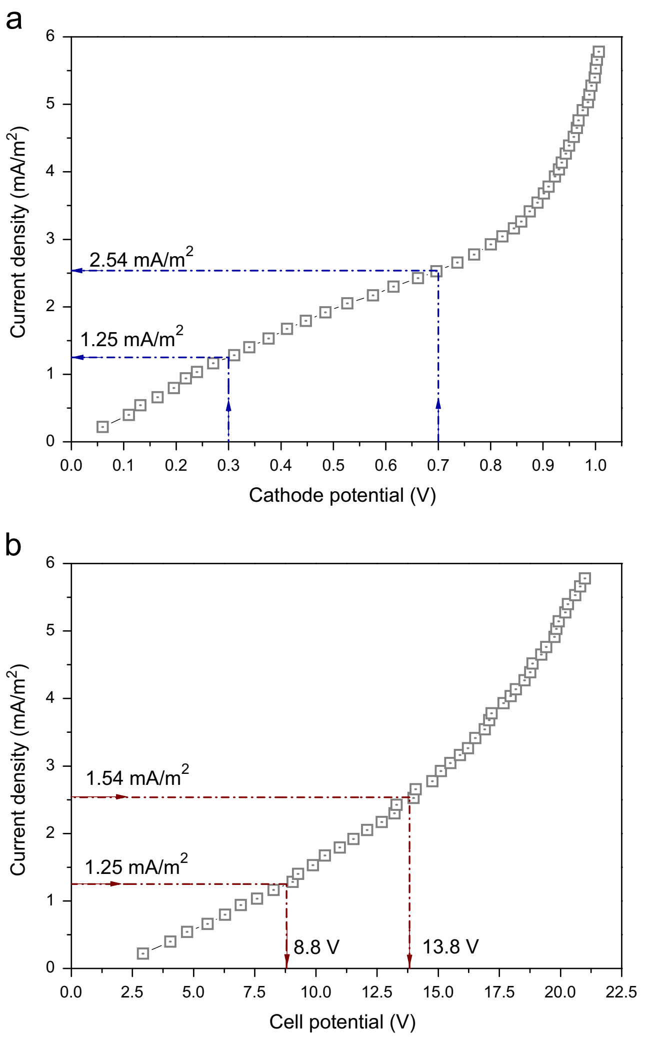

Fig. 4. Data of polarization curve of the cationic membrane for solution B (620 mg/L of NO_3^-). Current density vs cathode potential (a) and cell potential (b).

ohmic zone. In the second one, the current varies very slightly with voltage, corresponding to the so-called limiting current density. In region III, an over-limiting current takes place, and then the current intensity increases again with the applied voltage [41].

In Fig. 5b, it is possible to observe the current-potential curve of the membrane used for the nitrate reduction. The plot presents two regions and the estimated value of the limiting current

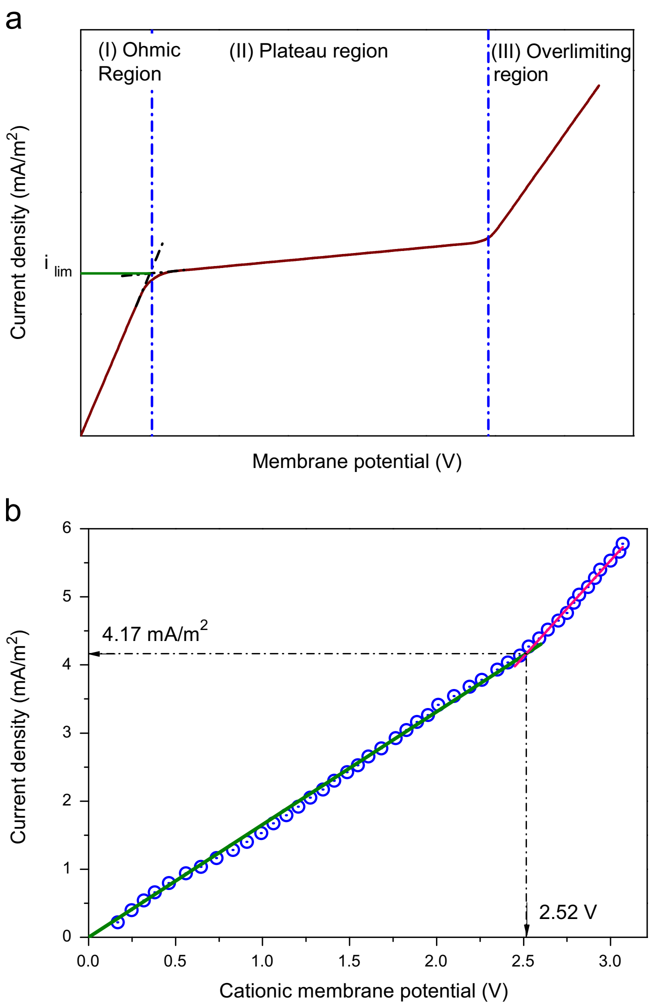

Fig. 5. The typical current potential curve (a) and the plot for our cationic membrane (b).

density is 4.17 mA/m^2 indicating that the selected range of the current density (from 1.25 to 2.54 mA/m^2) avoids polarization in the cation-exchange membrane.

During the achievement of the polarization curves, measurements of pH and electrical conductivity were carried out in both compartments (Fig. 6). It can be seen that there was an increase and a decrease of the pH with time in the cathode and anode compartments, respectively (Fig. 6a). On the other hand, the

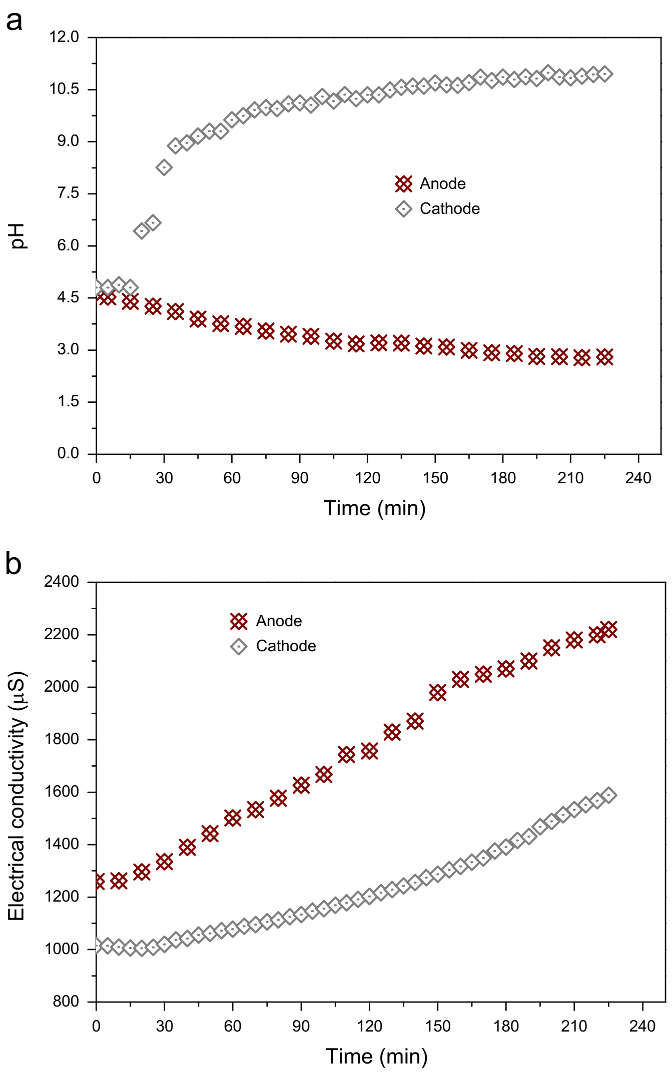

Fig. 6. Evolution of the pH (a) and conductivity (b) of solution B (620 mg/L of NO_3^-).

electrical conductivity recorded an increase with time in both containers (Fig. 6b). The pH and conductivity variation could be associated with the presence of H^+ and OH^-, which could be originated by the water redox reactions [32]:

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)} \quad E_0 = -0.83\ \text{V [32]}$$

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^- \quad E_0 = -1.23\ \text{V [32]}$$

It is important to observe that the Pourbaix diagram (Fig. 3a) displays a small domain for nitrite stability at high pH levels (10–11). Therefore, the reduction of nitrate toward this species (Eq. (1)) is thermodynamically favored in this zone.

3.2. *Membrane electrolysis*

Considering that in an undivided cell, nitrite ions can be oxidized to nitrate at the anode, strongly decreasing the efficiency of the paired electrolysis [33], the experiments were conducted by membrane electrolysis using a cationic membrane. The nitrate reduction data obtained by membrane electrolysis are presented in the next paragraphs. In these experiments, different initial concentrations of nitrate and applied cell voltage were evaluated and the concentrations of nitrate, nitrite and ammonium were monitored.

However, it would be important to keep in mind the different oxidation states of the nitrogen compounds:

$NO_3^-{}_{(aq)}$	$N_2O_4{}_{(g)}$	$NO_3^-{}_{(g)}$, $HNO_2{}_{(aq)}$	$NO_{(g)}$	$N_2O_{(g)}$	$N_2{}_{(g)}$	$NH_4^+{}_{(aq)}$, $NH_4OH_{(aq)}$, $NH_{3(g)}$
+5	+4	+3	+2	+1	0	−3

In the cathode, the production and coexistence of some compounds could be expected.

The operating parameters that have significant influence upon electrochemical denitrification processes include electrode material, cathode/anode surface area ratio, current input, pH, conductivity, sodium chloride (NaCl) concentration and initial concentration of nitrate ions [31,42]. The importance of the electrode composition and potential of the nitrate reduction has been studied by Reyter et al. [33,42].

3.2.1. *Influence of the nitrate concentration*

In the system here studied, when the initial concentration of nitrate was ca. 525 mg/L a significant nitrate reduction was observed at 13 V (Fig. 7a), with the generation of nitrite and ammonium. At 24 h, the concentrations of nitrite and ammonium were 138 and 61 mg/L, respectively. It could be said that the production of nitrite (Eq. (1)) and ammonium (Eq. (10)) was thermodynamically possible at higher pHs and cell potential of 13 V, in agreement with the Pourbaix diagram (Fig. 3a). In fact, a part of the produced nitrite was reduced to ammonium (Eq. (10)).

At 7 V (Fig. 7c), a slight depletion of the nitrate on time is observed for the minor initial concentration (374 mg/L); instead, its consumption increased considerably for the major one (759 mg/L). The experiment for 9 V (Fig. 7e and f) showed that nitrate consumption became important for both initial concentrations.

Again, for these cell potentials nitrate was mainly reduced toward nitrite (oxidation state of +3). The ammonium formation (oxidation state of −3) is even negligible for these potentials (7 and 9 V).

3.2.2. *Influence of the cell voltage*

Fig. 8 exhibits the influence of the cell potential in the reaction; it can be seen that from 5 V, the system begins to react. For low potential, the nitrate is transformed into nitrite mainly and at high voltages, the conversion to nitrite is stable. This plateau suggests similar rates of production (Eq. (1)) and consumption (Eq. (3)) of nitrite. The consumption is in agreement with the rise of the nitrate conversion to ammonium from the cell potential of 9 V (Fig. 8). Besides, the nitrite may participate in other reactions, producing compounds such as $NO_{(g)}$ (Eq. (7)), $N_2O_{(g)}$ (Eq. (8)), $N_{2(g)}$ (Eq. (3)) and $NH_{3(g)}$ (Eq. (11)). It can be seen that the gaseous compounds, except NH_3, have an intermediate oxidation state between nitrite and ammonium (or NH_4OH) and its stabilities would be limited to a narrow range of pH and cathode potential.

Finally, it can be seen that the rate of nitrate total reduction decreases with the cell voltage; at high voltages, even a plateau may be achieved (Fig. 8). However, this plateau could be ca. 90%.

A change in the behavior of the slope (Fig. 9) of the nitrate reduction with the initial concentration was observed at 7 and 9 V. Positive slopes were found at 7 V and negative ones at 9 V. It is possible that the ratio of nitrate mass (mg)/cathode area (m^2) and time were not sufficient to reduce all the nitrates present at high potential. In the graph, it can also be observed that the nitrite formation is the more important reaction to 7 V (Fig. 9);

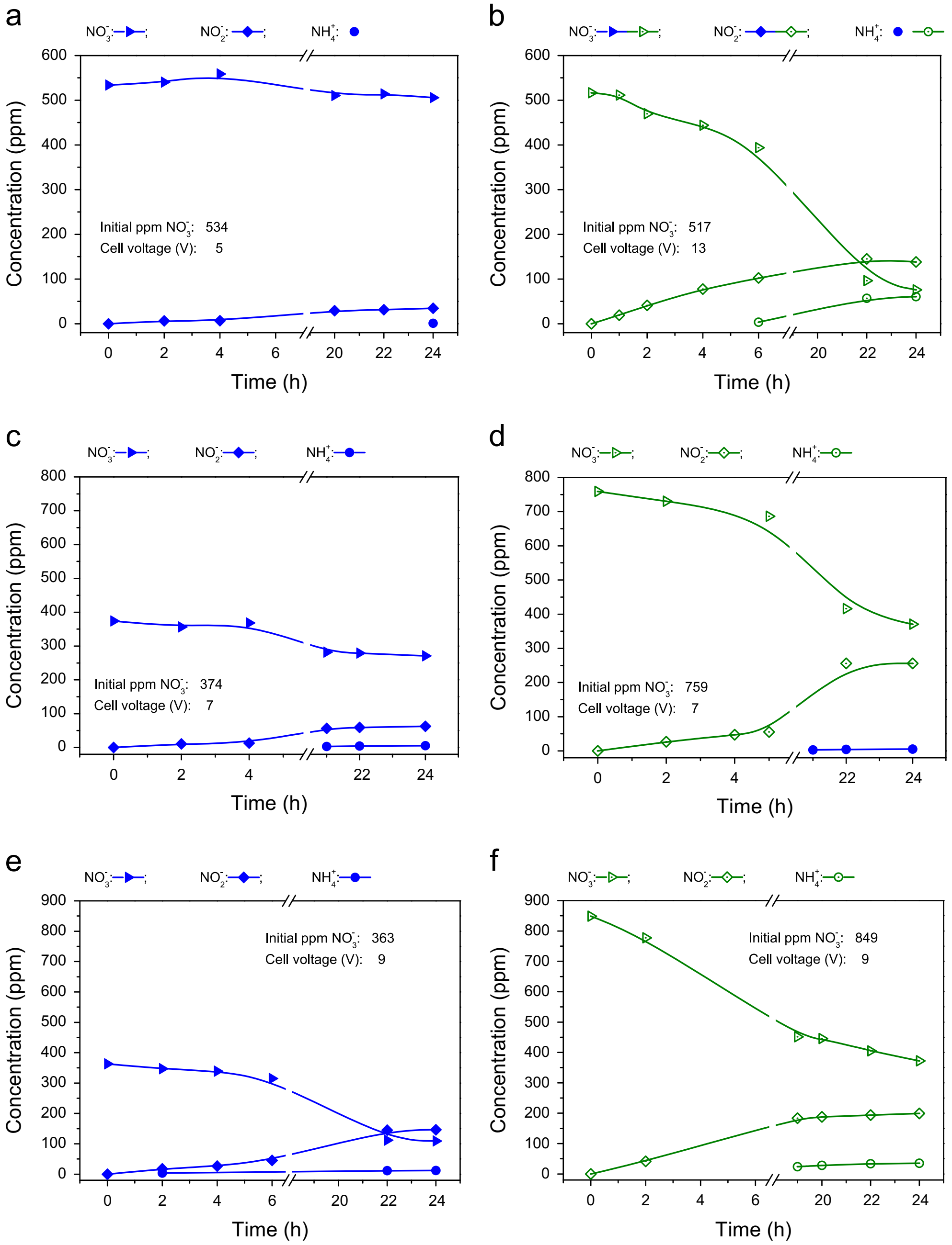

Fig. 7. Time-evolution of nitrogen species. Initial concentration of nitrate fixed at ~525 mg/L (a and b), cell potential fixed at 7 (c and d) and 9 V (e and f).

but nitrogen and other compounds could be formed at higher potentials (Fig. 9).

The reaction data is summarized in Table 3. The amount of nitrate consumed always increases with the initial concentration and cell voltage although the nitrate to nitrite conversion exhibits a decrease with initial mg/L of NO_3^- at 9 V.

The selected copper electrode shows a good performance to the nitrate reduction, achieving values as high as 85% (13 V); however, the reduction reactions do not show a high conversion to gaseous compounds and, therefore, the formation of the desired product (N_2) is low. The highest conversion to gaseous compounds was 17.9%, at 9 V and 526.3 mg/L of NO_3^-.

Probably, the use of other materials for the cathode would be necessary to improve the reduction toward nitrogen gas. Reyter et al. [33] obtained significant improvements in the nitrate removal by a paired electrolysis process with a Cu70Ni30 cathode and a DSA-type anode.

Dash et al. [43] evaluated the electrochemical denitrification of solutions simulating groundwater, with the aim of maximizing the conversion of nitrate to nitrogen gas. The solutions contained an initial concentration of 300 mg/L of NO_3^- and the pH was kept between 7.0 and 9.0. The evaluation was performed using aluminum, graphite, iron and titanium electrodes. While the electrodes of aluminum, iron and titanium nitrate showed high nitrate reductions (70–97%), the graphite electrode just yielded 8% of nitrate conversion. Nitrate was converted to ammonia with iron and aluminum electrodes. With titanium electrodes, the final product obtained in larger amounts was apparently nitrogen gas, but the presence of nitrites was also detected [43].

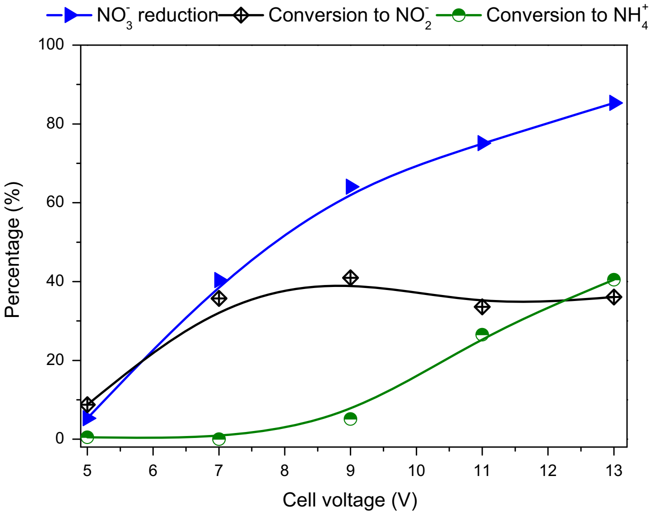

Fig. 8. The influence of the cell potential for NO_3^- reduction (average NO_3^- initial concentration = 531 mg/L).

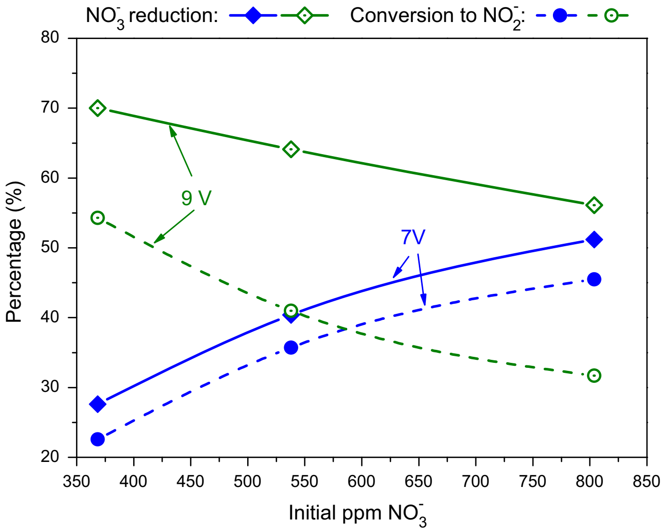

Fig. 9. The influence of cell potential and initial concentration on the reaction system.

Li et al. [44] evaluated the electrochemical denitrification of nitrate using Cu–Zn cathode and Ti/IrO_2–Pt anode. The authors reported that in the presence of chloride the formation of hypochlorite can act in the oxidation of ammonia and nitrites and they concluded that the presence of 0.5 mg/L of NaCl allowed nitrate oxidation without the detection of subproducts. The same experiments were performed using a cathode made of iron [45] and with cathodes of iron plus copper and titanium [46], always with an anode of Ti/IrO_2–Pt and the results obtained were also promising.

4. Conclusions

Although many membrane processes are already in use for water desalination, areas that need further research include discharge of ED and RO concentrate or brine. In this work, membrane electrolysis was applied to the denitrification of brines and showed promising results. Nitrite, ammonium and probably nitrogen gas were the reaction products. The best value was achieved at a cell potential of 9 V, which was obtained with a cathode potential of 0.9 V. Under these conditions, 64% of 526 mg/L of NO_3^- were converted into nitrite and gaseous compounds, with the formation of just 7.8 mg/L of ammonium. By the treatment method applied in this work, membrane electrolysis, the reduced products were not re-oxidized and there was no re-oxidation of the nitrite to nitrate. Membrane electrolysis is a valuable technique for nitrate reduction. Probably, a good nitrate reduction toward nitrogen gas could be accomplished using other materials for the cathode electrode, such as titanium and copper alloys.

Acknowledgments

The authors wish to acknowledge the financial support received from CAPES (Coordenação de aperfeiçoamento de pessoal de nivel superior), CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico), FAPERGS (Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul) and FUNASA (Fundação Nacional de Saúde) of Brazil, and from CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas), MINCYT (Ministerio de Ciencia, Tecnología e Innovación Productiva- Project PPCP 005) and UNL (Universidad Nacional del Litoral) of Argentina. Thanks are given to Elsa Grimaldi for the English language editing.

Table 3
Summary of electrochemical results.

Cell voltage (V_H)	Initial [a] (mg/L)		Residual mg/L [a,b] (after 24 h treatment)						Consumption [a,b]mg/L $N-NO_3^-$	$R_{NO_3^-}^{reduction}$ (%)[c]	$X_{NO_3^-/NO_2^-}$ (%)[c]	$X_{NO_3^-/NH_4^+}$ (%)[c]	$X_{compounds}^{NO_3^-/gaseous}$ (%)[c]
	NO_3^-	$N–NO_3^-$	NO_3^-	$N–NO_3^-$	NO_2^-	$N–NO_2^-$	NH_4^+	$N–NH_4^+$					
5	533.9	120.6	505.7	114.2	34.7	10.5	0.8	0.6	6.37	5.3	–	–	–
7	373.8	84.1	270.6	61.1	62.8	19.1	5.4	4.2	23.3	27.6	22.6	5.0	0.0
	549.6	124.1	327.7	74	145.6	44.3	0.0	0.0	50.1	40.4	35.7	0.0	4.7
	759.1	171.4	370.7	83.7	256.2	77.9	5.7	4.4	87.7	51.2	45.5	2.6	3.1
9	362.9	81.9	109.9	24.6	146.1	44.5	12	9.3	57.3	70.0	54.3	11.4	4.3
	526.3	118.9	189.2	42.7	160.0	48.7	7.8	6.1	76.1	64.1	41.0	5.1	17.9
	848.5	191.6	372.2	84.0	199.3	60.7	35.4	27.5	107.6	56.1	31.7	14.4	10.1
11	526.4	118.9	131.2	29.6	130.9	39.9	40.5	31.5	89.3	75.1	33.6	26.5	15.0
13	516.6	116.6	75.7	17.1	138.2	42.1	60.7	47.2	99.6	85.3	36.1	40.5	8.8

[a] Data obtained by ion chromatography.
[b] Measured after a 24-h treatment.
[c] Calculated from the ion chromatography data.

References

[1] D. Elyanow, J. Persechino, Advances in nitrate removal, Technical Paper, GE Water and Process Technologies ⟨https://knowledgecentral.gewater.com/kcpguest/salesedge/documents/Technical%20Papers_Cust/Americas/English/TP1033EN.pdf⟩, 2007 (accessed 03.09.13).

[2] C. Della Rocca, V. Belgiorno, S. Meriç, Overview of in-situ applicable nitrate removal processes, Desalination 204 (2007) 46–62.

[3] M.L. Bosko, F.A. Marchesini, L.M. Cornaglia, E.E. Miró, The effects of the support on the reduction of nitrite in water, Catal. Today 212 (2013) 16–22.

[4] F.A. Marchesini, L.B. Gutierrez, C.A. Querini, E.E. Miró, Chem. Eng. J. 159 (2010) 203–211.

[5] F. Garcia, D. Ciceron, A. Saboni, S. Alexandrova, Nitrate íons elimination from drinking water by nanofiltration, Sep. Purif. Technol. 52 (2006) 196–200.

[6] N. Voutchkov, Overview of seawater concentrate disposal alternatives, Desalination 273 (2011) 205–219.

[7] J.M. Ortiz, J.A. Sotoca, E. Expósito, F. Gallud, V. Garcıa-Garcıa, V. Montiel, A. Aldaz, Brackish water desalination by electrodialysis: batch recirculation operation modeling, J. Membr. Sci. 252 (2005) 65–75.

[8] H. Strathmann, Ion exchange membrane separation processes, Membr. Sci. Technol. 9 (2004) 1–22 (Chapter 1).

[9] R.W. Baker, Membrane Technology and Applications, Wiley and Sons Ltd., USA, 2012 417–451 (Chapter 10).

[10] F. Valero, A. Barceló, R. Arbós, 2011, in: Michael Schorr (Ed.), Electrodialysis Technology—Theory and Applications, Desalination, Trends and Technologies, InTech, Available from: ⟨http://www.intechopen.com/books/desalination-trends-and-technologies/electrodialysis-technology-theory-and-applications⟩, ISBN: 978-953-307-311-8, doi: 10.5772/14297. Croatia.

[11] Werner, Five Billion Gallons Later-Operating Experience at City of Suffolk EDR Plant, American Desalting Association, North American Biennial Conference and Exposition, 1998.

[12] GE Energy: GE Helps Catalonia Region Make the Most of Scarce Water Supplies, ⟨http://site.ge-energy.com/about/press/en/2009_press/051909.htm⟩. 2009.

[13] Info enviro, 2008. ⟨http://www.valoriza-agua.com/es_es/Images/ETAPABRERA_tcm20-5358.pdf⟩.

[14] Technical paper, GE and Public Water Supplies—Representative Installations (RO, NF, EDR), GE Water and Process Technologies, ⟨https://knowledgecentral.gewater.com/kcpguest/documents/Capability%20Profiles%20FAQ_Cust/Americas/English/IL1004EN.pdf⟩, 2009 (accessed on 11 09 2013).

[15] Astom Corporation, ⟨http://www.astom-corp.jp/en/en-usecase-007.html⟩. 2010.

[16] K. Salem, J. Sandeaux, J. Molénat, R. Sandeaux, C. Gavach, Elimination of nitrate from drinking water by electrochemical membrane processes, Desalination 101 (1995) 123–131.

[17] K. Kesore, F. Janowski, V.A. Shaposhnik, Highly effective electrodialysis for selective elimination of nitrates from drinking water, J. Membr. Sci. 127 (1997) 17–24.

[18] F. Hell, J. Lahnsteiner, H. Frischherz, G. Baumgartner, Experience with full-scale electrodialysis for nitrate and hardness removal, Desalination 117 (1998) 173–180.

[19] T. Sata, Studies on anion-exchange membranes having permselectivity for specific anions in electrodialysis—effect of hydrophilicity of anion-exchange membranes on permselectivity of anions, J. Membr. Sci. 167 (2000) 1–31.

[20] A.E. Midaoui, F. Elhannouni, M. Taky, L. Chay, M.A.M. Sahli, L. Echihabi, M. Hafsi, Optimization of nitrate removal operation from ground water by electrodialysis, Sep. Purif. Technol. 29 (2002) 235–244.

[21] A. Elmidaoui, M.A. Menkouchi Sahli, M. Tahaikt, L. Chay, M. Taky, M. Elmghari, M. Hafsi, Selective nitrate removal by coupling electrodialysis and a bioreactor, Desalination 153 (2002) 389–397.

[22] K.-H. Yeon, J.-H. Song, J. Shim, S.-H. Moon, Y.-U. Jeong, H.-Y. Joo, Integrating electrochemical processes with electrodialysis reversal and electro-oxidation to minimize COD and T-N at wastewater treatment facilities of power plants, Desalination 202 (2007) 400–410.

[23] M.A. Menkouchi Sahli, S. Annouar, M. Mountadar, A. Soufiane, A. Elmidaoui, Nitrate removal of brackish underground water by chemical adsorption and by electrodialysis, Desalination 227 (2008) 327–333.

[24] D.H. Kim, A review of desalting process techniques and economic analysis of the recovery of salts from retentates, Desalination 270 (2011) 1–8.

[25] A. Pérez-González, A.M. Urtiaga, R. Ibañez, I. Ortiz, State of the art and review on the treatment technologies of water reverse osmosis concentrates, Water Res. 46 (2012) 267–283.

[26] Y. Zhang, K. Ghyselbrecht, B. Meesschaert, L. Pinoy, B. Van der Bruggen, Electrodialysis on RO concentrate to improve water recovery in wastewater reclamation, J. Membr. Sci. 378 (2011) 101–110.

[27] M. Badruzzaman, J. Oppenheimer, S. Adham, M. Kumar, Innovative beneficial reuse of reverse osmosis concentrate using bipolar membrane electrodialysis and electrochlorination processes, J. Membr. Sci. 326 (2009) 392–399.

[28] Y. Zhang, K. Ghyselbrecht, B. Meesschaert, L. Pinoy, B.V. der Bruggen, Electrodialysis on RO concentrate to improve water recovery in wastewater reclamation, J. Membr. Sci. 378 (2011) 101–110.

[29] Y. Yang, X. Gao, A. Fan, L. Fu, C. Gao, An innovative beneficial reuse for seawater concentrate using bipolar membrane electrodialysis, J. Membr. Sci. 449 (2014) 119–126.

[30] C. Wisniewski, F. Persin, T. Cherif, R. Sandeaux, A. Grasmick, C. Gavach, F. Lutin, Use of a membrane bioreactor for denitrification of brine from an electrodialysis process, Desalination 149 (2002) 331–336.

[31] W.T. Mook, M.H. Chakrabarti, M.K. Aroua, G.M.A. Khan, B.S. Ali, M.S. Islam, M.A. Abu Hassan, Removal of total ammonia nitrogen (TAN), nitrate and total organic carbon (TOC) from aquaculture wastewater using electrochemical technology: a review, Desalination 285 (2012) 1–13.

[32] M. Pourbaix, Atlas D'equilibres Electrochimiques, Editorial, Gauthier-Villars, Paris, 1963.

[33] D. Reyter, D. Bélanger, L. Roué, Optimization of the cathode material for nitrate removal by a paired electrolysis process, J. Hazard. Mater. 192 (2011) 507–513.

[34] M. Pourbaix, Thermodynamics of Dilute Aqueous Solutions: With Applications to Electrochemistry and Corrosion, London, 1949, Edward Arnold & Co.

[35] L.J. Banasiak, T.W. Kruttschnitt, A.I. Schäfer, Desalination using electrodialysis as a function of voltage and salt concentration, Desalination 205 (2007) 38–46.

[36] F. Hell, J. Lahnsteiner, H. Frischherz, G. Baumgartner, Experience with full-scale electrodialysis for nitrate and hardness removal, Desalination 117 (1998) 173–180.

[37] C. Wisniewski, F. Persin, T. Cherif, R. Sandeaux, A. Grasmick, C. Gavach, Denitrification of drinking water by the association of an electrodialysis process and a membrane bioreactor: feasibility and application, Desalination 139 (2001) 199–205.

[38] B. Jingjing, P. Changsheng, X. Huizhen, A. Abou-Shady, Removal of nitrate from groundwater using the technology of electrodialysis and electrodeionization, Desalination Water Treat. 34 (2011) 394–401.

[39] D. Cardoso Buzzi, L.S. Viegas, M.A. Siqueira Rodrigues, A.M. Bernardes, J.A. Soares Tenório, Water recovery from acid mine drainage by electrodialysis, Miner. Eng. 40 (2013) 82–89.

[40] H. Strathmann, Chapter 6: electrodialysis and related processes, Membr. Sci. Technol. 2 (1995) 213–281.

[41] R.C.A. Moura, D.A. Bertuol, C.A. Ferreira, F.D.R. Amado, Study of chromium removal by the electrodialysis of tannery and metal-finishing effluents, Int. J. Chem. Eng. 2012 (Article ID 179312) (2012) 1–7.

[42] D. Reyter, D. Bélanger, L. Roué, Nitrate removal by a paired electrolysis on copper and Ti/IrO_2 coupled electrodes—influence of the anode/cathode surface area ratio, Water Res. 44 (2010) 1918–1926.

[43] B.P. Dash, S. Chaudari, Electrochemical denitrification of simulated groundwater, Water Res. 39 (2005) 4065–4072.

[44] M. Li, C. Feng, Z. Zhang, X. Lei, R. Chen, Y. Yang, N. Sugiura, Simultaneous reduction of nitrate and oxidation of by-products using electrochemical method, J. Hazard. Mater. 171 (2009) 724–730.

[45] M. Li, C. Feng, Z. Zhang, S. Yang, N. Sugiura, Treatment of nitrate contaminated water using an electrochemical method, Bioresour. Technol. 101 (2010) 6553–6557.

[46] M. Li, C. Feng, Z. Zhang, N. Sugiura, Efficient electrochemical reduction of nitrate to nitrogen using Ti/IrO_2–Pt anode and different cathodes, Electrochim. Acta 54 (2009) 4600–4606.