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**Gas Responsive Microgels as Novel Draw Agents  
for Forward Osmosis Desalination**

By

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*A thesis submitted for the degree of Master of Philosophy*

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# Declaration

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## 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<sub>2</sub>-responsive and O<sub>2</sub>-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<sub>2</sub>-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<sub>2</sub> purging, and can be recovered after CO<sub>2</sub> stripping by N<sub>2</sub> 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.

O<sub>2</sub>-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 O<sub>2</sub>-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 O<sub>2</sub>-responsive microgels as HEMA has –OH groups, which lead to high negative surface charges and affect the water recovery. FO desalination data show that O<sub>2</sub>-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 CO<sub>2</sub> or O<sub>2</sub> purging and they become smaller after removing these gases via N<sub>2</sub> purging. The swelling ratio for the microgels is up to 14 and 6.5 for CO<sub>2</sub> responsive and O<sub>2</sub>-responsive microgels, respectively.

As new polymer draw agents, CO<sub>2</sub>- and O<sub>2</sub>-responsive microgels demonstrate high water flux and water recovery capabilities as promising

draw solutes for energy-effective FO desalination. CO<sub>2</sub>-responsive DEAEMA microgels with 1wt% PEGDA crosslinker performed water flux of 56 LMH with 50 % water recovery ratio. DMAEMA CO<sub>2</sub>-responsive microgels perform smaller water flux due to lower pK<sub>a</sub> of DMAEMA than DEAEMA. O<sub>2</sub>-responsive microgels show relatively lower water flux than CO<sub>2</sub>-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

<b>Declaration</b> .....	<b>i</b>
<b>Acknowledgment</b> .....	<b>ii</b>
<b>Abstract</b> .....	<b>iii</b>
<b>Table of Contents</b> .....	<b>vi</b>
<b>Chapter 1</b> .....	<b>1</b>
<b>1 INTRODUCTION</b> .....	<b>1</b>
1.1 Background .....	2
1.2 Aims and objectives .....	5
1.3 Outline of the thesis.....	6
References .....	8
<b>Chapter 2</b> .....	<b>10</b>
<b>2 LITERATURE REVIEW</b> .....	<b>10</b>
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
<b>Chapter 3</b> .....	<b>53</b>

### **3 CO<sub>2</sub>-RESPONSIVE MICROGELS FOR ENERGY-EFFECTIVE FORWARD OSMOSIS DESALINATION** 53

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 CO <sub>2</sub> -responsive microgels.....	61
3.2.6 Microgels recycling evaluation.....	63
3.3 Results and Discussion.....	63
3.3.1 Synthesis and characterization of CO <sub>2</sub> -responsive microgels...	63
3.3.2 CO <sub>2</sub> and N <sub>2</sub> responsivity of microgels .....	66
3.3.3 Water flux of using CO <sub>2</sub> -responsive microgels as draw materials	67
3.3.4 Water recovery and recyclability of CO <sub>2</sub> -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 O<sub>2</sub>-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 O <sub>2</sub> -responsive microgels.....	98
4.2.3 Characterization of O <sub>2</sub> -responsive microgels.....	99
4.2.4 Evaluation on desalination performance of O <sub>2</sub> -responsive microgels.....	100
4.3 Results and Discussion.....	102



4.3.1	Synthesis and characterization of O <sub>2</sub> -responsive DEAEMA-FM/FS microgels.....	102
4.3.2	Water flux of O <sub>2</sub> -responsive DEAEMA-FM/FS microgels ....	105
4.3.3	Initial water flux, water recovery and recyclability of O <sub>2</sub> -responsive DEAEMA-FM/FS microgels .....	107
4.3.4	DMAEMA-based cationic O <sub>2</sub> -responsive microgels .....	110
4.3.5	Nonionic O <sub>2</sub> -responsive microgels.....	112
4.4	Conclusion.....	116
4.5	Supporting Information .....	117
	References .....	121
<b>Chapter 5</b>	<b>.....</b>	<b>127</b>
<b>5</b>	<b>CONCLUSIONS AND RECOMMENDATIONS.....</b>	<b>127</b>
5.1	Conclusions .....	128
5.2	Recommendations for future research.....	130

## **Chapter 1.**

### **INTRODUCTION**

## 1.1 Background

Water scarcity is one of the most severe issues that threatens people's life in many countries around the world. Statistics show that above two billion people are facing water shortage [1]. Providing safe and potable water for many countries is an urgent mission. Every year, millions of dollars are being spent on desalination of sea and brackish water in African and Middle East countries [2]. One of the main reasons for the water crisis is indeed global warming which has led to a high amount of greenhouse emission, rising of sea levels and drying riverbeds [3]. In addition, world population has been constantly increased during the last decades, and most of the accessible water possesses high salinity and cannot be used without further proper desalination [4].

Water treatment and desalination have been a very hot topic for researchers in the last decades. Particularly, membrane-based desalination technologies have been studied widely by many research groups around the world [5]. Currently, four major membrane-based desalination processes are Reverse Osmosis (RO), membrane distillation (MD), Electrodialysis (ED) and Forward Osmosis (FO) [6]. In addition to membrane processes, thermal processes like multi stage flash, multi stage distillation, humidification-dehumidification and vacuum compression are also considered. RO is by far the most popular desalination technique, and it works based on the applied pressure above the osmotic pressure of the saline water to separate water through a semi-permeable membrane [7]. Energy consumption is a major issue related to RO since high-pressure pumps are required. MD is a thermal process as the main driving force to vaporize the water and pass them through a super-hydrophobic membrane and subsequently condense the vapour in the form of fresh water [8]. MD needs thermal energy, which is a drawback to this process. In

addition, water flux of MD is relatively low. ED is an electrochemical separation process which works based on the potential difference between two electrodes and separation through two ion-exchange membranes [9]. ED is suitable for low-salinity feed, and it can only separate salt ions, thereby ED cannot remove other imperfections, like viruses and bacteria [10].

FO has promising advantages over other desalination techniques. First of all, FO uses a draw solution with high osmotic pressure and the natural osmotic pressure difference between the feed and draw solutions is the driving force for water permeation. Thereby, it is expected that energy consumption for the FO process can be much less than that for RO as FO uses the natural driving force. Moreover, FO is less prone to fouling and has a great potential to produce fresh water [11].

While FO has been recognised as a promising and energy-effective method of desalination, however, there are some technical issues, which are hindering its usage in a high scale FO process. The draw solution is the centre in FO process, as which needs to provide the enough driving force to achieve high water flux. Furthermore, the adsorbed water through the semi-permeable membrane via draw solution must be released easily. The appropriate draw solution must be non-toxic and economical, and importantly can be recovered from a long term operation without comprising its performance [12]. Any further process to separate draw solution from the adsorbed water requires energy and makes the process economically and technically less feasible. Thereby it is essential that draw solution can be recovered as simple as possible [13]. In addition, FO like RO is prone to membrane fouling and concentration polarization [14, 15].

Development of an FO desalination process is dependent on two main challenges: suitable membrane and draw solution. Water recovery as one of the most important

properties of a draw solution also plays a vital role. For having a high-performance FO desalination system, all these three parts must be precisely designed and selected. Many types of draw solutions have been considered for FO in the recent years, from different salts like  $\text{MgCl}_2$ ,  $\text{MgSO}_4$  and  $\text{NaCl}$ , thermolytic agents such as ammonium bicarbonate ( $\text{NH}_4\text{HCO}_3$ ) [16-18] to stimuli-responsive materials [13, 19]. Recently, thermo-responsive hydrogels and microgels, which are polymeric 3D materials have been synthesised as a draw solution for FO desalination [20, 21]. These hydrogels/microgels become hydrophobic at a certain temperature, but they swell and become hydrophilic at lower temperatures, providing osmotic pressure to draw water through the semi-permeable membrane [22]. However, the water flux of these microgels is not very high. Hartanto et al. functionalized thermo-responsive microgels with cationic and acidic monomers to use the power of charged agents to produce significantly higher water flux. However, this might lead to lower water recovery of the microgels as the charged monomers are not responsive to temperature. Microgels have advantages over bulk hydrogels as they offer high surface area which enhances the affinity between the membrane and draw solution [23]. In addition, microgels are still large enough and do not reverse diffuse to the feed side and concentration polarization is not as serious as liquid-state draw solutions. Microgels can be also attached to the surface of the membranes to have a continuous FO desalination process. Thereby, further investigation into the development of new microgels for FO desalination is necessary.

This thesis project develops novel and high-performance smart draw solutions for FO desalination. The draw solutions reported here are gas-responsive polymeric microgels. To the best of our knowledge, this is the first time using gas-responsive microgels as a draw agent for FO desalination.  $\text{CO}_2$ -responsive and  $\text{O}_2$ -responsive

microgels are fabricated and systematically evaluated as a draw agent for FO desalination. In addition, the proper method of water recovery has been studied for the microgels to find out if the responsivity of the microgels can enhance their recovery. Water recovery is carried out by purging the trigger/stripper gases ( $\text{CO}_2/\text{N}_2$  and  $\text{O}_2/\text{N}_2$ ), alternatively. Since the microgels are responsive to  $\text{CO}_2$  or  $\text{O}_2$ , their hydrophilicity changes upon using these gases or  $\text{N}_2$  as the neutral gas to remove  $\text{CO}_2$  or  $\text{O}_2$ .

## **1.2 Aims and objectives**

This thesis project is aimed to develop novel gas-responsive microgels as draw solutes for an energy-effective FO desalination. The main research objectives are listed below:

- ✓ To investigate monomers with tertiary amine moieties to synthesise microgels with responsivity to  $\text{CO}_2$ . A few monomers are selected and two types of them are considered and their FO desalination performance will be studied. DEAEMA and DMAEMA are selected as they show high responsivity to  $\text{CO}_2$  and their pure microgels can be synthesized via random polymerization.
- ✓ To consider fluoro-containing monomers as  $\text{O}_2$ -responsive agents to synthesise  $\text{O}_2$ -responsive microgels as draw solution. Two types of fluorine monomers will be selected to polymerize with four types of ionic and non-ionic monomers.
- ✓ To study precisely the structure of the microgels in terms of cross-linker type and concentration and different monomers that can be used for various gas-responsive microgels synthesis.

- ✓ To consider gas-responsivity of the microgels as a method for water recovery of the microgels.

### **1.3 Outline of the thesis**

This thesis is prepared by combination version. The two technical chapters (Chapters 3 and 4) are prepared as manuscripts which have been submitted to peer-review journals.

**Chapter 1** discusses background, and highlights research gaps, aims and objectives of the thesis project.

**Chapter 2** presents a literature review of forward osmosis technology and draw solution, particularly stimuli-responsive draw solutions. The fundamentals of forward osmosis technology are discussed. Update research progresses from recent studies on temperature and gas-responsive draw solutions are reviewed as the major part of this chapter.

**Chapter 3** is dedicated to study CO<sub>2</sub>-responsive microgels as a draw solution for FO desalination. This chapter is prepared as a manuscript and is submitted to Water Research journal for publication. The microgels for this chapter are synthesised via free radical polymerization and the effect of monomer and crosslinker type and concentration are studied. The microgels are further characterised and their water flux performance is investigated. As CO<sub>2</sub> is an acidic gas and changes pH, both effects of swelling ratio and charge moieties are contributing to better performance.

**Chapter 4** reports the synthesis and investigation of O<sub>2</sub>-responsive micorgels as a novel draw solution for forward osmosis. This chapter is written in manuscript style and is submitted to Environmental Science and Technology journal for publication. In this chapter, four ionic and no-ionic monomers with different properties are co-

polymerized with two fluoro containing monomers to synthesise O<sub>2</sub>-responsive microgels. Water flux and recovery performance of the microgels are studied systematically.

Finally, **Chapter 5** concludes the thesis and suggests further possible researches.

In this chapter, the key results are also summarized.



## References

- [1] R.R.T. John C. Crittenden, David W. Hand, Kerry J. Howe, George Tchobanoglous MWH's Water Treatment: Principles and Design, 3rd Edition, Wiley, 2012.
- [2] A. Fenwick, Waterborne infectious diseases--could they be consigned to history?, *Science*, 313 (2006) 1077-1081.
- [3] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Marinas, A.M. Mayes, Science and technology for water purification in the coming decades, *Nature*, 452 (2008) 301-310.
- [4] M. Elimelech, W.A. Phillip, The future of seawater desalination: energy, technology, and the environment, *Science*, 333 (2011) 712-717.
- [5] A.G. Fane, R. Wang, M.X. Hu, Synthetic Membranes for Water Purification: Status and Future, *Angewandte Chemie International Edition*, 54 (2015) 3368-3386.
- [6] I.O. Uribe, A. Mosquera-Corral, J.L. Rodicio, S. Esplugas, Advanced technologies for water treatment and reuse, *AIChE Journal*, 61 (2015) 3146-3158.
- [7] S.S. Shenvi, A.M. Isloor, A.F. Ismail, A review on RO membrane technology: Developments and challenges, *Desalination*, 368 (2015) 10-26.
- [8] S.M. Seyed Shahabadi, H. Rabiee, S.M. Seyedi, A. Mokhtare, J.A. Brant, Superhydrophobic dual layer functionalized titanium dioxide/polyvinylidene fluoride-co-hexafluoropropylene (TiO<sub>2</sub>/PH) nanofibrous membrane for high flux membrane distillation, *Journal of Membrane Science*, 537 (2017) 140-150.
- [9] Y. Tanaka, 12 - Electrodialysis, in: *Ion Exchange Membranes (Second Edition)*, Elsevier, Amsterdam, 2015, pp. 255-293.
- [10] M. Sadrzadeh, T. Mohammadi, Sea water desalination using electrodialysis, *Desalination*, 221 (2008) 440-447.
- [11] D.L. Shaffer, J.R. Werber, H. Jaramillo, S. Lin, M. Elimelech, Forward osmosis: Where are we now?, *Desalination*, 356 (2015) 271-284.
- [12] H. Luo, Q. Wang, T.C. Zhang, T. Tao, A. Zhou, L. Chen, X. Bie, A review on the recovery methods of draw solutes in forward osmosis, *Journal of Water Process Engineering*, 4 (2014) 212-223.
- [13] Y. Cai, X.M. Hu, A critical review on draw solutes development for forward osmosis, *Desalination*, 391 (2016) 16-29.

- [14] G.T. Gray, J.R. McCutcheon, M. Elimelech, Internal concentration polarization in forward osmosis: role of membrane orientation, *Desalination*, 197 (2006) 1-8.
- [15] W. kuang, Z. Liu, H. Yu, G. Kang, X. Jie, Y. Jin, Y. Cao, Investigation of internal concentration polarization reduction in forward osmosis membrane using nano-CaCO<sub>3</sub> particles as sacrificial component, *Journal of Membrane Science*, 497 (2016) 485-493.
- [16] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, A novel ammonia—carbon dioxide forward (direct) osmosis desalination process, *Desalination*, 174 (2005) 1-11.
- [17] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, Desalination by ammonia—carbon dioxide forward osmosis: Influence of draw and feed solution concentrations on process performance, *Journal of Membrane Science*, 278 (2006) 114-123.
- [18] R.L. McGinnis, J.R. McCutcheon, M. Elimelech, A novel ammonia—carbon dioxide osmotic heat engine for power generation, *Journal of Membrane Science*, 305 (2007) 13-19.
- [19] P. Liu, B. Gao, H.K. Shon, D. Ma, H. Rong, P. Zhao, S. Zhao, Q. Yue, Q. Li, Water flux behavior of blended solutions of ammonium bicarbonate mixed with eight salts respectively as draw solutions in forward osmosis, *Desalination*, 353 (2014) 39-47.
- [20] A. Razmjou, G.P. Simon, H. Wang, Polymer Hydrogels as Smart Draw Agents in Forward Osmosis Processes, (2015) 129-149.
- [21] Y. Hartanto, M. Zargar, X. Cui, Y. Shen, B. Jin, S. Dai, Thermoresponsive cationic copolymer microgels as high performance draw agents in forward osmosis desalination, *Journal of Membrane Science*, 518 (2016) 273-281.
- [22] D. Li, X. Zhang, G.P. Simon, H. Wang, Forward osmosis desalination using polymer hydrogels as a draw agent: Influence of draw agent, feed solution and membrane on process performance, *Water Research*, 47 (2013) 209-215.
- [23] Y. Hartanto, M. Zargar, H. Wang, B. Jin, S. Dai, Thermoresponsive Acidic Microgels as Functional Draw Agents for Forward Osmosis Desalination, *Environ Sci Technol*, 50 (2016) 4221-4228.

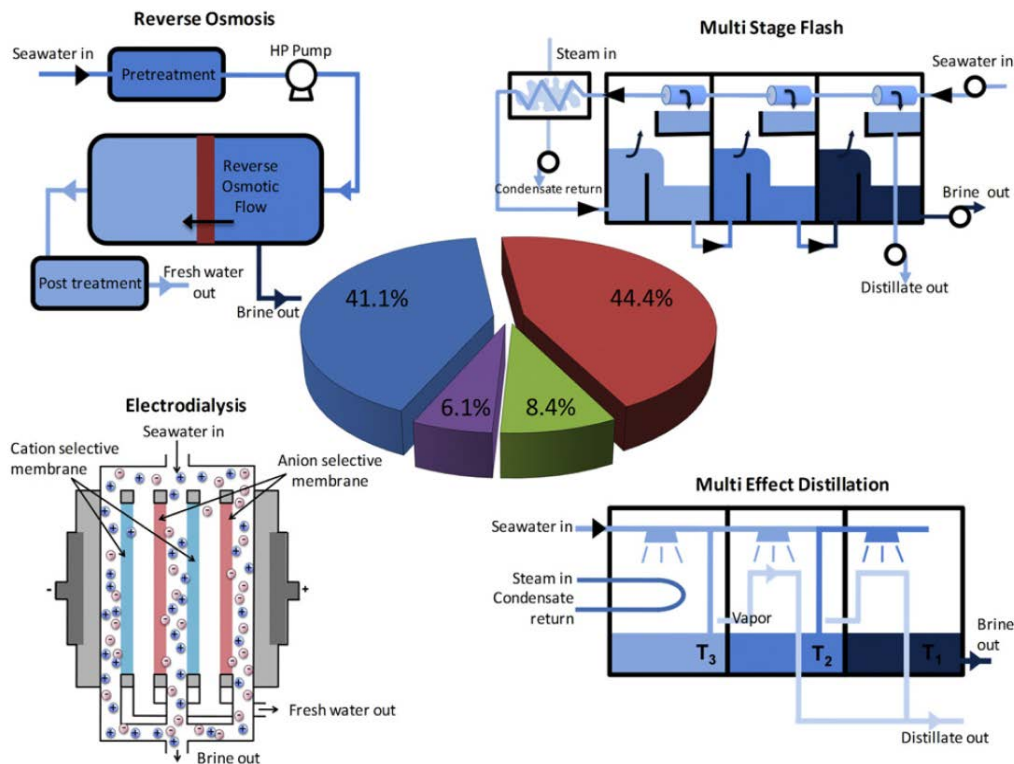
## **Chapter 2.**

# **LITERATURE REVIEW**

Forward osmosis is an emerging technology for desalination, which is able to overcome the issues related to high-energy consumption of other desalination techniques. One of the key features of developing forward osmosis is using a suitable draw solution, which performs high water flux and can be regenerated with the simplest method and lowest possible energy consumption. Different types of draw solutions have been studied and synthesised for this mission, however, more research is required in this regard. Consequently, the development of forward osmosis is dependent on the synthesising efficient draw solution. Thus, material development plays a major role to design the favourable draw solution. This chapter provides an update review of the principles and challenges of forward osmosis processes. Detailed research processes and discussion will be focused on recent studies and development of stimuli-responsive draw solutions.

## **2.1 Forward osmosis process**

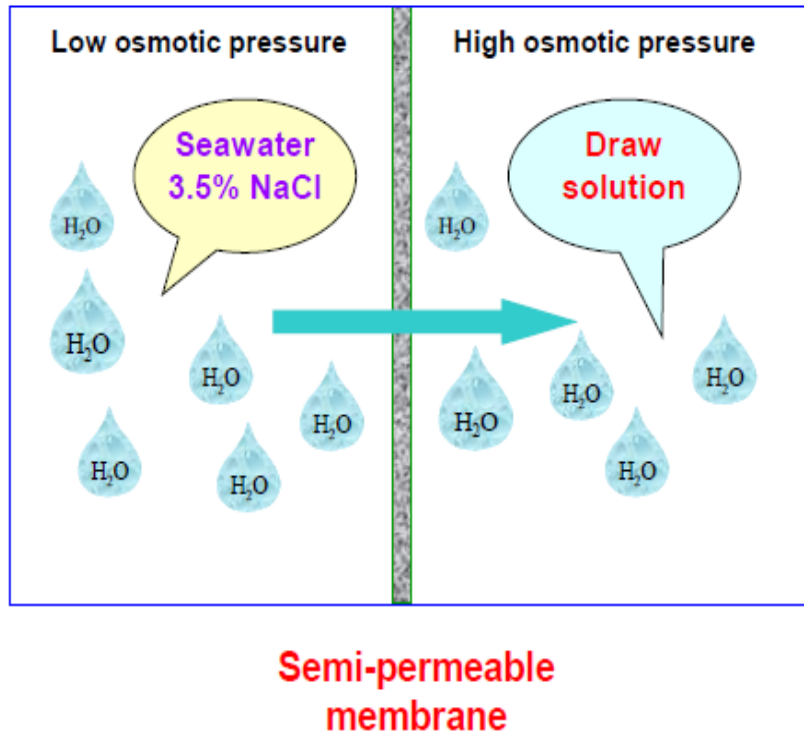
Desalination of brackish waters and seawater has attracted continuously increasing attention to overcome water scarcity in various continents with extreme water resources like Australia and Africa [1, 2]. Different thermal and membrane-based desalination methods have been utilised based on the required capacity, feed and output water quality and energy consumption to remove salt from water. Currently, Reverse Osmosis (RO) and Multi Stage Flash are the most applied techniques of desalination (Figure 1). Development of novel and new techniques with less environmental fingerprint and energy consumption has been a hot research topic for many researchers around the world.



**Figure 1** Schematic diagram of the most applied desalination methods and their contribution to the worldwide installed plants for producing freshwater from saline water (Re-printed from reference [3])

Forward osmosis is as an emerging membrane technology for water reuse and desalination [4]. Reverse Osmosis is currently the main membrane-based desalination process worldwide. Significant economic issues attributed to RO are the high energy consumption and severe membrane fouling. FO has attracted much attention in the last decade. Unlike pressure-driven membrane processes (such as RO), FO is a natural osmosis-driven process involving a semipermeable membrane and a draw solution [5]. Ideally, the semipermeable membrane performs as a barrier that rejects salts or unwanted elements, but allows water to pass through, while the draw solution has a higher osmotic pressure that extracts water from the feed across the membrane (Figure 2). Forward osmosis uses a concentrated draw solution to generate osmotic pressure, which extracts (draws) water across a semi-permeable membrane from the feed solution [6]. Consequently, the feed stream reduces in

volume, increasing the salt concentration, which results in a decrease in the permeate flux to the draw solution side.



**Figure 2** schematic structure of an FO process

### 2.1.1 Principles of forward osmosis

Forward Osmosis (or Osmosis or Direct Osmosis) is a natural physical phenomenon which has been discovered since the early days of mankind. FO follows the second law of thermodynamics, where movement of molecules from the low concentration solution to the high concentration solution through a semi-permeable membrane takes place naturally to equilibrate their overall chemical potential [7]. In other words, FO is the transport of water through a semi-permeable membrane due to the difference between the osmotic pressure across the membrane, from a solution of low solute concentration (with high water potential) to a solution of high solute

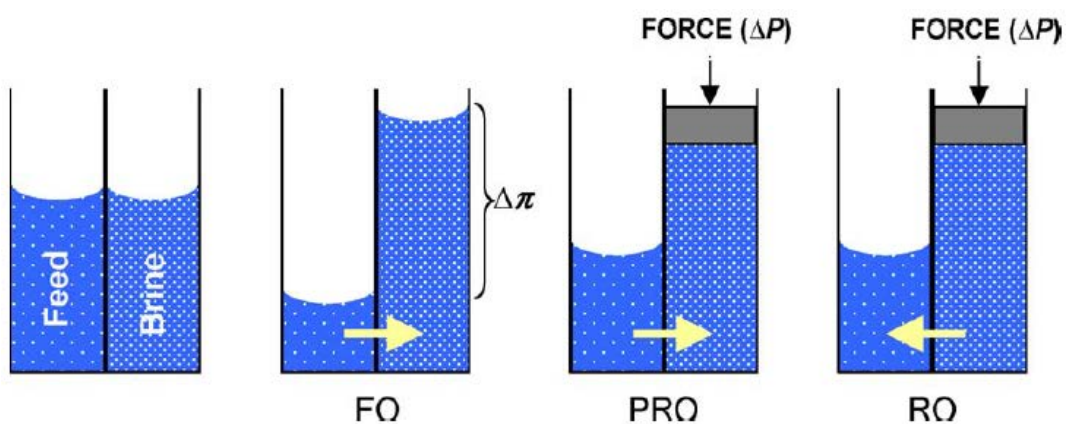
concentration (with lower water potential). The general equation for calculation of water flux of the osmotic processes is:

$$J = A(\sigma\Delta\pi - \Delta p) \quad (1)$$

where,  $J$  is water flux,  $A$  is the constant of membranes for water permeability,  $\sigma$  is the reflection coefficient.  $\Delta\pi$  is the osmotic pressure difference across the membrane and  $\Delta p$  is the applied external pressure. For RO  $\Delta p > \Delta\pi$ , and for pressure retarded osmosis (PRO)  $\Delta\pi > \Delta p$ . In FO process,  $\Delta p$  is zero, and water flux equation will be:

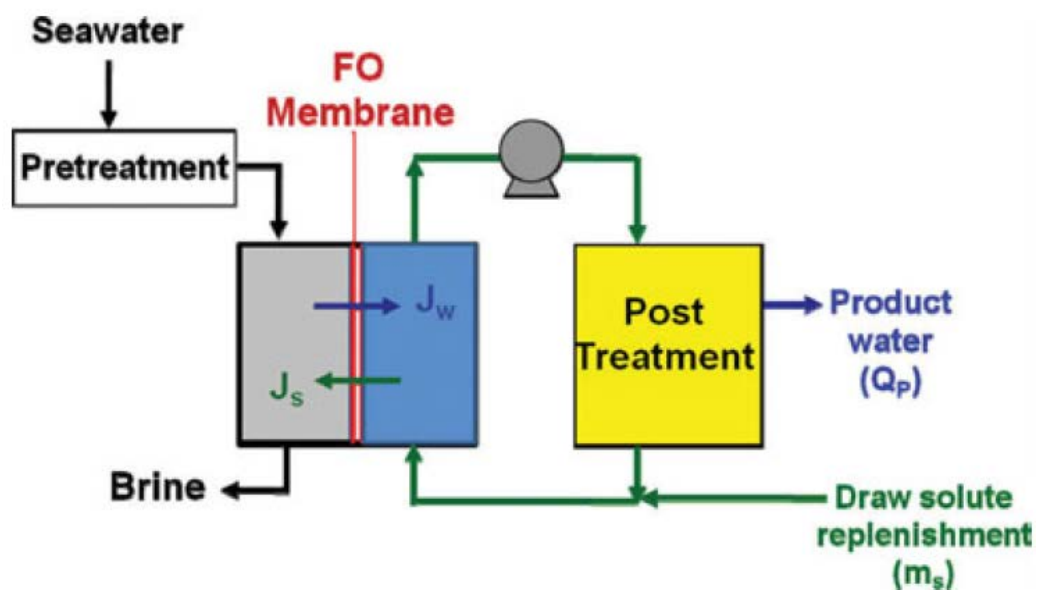
$$J = A\sigma\Delta\pi \quad (2)$$

Different osmotic processes are schematically shown in Figure 3. Unlike RO process, FO does not need an external pressure to perform. POR happens when the external applied pressure is neither zero nor more than osmotic pressure. Hence, this applied pressure is not able to reverse the water flux and convert it to RO. Some researchers have attempted to produce energy from this phenomenon (PRO), so called osmotic energy or salient gradient energy [8, 9].



**Figure 3** Different osmotic processes (Re-printed from reference [10])

After drawing water, a dewatering step is required to separate water from draw solution in an FO desalination process. This draw solution recovery (water recovery or draw solution regeneration) is of a great importance. Since FO process is performed based on the natural difference in the osmotic pressures, the only step that energy is consumed is draw solution recovery. A typical FO desalination process is shown in Figure 4.



**Figure 4** Schematic of an FO process with pre-treatment and post-treatment (Reprinted from reference [11])

### 2.1.2 Draw solution

The draw solution provides sufficient osmotic pressure as the driving force to transfer water molecules through the membrane. The draw solution is the centre of an FO process. A suitable draw solution not only leads to better performance of the FO process, but also results in lower recovery cost. An appropriate draw solution should have three main desirable characteristics: (1). The capability to generate high osmotic pressure, (2). Low reverse flux of draw solution through the membrane and (3). Easiness of recovery of the diluted draw solution. Other



parameters such as non-toxicity and low viscosity for pumping (for liquid-state draw solutions) are important as well.

Osmotic pressure of the draw solution is the only driving force in the FO process, thus it must be higher than that of the feed solution to be able to adsorb water molecules from the feed side through the membrane. According to Equation (2) ( $J_w = A\sigma\Delta\pi$ ) water flux of the FO process is directly related to the provided osmotic pressure of the draw solution. According to van't Hoff equation, ionic compounds are able to produce high osmotic pressure since they dissociate in water [12].

### **2.1.3 Operational challenges of FO process**

Despite desirable features of FO for desalination, there are three main challenges that are hindering FO desalination operation remarkably: concentration polarization, membrane fouling and draw solute back diffusion. These issues influence the performance of FO process negatively and need to be taken into consideration.

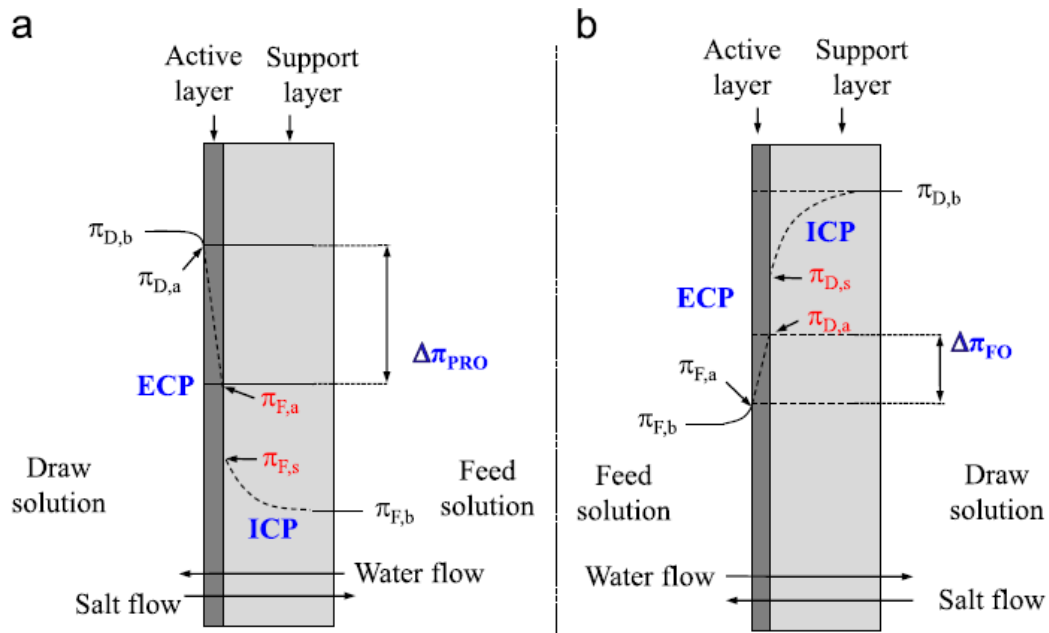
#### *2.1.3.1 Concentration polarization*

There are two types of concentration polarization for an FO process: internal concentration polarization (ICP) and external concentration polarization (ECP). In an FO process, the draw solution and the feed (saline water in desalination) diffuse to the selective and support layers of the membrane. A concentration distribution in the both sides occurs (Figure 5). Because of concentration polarization, the effective osmotic pressure across the membranes reduces and  $\pi_{D,a} - \pi_{F,a}$  will become lower than  $\pi_{D,b} - \pi_{F,b}$ .

In Figure 5,  $\pi_{D,a}$ ,  $\mu_{F,a}$ ,  $\pi_{D,b}$  and  $\pi_{F,b}$  are the osmotic pressures of the draw solution and the feed at membrane active layer surfaces, and bulky solutions in draw solution and feed solution, respectively [7]. The modified version of equation (2) after considering concentration polarization will be:

$$J = A\sigma\Delta\pi = A\sigma(\pi_{D,a} - \pi_{F,a}) \quad (3)$$

ECP takes place on the outer surface of the membrane selective layer. ECP can be concentrative ECP and dilutive ECP, depending on the orientation of membrane. If the saline feed is on the selective layer, as so-called FO-mode (Figure 5b), this is concentrative ECP. The dilutive ECP happens if the draw solution is facing selective layer or PRO-mode (Figure 5a). Dilutive refers to dilution of draw solution near the membrane and concentrative means accumulation of feed solutes near the membrane.



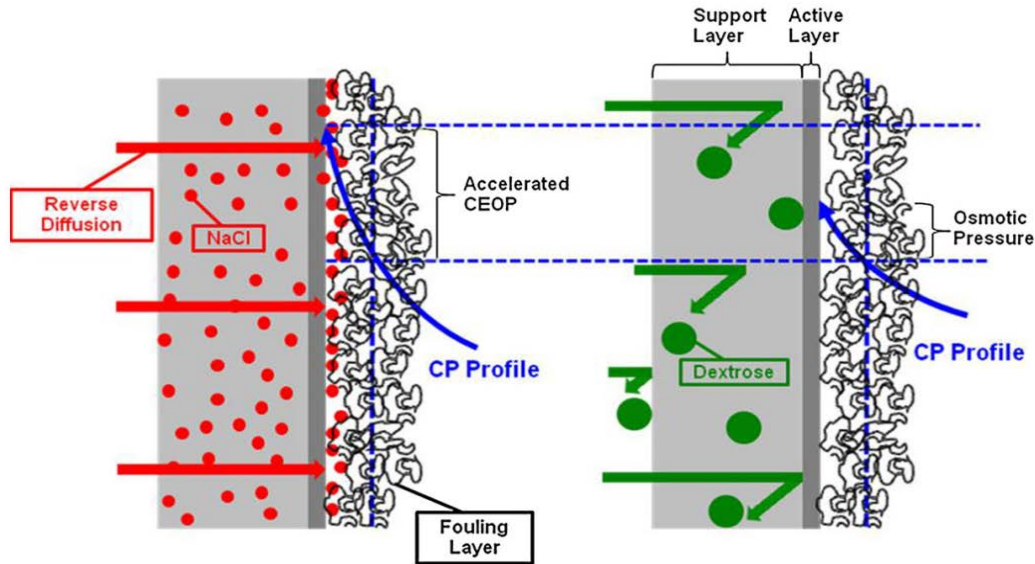
**Figure 5** Concentration polarization across a semi-permeable membrane in FO: (a) PRO-mode (b) FO-mode orientation (Re-printed from reference [7])

ICP takes place within the porous support layer and is more problematic than ECP. ICP is the main reason for water flux reduction in FO and it cannot be eliminated easily. It has been reported that ICP can lead to even 80% water flux drop [13]. ICP has two types similar to ECP, dilutive (in FO-mode) and concentrative ICP (in PRO-mode) [14]. The severity of ICP depends on a few factors, such as the structure of the support layer (thickness, tortuosity, and porosity) and also diffusion of draw solution in the support layer [15]. ICP and ECP can happen for a membrane simultaneously. Many researchers have tried to study the effects of them on FO water flux. At FO-mode membrane orientation, dilutive ICP should be considered and resolved because the effect of concentrative ECP is almost negligible. The concentrative ICP in a PRO-mode is negligible and dilution of draw solution has more severe influence on the water flux [16].

#### *2.1.3.2 Reverse draw solution diffusion*

Draw solution back diffusion happens when draw solution diffuses into the feed solution. This phenomenon is natural as the concentration of draw solution in the feed side is zero and the draw solution tends to move to feed side. Because of the back diffusion of draw solution, the osmotic difference across the membrane will be negatively influenced. Lee et al. illustrated that reverse diffusion of draw solution in the feed side results in cake-enhanced osmotic pressure (CEOP) effect and more severe membrane fouling as it is shown in Figure 6 [17]. According to this mechanism, permeate flux decline is not caused by the cake layer resistance, but rather due to the enhanced concentration polarization and hence osmotic pressure within the particle cake layer near the membrane surface [18]. This effect happens when draw solution accumulates on the surface of the membrane, contributing to concentration polarization and membrane fouling, and

consequently, leading to a reduction in the water flux. This issue is mainly related to liquid-state draw solutions with small molecules and for a draw solution with large molecular size, reverse diffusion is not a major issue.

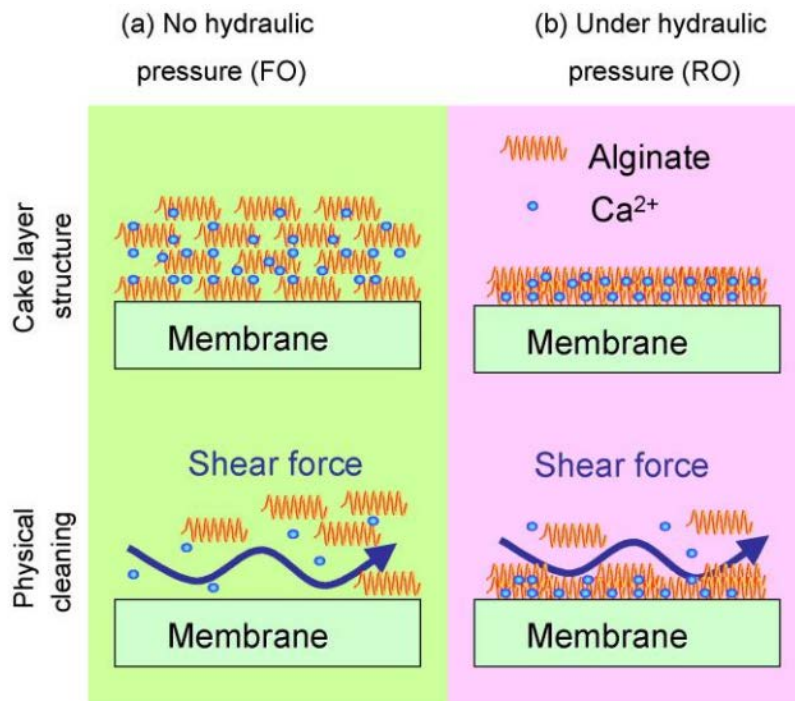


**Figure 6** Reverse diffusion of draw solution in an FO process (Re-printed from reference [17])

### 2.1.3.3 Fouling

Membrane fouling is another major issue in an FO process. Organic fouling, inorganic scaling and biofouling are the main types of fouling that can be seen for the membrane in an FO process (also RO process). Mi et al. reported that foulant-foulant interaction plays an important role in determining the rate and extent of fouling [19]. There are some factors that are important in organic fouling formation, such as permeation drag, hydrodynamic shear force and calcium binding [20]. Organic fouling can be removed without any chemical cleaning. After cleaning, FO had higher water flux recovery than RO. In fact, the hydraulic pressure in RO makes organic fouling more severe [21]. Figure 7 shows that organic foulants can be packed on the membrane surface. After cleaning, some amount of fouling will still remain and influence water flux. The process of compacting organic fouling on the

RO membranes might result in irreversible fouling, which is not observed in FO because no external high pressure is applied.



**Figure 7** Organic fouling on FO and RO membranes (Re-printed from reference [21])

Parida et al. investigated the effect of membrane orientation on the fouling and found that fouling in PRO mode is more severe [22]. This is due to the difference between the roughness of the selective layer and supportive layer. In PRO mode, where less smooth support layer is contacting the feed, the membrane is more prone to fouling.

Inorganic scaling is the precipitation of sparingly soluble salts, such as calcium sulphate, barium sulphate and calcium carbonate near or on the membrane surface, resulting in water flux reduction. It was seen that scaling of these salts on the membranes leads to decline in water flux similarly for FO and RO. However, FO process exhibited better water recovery. The reason is again the effect of hydraulic pressure, which leads to more compact scaling on the membrane surface [23].

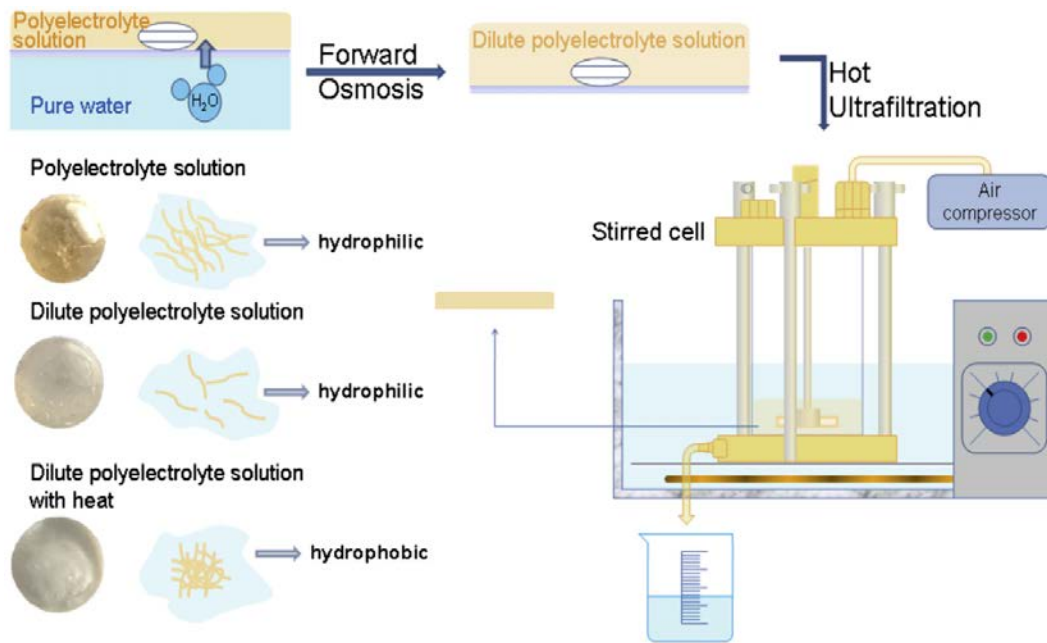
Another type of fouling for FO membranes is biofouling which is the formation of biofilm on the membrane surface and can result in water flux reduction by 10-15% of the initial flux [24]. Biofouling is a major issue for all the membrane technologies [25]. Biofouling can be formed with a few colonies of microorganisms, which exist in the feed, and form a bio film. Biofouling is a complicated process and ruled by several factors such as: properties of the feed water (temperature, osmotic pressure and pH) and the membrane surface topology (pore size, hydrophobicity, roughness, and electrokinetic charge) [20, 26]. Microfiltration, ultrafiltration and chlorination are used to prevent biofouling, however biofouling cannot be prevented completely as these methods do not remove all the existing microorganisms. Even if 99.9% of them are removed, there are still enough cells remaining which can continue to grow at the expense of biodegradable substances in the feed water [27]. Microfiltration and ultrafiltration are the most commonly used membrane processes for biofouling control. Chlorination can lead to formation of harmful compounds, membrane degradation, and shortening membrane lifespan.

## **2.2 Temperature-responsive draw solutions**

Physical properties of stimuli-responsive materials can be changed if they are processed with exposure of some stimuli like temperature, light, pH, etc. The most studied trigger for draw solution application is temperature [28, 29]. Temperature-responsive materials can be further subcategorized into two categories: Lower Critical Solubility Temperature (LCST) and Upper Critical Solubility Temperature (USCT). For LCST materials, they are miscible in water at the temperatures below LCST and they become hydrophobic and show phase separation above LCST. For USCT, this relation between temperature and hydrophilicity is vice versa, and they are hydrophilic at upper temperatures [30].

### 2.2.1 Linear polymers, hydrogels and microgels

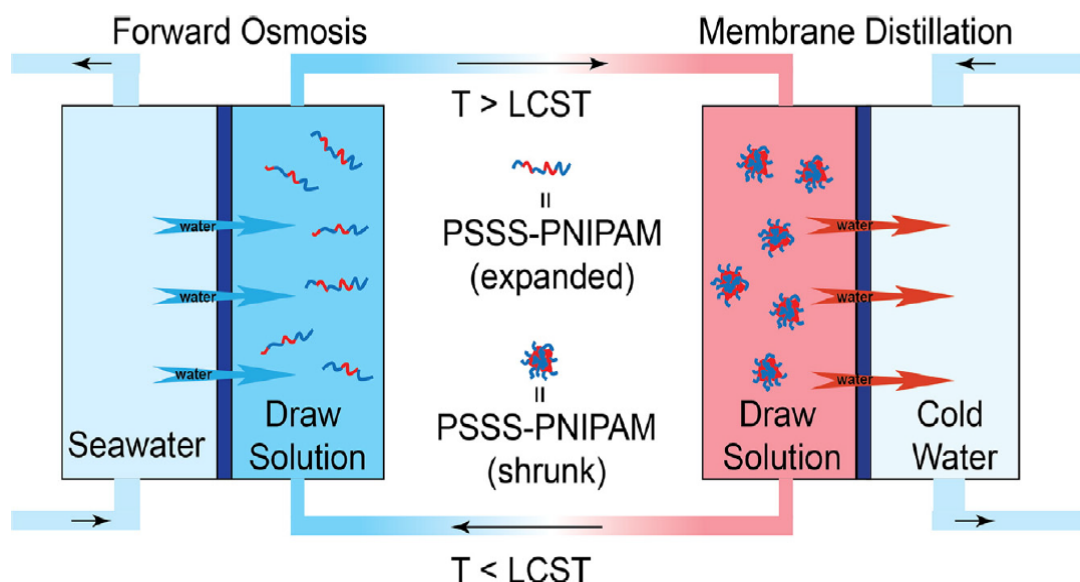
Poly (N-isopropylacrylamide) (PNIPAM) is the most studied polymer for fabrication of thermo-responsive draw solutions. PNIPAM shows a sharp transition from hydrophilic to hydrophobic at moderate temperature (32°C). The modified forms of this material have also been considered recently [31]. Ou et al. for the first time used PNIPAM and poly(NIPAM-co-Sodium Acrylate) P(NIPAM-SA) polymeric solution as draw solution [32]. These polymers are hydrophilic and water-miscible at room temperature and 15wt% water solution of these polymers were used as draw solution. They also used ultrafiltration at high temperature as the regeneration step (2 bar, 45 °C for 1 h) (Figure 8). At higher temperatures, the homogenous polymeric solution becomes suspension, and the polymeric molecules become hydrophobic. Thus, they are large enough to be separated via ultrafiltration. They also observed that high addition of SA into PNIPAM structure leads to reduction of PNIPAM temperature sensitivity. Using 50wt% SA addition, the polymeric solution showed no temperature responsivity, because SA is not thermo-sensitive [32]. Using P(NIPAM-SA) with 4wt% SA the polymer solution performed the best results with 0.35 LMH water flux and 65% recovery.



**Figure 8** Schematic diagram of the application of polyelectrolyte solution as draw agent for an FO-ultrafiltration process (Re-printed from reference [32])

Another polyelectrolyte as a potential draw solution was thermo-responsive copolymer of poly(sodiumstyrene-4-sulfonate-co-n-isopropylacrylamide) (PSSS-PNIPAM), which was synthesized by Zhao et al. [33]. They used solution of 15wt% as a draw solution and observed that this draw solution is able to produce adequate osmotic pressure for feeds with high salinity, like sea water with 0.6 M NaCl salinity. For draw solution regeneration, membrane distillation was considered as shown in Figure (9).



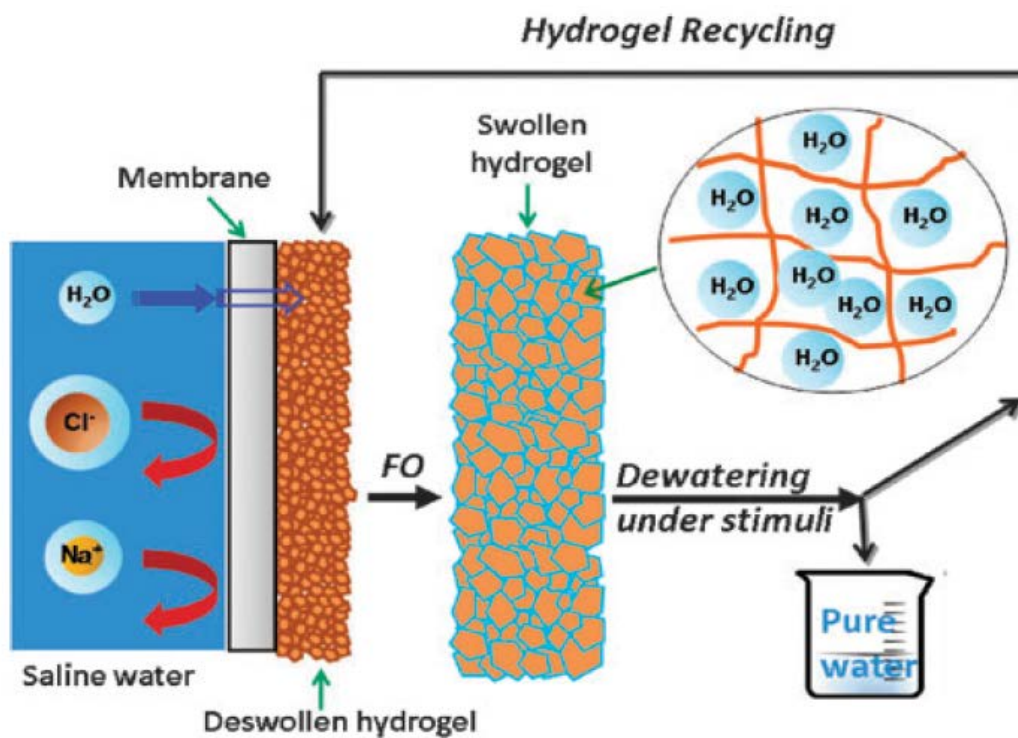


**Figure 9** Integration of FO with membrane distillation as regeneration step (Reprinted from reference [33])

Membrane distillation works with evaporation and condensation of the feed at 50 °C. The best water flux (around 4 LMH) was seen for 33% solution of the draw agent with 15wt% PSSS and 85% PNIPAM. Because of the presence of a large number of ions from ionic PSSS, the osmotic pressure was high enough for seawater desalination. One important issue, which hinders the application of thermo-responsive polymeric solution, is back diffusion as linear polymer molecular size is small enough to penetrate across the membrane and causing concentration polarization.

Hydrogels are another type of stimuli-responsive materials that have been fabricated as a draw agent. Hydrogels have 3D polymeric structure and are formed of loosely hydrophilic cross-linked polymers which have the capacity to undergo a drastic change in volume by absorbing and retaining several hundred times of their own weight of water while still remaining insoluble [34]. Temperature-responsive polymeric hydrogels were used as a draw solution for the first time by Professor Wang research team at Monash university in 2011 [35-40] (Figure 10). They synthesised four types of polymer hydrogels, two ionic hydrogels: poly(sodium

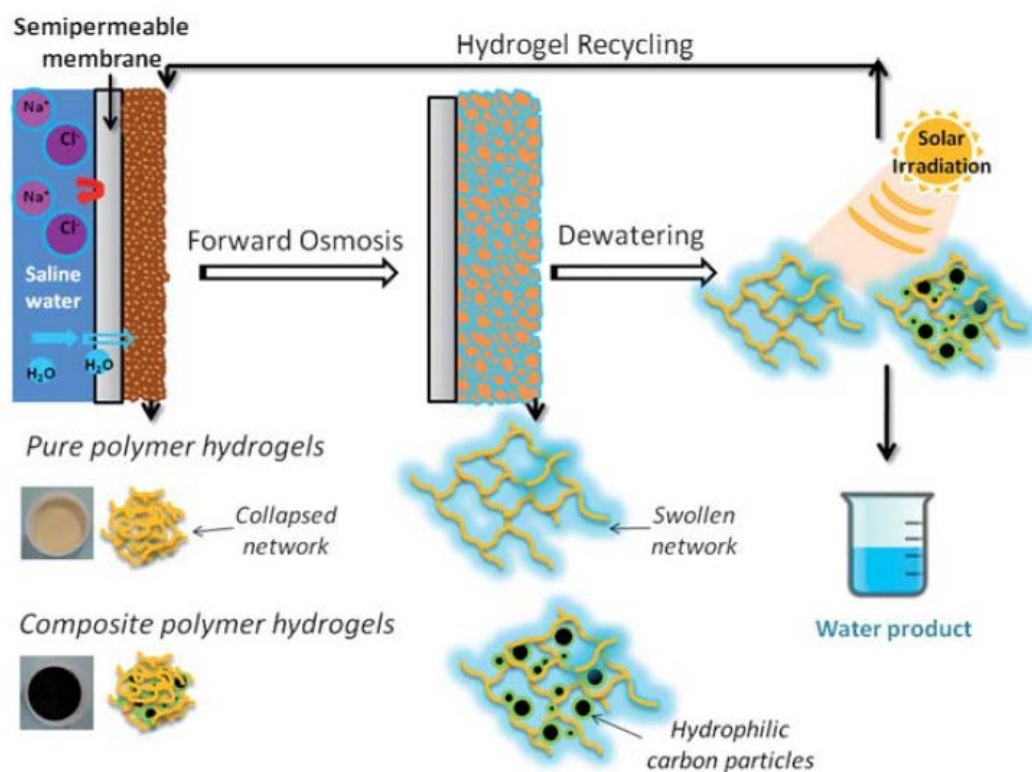
acrylate, PSA) and (poly(sodium acrylate)-co-poly(N-isopropylacrylamide) and two non-ionic hydrogels: poly(acrylamide), PAM) and poly(N-isopropylacrylamide), PNIPAM. These hydrogels were synthesised via bulk polymerization and the water flux was between 0.4 to 1.1 LMH, the higher values for the ionic hydrogels. The recovery of the hydrogels was carried out by increasing temperature until 50 °C. In this study, the hydrogels are put on the surface of the horizontal membrane and they are not attached to the membrane surface.



**Figure 10** Hydrogels as draw solution (Re-printed from reference [35])

In order to enhance the water recovery ability of the hydrogels, light-absorbing carbon particles were added to the structure of the hydrogels and solar irradiation was used for recovery [35] (Figure 11). The results showed that the addition of carbon particles leads to better penetration of heat into deeper layers of hydrogels and water recovery improved. For PNIPAM microgels with carbon particles, water recovery was almost 100% after 40 min exposure to the sunlight with an irradiation

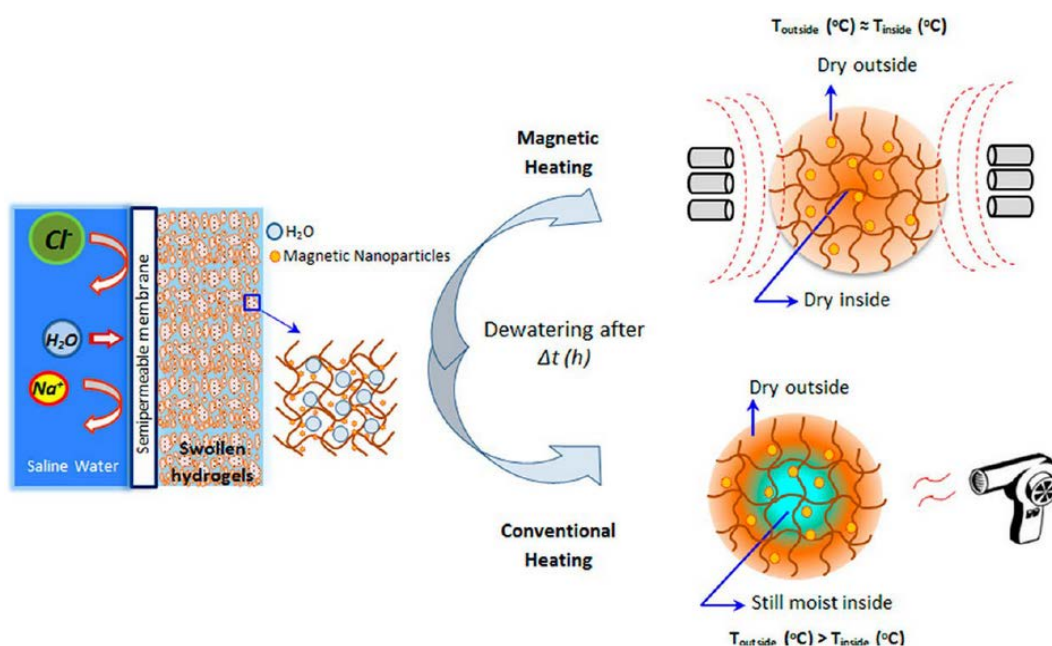
intensity of  $1.0 \text{ kW m}^{-2}$ . Carbon particle addition caused composite hydrogels to have higher swelling ratio and osmotic pressure than pure hydrogels and PNIPAM and PSA hydrogels showed improved water flux after carbon particle addition.



**Figure 11** Carbon composite hydrogels as draw solution in FO (Re-printed from reference [35])

Another method to enhance water recovery of hydrogels was synthesising composite hydrogels with magnetic nanoparticles. Sodium acrylate and NIPAM were copolymerized in the presence of  $\gamma\text{-F}_2\text{O}_3$  in order to use magnetic field-induced heating for dewatering of hydrogels. In thermo-responsive hydrogels some moist exists in the hydrogels. Therefore, recovery of the draw solutions cannot be done completely (Figure 12). Thereby, using magnetic particles will help heating up the deep part of the hydrogels and improve the dewatering of the hydrogels [40]. Magnetic heating at  $65 \text{ }^\circ\text{C}$  for 1 h resulted in 65% water recovery while this value was around 40% for 2 h convective heating at  $85 \text{ }^\circ\text{C}$ . Zhou et al. also used thermo-responsive magnetic nanogels as a draw solute [41]. They synthesised  $\text{Fe}_3\text{O}_4$

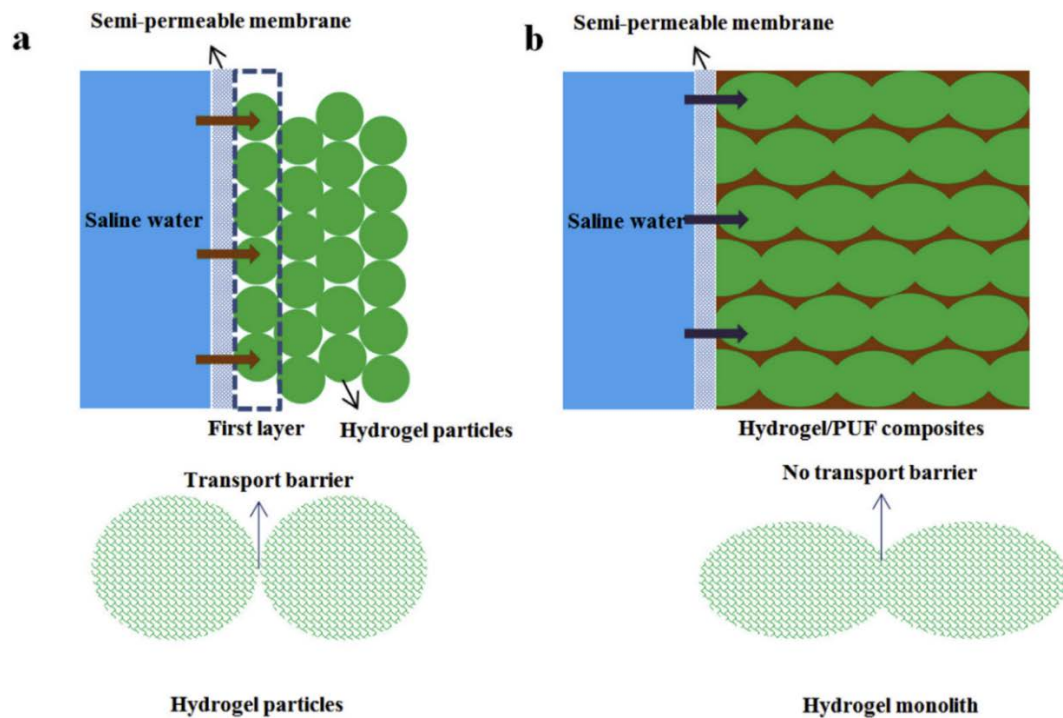
composite poly(N-isopropylacrylamide-co-sodium 2-acrylamido-2-methylpropane sulfonate) ( $\text{Fe}_3\text{O}_4@\text{P}(\text{NIPAM-co-AMPS})$ ) nanogels and used different concentration of these nanogels as draw solution. The results showed higher water flux for  $\text{Fe}_3\text{O}_4@\text{P}(\text{NIPAM-co-AMPS})$  nanogels than  $\text{Fe}_3\text{O}_4@\text{P}(\text{NIPAM-co-Acrylic acid})$  nanogels since AMPS has strong ionic moieties. In addition, larger water flux was performed at higher concentration of  $\text{Fe}_3\text{O}_4@\text{P}(\text{NIPAM-co-AMPS})$  nanogels (around 0.7 LMH for  $0.1 \text{ g.ml}^{-1}$ ). The regeneration step for draw solution was carried out by a combined stimulus of heating and magnetic field. The diluted draw solution was heated up to make the nanogels hydrophobic, then a magnetic field was utilised to separate them from water.



**Figure 12** Schematic diagram of the effect of magnetic and conventional heating on the dewatering of nanocomposite polymer hydrogels being used as draw solution in the FO process. (Re-printed from reference [40])

Bulk hydrogels cannot provide high water flux due to poor affinity between the membrane and the hydrogels. In addition, temperature distribution is not even during polymerization and a dense layer is formed on the hydrogels. Moreover,

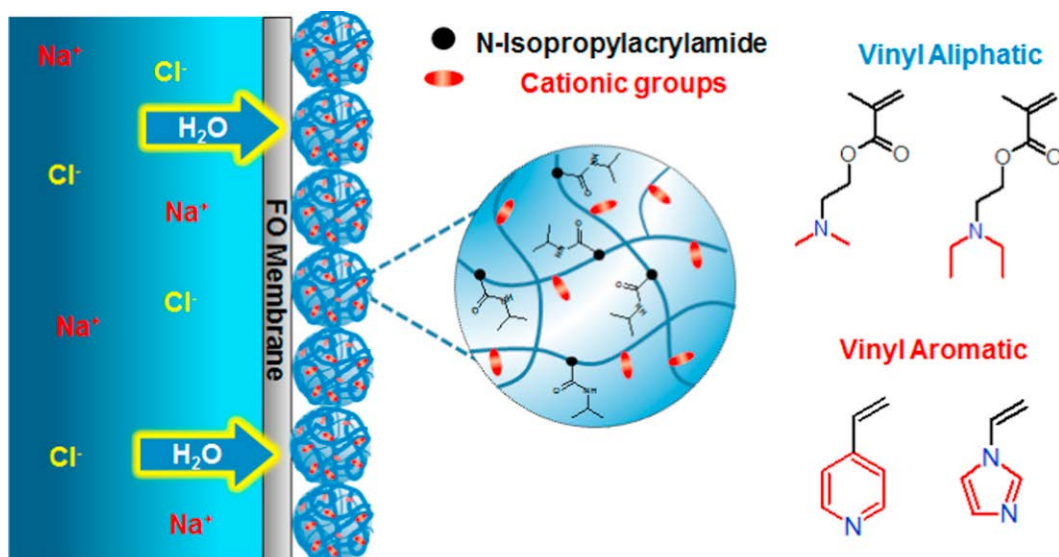
after bulk hydrogels synthesis, the hydrogels were grounded to particles, but the particle size cannot be even. Wei et al used hydrogel-polyurethane interpenetrating network material as an advanced draw agent [42]. As it can be seen in Figure (13), using this interpenetrating network resulted in no transport barrier on the way of water adsorption and it will make it possible to attach the hydrogels on the membrane surface by this method. For the hydrogel/ polyurethane: 8/1 draw solution, water flux of 25 LMH was performed, which showed a significant increment compared to the previous hydrogels.



**Figure 13** Water transport in the: (a) hydrogels powder (b) hydrogels/PUF composite (Re-printed from reference [42])

To deal with the technical issues related to hydrogels, microgels were introduced instead of hydrogels in 2015 by Hartanto et al. They functionalized PNIPAM microgels with acrylic acid (AA) via surfactant-free emulsion polymerization [43]. They found that addition of AA up to 8% leads to an increment in water flux; however, more AA addition causes very highly charged draw solution which is

difficult for dewatering. They also reported that high AA addition leads to the weak performance of hydrogels in dewatering. The microgels in this study performed high water flux of 25 LMH and water recovery of 50% for the microgels with 8wt% with AA. The results of this research were considerably better than the conventional hydrogels, as microgels are homogeneous and have a better affinity with the membrane. One interesting result from this study is that addition of charge moieties enhanced water flux. However, after a threshold, water recovery is negatively affected as charge monomers are not responsive to temperature and they are not likely to release the adsorbed water. This threshold for NIPAM-acrylic acid was 8wt% acrylic acid and for the microgels containing more than 8% acrylic acid, water recovery cannot be easily done via thermal process. It illustrates that higher amount of acrylic acid moieties lead to much less thermal sensitivity of the microgels. The PNIPAM microgels were further functionalised with cationic and anionic monomers to improve water flux [44, 45] (Figure 14). The presence of charged moieties within the microgels resulted in much higher water flux. For the microgels containing NIPAM with 2wt% itaconic acid or 2wt% DEAEMA water flux of 45 LMH was performed. The main reason for such a high water flux is dissociation of ionic moieties in water and adsorbing water by electrostatic force.



**Figure 14** Functionalised microgels as draw solution (Re-printed from reference [45])

### 2.2.2 Deep eutectic solvents

Deep eutectic solvents were recently investigated by Mondal et al. which were used as a new class of thermo-responsive draw solution to enrich low abundance DNA and proteins using an FO process [46]. They found that this draw solution can produce a very high osmotic pressure over 60 bar. This thermo-responsive draw solution can be regenerated by freezing the diluted draw solution. Upon reduction the draw solution temperature to below zero, the adsorbed water will be frozen. Thus, a phase separation (as shown in Figure 15) results in over 80% regeneration of draw solution. However, freezing processes are not as favourable as heating processes in the industry since heating can be done by various resources from waste energy [46].



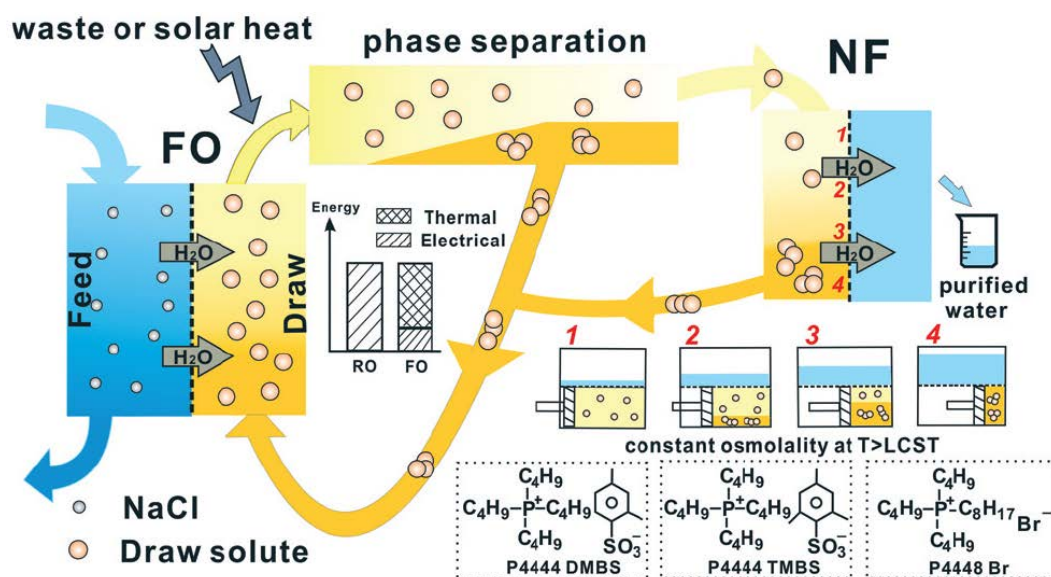
**Figure 15** Phase separation of water and deep eutectic solvents (Re-printed from reference [46])

### 2.2.3 Thermo-responsive Ionic Liquids

Ionic liquids are salts, which have liquid state in the room temperature. Thermo-responsive ionic liquids were investigated as a draw solution in 2015 by Cai et al. [47]. They used thermo-responsive ionic liquids ([P4444][TMBS], [P4444][DMBS] and [P4448][Br]) and found that these ionic liquids can produce sufficient osmotic pressure for feeds with high salinity as high as 0.6 M NaCl. These ionic liquids show LCST in temperature about 50 °C. After phase separation, the ionic liquid-rich phase can be used as draw solution. The water-rich phase after separation should be further purified by a low-pressure filtration process like nanofiltration (Figure 16). The water flux results revealed that a solution 80% [P4444][DMBS] as draw solution is able to produce above 10 LMH and 5 LMH for the feed with 0.15M and 0.6M salinity, respectively. This high water flux is due to the presence of natural counterions in the structure of ionic liquids which produce high osmotic pressure.



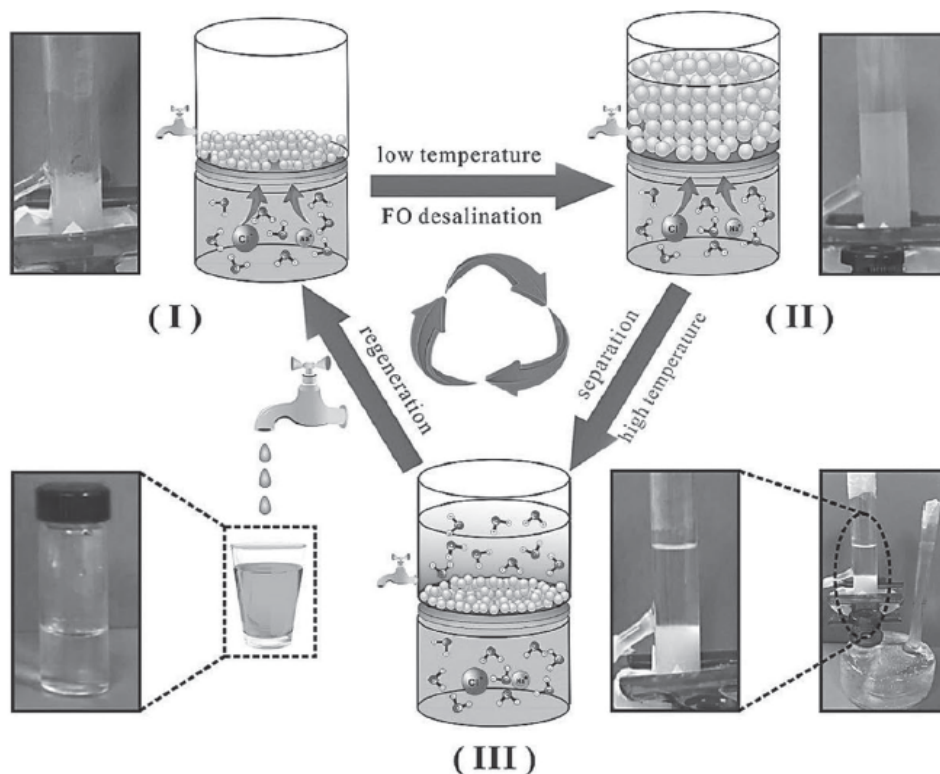
Poly (ionic liquid) thermo-responsive hydrogels were also utilised for forward osmosis desalination [48]. These hydrogels were synthesised by polymerization of thermo-responsive ionic liquid of tetrabutylphosphonium pstyrenesulfonate ([P4444][SS]) and tributylhexylphosphonium p-styrenesulfonate ([P4446][SS]). They compared the results of water flux performance with PNIPAM hydrogels and concluded that poly (ionic liquid) hydrogels [P4444][SS] and [P4446][SS] can perform water flux more than three times higher than that of PNIPAM microgels [48]. The regeneration of these hydrogels was performed at 60 °C and water recovery of poly (ionic liquid) was smaller than that of PNIPAM, due to the existence of ionic moieties, which are not responsive to temperature, and do not release water at upper temperatures.



**Figure 16** Thermo-responsive ionic liquids as draw solution (Re-printed from reference [47])

Fan et al. synthesised thermo-responsive tributyl-4-vinylbenzylphosphonium (TVBP)-based ionic liquid hydrogels for FO desalination [12]. These hydrogels were used for FO at 4 °C and regeneration was carried out at 20 °C. After water

recovery 20 °C and sedimentation of hydrogels (Figure 17), the released water had quality of potable water. However, the hydrogels were not able to perform a high water flux and this value for the best hydrogels was around 1 LMH. In addition, hydrogels performed the FO process at 4 °C, which is not an applicable temperature for the real applications.



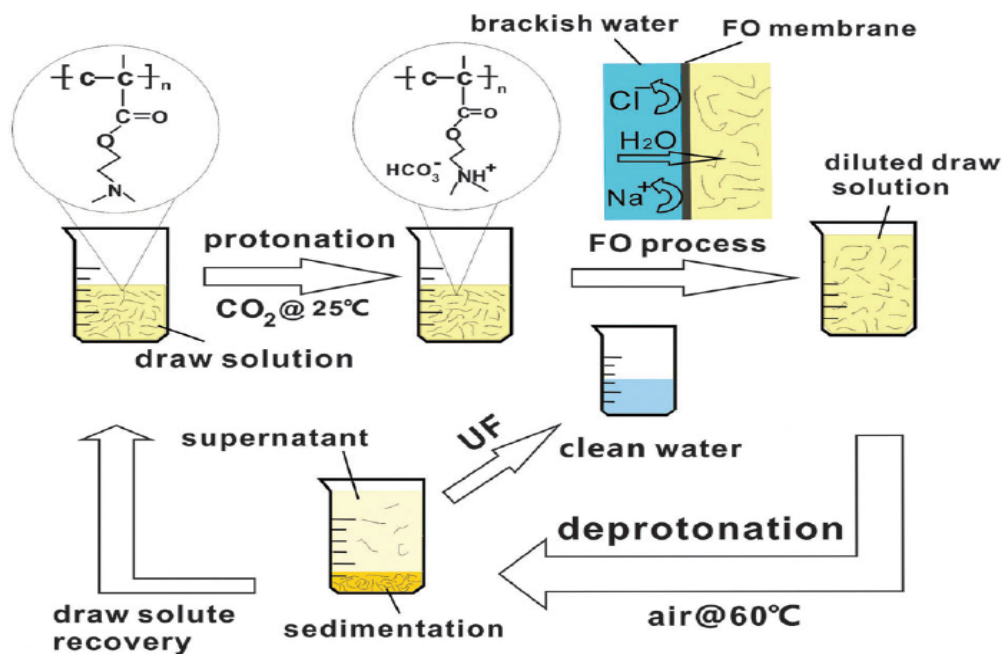
**Figure 17** Cyclic drawing–dewatering of poly (ionic liquid) hydrogels (Reprinted from reference [12])

### 2.3 Gas-responsive draw solutions

Gas-responsive materials show changes in their hydrophilicity once a trigger gas is purged [49, 50]. For example, CO<sub>2</sub>-responsive materials possess tertiary amine moieties in their structure and hydrophilicity of these materials switches upon purging or removing CO<sub>2</sub>. The gas-responsive materials are new draw solutions for the FO process. There were only a few case studies reported in the literature.

### 2.3.1 Gas-responsive linear polymers

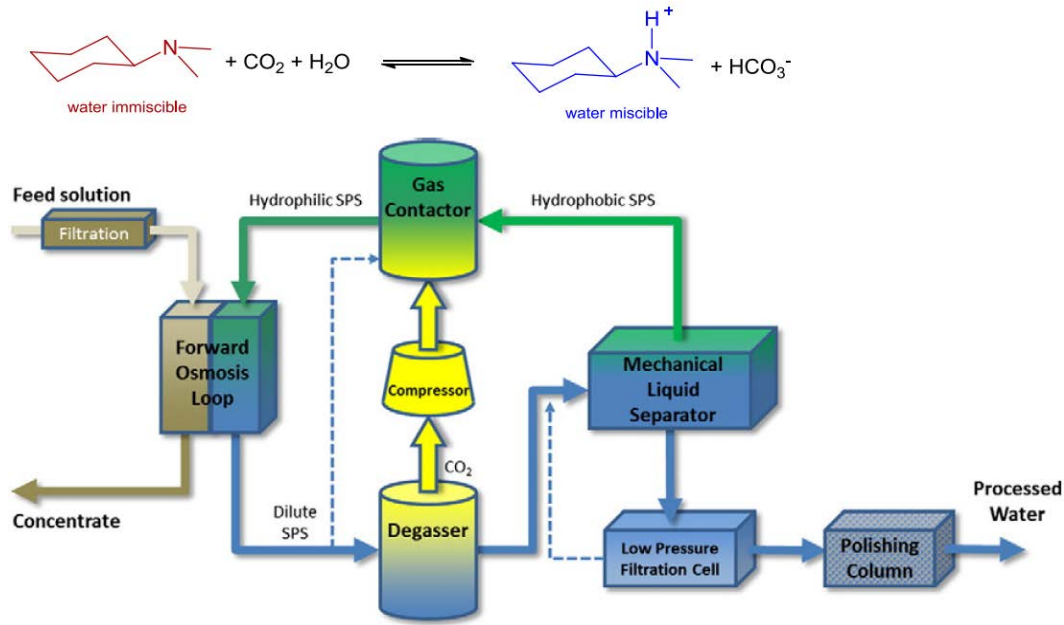
Using gas-responsive polymers as draw solution was first considered by Prof. Hu's group in 2013. CO<sub>2</sub>-responsive polyelectrolyte of poly [2-(dimethylamino) ethyl methacrylate] (PDMAEMA) was used as draw solution [51]. A solution of 60% DMAEMA was able to perform water flux of 6 LMH for the feed with 0.15 M NaCl salinity. As shown in Figure 18, the draw solution was purged by CO<sub>2</sub> before the FO process to protonate amine moieties of DMAEMA and enhance hydrophilicity. Afterwards, regeneration of draw solution was carried out by purging air at 60 °C since DMAEMA is dual responsive (both to temperature and CO<sub>2</sub>). After purging hot air, DMAEMA was precipitated and the separated water had the quality of the potable water after low-pressure ultrafiltration. PDMAEMA is hydrophobic in general, but it becomes water-soluble after CO<sub>2</sub>-protonation, due to reaction between its amine moieties and CO<sub>2</sub>. The draw solution used in this study was liquid-state. It is expected that it can diffuse to the feed side. In addition, heating is still required for the regeneration step.



**Figure 18** Schematic diagram of the dual responsive draw solute for forward osmosis desalination (Re-printed from reference [51])

### 2.3.2 Switchable polarity solvents

Switchable polarity solvents are another class of gas-responsive materials that have been recently studied as a draw solution for FO desalination. Switchable polarity solvents are naturally hydrophobic, but become hydrophilic after CO<sub>2</sub> exposure due to the presence of tertiary amine moieties. Amine moieties react with CO<sub>2</sub> and become hydrophilic and they can draw water through semi-permeable membranes [52, 53]. After removal of CO<sub>2</sub> by purging N<sub>2</sub>, they become hydrophobic again (Figure 19). These draw solutions show high osmotic pressure and perform purification at an operational scale of 480 m<sup>3</sup>/day (feed stream) for feed with salinities from 0.5 to 4.0 molal. The total equivalent energy requirement of the switchable polarity solvents FO process for seawater desalination applications was determined in a range of 2.4 - 4.3 kWh/m<sup>3</sup>, which is comparable with energy consumption RO, the most common used desalination technique (4 to 6 kWh/m<sup>3</sup> for 50% water recovery). Dimethylcyclohexylamine (DMCA) and 1-cyclohexylpiperidine are potential SPS candidates to be used as a draw solution for FO desalination [54]. A full study on several numbers of switchable polarity solvents has been done by Wilson et al. [55], which shows hydrophilicity-switchable behavior of the SPS and if they can be a proper candidate as a draw solution.



**Figure 19** Switchable polarity solvent as draw solution (Re-printed from reference [52])

## 2.4 Other types of draw solutions

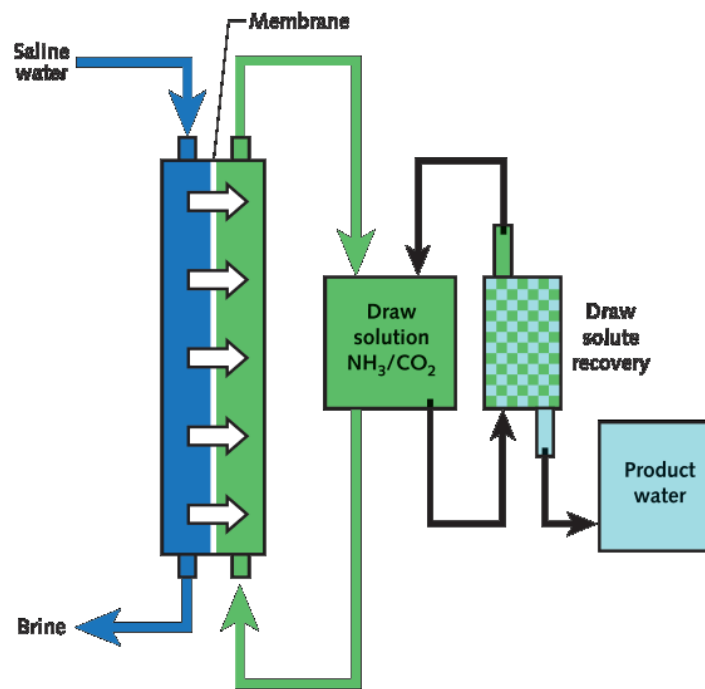
In addition to stimuli-responsive materials, which have been discovered recently, there are other types of draw solutions such as salts and synthetic draw solutions.

### 2.4.1 Salts

Achilli et al. used different inorganic salts as draw solution [56]. They stated that certain factors need to be considered in choosing proper salts, which should be water-soluble and exist as solid-phase, able to produce osmotic pressure above 1 MPa and non-hazardous. In addition, the selected salts should not cost more than 10  $\text{\$.L}^{-1}$ . Considering these parameters, they selected  $\text{CaCl}_2$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{KBr}$ ,  $\text{KCl}$ ,  $\text{KHCO}_3$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{MgCl}_2$ ,  $\text{MgSO}_4$ ,  $\text{NaCl}$ ,  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{HCO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$ . They made solutions of each salt to achieve draw solutions in three different osmotic pressures, 1.4, 2.8, and 4.2 MPa. Moreover, for draw solution recovery, reverse osmosis was considered. They found that internal concentration polarization is a major issue for these draw solutions and is strongly dependant on

diffusion coefficients of the ions. Combining high performance with low replenishment costs, three draw solutions ( $\text{KHCO}_3$ ,  $\text{MgSO}_4$ , and  $\text{NaHCO}_3$ ) were found to be the best for the FO process. However, in terms of water flux,  $\text{KBr}$  was the best salt with flux of  $3.74 (10^{-6} \text{ m/s})$ . Back diffusion of salts to the feed side is another drawback for salts. It was observed that divalent draw solutions ( $\text{MgSO}_4$ ,  $\text{MgCl}_2$ , and  $\text{CaCl}_2$ ) are highly rejected by the membrane and their back diffusion is very low.

Thermolytic mixture of  $\text{CO}_2$  and ammonia (ammonium bicarbonate,  $\text{NH}_4\text{HCO}_3$ ) in water is another well-established draw solution (Figure 20). This draw solution was first used by Neff et al. in 1964 [57]. Both ammonia and  $\text{CO}_2$  have high solubility in water and have low molecular weight, consequently, can be removed from water easily [58]. This draw solution is able to produce high osmotic pressure with proper management of ammonia and carbon dioxide ratios and ammonium salt speciation [59]. This draw agent performed water flux as high as 36 LMH. For water recovery, upon increasing the temperature to near  $60^\circ\text{C}$ , ammonium bicarbonate will be decomposed to ammonia and carbon dioxide. These gases can be further removed from the solution by low-temperature distillation, which uses relatively low energy [60]. However, back diffusion is always a problem for this draw solution that can lead to contamination of the feed and reduction in draw solution efficiency. It was calculated that  $\text{NH}_4\text{HCO}_3$  had a severe ratio of back diffusion to water flux, 0.9 g  $\text{NH}_4\text{HCO}_3$  per 1 litre of water [61]. In addition, It was also found that dilutive internal concentration polarization becomes more severe with increment in concentration of draw solution [62].

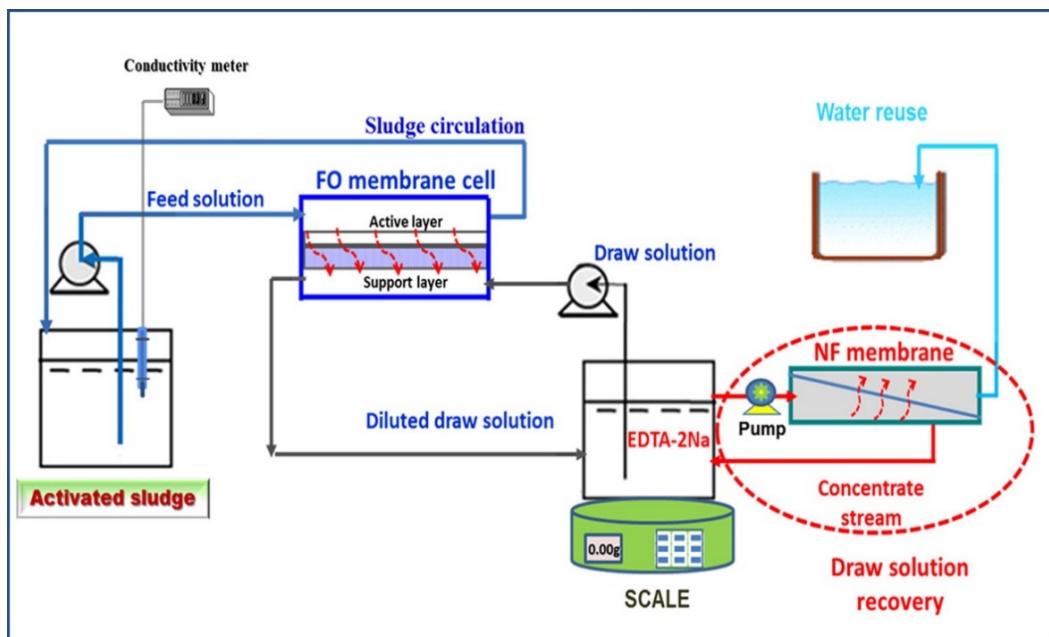


**Figure 20** Ammonium bicarbonate as draw solution for FO process, (Re-printed from [www.waterworld.com](http://www.waterworld.com))

In 2002, McGinnis used a novel FO process for seawater desalination by using potassium nitrate ( $\text{KNO}_3$ ) and  $\text{SO}_2$  [59]. Seawater is heated and fed to the FO unit and a heated saturated solution of  $\text{KNO}_3$  is used as draw solution. Subsequently, the diluted draw agent is cooled down by the coming seawater. After cooling, a significant amount of  $\text{KNO}_3$  will participate and osmotic pressure of the solution reduces. The diluted  $\text{KNO}_3$  solution will be fed to another FO unit, where dissolved  $\text{SO}_2$  acts as the draw solution. The saturated  $\text{SO}_2$  solution has higher osmotic pressure than the diluted  $\text{KNO}_3$  solution. Therefore, water will be drawn from diluted  $\text{KNO}_3$  side and  $\text{KNO}_3$  solution becomes recovered. After that,  $\text{SO}_2$  will be removed from the water by standard means such as heating, leaving the potable water.  $\text{SO}_2$  solution cannot be used as a draw solution for seawater desalination instead of  $\text{KNO}_3$ , as it does not produce sufficient osmotic pressure.

Ethylenediaminetetraacetic acid (EDTA) sodium salt was investigated as a draw agent for dewatering of high nutrient sludge by Hau et al. as EDTA is able to

produce high osmotic pressure [63, 64]. They observed that using 0.7 M EDTA sodium salt as draw solution achieved a high water flux of 8.45 LMH within the first hour and then water flux decreased sharply with the extension of experiment time due to both increases in deposition of sludge cake layer and diluted draw solution. Regeneration of EDTA sodium salt was done by nanofiltration as shown in Figure 21. They also considered using membrane distillation as the regeneration step of EDTA [65]. The results showed that using membrane distillation at 60 °C and condensation of permeated vapour at 20 °C, results in 100% rejection of ions in the diluted draw solution and high water quality for effective reuse.



**Figure 21** FO-Nanofiltration process for sludge dewatering using EDTA sodium salt as draw solution (Re-printed from reference [63])

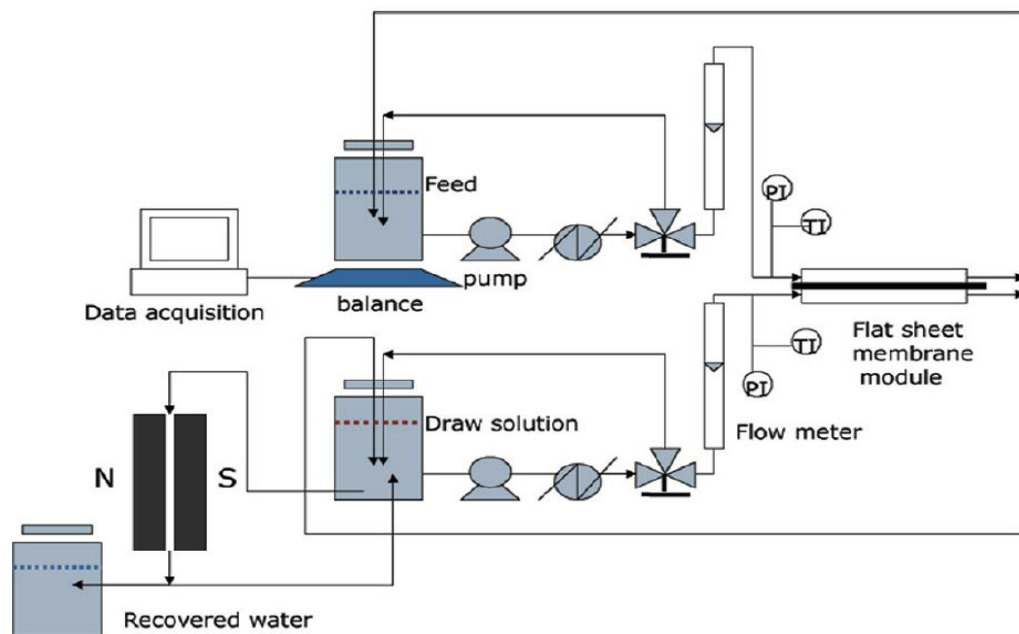
#### 2.4.2 Synthetic materials

Synthesis of advanced materials as a draw solution to deal with the issues related to conventional draw solutions, has been under attention by different research teams. Some of the synthesized materials have shown interesting results [66].



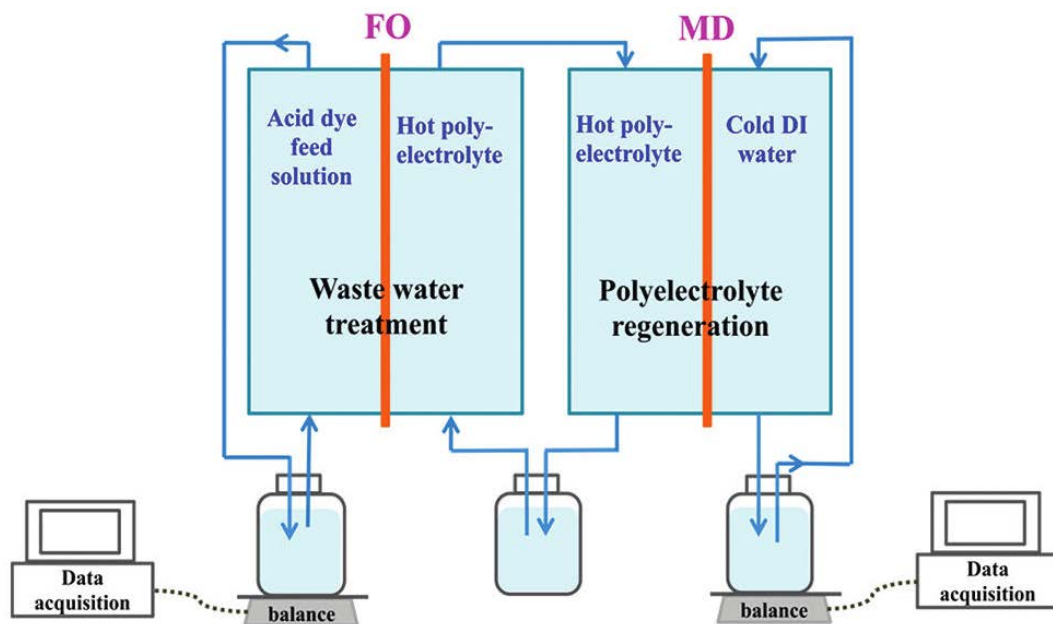
Several review papers about draw solution have been published in the recent years [67, 68] and here some of the efficient synthetic draw solutions are reviewed.

Chung et al. used hydrophilic magnetic nanoparticles (MNPs) capped by polyacrylic acid or poly (ethylene glycol) diacid (PAA-MNPs and PEG-(COOH)<sub>2</sub>-MNPs, respectively), which performed moderate water flux around 18 LMH [69, 70]. They used an external magnetic field to recycle the MNPs (Figure 22). They also showed that osmotic pressure generation is directly attributed to surface chemistry of MNPs and can be improved by increasing surface hydrophilicity and/or reducing their particle size. No reverse flux of the MNPs was detected due to their large particle size compared to inorganic species such as NaCl and MgCl<sub>2</sub>. Prevention of back diffusion is very important for some applications like protein enrichment where no reverse diffusion of draw solution to the feed is allowed. In addition to magnetic field, ultrafiltration can also be used to recycle the draw solution, as long as MNPs are large enough to be separated via ultrafiltration easily [69].



**Figure 22** Schematic diagram of an FO setup combined with a magnetic separator (Re-printed from reference [69])

To reduce material cost and reverse flux, polyelectrolytes of poly acrylic acid sodium (PAA-Na) salts were investigated as draw solutes by Ge et al. [71, 72]. They reported that PAA-Na showed very good results in terms of water flux and unfavourable back diffusion, and draw solution regeneration can be easily done by ultrafiltration. Multi-ionic PAA-Na performed better as draw solution. After recycle, they can be used again without any issue like agglomeration, which was seen for MNPs. However, one problem for this draw solution was the increment in viscosity with increasing their concentration, which make it difficult to pump. That is why integration of FO with membrane distillation, which works at relatively moderate temperatures, helps to reduce the viscosity of the draw solution for recycling (Figure 23) [71].

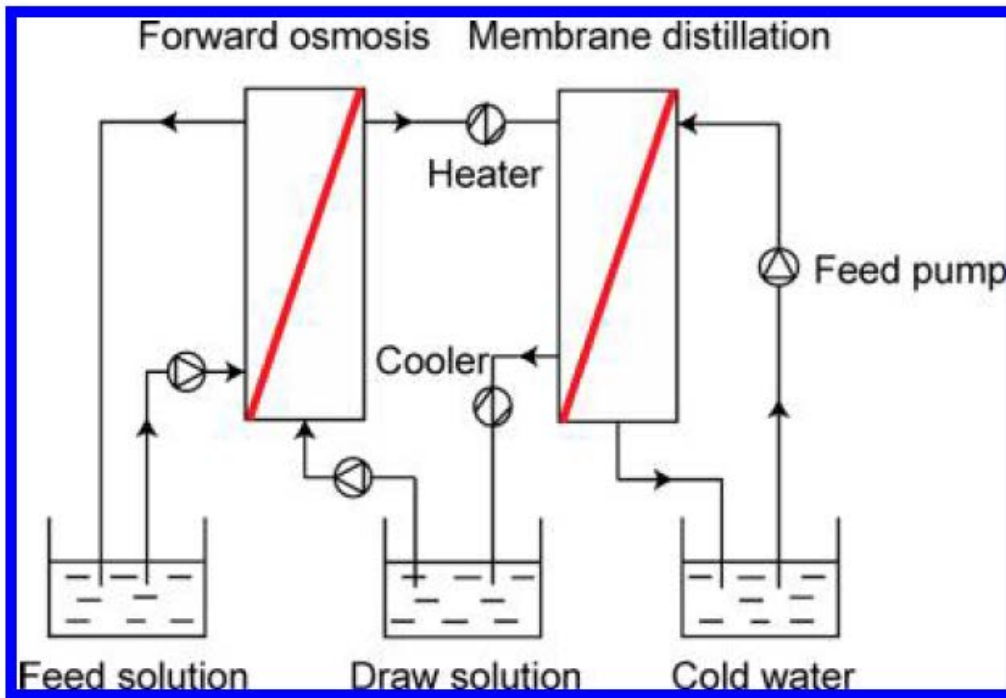


**Figure 23** Schematic diagram of the lab-scale FO–MD hybrid system. (Reprinted from reference [71])

Tian et al. used poly (sodium 4-styrenesulfonate) (PSS) as draw solute and their results showed that  $0.24 \text{ g}\cdot\text{mL}^{-1}$  PSS ( $70,000 \text{ g}\cdot\text{mol}^{-1}$ ) exhibits the best FO performance and the repeatability of FO performance can be improved with

increasing the PSS molecular weight [73]. They utilised a low pressure-driven ultrafiltration under two bar as the regeneration step. Zhao et al. explored the feasibility of using polyacrylamide (PAM, MW=3,000,000 g.mol<sup>-1</sup>) as a new draw solution [74]. 20 g.L<sup>-1</sup> PAM solution performed the highest water flux of 8 LMH and did not have any significant leakage to the feed side. It was also observed that PAM had superiority in terms of stability in water flux compared to the conventional ionic salts KCl.

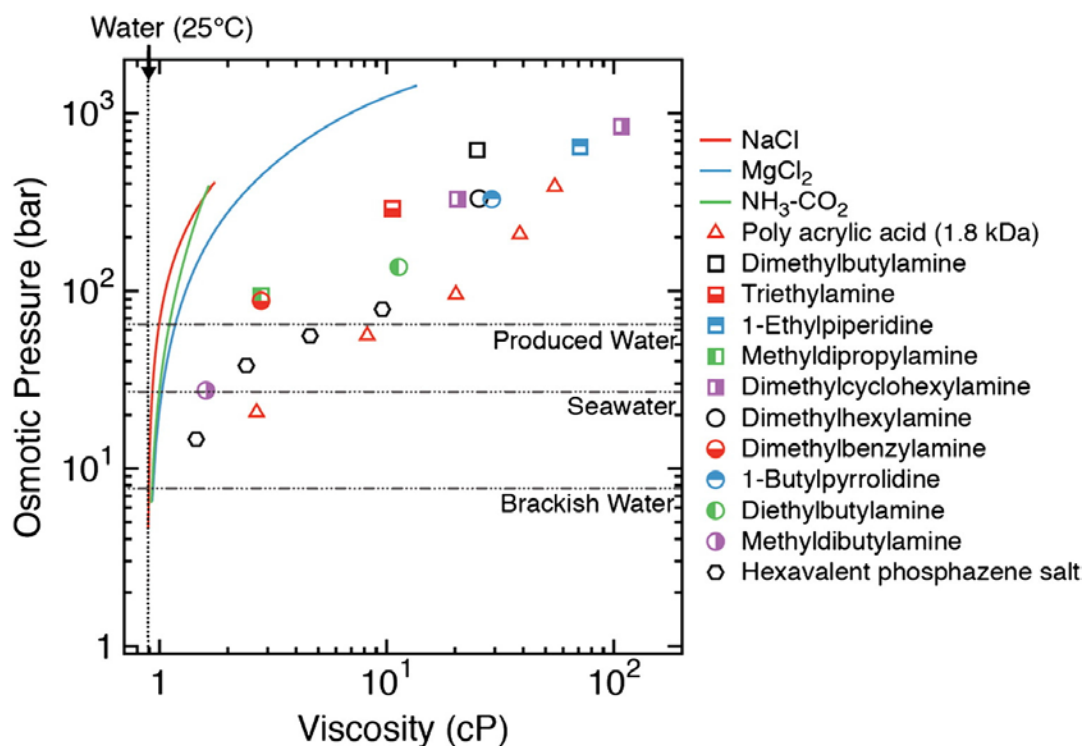
A dendrimer-based forward osmosis draw solute for seawater desalination was proposed by Zhao et al [75]. Poly(amidoamine) terminated with sodium carboxylate groups (PAMAM-COONa) was used for FO. It was seen that this draw solution has the following advantages: 1) The aqueous solution of (PAMAM-COONa) can produce high osmotic pressure because of the large number of -COONa groups. 2) Internal concentration polarization is reduced, as the viscosity of PAMAM-COONa solution is low. 3) PAMAM-COONa molecular size is relatively large, thereby back diffusion to the feed side is negligible. The water flux performance of this draw solution (33% aqueous solution) was 9 LMH for seawater as the feed. In addition, membrane distillation at 50 °C was applied for the regeneration of draw solution (Figure 24). Membrane distillation at this temperature had a water flux of 3.2 LMH.



**Figure 24** FO-membrane distillation system for PAMAM-COONa recovery (Reprinted from reference [75])

## 2.5 Research prospects

Many different draw solutions with various functionalities have been fabricated for the forward osmosis process. Draw solution is the most important part of the FO process since it provides the required driving force. Liquid-state draw solutions are susceptible to back diffuse to the saline feed. For large molecules with negligible reverse flux concentration polarization is a major issue. In addition, liquid-state draw solutions require pumping, and consequently, their viscosity is an important factor. As it can be seen in Figure 25, as the viscosity rises or the concentration of draw solution increases, the produced osmotic pressure also increases. Thus higher concentration/osmotic pressure results in more severe concentration polarization [76].



**Figure 25** Relationship between osmotic pressure and viscosity for different draw solutions (Re-printed from reference [76])

The solid-state draw solutions have recently attracted increasing research interests. Thermo-responsive hydrogels/microgels have shown great potentials to be used as draw solution. These draw solutions do not have any back diffusion to the feed side and concentration polarization. However, heating is still necessary for the recovery of hydrogels/microgels. Generally, microgels have better performance than hydrogels, owing to better affinity of the membrane with microgels than hydrogels. Gas-responsive draw agents can be recovered without using heat. To take advantage of both microgels and gas-responsive materials, gas-responsive microgels can be considered as a potential draw solution for FO desalination. These microgels are able to recover by purging a trigger gas instead of heating. In this study for the first time, the possibility of using the following gas-responsive microgels is studied:

1. CO<sub>2</sub>-responsive microgels with different crosslinker type and concentration;

2. O<sub>2</sub>-responsive microgels with considering two O<sub>2</sub>-responsive monomers with various ionic and nonionic monomers.

CO<sub>2</sub>-responsive microgels have monomers with amine moieties in their structure and purging CO<sub>2</sub> will lead to protonation of amines and swelling microgels. The microgels can perform high water flux owing to their charged amine moieties after CO<sub>2</sub> purging.

For O<sub>2</sub>-responsive microgels, fluorine monomers with responsivity to O<sub>2</sub> are selected. O<sub>2</sub>-responsive microgels exhibit weaker performance. However, one advantage of them compared to CO<sub>2</sub>-responsive microgels is that the pH of water does not change. Moreover, the diffusion of O<sub>2</sub> to the feed side does not affect the pH of the feed, while CO<sub>2</sub> diffusion can make it more acidic.

The detailed performances of these microgels are presented in the chapters 3 and 4 in manuscript style.

## References

- [1] A.A. Abufayed, M.K.A. Elghuel, M. Rashed, Desalination: a viable supplemental source of water for the arid states of North Africa, *Desalination*, 152 (2003) 75-81.
- [2] B.A. Bolto, The development of desalination in Australia, *Desalination*, 50 (1984) 103-114.
- [3] T. Humplik, J. Lee, S.C. O'Hern, B.A. Fellman, M.A. Baig, S.F. Hassan, M.A. Atieh, F. Rahman, T. Laoui, R. Karnik, E.N. Wang, Nanostructured materials for water desalination, *Nanotechnology*, 22 (2011) 292001.
- [4] B. Van der Bruggen, P. Luis, Forward osmosis: understanding the hype, *Reviews in Chemical Engineering*, 31 (2015) 1-12.
- [5] M.A. Darwish, H.K. Abdulrahim, A.S. Hassan, A.A. Mabrouk, A.O. Sharif, The forward osmosis and desalination, *Desalination and Water Treatment*, (2014) 1-27.
- [6] T.-S. Chung, S. Zhang, K.Y. Wang, J. Su, M.M. Ling, Forward osmosis processes: Yesterday, today and tomorrow, *Desalination*, 287 (2012) 78-81.
- [7] Q. Ge, M. Ling, T.-S. Chung, Draw solutions for forward osmosis processes: Developments, challenges, and prospects for the future, *Journal of Membrane Science*, 442 (2013) 225-237.
- [8] S. Chou, R. Wang, A.G. Fane, Robust and High performance hollow fiber membranes for energy harvesting from salinity gradients by pressure retarded osmosis, *Journal of Membrane Science*, 448 (2013) 44-54.
- [9] G. Han, S. Zhang, X. Li, T.-S. Chung, Progress in pressure retarded osmosis (PRO) membranes for osmotic power generation, *Progress in Polymer Science*, (2015).
- [10] T.Y. Cath, A.E. Childress, M. Elimelech, Forward osmosis: Principles, applications, and recent developments, *Journal of Membrane Science*, 281 (2006) 70-87.
- [11] J.-J. Qin, W.C.L. Lay, K.A. Kekre, Recent developments and future challenges of forward osmosis for desalination: a review, *Desalination and Water Treatment*, 39 (2012) 123-136.
- [12] X. Fan, H. Liu, Y. Gao, Z. Zou, V.S. Craig, G. Zhang, G. Liu, Forward-Osmosis Desalination with Poly(Ionic Liquid) Hydrogels as Smart Draw Agents, *Adv Mater*, 28 (2016) 4156-4161.

- [13] G.D. Mehta, S. Loeb, Internal polarization in the porous substructure of a semipermeable membrane under pressure-retarded osmosis, *Journal of Membrane Science*, 4 (1978) 261-265.
- [14] G.T. Gray, J.R. McCutcheon, M. Elimelech, Internal concentration polarization in forward osmosis: role of membrane orientation, *Desalination*, 197 (2006) 1-8.
- [15] S. Zhang, F. Fu, T.-S. Chung, Substrate modifications and alcohol treatment on thin film composite membranes for osmotic power, *Chemical Engineering Science*, 87 (2013) 40-50.
- [16] J. Su, Q. Yang, J.F. Teo, T.-S. Chung, Cellulose acetate nanofiltration hollow fiber membranes for forward osmosis processes, *Journal of Membrane Science*, 355 (2010) 36-44.
- [17] S. Lee, C. Boo, M. Elimelech, S. Hong, Comparison of fouling behavior in forward osmosis (FO) and reverse osmosis (RO), *Journal of Membrane Science*, 365 (2010) 34-39.
- [18] E.M.V. Hoek, M. Elimelech, Cake-Enhanced Concentration Polarization: A New Fouling Mechanism for Salt-Rejecting Membranes, *Environmental Science & Technology*, 37 (2003) 5581-5588.
- [19] B. Mi, M. Elimelech, Chemical and physical aspects of organic fouling of forward osmosis membranes, *Journal of Membrane Science*, 320 (2008) 292-302.
- [20] Y. Chun, D. Mulcahy, L. Zou, I.S. Kim, A Short Review of Membrane Fouling in Forward Osmosis Processes, *Membranes (Basel)*, 7 (2017).
- [21] B. Mi, M. Elimelech, Organic fouling of forward osmosis membranes: Fouling reversibility and cleaning without chemical reagents, *Journal of Membrane Science*, 348 (2010) 337-345.
- [22] V. Parida, H.Y. Ng, Forward osmosis organic fouling: Effects of organic loading, calcium and membrane orientation, *Desalination*, 312 (2013) 88-98.
- [23] B. Mi, M. Elimelech, Silica scaling and scaling reversibility in forward osmosis, *Desalination*, 312 (2013) 75-81.
- [24] C. Dreszer, A.D. Wexler, S. Drusova, T. Overdijk, A. Zwijnenburg, H.C. Flemming, J.C. Kruithof, J.S. Vrouwenvelder, In-situ biofilm characterization in membrane systems using Optical Coherence Tomography: formation, structure, detachment and impact of flux change, *Water Res*, 67 (2014) 243-254.
- [25] J.S. Vrouwenvelder, S.A. Manolarakis, J.P. van der Hoek, J.A. van Paassen, W.G. van der Meer, J.M. van Agtmaal, H.D. Prummel, J.C. Kruithof, M.C. van



Loosdrecht, Quantitative biofouling diagnosis in full scale nanofiltration and reverse osmosis installations, *Water Res*, 42 (2008) 4856-4868.

[26] R.M. Goulter, I.R. Gentle, G.A. Dykes, Issues in determining factors influencing bacterial attachment: a review using the attachment of *Escherichia coli* to abiotic surfaces as an example, *Letters in Applied Microbiology*, 49 (2009) 1-7.

[27] T. Nguyen, F.A. Roddick, L. Fan, Biofouling of water treatment membranes: a review of the underlying causes, monitoring techniques and control measures, *Membranes*, 2 (2012) 804-840.

[28] S. Dai, P. Ravi, K.C. Tam, Thermo- and photo-responsive polymeric systems, *Soft Matter*, 5 (2009) 2513-2533.

[29] D. Roy, W.L. Brooks, B.S. Sumerlin, New directions in thermoresponsive polymers, *Chemical Society reviews*, 42 (2013) 7214-7243.

[30] M.I. Gibson, R.K. O'Reilly, To aggregate, or not to aggregate? considerations in the design and application of polymeric thermally-responsive nanoparticles, *Chemical Society reviews*, 42 (2013) 7204-7213.

[31] M. Heskins, J.E. Guillet, Solution Properties of Poly(N-isopropylacrylamide), *Journal of Macromolecular Science: Part A - Chemistry*, 2 (1968) 1441-1455.

[32] R. Ou, Y. Wang, H. Wang, T. Xu, Thermo-sensitive polyelectrolytes as draw solutions in forward osmosis process, *Desalination*, 318 (2013) 48-55.

[33] D. Zhao, P. Wang, Q. Zhao, N. Chen, X. Lu, Thermoresponsive copolymer-based draw solution for seawater desalination in a combined process of forward osmosis and membrane distillation, *Desalination*, 348 (2014) 26-32.

[34] E.M. Ahmed, Hydrogel: Preparation, characterization, and applications: A review, *Journal of Advanced Research*, 6 (2015) 105-121.

[35] D. Li, X. Zhang, J. Yao, Y. Zeng, G.P. Simon, H. Wang, Composite polymer hydrogels as draw agents in forward osmosis and solar dewatering, *Soft Matter*, 7 (2011) 10048-10056.

[36] D. Li, X. Zhang, J. Yao, G.P. Simon, H. Wang, Stimuli-responsive polymer hydrogels as a new class of draw agent for forward osmosis desalination, *Chemical Communications*, 47 (2011) 1710-1712.

[37] A. Razmjou, G.P. Simon, H. Wang, Polymer Hydrogels as Smart Draw Agents in Forward Osmosis Processes, (2015) 129-149.

- [38] A. Razmjou, G.P. Simon, H. Wang, Effect of particle size on the performance of forward osmosis desalination by stimuli-responsive polymer hydrogels as a draw agent, *Chemical Engineering Journal*, 215–216 (2013) 913-920.
- [39] A. Razmjou, Q. Liu, G.P. Simon, H. Wang, Bifunctional Polymer Hydrogel Layers As Forward Osmosis Draw Agents for Continuous Production of Fresh Water Using Solar Energy, *Environmental Science & Technology*, 47 (2013) 13160-13166.
- [40] A. Razmjou, M.R. Barati, G.P. Simon, K. Suzuki, H. Wang, Fast Deswelling of Nanocomposite Polymer Hydrogels via Magnetic Field-Induced Heating for Emerging FO Desalination, *Environmental Science & Technology*, 47 (2013) 6297-6305.
- [41] A. Zhou, H. Luo, Q. Wang, L. Chen, T.C. Zhang, T. Tao, Magnetic thermoresponsive ionic nanogels as novel draw agents in forward osmosis, *RSC Adv.*, 5 (2015) 15359-15365.
- [42] J. Wei, Z.X. Low, R. Ou, G.P. Simon, H. Wang, Hydrogel-polyurethane interpenetrating network material as an advanced draw agent for forward osmosis process, *Water Res.*, 96 (2016) 292-298.
- [43] Y. Hartanto, S. Yun, B. Jin, S. Dai, Functionalized thermo-responsive microgels for high performance forward osmosis desalination, *Water Research*, 70 (2015) 385-393.
- [44] Y. Hartanto, M. Zargar, H. Wang, B. Jin, S. Dai, Thermoresponsive Acidic Microgels as Functional Draw Agents for Forward Osmosis Desalination, *Environ Sci Technol*, 50 (2016) 4221-4228.
- [45] Y. Hartanto, M. Zargar, X. Cui, Y. Shen, B. Jin, S. Dai, Thermoresponsive cationic copolymer microgels as high performance draw agents in forward osmosis desalination, *Journal of Membrane Science*, 518 (2016) 273-281.
- [46] D. Mondal, A. Mahto, P. Veerababu, J. Bhatt, K. Prasad, S.K. Nataraj, Deep eutectic solvents as a new class of draw agent to enrich low abundance DNA and proteins using forward osmosis, *RSC Adv.*, 5 (2015) 89539-89544.
- [47] Y. Cai, W. Shen, J. Wei, T.H. Chong, R. Wang, W.B. Krantz, A.G. Fane, X. Hu, Energy-efficient desalination by forward osmosis using responsive ionic liquid draw solutes, *Environ. Sci.: Water Res. Technol.*, 1 (2015) 341-347.
- [48] Y. Cai, R. Wang, W.B. Krantz, A.G. Fane, X.M. Hu, Exploration of using thermally responsive polyionic liquid hydrogels as draw agents in forward osmosis, *RSC Advances*, 5 (2015) 97143-97150.

- [49] M.F. Cunningham, P.G. Jessop, CO<sub>2</sub>-switchable materials, *Green Materials*, 2 (2014) 53-53.
- [50] S. Lin, P. Theato, CO<sub>2</sub>-Responsive polymers, *Macromolecular rapid communications*, 34 (2013) 1118-1133.
- [51] Y. Cai, W. Shen, R. Wang, W.B. Krantz, A.G. Fane, X. Hu, CO<sub>2</sub> switchable dual responsive polymers as draw solutes for forward osmosis desalination, *Chem Commun (Camb)*, 49 (2013) 8377-8379.
- [52] D.S. Wendt, C.J. Orme, G.L. Mines, A.D. Wilson, Energy requirements of the switchable polarity solvent forward osmosis (SPS-FO) water purification process, *Desalination*, 374 (2015) 81-91.
- [53] M.L. Stone, C. Rae, F.F. Stewart, A.D. Wilson, Switchable polarity solvents as draw solutes for forward osmosis, *Desalination*, 312 (2013) 124-129.
- [54] A.D. Wilson, C.J. Orme, Concentration dependent speciation and mass transport properties of switchable polarity solvents, *RSC Adv.*, 5 (2015) 7740-7751.
- [55] A.D. Wilson, F.F. Stewart, Structure–function study of tertiary amines as switchable polarity solvents, *RSC Advances*, 4 (2014) 11039.
- [56] A. Achilli, T.Y. Cath, A.E. Childress, Selection of inorganic-based draw solutions for forward osmosis applications, *Journal of Membrane Science*, 364 (2010) 233-241.
- [57] R.A. Neff, Solvent extractor, in, Google Patents, 1964.
- [58] M. Seker, E. Buyuksari, S. Topcu, D.S. Babaoglu, D. Celebi, B. Keskinler, C. Aydiner, Effect of pretreatment and membrane orientation on fluxes for concentration of whey with high foulants by using NH<sub>3</sub>/CO<sub>2</sub> in forward osmosis, *Bioresour Technol*, 243 (2017) 237-246.
- [59] R.L. McGinnis, Osmotic desalination process, in, Google Patents, 2002.
- [60] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, A novel ammonia—carbon dioxide forward (direct) osmosis desalination process, *Desalination*, 174 (2005) 1-11.
- [61] N.T. Hancock, T.Y. Cath, Solute Coupled Diffusion in Osmotically Driven Membrane Processes, *Environmental Science & Technology*, 43 (2009) 6769-6775.
- [62] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, Desalination by ammonia—carbon dioxide forward osmosis: Influence of draw and feed solution concentrations on process performance, *Journal of Membrane Science*, 278 (2006) 114-123.

- [63] N.T. Hau, S.-S. Chen, N.C. Nguyen, K.Z. Huang, H.H. Ngo, W. Guo, Exploration of EDTA sodium salt as novel draw solution in forward osmosis process for dewatering of high nutrient sludge, *Journal of Membrane Science*, 455 (2014) 305-311.
- [64] Y. Zhao, Y. Ren, X. Wang, P. Xiao, E. Tian, X. Wang, J. Li, An initial study of EDTA complex based draw solutes in forward osmosis process, *Desalination*, 378 (2016) 28-36.
- [65] N.C. Nguyen, S.-S. Chen, S.-T. Ho, H.T. Nguyen, S.S. Ray, N.T. Nguyen, H.-T. Hsu, N.C. Le, T.T. Tran, Optimising the recovery of EDTA-2Na draw solution in forward osmosis through direct contact membrane distillation, *Separation and Purification Technology*, (2017).
- [66] D. Li, H. Wang, Smart draw agents for emerging forward osmosis application, *Journal of Materials Chemistry A*, 1 (2013) 14049.
- [67] Y. Cai, X.M. Hu, A critical review on draw solutes development for forward osmosis, *Desalination*, 391 (2016) 16-29.
- [68] L. Chekli, S. Phuntsho, H.K. Shon, S. Vigneswaran, J. Kandasamy, A. Chanan, A review of draw solutes in forward osmosis process and their use in modern applications, *Desalination and Water Treatment*, 43 (2012) 167-184.
- [69] M.M. Ling, K.Y. Wang, T.-S. Chung, Highly Water-Soluble Magnetic Nanoparticles as Novel Draw Solutes in Forward Osmosis for Water Reuse, *Industrial & Engineering Chemistry Research*, 49 (2010) 5869-5876.
- [70] M.M. Ling, T.-S. Chung, X. Lu, Facile synthesis of thermosensitive magnetic nanoparticles as "smart" draw solutes in forward osmosis, *Chemical Communications*, 47 (2011) 10788-10790.
- [71] Q. Ge, P. Wang, C. Wan, T.-S. Chung, Polyelectrolyte-Promoted Forward Osmosis–Membrane Distillation (FO–MD) Hybrid Process for Dye Wastewater Treatment, *Environmental Science & Technology*, 46 (2012) 6236-6243.
- [72] Q. Ge, J. Su, G.L. Amy, T.S. Chung, Exploration of polyelectrolytes as draw solutes in forward osmosis processes, *Water Res*, 46 (2012) 1318-1326.
- [73] E. Tian, C. Hu, Y. Qin, Y. Ren, X. Wang, X. Wang, P. Xiao, X. Yang, A study of poly (sodium 4-styrenesulfonate) as draw solute in forward osmosis, *Desalination*, 360 (2015) 130-137.
- [74] P. Zhao, B. Gao, S. Xu, J. Kong, D. Ma, H.K. Shon, Q. Yue, P. Liu, Polyelectrolyte-promoted forward osmosis process for dye wastewater treatment –

Exploring the feasibility of using polyacrylamide as draw solute, *Chemical Engineering Journal*, 264 (2015) 32-38.

[75] D. Zhao, S. Chen, P. Wang, Q. Zhao, X. Lu, A Dendrimer-Based Forward Osmosis Draw Solute for Seawater Desalination, *Industrial & Engineering Chemistry Research*, 53 (2014) 16170-16175.

[76] D.L. Shaffer, J.R. Werber, H. Jaramillo, S. Lin, M. Elimelech, Forward osmosis: Where are we now?, *Desalination*, 356 (2015) 271-284.

## **Chapter 3.**

# **CO<sub>2</sub>-RESPONSIVE MICROGELS FOR ENERGY-EFFECTIVE FORWARD OSMOSIS DESALINATION**

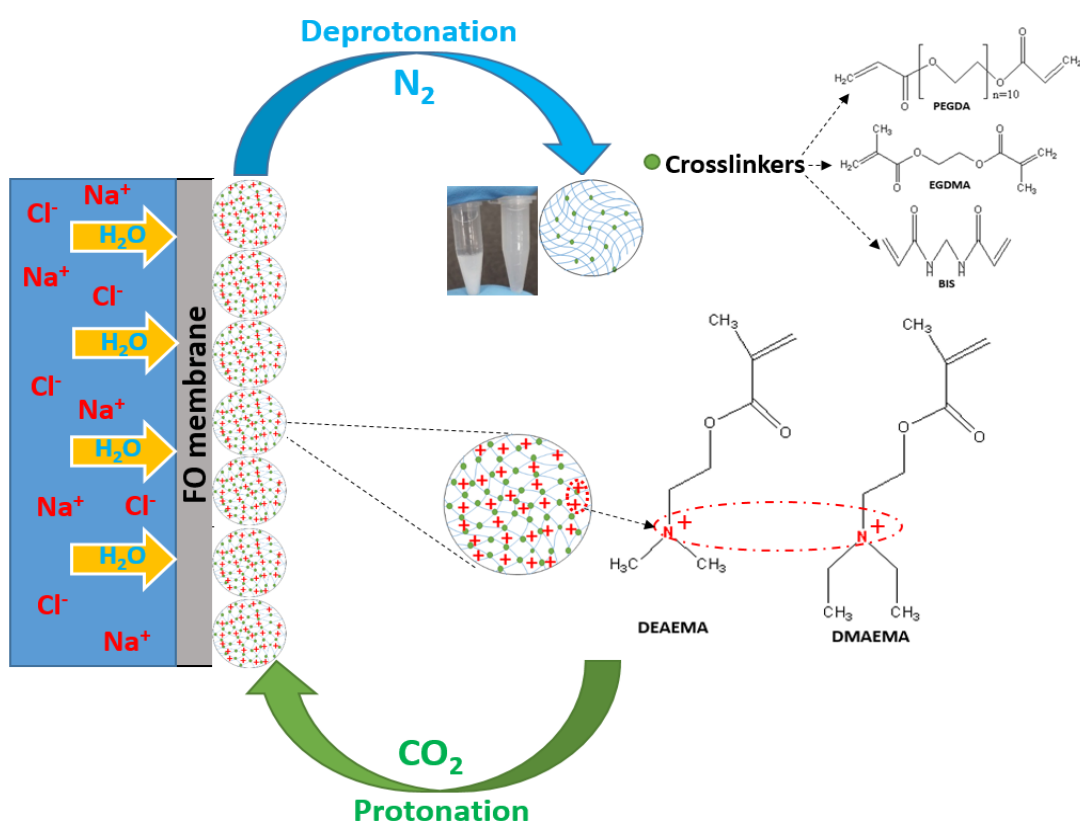
# Gas-Responsive Microgels for Energy-effective Forward Osmosis Desalination

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## Graphical Abstract



## Statement of Authorship

Title of Paper	Gas-Responsive Microgels for Energy-effective Forward Osmosis Desalination
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## Principal Author

Name of Principal Author (Candidate)	Hesamoddin Rabiee
Contribution to the Paper	Design the major experiments, material synthesis, data analysis and manuscript writing.
Overall percentage (%)	85%
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.
Signature	Date 27. Aug 2017

## Co-Author Contributions

By signing the Statement of Authorship, each author certifies that:

- the candidate's stated contribution to the publication is accurate (as detailed above);
- permission is granted for the candidate to include the publication in the thesis; and
- the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

Name of Co-Author	Bo Jin
Contribution to the Paper	Supervision and manuscript correction.
Signature	Date 28/08/2017

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Signature	Date 26/08/2017

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Contribution to the Paper	Supervision and manuscript correction.
Signature	Date 28/08/2017



## Abstract

Polymers as new draw materials for forward osmosis (FO) desalination have attracted much attention recently, where water adsorption and dewatering abilities of a draw material are crucial to its overall performance in desalination. Here, we for the first time develop smart gas-responsive microgels as new draw materials for energy-effective FO desalination in which the water adsorption and dewatering in FO desalination are driven by CO<sub>2</sub> and N<sub>2</sub> gases. A series of cationic microgels of 2-(diethylamino) ethyl methacrylate (DEAEMA) were prepared, and the CO<sub>2</sub> responsivity of these microgels on water flux and water recovery was systematically examined. CO<sub>2</sub> is able to protonate DEAEMA microgels to enhance water adsorption. The microgels with a polyethylene glycol diacrylate crosslinker perform comparably higher water flux than previously reported polymer draw materials. On the other hand, dewatering can be achieved by purging N<sub>2</sub> at room temperature to remove the dissolved CO<sub>2</sub>. At the isoelectric points, the adsorbed water can be released at room temperature due to the hydrophobic characteristics of deprotonated DEAEMA microgels. Comparing with the amphiphilic 2-(dimethylamino) ethyl methacrylate microgels (DMAEMA), DEAEMA microgels reveal better water flux and recovery due to their different dissociation constants. Our results suggest these gas-responsive microgels can be used as high performance and low-cost draw materials for future energy-effective FO desalination.

**Key Words:** Water, Desalination, Forward osmosis (FO), Smart microgels, CO<sub>2</sub>-responsive, Water Flux

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### 3.1 Introduction

During the last decades, membrane processes have received increasing attention for their broad separation/purification applications like water treatment, desalination [1-3], filtration [4, 5], gas separation [6, 7] and many others. Among these applications, desalination seems to be essential, as drinking water scarcity is becoming a severe and challenging issue for many countries around the world. Nowadays, only 2.5 % of freshwater are available on the earth, while almost 97 % of water resources are in the oceans with high salinity. Desalination is a sustainable process to produce fresh water to meet the need of increasing world population [8]. Currently, membrane processes and in particular, reverse osmosis (RO) process are the most commonly used technology for seawater desalination [2, 9-11]. Nevertheless, high energy consumption and fouling are big issues in the RO process. On the other hand, forward osmosis (FO) is a promising desalination technology due to low energy required [12]. In an FO process, water passes through a semi-permeable membrane due to the natural osmotic pressure provided by a draw solute, and subsequently; the adsorbed water can be separated from the draw solution by various separation processes. The main issue that hinders FO desalination in a large scale is the lack of efficient draw solutes that are able to overcome the thermodynamic constrain [13].

To date, many draw solutes have been taken into consideration, and the most favourable draw solutes must be able to provide high osmotic pressure and be environmental-friendly. In addition to good water adsorption ability, they should be able to release adsorbed water through a low-cost and efficient dewatering approach [14]. Inorganic salts like  $MgCl_2$ ,  $MgSO_4$ ,  $NaCl$ ,  $KCl$ ,  $KHCO_3$  and  $Ca(NO_3)_2$  are capable to provide high osmotic pressure and water flux. However,

further nanofiltration or RO process is needed to recover these salts for cyclic process [15]. Ammonium bicarbonate ( $\text{NH}_4\text{HCO}_3$ ) is another draw solute that shows desirable performance for FO desalination as it releases the adsorbed water after decomposition into ammonia and carbon dioxide using low-grade heat [16]. However, the solubility of ammonium bicarbonate in water is high and the treated water is not suitable to meet standard drinking water regulation.

The physicochemical properties of stimuli-responsive polymers can be tuned by an external stimulus such as temperature, pH, light, electric or magnetic field [17]. Over the last five years, these polymers have been considered as new draw materials for FO desalination as they are able to reversibly swell/deswell to adsorb/release water in the presence of a proper stimulus [18-21]. Thermo-responsive ionic liquid polymers have been utilized for FO desalination in the form of hydrogels [22, 23] or solutions [24-26]. These poly (ionic liquid) can provide high osmotic pressure owing to their innate ionic properties and display outstanding water flux [24]. However, better water flux always comes with the sacrifice of water recovery. Thermo-responsive N-isopropylacrylamide (NIPAM) hydrogels with other comonomers of sodium acrylate or acrylamide have been prepared [21], and the adsorbed water can be released upon heating to a temperature beyond the lowest critical solution temperature (LCST) of PNIPAM. Hartanto synthesized various thermo-responsive NIPAM microgels with different anionic and cationic comonomers [27, 28], and found water flux of using microgel draw materials is promising compared to that of hydrogels. The presence of charged comonomers promotes water flux, but it gives rise to the difficulty in water recovery. Introduction of cationic comonomers leads to a higher increment in water flux [28]. Besides, hydrogel composites have also been studied to enhance water recovery. Incorporating carbon particles [29] or magnetic nanoparticles [20, 30-33] to

thermo-responsive hydrogels facilitates water recovery. On the other hand, pH-responsive draw materials have been explored and their solubility can be tailored associated with protonation and deprotonation. For example, CO<sub>2</sub>-responsive poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA) solutions were used as the draw solutes [34], but CO<sub>2</sub> purging was not sufficient for dewatering and an extra heating to 60 °C was required to assist polarity switching [34]. Switchable-polarity solvents (SPS) reversibly switch their hydrophilicity-hydrophobicity upon pH change [35, 36], and low pressure filtration is enough to remove SPS from water [37]. However, back diffusion and internal concentration polarization (ICP) negatively affect their long-term performance [38, 39].

Having considered various aspects of current draw solutes in FO desalination, we here develop novel CO<sub>2</sub>-responsive microgel draw materials, where the protonation and deprotonation of the synthesized microgels can be triggered by CO<sub>2</sub> and N<sub>2</sub> purging. To the best of our knowledge, this is the first time to use gas-responsive microgels as a draw solution in an FO desalination process, where high water flux and energy-effective water recovery can be achieved simultaneously at room temperature.

## **3.2 Experimental**

### **3.2.1 Materials**

Monomers of 2- N,N'-(diethylamino)ethyl methacrylate (DEAEMA) and 2-N,N'-(dimethylamino) ethyl methacrylate (DMAEMA), and three crosslinkers of N, N'-methylene-bisacrylamide (BIS), poly (ethylene glycol diacrylate) (PEGDA, Mn = 575) and ethylene glycol dimethacrylate (EGDMA) were purchased from the Sigma-Aldrich. The chemical structures of monomers and cross-linkers is shown in Figure S1. Nonionic initiator of N,N'-azobisisobutyronitrile (AIBN) was supplied

by Acros Organics, and cationic initiator of 2,2'-azobis (2-methyl propionamide dihydrochloride) (V-50) was purchased from Novachem. Poly(vinyl pyrrolidone) (MW = 360,000 Da, Sigma) was used as the stabilizer for dispersion polymerization, and absolute ethanol was from Merck. Cellulose triacetate forward osmosis (CTA-FO) membranes were supplied by Hydration Technologies Inc. (HTI, USA). Sodium chloride was from the VWR. DI Water was from a Millipore water purification system.

### **3.2.2 Synthesis of DEAEMA microgels**

DEAEMA-based microgels were synthesised via a surfactant-free emulsion polymerization (SFEP) process [40]. Briefly, a 4 wt. % DEAEMA aqueous solution with different crosslinkers (three crosslinkers and three concentration levels) was prepared in a three-neck flask, which was fitted with gas outlet/inlet, a condenser and a mechanical stirrer. The solution was degassed for 1 h at 40 °C in an oil bath, and then the temperature was increased to 75 °C. After reaching 75 °C, the initiator (V-50), dissolved in 3 ml DI water and degassed for 5 min at room temperature, was injected to the flask. The solution turned to cloudy within 15 mins after initiator injection. After overnight polymerization under continuous stirring and nitrogen protection, the obtained microgels were purified against DI water by membrane dialysis (MWCO: 12–14kDa) for 4 days to ensure all unreacted compounds are removed. The microgels were dried at 70 °C and grounded into fine powders.

### **3.2.3 Synthesis of DMAEMA microgels**

Due to the difficulty of synthesizing DMAEMA microgels using a SFEP, DMAEMA microgels were prepared via dispersion polymerization [41, 42] using PEGDA as the crosslinker and PVP360 as the stabilizer. In detail, DMAEMA

monomer (10 wt. % to mixed solvent), AIBN initiator (1 wt. % relative to DMAEMA), PEGDA crosslinker (1 wt. % relative to DMAEMA) and PVP360 (2 wt. % relative to DMAEMA) were mixed with ethanol/water (9:1, wt:wt). The mixture was mechanically stirred (300 rpm) at room temperature for 1 h under N<sub>2</sub> bubbling. The oil-bath temperature was raised to 75 °C and the reaction continued for overnight. The resulting DMAEMA microgels suspension was purified against DI water dialysis for 4 days to remove ethanol and unreacted monomer.

### 3.2.4 Characterization of microgels

The hydrodynamic diameters ( $d_h$ ) and zeta potentials of the microgels at different pH were measured by a Zetasizer (Malvern, Nano-ZS). The swelling ratios (SR) of the microgels were calculated using the equation:

$$SR = \left( \frac{d_{h,pH}}{d_{h,pHr}} \right)^3 \quad (1)$$

where,  $d_{h,pH}$  is the hydrodynamic diameter of the microgel at a certain pH and  $d_{h,pHr}$  is the hydrodynamic diameter at the isoelectric point (IEP).

### 3.2.5 Evaluation on desalination performance of CO<sub>2</sub>-responsive microgels

#### *Water flux*

For water flux evaluation, a small amount of water (1 ml water per g dry microgels) was introduced to dry microgels for pre-wetting, and the paste-like wetted microgels were spread on the surface of FO membranes (the images of dry microgels, paste-like microgels, and microgels after the FO process is shown in Figure S2). CO<sub>2</sub> with a flow rate of 20 ml/min passed through a gas moisturizer before reaching microgel coated FO membranes. CO<sub>2</sub> was purged for ~ 1 h to ensure that microgels are fully protonated [43]. After that, the water flux of microgels were tested using a conductivity probe (probe cell constant,  $k = 1.0$ ),

which was immersed in the feed solution (2000 ppm NaCl) with changes in conductivity of the feed being continuously observed against time [27]. Conductivity data can be converted to NaCl concentration by a standard calibration curve. The experimental set-up is shown in Figure S3, and the following equations were used to calculate water flux:

$$V_t = \frac{C_i V_i}{C_t} \quad (2)$$

$$J_w = \frac{V_i - V_t}{A t} \quad (3)$$

where,  $V_i$  is the initial volume of feed (mL),  $C_i$  is the initial feed concentration (ppm), and  $V_t$  and  $C_t$  are the volume of feed and the feed concentration at time  $t$ , respectively.  $J_w$  is the water flux based on litre/m<sup>2</sup>/h (LMH),  $A$  is the effective membrane surface area and  $t$  (h) is the time when change in solution conductivity was observed.

#### *Water Recovery*

Water recovery measurement was done using a similar procedure [27] with a slight modification that gas was used as a stimulus here. For gas responsive FO systems, the amount prior added water must be considered in relevant calculation. After water adsorption, the microgels were collected and poured into a centrifuge container. The water-incorporated microgels were deprotonated by purging N<sub>2</sub>, using a needle to remove CO<sub>2</sub>. The flow rate of N<sub>2</sub> was 20 ml/min and pH was monitored using a pH meter to confirm the isoelectric point (IEP). At the IEP, the suspension was centrifuged at 12,000 rpm for 15 min to separate water from microgels. Water recovery was measured by gravimetric analysis using the following equations:

$$C_P = \frac{W_P}{W_P + W_W + W_A} \quad (4)$$

$$W_{WG} = W_H(1 - C_P) \quad (5)$$

$$R (\%) = \frac{W_R}{W_{WG}} \times 100 \quad (6)$$

where,  $W_P$  (g) represents the weight of dry microgel powders,  $W_w$  (g) is the weight of water adsorbed by the microgels being determined from water flux measurement, and  $W_A$  (g) is the weight of water added to dry microgels for pre-wetting.  $C_P$  (g/g) is the concentration of microgels in the centrifuge tube.  $W_H$  (g) is the weight of microgels in the centrifuge tube after FO.  $W_{WG}$  (g) is the total weight of water in microgels ( $W_w + W_A$ ).  $W_R$  (g) and  $R$  (%) are the weight and the percentage of water being recovered from microgels after centrifugation.

### **3.2.6 Microgels recycling evaluation**

After the first water adsorption-dewatering cycle, paste-like microgels were collected. The recovered microgels were weighted to confirm the amount of water retaining in microgels. The retained water in the recovered microgels was always higher than the water being added to pre-wet microgels prior to first desalination operation; hence slight heating was applied to ensure identical starting conditions for all cycling experiments. The recovered paste-like microgels were spread on the surface of FO membrane to repeat water flux and dewatering tests.

## **3.3 Results and Discussion**

### **3.3.1 Synthesis and characterization of CO<sub>2</sub>-responsive microgels**

The advantages of applying microgels as ideal draw materials rather than bulk hydrogels are not only attributed to the increase in surface areas but also due to no dense skin layer formation in interface [27]. In this study, CO<sub>2</sub>-responsive cationic DEAEEMA microgels were synthesized via batch surfactant free emulsion



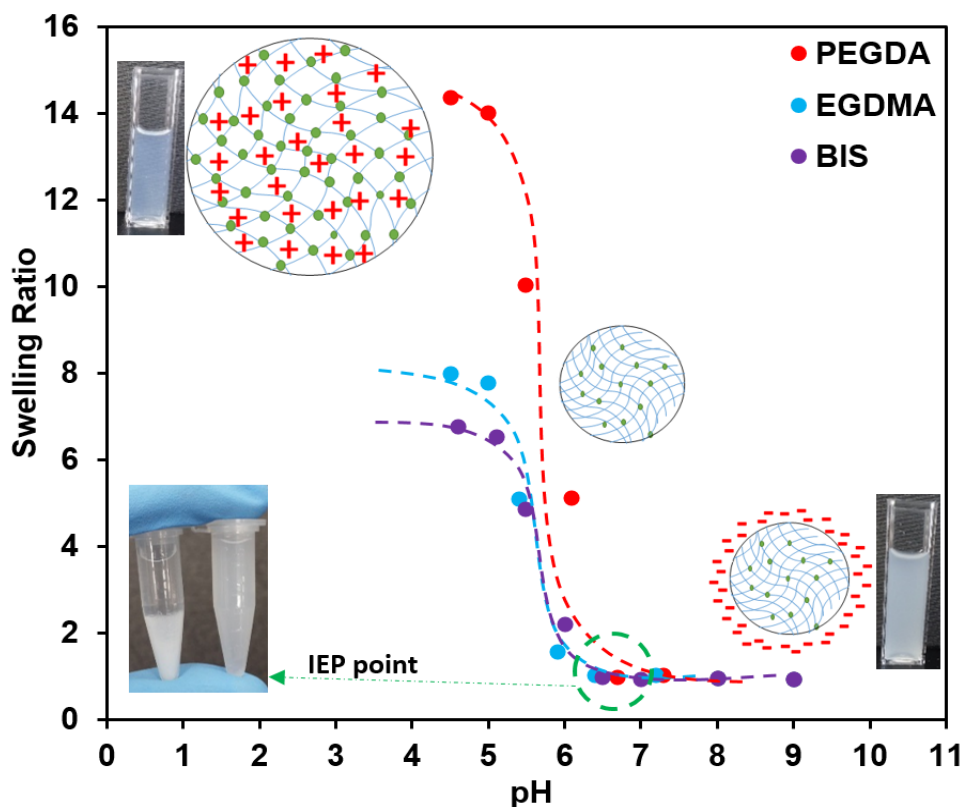
polymerization (SFEP) [44]. Since microgels are used as the draw materials for FO desalination, the process of SFEP is able to effectively eliminate adverse effects of surfactants in conventional emulsion polymerization. Moreover, SFEP is favourable to produce monodisperse microgels. Microgels are crosslinked polymers and the crosslinkers will influence their swellability and water adsorption capability. As such, three crosslinkers together with three concentration levels (0.5 wt. %, 1.0 wt. % and 2.0 wt. % to DEAEMA monomer) were varied in this study to understand their impacts on the physicochemical properties and the desalination performance of resulting microgels. The microgels after polymerization are in their non-protonated states [40] with a pH of 8.5 to 8.8.

DLS measurements were used to determine the hydrodynamic diameters of microgels at different pH, and these hydrodynamic diameters can be used to calculate their swelling ratios. In addition, zeta potentials of various microgels were also measured at different pH to identify their IEPs. For a dilute microgel solution ( $0.5 \text{ g.mL}^{-1}$ ), DLS reveals a narrow single-peak particle size distribution, indicating the presence of monodisperse microgels in solution. The hydrodynamic diameters of various microgels at different pH are shown in Figure S4. Three DEAEMA microgels with an identical amount of different crosslinkers possess a similar hydrodynamic diameter of about 200-250 nm at pH 7. Due to the hydrophobic characteristic of PDMAEMA at this pH, microgels are in their dense form and contribution from crosslinkers can be overlooked. However, they swell once being protonated to low pH associated with the positive charge repulsion of tertiary amine moieties [45]. The swollen microgels with PEGDA crosslinker have an average hydrodynamic diameter of 620 nm, but the one with BIS crosslinker only gives a diameter of 430 nm. A diameter of 500 nm is observed for the swollen DEAEMA microgels with EGDMA crosslinker. From Equation 1, swelling ratios of microgels

at different pH are calculated and shown in Figure 1. It is evident that the highest swelling ratio (~ 14.5) belongs to the microgels with PEGDA crosslinker. Both hydrodynamic diameters and swelling ratios of the DEAEMA microgels have suggested that smart microgel swelling follows the trend of PEGDA > EGDMA > BIS. Obviously, and the length and hydrophilicity of crosslinkers play important roles to affect swelling ratios of microgels [46, 47]. PEGDA and BIS are more hydrophilic and possess higher solubilities (22 mg/ml and 20 mg/ml for PEGDA and BIS) in comparison to EGDMA (1 mg/ml) [48]. On the other hand, in terms of chain length, PEGDA has a larger and more flexible bridging PEG chains (10 repetitive EG units) than BIS and EGDMA, but EGDMA has a larger size than BIS. The reason behind the highest swelling ratio of DEAEMA-PEGDA microgels than that of DEAEMA-EGDMA and DEAEMA-BIS microgels is that PEGDA is more hydrophilic and flexible.

Since the swelling/deswelling and water adsorption/release of these microgels are associated with their charges, zeta potentials were measured to study the change of microgels' charges at different pH (Figure S4). Three microgels follow a similar zeta-potential trend by varying pH in solution. Microgels are positively charged in the low pH range associated with tertiary amine protonation [49-51]. At high pH, zeta potentials of microgels are negative due to partial hydrolysis of the diethylaminoethyl ester groups and physical adsorption of OH<sup>-</sup> [52, 53]. By purging CO<sub>2</sub>, carbonic acid is able to protonate tertiary amines, and electrostatic repulsion pushes microgels expand and swell [40, 50]. While purging N<sub>2</sub>, deprotonation occurs till an isoelectric point (IEP) is achieved, where the zeta potentials of microgels are close to zero. Due to the sacrifice of electrostatic repulsion, microgels convert to non-charged and are prone to coagulate and shrink. The deswelling of microgels can be evident from the drop in hydrodynamic diameters and zeta-

potentials. Since water recovery is associated with the transition of hydrophilicity to hydrophobicity, the presence of charges in microgels will have an adverse effect on water release [54]. As a result, best microgel dewatering is achieved at the pH nearby IEP. By switching the protonation of microgels using CO<sub>2</sub>/N<sub>2</sub>, it is possible to combine the advantages of high water flux and high water recovery.



**Figure 1.** Comparison on the swelling ratios of the microgels with various crosslinkers at 25 °C and different pH.

### 3.3.2 CO<sub>2</sub> and N<sub>2</sub> responsivity of microgels

Cycling experiments on gas responsivity of microgels were investigated by alternatively purging CO<sub>2</sub> and N<sub>2</sub> to the microgels with their hydrodynamic diameters and zeta potentials being determined (Figure S5). CO<sub>2</sub> purging is to protonate microgels and N<sub>2</sub> purging is to deprotonate microgels. As the solubility of N<sub>2</sub> in water is lower than that of CO<sub>2</sub>, long time N<sub>2</sub> purging is required to remove CO<sub>2</sub>, i. e. 2-3 min CO<sub>2</sub> purging is able to drop solution pH to 4.5-4.8 but 20 min

N<sub>2</sub> purging is required to adjust pH back to 7.7-7.9. Despite some amine moieties of DEAEMA are partially hydrolysed as evident from the negative zeta potentials at high pH, both hydrodynamic diameters and zeta potentials of microgels show excellent reversibility in CO<sub>2</sub>/N<sub>2</sub> purging cycles. Thereby, the microgels have sufficient amine moieties to show reversible response to pH change [40, 53].

### **3.3.3 Water flux of using CO<sub>2</sub>-responsive microgels as draw materials**

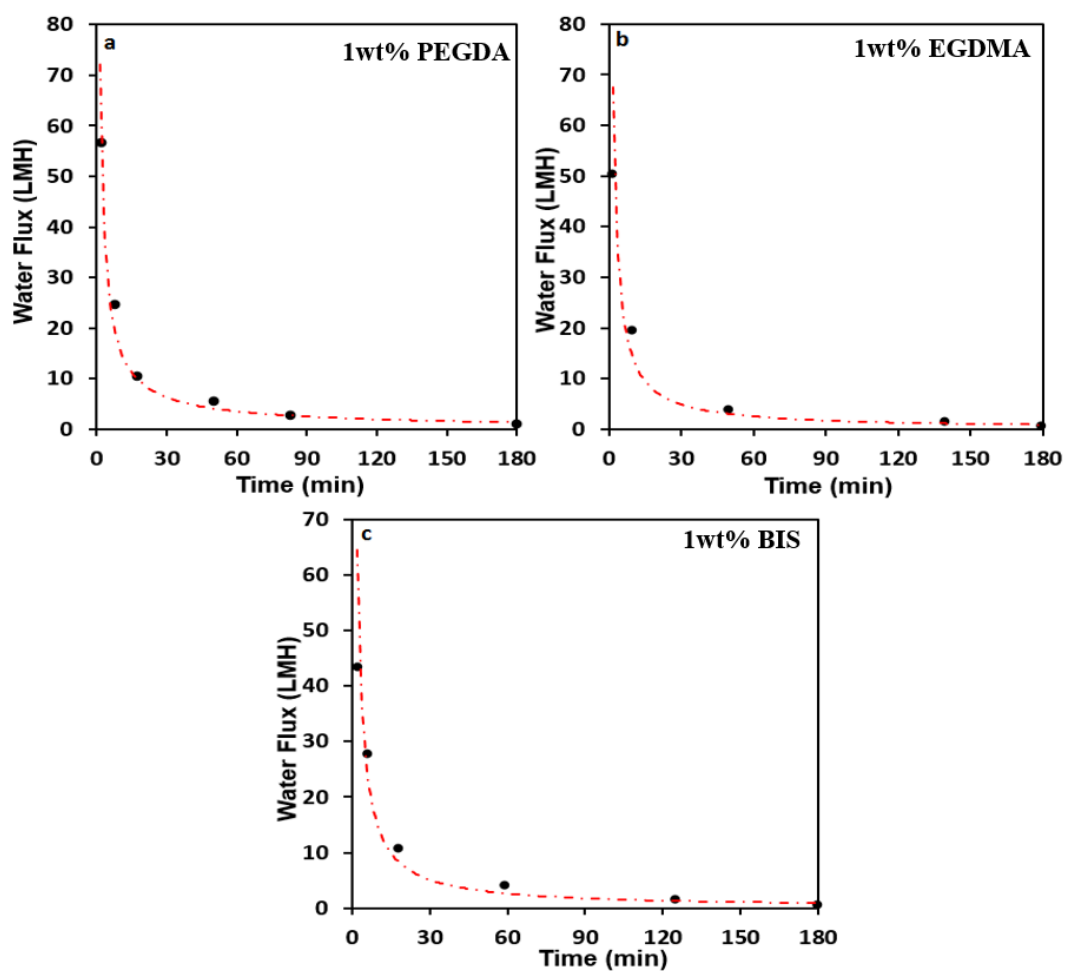
Water flux profiles using microgel draw materials are shown in Figure 2. FO membranes were pre-soaked to 2000 ppm NaCl solution overnight to saturate membranes prior to water flux measurement. CO<sub>2</sub> purging protonates DEAEMA, rendering the microgels be hydrophilic and active to adsorb water through a semi-permeable FO membrane. However, microgels are required to be pre-wetted to adsorb CO<sub>2</sub> [55]. Small amount of water addition promotes CO<sub>2</sub> adsorption [43] and facilitates interaction between microgels and FO membranes. After 1 h protonation of microgels by CO<sub>2</sub>, the membrane was put in contact with saline to monitor the water flux. The water fluxes of different microgels follow a similar pattern with a high flux within the first 10 minutes due to the high osmotic pressure gradient. After that, water flux declines and reaches a plateau (equilibrium state). The time required to reach the equilibrium state of microgels is faster than that of bulk hydrogels, and a higher water flux is observed, which is attributed to the high surface areas of microgels.

Water flux profiles of CO<sub>2</sub>-responsive microgels are comparable to those cationic or anionic thermo-responsive microgels [28, 54]. Figure 2 indicates that DEAEMA-PEGDA microgels give the highest water flux due to their best capability to swell. PDEAEMA has a pK<sub>a</sub> of about 7.4 and the microgels after protonation with CO<sub>2</sub> become hydrophilic to adsorb water [56, 57]. Therefore, fully-charged and more

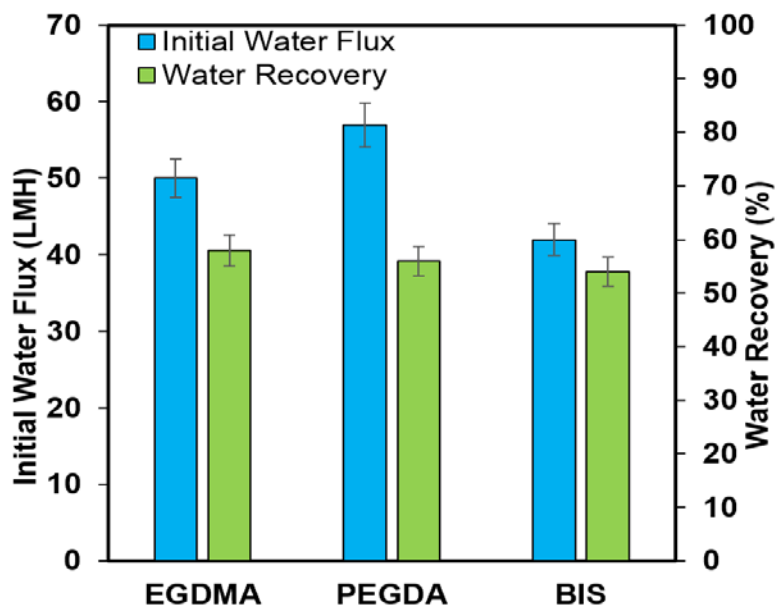
swellable microgels are able to provide high osmotic pressure and water flux. Moreover, according to the wetting angle-dependent Young-Laplace Equation, hydrophilic microgels are able to produce capillary pressure, which further enhances water flux [58]. Considering the microgels have large surface areas than bulk hydrogels [18], the capillary pressure between microgels is more remarkable to produce high osmotic pressure [22]. Compared with thermos-responsive cationic microgels and anionic microgels [28, 54], CO<sub>2</sub>-responsive DEAEMA microgels with 1 wt. % PEGDA perform a better water flux of 56 LMH.

### **3.3.4 Water recovery and recyclability of CO<sub>2</sub>-responsive microgels**

Comparison of the water recovery and initial water flux of various microgels is shown in Figure 3. The highest initial water flux belongs to the DEAEMA microgels with 1 wt. % PEGDA crosslinker. The water recovery for all microgels with different crosslinkers is quite close (54-58). Water recovery is dominated by the solvation and desolvation of microgels, and contribution from the small amount of crosslinkers is minor. Fan observed the variation in crosslinker hydrophobicity of thermo-responsive ionic liquid bulk hydrogels contributes to water flux and swelling ratio, but not water recovery [22].

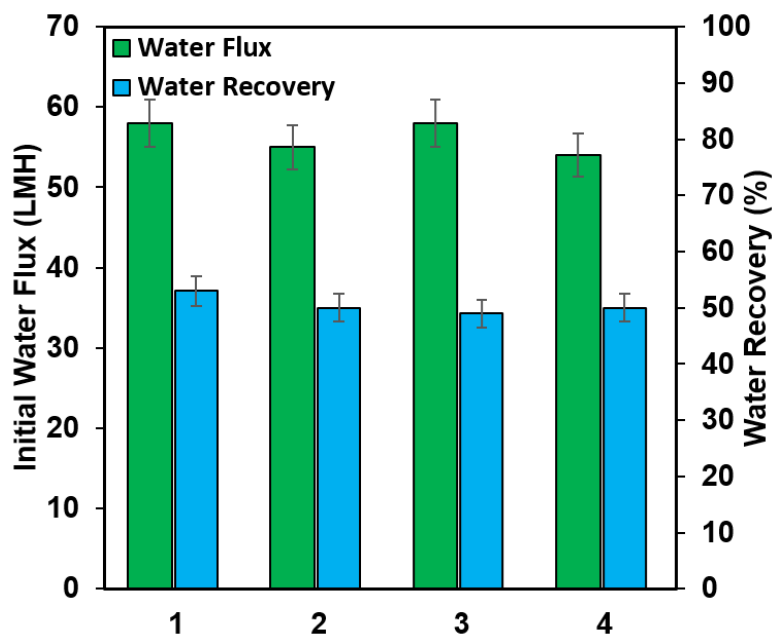


**Figure 2.** Water flux profiles for DEAEMA microgels with 1 wt. % of different crosslinkers at 25°C



**Figure 3.** Initial water flux and water recovery of the DEAEMA microgels with different crosslinkers

Recyclability performance plays an important role in microgel end-use application in FO desalination. Desired draw materials must be able to recover its capability to produce repeatable osmotic pressure for water adsorption after dewatering cycles. As evident from zeta potentials, microgels are able to reversibly protonate and deprotonate after CO<sub>2</sub> and N<sub>2</sub> cycling purging. In Figure 4, water flux and water recovery of the DEAEMA microgels with 1 wt. % PEGDA show acceptable repeatability after 4 drawing-dewatering cycles on both initial water fluxes and recovery ratios. The results are in good accordance with zeta potential measurements.



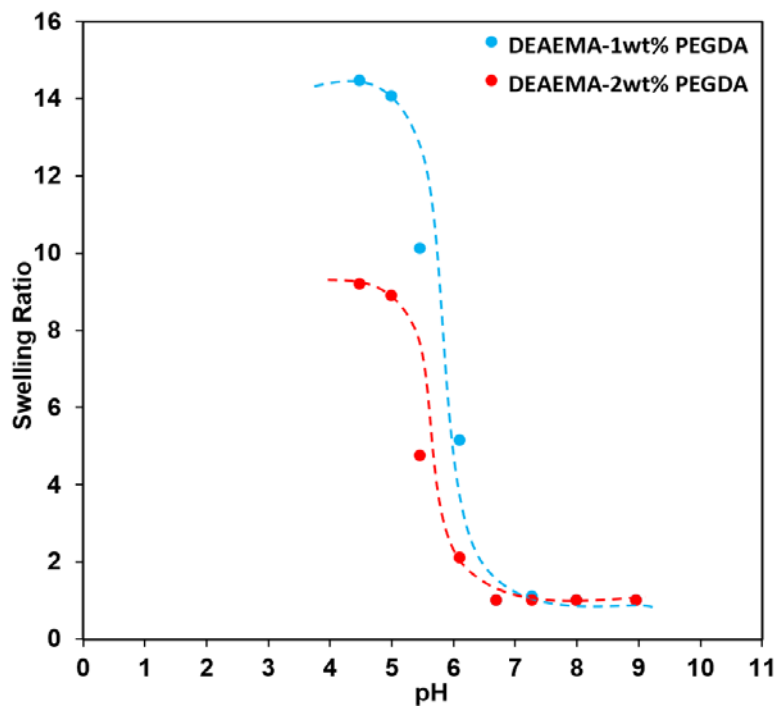
**Figure 4.** Recyclability of CO<sub>2</sub>-responsive DEAEEMA-PEGDA microgels as effective draw materials

### 3.3.5 Effect of crosslinker concentration

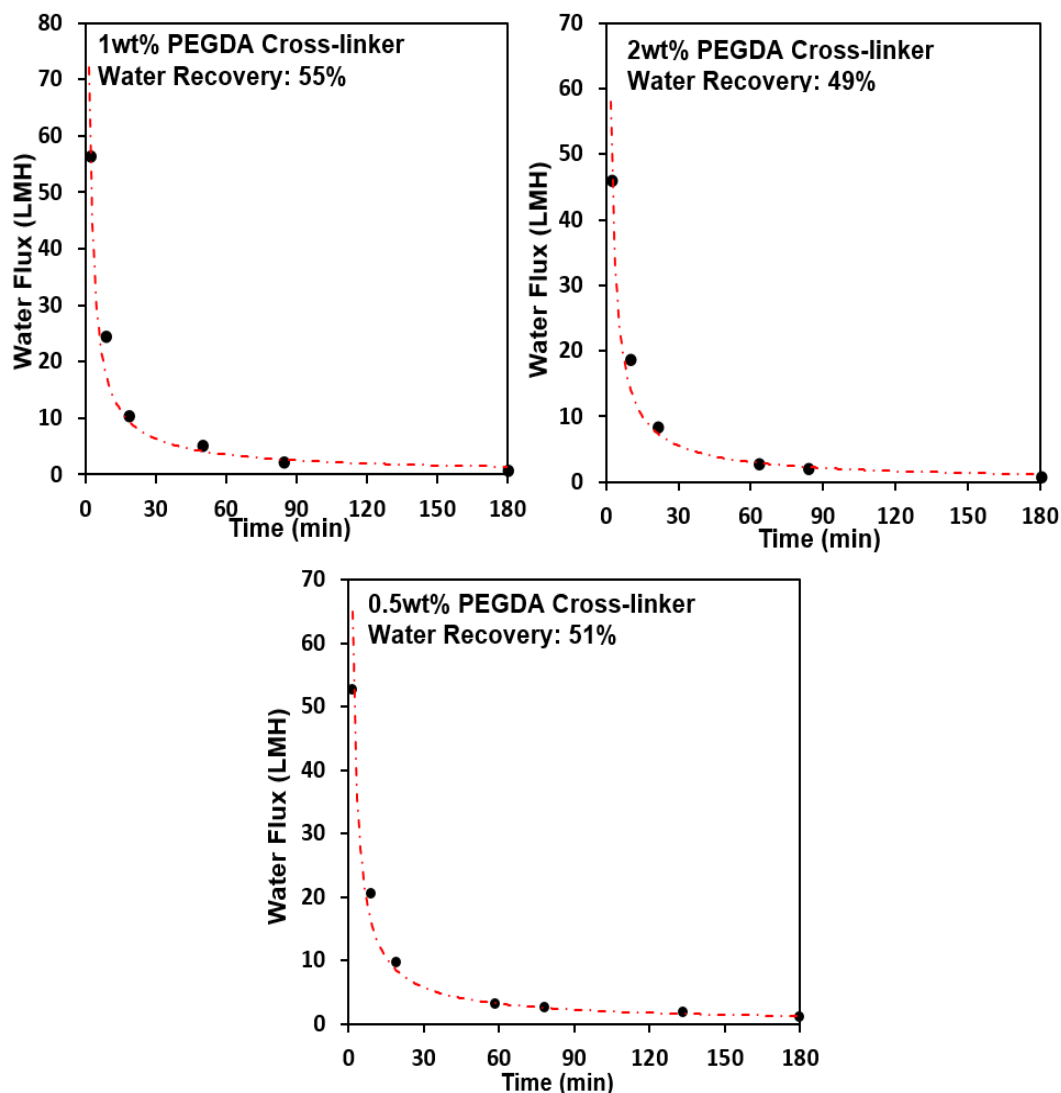
Amount of crosslinkers in microgels is another important variable to be investigated, PEGDA is selected as a model crosslinker and three concentration levels of 0.5, 1.0 % and 2.0 wt. % are applied to synthesize various microgels. From DLS measurements, the DEAEEMA microgels with 0.5 wt. % PEGDA show a multiple-peak size distribution, indicating that 0.5 wt. % crosslinker is not sufficient to produce homogenous microgels and some linear polymers co-exist with microgels in solution. On the other hand, the microgels with 1.0 and 2.0 wt. % PEGDA reveal one narrow size distribution, indicating the formation of homogenous microgels in solution. Comparison on swelling ratios of the microgels with different amount of PEGDA is shown in Figure 5, and the microgels with 1 wt. % PEGDA show a better swelling ratio (14 for 1 wt. % PEGDA and 8.5 for 2 wt. % PEGDA). Typically, microgels with less crosslinker have more chain flexibility and better swell capability [45]. Similarly, a high swelling ratio leads to a higher water flux for the microgels with 1 wt. % PEGDA (Figure 6, 56 LMH vs.



46 LMH for 1wt. % and 2wt. % PEGDA). The water flux for the microgels with 0.5 wt. % PEGDA is slightly lower than that with 1 wt. % crosslinker. Since such a system contains both microgels and linear polymers and linear polymers might back diffuse through membranes, the microgels with 0.5 wt. % crosslinker cannot be considered as a stable draw material for FO desalination operation.



**Figure 5.** Comparison on the swelling ratios of DEAEEMA microgels with 1 wt. % and 2 wt. % PEGDA

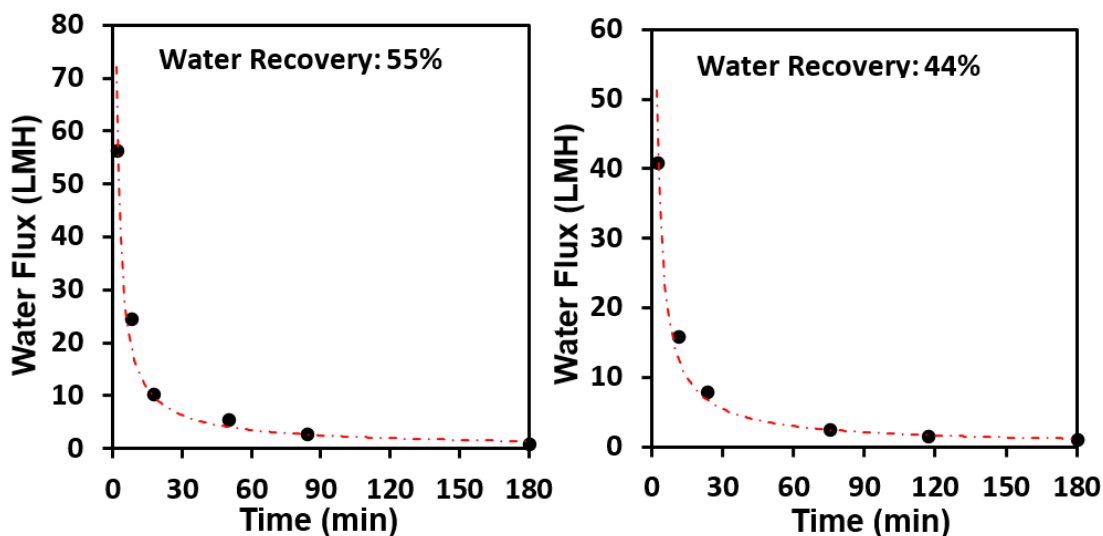


**Figure 6.** Water flux for the microgels with different amount of PEGDA crosslinker

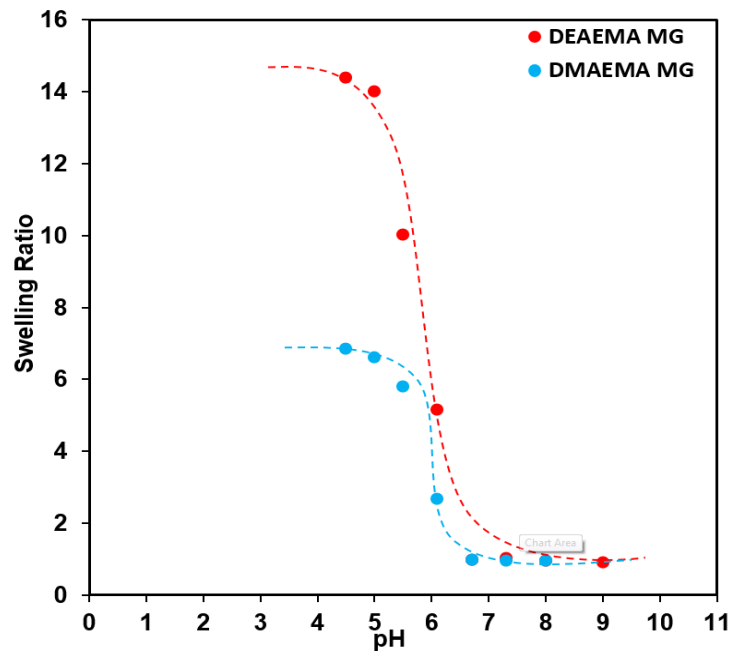
### 3.3.6 Effect of cationic monomers

DMAEMA microgels with 1 wt. % PEGDA crosslinker were also synthesised to elucidate the effect of different cationic monomers on the FO performance of microgels. Similar to DEAEMA, DMAEMA has tertiary amine moieties and can be responsive to CO<sub>2</sub> [41, 42]. However, linear PDMAEMA is soluble in water at room temperature, but PDEAEMA not [51, 59] due to their different pK<sub>a</sub> values and solubility parameters. DMAEMA microgels cannot be synthesised via the SFEP due to the difficulty in homogeneous nucleation, and dispersion polymerization was used to prepare monodisperse DMAEMA microgels. Figure 7

compares the initial water flux for both microgels. DEAEMA microgels show higher water flux (56 LMH) than that for DMAEMA microgels (41 LMH), which is attributed to their different dissociation constants ( $pK_a \sim 7.4$  and 7 for poly(DEAEMA) and poly(DMAEMA)) [57]. This observation agrees well with that of cationic thermo-responsive microgels, where microgels with DEAEMA show better water flux than that with an identical amount of DMAEMA. Comparison of the swelling ratios of both microgels is shown in Figure 8, and a better swelling capability of DEAEMA microgels consequently, results in a faster water flux. On the other hand, based on Hansen solubility parameter calculation, PDEAEMA is more hydrophobic than PDMAEMA, which suggests DEAEMA microgels are easier to release water at room temperature [28, 51]. Experimental results reveal the better water recovery ability for DEAEMA microgels (55 %) than that of DMAEMA microgels (44 %).



**Figure 7.** Water flux profiles for the microgels of (a) DEAEMA and (b) DMAEMA in the presence of 1 wt. % PEGDA crosslinker



**Figure 8.** Comparison on the swelling ratios of the DEAEMA and DMAEMA microgels at 25 °C

### 3.4 Conclusion

Energy-effective gas-responsive microgels are developed as efficient draw materials for forward osmosis desalination. Cationic DEAEMA and DMAEMA microgels are chosen as model systems with their tertiary amine moieties responsive to CO<sub>2</sub>/N<sub>2</sub> purging. Different cationic monomers, crosslinkers and crosslinker concentrations play crucial roles in the swelling/deswelling capabilities of the microgels together with FO desalination performance. For such systems, water adsorption and water release of can be simply tuned by CO<sub>2</sub> and N<sub>2</sub> purging at room temperature without any energy consumption. The DEAEMA microgels with 1 wt. % PEGDA crosslinker display an optimal water flux of 56 LMH. In terms of dewatering, the DEAEMA microgels show better water recovery ability than that of DMAEMA microgels. More importantly, such draw materials also display an outstanding reproducibility in both water flux and recovery. The output of this research will be a benefit for future energy-effective desalination.

## **Acknowledgement**

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### 3.5 Supporting Information

#### Gas-Responsive Microgels for Energy-effective Forward Osmosis Desalination

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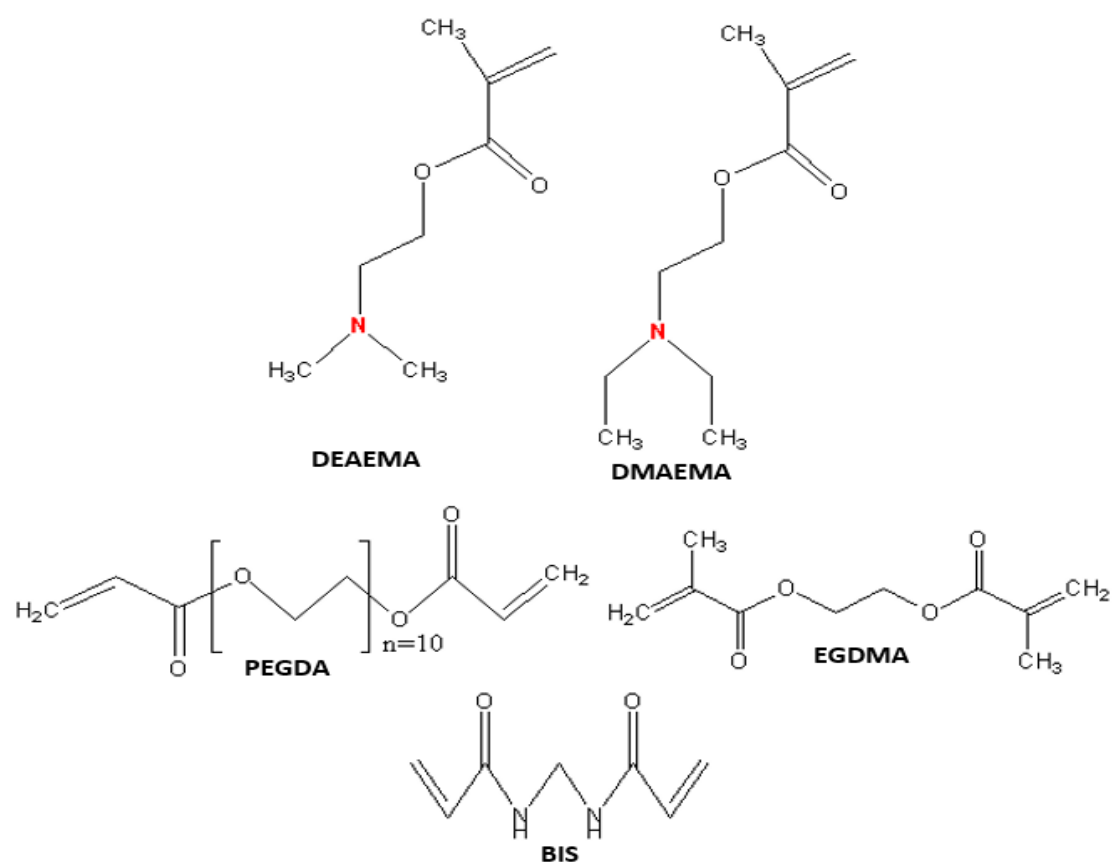
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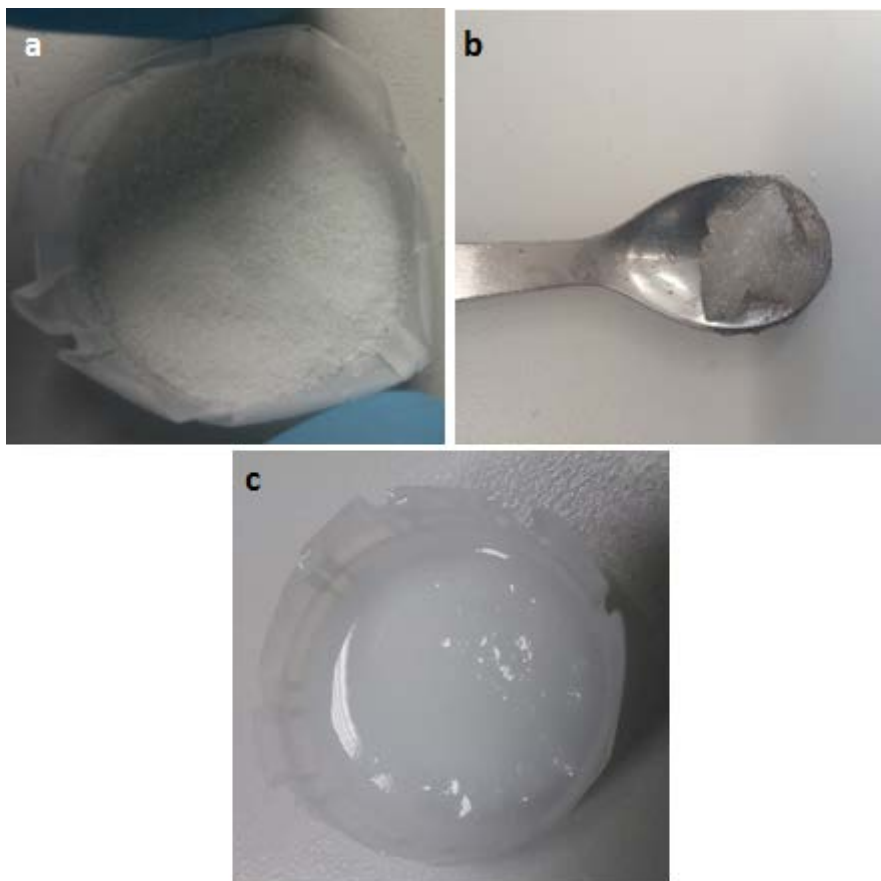
- Figure S1 Chemical structures of the monomers and crosslinkers used in this study
- Figure S2 Digital images of microgels: (a) dry microgels, (b) paste-like pre-wetted microgels (dry microgels + small amount of water) used for first FO process, and (c) microgels after FO process
- Figure S3 Experimental set-up for the water flux/recovery evaluation using CO<sub>2</sub>-responsive microgels as draw materials
- Figure S4 pH dependence of the (a) hydrodynamic diameters and (b) zeta potentials of DEAEMA microgels with different crosslinkers at 25 °C
- Figure S5 Cycling evaluation on the hydrodynamic diameters and zeta potentials of the DEAEMA-1 wt. % PEGDA microgels at 25 °C
- Figure S6 Dissolution of amine in aqueous system

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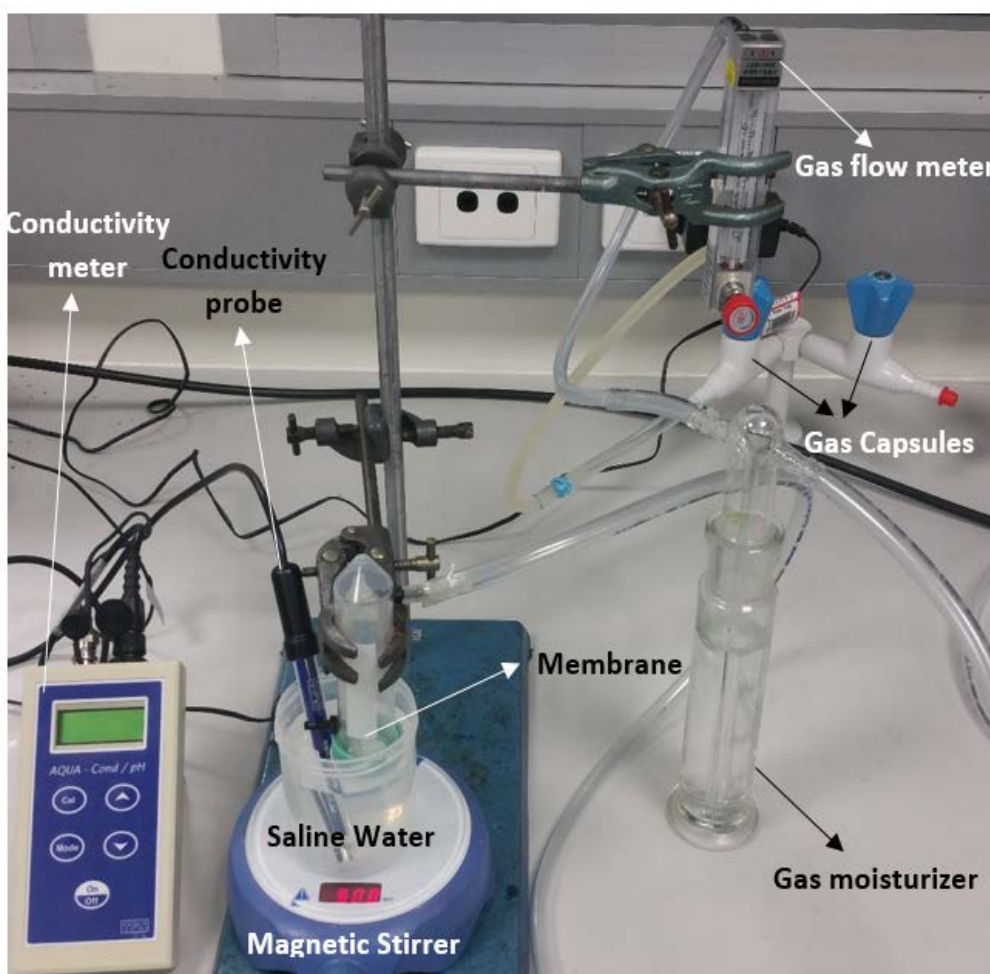
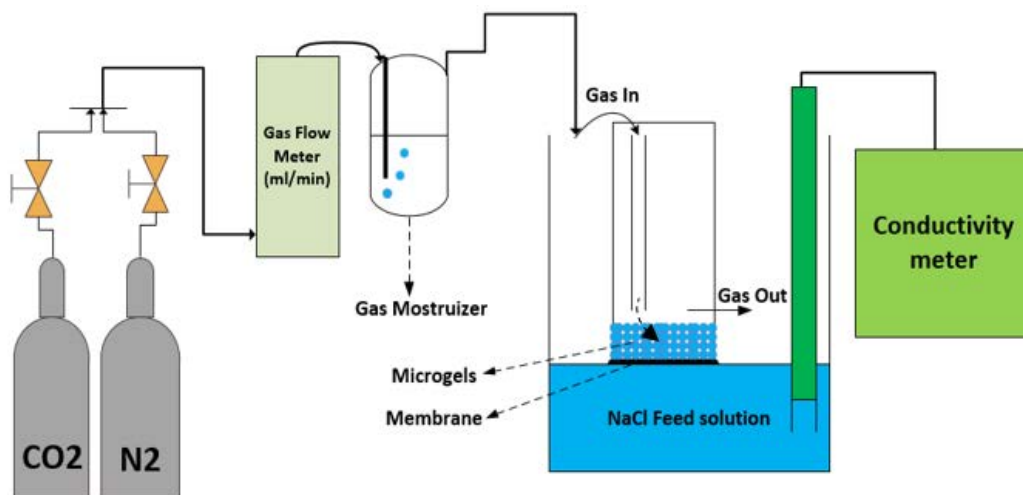


**Figure S1.** Chemical structures of the monomers and crosslinkers used in this study

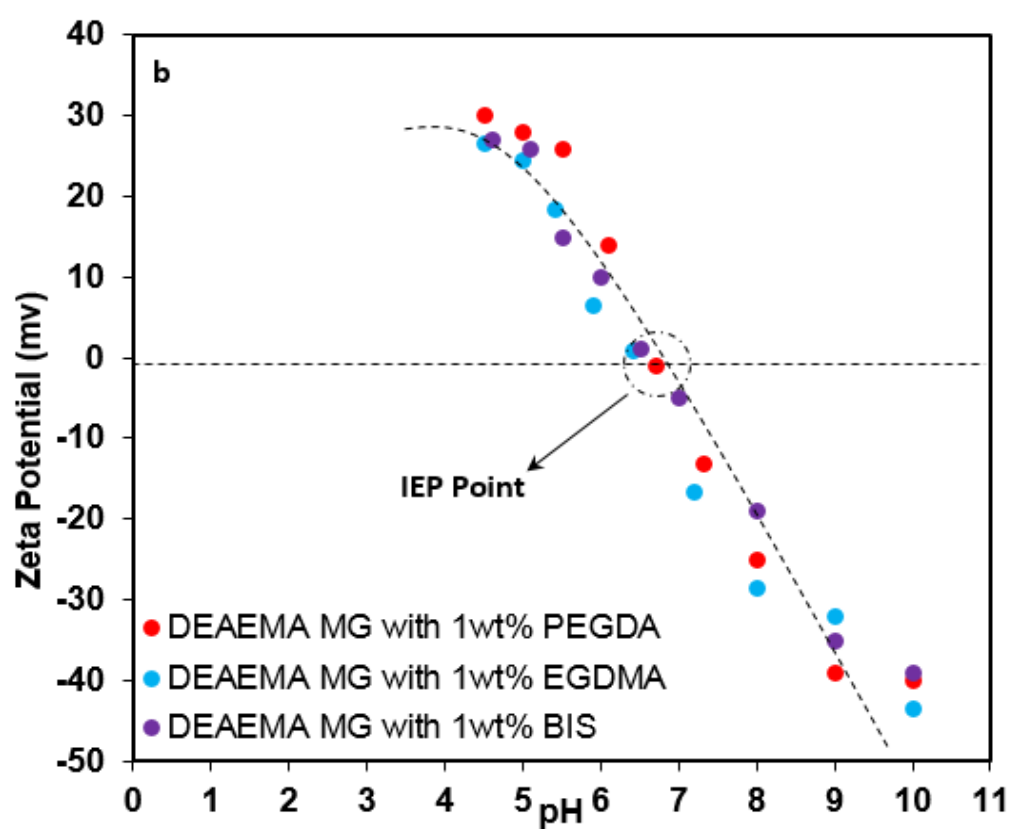
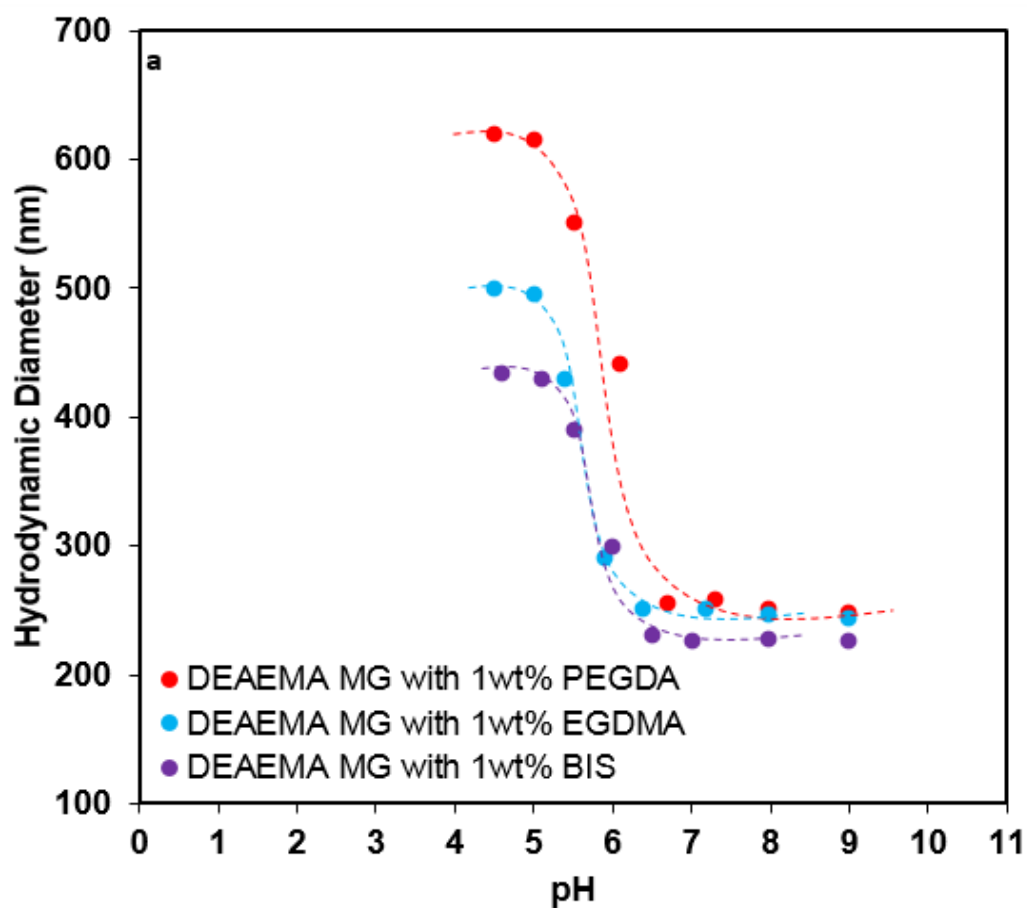


**Figure S2.** Digital images of microgels: (a) dry microgels, (b) paste-like pre-wetted microgels (dry microgels + small amount of water) used for the FO process and (c) microgels after FO process

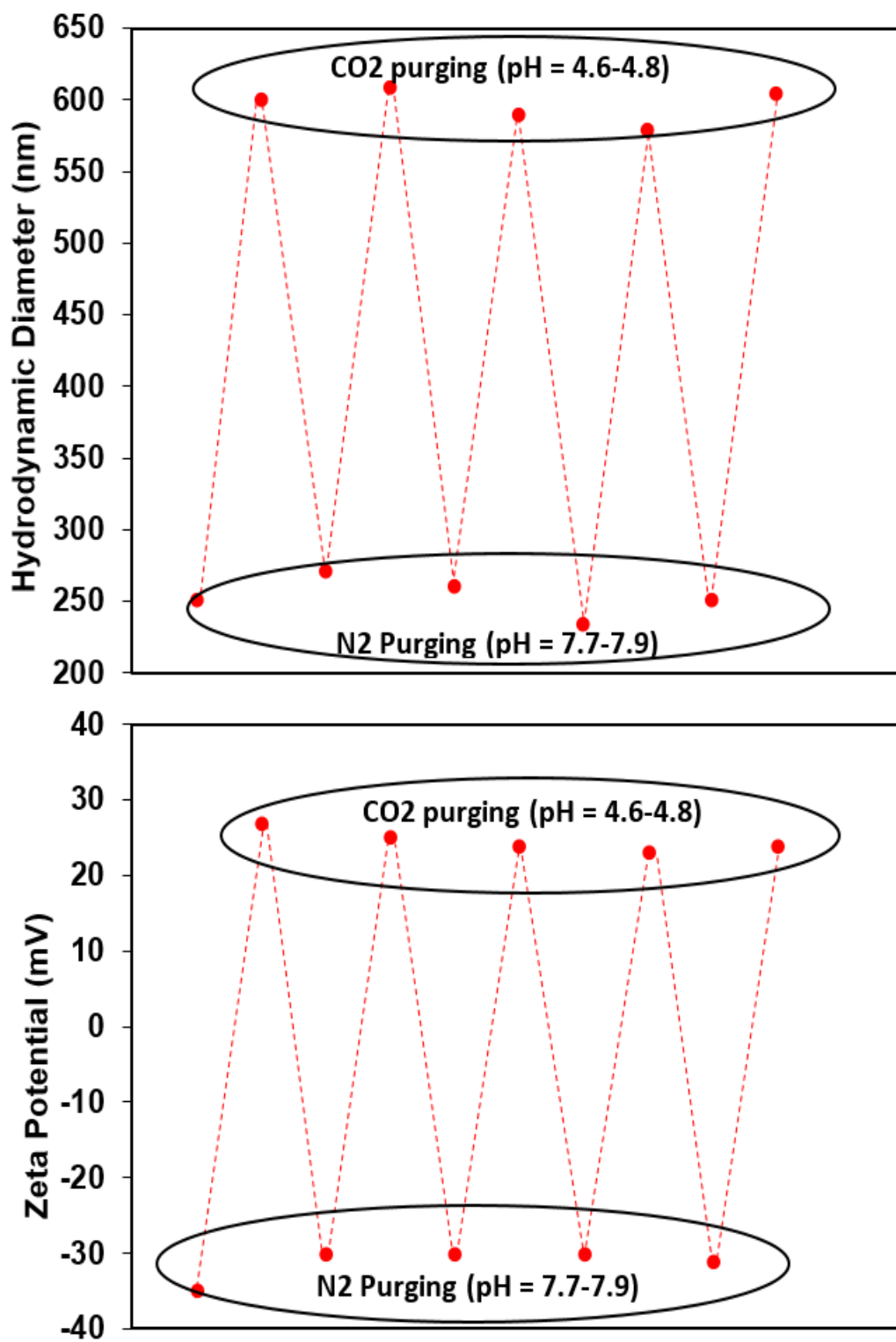




**Figure S3.** Experimental set-up for the water flux/recovery evaluation using CO<sub>2</sub>-responsive microgels as draw materials



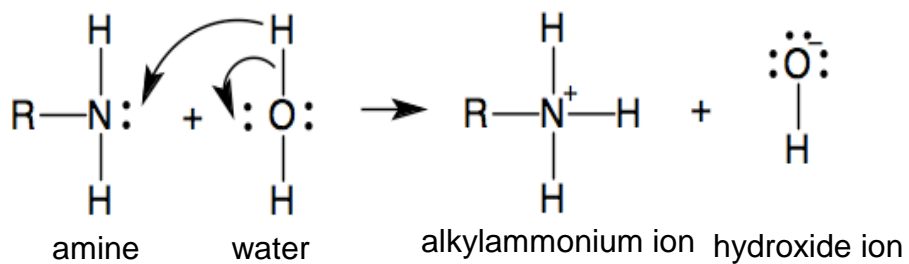
**Figure S4** pH dependence of the (a) hydrodynamic diameters and (b) zeta potentials of DEAEMA microgels with different crosslinkers at 25 °C



**Figure S5.** Cycling evaluation on the hydrodynamic diameters and zeta potentials of the DEAEMA-1 wt. % PEGDA microgels at 25 °C

### Partial Dissolution of Alkylamines in Aqueous solution

In aqueous solution, alkylamines dissolve and react with water as shown in Figure S6, where amine acts as a partial proton ( $\text{H}^+$ ) acceptor and water acts as a proton donor to produce  $\text{OH}^-$  in solution. The physical absorption of  $\text{OH}^-$  on microgel surfaces gives rise to negative zeta potentials of microgels at a high pH.



**Figure S6.** Dissolution of amine in aqueous system

## References

- [1] J.M. Dickhout, J. Moreno, P.M. Biesheuvel, L. Boels, R.G.H. Lammertink, W.M. de Vos, Produced water treatment by membranes: A review from a colloidal perspective, *Journal of Colloid and Interface Science*, 487 (2017) 523-534.
- [2] G.M. Geise, H.-S. Lee, D.J. Miller, B.D. Freeman, J.E. McGrath, D.R. Paul, Water purification by membranes: The role of polymer science, *Journal of Polymer Science Part B: Polymer Physics*, 48 (2010) 1685-1718.
- [3] S.M. Seyed Shahabadi, H. Rabiee, S.M. Seyedi, A. Mokhtare, J.A. Brant, Superhydrophobic dual layer functionalized titanium dioxide/polyvinylidene fluoride-co-hexafluoropropylene (TiO<sub>2</sub>/PH) nanofibrous membrane for high flux membrane distillation, *Journal of Membrane Science*, 537 (2017) 140-150.
- [4] H. Rabiee, S.M.S. Shahabadi, A. Mokhtare, H. Rabiee, N. Alvandifar, Enhancement in permeation and antifouling properties of PVC ultrafiltration membranes with addition of hydrophilic surfactant additives: Tween-20 and Tween-80, *Journal of Environmental Chemical Engineering*, 4 (2016) 4050-4061.
- [5] H. Rabiee, S.M. Seyedi, H. Rabiee, N. Alvandifar, Improvements in permeation and fouling resistance of PVC ultrafiltration membranes via addition of Tetronic-1107 and Triton X-100 as two non-ionic and hydrophilic surfactants, *Water Science and Technology*, 74 (2016) 1469-1483.
- [6] H. Rabiee, A. Ghadimi, T. Mohammadi, Gas transport properties of reverse-selective poly(ether-b-amide6)/[Emim][BF<sub>4</sub>] gel membranes for CO<sub>2</sub>/light gases separation, *Journal of Membrane Science*, 476 (2015) 286-302.
- [7] H. Rabiee, M. Soltanieh, S.A. Mousavi, A. Ghadimi, Improvement in CO<sub>2</sub>/H<sub>2</sub> separation by fabrication of poly(ether-b-amide6)/glycerol triacetate gel membranes, *Journal of Membrane Science*, 469 (2014) 43-58.
- [8] M. Elimelech, W.A. Phillip, The future of seawater desalination: energy, technology, and the environment, *Science*, 333 (2011) 712-717.
- [9] S.S. Shenvi, A.M. Isloor, A.F. Ismail, A review on RO membrane technology: Developments and challenges, *Desalination*, 368 (2015) 10-26.
- [10] M. Zargar, B. Jin, S. Dai, An integrated statistic and systematic approach to study correlation of synthesis condition and desalination performance of thin film composite membranes, *Desalination*, 394 (2016) 138-147.

- [11] M. Zargar, Y. Hartanto, B. Jin, S. Dai, Hollow mesoporous silica nanoparticles: A peculiar structure for thin film nanocomposite membranes, *Journal of Membrane Science*, 519 (2016) 1-10.
- [12] T.-S. Chung, L. Luo, C.F. Wan, Y. Cui, G. Amy, What is next for forward osmosis (FO) and pressure retarded osmosis (PRO), *Separation and Purification Technology*, 156 (2015) 856-860.
- [13] D.L. Shaffer, J.R. Werber, H. Jaramillo, S. Lin, M. Elimelech, Forward osmosis: Where are we now?, *Desalination*, 356 (2015) 271-284.
- [14] Q. Ge, M. Ling, T.-S. Chung, Draw solutions for forward osmosis processes: Developments, challenges, and prospects for the future, *Journal of Membrane Science*, 442 (2013) 225-237.
- [15] A. Achilli, T.Y. Cath, A.E. Childress, Selection of inorganic-based draw solutions for forward osmosis applications, *Journal of Membrane Science*, 364 (2010) 233-241.
- [16] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, A novel ammonia—carbon dioxide forward (direct) osmosis desalination process, *Desalination*, 174 (2005) 1-11.
- [17] A. Razmjou, G.P. Simon, H. Wang, Polymer Hydrogels as Smart Draw Agents in Forward Osmosis Processes, (2015) 129-149.
- [18] A. Razmjou, G.P. Simon, H. Wang, Effect of particle size on the performance of forward osmosis desalination by stimuli-responsive polymer hydrogels as a draw agent, *Chemical Engineering Journal*, 215–216 (2013) 913-920.
- [19] A. Razmjou, Q. Liu, G.P. Simon, H. Wang, Bifunctional Polymer Hydrogel Layers As Forward Osmosis Draw Agents for Continuous Production of Fresh Water Using Solar Energy, *Environmental Science & Technology*, 47 (2013) 13160-13166.
- [20] A. Razmjou, M.R. Barati, G.P. Simon, K. Suzuki, H. Wang, Fast Deswelling of Nanocomposite Polymer Hydrogels via Magnetic Field-Induced Heating for Emerging FO Desalination, *Environmental Science & Technology*, 47 (2013) 6297-6305.
- [21] D. Li, X. Zhang, J. Yao, G.P. Simon, H. Wang, Stimuli-responsive polymer hydrogels as a new class of draw agent for forward osmosis desalination, *Chemical Communications*, 47 (2011) 1710-1712.

- [22] X. Fan, H. Liu, Y. Gao, Z. Zou, V.S. Craig, G. Zhang, G. Liu, Forward-Osmosis Desalination with Poly(Ionic Liquid) Hydrogels as Smart Draw Agents, *Adv Mater*, 28 (2016) 4156-4161.
- [23] Y. Cai, R. Wang, W.B. Krantz, A.G. Fane, X.M. Hu, Exploration of using thermally responsive polyionic liquid hydrogels as draw agents in forward osmosis, *RSC Advances*, 5 (2015) 97143-97150.
- [24] Y. Zhong, X. Feng, W. Chen, X. Wang, K.W. Huang, Y. Gnanou, Z. Lai, Using UCST Ionic Liquid as a Draw Solute in Forward Osmosis to Treat High-Salinity Water, *Environ Sci Technol*, 50 (2016) 1039-1045.
- [25] J.-j. Kim, H. Kang, Y.-S. Choi, Y.A. Yu, J.-C. Lee, Thermo-responsive oligomeric poly(tetrabutylphosphonium styrenesulfonate)s as draw solutes for forward osmosis (FO) applications, *Desalination*, 381 (2016) 84-94.
- [26] Y. Cai, W. Shen, J. Wei, T.H. Chong, R. Wang, W.B. Krantz, A.G. Fane, X. Hu, Energy-efficient desalination by forward osmosis using responsive ionic liquid draw solutes, *Environ. Sci.: Water Res. Technol.*, 1 (2015) 341-347.
- [27] Y. Hartanto, S. Yun, B. Jin, S. Dai, Functionalized thermo-responsive microgels for high performance forward osmosis desalination, *Water Research*, 70 (2015) 385-393.
- [28] Y. Hartanto, M. Zargar, X. Cui, Y. Shen, B. Jin, S. Dai, Thermoresponsive cationic copolymer microgels as high performance draw agents in forward osmosis desalination, *Journal of Membrane Science*, 518 (2016) 273-281.
- [29] D. Li, X. Zhang, G.P. Simon, H. Wang, Forward osmosis desalination using polymer hydrogels as a draw agent: Influence of draw agent, feed solution and membrane on process performance, *Water Research*, 47 (2013) 209-215.
- [30] A. Zhou, H. Luo, Q. Wang, L. Chen, T.C. Zhang, T. Tao, Magnetic thermoresponsive ionic nanogels as novel draw agents in forward osmosis, *RSC Adv.*, 5 (2015) 15359-15365.
- [31] Q. Zhao, N. Chen, D. Zhao, X. Lu, Thermoresponsive magnetic nanoparticles for seawater desalination, *ACS Appl Mater Interfaces*, 5 (2013) 11453-11461.
- [32] M.M. Ling, T.-S. Chung, X. Lu, Facile synthesis of thermosensitive magnetic nanoparticles as "smart" draw solutes in forward osmosis, *Chemical Communications*, 47 (2011) 10788-10790.
- [33] M.M. Ling, K.Y. Wang, T.-S. Chung, Highly Water-Soluble Magnetic Nanoparticles as Novel Draw Solutes in Forward Osmosis for Water Reuse, *Industrial & Engineering Chemistry Research*, 49 (2010) 5869-5876.

- [34] Y. Cai, W. Shen, R. Wang, W.B. Krantz, A.G. Fane, X. Hu, CO<sub>2</sub> switchable dual responsive polymers as draw solutes for forward osmosis desalination, *Chem Commun (Camb)*, 49 (2013) 8377-8379.
- [35] M.L. Stone, C. Rae, F.F. Stewart, A.D. Wilson, Switchable polarity solvents as draw solutes for forward osmosis, *Desalination*, 312 (2013) 124-129.
- [36] K.K. Reimund, B.J. Coscia, J.T. Arena, A.D. Wilson, J.R. McCutcheon, Characterization and membrane stability study for the switchable polarity solvent N,N-dimethylcyclohexylamine as a draw solute in forward osmosis, *Journal of Membrane Science*, 501 (2016) 93-99.
- [37] D.S. Wendt, C.J. Orme, G.L. Mines, A.D. Wilson, Energy requirements of the switchable polarity solvent forward osmosis (SPS-FO) water purification process, *Desalination*, 374 (2015) 81-91.
- [38] G.T. Gray, J.R. McCutcheon, M. Elimelech, Internal concentration polarization in forward osmosis: role of membrane orientation, *Desalination*, 197 (2006) 1-8.
- [39] J.R. McCutcheon, M. Elimelech, Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis, *Journal of Membrane Science*, 284 (2006) 237-247.
- [40] A.J. Morse, S.P. Armes, K.L. Thompson, D. Dupin, L.A. Fielding, P. Mills, R. Swart, Novel Pickering emulsifiers based on pH-responsive poly(2-(diethylamino)ethyl methacrylate) latexes, *Langmuir*, 29 (2013) 5466-5475.
- [41] L. Hu, L.Y. Chu, M. Yang, H.D. Wang, C. Hui Niu, Preparation and characterization of novel cationic pH-responsive poly(N,N'-dimethylamino ethyl methacrylate) microgels, *J Colloid Interface Sci*, 311 (2007) 110-117.
- [42] C. Zhao, J. Zhang, G. Yuan, C.C. Han, CO<sub>2</sub>-triggered liquid–solid switching through a jamming mechanism, *RSC Advances*, 3 (2013) 9645.
- [43] M. Yue, Y. Hoshino, Y. Ohshiro, K. Imamura, Y. Miura, Temperature-responsive microgel films as reversible carbon dioxide absorbents in wet environment, *Angewandte Chemie*, 53 (2014) 2654-2657.
- [44] L. Lei, Q. Zhang, S. Shi, S. Zhu, Oxygen and carbon dioxide dual gas-responsive and switchable microgels prepared from emulsion copolymerization of fluoro- and amino-containing monomers, *Langmuir*, 31 (2015) 2196-2201.
- [45] K.E. Christodoulakis, M. Vamvakaki, pH-Responsive Microgel Particles Comprising Solely Basic or Acidic Residues, *Macromolecular Symposia*, 291-292 (2010) 106-114.



- [46] R. Acciaro, T. Gilányi, I. Varga, Preparation of Monodisperse Poly(N-isopropylacrylamide) Microgel Particles with Homogenous Cross-Link Density Distribution, *Langmuir*, 27 (2011) 7917-7925.
- [47] B.R. Saunders, On the Structure of Poly(N-isopropylacrylamide) Microgel Particles, *Langmuir*, 20 (2004) 3925-3932.
- [48] K. Kratz, A. Lapp, W. Eimer, T. Hellweg, Volume transition and structure of triethyleneglycol dimethacrylate, ethylenglykol dimethacrylate, and N,N'-methylene bis-acrylamide cross-linked poly(N-isopropyl acrylamide) microgels: a small angle neutron and dynamic light scattering study, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 197 (2002) 55-67.
- [49] D. Dupin, J. Rosselgong, S.P. Armes, A.F. Routh, Swelling kinetics for a pH-induced latex-to-microgel transition, *Langmuir*, 23 (2007) 4035-4041.
- [50] J.I. Amalvy, E.J. Wanless, Y. Li, V. Michailidou, S.P. Armes, Y. Duccini, Synthesis and characterization of novel pH-responsive microgels based on tertiary amine methacrylates, *Langmuir*, 20 (2004) 8992-8999.
- [51] S. Dai, P. Ravi, K.C. Tam, pH-Responsive polymers: synthesis, properties and applications, *Soft Matter*, 4 (2008) 435-449.
- [52] F.F. Al-Blewi, H.A. Al-Lohedan, M.Z.A. Rafiquee, Z.A. Issa, Kinetics of hydrolysis of procaine in aqueous and micellar media, *International Journal of Chemical Kinetics*, 45 (2013) 1-9.
- [53] Y. Chen, T. Zhao, B. Wang, D. Qiu, N. Ma, Highly Sensitive CO<sub>2</sub>-Responsive Polymeric Microgels That Respond Within Seconds, *Langmuir*, 31 (2015) 8138-8145.
- [54] Y. Hartanto, M. Zargar, H. Wang, B. Jin, S. Dai, Thermoresponsive Acidic Microgels as Functional Draw Agents for Forward Osmosis Desalination, *Environ Sci Technol*, 50 (2016) 4221-4228.
- [55] M. Yue, Y. Hoshino, Y. Miura, Design rationale of thermally responsive microgel particle films that reversibly absorb large amounts of CO<sub>2</sub>: fine tuning the pK<sub>a</sub> of ammonium ions in the particles, *Chem. Sci.*, 6 (2015) 6112-6123.
- [56] R.B. Karabacak, Emulsifier-free poly[2-(diethylamino) ethyl methacrylate] microgels with cationic quaternary ammonium monomers, *Journal of Applied Polymer Science*, 133 (2016) n/a-n/a.
- [57] V. Bütün, S.P. Armes, N.C. Billingham, Synthesis and aqueous solution properties of near-monodisperse tertiary amine methacrylate homopolymers and diblock copolymers, *Polymer*, 42 (2001) 5993-6008.

[58] P. Atkins, J.D. Paula, Physical Chemistry, W. H. Freeman and Company, New York, 2006.

[59] S. Dai, P. Ravi, K.C. Tam, B.W. Mao, L.H. Gan, Novel pH-Responsive Amphiphilic Diblock Copolymers with Reversible Micellization Properties, *Langmuir*, 19 (2003) 5175-5177.

## **Chapter 4.**

# **O<sub>2</sub>-RESPONSIVE MICROGELS FOR FORWARD OSMOSIS DESALINATION**

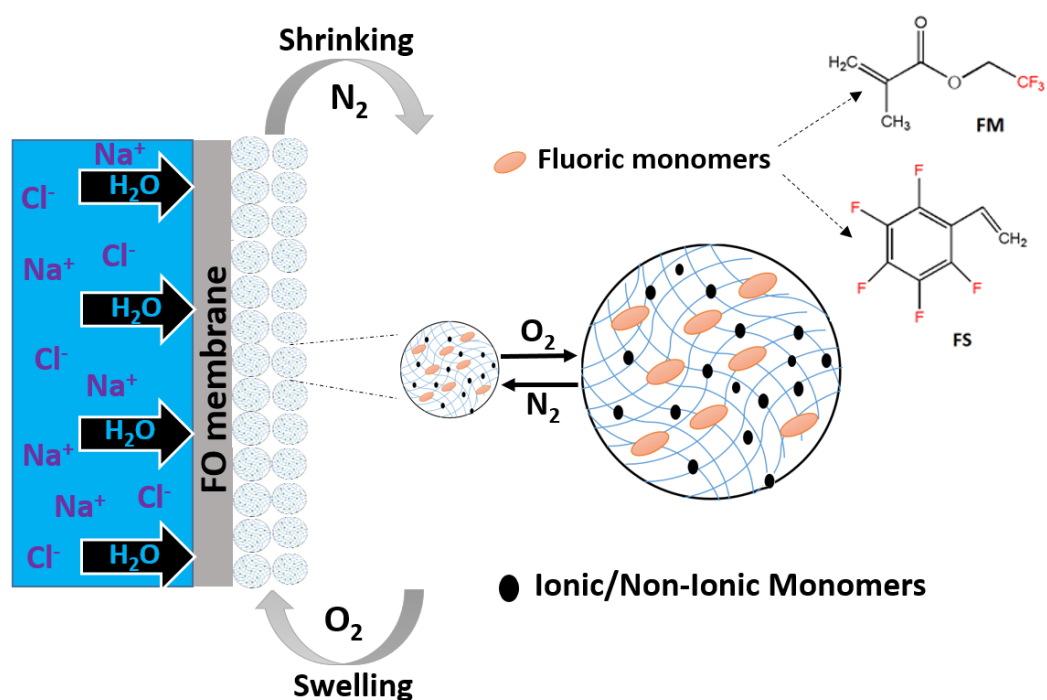
# O<sub>2</sub>-Responsive Microgels for Forward Osmosis Desalination

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Graphical Abstract:



## Statement of Authorship

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## Principal Author

Name of Principal Author (Candidate)	Hesamoddin Rabiee
Contribution to the Paper	Design the major experiments, material synthesis, data analysis and manuscript writing.
Overall percentage (%)	90%
Certification:	This paper reports on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I am the primary author of this paper.
Signature	Date 27 Aug 2017

## Co-Author Contributions

By signing the Statement of Authorship, each author certifies that:

- iv. the candidate's stated contribution to the publication is accurate (as detailed above);
- v. permission is granted for the candidate to include the publication in the thesis; and
- vi. the sum of all co-author contributions is equal to 100% less the candidate's stated contribution.

Name of Co-Author	Bo Jin
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Contribution to the Paper	Supervision and manuscript correction
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## Abstract

Gas responsive microgels have been recently developed for energy effective forward osmosis (FO) processes. In this study, smart O<sub>2</sub>-responsive copolymer microgels were synthesised and for the first time used as novel draw materials for FO desalination, where functional fluorine-containing monomers of trifluoroethyl methacrylate (FM) and pentafluorostyrene (FS) were selected to copolymerize with different water-soluble monomers to produce functional microgels. Water flux and water recovery performance in the presence of various O<sub>2</sub>-responsive microgels were systematically examined. Different fluorine monomers and monomer concentrations together with a variety of comonomers (diethylaminoethyl methacrylate (DEAEMA), dimethylaminoethyl methacrylate (DMAEMA), hydroxyethyl methacrylate (HEMA) and N-isopropylacrylamide (NIPAM)) were varied to optimize the desalination performance as draw materials. The microgels become reversibly active to draw water after purging O<sub>2</sub> and release water upon N<sub>2</sub> purging. The results showed that enhanced water flux was performed by the microgels with the more hydrophilic FM monomer. The microgels of DEAEMA-FM or DMAEMA-FM had a higher water flux up to 29 LMH, while the NIPAM-FM microgels showed the best recovery of 56 %.

**Key Words.** Forward osmosis, desalination, microgels, O<sub>2</sub>-responsive, draw materials

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## 4.1 Introduction

Membrane technology has become as one of the most prevalent methods for many separation processes over the last 5 decades. Currently, membrane processes have been used widely as cost-effective options for various industrial applications, such as gas separation (CO<sub>2</sub> capture [1], natural gas sweetening [2]), water treatment and desalination (reverse osmosis (RO) [3], membrane distillation (MD) [4], nanofiltration [5, 6] and forward osmosis (FO) [7]), etc. Desalination seems to be a necessary task for many countries around the world associated with the global population rise, and over 97 % of the water on the earth possess high salinity [8]. The RO process is the most commonly used membrane technology for water treatment and desalination to produce drinking water. However, FO has emerged as an energy-effective process during the recent years since it uses the natural osmotic pressure of a draw solution/material to drive water through a semi-permeable FO membrane to perform desalination [9].

In an FO process, a draw solution/material adsorbs water and releases it afterwards. Thereby, draw solution/material acts as the centre of the FO process regarding to provide the sufficient driving force [9]. A suitable draw solution/material should be able to provide high osmotic pressure, produce high water flux, possess low toxicity, and most importantly, to release the adsorbed water easily with minimum energy requirement [10]. In the recent years, many researchers have focused on development of efficient draw solutions/materials for FO process. Using divalent inorganic salts such as Na<sub>2</sub>SO<sub>4</sub> or MgSO<sub>4</sub> produces high water flux due to their high osmotic pressure [11]. For draw solution recovery and producing drinking water, FO process is hybridized by nanofiltration. However, using the nanofiltration

subsequent to FO is also an energy-consuming step and the membranes are prone to fouling [12].

Thermolytic materials as draw solutions/materials have attracted increasing attention over the last few years. Ammonia bicarbonate is the most-used draw solution in this category [13-15]. These materials are able to draw water from the salty feed and then release the adsorbed water by mild increasing temperature. Usually, the required heating for this transition can be provided by low-grade heat [16]. These kinds of draw solutions/materials in the liquid-state have drawbacks like reverse draw solution flux, membrane scaling, membrane stability and low water quality, which hinders the practical application of these draw solutions for real industrial usages [17]. In addition, trace residuals which are left behind during the separation process is not tolerated in producing potable water.

Thermo-responsive hydrogels that are 3D polymeric network materials have been developed to be used as new FO draw agents in the last few years [18, 19]. The main component of these materials is poly (N-isopropylacrylamide) (PNIPAM), which is well-known for its responsivity to temperature at 32 °C. One important advantage of using hydrogels as draw materials rather than salty solutions is dealing with internal concentration polarization (ICP) and reverse draw solution flux, which are common issues regarding to liquid-state and low molecular draw solutions, and thus influence their capability for long-term performance [20-23]. Although hydrogels are able to overcome the negative effect of reverse draw solutions, the water flux was not as high as conventional draw solutions. Some attempts have been explored to improve the performance of hydrogels by using various methods like composite/semi-interpenetrating network [24, 25] or bifunctional layers formation [26]. However, water flux did not increase considerably.



To deal with this issue, microgels offer some advantages over bulk hydrogels due to their high surface areas [27], which results in better contact with membrane and produces higher water flux [28]. Another advantage of microgels is the lack of dense skin of hydrogels. Hartanto et al. studied thermo-responsive microgels (non-ionic, acidic and cationic) as draw materials for FO process [27-29]. Their results clearly showed that these microgels can produce higher water flux than bulk hydrogels because of improved surface contact. They also observed that the copolymerization of NIPAM with cationic and anionic co-monomers can lead to remarkable improvement in water flux as these charges moieties are able to provide high osmotic pressures [28, 29]. However, addition of charged monomers above 5 % results in the significant reduction in water recovery.

On the other hand, our team recently synthesised the CO<sub>2</sub>-responsive microgels as the novel draw materials for FO desalination. CO<sub>2</sub> protonates the microgels and makes them be hydrophilic to adsorb water at low pH, and water recovery can be achieved at the isoelectric point (IEP) by purging N<sub>2</sub>. The key advantage of using CO<sub>2</sub>-responsive microgels was to deal with ICP and back diffusion of draw materials which leads to achieve high water flux was due to the presence of protonated amine moieties after CO<sub>2</sub> purging. Another advantage of using gas-responsive microgels is to use trigger gases in water recovery rather than moderate heat for thermo-responsive microgels, where higher water flux and efficient water recovery can be both achievable with less energy consumption. However, the issue related to application of CO<sub>2</sub>-responsive microgels is that the pH of the produced water might be inevitably different from that of potable water. On the other hand, there might be limited CO<sub>2</sub> back diffusion. Therefore, it is worth developing better gas-responsive microgels, which are responsive to a trigger gas without the above-mentioned issues. In this study, we reported the synthesis of O<sub>2</sub>-responsive

microgels and used them as new draw materials for FO desalination. Two commercially available fluoro-containing monomers were selected as O<sub>2</sub>-responsive segments to co-polymerize with different water-soluble monomers via surfactant-free emulsion or dispersion polymerization [30, 31]. Water flux and water recovery of resulting microgels were evaluated and optimised together with microgel recycling capability. The highest water flux can be obtained for the DEAEMA or DMAEMA microgels with 5 wt% FM, while the NIPAM microgels with 5 wt% FM gives best water recovery.

## 4.2 Experimental

### 4.2.1 Materials

Monomers of 2 - N,N'-(diethylamino)ethyl methacrylate (DEAEMA), hydroxyethyl methacrylate (HEMA), 2-N,N'-(dimethylamino) ethyl methacrylate (DMAEMA), 2,3,4,5,6 pentafluorostyrene (FS), 2,2,2-trifluoroethyl methacrylate (FM), N, N'-methylene-bisacrylamide (BIS) as crosslinker and anionic initiator of ammonium persulfate (APS) were purchased from Sigma-Aldrich. N-isopropylacrylamide (NIPAM, >98%), purchased from Tokyo Chemical Industry, was purified by recrystallization in n-hexane and dried at room temperature. Cationic initiator of 2,2'-azobis (2-methyl propionamide dihydrochloride) (V-50) was purchased from Novachem. N,N'-azobisisobutyronitrile (AIBN), as a non-ionic initiator was supplied from Acros Organics. Poly(vinyl pyrrolidone) (MW = 360,000 Da, Sigma) was used as the stabilizer for dispersion polymerization, and absolute methanol was from Merck. Cellulose triacetate forward osmosis (CTA-FO) membranes were supplied by the Hydration Technologies Inc. (HTI, USA). Sodium chloride was bought from the VWR. DI water is from a Millipore water purification system.

#### 4.2.2 Synthesis of O<sub>2</sub>-responsive microgels

*DEAEMA-Fluoro microgel synthesis.* DEAEMA-co-FS and DEAEMA-co-FM microgels were synthesised via a surfactant-free emulsion polymerization (SFEP) method by using V-50 as the initiator (2 wt% based on total monomer feed) [30]. FM content varied from 1 to 15 wt% relative to total monomer mass ( $m_{DEAEMA} + m_{FM}$ ). All the microgels had 1 wt% cross-linker (BIS), in respect to the total monomer. For the detailed synthesis of DEAEMA microgels with 5 wt% FM, 1.9 g of DEAEMA, 0.1 g of FM and 20 mg of BIS were charged to a three-neck flask. 45 ml deionised water was added. The flask was sealed and the mixed solution was mechanically stirred for 45 min under N<sub>2</sub> purging to degas. After that, the temperature was increased to 75 °C and the degassed initiator solution (40 mg in 5 ml water) was injected to start polymerization. The mixed solution turned to cloudy after 15 min. The polymerization was carried out overnight and subsequently purified against DI water for 4 days using membrane dialysis (MWCO: 12–14kDa) to remove all unreacted agents.

*DMAEMA-Fluoro microgel synthesis.* DMAEMA-FM microgels were synthesised via dispersion polymerization in a mixed solvent of (methanol:water = 1:9, vol:vol), as the SFEP was not applicable for DMAEMA [32, 33]. In this method, monomers of DMAEMA and FM were added to the water-ethanol mixture to have a 10 wt% solution. AIBN and BIS were used as the initiator and cross-linker (2 wt% for AIBN and 1 wt% for BIS relative to total monomer feed). 2 wt% PVP360 was charged as a macromolecular stabilizer. The mixture was mechanically stirred (300 rpm) at 40 °C for one hr under N<sub>2</sub> atmosphere. The oil bath temperature was raised to 75 °C to start polymerization, and it was left over night to complete the reaction. The resulting microgels were purified by dialysis against deionised water to remove any unreacted compounds and monomers.

*NIPAM-Fluoro and HEMA-Fluoro microgel synthesis.* The SFEP method was used to synthesise NIPAM-Fluoro and HEMA-Fluoro microgels, where semi-batch polymerization was considered according to our previous studies [27, 28]. Total monomer concentration in the batch was 1 wt% to avoid agglomeration of polymerization. The batch feed was degassed for 45 min under N<sub>2</sub> purging, then oil bath was heated to 75 °C and APS initiator was injected to start polymerization. During this period, the semi-batch feed was degassed. After the batch solution turned to cloudy, the semi-batch feed solution was added to the reactor at a flow rate of 3 mL/h. The total concentration of monomers after semi-batch feed was 4 wt%. Polymerization was completed overnight, and the same purification step with dialysis was considered to purify these microgels.

#### **4.2.3 Characterization of O<sub>2</sub>-responsive microgels**

*Fourier Transform Infrared Spectroscopy (FTIR).* FTIR spectra of microgels was obtained by using a Thermo Scientific NICOLET 6700 spectrometer equipped with a diamond ATR with wavenumber resolution of 4 cm<sup>-1</sup> in the range of 400–4000 cm<sup>-1</sup> under ambient conditions to study the functional groups of the microgels.

*Dynamic light scattering.* Dynamic light scattering was used to measure the hydrodynamic diameters ( $d_h$ ) of the synthesised microgels. The tests were handled by a Zetasizer (Malvern, Nano-ZS) and the swelling ratios (SR) of the microgels were calculated using the following equation:

$$SR = \left( \frac{d_{h,O_2}}{d_{h,O_2-free}} \right)^3 \quad (1)$$

where,  $d_{h,O_2}$  is the hydrodynamic diameter of the microgel after O<sub>2</sub> purging and  $d_{h,O_2-free}$  is hydrodynamic diameter after O<sub>2</sub> stripping. The Zetasizer was also used to measure the zeta potentials of microgels.

#### 4.2.4 Evaluation on desalination performance of O<sub>2</sub>-responsive microgels

*Water flux evaluation.* Water fluxes of the synthesised microgels were determined using a conductivity probe according to our previous studies [29]. In brief, changes in conductivity of the saline feed due to passing of water into the draw solution side is interpreted to water flux through the membrane [27]. For this evaluation, the microgels should be first activated by O<sub>2</sub>. For this purpose, microgels were slightly wetted to enhance the affinity to the membrane. A small amount of water (1 ml water per g dry microgels) was added to dried microgels. After water addition, the microgels became paste-like and were spread on the membrane. After that, O<sub>2</sub> was purged through the microgels for 1 h to activate microgels to become hydrophilic. A conductivity meter was used to measure the changes in feed conductivity and these data could be converted to NaCl concentration in the feed and calculate how much water has been adsorbed. The following equations were used to calculate water flux:

$$V_t = \frac{C_i V_i}{C_t} \quad (2)$$

$$J_w = \frac{V_i - V_t}{A t} \quad (3)$$

where,  $V_i$  and  $V_t$  are the initial volume of feed (mL) and the volume of feed at time  $t$ , respectively.  $C_i$  and  $C_t$  are the initial feed concentration (ppm) and the feed concentration at time  $t$ , respectively.  $A$  is the membrane surface area,  $J_w$  is attributed to the water flux based on litre/m<sup>2</sup>/h (LMH) and  $t$  (h) is the time of changing in solution conductivity.

*Water Recovery.* Water recovery measurement of the microgels was assessed based on purging and stripping of oxygen as the microgels were responsive to O<sub>2</sub>.

Gravimetric calculations based on the adsorbed water, weight of dried microgels and weight of added water are considered to calculate water recovery ratios of the microgels. In this method, swollen microgels after FO are collected and N<sub>2</sub> with a flow rate of 20 ml/min was purged to remove oxygen and make microgels be hydrophobic. N<sub>2</sub> purging was continued for 1 h to ensure that O<sub>2</sub> was fully removed. After that, the solution was centrifuged at 12,000 rpm for 15 min to release water. Water recovery analysis was calculated based on the following equations:

$$C_P = \frac{W_P}{W_P + W_W + W_A} \quad (4)$$

$$W_{WG} = W_H(1 - C_P) \quad (5)$$

$$R (\%) = \frac{W_R}{W_{WG}} \times 100 \quad (6)$$

In these equations,  $C_P$  gives the concentration of microgels in the centrifuge tube based on  $W_P$  (g) (weight of dry microgel powders),  $W_W$  (g) (weight of water adsorbed by the microgels) and  $W_A$  (g) (weight of water added to the dried microgels for wetting).  $W_H$  (g) is weight of microgels in the centrifuge tube after FO; thereby  $W_{WG}$  (g) is the total weight of water in the microgels in the swollen state, which includes the adsorbed water and the added water.  $W_R$  (g) is the amount of water recovered from the swollen microgels and  $R$  (%) will give the water recovery ratio.

*Microgels Recycling Evaluation.* Recycling evaluation of the microgels was launched after the centrifuge step. After centrifuge, the paste-like microgels were collected. The amount of water retained in the microgels was slightly higher than the amount of water added in the first stage to wet microgels. In order to apply identical initial condition of microgels, slight heating was considered to evaporate

extra water. After that, the recovered microgels were used again on the membrane to repeat water flux and recovery tests.

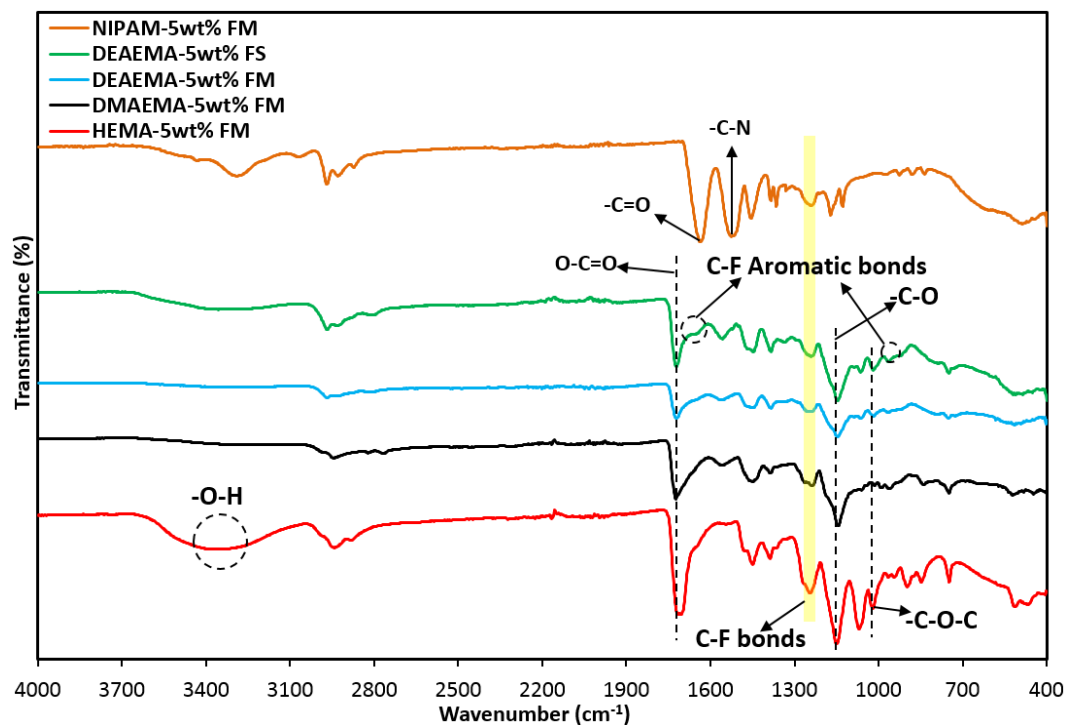
### **4.3 Results and Discussion**

#### **4.3.1 Synthesis and characterization of O<sub>2</sub>-responsive DEAEMA-FM/FS microgels**

The microgels were synthesised via the surfactant free emulsion polymerization (SFEP) to avoid the introduction of surfactants and microgel agglomeration, and the resulting microgels have better homogeneity compared to those being prepared by traditional emulsion polymerization. BIS was used as the crosslinker, and FM and FS were selected as the functional monomers due to the noticeable responsivity to O<sub>2</sub> of their polymers [30, 31, 34]. Detailed chemical structures of FS, FM, crosslinker and other comonomers are shown in Figure S1.

To confirm the successful copolymerization of these microgels, FTIR was carried out to identify various functional groups. The typical peaks corresponding to NIPAM at the bands around 1640 and 1545 cm<sup>-1</sup> are attributed to –C=O asymmetric stretching and the bending of C–N [28]. The stretching of the C–N bond and asymmetric bending of the C–H bond in the methyl groups of NIPAM are show as the peak at around 1450 cm<sup>-1</sup>. DEAEMA, DMAEMA and HEMA have a peak at around 1720 cm<sup>-1</sup> which is related to O–C=O. The peak at around 3370 cm<sup>-1</sup> is attributed to –O–H in HEMA structure [35, 36]. Stretching –C–O–C in DEAEMA, DMAEMA and HEMA can be found at around 1020 and 1150 cm<sup>-1</sup> [35]. Copolymerization of FM and FS has resulted in the presence of fluorine peaks in the microgels spectra. The peaks at highlighted areas of 1220-1250 cm<sup>-1</sup> are designated to functional C–F bonds [37-40] and the peaks at around 980 and 1655 cm<sup>-1</sup> are attributed to the aromatic –C=F=C– stretching of pentafluorostyrene [41,

42]. The existence of the above peaks verifies the presence of FM/FS in the microgels.

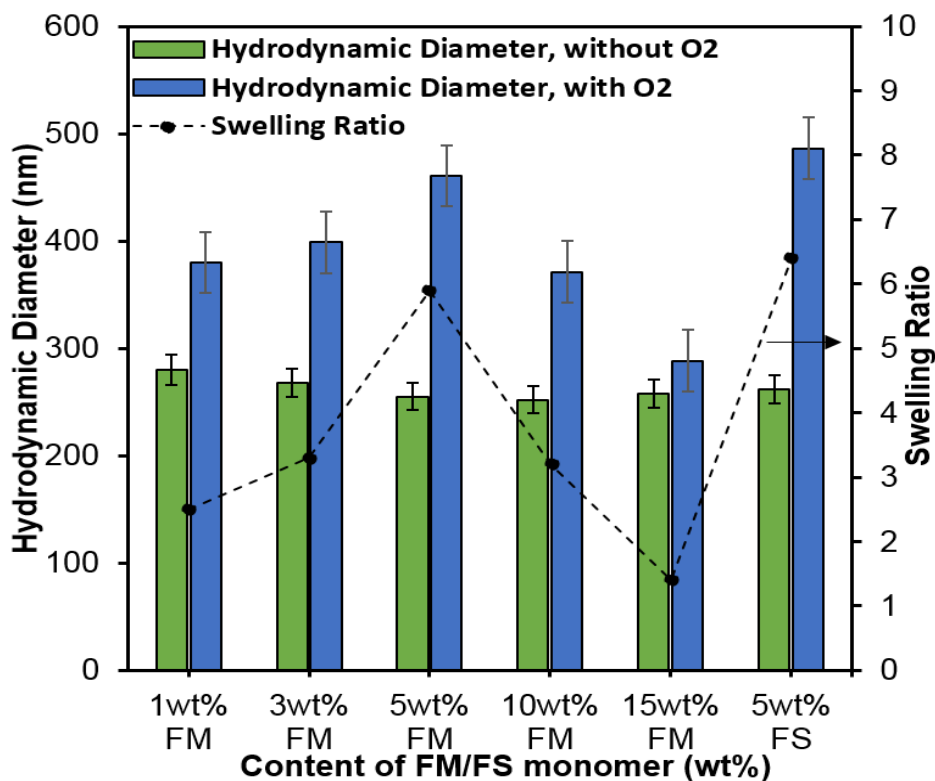


**Figure 1.** FTIR spectra of various O<sub>2</sub>-responsive microgels

Dynamic Light Scattering (DLS) was used to measure hydrodynamic diameters of microgels before and after O<sub>2</sub> purging at 25 °C and to calculate the swelling ratios of microgels. The particle size distributions of microgels are very narrow, indicating monodispersity in microgel sizes. The hydrodynamic diameters of different microgels are shown in Figure 2. After N<sub>2</sub> purging to remove any adsorbed oxygen, the sizes of all microgels in the non-swollen state are identical of around 255-280 nm. After that, the microgels are exposed to O<sub>2</sub> for half an hour to ensure the solution is saturated with O<sub>2</sub>, microgels turn to their swollen states as evident from the increase in their hydrodynamic diameters. When O<sub>2</sub> is purged, the interaction between the dissolved O<sub>2</sub> and the fluorine atoms leads to a reversible transparent-turbid transition. This transition confirms that the hydrophilicity of fluorine microgels improves and becomes more hydrophilic after O<sub>2</sub> purging [30,



31, 43]. Zhang et al. have reported such O<sub>2</sub>-responsiveness of polymers with carbon-fluorine bonds in their structure [44]. For our O<sub>2</sub>-responsive microgels, milky suspensions become transparent after O<sub>2</sub> purging (Figure S2) because the hydrophilicity of microgels can be triggered by oxygen.



**Figure 2.** Hydrodynamic diameters and swelling ratios of various DEAEMA-FM/FS microgels

The effect of fluorine moiety concentration on the swelling ratios of microgels shows that swelling ratios of the microgels in response to O<sub>2</sub> depend on FM concentration. In Figure 2, the swelling ratio of DEAEMA-FM microgels increases to around 5.9 for the microgels containing 5 wt% FM. However, further increment in the FM content up to 15 wt% leads to a reduction of swelling ratio. It means that presence of more fluorine monomer reduces the volume expansion of microgels in water [30]. The homopolymer microgels of FM and FS (poly(FM), poly(FS)) were synthesised, but they do not show any response to O<sub>2</sub>. Fluoro-polymers are known

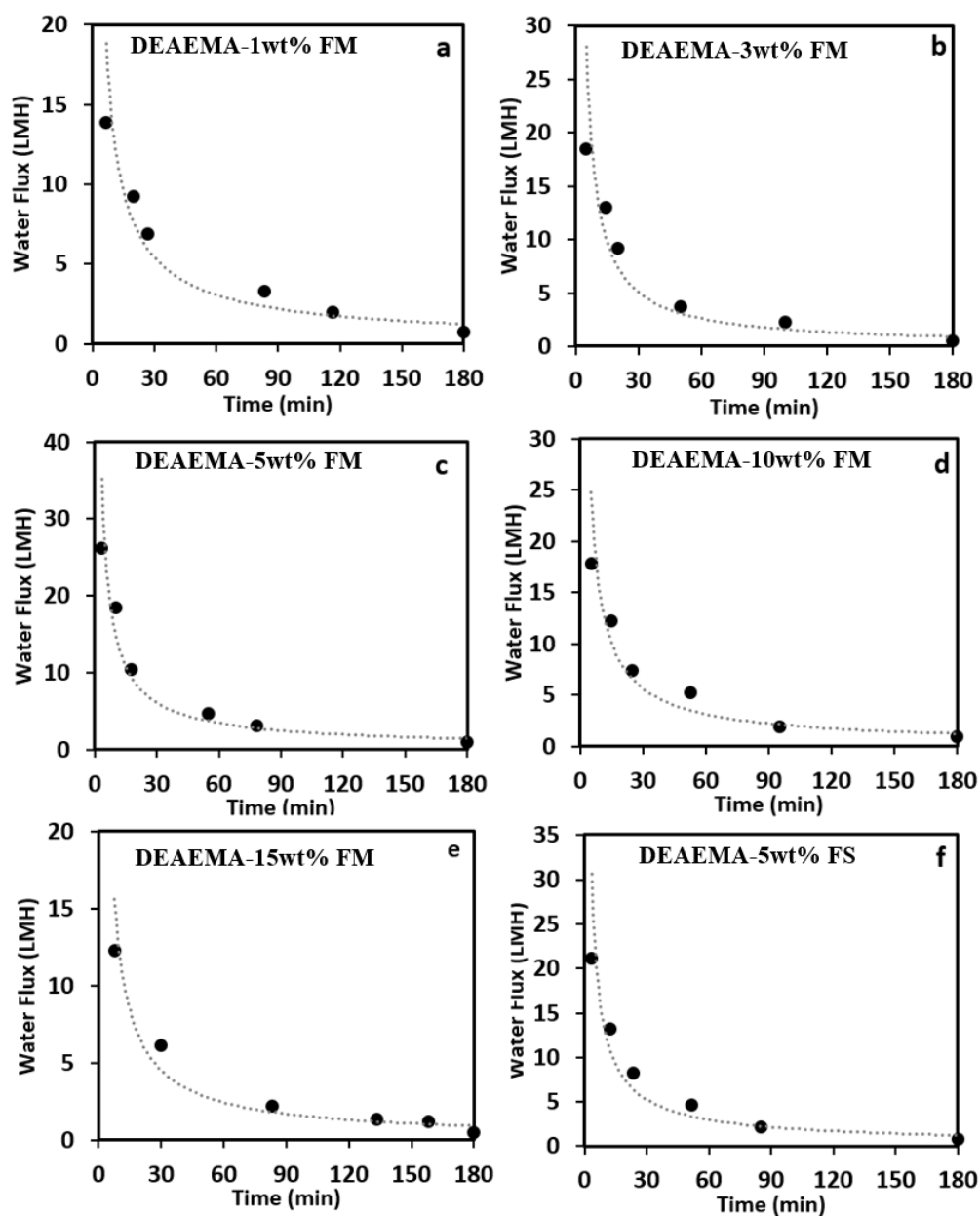
to be superhydrophobic and therefore, not able to swell and interact with oxygen in an aqueous system. Hence, it is necessary to choose fluorine monomers having their fluoro atoms as side groups and to co-polymerize with proper water-soluble comonomers to achieve O<sub>2</sub>-responsive microgels [31]. The introduction of water-soluble comonomers is able to produce either electrostatic repulsion or exclusive force to balance the hydrophobic interaction of fluorine monomers. As such, microgels are swellable in aqueous systems to ensure oxygen interaction with fluorocarbons.

In addition, the DEAEMA-5 wt% FS was also prepared with their swelling ratios being examined. As evident from Figure 2, it has a comparable swelling capability (6.4) as that of DEAEMA-5 wt% FM (5.9). FS has its fluorocarbon in the form of aromatic, but FM's fluorocarbon is in the form of aliphatic. The experimental finding further reinforces the importance of hydrophilic segments on the oxygen responsiveness.

#### **4.3.2 Water flux of O<sub>2</sub>-responsive DEAEMA-FM/FS microgels**

The water flux profiles using DEAEMA-FM/FS O<sub>2</sub>-responsive microgels as draw materials were obtained for 3 hr operation with detailed results shown in Figure 3. Prior to testing, FO membranes were soaked in saline water (2000 ppm NaCl) overnight to saturate the membrane with the saline feed [29]. Before starting the FO process, microgels were activated by purging oxygen to microgels. Since dry microgels do not have good affinity with membranes and the adsorption of O<sub>2</sub> is facilitated when microgels are wet, the microgels were slightly pre-wetted [45]. After O<sub>2</sub> purging to the paste-like pre-wetted microgels for 1 h to ensure the saturation of O<sub>2</sub>, the membrane was subsequently put in touch with saline feed to initiate the FO process. Figure 3 describes the water flux patterns of various

microgels at room temperature. High water flux is observed in the first 10 min (known as the initial water flux), which can be interpreted to the high osmotic pressure gradients between the saline feed and microgels [27]. As time goes on, water flux decreases and levels off after a semi-equilibrium period. This reduction in water flux is attributed to the drop of the osmotic pressure driving force associated with the saturation of microgels with adsorbed water [28].



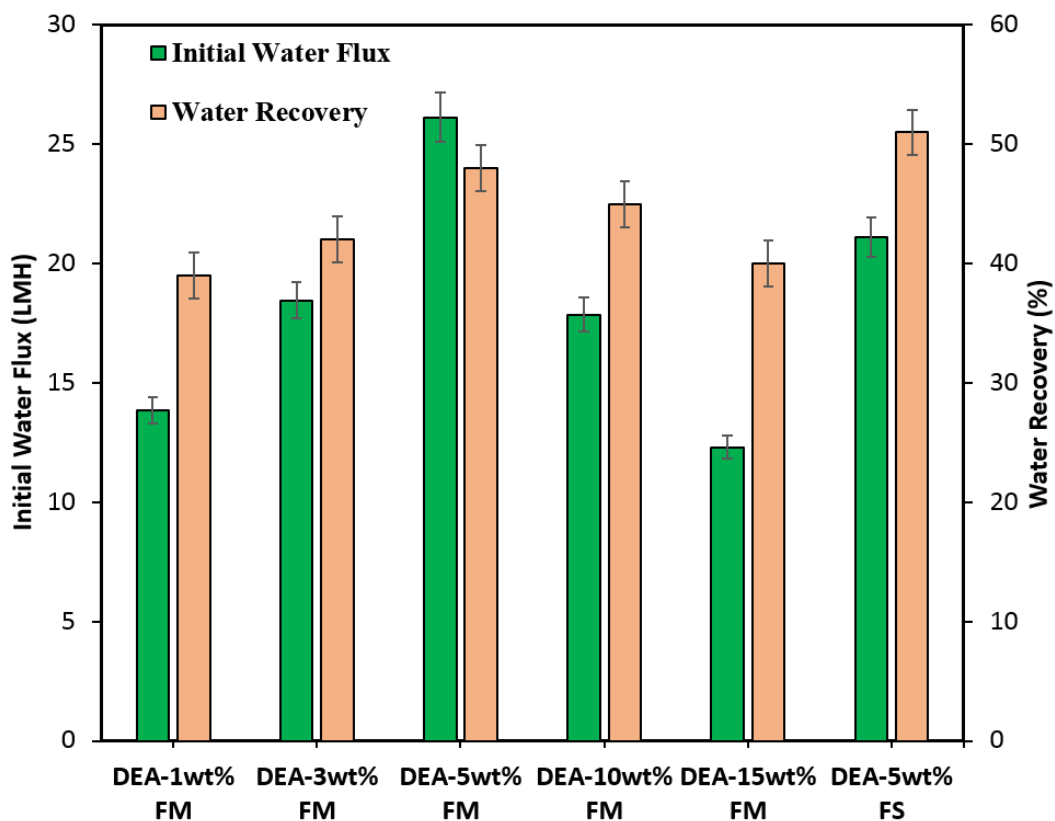
**Figure 3.** Water flux profiles of DEAEMA-FM/FS microgels

Although various microgels provide similar water flux profiles, they display different initial flux. DEAEMA-FM/FS O<sub>2</sub>-responsive microgels are able to provide a water flux up to 26 LMH, which is comparable to our previous studied on using CO<sub>2</sub>-responsive and thermo-responsive microgels [19, 27-29, 46]. The DEAEMA-5wt% FM microgels have a highest flux than other microgels containing lower and higher amounts of FM. This result is in accordance with DLS results, which show that DEAEMA-5wt% FM microgels has a highest swelling ratio among all DEAEMA-FM microgels. DEAEMA-5wt% FM microgels having high swelling ratio result in higher osmotic pressure and water flux. For the microgels with fluorocarbon contents below 5 wt%, not sufficient O<sub>2</sub>-responsive segments exist in the microgels, and therefore the swelling due to O<sub>2</sub> responsivity is less than that of DEAEMA-5wt% FM microgels. On the other hand, when FM content increases to 10 or 15 wt%, too much hydrophobic fluorocarbon segments hinder swelling in aqueous solution as well as water adsorption. In addition, the osmotic pressures and swelling ratios of the microgels are related to the balance of hydrophilic repulsion and hydrophobic attraction. The increment of hydrophobic segment to 10 wt% or 15wt% also leads to decrease the osmotic force created among hydrophilic moieties. In addition, DEAEMA-5wt% FS has a higher swelling ratio, but it provides lower water flux than that of DEAEMA-5wt% FM attributed to more hydrophilicity of FM than FS.

#### **4.3.3 Initial water flux, water recovery and recyclability of O<sub>2</sub>-responsive DEAEMA-FM/FS microgels**

DEAEMA-5wt% FM microgel has the highest initial water flux due to its higher swelling ratio over other DEAEMA-FM microgels and more hydrophilic compared to DEAEMA-FS. Microgels can be easily recovered to release the adsorbed water

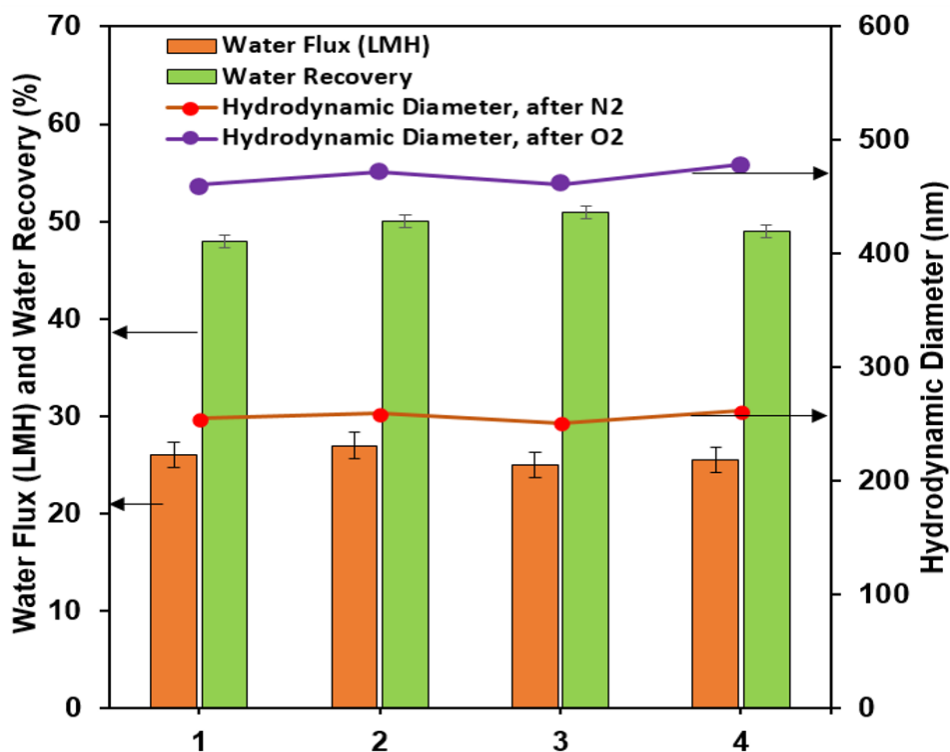
by purging  $N_2$  to remove  $O_2$  and make microgels be hydrophobic. Figure 4 shows that the DEAEMA-FM/FS microgels have their water recovery ratios in the range of 39 to 51 %. Increment in the water recovery ratio with FM increment is relevant to their swelling ratios. In addition, higher water recovery of DEAEMA-5wt% FS microgels compared to DEAEMA-5wt% FM is due to more hydrophobicity of FS than FM. Since microgels are charged, DLVO theory can be used to analyse the water releasing of the microgels [47]. The overall balance of hydrophobic interaction and electrostatic repulsion dominates water adsorption and recovery. In the present of  $O_2$ , both DEAEMA and FM/FS can be solvated and thus produce stable DEAEMA-FM/FS microgel dispersions because of the dominative electrostatic repulsion [48] (zeta potentials shown in Figure S3) and steric effect. On the other hand, after  $N_2$  purging, the shrinkage of FM/FS moieties associated with then increase in hydrophobic interaction results in water release. The water trapped within or close to the DEAEMA double layers cannot be recovered. However, these electrostatic double layers plays an important role for microgel recycling.



**Figure 4.** Initial water flux and water recovery of the DEAEMA-FM/FS microgels

Reversibility of the microgels is an important factor which determines their performance and operating costs for an FO desalination process. The microgel suspensions were purged by  $O_2/N_2$  alternatively for 30 min for several cycles. From these trails, we can observe the variation of their hydrodynamic diameters associated with swelling/deswelling processes (Figure 5). Associated with microgel swelling and shrinkage circles by alternative  $O_2/N_2$  purging, their hydrodynamic diameters are about 265 and 470 nm after  $N_2$  and  $O_2$  purging without considerable changes after various cycles. In addition, the microgels also show acceptable recyclability to adsorb and release water after four repeats of FO operation without significant reduction in their performance. The initial water flux and water recovery of DEAEMA-5wt% FM is shown in Figure 5. The water adsorption and dewatering performance do not change remarkably, and the results for the recyclability are

consistent with DLS measurements. These results confirm that the microgels have excellent reversibility to be used as draw materials in FO desalination.



**Figure 5.** Recyclability of O<sub>2</sub>-responsive DEAEMA-5wt% FM microgels in hydrodynamic diameters, water flux and water recovery.

The microgels with 5 wt% FM show better performance considering both water flux and water recovery, but hydrophilic comonomers also contribute significantly to the overall O<sub>2</sub>-responsiveness of the microgels. For this purpose, DMAEMA, NIPAM and HEMA were selected as model water-soluble comonomers to further elucidate their contribution to O<sub>2</sub>-responsive behaviour of microgels.

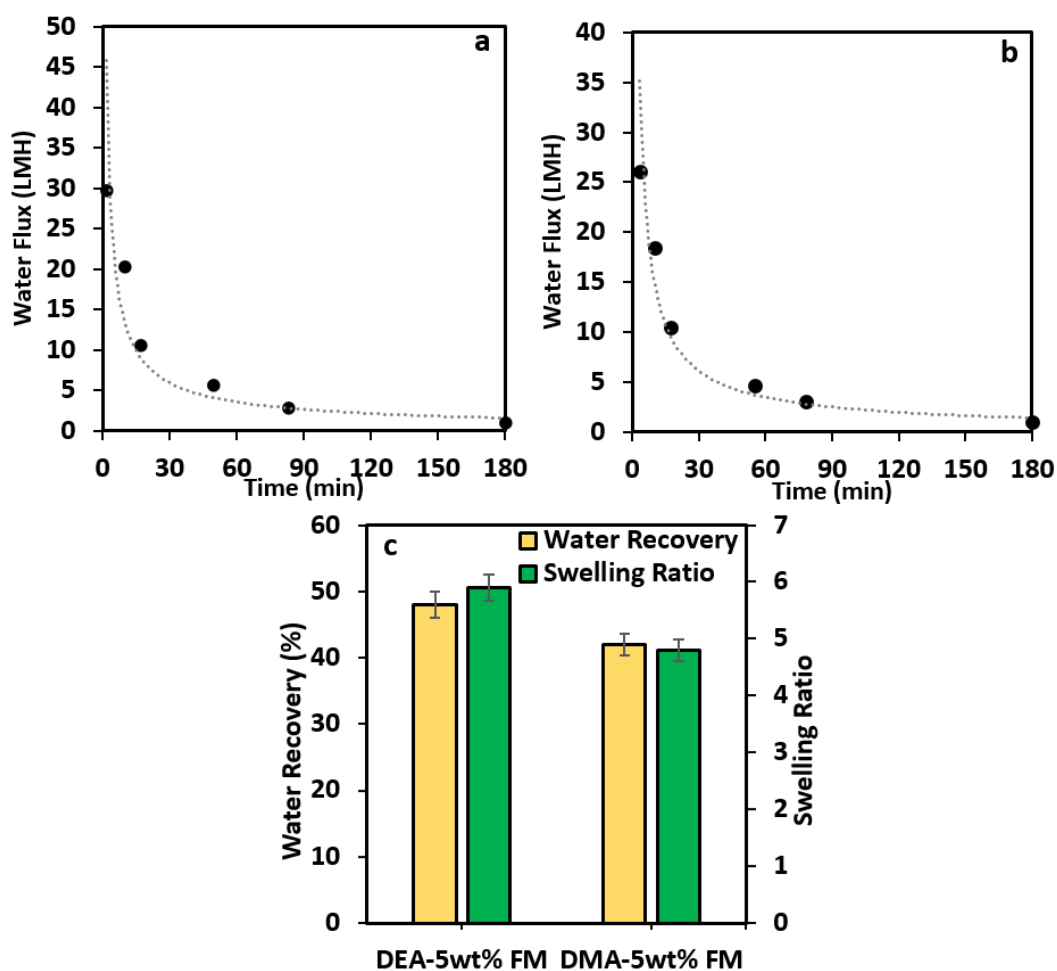
#### 4.3.4 DMAEMA-based cationic O<sub>2</sub>-responsive microgels

DMAEMA is a cationic monomer similar to DEAEMA. Unlike DEAEMA, linear poly (DMAEMA) is water-soluble in room temperature, but becomes hydrophobic beyond a temperature of 45 °C [49, 50]. The DMAEMA-5wt% FM microgels were prepared via dispersion polymerization [32, 33] due to the difficulty of homogenous

nucleation in the SFEP. Figure 6 shows the comparison of water flux, water recovery and swelling ratios of DEAEMA-5wt% FM and DMAEMA-5wt% FM. DMAEMA-5wt% FM microgels have slightly smaller swelling ratio compared to DEAEMA-FM/FS microgels (4.9 for DMAEMA microgels and 5.7 for DEAEMA microgels) due to their different pKa values. Figures 6a and 6b indicate that the water flux for DMAEMA-5wt% FM is 30 LMH while this value for DEAEMA-5wt% FM is 26 LMH. The water flux and water recovery of DMAEMA-5wt% FM microgels reveal that these microgels have slightly higher water flux compared to DEAEMA-5wt% FM. Although DMAEMA-FM swelling ratio is lower than DEAEMA-FM, however, a slightly higher water flux was performed by the DMAEMA-FM microgels due to the hydrophilic characteristic of DMAEMA. Water recovery ratios of the microgels are consistent with swelling ratios and as shown in Figure 6c, DMAEMA-5wt% FM has 41 % water recovery while this value for DEAEMA-5wt% FM was 48 %. However, it is noted that the DMAEMA-FM microgels with a higher water flux and lower swelling ratio lead in an overall lower water recovery, compared to DEAEMA-FM microgels. In addition, PVP macromolecular steric stabilizer is used for the dispersion polymerization of DMAEMA microgels. These hydrophilic PVP might keep some water and give a smaller water recovery ratio.

Experimental finding shows that there is a trade-off between water flux and water recovery abilities of the microgels used as draw materials for FO process [28, 29]. Draw materials with higher water recovery always have relatively lower affinity to water adsorption together with a low water flux. On the other hand, microgels which have high water flux cannot release the adsorbed water easily.





**Figure 6.** Comparison on different cationic O<sub>2</sub>-responsive microgels: a) Water flux profile of DMAEMA-5wt% FM b) Water flux profile of DEAEMA-5wt% FM c) water recovery and swelling ratio of DEAEMA/DMAEMA-5wt% FM microgels

#### 4.3.5 Nonionic O<sub>2</sub>-responsive microgels

HEMA and NIPAM were selected as model nonionic comonomers to synthesise uncharged O<sub>2</sub>-responsive microgels. HEMA-5wt% FM and NIPAM-5wt% FM microgels were synthesised using semi-batch SFEP. HEMA and NIPAM are both hydrophilic monomers but with different hydrophilicity when they are polymerized. After polymerization, linear P(HEMA) is slightly hydrophobic while P(NIPAM) is hydrophilic and water-soluble at room temperature [51, 52]. It has been reported that copolymerisation of NIPAM and HEMA results in the polymers to be more hydrophobic compared with P(NIPAM) due to the incorporation of hydrophobic

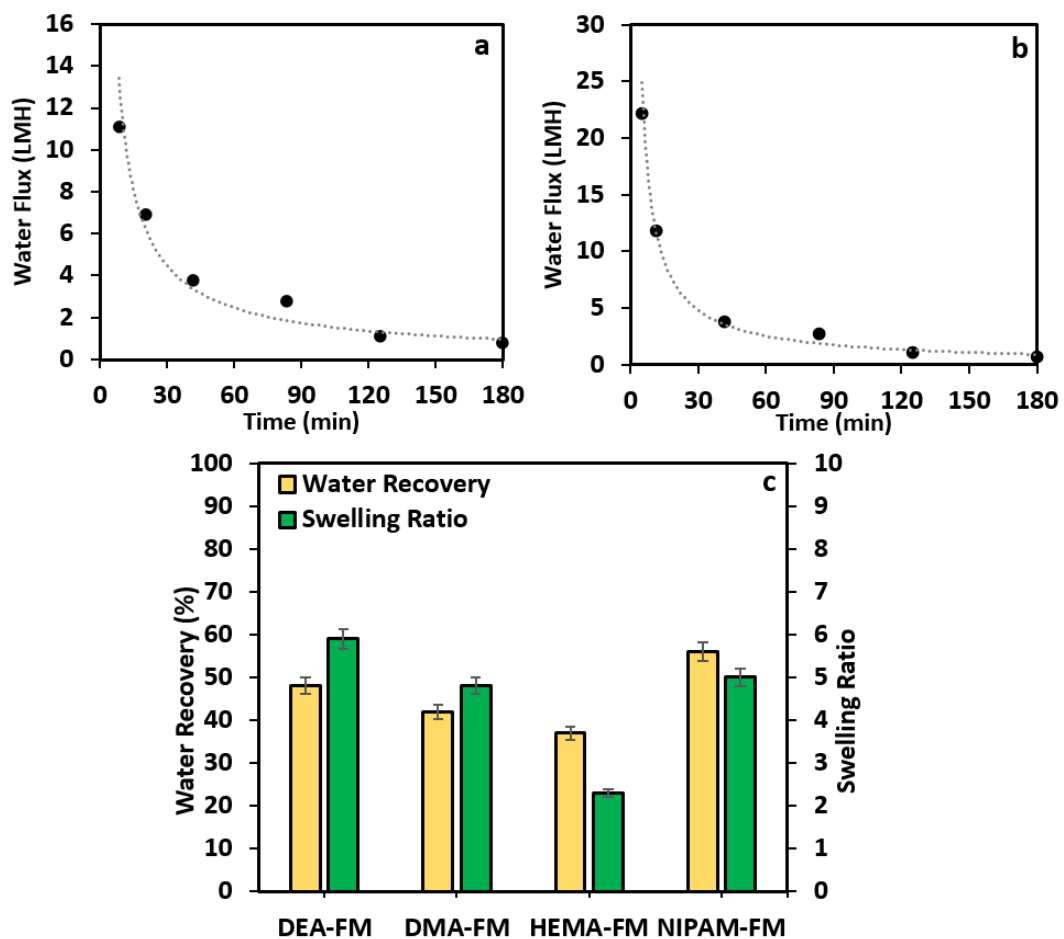
P(HEMA) [53, 54]. However, when poly (HEMA) is subjected to water, it will adsorb water and swell because of partial hydrogen bond formation between the -OH of HEMA and water [51].

The HEMA-5wt% FM microgels have a smaller swelling ratio than DEAEMA-5wt% FM and DMAEMA-5wt% FM microgels (Figure 7c). Consequently, the HEMA-FM microgels reveal a lower water flux (Figure 7a). In addition, HEMA-FM microgels also display poor water recovery than that of DEAEMA-FM and DMAEMA-FM. Zeta potential measurements show the HEMA-FM microgels be negatively charged (Figure S3), attributed to the partially hydrolysis of -OH groups of HEMA and the presence of negative charged APS initiator [55]. Although the zeta potential for HEMA-FM microgels of -25 mV is similar to that of DEAEMA-FM, but HEMA-FM microgels in Figure (7c) do not show a better water recovery performance due to the hydrophobicity after polymerization.

On the other hand, NIPAM-5wt% FM microgels have a lower zeta potential of -3 to -4 mV coming from the negative charges of APS initiator. [56]. NIPAM-5wt% FM microgels have higher responsivity to O<sub>2</sub> evident from their higher swelling ratio than that of HEMA-5wt%FM microgels and DEAEMA-FM microgels (Figure 7c). Since P(NIPAM) is water-soluble in room temperature, it reveals higher capability of swelling/deswelling and water flux compared to HEMA-FM microgels. Also, more hydrophilicity of P(NIPAM) than P(HEMA), results in a higher capillary pressure between the P(NIPAM) microgel particles, based on the wetting-angle-dependent Young–Laplace equation [57]. The initial water flux for NIPAM-5wt% FM is 23 LMH which is comparable with DEAEMA-5wt%FM microgels. Higher water flux of cationic O<sub>2</sub>-responsive microgels compared to NIPAM-FM microgels is due to dissociation of confined counterions to form

additional free counterions within the chain networks of the microgels. Consequently, more osmotic pressure and higher water flux are performed for cationic microgels.

In addition, NIPAM-FM microgels perform higher water recovery ratio than HEMA-FM microgels. Both NPAM and HEMA have the capability of hydrogen bond formation in aqueous solution. HEMA contains one carbonyl (C=O), which acts as proton acceptor, and one hydroxyl (-OH) group on the chain side, which acts as both proton donor and proton acceptor [58]. Therefore, both OH...OH and C=O...HO types of hydrogen-bonds exist in the poly (HEMA) aqueous system. NIPAM has -NH group as hydrogen-donor and C=O as hydrogen-acceptor [59]. Thereby, hydrogen bonding contributes to the solvation and water adsorption for the microgels. NIPAM-5wt% FM microgels show the highest water recovery of 56 % over other microgels. Improvement in the water recovery ratio of NIPAM-FM microgels can be explained by different solvation behaviour form that of cationic comonomers. Cationic microgels dissociate in aqueous system and produce osmotic force to control water adsorption and recovery. While NIPAM-FM microgels do not dissociate in water, hydrogen-bonding formation in aqueous solution dominates adsorb and release of water.



**Figure 7.** Comparison on the non-ionic O<sub>2</sub>-responsive microgels: a) HEMA-5 wt% FM b) NIPAM-5 wt% FM c) water recovery and swelling ratio

## 4.4 Conclusion

For the first time, O<sub>2</sub>-responsive microgels are developed as new draw materials for FO desalination. The fluorine monomers with aromatic and aliphatic structures, responsive to oxygen, are copolymerized with different ionic and non-ionic hydrocarbon monomers to produce functional microgels. Systematic studies show that aliphatic fluorine-containing monomers of FM appears to be more effective than the aromatic FS. 5 wt% FM sounds the best composition of fluoro-monomers in microgels to achieve optimum water adsorption and recovery. On the other hand, water-soluble comonomers also play an important role on FO desalination, where microgels with DMAEMA have higher water flux but a slightly lower recovery ratio than that the microgels prepared by DEAEMA owing to their different hydrophilicity. Moreover, NIPAM as the non-ionic comonomers provides similar water flux as those of charged comonomers but better water recovery due to their different water solvation mechanism.

## Acknowledgement

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**Supporting Information:** Chemical structures of the monomers, digital images of microgel suspensions before and after O<sub>2</sub>/N<sub>2</sub> purging and zeta potentials of the microgels are included as supporting information.

## 4.5 Supporting Information

### **O<sub>2</sub>-Responsive Microgels for Forward Osmosis Desalination**

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List of Figures:

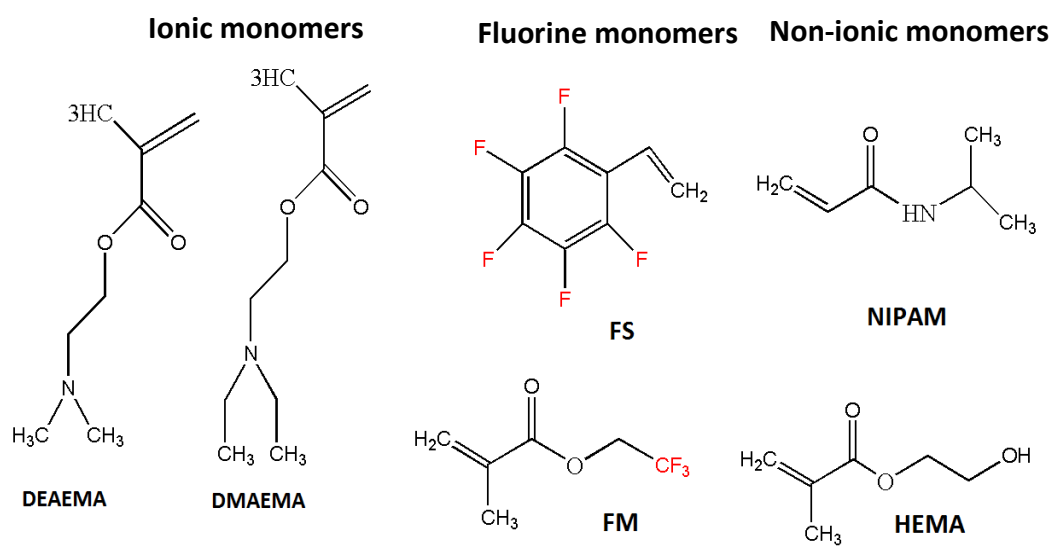
Figure S1 Chemical structures of the monomers used in this study

Figure S2 Digital images of DEAEMA-5wt% FM microgels: a) after O<sub>2</sub> purging  
b) after N<sub>2</sub> purging

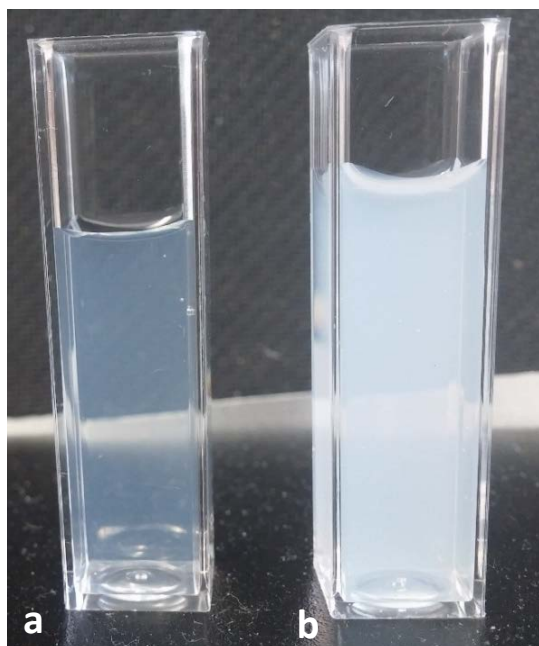
Figure S3 Zeta potentials of the microgels

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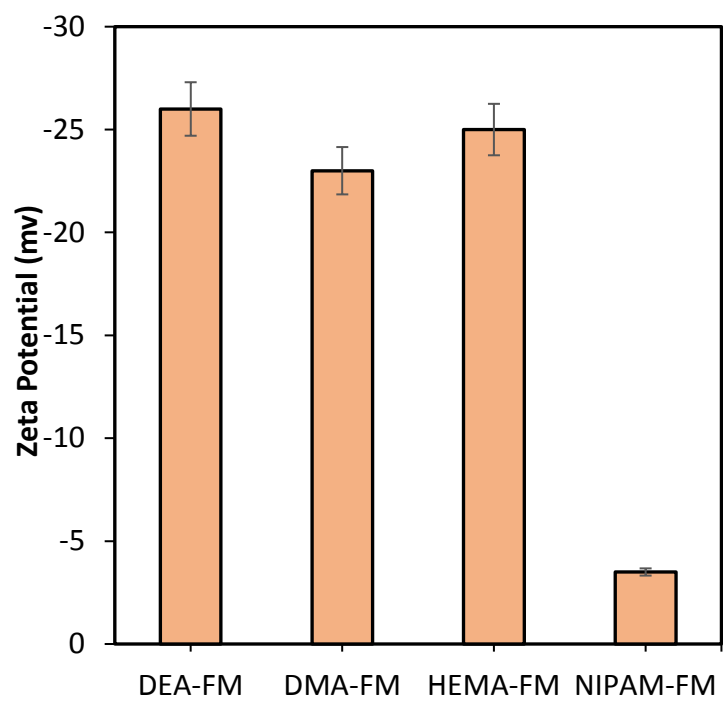


**Figure S1.** Chemical structures of the monomers used in this study



**Figure S2.** Digital images of DEAEEMA-5wt% FM microgels: a) after O<sub>2</sub> purging b) after N<sub>2</sub> purging





**Figure S3.** Zeta potentials of the microgels

## References

- [1] H. Rabiee, M. Soltanieh, S.A. Mousavi, A. Ghadimi, Improvement in CO<sub>2</sub>/H<sub>2</sub> separation by fabrication of poly(ether-b-amide6)/glycerol triacetate gel membranes, *Journal of Membrane Science*, 469 (2014) 43-58.
- [2] H. Rabiee, A. Ghadimi, T. Mohammadi, Gas transport properties of reverse-selective poly(ether-b-amide6)/[Emim][BF<sub>4</sub>] gel membranes for CO<sub>2</sub>/light gases separation, *Journal of Membrane Science*, 476 (2015) 286-302.
- [3] M. Zargar, Y. Hartanto, B. Jin, S. Dai, Hollow mesoporous silica nanoparticles: A peculiar structure for thin film nanocomposite membranes, *Journal of Membrane Science*, 519 (2016) 1-10.
- [4] S.M. Seyed Shahabadi, H. Rabiee, S.M. Seyedi, A. Mokhtare, J.A. Brant, Superhydrophobic dual layer functionalized titanium dioxide/polyvinylidene fluoride-co-hexafluoropropylene (TiO<sub>2</sub>/PH) nanofibrous membrane for high flux membrane distillation, *Journal of Membrane Science*, 537 (2017) 140-150.
- [5] H. Rabiee, S.M.S. Shahabadi, A. Mokhtare, H. Rabiei, N. Alvandifar, Enhancement in permeation and antifouling properties of PVC ultrafiltration membranes with addition of hydrophilic surfactant additives: Tween-20 and Tween-80, *Journal of Environmental Chemical Engineering*, 4 (2016) 4050-4061.
- [6] H. Rabiee, S.M. Seyedi, H. Rabiei, N. Alvandifar, Improvements in permeation and fouling resistance of PVC ultrafiltration membranes via addition of Tetronic-1107 and Triton X-100 as two non-ionic and hydrophilic surfactants, *Water Science and Technology*, 74 (2016) 1469-1483.
- [7] N. Akther, A. Sodiq, A. Giwa, S. Daer, H.A. Arafat, S.W. Hasan, Recent advancements in forward osmosis desalination: A review, *Chemical Engineering Journal*, 281 (2015) 502-522.
- [8] M. Elimelech, W.A. Phillip, The future of seawater desalination: energy, technology, and the environment, *Science*, 333 (2011) 712-717.
- [9] Q. Yang, J. Lei, D.D. Sun, D. Chen, Forward Osmosis Membranes for Water Reclamation, *Separation & Purification Reviews*, 45 (2015) 93-107.
- [10] Y. Cai, X.M. Hu, A critical review on draw solutes development for forward osmosis, *Desalination*, 391 (2016) 16-29.
- [11] A. Achilli, T.Y. Cath, A.E. Childress, Selection of inorganic-based draw solutions for forward osmosis applications, *Journal of Membrane Science*, 364 (2010) 233-241.

- [12] Y. Cai, W. Shen, J. Wei, T.H. Chong, R. Wang, W.B. Krantz, A.G. Fane, X. Hu, Energy-efficient desalination by forward osmosis using responsive ionic liquid draw solutes, *Environ. Sci.: Water Res. Technol.*, 1 (2015) 341-347.
- [13] Z. Li, R. Valladares Linares, S. Bucs, C. Aubry, N. Ghaffour, J.S. Vrouwenvelder, G. Amy, Calcium carbonate scaling in seawater desalination by ammonia-carbon dioxide forward osmosis: Mechanism and implications, *Journal of Membrane Science*, 481 (2015) 36-43.
- [14] Q. Ge, M. Ling, T.-S. Chung, Draw solutions for forward osmosis processes: Developments, challenges, and prospects for the future, *Journal of Membrane Science*, 442 (2013) 225-237.
- [15] L. Chekli, S. Phuntsho, J.E. Kim, J. Kim, J.Y. Choi, J.-S. Choi, S. Kim, J.H. Kim, S. Hong, J. Sohn, H.K. Shon, A comprehensive review of hybrid forward osmosis systems: Performance, applications and future prospects, *Journal of Membrane Science*, 497 (2016) 430-449.
- [16] M.L. Stone, C. Rae, F.F. Stewart, A.D. Wilson, Switchable polarity solvents as draw solutes for forward osmosis, *Desalination*, 312 (2013) 124-129.
- [17] P. Liu, B. Gao, H.K. Shon, D. Ma, H. Rong, P. Zhao, S. Zhao, Q. Yue, Q. Li, Water flux behavior of blended solutions of ammonium bicarbonate mixed with eight salts respectively as draw solutions in forward osmosis, *Desalination*, 353 (2014) 39-47.
- [18] A. Razmjou, G.P. Simon, H. Wang, Polymer Hydrogels as Smart Draw Agents in Forward Osmosis Processes, (2015) 129-149.
- [19] D. Li, X. Zhang, J. Yao, G.P. Simon, H. Wang, Stimuli-responsive polymer hydrogels as a new class of draw agent for forward osmosis desalination, *Chemical Communications*, 47 (2011) 1710-1712.
- [20] G.T. Gray, J.R. McCutcheon, M. Elimelech, Internal concentration polarization in forward osmosis: role of membrane orientation, *Desalination*, 197 (2006) 1-8.
- [21] K.Y. Wang, R.C. Ong, T.-S. Chung, Double-Skinned Forward Osmosis Membranes for Reducing Internal Concentration Polarization within the Porous Sublayer, *Industrial & Engineering Chemistry Research*, 49 (2010) 4824-4831.
- [22] W. kuang, Z. Liu, H. Yu, G. Kang, X. Jie, Y. Jin, Y. Cao, Investigation of internal concentration polarization reduction in forward osmosis membrane using nano-CaCO<sub>3</sub> particles as sacrificial component, *Journal of Membrane Science*, 497 (2016) 485-493.

- [23] N. Ma, J. Wei, S. Qi, Y. Zhao, Y. Gao, C.Y. Tang, Nanocomposite substrates for controlling internal concentration polarization in forward osmosis membranes, *Journal of Membrane Science*, 441 (2013) 54-62.
- [24] Z. Tai, J. Yang, Y. Qi, X. Yan, Q. Xue, Synthesis of a graphene oxide–polyacrylic acid nanocomposite hydrogel and its swelling and electroresponsive properties, *RSC Advances*, 3 (2013) 12751.
- [25] J. Wei, Z.X. Low, R. Ou, G.P. Simon, H. Wang, Hydrogel-polyurethane interpenetrating network material as an advanced draw agent for forward osmosis process, *Water Res*, 96 (2016) 292-298.
- [26] A. Razmjou, Q. Liu, G.P. Simon, H. Wang, Bifunctional Polymer Hydrogel Layers As Forward Osmosis Draw Agents for Continuous Production of Fresh Water Using Solar Energy, *Environmental Science & Technology*, 47 (2013) 13160-13166.
- [27] Y. Hartanto, S. Yun, B. Jin, S. Dai, Functionalized thermo-responsive microgels for high performance forward osmosis desalination, *Water Research*, 70 (2015) 385-393.
- [28] Y. Hartanto, M. Zargar, H. Wang, B. Jin, S. Dai, Thermoresponsive Acidic Microgels as Functional Draw Agents for Forward Osmosis Desalination, *Environ Sci Technol*, 50 (2016) 4221-4228.
- [29] Y. Hartanto, M. Zargar, X. Cui, Y. Shen, B. Jin, S. Dai, Thermoresponsive cationic copolymer microgels as high performance draw agents in forward osmosis desalination, *Journal of Membrane Science*, 518 (2016) 273-281.
- [30] L. Lei, Q. Zhang, S. Shi, S. Zhu, Oxygen and carbon dioxide dual gas-responsive and switchable microgels prepared from emulsion copolymerization of fluoro- and amino-containing monomers, *Langmuir*, 31 (2015) 2196-2201.
- [31] Q. Zhang, S. Zhu, Oxygen-nitrogen switchable copolymers of 2,2,2-trifluoroethyl methacrylate and n,n-dimethylaminoethyl methacrylate, *Macromolecular rapid communications*, 35 (2014) 1692-1696.
- [32] L. Hu, L.-Y. Chu, M. Yang, H.-D. Wang, C. Hui Niu, Preparation and characterization of novel cationic pH-responsive poly(-dimethylamino ethyl methacrylate) microgels, *Journal of Colloid and Interface Science*, 311 (2007) 110-117.
- [33] C. Zhao, J. Zhang, G. Yuan, C.C. Han, CO<sub>2</sub>-triggered liquid–solid switching through a jamming mechanism, *RSC Advances*, 3 (2013) 9645.

- [34] J.Y. Choi, J.Y. Kim, H.J. Moon, M.H. Park, B. Jeong, CO<sub>2</sub> - and O<sub>2</sub> -sensitive fluorophenyl end-capped poly(ethylene glycol), *Macromolecular rapid communications*, 35 (2014) 66-70.
- [35] S. Punyani, P. Narayanan, P. Vasudevan, H. Singh, Sustained release of iodine from a polymeric hydrogel device for water disinfection, *Journal of Applied Polymer Science*, 103 (2007) 3334-3340.
- [36] F.E. Erol, D. Sinirlioglu, S. Cosgun, A.E. Muftuoglu, Synthesis of Fluorinated Amphiphilic Block Copolymers Based on PEGMA, HEMA, and MMA via ATRP and CuAAC Click Chemistry, *International Journal of Polymer Science*, 2014 (2014) 1-11.
- [37] M.L. Becker, E.E. Remsen, K.L. Wooley, Diblock copolymers, micelles, and shell-crosslinked nanoparticles containing poly(4-fluorostyrene): Tools for detailed analyses of nanostructured materials, *Journal of Polymer Science Part A: Polymer Chemistry*, 39 (2001) 4152-4166.
- [38] J.B. DeCoste, G.W. Peterson, Preparation of hydrophobic metal-organic frameworks via plasma enhanced chemical vapor deposition of perfluoroalkanes for the removal of ammonia, *J Vis Exp*, (2013).
- [39] S.J. Lee, S.W. Han, K. Kim, Perfluorocarbon-stabilized silver nanoparticles manufactured from layered silver carboxylates, *Chemical Communications*, (2002) 442-443.
- [40] M.P.S. Andersen, M.D. Hurley, J.C. Ball, W.F. Schneider, T.J. Wallington, O.J. Nielsen, CF<sub>3</sub>CH(ONO)CF<sub>3</sub>: Synthesis, IR spectrum, and use as OH radical source for kinetic and mechanistic studies, *International Journal of Chemical Kinetics*, 35 (2003) 159-165.
- [41] M. Álvarez-Paino, A. Muñoz-Bonilla, G. Marcelo, J. Rodríguez-Hernández, M. Fernández-García, Synthesis and lectin recognition studies of glycosylated polystyrene microspheres functionalized via thiol-para-fluorine "click" reaction, *Polymer Chemistry*, 3 (2012) 3282.
- [42] N. Bilgin, C. Baysal, Y.Z. Menciloglu, Synthesis of fluorinated oligomers for supercritical carbon dioxide applications, *Journal of Polymer Science Part A: Polymer Chemistry*, 43 (2005) 5312-5322.
- [43] Q. Zhang, S. Zhu, Oxygen and Carbon Dioxide Dual Responsive Nanoaggregates of Fluoro- and Amino-Containing Copolymer, *ACS Macro Letters*, 3 (2014) 743-746.

- [44] Q. Zhang, L. Lei, S. Zhu, Gas-Responsive Polymers, *ACS Macro Letters*, 6 (2017) 515-522.
- [45] M. Yue, Y. Hoshino, Y. Ohshiro, K. Imamura, Y. Miura, Temperature-responsive microgel films as reversible carbon dioxide absorbents in wet environment, *Angewandte Chemie*, 53 (2014) 2654-2657.
- [46] X. Fan, H. Liu, Y. Gao, Z. Zou, V.S. Craig, G. Zhang, G. Liu, Forward-Osmosis Desalination with Poly(Ionic Liquid) Hydrogels as Smart Draw Agents, *Adv Mater*, 28 (2016) 4156-4161.
- [47] T. Missana, A. Adell, On the Applicability of DLVO Theory to the Prediction of Clay Colloids Stability, *J Colloid Interface Sci*, 230 (2000) 150-156.
- [48] A.J. Morse, S.P. Armes, K.L. Thompson, D. Dupin, L.A. Fielding, P. Mills, R. Swart, Novel Pickering emulsifiers based on pH-responsive poly(2-(diethylamino)ethyl methacrylate) latexes, *Langmuir*, 29 (2013) 5466-5475.
- [49] S. Dai, P. Ravi, K.C. Tam, B.W. Mao, L.H. Gan, Novel pH-Responsive Amphiphilic Diblock Copolymers with Reversible Micellization Properties, *Langmuir*, 19 (2003) 5175-5177.
- [50] S. Dai, P. Ravi, K.C. Tam, pH-Responsive polymers: synthesis, properties and applications, *Soft Matter*, 4 (2008) 435-449.
- [51] J.-P. Montheard, M. Chatzopoulos, D. Chappard, 2-Hydroxyethyl Methacrylate (HEMA): Chemical Properties and Applications in Biomedical Fields, *Journal of Macromolecular Science, Part C: Polymer Reviews*, 32 (1992) 1-34.
- [52] X.-P. Qiu, F. Tanaka, F.M. Winnik, Temperature-Induced Phase Transition of Well-Defined Cyclic Poly(N-isopropylacrylamide)s in Aqueous Solution, *Macromolecules*, 40 (2007) 7069-7071.
- [53] X. Zhang, L. Zhou, X. Zhang, H. Dai, Synthesis and solution properties of temperature-sensitive copolymers based on NIPAM, *Journal of Applied Polymer Science*, 116 (2010) 1099-1105.
- [54] Z. Shen, K. Terao, Y. Maki, T. Dobashi, G. Ma, T. Yamamoto, Synthesis and phase behavior of aqueous poly(N-isopropylacrylamide-co-acrylamide), poly(N-isopropylacrylamide-co-N,N-dimethylacrylamide) and poly(N-isopropylacrylamide-co-2-hydroxyethyl methacrylate), *Colloid and Polymer Science*, 284 (2006) 1001-1007.

- [55] W. Liu, X. Zhou, Z. Mao, D. Yu, B. Wang, C. Gao, Uptake of hydrogel particles with different stiffness and its influence on HepG2 cell functions, *Soft Matter*, 8 (2012) 9235.
- [56] Y. Utashiro, M. Takiguchi, M. Satoh, Zeta potential of PNIPAM microgel particles dispersed in water—effects of charged radical initiators vs. OH<sup>-</sup> ion adsorption, *Colloid and Polymer Science*, 295 (2016) 45-52.
- [57] P. Atkins, J.D. Paula, *Physical Chemistry*, W. H. Freeman and Company, New York, 2006.
- [58] S. Morita, Hydrogen-bonds structure in poly(2-hydroxyethyl methacrylate) studied by temperature-dependent infrared spectroscopy, *Front Chem*, 2 (2014) 10.
- [59] M. Keerl, V. Smirnovas, R. Winter, W. Richtering, Interplay between hydrogen bonding and macromolecular architecture leading to unusual phase behavior in thermosensitive microgels, *Angewandte Chemie*, 47 (2008) 338-341.

## **Chapter 5.**

# **CONCLUSIONS AND RECOMMENDATIONS**



This thesis focused on development of gas-responsive smart microgels as an efficient draw solution for forward osmosis desalination. CO<sub>2</sub> and O<sub>2</sub> were selected as the trigger gas and CO<sub>2</sub>-responsive and O<sub>2</sub>-responsive microgels were synthesised and analysed as efficient draw solutions. The key conclusions and recommendation for further research are mentioned here.

## 5.1 Conclusions

CO<sub>2</sub>-responsive microgels were synthesised via surfactant-free emulsion and dispersion polymerization. The key outcomes of regarding to CO<sub>2</sub>-responsive microgels are listed below:

1. Two types of cationic monomers were selected to synthesise CO<sub>2</sub>-responsive microgels, diethylaminoethyl methacrylate (DEAEMA) and dimethylaminoethyl methacrylate (DMAEMA). In terms of swelling ratio, water flux and water recovery, DEAEMA microgels exhibited better performance due to higher pK<sub>a</sub> of DEAEMA than DMAEMA.
2. DEAEMA CO<sub>2</sub>-responsive microgels with three different crosslinkers, polyethylene glycol diacrylate (PEGDA), Methylenebisacrylamide (BIS) and Ethylene glycol dimethylacrylate (EGDMA), were synthesised. Microgels with PEGDA crosslinker showed better water flux because of long chains of PEGDA. DEAEMA microgels with 1wt% PEGDA showed a water flux as high as 56 LMH with the water recovery ratio around 50%. In addition, crosslinker concentration above 1wt% resulted in less swellability of microgels.
3. Water recovery of CO<sub>2</sub>-responsive microgels was carried out at the isoelectric point, where the microgels are almost neutral and release the adsorbed water easily.

4. In addition to DEAEMA and DMAEMA, 1-vinylimidazole and 4-vinylpyrrolidone microgels were also selected for synthesis. Polymerization of 1-vinylimidazole was not successful via emulsion or dispersion polymerization and 4-vinylpyrrolidone microgels did not show any response to CO<sub>2</sub>/N<sub>2</sub> gas purging; therefore, they were not chosen for further study.

As, CO<sub>2</sub> can change the pH of the produced water and diffuse to the feed side and make the feed acidic, O<sub>2</sub>-responsive microgels were considered as another draw solution for FO desalination. The study on O<sub>2</sub>-responsive microgels resulted in the following outcomes:

1. Two commercially available fluoro containing monomers, trifluoroethyl methacrylate (FM) and pentafluorostyrene (FS), were selected to be co-polymerized with four ionic and non-ionic via emulsion and dispersion polymerization. Compared to FS, FM co-polymerized microgels showed better water flux as FM is more hydrophilic.
2. Results of DEAEMA-FM microgels revealed that concentration of FM above 5wt% leads to less swellability of the microgels.
3. DMAEMA-FM microgels had slightly higher water flux than DEAEMA-FM microgels, while less water recovery. DEAEMA/DMAEMA-5wt% FM microgels performed water flux between 26 to 29 LMH.
4. Hydroxyethylmethacrylate (HEMA)/ Isopropylacrylamide (NIPAM)-FM microgels were synthesised to analyse the effect of using non-ionic monomers. HEMA did not exhibit any improvement in water flux and recovery due to negative charges from –OH, but NIPAM showed better water recovery (56%) and comparable water flux.

5. Pure FM and FS microgels did not exhibit any response to O<sub>2</sub>, due to superhydrophobicity of fluorine polymers.

## **5.2 Recommendations for future research**

This study attempted to introduce the concept of using gas-responsive microgels as an efficient draw solution for FO desalination for the first time. However, more studies are required to understand the different aspects of these draw agents. First, other suitable materials with better water recovery must be developed to obtain complete recovery without applying any heating. In addition, ionic liquids can be a great option to provide high water flux as these materials are naturally ionic, and their responsivity to gas or temperature is not affected by their ionic feature very much. Gas-responsive ionic liquids have been synthesised recently, and they showed a sharp response to CO<sub>2</sub>. Therefore, synthesis of microgels with these ionic liquids might lead to better results. This study used several monomers for microgel synthesis, considering that some of them were not successful however, more investigation can result in materials that are more efficient.

Moreover, the process we used here was batch and it is not quite applicable for real application in desalination. Microgels are recovered after removing from the membrane and then they are used again. This is very important to concentrate on the technical part of using microgels or hydrogels as a draw solution for the FO process. In this regard, this is required to discover a way to attach the microgels to the surface of the membrane, without causing any defects and make a membrane module (flat-sheet or spiral wound). Thereby, it is suggested that more studies regarding to efficient materials and technical part should be carried out in the future.