Forward Osmosis in Wastewater Treatment Processes

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Abstract

In recent years, membrane technology has been widely used in wastewater treatment and water purification. Membrane technology is simple to operate and produces very high quality water for human consumption and industrial purposes. One of the promising technologies for water and wastewater treatment is the application of forward osmosis. Essentially, forward osmosis is a process in which water is driven through a semipermeable membrane from a feed solution to a draw solution due to the osmotic pressure gradient across the membrane. The immediate advantage over existing pressure driven membrane technologies is that the forward osmosis process per se eliminates the need for operation with high hydraulic pressure and forward osmosis has low fouling tendency. Hence, it provides an opportunity for saving energy and membrane replacement cost. However, there are many limitations that still need to be addressed. Here we briefly review some of the applications within water purification and new developments in forward osmosis membrane fabrication.

Keywords: Biomimetic membranes, Desalination, Draw solutions, Forward osmosis, Wastewater treatment

1. Introduction

The last decade has witnessed extensive research and technological achievements in water production and wastewater treatment processes. Also, it is being realized that water, energy and food are inter-connected – often expressed as the water-energy-food nexus. This necessitates further developments to establish more energy efficient solutions. Therefore, a growing number of academic and industrial research groups around the world are conducting work on water treatment and reuse – in particular, within membrane-based water treatment.

Forward Osmosis (FO) is one example of a promising membrane process and potentially a sustainable alternative/supplement to reverse osmosis (RO) process for wastewater reclamation and sea/brackish water desalination. FO has shown good performance in a variety of applications, such as desalination, concentration of wastewater and resource recovery, wastewater treatment and it is also attracting attention as a potential technology to augment water supplies using seawater and wastewater. However, Van der Bruggen et al (2015) stated that FO as stand-alone process is usually not viable for water treatment purposes. Nevertheless, membrane fouling limits its large-scale applications. To reduce the membrane fouling in FO, many improvements have been attempted, e.g. synthesis of different membrane materials, fabrication of membrane modules, membrane coatings etc. Further, there have been improvements in the productivity and decrease in the cost of synthetic membranes used for water and wastewater applications.

One of the novelties in membrane development research field is application of biomimetic membranes in separation processes including FO. Biomimetics is defined as the study of the structure and function of biological systems and processes as models or inspiration for the sustainable design and engineering of materials and machines. In particular the use of aquaporins (AQPs) – biological water channel proteins which are highly selective and effective has prompted considerable interest in recent years.
In this paper, we review, (i) the membrane process based on osmotic pressure, principles and transport of water molecules, (ii) applications of FO in water purification, and (iii) recent developments in FO membrane fabrication.

2. Osmotically Driven Membrane Processes

FO is a membrane process in which no hydrostatic pressure is applied. The transport of water molecules across a semi-permeable membrane occurs due to the osmotic pressure difference of solutions on either side of the membrane. The natural flow of water is from the low solute concentration side to the high solute concentration side across a semi-permeable membrane to equilibrate the osmotic pressure difference.

PRO is an osmosis process in which there is a hydraulic pressure applied to the high concentration solution, but the osmotic pressure difference is higher, so the water flux is still opposite to the flux in RO process. PRO possesses characteristics intermediate between FO and RO, where water from a low osmotic pressure feed solution (FS) diffuses through a membrane into a pressurized high osmotic pressure draw solution (DS). In order for water transport to occur, the osmotic pressure difference between the FS and DS should exceed the hydrostatic pressure on the DS side. The classical PRO application is electrical power generation which can be achieved by de-

Figure 1. Osmotic processes in membrane filtration. ΔP is applied hydraulic pressure; Δπ is osmotic pressure difference between the two solutions; \( J_w \) is water flux; \( J_s \) is salt reverse flux

Figure 2. Relationship between water flux and applied pressure in RO, PRO, FO, and AFO.
pressurizing the diluted seawater through a hydro-turbine or generator set.8

Pressure-assisted forward osmosis (AFO) has been proposed that applies the pressure at the feed side to further enhance the performance of the FO process to increase water flux. AFO adds a medium pressure pump to a conventional FO system. The system takes advantage of additional hydraulic pressure that results in water transport in both mechanisms: flux driven by hydraulic pressure (RO mechanism) and that by osmotic pressure (FO mechanism).

Figure 1 describes the flux directions of the permeating water in the RO, PRO, FO and AFO processes respectively. The theoretical water flux across the membrane \( J_w \) is calculated using a variation of Darcy’s law:

\[
J_w = A_w \times (\sigma \Delta \pi - \Delta P)
\]  

where, \( A_w \) is the pure water permeability coefficient of the membrane, \( \Delta P \) is the applied hydrostatic pressure, \( \Delta \pi \) is the differential osmotic pressure, and \( \sigma \) is the reflection coefficient which represents the rejection capability of a membrane. A perfect semipermeable membrane has \( \sigma = 1 \). Fig. 2 presents the relation between water flux and applied pressure.

In RO, solutes diffuse from the feed into permeate. However, in FO, solutes diffuse in two directions: from the feed into the DS (i.e., forward diffusion) and simultaneously from the DS into the feed (i.e., reverse diffusion). Reverse permeation of solutes from the DS into the FS decreases the osmotic driving force and consequently this reduces the water transport. In a FO system, this could dramatically increase the costs of the process.

The flux of a solute \( J_s \) through semipermeable membranes is governed by chemical potential gradients and is commonly described by Fick’s law:

\[
J_s = B(C_i - C_{Fm})
\]

where \( B \) is the solute permeability coefficient and \( C_i \) and \( C_{Fm} \) represent the solute concentration at the membrane-solution interface on the DS side and FS side, respectively.

### 3. The Forward Osmosis Process

In FO process, the water molecules are drawn from the FS through a semi-permeable membrane to the DS side (from a lower osmotic pressure to a higher osmotic pressure side). The driving force of the process is an osmotic pressure generated by the concentrated DS. The process ends when the hydraulic difference between the two solutions equals the osmotic pressure difference.

The semi-permeable membranes used in FO has comparable rejection range in size of pollutants (1nm and below) as RO membranes. Purified water is produced during the process and the DS is diluted. Thus, FO offers several advantages; (i) high rejection of a wide range of contaminants, (ii) reduction in energy consumption, (iii) lower brine discharge, and (iv) lower membrane fouling propensity compared to pressure-driven membrane processes.9

The main challenges in the FO process are related to:

- Development of high performance, such as higher water flux and lower salt reverse flux of FO membranes.
- Reduction in concentration polarisation of membranes.
- Ensuring low DS reverse solute flux across the membrane.
- Economical reuse and regeneration of the DS.

### 4. Types of DS

In the FO process, the concentrated solution is commonly known as the DS although different terms can be found in the open literature. The DS plays an important role in the efficiency and performance of the process, and the selection of appropriate DS is crucial.

The driving force involved in FO is shown in Fig. 3; where \( C_s, C_d, a_s, a_d \) and \( \mu_s, \mu_d \) are the solute concentrations, water activities and water chemical potentials in the feed (s) and draw (d) solution, respectively.

\[
C_d > C_s
\]

\[
a_d (H_2O) < a_s (H_2O)
\]

\[
\mu_d > \mu_s
\]

In this process it is the ability of the draw solution to generate the relevant osmotic pressure level that is paramount.11 The osmotic pressure of solution is affected by adding a second solute that can influence the solute–solvent interaction. Solutes disturb the solvent structure. In the case of water as the solvent, the presence of solute affects the structure of liquid water. In pure liquid water, the molecules are heavily hydrogen bonded in an ordered structure. The presence of ions disturb such structures by creating strong electric fields, the water dipoles are then arranged in an orderly manner and strongly bound, thus
affecting the freedom of water molecules and influencing their hydrogen bond system.\textsuperscript{12}

Osmotic pressure of a solution $\pi$ can be expressed by the Morse equation (applies to solutions with dilute concentrations, i.e. $<$0.5M), as follows:

$$\pi = iMRT = i \left( \frac{n}{V} \right) RT = -\frac{RT}{V_w} \ln(a_w)$$ \hspace{1cm} (3)

where $i$ is the van’t Hoff factor, $M$ is the molarity of the solute which is equal to the ratio of the number of solute molecules ($n$) to the volume of the solution ($V$), $R$ is the gas constant of 8.3145 J K$^{-1}$ mol$^{-1}$, and $T$ is the absolute temperature. The right side of the equation includes the chemical potential of water which allows for calculating the activity of water $a_w$ where $V_w$ is the molar volume of water.

Hence, to achieve a high osmotic pressure, a good solubility of the draw solute in water is required to get a high $n$ or $M$ value. In addition, an ionic compound which is able to fully dissociate to produce more ionic species is preferred because it may result in a high $i$ value. This indicates that multivalent ionic solutes are the most favourable. Therefore, compounds with high water solubility and a high degree of dissociation are potential candidates as draw solutes.

Different DS and their physio-chemical properties are presented in Table 1.

Since FO is an osmotic-driven process, a higher osmotic potential of DS than the feed solution is essential to induce a water flux. In addition, it must exhibit minimum reverse transport from the DS side to the feed side, be easily separated and re-used upon water extraction or be readily available if regeneration is not required.

Further to these characteristics, a desirable DS should be non-toxic, highly soluble, of neutral pH, inert and causing a minimum chemical or physical impact on the membrane, low molecular weight and low viscosity to reduce the concentration polarisation, be relatively low cost, and stable.

Many studies have been performed to identify appropriate draw solutes over the past few decades.\textsuperscript{22} Based on the available literature, NaCl appears to be the most promising DS (approximately 40% of experiments), due to its high solubility, low cost and relatively high osmotic potential. It has been used as a DS in concentrations from 0.3 M to 6 M, but is often used at 0.5 M simulating the osmotic pressure of seawater and prompting the use of real seawater or RO brine as a DS.\textsuperscript{3} Nevertheless, the type of wastewater (feed solution) and the required product purity have influence on the DS selection also. Some studies have used magnetic and/or hydrophilic nanoparticles as a DS.\textsuperscript{23,24} However, it seems that there are only few that can be selected as a perfect draw solute, since the regeneration step has to be included for draw solution. As such, the benefits of the process have to be larger than the costs of DS and the additional regeneration step.\textsuperscript{4}

### 4.1 Fouling in Osmotically Driven Membrane Processes

Fouling is due to the deposition of retained matter (particles, colloids, macromolecules, salts, etc.) on the membrane surface or inside the membrane pores. The interaction (chemical and hydrodynamic) between the foulants and the membrane surface reduces the membrane water flux either temporarily or permanently.\textsuperscript{25} There are

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**Table 1.** Overview of draw solutes used in FO processes.

<table>
<thead>
<tr>
<th>Draw solute(s)</th>
<th>Conc.</th>
<th>Osmotic pressure (bar)</th>
<th>Feed solution</th>
<th>$J_s$ (g/m$^2$h)</th>
<th>$J_{c^*}$ (L/m$^2$h)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDTA-2Na\textsuperscript{a}</td>
<td>0.61 M</td>
<td>60</td>
<td>Raw wastewater</td>
<td>0.1</td>
<td>3.3</td>
<td>13</td>
</tr>
<tr>
<td>NaOAc</td>
<td>1.49 M</td>
<td>60</td>
<td></td>
<td>0.4</td>
<td>5.4</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>1.27 M</td>
<td>60</td>
<td></td>
<td>2.4</td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>EDTA-2Na and NP7\textsuperscript{b}</td>
<td>0.1M and 15 mM</td>
<td>7.31</td>
<td>DI water</td>
<td>0.067</td>
<td>2.65</td>
<td>14</td>
</tr>
<tr>
<td>EDTA-2Na and NP9\textsuperscript{c}</td>
<td>0.1M and 15 mM</td>
<td>7.4</td>
<td>DI water</td>
<td>0.092</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PUF\textsuperscript{d}/hydrogel composites of hydrogel</td>
<td>50 to 89 wt%</td>
<td></td>
<td>DI water</td>
<td>3.9 to 17.9</td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>PSSP\textsuperscript{e}</td>
<td>20 wt%</td>
<td>20.85</td>
<td>DI water</td>
<td>0.14</td>
<td>14.50</td>
<td>16</td>
</tr>
<tr>
<td>PAspNa\textsuperscript{f}</td>
<td>0.3 g/mL</td>
<td>51.5 atm</td>
<td>DI water</td>
<td>4.9</td>
<td>31.8</td>
<td>17</td>
</tr>
<tr>
<td>Sucrose</td>
<td>1</td>
<td>26.7</td>
<td>DI water</td>
<td>12.9</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td>PAA-Na\textsuperscript{g}</td>
<td>0.72 g/mL</td>
<td>44</td>
<td>DI water</td>
<td>0.18</td>
<td>22</td>
<td>19</td>
</tr>
<tr>
<td>HCOONa\textsuperscript{h}</td>
<td>0.68</td>
<td>28</td>
<td>DI water</td>
<td>2.73</td>
<td>9.4</td>
<td>20</td>
</tr>
<tr>
<td>Sodium hexa-carboxylatophenoxy phosphazene</td>
<td>0.067</td>
<td>None</td>
<td>DI water</td>
<td>7</td>
<td></td>
<td>21</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Ethylenediaminetetraacetic acid disodium salt \textsuperscript{b} Nonylphenol ethoxylate surfactants, Tergitol NP7 \textsuperscript{c} Nonylphenol ethoxylate surfactants, Tergitol NP9 \textsuperscript{d} Polyurethane foam \textsuperscript{e} Oligomeric poly(tetrabutylphosphonium styrenesulfonate) \textsuperscript{f} Poly (aspartic acid sodium salt) \textsuperscript{g} Polyacrylic acid sodium salts \textsuperscript{h} Sodium formate
four major types of fouling: (1) organic fouling, which is caused by macromolecular organic compounds such as alginate, protein, and natural organic matters; (2) inorganic fouling, which is due to crystallization of sparingly soluble mineral salts when the salt concentration exceeds saturation; (3) biofouling, which involves bacteria deposition, attachment, and subsequent growth to form biofilm; and (4) colloidal fouling, which results from the deposition of colloidal particles. Depending on its severity, fouling can have varied degree of adverse impact on membrane performance, such as decreasing water flux, deteriorating product water quality, and increasing maintenance burden. Furthermore, the foulants might also chemically degrade the membrane material. Fouling is a considerable problem that occurs in most liquid membrane processes and consequently influences the economics of the operation. Hence, a lot of research has been done to reduce the impacts of fouling in pressure driven membrane processes. The problem can be addressed by changing operational conditions, cleaning, membrane surface modification, and membrane material choices.

However, fouling in osmotically driven membrane processes is different from fouling in pressure driven membrane processes (Figure 4). Depending on the membrane orientation, the deposition of foulants occurs on different membrane surfaces. In FO process, foulant deposition occurs on the relatively smooth active layer. In PRO and other pressure driven processes, the foulant deposition takes place on the rough support layer side, or even within the support layer. Recent studies have demonstrated that membrane fouling in FO process is relatively low compared to the pressure driven processes (Figure 4). Depending on the membrane orientation, the deposition of foulants occurs on different membrane surfaces. In FO process, foulant deposition occurs on the relatively smooth active layer. In PRO and other pressure driven processes, the foulant deposition takes place on the rough support layer side, or even within the support layer. In FO process, fouling due to organic materials is more severe than inorganic material. Alginate as a model foulant was studied in FO and RO. NaCl was used as draw solute in FO and feed solute in RO, severe flux decline in FO was observed than in RO. However, when dextrose was used as draw solute in FO, the flux decline was almost identical to RO. This indicates a cake formation from reverse salt flux. Humic acid filtration shows higher flux decline in FO than in RO. This also occurs in colloidal fouling with silica particles. The flux decline is attributed to intermolecular bridging of humic acid molecules by the salt ions.

A strong correlation between intermolecular adhesion and fouling in FO was observed. Strong foulant-foulant interactions, such as adhesion, causes faster accumulation of foulant on the membrane surface. Fouling is a considerable problem that occurs in most liquid membrane processes and consequently influences the economics of the operation. Hence, a lot of research has been done to reduce the impacts of fouling in pressure driven membrane processes. The problem can be addressed by changing operational conditions, cleaning, membrane surface modification, and membrane material choices.

Motsa et al. (2014) reported that membrane orientation had an impact on fouling behaviour since the membrane fouled more easily when operated in PRO mode than in FO mode. There was severe permeate flux decline in PRO mode mainly due to the calcium–alginate complexes blocking the pores in the support layer. Yong Ng and Parad, focused on the impact of lower organic loads (10, 30, 50 ppm) in secondary effluents with calcium inclusion on
the fouling characteristics of FO membranes both in the FO and PRO modes. In their work, they demonstrated that the FO mode had lower fouling compared to the PRO mode, which was also seen by other authors. This was attributed to the denser, smoother and tighter structure of the membrane active layer which prevented the adhesion and accumulation of foulants on the membrane surface, while the porous support layer, being a looser structure, allowed the accumulation and deposition of the foulants on its surface and inside the membrane, by the mechanisms of direct interception and subsequent pore plugging.

Thus it is clear that the nature of fouling in osmotically driven membrane process is different from fouling in pressure driven membrane processes. Further investigations of the mechanism of FO fouling are required to fully understand the differences. The mechanism of fouling is complex and depends on many factors such as water quality, temperature, system design, membrane cleaning, water flow, membrane surface etc. To mitigate fouling, these factors need to be considered in the process design and development.

5. Forward Osmosis Applications

FO has a potential benefit as it requires a low hydraulic pressure compared to the pressure-driven process (RO). FO has low energy consumption therefore it involves lower costs, and with appropriate draw solutes and its regeneration methods, the process could be developed to be economically feasible and technically sound.

While FO has been investigated in a wide range of applications, including power generation, seawater/brackish water desalination, wastewater treatment and food processing, this review focuses mainly on wastewater treatment.

In general, there are two clusters of applications concerning FO in the water production and water treatment industry (Figure 5), (i) desalination and (ii) water reuse.11

5. 1. Desalination

In early 1970s, the FO process was proposed as pretreatment step to the RO process. However, the advent of commercial FO cellulose triacetate (CTA) membranes prompted applications within seawater/brackish water desalination. With the FO desalination process, fresh water can be obtained directly (Figure 6) obtained from saline water (seawater or brackish water) at low (or no) pressure. This can be obtained by using an osmotic reagent based on volatile salts such as NH₄HCO₃ as the DS. A DS recovery process is needed to separate the draw solute from the solution, and in this case raising the DS temperature abo-
ve 60 °C will produce CO₂ and NH₃ which can then be reused to produce NH₄HCO₃ in the next cycle. Also, polymer hydrogels and modified magnetic particles have been suggested as DS in FO desalination with no pressure required.

**Indirect FO desalination** uses a high salinity water (e.g. seawater/brackish water) as the DS and a poor-quality water source such as wastewater effluent or urban storm water runoff as FS. The diluted seawater/brackish water DS can then be desalinated using low pressure reverse osmosis (LPRO). The FO-LPRO hybrid process reduces the cost of the total desalination process compared to pure RO. This is due to the fact that desalination occurs with a lower salinity and can run at 50% recovery. Nicoll (2013) compared three different desalination systems: i) conventional pre-treatment with a dual media filter (DMF), cartridge filtration and SWRO; ii) UF based pre-treatment with SWRO; and iii) conventional pre-treatment feeding a FO/RO plant. The summary calculations showed that the DMF/FO/RO configuration has the lowest energy consumption.

Many studies were focused on DS and their recovery for FO desalination. Different draw solutes (i.e. NaCl, KCl, CaCl₂, MgCl₂, MgSO₄, Na₂SO₄, and C₆H₁₂O₆) were investigated for seawater desalination using a hybrid FO–NF process. Nanoparticles (superparamagnetic) were also tested as a DS in FO desalination, where the nanoparticles could be regenerated by UF.

### 5.2. Wastewater Treatment

Most FO approaches for poor quality water treatment and reuse are similar to the direct seawater desalination method, where poor-quality water is used as feed, while a DS is used to reduce the volume of the feed. The DS is further treated by other post-treatment process for the recovery of the salt (e.g. RO, membrane distillation).

In general, wastewater has lower osmotic pressure and higher fouling propensity. FO integrated with membrane distillation (MD) process was studied for treatment of municipal wastewater, where stable water flux was attained in a continuous operation at the recovery rate up to 80%. The FO showed a moderate to high rejection of most organic contaminants while MD rejected the residual contaminants to achieve a near complete rejection in the hybrid process. To recover clean water from secondary wastewater effluent, a photovoltaic powered FO – electrodialysis (FO-ED) process was tested. The process resulted in high removal of total organic carbon (TOC) from the feed wastewater and production of fresh water. By using FO and ED through solar energy, this process has been able to supply potable water in isolated and remote areas and islands. In addition, FO process showed several benefits for space missions, including high wastewater recovery, low energy cost and minimized resupply. Further, natural steroid hormones were removed from wastewater by FO membrane contactors. FO has also been used for other wastewater such as oily wastewater, industrial and municipal wastewater, nuclear wastewater, landfill leachate, oil-water separation. Additionally, application of FO for wastewater treatment was performed in membrane bioreactor (Figure 7), called osmotic membrane bioreactor (OsMBR).

Submerged membrane bioreactors (MBRs) involve biodegradation and membrane filtration in a single reactor. It has become one of the most commonly applied technologies in the treatment of different types of wastewater. FO process replaces the pressure driven membrane process (microfiltration, ultrafiltration) used in MBR. Integration of FO in MBR provides lower fouling propensity, no applied hydraulic pressure, and equally good quality effluent. Unlike the conventional MBR, FO-MBR does not involve high pressure diffused air for reducing the cake layer formation on the membrane surface and pump for collecting the effluent. In addition, FO provides a more sustainable flux and reliable removal of contaminants. The study of novel FO-MBR or osmotic MBR (Os-MBR) has been initiated in the last five years. A salt accumulation model to investigate FO performance in Os-MBR shows that the ratio of the membrane salt permeability (B) to the water permeability (A) (i.e. B/A) and the ratio of hydraulic retention time (HRT) to sludge retention time (SRT) (i.e. HRT/SRT) are two important parameters for the optimization of OsMBR operation. To minimize the flux decline caused by salt accumulation, these two ratios should be low.

### 6. Recent FO Membrane Developments

The ideal FO membrane exhibits high water permeability and solute rejection, minimal external and internal concentration polarization (ICP) as well as high chemical and mechanical stability. These features are somewhat contradictory. For example, a low ICP requires a low...
S-value (structural parameter) which in turn requires a low thickness and high porosity. Thus, providing sufficient mechanical stability to a thin highly porous membrane is one of the key outstanding problems in FO membrane development.

The membrane structural parameter $S$ is defined as:

$$S = K \times D = \frac{t_s \times \tau}{\varepsilon}$$

where $D$ is the diffusion coefficient of the draw solute, $t_s$ is the support layer thickness, $\tau$ the tortuosity, and $\varepsilon$ the porosity.52

Several materials have been investigated for FO membrane fabrication. These include materials based on cellulose, polyamide (and other polymers), and polyelectrolytes. Also so-called mixed matrix membranes have been investigated. These membranes typically consist of ‘fillers’ or inclusions (e.g. zeolites) embedded in a polymeric matrix. A special case is the concept of biomimetic FO membranes where aquaporin proteins are incorporated in the membrane enhancing water flux while preserving high solute rejection.

Cellulose acetate (CA) and cellulose triacetate (CTA) have been used in RO membrane fabrication since the 1960s so it is perhaps not surprising that FO membrane.

### Table 2. An overview of various FO application in last five years

<table>
<thead>
<tr>
<th>Feed</th>
<th>Process / FO membrane material / DS / module: Objective</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic wastewater with sludge</td>
<td>Submerged OsMBR / CTA / NaCl (aq.) / Flat-sheet: Water reclamation from wastewater</td>
<td>The bioinspired surface modification improved the antifouling ability of the CTA FO membrane.53</td>
</tr>
<tr>
<td>Polyvinyl chloride (PVC) latex</td>
<td>FO / CTA / NaCl (aq.) / Flat-sheet: Condensation of PVC latex with FO as a pretreatment step</td>
<td>The apparent TOC rejection in the FO process is slightly higher than that in RO.54</td>
</tr>
<tr>
<td>Boiler feed water (BFW)</td>
<td>FO / PA-TFC / NaCl (aq.) / Flat-sheet: treatment of BFW of steam assisted gravity drainage (SAGD) process</td>
<td>Reducing the temperature (during fabrication) of the organic solution down to −20 °C effectively reduced the thickness of the PA selective layer.55</td>
</tr>
<tr>
<td>High-nutrient sludge</td>
<td>FO-MD / TFC / Na3PO4 (aq.) / Flat-sheet: concentrating high-nutrient sludge in an FO–MD hybrid system</td>
<td>At pH 9, the Na3PO4 was providing a high water flux and mitigating salt leakage resulting from the formation of the high charge of phosphate and complexon.56</td>
</tr>
<tr>
<td>Wastewater with sludge</td>
<td>OsMBR / − / Fertilizer / − / anaerobic fertilizer-drawn forward osmosis membrane bioreactor (AnFDFOMBR) for biogas production</td>
<td>Mono-ammonium phosphate (MAP) showed the highest biogas production while other fertilizers exhibited an inhibition effect on anaerobic activity with solute accumulation.57</td>
</tr>
<tr>
<td>Raw sewage</td>
<td>FO-MD / CTA / NaCl (aq.) / Flat-sheet: Direct sewer mining</td>
<td>Trace organic contaminants (TrOC) transport through the FO membrane is governed by “solute-membrane” interaction, whereas that through the MD membrane is strongly correlated to TrOC volatility.48</td>
</tr>
<tr>
<td>Secondary wastewater effluent</td>
<td>FO-ED / CTA / NaCl (aq.) / Flat-sheet, parallel plate-and-frame module: Potable water production, utilization of natural energy for water treatment and reuse</td>
<td>In the ED unit, the diluted draw solution was desalted and high-quality water was produced; the concentrate was recycled to the FO unit and reused as the draw solution.59</td>
</tr>
<tr>
<td>Synthetic wastewater</td>
<td>FO / CTA / NaCl (aq.) / Flat-sheet: Tetracycline recoverable separation from antibiotic wastewater</td>
<td>An effective treatment of tetracycline antibiotic wastewater as well as the recovery of antibiotics from the wastewater.58</td>
</tr>
<tr>
<td>Synthetic surfactant wastewater</td>
<td>FO / CTA / NaCl (aq) / Flat-sheet: Dehydrate and treat Olive Mill Wastewater (OMWW)</td>
<td>Complete decolorization of permeate, and more than 98% rejection to OMWW components, including biophenols and ions.59</td>
</tr>
<tr>
<td>Synthetic dye wastewater</td>
<td>FO-CF(coagulation/flocculation) / TFC / Poly(acrylic acid) NaCl (aq) / Flat-sheet: treatment and reuse of textile wastewater</td>
<td>Remarkable reverse fouling behaviour has been observed where the Jw of the fouled membrane was fully restored to the initial value by physical flushing without using any chemicals.60</td>
</tr>
<tr>
<td>Wastewater containing heavy metals</td>
<td>FO / cellulose acetate butyrate (CAB) / NaCl (aq.) / Hollow fiber: Water reclamation from emulsified oily wastewater through FO under the PRO mode</td>
<td>Water flux declines slightly by 10% after a 12 h oil/water test under the PRO mode and water flux of the fouled membrane can be restored to 97% by simple water rinse.61</td>
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nes based on CTA were amongst the first to be commercially available from Hydration Technologies Incorporated (HTI). In recent years there have been significant developments in CA and CTA based FO membrane both in flat sheet and hollow fibre geometries. Generally, these membranes are fabricated in a phase inversion process where a polymer is transformed in a controlled way from a solution state to a solid state. Thus, when a polymer solution (polymer plus solvent) is cast on a suitable support and immersed in a coagulation bath containing a non-solvent precipitation occurs because of the exchange of solvent and non-solvent. The procedure allows for making membranes with very low S-values (of the order of 50 μm) which makes them potentially good FO membranes. The general trend is that CA membranes have acceptable water fluxes but tend to have lower rejection (and thus higher reverse solute fluxes) whereas the opposite trend is the case for CTA based FO membranes.

The cellulose hydroxyl can be reacted with reagents to generate cellulose esters beyond CA and CTA. These include materials such as cellulose propionate (CP), cellulose acetate butyrate (CAB) or cellulose acetate propionate (CAP). Dual layer FO hollow fibres made from CA and CAP show superior performance compared to CA-based flat sheet or hollow fibre membranes. However, the limited stability to temperature and pH generally restricts the use of cellulose-based materials.

Cellulose-based membranes were dominant throughout the 1960s until the advent of thin film composite (TFC) membranes in the 1970s. Most TFC membranes are made with a porous, highly permeable support such as polysulfone, which is coated with a cross-linked aromatic polyamide thin film. The coating — also sometimes referred to as the active layer — provides the solute rejection properties while the support provides the mechanical stability. The typical coating is made by interfacial polymerization to create a 100–200 nm thick polyamide coating exemplified by the reaction between m-phenylene diamine and trimesoyl chloride monomers.

A good polyamide layer requires optimization of the exact monomer composition, reaction time, temperature and ambient humidity. In FO membranes, addition of the detergent sodium dodecyl sulfate (SDS) can enhance solute rejection without major impact on the water flux, and post treatment using SDS/glycerol followed by thermal annealing facilitates removal of unreacted monomers resulting in increased free volume and reduced thickness leading to improved flux without detrimental effects on rejection. The presence of cetyltrimethylammonium chloride (CTAC) which can react with the m-Phenylene diamine (MPD) can decrease water flux while increasing the solute rejection. Thus, there are a number of possibilities for fine-tuning FO membrane active layers.

A good support for a TFC membrane shows a low ICP and typically supports are based on polysulfone or polyethersulfone. Also bucky papers made from Carbon Nanotubes (CNTs) and nanofiber mats formed from electrospun fibres have been suggested as good FO membrane support due to high porosity and tensile strength. Structurally it has been argued that an open ‘finger’ like structure of the support is to be favoured over a dense ‘sponge’ like structure. However a more open structure is also mechanically weaker and a more dense structure also may have a higher ICP. An obvious compromise would be to have an anisotropic support with a sponge structure interfacing the active layer supported by a finger like structure below. But the structural features are not the only determinants for FO membrane performance. A sponge like support structure may in fact give rise to a higher water flux than a finger like structure provided that hydrophilicity and thickness are well controlled. This illustrates the complexity behind ICP where many specific physico-chemical factors give rise to a phenomenological effect.

Polyelectrolytes have attracted considerable attention over the last decade as an alternative to the TFC approach. The typical polyelectrolyte membrane consists of a layer-by-layer (LbL) deposition of alternating cationic and anionic electrolyte-films onto a suitable support where hydrolysed (and thus negatively charged) polyacrylonitrile is an exemplary material. Large scale production of LbL assembled membranes has proved to be difficult; nevertheless, the approach offers the potential of fabricating membranes with good rejection combined with good solvent resistance and thermal stability.

One of the latest design approaches for FO (and RO) membranes is based on the concept of membrane biomimetics where technological developments take cues from nature. The basic concept is based on the fact that biological membranes have excellent water transport characteristics.

### Table 3. List of commercial producers and developers of FO membranes

<table>
<thead>
<tr>
<th>Company</th>
<th>Membrane Type</th>
<th>Configuration</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aquaporin A/S</td>
<td>Biomimetic aquaporin</td>
<td>Hollow fiber and flat sheet</td>
<td>Commercial</td>
</tr>
<tr>
<td>Oasys Water</td>
<td>Thin film composite</td>
<td>Flat sheet</td>
<td>Commercial</td>
</tr>
<tr>
<td>Fluid Technology Solutions, Inc.</td>
<td>Cellulose tri-acetate</td>
<td>Flat sheet</td>
<td>Commercial</td>
</tr>
<tr>
<td>Nitto Denko</td>
<td>Composite semipermeable membrane</td>
<td>-</td>
<td>Development</td>
</tr>
<tr>
<td>Woongjin Chemical Co., Ltd.</td>
<td>Composite membrane</td>
<td>-</td>
<td>Development</td>
</tr>
<tr>
<td>Porifera</td>
<td>Thin film composite</td>
<td>Flat sheet</td>
<td>Commercial</td>
</tr>
</tbody>
</table>

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They employ natural proteins known as aquaporins (AQPs) to regulate the flow of water, providing increased permeability and near-perfect solute rejection.79 Thus by using reconstituted AQPs as building blocks one can create membranes with unique flux and rejection properties.80 AQP membrane design approaches have been recently reviewed.7 According to membrane structural design, AQPs incorporated biomimetic membranes can be classified into two basic types, (1) AQPs containing vesicle encapsulated membranes (VEMs), where AQPs containing vesicles (proteoliposomes or proteo-polymersomes) are immobilized in a dense polymer layer and (2) AQP containing supported (lipid or polymer) membrane layers (SMLs).

AQP-based membranes are currently being produced and commercialised by the Danish company Aquaporin A/S, its Singaporean affiliate, Aquaporin Asia Pte. Ltd., and its Joint Ventures AquaPoten Limited in China and Aquaporin Space Alliance in Denmark in flat sheet and hollow fibre geometries. The membranes are currently tested in several processes including pesticide removal, CO₂ capture, and water reuse in space and textile wastewater treatment.81–84

7. Conclusions

The FO process used in wastewater treatment and water purification shows promising results, and has many advantages in comparison to the conventional water/wastewater treatment processes.

The studies are focused on improving the FO process by developing new membranes, membrane surface modifications, different DSs and their compatibility with various wastewaters. However, there are other issues (e.g. membrane fouling, raw water characteristics) in FO process that needs to be studied. FO processes are highly compatible with other treatment processes therefore, the whole treatment process could become more cost effective by incorporating FO process. As it is seen from the literature, many studies and improvements were done on the membrane materials and their surface, and new technologies were implemented, such as membranes with biological materials (aquaporins).

Higher quality water is in demand due to the imposition of new and ever-changing water quality standards. Therefore, interest in FO technology is growing as a potential, cost-competitive and reliable alternative.

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9. References