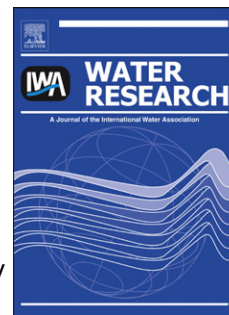


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# **Towards Temperature Driven Forward Osmosis Desalination Using Semi-IPN Hydrogels as Reversible Draw Agents**

Yufeng Cai<sup>1,2</sup>, Wenming Shen<sup>1,2</sup>, Siew Leng Loo<sup>2,3</sup>, William B. Krantz<sup>2,4</sup>, Rong Wang<sup>2,3</sup>, Anthony G. Fane<sup>2,3</sup>, Xiao Hu<sup>\*1,2</sup>

<sup>1</sup>School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, <sup>2</sup>Singapore Membrane Technology Centre, <sup>3</sup>School of Civil and Environmental Engineering, Nanyang Technological University, Singapore, <sup>4</sup>School of Chemical Engineering, University of Colorado, USA

## **Abstract**

We report a study to explore new materials and a new concept for temperature driven quasi-continuous desalination using hydrogels as draw agents in forward osmosis (FO). This concept is enabled by the design and preparation of thermally responsive hydrogels having a semi-interpenetrating network (semi-IPN) structure. Thermally responsive semi-IPN hydrogels were synthesized by polymerization of N-isopropylacrylamide (NIPAm) in the presence of polysodium acrylate (PSA) or polyvinyl alcohol (PVA). Their functions as draw agents in FO were systematically studied and compared with hydrogels prepared from the PNIPAm homopolymer or the NIPAm-SA copolymer. While the semi-IPN hydrogels displayed the desirable balanced thermally responsive swelling and dewatering behavior, the NIPAm-SA copolymer hydrogels were found to have poor dewatering behavior, making them unsuitable for a continuous temperature driven desalination process. At 40 °C, the semi-IPN hydrogels rapidly release

nearly 100% of the water absorbed during the FO drawing process carried out at room temperature. Results clearly indicate the potential of semi-IPN hydrogels as semi-solid draw agents in the FO process, in which quasi-continuous desalination could be achieved by cyclic heating and cooling within a moderate temperature change.

**Keywords:** Forward osmosis, Temperature-driven, Desalination, Thermally responsive semi-IPN hydrogel, Reversibility

\*Corresponding Author: Hu X (Email: asxhu@ntu.edu.sg)

## Introduction

Forward osmosis as a novel membrane separation technology has attracted much attention because of its advantages over reverse osmosis such as low energy consumption, less fouling problems and high water recovery (Cath et al., 2006; Chekli et al., 2012). One of the key challenges in FO processes is the limited choice of draw solutes. An ideal draw solute should generate a high osmotic pressure and subsequently a high water flux while being readily recovered and reused at low energy consumption (Chekli et al., 2012). In addition, other criteria such as low reverse ion diffusion, non-toxicity and minimal membrane degradation should also be taken into consideration. Sugar (J.O.Kessler and C.D.Moody 1976; Kravath and Davis 1975) and ammonium carbonate (McCutcheon et al., 2006) have been studied as draw solutes to desalinate seawater via the FO process. However, the application of edible sugar as a draw solute is usually limited to emergency life saving hydration devices rather than large scale desalination. Ammonium carbonate encounters problems including reverse ion diffusion, an

unpleasant odor and underlying health issues. Polymer decorated superparamagnetic nanoparticles (Ge et al., 2011) have attracted much attention since they may be easily recovered by a magnetic field and provide a reasonable osmotic pressure owing to their nano-scale dimension. However, problems associated with the agglomeration of magnetic nanoparticles under a strong magnetic field and the consequent decreased osmotic pressure during reuse of such particles have not been resolved (Ling et al., 2011). A range of other possible draw solute candidates including polypropylene glycol (Jorgensen 2009), polyelectrolytes (Ge et al., 2012), positively charged inorganic salt/negatively charged magnetic nanoparticles complex (Liu et al., 2011) and ionic liquids (Yen et al., 2010) have also been studied in the search for the “ideal” draw solute.

Recently, hydrogels as a new class of draw agent for FO have been proposed. Hydrogels can absorb water through a FO membrane driven by swelling pressure; their insoluble crosslinked network enables dewatering under thermal and mechanical stimuli. An ionizable poly sodium acrylate (PSA) hydrogel produces the highest water flux but only less than 5% of the absorbed water can be released at 50 °C and 3 MPa. Although the PNIPAm hydrogels were shown to release about 70% of the absorbed water, they had a much lower water flux. Surprisingly, attempts to use copolymers of sodium acrylate (SA) and NIPAm did not result in the anticipated synergy of water flux and water recovery (Li et al., 2011a). Although the water flux was increased relative to a pure PNIPAm hydrogel by using a copolymer due to the incorporation of SA, the thermally responsive dewatering behavior was not observed in the copolymer. In more recent studies (Li et al., 2013; Li et al., 2011b; Zeng et al., 2013), hydrophilic carbon particles and graphene oxide were incorporated into a NIPAm-SA copolymer hydrogel as solar energy

absorbents. It is interesting that dewatering of this composite hydrogel was achieved via simple exposure to simulated sunlight by which the temperature was increased to up to 55 °C. Significantly better water release was reported in the composite hydrogel although the dewatering time was still long. However, the fact that the water released was mostly in the vapor state indicates that the release was through a heat assisted desiccation mechanism rather than through the stimulus induced dewatering of a thermally responsive hydrogel. The reliance on light irradiation may pose additional challenges for its practical implementation into a desalination module. Therefore, although hydrogels are very attractive candidates as FO draw agents because of their potential to circumvent the problems associated with the recovery of the draw agent, the challenge to improve the water flux while maintaining facile and efficient dewatering needs to be addressed.

In this paper we will discuss the preparation of PNIPAm-PSA or PNIPAm-PVA semi-IPNs and the mechanisms whereby they can be used as draw agents for temperature driven FO desalination of brackish water. Although the synthesis of semi-IPNs has been earlier reported (Dhara et al., 2001; Harmon et al., 2003), there is no discussion relative to the mechanisms or processes of desalination. Our findings show that a balanced water absorbing and dewatering behavior of the semi-IPN hydrogels is essential towards a temperature driven quasi-continuous FO desalination.

## 1. Material and methods

### 1.1. Materials

N-isopropylacrylamine (NIPAm,  $\geq 98\%$ ) was purchased from Wako Pure Chemical Industries Ltd. (Japan). N,N'-methylenebis(acrylamide) ( $\geq 99\%$ , crosslinker), sodium acrylate (97%), polyvinyl alcohol (PVA,  $M_w=61,000$ ) and N,N,N',N'-tetramethylethylenediamine (TEMED, accelerator, 99%) were purchased from Sigma-Aldrich. Ammonium peroxydisulfate (initiator, 98%) was purchased from Alfa Aesar. Linear PSA was prepared by free radical polymerization via standard methods (Li et al., 2004; Yamashita et al., 2003). FO membranes made from cellulose triacetate (lot No. 110707-ES-1) were supplied by Hydration Technologies Inc. (HTI), USA. Deionized water ( $18\text{M}\Omega\cdot\text{cm}$ ) was used for all experiments; all chemicals were used as received.

### 1.2. Preparation of Hydrogels

The PNIPAm/PSA and PNIPAm/PVA semi-IPNs were synthesized by polymerizing NIPAm in the presence of linear PSA and PVA, respectively. As a comparison, PNIPAm/PSA copolymer hydrogel was synthesized by random copolymerization of NIPAm and SA. The feed compositions are summarized in Table 1.

**Table 1 Synthesis compositions for hydrogels<sup>a</sup>**

Sample	Code	NIPAm(M)	SA(M)	PVA(M)	MBA <sup>b</sup> (mM)	APS <sup>c</sup> (mM)	TEMED <sup>d</sup> (mM)
1M PNIPAm	PNIPAm	1	-	-	20	10	10
PNIPAm-co-PSA(0.8M:0.2M)	co-0.2PSA	0.8	0.2	-	20	10	10
PNIPAm-IPN-PSA(0.8M:0.2M)	SI-0.2PSA	0.8	0.2 <sup>e</sup>	-	16	8	8
PNIPAm-IPN-PVA(0.8M:0.2M)	SI-0.2PVA	0.8	-	0.2	16	8	8

PNIPAm-IPN- PVA (0.5M:0.5M)	SI- 0.5PVA	0.5	-	0.5	10	5	5
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a. Initiator, accelerator and crosslinker are 1 mol%, 1 mol%, 2 mol% with respect to to monomer (NIPAm for all semi-IPNs; NIPAm and SA for copolymerization), respectively. b. In 2% (w/v) aqueous solution. c. In 10% (w/v) aqueous solution. d. In 5% (v/v) aqueous solution. e. refers to concentration of PSA monomer unit.

In this study the total repeat unit concentration is 1M. For example, to prepare SI-0.5PVA, the NIPAm concentration and PVA repeat unit were both 0.5M. In actual synthesis the predetermined amount of NIPAm, MBA and PSA or PVA were first dissolved in DI water at 70°C under constant stirring until a homogeneous solution was made. The solution was then cooled to room temperature and bubbled with pure nitrogen for 30 minutes before TEMED and APS were added in sequence. The polymerization was carried out for 24 hours at room temperature. The semi-IPN hydrogels were washed with large quantities of DI water for 5 days with a change of water every 8 hours to leach the low molecular weight molecules.

### 1.3. Characterization

The hydrogels were immersed in DI water for 3 days to ensure that the equilibrium swollen state was reached. The swollen hydrogels were cut into disks with a diameter of 24mm and thickness of approximately 3mm, and then immersed into 40 °C water for 10 minutes to measure the dewatering profile. The excess free water on the hydrogel surface was removed by a gentle vacuum suction for 2 seconds before each weighing. The hydrogel disks after the deswelling measurement at 40 °C were dried in a vacuum oven at 50 °C until a constant weight ( $W_d$ ) was reached, based on which the swelling ratios and water retentions during the deswelling period could be calculated. The swelling ratio is defined as  $(W_t - W_d)/W_d$ , where  $W_t$  is

weight of hydrogel at particular time during deswelling,  $W_d$  is the weight for the completely dry state.

The lower critical solution temperature (LCST) of each hydrogel was determined by a differential scanning calorimeter (TA Q10 Modulated DSC, TA Instruments). The hydrogels were swollen to equilibrium before the DSC measurement. For each DSC measurement, approximately 20 mg of swollen hydrogel was placed into a hermetically sealed aluminum pan. The temperature range was from 20 °C to 50 °C at a heating rate of 3 °C/min. Dry nitrogen was used for purging at a flow rate of 50 mL/min.

#### 1.4. Hydrogel dewatering and FO draw agent assessment

A 24mm diameter, disk-shaped, hydrogel aggregate was fabricated using 400 mg of dry polymer particles of <200  $\mu\text{m}$  in size. The disk was allowed to swell to a swelling ratio of approximately 2 to form an integral aggregate with a typical thickness of approximately 3 mm, as shown in Figure 1(c). The swollen disk then was allowed to deswell at 40 °C in water. The deswelling profile was obtained by monitoring its weight decrease as a function of time. The hydrogel discs maintained excellent mechanical integrity during the swelling and deswelling studies. The hydrogel disc, after pre-conditioning by first swelling to a ratio of 2 followed by deswelling to an equilibrium plateau at 40 °C, was then placed on the FO membrane to measure its performance as a draw agent for brackish water. The water flux is defined as  $V/(A \cdot t)$ , where  $V$  is the volume (L) of water permeating through the membrane,  $A$  is the contact area ( $\text{m}^2$ ) between the hydrogel and membrane, and  $t$  is the FO process time (h). In this study the water flux measurement was conducted for 5 hours using an apparatus built in-house as shown in Figure 1 (a and b). The chamber filled with an aqueous solution of 2000 ppm NaCl



(brackish water) and an FO membrane was sealed with a rubber O-ring that was compressed via screws. A small tube linked the chamber with the ambient air. The water level was maintained approximately 5 cm higher than the FO membrane to ensure that the brackish solution was always in contact with the FO membrane and that the hydraulic pressure in the small tube had a negligible effect. The water flux was determined by monitoring the hydrogel weight increase. Magnetic stirring in the brackish water was used to minimize concentration polarization. After the FO process the hydrogel disc was immersed into 40 °C water to release the absorbed water. The cycle was repeated 3 times to study the reversibility of these hydrogels as a FO draw agent.

## **2. Results and discussion**

### **2.1. Swelling and Deswelling of semi-IPN hydrogels**

Figure 2(a) shows that both hydrophilic linear PVA and PSA chains incorporated into the thermally responsive PNIPAm networks substantially increase the equilibrium swelling ratio of the hydrogels. Furthermore, all the semi-IPN hydrogels display excellent thermally responsive water recovery or dewatering efficiency at 40 °C, with the resulting percentage recoveries being even higher than that for the pure PNIPAm hydrogel. This behavior was attributed to the presence of linear hydrophilic chains, such as PSA or PVA, forming a type of water release 'channel', which enhances thermally induced water release even though the semi-IPN are more hydrophilic than PNIPAm (Zhang et al., 2003). Although the NIPAm-SA copolymer hydrogel (co-0.2PSA), which has the same chemical composition as the semi-IPN (SI-0.2PSA), also shows similar improved equilibrium swelling ratio, the copolymer hydrogel gives virtually no water

recovery efficiency under the same conditions. The PNIPAm and the semi-IPN hydrogel discs formed from particle aggregates can rapidly dewater and shrink from even a low swelling ratio (SR) of about 2 at 40°C (Figure 2(b)). All the thermally responsive semi-IPN hydrogels reached equilibrium, i.e., the minimum plateau swelling ratio at 40 °C, after only 10 minutes of deswelling, while the NIPAm-SA copolymer continues absorbing water at the same temperature and shows no water release. Note that in this study we have focused in particular on the dewatering behavior of the hydrogels from a low initial swelling ratio of 2, although studying the dewatering behavior of the hydrogels from a high swelling ratio (e.g., from their maximum or equilibrium swell ratios) is still useful (Figure 2(a)). We believe, an understanding of the dewatering from a low swelling ratio is more relevant to their use as draw agents in an FO process because the water flux generated by the hydrogels diminishes when the swelling ratio is higher than 2 according to our study. The rapid and efficient thermally induced water recovery (dewatering) of the semi-IPN hydrogels at the low swelling ratio is an advantageous characteristic for the semi-IPN hydrogels for use as FO draw agents, which will be discussed in more detail later. For better comparison, the plateau swelling ratio at 40°C was defined as the onset point swelling ratio (OPSR) from which the hydrogels start to draw water across the membrane in the FO process in this work. In other words, for the subsequent FO process studies, all hydrogels were first pre-conditioned at 40 °C before being used as draw agents. Based on Figure 2(b), the OPSRs for PNIPAm, SI-0.2PVA, SI-0.5PVA and SI-0.2PSA are  $0.50 \pm 0.01$ ,  $0.73 \pm 0.01$ ,  $0.75 \pm 0.01$  and  $0.92 \pm 0.01$  respectively. The hydrophilic polymer, especially ionic PSA, enhances the OPSR due to its affinity for water molecules; however, the thermo-sensitivity is preserved and makes it possible for semi-IPNs to effectively release water under a thermal

stimulus. Another point worth discussing is the deswelling distinction between SI-0.2PSA and co-0.2PSA despite their similar room temperature equilibrium swelling ratios. Ionic SA incorporated during the copolymerization with NIPAm would increase the copolymer's LCST to higher than 80 °C with the SA/NIPAm ratio of 1:4 for co-0.2PSA (Hirose et al., 1987), while the semi-IPN hydrogel with the same SA/NIPAm dose ratio maintained the PNIPAm's thermosensitivity. This distinction can be ascribed to the charge distribution inside the hydrogels. Randomly distributed charges from copolymerization would jeopardize the formation of hydrophobic aggregates due to the hydration of immobilized  $\text{COO}^-$  and  $\text{Na}^+$  ions as well as strong electrostatic repulsion (Kokufuta et al., 1998); while the localized charge from semi-IPN and the mobility of the linear polymer mitigate these influences on the hydrophobic aggregate formation.

Figure 3 shows that all the semi-IPN hydrogels are thermally sensitive with LCSTs between 33 to 35 °C close to that of the PNIPAm. Interestingly, the LCSTs of the semi-IPN hydrogels are counter-intuitively lower than those of the PNIPAm. This phenomenon was ascribed to a unique effect due to hydrogen bonding between PVA and PNIPAm for PNIPAm/PVA semi-IPNs (Shin et al., 1998). However, no one has reported the lowering of the LCST for PNIPAm/PSA semi-IPNs for which the mechanisms might be complex. It is believed that, while there still may be hydrogen bonding between PSA and NIPAm, the PSA, being a polyelectrolyte, may have an effect analogous to other inorganic electrolytes (e.g., NaCl or  $\text{NaNO}_3$ ), which were shown to have caused the lowering of the LCST of PNIPAm (Zhang and Cremer 2006). The existence of the LCSTs in the semi-IPNs containing linear hydrophilic polymers is the basis for these hydrogels to have a substantially higher swelling ability than the PNIPAm while maintaining an excellent

thermally responsive behavior. Note that no LCST was detected in the same temperature range for the NIPAm-SA copolymer co-0.2PSA (see Figure 3).

## 2.2. FO process and reversibility

In contrast to prior studies using hydrogels as a draw agent in which the one-time FO process was started with completely dry hydrogels (Li et al., 2011a; Li et al., 2011b), the FO process reported in this work started with partially-swollen hydrogels pre-conditioned to the respective OPSRs at 40°C. This is because in our subsequent cyclic reversibility study the dewatering was always carried out at 40 °C. The pre-conditioned hydrogel discs at the OPSRs were then put onto the FO membrane as draw agents. Figure 4 shows the water flux in liters per square meter per hour (LMH) and corresponding swelling ratio as a function of time for each hydrogel during the FO process. The incorporation of a linear hydrophilic polymer or polyelectrolyte imparts two contrasting effects on the FO process in terms of the water flux. On the one hand, a hydrophilic polymer, especially a polyelectrolyte, PSA, increases the water flux dramatically. For example, it is clearly visible in Figure 4 that all the semi-IPN hydrogels generate a higher water flux than the pure PNIPAm hydrogel; moreover, SI-0.2PSA generates a higher water flux than SI-0.2PVA. A more meaningful way to compare the ability to absorb water among the different hydrogels is to compare the water flux at the same swelling ratio. The plots of LMH versus swelling ratio for the hydrogels, shown in Figure 5(a), clearly indicate the decreasing trend of flux with increasing swelling ratio. All the semi-IPN hydrogels generate a higher water flux than the PNIPAm hydrogel at each swelling ratio. For example, at a swelling ratio of 1, the water fluxes generated by the semi-IPN hydrogels are expected to be 0.18, 0.18 and 0.12 LMH

for SI-0.2PSA, SI-0.5PVA and SI-0.2PVA, which are 2.6, 2.6 and 1.7 times the 0.07 LMH observed for the PNIPAm hydrogel. On the other hand, as discussed earlier (Figure 2(b)), the incorporation of PVA or PSA increases the OPSRs which are the points from which the FO process commences (OPRS was earlier defined as the plateau swell ratio after dewatering at 40 °C with reference to Figure 2). Therefore, the semi-IPNs as draw agents were operated at higher swelling ratios than the PNIPAm. This is disadvantageous in terms of water flux. Fortunately, the enhancement of the drawing effect of PVA or PSA incorporation outweighs the negative effect of increasing the OPSR in the semi-IPNs as shown in Figure 4. For example, the average water fluxes generated by SI-0.5PVA and SI-0.2PSA are still 85% and 58% higher than that of the PNIPAm for the first hour in the FO process.

The competition between these two effects for the three semi-IPNs also determines their performance in the FO process. At the same swelling ratio, the water flux generated by the SI-0.2PSA (0.183LMH at SR=1) is virtually the same as that for the SI-0.5PVA (0.177LMH at SR=1), as seen in Figure 5(a). However, the SI-0.5PVA has a lower OPSR and therefore a larger swelling ratio difference between the swelled state (at room temperature) and deswelled state (at 40 °C) than that observed for the SI-0.2PSA during the FO process. Actually in using reversible hydrogels as draw agents, the reversible swelling ratio span (between the drawing and dewatering temperatures) is also a critical parameter to be considered besides the LMH values. For example, Figure 5 (a) shows that during the FO process, the swelling ratios increased in comparison to their OPSRs by 0.54, 0.66, 0.74 and 0.87 for PNIPAm, SI-0.2PVA, SI-0.2PSA and SI-0.5PVA, respectively. This means that while SI-0.2PSA drew and recovered 37% more water than PNIPAm, the SI-0.5PVA drew and recovered 61% more water than PNIPAm, even though

250 they have generated similar water fluxes at the same swelling ratio. In fact, the LMH versus SR  
 251 plots in Figure 5(a) for SI-0.2PSA and SI-0.5PVA virtually overlap each other. In order to further  
 252 understand the FO drawing and dewatering performance of the hydrogels, it is useful to  
 253 introduce the reversible swelling ratio span parameter, which is the difference between the  
 254 OPSR (defined earlier) and the EPSR (end point swelling ratio). The EPSR is the swelling ratio of  
 255 the hydrogel at the end of the room temperature FO drawing process, prior to the dewatering  
 256 process by heating to 40 °C. Figure 5(b) schematically shows that during the FO process using a  
 257 hydrogel as the draw agent, the hydrogel swells from the OPSR to the EPSR while the water flux  
 258 reduces from  $LMH_{onset}$  to  $LMH_{end}$ . Because of their thermally responsive behavior, the swollen  
 259 hydrogels will undergo dewatering and shrink to the OPSR upon heating to 40 °C. (This allows  
 260 the next cycle of FO drawing using the dewatered hydrogels.) The amount of water,  $m_{w, recovered}$ ,  
 261 that can be recovered from a hydrogel during one FO drawing and de-watering cycle is  
 262 determined by the reversible swelling ratio span, i.e.,  $EPSR - OPSR$ . In fact,  $m_{w, recovered} = (EPSR -$   
 263  $OPSR) \times m_{gel, dry}$ , where  $m_{gel, dry}$  is the mass of the dried hydrogel used. If for ease of comparison  
 264 between the hydrogels for example in this work we define the EPSR to be the SR when the  
 265 water flux is reduced to 0.1 LMH, the EPSRs of the PNIPAm and the semi-IPN hydrogels can be  
 266 determined from Figure 5(a). Table 2 tabulates the values of the OPSR, EPSR and  $(EPSR - OPSR)$  of  
 267 these hydrogels. It can be clearly seen that all the semi-IPN hydrogels have a higher EPSR than  
 268 the PNIPAm hydrogel. The reversible swelling ratio spans  $(EPSR - OPSR)$  of the semi-IPN  
 269 hydrogels are also larger than that of the PNIPAm hydrogel despite higher OPSRs for the semi-  
 270 IPNs. For example, the reversible swelling ratio span for SI-0.5PVA is 0.75 (g/g) is 240% larger

than that of the PNIPAm hydrogel. For the NIPAm and SA based hydrogels, the PSA is expected to have the highest swelling and drawing power and hence the highest EPSR. However, its

Table 2 OPSR, EPSR and the reversible swelling ratio span of the PNIPAm and the semi-IPN hydrogels\*

Hydrogel Code	OPSR	EPSR	EPSR-OPSR
<b>PNIPAm</b>	0.50	0.72	0.22
<b>SI-0.2PVA</b>	0.73	1.18	0.45
<b>SI-0.2PSA</b>	0.92	1.50	0.58
<b>SI-0.5PVA</b>	0.75	1.50	0.75

\*Note that the EPSR is defined as the swelling ratio when the water flux is reduced to 0.1 LMH.

OPSR is also high (virtually the same value as the EPSR because the PSA hydrogel is not expected to dewater at 40 °C). Hence the  $m_{w, \text{recovered}}$  is virtually 0 during the thermal cycles between room temperature and 40 °C. On the other hand, although the thermally responsive PNIPAm hydrogel has the lowest OPSR, its EPSR is also low. Hence, in either case, the amount of recovered water is small. For the semi-IPN hydrogels, the incorporated hydrophilic PVA or PSA chains not only increase the water flux and EPSR substantially, but also preserve the excellent thermally responsive properties. Although the OPSR values are higher in the semi-IPNs compared to the PNIPAm, they still yielded larger amounts of water during the temperature-driven FO drawing (at room temperature) and dewatering (at 40 °C) cycle. Therefore, balanced FO drawing and dewatering properties are the essential characteristics that make these semi-IPNs suitable candidates as FO draw agents. Based on this understanding, future materials optimization or new hydrogel development aimed at maximizing  $m_{w, \text{recovered}}$  should target

hydrogels with an OPSR after heat induced dewatering that is as low as possible and with an EPSR that is as high as possible for a given  $LMH_{end}$  as suggested by Figure 5(b).

Figure 6 shows the water flux versus time for three consecutive cycles for the semi-IPN and the PNIPAm hydrogels, which indicates that the drawing and dewatering cycles are highly reversible. The reversibility of these hydrogels was imparted by the thermo-sensitivity of the PNIPAm structure, while incorporated hydrophilic linear polymers that enable the semi-IPN hydrogels to absorb and subsequently release more water during one cycle.

### 2.3. Quasi-continuous FO desalination using a semi-IPN hydrogel

Note that although the water flux (LMH) of hydrogel draw agents are still low compared to those of a solution based draw agent such as  $NH_3HCO_3$ , they are still interesting because hydrogels eliminate the need of draw solute regeneration during water treatment. Furthermore, flux does not always depict accurately the actual FO performance for hydrogel draw agents since the LMH and drawing rate are significantly affected and tuned by the contact area between the hydrogel and the FO membrane. It is clearly seen in Figure 7 that a larger contact area led to significantly faster water absorption. In this case, when a hydrogel of the same weight (400 mg) is spread onto a larger membrane area, the water diffusion path is decreased, thereby facilitating more rapid swelling. These results suggest that by optimizing the hydrogel thickness and its contact area with the FO membrane, better performance would result and the duration of the FO process can be further reduced. It is envisioned that a potential embodiment of the use of semi-IPN hydrogels as draw agents is to integrate them into



a FO hollow fiber module. Figure 8 shows a conceptual design of a quasi-continuous temperature driven desalination module with a semi-IPN hydrogel coated onto the outside surface of the FO hollow fiber membranes. In the FO process the water from the feed solution (which flows through the lumen of the hollow fibers) permeates through the membrane at room temperature (e.g., 25 °C) due to drawing by the hydrogel as it swells. Subsequently the dewatering process is enabled by a moderate heating to 40 °C at which the swollen hydrogel releases the desalinated water. The 'cooling and heating' cycles suggested schematically in Figure 8 can be continued to allow an essentially temperature-driven FO desalination. The design is regarded as quasi-continuous since the desalinated water can be collected during each heat induced deswelling stage at 40 °C. Using the semi-IPNs discussed in this work, a temperature modulation of about 15 °C (e.g., between 25 to 40 °C) could drive the desalination process. A mild dewatering condition of 40 °C is very important because it not only saves energy and reduces the cost, but also avoids possible membrane degradation. For example, it is known that 43 °C is the upper limit for long term housing of the FO membrane from HTI (HTI data sheet). The hydrogels swell to absorb water from the brackish water at a temperature below their LCST, while they deswell to release desalinated water for collection at a temperature above their LCST. Apart from the energy needed to pump the saline water feed through the lumen of the hollow fibers, the periodic temperature modulation is essentially the only driving force for desalination in this hydrogel enabled FO process. This temperature difference can be readily obtained using hot air/water generated from industrial waste heat. In addition, it is also possible, by optimizing the molecular structure of the hydrogels, to further reduce the temperature difference required between the 'cooling and heating' cycles. Therefore, it is

believed that this concept has the potential to be advanced to commercialization after further optimization of the hydrogels to obtain better performance in terms of drawing and dewatering ability and rate.

## Conclusions

We have successfully prepared a series of hydrogels based on PNIPAm-PSA and PNIPAm-PVA semi-IPNs with superior and balanced thermally responsive swelling and dewatering behavior. They were shown to be suitable candidates as draw agents for continuous temperature driven FO desalination while the copolymer counterpart with the same chemical or monomer compositions showed no such potential. A conceptual design of a quasi-continuous FO drawing/dewatering desalination is proposed that employs a membrane module containing hollow fibers coated with a layer of the semi-IPN hydrogels. The process is essentially driven by temperature cycles within a moderate range, e.g., 15 °C. The low energy consumption and quasi-continuous characteristics make semi-IPN hydrogels attractive as draw agents for potential large scale forward osmosis desalination. Furthermore, through detailed analysis of the drawing and dewatering behavior of different semi-IPN hydrogels, the reversible swelling ratio span (EPSR-OPSR) parameter was defined to provide a quantitative performance metric for hydrogel FO drawing agents. The results of this study are significant in that they provide further insight into the future research direction required to develop an 'ideal' hydrogel drawing agent. We trust that this work will encourage further studies and development focused on applying hydrogels to desalination.

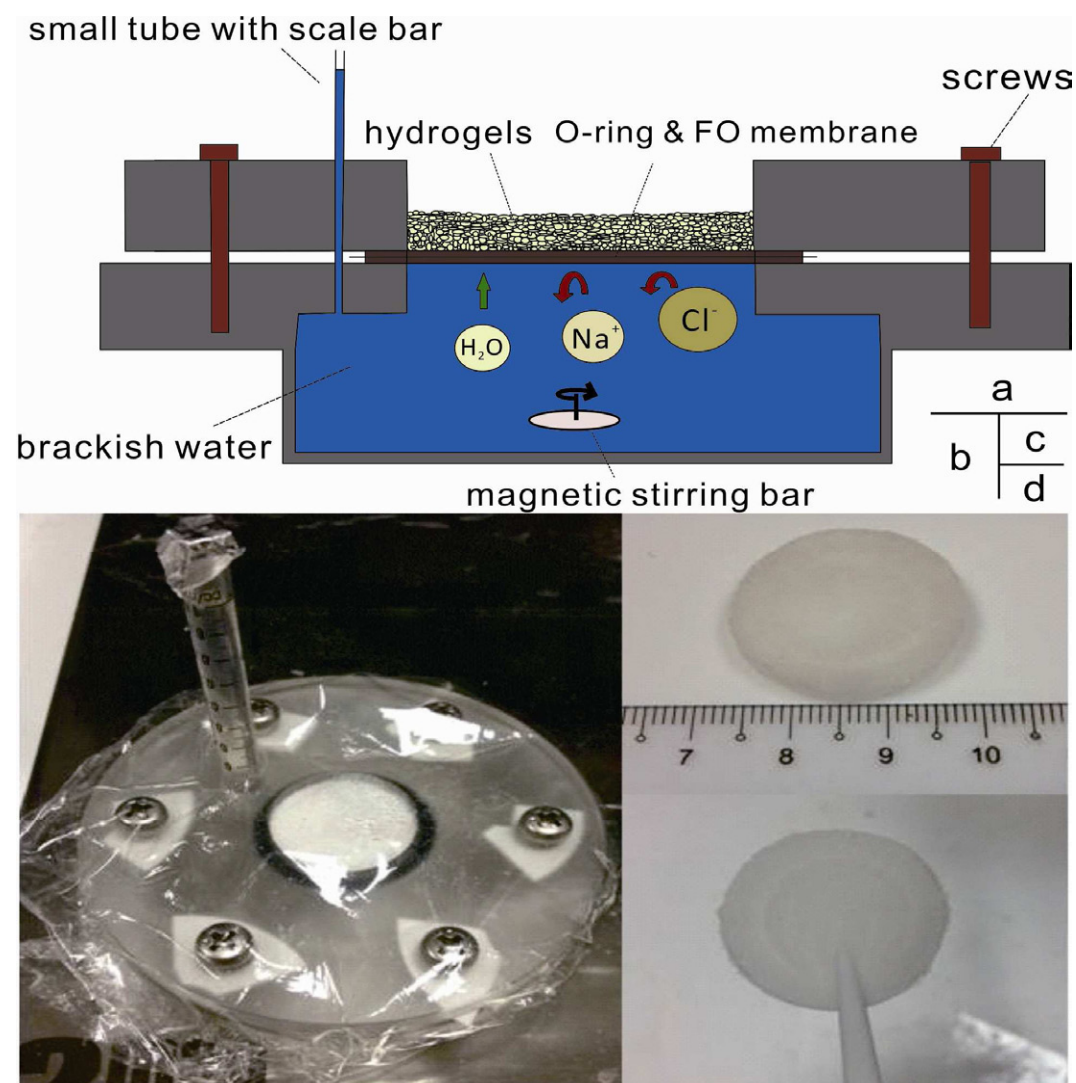
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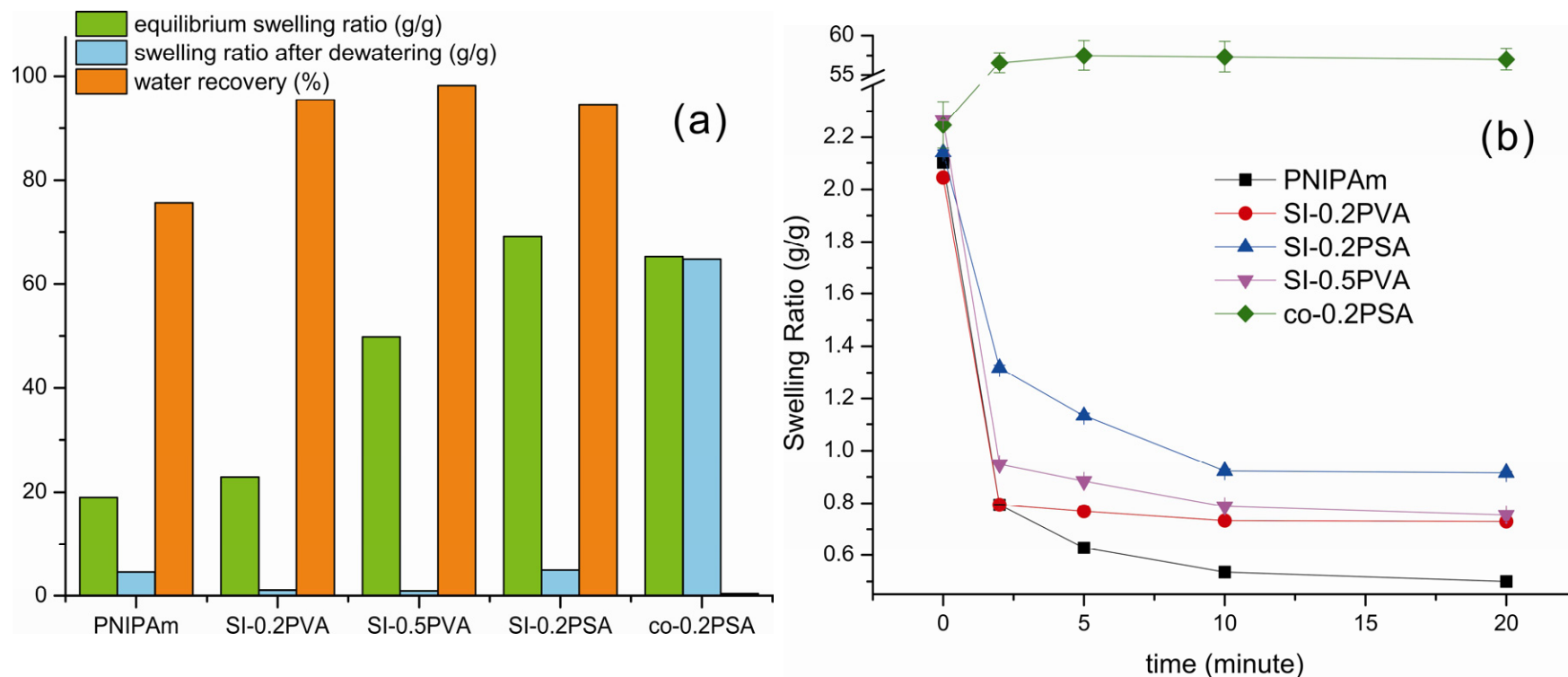
## References

- Cath, T., Childress, A. and Elimelech, M. (2006) Forward osmosis: Principles, applications, and recent developments. *Journal of Membrane Science* 281(1-2), 70-87.
- Chekli, L., Phuntsho, S., Shon, H.K., Vigneswaran, S., Kandasamy, J. and Chanan, A. (2012) A review of draw solutes in forward osmosis process and their use in modern applications. *Desalination and Water Treatment* 43(1-3), 167-184.
- Dhara, d., Nisha, C.K. and Chatterji, P.R. (2001) Interpenetrating networks of poly(N-isopropylacrylamide) with anionic and cationic polymers. *Macromolecular Chemistry and Physics* 202, 3617-3623.
- Ge, Q., Su, J., Amy, G.L. and Chung, T.S. (2012) Exploration of polyelectrolytes as draw solutes in forward osmosis processes. *Water research* 46(4), 1318-1326.
- Ge, Q., Su, J., Chung, T.-s. and Amy, G. (2011) Hydrophilic superparamagnetic nanoparticles synthesis characterization and performance in forward osmosis processes. *Ind.Eng.Chem.Res.* 50, 382-388.
- Harmon, M.E., Schrof, W. and Frank, C.W. (2003) Fast-responsive semi-interpenetrating hydrogel networks imaged with confocal fluorescence microscopy. *Polymer* 44(22), 6927-6936.
- Hirose, Y., Amiya, T., Hirokawa, Y. and Tanaka, T. (1987) Phase transition of submicron gel beads. *Macromolecules* 20, 1342-1344.
- J.O.Kessler and C.D.Moody (1976) Drinking water from sea water by forward osmosis. *Desalination* 18, 297-306.
- Jorgensen, M.K. (2009) Investigation of Polypropylene Glycol 425 as a Draw Solution for Forward Osmosis, Aalborg University, Denmark.
- Kokufuta, E., Wang, B., Yoshida, R., Khokhlov, A.R. and Hirata, M. (1998) Volume phase transition of polyelectrolyte gels with different charge distribution. *Macromolecules* 31, 6878-6884.
- Kravath, R.E. and Davis, J.A. (1975) Desalination of sea water by direct osmosis. *Desalination* 16, 151-155.
- Li, D., Zhang, X., Simon, G.P. and Wang, H. (2013) Forward osmosis desalination using polymer hydrogels as a draw agent: influence of draw agent, feed solution and membrane on process performance. *Water research* 47(1), 209-215.
- Li, D., Zhang, X., Yao, J., Simon, G.P. and Wang, H. (2011a) Stimuli-responsive polymer hydrogels as a new class of draw agent for forward osmosis desalination. *Chemical communications* 47(6), 1710-1712.
- Li, D., Zhang, X., Yao, J., Zeng, Y., Simon, G.P. and Wang, H. (2011b) Composite polymer hydrogels as draw agents in forward osmosis and solar dewatering. *Soft Matter* 7(21), 10048.

- Li, Y., Li, X., Zhou, L., Zhu, X. and Li, B. (2004) Study on the synthesis and application of salt-resisting polymeric hydrogels. *polymers for advanced technologies* 15(12), 34-38.
- Ling, M.M., Chung, T.S. and Lu, X. (2011) Facile synthesis of thermosensitive magnetic nanoparticles as "smart" draw solutes in forward osmosis. *Chemical communications* 47(38), 10788-10790.
- Liu, Z., Bai, H., Lee, J. and Sun, D.D. (2011) A low-energy forward osmosis process to produce drinking water. *Energy & Environmental Science* 4(7), 2582.
- McCutcheon, J.R., McGinnis, R.L. and Elimelech, M. (2006) Desalination by ammonia-carbon dioxide forward osmosis: Influence of draw and feed solution concentrations on process performance. *Journal of Membrane Science* 278(1-2), 114-123.
- Shin, B.C., Jhon, M.S., Lee, H.B. and Yuk, S.H. (1998) Temperature-induced phase transition of semi-interpenetrating polymer networks composed of PNIPAm and hydrophilic polymers. *European Polymer Journal* 34(2), 171-174.
- Yamashita, K., Nishimura, T. and Nango, M. (2003) Preparation of IPN-type stimuli-responsive heavy-metal-ion adsorbent gel. *polymers for advanced technologies* 14, 189-194.
- Yen, S.K., Mehnas Haja N, F., Su, M., Wang, K.Y. and Chung, T.-S. (2010) Study of draw solutes using 2-methylimidazole-based compounds in forward osmosis. *Journal of Membrane Science* 364(1-2), 242-252.
- Zeng, Y., Qiu, L., Wang, K., Yao, J., Li, D., Simon, G.P., Wang, R. and Wang, H. (2013) Significantly enhanced water flux in forward osmosis desalination with polymer-graphene composite hydrogels as a draw agent. *RSC Advances* 3(3), 887.
- Zhang, J.-T., Cheng, S.-X. and Zhuo, R.-X. (2003) Poly(vinyl alcohol)/poly(N-isopropylacrylamide) semi-interpenetrating polymer network hydrogels with rapid response to temperature changes. *Colloid and Polymer Science* 281(6), 580-583.
- Zhang, Y. and Cremer, P.S. (2006) Interactions between macromolecules and ions: The Hofmeister series. *Current opinion in chemical biology* 10(6), 658-663.



**Figure 1 (a) Schematic and (b) photo of the apparatus built in-house for the FO flux measurements. (c) The hydrogel disc formed from dry polymer particles. (d) Photo indicating that the hydrogel disc is robust for handling and maintaining its integrity.**



**Figure 2 (a)** Equilibrium swelling ratio at room temperature, percentage water recovery after 10 minutes dewatering at 40°C for the bulk hydrogels, and swelling ratio after complete dewatering of the hydrogels at 40 °C. **(b)** Deswelling profile of hydrogel particle aggregate discs from a relatively low swelling ratio of 2. All the hydrogels had a 24 mm diameter and 3mm thickness. The dewatering was conducted at 40°C in water.

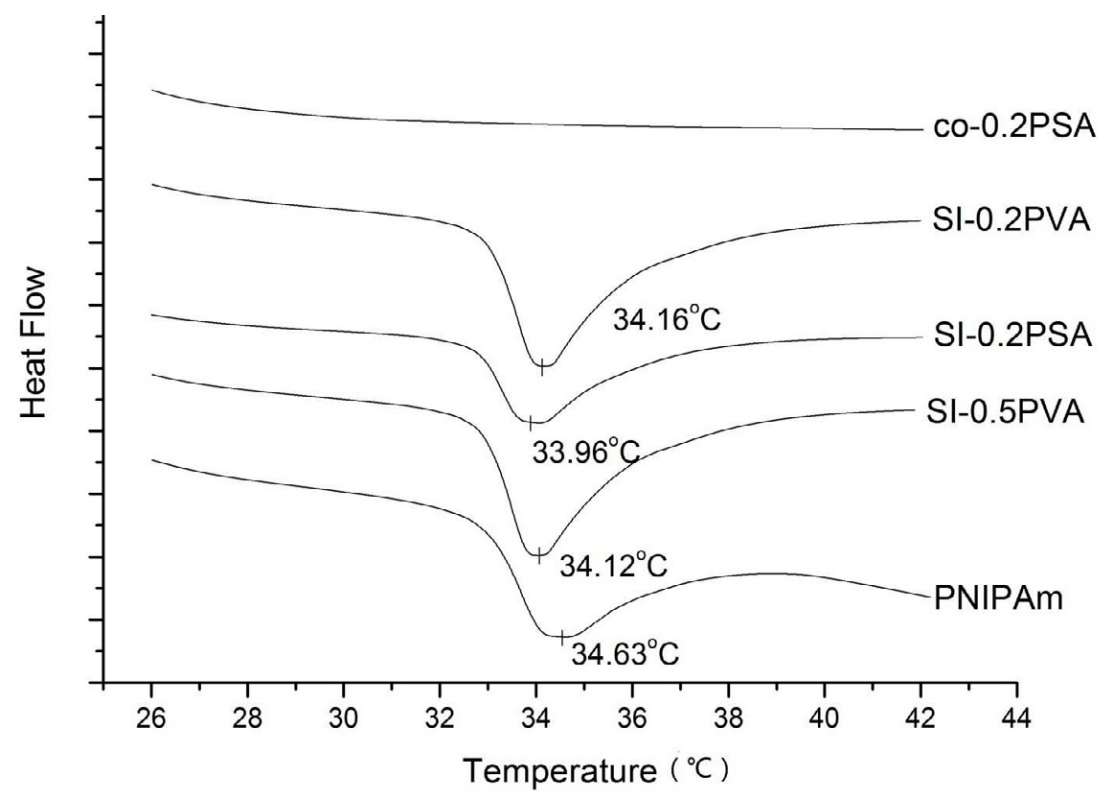
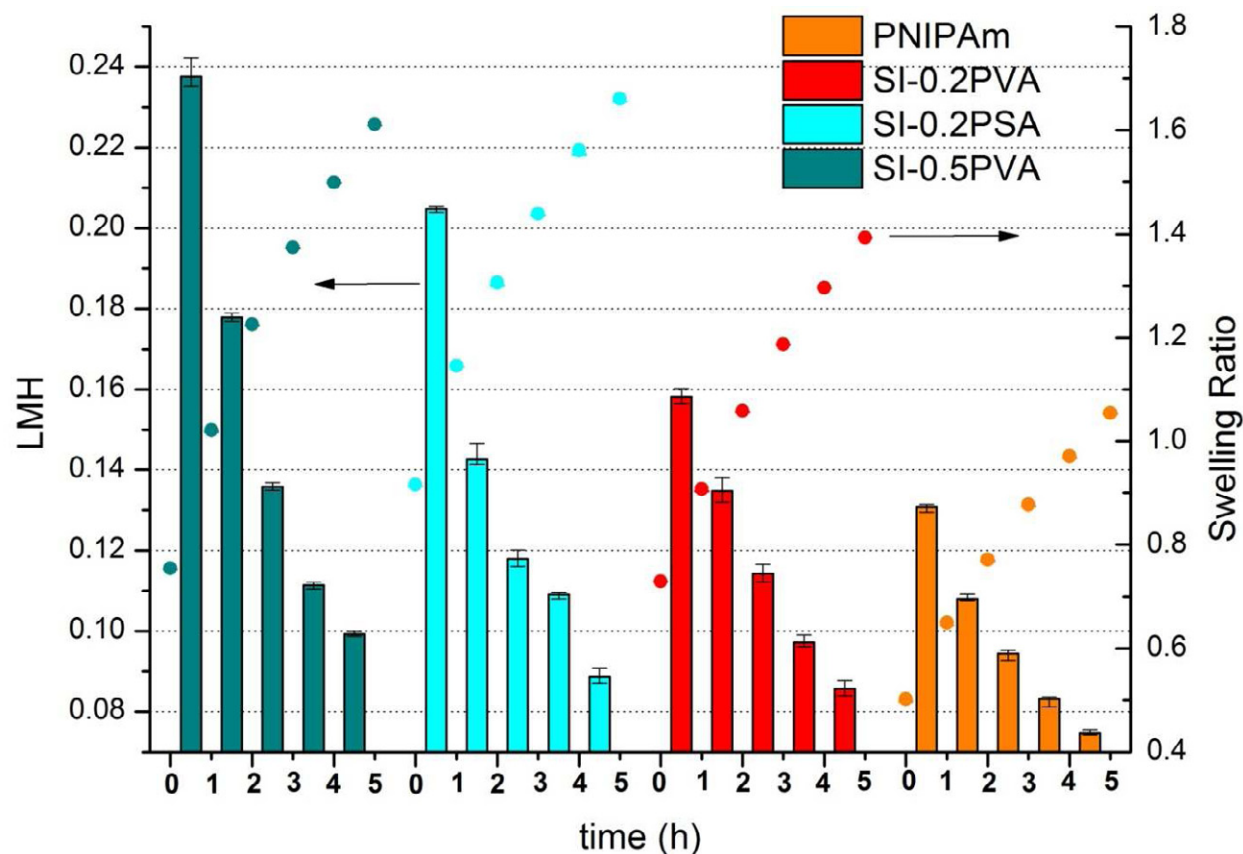
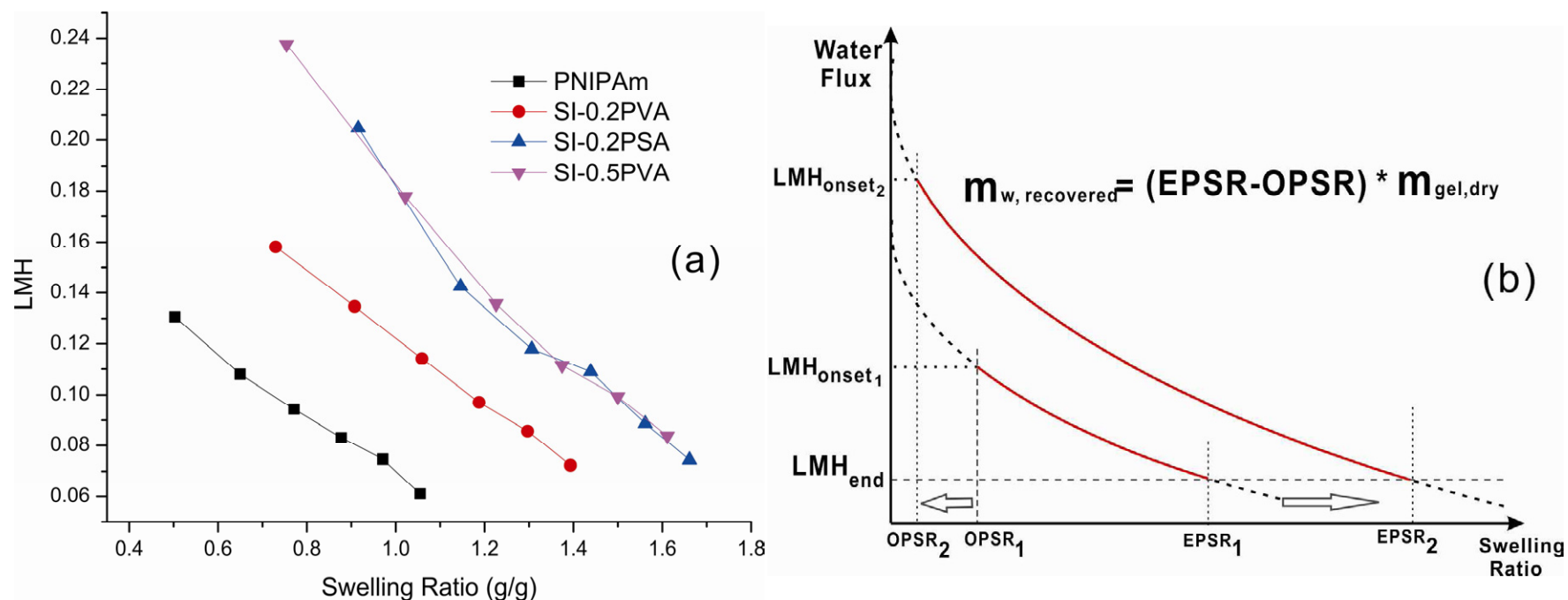


Figure 3 DSC traces of the hydrogels showing the LCST transition in the hydrogels.

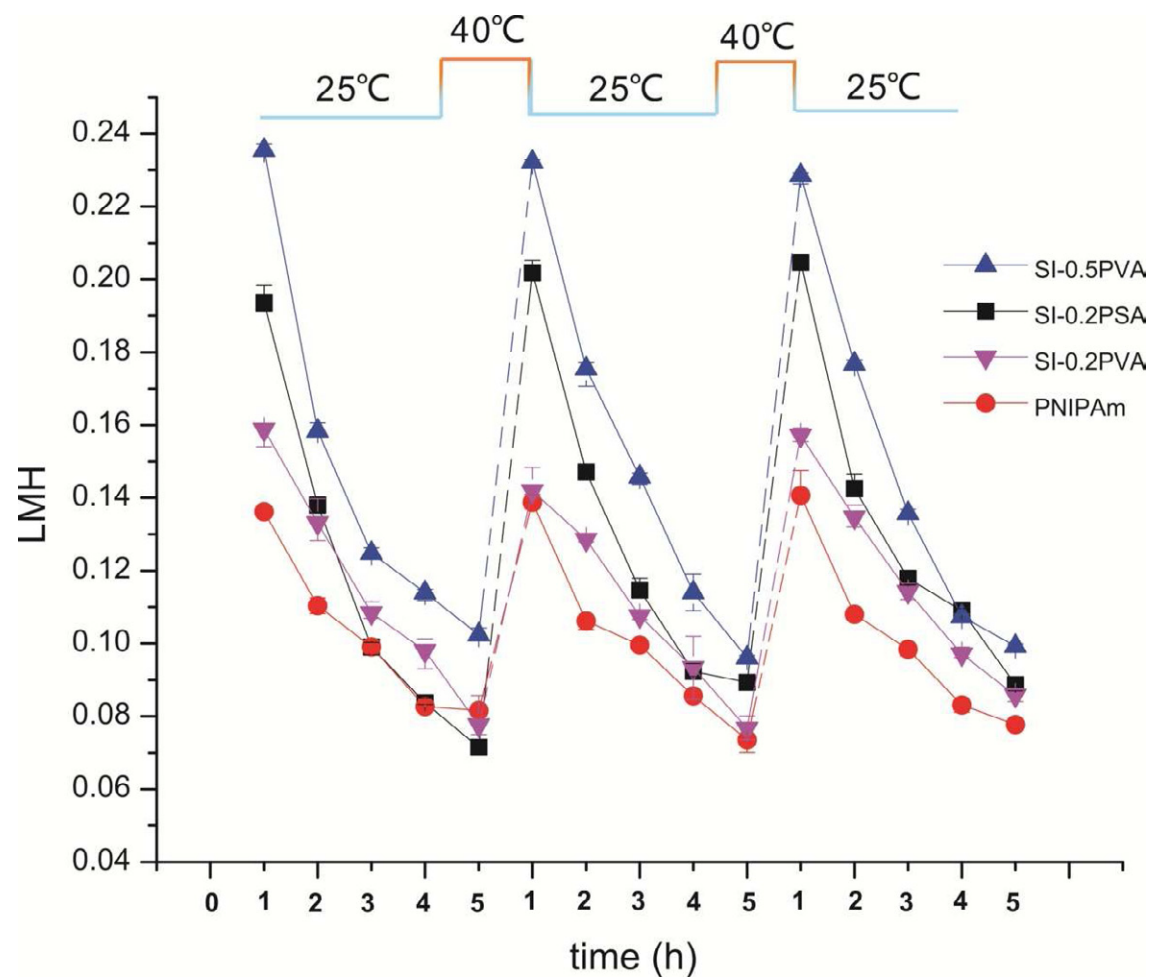


**Figure 4** The average water flux generated by the hydrogels during each hour (column) and the corresponding swelling ratio (dot) in the FO experiments. The column represents the average flux calculated from the weight increment in the hydrogel during each hour. For example, the first column of each hydrogel represents the average water flux generated in the first hour, and the first two dots are the swelling ratio before and after the first hour swelling. The dots at 0 hour represent the OPSRs.

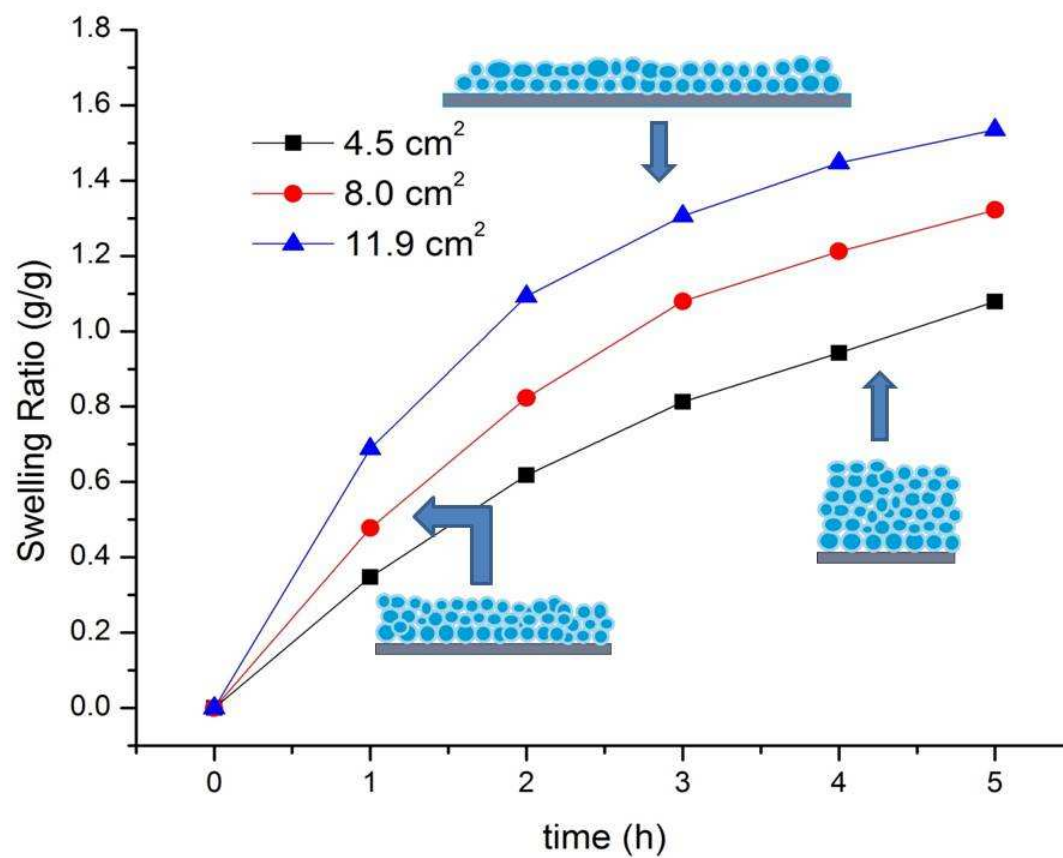




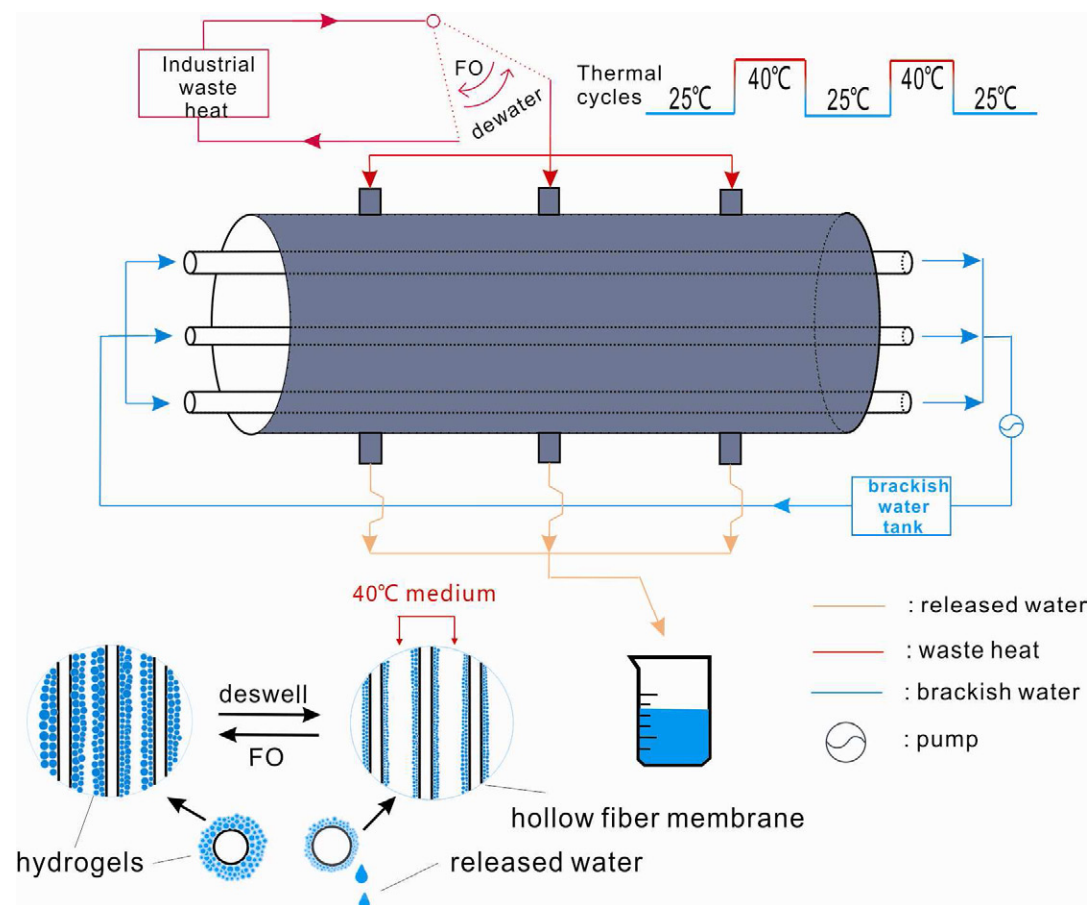
**Figure 5 (a) The water flux and swelling ratio correlation curve for hydrogels for a 5 hour FO process. (b) Schematic for the reversible hydrogel design optimization. The ideal situation is that the reversible hydrogel has larger EPSR and lower OPSR simultaneously to enlarge the reversible span. The EPSR represents the swelling ratio at which the water flux reaches an arbitrary set value and OPSR shares the definition mentioned above in the text. The red solid line represents the reversible span with the swelling ratio difference between EPSR and OPSR.**



**Figure 6** Reversibility of hydrogels for three FO-deswelling cycles. The five dots in each cycle represent the average water flux for the corresponding one hour. The deswelling process (dashed line) duration is 10 minutes and is not to scale relative to the FO process duration.



**Figure 7** The influence of membrane/hydrogel contact area on the FO performance of SI-0.2PSA. 2000 ppm brackish water is feed solution and the dry hydrogel weight in all three cases is approximately 400 mg.



**Figure 8** Quasi-continuous FO desalination using a semi-IPN hydrogel as the draw agent. Apart from the energy needed to pump the saline water feed through the lumen of the hollow fibers, the periodic temperature modulation within 15 °C (e.g., between 25 to 40 °C) is essentially the only driving force for desalination in this configuration. This temperature difference can be readily obtained using warm air generated from industrial waste heat.

- Temperature cycle driven FO desalination using responsive semi-IPN hydrogels as draw agents.
- Desalination driven by a temperature modulation, e.g., between room temperature and 40 °C.
- FO desalination without the need of draw solute recovery.
- A conceptual design is advanced for a hydrogel incorporated into a quasi-continuous FO module.
- A parameter is defined as a metric to guide in the search for better and better hydrogel in future.