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5	Membrane capacitive deionisation as an alternative
6	to the 2 nd pass for seawater reverse osmosis
7	desalination plant for bromide removal
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10	Desalination
11	October 2017
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Abstract

Most Australian surface and ground waters have relatively high concentration of bromide between 400-8,000 μ g/L and even higher concentration in seawater between 60,000-78,000 μ g/L. Although bromide is not regulated, even at low concentrations of 50-100 μ g/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 (BrO₃-), 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 μ g/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 deionization (MCDI) as one of the alternatives to the 2nd pass BWRO for effective bromide removal in a more energy efficient way.

Keywords: desalination, membrane capacitive deionization, bromide, disinfection byproducts, reverse osmosis

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 pressure to produce freshwater is pursued as a major technology to augment fresh water supplies. Globally, about 38 billion m³/year of desalinated water is currently produced from more than 18,000 desalination plants located in 150 countries, and it is projected that the capacity will reach 54 billion m³/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]. More than 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 μ g/L whereas other countries such as the US, China, Canada, EU, Japan and WHO guidelines set the bromate limit to be 10 μ g/L [12]. The Australian Beverages Council Ltd. recommends a very strict bromide level of 10 μ g/L before disinfection to comply with a bromate limit of 20 μ g/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 μ g/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 $100~\mu g/L$ to $1,000~\mu g/L$ 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 significant 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 Deionization (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 stabilize permeate from NF/LPRO [37].

In this paper, the application of MCDI for bromide removal from the 1st pass SWRO permeate was systematically 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.

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 x 100 mm dimensions coated on a graphite current collector. The electrodes were separated by a nonconductive 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 m²/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 two minutes 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).

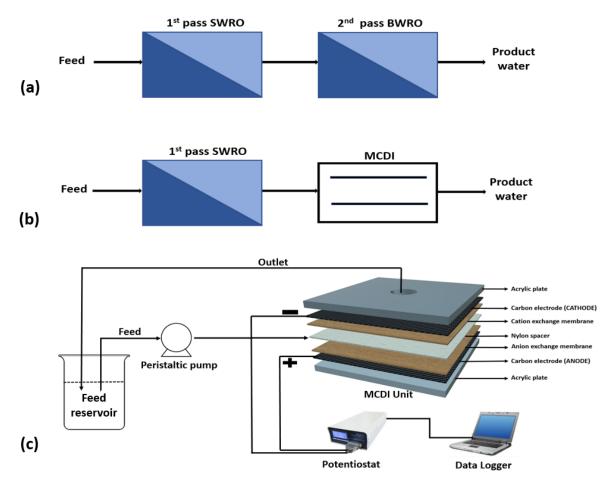


Figure 1: Schematic process diagram (a) existing second-pass SWRO configuration (b) proposed SWRO-MCDI hybrid (c) process schematic of lab-scale MCDI operation.

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 (TDS) on bromide removal, NaCl (AnalaR, MERCK Pty. Limited, Australia) solution with different TDS of 100, 200, 300, 400 mg/L was used with a bromide concentration at 1 mg/L.

To demonstrate the practical applicability of the MCDI, the 1st pass SWRO permeate was obtained from a lab-scale SWRO unit operation using SWC5 RO membrane (Hydraunatics,

167 USA). The lab-scale SWRO used in this study consisted of a stainless steel RO membrane cell (14.5 cm x 9.5 cm x 0.185 cm) with an effective membrane area of 137.75 cm² connected to 168 169 a high-pressure pump controlled manually using a feed valve, by-pass valve, back pressure 170 regulator, pressure gauge and a flow meter. A 10 L actual seawater collected from Rose Bay, 171 New South Wales in Australia with a TDS of 38,400 and bromide concentration of 75.8 mg/L 172 was passed through the RO membrane at a crossflow rate of 1 L/min and an applied pressure 173 of 60 bar. The RO permeate was collected while the brine was constantly recycled into the feed 174 water reservoir. The 1st pass SWRO permeate from the lab-scale unit was further diluted using DI water to obtain the 1st pass permeate with different TDS (100, 200, 300 and 400 mg/L) to 175 represent typical 1st pass SWRO permeate in actual desalination plants. 176

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2.3 Sample analysis

The water samples were analysed using ICP-MS 7900 (Agilent Technologies, Japan) after calibration using a standard Br⁻ solution (TPS, Water Quality Instruments, Australia) for a concentration range from 0-5 mg/L. All the tests were done in duplicates, and average values are presented. The bromide removal efficiency was calculated using the equation (1) as follows:

184 Bromide removal efficiency (%) =
$$\frac{C_0 - C}{C_0} * 100$$
 (1)

185 Where C_0 and C represent initial and final bromide concentrations (mg/L) in the feed water and 186 treated water, respectively. The same methodology was used to calculate the TDS removal 187 efficiencies by monitoring the electrical conductivity. The energy consumption was calculated 188 using the equation (2):

189 Energy (kWh/m³) =
$$\frac{E_{ads} \int_0^t I_{ads}(t)dt + E_{des} \int_0^t I_{des}(t)dt}{V}$$
 (2)

Where, *E*, *I* and *t* represent voltage, current and time respectively. The subscripts ads and des refer to adsorption and desorption stages, and *V* is the amount of treated water produced per cycle.

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Table 1 Water quality and experimental conditions in the lab-scale MCDI.

Test parameter	Water quality			Operational condition		
	Ion composition	TDS (mg/L)	pН	Applied	Flow rate	Operating time
				Voltage (V)	(ml/min)	(min)
Br Conc. (mg/l)	Na ⁺ , Br ⁻	1, 5, 10	7	1	40	10
TDS (mg/L)	Na ⁺ , Cl ⁻ , Br ⁻	100, 200, 300, 400	7	1	40	10
pH	Na ⁺ , Br ⁻	1, 5, 10	4, 7, 10	1	40	10
Applied voltage (V)	Na ⁺ , Br ⁻	1, 5, 10	7	0.4, 0.7, 1	40	10
Operating time (min)	Na ⁺ , Br ⁻	1, 5, 10	7	1	40	1, 3, 5, 10
Flow rate (ml/min)	Na ⁺ , Br ⁻	1, 5, 10	7	1	20, 40	10
SWRO permeate (mg/L)	Mixed ions	100, 200, 300, 400	7	1	40	1, 2, 3, 4, 5, 10

Results and discussions

3.1 Influence of water quality on the bromide removal

The feed water quality such as bromide concentration, background TDS and pH are important parameters, which determine the overall performance of the MCDI. Therefore, the influence of each of the water quality parameter in the removal of bromide by MCDI is presented in the following sections.

3.1.1 Influence of bromide concentration and the feed water TDS

To evaluate the effect of bromide concentration on MCDI performance, three different types of feed water with different bromide concentration (1, 5 and 10 mg/L as Br⁻ prepared in Milli-Q water) were tested. Fig. 2(a) shows the bromide removal efficiency ranged from 99.5% to 99.9% for all the water tested. A slightly lower removal efficiency for 1 mg/L bromide feed water was observed probably due to the higher electrical resistance of the dilute feed water with low electrical conductivity due to very low Br⁻ concentration. Since the overall TDS of the feed water tested was low (Br⁻ solution prepared in MQ water), higher bromide removal is not unusual because the Br⁻ ions have more accessible surface area to be adsorbed on the electrodes. However, the presence of competing ions can have a significant influence on bromide removal depending on the ionic charge, hydrated radius and the concentration of competing ions [38].

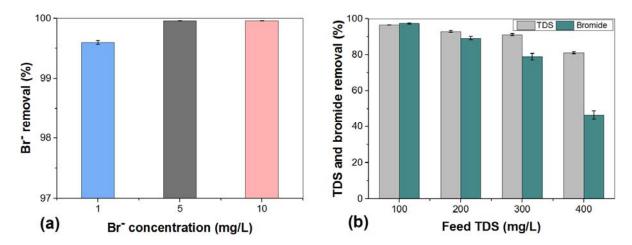


Figure 2: (a) effect of bromide concentration containing only single electrolyte on bromide removal efficiency (b) bromide removal under various background TDS mainly consisting of NaCl with a fixed bromide concentration of 1 mg/L for all types of feed water. The operational voltage and operating time were 1 V and 10 minutes, respectively.

Fig. 2(b) illustrates the influence of background TDS on the bromide removal by MCDI process. The desalination efficiency in CDI process is highly dependent on the feed water TDS since the ions removal mechanism in MCDI involves temporary storage of adsorbed ions on the limited electrode surface. While the bromide removal was 97.4% and 90% in the presence of 100 and 200 mg/L NaCl respectively, the bromide removal efficiency was significantly reduced to about 79% and 46 % as the background NaCl concentration was increased to 300 and 400 mg/L. The TDS removal, however, varied from 81% to 96 % for all the feed water types tested in this study. The results show that bromide removal is drastically affected in the presence of background competing ions such as from NaCl mainly due to the presence of a much higher concentration of chloride ions compared to bromide ions. It is interesting to note that at lower TDS, bromide removal was quite significant probably due to the smaller hydrated size of Br compared to Cl ions, findings which are consistent with these studies [38-40]. However, at higher TDS, the high concentration of chloride ions severely impedes the adsorption of bromide ions, which further confirms that under mixed ionic environment, the ions with the highest concentration have more selectivity for adsorption [41, 42]. In practical application, however, the 1st pass SWRO permeate contains multiple ions with different ionic properties. Therefore, bromide removal efficiencies can significantly vary when multiple ions are present in the feed water.

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3.1.2 pH of the feed water

The bromide removal efficiencies at different pH conditions were above 99% for all types of feed water (Fig. 3) indicating that pH variation did not have any significant impact on bromide removal for the given bromide concentrations. It is expected that there will be competition between Br and OH for adsorption at high pH condition, which partially explains the slight reduction in bromide removal from 99.5% at pH 4 to 99.1% at pH 10. Other studies on bromide removal also did not observe any specific pH effect on bromide removal [4]. Unlike boron and phosphate whose removal with CDI depends on pH since they take different chemical forms based on the pH [20, 43], bromide removal does not seem to have any specific association with pH variation.

100 1 mg/L 5 mg/L 10 mg/L 99 - 10 mg/L 99 -

pH

Figure 3: The influence of pH on bromide removal at a flow rate of 40 ml/min, applied voltage of 1 V and adsorption time of 10 minutes.

3.2 Influence of operating parameters

The voltage, operating time and flow rate are some of the critical operational parameters to be considered in optimising the performance of the MCDI system. The following sections highlight the results of these parameters on bromide removal.

3.2.1 Applied voltage and operating time

The desalination efficiency of any CDI or MCDI operation is directly proportional to the applied voltage because, at a higher voltage, a thicker electrical double layer is formed which

leads to higher ion storage capacity of the electrodes. However, exceeding the voltage threshold of 1.23 V is not recommended due to excessive current leakage because of the splitting of water molecules by electrolysis [44]. For the feed water containing only NaBr, bromide removal ranged from 98.4% to 99.9% for the entire range of voltage applied (0.4, 0.7 and 1 V) as shown in Fig. 4(a). This high bromide removal is expected since the TDS of the feed was not high enough to completely saturate the electrodes. Although the bromide removal efficiencies were consistently high (>99.91%) for feed water containing 5 and 10 mg/L of bromide for the applied voltage range, a slightly lower removal efficiency (98%) is observed for the feed water containing 1 mg/L of bromide at 0.4 V. This lower bromide removal may be explained by the fact that, the low applied voltage was not able to overcome the higher resistance of the dilute feed water with low electrical conductivity. However, with the increase in voltage to 0.7 and 1 V, bromide removal efficiency exceeded 99.5% mainly by overcoming the higher resistance of the dilute feed water.

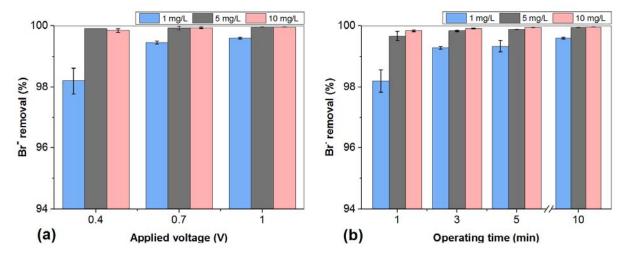


Figure 4: The effect of (a) applied voltages at 10 minute adsorption time (b) operating time on bromide removal at 1 V pH 7.

Another important parameter for process optimisation in MCDI operation is the effect of operating time, which has a significant influence on the treated water quality and energy consumption. The operation time in this study refers to the adsorption duration in which the MCDI unit was operated in a batch mode. As observed in Fig. 4(b), bromide removal efficiency ranged from 98.2% to 99.9% for the operating time tested between 1 to 10 minutes, indicating that at these Br⁻ concentrations and TDS values, the adsorption process is quite rapid. Within about 5 minutes of operation, the bromide removal has already reached higher than 99.9%, which is more than adequate for water quality, and MCDI operation beyond this time duration

is only likely to increase the water cost. Further, by getting better insights into the time selectivity of various ion (removal of one type of ion relative to other ions) removal from the feed water [45], it is possible to optimise the MCDI operation.

3.2.2 Effect of feed water flow rate

The effects on bromide removal by MCDI process at different feed flow rates of 20 and 40 ml/min are shown in Fig. 5. The bromide removal efficiencies for all the three feed water types were within 99.5% to 99.9%, indicating the minimum effect of the flow rates on the MCDI performance, which is normally the case under a batch-mode process [44]. This is likely because enough time is available for ion adsorption on the electrodes since the treated water is constantly recycled into the feed reservoir when operated in a batch mode. A similar phenomenon was also observed by, where varying flow rates in a batch-mode CDI process (larger CDI module) had little influence on electrosorption from a solution containing only single electrolyte [21]. In contract, however, for a single-pass MCDI operation, which is more representative of the practical application of MCDI, flow rates invariably affect the adsorption efficiency [38]. Therefore, optimising the flow rate for optimum energy consumption and water quality is an important parameter for optimal MCDI performance.

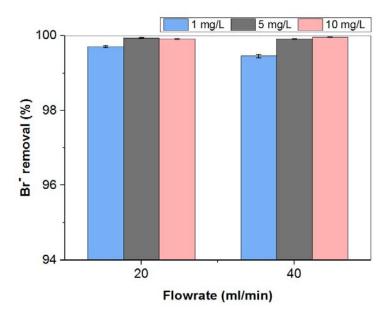


Figure 5: Influence of flow rates on bromide removal efficiency at the applied voltage of 1 V and operating time of 10 minutes.

3.3 Bromide removal from a real 1st pass SWRO permeate

3.3.1 Bromide removal from the 1st pass SWRO permeate

The bromide removal from the actual 1st pass SWRO permeate was evaluated for feed water with varying TDS of 100, 200, 300 and 400 mg/L to cover a wide range of SWRO permeate depending upon the plant operational parameters. Fig. 6(a) shows the final bromide concentration after treatment with MCDI. For feed TDS of 100, 200 and 300 mg/L, the final bromide concentration was 8, 14 and 74 µg/L, respectively after 10 minute adsorption, which is lower than 100 µg/L, a standard design requirement in most SWRO plants in Australia. However, depending on the feed TDS, even shorter adsorption time is adequate to meet the guideline value for bromide as depicted in Fig. 6(a). For SWRO permeate TDS of 400 mg/L however, the final bromide concentration was 197 µg/L after 10 minute adsorption, which means additional treatment is required to meet the Australian standard for bromide in the drinking water. When the voltage was increased to 1.2 V, the final bromide concentration for the feed TDS of 400 mg/L was reduced to 84 µg/L corresponding to 89 % removal and also the TDS removal was increased from 78.4% at 1 V to 90% at 1.2 V, mainly due to the formation of thicker electrical double layer which enhanced the overall salt adsorption capacity of the electrodes. For comparison, a study by using 24 pairs of eletrodes in CDI on diluted seawater observed bromide removal of 86 % (feed Br concentration of 340 µg/L and feed TDS of 1000 μS/cm) even in the presence of competing ions [46]. Other research showed the following selectivity SO₄²> Br>Cl>F>NO₃ with 97% bromide removal with initial bromide concentration of 8.6 mg/L of Br⁻ [38].

On the other hand, the TDS adsorption capacity is between 1.3 to 9.8 mg of TDS/g of activated carbon for the four different types of feed water as shown in Fig. 6(b). It can be observed that the TDS adsorption capacity increased with the increase in feed water TDS until the electrode is completely saturated (Fig. S1). This phenomenon is in agreement that the increased TDS results in increased electrosorption capacity of the activated carbon due to improved diffuse double-layer capacity, which is directly related to feed water TDS [38]. The TDS removal, however is in fact not very critical given the already low TDS of the 1st pass SWRO permeate which requires remineralisation.

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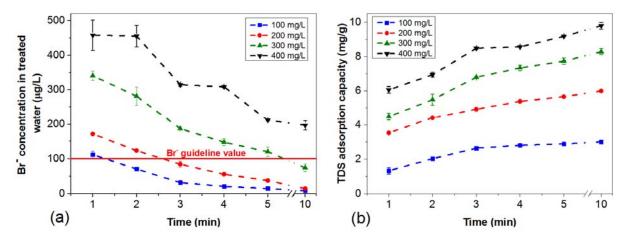


Figure 6: (a) bromide removal from 1st pass SWRO permeate with different feed water TDS at 100, 200, 300 and 400 mg/L TDS with initial bromide concentration of 192, 382, 561 and 774 μg/L as Br⁻ respectively at 1 V. The solid red line represents the guideline value for Br⁻ concentration in the product water in most desalination plants (b) TDS adsorption capacity for different TDS feed water with the same experimental conditions as above.

3.3.2 Energy consumption in MCDI vs the 2nd pass SWRO

The energy consumption in MCDI directly relates to the feed water TDS, and it is known to be energy-efficient when the feed water TDS is less than 2000 mg/L [47]. Therefore, MCDI presents an alternative solution to the 2nd pass SWRO since the average TDS range of the 1st pass SWRO permeate is 250-300 mg/L. The specific energy consumption ranges from 0.05 to 0.3 kWh/m³ based on the optimum operating time (Fig. S2) for each feed water to ensure that the bromide concentration of less than 100 µg/L is maintained in the treated water (Fig. 7). The calculated energy includes the total energy required for both the adsorption and desorption phase but does not include the energy used in pumping the feed water into the MCDI unit. For comparison, the average energy consumption of the 2nd pass BWRO unit at Perth desalination plant in Australia has been reported to be 0.35 kWh/m³ (personal communication), which is 40% higher compared to the energy requirement of 0.21 kWh/m³ for average feed TDS of 300 mg/L using MCDI. Furthermore, with optimization of the reverse voltage during desorption period, the energy consumption could be significantly reduced. However, as desorption voltage directly affects desorption time which determines the entire water recovery, further research should be carried out for the system optimization. More energy savings can be possible in MCDI since it was demonstrated that up to 83% of the energy used during adsorption stage could be potentially recovered during desorption phase through controlled charging and discharging of the MCDI cell at different currents under constant current operation mode [27]. A further research indicated energy recovery up to 47 % by transferring the energy from the MCDI unit to a supercapacitor using buck-boost converter during discharging step [28].

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Therefore, MCDI could be a highly competitive technology for treating the 1st pass SWRO permeate to replace the 2nd pass BWRO usually adopted to meet the bromide concentration standard.

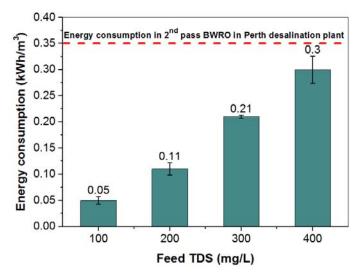


Figure 7: Total energy consumption during adsorption and desorption in MCDI. For 100, 200 and 300 mg/L TDS feed water, the optimum operating time was 2, 3 and 10 minutes respectively at 1 V. For feed water with 400 mg/L, the operating time was 10 minutes at 1.2 V.

Conclusions

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In this work, the fundamentals of bromide removal under various water quality and operational parameters were systematically evaluated using a lab-scale MCDI unit. It was demonstrated that bromide can be effectively removed by MCDI for the TDS range that is normally associated with the 1st pass SWRO permeate. The bromide removal could also be further improved if a specific bromide selective ion-exchange membrane is incorporated in the MCDI application as opposed to the use of generic anion exchange membrane used in the current study. Such selective resin incorporated in ion exchange membrane is expected to enhance the kinetics of bromide ion transport to the electrode surface effectively through improved selectivity of bromide ions. The average energy consumption of the 2nd pass BWRO unit at Perth desalination plant in Australia is 0.35 kWh/m³, which is 40% higher compared to the energy requirement of 0.21 kWh/m³ (considering total energy use for both adsorption and reverse voltage desorption) for average feed TDS of 300 mg/L using MCDI. The energy efficiency can be further optimised if the energy recovery from MCDI can be applied on a practical scale since energy recovery from MCDI as high as 83% has been reported. Finally, the detail comparative cost related to capital investment between MCDI and 2nd pass BWRO has to be further investigated in the future study.

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Acknowledgments

- 396 This work is supported by the Korea Agency for Infrastructure Technology Advancement
- 397 (KAIA) grant funded by the Ministry of Land, Infrastructure and Transport (Grant 17IFIP-
- 398 B116952-02). The support was also provided to HKS by the Australian Research Council
- 399 (ARC) through Future Fellowship (FT140101208) and to SP under the UTS Chancellor's
- 400 postdoctoral research fellowship.

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