

Membrane Capacitive Deionization Using Ion-exchange Polymer Coated Electrodes for Resource Recovery from Wastewater

by David Kim

Thesis submitted in fulfilment of the requirements for
the degree of

Doctor of Philosophy

under the supervision of Hokyong Shon

University of Technology Sydney
Faculty of Engineering and Information Technology

November 2020

Certificate of Original Authorship

Required wording for the certificate of original authorship

CERTIFICATE OF ORIGINAL AUTHORSHIP

I, David Kim 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.

This research is supported by the Australian Government Research Training Program.

Signature: Production Note:
Signature removed prior to publication.

Date: 14 November 2020

Collaborative doctoral research degree statement

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of the requirements for a degree at any other academic institution except as fully acknowledged within the text. This thesis is the result of a Collaborative Doctoral Research Degree program with Korea University.

ACKNOWLEDGEMENTS

First of all, I really appreciate my beloved wife, Gimun Gwak, for her sacrifice in support of my PhD study at UTS. Also, I would like to truly thank my parents, Dr. Kyunghoon Kim and Mrs. Haekyung Park, for their support and encouragement. I also Thanks also to my sister Dr. Johanna Inhyang Kim Kim. Without their support, I could not achieve a successful Ph.D. study outcome. My dear son, Haon Kim, I love you all from the bottom of my heart.

I would also like to thank my colleagues, Pema Dorji and Jade Jiayi Jiang, for their sincere co-operation. Besides, I would like to appreciate the invaluable time and memories that I shared with my friends, Ralph Rolly Gonzales, Seongchul Ryu, Federico Volpin, Dr. Jungeun Kim, Dr. Myoung Jun Park, Dr. Yunchul Woo, Dr. Youngkwon Choi, Yunju Jo, Dr. Sungil Lim, Nawsahd Akther, Van Huy Tran, Syed Muztuza Ali, Minwei Yao, Ugyen Dorji, Dr. Nirenkumar Pathak, Jiawei Ren, Dr. Mohammed Johir, Dr. Leonard Tijing, and Dr. Laura Chekli.

I would like to express my heartfelt appreciation to my principal supervisor Prof. Ho Kyong Shon for giving me the opportunity to work with him at University of Technology Sydney. I also am very thankful to my co-supervisor Dr. Sherub Phuntsho for his encouragement, mentorship, and support. The thesis could not be completed without their supervision

Thanks to all the people I have met during my PhD career at University of Technology Sydney. The journey of my life in Sydney for a year and a half was truly unforgettable.

Book chapters and Journal Articles Published or Submitted**

1. Min Zhan, Gimun Gwak, **David Inhyuk Kim**, Kiho Park, Seungkwan Hong, Quantitative analysis of the irreversible membrane fouling of forward osmosis during wastewater reclamation: Correlation with the Modified Fouling Index, *Submitted to Journal of Membrane Science*.
2. Pema Dorji, **David Inhyuk Kim**, Seungkwan Hong, Sherub Phuntsho, Ho Kyong Shon, Pilot-scale membrane capacitive deionisation for effective bromide removal and high water recovery in seawater desalination, *Submitted to Desalination*.
3. HyunJun Chung, Jungbin Kim, **David Inhyunk Kim**, Gimun Gwak, Kyeongil Kim, Seungkwan Hong, Feasibility study of reverse osmosis–flow capacitive deionization (RO-FCDI) for energy-efficient desalination using seawater as the flow-electrode aqueous electrolyte, *Submitted to Desalination*.
4. ***David Inhyuk Kim**, Ralph Rolly Gonzales, Pema Dorji, Sherub Phuntsho, Seungkwan Hong, Hokyong Shon, Efficient Removal and recovery of nitrate from wastewater in MCDI using a nitrate selective resin/anion-exchange polymer coated activated carbon electrode, *Submitted to Separation and Purification Technology*.
5. Gimun Gwak, **David Inhyuk Kim**, Seungkwan Hong, Draw solutes for FO: Model, polymer hydrogels, and nanoparticles, Current Trends and Future Developments on (Bio-) Membranes: Reverse and Forward Osmosis: Principles, Applications, Advances, (2019) 37-56.
6. ***David Inhyuk Kim**, Pema Dorji, Sherub Phuntsho, Seungkwan Hong, Hokyong Shon, Reuse of municipal wastewater via membrane capacitive

- deionization using ion-selective polymer-coated carbon electrodes in pilot-scale, *Chemical Engineering Journal*, 372 (2019) 241-250.
7. Gimun Gwak, **David Inhyuk Kim**, Seungkwan Hong, An integrated system for CO₂ capture and water treatment by forward osmosis driven by an amine-based draw solution, *Journal of Membrane Science*, 581 (2019) 9-17.
 8. ***David Inhyuk Kim**, Pema Dorji, Gimun Gwak, Sherub Phuntsho, Seungkwan Hong, Hokyong Shon, Effect of brine water on ion discharge in membrane capacitive deionization and its implication on nitrogen recovery from wastewater, *ACS Sustainable Chemistry & Engineering*, 7(13) (2019) 11474-11484.
 9. Pema Dorji, **David Inhyuk Kim**, Sherub Phuntsho, Hokyong Shon, Bromide and iodide selectivity in membrane capacitive deionization, and its potential application to reduce the formation of disinfection by-product in water treatment, *Chemosphere*, 234 (2019) 536-544.
 10. *Jiaxi Jade Jiang¹, **David Inhyuk Kim**¹, Pema Dorji, Sherub Phuntsho, Seungkwan Hong, Hokyong Shon, Phosphorus removal mechanisms from domestic wastewater by membrane capacitive deionization and system optimization for enhanced phosphate removal, *Process Safety and Environmental Protection*, 126 (2019) 44-52.
 11. **David Inhyuk Kim**, Gimun Gwak, Seungkwan Hong, Sustainable dewatering of grapefruit juice through forward osmosis: Improving membrane performance, fouling control, and product quality, *Journal of Membrane Science*, 578 (2019) 53-60.
 12. Pema Dorji, Jongmoon Choi, **David Inhyuk Kim**, Sherub Phuntsho, Seungkwan Hong, Ho Kyong Shon, Membrane capacitive deionisation as an alternative to

the 2nd pass for seawater reverse osmosis desalination plant for bromide removal, *Desalination*, 433 (2018) 113-119.

13. Gimun Gwak, **David Inhyuk Kim**, Seungkwan Hong, New industrial application of forward osmosis (FO): Precious metal recovery from printed circuit board (PCB) plant wastewater, *Journal of Membrane Science*, 552 (2018) 234-242.
14. ***David Inhyuk Kim**, Gimun Gwak, Pema Dorji, Di He, Sherub Phuntsho, Seungkwan Hong, Hokyong Shon, Palladium recovery through membrane capacitive deionization (MCDI) from metal plating wastewater, *ACS Sustainable Chemistry & Engineering*, 6 (2018) 1692-1701.
15. **David Inhyuk Kim**, Jongmoon Choi, Seungkwan Hong, Evaluation on suitability of osmotic dewatering through forward osmosis (FO) for xylose concentration, *Separation and Purification Technology*, 191 (2018) 225-232.
16. Jungwon Kim, **David Inhyuk Kim**, Seungkwan Hong, Analysis of an osmotically-enhanced dewatering process for the treatment of highly saline (waste)waters, *Journal of Membrane Science*, 548 (2018) 685-693.
17. Byeong Gyu Choi, **David Inhyuk Kim**, Seungkwan Hong, Fouling evaluation and mechanisms in a FO-RO hybrid process for direct potable reuse, *Journal of Membrane Science*, 520 (2016) 89-98.
18. **David Inhyuk Kim**, Jungwon Kim, Seungkwan Hong, Changing membrane orientation in pressure retarded osmosis for sustainable power generation with low fouling, *Desalination*, 389 (2016) 197-206.
19. Jungwon Kim, Bongchul Kim, **David Inhyuk Kim**, Seungkwan Hong, Evaluation of apparent membrane performance parameters in pressure retarded

osmosis processes under varying draw pressures and with draw solutions containing organics, *Journal of Membrane Science*, 493 (2015) 636-644.

20. **David Inhyuk Kim**, Jungwon Kim, Ho Kyong Shon, Seungkwan Hong, Pressure retarded osmosis (PRO) for integrating seawater desalination and wastewater reclamation: Energy consumption and fouling, *Journal of Membrane Science*, 483 (2015) 34-41.
21. Eunjeong Mun, Sangyoun Lee, **Inhyuk Kim**, Boksoon Kwon, Heedueng Park, Seungkwan Hong, Measurements of assimilable organic carbon (AOC) in high saline conditions using P17, *Water Science & Technology: Water Supply*, 13 (2013) 265-272.

** Publications made during the PhD candidature include articles not related to the thesis.

* Articles related to the thesis.

Conference papers and presentation

1. Gimun Gwak, Jungwon Kim, **David Inhyuk Kim**, Seungkwan Hong, “Integrating system for carbon dioxide (CO₂) capture and water reuse: Application of forward osmosis (FO) with amine-based draw solution”, The 11th Conference of the Aseanian Membrane Society (AMS 11), July 3-6, 2018, Brisbane, Australia.
2. **David Inhyuk Kim**, Gimun Gwak, Seungkwan Hong, “Sustainable dewatering of grapefruit juice by forward osmosis (FO): FO performance, fouling control and product quality”, The 11th Conference of the Aseanian Membrane Society (AMS 11), July 3-6, 2018, Brisbane, Australia.
3. Gimun Gwak, **David Inhyuk Kim**, Seungkwan Hong, “New Industrial Application of Forward Osmosis (FO): Precious Metal Recovery from Printed Circuit Board (PCB) Plant Wastewater”, International Environmental Engineering Conference (IEEC), November 15-17, 2017, Jeju, Korea.
4. Gimun Gwak, **David Inhyuk Kim**, Jihoon Alex Lim, Seungkwan Hong, “New industrial application of forward osmosis: precious metal recovery”, 8th IWA Specialist Conference on Membrane Technology for Water and Wastewater Treatment, November 05-09, 2017, Singapore, Singapore.
5. **David Inhyuk Kim**, Gimun Gwak, Sherub Phuntsho, Seungkwan Hong, Ho Kyong Shon, The potential of CDI for recovery of precious metals: Palladium from plating industry wastewater, International Conference on Capacitive Deionization, Electrosorption & Electrodialysis (CDI&E 2017), July 3-6, 2017, Seoul, Korea.
6. **David Inhyuk Kim**, Jongmoon Kim, Seungkwan Hong, “Feasibility of forward osmosis (FO) for food processing: A comparison to nanofiltration (NF)”, 5th

IWA Regional Conference on Membrane Technology (IWA-RMTC), August 22-24, 2016, Kunming, China.

7. **David Inhyuk Kim**, Jungwon Choi, Seungkwan Hong, “A hybrid process of PRO-RO for sustainable water production with low fouling: Changing membrane orientation in PRO”, 5th IWA Regional Conference on Membrane Technology (IWA-RMTC), August 22-24, 2016, Kunming, China.
8. **David Inhyuk Kim**, Jungwon Kim, Junghyun Kim, Seungkwan Hong, "A hybrid process of pressure retarded osmosis and reverse osmosis (PRO-RO) for sustainable water-energy generation with low fouling, The 8th International conference on separation science and technology, July 5-8, 2016, Tianjin, China.
9. Byeonggyu Choi, **David Inhyuk Kim**, Seungkwan Hong, “Sustainability of forward osmosis-reverse osmosis (FO-RO) hybrid process: Water quality and membrane fouling", The 8th International Desalination Workshop, November 18-21, 2015, Jeju, Korea.
10. **David Inhyuk Kim**, Byeonggyu Choi, Seungkwan Hong, "Changing membrane orientation for pressure retarded osmosis (PRO) with low fouling”, The 8th International Desalination Workshop, November 18-21, 2015, Jeju, Korea.
11. **David Inhyuk Kim**, Seungkwan Hong, "Effect of pressure on performance of pressure assisted osmosis (PAO) membrane processes", International Environmental Engineering Conference (IEEC 2015), October 28-30, 2015, Busan, Korea.
12. Byeonggyu Choi, **David Inhyuk Kim**, Seungkwan Hong, "Innovation of osmosis membrane technology for the direct potable reuse of wastewater”, The 6th IWA-ASPIRE Conference &Exhibition, September 20-24, 2015, Beijing, China.

13. **David Inhyuk Kim**, Jungwon Kim, Junghyun Kim, Seungkwan Hong, " PRO for wastewater reclamation and seawater desalination with low energy consumption", 4th International Conference on Environmental Engineering, Science and Management, May 27-29, 2015, Chiang Mai, Thailand.
14. Jungwon Kim, Bongchul Kim, **David Inhyuk Kim**, Seungkwan Hong, "Evaluation of RSF in PRO process at the presence of organic matters", 7th International Desalination Workshop, November 5-8, 2014, Jeju, Korea.
15. **David Inhyuk Kim**, Jungwon Kim, Seungkwan Hong, "Pressure retarded osmosis (PRO) for seawater desalination and wastewater reclamation with low energy consumption", The 10th International Congress on Membranes and Membrane Processes, July 20-25, 2014, Suzhou, China.
16. Yoontaek Oh, Younggil Ju, **David Inhyuk Kim**, Jungwon Kim, Seungkwan Hong, Sangho Lee, Seukhun Lee, Menachem Elimelech, "Effect of externally induced hydraulic pressure on water flux in pressurized forward osmosis (PFO) with different membrane orientations", The 7th IWA Specialized Membrane Technology Conference and Exhibition for Water and Wastewater Treatment and Reuse, August 25-29, 2013, Toronto, Canada.
17. Jungwon Kim, Bongchul Kim, **David Inhyuk Kim**, Seokheon Lee, Seungkwan Hong, "Membrane fouling and analysis in pressure retarded osmosis", The 8th conference of the Aseanian Membrane Society, July 16-19, 2013, Xian, China.
18. **David Inhyuk Kim**, Bongchul Kim, Seungkwan Hong, "Developing the methods for evaluating FO membrane performance", The 5th International Desalination Workshop, October 28-31, 2012, Jeju, Korea.

Presentation made during the PhD candidature including proceedings, oral and poster presentations.

Abstract

In the face of major global challenging issues of water scarcity, the water industry has been undergoing a paradigm shift. The limited availability of nutrients resources, such as nitrogen and phosphorus, and their oversupply as fertilizer are projected to risk the global demands for food production. Therefore, the global needs of renewable resources have driven the wastewater facilities to recycle nutrients. Wastewater has been considered an important source of recoverable nutrients and other valuable materials, and thus, resource recovery from wastewater has become attractive where technological innovation is being used to provide additional social, environmental, and economic benefits.

Membrane capacitive deionization (MCDI), driven by an electrochemical potential between two electrodes across ion-exchange membranes (IEMs), has been shown to be an effective system for recovering valuable nutritional resources dispersed in wastewater via the enrichment and selective collection of the ions present in small amounts in low salinity wastewater resources. In particular, the recovery of nitrogen and phosphorus from municipal wastewaters has been noted as one of the most feasible targets to prevent environmental issues, such as the eutrophication of water resources and procuring these biological nutrients essential for food production. However, the application potential of MCDI for the resource recovery has not been verified due to lack of its full investigation from practical perspectives.

In this study, the application potential of MCDI was explored to recover nutrient resources present in wastewater, especially converging the ion selectivity and performance efficiency during electrosorption and electrode regeneration. Carbon electrodes coated with a thin cation- or anion-exchange polymer layer which acted as an

IEM in the conventional MCDI have been mainly used as an advanced configuration for the electrosorptive process with both inducing lower membrane electrical resistance and inhibiting the electrosorption of the counter-ions during regeneration of electrodes.

The ion transport during resource recovery via MCDI, from feed water to a carbon electrode in electrosorption and then from the carbon electrode into highly enriched brine solution in regeneration, was examined. The ion discharge was retarded by a reverse-ionic strength gradient induced by the enriched brine solution. The regeneration was further hindered when a dilute feed solution concentration was used (<10 mM), attributing to the enhanced resistance of the ion-exchange (IX) layer. Energy-efficient regeneration methods, such as short-circuiting, were constrained owing to lack of electrochemically repulsive force capable of overcoming the reverse gradient. The preferential desorption order under a mixture of cations was $K^+ > Na^+ > Mg^{2+}$, as mainly determined by their physiochemical properties, whereas the permselectivity through the cation-exchange membrane (CEM) was insignificant.

The application potential of MCDI using IX layer coated electrodes was systematically explored demonstrating its effective performance in resource recovery from wastewater, and the operating conditions were optimized considering the complex nature of the characteristics of real municipal wastewater. A higher salt adsorption capacity and charge efficiency could be attained owing to the lower resistance induced by the thinly coated layer facilitating faster ionic transport. The organic substances had an insignificant impact on the electrodes' performance in a longer operation, as the fairly adsorbed negatively charged organic compounds were well released in the consequent desorption stage. The fouling-free operation was attributed to the flat morphology of the coated IX layer surface

with low roughness offering a smaller chance for the impurities to accumulate on the electrode surface.

The electrosorption selectivity followed the permselectivity through the IX layers, and was impacted by the change in their mobility under different applied potential. The selective electrosorption of NO_3^- can be enhanced by decreasing applied potential to increase relative ion mobility and by increasing water flow rate to reach faster electrode saturation. The recovery of phosphate has been examined considering the effect of phosphate speciation reactions at a typical pH range in wastewater (between 6.5 and 8.5). The overall P adsorption capacity was apparently higher in the lower pH, where H_2PO_4^- dominantly presents in wastewater, owing to the smaller hydrated radii monovalent ions occupying less space within the electric double layer (EDL) for charge neutralization. However, the effect of phosphate speciation on selective phosphorus removal from wastewater was insignificant, as in reality it presents in a low amount compared to the other anions.

One of the major disadvantages of MCDI for resource recovery is the inability of electrodes to selectively remove target ions. Therefore, a nitrate selective composite electrode coated with an anion-exchange polymer with A520E resins was fabricated for enhanced recovery of nitrate. The low-contact resistance of the coated IX layer enhanced the electrosorption capacity, whereas the granular nitrate—selective resin incorporated in the IX layer rather increased the electrical resistivity. The adsorbed mole fraction of NO_3^- kept increased even after saturation, attributing to the ion exchange between Cl^- on the resin coating layer and NO_3^- contained in the bulk feed solution. However, its desorption efficiency for NO_3^- was lowered as the NO_3^- were temporarily intercepted by being

exchanged with Cl^- ions in the resin at the IX layer during the ion migration towards the bulk brine solution.

The possible application of MCDI was further tested on the recovery of palladium from metal plating wastewater. The highly efficient adsorption of Pd from a single Pd solution, higher than 98.38% even at 0.3 V of low applied potential, was driven by both electrosorptive and physical adsorption. Its removal was remained to be high even under co-existence of different cations present in the metal plating wastewater, since the Pd species with high initial concentration and ionic charge valency competitively took place within the EDL. High concentration of Pd was obtained after five successive operation cycles (925.48 mg/L) from a 100 mg/L Pd catalyst solution. However, an apparent decrease in Pd removal and desorption in the successive cycles implied the deterioration of electrodes attributing to physisorption or complexation of Pd metal ions within the porous structure of electrode, resulting in reduced available surface area of electrode for additional electrosorption.

This thesis finally concludes with recommendations to provide future insights into realizing the practical use of MCDI for the recovery of resources from wastewater. The operating conditions of MCDI are important in order to achieve selective and highly efficient resource recovery. Enriching the target resource above a desired amount could be limited due to the reverse-ionic strength gradient. Reversing polarity is expected work best for discharging ions into brine, but however, its optimized condition has to be determined carefully as its energy demand could compensate the feasibility of MCDI. Employing lower potential and higher flow rate for selective nitrate removal may rather result in poor total removal of ions in the wastewater, whereas selective collection of phosphate at the current technological level is likely to be challenging due to its low

amount present in wastewater and low permselectivity through the IEM. The carbon electrodes can be customized for the enhanced extraction of target species by coating IX polymer solution. New coating techniques for a thinner selective layer incorporating micro-fine resins will further improve the charge efficiency and ion selectivity. The application of MCDI on recovery of precious metals requires preventive maintenance or cleaning strategies to inhibit the physisorption, complexation or crystal formation of the metallic species on the IX layer surface.

Table of Contents

Abstract.....	x
Table of Contents	xv
List of Figures	xxii
List of Tables	xxvii
CHAPTER 1	1
Introduction	1
1.1 Research background.....	2
1.2 Objectives and scope of the research.....	5
1.3 Structure of the thesis	5
CHAPTER 2	9
Literature Review.....	9
2.1 Introduction.....	10
2.2 Water scarcity.....	10
2.3 Sustainable development of wastewater.....	11
2.4 Municipal wastewater	13
2.5 Advanced wastewater treatment technologies	14
2.5.1 Adsorption	14
2.5.2 Ozonation	15
2.5.3 Advanced oxidation processes (AOPs).....	16
2.5.4 Membrane-based technologies	17
2.5.5 Overall comparison	18
2.6 Wastewater-based resource recovery	19

2.7	Review of membrane-based technologies for resource recovery	22
2.7.1	Pressure-driven membrane processes.....	24
2.7.2	Osmotically-driven membrane processes	26
2.7.3	Thermally-driven membrane processes.....	28
2.7.4	Electrically-driven membrane processes	31
2.8	Historical background theory in capacitive deionization.....	33
2.9	Electric double layer.....	34
2.10	Membrane capacitive deionization: Basics and principles.....	35
2.11	Preferential order of electrosorption of ions	38
2.12	Energy efficiency and recovery in CDI	40
2.13	Applications of capacitive deionization	42
2.13.1	A RO-CDI hybrid system for brackish water desalination.....	43
2.13.2	Water softening through CDI process	46
2.13.3	CDI for resource recovery	48
2.14	Conclusion	51
CHAPTER 3	53
Materials and Methods	53
3.1	Introduction.....	54
3.2	Experimental materials.....	54
3.3	Fabrication of ion-exchange polymer coated carbon electrode .	54
3.4	Membrane capacitive deionization tests.....	56
3.5.1	Bench-scale MCDI experiments.....	56
3.5.2	Pilot-scale MCDI experiments	58
3.5	Analytical methods	59

3.5.1	Scanning electron microscope	59
3.5.2	Atomic force microscopy	59
3.5.3	Measurement of water quality	60
CHAPTER 4		61
Investigation of Ion Transport During Electrode Regeneration and Its Implications on Mineral Recovery from Wastewater		61
Research highlights		62
4.1	Introduction	62
4.2	Experimental	65
4.2.1	Synthetic and wastewater solutions	65
4.2.2	Carbon electrodes and ion-exchange membranes	66
4.2.3	Bench-scale MCDI setup	66
4.2.4	Investigation of ion desorption behavior	67
4.2.5	Successive, five-cycle operation for concentrating ammonium	68
4.2.6	Measurement of water quality	69
4.3	Results and discussion	69
4.3.1	Effect of brine water concentration on cation desorption	69
4.3.2	Desorption rate change in electrode regeneration with different ions in brine 72	
4.3.3	Comparison of reverse polarity and short-circuiting for mineral resource recovery	74
4.3.4	Competitive ion desorption under the co-existence of different ions	77
4.3.5	Desorption kinetics using pseudo-first-order and pseudo-second-order models 81	
4.3.6	Implications for the recovery of ammonium from wastewater	84
4.4	Concluding remarks	87
CHAPTER 5		90

Selective Nitrate Recovery from Municipal Wastewater for Water Reuse via Membrane Capacitive Deionization	90
Research highlights	91
5.1 Introduction	91
5.2 Experimental methods	95
5.2.1 Activated carbon electrodes coated by ion-selective polymers.....	95
5.2.2 Experimental protocol of lab-scale MCDI.....	96
5.2.3 Configuration of the pilot-scale MCDI unit	97
5.2.4 Measurement of water quality	98
5.3 Results and discussion	100
5.3.1 SEM analysis of the ion-selective carbon electrodes	100
5.3.2 Lab-scale performance of the coated electrodes	101
5.3.3 Removal efficiency of ions during wastewater reuse.....	104
5.3.4 Enhancing water quality by changing electrosorption time.....	109
5.3.5 Changing applied potential and flow rate for selective NO ₃ ⁻ removal.....	111
5.3.6 Successive operation of the pilot-scale MCDI system in a 15 d period	113
5.4 Concluding remarks	117
CHAPTER 6	119
Phosphorus Removal Mechanisms from Domestic Wastewater and System Optimization for Selective Phosphate Recovery	119
Research highlights	120
6.1 Introduction	120
6.2 Materials and methods	123
6.2.1 Lab-scale MCDI unit setup	123
6.2.2 Feed solution preparation	124

6.2.3	Experimental operating conditions	126
6.2.4	Sample analysis	127
6.3	Results and discussion	128
6.3.1	Speciation of phosphate.....	128
6.3.2	The influence of co-existing anions in domestic wastewater on T-P removal 133	
6.3.3	Optimization of MCDI system for highly efficient total phosphorus removal 135	
6.4	Concluding remarks.....	139
CHAPTER 7	142
	Enhanced Recovery of Nitrate from Municipal Wastewater using Anion-exchange Polymer Coated Electrode Embedded with Nitrate Selective Resins	142
	Research highlights	143
7.1	Introduction.....	143
7.2	Materials and methods.....	147
7.2.1	Fabrication of the ion-exchange polymer coated carbon electrode with embedded A520E	147
7.2.2	Bench-scale MCDI using ion-exchange layer-coated electrodes	148
7.2.3	Investigation of preferential electrosorption and discharge of nitrate using A520E/IX electrode.....	149
7.2.4	Successive five-cycle operation for concentrating nitrate	149
7.2.5	Measurement of concentration of anions and their removal	150
7.3	Results and discussion	151
7.3.1	Morphology of the IX and A520E/IX layered electrodes	151
7.3.2	Electrosorption performance using the nitrate-selective electrode.....	152
7.3.3	Preferential adsorption of anions in MCDI using A520E/IX layered electrodes 156	

7.3.4	Preferential discharge of anions during regeneration of A520E/IX layered electrodes.....	159
7.3.5	Recovery of nitrate from real municipal wastewater effluent with A520E/IX layered electrode	162
7.4	Concluding remarks.....	166
CHAPTER 8		168
Expanding the Potential Application of Membrane Capacitive Deionization on Recovery of Palladium from Metal Plating Wastewater		168
Research highlights		169
8.1	Introduction.....	169
8.2	Materials and methods.....	172
8.2.1	Model palladium and palladium catalyst solution for electroless plating.....	172
8.2.2	Carbon electrodes and ion exchange membranes	173
8.2.3	Bench-scale MCDI setup.....	173
8.2.4	Multiple cycles operation for concentration of Pd	174
8.2.5	Measurement of water quality	175
8.3	Results and discussion	176
8.3.1	Removal of Pd in CDI under different operating conditions	176
8.3.2	Enhancing Pd concentration through multiple MCDI adsorption and desorption cycles	177
8.3.3	Effect of feed water concentration and composition on Pd removal rate	179
8.3.4	Effect of concentration of concentrate solution on Pd desorption efficiency in MCDI	182
8.3.5	Enhancing desorption efficiency through increasing desorption time or applied potential for higher Pd concentration	184
8.3.6	Deterioration of Pd adsorption performance under longer operation cycles	186
8.3.7	Potential integration of MCDI and ion selective electrode for Pd recovery	188

8.4	Concluding remarks	189
CHAPTER 9	191	
Conclusions and Recommendations	191	
9.1	Summary of major outcomes	192
9.1.1	Ion discharging behavior during electrode regeneration and its implications on mineral recovery	192
9.1.2	Selective nitrate and phosphate recovery from municipal wastewater	193
9.1.3	Development of nitrate selective electrode for enhanced recovery	195
9.1.4	Membrane capacitive deionization for recovery on palladium waste.....	195
9.2	Recommendations	196
REFERENCES.....	199	

List of Figures

Figure 1.1. Schematic of an MCDI process. Upon an applied electrical potential between two porous carbon electrodes, ions attract toward the electrodes: cations toward the cathode (on top) and anions toward the anode (bottom).	4
Figure 2.1. Global economic and physical water scarcity (Molden 2013).....	11
Figure 2.2. 17 Sustainable Development Goals to be achieved by 2030 (Connor et al. 2017).	12
Figure 2.3. Global consumption of freshwater resources (Mateo-Sagasta, Raschid-Sally & Thebo 2015).....	13
Figure 2.4. Schematic illustration of RO with a high-pressure pump (Elimelech & Phillip 2011).	25
Figure 2.5. Schematic illustration of osmosis-based FO process (Haupt & Lerch 2018).	27
Figure 2.6. Beneficial reverse diffusion of draw solutes in FO promoting nutrient recycle from wastewater (Xie et al. 2014).....	28
Figure 2.7. Schematic illustration of the basic principles of MD process (Shirazi, Mahdi & Kargari 2015).	29
Figure 2.8. A direct contact MD process for the recovery of ammonia from wastewater using H₂SO₄ as stripping solution (Guo et al. 2019).....	30
Figure 2.9. Comparison of energy consumption between RO and MCDI (Zhao, Porada, et al. 2013).....	41
Figure 2.10. Schematic illustration of possible applications of (M)CDI (Choi et al. 2019).	43
Figure 2.11. Schematic illustration of the two-pass (a) RO-RO system and (b) RO-CDI system for the production of high quality water (Choi et al. 2019).....	44
Figure 2.12. Schematic illustration of the two-stage (a) RO-RO system and (b) RO-CDI system for enhanced water recovery (Choi et al. 2019).	45
Figure 2.13. Schematic illustration of CDI for hardness removal (Tuan et al. 2015).	46
Figure 3.1. (a) Automatic film applicator (Elcometer 4340, Elcometer Aisa Pte. Led.).....	56

Figure 3.2. Schematic illustration of the bench-scale MCDI test units.....	58
Figure 3.3. Schematic illustration of the pilot-scale MCDI test unit for wastewater reuse.....	59
Figure 4.1. Experimental procedure of MCDI tests for the investigation of ion discharge into a high-concentration brine solution.	68
Figure 4.2. Average concentration of Na^+ desorbed into brine solution (0 to 10 mM of NaCl). The samples were collected every minute and Na^+ was collected on the electrode from a 100 mL feed solution containing (a) 0.1, (b) 1, and (c) 10 mM of NaCl. The average Na^+ adsorption capacity after the electrosorption stage from the 0.1, 1, and 10 mM NaCl feed solution was 0.24, 2.47, and 10.81 Na^+ mg/carbon g, respectively.....	72
Figure 4.3. Average concentration of Na^+ desorbed into the brine solution: ((a) 1 mM and (b) 10 mM of NaCl, KCl or MgCl_2) and (c) the corresponding desorption capacity of the used carbon electrode. Na^+ was adsorbed on the electrode from a 100 mL feed solution containing 1 mM of NaCl, and the Na^+ adsorption capacity after the electrosorption stage was 2.47 Na^+ mg/carbon g.....	73
Figure 4.4. Effect of desorption methods on the ion discharge performance in MCDI. The average concentration of desorbed Na^+ driven by (a) reverse polarity and (b) short-circuiting, and (c) the corresponding desorption capacity when disposed into 10 mM of NaCl brine. Na^+ was adsorbed onto the electrode from a 100 mL feed solution containing 1 mM of NaCl; the Na^+ adsorption capacity after the electrosorption stage was 2.47 Na^+ mg/carbon g.....	75
Figure 4.5. Competitive desorption among Na, K, and Mg ions. (a) The average concentration of desorbed ions, (b) desorption efficiency, (c) and discharge selectivity of three different cations. The electrosorption tests were run using a mixed feed solution containing 0.33 mM of NaCl, KCl, and MgCl_2 for each. The average removal efficiency of Na^+ , K^+ , and Mg^{2+} from the feed solution was 71%, 96%, and 97%, respectively. The adsorbed ions were then desorbed in to DI water during regeneration.	80
Figure 4.6. Discharge selectivity of Na, K, and Mg in the 1 st min of electrode regeneration. The ions were discharged into 0, 1, and 10 mM NaCl brine solutions. The average removal efficiency of Na^+ , K^+ , and Mg^{2+} from the feed solution was 71%, 96%, and 97%, respectively.....	81
Figure 4.7. Linearized (a) pseudo-first- and (b) -second-order kinetics fitting for the results of discharged Na, K, and Mg ions.	83
Figure 4.8. Concentration and portion of NH_4^+ in synthetic wastewater feed and brine solutions after the 1 st , 3 rd , and 5 th operation cycle.....	87
Figure 5.1. Schematic diagram of the (a) lab- and (b) pilot-scale MCDI test units using ion-selective electrodes for wastewater reuse.....	97

Figure 5.2. SEM images of the surface of (a) the original, (b) cation-selective, and (c) anion-selective carbon electrodes.	101
Figure 5.3. SAC of the (a) ion-selective and (b) conventional MCDI systems at different potentials (0.6–1.2 V).	103
Figure 5.4. Average charge efficiency for ion-selective and conventional MCDI systems at 1.2 V.	104
Figure 5.5. Specific selectivities of (a) cations and (b) anions on ion-selective polymer-coated electrodes in wastewater. The left axis shows the selectivity derived by the number of adsorbed ions divided by the total number of removed cations or anions. The right axis shows the selectivity derived by the ion removal efficiency divided by the average removal of the total number of ions (61.3% total removal efficiency).	109
Figure 5.6. Changes in permeate (a) cation and (b) anion concentrations obtained from ion-selective MCDI cells during the treatment of wastewater.	111
Figure 5.7. (a) Removal efficiency and (b) selectivity of NO_3^- at different potentials and flow rates.	112
Figure 5.8. Average conductivity profile of the permeate (blue) and concentrate (gray) for 2-min adsorption/desorption cycles on each day. The long-term MCDI operation was carried out for a period of 15 d.	115
Figure 5.9. Removal of DOC from the feed and permeate of the wastewater.	115
Figure 5.10. Root-mean-square roughness of the originally activated carbon electrode, AEM (Neosepta AMX), and anion-selective electrode.	117
Figure 6.1. Schematic diagram of the proposed single-pass lab-scale MCDI unit setup	124
Figure 6.2. Effects of equilibrium system on variation of the effluent TP concentration for highly concentrated feed streams when feed solution containing phosphate salt only, during electrosorption process operated at 1.2 V (Experimental conditions: $[\text{P}]_0 = 4 \text{ mM}$, Flow rate = 8 mL/min.).	129
Figure 6.3. Effects of equilibrium system on variation of the effluent total phosphorus concentration for feed simulating P concentration in real domestic wastewater at (a) low concentration of TDS, $[\text{P}]_0 = 0.4 \text{ mM}$ (b) high concentration of TDS, $[\text{P}]_0 = 0.4 \text{ mM}$, $[\text{Cl}^-]_0 = 3.6 \text{ mM}$ (Experimental conditions: Flow rate = 8 mL/min; Voltage = 1.2 V).	131
Figure 6.4. Experimental salt adsorption capacity for both concentrated feed streams ($[\text{P}]_0 = 4 \text{ mM}$), low TDS feed streams ($[\text{P}]_0 = 0.4 \text{ mM}$), and high TDS feed streams ($[\text{P}]_0 = 0.4 \text{ mM}$, $[\text{Cl}^-]_0 = 3.6 \text{ mM}$) (Experimental conditions: Flow rate = 8 mL/min; Voltage = 1.2 V).	133

Figure 6.5. The electrosorption competition of Cl^- , SO_4^{2-} and TP in terms of (a) effluent concentration, and (b) salt adsorption capacity in MCDI in a mixed electrolyte at 1.2 V (Experimental conditions: Flow rate = 8 mL/min, Feed solution pH = 7.2).....	135
Figure 6.6. Experimental average ion removal efficiency (E) and relative ion removal ratio (RE) results for SP mode MCDI operated at various (a) adsorption time, (b) voltage, (c) flow rate. The details of individual control parameters are described in Table 6.2.	138
Figure 6.7. The effect of applied voltage on the variation of removal efficiency of phosphorus and other anions for MCDI electrosorption process operated at (a) 0.6 V, and (b) 1.2 V (Experimental conditions: Flow rate = 8 mL/min, Feed solution pH = 7.2).....	138
Figure 6.8. The effect of supplied flow rate on the variation of removal efficiency of phosphorus and other anions for adopted flow rate at (a) 24 mL/min, and (b) 8 mL/min (Experimental conditions: Voltage = 1.2 V, Feed solution pH = 7.2).....	139
Figure 7.1. SEM images of the surface of (a) the original, (b) IX layered, and (c) A520E/IX layered carbon electrodes.	152
Figure 7.2. Salt adsorption capacities of A520E/IX layered-, IX layered-, and conventional- MCDIs in the removal of (a) NaCl and (b) NaNO_3 during experiments involving single salt species. The applied potential and feed solution flow rate during the MCDI tests were 1.2 V and 30 ml/min, respectively, under single-pass mode.....	154
Figure 7.3. Charge efficiency among A520E/IX layered-, IX layered-, and conventional-MCDIs.....	156
Figure 7.4. Salt adsorption capacity of the (a) IX layered- and (b) A520E/IX layered-MCDIs from a mixture of 3.3 mM of NaNO_3 , Na_2SO_4 , and NaCl, for each.	158
Figure 7.5. Mole fraction of adsorbed NO_3^- in the IX layered- and A520E/IX layered-MCDIs.....	159
Figure 7.6. Competitive desorption among NO_3^- , Mg^{2+} , and Cl^- . The average concentrations of desorbed ions and corresponding desorption efficiency in (a and b) IX layered- and (c and d) A520E/IX layered-MCDIs.....	161
Figure 7.7. (a) Concentration of major anions in wastewater and the effluent, and the corresponding (b) specific selectivity of each ion in terms of removal $\%/\%_{\text{total}}$	163
Figure 7.8. Concentration and portion of NH_4^+ in municipal wastewater feed and brine solutions after the 5 th operation cycle using IX layered and A520E/IX layered electrodes.....	166

Figure 8.1. The protocol for MCDI test with multiple cycles.	175
Figure 8.2. Removal rate of Pd using the synthetic solution containing 100 mg/L of palladium under different potentials (0.6 to 1.2 V) operating times (2 to 8 min) in adsorption step.	177
Figure 8.4. Concentration of Pd in concentrate solution after desorption of ions from the carbon electrodes. After adsorption of ions from new catalyst solutions containing (a) 1,.....	179
Figure 8.3. Removal rate of Pd in synthetic Pd and Pd catalyst solutions containing 1, 10, and 100 mg/L of Pd in adsorption step. The electrosorption was conducted at 0.9 V for 8 min.....	182
Figure 8.5. Concentration of Pd in residual solution after secondary desorption in each cycle. After adsorption/desorption using new catalyst solutions containing (a) 1, (b) 10, and (c) 100 mg/L of Pd, the remained ions on the electrode surface was further released in a new DI water (residual water) for 8 min at 0.9 V. New feed solution was then replaced to initiate another Pd recovery cycle, whereas the concentrate water was kept being used over every cycles. New DI water was then replaced to measure the concentration of residual water after each cycle.	184
Figure 8.6. The enhanced concentration of Pd concentrate and the corresponding concentration of Pd in residual solutions after secondary desorption with increased (a) desorption time and (b) applied potential. The secondary desorption to release residual Pd ions from the carbon electrode was performed at 0.9 V and 8 min...	185
Figure 8.7. Pd removal rate from catalyst solution for ten cycles.	187
Figure 8.8. SEM images of virgin (a) carbon cathode and (b) cation exchange membrane, and used (c) carbon cathode and (d) cation exchange membrane after ten cycles CDI test. Plus, the Pd/C ratio described in this figure was measured by EDS analysis.....	188
Figure 8.9. Possible application of MCDI: (a) an integrated Pd recovery process consisting of MCDI and electrowinning, and (b) single MCDI process using a Pd selective electrode material.	189

List of Tables

Table 2.1. Comparison of different technologies for wastewater treatment for advanced wastewater treatment (González et al. 2016).....	18
Table 2.2. Literature of nutrient recovery from wastewater resource by membrane-based processes.....	23
Table 2.3. Hardness removal via CDI under various operating conditions and electrode types ((Choi et al. 2019)).	47
Table 2.4. Removal of heavy metals via MCDI under various feed chemistries and electrode types.	49
Table 2.5. Recovery of nutrient resources via MCDI under various feed chemistries and electrode types.	50
Table 4.1. Chemical compositions of the synthetic wastewater feed.	65
Table 4.2. Parameters derived by the fitting of pseudo-first- and -second-order kinetics for the desorption performance.	84
Table 4.3. Ionic compositions of the feed and brine solutions after successive cycles of operation (Hertz & Franks 1973; Nightingale Jr 1959; Picioreanu, Van Loosdrecht & Heijnen 1997).....	86
Table 5.1. Average removal of ionic species in wastewater effluent during pilot-scale layered-MCDI operated at 1.2V for 2 min.	105
Table 6.1. The proportion of different phosphorus species under various pH. ...	122
Table 6.2. Composition of synthetic wastewater feed solution. HCl was added to adjust pH between 7 and 8.....	125
Table 6.3. Proposed experimental conditions and control parameters.....	126
Table 7.1. Ionic compositions of anions in the feed and brine solutions after five successive cycles of operation.	163
Table 8.1. Major characteristics of 1, 10, and 100 mg/L of diluted Pd catalyst solutions.....	173