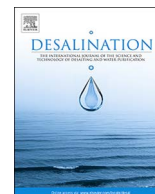




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Electrodialysis for water desalination: A critical assessment of recent developments on process fundamentals, models and applications

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ABSTRACT

The need for unconventional sources of fresh water is pushing a fast development of desalination technologies, which proved to be able to face and solve the problem of water scarcity in many dry areas of the planet. Membrane desalination technologies are nowadays leading the market and, among these, electrodialysis (ED) plays an important role, especially for brackish water desalination, thanks to its robustness, extreme flexibility and broad range of applications. In fact, many ED-related processes have been presented, based on the use of Ion Exchange Membranes (IEMs), which are significantly boosting the development of ED-related technologies. This paper presents the fundamentals of the ED process and its main developments. An important outlook is given to operational aspects, hydrodynamics and mass transport phenomena, with an extensive review of literature studies focusing on theoretical or experimental characterization of the complex phenomena occurring in electromembrane processes and of proposed strategies for process performance enhancement. An overview of process modelling tools is provided, pointing out capabilities and limitations of the different approaches and their possible application to optimisation analysis and perspective developments of ED technology. Finally, the most recent applications of ED-related processes are presented, highlighting limitations and potentialities in the water and energy industry.

1. Introduction

Seawater desalination is the main non-conventional source of fresh water in many countries all around the world. In some specific areas, facing severe water scarcity conditions, it is indeed the first source of fresh water for the local population. Recent figures about desalination industry indicate a cumulative contracted capacity of desalination plants in 2016 of almost 100 Mm³/day, with an average contracted capacity per year between 3 and 5 Mm³/day in the last 5 years [1], and a continuous increasing trend is expected in the next decades. Interestingly, seawater desalination led the desalination market in the first decade of the third millennium, with a dramatic capacity increase for SW-desalination plants in those years. Conversely, during the second decade the desalination industry experienced a growth of the applications to the desalination of brackish water and other types of water streams (e.g. tertiary waste waters, surface saline waters, etc.), where the typical capacities are small or medium (below 50.000 m³/day) [1].

Among several different technologies, membrane processes nowadays have the leading role. In particular, looking at the new contracted plants (2010–2016), reverse osmosis now holds by far the majority of the global market share, ranging from 60% to 90% depending on the

geographical areas. Thermal evaporative processes (mainly Multiple Effects Distillation and Multiple Stage Flash technologies) are still keeping an important role in Gulf countries, historically characterized by the operation of huge thermal desalination plants, thanks to their robustness, small sensitivity to low quality seawater feed and salt concentration and to the large availability of low-temperature waste heat for powering the thermal evaporative plants.

Within this context, electromembrane processes, e.g. electrodialysis (ED), electrodialysis reversal (EDR) and electrodeionization (EDI), have a small, yet stable share in low-salinity desalination applications. New ED/EDR and EDI contracted plants in 2015–2016 covered between 1 and 2% of the total desalination installed capacity, with the majority of plants processing brackish water and with a size ranging between few tens of m³/day up to a maximum of 10,000 m³/day, reached by an EDR plant installed in South Africa [1].

Such limitation in installed capacity and type of treated feed is mainly due to the relatively higher cost of ion exchange membranes (IEMs) compared to RO membranes, and to the significant reduction of membrane selectivity when seawater is used as the feed solution.

A very recent development in the field of electromembrane processes has been the launching of reverse electrodialysis (RED) for

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energy generation from salinity gradients. In this new application, the salinity difference between two streams (e.g. seawater and river water, or concentrated brines and brackish water) is converted into electricity by means of a controlled mixing of the two solutions. RED significantly promoted the development of new membranes and new plant configurations suitable for operations at high salinity, with optimized process efficiencies [2–8].

Electromembrane processes are thus experiencing a very promising revival era, pushed by R&D and industrial developments carried out by research institutions and major industrial stakeholders in the US, Europe and Japan [9].

In addition to that, a number of novel applications have been proposed in other industrial sectors, where the features of ED (or EDI) are more suitable than RO. Examples of these applications are the use of ED for brine concentration in sea-salt production facilities in Japan [10,11]; in food industry (e.g. for juice de-acidification) [12–14]; in electronics (e.g. for ultrapure water production) and wastewater treatment, especially for heavy metals removal [15–17]. Moreover, the recent trends in the field of renewable energy desalination have also highlighted the promising features of photovoltaic (PV)-ED coupling, made possible by the extreme flexibility of the ED process, which can follow the oscillating behaviour of PV power production [18]. The same features make ED extremely suitable also for coupling with other off-grid sources, such as wind energy [19].

Finally, several special applications of electromembrane processes are gaining room in the scientific-technological community, which is more and more engaged in developing new IEMs and devices, enlarging the potential for the application of this flexible and multi-faceted class of technologies. Among these, it is worth to mention the growing field of bipolar membranes for acid and alkali production and electrochemistry applications [20–26], the development of selective-electrodialysis for selective salt separation from saline streams [26–29], and the application of the electrochemical metathesis (EDM) in zero liquid discharge (ZLD) desalination [30–33].

An overview of ED technologies for water desalination and related processes is presented here, with a specific focus on the most challenging topics for the growth of the technology, such as IEM development, modelling tools for process optimization, and innovative applications.

In particular, an extensive review of literature studies on the hydrodynamics, mass transport and fundamental phenomena governing the operation of electromembrane processes is given, with the aim of providing the reader with a comprehensive collection of all the main findings published in this field so far. The most important physico-chemical phenomena are critically analysed for an in-depth knowledge of what governs ED and related processes. Finally, the most significant mathematical modelling approaches to the design and simulation of electromembrane processes are presented.

2. Historical development and working principle

2.1. From early steps to commercialisation

ED was proposed for the first time in 1890 by Maigrot and Sabates [34]. They built an early concept unit to demineralize sugar syrup by using carbon as electrodes and permanganate paper as membrane. A dynamo served as current supply.

However, Maigrot and Sabates never used the term electrodesalination, which can be officially found for the first time in a patent in 1900 [35]. In this patent, Schollmeyer aimed to purify sugar syrup using the same technology as in [34], but with soluble zinc or iron anodes. Despite this, it is generally argued that ED was not actually theorized until 1911 [35–37], when Donnan presented his exclusion principle, experimentally confirmed by Teorell few years later. According to this principle, it is possible to manufacture membranes selective to cations using fixed negative charges and membranes selective to anions using fixed positive charges.

The theorisation of electrochemical principles governing the behaviour of IEMs opened the way to the development of new membranes and to the conceptualisation of an electrodesalinator with multiple compartments [34]. However, the actual concept of multi-compartment ED where anion and cation exchange membranes are alternated could be only realised in 1950, when W. Juda and W. A. McRay manufactured the first synthetic ion-exchange membranes from ion exchange resins [35]. These membranes were used by Ionics (US) in 1954 to build the first ED desalination plant for Aramco (Saudi Arabia) [35]. Since that year, many other ED units were built.

In 1974, ED faced the main breakthrough with the development of the electrodesalination reversal concept (EDR) [35,38]. This new operational strategy allowed ED to work by periodically inverting the current, offering the main advantage of membrane fouling control and generating a breakthrough in the implementation of ED at the larger industrial scale.

By then, a number of “ED-derived” alternatives, applications and processes have been developed and presented in the literature, providing a further booster to the development of electromembrane technologies in general. Fig. 1 represents a synthetic timeline of the most critical development steps for ED and related technologies, indicating from the first important milestones to the more recent and very differentiated applications presented so far, including the first laboratory- or pilot-scale experiences and the first commercialisation attempts of the most recent ED derived processes. A deeper insight on these special applications will be given in Section 6.

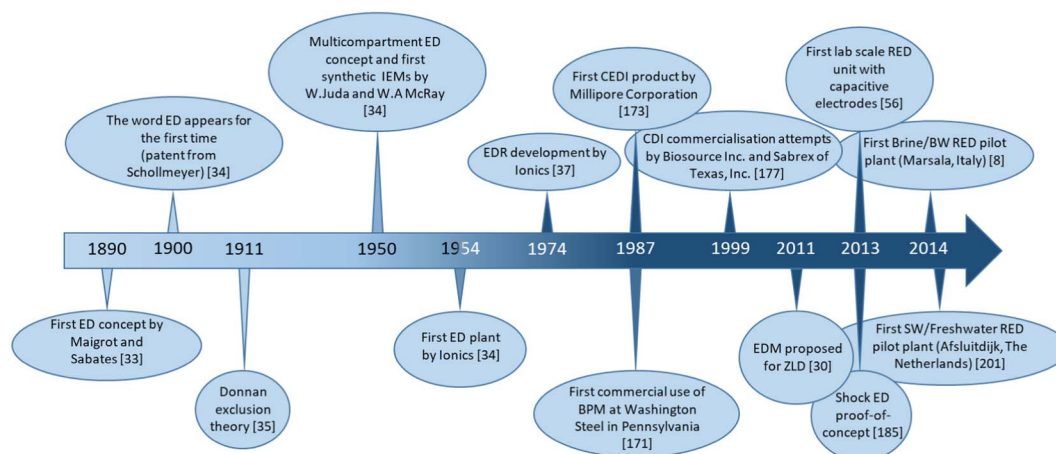


Fig. 1. Timeline of the most important developments for ED and related processes.

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