

## Review

## A review on the recovery methods of draw solutes in forward osmosis



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## ABSTRACT

Recently, there has been an increasing use of forward osmosis (FO) technique for energy-efficient water treatment, leading to significant public concerns. One key know-how to make FO practical is developing an ideal draw solute characterized by high water flux, low reverse solute flux, and easy recovery. The recovery of draw solutes takes a significant energy cost in FO technology implementation. To this end, it is necessary to enhance the understanding of how different kinds of draw solutes are regenerated during the dewatering process. This review aims to provide a comprehensive overview of current knowledge of draw solutes in terms of recovery from water. A variety of existing recovery methods developed so far to overcome the recovery barriers, including thermal separation, membrane separation, precipitation, stimuli–response, combined processes, and direct use without recovery are presented. Discussions on the advantages and limits of the existing recovery methods are made based on acquired knowledge from the literature. Future directions for the effective and energy-efficient recovery of draw solutes are also provided. Information summarized in the paper further highlights the potential applications of the FO process.

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## Contents

1. Introduction .....	213
2. Approaches to DSs recovery .....	213
2.1. Thermal separation .....	213
2.2. Membrane separation .....	214
2.2.1. RO .....	214
2.2.2. NF .....	215
2.2.3. UF .....	216
2.2.4. Membrane distillation (MD) .....	216
2.2.5. Electrodialysis (ED) .....	216
2.3. Precipitation for recovery .....	217
2.4. Stimuli–response for recovery .....	217
2.4.1. Response to heat, hydraulic pressure, sunlight, and gas pressure .....	217
2.4.2. Magnetic response .....	219
2.5. Combined processes for recovery .....	219
2.5.1. Precipitation combined with magnetic response .....	219
2.5.2. Integrated electric-field NF .....	219
2.5.3. Hot ultrafiltration (HUF) .....	219
2.6. Direct use for drinks, irrigation, and desert restoration .....	219

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3. Challenges and prospects for the future .....	220
Acknowledgements .....	221
References .....	221

## 1. Introduction

Since the beginning of the 2000s, forward osmosis (FO) has gained increasing popularity. It has been viewed as one of the most promising technologies in the 21st century [1–6], as it is a green membrane technology for desalination and water treatment with advantages of lower energy cost and less membrane fouling compared with traditional membrane processes such as reverse osmosis (RO), ultrafiltration (UF), nanofiltration (NF), and microfiltration (MF) [4,7–10]. In a FO process, a draw solution is used to “attract” water from feed solution by osmotic pressure difference through a semi-permeable membrane, while most solutes are rejected by the FO membrane. This is followed by a process to reconcentrate the diluted draw solution and produce clean water. Although not all FO applications require recovery of draw solutes (DSs) (e.g., for nutritious drinks during emergencies [11], irrigation [12], and desert restoration [13]), several major FO applications (e.g., desalination for drinking water, wastewater reclamation, etc.) need DSs to be separated from water or reconcentrated for reuse [14,15]. The selection and use of a suitable draw solute can greatly influence the efficiency and sustainability of FO operations. Typically, an ideal draw solute in FO for water production should have the desired properties of high osmotic pressure, minimal reverse solute diffusion, easy separation from water, economic feasibility, reusability, nontoxicity, and compatibility with FO membranes [16–19].

In recent years, a number of novel DSs have been proposed together with a variety of remarkable recovery technologies besides traditional DSs like sodium chloride (NaCl) [20] to advance FO technology for various applications (Table 1). These DSs may be generally classified into inorganic salts, and organic compounds according to their physicochemical properties. The inorganic salts including ammonia–carbon dioxide ( $\text{CO}_2/\text{NH}_3$ ) [21], fertilizers [12], seawater [22,23], and aluminum/copper/magnesium sulfate [24–26], have been proposed to reduce the energy cost for regeneration. However, the inorganic DSs with monovalent ions may cause high reverse solute flux. The organic compounds include 2-methylimidazole-based compounds [27], polyacrylic acid sodium salts (PSA) [28], hexavalent phosphazene salts [29], switchable polarity solvents (SPS) [30], hydroacid complexes [31], EDTA sodium salts [32], sodium lignin sulfonate (NaLS) [13], zwitterions [33],  $\text{Na}^+$ -functionalized carbon quantum dots (Na-CQD) [34], and smart materials [18], which are expected to have minimal reverse solute flux and require low energy cost for recovery. Among the organic DSs, smart materials with intelligent response have attracted growing interest for FO applications recently, including functionalized magnetic nanoparticles (MNPs) [35–42], thermosensitive polyelectrolytes [43–46], and stimuli-responsive hydrogels responding to different stimuli such as heating [10,47], a combination of heating and hydraulic pressure [48], sunlight [49–51], gas pressure [52], and magnetic heating [53]. These smart DSs may be recovered at a relatively low-energy cost under different stimuli, and induce minimal reverse solute flux due to their large sizes. However, a comprehensive review of the recovery methods of these DSs is not available. Thus the objectives of this paper are (1) to conduct a critical and detailed review on the existing recovery methods of DSs, and (2) to illustrate how the newly developed technical innovations on recovery of DSs have led to preference for FO technology as a membrane-based separation process.

## 2. Approaches to DSs recovery

### 2.1. Thermal separation

In as early as the 1960s, a variety of reagents were tested for use as DSs in the FO process for seawater desalination. However, previous efforts on these reagents are mostly presented for patents; thus, they have limited technical and performance details. In 1965, Batchelder used volatile solutes such as sulfur dioxide ( $\text{SO}_2$ ) in FO [54].  $\text{SO}_2$  was added to seawater or freshwater to create a solution with high osmotic pressure, which could be used as the driving force to extract water from seawater. After FO,  $\text{SO}_2$  was separated from water by heating or air stripping. However, the experiments only demonstrate that a desirable water flux is observed without providing detailed data on the recovery rates. Later, McGinnis described a two-stage FO process using a combination of potassium nitrate ( $\text{KNO}_3$ ) and  $\text{SO}_2$  for seawater desalination [55]. This process utilized the temperature-dependent solubility of  $\text{KNO}_3$  and  $\text{SO}_2$  to enhance the water recovery rate. However, it is costly as cooling and heating are required to recycle  $\text{KNO}_3$  and  $\text{SO}_2$ . Despite the fact that the recovery of  $\text{SO}_2$  from water is easily available, the process involving  $\text{SO}_2$  may be very dangerous because  $\text{SO}_2$  is volatile, corrosive, and highly reactive toward both oxidants and reductants.

McCutcheon et al. and McGinnis et al. made a great breakthrough with the use of ammonia–carbon dioxide ( $\text{NH}_3/\text{CO}_2$ ) draw solution in the FO process (Fig. 1) [21,56–58]. The  $\text{NH}_3/\text{CO}_2$  draw solution could be formed by dissolving  $\text{NH}_3$  and  $\text{CO}_2$  gases in water at appropriate proportions, which could generate a high osmotic pressure. The recovery of the DS could be achieved easily. Heating ( $\sim 60^\circ\text{C}$ ) of these ammonium salts led to their decomposition into  $\text{NH}_3$  and  $\text{CO}_2$  gases, which were then separated from water. The recovered gases could then dissolve in water for reuse. Experiments demonstrated that the average water recovery rate of this system was as high as 64% [58], and the energy consumption was as low as an electrical power of less than  $0.25\text{ kWh/m}^3$  [57]. The waste heat (e.g., from power generation plants) could be utilized to enhance the energy-efficiency advantage for recovery. However, the removal of ammonia residue from product water remains a critical issue, and even trace amounts of residue may deteriorate the product water. It may be difficult to eliminate ammonia from

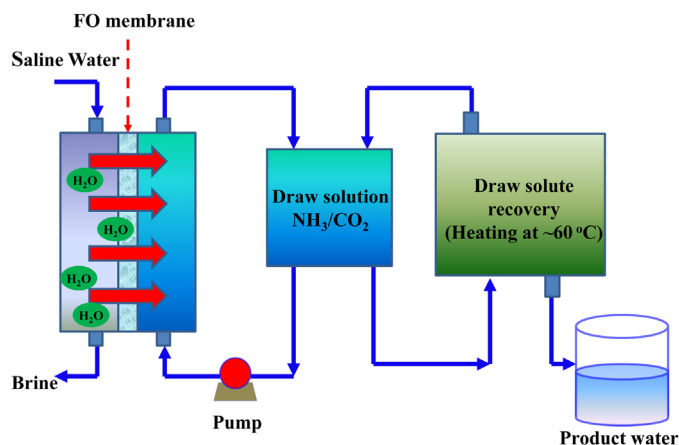


Fig. 1. Schematic diagram of the  $\text{NH}_3/\text{CO}_2$ -driven FO process.

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