CHAPTER 3

Literature review II – Thin film composite Reverse Osmosis Membrane Productivity Improvement

With increasing population and industrialization, the demand for fresh water also increases. In the 21st century, the most vital problems affecting people across the world are sufficient clean water to satisfy municipal, agricultural and industrial needs and reliable/continuous power supply. The rapid growths in population and economy have resulted in greater demand of good quality water, leading to catastrophic water shortage in water-stressed areas [1].

3.1 Overview

With the fact that only around 0.8% of the total earth's water is fresh water [2], numerous researches have been conducted in an effort to develop more sustainable technological solutions that would meet the water demand.

Desalination of seawater/brackish water and reuse of industrial and municipal waste water are the best technology based alternatives to mitigate the increasing water demand. With development of technology and reduction in cost, Reverse Osmosis has become a standard option for water treatment and reuse. In general, desalination technologies can be categorized into two different modes of separation, i.e. thermal and membrane-based desalination. Thermal processes include multi-stage flash (MSF), multiple effect distillation (MED) and vapor compression distillation (VCD), whereas membrane-based processes include reverse osmosis (RO), nanofiltration (NF) and electro-dialysis (ED). Among these technologies, RO membrane desalination is the primary choice owing to its low energy demand as compared to the other technologies [2].
Figure 3.1 presents the total amount of water produced by membrane desalination plants and thermal desalination [3].

It can be seen from figure 3.1 that membrane based desalination has increased exponentially in last few years whereas; thermal desalination is almost constant for past many years.

The global installed desalination capacity by water sources and the use of seawater as feed water has contributed more than half of the total capacity produced worldwide [4]. The scale of water desalination is extra-ordinarily large. In 2010, approximately 61 billion litres of desalinated water was produced worldwide per day as compared to 14 billion litres of crude oil being processed in the same year.

Since the first invention of an asymmetric membrane, reverse osmosis membrane technology has undergone a significant progress in its capacity to desalinate water. It is
acknowledged that the scientific breakthrough in developing ultra-thin film onto microporous substrate is equivalent to the historic announcement of Loeb–Sourirajan asymmetric membrane in 1960. This is because of the wide-spread replacement of cellulose acetate membranes by thin film composite RO membranes owing to their better solute rejection and water-flux performance.

### 3.2 Reaction to form polyamide membrane

Figure 3.2 shows the reaction taking place to form a thin film of polyamide over porous support membrane [48].

![FIGURE 3.2 Reaction between amine and acyl chloride to form polyamide film](image)

Despite the high performance of composite membranes, the research on how to further improve the properties of top active skin layer still remains as high-priority domain over the years. This comes from the fact that the polyamide barrier layer can be modified to yield a high permeability membrane in order to increase its productivity. The polyamide membrane performance can be enhanced not only by newly synthesized monomers but also by surface modification as post treatment.

Thickness of the polyamide layer has a direct correlation with its permeability. Thicker the polyamide layer, the lower is the permeability. It has been demonstrated that increasing thickness poses greater resistance for water to pass through the polyamide layer and therefore causes decline in flux [5].
A key limitation to commercial polyamide membranes is membrane degradation through contact with oxidative environment and chlorine — one of the common disinfectants used in water and wastewater treatment. Previous studies have revealed that the changes in chemical nature of polyamide upon exposure to chlorine can affect membrane performance, shortening the lifespan of membrane [6-8]. It has been demonstrated that the conversion of amide N-H group to N-Cl group upon chlorine exposure is the main factor causing the remarkable selectivity deterioration.

### 3.3 Transport through membrane

Many mathematical and mechanistic models have been proposed in 1980s to demonstrate the transport through reverse osmosis membranes. Researchers like Jonsson (1980), Soltanieh, Mazid (1984), Pusch (1986), Dickson (1988), Rautenbach (1989) studied the transport of water through membrane and proposed models [9-13].

#### 3.3.1 Solution diffusion model:

The solution diffusion model assumes that the pressure within the membrane is uniform and concentration potential gradient is linearly manifested in the membrane layer. The feed side of the membrane has higher chemical potential than the permeate side. Chemical potential gradient can be expressed as concentration gradient. The schematic presentation of solution diffusion model is shown below.
3.3.2 Pore diffusion model: The pore-flow model assumes that the chemical potential gradient across the membrane is expressed only as pressure gradient. It suggests that the pressure also declines in the membrane layer.

Although the solution-diffusion model seems to be a dependable method of describing transport in many membranes, it does not apply to coarser ultrafiltration membranes used to separate large molecules, proteins, bacteria, viruses etc. from water. In case of ultrafiltration membranes, the actual water fluxes are significantly higher than that can be obtained by solution-diffusion using reasonable values for the partition and diffusion.
coefficients of water. Many small solutes have the same permeation rate as that of water and, hence, no rejection by the ultrafiltration membrane. This observation can be readily rationalized by the filtration-type mechanism of a pore-flow membrane, but it is not easily explained by a solution diffusion membrane. Thus, Transport in such membranes can be best described by a pore-flow model.

The transition between a pore-flow and a solution diffusion mechanism seems to occur with membranes having very small pores. The difference between pore-flow and solution-diffusion mechanisms lies in the relative permanence of the pores. In a solution-diffusion membrane, free-volume elements (pores) that exist in the membrane are present in about the same time scale as the motions of the permeants traversing the membrane. On the other hand, in a pore-flow membrane, the free volume elements (pores) are relatively fixed and do not fluctuate in position or volume on the time scale of permeant motion [14].

3.4 Water/salt trade-off relationship in swollen polymers

For the majority of membrane applications, polymers with high selectivity and permeability are desirable. Membrane chemical structure and morphology dictates its performance i.e. permeability and selectivity, thus the structure-property relations are very important to study. It is understandable that a membrane with higher permeability will have lower selectivity. An empirical trade-off of water permeability, sorption and diffusivity selectivity has been reported [15].

Trade-off between output and separation performance is very general and observed across many areas of membrane science, including ultrafiltration, gas separation and fuel cells, despite the fact that the polymers, separation problem and molecular transport mechanisms are quite different in various cases [16-22].

Thin film composite polyamide membranes follow a similar trade-off relationship, though their water permeability depends on an assumed effective active-layer thickness. Existence of this trade-off relationship is qualitatively consistent with free-volume theory.
Free volume theory relates diffusion coefficient of penetrant i (Di) to the polymer’s average free volume vf as follows:

\[ Di = a_i \times \exp \left( -\frac{b_i}{vf} \right) \]

Where, \( a_i \) and \( b_i \) are constants. \( b_i \) is proportional to the size of penetrant i.

If the polymer’s average free volume increases, the diffusion coefficients of the penetrants will increase. At the same time, the diffusion selectivity of the smaller penetrant over the larger will decrease because \( b_i \) is proportional to penetrant size [15].

### 3.5 Modification in TFC RO membrane for performance improvement

Thin film composite reverse osmosis Reverse Osmosis membrane has undergone significant improvement in performance since inception. Over the last decade, there have been continuous efforts to improve the performance of TFC RO membrane in terms of its productivity and selectivity as well as its tolerance against chlorine, solvent, fouling, etc. [23].

The peculiar advantage of Thin film composite reverse osmosis membrane lies in independent control and optimization of each layer (i.e. top selective layer and bottom porous substrate) while offering excellent compression resistance and mechanical strength [23]. Many scientists and researchers attempted to modify the Thin film Composite Reverse Osmosis (TFC RO) membrane by surface modification. Polyvinylpyrrolidone (PVP) immobilized on RO membrane for better surface hydrophilicity and fouling resistance has been reported [24]. Thermally initiated free radial grafting of Polyvinyl alcohol (PVA) on TFC RO membrane to make the Surface smoother and more hydrophilic has been reported [25]. However, the permeability improvement by such modification was insignificant.

A significant improvement in water flux of thin film composite Reverse Osmosis membrane by controlled sodium hypochlorite treatment for controlled time and high pH has been observed [26]. With exposure to oxidizing agent sodium hypochlorite, the amide bond gets chlorinated to CO-N-Cl, which in turn leads to ring chlorination by orton rearrangement. The surface of this membrane is hydrophilic. However, prolonged exposure
to oxidizing agent leads to complete degradation of the aromatic polyamide and the membrane solute rejection drastically reduces. Thus, controlled sodium hypochlorite treatment can increase the water-flux of the membrane.

![Mechanism of aromatic polyamide membrane oxidation](image)

The polyamide layer was made more hydrophilic by a supra-molecular assembly over its surface [27]. It has been demonstrated that chlorine exposed membranes have better performance in terms of boron removal [28]. It has been studied that the glass transition temperature decreases with free chlorine treatment and it can be correlated with the reduction in salt rejection of the TFC RO membrane [29].

It has been shown that RO membrane performance can be significantly improved by post-treatment with an activating solvent such as Di-methyl formamide [30].

A hydrophilic membrane support layer was fabricated with Polydopamine for increased support layer hydrophilicity without reduction in membrane selectivity [31]. It has been reported that end-of-life reverse osmosis membrane elements can also be rejuvenated by successive treatment with sodium hypochlorite and such membrane has higher hydrophilicity and lower fouling [32].
3.6 Nano-composite membrane

Nano-scale materials embedded in the polyamide barrier layer can improve the performance of Thin Film Composite RO membrane [33-42]. Many researchers have attempted to synthesize Thin Film Composite RO membrane and evaluate their performance. For example, it has been reported that thin film nanocomposite membrane comprised of NaA zeolite exhibited smoother and more hydrophilic, negatively charged surfaces. It was shown that nanoparticle pores played an active role in water permeation and solute rejection [33]. Zeolite-polyamide thin film nanocomposite (TFN) membrane was prepared on a polysulfone (PSf) porous substrate tailored for forward osmosis i.e. thin support, high porosity, and straight needle-like pores. The embedded NaY zeolite nanoparticles in the polyamide barrier layer significantly increased its water permeability [34]. Thin Film Nanocomposite formed with higher loading (~5 w %) of TiO$_2$ nanoparticles and more robust structure of PA-TiO$_2$ nanocomposite membrane has been reported [35]. Nanocomposite with silica exhibited superior thermal stability than the pure polyamide membranes and better performance in terms of separation efficiency and water-flux [36].

Loading silver nanoparticles on thin-film composite (TFC) reverse osmosis membrane reduced its permeability but showed strong anti-bacterial activity leading to reduction of more than 75% in the number of live bacteria attached to the membrane [37]. Polysulfone-TiO$_2$ substrate was prepared for forward osmosis application and it was found that both hydrophilicity and porosity of the substrate were increased upon addition of TiO$_2$ [38]. Results revealed that both hydrophilicity and porosity of the substrate were increased upon addition of TiO$_2$ nanoparticles [39]. PSf-TiO$_2$ substrate was formed and the results revealed that the hydrophilicity and the porosity of the substrate were improved upon the TiO$_2$ addition, leading to significant enhancement in water-flux [40].

The titanate nanotubes (TNTs) were self-synthesized and amino functionalized to produce titanate nanotubes (NH$_2$-TNTs) for thin film nanocomposite (TFN) reverse osmosis (RO) membrane fabrication. The novel RO membrane fabricated by embedding NH$_2$-TNTs into polyamide (PA) layer exhibited 93% higher water-flux [41]. Hybrid thin-film-composite
(TFC) membrane was prepared by self-assembly of the TiO$_2$ nanoparticles showed significant prevention against the microbial fouling [42].

Graphene oxide was incorporated into polyamide composite membrane where Graphene oxide sheets enhanced the water permeation properties of fabricated polyamide membrane [43]. The graphene oxide nano-sheet composite membrane showed lower membrane surface energy and an enhanced hydrophilicity. The presence of carboxyl, hydroxyl or epoxy groups on the surface of the Graphene oxide sheets make the materials highly hydrophilic, therefore allowing for facilitated transport of water between the graphene sheets upon wetting.

Nano-scale materials embedded in polyamide barrier layer can improve the performance of thin film composite RO membrane [33-42]. Influence of zeolite crystal size in zeolite-PA nanocomposite was evaluated where it was found that smaller size of zeolite produced greater permeability enhancement whereas, larger size of zeolite produced more favourable surface properties [44]. Metal organic framework nanoparticles were dispersed in organic phase containing trimesoyl chloride prior to interfacial reaction. Membrane performance in organic solvent nanofiltration was evaluated and found that the permeance increased when MOFs were embedded in PA layer [45].

Figure 3.3 depicts the concept of embedding nanoparticles in the top selective layer in the preparation of thin film nanocomposite (TFN) membrane.

![Figure 3.3: Incorporation of nanoparticles in polyamide film](image)

**FIGURE 3.6: Incorporation of nanoparticles in polyamide film**

In order to enhance the transport rate of water molecules, Fathizadeh et al. imparted bigger pore size of zeolite NaX in the thin film layer with the objective of creating larger molecular tunnels for water to flow. The new Thin film nanocomposite membrane of polyamide and nano-NaX zeolite was synthesized by the interfacial polymerization.
method. Results showed that nano-NaX zeolite increased physical and chemical stability properties. An enhancement in the concentration of m- pheylenediamine (MPD) and trimesoylchloride (TMC) monomers lead to production of Thin Film Nanocomposite (TFN) membrane with high water permeability and low solute rejection [46].

Multiwalled nanotube/polyester composite membrane was prepared to overcome the trade-off between permeability and selectivity [47]. Thus, many researchers tried to impart nanomaterial in Thin Film Composite RO membrane to make it more robust in performance.

### 3.7 Concluding remarks

The concept of interfacial polymerization has been known for more than 45 years since it was first introduced by Mogan in 1965. Through this concept, an ultrathin film of a few nanometer thickness can be made over polysulfone support layer by interfacial polymerization. Currently, TFC membranes have found widespread applications in NF and RO and have shown huge potential to be further used in applications involving gas separation, pervaporation, hydrocarbon fractionations, etc. It cannot be concluded that this technology has already reached the maturity while many opportunities still exist. Efforts should continue on the development of high flux/low pressure composite membrane with enhanced salt rejection as well as improved resistances of fouling, chlorine, solvent, etc. By modifying structure and morphology of the top polyamide layer of the membrane, high flux membrane can be obtained. Efforts should also continue in the direction of making such high flux membrane by surface modification as they are of particular interest in renewable energy powered desalination.

### References


