

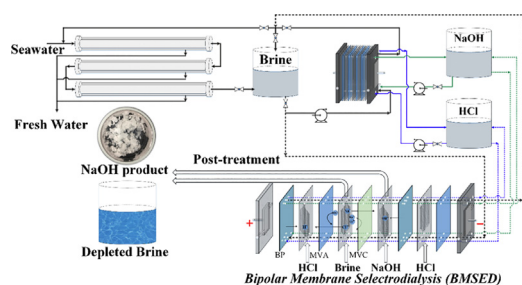
Selectrodialysis with bipolar membrane for the reclamation of concentrated brine from RO plant

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GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Selectrodialysis
Bipolar membrane
Concentrated brine
Reclamation
Desalination

ABSTRACT

Reverse osmosis (RO) is increasingly becoming the dominant strategy for seawater desalination owing to its excellent desalination performance over the past few decades. It produces a considerable amount of concentrated brine, which is a threat to marine ecosystems accompanying freshwater production. Electrodialysis has been demonstrated to be a feasible process for brine treatment. In this work, a novel process called Selectrodialysis with Bipolar Membranes (BMSSED) was firstly proposed for treating concentrated brine. BMSSED uses bipolar membranes and monovalent selective ion exchange membranes inside the ED stack and thus combines the selectrodialysis (SED) and bipolar membrane electrodialysis (BMED) processes into a single step. BMSSED can desalinate concentrated brine, selectively regenerate monovalent ions and produce acids/bases in a single route. The feasibility of the process was investigated by using different commercial membranes. The factors, including the current density and brine concentrations, were investigated. The results indicated that brine was successfully treated by using BMSSED and that a HCl and NaOH solution (up to an approximate 2 mol/L concentration) with high purity was eventually produced. Therefore, BMSSED is a pertinent environmentally and economically friendly process for RO concentrated brine management.

1. Introduction

Freshwater, which is the most indispensable element for life on

Earth, is drawing increasing public attention due to its uneven distribution and use in human activities [1,2]. The freshwater crisis prompts us to accelerate the pace of obtaining fresh water by taking

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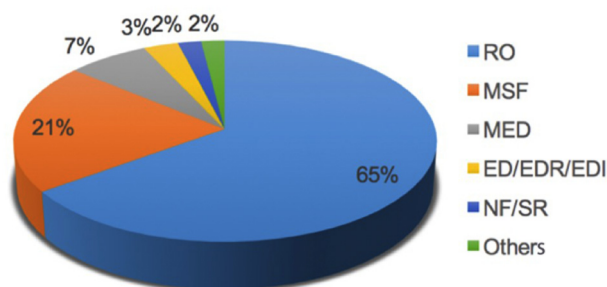


Fig. 1. Distribution of the total installed water desalination capacity worldwide [7].

advantage of advanced technologies, such as seawater desalination. Seawater desalination is a very developed industrial practice [3] since almost 97% of the water on Earth is stored in the ocean [4].

To date, several feasible technologies are available for seawater desalination, including reverse osmosis (RO), multi-stage flash (MSF), multiple effect distillation (MED), electrodialysis (ED), nanofiltration (NF), among others. The distribution of these technologies for producing fresh water is shown in Fig. 1 [5]. It is obvious that RO occupies approximately 65% of the total installed capacity of seawater desalination and is increasingly becoming the dominant seawater desalination technology due to its excellent desalination performance, high water recovery efficiency and relatively low cost [6].

However, after transferring water molecules across RO membranes under an appropriate pressure exerted above seawater, salts and other chemicals are concentrated and brine with high salt concentrations is simultaneously produced. Conventionally, concentrated brine is directly discharged back to the ocean, which may cause adverse effects to the environment, i.e., transformation of sediment quality, impairment of marine life and damage to coastal ecosystems [8], especially where the ecosystem is sensitive [9]. Therefore, brine from RO processes should be appropriately treated before its disposal. Currently, some efforts have been made regarding concentrated brine treatment. Solar evaporation is the most well-known technique [10]. Although solar evaporation apparatuses are relatively easy to construct and require infrequent maintenance, large land areas as well as long operating periods are needed [11,12]. Nanofiltration (NF) is an alternative method that separates monovalent ions from brine and achieves value-added byproduct reclamation [13]. However, NF requires a particularly high pressure and is accompanied by serious membrane fouling.

Electrodialysis (ED) is an emerging technology for the brine treatment. ED processes typically include conventional electrodialysis (CED), selectrodialysis (SED) and bipolar membrane electrodialysis (BMED). These processes have been used in the field of water treatment; environmental protection; chemical/biochemical engineering, i.e., seawater desalination [14,15]; CO₂ capture/regeneration [16,17]; and organic acid/base production [18]. ED has also been used in brackish water treatment and to treat highly concentrated salinity wastewaters [19–21]. Zhang et al. [22] presented a systematic techno-economic analysis and an environmental impact evaluation of a RO concentrate treatment process by using ED. Jiang et al. [23] previously used a multi-stage ED process to treat RO concentrated brine and obtained a coarse salt/fresh water byproduct. Yang et al. [24] utilized BMED to treat Ca²⁺/Mg²⁺ free brine and obtained a pure NaOH/mixed acid byproduct. Unfortunately, a pretreatment was required to remove multivalent ions (contaminants).

For the separation of different charged ions in the brine, mono-valent selective membranes were introduced as an alternative. A typical SED stack configuration is shown in Fig. 2. Conventionally, mono-valent selective cation exchange membranes (MVCs) and mono-valent selective anion exchange membranes (MVAs) were repeatedly installed between two electrodes. Under the driven force of current and the

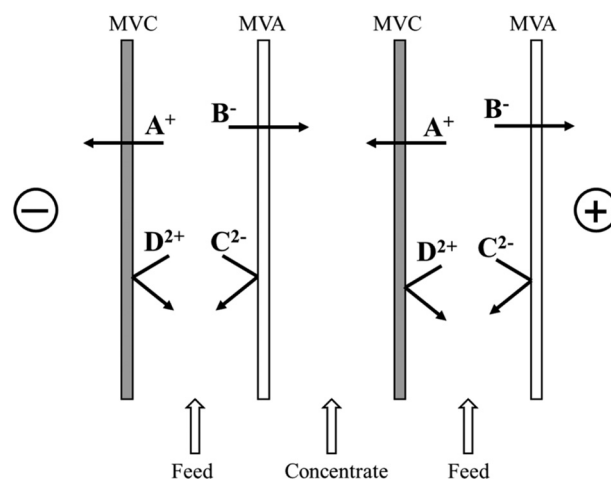


Fig. 2. Configuration of a typical selectrodialysis membrane stack.

permselectivity of mono-valent selective membranes, the mono-valent ions were selectively removed, and bivalent ions were blocked inside feed solution. Compared with CED process, SED can achieve a normal ED function and simultaneously separate different ions, making it a more versatile technology that can be used in special fields, particularly when dealing with mixed wastewater. Zhang et al. [25] designed a novel selectrodialysis membrane stack, and a subsequent study [26] indicated that selectrodialysis was able to successfully concentrate phosphate from wastewater. Reig et al. [27] reclaimed H₂SO₄, HCl and NaOH from brine by the cooperative use of independent BMED and SED units. Typically, the processes include two independent techniques, i.e., BMED and SED for the concentrated brine treatment. Thus, the complex operation and multi-integrated units limit their industrialization.

Considering the processes discussed above, pretreatment to remove multivalent ions by chemical methods or SED is indispensable. Here, we propose a novel process, selectrodialysis with bipolar membranes (BMSED). By replacing the normal AEM and CEM in the BMED stack with corresponding monovalent selective membranes (MVA and MVC), manifold goals, including the desalination of concentrated brine, separation of monovalent ions and multivalent ions, and production of high purity acid/base, were achieved within a single BMSED operation without any pretreatment. The present study is organized as follows: 1) the influence of the power supply mode, 2) effect of the current density, 3) impact of brine concentration and 4) long-term evaluation.

2. Experimental section

2.1. Materials

The membranes used in the experiments were ASV (monovalent selective AEM, from AGC Engineering Co. Ltd., Japan), CSO (monovalent selective CEM, from AGC Engineering Co. Ltd., Japan), ACS (monovalent selective AEM, from ASTOM Co., Japan), CIMS (monovalent selective CEM, from ASTOM Co., Japan), and BP-1E (bipolar membrane, BM, from ASTOM Co., Japan). The main properties of the membranes are listed in Table 1. Brine was prepared by dissolving seawater crystal in deionized water (before the brine was prepared, crystals were dried at 60 °C for several days to remove crystallized water). Brine concentrations of 70 and 105 g/L were used to simulate the RO concentrate, which is generally 2–3 times higher than that of natural sea water [28]. All reagents were of analytical grade.

2.2. Experiment set-up

The BMSED process was conducted with lab-scale equipment that was designed and assembled in our lab. Three pieces of BMs, two pieces

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