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Nitrate reduction of brines from water desalination plants by membrane electrolysis

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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].

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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].