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A critical review on draw solutes development for forward osmosis

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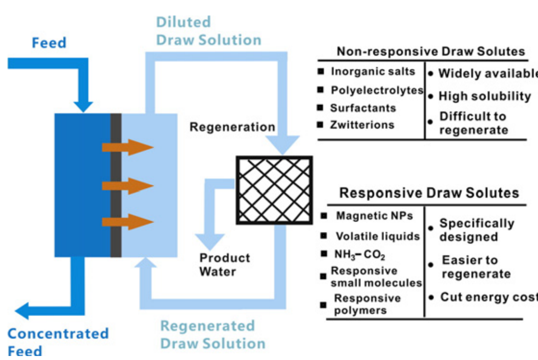
HIGHLIGHTS

- 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



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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.

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_2SO_4, $(NH_4)_2SO_4$, $Ca(NO_3)_2$, $KHCO_3$, 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 nonionic 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