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Membrane capacitive deionisation as an alternative to the 2nd pass for seawater reverse osmosis desalination plant for bromide removal

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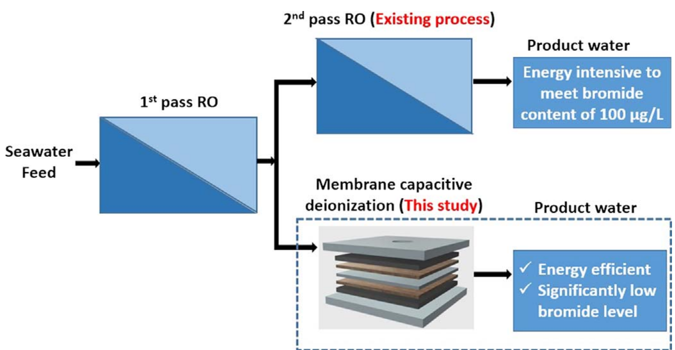
GRAPHICAL ABSTRACT



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ABSTRACT

Most Australian surface and ground waters have relatively high concentration of bromide between 400 and 8000 µg/L and even higher concentration in seawater between 60,000–78,000 µg/L. Although bromide is not regulated, even at low concentrations of 50–100 µg/L, it can lead to the formation of several types of harmful disinfection by-products (DBPs) during the disinfection process. One of the major concerns with brominated DBPs is the formation of bromate (BrO_3^-), a serious carcinogen that is formed when water containing a high concentration of bromide is disinfected. As a result, bromate is highly regulated in Australian water standards with the maximum concentration of 20 µg/L in the drinking water. Since seawater reverse osmosis (SWRO) desalination plays an important role in augmenting fresh water supplies in Australia, SWRO plants in Australia usually adopt 2nd pass brackish water reverse osmosis (BWRO) for effective bromide removal, which is not only energy-intensive to operate but also has higher capital cost. In this study, we evaluated the feasibility of membrane capacitive deionisation (MCDI) as one of the alternatives to the 2nd pass BWRO for effective bromide removal in a more energy efficient way.

1. Introduction

Australia is one of the driest regions on earth, and it has experienced severe droughts in the past that significantly affected rain-dependent water sources. As a result, Seawater Reverse Osmosis (SWRO), where, seawater is passed through a semi-permeable membrane at high

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pressure to produce freshwater is pursued as a major technology to augment fresh water supplies. Globally, about 38 billion m^3/year of desalinated water is currently produced from > 18,000 desalination plants located in 150 countries, and it is projected that the capacity will reach 54 billion m^3/year by 2030 [1]. Similarly, a significant investment is made in desalination plants in Australia to secure country's water supply. Its current and planned large-scale SWRO plants have a total capacity of 1874 ML/d [2] with a total investment in desalination plants exceeding AU$ 10 billion already [3]. However, the presence of high concentration of bromide in seawater presents a unique challenge. Unlike the conventional single-pass SWRO plants operated globally, most of the SWRO plants in Australia have to adopt two-stage RO process; 1st pass SWRO followed by 2nd pass BWRO to achieve effective bromide removal as depicted in Fig. 1(a). This additional pass increases both the capital cost and the operation cost. Therefore, any alternative energy efficient process with effective bromide removal could significantly help reduce SWRO desalination cost.

Bromide is a precursor for the formation of several types of disinfection by-products (DBPs) during water disinfection process [4–6]. > 600 types of DBPs have been recorded [7] with much more yet to be identified. It is also well-established that, not only greater health risks are associated with brominated DBPs than chlorinated DBPs, but when a high concentration of bromide is present, the brominated DBPs are more dominant as well [5, 8, 9].

One of the major concerns with bromide-related DBPs is the formation of bromate, a highly regulated carcinogen [10, 11]. Currently, Australian standard for bromate is 20 μg/L whereas other countries such as the US, China, Canada, EU, Japan and WHO guidelines set the bromate limit to be 10 μg/L [12]. The Australian Beverages Council Ltd. recommends a very strict bromide level of 10 μg/L before disinfection to comply with a bromate limit of 20 μg/L. Several factors such as bromide concentration, the presence of organic matter, pH, ozone dose and reaction time are known to contribute to bromate formation [13]. Even with the bromide concentration of 50–100 μg/L, excessive formation of bromate is a serious concern, and once it is formed, its removal is reported to be uneconomical and difficult [14].

There are several technologies used and evaluated for bromide removal from water such as RO, NF, electrodialysis and adsorption techniques [15]. Among these processes, SWRO has the highest bromide rejection rates. However, despite its effectiveness, SWRO is still considered to be an expensive process for water production. Depending on the SWRO membranes used, a bromide concentration of 100 μg/L to 1000 μg/L is still expected in most first pass SWRO permeate. Therefore, SWRO desalination plants in Australia generally have to adopt two-stage RO process as mentioned above mainly for effective bromide removal but at a signficant additional cost. Other conventional treatment processes such as coagulation and flocculation processes and media filtration are found to be ineffective for bromide removal [15, 16].

The Capacitive Deionisation (CDI) is an electrosorption process to remove ionic impurities from the wastewater due to the formation of electric double layer (EDL), where the ions are temporarily adsorbed on the surface of the charged electrodes [17]. The technology is primarily suitable for desalination of brackish water. However, recently, the CDI application has significantly widened to include other water treatment processes such as water softening and selective removal of specific cations such as heavy metals [18, 19]. It has also been used for removal of nitrate and phosphates [20, 21] and production of ultra-pure water [22–24]. Unlike other desalination processes such as RO, CDI process operates at low pressure, and it is found to be energy efficient to treat low salinity water [25, 26]. Moreover, the fact that 47–83% of the energy spent in CDI can be recovered makes CDI an energy efficient process for desalination [27, 28]. Further, it has been demonstrated that the operational parameters can be tuned to obtain the required effluent quality [29, 30].

The membrane CDI (MCDI), which incorporates cation and anion ion exchange membranes to improve ion selectiveity in CDI is found to improve desalination efficiency and reduce energy consumption. This is due to better ion selectivity as well as inhibition of co-ion desorption from the electrodes during desorption [31–33]. Since the first demostration of MCDI in desalination of thermal power wastewater [34], the MCDI configuration has been widely adopted as a promising technology for water treatment. The use of ion exchange membranes has also made it possible to innovatively use the MCDI for selective removal of ions by coating ion exchange resin on the electrode for better selectivity such as nitrate and lithium ions from mixed solution [35, 36]. Recently, a novel and innovative concept was introduced, where a monovalent cation selective membrane was used in MCDI to produce divalent cation-rich solution as a means to stabilise permeate from NF/LPRO [37].

In this paper, the application of MCDI for bromide removal from the 1st pass SWRO permeate was systematiclly investigated as a potential alternative to the 2nd pass BWRO as shown in Fig. 1(b). The effect of feed water qualities such as bromide concentration, TDS and pH were varied to understand their influences on bromide removal. Similarly, the effect of operating conditions such as applied voltage, flow rates and operating time on bromide removal were assessed to determine the optimum operating conditions for MCDI operation. Finally, for practical application purpose, a real 1st pass SWRO permeate was used as an actual feed to determine bromide removal efficiency. A detailed assessment of bromide removal efficiency and energy consumption in MCDI and the 2nd pass BWRO was compared, and recommendations to further improve bromide removal and energy efficiency in MCDI were also discussed.

2. Materials and methods

2.1. Lab-scale MCDI

The lab-scale MCDI cell consisted of a pair of porous carbon electrodes (Siontech Co., Korea) made of activated carbon P-60 (Kuraray Chemical Co., Japan) of 100 mm × 100 mm dimensions coated on a graphite current collector. The electrodes were separated by a non-conductive nylon spacer (200 μm) to prevent electrode short-circuit, and it also served as flow distribution within the cell. The BET surface area and the weight of the activated carbon as per the manufacturer were 1689.5 m^2/g and 1.6 g, respectively. The cation (CMB) and anion (Neosepta AFN) exchange membranes (ASTOM Corp., Japan) were placed in front of cathode and anode respectively to enhance ion selectivity. The whole unit was supported by a pair of acrylic plate. The feed water was pumped using a peristaltic pump (GTS 100, Green Tech, Korea) from a fixed feed volume of 50 ml, and the effluent was constantly recycled into the feed reservoir under a batch-mode MCDI operation. An electrical voltage applied to the electrodes was regulated using a potentiostat (ZIVE SP1, WonATech Co., Korea). Before each experiment, the MCDI unit was stabilised by repeated adsorption and desorption for 2 min each until a dynamic equilibrium was reached to ensure cycle replicability. All the experiments were done as per the experimental design (Table 1) with reverse voltage desorption for the same duration as the adsorption time using 800 ml Milli-Q water. The schematic of the CDI unit and its operation is presented in Fig. 1(c).

2.2. Feed water preparation

Feed water was prepared by dissolving analytical grade NaBr (Sigma Aldrich, Israel) in 18 MΩ cm resistivity Milli-Q water. Firstly, to understand the fundamental response of bromide removal under different types of water quality and operational parameters, feed water with Br^- concentrations of 1, 5 and 10 mg/L as Br^- (single electrolyte solution with NaBr) was prepared. This concentration range simulates real water bromide concentration in the 1st pass SWRO permeate, as well as bromide concentration in other surface water system in Australia. To understand the effect of background total dissolved solids