UNIVERSITY
OF TECHNOLOGY
SYDNEY

Enhancing the performance of lithium recovery in seawater with membrane distillation and manganese oxide metal-organic framework nanoparticles

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Thesis submitted in fulfilment of the requirements for the degree of

Master of Engineering.

under the supervision of Prof. Saravanamuthu Vigneswaran and Dr. Gayathri Naidu

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August 2021

Certificate of original authorship

I, Sharaniya Roobavannan declare that this thesis, is submitted in fulfilment of the requirements for the award of Master of Engineering, in the 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. This research is supported by the Australian Government Research Training Program.

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Acknowledgements

I would like to express my sincere gratitude to my principal supervisor Professor S. Vigneswaran and my co-supervisor, Dr. Gayathri Naidu, for their supervision, continuous guidance, encouragement, and support at all levels during my study at UTS.

In addition, I would like to thank Dr. Md Johir who has taught me how to use the analytical instruments in the UTS laboratory and Dr. Niren Pathak who has supported me in the laboratory analysis.

I am also thankful for the academic and technical support of the University of Technology Sydney and its staff. I appreciate the support of my friends Charith Fonseka, Alex Hienphuong and SeongChul Ryu at CTWW and all my friends in Sydney.

Finally, I wish to thank my husband Mahendran Roobavannan for his unconditional love and encouragement throughout the whole journey that he has taken with me. It would not have been possible without you. Furthermore, I would like to thank my father, my sisters and my loving son for their support and love.

Journal article published.

Roobavannan, S., Vigneswaran, S. & Naidu, G. 2020, 'Enhancing the performance of membrane distillation and ion-exchange manganese oxide for recovery of water and lithium from seawater', Chemical Engineering Journal, vol. 396, p. 125386.

LIST OF ABBREVIATIONS

SWRO	Sea Water Reverse Osmosis
DCMD	Direct Contact Membrane Distillation
MD	Membrane Distillation
HMO	Hydrogen Manganese Oxides
ZIF-8	Zeolitic Imidazolate Framework 8
MOF	Metal Organic Framework
LMO	Lithium Manganese Oxides
LIBs	Lithium-Ion Batteries
AGMD	Air Gap Membrane Distillation
VMD	Vacuum Membrane Distillation
SGMD	Sweeping Gas Membrane Distillation
MOFs	Metal-Organic Frameworks
PTFE	Polytetrafluoroethylene
Hmim	2-Methylimidazole
VCF	Volume Concentration Factor
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
TDS	Total Dissolved Solids
LC-OCD	Liquid Chromatography with Organic Carbon Detection
SEM	Scanning Electron Microscope
EDS	Energy-Dispersive Spectroscopy
XRD	X-Ray Powder Diffraction
PFO	Pseudo First Order
PSO	Pseudo Second Order

CAPEX	Capital Expenditure
OPEX	Operational Expenditure

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Abstract

Growing population and climate change have significantly increased the demand for drinking water. Desalination plants are used to convert seawater into fresh drinking water using the reverse osmosis process. In sea water reverse osmosis (SWRO) process, water from a pressurized saline solution is separated from the dissolved salts by flowing through a water-permeable membrane. This process needs to dispose the waste containing concentrated brine. The concentrated brine from these plants contributes approximately 40% of their output and must be dealt immediately. Disposal of this waste directly into the sea has significant damage to the marine environment and it must be addressed. Conventional approaches to the problem presented by the concentrate involve treating the concentrate and then discharging the treated water into open water bodies or reusing it. However, these approaches typically have high operational costs, a necessity for large-scale operations, low productivity, and are chemically intensive. Consequently, an alternative approach is to adopt zero liquid discharge with resource recovery, generating additional revenue as well as protecting the environment.

Seawater contains economically valuable metals, such as Lithium (Li^+) but these are present at relatively low concentrations compared with Sodium (Na^+), Potassium (K^+), Calcium (Ca^{2+}) and Magnesium (Mg^{2+}) and are currently not recovered commercially. Recovering lithium (Li^+) from seawater is a sustainable alternative to meet its high demands. Li^+ recovery from seawater must be enhanced to attain economic efficiency.

In this work, the potential of enhancing Li^+ recovery from seawater is evaluated by firstly treating and concentrating seawater to produce fresh water while increasing Li^+ concentration using direct contact membrane distillation (DCMD) and reducing competitive ions; and thereafter to develop an efficient novel adsorbents, acid treated manganese oxide ion sieve (HMO) for converting waste brine from desalination plants into a desirable resource through extracting economically valuable lithium (Li^+)

Membrane Distillation (MD) ia an alternative membrane approach for treating concentrate. MD is a thermally driven membrane process based on mass transfer through a microporous hydrophobic membrane. The driving force is normally a temperature gradient between the heated side (feed) and cold side (permeate) of the membrane. The hydrophobic nature of the membrane prevents liquid intrusion into the pores, so only water vapour is transported through the membrane and condensed on the cooling side (permeate). MD has features that make it attractive for seawater concentrate treatment: (i) the low thermal requirement (45–60°C) allows

integration with alternative thermal sources such as solar, making it a sustainable process; (ii) it can produce high-quality fresh water suitable for reuse; (iii) it can concentrate seawater up to its saturation limit, reducing volume while increasing concentrations of valuable metals for selective recovery. In this study a lab scale direct contact membrane distillation (DCMD) was used to treat and concentrate seawater and pre-treated seawater (caustic soda ash and oxalic acid). DCMD performance with seawater and pre-treated seawater as feed solutions achieved an initial permeate fluxes of 25.5±0.8 L/m2h (LMH) with high quality permeate/freshwater characteristics (> 96% ion rejection). However, DCMD operated with seawater and caustic soda pre-treated seawater exhibited rapid decline of permeate fluxes (86-90%) by a volume concentration factor of 3 times onwards. Typically, seawater, in its original condition contain Ca2+ in the range of 350 - 400 mg/L. It is highly challenging for MD to treat original seawater due to the inevitable development of Ca^{2+} based scaling in thermal condition, namely, CaSO4. DCMD achieved enhanced water recovery upon pre-treatment with oxalic acid (88–91%) compared to caustic soda ash (65–68%) and without pre-treatment (47–51%). Caustic soda ash required Na+ addition in alkaline condition for Ca^{2+} removal, while oxalic acid removed Ca^{2+} in acidic condition without any inorganic ion addition. The low ion concentration in acidic condition upon oxalic acid pre-treatment enabled DCMD to concentrate seawater to high levels, increasing Li^+ concentration by 7 times.

In Li^+ solution, HMO achieved a maximum adsorptive capacity of 17.8 mg/g in alkaline condition. Multiple cycles of desorption and regeneration of HMO showed only 7–11% decline of Li^+ uptake and minimal Mn dissolution, which, established HMO's reuse capacity. Selective Li^+ mechanism is attributed to H/Li exchange as well as high negative surface charge of HMO. In seawater, Li^+ uptake by HMO reduced by 44–46% due to the presence of Mg^{2+}. Seawater with minimal Mg^{2+} was favourable for enhancing Li+ uptake by HMO. Seawater treatment in stages – divalent pre-treatment and concentrating seawater, followed by HMO, provided a favourable scenario for attaining high.

quality water, selective Li^+ recovery, and other resources – Ca^{2+} and Mg^{2+}. The drawback of this method is HMO can only recover Li at high pH (11-12). Therefore, in this study, a new HMO with metal organic framework -ZIF-8@MOF was synthesised for the first time. The ZIF-8@MOF showed higher Li+ adsorption capacity compared to HMO. More importantly, ZIF-8@MOF can selectively extract Li^+ in seawater at its original pH (7.5-8.0). This is favourable in attaining selectively Li^+ recovery from seawater without the need for pH adjustment to 11 with chemical addition (NaOH).