

**The Examination and Comparison between Reverse and Forward Osmosis:
Which Is the Solution for the Future?**

Jialing Geng

BScH Environmental Chemistry Candidate 2015

Queen’s University

Abstract

Water shortages are becoming a global problem which is further aggravated by rapid population and economic growth. Owing to the scarce amount of fresh water available, various water desalination and purification methods have been developed over the past decades to mitigate the scarcity of fresh water. Reverse osmosis (RO) emerged as one of the most viable techniques due to its reduced energy cost compared to distillation, which requires massive amount of heat. RO uses hydraulic pressure to push the flow of water across a semi-permeable membrane to separate water from the salt it dissolves. The past few decades have seen the development of RO membranes, through which optimized materials and compositions have been synthesized for excellent water flux and salt rejection. Recently, forward osmosis (FO) has been gaining attention because no hydraulic pressure needs to be applied. By using a draw solution, a spontaneous flow of water occurs in a FO system, allowing for much lower energy consumption compared to RO. In addition, RO suffers from severe membrane fouling that is intensified by the pressure applied. In contrast, FO membranes show less fouling. However, internal polarization of FO is a major obstacle that causes a severe flux decline. In addition, FO lacks truly optimized membranes since the majority of FO membranes are modified RO membranes. Furthermore, FO needs an optimized draw agent that is easily removable and non-toxic. Hence, a literature review addressing the advantages and limitations of FO with regard to membranes, energy cost, draw agents and fouling problems has been conducted. A comparison between FO and RO in each aspect has been drawn, and the challenges as well as future research directions for FO have been highlighted.

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1.0 Introduction

Water scarcity has been one of the major environmental issues faced by many societies in the world due to the limited amount of fresh water and its uneven distribution on Earth. Out of the total volume of 1.4 billion km³ of water on Earth, 97.5 % is salt water and only 2.5 % is fresh water. Out of this 2.5 % of fresh water, only 0.3 % is in liquid form that is available for human consumption (Gleick, 1996). Since the global population is growing rapidly, the shortage of fresh water has become an increasingly pressing problem which needs a viable solution in the near future. Furthermore, the water scarcity problem has been intensified by water pollution due to overpopulation and rapid industrialization of developing countries. According to statistics, currently one out of every six people in the world is water stressed, and about one billion people in developing countries are faced with water scarcity problems (Watkins, 2006).

The water scarcity problem would be significantly mitigated if an ideal purification method can be developed to turn salty seawater or contaminated fresh water into potable water. Over the past decades, a lot of research has focused on developing water treatment methods, and one of the most applicable methods is reverse osmosis (RO). Reverse osmosis is a membrane technique which utilizes pressure applied across a semi-permeable membrane for water filtration. It is an important process for desalination of seawater because it does not require heat and the

energy demand is a lot lower than distillation. The first practical seawater desalination with RO was demonstrated by Sidney Loeb in the 1960s (Loeb and Sourirajan, 1964). Since then, a lot of research has been done on RO (Spiegler and Kedem, 1966; Sourirajan, 1970; Peterson, 1993). Recently, forward osmosis (FO) in desalination has started to gain attention due to its potentially lower energy cost than RO (Cath *et al.*, 2006; McCutcheon and Elimelech, 2006; Yip *et al.*, 2010).

My research will focus on the comparison between FO and RO, and my final goal is to find out if FO or RO would be the better method for water purification. To this day, there has been a large amount of literature about the development of either RO or FO in water desalination, including the development of membranes, draw solutions, reducing energy input and fouling, etc. In recent years, most of the research papers prefer FO to RO for two reasons. First, RO requires a high pressure to force the water to go from high to low concentrations, opposing the normal osmotic properties. Hence, RO is very energy intensive, which requires 3.6-5.7 kWh to produce a cubic meter of clean water (Humplik *et al.*, 2011). Second, RO has inevitable fouling problems which require chemical cleaning (Lahoussine *et al.*, 1990). However, McCutcheon and Elimelech (2006) suggested that the internal concentration polarization of FO is a major obstacle which can cause a severe water flux decline. In addition, FO needs an optimized draw agent that displays non-toxicity while maintaining a high osmotic pressure. Therefore, a thorough comparison between FO and RO needs to be made before the statement that “FO is better than RO” is confirmed. In this report, FO and

RO methods will be compared in different aspects such as membranes, energy cost, and fouling problems. In addition, different draw agents for FO will be studied to further assess the advantages and disadvantages of FO. Through the comparison of all the factors above, it could be determined that whether FO or RO is a more practical method for water treatment or desalination.

2.0 An Overview of Reverse Osmosis

2.1 A Brief history of Reverse Osmosis

Osmosis was first demonstrated in 1748 by a French scientist Jean-Antoine Nollet, who proved that solvent could flow from a region with a lower concentration of solute to a region with a higher concentration of solute due to the existence of osmotic pressure. Using a pig's bladder as a membrane, Nollet found that the solvent would keep flowing through the membrane until equilibrium is reached on both sides. There was no significant progress until 1867 when Traube prepared the first inorganic membrane, which was a thin film composed of copper ferrocyanide that displayed high selectivity (Glaser, 1998). Since then, osmosis technique has attracted increasing attention and developed rapidly.

The first pressure-driven osmosis process emerged in 1907, when Bechold (1907) carried out ultrafiltration experiments that drove the flow of solvents through a filter paper filled with acetic acid solutions under an applied pressure. Meanwhile, the first

membrane made of polymeric materials was synthesized from cellulose extracted from natural products (Glater, 1998). With the applications of these methods, the first experiment on seawater desalination was conducted by researchers in the University of California. However, due to the low water flux, this technique was not commercialized until asymmetric membranes were characterized by Leob and Sourirajan (1964) in the 1960s. (Leob and Sourirajan, 1964).

Leob and Sourirajan were two scientists from UCLA, where they worked on developing a membrane that would display high water permeability meanwhile maintaining a high level of salt rejection (Leob and Sourirajan, 1964). From their research, it was found that the membrane was asymmetric with one side being active and showing high salt rejection. With this finding, Leob and Sourirajan carried on the invention of an economically viable membrane by making it asymmetric with an active layer on one side but a supporting layer on the other. The membrane was made from cellulose acetate dissolved in acetone solution which was casted on a sheet of glass and let to be dried by air. To ensure the porosity of the supporting layer, liquid magnesium perchlorate was used to swell up the polymer. The other side was exposed to air to form the dense active layer (Leob and Sourirajan, 1964). With the significantly improved water flux and salt rejection, the practice of RO became practical for water desalination and allowed RO membranes to be commercially available. The Leob-Sourirajan membrane entered the market in 1961, which attracted the interests of a few companies including Heaven's industries, which was the first

one to apply the new membrane. In this company, a tube-shaped membrane was invented which worked as both a membrane supporter and a pressure vessel (Glater, 1998). Later on, the first RO commercial plant was built in California and applied Loeb and Sourirajan's technologies in the pilot program. With the emergence of this program, the desalination technology drew the interests from industries worldwide, and global desalination capacity has grown exponentially since then (Fig.1). Nowadays, there are more than 15 000 desalination plants in the world, and a half of them are RO plants (Greenlee *et al.*, 2009)

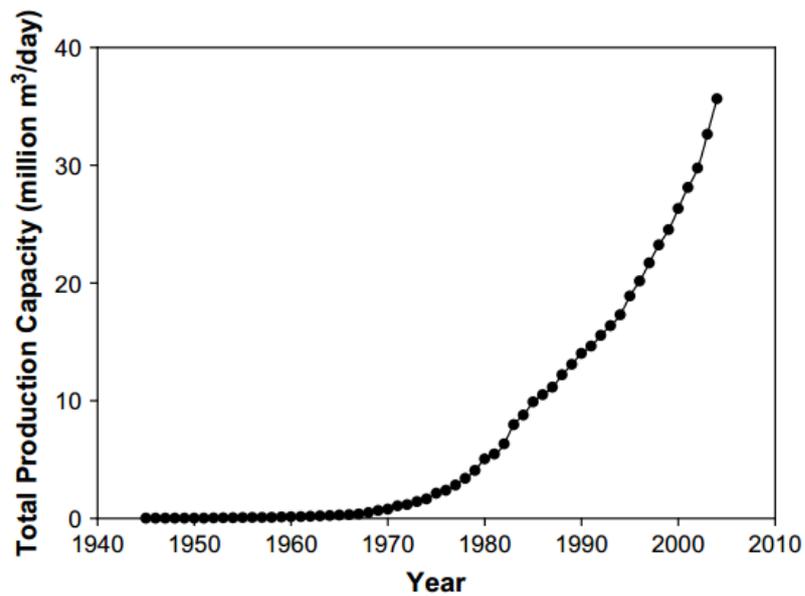


Fig.1 – Desalination capacity in the world from 1945 through 2006 (Gleick, 2006)

2.2 Working Principles

Osmosis is a natural phenomenon which involves the flow of a solvent through a semi-permeable membrane to a region with more concentrated solutes. This process is driven by the tendency to keep equal concentrations on each side, producing an osmotic pressure. Reverse osmosis is operated by reversing the natural flow of solvents, which are forced to flow from a concentrated region to a more diluted region. To achieve this, an external pressure has to be applied to overcome the osmotic pressure and enable the flow of solvent. A semi-permeable membrane is used in order to separate salt from the feed solution by allowing only solvent to flow through.

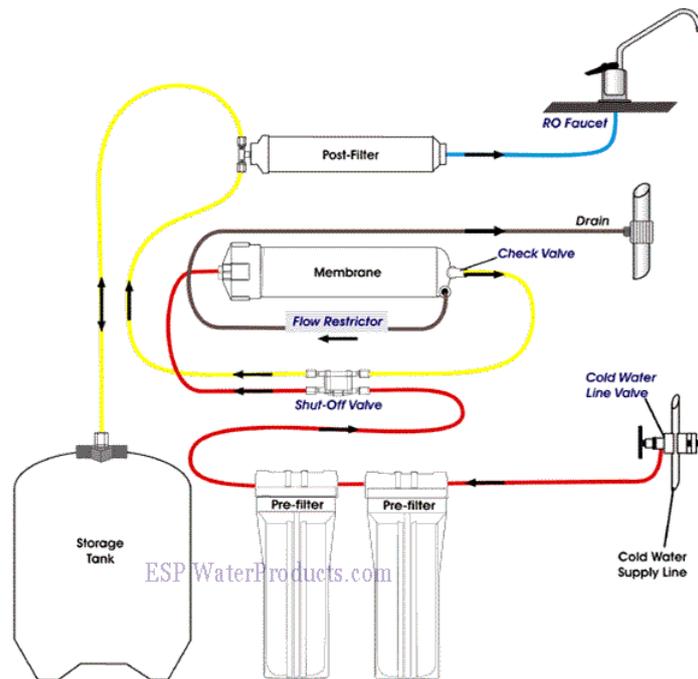


Fig.2 – A schematic diagram of a reverse osmosis system (Esp water products)

Fig.2 shows a schematic diagram of a residential reverse osmosis system, in which the feed solution enters the system from the cold water line valve, and the

sediment, soil and clay are separated in the pre-filters. The filtered water enters the reverse osmosis membrane which is usually embedded in a pressure vessel, and is then eluated into the RO water storage tank. The purified water from the storage tank goes through a post-filter before entering the RO faucet so that the remaining impurities can be removed. The RO membranes are usually cylinder-shaped and loaded into a pressure vessel. When the feed water is pumped into the membrane, the pressure pump forces water to diffuse through the membrane and leave behind the salt onto the membrane. There is a perforated central tube in the middle of the cylinder which keeps the desalted water within the envelope from contamination.

2.3 RO membranes

2.3.1 Introduction to RO membranes

Conventional RO membranes include cellulose acetate membrane (Loeb and Sourirajan, 1964), cellulose triacetate membrane (Sudak, 1990), blended cellulose diacetate and cellulose triacetate membrane (King *et al.*, 1970) and polyamide membrane (Credali and Parrini, 1971). Currently, the dominant RO membrane materials are thin film composite (TFC) polyamide which consists of a polyester web as the supporting layer, the microporous interlayer and the barrier layer on the surface (Peterson and Cadotte, 1990). RO membranes can have different modules, of which the dominant type is spiral wound module with membrane sheets wound around the

central tube (Baker, 2004). Recent years have seen the emergence of novel RO membranes such as rigid star amphiphiles membrane (Lu *et al.*, 2007), ceramic membranes (Pabby *et al.*, 2009), carbon nanotube membranes (Noy *et al.*, 2007), biomimetic membrane (Kaufman *et al.*, 2010) and membranes with incorporated hydrophilic additives (Zhao and Ho, 2014).

Two factors that determine the performance of membranes are water flux and salt rejection levels. Water flux is an important factor since it examines how efficient the filtration can be. Factors including membrane porosity, void volume of the membrane, the distance a molecule needs to travel through the membrane, the tortuosity and the thickness of the membrane all contribute to the outcome of water flux. The relationship can be expressed as the following equation (Bird *et al.*, 2012):

$$N_{Ax} = \frac{\rho_A k}{\mu} \frac{d\rho}{dx} - D_{AB} \frac{d\rho_A}{dx}$$

where N_{Ax} is the mass flux of the substance A, ρ_A is the mass density of A, k is the permeability, μ is the viscosity of A, and $\frac{d\rho}{dx}$ is the pressure gradient in x-direction, and D_{AB} is the diffusion coefficient for A to diffuse in B. In order to force the water to flow through the membrane, the applied pressure must exceed the osmotic pressure of the solution, which is expressed as (Perry and Green, 1997):

$$\pi_{concentrate} = \left(\frac{1}{1 - R_w} \right)$$

where R_w is the recovery factor of a membrane.

The salt rejection level is another indicator for membrane performance, and the

equation is expressed as (Baker, 2004):

$$N_s = B(C_{feed} - C_{permeate})$$

where N_s is the salt flux, C_{feed} is the concentration of the feed solution, $C_{permeate}$ is the concentration of the permeate, and B is a constant that follows the relationship:

$$B = \frac{D_s K_s}{l}$$

where D_s is the salt diffusivity, K_s is the partition coefficient of the salt and l is the thickness of the membrane. For a spiral wound membrane, the salt rejection can be describe by the following equation (Bartels *et al.*, 2005):

$$R_s = \left(1 - \frac{C_{permeate}}{\left(\frac{C_{feed} + C_{concentrate}}{2} \right)} \right) \times 100\%$$

where R_s is the salt rejection for a crossflow operation.

2.3.2 Conventional RO membranes

Early membranes were mostly made of cellulose triacetate (CA), which displayed high salt rejections but low water flux. In 1960s, Loeb and Sourirajan developed asymmetric CA membranes which exhibited much improved water fluxes (Loeb and Sourirajan, 1964). Later cellulose triacetate (CTA) was also used as a RO membrane materials due to their high pH durability and stability, but they were prone to compaction problems which could cause a great loss in water flux (Sudak, 1990). To solve the compaction issues, cellulose diacetate and CTA were blended into the membrane, and results indicated that they showed greater permeability and selectivity

(King *et al.*, 1970). In addition, aromatic polyamide was also used in RO membranes but not extensively due to their low flux and salt rejection. The same flaw also existed in chlorine resistive membranes despite their high tolerance towards a wide pH range (Credali and Parrini, 1971).

A great breakthrough in membrane science was the development of composite -membrane which was an anisotropic membrane with different compositions through the multiple layers. One-step casting was difficult to perform because each layer had their different optimization requirement, thus two-step casting methods were developed to ensure the optimization for each layer. This also enabled the use of various materials for different layers, which broadened the selection of polymers.

Early casting methods for TFC membranes included float-casting and dip-casting. Float casting was a process in which the CA film was casted on water and then laminated onto a support layer (Francis, 1966). However, this technique was not applicable to industrial scales and did not gain much commercial attention. Later a dip-casting method was invented to replace the float casting method. Dip coating involved acid polycondensation of small hydroxyl compounds, which could be applied in large scales (Riley *et al.*, 1968). Instead of CA support layer, polysulfone was found to be the optimized material for support layer because of its improved flux and resistance to compaction, and also the stability in low pH environments (Rozelle *et al.*, 1968)

Following the invention of polysulfone support layers, the technique of interfacial polymerization was developed for RO membrane synthesis. Interfacial polymerization is a process in which two reactants react to produce polymers on the interface between two liquid phases. This process allows reaction to occur under ambient temperatures and enables the use of polymers unstable at high temperatures. The first important interfacial polymerization was the formation of NS-100, which was synthesized from toluene di-isocyanate and polythylenimine (Cadotte, 1977). Later on, membrane made of PA-300 polymerized from polyepiamines with improved water flux and salt rejection was developed for spiral wound membranes (Hickman *et al.*, 1979). Polymerizations of monomeric amines were also tested by Cadotte, and he discovered that membranes made from monomeric aromatic amines and aromatic acyl halides with more than three carbonyl halide groups could give the best result. With this reaction, polymerization and crosslinking occurred very fast without heat curing (Koo *et al.*, 1986).

Surface modification is another important step for RO membrane synthesis. It is crucial in enhancing water permeability and recovery of fresh water. Although there are various methods for membrane polymer synthesis, their performance could not be optimized without modifying the membrane surface. Techniques including soluble solvent such as a mixture of acid and alcohol have been used to improve the hydrophilicity and water permeability due to the existence of hydrogen bonding

(Mukherjee *et al.*, 1996). In addition, gas plasma treatment can also be used for surface modification to increase the hydrophilicity and cross-linking (Wu *et al.*, 1997). In addition to post treatments, the properties of membranes could also be optimized during the interfacial polymerization process. Recently, Tang *et al.* (2010) found that the introduction of LiBr salt into the aqueous solution could produce a smoother membrane surface and a higher salt rejection rate due to the interaction between Li⁺ ions and hydroxyl groups. Kong *et al.* (2010) discovered that the addition of a co-solvent containing acetone would decrease the immiscibility gap between aqueous and organic phase, which led to a very high water flux without compromising the salt rejection.

2.3.3 Novel RO membranes

Currently, most of the membranes used in industries are polymeric membranes. However, as nanotechnology develops rapidly, novel RO membranes made from nanomaterials have been synthesized. Although these novel membranes have not been commercialized, their emergence opened a new potential route to produce RO membranes. A recent study showed a development of a membrane for nanofiltration, in which the membranes were made from percolating methanol through rigid star amphiphiles. The rigid star amphiphiles were synthesized from cyclization processes which enabled the membranes to be extremely smooth with doubled water flux and high salt rejection (Lu *et al.*, 2007).

Another type of membranes made of ceramics containing silica or zirconia have also been developed. Ceramic membranes have a macro-porous support layer and a meso-porous active layer, and they display more robustness than conventional RO membranes (Pabby *et al.*, 2009). However, this type of membranes has not been widely applied due to the high manufacturing cost. Membranes made of nanoparticles have also gained a lot of interests in recent years. Membranes made of titanium oxide nanoparticles were found to exhibit excellent anti-bio fouling properties (Kim *et al.*, 2003). Zeolite nanoparticles have also been studied and results showed that membranes made from zeolite were smoother and more hydrophilic, which allowed for a higher water flux and salt rejection than conventional TFC membranes (Jeong *et al.*, 2007). Carbon nano-tube membranes have also caught increasing attention these years due to their enhanced performance. The nano-tubes inside the membrane allowed for high water transportation inside the channels, giving rise to improved water permeability (Noy *et al.*, 2007). Recent studies have also shown that incorporating hydrophilic additives such as o-ABA-TEA salt into the membrane could improve the water flux up to 99.41% (Zhao and Ho, 2014). In addition, TFC membranes that displayed superior anti-organic fouling performance have been made from adding agents such as titanate nanotubes, nitric oxide and N-chlorosuccinimide (Emadzadeh *et al.*, 2014) (Barnes *et al.*, 2015) (Yu *et al.*, 2015).

2.3.4 RO membrane fouling problems

Fouling has been an obstacle for RO membranes, which results in significant

decrease in water flux and shortened membrane lifetime. Fouling occurs when particles, salts, sands and other contaminants are absorbed onto the membranes. For water desalination, the major source of fouling is humic acid, a natural organic matter (NOM) present in most natural water. Tang *et al.* (2006) conducted fouling experiments and showed that humic acid on RO membranes could lead to a drop in water permeability. In their experiments, the impacts of hydrodynamic conditions and solution compositions were examined, and the results indicated that the flux reduction due to humic acid fouling was dependent on the feedwater composition and the initial flux. A more pronounced reduction in water flux was seen in solutions with a lower pH and higher Ca^{2+} ion concentration.

In addition to humic acid fouling, concentration polarization was also found to be a source of RO membrane fouling. Pressure-driven systems are prone to concentration polarization which is a result of transfer of some species through the membrane. In RO systems, the mass transfer can cause a higher concentration on the feed side and a lower concentration on the permeate side. This difference can increase the osmotic pressure at the membrane surface and significantly reduce water flux (McCutcheon and Elimelech, 2006). Hoek and Elimelech (2003) conducted experiments on colloidal fouling of RO membranes and found that the cake-enhanced concentration polarization was a new source of fouling. In a filtration system, the colloidal substances that remain on the membrane grow into a layer which is called “cake”. Hoek and Elimelech found that the flux decline of the membrane was associated with

the cake model, which significantly altered the hydrodynamics of cross-flow membranes and hindered the diffusion of salt ions.

Using the cake model, the cake-enhanced osmotic pressure could be described using the following equation (Hoek *et al.*, 2002):

$$\Delta\pi_m^* = \Delta P - v\mu R_m - v\mu \frac{180(1-\epsilon)}{\rho_p d_p^2 \epsilon^3} M_d$$

where $\Delta\pi_m^*$ is the cake-enhanced osmotic pressure, ΔP is the applied pressure, v is the permeate flux, μ is the dynamic viscosity of water, R_m is the membrane hydraulic resistance, and $\frac{180(1-\epsilon)}{\rho_p d_p^2 \epsilon^3} M_d$ is the term describing Rc (the transient hydraulic resistance), which depends on the cake layer porosity, particle diameter and particle density. To verify the cake-enhanced concentration polarization model, they compared membranes with similar hydraulic resistance and salt rejection and membranes with similar hydraulic resistance and different salt rejection, results of which indicated that cake-enhanced polarization was the major factor causing an elevated trans-membrane pressure that subsequently significantly decreased the water flux. Due to the fouling problems, RO membranes need constant maintenance and replacement in order to maintain their performance.

2.3.5 Energy Cost and Energy Recovery Method

High energy consumption has always been a limitation for reverse osmosis. For seawater reverse osmosis plants (SWRO), energy takes up the largest portion of consumption in their operations. The energy is consumed from processes such as pumping, pre-treatment, and mostly importantly, the high pressure demand for RO. It has been estimated that the high-pressure pump takes up about 84% of the entire energy consumption in SWRO, and other combined components including pre-treatment, abstraction and product transfer pump take up about 15% (Fig.3).

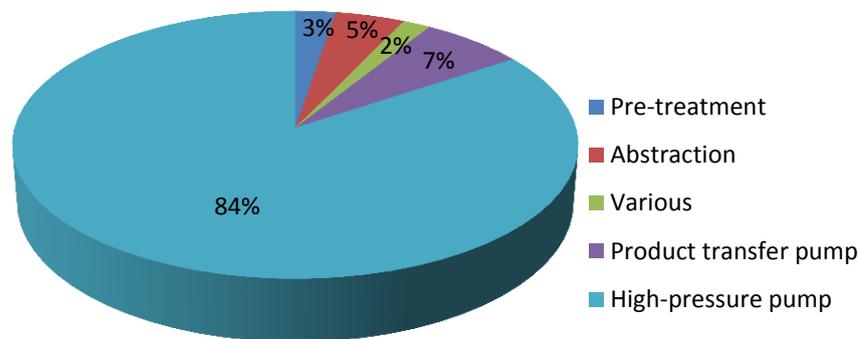


Fig.3-Energy consumption of different stages for SWRO (Wilf, 2004)

Although the energy cost in SWRO plants has decreased from 20 kWh/m³ in 1970s to about 2.0 kWh/m³ today, a considerable amount of energy is still needed to produce sufficient desalinated water (McHang and Truby, 2004). To decrease the energy cost of reverse osmosis, several energy recovery systems have been developed.

Nowadays, energy recovery devices (ERD) can reuse the remaining energy in brine and apply it to the feed solutions. There are two common recovery systems currently in use, which are pressure exchangers and turbine systems (Fritzmann et al., 2007). In the exchanger system, the pressure remaining in the brine is transferred into the feed water. There are three chambers connecting the brine system and the feed system: chamber A is responsible for transporting the pressure from brine to feed, chamber B adjusts the pressure and chamber C is responsible for the back filling from feed to brine (Fig.4) (Rautenbach and Melin, 2003).

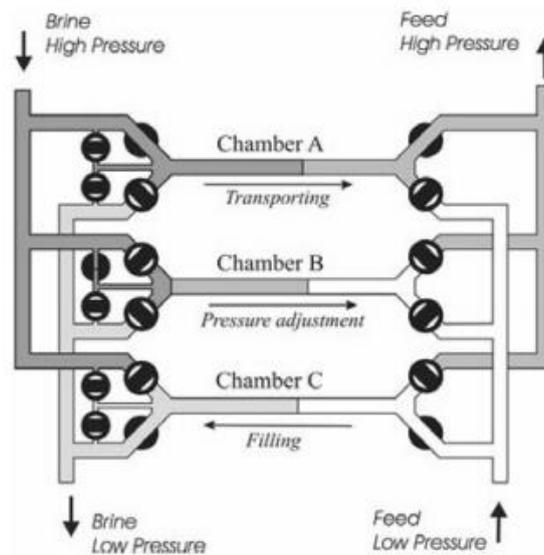


Fig.4 – Schematic diagram of a pressure exchanger (Rautenbach and Melin, 2003)

A turbine system consists of a pump and a turbine which contain a rotor. The high pressure from brine drives the rotation of the rotor which then produces power for the turbine and the high pressure pump to drive the main electric motor. The motor pressurizes the feed solutions which are subsequently pressurized by the turbocharger (Fritzmann et al., 2007).

The application of energy recovery system has reduced RO energy consumption to 2-4 kWh/m³ for seawater desalination (Wilf, 2004). However, there are some drawbacks associated with pressure exchangers such as the demand for auxiliary equipment which is costly. In addition, pressure exchangers can also increase the salinity of the feed solution after being mixed with brine, leading to a higher osmotic pressure (Fritzmann et al., 2007). Turbine systems were found to have reduced efficiencies if changes out of the actual design point occur, whereas pressure exchangers are capable of maintaining a higher efficiency (Fritzmann et al., 2007).

3.0 An Overview of Forward Osmosis

3.1 A Brief history of Forward Osmosis

Forward osmosis is a process in which the separation of solute from water is achieved by the flow of water through a semi-permeable membrane. Different from RO, water flows from a region of lower concentration to a region of higher concentration due to the introduction of a draw solution. This process generates a spontaneous flow of water, and the use of hydraulic pressure could be avoided. The easily-removable draw agents are then removed from the draw solutions to regenerate fresh water. Pressure-retarded osmosis (PRO) is a similar process which pressurizes the saline water using the pressure difference between seawater and fresh water, thus it is an intermediate process between FO and RO.

Since FO is not as energy-intensive as RO, it has attracted increasing interests in both academics and industries in recent years. However, the emergence of FO can be traced back to 1965 when Batchelder published a patent. In his work, ammonia gas was used dissolved in water to produce a concentrated draw solution, into which the water from feed solution flew through a cellulosic membrane (Batchelder, 1965). The history of FO can be linked to the development of various draw solutions, since effective removal of solutes from draw solutions is the most important step to FO becoming a viable alternative to RO.

In recent years, new types of draw solutions containing smart drawing agents and various types of membranes have been developed due to the rapidly growing interests in FO techniques. Between 2005 and 2011, the number of publications about FO has increased by almost 20 folds (Fig. 5).

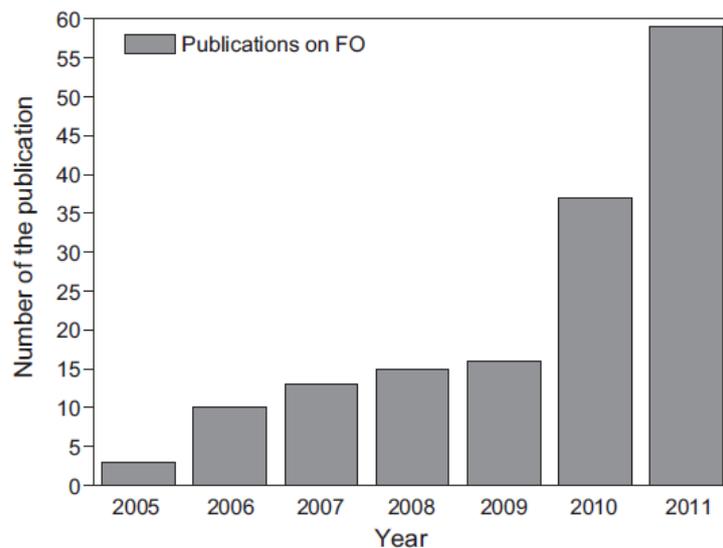


Fig.5 – Increase in number of publications between 2005 and 2011 (Zhao *et al.*, 2012)

3.2 Working Principles of Forward Osmosis

In general, the equation that describes the relationship between osmotic pressure and hydraulic pressure for FO, RO and PRO is (Cath *et al.*, 2006):

$$J_w = A(\sigma\Delta\pi - \Delta P)$$

where J_w is the water flux, A is the water permeability constant, σ is the reflection coefficient, $\Delta\pi$ is the osmotic pressure difference across the membrane and ΔP is the applied pressure. Since FO does not require an applied pressure, the ΔP equals to zero. For RO, this term is greater than zero due to the need of hydraulic pressure, and it is also greater than 0 for PRO since the saline solution needs to be pressurized. This relationship is illustrated in Fig. 6.

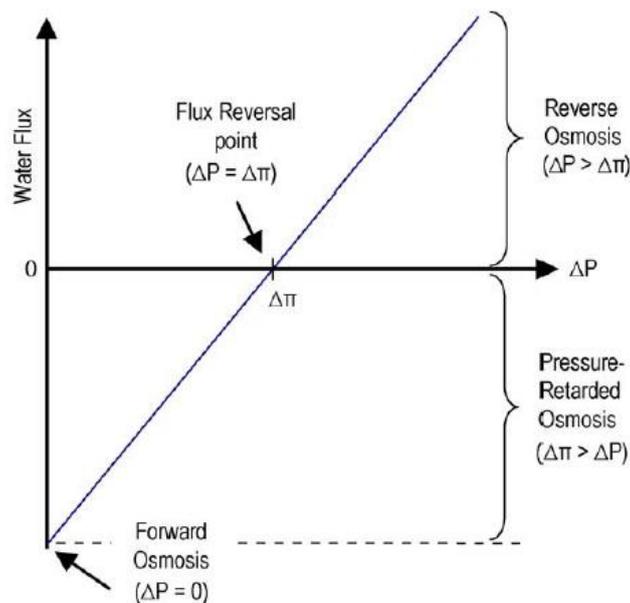


Fig.6 – Relationship between hydraulic pressure and osmotic pressure for FO, RO and PRO. FO occurs when the hydraulic pressure is zero, RO occurs when the hydraulic pressure equals to osmotic pressure and PRO occurs when the applied pressure is

greater than osmotic pressure (Cath *et al.*, 2006).

3.3 Conventional Draw Agents

In the past few decades, there have been several types of draw agents used for FO. The first attempt was the use of sulphur dioxide as a draw agent which could be easily recovered from heating or distillation (Batchelder, 1965). However, its performance as a draw agent was not extensively studied and no evidence suggests that it is an efficient agent for osmosis. In addition, SO₂ can lead to a high acidity and toxicity in water, which might not be suitable for practical applications. However, Batchelder's use of easily removable gases inspired a lot of researchers. In 1965, another osmotic experiment was conducted in which sulfur dioxide was added into a two-phase system. An inorganic membrane was used for this process, and materials including copper ferrocyanide and glass were used. After the osmotic process, the dissolved gases were removed from the draw solutions and the freshwater was regenerated. This was the first time that the draw solute was separated and reused (Glew, 1965).

In 1972, another draw solution was developed which contained aluminium sulfate which could be easily removed by adding calcium sulfate after use. The calcium hydroxide was then separated from the draw solution by introducing carbon dioxide into the solution to produce calcium carbonate precipitates (Frank, 1972). Glucose draw solutions were developed by Kravath (1975), and this technique was designed

for water desalination on emergency lifeboats. Although the salinity could not be completely reduced, its residual concentration was safe enough for human consumption. In 1989, Stache invented semi-permeable membrane bags with fructose or glycine solutions which were later made into hydration bags. This was the first time the FO technique in desalination became commercially available. Compared to glucose, fructose and glycine could generate a higher osmotic pressure and they are still involved in emergency use today (Ge *et al.*, 2013)

In 2002, a two-stage process was developed in which water was recovered in two steps. Potassium nitrate was used as the draw agent, and the solubility of it changed upon temperatures. Under high temperatures, it could dissolve in water and participate in the osmotic processes; under low temperatures, its solubility significantly decreased and it could be easily removed as a precipitate (McGinnis, 2002). The breakthrough was the development of the mixture of NH_3 and CO_2 , which was able to generate a high osmotic pressure and water flux. The recovery could also be achieved from simply heating up the solution to about $60\text{ }^\circ\text{C}$ (Cath, 2006). However, the largest drawback of this technique was the residual ammonia left in water. It was difficult to completely remove ammonia from water and lower its concentration to the standard drinking water level set by the World Health Organization (Miller and Evans, 2006).

3.4 Smart Draw Agents

A significant obstacle through the development of FO was the lack of a suitable draw agent which could produce a high water flux but could also be thoroughly removed from water. Currently, a FO-RO hybrid system is used so that the RO can remove the draw agents from water. Although this process is not as energy-intensive as RO, it can still cost energy up to 25,000 kW a day (Altaee, *et al.*, 2014). In recent years, a new type of draw agent, smart draw agents have been developed to improve the performance of FO. Smart draw agents are the substances which are sensitive towards changes of temperature, magnetic field and pressure. The use of RO could be avoided since they are easy to be removed, in turn lowering the energy cost. This opened a new way in the FO draw solution designs, and would create a high potential for the progress of FO development.

Currently, there are several types of smart draw agents that have been studied including thermoresponsive polyelectrolyte solutions, functionalized magnetic nanoparticles, stimuli-responsive polymers and switchable water. The working principles and properties will be outlined and limitations of these draw solutions will be reviewed.

3.4.1 Functionalized magnetic nanoparticles

Functionalized magnetic nanoparticles are very promising draw agents which have attracted a lot of research interests these years. Their special properties of response to magnetic fields make them ideal draw agents which can be easily removed in the presence of a magnetic field. The first attempt of desalination using functionalized magnetic nanoparticles was conducted and patented by Warne *et al* (2008). Later, hydrophilic magnetic nanoparticles with different functional group coatings were synthesized by Chung's group (2012). They tested several functional groups such as triethylene glycol, poly(ethylene glycol)diacid, poly (acrylic acid) (PAA) and 2-pyrrolidone. The functionalized magnetic particles were found to display both good osmotic and recovery efficiency. The separation was carried out applying a magnetic field or heating. Among all the functional groups examined, PAA was discovered to produce the highest osmotic pressure and water flux, which suggested that smaller particles could improve the osmotic pressure. Although it was found before that higher concentration of nanoparticles could also improve osmotic pressure, a higher viscosity could also be produced which might lower the dissociation of ligands (Ling *et al.*, 2010). Despite of the drawbacks, results showed that PAA-modified magnetic particles at high concentrations yielded very high water fluxes.

However, the limitation of magnetic nanoparticles was the potential of particle

agglomeration, which could reduce water flux over time (Ling *et al.*, 2010). Chung's group suggested using ultrasonic treatment, but this led to degradation of magnetic nanoparticles and a drop of over 40% in water flux was observed (Ling and Chung, 2011). It was reported that the separation problem could be fixed by using magnetic nanoparticles functionalized with poly (N-iso-propylacrylamide) and triethylene glycol (PNIPAM/TRI-MNPs) instead of PAA (Ling *et al.*, 2011). PNIPAM was a thermal responsive material which could undergo solution-gel transitions when exceeding the lower solution critical temperature (LSCT), and the agglomeration could be thus avoided.

There are a few problems associated with poly-electrolyte magnetic nanoparticles such as low recovery rate, which is a result of them being easily affected by small particle sizes and thick polymer coating layers. In addition, the heating method of separation is only restricted to magnetic particles coated with thermoresponsive layers (Ling *et al.*, 2011). Furthermore, the long-term stability has not been fully studied.

3.4.2 Thermoresponsive Polyelectrolyte Solutions

Thermoresponsive polyelectrolyte materials are compounds which are responsive under temperature change through which the recovery is achieved. Materials that have been studied include 2-methylimidazole-based solutes, hexylammonium hydrogen carbonate, dendrimers and polyelectrolytes (Li and Huang, 2013). One material that

has attracted lots of attractions is N,N',N''-triacylated tris (2-aminoethyl)amine (acryl-TAEA), of which the derivatives have a high solubility in water (Noh *et al.*, 2012). It is a weak base which causes less damage membrane, but its high LCST could result in higher energy consumption in the dewatering process.

Another draw solution studied is poly (sodium acrylate) (PSA) which has a greater ionization capacity and degree of dissociation. It also shows a higher conductivity and osmotic pressure. A higher water flux was also observed for PSA draw solutions, and the flux could be further improved by functional group optimizations. However, it was found that water flux could be impacted by changes in concentrations, viscosity and concentration polarization. Therefore, the concentration and viscosity of the electrolyte solution is very crucial. Later on, polyelectrolyte solutions with N-isopropylacrylamide (NIPAM) and sodium acrylate (SA) were developed in order to decrease the energy consumption in FO (Ou *et al.*, 2013). It was found that a higher SA concentration could give rise to a greater degree of dissociation, improving the osmotic pressure produced. Currently, there have been a few ways of separating the polyelectrolytes from water studied. However, the quality of water has not been completely investigated.

3.4.3 Stimuli-responsive Polymer Hydrogels

Stimuli-responsive hydrogels are smart draw agents which uptake water by extending the polymer chains, creating a swelling pressure to drive the FO process (Li

et al., 2011). This type of draw agent shows reversible properties because they can go through reversible volume change upon changes in temperature, solvent, pressure, etc. Several hydrogels that have been studied include polyacrylamide (PAM-MBA), poly(sodium acrylate) (PSA-MBA) and poly(N-isopropylacrylamide)-co-poly(sodium acrylate) (PNIPAM-co-SA) (Li and Huang, 2013).

Hydrogels with different properties can significantly affect the performance of FO. For instance, hydrogels with ionic groups could attract more water due to the balance with counter ions, producing a higher water flux (Li and Huang, 2013) (Li *et al.*, 2011). It was also found that smaller particles could generate a higher osmotic pressure because of the greater surface area exposed and larger interstitial volume (Razmjou *et al.*, 2013). An increase in the surface area could let in more water into the internal networks, producing a higher osmotic pressure. The FO performance could also be enhanced using composite hydrogels such as hydrophilic carbon fillers (Zeng *et al.*, 2013). Hydrogels made from composite materials were found to have larger swelling ratios which resulted in higher water fluxes.

Reduced graphene oxide (rGO) was an important composite hydrogel that was discovered. The introduction of rGO into the hydrogels could reduce crosslinking densities and enhance the transport of water. A higher porosity and increased accessible surface area was also found in rGOs (Zeng *et al.*, 2013). However, it was reported that the rGO sheets could restrict the swelling of hydrogel networks and

reduce water fluxes.

Recovery methods for hydrogels that have been investigated so far include hydraulic pressure, sunlight irradiation and temperature. Sunlight is a more effective and sustainable way compared to the application of temperature and hydraulic pressure. It was found that 86.6% water recovery was achieved for PNIPAM-MBA-C composite hydrogels after 20 minute exposure to sunlight (Ling *et al.*, 2010).

3.4.4 Switchable Water

Switchable water is another type of draw solution that can be used in the process of FO developed by Jessop group. Switchable water is an aqueous solution of a switchable amine which could exhibit switchable ionic strengths (Su *et al.*, 2012). It is also a stimuli-responsive smart draw solution, which is more sensitive to CO₂ than conventional surfactant sodium dodecyl sulfate (SDS) (Su *et al.*, 2012).

CO₂ is used as a trigger for this process: the amine has a very low ionic strength in water with the absence of CO₂ and a high ionic strength with the presence of CO₂. The introduction of CO₂ can protonate the amine and a bicarbonate salt is generated, which in turn increases the ionic strengths of the solution (Fig. 7). Switchable water is a promising draw solution for FO because the solution with a high ionic strength with the presence of CO₂ can enable a high water flux, and the CO₂ can be easily removing by heating (Mercer and Jessop, 2010).

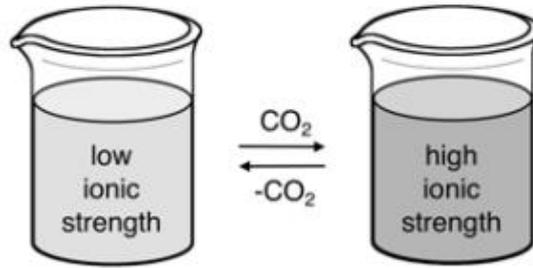


Fig.7 – The change in ionic strengths switchable water with the introduction and removal of CO₂ (Mercer and Jessop, 2010)

3.5 FO membranes

3.5.1 Introduction to FO membranes

The earliest FO membranes were synthesized by Loeb (1997), who used asymmetric aromatic polyamide for FO and PRO membranes. However, all later research of FO used RO flat sheet or tubular membranes, and a lower flux was always observed than expected (Cath *et al.*, 2006). For example, Votta *et al.* (1974) used cellulose acetate RO membranes for FO processes; Kravath and Davis (1975) used flat sheet RO membranes. The first specialized FO membrane emerged in 1990s, and it was designed by Osmotek Inc. After its properties being tested by a lot of researchers, this membrane became commercially available for water purification for military and emergency use (Cath *et al.*, 2006). The membrane was made of CTA with a thickness much lower than RO membranes, and it also lacked a support layer.

Nowadays, most of the FO membranes in used are also modified RO membranes and thereere have not been membranes optimized for FO. There are only two companies making commercial FO membranes: the abovementioned Osmotek Inc. also known as HTI and Catalyx Inc. (Wang *et al.*, 2010). In general, an ideal FO membrane should have a high salt rejection, a thin membrane and a higher water flux. Since FO does not require an applied pressure, the demand for FO membranes is very different from RO.

3.5.2 Membrane Modules

Membranes can have different configurations used to pack membranes for FO. There are three major types of modules: plate-and-frame membranes, spiral wound membranes and tubular membranes. Different modules are used with different operation modes, and the two major modes are continuous flow and batch operation (Cath *et al.*, 2006). In a continuous flow system, the draw solution keeps being reconcentrated and the draw solution is recirculated. Modules made of flat sheet membranes such as spiral wound modules cannot be used in this mode because of the lack of stream flow on the support side. For operation in this modes, the membrane has to be supported and tolerant towards permeate side pressure, and the flow channels have to be accessible (Cath *et al.*, 2006). In the batch operation mode, the draw solution is only diluted once and not reused. Applications such as hydration bags

and osmotic pumps are used (Theeuwes and Yum, 1976).

The simplest module for FO is plate-and-frame membrane, which can vary in size and shape. Although this type of membranes can be made in large scales, the construction can be very complex. Limitations associated with this type of module include lack of sufficient membrane support and low density of packing. In addition, there are difficulties in sealing and monitoring membrane integrity, and the operation conditions are limited (Cath *et al.*, 2005). Another type of module is the spiral-wound membrane, which is operated with a single stream. The flow of the streams is very slow and the flow velocity is controlled by membrane properties and operating conditions. Since the draw solution cannot be forced to flow inside the envelope in the membrane, the spiral-wound membranes cannot be used for FO. Modifications to spiral-wound membranes were for FO, producing a membrane that could allow streams to flow through the same way as RO. Different from RO membranes, the feed solution can only flow through one side since the central tube is blocked halfway (Mehta, 1982).

Tubular/hollow module is considered to be the most practical membrane for RO since tubular membranes can be self-supported, which means that packing and supporting are easy without deforming the membranes (Cath *et al.*, 2006). In addition, tubular membranes are easier to fabricate, and they also allow liquids to flow on both sides. Furthermore, Cath (2006) argued that hollow fiber membranes were better for

FO because they did not need for a thick support layer like that in flat sheet RO membranes, which could reduce internal concentration polarization and improved performance.

The major difference between hollow fiber and tubular membranes is the flow scale. Only laminar flow can be achieved for hollow fibers, thus mixing is limited at membrane surface. These can increase the chance for concentration polarization, fouling and reduced mass transfer. In comparison, tubular membranes have more than twice as much of internal diameter, which in turn reduce concentration polarization and fouling problems.

3.5.3 Membrane Materials

Currently, the major material used for FO membrane is the TFC, which is also commonly used for RO membranes. TFC membranes are semi-permeable membranes that are made from polyamide with a three-layer construction, giving a high rejection rate and high mechanical strength. However, since TFC membranes are designed for RO, the support layer is very thick due to the demand for high pressure. This is not an ideal situation for FO since the thick layer results in a poor permeate water flux due to the lack of applied pressure in FO processes. To yield a good FO performance, RO membranes are modified through processes such as fabrication which could significantly increase the water flux for FO (Yip *et al.*, 2010).

There are three newly-developed types of modified membranes including phase-inversion-formed cellulose membranes, fabricated TFC membranes and chemically modified membranes. Chung's group (2007) developed polybenzamidazole (PBI) hollow membrane fabricated by dry-jet wet phase inversion, which allowed for robust mechanical strengths and excellent chemical stability. However, the salt rejections could not satisfy for sodium chloride, sodium sulfate and magnesium sulfate. Later, Yang et al. (2009) optimized the PBI membrane by adding polyethersulfone (PES) and polyvinylpyrrolidone (PVP) into the casting solution, which produced a dual layer membrane and an ultrathin selective skin. In addition, the porous water channels and microporous sponge like support layer also gave rise to a better FO performance. Phase inversion techniques could also be used on cellulose acetate membranes, which could improve salt rejection. Compared to other materials, cellulose acetate displays a higher hydrophilicity, which means a higher water flux and a lower fouling propensity. Furthermore, Chung's group has developed a double-skinned membrane which has reduced internal concentration polarization. However, cellulose acetate membranes are not very resistant to hydrolysis and biological attack. They are also restricted to a narrow pH and temperature range.

Fabricated thin film composite membranes have gained a lot of research interests. There are two types of fabricated TFC membranes in use, with one being thinner ($\sim 50 \mu\text{m}$) and one being thicker ($>100 \mu\text{m}$), and they are both asymmetric and made of CTA (Zhao *et al.*, 2012). An ideal FO membrane should have a small portion of

sponge-like layer and a highly porous substrate. Straight finger-like pores are more preferred than spongy pores because of the reduced internal concentration polarization (Wei *et al.*, 2011). In addition, a desirable FO membrane should also have a highly hydrophilic support with low tortuosity to reduce the concentration polarization problem, and a selective active layer is required to enhance salt rejection and minimize reverse solute diffusion. Chemically modified membranes are another type of new FO membranes. Recently, a novel hydrophilic polymer, polydopamine (PDA) was used to modify the support layer of RO membranes, and it was found out to have a low internal concentration polarization and improved water flux (Arena *et al.*, 2011).

3.5.4 Internal Concentration Polarization

Internal concentration polarization (ICP) is the major problem associated with FO, which is a result of asymmetric membrane constructions. It has been found that the orientation of the membrane is closely related to the ICP effect of FO membranes.

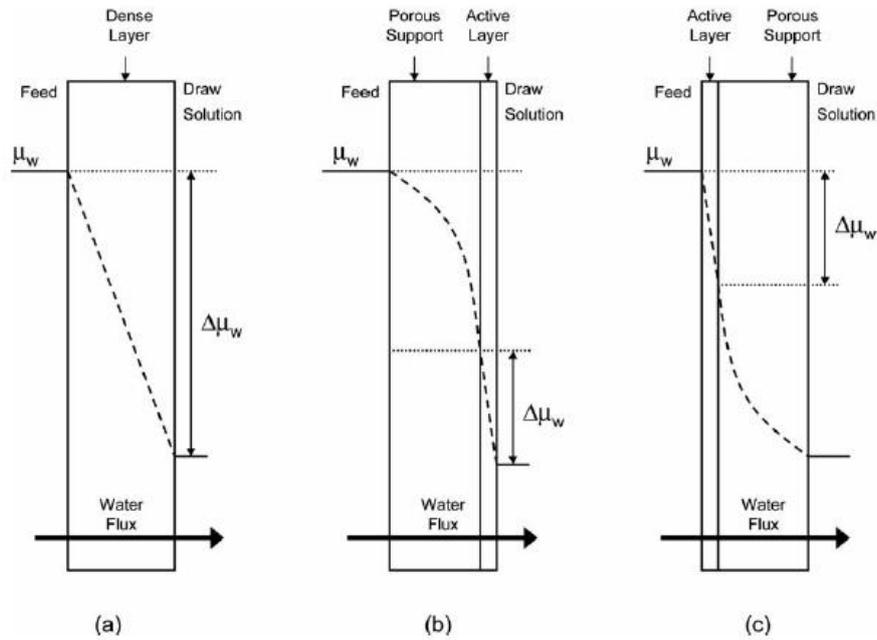


Fig.8 – Different effects of ICP as a result of symmetric membrane (a), an asymmetric membrane with the porous support layer facing the feed solution (b) and an asymmetric membrane with the dense active layer facing the feed solution (c) (Cath *et al.*, 2006)

As shown in Fig.8, if the support layer faces the feed solution, water can enter the support layer and diffusion into the draw solution might occur. If this happens, a polarized layer will be created along the side of active layer where salt cannot penetrate the active layer from the support layer. Therefore, a phenomenon called “concentrative polarization” happens when an increased concentration happens within the porous layer. Conversely, if the active layer faces the feed solution, water can flux through the support layer and solute in the draw solution can diffuse through the support layer into the interior surface, diluting the draw solution. This phenomenon is known as “dilutive polarization”. Dilutive polarization depends on the concentration of draw solution and the molecular weight of the draw agents. Large molecules cannot diffuse fast enough through the support layer, which might lower the water flux. Both

concentrative and dilutive ICP can cause significant reduction in water fluxes.

For concentrative ICP, the relationship between water flux and membrane orientation can be described by (Lee et al.,1981) (Loeb et al., 1997):

$$J_w = \frac{1}{K} \ln \frac{\pi_{Hi}}{\pi_{Low}}$$

where J_w is the water flux, π is the osmotic pressure, K is the resistance to solute diffusion within the support layer, π_{Hi} and π_{Low} are the osmotic pressures of draw and feed solutions. K is described as:

$$K = \left(\frac{1}{J_w} \right) \ln \left(\frac{B + A\pi_{Hi} - J_w}{B + A\pi_{Low}} \right)$$

where B is the solute permeability coefficient of active layer. Similarly, K was also defined for dilutive ICP:

$$K = \left(\frac{1}{J_w} \right) \ln \left(\frac{B + A\pi_{Hi}}{B + J_w + A\pi_{Low}} \right)$$

K is defined as the resistance to diffusion, which can be described as

$$K = \frac{t\tau}{\varepsilon D_s}$$

where t is the membrane thickness, τ is the tortuosity, ε is the porosity, and D_s is the diffusion coefficient of the solute. The larger the K value, the more reduction in water flux will happen. In the equation, all other terms except the diffusion coefficient are fixed, which means the effect of ICP is completely dependent on the draw solutes.

4.0 RO vs. FO

4.1 Energy Cost

High energy demand has always been a problem associated with RO due to the requirement for a high hydraulic pressure in the process. In comparison, FO is a less energy-intensive process since it does not need an external pressure source which significantly reduces the energy consumption. Although there have been various recovery methods developed to reduce the energy input, RO still costs about 2 kWh to produce each cubic meter of water with recovery techniques applied (McHang and Truby, 2004). In comparison, FO consumes less than 0.25 kWh to produce per cubic meter of desalinated water (Elimelech, 2007). Osmosis has a great potential to be the dominant seawater desalination method in the near future, and it is crucial that the technology should be sustainable when being applied in global scales. With the intensive energy consumption of RO (8 times of FO), issues associated with energy will arise soon. FO, compared to RO, is a more sustainable desalination technique in the aspect of energy cost.

4.2 Fouling and Concentration Polarization

Fouling is an issue that exists both in FO and RO and can result in a great decrease in water flux. Studies have shown that the major fouling issue associated with both FO and RO are cake-enhanced concentration polarization due to the reverse

diffusion of solvents (Hoek and Elimelech, 2003) (Tang *et al.*, 2010). However, the fouling in RO process was found to be irreversible whereas that in FO was reversible. Without the application of hydraulic pressure, the organic foulant could be easily removed (Tang *et al.*, 2010). In addition, the cake-enhanced concentration polarization effect in FO could be minimized from choosing a proper draw solution, but this cannot be achieved by RO. On the other hand, FO is also prone to internal concentration polarization, which could also significantly reduce the water flux. However, it was found that the impact on water flux is dependent only on the diffusion coefficient of the draw solutes for FO (Loeb *et al.*, 1997), which means solving the problem for FO would be more feasible than RO if an ideal draw solution could be designed.

4.3 Membranes

There has been much more research on RO membranes over the past few decades, the development of RO membranes is more mature than FO membranes. Currently, most of the FO membranes used in research are still modified RO membranes, and there are only two companies producing commercial FO membranes. In RO industries, the major types of membrane used in both FO and RO are TFC membranes, with a minor amount of novel membranes such as nanomaterials. Both FO and RO membranes are shown to display good water flux and salt rejection rate above 98% (Yip *et al.*, 2010;Fritzman *et al.*, 2006). However, it has been suggested that the price

of FO membranes is about ten times higher than RO membranes (Ge *et al.*, 2013). Since most of the existing FO membranes are modified from RO membranes, and the development of new FO membranes is still in progress, a conclusive comparison between FO and RO membranes cannot be made.

5.0 Conclusions

- As the global water shortage issue intensifies, the need for water desalination is increasing. The technology of osmosis provides an efficient desalination method to mitigate the water scarcity problem. Reverse osmosis has been studied extensively for the past few decades, and it is a mature desalination method which works efficiently and produces a high water flux and salt rejection. However, the high energy cost is the major obstacle associated with RO. In addition, fouling is another significant problem which is a result of enhanced-cake concentration polarization. The fouling problem could lead to a considerable decrease in water flux.
- Forward osmosis is a new technique compared to RO but has drawn increasing attention in recent years because of its low demand for energy. The spontaneous flow of water without requiring a hydraulic pressure makes FO a more sustainable technique in terms of energy consumption. Moreover, it has also been found that fouling in FO processes is reversible, which makes it more feasible to remove the foulant. However, current limitations with FO

include internal concentration polarization, which is the major factor causing water flux reduction. In addition, FO also lacks a suitable draw agent which could produce a high osmotic pressure, low cost, non-toxicity, low energy consumption, long-term stability and lower ICP. In addition, the development of FO membranes is not mature since most of the FO membranes are still modified from RO membranes. Hence, a conclusive comparison between FO and RO cannot be made for the time being.

- Nonetheless, the technique of FO is very promising as a seawater desalination method for the near future because of its lower energy cost and lower chance of fouling. The main focus of research on FO should be emphasized on the development of optimized draw agents and more suitable membranes for FO. If proper draw agents could be developed to decrease the internal concentration polarization problem, the major drawback of FO would be eliminated. On the other hand, membranes that are designed and optimized for FO should be developed so that improved membrane efficiency and a lower manufacturing cost could be achieved. If these could be achieved, FO would possibly be the more practical and sustainable method for seawater desalination.

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