Gas Responsive Microgels as Novel Draw Agents for Forward Osmosis Desalination

By

Hesamoddin Rabiee

Thesis advisors:
Associate Professor Bo Jin, Professor Sheng Dai

A thesis submitted for the degree of Master of Philosophy

School of Chemical Engineering
Faculty of Engineering, Computer and Mathematical Sciences
The University of Adelaide

October 2017
Declaration

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission in my name for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint award of this degree. I give consent to this copy of my thesis when deposited in the University Library, being made available for loan and photocopying, subject to the provisions of the Copyright Act 1968. The author acknowledges that copyright of published works contained within this thesis resides with the copyright holder(s) of those works. I also give permission for the digital version of my thesis to be made available on the web, via the University's digital research repository, the Library Search and also through web search engines, unless permission has been granted by the University to restrict access for a period of time.

I acknowledge the support I have received for my research through the Adelaide Scholarship International (ASI) award, when I started my study as an international student.
Acknowledgment

I would like to take this opportunity to thank all the people who helped me to do this research during my study as a master of philosophy.

My kindest gratitude to my caring supervisors, Prof. Bo Jin and Prof. Sheng Dai, who provided sufficient and knowledgeable suggestions for me during my research. Their supervision was truly beneficial and efficient for me.

I also thank Dr. Yusak Hartanto, the previous Ph.D. student of our group who helped me to design the experiments. I like to thank my friend and teammate Mr. Seonho Yun, who helped me in the experiments and I enjoyed his suggestions during my study. Dr. Masoumeh Zargar whom I worked with in the first months of my candidature and I used her recommendations for my research. Finally, I thank all the researchers at Polymer, Pharmaceutical and Bionanotech Labs and I will have their friendship for the rest of my life.

I must thank the University of Adelaide for the financial support and giving Adelaide Scholarship International (ASI) award to me. In addition, the staff of chemical engineering school who provided a friendly atmosphere and kind support.

Finally yet importantly, my warmest and deepest gratitude goes to my beloved parents and family. They supported me all the time and their love made this journey possible.
Abstract

Forward Osmosis (FO) process is a low-energy membrane separation technique, which has attracted increasing attention recently for desalination applications. Unlike Reverse Osmosis, which needs a high-pressure pump; FO works via natural osmotic pressure provided by a draw solution. Therefore, development of efficient draw solutions is quite important. Polymeric stimuli-responsive microgels/hydrogels are promising options as they can be recovered by applying the proper stimulus heating or gassing processes. The temperature-responsive microgels/hydrogels have been developed for FO application in recent years. This thesis study was aimed to the development of gas-responsive microgels as draw solutions for FO desalination. Two main series of microgels: CO\textsubscript{2}-responsive and O\textsubscript{2}-responsive microgels are for the first time fabricated and evaluated for FO desalination throughout the thesis. The feed saline water used here is 2000 ppm NaCl, which is considered as brackish water.

A few of polymer monomers with tertiary amine moieties are selected for synthesizing CO\textsubscript{2}-responsive microgels. Water flux of the microgels was measured by monitoring conductivity of the saline feed water and interpreting it to the water flux through the membrane. The microgels are active and protonated as a draw solution after CO\textsubscript{2} purging, and can be recovered after CO\textsubscript{2} stripping by N\textsubscript{2} purging. Microgels synthesised with diethylaminoethyl methacrylate (DEAEMA) can provide water flux as high as 56 LMH. Characterization tests are carried out to explore the most-effective microgels with respect to cationic monomers: DEAEMA and dimethylamino ethyl methacrylate (DMAEMA), and the type and concentration of crosslinkers:
poly (ethylene glycol diacrylate) (PEGDA), N,N'-methylene-bisacrylamide (BIS) and ethylene glycol dimethacrylate (EGDMA). The microgels are recovered at their isoelectric point, where microgels are not charged and release water easily.

O2-responsive microgels are synthesised and their FO desalination performance is studied systematically. Two Fluoro-containing monomers (2,3,4,5,6 pentafluorostyrene (FS), 2,2,2-trifluoroethyl methacrylate (FM)), which are responsive to oxygen, are selected to copolymerize with four suitable ionic and non-ionic monomers: DEAEMA, Hydroxyethyl methacrylate (HEMA), DMAEMA and N-isopropylacrylamide (NIPAM). The results show that the water recovery ratio can be enhanced if a proper non-ionic monomer like NIPAM is used. The O2-responsive microgels synthesised by DMAEMA and 5wt% FM monomer can perform the highest water flux up to 29 LMH. The experimental data reveal that HEMA is not a suitable non-ionic monomer to synthesise O2-responsive microgels as HEMA has –OH groups, which lead to high negative surface charges and affect the water recovery. FO desalination data show that O2-responsive microgels perform comparable water flux and water recovery capability.

Dynamic light scattering (DLS) as the main characterization test for microgels is done. The microgels show larger hydrodynamic diameter after CO2 or O2 purging and they become smaller after removing these gases via N2 purging. The swelling ratio for the microgels is up to 14 and 6.5 for CO2 responsive and O2-responsive microgels, respectively.

As new polymer draw agents, CO2- and O2-responsive microgels demonstrate high water flux and water recovery capabilities as promising
draw solutes for energy-effective FO desalination. CO$_2$-responsive DEAEMA microgels with 1wt% PEGDA crosslinker performed water flux of 56 LMH with 50 % water recovery ratio. DMAEMA CO$_2$-responsive microgels perform smaller water flux due to lower pK$_a$ of DMAEMA than DEAEMA. O$_2$-responsive microgels show relatively lower water flux than CO$_2$-responsive microgels. The best water flux performance is observed for DEAEMA/DMAEMA-5wt% FM microgels with 26-29 LMH, while the highest water recovery is given by NIPAM-5wt% FM microgels with 56%.
Table of Contents

Declaration ........................................................................................................... i
Acknowledgment ........................................................................................... ii
Abstract .......................................................................................................... iii
Table of Contents ............................................................................................. vi

Chapter 1. ........................................................................................................ 1

1 INTRODUCTION ......................................................................................... 1
  1.1 Background ............................................................................................ 2
  1.2 Aims and objectives .............................................................................. 5
  1.3 Outline of the thesis .............................................................................. 6

References ........................................................................................................... 8

Chapter 2. ....................................................................................................... 10

2 LITERATURE REVIEW ............................................................................. 10
  2.1 Forward osmosis process ..................................................................... 11
    2.1.1 Principles of forward osmosis....................................................... 13
    2.1.2 Draw solution ............................................................................... 15
    2.1.3 Operational challenges of FO process ....................................... 16
  2.2 Temperature-responsive draw solutions ............................................ 21
    2.2.1 Linear polymers, hydrogels and microgels................................. 22
    2.2.2 Deep eutectic solvents ............................................................... 30
    2.2.3 Thermo-responsive Ionic Liquids .............................................. 31
  2.3 Gas-responsive draw solutions .......................................................... 33
    2.3.1 Gas-responsive linear polymers ............................................... 34
    2.3.2 Switchable polarity solvents ..................................................... 35
  2.4 Other types of draw solutions ............................................................ 36
    2.4.1 Salts ......................................................................................... 36
    2.4.2 Synthetic materials ................................................................. 39
  2.5 Research prospects .............................................................................. 43

References ........................................................................................................... 46

Chapter 3. ...................................................................................................... 53
3 CO₂-RESPONSIVE MICROGELS FOR ENERGY-EFFECTIVE FORWARD OSMOSIS DESALINATION

Abstract ............................................................................................................. 56

3.1 Introduction ................................................................................................. 57

3.2 Experimental ............................................................................................... 59

3.2.1 Materials .................................................................................................... 59

3.2.2 Synthesis of DEAEMA microgels ............................................................ 60

3.2.3 Synthesis of DMAEMA microgels ........................................................... 60

3.2.4 Characterization of microgels ................................................................. 61

3.2.5 Evaluation on desalination performance of CO₂-responsive microgels ....................................................................................................................... 61

3.2.6 Microgels recycling evaluation ............................................................... 63

3.3 Results and Discussion ................................................................................ 63

3.3.1 Synthesis and characterization of CO₂-responsive microgels ... 63

3.3.2 CO₂ and N₂ responsivity of microgels ................................................... 66

3.3.3 Water flux of using CO₂-responsive microgels as draw materials 67

3.3.4 Water recovery and recyclability of CO₂-responsive microgels 68

3.3.5 Effect of crosslinker concentration ....................................................... 71

3.3.6 Effect of cationic monomers ................................................................. 73

3.4 Conclusion ................................................................................................... 75

3.5 Supporting Information ............................................................................... 77

References ......................................................................................................... 84

Chapter 4......................................................................................................... 90

4 O₂-RESPONSIVE MICROGELS FOR FORWARD OSMOSIS DESALINATION................................................. 90

Abstract ........................................................................................................... 93

4.1 Introduction .................................................................................................. 94

4.2 Experimental .............................................................................................. 97

4.2.1 Materials .................................................................................................. 97

4.2.2 Synthesis of O₂-responsive microgels ..................................................... 98

4.2.3 Characterization of O₂-responsive microgels ........................................ 99

4.2.4 Evaluation on desalination performance of O₂-responsive microgels ..................................................................................................................... 100

4.3 Results and Discussion ............................................................................. 102
4.3.1 Synthesis and characterization of O2-responsive DEAEMA-FM/FS microgels ................................................................. 102
4.3.2 Water flux of O2-responsive DEAEMA-FM/FS microgels .... 105
4.3.3 Initial water flux, water recovery and recyclability of O2-responsive DEAEMA-FM/FS microgels .............................................. 107
4.3.4 DMAEMA-based cationic O2-responsive microgels ......... 110
4.3.5 Nonionic O2-responsive microgels ........................................... 112
4.4 Conclusion .............................................................................. 116
4.5 Supporting Information ........................................................... 117
References .................................................................................... 121

Chapter 5 ...................................................................................... 127

5 CONCLUSIONS AND RECOMMENDATIONS ............ 127
5.1 Conclusions ........................................................................... 128
5.2 Recommendations for future research................................. 130