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Boron removal from saline water by a microbial desalination cell integrated with donnan dialysis

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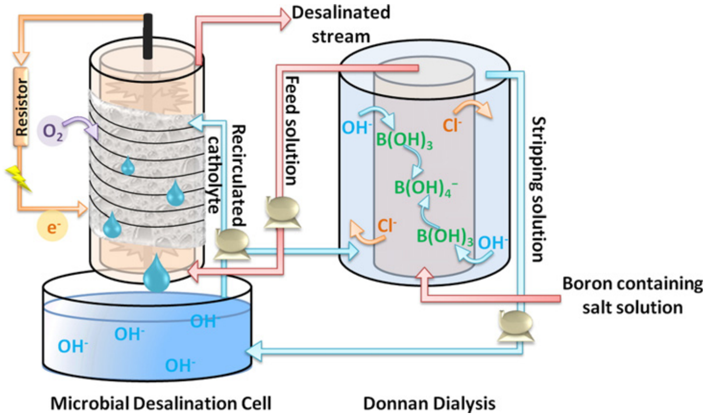
HIGHLIGHTS

- Donnon dialysis can assist with boron removal in an MDC system.
- The alkaline solution generated by the MDC acts as a stripping medium.
- The key challenge is to convert boron to borate ions.
- Boron removal is via both diffusion and ion exchange.
- Salinity of the salt solution can affect boron removal through ion competition.

GRAPHICAL ABSTRACT



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ABSTRACT

Boron has toxic effects on plant growth and thus its removal is necessary from desalinated saline water for irrigation application. Microbial desalination cells (MDCs) are a new approach for effective desalination but boron removal has not been addressed before. Herein, MDCs were studied for boron removal with aid of Donnan Dialysis (DD). The alkaline solution generated by the MDC cathode was used to ionize boric acid to facilitate boron removal. An MDC system with DD pretreatment removed 60 or 52% of boron with the initial boron concentration of 5 or 20 mg L^{-1}. In the absence of DD, direct cathodic alkalinization of boron in an MDC was not effective in terms of boron removal and had a serious issue of salt accumulation. The MDC with DD post-treatment could reduce the boron concentration below 2 mg L^{-1}, although the high pH of its final effluent needs to be further addressed. Further investigation will consider an MDC system with both DD pre-treatment and post-treatment for improving boron removal.

1. Introduction

Boron is a common element in brackish water having a concentration up to 40 mg L^{-1} and in seawater around 5 mg L^{-1} [1,2]. Boron is an essential element for plant growth, but the high-concentration boron in the irrigation water could damage plants. Many plants

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encounter toxicity problems when the concentration of boron exceeds 2 mg L^{-1}, and some sensitive plants cannot tolerate a boron concentration greater than 0.3 mg L^{-1} [1]. Thus, when desalinating saline water for irrigation use, boron removal will be necessary. The world's largest desalination plant, the Ashkelon Seawater Reverse Osmosis (SWRO) plant in Israel, has incorporated boron removal as post-treatment after the multi-stage RO. Boron exists in water in the form of boric acid, and because of boric acid's non-dissociative character, pH amendment must be applied according to the pKa value of boric acid (9.14) to ionize boric acid before treating boron-containing water (as shown in Eq. (1)). Effective removal of boron has been accomplished by electro-flocculation, ED, or RO, and no matter which method is applied, the key is to raise pH ionizing boric acid to the charged form (borate) [1,3,4]. The pH adjustment is usually conducted by adding sodium hydroxide, thereby increasing the operating cost and thus the price of the desalinated water.

$$B(OH)_3 + H_2O \Leftrightarrow B(OH)_4^- + H^+ \quad (1)$$

High-pH solution is a side product of desalination by microbial desalination cells (MDCs), and this feature may be used to facilitate boron removal. MDCs are bioelectrochemical systems through integrating electrodialysis into microbial fuel cells (MFCs) [5], and the overview of this technology can be found in the recent review papers [6–8]. Although still at an early stage of development, the MDC technology has been advanced with improved desalination through optimizing reactor configurations [9–12], applying resin in the desalination compartment to reduce internal resistance [13,14], or adjusting pH with electrolyte recirculation [15,16]. Fundamental studies have revealed the diverse microbial community in the anode of an MDC [17,18], and mathematical modeling has helped to explicitly analyze the desalination process [19,20]. In a recent study, an MDC system with a total liquid volume of 105 L was developed with a desalination rate up to 9.2 ± 0.2 kg TDS m^{-3}-d^{-1} by applying an additional external voltage [21]. Considering the low desalination rate, MDCs may be applied for 1) desalinating seawater as pretreatment followed by conventional desalination methods and offsetting energy consumption via extracting bioenergy from wastewater; and 2) desalinating brackish water for irrigation application. MDCs have been demonstrated for successful removal of multiple ions from brackish water, such as sodium, calcium, magnesium, chloride and sulfate, to meet irrigation guidelines [19]. However, boron removal has not been studied in MDCs. If MDCs will be applied for desalination, boron issues must be properly addressed.

Oxygen reduction reaction on the cathode of an MDC accumulates hydroxide ions [22] with a side product of alkaline solution:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (2)$$

This hydroxide-ion abundant catholyte from an MDC can serve as an alkaline solution in Donnan Dialysis (DD) that may be used to produce dissociated borate for boron removal in the MDC and/or through ion exchange. DD is a pH modifying treatment process that the pH of the target solution can be elevated without raising conductivity. When an alkaline solution is used as the stripping solution and a target solution as the feed solution in a DD device equipped with AEM (anion exchange membrane), the difference in chemical potential of hydroxide ions drives the diffusion of hydroxide ions from the stripping solution into the feed solution, and meanwhile extracts negative ions from the target solution. In the case of pretreatment of boron-containing saline solution, anions such as chloride ions will likely compete with borate ions for extraction because of its abundance.

In this study, we have proposed and investigated an MDC system integrated with DD to treat boron-containing saline water. In the system where DD acts as a pre-treatment process (Fig. 1), the saline water is firstly treated in the DD device that uses the catholyte of the MDC as a stripping solution and converts boric acid to borate; then, the DD feed effluent is desalinated in the MDC for boron removal that has borate moving from the desalination compartment into the anode effluent. Such a process takes advantage of ion separation and accumulation of hydroxide ions in an MDC and ion exchange in the DD. The objectives of this study were to: (1) examine the feasibility of the system; (2) study the effect of pH in DD stripping solution and salt loading on boron removal; and (3) examine different integration approaches including direct cathodic alkalinization of the salt solution, DD as pretreatment before MDC, and DD as post-treatment after MDC.

2. Materials and methods

2.1. MDC setup and operation

The MDC was constructed as a tubular reactor similarly to the one in the previous studies [19,20], consisting of two layers of ion exchange membranes (IEM): anion exchange membrane (AEM, AMI-7001, Membrane International, Inc., Glen Rock, NJ, USA) with a 3.8-cm diameter and a 20-cm length forming the anode compartment (300 mL), and cation exchange membrane (CEM, CMI-7000, Membrane International, Inc.) that had a diameter of 5 cm and a length of 20 cm wrapping the AEM tube and creating a space between the two membrane tubes that formed a desalination compartment (150 mL). The distance between the AEM and the CEM was 0.6 cm. The anode electrode was a 20-cm long carbon fiber brush, and the cathode electrode was a piece of carbon cloth coated with activated carbon supported platinum (Pt/C) as a catalyst at a loading rate of 0.2 mg Pt cm^{-2}. An external resistor of 0.1 Ω connected the two electrodes by using titanium wire. The anode feed solution contained (per L of tap water): NaAc, 3 g (to ensure sufficient substrate supply); NH_4Cl, 0.15 g; NaCl, 0.5 g; $MgSO_4$, 0.015 g; $CaCl_2$, 0.02 g; KH_2PO_4, 0.53 g; and K_2HPO_4, 1.07 g. The anolyte was fed at a rate of 0.5 mL min^{-1} (HRT of 10 h), unless elsewhere stated, and was recirculated at 100 mL min^{-1}. The salt solution (saline water) was prepared to mimic brackish water, and contained (per L of tap water): NaCl, 3 g; and H_3BO_3, 0.028 or 0.112 g. The catholyte was either tap water or prepared by dissolving NaOH in tap water, dripping from the top to the bottom of the outer tube for rinsing the cathode electrode at a recirculation rate of 35 mL min^{-1}.

2.2. Donnan dialysis

The DD device was an AEM tube with the volume of 300 mL submerged in a 1 L container. The tube was filled with salt solution (feed solution) recirculated at 35 mL min^{-1}, and the container was filled with alkaline solution (stripping solution) either from the MDC catholyte or prepared by dissolving NaOH in tap water.

2.3. Measurement and analysis

The MDC voltage was recorded every 3 min using a digital multimeter (Keithley Instruments, Inc., Cleveland, OH, USA). The conductivity of the salt solution was measured using a benchtop conductivity meter (Mettler-Toledo, Columbus, OH, USA). The pH was measured by a benchtop pH meter (Oakton Instruments, USA). The boron concentration was measured by using the Carmine method (HACH Co., Ltd., USA, method 10252).

3. Results and discussion

3.1. Feasibility of boron removal

The feasibility of boron removal was examined by using an additional alkaline solution as a stripping solution in the DD. The MDC system was operated in a batch mode. The reason why a synthetic alkaline solution was applied instead of the MDC catholyte was to achieve better manipulation of the pH. A control experiment without the DD