A critical review on draw solutes development for forward osmosis
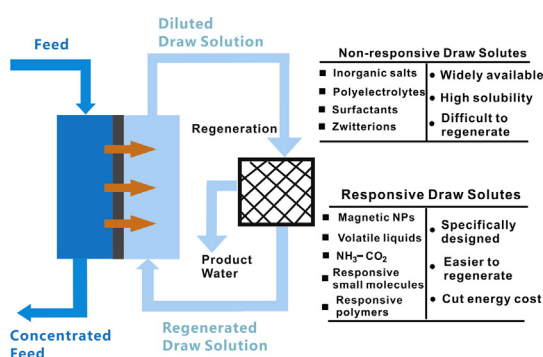
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HIGHLIGHTS

- FO draw solutes have been comprehensively and critically reviewed.
- FO enabled by responsive draw solutes can have a significant energy cost saving.
- FO has advantages in niche applications where RO alone is unsuitable.
- Ideal draw solute development calls for interdisciplinary efforts.

GRAPHICAL ABSTRACT

ABSTRACT

Despite the impressive progress in forward osmosis (FO) membranes and pilot scale testing of FO process, lack of draw solutes that can be efficiently regenerated is still a limiting factor for more prolific commercial applications of FO technology. In the past decade, a large variety of draw solutes have been investigated. While many promising concepts were discussed, efforts are still needed to search for an 'ideal' draw solute which could enable the next breakthrough in FO technology. Besides giving a critical review on the development of FO draw solutes, we attempt to clarify some of the most important issues about draw solutes, to define the criterion for draw solutes, and to offer insights into challenges and opportunities concerning their future development. We intentionally avoid very detailed discussion on the issue of viability of FO, which was covered in several earlier reviews. Draw solutes are categorized into either non-responsive or responsive type according to their response toward external stimuli, such as heat and electromagnetic field. While the focus is on responsive draw solutes whose regeneration relies on their smart response to stimuli, non-responsive draw solutes are also discussed not only for a historic reason, but also for the valuable lessons learnt from these earlier systematic studies.

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1. Introduction

Forward osmosis (FO) has experienced a typical cycle of discovery, over hype, disappointment, condemnation and gradual restitution.

The harsh criticism of FO largely stems from its inability to compete with reverse osmosis (RO) process for sea water desalination. More recently, FO has started to be recognized as a viable complementary technology to RO for certain important niche applications, particularly for applications where the use of sole RO is impractical or impossible. Although thermodynamically FO process consumes more energy than RO for desalination, one can still expect significant saving on energy cost and reduction of carbon footprint by using suitable draw solutes. In the community of forward osmosis, the argument is no longer on if

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FO has a future, but on whether one could develop draw solutes that can be cost effectively regenerated and reused. It is believed that the availability of suitable draw solutes is crucial for the future of FO.

Forward osmosis (FO) as an emerging and promising technology has attracted much attention [1]. In FO, a concentrated draw solution with a lower water chemical potential and a more diluted feed solution with a higher water chemical potential are separated by a membrane that rejects the salt but allows the passage of water. The water permeation from feed solution to draw solution is a spontaneous process driven by the chemical potential gradient [2]. The absence of large hydraulic pressure in FO process in comparison to RO may help reduce the energy consumption in electrical pumping, and the lower fouling propensity as well as higher fouling reversibility [3–5] may prolong the membrane's service life-time and reduce overall operational cost.

In FO, the draw solutes, also known as draw agents, dispersed and/or dissolved in water to form homogeneous draw solutions, are of paramount importance. As an osmotically driven process, the draw solute should be able to significantly reduce the water chemical potential, and consequently generate a high osmotic pressure in FO process. On the other hand, the draw solute is also expected to be easily separated from the diluted draw solution in the subsequent process to regenerate the draw solute for reuse and to produce purified water. The paradox of draw solute lies in these two conflicting basic requirements, because the need to generate a high osmotic pressure requires a strong affiliation between the draw solute and water molecules, e.g., via hydration or ionization, while such strong affiliation makes its separation from water more difficult during regeneration. In the design or selection of draw solute, it is important to have a holistic consideration of all requirements or criteria which are summarized herein. In addition to satisfying the conflicting requirements of producing high osmotic pressure and being easily regenerated, a successful draw solute must fulfill the following conditions: (i) being benign to the FO membrane, i.e., causing no damage to the delicate membrane rejection and support layers even after prolonged usage; (ii) low-toxicity with no adverse effect on human health and environment; (iii) low or zero draw solute reverse diffusion; (iv) low viscosity even at high concentrations; (v) chemically stable for repeated use; and (vi) cost effective. These criteria have no doubt posed great challenges toward developing ideal draw solutes.

Up to now, there have been several very good reviews on forward osmosis processes [6–11] and a few others have specifically highlighted the importance of draw solutes [12–14]. However, most of these reviews focused mainly on the processes and theories such as concentration polarization and osmotic pressure in FO. Specific discussion on draw solutes was either very brief or just a factual listing of the draw solutes reported. It is believed that a critical review with insights into the future trend of draw solutes in the context of the future of FO is timely and highly necessary. In addition, a significant number of earlier research papers were highlighting FO's perceived low energy input, and the discussion on draw solutes was focused on achieving high water flux comparable to that in RO, with a misplaced expectation of outperforming RO energetically for seawater desalination.

Herein we review the development of draw solutes, and categorize them as non-responsive or responsive draw solutes. Non-responsive draw solutes are referring to those draw solutes that do not have significant change in their water affinity in response to stimuli such as temperature, pH, electro-magnetic field or light. On the other hand, the responsive draw solutes, upon exposure to stimuli, undergo substantial changes in water affinity that are often accompanied by phase transitions between two states with different water affinities. This allows ease of regeneration while maintaining sufficiently high drawing ability. More importantly, we share our opinions on future prospects of FO and developing trend of draw solutes based on a critical assessment of various types of draw solutes investigated. We also hope that this would help define the future role of FO among other water-related technologies and provide guidance to developing successful draw solutes to enable FO to fulfill its potential.

2. Non-responsive draw solutes

2.1. Inorganic salts

From the first trials of using saccharide or sugar as draw solutes to extract water from seawater in 1970s, low cost and easily available substances were studied as possible draw solutes [15–17]. Besides sugars, inexpensive inorganic salts including NaCl, MgCl$_2$, Na$_2$SO$_4$, (NH$_4$)$_2$SO$_4$, Ca(NO$_3$)$_2$, KHCO$_3$, and others have been systematically studied as draw solutes [18]. These initial studies established helpful protocols to evaluate a comprehensive list of inorganic salts as draw solutes by comparing the essential parameters, such as water flux, draw solute reverse diffusion, draw solute loss in RO regeneration as well as replenishment cost. These studies were very useful even though no single draw solute emerged to excel in all the performance parameters evaluated. For example, KCl was found to generate the highest water flux, while MgSO$_4$ achieved the highest retention rate during regeneration via RO owing to its larger divalent ions [18]. The study of widely available inorganic salts as draw solutes is very convenient and helpful in understanding the relevant issues associated with FO such as concentration polarizations (CP) and mass transport [19–24]. However, the discussion on their regeneration after the FO process is lacking. One possible reason is that the regeneration of such inorganic salts relies on conventional and mature technologies, e.g., thermal distillation, membrane distillation (MD) or pressurized membrane filtration such as nanofiltration (NF) and RO. Therefore, because mature technologies were used in regeneration process, the FO process itself was the natural focus of their study.

2.2. Polymers and organic molecules

Besides simple inorganic salts, many water soluble polymeric and organic compounds were also investigated as non-responsive draw solutes. Linear poly(sodium acrylate) (PSA), a typical polyelectrolyte, has been tested as draw solute by Ge et al. for FO seawater desalination [25]. An initial water flux of about 5 litre per square meter per hour (LMH) in FO was reported against seawater and nano-filtration (NF) was used for draw solute regeneration. Compared to simple inorganic salts with lower molecular weights, the polyelectrolytes have the advantage of much reduced reverse diffusion into feed solution due to higher molecular weight. However, the higher viscosity of polyelectrolyte solutions would aggravate problems like CP in FO process and circulation difficulties in both FO and regeneration processes. These adverse effects are more detrimental with increasing polyelectrolyte molecular weights [26]. Besides PSA, sodium salt of poly(aspartic acid) were also evaluated [27]. Modification via random copolymerization of monomeric electrolyte (i.e., sodium acrylate, SA) with thermally responsive monomers such as N-isopropylacrylamide (NIPAm) may facilitate regeneration via MD or NF [28,29]. However, since non-ionic species have lower osmotic pressure due to the absence of counter-ions [30–32], copolymerization with any non-ionic monomer would decrease the charge density in the draw solute, resulting in reduced osmotic pressure [33]. Apart from modifying the monomer structure and compositions of polyelectrolytes, the effect of molecular architecture was also investigated, ranging from linear chain to hyperbranched or dendritic chain structure. Dendritic polyelectrolytes produced higher water flux in FO and improved draw solute regeneration because of its lower viscosity and higher radius of gyration than the linear polyelectrolyte counterpart at similar osmotic pressures [34,35].

In the meantime, organic salts or organic electrolytes whose molecular weights (between 100 to 1000 g/mol) are typically higher than that of the inorganic salts but lower than that of polyelectrolytes were also

investigated. Their draw solutions have lower viscosities and generate higher water fluxes than their polymer counterparts, while retaining the advantage of lower reverse diffusion than the inorganic salts. A variety of possible draw solutes were investigated, including hexavalent phosphazene salts [36], ethylenediamine tetrapropionic salts [37], ethylenediamine tetraacetic based salts [38], zwitterions [39], hydroacid complexes [40–43] and ionic liquids [44]. Similar to polyelectrolytes, their regeneration depends on NF or MD and their role is to replace monovalent inorganic salts like NaCl owing to a lower reverse diffusion and a comparable water flux. Nevertheless, among the few reports on the economics of these draw agents to replace NaCl, even the commercially available zwitterions were found to have a higher cost than NaCl despite lower reverse diffusion [39]. Probably the cost would be even higher for those elaborately synthesized organic salts. Surfactants are another interesting group of organic draw solutes reported, and their micellar draw solutions have been studied in FO based membrane bioreactor [45,46]. The relatively constant, though moderately high, osmotic pressure at concentrations above the Critical Micelle Concentration is responsible for a stable water flux. This unique characteristic of surfactants should perhaps be further explored in future.

2.3. Limitation of non-responsive draw solutes

There have been a large number of reports that investigated several classes of non-responsive draw solutes, some of which with very elaborate molecular designs. These studies are academically interesting and helpful because most of them were focusing on maximizing the drawing ability, i.e., high osmotic pressure, while minimizing the reverse diffusion. In addition, NF instead of RO can be used to regenerate most of these draw solutes. While such systematic and intensive studies of non-responsive draw solutes are perhaps essential in the course of draw solute development, their practical applications are very limited. One attempted application is the FO–NF hybrid process for seawater desalination with the underlying rationale that the NF membrane used in regeneration process has a higher permeability than RO membrane, and hence FO–NF might be energetically superior to RO (a notion now considered naive). There were reports claiming that an FO–NF or FO–RO hybrid process, such as the one shown in Fig. 1, consumes less energy than RO for seawater desalination [47–49]. However, further investigation through simple derivation below reveals that FO–NF or FO–RO hybrid

cannot energetically outperform RO, at least theoretically, if the membrane has 100% salt rejection.

In fact, the following deduction is helpful to clarify the energy consumption issue. Since water flux in FO is driven by water chemical potential (μ_A), which is a function of pressure (P) and water activity (α_w) at a constant temperature

$$\mu_A = f(P, \alpha_w) \tag{1}$$

When a hydraulic pressure equivalent to osmotic pressure (Π) is exerted on the side of lower water chemical potential, equilibrium is achieved and $d\mu_A = 0$, namely

$$d\mu_A = \left(\frac{\partial \mu_A}{\partial P}\right)dP + \left(\frac{\partial \mu_A}{\partial \alpha_w}\right)d\alpha_w = 0 \tag{2}$$

Because $\left(\frac{\partial \mu_A}{\partial P}\right) = V_A$, $\left(\frac{\partial \mu_A}{\partial \alpha_w}\right) = \left(\frac{RT}{\alpha_w}\right)$, where V_A is the molar volume of water, therefore,

$$V_A dP + \frac{RT}{\alpha_w}d\alpha_w = 0 \tag{3}$$

Integrate for α_w (from 1 to α_w) and P (from P to P+Π), then

$$-RT\int_1^{\alpha_w} d\ln(\alpha_w) = \int_P^{P+\Pi} V_A dP \tag{4}$$

If molar volume of water is not a function of pressure, namely water is incompressible,

$$\Pi V_A = -RT\ln\alpha_w \tag{5}$$

According to another work [50], the theoretical minimum energy requirement (W_{min}) for desalination is derived to be a function of water activity, solution's temperature and water recovery (Y)

$$W_{min} = -\frac{RT}{Y} \cdot \ln(\alpha_w) \cdot \ln\left(\frac{1}{1-Y}\right) \tag{6}$$

This minimum energy requirement is derived on the assumption that the desalination occurs as a reversible thermodynamic process and is independent on the specific desalination method. By combining
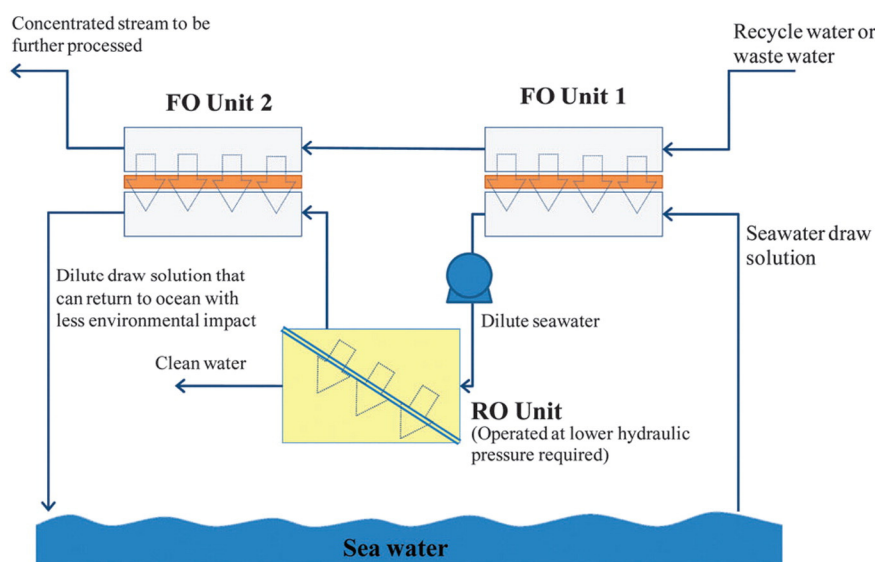

Fig. 1. Schematic diagram of using FO–RO hybrid system for low energy desalination. Reprinted with permission from Reference [8]. Copyright 2013, Royal Society of Chemistry.

Eqs. (5) and (6), we have

$$W_{min} = V_A \cdot \frac{\Pi}{Y} \cdot \ln\frac{1}{1-Y} \qquad (7)$$

When the water recovery is approaching zero, or the osmotic pressure stays constant with water recovery, then the theoretical minimum energy requirement is

$$W_0 = V_A \cdot \Pi \qquad (8)$$

From Eqs. (7) and (8), it is clear that minimum energy requirement for desalination is a function of the osmotic pressure of feed solution. Although the water permeation in FO is indeed a spontaneous process, this exemption from an externally applied hydraulic pressure in FO is not free. It is at the cost of introducing a draw solution with a higher osmotic pressure than feed solution, and the draw solute needs to be regenerated later. As seen in Fig. 2, in either a co-current or counter-current module, the diluted draw solution at the exit of FO module always assumes a higher osmotic pressure than that of initial feed solution (more quantitative analysis can be found in reference [51]). Therefore, according to Eq. (7), theoretically, higher energy consumption should be anticipated in either FO–NF or FO–RO hybrid process than in RO alone because higher hydraulic pressure is needed to regenerate draw solute from the diluted draw solution after FO.

Actually, for the sake of fairness, the claim that FO–NF or FO–RO hybrid process (Fig. 1) has lower energy consumption than seawater RO desalination is not completely unfounded, albeit somewhat misleading. This is because in those reports, NF or RO only deals with diluted seawater after FO process, and a great portion of product water actually originated from municipal wastewater as the 'hidden' diluent. In other word, that hybrid system was not entirely desalinating seawater. This is the reason why it appears that the hybrid processes have the reported advantage on energy consumption. In another study, Altaee et al. found that FO–RO hybrid process consumes more energy than RO alone in seawater desalination [52], and McGovern et al. claimed that FO–RO is unlikely to approach the energy efficiency of RO in seawater desalination [53], which corroborates our theoretical deduction above. Perhaps the strongest negative views towards FO using non-responsive draw solutes in water production were expressed by Field et al. [54] and Van der Bruggen et al. [55]. Their views against FO possibly stem from their countervailing reaction to some of the unrealistic and over-hyped claims in earlier FO reports.

It is worth mentioning that some non-responsive draw solutes have also been exploited in indirect desalination, where there is no regeneration process and the diluted draw solution can be utilized "directly" in life-saving hydration bags [2], irrigation [56–58] and desert restoration

[59]. This is one of the very promising applications for FO. However, as mentioned above that FO process alone produces a solution with a higher osmotic pressure, the viabilities of these indirect desalination applications largely hinge on the feed solution salinity. If feed solution is of high salinities like seawater, then the fertilizer solution after FO process still needs further treatment to reduce its concentration before it is suitable for usage (e.g., irrigation), by either diluting with fresh water [59] or consuming energy to remove a portion of the draw solute [60].

2.4. Is there any silver lining for non-responsive draw solute?

Although FO–RO or FO–NF hybrid systems enabled by non-responsive draw solutes are found to be unable to compete with direct RO for seawater desalination in terms of energy consumption and mass transfer efficiency (concentration polarization), they still have potentials to contribute to desalination. Blandin et al. [61] suggested that if water flux in FO is above 30 LMH, then the hybrid FO–RO process may become comparable to RO in seawater desalination. We believe that this is an interesting point even though such a high water flux requirement sets a formidable task for the current generation of FO membranes technology. Mazlan et al. [62] found although FO–NF cannot compete with RO because of its higher energy consumption and additional capital investment, other unique advantages of FO might still make it attractive. One of the advantages is the lower fouling propensity and high fouling reversibility, which might enable FO to serve as the pretreatment step to remove the dissolved solids, especially in wastewater with a high fouling or scaling propensity [63]. Another hidden advantage is that FO membrane seems to achieve a higher rejection of trace organic compounds, boron and chloride than RO membrane [64–66]. Therefore, Shaffer et al. [67] envisioned a special scenario where FO–RO can outperform RO in seawater desalination in overall energy consumption. The desalinated water can be used for irrigation where there is a more stringent standard for boron and chloride. In this case, FO–RO hybrid process consumes less chemicals and energy in pretreatment, and the FO–RO double-barrier can effectively reduce boron and chloride to the acceptable level. This cannot be achieved by RO alone and hence post-treatment is needed to guarantee the same level of boron and chloride in product water. In such scenario, the need of post-treatment for RO and savings in pretreatment of FO–RO make the hybrid system more attractive.

Apart from desalination, FO processes using non-responsive draw solutes have many other applications. Although the scope of using diluted draw solution after sole FO process is limited by feed solution salinity, the spontaneous water permeation process itself and the volume reduction of feed solution for enrichment are the two possible areas where FO could be useful. FO may be able to lower the impact of desalination process on marine ecosystem [68]. The prospect of less fouling
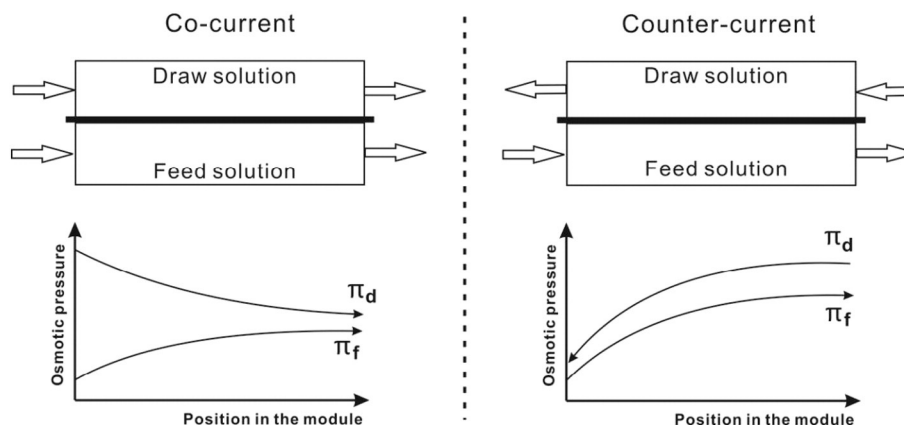

Fig. 2. Osmotic pressure profiles of feed solution and draw solution in co-current and counter-current module. Π_d and Π_f are osmotic pressure of draw solution and feed solution, respectively. Note that the osmotic pressure of draw solution at the end of FO is always higher than that of initial feed solution at the entry.

of FO makes it suitable in concentrating solutions which cannot be effectively achieved by thermal methods or RO [69]. For example, the enrichment of toxic substances and nutrients in wastewater enabled by FO bioreactor was effective [70–73], and FO also seems to be promising in sludge and oil dewatering [74–77] and in the treatment of effluents from food [78–80], pharmaceutical/personal care [81,82], and oil and gas industry [83–85]. In addition, applications of FO have also been extended to replenish water in cooling tower [86,87]. More information on the promising applications of FO hybrid systems using non-responsive draw solutes can be found in an excellent review paper published recently [88]. Nevertheless, it should be noted that the role of draw solutes in some of these applications is comparatively minor and the concentration of feed solutions or the water permeation process is the more important aspect. In some cases, the draw solute regeneration is not a must so that the draw solution can either be further diluted for safe discharge or be naturally decomposed [89]. Looking forward, the availability of draw solutes that can be easily and cost effectively regenerated should expand the applications of FO.

3. Responsive draw solutes

Responsive draw solutes are a class of smart draw solutes that can cause significant reduction in the osmotic pressure of diluted draw solutions upon exposure to an external stimulus, which may be electric or magnetic field, temperature, pH or light. Although traditional methods such as NF or RO may still be needed as the final step in regeneration process to polish the product water quality, the response of draw solutes to external stimuli enables a first stage facile separation of draw solute from the diluted draw solutions. Therefore, the use of appropriate responsive draw solutes can significantly alleviate the problems associated with the regeneration of non-responsive draw solutes. Two caveats must be made before we dive into the status of responsive draw solutes. (i) One must not expect any violation of thermodynamic laws by using responsive draw solutes. While FO consumes more energy than direct RO regardless which type of draw solute is used, it is possible to substantially reduce the energy cost by reducing the electric energy usage in regeneration and replacing it with other less expensive form of energy, e.g., thermal energy, including low grade industrial waste heat. It is not inconceivable that one could reduce the usage of electric energy to virtually zero. (ii) Not all types of responsive draw solutes reported in the literature are equally suitable for FO application despite the respective claims. Some of them are still in the development stage, while others are of academic interest only.

3.1. Nanoparticles

Nanoparticles are particles with dimension between 1 nm to 100 nm [90]. Draw solution prepared by nanoparticles dispersed in water could theoretically have very low draw solute back diffusion since their dimension is larger than the pore size of FO membrane. Ionic species are always decorated on the surface of nanoparticles to increase the osmotic pressure of the draw solutions. For instance, Na^+ paired carbon quantum dots were found to be able to generate a water flux against seawater feed solution [91]. However, the carbon quantum dots are still non-responsive and perhaps difficult to have a distinct energetic advantage over those polyelectrolytes discussed earlier.

The focus of using nanoparticles as draw solutes has been mostly on paramagnetic nanoparticles. It was assumed that these magnetic nanoparticles, e.g., Fe_3O_4 with surface decoration, would generate the osmotic pressure needed to extract water through the FO membrane and the magnetic nanoparticles can be rapidly separated from draw solution in a magnetic field, as demonstrated in Fig. 3. Although this idea was probably first proposed by a company named NanoMagnetics in UK for contaminants removal by FO [92], it has been studied by several research groups in academia for desalination purposes. Fe_3O_4 nanoparticles capped by a series of hydrophilic species were studied as magnetically
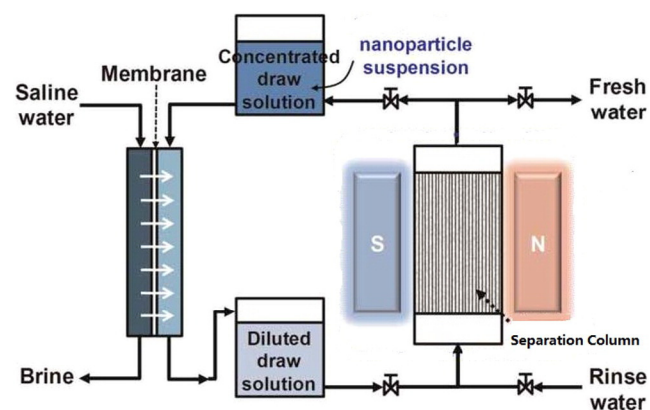
Fig. 3. Schematic illustration of using magnetic nanoparticles as draw solute in FO desalination. Reprinted with permission from Reference [99]. Copyright 2011, IWA Publishing.

responsive draw solutes [93–98]. The concept of using magnetic particles as the draw solutes is highly attractive due to the ease of regeneration by using a magnet while maintaining very low back diffusion. However, the FO water flux is much less impressive even when the feed solution is deionized water [95–98] or diluted brackish water (2g/l $MgSO_4$) [94]. Kim et al. [99] found that although smaller nanoparticles are preferred in FO process, nanoparticles less than 11 nm were not easy to be separated even under a strong magnetic field; whereas even bigger nanoparticles (>20 nm) were difficult to recover from the magnetic separation column. In addition, nanoparticles with uniform dimension are desirable for efficient regeneration via a membrane process. However, achieving this in large quantity is still a challenge. Another issue is agglomeration of nanoparticles under magnetic field during regeneration, which is difficult to be completely resolved even with intense ultrasonication. One possible solution is to introduce hydrophobic association between particles to aid the regeneration process, and hence a weaker magnetic field can be used during regeneration to alleviate the agglomeration. Polymers or hydrogels synthesized from copolymerization of electrolyte and NIPAm have been coated onto the nanoparticles to prevent the core particles from irreversible agglomeration [100–102]. A reasonable water flux of ~2 LMH can be generated even against seawater [100], and stable water flux in FO can be maintained after 5 FO-regeneration cycles. However, the synthesis of the nanoparticles is complex and only 50% recovery can be achieved by a magnetic field at temperatures above the Lower Critical Solution Temperature (LCST), while the other half of the particles still needs to be recovered by NF [100]. It was reported that using electric field instead of magnetic field for particle recovery can reduced particle agglomeration [103]. Although there is no clear strategy in sight to further increase the osmotic pressure in order for such nanoparticle draw solutes to be used for large scale desalination, such nanoparticles may find other applications such as protein enrichment and separation [104].

3.2. Hydrogels

Hydrogels are crosslinked hydrophilic polymers with water entrapped within the network. Their potential role in desalination was first tested by directly immersing and swelling polyelectrolyte hydrogels in seawater [105–107]. However, the salinity of the water squeezed from hydrogel under a very high hydraulic pressure revealed that sole Donnan effect is insufficient to achieve a high salt rejection and the water recovery is also low. Therefore, in most of the later studies, hydrogels served as semi-solid draw solutes in FO as shown in Fig. 4. The water extracted and entrapped by hydrogels during FO process should be theoretically pure (if salt rejection of membrane is 100%). In addition, as shown in Fig. 4, the water can be released in regeneration
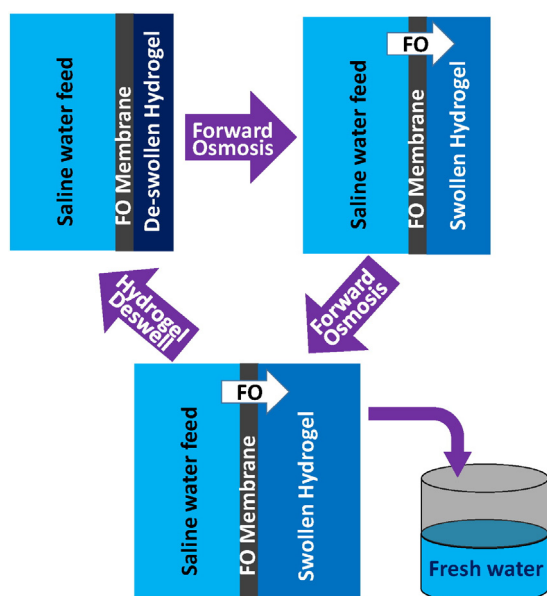
Fig. 4. Schematic diagram of using stimuli responsive hydrogels as draw solutes. Swelling is a spontaneous process while deswelling is triggered by external stimuli, which may include heat, magnetic and electric fields.

process by triggering responsive hydrogels to shrink under various external stimuli. Hydrogels draw agents have the advantages of intrinsically zero draw solute reverse diffusion and there is no need to further polish the released water since hydrogel networks do not dissolve in water. Unlike traditional draw solutes that dissolve or disperse in water to form draw solution, this special semi-solid form of draw solute (sometimes also named as draw agent for the hydrogel case) has once raised questions about whether its swelling process is truly FO in nature since the concept of osmotic pressure does not fit in hydrogels [108,109]. It is necessary to clarify that water flux in FO is actually driven by water chemical potential, or water activity. Osmotic pressure is only a more tangible and convenient parameter characterizing liquid solutions. The close relationship between water activity and osmotic pressure can be found in Eq. (5) (see earlier Section 2.3).

Li et al. [110] was the first to study the potential of hydrogels as draw solutes. Doubtlessly, hydrogels made from crosslinked PSA (or other polyelectrolytes [111]) generated the highest water flux in FO. This is because the strong interactions between PSA and water molecules (e.g., hydration and ionization) reduce the water chemical potential and increase the chemical potential gradient across the membrane. Unfortunately, water recovery from PSA is so poor that simultaneous heating and squeezing by hydraulic pressure can only recover a small portion of the water from the hydrogel. Hydrogels based on thermally responsive PNIPAm achieved the best water recovery of >75% at temperatures above its LCST, whereas its water drawing ability via swelling is poor. Copolymerization of SA with NIPAm was an obvious compromise, but it failed to produce significant improvement because of the diminishing responsive behavior with increasing SA content owing to electrostatic repulsion and hydration of ions [112]. Other reports investigated the effect of extrinsic parameters of hydrogels [113,114], and incorporation of different additives [115–118] and construction of a double layered structure [119] were attempted to enhance the deswelling of hydrogels based on poly(SA-NIPAm) random copolymers. However, majority of the water released is still believed in vapor form because there is little or no rapid macroscopic shrinkage of hydrogel to release absorbed liquid water. The regeneration mechanism is still essentially heat-induced evaporation through indirect heating using light irradiation or induction. The imbalance between swelling and de-swelling rates of the thermally responsive hydrogels was a major obstacle.

Cai et al. [120] resolved the problem of this imbalance by preparing hydrogels with a semi-interpenetrating network (semi-IPN) structure. The breakthrough of this work is that FO and regeneration cycles can be reversibly switched between 25 and 40 °C. Based on these unique semi-IPN hydrogels, a fresh concept of quasi-continuous desalination process driven by temperature cycling was proposed (between 25 and 40 °C, see Fig. 5). For the first time, a sustained water flux was demonstrated by using a hydrogel draw agent although the value is still very low. Another important contribution of this work is the proposition of a preliminary criterion towards high performance hydrogel draw solutes. This has posed a challenge to both desalination and polymer science communities. Instead of continuing using PNIPAm based hydrogels, Cai et al. [121] later synthesized new hydrogels based on thermally responsive polyionic liquids, and the water flux more than quadrupled that attained by PNIPAm based semi-IPN hydrogels. Furthermore, the hydrogel criterion was further refined to explicitly include the time factor which is important for further advancement of hydrogel draw solutes.

So far, in most of the studies of hydrogels draw agents, the evaluations of FO and regeneration performances are disconnected. FO performance was often conducted with dry hydrogel, which gave a high water flux value but this is not sustainable because after external stimuli the deswollen hydrogel is not in the dry state but contains significant amount of water. The performance reversibility and the concept of integrating hydrogels into a desalination module were only envisaged by a few studies [119–121]. Another obstacle for hydrogels is the low water flux. Therefore hydrogels may only be more suitable for brackish or other low salinity water treatment unless new materials can be found. Nevertheless, the recently reported FO water flux of 20 LMH by Hartanto et al. [122] using emulsion polymerized micro-gel particles is indeed exciting. If such high flux can be proved reversible and sustainable, it might be interesting to combine the micro-gel approach with an electro-responsive hydrogel reported earlier [123].

3.3. Metathesis precipitable salts

Draw solute regeneration by precipitation was reported as early as in 1970s, where the draw solute of aluminum sulfate was precipitated by adding calcium hydroxide [124]. However, it was not until very recently that several other inorganic salts such as $CuSO_4$ and $MgSO_4$ were tested as "smart" draw solutes by Alnaizy et al. since their regeneration is not by NF but via a metathesis reaction [125, 126]. After the FO process, stoichiometric barium hydroxide was added into the diluted draw solution to chemically generate $BaSO_4$ and $Cu(OH)_2$ or $Mg(OH)_2$ precipitation. Fresh water can be obtained by microfiltration (MF), and these precipitation mixtures are washed with sulfuric acid to recover the $CuSO_4$ or $MgSO_4$ draw solute while $BaSO_4$ is easily separated as a byproduct. These draw solutes are found to be effective for brackish water feed solutions. Liu et al. [127] reported $Al_2(SO_4)_3$ as draw solute for FO. In regeneration process, CaO was added to form a gel-like mixture consisting of $CaSO_4$ and $Al(OH)_3$. This positively charged mixture can be destabilized by addition of negatively charged colloids, e.g., SiO_2 coated magnetic Fe_3O_4 nanoparticles. Draw solutes can then be removed by external magnetic field and recovered by addition of sulfuric acid with insoluble $CaSO_4$ as the byproduct. However, no evaluation of FO performance or water quality was reported. In summary, this group of draw solutes may only be applicable for brackish water treatment, and not suitable for drinking water production because of the residue of Al^{3+} and Cu^{2+} ions in final water product. Other disadvantage of these draw solutes include the use of large amount of chemicals, tedious multi-step reaction/precipitation procedures and formation of byproducts during regeneration.
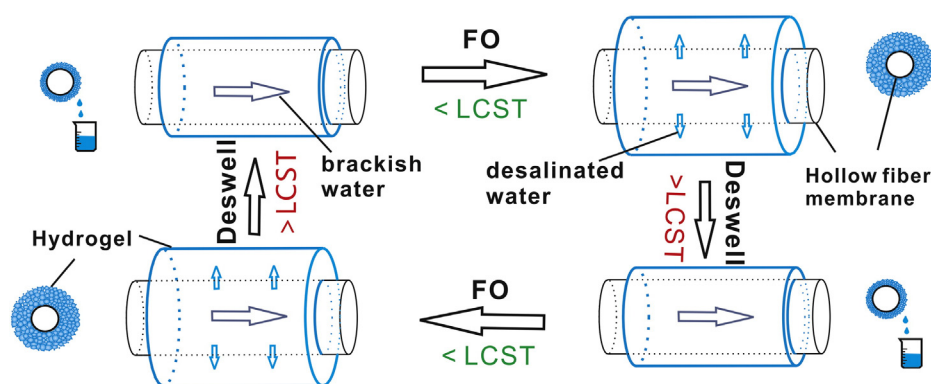
Fig. 5. Schematic illustration of temperature-modulated FO desalination enabled by thermally responsive hydrogels. At temperatures below the Lower Critical Solution Temperature (LCST), the hydrogel absorbs desalinated water through FO membrane from brackish water; at temperatures above the LCST, the hydrogel undergoes a phase separation to squeeze liquid water out to regenerate the hydrogel ready for next FO process.

3.4. Soluble gases or volatile liquids

Instead of liquid–solid phase separation in the regeneration process of metathesis precipitation, liquid–gas phase separation has also been studied by many researchers. Batcheler [128] proposed to use gases including SO_2 and NH_3 as draw solutes in 1965. Since these gases are quite soluble in water, the osmotic pressure would be desirably high albeit no experimental results were given. In the regeneration process, it was conceivable that removal of these gases could be done by air-stripping or evaporation under controlled temperature and pressure. Later, in his dual-stage draw solution system, McGinnis [129] also utilized soluble gases such as SO_2 or CO_2 as the second draw solutes to extract water from the first draw solution. However, the acidic or basic gases tend to ionize after dissolution, which caused difficulties in regeneration process since there is inevitably a small amount of draw solute in water even after air-stripping.

Sato et al. [130] explored a water-inert low boiling gas or highly volatile liquid, dimethyl ether, as the draw solute in FO desalination. Due to the moderate solubility (71 g/l) and low boiling point in atmosphere (-24 °C), the dimethyl ether draw solution generates an osmotic pressure of 24 bar and fresh water can be obtained after draw solute evaporation at room temperature. Interestingly, for this draw solute, energy consumption does not take place in regeneration but in draw solution preparation since external pressure is needed to aid the dissolution of the draw solute. Unfortunately, due to the presence of hydraulic pressure in the draw solution side, only thicker and robust RO membranes and static FO module were used to measure water flux. We suspect that the large operation hydraulic pressure in the draw solution side may cause complications on its actual implementation, and a matching pressure is also needed at the feed solution side. Therefore, more efforts are needed to tackle such challenges. A recent report screened a number of such compounds [131], and a very high osmotic pressure of up to 200 bar was reported. However, data on water flux in FO process, draw solute reverse diffusion and energy consumption were not reported. Reduction of water flux due to draw solute reverse diffusion could be a practical problem since current FO membranes are designed for rejecting salts [132]. There would be future requirements for FO membranes to have a better water-organic liquid selectivity in order to explore the potential of these types of draw solutes.

3.5. NH₃–CO₂ draw solutes

The thermolytic NH_3–CO_2 system is by far one of the most studied draw solutes and has shown good promise in several pilot scale operations. Therefore it is discussed separately from other soluble-gas draw solutes. Although this draw solute was first discovered in 1964 [133], it was not widely recognized as a promising draw solute for desalination until McCutcheon et al. [134,135] fully tested the essential parameters in the FO process, including water flux, draw solute reverse diffusion as well as salt rejection. As shown in Fig. 6, thermolytic salts made from the reaction between CO_2, NH_3 and H_2O can generate a very high osmotic pressure in FO process. In regeneration process, the draw solutes decompose to form the original gases, theoretically leaving fresh water product. In reality, due to the insufficient solubility of ammonium bicarbonate, the molar ratio of NH_3 to CO_2 is usually higher than 1 in order to form more soluble salts like ammonium carbonate and ammonium carbamate, resulting in an alkaline draw solution with a high pH [136]. Pilot-scale setups have been attempted to develop closed-loop operation [136,137]. In addition, applications other than desalination were also reported [138,139].

However, like many other draw solute candidates, NH_3–CO_2 system also has its drawbacks. The ammonium salts in draw solution suffer from rather severe back diffusion. Consequently there is a strong propensity of membrane scaling with carbonate ions at the feed solution side in alkaline condition [140]. A more thorough feed solution pretreatment to remove ions like Ca^{2+} can alleviate the scaling problem but with added cost. In addition, regenerating these gaseous draw solutes is often accompanied by undesirable water evaporation [141]. Water evaporation not only increases the energy consumption, but also causes difficulties in achieving a stable draw solution concentration after regeneration. Furthermore, there is inevitably trace amount of ammonia residue in the product water due to high solubility of ammonia. It is very unlikely, or not economically viable, to reduce the ammonia
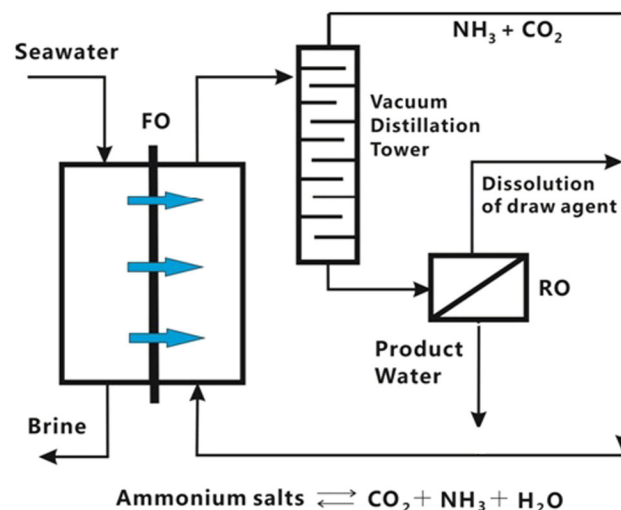

Fig. 6. Schematics of ammonium thermolytic salts as draw solutes in FO desalination.

concentration below the drinking water standard of 1.5 mg/l. However, NH_3–CO_2 draw solute has been used to treat high-salinity wastewater from shale-gas industry [142,143]. Also, replacing ammonia with trimethylamine could significantly reduce the draw solute back diffusion [144]. However, thorough removal of amine is still a challenge, and there are also concerns about odor and toxicity. Despite all these shortcomings, it is still one of the most studied draw solutes and has shown very good promise.

3.6. Polarity-switchable draw solute

Switchable polarity solvents (SPS) that change their affinity with water had been widely applied in several industrial applications including facile emulsion/demulsion [145] and polystyrene foam recycling [146]. Stone et al. [147] is the first to introduce this class of molecules as draw solutes. As shown in Fig. 7, the hydrophobic amine becomes hydrophilic and ionizes upon reaction with CO_2, to produce a draw solution with a very high osmotic pressure. In the regeneration process, CO_2 is removed and the amine restores to its hydrophobic non-ionic neutral state, facilitating phase separation from water. Final product water is polished by RO. The use of SPS draw solute is an interesting idea. However, one of the challenges is their compatibility with FO membranes because small molecular amines tend to swell and damage the membrane rejection layer and deteriorate its selectivity. In addition, the removal of CO_2, or deprotonation of the draw solute, may not be easy since, unlike the NH_3–CO_2, the ammonium salts from switchable polarity solvents are not considered thermolytic. In fact, the paper reported the adding of NaOH into the diluted draw solution to deprotonate the amine during regeneration [147]. Furthermore, even the deprotonated SPS still has a relatively high solubility of 18g/l in water. RO was used to remove the dissolved amine residue but the product water is still unsuitable to drink.

Such type of SPSs can be deemed as CO_2 responsive draw solutes, because of the presence of tertiary amines in their structures [148]. Wilson et al. [149,150] systematically studied the influence of tertiary amine structure on the properties of draw solute, including viscosity, molecular diffusion coefficients, osmotic pressure and density. A FO prototype using an amine-CO_2 mixer was designed [149], but further study in regeneration, especially CO_2 removal was not discussed. Recently, Orme et al. [151] studied 1-cyclohexylpiperidine as the polarity switchable draw solute. The unique feature of this draw solute is that air-stripping by bubbling inert gas is no longer a necessity, and regeneration can be achieved by heating alone, e.g., at 80 °C for 3 h. Therefore, this draw solute can also be categorized as a thermolytic salt as it bears

similarity to the NH_3–CO_2 system. Preliminary results showed that heating can reduce the solution's osmolality to about 0.2 osmol/kg, or about 5 bar in osmotic pressure. However, no discussion on product water quality was reported.

Apart from using hydrophobic amines, thermally responsive polymer of poly[2-(dimethylamino) ethyl methacrylate] (PDMAEMA) was also investigated by Cai et al. [152]. Compared with the aforementioned polarity switchable draw solutes with small molecular weights, this CO_2 and thermally dual responsive polymer draw solute is benign to membrane. In addition, the synthesis of PDMAEMA is scalable and it has low reverse diffusion. For PDMAEMA, the draw solute to water flux ratio is two orders of magnitude lower than that of 1-cyclohexylpiperidine [151]. The larger size of the polymer draw solute assists in regeneration process and, in addition, PDMAEMA is thermally responsive with the LCST behavior (see next section for details). Therefore phase separation via precipitation of the draw solute at 60 °C after CO_2 removal is effective, leaving a supernatant phase so diluted that a 2 bar ultrafiltration (UF) step can achieve a 95% water recovery. Further investigation on such dual responsive polymers should focus on optimization of molecular weight and molecular architecture. Thorough studies on concentration polarization with these new draw solutes are also necessary.

3.7. Thermally responsive molecules

Exploring draw solutes with a strong temperature-dependent solubility dates back to 1970s. Hough [153] listed compounds with a higher water solubility at a either high or low temperature. Experiments to assess the performance of these compounds as draw solutes were lacking, possibly limited by the lack of suitable membranes at that time. Draw solutes with Lower Critical Solution Temperature (LCST) in water are another group of candidates responsive to temperature. The draw solution in FO process is a homogeneous single phase solution at temperatures below the LCST. At temperatures above LCST, the draw solution undergoes a phase separation, typically resulting in a draw solute-rich phase and a water-rich phase that can be further polished for fresh water production. Ideally, the phase separation should be as complete as possible to recover concentrated draw solute-rich phase with a sufficiently high osmotic pressure, while the water-rich phase is as dilute as possible for ease of further treatment. Conventional LCST-type polymer such as PNIPAm and its copolymers are unable to extract water from seawater due to the neutral non-ionic state and high molecular weight. Studies were more focused on LCST-type small molecules so far.

An earlier study used polypropylene glycol (PPG) with an average molecular weight of 425 g/mol [154]. An osmotic pressure of about
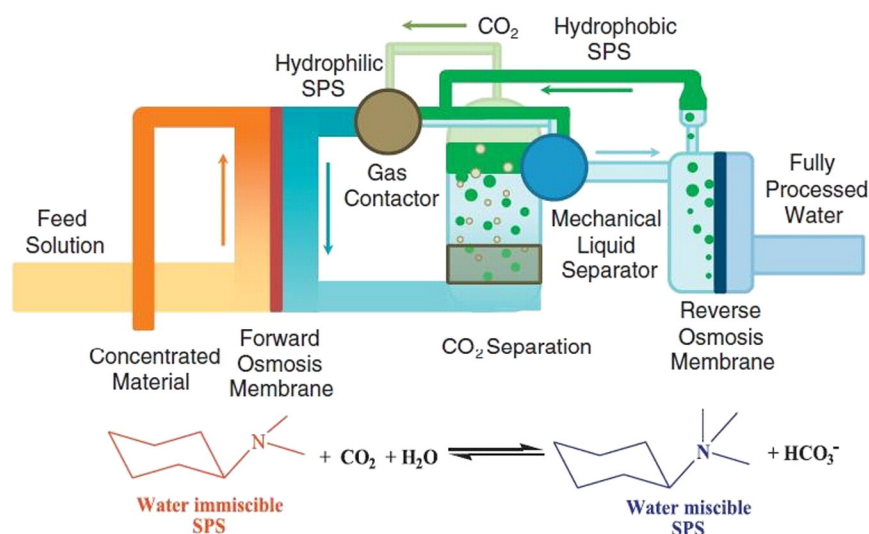

Fig. 7. Illustration of using hydrophobic tertiary amine as polarity switchable draw solute. This figure is modified from reference [147]. Reprinted with permission. Copyright 2013, Elsevier.

40 bar can be achieved to treat seawater in a bench-scale FO test set-up. However, the performance in the regeneration process is poor, due to the polydispersity in molecular weight. Nok et al. [155,156] and Nakayama et al. [157] studied N-acrylate polyethylenimine (PEI) derivatives and glycol ethers as possible LCST-type draw solutes. These draw solutes have a very stable phase separation behavior above LCST due to the uniform molecular weight. Unfortunately they have low osmotic pressure and can hardly draw water from artificial seawater feed solution (0.6 M NaCl). A study by Cai et al. [158] was the first to introduce LCST-type ionic liquids as draw solutes. Their molecular structures are given in Fig. 8, together with the schematics describing the FO-regeneration processes. The synthesized thermally responsive ionic liquids showed great potential as desalination draw solutes, with high osmotic pressure capable of drawing water from a 1.6 M NaCl feed solution, which is equivalent to a salinity about 3 times that of seawater. At the same time, only a mild heating to 60 °C is needed in regeneration process, leading to phase separation into a draw solute-rich phase that can be directly reused as draw solution without further treatment, and a water-rich phase that can be further treated by NF or RO at as low as 5 bar. Study revealed that the enthalpy of the phase separation of these responsive ionic liquid draw solutes (3 to 5 kJ/kg) is substantially lower than the decomposition enthalpy of ammonium salts such as NH_4HCO_3, making them more attractive. The liquid–liquid phase separation behavior is also much more favorable for draw solute regeneration compared to the two stage regeneration involving a liquid-to-gas followed by a gas-to-liquid transition in the case of $NH_3–CO_2$, which may require vacuum or pressure for rapid gas removal or re-dissolution.

The LCST-type ionic liquids should be intrinsically superior over non-ionic organic compounds of similar molecular weight to produce a higher osmotic pressure at similar concentration. Ionic liquids are also non-volatile with excellent thermal and chemical stability. These are all desirable attributes of a good draw solute. Future development in responsive ionic liquid draw solutes with more careful molecular structure design may achieve better balance between hydrophobicity and hydrophilicity. Interestingly, based on the mechanism of the LCST behavior, more hydrophobic molecules facilitate easier regeneration and are perhaps more suitable for colder climate because both FO and regeneration are done done at respective lower temperatures. More hydrophilic versions could be designed for use in the warmer climate. The goal is to produce high osmotic pressure during FO while regeneration can be carried out with the lowest possible energy cost. Apart from the LCST-type draw solutes, a few UCST-type draw solutes whose phase separations occur during cooling, were also studied recently [159,160].

4. Some important issues

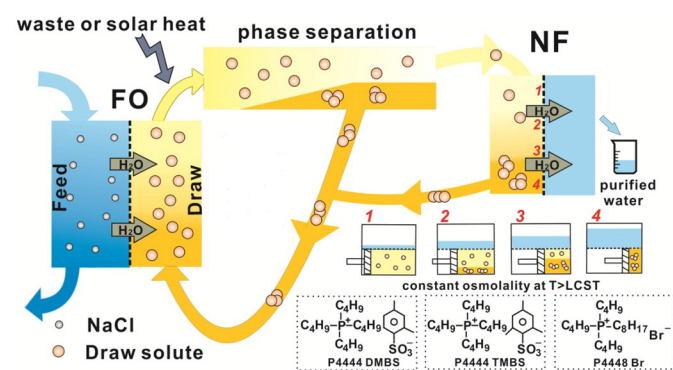It is our wish and belief that the role of FO technology and the future trend of draw solutes should be clarified through a critical and thorough review. We also hope that sharing of our personal experience and opinion would catalyze discussion and accelerate future development in this exciting and important field. Therefore, we further outline below several critical issues that are ambivalent or overlooked in the literature. We hope that the awareness and understanding of these issues would help readers from both academia and industry to reach a more balanced view on the future development of FO draw solutes and FO technology.

4.1. Energy consumption and energy cost

Although there are dozens of research papers on responsive draw solutes and a lot of them mentioned "low energy" in the context, yet only few research papers attempted to calculate the theoretical energy consumption of FO enabled by the corresponding responsive draw solutes. The energy consumption of $NH_3–CO_2$ system for seawater desalination was calculated to be only 0.84 kWh/m^3 at 75% water recovery [161], which stirred some discussion and debate since this value is lower than the theoretical minimum. We believe that there is a possibility that this energy consumption estimation did not include the energy for further treatment needed to completely remove the residue $NH_3–CO_2$ in the water exiting the regeneration vacuum column. The report also did not discuss the possible energy consumption due to water evaporation while NH_3 and CO_2 were librated during the draw solute regeneration. Kim et al. [162] studied the FO seawater desalination enabled by draw solutes with temperature-dependent solubility. The theoretical minimum energy consumption during the regeneration via crystallization and RO was found to be 2.15 kWh/m^3 at 30% water recovery, which is higher than that of standalone RO for seawater desalination at the same water recovery. Actually, this is understandable because, similar to the non-responsive draw solute, the responsive draw solute regeneration process is still dealing with a diluted draw solution with a higher osmotic pressure than the feed. Although operating at high pressure, RO is currently the most energy efficient seawater desalination technology with an energy consumption very close to the theoretical minimum [141,163]. Developing new draw solutes is unlikely to enable FO to consume less energy than its RO counterpart.

However, energy consumption and energy cost are two different concepts. One of the merits of using responsive draw solutes is that pre-separation of draw solute and water is done by a certain external stimulus, leaving a much more diluted stream for the electricity-consuming process, e.g., RO, to treat. Therefore, it is anticipated that the electric energy consumption of FO enabled by responsive draw solutes could be lower than that of RO. Cai et al. [158] found that although the theoretical total energy consumption of FO is higher than RO in seawater desalination assuming 50% water recovery, the hydraulic pressure needed in the NF polishing step is only less than 5 bar and the electric energy consumption is only about 13% that of RO. By exploiting the possibility of using inexpensive thermal energy, e.g., low grade industrial waste heat or solar source, in place of the expensive electric energy, FO has the potential for significant cost saving compared to RO. For instance, FO enabled by thermally responsive hydrogel draw solutes can virtually be operated by only thermal energy [119–121] (excluding the normal pumping energy needed for circulation), although more efforts are needed before it can be widely accepted for commercial applications.

4.2. Treatment of streams with high salinity or fouling propensity and zero liquid waste discharge

The new development in responsive draw solutes may enable FO to find its niche to achieve extremely high water recovery where near zero liquid discharge is preferred or demanded. In addition, FO might be particularly useful to treat difficult feed streams such as those with very high salinities. In such cases, FO can be highly complementary to RO because RO has a practical upper limit in operation hydraulic pressure, while in FO, the feed stream can be continuously concentrated as

Fig. 8. Illustration of LCST-type ionic liquids as draw solutes in forward osmosis desalination. This figure is adapted from Reference [158]. Reprinted with permission. Copyright 2015, Royal Society of Chemistry.

long as the draw solution maintain a higher osmotic pressure than the feed. To put into perspective, it appears that thermal distillation methods including multi-stage flash (MSF) and multiple effect distillation (MED) are probably the only alternatives to FO in treating high salinity feed streams. However, instead of the need for evaporating large amount of water, the draw solute regeneration process in FO involves only a phase change (e.g., liquid–liquid phase change) of the draw solute with a much lower enthalpy than that of water vaporization, making FO potentially more energetically favorable than MSF and MED. In a recent study, Wendt et al. [164] found that the energy consumption of concentrating seawater to saturated NaCl solution by FO enabled by polarity switchable draw solute is only less than 4.3 kWh/m^3. This amazing water recovery of up to 90% cannot be achieved by RO alone, and the 4.3 kWh/m^3 energy consumption value is lower than that from MSF and MED. If FO is combined with a crystallizer to achieve zero-liquid discharge, then the saturated NaCl solution effluent from FO can save a vast amount of energy in the crystallizer [165]. The production of crystal salts from crystallizer may be additional revenue for the desalination plant, and the absence of liquid discharge not only preserves the environment, but saves the cost in brine disposal [164]. The same concept is applicable to other applications such as treating high salinity waste water from mining or shale gas industry. It is worth mentioning that one should take the advantage of the low hydraulic pressure and high fouling reversibility in FO processes based on responsive draw solutes and explore in future for applications in concentrating effluents or products from food, pharmaceutical and diary industries. Of course, for such applications, special attention should be given to the toxicity and reverse diffusion issues of the draw solutes.

4.3. Water recovery

The water recovery in RO is a straightforward parameter defined as the fraction of product water weight (flux) over the feed solution weight (flux). Whereas in FO desalination, there are FO process and regeneration process, and the term "water recovery" was sometimes less clearly defined. For example, in some reports [110,116,117], the term "water recovery" is only used to quantify draw solutes performance in regeneration process, rather than the water recovery of the entire FO-regeneration process. Similar discussion was also found in other reports using NF or RO as the regeneration methods [28]. It should be highlighted that, in a stable closed-loop FO-regeneration desalination process, overall water recovery is equivalent to the water recovery of the FO process only that is defined as the ratio of mass of water permeating through the FO membrane to the mass of feed solution, and should not be confused with 'water recovery' mentioned during regeneration process. The regeneration process is to restore the diluted draw solution to its initial concentration, and the "water recovery" value discussed in the regeneration process is just an indicator of the performance of the draw solutes under the chosen regeneration conditions. In fact, only a very few reports mentioned the 'true' FO water recovery when evaluating the performance of draw solutions. This is due to the fact that closed-loop FO-regeneration was not realized in many bench-scale experiments, and in most academic papers, the reported water flux data are often measured under conditions where there is virtually no concentration variation in both draw solution and feed solution.

4.4. Draw solute reverse diffusion

The reverse diffusion of draw solute into feed solution becomes more severe when the draw solute's molecular weight is reduced to favor a higher water flux. The situation is further aggravated when treating high salinity feed streams. For example, based on the reported reverse diffusion data of 1-cyclohexylpiperidine [151], one could estimate that there would be substantial daily loss of draw solute due to back diffusion if such draw solutes were used in a large scale water treatment plant. Sometimes it is not realised that such loss not only

leads to a higher cost but may also pose a threat to the environment. In fact, both the amine based polarity switchable solvents and NH$_3$–CO$_2$ system contain nitrogen, and any possible release into the environment could lead to pollution or eutrophication. Although the environmental impact can be reduced by feed solution post-treatment, e.g., using anaerobic ammonium oxidization (anammox) [166], the cost might increase significantly. In addition, mineral scaling due to reverse diffusion of carbonate of NH$_3$–CO$_2$ draw solute has been reported [140]. In another study [136], as shown in Fig. 9, the feed solution was distilled after FO to recover the reverse diffused ammonium salts. This again would definitely increase the energy consumption. Recently, Nguyen et al. [167–169] found that addition of surfactants into certain salts can significantly reduce draw solute reverse diffusion without severely compromising the water flux. This is very interesting and should be studied further to explore its usage in other responsive draw solutes discussed in this review. Clearly, there are opportunities to minimize reverse diffusion of draw solutes. Three possible approaches should be considered simultaneously, i.e., through developing new draw solutes, enhancing FO membrane selectivity and optimizing the FO operation parameters.

4.5. Concentration polarization

Concentration polarization (CP) is a prevalent phenomenon in any membrane based process and not exclusive to FO. Interestingly, almost every review paper on FO and some research papers on draw solutes included some basic introduction of CP as general background information. However, there is virtually no discussion on quantifying the influence of the draw solute type on CP in FO process. This is probably because CP in FO is more complex as it is not only affected by membrane structures and operation parameters (e.g., flow rate, temperature and membrane cell configuration) as in RO or NF. The introduction of a new draw solute and its associated issues such as viscosity and reverse diffusion may further complicate the assessment of CP in FO. The reported quantitative study on CP only compared the effect of different operation parameters, such as draw solution concentration, feed solution concentration and membrane orientation for a given draw solute. Up to now, there is no systematic study carried out to quantitatively
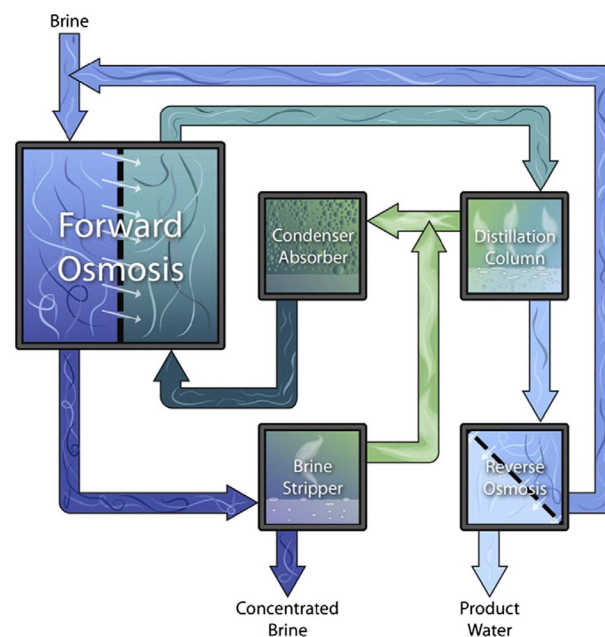
Fig. 9. The illustrative diagram of NH$_3$–CO$_2$ as draw solute in a pilot-scale experiment. Distillation of feed solution is adopted to recover the back-diffused draw solute. Reprinted with permission from Reference [136]. Copyright 2013, Elsevier.

Table 1
Summary of various types of draw solutes for forward osmosis.

Draw solutes	Examples	Comments and remarks	Ref
Inorganic salts	NaCl, MgCl$_2$, Na$_2$SO$_4$, (NH$_4$)$_2$SO$_4$, Ca(NO$_3$)$_2$, KHCO$_3$	Useful fundamental study; helpful in understanding important parameters affecting FO performance; non-responsive; limited application.	[18–23]
Polymers	PSA, poly(aspartic acid), copolymers	Non-responsive; low back diffusion but also low water flux; copolymers with non-ionic monomers producing even lower water flux; high viscosity; limited application.	[25–35]
Organic compounds	Sodium salts of organic acids, zwitterions, hydroacid complexes	Better water flux than polymers; mainly focused on lowering back diffusion; complex synthesis procedures; non-responsive; limited application.	[36–46]
(Magnetic) nanoparticle	Carbon quantum dots and Fe$_3$O$_4$ with surface modification	Ease of regeneration via magnet; low to moderate water flux; low back diffusion; issue of particle agglomeration; possibility for very special applications.	[93–104]
Thermally responsive hydrogels	PNIPAm, copolymers with PSA, semi-IPNs, polyionic liquids	Unique auto- or self-regeneration characteristics; zero back diffusion; possibility of quasi-continuous FO process demonstrated; low water flux though significant improvement in new responsive hydrogels based on polyionic liquids; opportunities for dewatering of low salinity feed streams.	[110–123]
Metathesis precipitable salts	CuSO$_4$/MgSO$_4$ + Ba(OH)$_2$ + H$_2$SO$_4$, Al$_2$(SO$_4$)$_3$ + CaO	Academically interesting; chemicals and acid/base needed in regeneration; tedious regeneration steps; concerns of toxicity; no apparent viable application.	[124–127]
Dissolved gases or volatiles	SO$_2$, NH$_3$, CO$_2$, dimethyl ether	High osmotic pressure possible; draw solutions prepared under pressure; possible operational issues; severe back diffusion likely; toxicity issue; more studies needed.	[128–131]
NH$_3$–CO$_2$ combination	Ammonium bicarbonate, carbonate and carbamate	High osmotic pressure; most widely studied; incomplete removal of NH$_3$; not suitable for drinking water; serious back diffusion; scaling; pilot scale plant demonstrated, regeneration requiring both liquid-to-gas and gas-to-liquid transitions.	[133–144]
Switchable polarity solvents	Tertiary amines-CO$_2$, PDMAEMA-CO$_2$	CO$_2$ used for protonation; liquid–liquid phase separation during regeneration; possible damage to membranes; liquid–solid phase separation, no damage to membrane and low back diffusion for PDMAEMA; more investigation needed for implementation.	[147–152]
Thermally responsive organic compounds	PPG, PEI, glycol ether, ionic liquids	Most studies on LCST type molecules; high water flux possible; thermally responsive ionic liquids outperforming the rest; significant saving on energy cost possible; pilot scale studies needed, UCST type molecules to be explored.	[153–158]

compare the CP effect between different types of draw solutes. However, qualitatively it is known that CP is related to the draw solution viscosity and diffusivity of draw solute molecules. Therefore, it is believed that reducing draw solute molecular weight and/or optimizing the molecular architecture are two of the possible ways to reduce CP from draw solute perspective. More studies also need to be carried out on the effect of draw solute/membrane interaction on CP. Addressing complex issues such as CP in FO calls for interdisciplinary research with combined efforts not only from chemists and materials scientists, but also from membrane manufacturers and process engineers.

5. Summary

The subject of draw solutes for forward osmosis has been comprehensively reviewed in this report. We strived not to make just a collection of a long list of draw solutes reported in the literature but to examine each category of draw solutes carefully and critically. We also highlighted several important issues concerning draw solutes because tackling these challenges requires multidisciplinary effort and knowledge in chemistry, materials science, membrane science and process engineering. For example, the concentration polarization in the FO process can be alleviated by adopting not only responsive draw solutes with smaller molecular weights, but also new FO membranes with advanced structures and operation conditions with optimized cross-flow parameters. The draw solutes discussed in this reports are not all equal and each is at its own stage of development. It is certain that the searching for 'ideal' draw solutes will continue as the results so far have shown that, with suitable responsive draw solutes, FO can be a viable complementary technology to other technologies including RO. FO has been shown to have niche applications where RO is uneconomical or inapplicable, e.g., for treating feed streams with high salinity or high fouling propensity. It is now clarified and widely accepted that FO is unlikely to reduce total energy consumption for seawater desalination as compared to its RO counterpart. However, there is potential for substantial energy cost saving with FO when low grade thermal energy is used in place of electricity by using suitable responsive draw solutes. We therefore made a deliberate effort to analyze the rationale, advantages and disadvantages of these draw solutes with the ultimate goal to provide a guidance for future development of new and better draw solutes and to minimize the unnecessary mistakes and confusions. We

anticipate that an accelerated development in new draw solutes in the near future will further propel the FO and related technology.

The current endeavor to explore new draw solutes through chemistry and materials science approaches has been fruitful, especially in the effort towards achieving enhanced overall performance, i.e., (i) high osmotic pressure, (ii) being easily regenerated with only low grade heat, (iii) low reverse diffusion, (iv) low viscosity, (v) good chemical and thermal stability, and (vi) low toxicity. The main categories of draw solutes discussed in this review are outlined in Table 1 for ease of comparison. It is clear that further work is needed as none of these draw solutes is perfect.

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