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

by Pema Dorji

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the degree of

Doctor of Philosophy

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Dr Sherub Phuntsho

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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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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.