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An innovative beneficial reuse of seawater concentrate using bipolar membrane electrodialysis

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A B S T R A C T

Because of the demand for acid solutions in seawater desalination pretreatment and the difficulty of transporting sulfuric acid or hydrochloric acid, seawater concentrate from an RO system was used as the feed for the production of mixed acid by bipolar membrane electrodialysis (BMED) after the removal of calcium ions and magnesium ions. In this experiment, the feasibility of the process was tested using a laboratory ED-cell with an effective area of 88 cm^2. Based on the configuration of the BP-C-A-BP, the mixed acid solution was produced in the acid compartment, and the base solution was produced in the base compartment. The results showed that 1 mol/L mixed acid and sodium hydroxide could be produced continuously at a constant current density of 57 mA/cm^2 and a flow rate of 0.30 L/h in the continuous-mode BMED. After the production of the acid and base solution, membrane fouling was inspected by measuring the stack resistance and using electron microscopy and surface elemental analysis. No visible fouling deposits on the surface of the CEMs (AEMs) were observed, and there was an increased stack resistance, thus proving that the BMED process for mixed acid production with pretreated RO concentrate is suitable for a long-term run.

1. Introduction

Because of the decreasing availability of natural water resources and the increasing water demand, the lack of potable water is one of the greatest challenges around the world. The supply of water resources is falling behind the needs of a rapidly growing population. Seawater desalination, an effective means to obtain fresh water, eases the worries about the water resource crisis [1–4].

Seawater desalination technology includes multistage flash (MSF), multi-effect distillation (MED), reverse osmosis (RO) and electrodialysis (ED) [5], and each technology plays a special function for different water quality and different areas. RO has developed rapidly due to the simplicity of the process, the stable quality of the water produced and the relatively low cost of the process. Regardless of the technique, a pretreatment process is necessary to avoid fouling, scaling and corrosion problems; this is especially the case for RO. pH control by the addition of acid solution (sulfuric acid or hydrochloric acid) is one pretreatment step for controlling membrane scaling; however, the transportation and storage of a large amount of sulfuric acid or hydrochloric acid lead to some hidden risks, especially for desalination plants located far from sulfuric or hydrochloric acid plants.

For the application of RO and other desalination technologies, one of the most important issues is the treatment of RO concentrate as a by-product generated from the desalination process. Traditionally, RO concentrate has been discharged directly into seawater, which is the most economical choice but is not environmentally friendly [6]. Based on 40% recovery, 60% of the RO concentrate would be discharged back to the offshore areas, where it becomes a potentially serious threat to marine ecosystems and the environment. Gonzaález et al. [7] have given a brief overview of potential treatments to overcome the environmental problems associated with the direct discharge of RO concentrate, and many other researchers have made continuous efforts toward increasing the water recovery or zero liquid discharge (ZLD). The conventional technique (solar evaporation) and emerging technologies (including membrane distillation, electrodialysis and forward osmosis) for dealing with the concentrate have been tested; however, the above mentioned methods have either high capital costs or technical obstacles, and direct discharge is still regarded as the first choice in many countries. On the other hand, RO concentrate contains a large amount of dissolved ions, which is approximately two times higher than that of natural seawater. Direct discharge not only increases the salinity of offshore areas but also squanders resources, so an economical method would take advantage of the useful ingredients in the RO concentrate.

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In particular, Badruzzaman et al. [8] reused RO concentrate from a wastewater treatment plant (WWTP) using bipolar membrane electrodialysis (BMED) and electrochlorination techniques to convert the dissolved ions, such as sodium ions and chloride ions, into useful chemical products. In contrast to RO wastewater concentrate, RO concentrate from SWRO has a higher salinity, with an especially high content of sodium ions and chloride ions that can be used to produce hydrochloric acid and sodium hydroxide.

To meet the requirements of the acid solution for the RO seawater desalination pretreatment process and to take advantage of the useful ingredients in RO concentrate, BMED was used to convert RO concentrate into acid and base, and the acid was then applied to the pretreatment process for seawater desalination. As a traditional, established process, electrodialysis has been used for more than 50 years on a large industrial scale for the production of potable water from brackish water sources [9]. More recently, electrodialysis, in combination with bipolar membranes, has been the focus of several new applications in the chemical processing industry, in the food and drug industry and in environmental protection [10–18]. In terms of the production of acid and base from industrial wastewaters [19–21], many experimental studies have shown promising results. However, the application of BMED to produce acid and base from waste streams such as RO concentrate has rarely been investigated. This research has successfully demonstrated the proof of principle of the above-mentioned technologies for RO seawater concentrate management. The specific objectives of this study were (a) optimization of the BMED processes using simulated RO seawater concentrate and (b) the production of acid and base using BMED from RO seawater concentrate. We created an internal circulation between the seawater desalination pretreatment process and the SWRO concentrate. The results showed that 1 mol/L mixed acid and sodium hydroxide could be produced continuously at a constant current density of 57 mA/cm^2 and a flow rate of 0.30 L/h in the continuous-mode BMED, and no visible fouling deposits were observed on the surface of the CEMs (AEMs), thus proving that the BMED process for mixed acid production from pretreated SWRO concentrate is suitable for a long-term run.

2. Theory

BMED is a technique that utilizes conventional electrodialysis and operates by utilizing enhanced ionic mobilities under an applied potential and by limiting the movement of ions using ion selective membranes in conjunction with a bipolar membrane [8], which is used to split water into hydrogen ions and hydroxide ions. The application of BMED is shown in Fig. 1. When a direct electrical potential is established, the water molecules at the interphase of the bipolar membrane are split into hydrogen ions and hydroxide ions, and the hydrogen ions combine with anions migrating from the feed/salt compartment through the anion exchange membrane (AEM) to generate acid in the acid compartment. Meanwhile, the hydroxide ions combine with cations migrating from the feed/salt compartment through the cation exchange membrane (CEM) to produce the corresponding base in the base compartment [22]. In this experiment, RO concentrate, after the removal of calcium ions and magnesium ions, was pumped to a BMED system as the feed. Sodium ions (main cation) in the RO concentrate were driven across the cation exchange membrane and combined with hydroxide ions to produce a base under a direct current (DC) voltage applied to the electrodes. Similarly, chloride ions and sulfate ions (main anions) migrating toward the anode passed through the anion exchange membrane and combined with hydrogen ions to produce the mixed acid. The conversion from the dissolved ions in the RO concentrate into acid and base is shown:

$$H_2O \rightarrow H^+ + OH^- \quad \text{(Interphase of bipolar membrane)} \tag{1}$$

$$H^+ + Cl^- + SO_4{}^{2-} \rightarrow HCl + H_2SO_4 \quad \text{(Acid compartment)} \tag{2}$$

$$OH^- + Na^+ \rightarrow NaOH \quad \text{(Base compartment)} \tag{3}$$

The current efficiency and energy consumption are important for the characterization of the bipolar electrodialysis process [8]. The current efficiency (%) is given by

$$\eta = \frac{n(c_t - c_0)VF}{NIt} \tag{4}$$

where C_t and C_0 are the concentrations of acid in the acid compartment at time t and 0, respectively. V is the circulated volume of solution in each tank, I is the current, F is the Faraday constant, and N is the number of cell triplets. The energy consumption can be defined by the following equation.

$$E = \int \frac{UIdt}{C_t VM} \tag{5}$$

Here, U is the potential across the cell stack (V), and M stands for the molar weight of hydrochloric acid.

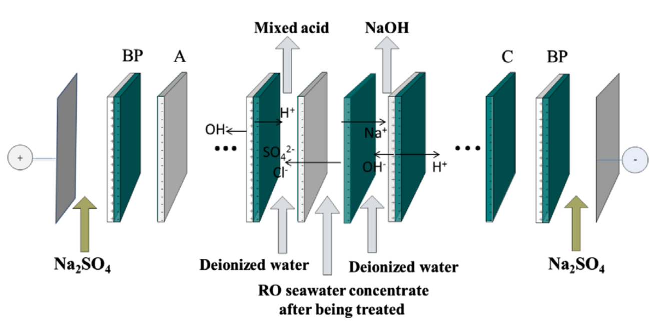

Fig. 1. Schematic of the BMED system operating principle for the conversion of acid and alkali from the RO concentrate (BP: bipolar membrane, A: anion exchange membrane, C: cation exchange membrane).

3. Materials and methods

3.1. Reagents and membranes

All of the reagents were of analytical grade, and deionized water was used throughout. The heterogeneous cation exchange membrane and the anion exchange membrane were purchased from Qianqiu Environmental Protection & Water Treatment Corporation (China), and the bipolar membranes were commercially obtained from FuMA-Tech GmbH (Germany). The characteristics of these membranes are identical to those of the membranes used in the literature [23], and they were installed in a laboratory-scale ED stack purchased from

Table 1
The main characteristics of the membranes.

Membrane	Area resistance (Ω cm^2)	Thickness (mm)	IEC (meq g^{-1})	Selectivity (%)	Efficiency (%)
BPM	<3	0.18–0.2			98
AEM	15	0.6	1.8	>392	
CEM	20	0.6	2.0	>394	