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Keywords: Energy, regeneration, membrane separation, draw solutes, forward osmosis

Abstract:

In recent years, membrane technologies have been developed to address water shortage and energy crisis. Forward osmosis (FO), as an emerging membrane-based water treatment technology, employs an extremely concentrated draw solution (DS) to draw water pass through the semi-permeable membrane from a feed solution. DS as a critical material in FO process plays a key role in determining separation performance and energy cost. Most of existing DSs after FO still require a regeneration step making its return to initial state. Therefore, selecting suitable DS with low reverse solute, high flux, and easy regeneration is critical for improving FO energy efficiency. Numerous novel DSs with improved performance and lower regeneration cost have been developed. However, none reviews reported the categories of DS based on the energy used for recovery up to now, leading to the lack of enough awareness of energy consumption in DS regeneration. This review will give a comprehensive overview on the existing DSs based on the types of energy utilized for DS regeneration. DS categories based on different types of energy used for DS recovery, mainly including direct use based, chemical energy based, waste heat based, electric energy based, magnetic field energy based, and solar energy based are proposed. The respective benefits and detriments of the majority of DS are addressed respectively according to the current reported literatures. Finally, future directions of energy applied to DS recovery are also discussed.

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Review

Recent Advance on Draw Solutes Development in Forward Osmosis

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Abstract: In recent years, membrane technologies have been developed to address water shortage and energy crisis. Forward osmosis (FO), as an emerging membrane-based water treatment technology, employs an extremely concentrated draw solution (DS) to draw water pass through the semi-permeable membrane from a feed solution. DS as a critical material in FO process plays a key role in determining separation performance and energy cost. Most of existing DSs after FO still require a regeneration step making its return to initial state. Therefore, selecting suitable DS with low reverse solute, high flux, and easy regeneration is critical for improving FO energy efficiency. Numerous novel DSs with improved performance and lower regeneration cost have been developed. However, none reviews reported the categories of DS based on the energy used for recovery up to now, leading to the lack of enough awareness of energy consumption in DS regeneration. This review will give a comprehensive overview on the existing DSs based on the types of energy utilized for DS regeneration. DS categories based on different types of energy used for DS recovery, mainly including direct use based, chemical energy based, waste heat based, electric energy based, magnetic field energy based, and solar energy based are proposed. The respective benefits and detriments of the majority of DS are addressed respectively according to the current reported literatures. Finally, future directions of energy applied to DS recovery are also discussed.

Keywords: forward osmosis; draw solutes; membrane separation; regeneration; energy

1. Introduction

With the development of economy, population boom and increasing urbanization, water shortage has become a global problem. To address the water scarcity and prevent water pollution, the seawater desalination and wastewater reuse has been considered as a good solution to solving mentioned above [1–5]. In the past decade, numerous desalination technologies, including multistage flash evaporation, low-temperature multi-effect distillation, electrodialysis, reverse osmosis (RO) have been developed to desalinate seawater. Among them, RO is one of the most widely used desalination technology, due to its high salt rejection and easy large-scale operation. The energy consumption of 1 m³ fresh water produced by RO is still up to 1.5–2.5 kWh, which is 5~10 times lower than that of distillation [6]. However, the discharge of concentrated salt solution produced by RO may give rise to the secondary pollution [1,7–11].

Forward osmosis (FO) is an emerging water treatment technique [12]. In FO process, the net osmotic pressure difference generated by the draw and feed solution with different concentrations on both sides of the membrane impels water molecules to permeate from the side of feed solution to the draw solution (DS). Since water molecules spontaneously permeate without additional pressure, the energy consumption of seawater desalination by FO alone without DS recovery is around 0.84 kWh/m^3 , which is 72.1% lower than that of RO [13]. Compared with RO, FO possesses a stronger antifouling capability [2,14–17], higher water recovery, and less salt discharge. Therefore, it has good prospect of application in such fields as seawater desalination [18,19], agricultural irrigation [20], anaerobic sludge disposal [8,21,22], osmotic power generation [23–25], wastewater treatment [19,26], protein enrichment [27,28], drug delivery and release [14,29], aerospace [30], and food industry [31].

Although FO is well considered as an energy-saving process by using some smart agents as DS, the result of thermodynamic calculations shows that reducing energy consumption in FO process isn't a "free lunch" [15]. In general, FO desalination process includes two steps: The concentrative DS is diluted, and the dilutive DS is re-concentrated. This means the use of higher osmotic pressure DS dewater from feed solution in the first step and the diluted DS should be regenerated to initial state by using other technologies in the second step. Especially, considering DS regeneration in seawater desalination, the energy consumption of a standalone FO process far surpasses than that of RO [15]. However, FO hybrid systems (i.e., FO-RO) are capable of desalinating the high-salinity waters, which RO process is limited, such as those highly fouled or specific waste stream or high osmotic pressure feeds [15]. In addition, FO as an immature technology suffers some limitations, such as severe DS leakage, which may decrease the quality of product water or reduced FO performance or increase DS recycling costs, leading to hinder its practical industrial application. However, FO still has the opportunities by employing the low-cost thermal energy for DS regeneration. For example, the use of thermolytic compounds as DSs in FO hybrid systems can reduce total energy requirement for desalting high-salinity waters, which is more energy-saving than other desalination solutions [15]. This case shows the advantages of FO over RO, such as low energy cost, considerably high water recovery, and minimal fouling. These advantages imply that FO is facing some accompanied challenges. In fact, FO could not be applied in widespread applications, mainly due to the limited choices of DSs.

DS as one of critical materials of FO has a great impact on the energy efficiency. Although FO is common an energy-efficient process without DS recovery, it, in most instances, still requires the secondary step to concentrate DS, which would directly increase the relevant energy cost. Therefore, it is necessary to develop suitable DS so as to break through the bottleneck of FO's development toward the practical application. An ideal DS should have some characteristics [2,32], including high solubility, high osmotic pressure, low molecular weight (MW), low-cost regeneration, good compatibility with the membrane, low reverse solute flux, nontoxicity, and so forth.

In the past few decades, plenty of materials have been investigated as DS in FO. Several review articles on traditional and advanced DS have been published [1,4,10,18,21–25,33–44], these DSs are shown in Table 1, which include (1) inorganic compounds, (2) organic compounds (e.g., polyacrylic acid sodium, methylimidazole-based compounds, hexavalent phosphazene salts, stimuli-responsive hydrogels), (3) functionalized nanoparticles (e.g., magnetic nanoparticles (MNPs)), Na^+ -functionalized carbon quantum dots (Na-CQD). However, none has systematically addressed the energy type of DS in recovery process. Most of these reviews focused mainly on the synthesis, application, performance, and theories of DS in FO process. Specific discussion on the energy used to re-concentrate dilutive DS was rather brief. Moreover, lots of earlier research literatures were highlighting FO's feature of low energy consumption, and more discussion on DSs was focused on achieving superior FO performance, but mentioned lightly on the energy cost, resulting in a misplaced expectation of FO with higher energy efficiency than RO desalination. Therefore, in order to strengthen a comprehensive understanding on DS regeneration. A review that analyzes the types of energy applied in DS regeneration is crucially needed. Up to now, there are no relative reports on DS's classification based on the type of energy used for DS recovery [10,20].

Table 1. Overview of the traditional classification of draw solutions (DSs) in forward osmosis (FO) process.

Categories	Draw Solutes	Recovery Methods	Ref.
Inorganic compounds	NaCl	reverse osmosis (RO)	[33]
	inorganic fertilizer	direct use	[45]
	potassium sulfate (K ₂ SO ₄)	RO	[33]
	sodium nitrate (NaNO ₃)	direct use	[46]
	aluminum sulfate (Al ₂ (SO ₄) ₃)	precipitation	[47]
	magnesium sulfate (MgSO ₄), copper sulfate (CuSO ₄)	precipitation	[48,49]
Organic compounds	Switchable polarity solvent (SPS)	RO	[50]
	sodium polyacrylate (PAA-Na)	ultrafiltration (UF), membrane distillation (MD)	[51,52]
	CO ₂ -responsive polymers (PDMAEMA)	UF	[53]
	poly(sodium styrene-4-sulfonate-co-N-isopropylacrylamide) (PSSS-PNIPAM)	MD	[54]
	poly (aspartic acid sodium salt)	MD	[55]
	<i>N,N</i> -dimethylcyclohexylamine (N(Me) ₂ Cy)	heating	[56]
	1-Cyclohexylpiperidine (CHP)	heating	[57]
	Micellar solution	UF	[58]
	oxalic acid complexes with Fe/Cr/Na	nanofiltration (NF)	[59]
	2-Methylimidazole compounds	MD	[60]
	trimethylamine–carbon dioxide	heating	[61]
	glucose, fructose	RO	[62–64]
	polyelectrolyte incorporated with triton-x114	MD	[65]
	dimethyl ether	heating with solar energy	[66]
	poly(4-styrenesulfonic acid-co-maleic acid)	NF	[67]
Functional nanoparticles	Super hydrophilic nanoparticles	UF	[40]
	hydrophilic superparamagnetic nanoparticles	magnetic separation	[68]
	magnetic core-hydrophilic shell nanosphere	magnetic separation	[69]
	thermoreponsive Magnetic Nanoparticle	magnetic separation	[42]
	dextran-coated MNPs	magnetic separation	[36]
	hyperbranched polyglycerol coated MNPs	magnetic separation	[70]

In this review article, we critically classified the DS's categories in terms of their energy types applied in recovery process; discuss its potential in recovery process, FO performance, and suitable applications in FO. Specifically, we address the development and the advantages or demerits of existing DSs based on the new DS classification, categorizing them as directly use based, chemical energy based, waste heat based, electric energy based, solar energy based, and magnetic field energy based. Addressing these DS categories and understanding the limits of different DS in FO process will provide vital information to guidance the exploration of successful DS for expanding the range of its application.

2. Classifications of DS Based on the Types of Energy Used in Regeneration Process

The remaining defects of DS, such as high reverse solute flux, low osmotic pressure and high energy cost in recovery seriously hinder FO application. Therefore, the development of a novel DS to solve above problems is still a great challenge. Previously, several reviews have simply classified the known DSs (inorganic and organic compounds) based on the chemical properties. Later, these DSs were further subdivided into inorganic salts, organic salts, polymers, nanoparticles, micelle solutions,

gels, and so forth [71]. Recently, the types of DSs based on different regeneration methods were reported, which included directly use, thermal separation, membrane separation (RO, nanofiltration (NF), ultrafiltration (UF), microfiltration (MF), chemical precipitation, stimuli-responsive (e.g., light, electricity, magnetic field). In this review, the classification of DSs based on types of energy employed in regeneration process is summarized (Table 2).

Table 2. Overview of DSs based on the types of energy used in recovery process.

Categories	Recovery Methods	Draw Solutes
Direct use	Without recovery	Saccharides (glucose, fructose) [72,73], fertilizer [20,46], liquid fertilizer [74], sodium lignin sulfonate (NaLS) [75]
Chemical energy	Precipitation	$\text{Al}_2(\text{SO}_4)_3$ [47,76], MgSO_4 [49], CuSO_4 [77]
	Heating	Sulfur dioxide (SO_2) [78], ammonia and carbon dioxide ($\text{NH}_3\text{-CO}_2$) [79]
	heating	<i>N,N</i> -dimethylcyclohexylamine ($\text{N}(\text{Me})_2\text{Cy}$) [56], 1-Cyclohexylpiperidine (CHP) [57], trimethylamine-carbon dioxide ($\text{N}(\text{CH}_3)_2\text{-CO}_2$) [61], switchable polarity solvents [50], ionic polymer hydrogels with thermal responsive units [80]
Waste heat	phase separation	Upper critical solution temperature (UCST) ionic liquid [81], ammonium iodide salts [82], lower critical solution temperature (LCST) ionic liquid [83], thermally responsive polyionic liquid hydrogels [84–86], thermosensitive copolymer [54], ionic hydrogels [34], thermo-sensitive polyelectrolyte [87], phase transition materials [88], CO_2 switchable dual responsive polymers [89,90], thermosensitive polymer coated magnetic nanoparticles [38], gas-responsive cationic microgels [91]
	MD	2-Methylimidazole salt [60], Na^+ -functionalized carbon quantum dots (Na-CQDs) [92], dendrimer [93], poly (aspartic acid sodium salt) [55], multi-charged oxalic acid complexes [94]
Electric energy	RO	Inorganic salt (NaCl [95,96], MgCl_2 [95], KNO_3 [33]), organic ionic salts [97], glucose and sucrose miscible liquids [63]
	NF	divalent metal salt (Na_2SO_4 , MgSO_4) [98], EDTA sodium salt [21], metal complexes [27,59,99], poly (4-styrenesulfonic acid-co-maleic acid) [69], novel carboxyethyl amine sodium salts [100], organic phosphonate salts [101]
	UF	Thermosensitive polyelectrolyte [102], surface modified MNPs [37,39], phosphatic surfactant [103], micellar solution [58,104], sodium polyacrylate [52], carboxylate polyelectrolyte [105], natural polymer-based cationic polyelectrolyte [106]
	MF	Thermo-responsive copolymers [107]
Solar energy	Irradiating	Bifunctional polymer hydrogel layers [108], graphene gels [109], thermo-responsive nanoparticles [110], composite hydrogel monoliths containing thermoplastic polyurethane microfibers [111], composite hydrogels (carbon particles and sodium acrylate-isopropylacrylamide) (SA-NIPAM) [112,113], composite hydrogels based on graphene and SA-NIPAM [114], dimethyl ether [66]
Magnetic field energy	Magnetic separation	Functionalized MNPs [37], citrate-coated MNPs [115], PAA-Na coated-MNPs [34,116], thermosensitive magnetic nanogels [38,42], dextran coated Fe_3O_4 magnetic nanoparticles [36], triethylene glycol-coated magnetic nanoparticles, polyacrylic acid-coated magnetic nanoparticles [37], poly(oxy-1,2-ethanediy)-coated magnetic nanoparticles [39], poly(ethylene glycol) diacid-coated (PEG-(COOH) ₂ -coated) MNPs [39], hyperbranched polyglycerol coated MNPs [70], polyacrylic acid-coated MNPs [37,40,41]

2.1. Direct Use without Recovery

Since FO itself does not produce fresh water, a second regeneration process is needed to obtain the pure water. DS regeneration is considered as a potentially energy-intensive process, its energy cost in DS recovery significantly depends on the as-selected DS. For one case, FO without the step

of DS regeneration is the lowest energy-saving. These FO processes without DS recovery have been successfully used for drinking, fertilization, irrigation and soil prevention in arid areas [20,46,72–75,78]. Natural sugar DSs (e.g., glucose, fructose and sucrose) [72,73,88] diluted after FO could drink and use in some emergency boats [62]. In addition, other edible sugars (e.g., beverage powders or fructose) were produced to hydration packs for military or emergency purpose. However, the as-obtained product is the sweet water, which is unsuitable for long-term drinking [117]. Another example without DS regeneration is the use of the concentrated fertilizer solution [20,45,118,119]. Phuntsho et al. investigated the conventional inorganic fertilizers as DS. Results showed that 1 kg of fertilizer can take up 11–29 L of fresh water from seawater. In this fertilizer-driven FO process, inorganic fertilizers with high osmotic efficiency can draw water feasibly from wastewater resource or seawater, where the diluted DS can use for fertigation [120]. However, the concentration of the spent DS is commonly too concentrated for the direct fertigation of crops, requiring another dilution with fresh water before it is suitable [20,45]. Recently, Duan et al. [75] also reported an interesting case of using sodium lignin sulfonate (NaLS) as DS in FO, which does not require DS regeneration, the diluted NaLS can use for desert regeneration directly, preventing soil erosion as a soil stabilizer, and providing nutrients for plant growth. In addition, seawater itself can be used as a DS for the reuse of toxic wastewater; it would be safely discharged into the sea after FO, simultaneously retaining the toxic compounds by the membrane [121].

2.2. Chemical Energy

Traditional multivalent inorganic salts, such as $\text{Al}_2(\text{SO}_4)_3$, CuSO_4 , MgSO_4 , have been extensively used as DS for seawater desalination, because of its reasonably high water fluxes. The solubility of these salts may be adjusted with the change of temperature or pH. Once DS transforms into precipitate from the dilutive solution after FO, then the fresh water can be separated by filtration and the clean precipitate may be dissolved with acid into new DS and then return to the next cycle [6]. An early case of using $\text{Al}_2(\text{SO}_4)_3$ as DS in FO was reported by Frank in 1972 [47]. After FO, the diluted $\text{Al}_2(\text{SO}_4)_3$ would be reacted with calcium hydroxide ($\text{Ca}(\text{OH})_2$) solution to produce aluminum hydroxide precipitation and the product water after filtration, the resultant precipitate was then dissolved with sulfuric acid to recover $\text{Al}_2(\text{SO}_4)_3$ solution and insoluble $\text{Al}(\text{OH})_3$ for reuse. In 2011, a composite of $\text{Al}_2(\text{SO}_4)_3$ and MNPs as DS was proposed by Liu et al. [76], it can be separated by magnetic field to produce fresh water.

In 2013, Alnaizy et al. [49,77] used CuSO_4 and MgSO_4 as DS to desalinate brackish water, and the diluted DS may be recovered by adding barium hydroxide $\text{Ba}(\text{OH})_2$ to generate precipitation and the product water [18,19]. (Figure 1) However, although this process doesn't consume additional energy except chemical energy itself, the trace of heavy metal salt retained in water will pose a threat to the environment and people's health. The product water requires further purification, which is adverse to reduce the energy cost; the storage of toxic precipitation may arouse the environmental concern. Therefore, the regeneration method by chemical precipitation may not be feasible for large-scale application, although it does not use external energy apart from chemical energy itself.

2.3. Thermal Energy

The use of geothermal energy and low-grade waste heat for DS recovery is deemed to be a more cost-effective solution. In some cases, DS regeneration does not require the heat source strictly; this general low-grade heat (e.g., waste heat or geothermal energy) can be directly used for heating separation process. At present, several kinds of DS regeneration by heating separation were reported. For instance, (1) gas and volatile compounds, (2) phase transition materials (such as lower critical solution temperature (LCST), and upper critical solution temperature (UCST) compounds, and thermo-sensitive gels), and (3) membrane distillation (MD).

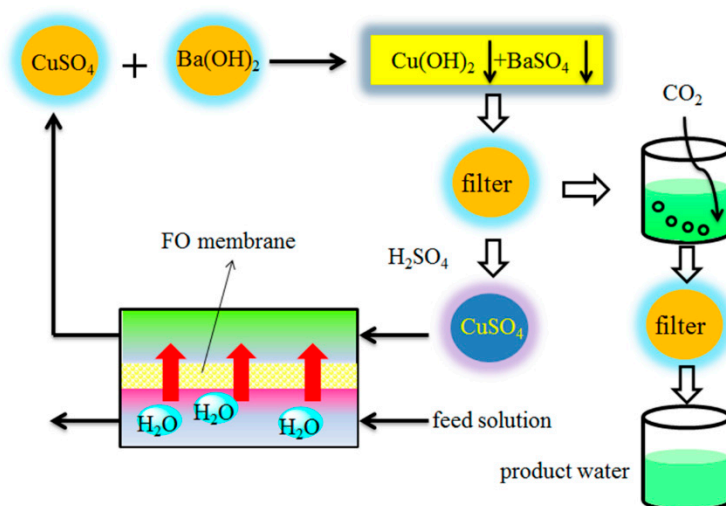


Figure 1. Schematic illustration of the use of precipitate method to regenerate CuSO_4 draw solution (DS) after forward osmosis (FO) process.

2.3.1. Gas and Volatile Compounds

Some gases, such as SO_2 and $\text{NH}_3\text{-CO}_2$, may easily dissolve in water and their aquo-complexes in water can generate high osmotic pressure. In 1965, Batchelder et al. [78] used volatile SO_2 water solution as DS for seawater desalination. However, the toxic SO_2 gas has strong corrosion to the equipment, which has not been further used. Up to 2005, Elimelech et al. proposed a new DS by the mixing of ammonia and carbon dioxide. McCutcheon et al. [79] found that the solution mixed with a certain proportion of $\text{NH}_3\text{-CO}_2$ can generate the extremely high osmotic pressure, mainly due to the generation of ammonium bicarbonate salt (NH_4HCO_3). A high water flux and water recovery can be achieved by using $\text{NH}_3\text{-CO}_2$ solution as DS in FO. Moreover, the diluted NH_4HCO_3 solution after FO could be easily decomposed into the gas of NH_3 and CO_2 again when heated to 60°C with waste heat; meanwhile the product water was also obtained. The collected NH_3 and CO_2 will back for reuse again. Results showed that FO fluxes achieved by this system are about $3.6\text{--}36\text{ L}/(\text{m}^2\cdot\text{h})$. Since the low-grade waste heat is used to decompose NH_4HCO_3 at low temperature (60°C), this FO desalination employing NH_4HCO_3 DS can save 85% of energy cost compared with other desalination technologies, showing a great application potential [13]. However, the drawback of NH_4HCO_3 DS is that the high reverse flux caused by its low MW may lead to the reduction water flux and the deterioration the quality of water [33]. Besides, the removal of the trace amounts of ammonia in product water is still a big challenge. Later, to overcome the mentioned defects above, a series of ammonium carbonate salts with similar function of $\text{NH}_3\text{-CO}_2$, such as *N,N*-dimethylcyclohexylamine ($\text{N}(\text{Me})_2\text{Cy}$) [56], 1-Cyclohexylpiperidine (CHP) [57], trimethylamine ($\text{N}(\text{CH}_3)_2$) [61] and switching polarity solution (SPS) [50] have been reported.

2.3.2. Phase Transition Materials

Phase transition materials [88] may reversibly change the phase between solid and liquid with the various factors (e.g., temperature, pH, CO_2 et al.). According to the different critical dissolution temperatures, they are divided into UCST [81] and LCST materials [83–85,107]. This category of solutes mainly includes the ionic gels [34], the thermo-sensitive copolymer [54], the CO_2 response SPS [89,95], and the thermosensitive polyelectrolyte [87].

A recent study reported the use of a series of LCST materials as DS. Three organic ionic liquids [85] (e.g., tetrabutylphosphonium 2,4-dimethylbenzenesulfonate ($\text{P}_{4444}\text{-DMBS}$), tetrabutylphosphonium 2,4,6-trimethylbenzenesulfonate ($\text{P}_{4444}\text{-TMBS}$), and tetrabutylphosphonium bromide ($\text{P}_{4448}\text{-Br}$)) with different hydrophilicity were investigated. Results showed that the osmolality and molality have a non-linear correlation relationship, due to the occurring of molecules hydrophobic association at high

concentration. These solutes whose osmotic pressure is approximately three times higher than that of seawater were applied to dewatering from seawater. DS regeneration after FO was carried out when heated to above LCST (30~50 °C), resulting in the phase separation. Recently, Zhong et al. [81] proposed to the use of a UCST ionic liquid [protonated betaine bis(trifluoromethylsulfonyl)imide (donated as [Hbet] [Tf2N])] as DS to dewater from high salt water. Results showed that the 3.2 M [Hbet] [Tf2N] solution over the UCST of 56 °C was able to draw water from 3.0 M saline water. Consequently, the diluted solution was cooled to below the UCST to form two phases of ionic liquid and water. The phase of rich ionic liquid could be used directly without additional re-concentration.

The CO₂ response SPS may change their miscibility by injecting of CO₂. Stone et al. [50] first proposed the use of SPS as DS. The phase transformation was easily achieved through the injection of CO₂, because the cloudy solution of amine reacts with CO₂ to form a protonation product, which is readily dissolved in water. The diluted SPS after FO can be recovered to the immiscible state through the removal of CO₂ by heat with a low-grade source. The regeneration process was allowed to mechanically recover the majority of amine solution. However, the residual amine in water still required to be removed using RO. Moreover, the later study found that the cellulose triacetate membrane could be damaged by the DS of N(Me)₂Cy, leading to the solute leakage [50]. An improved solution that the polymer with dual temperature and CO₂ response was synthesized as DS for desalination was proposed by Cai et al. [90]. After the injection of CO₂, the ionized polymers can fully dissolve in water and generate high osmotic pressure; the diluted solution can be recovered through the phase separation when heated to 60 °C. The use of dual-response polymer as DS could effectively reduce reverse solute flux. Similarly, 1-cyclohexylpiperidine as a SPS DS showed a comparable performance of that the N(Me)₂Cy, but a good compatibility with polyamide membranes [57].

2.3.3. MD

MD is a thermo-driving membrane separation technology, it being not affected by the concentration of feed solution, becomes possible to desalinate high salt wastewater [122]. In MD process, the water vapor on the side of hot feed solution (heated by low-value heat source) diffuses across a hydrophobic porous membrane into the cold liquid water [87,123–127]. In general, a suitable temperature gradient of 10~20 °C on both sides of the hot and cold solutions should be stably maintained to produce distilled water [124]. Since MD has the high selectivity and the 100% theoretical rejection rate for nonvolatile solutes [124,127], it is probably a good candidate for the recovery of diluted DS and can replace traditional separation technologies [55,60,92,93]. In addition, MD can use the low-value waste heat to minimize the capital cost [52,127]. However, there are several limitations about the current MD, including (1) low and unstable permeate flux, (2) membrane fouling, and (3) high heat lost [128–130].

The use of MD to recover 2-methylimidazole compounds was reported by Yen et al. [20]. A water flux of 8 LMH could be achieved. Later, numerous researchers, such as Wang et al. [131], Xie et al. [132], and Zhang et al. [133] investigated MD to recover the diluted solution of NaCl after FO for sustainable water recovery of protein concentration and oil-water separation. Guo et al. [92] used MD to recover Na-CQDs DS for seawater desalination, and a stable water flux of 3.5 L/(m² h) could be maintained after several cycles at 45 °C. Another hybrid FO/MD system for the recovery of polyelectrolytes (PAA-Na) after FO was investigated by Ge et al. [134]. Results showed that the high rejection of PAA-Na was carried out in MD at the temperatures of 50–70 °C. The most efficient performance of this hybrid FO-MD system can be achieved when it is conducted under the condition of 0.48 g/mL solution at 66 °C. Afterwards, the hybrid FO-MD process was also used to treat dye wastewater and toxic wastewater [52,135]. (Figure 2) To minimize the leakage of DS in MD process, the large size of thermoresponsive polymer (PSSS-PNIPAM) is used as DS for seawater desalination [54]. The osmotic pressure of PSSS-PNIPAM decreases with the temperature increases due to the agglomeration of the polymer chains, leading to a higher water vapor pressure. After three recycles, a stable water flux of 2.5 L/(m² h) and product of water could be achieved. In fact, however, MD still needs to overcome lots

of defects, including low water flux, membrane scaling and high hot loss, which is adverse to reduce the energy cost.

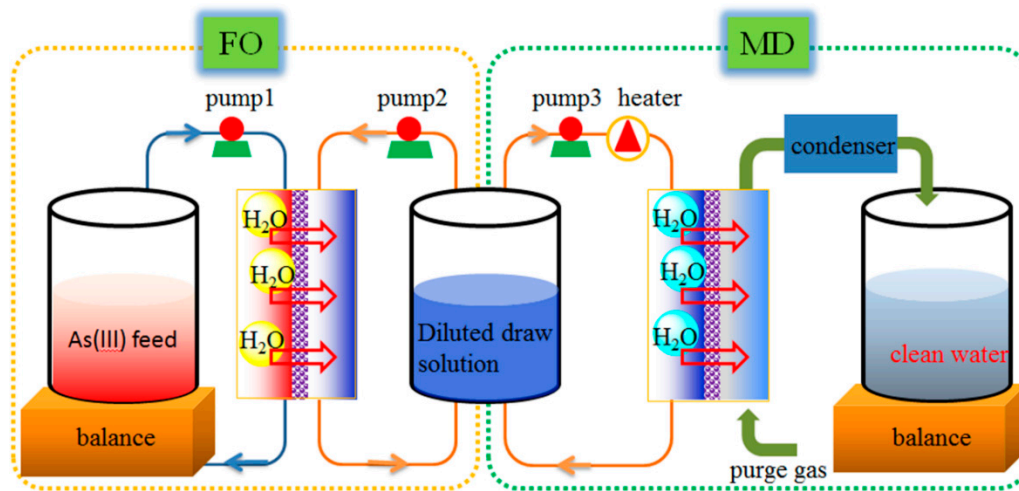


Figure 2. Schematic illustration of using a hybrid FO-MD process for wastewater treatment.

2.4. Electric Energy

At present, membrane separation method is frequently used for DS regeneration, because of its high solute rejection and simple operation. It is well-known that all membrane separation processes consume electricity except MD. Different membrane separation technologies have different energy consumption depending on the osmotic pressure of feed solution and membrane types. Currently, the membrane separation technologies used for DS recovery mainly include RO, NF, and UF.

2.4.1. RO

Considering the low molecular weight cut-offs and high solute rejection, RO is a good option for DS recovery when using monovalent salts (e.g., NaCl, seawater) as DS [136]. In the past few years, most of inorganic salts, including NaCl (seawater), MgCl₂, MgSO₄ and Na₂SO₄, were frequently used as DS, due to their high osmotic pressure. However, these diluted monovalent salts solution after FO often require extremely high energy costs to be regenerated. It seems impossible to use RO for DS recovery. In spite of this, the hybrid FO-RO for seawater desalination was also proposed (Figure 3) [33], FO and RO can be used as the front end pretreat and post-treatment desalination technologies, respectively [136]. The advantages of this system are greatly reducing membrane fouling after FO treatment [137] and the energy cost in RO units, because of seawater diluted after FO [137].

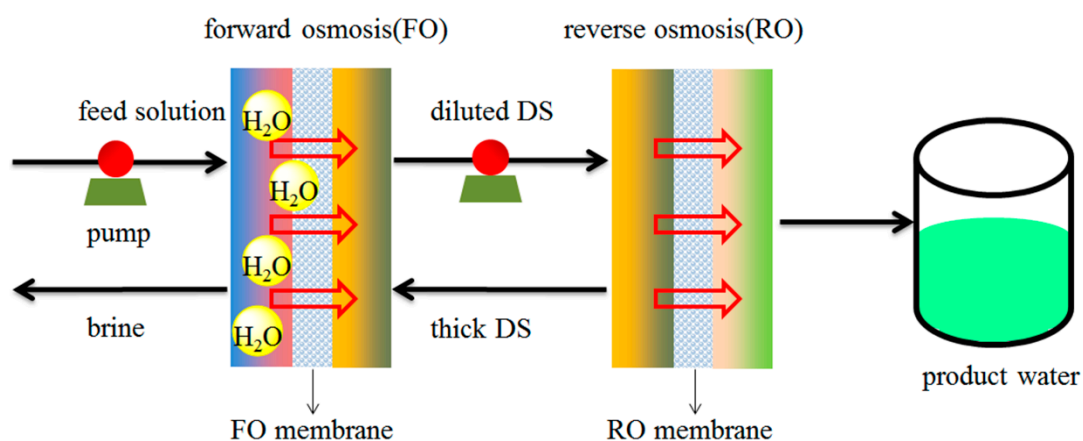


Figure 3. Schematic illustration of using a hybrid FO-RO process for desalination seawater.

Yangali et al. [138] used low-pressure RO for DS recovery employing FO to desalinate seawater. Results showed that this hybrid FO-RO system can save 50% of energy consumption ($\sim 1.5 \text{ kWh/m}^3$) compared with independent RO desalination ($2.5\text{--}4 \text{ kWh/m}^3$). Its cost efficiency would surpass RO only if the water flux above $5.5 \text{ L}/(\text{m}^2 \text{ h})$ can be achieved. In addition, Bowden et al. [97] used RO to recover the organic acid salt. DS regeneration with the average solute rejection rate of near 99% was conducted under the pressure of 28 bar, indicating the feasibility of DS recovery by RO. Another hybrid FO-RO system combination of wastewater as feed using seawater as DS was proposed by Cath et al. [15]. The diluted seawater after FO providing a low saline solution, subsequently, flow into RO units to desalinate. This hybrid system with impaired sources as feed can produce high quality of drinking water and achieve a favorable economic return with the water recovery rate up to 63% [15]. It can be seen that the hybrid FO-RO process may be a competitive choice for desalination of high saline water compared with RO alone. However, considering its energy cost and efficiency, RO recovery for DS regeneration may be discouraged under high operating pressure.

2.4.2. NF

NF membrane with the 1–2 nm of pore size can effectively remove organic compounds with MWs between 200–1000 Da, but its rejection rate of multivalent salts (99%) is higher than that of monovalent salts. A sort of looser membrane, with relative high molecular weight cut-offs, it can produce higher water flux than RO under a given pressure. In recent years, it is intensively used to remove the organic matters and dissolve salts in water treatment, food and medicine industry [21,27,59,98,99]. The use of NF to recover DS has received great attention [71]. Tan and Ng [98] investigated the NF recovery rate of a series of different DSs (e.g., MgCl_2 , MgSO_4 , Na_2SO_4 and ethanol) after FO. The stable water fluxes as high as $10 \text{ L}/(\text{m}^2 \text{ h})$ can be achieved in both FO and NF process, the reachable NF rejection rates of 97.4% can be observed. They found that the total dissolved solid (TDS) is as low as 113.6 mg/L of the product water after two-pass NF treatment process, which meets the drinkable standard (TDS < 500 mg/L) required by world health organization [137]. After that, Zhao et al. [122] used NF to regenerate the diluted bivalent salt solution (MgSO_4 and Na_2SO_4) after FO. According to their findings, the performance of hybrid FO–NF process for desalination of brackish water is superior to that standalone RO process, because of its lower hydraulic pressure, lower membrane fouling, and higher flux recovery after cleaning. Besides, Su et al. [73] proposed the use of NF to regenerate the dilute sucrose after FO, the rejection rates of as high as 99.6% can be achieved, due to the sucrose with large molecule size. Consequently, the concentrated sucrose DS return to FO units may continually draw water from wastewater while producing clean water in NF units. The NF recovery of EDTA sodium salts under external pressure of 5.5 bar was reported by Hau et al. [25]. They found that a rejection rate of 93% for high charged salts was achieved well. Afterward, the regeneration of hydroacid complex solutions using NF with a low-pressure of 10 bar were conducted by Ge et al. [27,59,99]. These compounds had expanded configurations and charged groups, leading to an achievable high rejection rate of 97%. Later, the diluted DS of carboxyethyl amine sodium salts [100], and the organic phosphonate salts [101] were also used NF regeneration after FO. It can be seen that NF is a good choice for DS recovery, due to its low extremal pressure and high rejection rate of valent salts.

2.4.3. UF

UF membrane with a bigger pore size than RO and NF can bring about a higher water flux and lower energy cost [139,140]. UF is suitable for the regeneration of these DSs with big size (such as macromolecules, polyelectrolytes, or particles). Recently, the regeneration of MNPs through magnetic separation was feasible to produce clean water. Ling et al. [38,43] proposed the use of UF to regenerate hydrophilic nanoparticle DS. They found that, unlike magnetic separation, the collected MNPs after UF in concentrated solution didn't agglomerate again, which make it retain the initial osmotic pressure well even after five regeneration cycles. After FO desalination, Ge et al. [52] adopted UF to recover diluted solution of sodium polyacrylate (PAA-Na). For the PAA-Na with the MW of 1800 Da, a rejection

rate of 99% can be achieved under the external pressure of 10 bar, because of the MWs and expanded structure of polymer. The water flux in this FO-UF slightly decreased after nine regeneration cycles, which was explained by the loss of PAA-Na during UF [76]. Other DSs, including MNPs modified with PAA (~5 nm) [40], polystyrene sulfonic acid sodium (PAS-Na) [53], phosphate surfactants [103], micellar solution [58,104], thermo-sensitive polyelectrolyte [102], and phase change materials [88], were all used UF to regenerate. As a pressure-dependent membrane process, however, the regeneration performance of UF still relies on the osmotic pressure of DS. In term of the analysis of energy balance, Shaffer et al. [15] reviewed that the object of DS regeneration is to concentrate diluted solution and make it return to the initial osmotic pressure, which the same external pressure will be provided by UF even RO. Therefore, the minimum energy consumption for both processes are the same. The energy cost being equal, RO would be given the priority for its superior rejection rates.

2.5. Magnetic Energy

Magnetic nanoparticles (MNPs) have been intensively investigated as a very promising DS, because it can be recover using magnetic field (Figure 4) [37,38,40,43]. The advantages of magnetic separation are high efficiency and energy conservation compared with other DSs regeneration methods. Recently, to improve the water solubility and surface hydrophilicity, MNPs functionalized with strong hydrophilic groups are considered as one of the feasible solutions to enhance their osmotic pressure, as well as easy recycle utilization [141]. Ling et al. conducted an in-depth study on the first use of hydrophilic functionalized MNPs as DS [37]. The target MNPs coated with 2-pyrrolidine, triethylene glycol, and PAA were synthesized based on the precursor of ferric triacetyl acetonate ($\text{Fe}(\text{acac})_3$) through a thermal decomposition method. The sizes of functionalized MNPs were all less than 20 nm and were successfully used in the FO process. At an extreme low concentration of 0.05 mol/L, all functional MNPs showed the improved osmotic pressure and water flux. Water fluxes of three functional MNPs followed the order of MNPs-PPA > MNPs-pyrrolidine > MNPs-triethylene glycol, mainly because of the higher potential energy on the surface of MNPs-PPA. The MNPs separation was conducted with a commercially available magnetic separator. However, these DSs showed a decreased (about 21%) water flux after nine cycles because of MNPs agglomeration.

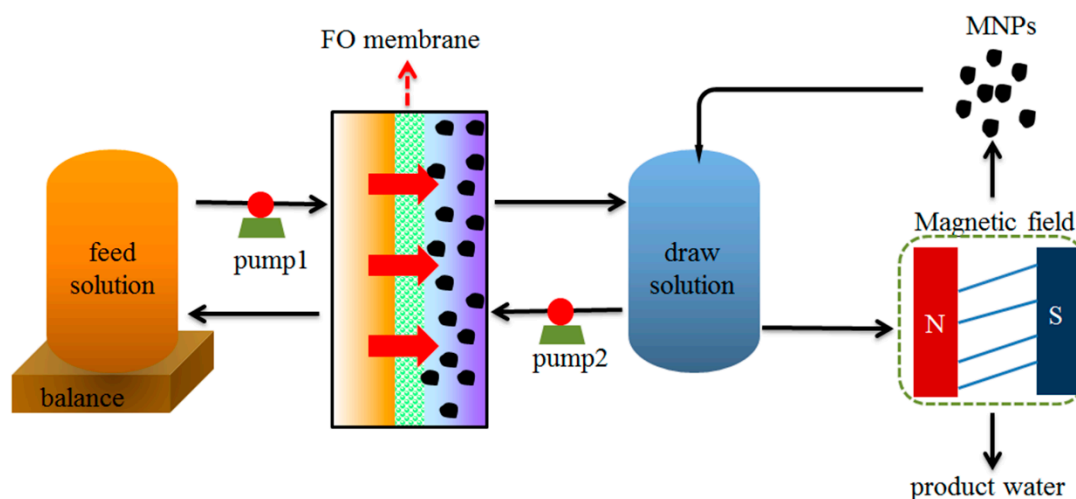


Figure 4. Schematic illustration of using functionalized magnetic nanoparticles as DSs in FO process. (MNPs, magnetic nanoparticles).

Later, Ge et al. [39,68] explored a new MNPs coated with poly (ethylene glycol) diacid ($\text{PEG}-(\text{COOH})_2$) with different MWs through a one-pot reaction. Results of transmission electron microscopy showed that these particles had the spherical sizes ranging from 4.2 to 11.5 nm. In addition, higher water flux was found with the use of PEG with lower MWs. The water fluxes of 13.5, 13, and 11.5 $\text{L}/(\text{m}^2 \cdot \text{h})$ belong to those MNPs coated with PEG MWs of 250, 600 and 4000, respectively [43].

The above results indicated that the factors like particle size, hydrophilic group distribution, and the number of hydrophilic groups were greatly related to FO performance. Besides, one type of MNPs coated with dextran [36] and a thermo-responsive PNIPAM-modified MNPs [38] as DS were proposed. Since the reverse solute flux is almost negligible using MNPs as DS, it could be applied to concentrating the proteins and drugs. At present, however, the product water separated by magnetic field is still hard to meet the drink water standards. An additional purification step is needed, which would sacrifice the separation efficiency. Therefore, more studies are dedicated to producing the high quality of water and improve the recovery efficiency.

2.6. Solar Energy

Smart materials may undergo a reversibly change between water absorption and dehydration with the change of surrounding stimuli (e.g., sunlight, pressure, heat). Recently, a series of stimuli-response hydrogels were proposed as DS in FO. This novel type of hydrogels-driven FO process (Figure 5) employing the solar energy for the DS regeneration have been attracting more and more attentions. Especially, the light or thermoresponse hydrogels can release fresh water when it is exposed to sunlight, because of the structure's own shrinkage. For instance, the light or thermoresponse hydrogels can take up enough water under the temperature of maximum volume phase transition and dewater at temperatures above the volume phase transition temperature [34,49,142–145]. The graphene-doped hydrogels as DS were proposed by Li et al. [109]. The efficiency of water release was significantly improved; because of the heat absorption was enhanced by adding an appropriate amount of graphene. In addition, the hydrogels doped with light-absorbing carbon particles (10~25 μm) was also reported [112]. Under the irradiation intensity of 1.0 kW/m^2 for 20 min, a water recovery rate of 50% was achieved, which is superior to than that of p(NIPAM-co-SA) hydrogels (around 17%). However, the doping of the carbon materials, if beyond a certain scope, may scarify water fluxes, for the direct contact area reduced between hydrogels particles and FO membrane. Similarly, other hydrogels, such as dual-functional polymer gels and photosensitive particles [108] and photosensitive particles [37] all show the same effects of taking up and releasing. The eco-friendly dewatering process by using solar energy may obviously reduce the cost. However, the collection of clean water released by the exposure of thermoresponse hydrogels under sunlight remains a big challenge now [146].

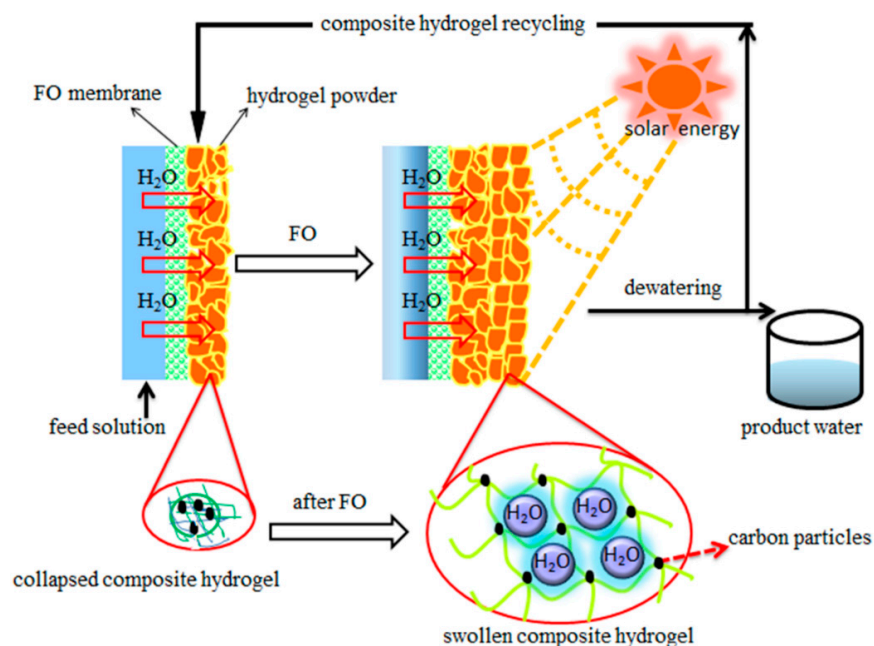


Figure 5. Schematic illustration of using solar energy to recover the thermoresponsive hydrogels DSs in the hydrogels-driven FO process for desalination.

3. Future Challenges or Perspectives

The use of FO for the production of clean water has been proposed since 1960's, it really booms in the improvement of water recovery only within the last decade. FO process with high water flux would be to compare with other existing membrane-based process in seawater desalination and wastewater reuse. Numerous efforts have been dedicated to developing and improving the high performance of FO membranes, but there is also a need for the parallel develop of superior DS with high osmotic pressures to produce high water flux. The lack of powerful DS bearing high water flux, low reverse flux, and easy recovery has become the obstacles to the progress of FO.

FO employed the direct use of DS may be economical and technical sound when using two solutions with a high osmotic pressure difference, due to the lack of DS recovery. However, only few water sources are available to dewater using these specific DSs (e.g., saccharides [72,73], fertilizer [20,46], liquid fertilizer [74], sodium lignin sulfonate [75]). (Table 2) For instance, the drinkable diluted glucose DS after FO can be used for emergency rescue. Besides, the diluted sodium lignin sulfonate solution is utilized in the land as nutrient; whose energy cost in this process only includes the power input of pumping, storage and others. In this case, the total energy cost of FO alone for seawater desalination is approximately $0.59 \text{ kWh}\cdot\text{m}^{-3}$ [13], which is about one third of that of RO water desalination ($1.5 \text{ kWh}\cdot\text{m}^{-3}$) [1] and one-seventh of that of other technologies ($4 \text{ kWh}\cdot\text{m}^{-3}$) [13]. However, most of the expensive DS still requires recovery.

DS regeneration method based on the chemical energy is unlikely to be used on large-scale, due to the environment concern caused by the discharge of by-products. Especially, since the trace amount of heavy-metal ions after precipitation can't be removed completely from the diluted DS, it is often required a secondary treatment using RO to obtain clean water, which leads to the massive energy consumption.

The most commonly used method according to the reported literature is the membrane-based separations (e.g., RO, NF), which uses electricity to recover those small molecules, including inorganic salts, organic salts, and electrolytes. However, it is widely accepted in both academia and industry that a hybrid FO-RO process does not minimize the lower energy consumption for desalination than RO alone. Except the case of using hybrid FO-RO process for the desalination seawater, FO as the front-end treatment and RO as the post-treatment step still attract attentions. Another case is that the use of UF has the potential of higher water fluxes and lower energy costs for regenerating these sufficiently large solute molecules or particles [139,140]. Among all the membrane-based recovery methods, a number of studies are focused on investigating MD regeneration of the diluted DS. In the case of regeneration PSSS-PNIPAM using a hybrid FO-MD system, the calculated energy consumption of 29 kWh m^{-3} is required at $50 \text{ }^\circ\text{C}$ [54], which is much higher than the use of FO-RO or RO alone. However, it still has the considerable potential for energy cost when the use of low-grade waste heat replaces the electricity. The use of new energy for DS recovery was intensively investigated recently.

Take the magnetic field energy as example, the use of functionalized MNPs as DS after FO may be quickly and cheaply concentrated by a magnetic separator [36,37,39,40,147]. However, the MNPs aggregation during separation process has severely impacted the reused performance, and in some cases, the water quality produced by magnetic separator is not always as good as desired. Moreover, the synthesis of large amount of functionalized nanoparticles are extremely expensive [33,148].

The light or thermo-responsive hydrogels as DS has been demonstrated in the FO process. These smart DSs are of the negligible reverse solute flux and can be recovered with solar energy. However, the water flux in FO is extremely low (most of ranging from $0.5\text{--}3 \text{ L}/(\text{m}^2\cdot\text{h})$) [113]. The swelling pressure and light or thermo-responsive property of hydrogels need to be further optimized on their physical-chemical properties. More studies need to design continuous smart materials-driven FO process for practical applications. There is no doubt that smart DSs driven FO processes using renewable energy for DS recover may be the first choice in the future.

4. Conclusions

This review has been tried to categorize the current DSs in terms of the types of energy used for DS regeneration process, and also analyzes the potential of DS in the case of seawater desalination and wastewater reuse that it can be capable of reducing energy cost. Publications reported in the past few years are examined apart from some older cases to know how current DS developments have been impacted by past efforts and challenges. Selection of a suitable DS is very important to the energy efficient and cost-effective running in FO. An ideal DS must be cheap and abundant, be high water flux and low reverse solute flux, be nontoxic, and be easy to regenerate. Considering the non-negligible problem with FO is that a second step is needed to recover fresh water from the diluted DS and to simultaneously regenerate the DS. This second step requires having low energy consumption and high efficient output.

All of DS recovery methods have their potentials and limitations in the process of FO application, and that each regeneration method involves at least one or two different types of energy consumption depends on different DS. However, not all DSs are always available for complex water source, which often requires a hybrid technology solution to producing clean water. Considering the selection of DS at a certain application, the main problems of how much energy is consumed and how effective the recovery process (the cost of the DS themselves and the energy cost payed out for solute regeneration) is should be taken into consideration. This review (Table 2) covers most of example matters, which have been employed as potential DS. Several classifications of DS in terms of the different types of energy employed for DS regeneration have been summarized and highlighted, including direct use without recovery, chemical energy, low grade waste heat, electric energy, magnetic field energy, and solar energy. Among them, the “direct use”-based DS is the most save-energy solution in FO, but its application is restricted by the few of available DS. However, DS recovery using chemical energy is unpromising, because it not only requires additional chemicals, but also generates more by-products. Besides, the DS recovered by electric energy (i.e., RO, NF) is still the most popular one in recent years, due to the high salt rejection, but it is incapable of treating that solution of high osmotic pressure. The innovative hydrogels, stimuli responsive polymers, and MNPs coated with hydrophilic groups can be used as DSs, showing the low reverse salt flux and innovative recovery pathways. Those DSs recovered after FO using solar energy, waste heat or magnetic field energy makes DS regeneration process become greener and energy-saving. It is likely that this type of DSs may be the most development promising one in the future, even if there is no any single perfect DS to be discovered for the needs of specific situations. We would like to hope that the main categories of DSs discussed in this review may help the development of further work of DSs innovation.

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