Potential application of membrane capacitive deionisation for bromide removal in seawater desalination

by Pema Dorji

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CERTIFICATE OF ORIGINAL AUTHORSHIP

I, **Pema Dorji** declare that this thesis, is submitted in fulfilment of the requirements for the award of **Doctor of Philosophy**, in the School of Civil and Environmental Engineering, Faculty of Engineering and Information Technology at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise referenced or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

This document has not been submitted for qualifications at any other academic institution.

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JOURNAL ARTICLES PUBLISHED OR SUBMITTED**

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LIST OF ABBREVIATIONS

AC	Activated carbon
BM	Batch-mode
BWRO	Brackish water reverse osmosis
CA	Carbon aerogel
CC	Constant current
CDC	Carbide-derived carbon
CDI	Capacitive deionisation
CNFs	Carbon nanofibers
CNT	Carbon nanotubes
CS	Carbon spheres
CV	Constant voltage
DBPs	Disinfection by-products
ED	Electro-dialysis
EDL	Electrical double layer
FCDI	Flow capacitive deionisation
G	Graphene
GCS	Gouy-Chapman-Stern
HCDI	Hybrid electrode capacitive deionisation
HRT	Hydraulic residence time
LDHs	Layered double hydrous oxides
LPRO	Low-pressure reverse osmosis
MCDI	Membrane capacitive deionisation
MCL	Maximum contaminant level
MCS	Mesoporous carbon spheres
mD model	modified Donnan model
MIEX	Magnetic ion exchange
mM	Millimolar
NF	Nanofiltration
NMO	Sodium manganese oxide
PFO	Pseudo-first-order
PSO	Pseudo-second-order
RG	Reduced graphene
RO	Reverse osmosis
SAC	Salt adsorption capacity
SP	Single-pass
SWRO	Seawater reverse osmosis
TDS	Total dissolved solids
TFC	Thin-film composite
UF	Ultrafiltration
UV	Ultraviolet
WHO	World Health Organization
WR	Water recovery
ZVD	Zero voltage discharge

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ABSTRACT

The freshwater shortage is becoming an increasingly scarce resource due to rapid population growth and increased freshwater demand for industrial activities. The situation is further getting worse due to the effect of climate change as evident from extreme events such as droughts. In order to secure freshwater availability, most countries, including Australia are resorting to seawater desalination because seawater provides a reliable and climate-independent water source. Among desalination technologies, seawater reverse osmosis (SWRO) is the dominant technology due to its better energy efficiency and also its high salt rejection rates. While single-stage SWRO is adequate for the production of high-quality drinking water in most countries, in Australia, due to the strict requirement for bromide removal to prevent the formation of toxic bromide related disinfection by-products in the water, additional stage such as 2nd pass brackish water reverse osmosis (BWRO) has to be used. As a result, all the SWRO plants are designed as two-stage SWRO, which adds significant cost to the overall SWRO plant.

Recently, capacitive deionisation (CDI) has emerged as a suitable alternative for desalination of low-saline water sources compared with membrane processes. CDI is an electrosorption process where ions are removed by the charged carbon electrodes. Some of the advantages of CDI technology are low energy consumption, removal of all types of charged ions such as bromide and its ability to effectively desalinate water at a very low voltage (1 V) application. Therefore, in this research, the application potential of membrane CDI, which is an advanced version of CDI, is investigated for bromide removal. A detailed assessment of bromide removal efficiency and energy consumption were compared with that of conventional 2nd pass BWRO.

Several investigations related to bromide removal in MCDI were evaluated both at lab-scale and pilot-scale studies. The fundamental studies using lab-scale showed that bromide could be effectively removed using a commercially available carbon electrode. Further, a pilot-scale MCDI demonstrated that MCDI can be operated at high water recovery using variable flow rates during the adsorption and desorption stages. It was also found that using a much lower flow rate during desorption compared to adsorption stage can produce an acceptable water quality with high water recovery. The energy consumption of lab-scale and pilot-scale studies were between 0.11-0.16 kWh/m^3 of

treated water, which is only about 30-45% of the energy consumed by the 2nd pass BWRO in Perth desalination plant.

A fundamental lab-scale study on the selectivity between bromide and iodide, which is another important inorganic halide for the formation of toxic disinfection by-products was also conducted. The results showed that iodide was more selectively removed over bromide even in the presence of significant background concentration of sodium chloride mainly due to the high partial-charge transfer coefficient of iodide compared to bromide ions although both these ions have similar ionic charge and hydrated radius. The result also showed that MCDI could be a potential alternative for the removal of both bromide and iodide during water treatment.

One of the major disadvantages of capacitive deionisation-based desalination is the inability of the electrodes to selectively remove the target ions from a mixture of other background ions. Although bromide can be effectively removed in MCDI, especially in low salinity water, its removal efficiency can be reduced if the total salt content in the feed water is high. Therefore, a bromide selective composite electrode was developed by coating a slurry of grounded bromide selective resin and anion exchange polymer on the surface of the commercial carbon electrode. The composite electrode demonstrated high selectivity for the bromide, which was 3.4 times that of conventional MCDI. A further test on bromide selectivity in a complex mixture of several anions showed that bromide removal was 10 times that of conventional MCDI. The incorporation of bromide selective resin enhanced the capture and transport of bromide ions onto the carbon electrode while impeding the transport of other competing ions. The use of bromide selective electrodes in MCDI is expected to further reduce energy consumption while improving bromide removal efficiency.

CHAPTER 1

INTRODUCTION

1.1 Background

Freshwater is a key resource to realize the post-2015 Sustainable Development Goals (Harrison et al. 2016). However, it is increasingly becoming a scarce resource as a result of rapid population and industrial growth, and climate change is further worsening the situation (Hotloś 2008; IPCC 2014). It is estimated that about four billion people will face some level of scarcity (Mekonnen & Hoekstra 2016). Globally, freshwater accounts for only about 2.5% of global water resource, much of which is inaccessible for human use, and the rest 97.5% exist as seawater (Gleick 1993). Therefore, it is critical that other reliable and sustainable options to produce freshwater are evaluated.

In order to address the challenges of freshwater scarcity throughout the world, seawater resource is increasingly viewed as a potential reliable water source that is climate-independent. Globally, More than 15,906 desalination plants produce 34,675 million m^3/year of desalinated water globally (Jones et al. 2019). Among desalination technologies, 69% of the desalination plants use Seawater Reverse Osmosis (SWRO) system, which forces water through RO membrane under high pressure, and currently, it accounts for 70% of the global desalinated water (Jones et al. 2019).

Australia is one of the driest regions on earth, and since the millennium drought in Australia in early 2000 significant investment in SWRO desalination system was made with a total current production capacity of 500 million m^3/year (Heihsel et al. 2019). However, the desalination system such as SWRO is considered to be the most expensive option for freshwater production mainly due to significant capital investment, and high operational and maintenance cost required (Heihsel et al. 2019; Wakeel et al. 2016; Ziolkowska 2015). The situation of installation and operation of SWRO plants is little more complicated in Australia due to a specific legal requirement. For example, all the SWRO desalination plants in Australia have to be designed as a two-stage RO process where the desalinated water from the 1st stage SWRO has to be treated again in the 2nd stage brackish water RO (BWRO) for the production of high-quality drinking water. This requirement is mainly due to the high bromide reduction requirement in Australia, which is currently set at less than 100 μg/L in the product/desalinated water. Such addition of the second stage RO process adds significant additional cost on the technology which is already the most expensive technology for freshwater production (Bartels et al. 2009;

Choi, Oh, et al. 2019; Dorji et al. 2018). Among natural water sources, seawater contains a very high concentration of bromide between 65-75.8 mg/L (Dorji et al. 2018; Watson, Farré & Knight 2012).

Bromide is an inorganic precursor known for the formation of several types of disinfection by-products (DBPs) during water disinfection process especially when organic matters are present in the water source (Gyparakis & Diamadopoulos 2007; Hua, Reckhow & Kim 2006; Kampioti & Stephanou 2002; Liu, Wang, et al. 2016). Most of the DBPs are now considered to be an "emerging" environmental contaminants, and more than 600 types have been reported (Richardson & Kimura 2017; Richardson et al. 2007). One of the major concerns with bromide-related DBPs is the formation of bromate (BrO_3^-), a highly regulated carcinogen (Genuino & Espino 2012; Winid 2015). Currently, Australian standard for bromate is 20 µg/L whereas other countries such as the US, China, Canada, EU, Japan and WHO have strict bromate limit of 10 µg/L (Wang, Mao, et al. 2014).

While water disinfection is important to ensure that the water is free from any harmful bacteria and viruses, it is also clear that hundreds of toxic DBPs are unintentionally added into our drinking water (Richardson et al. 2007). Therefore, one of the major challenges for water treatment plants is to ensure effective water disinfection while minimising the formation of toxic DBPs (Simpson & Hayes 1998). Currently, chlorination, chloramination, ozonation and ultraviolet radiations are some of the common disinfection processes adopted in water treatment (Krasner 2009). Among these disinfectants, the use of ozonation has been identified as a major problem for the production of brominated DBPs including bromate (Pinkernell & Von Gunten 2001; Von Gunten & Hoigne 1994; Wu et al. 2019). One important strategy to reduce the formation of bromide related DBPs is by ensuring that bromide concentration is reduced as far as possible before the water is disinfected.

There are several technologies used and evaluated for bromide removal from the water such as membrane process, electrochemical and adsorption techniques (Watson, Farré & Knight 2012). Among these processes, SWRO was found to have the highest bromide rejection rates of 99.78% (Bartels et al. 2009). However, even the state-of-art SWRO plant is not able to produce product water within the threshold bromide level of less than 100 µg/L in a single-pass configuration because the bromide concentration ranges from 0.3-1 mg/L depending on SWRO operation parameters. As a result, additional treatment stags are required. Other conventional treatment processes such as coagulation and flocculation processes and media filtration are found to be ineffective for bromide removal, whereas the use of commercial ion exchange resins are not found to be suitable for practical application for large–scale water treatment due to high chemical demand for their regeneration and also generation of significant wastewater in the form of secondary pollution (Bartels et al. 2009; Watson, Farré & Knight 2012). As an alternative to the above processes for bromide removal, the application of capacitive deionisation is explored, which can demonstrate an excellent bromide removal at much lower energy requirement compared to conventional BWRO process used in two-stage desalination plants across Australia.

Capacitive Deionization (CDI) is an emerging desalination technology which removes ionic impurities from the feed water due to the formation of an electric double layer (EDL) on the surface of the charged electrodes when an electric field is applied (AlMarzooqi et al. 2014; Kim & Choi 2010b; Pekala et al. 1998). Some of the major of advantages of CDI is its ability to remove a wide range of ionic contaminants, has high water recovery and uses inexpensive components such as readily available activated carbon electrodes in its construction (Weinstein & Dash 2013). Unlike other desalination processes, the CDI process operates at low pressure and is found to be energy efficient for desalination of low salinity water (Farmer et al. 1995; Suss et al. 2012). The absence of hydraulic pressure not only reduces the operating cost of CDI but can also be beneficial for fouling control compared to the pressure-driven membrane processes. Moreover, relatively low voltage (1-1.2 V) is required for CDI operation over conventional electrochemical-driven processes such as electrolysis (>20 V), as a result, CDI shows significant advantages in terms of low energy requirements for the treatment of low-salinity water (Ahmad et al. 2016). Also, the fact that CDI can be operated at a very low voltage means that it is possible to power CDI using renewable solar energy, which will be advantageous for small-scale desalination system in remote locations. Unlike other adsorption techniques, CDI does not involve the use of chemicals for the regeneration of the electrodes since it can be achieved by polarity reversal. It is, therefore, only appropriate that research and development of CDI and its applications for a wide range of water and wastewater treatment have been intensively investigated by both the academic and industry communities as detailed in the later sections of this thesis.

Significant progress has been made in CDI development over the last decade. Since 2005 more than 1130 CDI research papers have been published with exponential growth in CDI research occurring from 2010. It is interesting to note that most of the CDI studies focused on electrode development (53%), followed by CDI applications (20%) and other fundamental CDI studies (12%). It is obvious that high-efficiency electrode development will continue to be a major focus of the CDI research for some time to come, due to the critical role of the electrode for CDI performance regarding high salt adsorption capacity, high salt removal rate and better energy efficiency. A total of 15 review papers related to CDI have been published in the last five years, which also strongly indicates the rapid evolution of the emerging CDI technology.

There are currently three most common types of CDI in use with specific advantages and disadvantages: (1) conventional CDI that uses a pair of static electrodes, (2) membrane CDI (MCI) which uses ion exchange membranes in combination with static carbon electrodes (Lee et al. 2006) and (3) Flow CDI (FCDI) which uses, as the name suggests, slurry electrodes made of carbon particles (Jeon et al. 2013) instead of static electrodes used in CDI or MCDI. Among these, the conventional CDI is found to be limited by lower salt adsorption capacity and high energy consumption due to a certain phenomenon of counter-ion adsorption and co-ion desorption in the feed channel during charging and discharging of the CDI cell, however, it is the simplest form of CDI construction and operation that can be practically used. A slightly advanced version of CDI called MCDI was developed which significantly showed better salt removal efficiency as well as energy efficiency because of the use of ion exchange membrane, which prevented unnecessary movement of ions between the electrodes during repeated charging and discharging of the cells. However, the use of separate layers of ion exchange membranes in MCDI had some cost implications because it requires an ion exchange membrane which is generally expensive. The recent trend in MCDI has been to coat a thin layer of ion exchange polymer directly on the surface of the electrode, which is expected to significantly reduce the cost of the overall system of MCDI. Lastly, there is also significant interest in investigating the performance of FCDI, which demonstrated the ability to continuously desalinate water and also showed its applicability to desalinate high salinity water such as seawater. However, further investigation is required to assess its practicability and energy consumption since it is a rather complex process to operate, and so far all the studies on FCDI have been limited to lab-scale model.

Within the challenges highlighted above, under this research, a detail investigation of bromide removal using MCDI was carried out. This study evaluated the feasibility of MCDI as a suitable alternative to the 2nd pass BWRO using both lab-scale and pilot-scale study and optimised MCDI operation for high water recovery and better energy efficiency. The energy consumption of lab-scale and pilot-scale studies were between 0.11-0.16 kWh/m^3 of treated water, which is only about 30-45% of the energy consumed by the 2nd pass BWRO in Perth desalination plant (0.36 kWh/m^3). Further, the commercial activated carbon electrode was modified by incorporating bromide selective resin in the ion exchange matrix to improve bromide selectivity. The composite electrode demonstrated high selectivity for the bromide, which was 3.4 times that of conventional MCDI. The incorporation of bromide selective resin enhanced the capture and transport of bromide ions onto the carbon electrode while impeding the transport of other competing ions. The use of bromide selective electrodes in MCDI is expected to further reduce energy consumption while improving bromide removal efficiency. Additionally, a fundamental study on the selectivity between bromide and iodide, which is also another key halide for the formation of DBPs was carried out to assess inherent selectivity between bromide and iodide using MCDI coated with ion exchange polymer in MCDI. The results from this research favorably indicate the suitability of membrane capacitive deionisation for effective bromide removal compared to the conventional end pass BWRO. However, some challenges and opportunities for further improvement are recommended.

1.2 Research aim, objectives and scope

This study aimed at exploring the potential application of membrane capacitive deionisation for effective bromide removal from seawater by integrating MCDI in the current SWRO to replace the 2nd stage BWRO process from the plant.

The specific objectives of the research were to:

- Conduct a detailed literature review on the current status of capacitive deionisation and its application potential in water and wastewater treatment;
- Investigate the fundamentals of bromide removal by MCDI using commercial electrodes in a lab-scale MCDI system and quantify energy consumption with the conventional membrane process;
- Evaluate bromide removal in a pilot-scale MCDI and optimising the operating parameters for high water recovery and energy efficiency;
- Determine preferential selectivity between bromide and iodide (similar charge and hydrated radius) in MCDI since iodide is also one of the major halides for DBP formation; and
- Modify the commercial carbon electrode to make it bromide selective by incorporating bromide selective resin on the electrode surface.

The main focus of the research is on the application of membrane capacitive deionisation for bromide removal, therefore, an extensive review has been conducted on the application potential of MCDI for water treatment. Since there are limited information and data on capital cost and practical application of CDI, it is not the intention of this research to provide an extensive cost-benefit analysis between CDI and other technologies regarding the capital cost and their operating cost. The science behind CDI and MCDI have been covered in less detail, and not exhaustive enough to cover all aspects and types of CDI operation and development. Although there are several discussions related to the formation of DBPs due to the presence of bromide during water disinfection, it is not the intention of this study to quantify the formation of DBPs under various disinfection process.

1.3 Thesis structure

This dissertation contains seven chapters, some of which includes published materials during the research tenure as a PhD candidate. Chapter one provides a brief background on the need and motivation for the research, and the main research objective and the scope of research.

Chapter two provides a detailed literature review on the application of capacitive deionisation process in water and wastewater treatment. Some parts of the materials in this section is adapted from the review paper that was published during the PhD candidature in Desalination (Choi, Dorji, et al. 2019) titled "*Applications of capacitive deionization: desalination, softening, selective removal, and energy efficiency*". It also includes a comprehensive review of capacitive deionisation technology, how it has evolved, and the major advantages and challenges are reviewed, and strategies for further development have been identified.

Chapter three assesses the application of membrane capacitive deionisation for bromide removal from seawater using a lab-scale MCDI system as a potential alternative to the 2nd pass BWRO in the desalination process. A detailed fundamental assessment of bromide removal was conducted and the effect of water characteristics and MCDI operating parameters such as flow rate, applied voltages and adsorption time were optimised. In addition, the performance of the MCDI unit was also compared with a conventional RO process for the treatment of actual seawater to quantity bromide removal efficiency and energy consumption, and some areas for improvement were identified. The result of this chapter was published in Desalination (Dorji et al. 2018), which is titled as "*Membrane capacitive deionisation as an alternative to the 2nd pass for seawater reverse osmosis desalination plant for bromide removal*".

Chapter four presents results from the pilot–MCDI unit with water treatment capacity that is almost 100 times that of the lab-scale unit. Since it is difficult to optimise the MCDI operation at a lab-scale unit due to limited flexibility in controlling the unit, pilot-MCDI unit was used, which provided much greater flexibility to operate the MCDI system under a very realistic operating condition, so that the results from the pilot MCDI unit can be directly extrapolated in the real world application. The results from this chapter was published in Desalination as *"Pilot-scale membrane capacitive deionization for effective bromide removal and high water recovery in seawater desalination"*. The result from this study was also presented during the CDI&E International Conference in Beijing, 20-23 May 2019.

Chapter five evaluates the selectivity of bromide and iodide ions, which is also another inorganic halide precursor for the formation of DBPs in MCDI using a composite MCDI electrode with an ion exchange membranes coated on the surface of the carbon electrode. Both bromide and iodide are the major halide precursors for the formation of DBPs. While the effect of different charge and hydrated radius of ions on selectivity in CDI and MCDI have been extensively studied, this chapter evaluated the effect on ion selectivity between bromide and iodide which have similar hydrated radius and ionic charge, and it was determined that there is inherent ion selectivity in MCDI even between ions with similar chemical characteristics. The result from this chapter was published in Chemosphere (Dorji et al. 2019) titled *"Bromide and iodide selectivity in membrane capacitive deionisation, and its potential application to reduce the formation of disinfection by-products in water treatment".*

Chapter six investigated the performance of novel bromide selective electrode, which was developed by coating a mixture of bromide selective resin and anion exchange polymer on the surface of commercial carbon electrode. Like many other water treatment technologies, MCDI application is also limited by its inability to have preferential selectivity over other ions. Under this study, the potential of enhancing bromide selectivity was evaluated so that MCDI electrodes can be made highly target-ion selective to improve removal of target ions more efficiently. The results from this chapter has been submitted to Desalination titled "*Novel composite electrode for selective bromide removal in membrane capacitive deionisation for seawater desalination*".

Chapter seven provides a summary of major conclusions from the research and provides recommendations for further improvement on bromide removal, and enhancing energy efficiency in MCDI have been discussed.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter provides a comprehensive review of the current status of capacitive deionisation technology and its applications for various water and wastewater treatment options. The review starts by describing the current challenges on freshwater shortages and how seawater desalination is becoming an important technology, globally and also in Australia for the production of reliable freshwater from the abundant seawater resource. The review then discusses specific challenges for Australian desalination plants due to the strict requirement for low bromide concentration in the desalinated water mainly because bromide is known to form several toxic disinfection by-products during water disinfection. A detailed review of bromide removal using current water treatment technologies and their limitations are also highlighted. Later sections of the review provide an extensive review of capacitive deionisation technology, its wide range of application potential, and strategies to improve energy efficiency and selective removal is discussed.

2.2 Seawater: a source of unlimited water resource

Freshwater is a key resource to realize the post-2015 Sustainable Development Goals by the United Nations (Harrison et al. 2016), but it is increasingly becoming a scarce resource. It is estimated that about four billion people will face severe water scarcity at least one month per year (Mekonnen & Hoekstra 2016). Globally, freshwater accounts for only about 2.5% of global water resource, much of which is inaccessible for human use, and the rest 97.5% exist as seawater (Gleick 1993). Although rapid population growth and industrial development led to over-exploitation of limited freshwater, the effect of climate change is expected to further worsen the freshwater availability (Hotloś 2008; IPCC 2014; Peters & Meybeck 2000). Therefore, it is critical that other reliable and sustainable options to produce freshwater are evaluated.

To address the challenges of freshwater scarcity throughout the world, seawater desalination system is playing an important role in many countries because seawater is a climate-independent resource, which is a source of unlimited and highly reliable water source. Although significant efforts have been made to conserve freshwater resources through water recycling and other water conservation efforts, these methods do not add additional freshwater to the current freshwater availability. Further, there is also a larger issue that needs to be addressed on the acceptance of the use of recycled water for the general population in some communities (Furlong et al. 2019). Currently, there are more than 15,906 desalination plants with a total capacity to produce 34,675 million m^3/year of desalinated water globally, of which, the Middle East and North African regions account for almost 50% of this capacity (Jones et al. 2019). Fig. 2-1 shows the distribution of desalination plants and water users in various parts of the world. About 62% of desalinated water is used for municipal water supply as potable water. Among desalination technologies, 69% of the desalination plants use Seawater Reverse Osmosis (SWRO) system, where fresh water is produced by permeating seawater across a reverse osmosis membrane under extremely high pressure. Global share of desalination using SWRO accounts for 65.5 million m^3/day (Fig. 2-2), which is almost 70% of the global desalinated water (Jones et al. 2019). It is predicted that SWRO will experience unprecedented growth in the coming years as more countries start to make a significant investment in desalination technology to augment freshwater resources (Gude 2016; Ziolkowska 2015). However, SWRO plants also have significant environmental cost due to extensive energy usage and disposal of high-concentration brine back into the oceans (Miller, Shemer & Semiat 2014; Shannon et al. 2008). Therefore, although SWRO plants are highly energy efficient desalination system, further innovation to improve the technology is expected to reduce the overall cost of water production, and also to make the overall desalination system more energy efficient (Mayor et al. 2016).

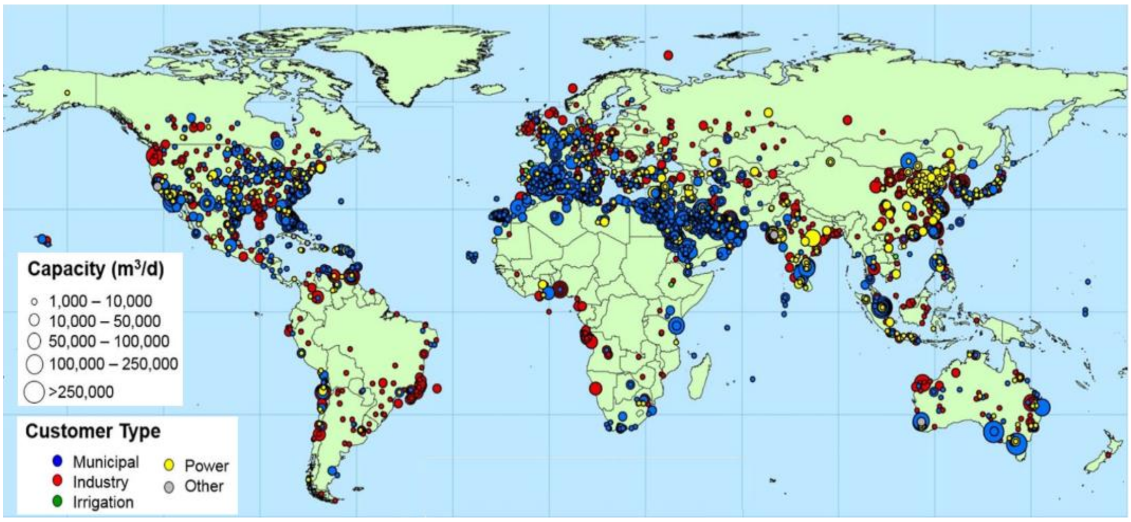

Figure 2-1: Global desalination capacity (Jones et al. 2019).

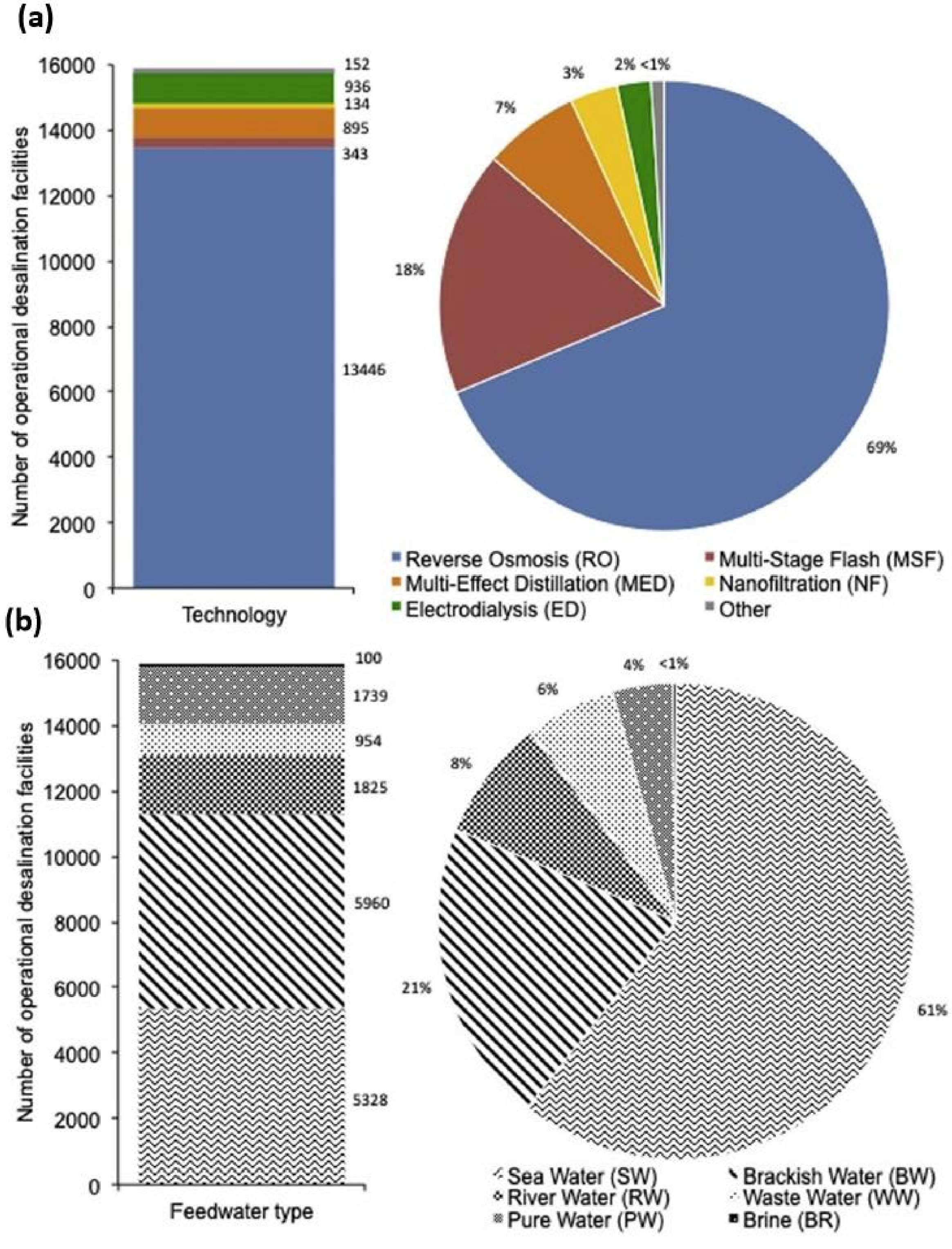

Figure 2-2: Global desalination capacity by (a) technology (b) feed water type (Jones et al. 2019).

2.3 Australia's experience in seawater desalination

Since the millennium drought in Australia about a decade ago, significant investment in SWRO desalination system has been made to address the water shortage. Its current planned desalination capacity is about 690 million m^3/year with a total investment in desalination exceeding AU$ 10 billion already (Crisp, Swinton & Palmer 2010; Gude 2016). As per the recent data, the current operational capacity of 20 largest desalination plants in Australia produces about 500 million m^3/year (Table 2-1), and the majority of the desalinated water is intended for the municipal supply (Heihsel et al. 2019). However, the desalination system such as SWRO is considered to be the most expensive option for freshwater production mainly due to significant capital investment, and high operational and maintenance cost required (Heihsel et al. 2019; Wakeel et al. 2016; Ziolkowska 2015). The Victorian desalination plant in Australia is estimated to cost AU$ 18 billion in capital and operation cost over 27-year contract even when no water is used from the plant when it is on standby mode (Furlong et al. 2019). It is a similar situation for major desalination plants in Australia because all of these plants operate under similar modality for installation and operation.

Although the SWRO process is highly energy efficient compared to other thermal-based desalination systems, the operation of SWRO in Australia seems to encounter a specific challenge, unlike other countries. For example, all the SWRO desalination plants in Australia have to be designed as a two-stage RO process (Fig. 2-3) where the desalinated water from the 1st stage SWRO has to be treated again in the 2nd stage brackish water RO (BWRO) for the production of high-quality drinking water. This requirement is mainly due to the high bromide reduction requirement in Australia, which is currently set at less than 100 μg/L in the product/desalinated water since the presence of bromide leads can lead to the formation of toxic disinfection by-products. Such addition of the second stage RO process adds significant additional capital cost and operation cost, which further increases the overall cost of the desalinated water (Bartels et al. 2009; Choi, Oh, et al. 2019; Dorji et al. 2018). Among natural water sources, seawater contains a very high concentration of bromide between 65-75.8 mg/L (Dorji et al. 2018; Watson, Farré & Knight 2012). It is also reported that some Australian surface and groundwater water sources, especially in Western Australia contain high concentration of bromide in excess of 8 mg/L, which is 80 times the required threshold in desalinated water, therefore it poses a significant risk of formation of toxic brominated DBPs in the water (Gruchlik, Heitz, et al. 2014; Gruchlik, Tan, et al. 2014).

Table 2-1: Desalination capacity in Australia (Heihsel et al. 2019).

Desalination plant	Capacity [m^3/d]	Location	Award year	Online year
Victorian Desalination Plant	444,000	Victoria	2009	2012
Port Stanvac	274,000	South Australia	2009	2012
Sydney Desalination Plant (Kurnell)	250,000	New South Wales	2007	2010
Kwinana	143,700	Western Australia	2005	2006
Southern Seawater desalination plant	140,000	Western Australia	2009	2011
Sino Iron Ore Project, Cape Preston	140,000	Western Australia	2008	2012
Southern Seawater Desalination Plant (expansion)	140,000	Western Australia	2011	2013
Tugun (Gold Coast)	133,000	Queensland	2006	2009
Browse downstream engineering processes	10,560	Western Australia	2011	2012
Agnes Water Integrated Water Project	7500	Queensland	2008	2011
Bechtel Wheatstone construction	7500	Western Australia	2012	2012
Onslow	7500	Western Australia	2013	2013
Gorgon	7000	Western Australia	2010	2012
Curtis LNG Project	5000	Queensland	2010	2011
Jabiru	5000	Northern Territory	2006	2007
Bechtel Wheatstone compaction 2	4500	Western Australia	2011	2012
Onslow2	4500	Western Australia	2013	2013
Onesteel Whyalla Plant	4100	South Australia	2010	2011
Penrice	4050	South Australia	2005	2006
Fortescue Metals Group Port Headland	4000	Western Australia	2011	2012

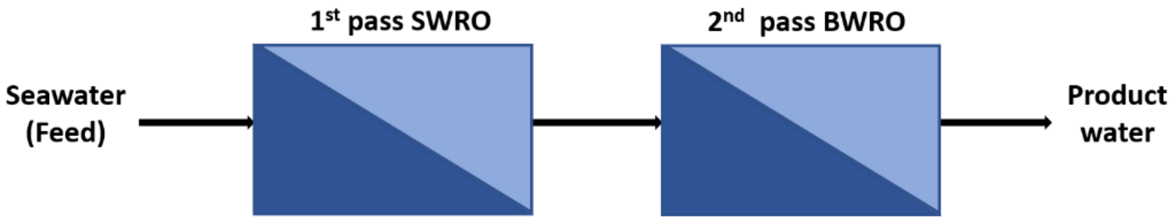

Figure 2-3: SWRO configuration in Australian desalination plants using two-stage RO process for the production of high-quality drinking water.

2.4 Bromide, a source of toxic disinfection by-products in water

Bromide is an inorganic precursor known for the formation of several types of disinfection by-products (DBPs) during water disinfection process especially when organic matters are present in the water source (Gyparakis & Diamadopoulos 2007; Hua, Reckhow & Kim 2006; Kampioti & Stephanou 2002; Liu, Wang, et al. 2016). Most of the DBPs are now considered to be an "emerging" environmental contaminants, and more than 600 types have been reported (Richardson & Kimura 2017; Richardson et al. 2007). The growing number of DBPs in water treatment is of particular concern because the current level of knowledge is this field is not comprehensive enough. 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 (Bichsel & Von Gunten 1999; Kampioti & Stephanou 2002; McTigue et al. 2014; Myllykangas 2004). One of the major concerns with bromide-related DBPs is the formation of bromate, a highly regulated carcinogen (Genuino & Espino 2012; Winid 2015). Currently, Australian standard for bromate is 20 µg/L whereas other countries such as the US, China, Canada, EU, Japan and WHO have strict bromate limit of 10 µg/L (Wang, Mao, et al. 2014). 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 (Bonacquisti 2006). Even with the bromide concentration of 50-100 µg/L, excessive formation of bromate is a serious concern, and once it is formed, there is no practical technology for its removal (Richardson et al. 2007; Tan et al. 2016; von Gunten

2003; Winid 2015). An experimental investigation of bromate formation from groundwater sources in Greece with an initial bromide concentration of 161 μg/L led to the formation of 23 μg/L of bromate, which is more than twice the maximum contaminant level (MCL) in the US, China, Canada, EU and Japan. Another concern with the presence of bromide is that if it's concentration is greater than 0.2 mg/L, then it will be difficult to maintain a desired residual chloramine level to further prevent water contamination since chloramine reacts with bromide to form bromamine (Bartels et al. 2009).

2.5 Water disinfection: benefits and challenges

Water disinfection is a critical component of water and wastewater treatment system to ensure that the water is free from any harmful bacteria and viruses. In fact, our ability to disinfect our water and produce safe drinking water is considered as one of the top five engineering achievements of the 20th century (Constable & Somerville 2003). However, with further progress and understanding of the disinfection system and its risk, it is also clear that hundreds of toxic DBPs are unintentionally added into our drinking water (Richardson et al. 2007). Therefore, one of the major challenges for water treatment plants is to ensure effective water disinfection while minimising the formation of toxic DBPs (Simpson & Hayes 1998).

Currently, chlorination, chloramination, ozonation and ultraviolet radiations are some of the common disinfection processes adopted in water treatment (Krasner 2009). All these disinfectants have different disinfection potential, but they also react differently with various DBP precursors such as bromide and iodide to produce a wide range of DBPs (Richardson & Kimura 2017). Among these disinfectants, the use of ozonation has been identified as a major problem for the production of brominated DBPs including bromate (Pinkernell & Von Gunten 2001; Von Gunten & Hoigne 1994; Wu et al. 2019). Even in chlorinated water, which is the most widely used disinfectant, the formation of brominated DBPs has been reported (Kampioti & Stephanou 2002; Pan & Zhang 2013). Since the DBPs are highly regulated, many water treatment plants have started to explore alternative disinfectants to comply with the regulatory requirements on DBPs (Wang, Mao, et al. 2014). For example, water treatment plants using chloramination were able to meet the regulatory requirement for regulated DBPs compared to chlorination (Goslan et al. 2009).

2.6 Strategies in reducing the risk of bromide related disinfection by-products

In order to mitigate the risk of formation of bromide related DBPs during water treatment, there are three different interventions that can be adopted during water treatment. Firstly, it is clear that the presence of bromide in the water, even in minute concentration, can be a potential source for the formation of DBPs during water disinfection. Therefore, if the bromide concentration can be significantly reduced before the water is disinfected, this would be a preferred strategy because this stage significantly reduces the DBP formation potential due to bromide.

Secondly, it is also possible to control the disinfection process itself to reduce the risk of DBP formation. However, disinfection is a rather complex process with many variables to control and monitor, such as the type of disinfectants, dosages, contact time etc. The resources required to ensure that the disinfection process is always working at an optimum level will be an enormous task. Since our understanding of DBP formation pathways is still limited, there will be a lot of uncertainties and risks involved to rely on optimum disinfection process to control the formation of DBPs.

The last intervention in risk mitigation of bromide related DBPs formation is by actually monitoring the formation of DBPs in the treated water and if required, adding further treatment for their removal. This stage is practically challenging because, it is difficult to remove DBPs when they are present in such a minute (parts per trillion) level, and as mentioned above, the removal of DBPs once formed is not economical at all, and there is no practical technology that is currently in use. Moreover, water disinfection is normally the final stage of the treatment to ensure that bacteria and viruses are not present in the water before the water is distributed to the consumers. Any additional treatment process after disinfection will increase the risk of cross-contamination of the water. It is, therefore, obvious that from the three different interventions to mitigate the risk of bromide related DBPs, the best option is to ensure that the source water has significantly low levels of bromide before it is being disinfected.

There are several technologies used and evaluated for bromide removal from the water such as membrane process, electrochemical and adsorption techniques (Watson, Farré & Knight 2012). Among these processes, SWRO has the highest bromide rejection rates. However, even the state-of-art SWRO plant is not able to produce product water within the threshold bromide level of less than 100 µg/L in a single-pass configuration. Depending on the SWRO membranes used, a bromide concentration of 100 µg/L to 1,000 µg/L is still expected in most first-pass SWRO permeate as per DOW FILMTEC^{TM} advisory note on their SWRO membranes. Therefore, SWRO desalination plants in Australia generally have to adopt a two-stage RO process as mentioned above mainly for effective bromide removal but at a significant additional cost to the overall SWRO system that is already expensive to built and operate. Other conventional treatment processes such as coagulation and flocculation processes and media filtration are found to be ineffective for bromide removal, whereas use of commercial ion exchange resins although available are not found to be practical for large–scale application because of high chemical demand for their regeneration and also generation of significant wastewater (Bartels et al. 2009; Watson, Farré & Knight 2012).

2.7 Review of current technologies for bromide removal

Since bromide is an important inorganic salt responsible for the production of many forms of toxic DBPs including bromate, several water treatment options are available for its removal. In general, the most common technologies for bromide removal are categorized as membrane, electrochemical and adsorption techniques as presented in the review article for halide removal (Watson, Farré & Knight 2012). This review paper made a comprehensive assessment of bromide removal using several types of technologies, identified major challenges and limitations of the technologies including their practical application.

2.7.1 Bromide removal in membrane process

The membrane technologies include reverse osmosis (RO) membrane and nanofiltration (NF) membranes. The investigation for removal of bromide by SWRO membrane is limited, however, bromide rejection of 99.34-99.78% (Table 2-2) has been reported from the pilot and full-scale plants depending on high rejection and high flow SWRO membranes (Bartels et al. 2009). The performance of Polyamide NF membranes has shown bromide rejection of 80-97% from synthetic water. Despite the high rejection of bromide by both NF and RO membranes, and their ability to simultaneously remove organic matter, the extensive need for pretreatment and high energy requirement, and their high propensity for fouling and scaling are found to be major challenges (Watson, Farré & Knight 2012). Other studies evaluated the hybrid coagulation-ceramic membrane system for the removal of organics and bromide from surface waters (Alansari et al. 2016). While some removal of dissolved organic carbon (30%) was achieved, there was hardly any bromide removal observed in the process.

Table 2-2: Bromide rejection by RO and NF membrane (Watson, Farré & Knight 2012)

Membrane	**Type**	**Water source**	**Initial Br^- concentration (mg/L)**	**Br^- rejection (%)**	**Ref.**
SWC4+	Composite Polyamide (RO)	seawater	70.9	99.78	(Bartels et al. 2009)
SWC5	Composite Polyamide (RO)	seawater	64.4	99.34	(Bartels et al. 2009; Pontié, Diawara & Rumeau 2003)
NF-90 (200 Da)	Polyamide TFC	Synthetic	1030	94-96	(Harrison et al. 2007)
NE-90 (200 Da)	Polyamide TFC	Synthetic	1030	94-97	(Harrison et al. 2007)
NF-70 (200 Da)	Polyamide TFC	Natural	51.3	>93	(Pontie et al. 2003)
NF-90 (200 Da)	Polyamide TFC	Natural	51.3	80	(Drewes et al. 2009)

2.7.2 Bromide removal by ion exchange and adsorption technology

Several ion exchange resins such as Magnetic Ion Exchange (MIEX®) which are generic anion exchange resin were also used to evaluate their selectivity in bromide removal (Watson, Farré & Knight 2012). It was reported that bromide removal was dependent on the carbonate concentration, for example, a bromide removal efficiency decreased from 94% to 43% when source water $CaCO_3$ concentration increased from 91 mg/L to 155 mg/L (Singer & Bilyk 2002). Recently, a MIEX/UF hybrid was studied to assess bromide removal from a source water (0.62 mg/L as bromide) and depending on the dose of MIEX, bromide removal of 16% and 37% were observed with high MIEX being more favourable for bromide removal (Gibert et al. 2017). However, it was found that the bromide saturation occurred much faster than that of DOC, and even release of bromide ions back into the solution at a later stage have been reported mainly due to the lower affinity of MIEX towards bromide ions. One of the major challenges in the use of ion exchange process is their inapplicability on a large-scale water treatment plants due to their cost, reduced treatment efficiency in the presence of competing ions, and also production of significant about of wastewater during their regeneration. Another issue is related to the processing time, which is significantly longer, which is also not very practical.

The use of adsorption technology using various adsorbents such as layered double hydrous oxides (LDHs), carbon composites such as silver-doped carbon aerogels and aluminium-based adsorbents have been reported (Watson, Farré & Knight 2012). The common limitations of adsorption techniques are that their bromide removal capacity can be severely limited by the competing ions. The use of LDH such as Mg-Al showed bromide removal between 27.5-94% from feed water containing single electrolyte of 100 mg/L of bromide however, this study was limited to study the fundamental mechanism of bromide removal by LDH (Lv et al. 2008). The use of high concentration of bromide only solution and the long adsorption duration of 24 hours will limit its large-scale practical application. Other types of LDH such as sol-gel double hydrous oxide were also used for bromide removal, and bromide removal between 9-80% was observed in synthetic solution with initial bromide concentration of 198.2 mg/L (Chubar 2011; Chubar et al. 2005). Silver-doped carbon aerogels were also studied to remove bromide from a natural water source (0.15 mg/L Br^-) but its removal efficiency was reduced to just 30% when background chloride concentration was 40 mg/L (Sánchez-Polo et al. 2006) (Sánchez-Polo et al. 2007), which makes it impractical for application in water treatment.

2.7.3 Bromide removal by electrodialysis (ED)

An electrodialysis was used for the treatment of groundwater in central Australia with a bromide concentration of 10.6 mg/L and water TDS of 5300 mg/L (Onorato, Banasiak & Schäfer 2017). The average bromide removal was 99.4%, and the pH did not have any effect on its removal as determined in our study as well (Dorji et al. 2018) because bromide does not form multiple species like boron and phosphate, whose removal depends on the pH variation. It is also reported that membrane fouling due to precipitation of insoluble species was an issue in ED and further highlights that long-term chemical and mechanical stability could be a concern for practical applicability. The study did not make detail assessment on the energy consumption, however, the fact that voltage applied were 12 V and 18 V, which is significantly higher than 1.2 V which is normally applied in CDI process. In a separate study, donnan-dialysis approach, where anion exchange process allows for the removal of bromide from feed water containing 500 µg/l bromide with that of less harmful sodium chloride solution (receiving water 200 mM NaCl) was studied (Wlśnlewskl & Kabsch-Korbutowicz 2017). It was found that bromide removal of 74-77% was achieved for different types of anion exchange membranes used.

2.7.4 Bromide removal in CDI

There are limited investigations on the applicability of capacitive deionisation on the removal of bromide although an extensive review on the halide removal technologies suggested that, with proper optimisation and further development, capacitive deionization could rival membrane process for water treatment (Watson, Farré & Knight 2012). The assessment of bromide removal in CDI was conducted in 2005 where bromide removal of 86 % was observed for an initial bromide content of 0.36 mg/l in the diluted seawater (Welgemoed 2005). The competitive removal of bromide and iodide was evaluated from brackish water generated during natural gas mining with a removal efficiency of 50% and 69.7% for Br and I respectively, for feed water concentration of about 50 mg/l of bromide and iodide (Xu et al. 2008). Our research on bromide removal from synthetic water showed reduced bromide removal efficiency between from 97% to 46% when the background TDS of the feed water increased from 100 mg/L to 400 mg/L showing that the effect of background ions can be detrimental for bromide removal (Dorji et al. 2018). It was also reported that the parameters such as pH and flow rate (in batch-mode) did not have an effect on bromide removal. Further investigation on the anion selectivity between bromide, chloride and iodide showed the removal trend in the order of $I^->Br^->Cl^-$ (Dorji et al. 2019). The highest removal of iodide in CDI was reported to be mainly due to the high partial charge transfer coefficient of iodide compared to chloride and bromide as reported earlier (Xu et al. 2008).

2.8 Capacitive deionisation: basics and principles

Capacitive Deionization (CDI) is an emerging desalination technology with a wide range of application potential for water and wastewater treatment. It is an electrosorption process to remove ionic impurities from the feed water due to the formation of an electric double layer (EDL), where the ions are temporarily adsorbed on the surface of the charged electrodes (AlMarzooqi et al. 2014; Kim & Choi 2010b; Pekala et al. 1998). It has a distinct advantage in removing ionic contaminants, has high water recovery, and uses inexpensive components such as readily available activated carbon electrodes in its construction (Weinstein & Dash 2013). Unlike other desalination processes, the CDI process operates at low pressure and is found to be energy efficient for low salinity water treatment (Farmer et al. 1995; Suss et al. 2012). However, with recent advancements in electrode materials and process optimisation, use of CDI to treat feed water with much higher salinities have also been demonstrated. Moreover, it has high flexibility to customise the operating parameters as per the required effluent quality (Huyskens, Helsen & de Haan 2013; Zhao, Satpradit, et al. 2013). As the absence of hydraulic pressure not only implies the potential to reduce operating cost but can also be beneficial for fouling control, compared to the pressure-driven membrane processes. Furthermore, relatively low voltage is required for CDI operation over conventional electrochemical-driven processes, as a result, CDI shows significant advantages in terms of low energy requirements with substantial water recovery (Ahmad et al. 2016).

Significant progress has been made in CDI related studies over the last decade. Since 2005 more than 1130 CDI research papers have been published as evident from Fig. 2-4, where exponential growth in CDI research occurred from 2010. It is interesting to note that most of the CDI studies focused on electrode development (53%), followed by CDI applications (20%) and fundamental CDI studies (12%). It is obvious that the search for ideal CDI electrode development will be the dominating focus of the research for some time to come, due to the critical role of the electrode for CDI performance. However, as discussed in the subsequent sections of the thesis, there is a significant gap between the academic research and the practical application potential of the novel electrodes. A total of 15 review papers related to CDI have been published in the last five years, which also strongly indicates the rapid evolution of the emerging CDI technology.

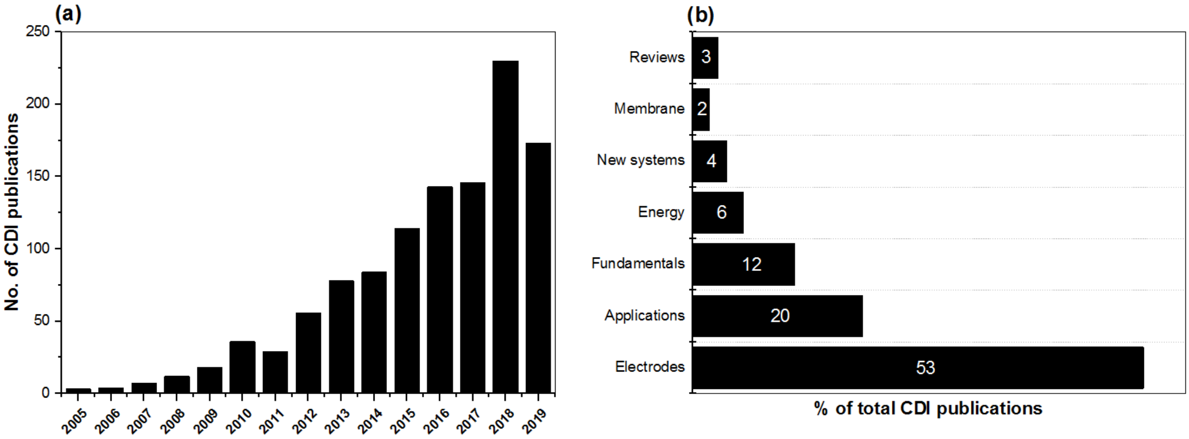

Figure 2-4: The research progress in CDI (a) Number of CDI related publications between 2005-2019 (accessed from Scopus on 30th June 2019) (b) the research areas in CDI between 2012-2017.

2.8.1 Major components in CDI and its operating principle

The CDI uses a pair of porous conductive electrodes, mostly carbon-based materials such as activated carbon (Porada et al. 2013) to attract dissolved ions on the surface of the electrodes when an external potential is applied on the electrodes. The most common electric conductor used is a graphite sheet on which the slurry activated carbon is coated. The pair of electrodes are normally separated with a non-conductive nylon spacer to prevent electrode short-circuit but it also serves an important role in flow distribution. The major components of CDI unit are shown in Fig. 2-5. Most lab-scale CDI experiments are conducted using a single pair of electrodes for fundamentals studies. Larger commercial CDI modules basically consist of multiple pairs of electrodes, where positive and negative electrodes are alternately arranged, and all the positive electrodes and negative electrodes are connected on a common positive and negative terminals respectively (Kim et al. 2019). However, unlike conventional adsorption process, CDI is effective only for the removal of charged ions, and uncharged pollutants such as organic compounds and silica cannot be removed adsorption.

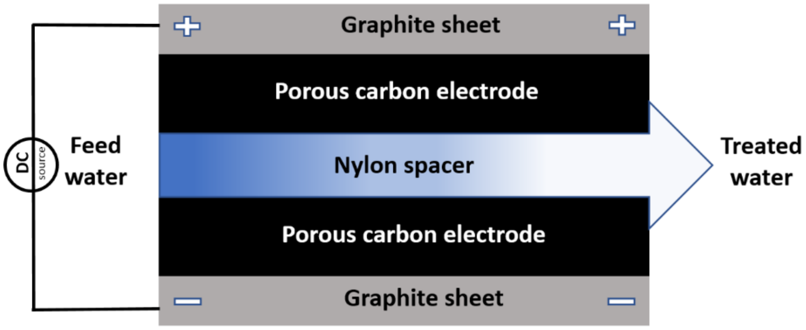

Figure 2-5: Schematics of typical CDI components.

In principle, CDI operation is a two-step process where ion removal occurs during the adsorption phase followed by ion desorption during the electrode regeneration phase. The ion adsorption phase, which is also sometimes referred to as charging phase of the CDI is normally achieved by two different approaches: Constant Voltage (CV) or Constant Current (CC) charging (Porada et al. 2013). Most commercial CDI units are operated on CV mode due to its simplicity in operation compared to CC mode. One major implication of CV operation is that the effluent quality becomes inferior with time, whereas under CC operation, the quality of the effluent can be maintained at fairly constant. It is reported that when the applied voltage exceeds a certain threshold (theoretically 1.23 V) will cause Faradaic reaction due to water electrolysis, which leads to decreased desalination performance, decrease energy efficiency, and reduce electrode lifespan (Zhang et al. 2018). A hybrid CV-CC operation of CDI for adsorption has also been demonstrated to take advantage of both CV and CC operation mode, where charging of the CDI cell starts with CV followed by CC at a later stage of the charging process (Saleem et al. 2016). Earlier research showed that CC charging was found to be more energy efficient (Qu et al. 2016) although a recent analysis on the energy efficiency between CV and CC charging of CDI cell did not find any significant difference in the energy consumption between the two operating modes to achieve a similar adsorption threshold (Wang & Lin 2018).

For desorption or regeneration of electrodes, zero voltage discharge (ZVD), short-circuit and reverse voltage application is generally applied to force the ions out of the electrode surface into the bulk solution in the spacer, where they are finally flushed out of the system as a highly concentrated brine stream, depending on the desorption flow rates and application of reverse voltage. Under short-circuit regeneration, a direct connection is made between the electrodes so that the potential difference gradually becomes zero. One major advantage of short-circuit regeneration of the electrodes is that no electrical energy is required to drive the process, however, the regeneration rate is slower (Yao & Tang 2017). Another approach for the regeneration of the electrodes is the application of reverse voltage. As the name indicates, the voltage is reversed or switched between the positive and negative terminal, therefore, faster regeneration is achieved. However, reverse voltage desorption requires a significant amount of energy, which is almost 50% of the total energy required for deionization. It is also possible to have a combination of short-circuit and reverse voltage desorption to optimize energy consumption, which is adopted in this research (chapter 4).

2.8.2 Electrode materials for CDI

Electrode material in CDI is one of the most important components, which directly determines the desalination capacity and energy efficiency in desalination. Several important characteristics of ideal CDI electrode were highlighted by (Oren 2008). The ideal electrode materials should have a high specific surface area, high electronic conductivity, high tolerance to pH and voltage fluctuations, ease of manufacturing for various design and shape requirement and have a low propensity for scaling and biofouling. Therefore, it is not surprising that research on electrode material development has been a major focus in CDI research (Fig. 2-4). In fact, there is so much competition among many research groups in the development of ideal CDI electrodes that several review papers dedicated to CDI electrodes have been published in the last few years to account for rapidly increasing new materials developed for CDI application (Liu, Nie, et al. 2015; Oladunni et al. 2018; Thamilselvan, Nesaraj & Noel 2016). As noted in these review papers, while porous carbon-based electrodes such as activated carbon, carbide-derived carbon (CDC), carbon aerogel, carbon nanotubes (CNTs), carbon nanofibers (CNFs), composites, graphene etc. have been used as standalone electrodes, many other materials such as carbon composites have been explored as shown in Table 2-2 and Table 2-3.

Activated carbon is the most common electrode material due to its high surface area and optimized pore size distribution for the CDI process with relatively cheap and easy manufacturing characteristics (Villar et al. 2011). Significant efforts have been conducted on improving the performance of CDI by employing the novel electrodes. The newly synthesized or developed electrodes exhibited innovative removal efficiency, however, the essence lies not only on the improved electrode performance but on the commercialization and practical application (i.e., cheap and easy to scale-up). That is the reason why most of the CDI suppliers Voltea (Nederland), EST Water & Technologies CO., Ltd (China), and Siontech (South Korea) supply CDI units manufactured the CDI modules with the conventional activated carbon.

However for better removal efficiency, other aforementioned materials have been widely investigated as the next generation electrodes due to (1) improved surface area (carbide-derived carbon (CDC) for about 1100 - 1300 m^2/g, graphene for 2630 m^2/g, and CNT for 77,415 m^2/g) (Frackowiak & Beguin 2001; Li et al. 2011; Porada et al. 2012), (2) high salt adsorption capacity (CDC for 28-44% increment) (Porada et al. 2012), (3) low electrical resistivity (carbon aerogel for <40 mΩ/cm) (Hou, Huang & Hu 2013), or (4) optimized pore size distribution (carbon aerogel for < 50 nm) (Pröbstle, Wiener & Fricke 2003). Furthermore, anion and cation exchange polymers integrated with CNTs electrodes were fabricated. It showed much higher removal efficiency (93%) compared to that of CDI (25%) or MCDI (74%) (Liu et al. 2014). Regarding salt adsorption capacity of the carbon-based electrodes, only the electrodes that have at least salt adsorption capacity of 8 mg/g at 1.2 V, which is a minimum recommend for CDI application (Porada et al. 2013) have been presented in Table 2-3 (Ahmed & Tewari 2018; Oladunni et al. 2018) since it was recommended that for practical application, CDI electrodes should have at least a salt adsorption capacity of 8 mg/g. Among carbon-based electrode, the CNT-based composite electrode showed the highest salt adsorption capacity of about 44 mg/g followed by graphene aerogel composite at 24 mg/g of SAC, which is about 2-3 times the salt adsorption capacity of the most common activated carbon electrode.

There is also a recent trend in the application of intercalation materials as CDI electrodes where the deionisation is mainly driven by redox activity instead of the electric field that is commonly used in CDI (Singh et al. 2019). As reported, the intercalation materials in CDI shows similar salt adsorption capacity (SAC) to that of carbon electrodes but at a much lower voltage, thereby making the overall process more energy efficient. Another advantage of interaction materials is that they do not require ion exchange membranes to improve selectivity since they can be either cation or anion selective, therefore, counter-ion adsorption and co-ion desorption do not occur.

Table 2-3: Salt adsorption capacities of selected electrode materials obtained (Oladunni et al. 2018).

Electrode material	**Surface area (m^2/g)**	**Initial feed concentration (mg/L)**	**Salt adsorption capacity (mg/g)**	**Ref.**
Activated carbon (AC)	700	100	14.32	(Wang et al. 2015)
Carbon aerogel (CA)	2600	200	10.45	(Kumar et al. 2016)
CNTs-CNTs	200.74	1000 (µS/cm)	11	(Wang, Zhang, et al. 2014)
CNTs-GR	391	780	26.42	(Wimalasiri & Zou 2013)
CNT-polypyrrole	185.21	1000 (µS/cm)	43.99	(Wang, Zhang, et al. 2014)
Mesoporous Carbon Spheres (MCS)	1099	100	11.5	(Li et al. 2017)
Nitrogen-doped graphene sponge	526.7	500	21	(Xu et al. 2015)
AC-TiO_2	-	584.4	17	(Kim et al. 2014)
AC-MnO_2	625	584	9.3	(Liu, Hsi, et al. 2016)
RG-TiO_2	658.6	300	16.4	(El-Deen et al. 2015)
G-TiO_2	187.6	500	15.1	(Yin et al. 2013)
Graphene Aerogel (GA- TiO_2)	187.6	6000	24.2	(Yin et al. 2013)
CNTs-Chitosan (CS)	106	58.44	10.7	(Hou, Huang & Hu 2013)
Graphene-CS-Mn_3O_4	240	300 (µS/cm)	12.6	(Gu et al. 2015)

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materials in CDI shows similar salt adsorption capacity (SAC) to that of carbon electrodes but at a much lower voltage, thereby making the overall process more energy efficient. Another advantage of interaction materials is that they do not require ion exchange membranes to improve selectivity since they can be either cation or anion selective, therefore, counter-ion adsorption and co-ion desorption do not occur.

2.8.3 Types of CDI architectures, and their performance in water desalination

There are three most common types of CDI in use today (Fig.2-7) although other new CDI systems have also been developed. They are conventional CDI, membrane CDI and Flow CDI (FCDI), all of which have different desalination capabilities, and have unique features in their construction and operating processes. The conventional CDI is the earliest form of CDI which uses a pair of carbon electrode for desalination. The advanced version of CDI is the development of membrane CDI which used cation and anion exchange membranes to improve desalination efficiency. Both CDI and MCDI uses static flat sheet electrodes, where water flows parallel to the electrodes, and sometimes referred to as flow by CDI/MCDI (Tang et al. 2018). The flow CDI is a new generation CDI design, which uses suspended carbon particles, which are constantly being replenished, as a result, continuous desalination of water is possible, unlike CDI and MCDI, which require adsorption and desorption stages due to faster saturation of the electrodes. The subsequent sections provide more detail on their working principle, their advantages and limitations are discussed. Further, a brief description of other advances in CDI configurations is also provided.

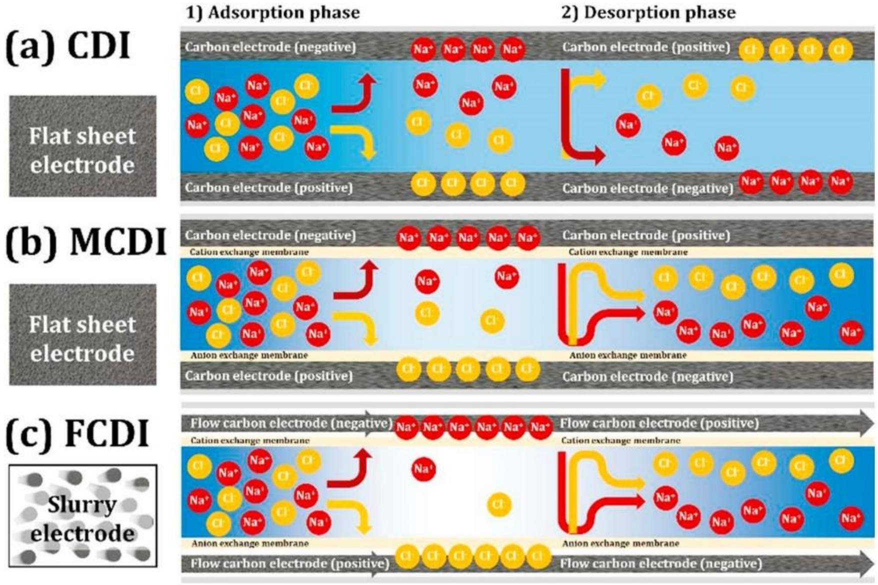

Figure 2-6: Removal mechanisms of (a) CDI, (b) membrane CDI, and (c) flow electrode-CDI (Choi, Dorji, et al. 2019).

Capacitive deionisation is a promising technology for desalination of low-saline water sources such as brackish water, and therefore, a large portion of CDI research is dedicated for brackish water desalination. Currently, several technologies are used for brackish water desalination: membrane-based pressure driven (i.e., reverse osmosis (RO) and nanofiltration (NF)) and electrochemically driven (i.e., electrodialysis (ED) and (electro-deionisation (EDI)) processes are by far the dominant technologies producing fresh water from various water resources (Rautenbach & Voßenkaul 2001; Xu & Huang 2008). Although significant improvement of desalination technologies has been achieved, limitations such as high energy consumption and/or membrane fouling have been reported to be the critical problem (Ghalavand, Hatamipour & Rahimi 2015; Jamaly et al. 2014). Therefore capacitive deionization (CDI), an electrochemical process removing the salt or charged species from the feed solution by the porous electrodes has emerged as the next-generation desalination technique (Porada et al. 2013). The following sections summarizes the use of most common CDI types for desalination.

2.8.3.1 Conventional CDI

The conventional CDI involves the use of static porous electrodes, mostly carbon-based to remove the salt ions from an aqueous solution when an electric potential is applied across the electrodes. In a conventional CDI process, due to the use of static electrodes, the salt removal capacity is severely limited (Suss et al. 2015). However, with the recent development of high capacity electrodes such as graphene, graphite, carbon composite and hybrid CDI electrodes, the adsorption capacity has significantly increased in the last few years between 30-78 mg/g compared to just about 15 mg/g for carbon aerogel electrodes even for conventional CDI system (Lee et al. 2014; Liu, Liao, et al. 2015; Liu et al. 2012). As shown in Table 2-4, a wide range of electrode materials with salt adsorption capacities as high 78 mg/g have been reported for CDI application under various feed water TDS of 500–4500 mg/l with desalination efficiency between 17-86% has been achieved for CDI.

2.8.3.2 Membrane capacitive deionisation (MCDI)

One of the major issues experienced by CDI is the occurrence of simultaneous adsorption of counterions and expulsion of co-ions in the spacer channel during adsorption and desorption phases, which reduces the desalination performance (Biesheuvel et al. 2011; Porada et al. 2013). However, with the integration of ion exchange membranes with CDI, this phenomenon is greatly reduced as indicated by various studies, thereby providing complete regeneration of the electrode capacity and also drastically increasing both desalination efficiency and energy efficiency (Kim & Choi 2010c; Li & Zou 2011). Table 2-3 provides selected data on MCDI performance on desalination.

The first MCDI was used in desalination of thermal power wastewater, where salt removal rate for MCDI was 19 % higher than CDI (Lee et al. 2006). Several desalination experiments then followed, which further demonstrated the superior performance of MCDI over conventional CDI process. Similarly, the MCDI salt removal of higher than 92 % was reported by (Lee et al. 2006; Li et al. 2008; Liu et al. 2014), where MCDI was found to remove between 25-44 % higher removal efficiency than CDI. In another study, MCDI performance was found to be 130 % higher than CDI for 1000 mg/L feedwater (Liang et al. 2013). More importantly, the MCDI exhibited better overall performance over long operation hours compared to CDI (Omosebi et al. 2014). In a similar study, Kim & Choi (2010a) determined 50 % better salt removal and higher energy efficiency in MCDI than CDI. It was also observed that at Constant Current (CC) operation, MCDI not only produces stable effluent but also consumes lower energy than RO however, its application is limited only at feed TDS of less than 2000 mg/l (Zhao, Biesheuvel & Van der Wal 2012). It has been proved that among the most common CDI architecture such as conventional CDI, MCDI and flow CDI, only MCDI can operate at thermodynamic efficiencies similar to that of reverse osmosis accounting for energy recovery (Hand et al. 2019). Although CDI is prone to organic fouling such as sodium alginate and humic acid with salt adsorption reduction between 70-75%, and charge efficiency reduction between 65-90%, the effect on MCDI for both adsorption capacity and charge efficiency were was rather limited, which clearly shows the advantage of incorporation ion-exchange membrane in CDI (Hassanvand et al. 2019). Even in the treatment of membrane bioreactor effluent with significant TOC content, continuous operation of MCDI pilot unit for 15 days showed only slight reduction in the adsorption capacity as reported in our earlier study (Kim et al. 2019). Therefore, it is not surprising that most commercial suppliers of CDI technology have preferential use of MCDI as the main CDI technology for commercialization.

Another important development in MCDI is the use of a direct coating of ion exchange polymers on the electrode surface as introduced in 20111 (Lee et al. 2011) instead of using a separate ion exchange layers normally used in MCDI. Such a technique is not only found to be energy efficient due to the thinner layer of ion exchange layers, but the application of MCDI has also widened significantly. For example, it is possible to coat the commercial activated carbon with ion-selective resin and polymers to make MCDI more selectivity as done in this research, and also for specific nitrate and lithium recovery (Ryu et al. 2013; Yeo & Choi 2013). Further significant progress has been made on the use of alternative electrode materials to carbon such as intercalation materials which provide similar salt adsorption capacity to carbon electrodes by operating at a much lower voltage, but without the use of ion exchange layers, thereby making the overall process more energy efficient (Singh et al. 2019).

2.8.3.3 Flow CDI (FCDI) and other advance CDI

The flow electrode CDI (FCDI) introduced by (Jeon et al. 2013) integrated with the ion-selective membrane is a novel concept where the carbon electrodes are rather suspended and mobile, as opposed to static electrodes found in conventional CDI (Fig. 2-7). They demonstrated over 95 % salt removal efficiency for a feed TDS of 32000 mg/l, making it feasible to even desalinate seawater, however, details on energy consumptions were not evaluated. The FCDI fundamentally addresses most of the limitations experienced earlier related to the limited salt adsorption capacity of electrodes and provided a solution for continuous operation of the CDI due to a constant replenishment of suspended carbon particles into the system. Following up on the discovery of the FCDI concept above, the possibility of incorporating continuous energy generation from FCDI due to its continuous operation mode was also evaluated (Porada et al. 2014). This development obviously will lead to better CDI operation design and also incorporate higher energy efficiency in the system. Although FCDI is a novel and promising CDI technology, most studies are confined to lab-scale and any practical application and field demonstration are severely limited. The current lab-scale studies using FCDI focus more on the salt removal efficiency, and there is no clear assessment of the charge efficiency of such a system, which determines the total energy consumption of desalination. Recent energy consumption in different CDI system concluded that MCDI is much more energy efficient compared to CDI or even FCDI (Hand et al. 2019).

Another evolution of CDI is the use of Hybrid electrode CDI (HCDI) as introduced by Lee et al. (2014), which is basically a combination of CDI and battery system using asymmetric electrodes: one electrode containing sodium manganese oxide (NMO) and the other is a conventional carbon electrode. During the adsorption process, sodium ions are held by the NMO due to a chemical reaction, whereas the chloride ions are attracted to the carbon electrode. Significantly high adsorption capacities between 27.7-31.2 mg/g were reported for a varying feed water TDS of 292-5844 mg/l compared to just about 15 mg/g for carbon-based electrodes.

Table 2-4: Salt adsorption rate and removal efficiency of different types of CDI electrode materials and system types. As the salt adsorption rate and removal efficiency results were obtained from the lab-scale experiments, capacity of the CDI system was not stated (Dorji et al. 2019).

Feed water TDS conc. (mg/l)	**Flow rate (mL/min)**	**Salt adsorption rate (mg/g)**	**Salt Removal efficiency (%)**	**Applied voltage (V)**	**Electrode materials**	**CDI types**	**Remarks**	**Ref.**
1506	7000	-	75-82	1.5	Activated carbon	**CDI**	Effect of hardness on long-term CDI operation	(Zhang, Mossad & Zou 2013)
1676		-	55-86					
1500	7000	-	75-80	1.5			Performance of commercial portable CDI unit	(Mossad, Zhang & Zou 2013)
2500	5	10.5	27	1.6	Activated carbon cloth		Desalination and disinfection properties of CDI	(Laxman et al. 2015)
1500		8.9	32	1.6				
2000	25	7.7	84	1.8	Activated carbon with TiO_2		Fabrication and performance evaluation of the electrodes prepared with titanium dioxide and activated carbon	(Ahmad et al. 2016)
2500		10.4	82					
3000		11.2	71					
4000	6	8.9		1.2	Activated carbon fibre		Evaluation of performance of different types of activated carbon fibre electrodes in desalination	(Huang et al. 2012)
2000	-	7	-	1.3	Carbon aerogel		Desalination performance of brackish water and iodine recovery using CDI	(Xu et al. 2008)
1168	-	13	-	1.2			Desalination application using carbon aerogel electrode in CDI	(Hou, Huang & Hu 2013)
600	500	8.4	66	1.2			Electrode fabrication and assessment of desalination performance	

700			60		Mesoporous carbon aerogel			(Kohli et al. 2016)
1000			80					
1200			86					
1500			84					
1000	80	-	60	1.4	Carbon composite		Fabrication of composite electrode and evaluation of desalination performance	(Lee et al. 2009)
							Preparation of 3-Dimensional hierarchical porous carbon composite electrode	(Wen et al. 2012)
800	20	20.76	-	1.2	Graphene oxide/resorcinol-formaldehyde		Synthesis of graphene-composite electrode for CDI	(Liu, Liao, et al. 2015)
		33.52	-	1.8				
500	25	16.1	-	1.2	Flexible cotton derived carbon sponge		Fabrication of cotton-derived carbon sponge electrode	
3970	30	14.6	35	1.2	Mesoporous carbon flat sheet with graphite		Synthesis of mesoporous carbon electrode for desalination	(Tsouris et al. 2011)
4460		14.5	31					
3000		5.3	17.6					
1000	-	78.73	-	1.4	Polypyrrole/graphite		Investigation of dopants on the adsorbing performance of polypyrrole/graphite electrodes for CDI	(Liu et al. 2012)
500	1000	-	90.6	-	Activated carbon	**MCDI**	Study demonstrating energy recovery potential of MCDI during desorption phase	(Długo ki & van der Wal 2013)
503	-	-	70	-			Practical application of MCDI for desalination of cooling tower feed water	(Van Limpt & van der Wal 2014)
1000	40	-	92	1.2	Activated carbon cloth		performance comparison between CDI and MCDI	(Lee et al. 2006)

-	40		93.5	1.6	Carbon nanotube-nanofibre	Fabrication of carbon nanotube-carbon fibre composite electrode for MCDI desalination	(Li et al. 2008)
-	50	5.6	93	1.2	Carbon nanotubes	Incorporation of ion exchange polymer directly on the electrode as modified MCDI	(Liu et al. 2014)
1000	9		90	1.2	Carbon fibre	Performance of different types of ion exchange membranes on MCDI	(Liang et al. 2013)

2.8.4 CDI operation mode and factors affecting CDI performance

2.8.4.1 CDI operation mode

The two main types of CDI experimental design or CDI operation involves a single-pass (SP) operation or a batch-mode (BM) operation as shown in Fig. 2-9 (Porada et al. 2013). In a single-pass mode, the feed water passes through the CDI system only once, and the treated water quality parameters such as conductivity profile, pH and ion concentration are measured at the outlet of the CDI unit to evaluate the performance of the CDI unit. Under a batch-mode operation, the treated water from the reservoir is recycled back to the reservoir, therefore, feed water flows between the electrodes multiple times, and the water quality is assessed in the reservoir. Most fundamental studies to evaluate the performance of the electrodes are conducted under a batch-mode operation as conducted in this research using a single pair of electrodes. However, due to the rapid adsorption of ions in CDI during the application of the voltage, most large-scale CDI system uses a single-pass approach because it is more efficient than a batch-mode. A similar methodology was adopted in the operation and optimisation of the performance of the pilot-MCDI unit in this research.

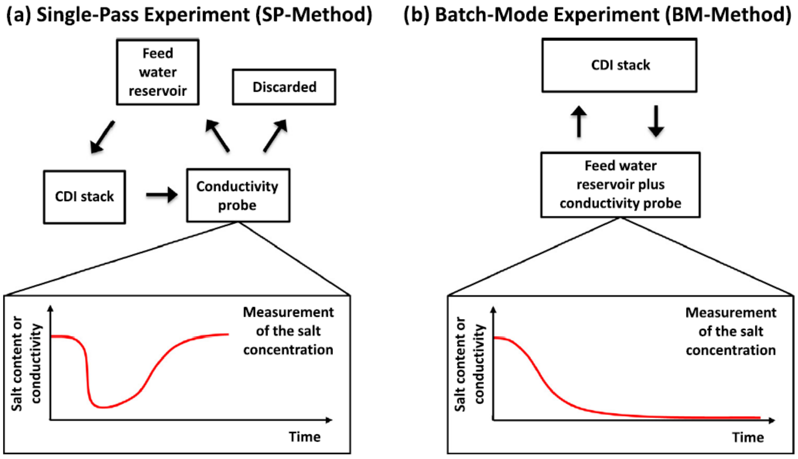

Figure 2-7: Schematics and expected conductivity profiles of (a) Single -pass (SP) and (b) Batch-mode (BM) CDI operation (Porada et al. 2013).

2.8.4.2 Effect of operational parameters

There are several operational parameters in CDI which can be controlled to determine the level of deionisation required. The two most important parameters that can be easily tuned are the applied voltage and the flow rates. As stated earlier, the removal of the ions is related to the formation or thickness of the EDL layer, which is proportional to the applied voltage (Dorji et al. 2018; Dorji et al. 2019). Therefore, high voltage application provides better deionisation however, application of a voltage in excess of 1.2 V is not recommended to prevent water electrolysis, which can be counterproductive for deionisation (Porada et al. 2013). Similarly, operating the CDI at high constant current results in superior deionisation however, the applied current has to be lower than the threshold current to prevent water electrolysis.

The flow rate used for adsorption and desorption also plays a significant role in determining the efficiency of the CDI system operation. The effect of flow rate on single-pass CDI operation is more sensitive where slower flow rates result in superior performance and the use of high flow rates produce treated water that is inferior in quality. These observations are related to the hydraulic resident time (HRT), which is more favourable at slower flow rates compared to high flow rates (Mossad & Zou 2012). However, it is important to note the unit productivity of treated water decreases at low flow rate although the quality of the treated water can be much better than operating the unit at high flow rates. The flow rate can also have a significant effect on the energy consumption where high flow rates normally indicate lower energy consumption per unit of treated water produced but the quality of the treated water is compromised. Therefore, it is important that the optimisation of CDI operation should be dictated by the level of treatment required, based on which energy consumption can be optimized (Chapter 4). The effect of flow rate on the CDI performance operated under a batch-mode is less sensitive due to increased HRT, as feed water make multiple passes through the electrode stack as determined in the lab-scale study in this research (Dorji et al. 2018).

2.8.4.3 Effect of water quality parameters

The major water quality parameters that affect deionisation in CDI are feed water composition and pH of the feed solution. Since the electrosorption in CDI is mainly dependent on the removal of ions from water rather than separating water molecules as is normally the case with membrane process, the concentration of total dissolved salts significantly determines the CDI removal efficiency for deionisation. As a result, CDI application is mainly limited to the brackish water desalination, which is one of the major challenges for CDI application (Porada et al. 2013; Suss et al. 2015). It was reported that CDI is more energy efficient than RO only for feed water TDS of less than 2000 mg/L, and thus far, the overall salt adsorption is limited by the adsorption capacity of the electrodes, and not so much by the salt adsorption rate. The effect of high background ion concentration significantly affects the selective removal of target ions because ions that have the highest concentrations tend to occupy more space on the electrodes (Choi, Lee & Hong 2016; Dorji et al. 2018). Removal selectivity of CDI is governed by the characteristics of the ionic composition in the feed water (i.e., ionic charge, hydrated radius, and initial concentration of ions), operating conditions (i.e., applied voltage), and electrode properties (i.e., pore size, pore size distribution, and structure) (Avraham et al. 2008; Hou & Huang 2013; Huang et al. 2016; Rana-Madaria et al. 2005).

2.8.4.4 Increasing water recovery in CDI

Water recovery, which is the ration of treated water produced over total water used is an important parameter to assess water treatment technologies. In CDI, it is common to operate CDI at 50% recovery using the same water flow rates for adsorption and desorption stages for a single pass system. However, the water recovery can be significantly increased up to 90% in CDI by adopting a variable flow operation (Ramachandran et al. 2019), where adsorption flow rates can be much higher than desorption flow rates, thereby producing more treated water than wastewater per cycle of operation. In fact, a similar approach to increase water recovery was used in the operation and optimization of the pilot-MCDI unit (Chapter 4). Besides, since the adsorption and desorption process in CDI is rather quite rapid, it is also possible to use shorter desorption time compared to adsorption time so that the amount of treated water produced per cycle is greater than 50%. It is important, however, to ensure that the electrode regeneration is effective for the flow rates and desorption time used so that the performance of the CDI system is consistent. A long-term pilot-scale CDI study for the treatment of cooling tower water reported water recovery between 80-84% (Van Limpt & van der Wal 2014). For batch-mode CDI application, the wastewater from desorption stage can be used again during the adsorption stage to recover more water, although the overall performance of the CDI will be compromised in terms of desalination efficiency, and more energy will be required since high concentration feed water has to be treated in the subsequent stages.

2.8.5 Origin and evolution of CDI

The review by Porada et al. (2013) provides a detailed account on the origin and how CDI has evolved over time since the 1960s when a conceptual study on CDI was developed (Fig. 2-8). It can be seen that significant progress was made from the 1990s in CDI to better understand the theoretical concepts of CDI and advances in the development of high capacity electrodes and the innovation on alternative CDI architectures. For example, the experimental and theoretical concept of MCDI was developed in 2006, which till this day is the next-generation CDI, which has found practical and commercial applications due to its improved desalination capacity and higher charge efficiency compared to conventional CDI. Another area of improvement was made on the production of high capacity electrodes such as carbon aerogel, carbon nanotubes, graphene and surface modified carbon electrodes. By 2012, CDI application has moved from a generic desalination system without much ion-selectivity to make MCDI for more selective for the removal of target ion such as nitrate. Also, constant current operation mode for CDI and MCDI was discovered, which has drawn many research interests, not only due to its better energy efficiency for desalination but also its potential application in energy recovery from MCDI operation compared to Constant Voltage operation.

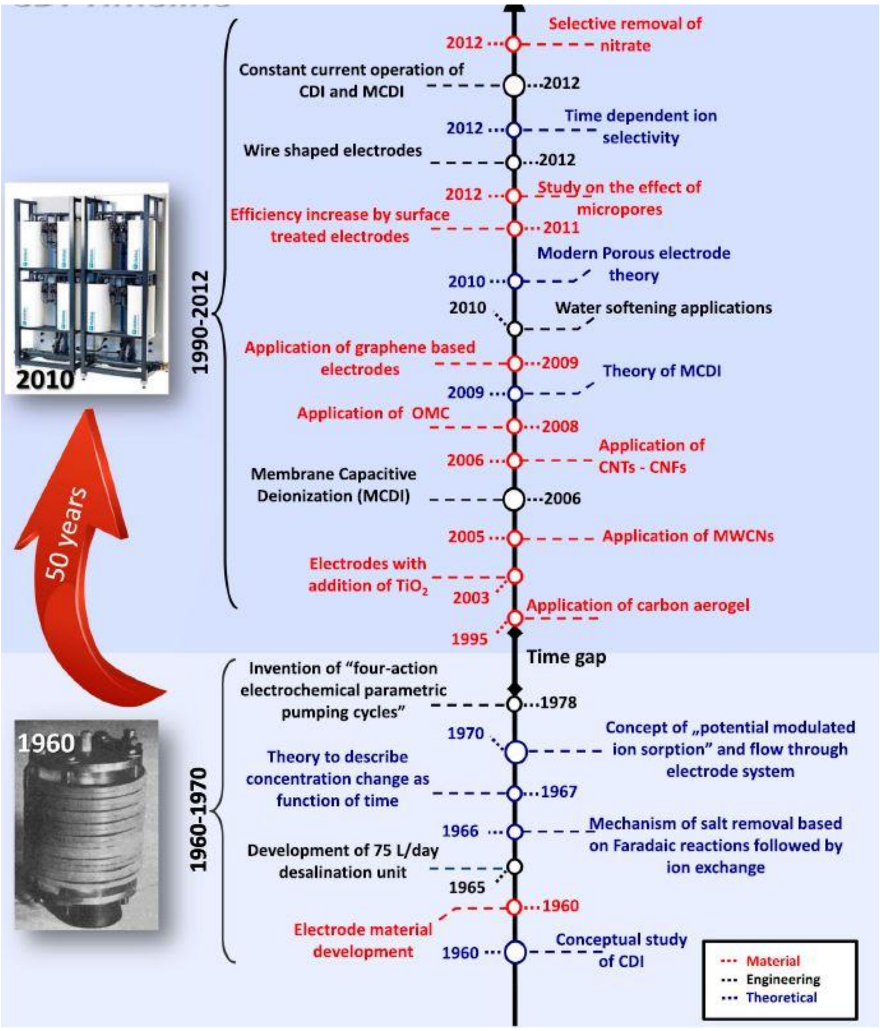

Figure 2-8: Timeline of scientific developments of CDI since 1960 (Porada et al. 2013).

A recent review paper by Tang et al. (2018) highlights further CDI development till 2016 where significant developments have occurred in CDI such as the development of desalination battery, flow electrode CDI, Hybrid CDI, Inverted CDI and use of cation intercalation desalination system (Fig. 2-9). Although these CDI processes and electrodes have demonstrated increased salt adsorption capacities, their production at commercial scale is limited, which will limit practical application in the field. Moreover, their reliability and cost will be a critical factor for a successful application.

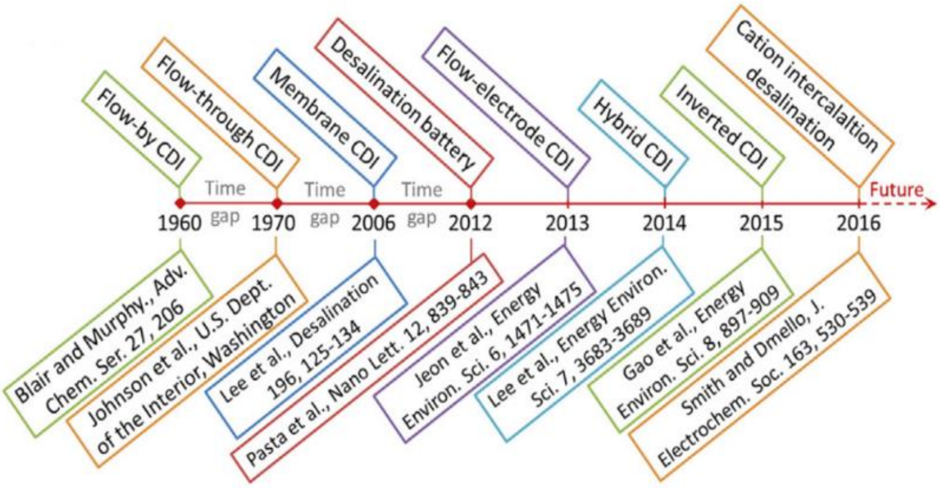

Figure 2-9: Evolution of CDI cell architectures (Tang et al. 2018).

2.8.6 Theoretical models for ion transport and removal in CDI

The review on the science and technology for water desalination by capacitive deionization by (Porada et al. 2013) provides a detail analysis of different EDL models (Fig. 2-10). It is briefly summarized in this section. The earliest concept of formation of an electrical double layer (EDL) at the interface of charged electrode and electrolyte is the Helmholtz model as illustrated in Fig. 2-10 (a) (Helmholtz 1853). In this model, when the electrode is charged either positively or negatively, the accumulated charge on the electrode is completely compensated by the redistribution of the ions of oppositely charged ions from the electrolyte on the respective electrodes, as a result, ion adsorption and desorption takes place during repeated charging and discharging of electrodes. However, this model inadequately described the salt adsorption in porous carbon electrode because not all the ions condensed onto a plane next to the electrode surface, rather ions remain diffusively distributed in a layer close to the surface. As a result, the Gouy-Chapman-Stern (GCS) model (Fig. 2-10 (b)) was developed to account for this discrepancy, however, both Helmholtz and GCS model failed to account for ion adsorption in the micropores and the EDL overlapping phenomenon. As a result, modified Donnan (mD) model (Fig. 2-10 (c)) was formulated in 2011, which was able to model salt adsorption capacity and charge storage as a function of various cell voltage, salt concentration and ion composition (Suss et al. 2015).

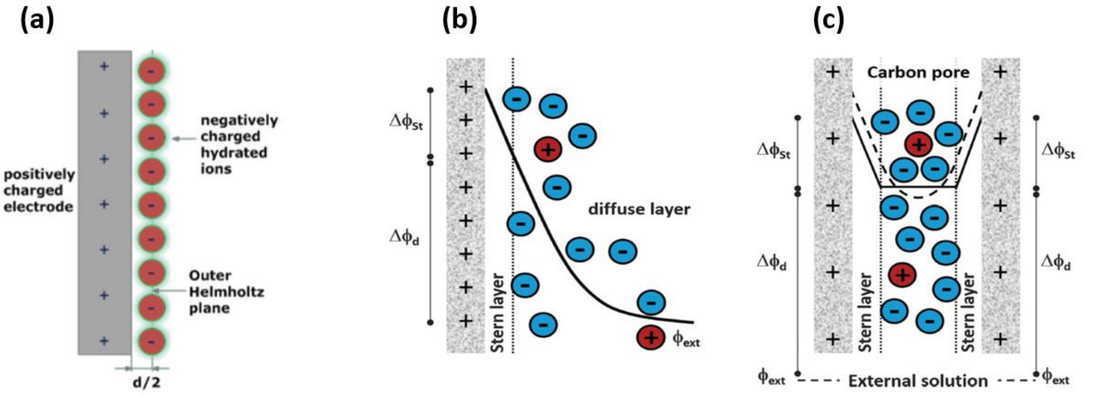

Figure 2-10: Models for charge and ions storage in porous CDI electrode (a) Helmholtz model (Gongadze et al. 2009) (b) Structure of the electrical double layer (EDL) as per Gouy-Chapman-Stern theory for non-overlapping EDL (c) mD model for overlapping EDL (Suss et al. 2015).

2.8.7 Modelling adsorption isotherms and adsorption kinetics in CDI

The classical adsorption isotherms such as Langmuir and Freundlich isotherms have been used in some CDI studies to interpret and fit the experimental data because CDI in principle is quite similar to adsorption process (Li et al. 2016; Wimalasiri, Mossad & Zou 2015). However, these adsorption models do not adequately represent and describe ion adsorption in CDI, which is an electrosorption process, a mechanism not experienced in a conventional application of adsorption technologies (Suss et al. 2015). As reported, the classical adsorption models are for adsorption of uncharged molecules over a common electrode, whereas in CDI, the ion removal is due to the formation of EDL structure, where cations and anions are removed using separate electrodes, therefore, classical models for adsorption becomes irrelevant (Porada et al. 2013).

The use of both linear and non-linear pseudo-first-order (PFO) and pseudo-second-order (PSO) rate equations are commonly used models to understand and quantify the adsorption kinetics in CDI study as per the equations (1) and (2) (Blanchard, Maunaye & Martin 1984; Lagergren 1898; Tran et al. 2017). However, such rate kinetics provide limited information on the adsorption kinetics in CDI for certain operating conditions, and they do not provide holistic information as a result of other important parameters such as applied voltage, and flow rates.

$$q_t = q_e \ [1 - \exp(-k_1 \ t)] \tag{1}$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 {q_e}^2} \tag{2}$$

where q_t is the amount of adsorbed solute over the total mass of adsorbent (µmol/g), q_e is the maximum adsorption capacity (µmol/g), k_1 (min^{-1}) and k_2 ($g^{-1}.min^{-1}$/ µmol) are the pseudo-first-order and second-order rate constants, and t the time.

2.8.8 Evaluating CDI performance

2.8.8.1 Charge efficiency and energy consumption in CDI

Charge efficiency, Λ is a ratio between moles of salt removed over moles of charge transferred to the electrodes, and it is a key parameter to evaluate the energy efficiency of CDI system, (Zhao et al. 2009) (Suss et al. 2015). It is reported that higher the charge efficiency, lower the energy consumption for the given CDI operation. Also, MCDI generally shows higher charge efficiency compared to CDI. In a recent study comparing the energy efficiency of CDI, MCDI and flow CDI, it was reported that only MCDI can operate at thermodynamic efficiencies similar to that of reverse osmosis accounting for energy recovery from the process (Hand et al. 2019). As discussed above, the charge efficiency of CDI is lower than that of MCDI, but for FCDI, while it demonstrated higher salt removal compared to CDI or MCDI, its energetic performance is significantly affected by higher overall resistance of suspended carbon particles.

The energy consumption in CDI is calculated using the following equation

$$\text{Energy (kWh/m}^3\text{)} = \frac{E_{ads} \int_0^t I_{ads} \ (t)dt \ + \ E \ _{des} \int_0^t I_{des} \ (t)dt}{V}$$

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. The energy consumption in pumping the feed water in CDI is normally neglected because, compared to the energy required for actual deionisation in CDI, pumping energy is negligible (Qin et al. 2019; Zhao, Porada, et al. 2013).

2.8.8.3 Salt removal efficiency (%) and Salt adsorption capacity (SAC)

The salt removal efficiency in CDI is normally calculated using the equation:

$$\textit{Salt removal efficiency (\%)} = \frac{C_0 - C}{C_0} * 100$$

Where C_0 and C represent initial and final salt concentrations (mg/L) in the feed water and treated water, respectively. The same methodology is used to calculate the TDS removal efficiencies by monitoring the electrical conductivity. Although representing CDI desalination efficiency in terms of % removal is a standard practice in water treatment, such results are difficult for cross comparison among different CDI types especially when different feed water characteristics and feed water volumes are used. Therefore, it is common in CDI to represent CDI performance by determining the salt adsorption capacity (eg. mg/g) (ratio of the mass of salt removed/total mass of electrode (mass) or by representing salt adsorption capacity as a ratio of total salt removed/unit surface area of both electrodes. The total mass of salt removed is determined based on the concentration change in the feed water and the treated water by specific ion analysis if the feed water contains mixed ions, or through simple monitoring of conductivity reading if the feed water contains only single electrolyte such as NaCl.

2.8.8.4 Energy consumption

The energy consumption is calculated using the equation:

$$\text{Energy (kWh/m}^3\text{)} = \frac{E_{ads} \int_0^t I_{ads}\ (t)dt\ +\ E_{\ des} \int_0^t I_{des}\ (t)dt}{V}$$

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.

2.9 Review of other applications of CDI in water treatment

2.9.1 Water softening

Water hardness due to the presence of minerals such as calcium and magnesium ions causes serious problems for boilers and heat exchangers due to scale formation. Several processes have been adopted to reduce water hardness such as chemical precipitation, ion exchange processes, NF, RO, and ED (Seo et al. 2010). However, most of these unit operations either consume high energy or require excessive chemicals usage, or generate a significant scaling on the surface of the membranes. Therefore, CDI has been examined as an alternative water softening process. The stronger attraction between the electrodes and multivalent ions makes the CDI technology suitable for removal of hardness ions. As such, some studies investigated the feasibility of CDI technology on the water softening application (Table 2-5).

Specifically, novel CDI electrodes for water softening have been investigated. The removal of calcium ions was 44% higher with Ca-alginate coated electrode compared to conventional CDI due to increased charge efficiency (55% for CDI against 85% for Ca-alginate-CDI (CA-CDI)) (Yoon et al. 2016). Another coating material, nanoporous γ-Al_2O_3 or SiO_2 was coated on Porvair carbon for increasing the Ca^{2+} removal efficiency (Lado et al. 2013; Wouters et al. 2013). With the coating on the surface of the carbon electrodes, specific surface area, as well as the electrochemical properties of the electrodes, was improved and the quantity of the removed Ca^{2+} was between four and five times higher than the uncoated electrodes. However, the choice of carbon materials also makes a major impact on ion selectivity. When SiO_2 was coated on the carbon foam, it showed good removal efficiency (about 89-98%), on the other hand, the removal efficiency of the carbon cloth with SiO_2 coating was only 16% (Wouters et al. 2018). It should be also noted that applied voltage and flow rate directly determine the removal efficiency. Increasing voltage and flow rate resulted in increased removal efficiency (Lado et al. 2014).

Table 2-5: Removal efficiency of hardness depending on the CDI types and electrodes under various operating conditions (i.e., applied voltage and flow rate).

Hardness ion/ concentration	Applied voltage (V)	Flow rate (mL/min)	Removal efficiency	CDI type/electrode		Remarks	Ref.
350 mg/L as $CaCO_3$	1.5	4	73%	CDI with carbon cloth electrode		Application of CDI in hardness removal using different types of activated carbon electrodes	(Seo et al. 2010)
10 mM, $CaCl_2$	1.2	2	14.2 mg Ca^{2+}/g	Ca-alginate coated on carbon electrode		Application of Ca-alginate coated MCDI for hardness control	(Yoon et al. 2016)
10 mM, $CaCl_2$		2	9.8 mg Ca^{2+}/g	CDI with carbon electrode			
35 mg/L as $CaCO_3$	2	10	3.5 mg $CaCO_3$/g	CDI with purified reduced graphene oxide electrode		Ultra-pure graphene oxide and reduced graphene oxide electrode for hardness control	(Tuan et al. 2015)
266 mg/L, $CaCl_2$	2	20	90%	CDI with activated carbon cloth electrode		Fabrication of carbon cloth electrode for hardness removal	(Dong et al. 2015)
46 mg/L, Ca^{2+}	1.2	28,000	74%	MCDI with porous carbon electrode		Application of MCDI for cooling tower feed water desalination	(Van Limpt & van der Wal 2014)
5.1 mg/L, Mg^{2+}		28,000	71%				
1.45 mM, Ca^{2+}	2	10	58%	CDI with activated carbon electrode in a multi-ionic environment		Ion selectivity study using CDI in a multi-ionic environment	(Hou & Huang 2013)
2.41 mM, Mg^{2+}		10	47%				
2.5 mM, $CaCl_2$	1.5	-	~98%	CDI with SiO_2 coating carbon electrodes	Carbon foam	Removal efficiency of CDI depending on carbon materials and the effect of coating on the surface of the electrodes	(Wouters et al. 2018)
			~89%		Carbon nanofoam		
			~16%		Carbon cloth		
			~82%		Carbon sheet		
3 mM, $CaSO_4$	0.8	110	1.35 mg, $CaSO_4$/g	CDI with SiO_2 coating carbon electrodes		Effect of applied voltage and flow rate on the ion removal/regeneration, charge efficiency and energy consumption	(Lado et al. 2014)
	1.0		2.97 mg, $CaSO_4$/g				
	1.2		4.38 mg, $CaSO_4$/g				
		45	3.38 mg, $CaSO_4$/g				

In addition, a higher removal for calcium ions was reported for carbon cloth over composite electrode due to better wettability of the carbon cloth (Seo et al. 2010). The authors also noted the importance of optimizing the pore size of the electrodes to improve the ion selectivity for divalent ions for possible water softening applications (Seo et al. 2010). The interesting approach for hardness removal using ion exchange process under CDI was also reported by adopting zeolite modified carbon electrode for hardness removal through CDI-assisted ion exchange mechanism (Kim et al. 2016). The application of external voltage led to a remarkable increase in calcium removal. In a slightly different study, a novel concept was introduced, where a monovalent cation selective membrane was used in MCDI to produce a divalent cation-rich solution as a means to stabilize permeate from NF or low-pressure RO (LPRO) (Choi, Lee & Hong 2016). This is another example where MCDI can be innovatively configured to serve specific needs for different applications.

2.9.2 Selective removal

In recent years, the selective removal of specific ions from the feed solution has become a critical issue in many industrial processes such as valuable resources recovery or toxic ion removal (Choi, Choi & Hong 2015; Lahav & Birnhack 2007; Reig et al. 2016). As a result, there are lots of innovations in technologies, however, generation of the secondary waste stream, higher energy consumption and higher capital cost were noted to be the inherent challenges (Fu & Wang 2011; Rana-Madaria et al. 2005). Therefore, the feasibility of the CDI process for selective removal has been extensively explored in this section.

2.9.3 Heavy metal removal

Due to rapid industrial development, an increasing amount of toxic heavy metals such as lead, cadmium, chromium etc. are released into the environment. A comprehensive review of the existing technologies for heavy metal removal was conducted by (Fu & Wang 2011). The most common heavy metal removal technologies include chemical precipitation, ion-exchange, adsorption, membrane processes, coagulation and flocculation, and electrochemical processes. The review found certain disadvantages of the above processes. For example, chemical precipitation produces a large volume of sludge and secondary waste, and they are good only for water containing a high concentration of ions. Similarly, ion-exchange also generates secondary waste during regeneration of resin, and they have limited large-scale applicability. The membrane processes are known to be efficient in heavy metal removal but they have higher operating cost, and electrochemical processes have higher energy and capital cost. Since CDI is proven to be an energy efficient technology for low TDS water, and it does not use any chemical in the processes, it can be a viable technology for heavy metal removal.

There are several studies on CDI application in removing different species of heavy metals from various water sources (Table 2-6). The removal efficiency difference between lead and sodium was critically investigated depending on the pH, initial lead concentration, and time (Liu et al. 2017). Lead was more sensitively affected by the pH changes and the removal efficiency was highest at the neutral pH condition (pH was 6). Other interesting results were the adsorption rate of lead and sodium. Due to the relatively high charge of lead compared to sodium, the adsorption equilibrium of lead was reached in a very short time, which indicates that highest removal selectivity between lead and sodium could be achieved with relatively lower operating time and neutral pH condition.

In addition to the study on lead removal, fundamental research on the removal efficiency of the two kinds of arsenic (As(Ⅴ) and As(Ⅲ)) was also studied with a different initial concentration of arsenic and applied voltage on the CDI system (Fan et al. 2016). As expected, increased applied voltage and initial arsenic concentration resulted in the increased removal efficiency of both As (Ⅴ) and As (Ⅲ). However, the sorption capacity of As (Ⅴ) was higher than that of As (Ⅲ) under all of the operating conditions. Additionally, with the presence of NaCl or natural organic matter (NOM), the removal efficiency of both arsenic ions was declined due to the competition effect. Specifically, NOM could potentially obstruct the electrode pores and therefore, the specific surface area would be reduced.

As the CDI process is operated with the potential difference between the pairs of the electrodes, charge and hydrated radius of the ions in the water determine the removal efficiency. Therefore, when considering the individual removal test, although cadmium and lead exhibit identical charge valence, due to the relatively large hydrated radius of the cadmium (4.26 and 4.01 Å of cadmium and lead, respectively), lead was more favourably removed. However, it should be noted that despite the larger hydrated radius of chromium than that of cadmium or lead, the removal efficiency of the chromium was much higher (Huang et al. 2016). Similar removal efficiency trend was observed when three metals were mixed in the solution with the same concentration. Specifically, the removal efficiency of cadmium was significantly inhibited due to the combined effect of hydraulic radius and charge valance (Rana-Madaria et al. 2005).

Table 2-6: Removal efficiency of heavy metal ions by CDI.

Pollutants	Concentration	Electrodes	Removal efficiency	Remarks	Ref.
Arsenic	0.02-0.1 mg/L	Activated carbon	86-98%	Use of solar-powered CDI unit for arsenic removal from synthetic water	(Zhang et al. 2016)
	0.1-200 mg/L	Activated carbon	0.01 - 0.025 mg, As(Ⅴ)/g	Effect of applied voltage and initial concentration on the removal efficiency of As(Ⅴ) and As(Ⅲ)	(Fan et al. 2016)
			0.005 - 0.014 mg, As(Ⅲ)/g		
	0.2 mg/L	Activated carbon	98.51%	Practical application of commercial CDI module for arsenic and lead removal in Mexico	(Garrido et al. 2009)
Lead	0.0267 mg/L		>60%		
	5-100 mg/L	3D graphene	60-99%	Heavy metal separation from wastewater by CDI with 3D graphene-based asymmetric electrodes	(Liu et al. 2017)
	0.5 mM	Activated carbon	43%	Assessment of CDI application in heavy metal (i.e., lead, cadmium, and chromium) removal	(Huang et al. 2016)
Cadmium	0.5 mM		32%		
Chromium	0.5 mM		52%		
	2 mg/L	Carbon aerogel	99.6%	Application of CDI in the removal of chromium from wastewater using carbon aerogel electrode	(Rana-Madaria et al. 2005)
	0.035 mg/L	Carbon aerogel	94%	Chromium ions removal using carbon aerogel electrodes for ground water remediation	(Farmer et al. 1997)
	0.025 mg/L		88%		
Copper	50 mg/L	Activated carbon	>90%	Copper ions removal from aqueous solution with CDI	(Huang, Fan & Hou 2014)

2.9.4 Phosphate and nitrate removal

Similar to heavy metal species, high concentration of phosphates and nitrates contained in the wastewater from agriculture and industrial applications should be removed for preventing the environmental concerns such as eutrophication of water source (Conley et al. 2009; Majumdar & Gupta 2000). While phosphorus is an environmental pollutant, it is also an essential element for food production, which is in short supply, therefore, it is not only important to treat water for phosphorus removal but it also has to be recovered (Cordell et al. 2011). The common unit process for phosphorus removal and recovery from wastewater is the struvite precipitation and sludge incineration where phosphorus recovery between 90-98% and 75% respectively can be achieved but it has substantial investment due to high chemical and energy demand (Cieślik & Konieczka 2017; Cordell et al. 2011). Several full-scale technologies exist for nitrate removal (Shams 2010), where maximum nitrate removal efficiency reported was 100% for the biological process followed by membrane processes such as RO (97%), ion-exchange (90%) and chemical process (70%). While the removal efficiencies have been reported to be quite good, the review also highlighted the issues of high operational cost, the extensive requirement of pre-treatment and post-treatment, and generation of secondary pollution as some of the challenges of these technologies. Therefore, several studies evaluated the removal efficiency of the phosphate and nitrate by the CDI process.

A pilot CDI unit (AQUA, EWP) was tested to evaluate phosphate removal and the removal efficiencies were 86% and 77% for feed water containing 50 and 300 mg/L phosphate, respectively (Huang et al. 2014). They also observed lower removal efficiencies for higher initial phosphate concentration and higher flow rates with optimum pH between 5 and 6, achieving 98% removal with a three-stage system. Another study also utilized same CDI unit for investigating the removal efficiency of nitrate at different initial nitrate (100, 300, and 500 mg/L of nitrate with 2.0 g/L, NaCl) and NaCl (300 mg/L of nitrate with 1.5, 2.0, and 3.0 g/L, NaCl) concentration, respectively (Tang et al. 2015). Although the experimental data was obtained from the batch mode CDI system operation, developed transport model was in good agreement with the tested results. Based on the model, removal trends of more diverse ion species could be further investigated. Likewise, a commercial CDI unit (DesEL Technology, ENPAR Tech. Inc.) was also used to assess nitrate removal from wastewater (88-98%, removal rate) (Broséus et al. 2009).

In the separate study, the removal efficiency and selectivity of nitrate were significantly improved with the coated anion-exchange resin (BHP 55) with high nitrate selectivity (Kim & Choi 2012; Yeo & Choi 2013). The resin employed in both studies preferentially adsorbed nitrate ions over other anions. Similar to BHP 55 coating, asymmetric carbon electrodes coated with SiO_2 and $Al_2O_3^-$ were used, and higher nitrate removal capacity was observed compared to the uncoated symmetric carbon electrodes (Lado et al. 2017). The faster ion transport due to the reduced hydrophobicity, increased specific surface area, and increased adsorption sites were identified as the major factors for higher removal (Fig. 2-11). Aforementioned studies improved the nitrate removal efficiency with coating on the surface of the carbon electrodes, on the other hands, a novel CDI electrode (Pd/NiAl-LMO film electrode) was also developed (Hu et al. 2018). Pd/NiAl-LMO electrode effectively captured nitrate to convert it to nitrogen (N_2) through the regeneration phase.

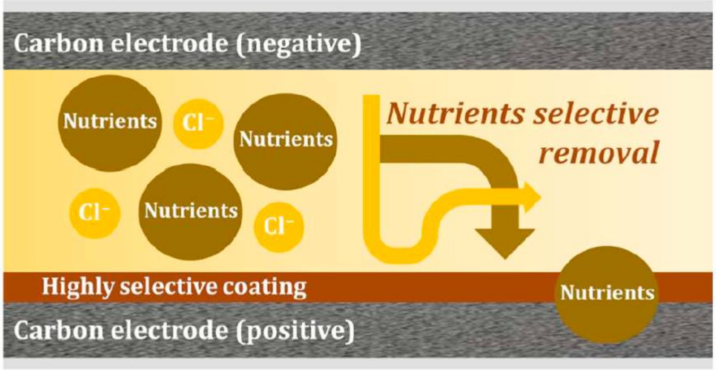

Figure 2-11: Use of nutrient selective coating materials to increase nutrient selectivity in the CDI process (Choi, Dorji, et al. 2019).

2.10 Improving energy efficiency in CDI

Due to the intensive energy consumption of conventional desalination techniques, CDI has emerged as the new technology for energy and cost-effective desalination process. However, there still exists a tremendous potential for reducing or recovering the energy used in charging the CDI unit. There have been great efforts on improving the energy efficiency of the MCDI technology and the energy recovery during the desorption stage (Fig. 2-12) (Anderson, Cudero & Palma 2010; Demirer et al. 2013; Jeon et al. 2014;

Pernia et al. 2014; Zhao, Biesheuvel & Van der Wal 2012). The adsorbed ions in the electrical double layers move from the electrode into the feed stream and the electrons get transported over the external load simultaneously, which resulted in the energy recovery (Długołęcki & van der Wal 2013).

As summarized in Table 2-7, with the introduction of nanoporous activated carbon electrode, 30 to 45% of the consumed energy could be recovered (Han, Karthikeyan & Gregory 2015), while under the optimized operating condition, up to 83.2% of energy recovery can be achieved. Indeed, the energy recovery rate can be more than 70% with inexpensive hydrophilic activated-charcoal based electrodes (Andres & Yoshihara 2016). It was also found that the energy recovery of 40% can be possible even for the conventional CDI cell (Demirer et al. 2013). Moreover, up to 83% of the used energy can be recovered in the regeneration phase under constant current condition using a MCDI stack (Długołęcki & van der Wal 2013). In order to identify optimum operating mode for higher energy recovery, energy recovery was tested under different voltages and currents for CV and CC mode, respectively (Kang et al. 2016). From the results, CC mode operation was found to be more advantageous than CV mode due to the higher energy storage and it was determined up to 47 % of the energy can be recovered for CC operation. However, in a separate study earlier, it was reported that up to 83% of the energy can be recovered (Długołęcki & van der Wal 2013). Since CDI desalination is already a low energy process, optimising energy recovery will further make the CDI technology more favourable and energy efficient over other desalination processes.

However, the resistance of the CDI cell seems to play a major role in determining the energy efficiency of the overall system. The contact resistance between current collector and the electrode was found to contribute about 90 % of the cell resistance (Qu et al. 2015)and suggests that sufficient pressure and close contact between the current collector and electrode should be maintained. They also state that cell resistance should be one of the parameters in CDI performance evaluation alongside salt adsorption capacity and salt removal rate.

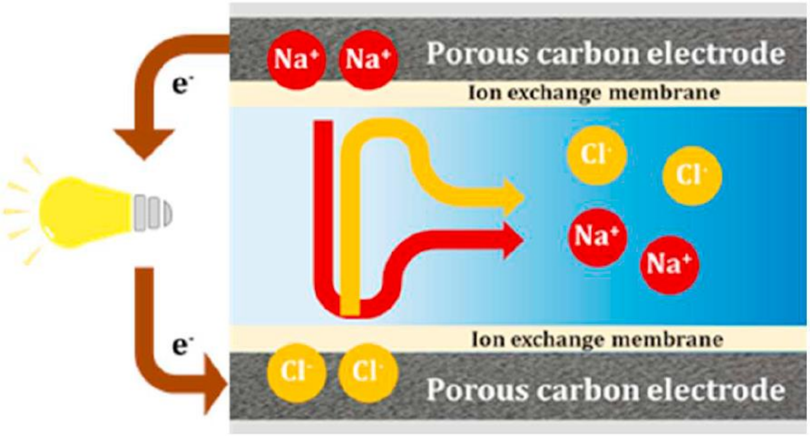

Figure 2-12: Release of stored energy from CDI during the desorption/discharging phase (Choi, Dorji, et al. 2019).

The energy recovery ratio of various operating conditions (operating time, feed solution salinity, and charging current) and system configuration of CDI (cell size and electrode surface) were also investigated (Álvarez-González et al. 2016; Demirer et al. 2013). The energy recovery ratio of the CDI system increased with the increment of feed solution salinity, applied voltage, but decrement of the cycle duration. Specifically, optimum electrode surface and current for minimizing the energy losses was critically simulated and validated (Álvarez-González et al. 2016; García-Quismondo et al. 2013). On the other hand, the size of the CDI system has little impact on the energy recovery ratio although increased system size may enhance the thermodynamic efficiency.

Table 2-7: Recent improvements on energy recovery of the CDI process. CC and CV respectively indicate constant current and constant voltage.

Maximum energy recovery (%)	**CDI type**	**Experimental conditions**					**Ref.**
		Electrodes	Recovery mode	Feed solution concentration	Applied current for desorption	Remarks	
83	MCDI	Activated carbon	CC mode	8.6 - 86 mM	2 - 15 A	Energy recovery of MCDI depending on the feed solution quality and applied current	(Długoł cki & van der Wal 2013)
40	MCDI	Activated carbon	CC mode	20 mM	8.64 mA	Energy recovery in MCDI and CDI under CC and CV mode	(Zhao, Biesheuvel & Van der Wal 2012)
20	FCDI	Activated carbon	CC mode	35 g/L	0.1 A	Performance and energy recovery in FCDI	(Jeon et al. 2014)
29	CDI	Carbon aerogel	CV mode	0.5 g/L	1 mA	Effect of operating time, feed solution concentrations, and CDI system sizes on energy recovery in CDI	(Demirer et al. 2013)
39				1.0 g/L			
63				1.5 g/L			
83	MCDI	Activated carbon	CC mode	0.5 - 1 g/L	1 A	Effect of water recovery and flow rate on energy recovery in MCDI	(Zhao, Porada, et al. 2013)

2.11 Challenges in CDI technology: fouling, scaling, and scale-up

With rapid development in CDI technology, unconventional water resources such as seawater or municipal wastewater have been gradually investigated as the feed solution. Although the regeneration stage of CDI process mitigates the formation of fouling layer or precipitation of components from the solution onto the electrode surface (Kim & Choi 2010a; Lee et al. 2006), organic fouling or scaling potential still deteriorates the sustainability of CDI (AlMarzooqi et al. 2014). Specifically, fouling and/or scaling could decrease removal efficiency and permeate flow rate as well as increase energy consumption (Mossad & Zou 2013). It is also noteworthy that sustainable operation of CDI is as critical as developing high removal performance electrodes or system, however, there have been only a few studies on organic fouling in CDI. For better understanding and improving the CDI sustainability, fundamental investigations of CDI on fouling/scaling mechanism should be a priority. Then, optimized pretreatment processes and cleaning methods with different feed solution properties for organic fouling control are considered to be essential. With these advances, successful and sustainable operation of CDI in the real application could be achieved.

2.12 Conclusion and future direction for expanding the CDI applications

As an emerging desalination technology, CDI is fast gaining momentum as reported from the significant number of publications related to CDI development. A lot of progress has been made in CDI including the development of several new CDI types such as membrane CDI and Flow CDI as well as other innovative hybrid CDI system, each with its own advantages and disadvantages. For example, while conventional CDI is the simplest form of CDI, its desalination and energy efficiency was compromised due to its inability to control counter ions adsorption and co-ion desorption process. A slightly advanced version of CDI called MCDI was developed which significantly showed better desalination efficiency as well as energy efficiency. Although the use of separate layers of ion exchange membranes in CDI had some cost implications because of expensive ion exchange membranes, the ability to coat ion exchange polymers directly on the surface of the electrodes is expected to significantly reduce the cost of the overall system of MCDI. There is also significant interest on better understanding the performance:

desalination efficiency and energy efficiency of flow CDI, which has the ability to continuously desalinate water and also showed its applicability to desalinate high salinity water such as seawater at lab-scale investigation. However, further investigation is required to assess its practicability and energy consumption since it is a rather complex process to operate.

A significant focus on CDI research is related to the development of novel CDI electrode, which accounts for more than 50% of CDI related research. While the development of high capacity electrodes is crucial, not only the performance of the electrodes but also the ease of manufacturing and cost have to be considered for commercial and practical application purpose, and their long-term performance under repeated charging and discharging should also be investigated.

As reviewed in this chapter, CDI has been found to be a promising solution for water and wastewater treatment especially due to its ability to remove a wide range of charge ions from aqueous solution. The range of applications includes brackish water desalination, water softening, selective removal of ions including nutrient removal and recovery. Although CDI faces a major problem in selective or target removal of specific ions, recent studies have demonstrated that CDI electrodes can be tuned by coating selective ion selective solution for the removal of target contaminants. It is expected that the future works on CDI will involve more research into CDI application for removal and recovery of target ions from water sources.

Bromide is an important precursor for the formation of several different types of disinfection by-products during water disinfection. As reviewed in this chapter, most of the current water treatment technologies such as membrane, ion exchange and adsorption processes have the ability to remove bromide from various sources. However, most of these technologies have reported certain limitations. For example, membrane processes are associated with high energy demand, use of ion exchange resins and adsorption technology are limited by the high cost of materials, generation of wastewater and their inability to scale-up to be applied on large-scale water treatment plants. The application of capacitive deionization for bromide have been reported mostly for their removal using conventional CDI process. However, the use of membrane capacitive deionisation (MCDI) for bromide removal can be highly efficient compared to conventional membrane process.

There is a clear gap for the need to investigate in greater detail, on the technical and economic assessment of bromide removal using MCDI. Further, the recent development on the improving ion selectivity in MCDI by surface modification of the carbon electrodes by incorporating specific ion selective resin can also be a potential opportunity for investigation.

CHAPTER 3

MEMBRANE CAPACITIVE DEIONISATION AS AN ALTERNATIVE TO THE 2ND PASS FOR SEAWATER REVERSE OSMOSIS DESALINATION PLANT FOR BROMIDE REMOVAL

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P. Dorji, J. Choi, D.I. Kim, S. Phuntsho, S. Hong, H.K. Shon, 'Membrane capacitive deionisation as an alternative to the 2nd pass for seawater reverse osmosis desalination plant for bromide removal', *Desalination*, 433 (2018).
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3.1 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 pressure to produce freshwater is pursued as a major technology to augment fresh water supplies. A significant investment is made in desalination plants in Australia to secure the country's water supply and it's current and planned large-scale SWRO plants have a total capacity of 1874 ML/d (Crisp, Swinton & Palmer 2010) with a total investment in desalination plants exceeding AU$ 10 billion already (Gude 2016). However, the presence of a high concentration of bromide in seawater presents a unique challenge since high concentration of bromide in water can lead to formation of toxic and harmful disinfection by-products during water disinfection process (Hua, Reckhow & Kim 2006; Kampioti & Stephanou 2002; Liu, Wang, et al. 2016). 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. 3-1(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.

There are several technologies used and evaluated for bromide removal from the water such as RO, NF, electrodialysis and adsorption techniques (Watson, Farré & Knight 2012). 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 mainly due to high capital investment, and operating cost due to high energy requirement. Depending on the SWRO membranes used, a bromide concentration of 100 µg/L to 1,000 µg/L is still expected in most first pass SWRO permeate. Therefore, SWRO desalination plants in Australia generally have to adopt a two-stage RO process as mentioned above mainly for effective bromide removal but at a significant additional cost. The Capacitive Deionization (CDI) is an electrosorption process to remove ionic impurities from the wastewater due to the formation of an electric double layer (EDL), where the ions are temporarily adsorbed on the surface of the charged electrodes (Pekala et al. 1998). 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 (Farmer et al. 1995; Suss et al. 2012). Moreover, the fact that 47-83% of the energy spent in CDI can be recovered makes CDI an energy efficient process for desalination (Długołęcki & van der Wal 2013; Kang et al. 2016). Further, it has been demonstrated that the operational parameters can be tuned to obtain the required effluent quality (Huyskens, Helsen & de Haan 2013; Zhao, Satpradit, et al. 2013).

In this chapter, a fundamental study on 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 in a lab-scale MCDI setup, using a pair of commercial activated carbon electrodes and cation and anion exchange membranes as shown in Fig. 3-1. 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 was 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.

3.2 Materials and methods

3.2.1 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 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 two minutes each until a dynamic equilibrium was reached to ensure cycle replicability. All the experiments were done as per the experimental design (Table 3-1) 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. 3-1(c).

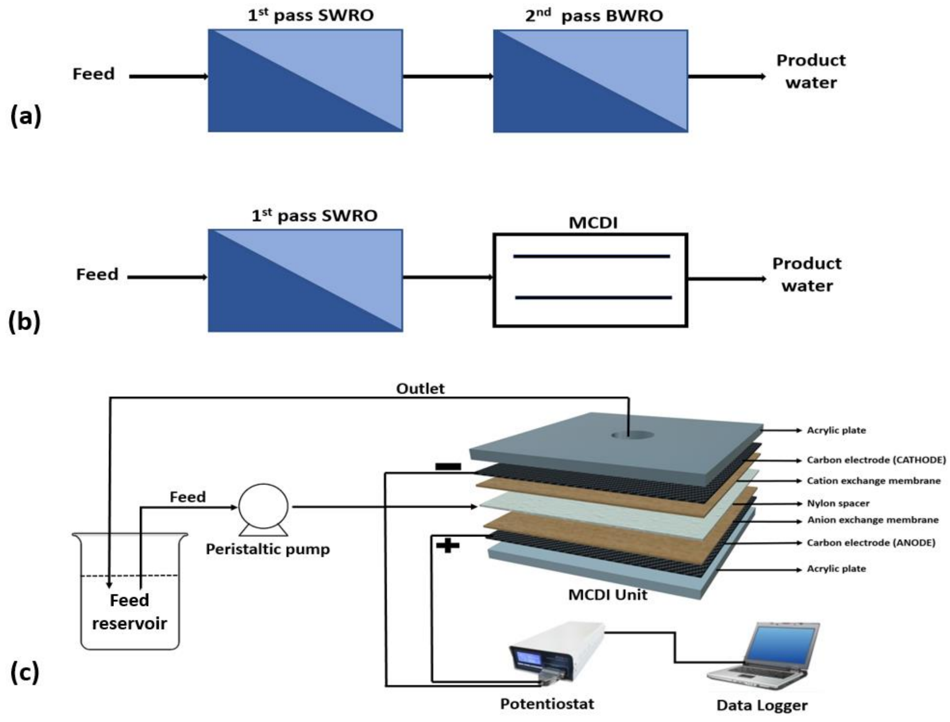

Figure 3-1: Schematic process diagram (a) existing second-pass SWRO configuration (b) proposed SWRO-MCDI hybrid (c) process schematic of lab-scale MCDI operation.

3.2.2 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, 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 cm^2 connected to a high-pressure pump controlled manually using a feed valve, by-pass valve, back pressure regulator, pressure gauge and a flow meter. A 10 L actual seawater collected from Rose Bay, New South Wales in Australia with a TDS of 38,400 and bromide concentration of 75.8 mg/L was passed through the RO membrane at a cross-flow rate of 1 L/min and applied pressure of 60 bar. The RO permeate was collected while the brine was constantly recycled into the feed 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 represent typical 1st pass SWRO permeate in actual desalination plants.

3.2.3 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:

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

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

$$\text{Energy (kWh/m}^3\text{)} = \frac{E_{ads}\int_0^t I_{ads}\ (t)dt\ +\ E\ _{des}\int_0^t I_{des}\ (t)dt}{V} \qquad (2)$$

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.

Table 3-1: Water quality and experimental conditions in the lab-scale MCDI.

Test parameter	**Water quality**			**Operational condition**		
	Ion composition	**TDS (mg/L)**	**pH**	**Applied Voltage (V)**	**Flow rate (ml/min)**	**Operating time (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

3.3 Results and discussions

3.3.1 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.

3.3.2 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. 3-2 (a) shows the bromide removal efficiency ranged from 99.5% to 99.9% for all the water tested. 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 (Mossad & Zou 2012).

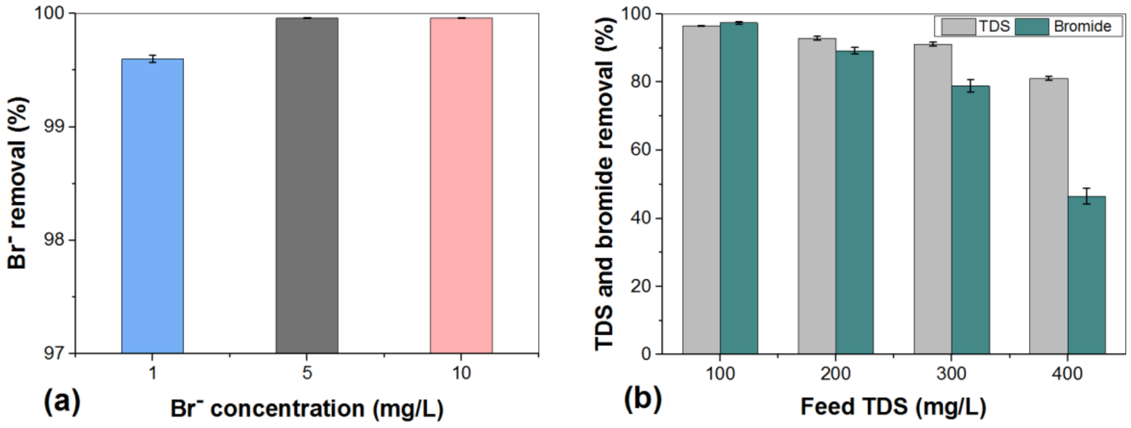

Figure 3-2: (a) Effect of bromide concentration containing only single electrolyte on bromide removal efficiency (b) bromide removal under various background TDS mainly consisting of NaCl with a fixed bromide concentration of 1 mg/L for all types of feed water. The operational voltage and operating time were 1 V and 10 minutes, respectively.

Fig. 3-2 (b) illustrates the influence of background TDS on the bromide removal by MCDI process. The desalination efficiency in the 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 (Chen et al. 2015; Hou & Huang 2013; Mossad & Zou 2012). 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 (Xu et al. 2008). 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.

3.3.3 pH of the feed water

The bromide removal efficiencies at different pH conditions were above 99% for all types of feed water (Fig. 3-3) 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 (Liu, Wang, et al. 2016). Unlike boron and phosphate whose removal with CDI depends on pH since they take different chemical forms based on the pH (Avraham et al. 2011; Huang et al. 2014), bromide removal does not seem to have any specific association with pH variation.

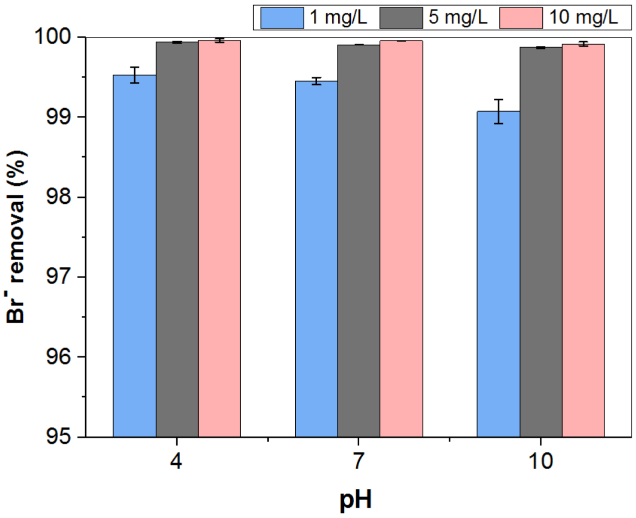

Figure 3-3: The influence of pH on bromide removal at a flow rate of 40 ml/min, applied voltage of 1 V and adsorption time of 10 minutes.

3.3.4 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.

3.3.5 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 the 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 (Porada et al. 2013). 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. 3-4(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.

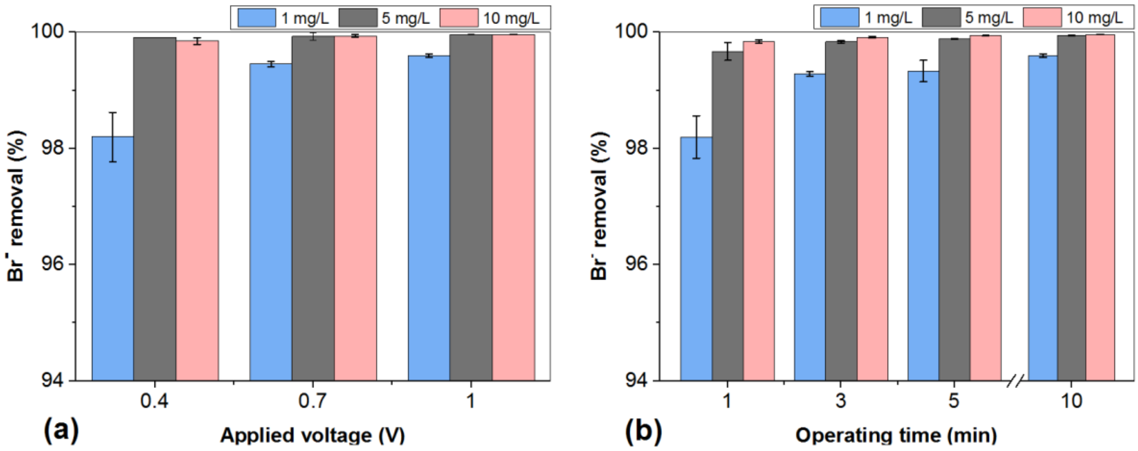

Figure 3-4: The effect of (a) applied voltages at 10 minute adsorption time (b) operating time on bromide removal at 1 V at pH 7.

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. 3-4 (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 (Zhao et al. 2012), it is possible to optimise the MCDI operation.

3.3.6 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. 3-5. 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 (Porada et al. 2013). 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 (Tang et al. 2015). 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 (Mossad & Zou 2012). Therefore, optimising the flow rate for optimum energy consumption and water quality is an important parameter for optimal MCDI performance.

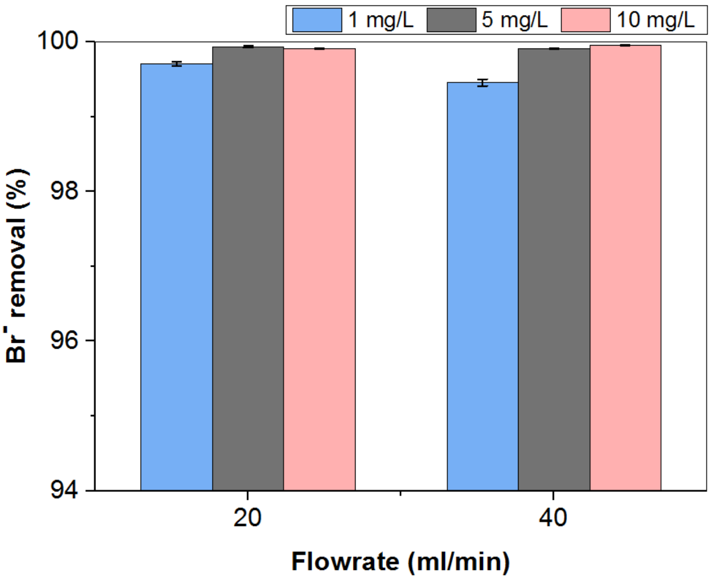

Figure 3-5: Influence of flow rates on bromide removal efficiency at the applied voltage of 1 V and operating time of 10 minutes.

3.4 Bromide removal from a real 1st pass SWRO permeate

3.4.1 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. 3-6(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. 3-6(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 electrodes 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 (Welgemoed & Schutte 2005). Other research showed the following selectivity $SO_4^{2-}>Br^->Cl^->F^->NO_3^-$ with 97% bromide removal with initial bromide concentration of 8.6 mg/L of Br^- (Mossad & Zou 2012).

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. 3-6 (b). It can be observed that the TDS adsorption capacity increased with the increase in feed water TDS until the electrode is completely saturated. 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 (Mossad & Zou 2012). The TDS removal, however, is in fact not very critical given the already low TDS of the 1st pass SWRO permeate which requires remineralisation.

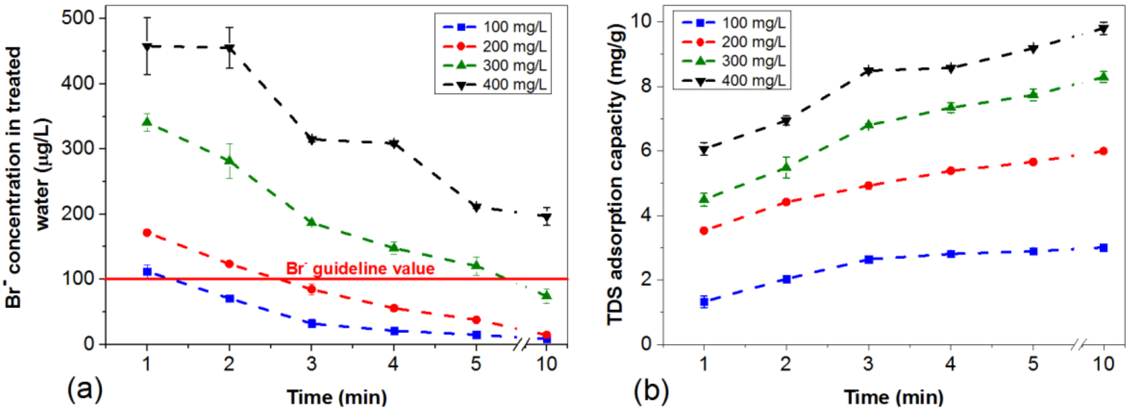

Figure 3-6: (a) bromide removal from 1st pass SWRO permeate with different feed water TDS at 100, 200, 300 and 400 mg/L TDS with initial bromide concentration of 192, 382, 561 and 774 µg/L as Br- respectively at 1 V. The solid red line represents the guideline value for Br^- concentration in the product water in most desalination plants (b) TDS adsorption capacity for different TDS feed water with the same experimental conditions as above.

3.4.2 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 (Zhao, Porada, et al. 2013). 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/m^3 for each feed water to ensure that the bromide concentration of less than 100 µg/L is maintained in the treated water (Fig. 3-7). 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 since the pumping energy in CDI is negligible compared with the energy required for adsorption and desorption of ions (Qin et al. 2019). 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/m^3 (personal communication), which is 40% higher compared to the energy requirement of 0.21 kWh/m^3 for average feed TDS of 300 mg/L using MCDI. Furthermore, with the optimization of the reverse voltage during the desorption period, 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 (Długołęcki & van der Wal 2013). Further research indicated energy recovery up to 47 % by transferring the energy from the MCDI unit to a supercapacitor using buck-boost converter during the discharging step (Kang et al. 2016). 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.

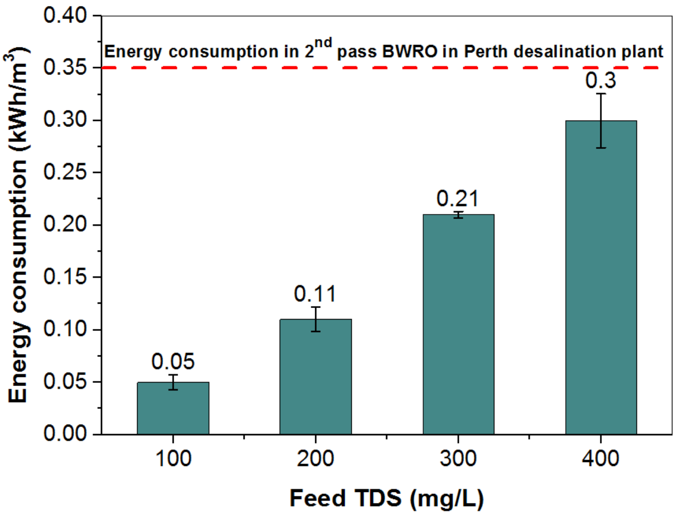

Figure 3-7: Total energy consumption during adsorption and desorption in MCDI. For 100, 200 and 300 mg/L TDS feed water, the optimum operating time was 2, 3 and 10 minutes respectively at 1 V. For feed water with 400 mg/L, the operating time was 10 minutes at 1.2 V.

3.5 Conclusions

In this chapter, 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 the 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/m^3, which is 40% higher compared to the energy requirement of 0.21 kWh/m^3 (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.

The next chapter investigates bromide removal in a pilot MCDI unit, which is 100 times the capacity of the lab-scale MCDI unit to provide a detailed approach for a realistic application of MCDI. Specifically, detailed energy consumption and efficient desorption methods using the variable flows: combination of different flows for adsorption and desorption stages, including hybrid desorption method with a combination of short-circuit and polarity reversal were investigated to reduce energy consumption and to increase water recovery in MCDI.

CHAPTER 4

PILOT-SCALE MEMBRANE CAPACITIVE DEIONIZATION FOR EFFECTIVE BROMIDE REMOVAL AND HIGH WATER RECOVERY IN SEAWATER DESALINATION

***This chapter was published in Desalination (2020)**

P. Dorji, D.I. Kim, S. Hong, S. Phuntsho, H.K. Shon, 'Pilot-scale membrane capacitive deionisation for effective bromide removal and high water recovery in seawater desalination', *Desalination*, 479 (2020).

View/Download from: https://doi.org/10.1016/j.desal.2020.114309

[Production Note: This paper is currently embargoed and not included in this digital copy.]

CHAPTER 5

BROMIDE AND IODIDE SELECTIVITY IN MEMBRANE CAPACITIVE DEIONISATION, AND ITS POTENTIAL APPLICATION TO REDUCE THE FORMATION OF DISINFECTION BY-PRODUCTS IN WATER TREATMENT

[*]This Chapter was published in Chemosphere (2019)

P. Dorji, D.I. Kim, J. Jiang, J. Choi, S. Phuntsho, S. Hong, H.K. Shon, ‘Bromide and iodide selectivity in membrane capacitive deionisation, and its potential application to reduce the formation of disinfection by-products in water treatment’, *Chemosphere*, 234 (2019).

View/Download from: *https://doi.org/10.1016/j.chemosphere.2019.05.266*

CHAPTER 6

NOVEL COMPOSITE ELECTRODE FOR SELECTIVE BROMIDE REMOVAL IN MEMBRANE CAPACITIVE DEIONISATION

*** This chapter is submitted, and under review in *Desalination* (2020)**

P. Dorji, S. Phuntsho, D.I. Kim, S. Lim, M. J. Park, H.K. Shon, 'Novel composite electrode for selective bromide removal in membrane capaitive deionization for seawater desalination', Under review in *Desalination* (2020).

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 General conclusion and recommendations on CDI technology

1. As an emerging desalination technology, CDI is fast gaining momentum as reported from the significant number of publications related to CDI development. A lot of progress has been made in CDI, including the development of several new CDI types such as membrane CDI and Flow CDI as well as other innovative hybrid CDI system, each with its own advantages and disadvantages. However, further investigation is required to assess the process configuration for its practicability.
2. A significant focus on the CDI research is related to the development of novel CDI electrode, which accounts for more than 50% of CDI related research. While the development of high capacity electrodes is crucial to increase desalination performance and also to reduce energy consumption, other important factors such as ease of manufacturing and cost have to be considered for commercial and practical application purpose. Moreover, the novel electrodes also have to demonstrate reliable performance under repeated charging and discharging during operation should be investigated.
3. CDI is found to be a promising solution for water and wastewater treatment especially due to its ability to remove a wide range of charge ions from aqueous solution. The range of applications includes brackish water desalination, water softening, selective removal of ions including nutrient removal and recovery. Although CDI faces a major problem in selective or target removal of specific ions, recent studies have demonstrated that CDI electrodes can be customised by coating selective ion selective solution for the removal of target contaminants. This aspect of improvised MCDI will further widen MCDI application for the removal of specific contaminants effectively using far less energy consumption. It is expected that the future works on CDI/MCDI will involve more research into CDI application for removal and recovery of target ions from water sources.

4. Finally, a significant amount of research has gone into improving energy efficiency in CDI. As discussed earlier, CDI is found to be energy efficient

compared to membrane processes for the treatment of low saline water sources. Due to its unique two-step adsorption and desorption cycle operation, the stored charged during the adsorption stage can be harvested during the desorption phase. Therefore, for CDI to be even more competitive with membrane treatment processes, a practical strategy has to be developed to harvest and reuse the energy, a fact that has only been demonstrated through small-scale lab studies thus far.

7.2 Conclusion and recommendations on bromide removal in MCDI

1. It was demonstrated that bromide can be effectively removed by commercial MCDI for the TDS range that is normally associated with the 1st pass SWRO permeate. The energy consumption of lab-scale and pilot-scale studies were between 0.11-0.16 kWh/m^3 of treated water, which is only about 30-45% of the energy consumed by the 2nd pass BWRO in Perth desalination plant (0.36 kWh/m3).
2. The pilot-MCDI unit showed consistent performance in TDS and bromide removal. The use of lower desorption flow rates compared to adsorption flow rates was found to be effective for electrode regeneration. This is possible because when the voltage is reversed or cell is short-circuited during desorption, the electrostatic forces that hold the ions are basically removed, which allows even low flow rates to be effective to flush the adsorbed ions from the electrodes. Further, the use of shorter desorption time showed some deterioration in the treated water quality due to incomplete electrode regeneration however, desorption time of 2 minutes against adsorption time of 4 minutes (50% of adsorption time) still produced treated water with average TDS of 13.4 mg/L with overall TDS removal of higher than 91% for similar feed water quality for 2nd pass BWRO. The energy consumption in MCDI decreases with the increase in flow rates because of more desalinated water produced per unit time but the quality of the treated water is compromised, which is inferior compared to using lower flow rates. While the pilot MCDI unit had some flexibility to tune the operational parameters, for the practical application, it would be ideal to have additional features to automatically control the flowrates, adsorption and desorption time

sequence based on the conductivity detection by setting a certain threshold. Such simple automation will allow the MCDI unit at an optimum condition.

3. The selectivity study between bromide and iodide showed that iodide has a much higher individual adsorption capacity compared to bromide in binary solutions as well as in the presence of significant amount of NaCl ions. In a mixed solution of bromide and iodide, and also in the presence of background NaCl TDS, iodide was more preferentially removed than bromide. Finally, this study clearly demonstrates the feasibility of MCDI for effective removal of both bromide and iodide from the water even though they are present in relatively smaller quantities compared to other anions, and it can be practically applied for targeted bromide and iodide removal, which will result in a significant reduction in the formation of toxic disinfection by-products.

4. Finally, a novel bromide selective electrode was developed by coating a mixture of bromide selective resin and anion exchange polymer on the surface of a commercial activated carbon electrode. The bromide selectivity of the composite electrode was compared with that of conventional MCDI system with a separate ion exchange layers. The composite electrode demonstrated slightly higher charge efficiency compared to conventional MCDI system, as a result, it was more efficient in desalination. Further, the composite electrode also demonstrated high selectivity for bromide, where bromide removal was almost 3.4 times that of MCDI in a binary solution containing bromide and chloride ions at 1:5 ratio. A further study on bromide selectivity in a complex mixture of several anions showed that the composite bromide selective electrode removed 10 times more bromide compared to the commercial electrode. It is believed that the incorporation of bromide selective resin enhanced the capture and transport of bromide ions onto the carbon electrode while impeding the transport of chloride ions in a binary solution. However, in the complex mixture of anions, although the composite electrode demonstrated significant selectivity for bromide ions, it also showed some preferential rejection of sulphate and phosphate, whereas no specific selectivity was observed for chloride, nitrate and iodide. The composite electrode also showed reproducible results within five consecutive cycles. This

study demonstrates the potential application of MCDI for selective removal of target ions from water sources by simple surface modification of electrodes, which can increase the total adsorption capacity of target ions compared to the generic CDI electrodes. owever, since CDI/MCDI operation is a cyclical process where the cells undergo repeated charging and discharging process, it is important for any novel electrodes to be able to maintain their integrity and performance over a long-term period of at least few years to be of commercial value.

5. A detail evaluation of composite electrodes such as the one developed to enhance bromide selectivity can address one of the fundamental issues in water treatment: removal of target ions for water treatment or it can be applied for resource recovery due to the cyclical nature of the MCDI operation: adsorption followed by desorption. This area in MCDI is rapidly evolving where cation and anions specific composite electrodes are developed by coating ion exchange resins on the carbon electrode surface. However, long-term performance of such electrodes have to be further studied, specifically their assessment upon several thousand adsorption and desorption cycles, and future studies could also address optimisation of the thickness of electrodes prepared with different loading and size of ion exchange resins.

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