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Integration of monopolar and bipolar electrodialysis for valorization of seawater reverse osmosis desalination brines: Production of strong acid and base

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HIGHLIGHTS

- Seawater desalination reverses osmosis (SWD-RO) brine was valorized as NaOH and HCl.
- ED was used to purify and concentrate SWD-RO brine into divalent-free NaCl solutions.
- 100 to 200 g NaCl/L brines were achieved by ED depending on current and temperature.
- EDBM was applied to produce HCl and NaOH as chemicals for pH adjustment treatments.
- NaOH and HCl up to 2 M were obtained at 9 V by EDBM using an ED pretreated brine.

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ABSTRACT

Water scarcity in the Mediterranean basin has been solved by using seawater desalination reverse osmosis technology (SWD-RO). This technology produces brine which is discharged back into the sea resulting in an environmental impact on marine ecosystems. Under the circular economy approach, the aim of this work is to recover resources from NaCl-rich brine (~60–70 g/L), e.g. in the form of NaOH and HCl, by integration of two ion exchange-based membrane technologies and quantify the electrical energy consumption. Electrodialysis (ED) incorporating monovalent selective cation exchange membranes as divalent ions purification and concentration of the NaCl present in the SWD-RO brine, was integrated with bipolar membrane ED (EDBM) to produce NaOH and HCl. Current densities of 0.30–0.40 kA/m^2 at two temperature ranges simulating different seawater temperature regimes (15–18 °C and 22–28 °C) were tested and a pure NaCl solution was used as starting concentrate stream. NaCl-rich brines with 100 or 200 g NaCl/L were obtained by ED and then introduced in the EDBM stack producing HCl and NaOH up to 2 M, depending on the initial concentrations. A minimum energy consumption of 1.7 kWh/kg NaOH was calculated when working by EDBM with initial concentrations of 104 g NaCl/L and 0.24 M HCl and NaOH.

1. Introduction

Water scarcity in the Mediterranean basin has been solved by using seawater and reverse osmosis as desalination technology (SWD-RO). The process produces brine which is discharged back into the sea resulting in an environmental impact on marine ecosystems [1]. Initially, managing the generated brines was considered as an environmental problem, but it has recently been identified as an opportunity to develop circular economy concepts to transform a waste (the brine) to a resource for materials production [2]. Any medium to large SWD-RO plant drives so large amount of dissolved elements that may be considered as a mine and then, the waterworks site could be seen not only as a "water factory" but also as a potential chemicals production site. Although revalorization of SWD-RO brines represents a promising and sustainable alternative it has been applied so far only on a limited scale because of the large number of technological gaps to be covered for making it economically feasible [3].

Seawater contains almost all elements in the periodic table [4]. However, only a few are nowadays profitable extracted conventionally by evaporation: sodium chloride, potassium chloride, magnesium and bromide salts. Several extraction schemes for a list of eight elements have been identified as being potentially economically and technically viable (Na, K, Mg, Rb, P, Cs, In, Ge) [5]. Valorization approaches of SWD-RO brine to produce salts through different concentration/precipitation technologies have been widely reviewed by Kim [6], Van der Bruggen

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et al. [7] and Pérez-González et al. [8] in an attempt to attain the zero liquid discharge (ZLD) objectives [9]. Due to the high salinity and consequently high ionic conductivity, electrically driven membrane processes such as electrodialysis (ED) based on the selective passage of some constituents through an ion-exchange membrane (IXM) have been widely researched. Several studies have been oriented to the brine reuse by the chlor-alkali industry from SWD-RO brines [10–14]. This industry uses NaCl-rich brines to produce Cl_2, NaOH and H_2 by means of ED as a salt valorization option. It was demonstrated that ED technology concentrates NaCl from SWD-RO brines with competitive electrical consumptions around 0.20 kwh/kg NaCl to produce 200 g NaCl/L.

Such solutions could be also used as raw materials to produce chemical commodities as HCl and NaOH if bipolar membranes (BM) are integrated. However, ED combination with bipolar membranes (EDBM) has been only applied successfully for chemical and biochemical applications, food processing and in less extension for waste management of metallurgical industries [1,15–19]. When electric current is applied between the electrodes of the EDBM stack, water splitting is produced in the BM. Therefore, the produced H^+ and OH^- ions can be used to generate acid (HX) and base (MOH) from salts (MX), for example NaCl from the chemical industry to produce HCl and NaOH, without production of hydrogen, oxygen or undesirable products. Another of the main features of EDBM process is that water dissociation is accelerated up to 50 million times compared to the rate of water dissociation in aqueous solutions. Moreover, EDBM has low voltage drop, maximal energy utilization, space saving, easy installation and operation, low start-up and running costs and last but not least it can provide products of high quality. However, one of the drawbacks of EDBM, when applied to waste valorization, is that it is not as economically competitive as other membrane separation technologies, due to the electrodes and ion exchange membranes cost and the capital cost. Despite this economical limitation, all the features previously commented have made EDBM an environmentally friendly technology for valorization and management of industrial brines [1,20–22]. A clear application is, thus, the salt-rich waste valorization for the production of acids and bases and a growth number of applications with industrial brines are reported [1,16,17,23,24]. However more limited applications are devoted to SWD-RO brines to produce acid and base with EDBM at lab or pilot scale [15,25]. These studies have concluded that the economic and technical feasibility will be improved if the electrical consumption could be reduced with the increase of brine concentration and with the reduction of scaling compounds in the brines (HCO_3^-, Ca^{2+}, Mg^{2+}). In our previous study [26], SWD-RO brines (60 g/L NaCl) were purified in divalent elements by using NF membranes and 1 M HCl and 1 M NaOH were produced by using EDBM with electrical consumptions of 2.6 kwh/kg NaOH. However, scarce data and studies could be found on the influence of the brine concentration (e.g. NaCl) on the process efficiency in terms of the production of the highest NaOH and HCl concentrations and the specific electrical consumption.

The aim of this work is to quantify the performance and the electrical energy consumption of: a) the concentration and purification of NaCl from SWD-RO brines by using monovalent selective ion exchange membranes to avoid the presence of divalent metal ions (Ca, Mg) in ED cells; and b) the integration of an EDBM system for in-situ production of HCl and NaOH from concentrated NaCl brine (e.g. 100–200 g NaCl/L). The specific objectives are to find optimal operation conditions of the integrated processes of ED and EDBM to achieve the lowest specific electrical consumption and the highest acid and base concentrations.

2. Materials and methods

SWD-RO brine from the seawater desalination plant of El Prat (Barcelona, Spain) was used as feed solution for the ED system. Mainly, this brine was rich in NaCl (65.1 ± 6.1 g NaCl/L), although it also contained other major components such as sulfate (5.4 ± 0.2 g/L), Mg^{2+} (2.6 ± 0.2 g/L), and Ca^{2+} (0.7 ± 0.04 g/L). Two different ranges of brine temperature were evaluated: 15 to 18 °C from a spring season and 22 to 28 °C from a summer season. Moreover, a pure NaCl solution was used as initial solution for the concentrate loop.

In a previous study, Casas et al. [27] evaluated the removal of Ca^{2+} and Mg^{2+} as a potential valorization pathway for seawater desalination brines. Treated brines contained concentration of Ca^{2+} and Mg^{2+} below 10 mg/L. For practical purposes and taking into account that the Ca-Mg purification process was evaluated previously, fresh pure NaCl brines simulating the composition of the feed concentrated brines to be used in the valorization as HCl and NaOH by EDBM were prepared in the present study. Fig. 1 shows also this procedure were pure NaCl was used as input brine for the ED concentrated loop.

Then, the ED cell was working with an open diluate loop and a NaCl recirculated concentrate stream. Sequentially, the NaCl-rich concentrated solution produced by the ED system was introduced in the EDBM cell which was used to produce NaOH and HCl. Details on the operation conditions are described as follows.

2.1. Experimental description and operation of the ED plant

An ED pilot using an Eurodia Aqualizer SV-10 stack (620 × 450 × 313 mm) with 50 cell pairs made of Neosepta cation-exchange membranes (CIMS) and anion-exchange membranes (ACS) (0.1 m^2 effective surface area per membrane) was used [13,14,28]. The main characteristics of the membrane are listed in Table 1.

The intermembrane distance was 0.43 mm and linear flow velocity at the inlet of desalting and concentrating cells was 11 cm/s. The feeding and the electrolyte circuits were operated in a single-pass design to achieve higher current densities and minimize the problems of the increase of temperature in the cell. The concentrate (divalent-free NaCl-rich) stream was re-circulated to reach the maximum NaCl concentration with sustainable electrical specific consumption (e.g. current densities <0.4 kA/m^2 and specific electric consumption <0.3 kWh/Kg NaCl) under the two given brine temperature ranges evaluated. The SWD-RO brine flow rate through the stack was 0.5 m^3/h in both the feeding and the concentrating stream compartments and 0.15 m^3/h in the electrodes chambers. HCl was added to keep the pH below 4 for the cathodic circuit, below 7 in the feeding circuit and below 5.5 in the concentrate circuit.

Two temperature ranges simulating different seawater temperature regimes (15–18 °C and 22–28 °C) were tested and current densities were varied between 0.3 and 0.40 kA/m^2 in order to obtain a NaCl-rich brine with the lower specific electrical consumption (<0.3 kWh/kg NaCl). The SWD-RO brine concentration process was monitored by in-line measurements of temperature, flow-rate, pressure, current intensity, voltage, electrical conductivity and pH as it can be seen in Fig. 2.

2.2. Experimental description an operation of the EDBM plant

A lab-scale pilot incorporating an EDBM stack PCCell ED 64-004 (PCCell GmbH, Germany) was used. The dimension of the cell was 0.11 × 0.11 m. A scheme of the EDBM stack is shown in Fig. 3. It was a 4 chamber system (electrode rinse, acid, base and salt) with an active membrane area of 64 cm^2 per membrane. The stack configuration was composed of three cell triplets; each cell triplet had one cationic exchange membrane (CEM) (PC-SK), one anionic exchange membrane (AEM) (PC Acid 60) and one bipolar membrane (BM). The main characteristics of the membrane are listed in Table 1. The EDBM cell worked under close loop configuration for the four streams. Two electrodes rinse compartments formed a single circuit located at the cell ends.

Four pumps were used to impulse each stream into the EDBM unit. All the performances were carried out at constant voltage (9 V) until the conductivity in the feed tank was almost zero (values around 2 or 3 mS/cm). Some other parameters were constant during the