

Thin Film Composite and/or Thin Film Nanocomposite Hollow Fiber Membrane for Water Treatment, Pervaporation and Gas/Vapor Separation

by

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Abstract

Nowadays asymmetric thin film composite (TFC) polymeric hollow fiber (HF) membranes are extensively used in industrial gas/vapor separations, water treatment etc. There are numerous advantages to use hollow fibers such as: low energy requirements, simplicity of operation, and high specificity. In the present article we discuss the progress made during the past decade in the preparation of the HF substrate and preparation/modification of the thin selective layer. Their applications in water treatment, dehydration of alcohols via pervaporation and gas/vapor separation are also demonstrated.

Key words: Thin composite hollow fiber; water treatment; water vapor separation; dehydration of alcohols; pervaporation.

1. Introduction

Hollow fiber membranes (HFMs) are a class of artificial membranes containing a semi-permeable barrier in the form of a hollow fiber. Originally developed in the 1960s for reverse osmosis applications, hollow fiber membranes have since become prevalent in water treatment, desalination, cell culture, medicine, and tissue engineering.^[1] Most commercial hollow fiber membranes are packed into cartridges which can be used for a variety of liquid and gaseous separations [1]. Hollow fiber membranes deliver highly efficient operation in a small footprint. The advantages are numerous: low energy requirements, simplicity of operation, and high specificity. An optimized hollow fiber NF module would give a 100% increase in performance compared to an optimized spiral-wound module [2] The single greatest advantage of hollow-fibre modules is the ability to pack a very large membrane area into a single module.

Thin film composites usually consist of a highly porous substrate coated with a thin dense film of a different polymer. A thin film composite reverse osmosis membrane can be defined as a multi-layer membrane in which an ultrathin semipermeable membrane layer is deposited on a preformed, finely microporous support structure [3] The composite membrane fabrication technique is one of the most effective methods to prepare membranes A composite membrane is obtained by forming an ultra-thin dense layer on a porous support layer. Several processes have been reported for the preparation of composite membranes, interfacial polymerization is one of the most commonly used processes. Cadotte [4] presented first time the selective polyamide film by interfacial polymerization of *m*-phenylene diamine (MPD) and trimesoyl chloride (TMC).

2. Method of making Thin Film Composite (TFC) Hollow Fiber (HF)

2.1 Fabricating Hollow Fiber

The fabrication of HFM can be divided in four general groups.

- i) Melt Spinning, in which a thermoplastic polymer is melted and extruded through a spinneret into air and subsequently cooled.
- ii) Dry Spinning, in which a polymer is dissolved in an appropriate solvent and extruded through a spinneret into air.
- iii) Dry-Jet Wet Spinning, in which a polymer is dissolved in an appropriate solvent and extruded into air and a subsequent coagulant (usually water).
- iv) Wet spinning, in which a polymer is dissolved and extruded directly into a coagulant (usually water).

Common to each of these methods is the use of a spinneret (Fig. 1), a device containing a needle through which solvent is extruded and an annulus through which a polymer solution is extruded. A schematic diagram for the formation of hollow fiber is shown in Fig.1. As the polymer is extruded through the annulus of the spinneret, it retains a hollow cylindrical shape. As the polymer exits the spinneret, it solidifies into a membrane through a process known as phase inversion. The properties of the membrane, such as average pore diameter and membrane thickness can be finely tuned by changing the dimensions of the spinneret, temperature and composition of "dope" (polymer) and "bore" (solvent) solutions, length of air gap (for dry-jet wet spinning), temperature and composition of the coagulant, as well as the speed at which produced fiber is collected by a motorized spool.

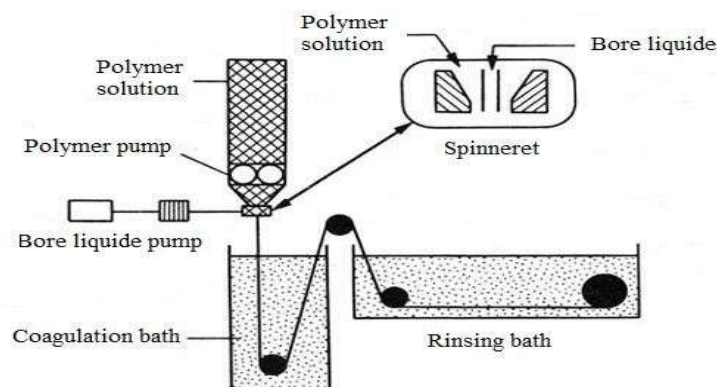


Fig. 1 Apparatus for forming a hollow fiber gas separation [5].

Spinning process involves several stages:

- i) The diffusion of internal precipitant molecules into the concentrated hollow fiber forming polymer solution. At the same time polymer coagulates (precipitates from solution) to form a solid phase.
- ii) A cross-diffusion of solvent molecules from the polymer solution into the internal nonsolvent. This speeds up the process of coagulation of the polymer and the formation of the porous structure of the fiber body.
- iii) Evaporation of the solvent molecules from the outer surface of the fiber into the air. The concentration of polymer on the outer surface of the fiber is increased and the dense (selective) polymer layer is formed.

Chung's group [6] developed novel tri-bore thin-film composite (TFC) hollow fiber (HF) membranes for forward osmosis (FO) processes by employing a specially designed tri-bore blossom spinneret. Fig. 2 shows schematic diagram of tri-bore hollow fiber formation.

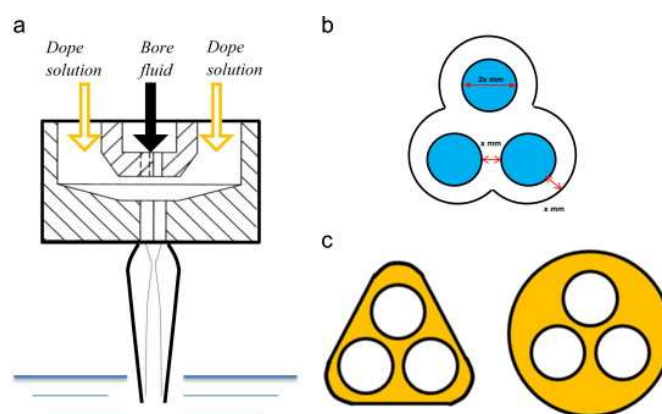


Fig. 2 (a) Single layer tri-needle spinneret; (b) bottom view of the tri-needle spinneret; (c) cross section [6]

2.2 TFC Hollow Fiber Fabrication

A composite membrane is provided by forming a nano-thin selective dense layer on a porous substrate. The top selective layer and bottom porous substrate of the composite membrane can be modified to maximize the overall membrane performance. There are many ways or techniques to make thin composite layers on the surface of a support. Most common ones are:

- a) Interfacial polymerisation reaction.
- b) Dipping method.
- c) Plasma treatment
- d) Chemical reaction

Others are [7]:

- i) Chemical vapour deposition (CVD)
This method involves the deposition of a desired component in the vapour state on a substrate by means of a chemical reaction.
- ii) Sputtering
This technique involves bombarding a target with energetic particles, which cause surface atoms to be ejected and then deposited on a substrate close to the target.
- iii) Spray pyrolysis
This method involves spraying a solution of metal salts into a heated gas stream where it is pyrolyzed. The method has been successfully applied for the production of fine metals or metal oxide particles. Li et al. [8] obtained a Pd–Ag alloy membrane on the surface of a porous alumina hollow fibre by spray pyrolysis of a $\text{Pd}(\text{NO}_3)_2$ and AgNO_3 solutions on a $\text{H}_2\text{--O}_2$ flame.

2.2.1. Dip Coating

Dip coating is an industrial coating process which is used, for example, to manufacture bulk products such as coated fabrics etc. and is also commonly used in academic research, where many chemical and nanomaterial engineering research projects need to create thin-film coatings. Dip-coating methods are frequently employed to produce thin films on the surfaces of hollow fibers to produce thin film composite hollow fiber membranes. Dip-coating process can be separated into five stages [9].

- i) Immersion: The substrate is immersed in the solution of the coating material at a constant speed (preferably jitter-free).
- ii) Start-up: The substrate has remained inside the solution for a while and is starting to be pulled up.
- iii) Deposition: The thin layer deposits itself on the substrate while it is pulled up. The withdrawing is carried out at a constant speed to avoid any jitters. The speed determines the thickness of the coating (faster withdrawal gives thicker coating material) [10,11].

- iv) Drainage: Excess liquid will drain from the surface.
- v) Evaporation: The solvent evaporates from the liquid, forming the thin layer. For volatile solvents, such as alcohols, evaporation starts already during the deposition and drainage steps.

The dip coating technique is used for making thin films by self-assembly and with the sol-gel technique. Self-assembly can give film thicknesses of exactly one monolayer. The sol-gel technique creates films of increased, precisely controlled thickness that are mainly determined by the deposition speed and solution viscosity. Functional coatings applied to change the surface properties of the substrate such as adhesion and wettability. In general, TFC hollow fiber membrane is prepared by using a fluid precursor which undergoes a chemical change at a solid surface, leaving a solid layer.

2.2.2. In-situ Polymerization

The most common technique to make TFC hollow fiber membrane is IP reaction. Interfacial polymerization (IP) reaction to form polyamide dense layer is based on 1,3,5-benzenetricarbonyl trichloride (TMC) and 1,3-phenylenediamine (MPD). Fig. 1 shows the IP between TMC and MPD. Interfacial polymerization is a type of step-growth polymerization in which polymerization occurs at an interface between an aqueous solution containing one monomer and an organic solution containing a second monomer. IP occurs in a mixed monolayer of the adsorbed monomers. When the interfacial pressure of the adsorbed mixed monolayer exceeds the equilibrium spreading pressure of the polymer, the latter is precipitated from the monolayer, giving rise to a thick film at the interface. In polymer chemistry, in situ polymerization means "in the polymerization mixture." There are numerous unstable oligomers (molecules) which must be synthesized in situ (i.e. in the reaction mixture but cannot be isolated on their own) for use in various processes. Mostly, in hollow fiber, TFC composite membrane formation, the selective layer is deposited on the lumen side of the fiber.

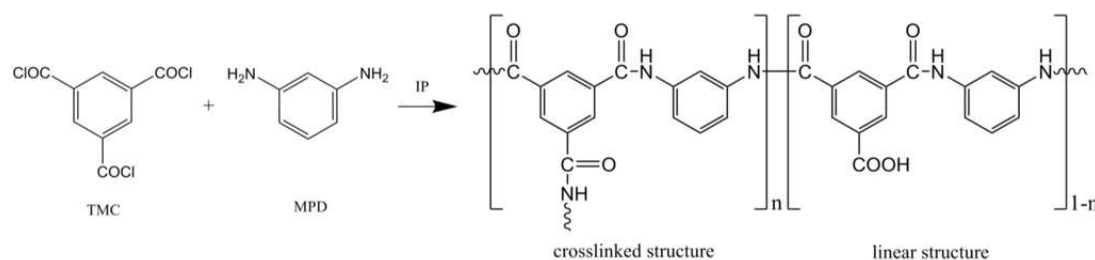


Fig. 3 IP between TMC and MPD

Urper et al. [12]. discussed the recent developments in the design of TFC hollow fiber nanofiltration membranes and provided a comparative analysis of two main methods of their fabrication;

- i) interfacial polymerization
- ii) phase inversion.

To prepare integrally skinned hollow NF, direct PI method is commonly used where the porous sublayer and the separation layer (membrane skin) are made of same polymer). On the other hand, IP on phase-inverted membranes is used to prepare thin film composite (TFC) membranes where the porous support is made of a different material (typically polysulfone) than the skin (typically aromatic polyamide (PA)).

3. Water Treatment

Different types of membranes are used for softening, disinfection, organic removal, and desalination of water and wastewater. There are four types of membranes which are used for water treatment.

- i) Ultrafiltration (UF).
- ii) Reverse osmosis (RO).
- iii) Nanofiltration (NF).
- iv) Microfiltration (MF).

Fig. 4 shows the range of nominal membrane pore sizes [13].

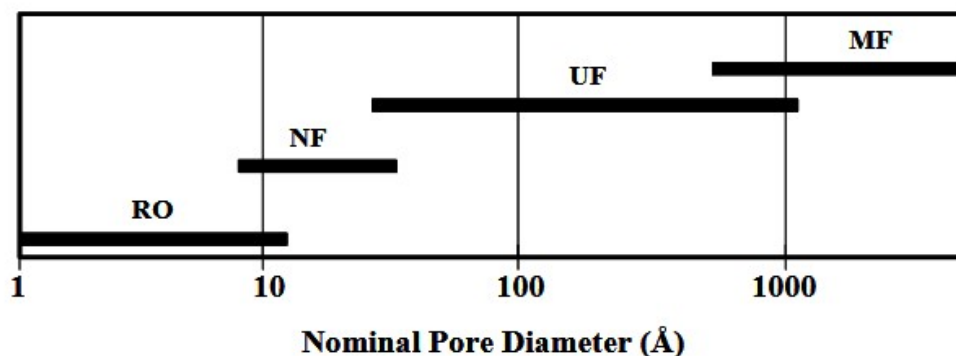


Fig. 4 Range of nominal membrane pore sizes

3.1 RO

Thin film composite reverse osmosis membrane can be defined as a multi-layer membrane in which an ultrathin semipermeable membrane layer is de-posed on a preformed, finely microporous support structure. It is difficult to make RO HF. So far, the use of hollow fibers in RO has not been completely successful. The hollow fiber modules that have been frequently used for RO have the selective skin on the outer side of the fiber, which creates problems such as concentration polarization and enhanced fouling, and it leads to decrease in the efficiency [14]. Veríssimo et al. [15] presented a new technique for the preparation of RO composite hollow fibers with the selective film in the bore side of the fiber and the optimization of the preparation. The technique was by introducing an inert liquid buffer between the aqueous *m*-phenylene diamine and the organic trimesoylchloride solution. Hollow fibers presented by Veríssimo et al were specifically applied to low pressure RO. However, those fibers can be used for other applications.

Verissimo et al. [15] used polyetherimide (PEI) hollow fiber membranes with PA coated on the bore side for desalination etc. By using the organic liquid as the buffer layer, average water permeability of $0.6 \times 10^{-5} \text{ L m}^{-2} \text{ h}^{-1} \text{ Pa}^{-1}$ and a NaCl rejection of 99.5% under a pressure of $10 \times 10^5 \text{ Pa}$ (10 bar) feed pressure were observed, which is very high rejection obtained with MPD/TMC based TFC-membranes. It suggested that the membrane prepared by using inert organic liquid was virtually defect free. The performance of the membranes could be further improved by formic acid treatment to an average water permeability of $3 \times 10^{-5} \text{ L m}^{-2} \text{ h}^{-1} \text{ Pa}^{-1}$ with rejections higher than 95%.

Ni et al. [16] fabricated hollow fiber composite reverse osmosis membranes by the inter-facial polymerization of *m*-phenylenediamine (mPDA) and trimesoyl chloride (TMC) using polysulfone ultrafiltration membrane as the support. It was revealed that the performance of membranes (RO) can be improved by post treatments with

NaOCl and polyvinyl alcohol (PVA) solution. It was observed that the salt rejection of the membranes increases dramatically after NaOCl and PVA solution treatment, but the permeate flux decreases slightly. Salt rejection of 96.3% and pure water flux of $10.9 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ were obtained when the membrane was treated 500 ppm of NaOCl solution and 20 ppm of PVA solution. Kim and Deng [17] modified the surface of commercial thin-film composite (TFC) membranes (six commercial TFC membranes - three nanofiltration (NF) (NF90, NF270 and DK) and three reverse osmosis (RO) membranes (XLE, BW30 and SG)) via low-pressure ammonia (NH_3) plasma treatment. It was reported that a 10 min NH_3 plasma treatment at 90 W was found to be adequate for the TFC membrane modification. The contact angles of NH_3 plasma treated membranes were decreased with increasing plasma treatment time. It was also revealed that modified membranes showed better characteristics in comparison with TFC membranes without modification for water treatment.

3.2 NF

Significant research work on the TFC hollow fiber membrane for the application in nanofiltration has been done. Sun et al. [18] first time fabricated dual-layer thin-film composite nanofiltration hollow fiber (Torlon® 4000T-MV polyamide-imide (PAI)) via IP of hyper branched polyethyleneimine (HPEI) and isophthaloyl chloride (IPC). The substrate possesses a unique cross-section structure comprising a layer full of macrovoid located in the middle and sandwiched by two thin spongy-like layers. The final composite membrane possesses a negatively charged substrate and a positively charged selective layer. Such a sandwich-like sublayer structure provides minimal transport resistance and sufficient mechanical strength for water permeation under high pressures. The possible chemical structure of the interfacial polymerized thin film is proposed in Fig. 5.

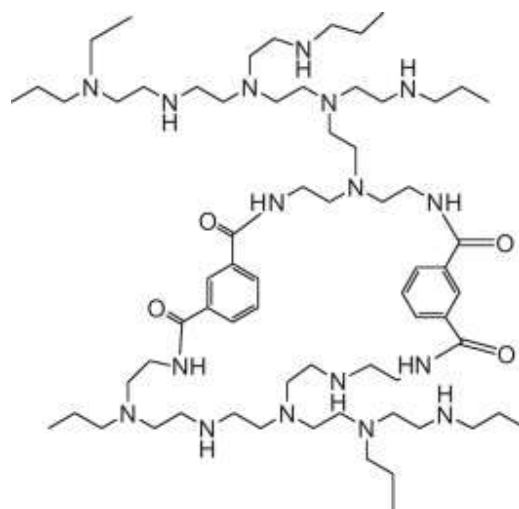


Fig. 5 The possible chemical structure of the interfacially polymerized network formed with hyperbranched polyethyleneimine and isophthaloyl chloride [18].

Together with the steric-hindrance and the solute electro-neutrality effects, due to double-repulsion effect, the newly developed NF membrane showed superior rejections (over 99%) for both positively and negatively charged dye molecules. It was reported that optimized NF membrane had a mean effective pore radius of 0.36 nm, molecular weight cut off of 500 Da, and pure water permeability of $4.9 \text{ L m}^{-2} \text{ bar}^{-1} \text{ h}^{-1}$.

Liu et al. [19] fabricated a high-flux thin film composite (TFC) hollow fiber nanofiltration (NF) membrane. It contains a barrier layer of polypiperazine amide synthesized via interfacial polymerization (IP) on a previously prepared dual-layer (PES/PVDF) hollow fiber substrate, which was synthesized via the two-step TIPS/NIPS method. It was reported that the novel hollow fiber NF membrane has a permeability of $16.6 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, a MWCO of 330 Da and a tensile strength of 10.3 MPa. Membrane also revealed a higher rejection of total organic carbon and a lower rejection of total dissolved solids of the secondary effluent from a petrochemical industry plant. This study supports that it could be used in municipal, agricultural and industrial wastewater treatment.

Zheng et al. [20] prepared positively charged thin-film composite hollow fiber nanofiltration membranes by the dip-coating method using polypropylene hollow fiber microfiltration membrane as support. The coating materials were polyvinyl alcohol (PVA) and polyquaternium-10 (the reaction product of hydroxyethyl cellulose with a trimethylammonium substituted epoxide, PQ-10) and glutaraldehyde used as cross-linking agent. By using the submerged filtration technique, it was observed that the rejections of Brilliant Green, Victoria Blue B and Crystal Violet were 99.8%, 99.8% and 99.2%, respectively. The permeation properties were estimated through pressurized cross-flow permeation technique. Inorganic salts such as CaCl_2 , MgCl_2 , NaCl , MgSO_4 and Na_2SO_4 of analytical grade were used as the model solutes to determine the permeation characteristics of the resultant membrane. It was found that the salt rejection order of the membrane was $\text{CaCl}_2 > \text{MgCl}_2 > \text{NaCl} > \text{MgSO}_4 > \text{Na}_2\text{SO}_4$ at neutral pH.

Maurya et al. [21] fabricated TFC hollow fiber nanofiltration membranes by coating a thin polyamide layer on to polysulfone hollow fiber ultrafiltration membrane via IP (*m*-phenylenediamine and trimesoyl chloride) under different conditions. These membranes exhibited molecular weight cut-off values in the range of 490 to 730 g/mole and showed the rejections in the range of 60–97% for reactive black-5

and rhodamine-B with water flux of $10\text{--}35\text{ mL m}^{-2}\text{ h}^{-1}$ at 25 psi for feed solutions containing 400–2000 ppm dye. These membranes could be applied for the removal of dye from water. Yu et al. [22] fabricated the CMCNa/PP thin-film composite membranes via coating CMCNa (sodium carboxymethyl cellulose) skin layer on the outer surface of polypropylene (PP) microporous hollow fibers followed by cross-linking with FeCl_3 . From the permeation tests it was observed that its MWCO was about 700 Da and it could effectively remove anionic dyes (Congo red and Methyl blue) from aqueous solution. The dye retention, water permeability and salt rejection rate to aqueous solution containing 2000 mg/l Congo red and 10,000 mg/L NaCl were 99.8%, $7.0\text{ L m}^{-2}\text{ h}^{-1}\text{ bar}$, and lower than 2.0 %, respectively.

Wei et al. [23] removed heavy metals from actual electroplating wastewater by using thin-film composite nanofiltration (NF) hollow-fiber membranes. Thin-film composite NF hollow-fiber membranes were prepared by an interfacial polymerization technique. PIP and TMC were used as reactive monomers to form the polyamide film on the inner surface of the hollow-fiber membrane. The supporting hollow fiber membrane was made of polysulfone/poly(ether sulfone) (PS/PES) and had a pure water flux of approximately $152\text{ L m}^{-2}\text{ h}^{-1}$ at 0.1 MPa. It was reported that the permeate flux and heavy-metal rejection rates of the membrane increased with increasing operating pressure. The rejection rates for chromium, copper, and nickel ions were 95.76%, 95.33%, and 94.99%, respectively. The concentration of chromium, copper, and nickel ions in the retentate were 5.72, 5.66, and 5.63 times compared with their original feed concentrations.

Liu et al. [24] fabricated PA/PVDF hollow fiber composite NF membranes by IP using (TMC) and piperazine (PIP) as the interfacial polymerization reaction reagents. Only the external surface during the dipping process had come in contact with reactants to form polyamide skin layer. By using the feed solution of 2 g L^{-1} Na_2SO_4 , MgCl_2 , KCl, NaCl, PEG600 and PEG1000, its separation performance was studied. It was observed that the rejections of PA/PVDF hollow fiber composite NF membranes for Na_2SO_4 , MgCl_2 , KCl, NaCl, PEG600 and PEG1000 were 92.3%, 7.0%, 9.5%, 14.2%, 88.4% and 89.3%, respectively.

Plisko et al. [25] incorporated fulleranol $\text{C}_{60}(\text{OH})_{22-24}$ into the polyamide (PA) selective layer and developed thin film nanocomposite (TFN) hollow fiber membranes for low molecular weight cut-off ultrafiltration. The membranes were fabricated via interfacial polymerization technique by alternately pumping fulleranol dispersion in triethylenetetramine (TETA) aqueous solution and isophthaloyl chloride solution in hexane through polysulfone hollow fiber membranes. It was suggested by authors that fulleranol may form hydrogen bonds with amine and

amide groups of the polyamide obtained by interfacial polymerization including ester bonds with unreacted acyl chloride groups. Anti fouling properties of the membranes were evaluated by using the flux changes during alternative filtration of pure water and foulant – 0.4 g L⁻¹ lysozyme solution in phosphate buffer (0.05 M, pH=7.0). It was revealed that on incorporation of fulleranol to the PA skin layer, pure water flux decreased with slight increase in lysozyme rejection. It was reported that the properties of the modified membrane were superior to the initial membrane.

Abolfazli and Rahimpour [26] investigated the effect of adding silica nanoparticles and TETA (triethylenetetramine) on the permeation performance and morphology of thin-film composite hollow fiber membranes. In this study, PSF (polysulfone) HF UF was used as a support layer and trimesoyl chloride and piperazine were used as monomers for IP reaction. TETA and SiO₂ nanoparticles were in aqueous phase of interfacial polymerization reaction. The TFC skin layer was deposited on the external surface of the hollow fiber. Using cross-flow hollow fiber filtration setup, membrane performances were investigated by using 2000 ppm of NaCl as feed at pressure of 5 bar. It was observed that salt rejection increased from 15.17 to 25.44% with increasing the TETA concentration from 0.5 to 10% (w/v). Further, it was also observed that the structure and performance of the composite membrane can be effectively controlled by adjusting the concentration of additives.

Fang et al. [27] fabricated composite hollow fiber with thin-film selective layer on the inner surface of a polyethersulfone (PES) UF membrane as substrate. The selective layer was formed by interfacial polymerization using branched polyethyleneimine (PEI) and trimesoyl chloride (TMC) as the monomers in aqueous and organic phases, respectively. The membrane prepared with optimized preparation parameters showed a positively charged thin-film selective layer with pure water permeability (PWP) of about 17 L m⁻² h⁻¹ bar and a molecular weight cut-off (MWCO) of around 500 Da. It was observed that the membrane rejections for Mg²⁺ and Ca²⁺ ions were found to be around 90% and the water flux was about 20 L m⁻² h⁻¹ at 2 bar pressure. It was suggested by authors that these membranes could be used in water softening applications.

3.3 FO

Forward osmosis (FO) is an emerging, low-energy, and green membrane process in comparison to conventional desalination and wastewater treatment processes. FO desalination utilizes osmotic pressure difference between a feed solution (FS) and a draw solution (DS) to drive water across a semi-permeable membrane. Higher rejections to a wide range of contaminants and low membrane fouling properties

compared to the conventional RO process are drawing the attention significantly to use FO process in water treatment.

Sukitpaneenit and Chung [28] presented TFC FO HF for forward osmosis (FO) applications. Functional selective polyamide layer was formed by highly reproducible IP on a polyethersulfone (PES) hollow fiber support. PES HF support was made by dual-layer coextrusion technology to get desirable macrovoid-free and fully sponge-like morphology. Fig. 6 shows strategies to control the phase inversion process with the aid of coextrusion technology employing a dual-layer spinneret.

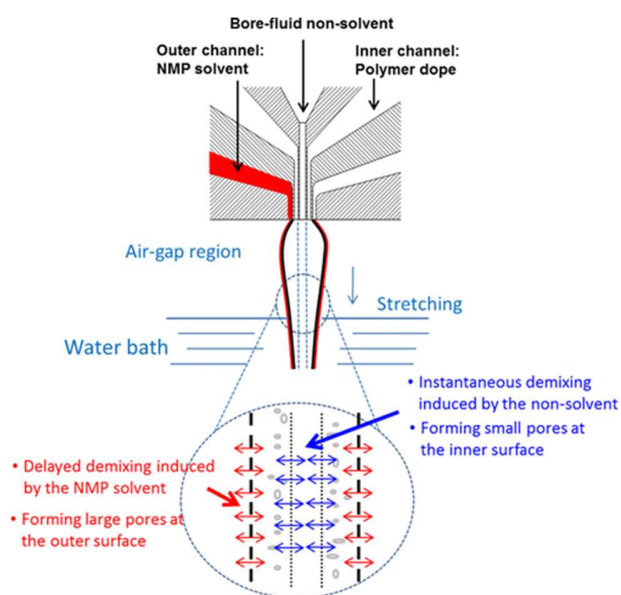


Fig. 6 Strategies to control the phase inversion process with the aid of coextrusion technology employing a dual-layer spinneret [28].

Sukitpaneenit and Chung [28] developed thin-film composite (TFC) hollow fiber membranes for forward osmosis (FO) applications. It consisted a functional selective polyamide layer formed by highly reproducible interfacial polymerization on a polyethersulfone (PES) hollow fiber support. The membrane exhibited relatively high water fluxes of 32–34 LMH ($\text{Lm}^{-2}\text{h}^{-1}$) and up to 57–65 LMH from pure water feed to 2 M NaCl draw solution tested under the FO and pressure retarded osmosis (PRO) modes, respectively. Authors claimed that the membranes could display a high water flux up to 15–18 LMH with seawater which is comparable to the best value reported for seawater desalination applications.

Low et al. [29] used new polyethersulfone-based ultrafiltration membrane which was incorporated with Zn_2GeO_4 nanowires. The composite membrane was used as

a substrate for the fabrication of TFC FO membrane, by coating a thin layer of polyamide on top of the substrate. In RO mode, the Zn_2GeO_4 -modified membrane showed ~45% increase in water permeability and NaCl salt rejection of 80%. In FO mode, the ratio of water flux to reverse solute flux was also improved. The membrane may also be used as nanofiltration (NF) or RO membrane since they are less affected by ICP effects (internal concentration polarization). It is a characteristic problem for asymmetric thin-film composite (TFC) FO membrane which leads to lower water flux. Authors demonstrated that the incorporation of nanomaterials to the membrane substrate may be an alternative approach to improve the formation of polyamide skin layer to achieve better FO performance.

Gang et al. [30] deposited a polyamide skin onto the outer and inner surfaces of the PES fiber via interfacial polymerization between m-phenylenediamine (MPD) and trimesoyl chloride (TMC), separately. FO and PRO tests were done to see its performance and the draw solution flowed against the inner polyamide selective layer of the double skin TFC(dTFC)-PES membrane. Superior antifouling performance has been demonstrated by the dTFC-PES membrane when the feed was real wastewater brine (WWBr). The membrane water flux slightly drops to 71% of the initial value at a high feed recovery of 80% in FO mode. Stable performance was observed in PRO mode where the power density only decreases to 90.8% of the initial value after a 12 h test at $\Delta P=15$ bar. Figure 7 shows the fouling mechanisms of conventional TFC FO membranes and developed double-skin dTFC-PES membrane. Insignificant fouling was observed on the draw solution side. This phenomenon was due to the outstanding rejection of the polyamide skin facing the draw solution and the transmembrane water permeation from the feed side.

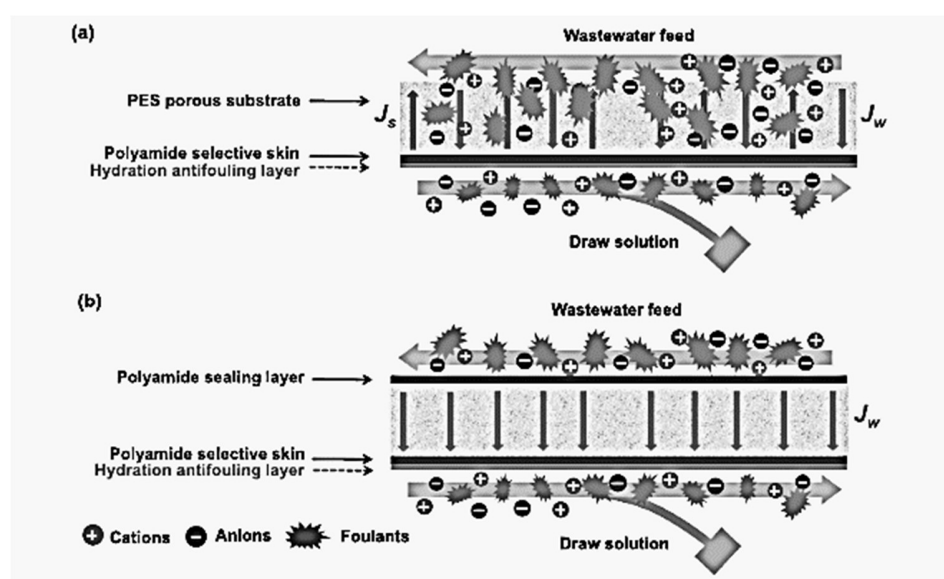


Fig. 7. Schematic of fouling phenomena: (a) the conventional TFC membrane and (b) the newly developed double-skin TFC membrane in FO (under the PRO mode) and PRO processes [30]

Chou et al. [31] developed FO hollow fiber membrane, which was fabricated by interfacial polymerization on the inner surface of a polyethersulfone(PES) hollow fiber using m-phenylenediamine (MPD) aqueous solution and trimesoyl chloride (TMC) hexane solution. It was observed that this hollow fiber membrane can achieve a water flux of $12.4 \text{ L m}^{-2} \text{ h}^{-1}$ for 3.5 wt.% (0.59 M) NaCl feed solution and 2 M NaCl draw solution. It was suggested by authors that this new FO hollow membrane have potential for seawater. Chou's membrane also exhibited excellent intrinsic separation properties, with a water flux of $42.6 \text{ L m}^{-2} \text{ h}^{-1}$ using 0.5 M NaCl as the draw solution and DI water as the feed with the active layer facing the draw solution orientation at 23°C [32].

Chung's group [33] developed novel tri-bore thin-film composite (TFC) hollow fiber (HF) membranes for forward osmosis (FO) processes by employing a specially designed tri-bore blossom spinneret. A polyamide selective layer was fabricated on the inner surface of the Matrimid[®] HF substrates by interfacial polymerization between MPD and TMC monomers. The tri-bore thin-film composite (TFC) hollow fiber (HF) membranes exhibited high water fluxes of 50.5 LMH and 11.8 LMH with salt leakages as low as 3.5 gMH ($\text{g m}^{-2}\text{h}^{-1}$) and 2.5 gMH, in pressure retarded osmosis (PRO) and FO modes, respectively, when using 2 M NaCl as the draw solution and pure water as the feed. In desalination experiments, water flux was 5.8 LMH using a 2 M NaCl draw solution and a model seawater solution as the feed. Theoretically it was found that the advantages of triangle TFC tri-bore HF membranes over round ones was higher water output per module than the latter at the same packing density due to larger effective membrane area in the former one.

Fang [34] fabricated thin film composite forward osmosis PES hollow fiber membranes by depositing thin film active layer on the lumen side via IP. Two monomers i.e. m-phenylene-diamine (MPD) and TMC. were used for polymerization. From their studies, it was revealed that two different chemicals can successfully work together as the additives of aqueous solution to achieve a better performing membrane than applying each additive separately. Under optimized conditions, water flux can reach $42.6 \text{ L h}^{-1} \text{ m}^{-2}$ using 0.5M NaCl as draw solution

with the fabricated membrane. Thus the performance of the fabricated FO hollow fiber was believed to be superior to all FO membranes reported in the open literature.

Shibuya et al. [35] fabricated two types (different inner diameters) TFC polyketone (as support) HFs with a PA layer on the shell side of the fiber. The PA layer was deposited via IP of TMC and MPD. The prepared TFC-FO membrane using the HF with smaller diameter (TFC-FO (HF-A)) showed higher FO flux and better mechanical properties than those of the membrane prepared using the HF with larger diameter (TFC-FO (HF-B)).

3.4 PRO

PRO can be viewed as an intermediate process between FO and RO, where hydraulic pressure is applied in the opposite direction of the osmotic pressure gradient (similar to RO). Loeb and Norman [36] proposed pressure-retarded osmosis (PRO) process. In a PRO process, water flows naturally from a low salinity stream (feed water) at an ambient pressure across a semi-permeable membrane to a pressurized high salinity stream (draw solution) driven by the osmotic pressure difference across the membrane. Chou et al. [37] first time reported the fabrication of thin-film composite hollow fiber membranes which could be used in PRO process. Composite hollow fiber membrane was prepared by depositing a thin layer of PA on PES hollow fiber via IP. The main reagents used were m-phenylenediamine (MPD), trimesoyl chloride (TMC) and cyclohexane. From the performance test, it was revealed that The TFC PRO hollow fiber membranes have a water permeability (A) of 9.22×10^{-12} m/(s Pa), salt permeability (B) of 3.86×10^{-8} m/s and structural parameter (S) of 4.6×10^{-4} m.

Ingole et al. [38] developed a high flux and high power density TFC-PRO membrane from the polyethersulfone (PES) membrane support which was modified by coating with polydopamine (PDA), based on the easy self-polymerization and strong adhesion characteristics of dopamine (DA) under mild conditions. It was found that this improved process resulted in TFC-PRO membranes with simultaneous enhancements in both water permeability and salt rejection properties. On studying the performance of the thin film composite (TFC) membrane with polydopamine layer, it was revealed that the PDA-TFC membrane has very high flux, excellent power density performance and good stability. It was suggested by authors these membranes can be used in all engineered osmosis applications including pressure retarded osmosis.

Wan et al. [39] developed an inner-selective thin-film composite (TFC) PRO hollow fiber membrane with a high operating pressure and a high power density by adding an inorganic salt, CaCl_2 to the PES dope solution. The presence of CaCl_2 increases the dope viscosity, reduces the mean pore size and narrows the pore size distribution. PA selective layer was deposited on the lumen side of the hollow fibers via IP. First MPD aqueous solution containing 0.1 wt.% SDS was circulated followed by purging air. Second a hexane solution with 0.15 wt.% TMC was reacted with MPD, resulting in absorption of polymer on the inner surfaces of the hollow fiber substrate to form a thin polyamide selective layer. It was revealed that TFC-PES membrane has the highest pure water permeability and smallest salt permeability. Further, it showed highest ever reported power density of 38 W/m^2 at 30 bar using 1.2 M NaCl solution and DI water as the draw and feed solutions, respectively.

Table 1 summarizes TFC hollow fiber membranes for water treatment.

Table 1

TFC hollow fiber membrane for water treatment.

Membrane	Use	Results	Ref
PDA - PES	Desalination	Reverse Osmosis High flux, excellent power density performance and good stability. Can be used in all engineered osmosis applications including PRO.	[15]
PA-PSF, post treated with NaOCl and sodium hydroxide.	Desalination	Salt rejection of 96.3% and pure water flux of $10.9 \text{ l} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$	[16]
Low-pressure NH_3 plasma treatment(six commercial TFC membranes (3 NF, 3 RO))	Water treatment	Contact angles of NH_3 plasma treated membrane were decreased with increasing plasma treatment time. increased the surface hydrophilicity,	[17]
polypiperazine amide - PES/PVDF (NF)	Waste water treatment	Nano filtration High-flux and outstanding selectivity of TOC/TDS.	[19]
HPEI-Torlon® PAI (NF)	Removal of organic matters from water	Pure water permeability of $4.9 \text{ l m}^{-2} \text{ bar}^{-1} \text{ h}^{-1}$.	[18]
PVA+PQ-10-PP (NF)	Desalination	Salt rejection order $\text{CaCl}_2 > \text{MgCl}_2 > \text{NaCl} > \text{MgSO}_4 > \text{Na}_2\text{SO}_4$.	[20]
PA-PSF (NF)	Removal of Dye etc. Water treatment	Cationic dye removal (submerged filtration). MWCO in the range of 490 to 730 g/mole. Rejections in the range of 60–97% for reactive black-5 and rhodamine-B with water flux of $10\text{--}35 \text{ mLm}^{-2} \text{ h}^{-1}$ at 25 psi for feed	[21]

		solutions containing 400–2000 ppm dye.	
CMCNa/PP (NF)	Water treatment	MWCO of about 700 Da. Remove anionic dyes. The dye retention, water permeability and salt rejection rate to aqueous solution containing 2000 mg/l Congo red and 10,000 mg/l NaCl were 99.8%, 7.0 Lm ⁻² h ⁻¹ bar, and lower than 2.0%, respectively.	[22]
PIP+TMC-PSF+PES (NF)	Heavy metal removal	Pure water flux of approximately 152 Lm ⁻² h ⁻¹ at 0.1 MPa. Rejection rates for chromium, copper, and nickel ions were 95.76%, 95.33%, and 94.99%, respectively	[23]
PA (TMC+PIP)-PVDF	TMC) and piperazine (PIP)	Rejections Na ₂ SO ₄ , MgCl ₂ , KCl, NaCl, PEG600 and PEG1000 were 92.3%, 7.0%, 9.5%, 14.2%, 88.4% and 89.3%, respectively	[24]
Si NPTs + TETA – PSF	Desalination	Rejection increased from 15.17 to 25.44% with increasing the TETA concentration from 0.5 to 10% (w/v). Structure and performance of the composite membrane can be effectively controlled by adjusting the concentration of additives.	[26]
Fullerene C ₆₀ (OH) ₂₂₋₂₄ +PA – PSF (UF)	Water treatment	Superior antifouling properties. Decrease of pure water flux and a slight increase of rejection of lysozyme and PVP K-15. Antifouling properties of the PA/fullerenol membranes are superior to the pristine membrane. A correlation between surface properties and fouling behavior is established.	[25]
PA-PEI		PWP about 17 L m ⁻² h ⁻¹ bar. Rejections for Mg ²⁺ and Ca ²⁺ ions were found to be around 90% and the water flux was about 20 L m ⁻² h ⁻¹ at 2 bar pressure. It could be use in water softening applications.	[27]

Forward Osmosis, Pressure Retarded Osmosis

Functional selective PA layer-PES (FO, PRO)	Desalination application	Relatively high water fluxes of 32–34 LMH (FO) and up to 57–65 LMH (PRO) against a pure water feed using 2 M NaCl as the draw solution. With model seawater solution as the feed, the membranes could display a high water flux up to 15–18 LMH.	[28]
Zn ₂ GeO ₄ -PES (FO, RO, NF)	Water treatment	RO mode, 45% increase in water permeability and NaCl salt rejection of 80%. FO mode, ratio of water flux to reverse solute flux improved	[29]
PA-PES (dTFC-PES) (FO, PRO)	Waste water treatment	High feed recovery of 80% in FO mode. Stable performance was observed in PRO mode.	[30]
PA-PES (FO)	Water treatment, desalination.	Water flux of 12.4 Lm ⁻² h ⁻¹ for 3.5 wt.% (0.59 M) NaCl feed solution and 2 M NaCl draw solution.	[31]
PA-PES (FO)	Water treatment, desalination.	Excellent intrinsic separation properties, with a water flux of 42.6 Lm ⁻² h ⁻¹ , with a water flux of 42.6 Lm ⁻² h ⁻¹ using 0.5 M NaCl as the draw solution.	[32]
PA-Matrimid [®] (Tri-bore-composite) (PRO, FO)	Saline water treatment	High water fluxes of 50.5 LMH and 11.8 LMH with salt leakages as low as 3.5 gMH and 2.5 gMH, in pressure retarded osmosis (PRO) and FO modes, respectively, when using 2 M NaCl as the draw solution and pure water as the feed.	[33]
PA-polyketone (IP shell side)	Saline water treatment	HF with smaller diameter showed higher FO flux and better mechanical properties than those of the membrane prepared using the HF with larger diameter.	[35]

PA-PES	Desalination	Under optimized conditions, water flux can reach $42.6 \text{ Lh}^{-1}\text{m}^{-2}$ using 0.5M NaCl as draw solution with the fabricated membrane. Thus the performance of the fabricated FO hollow fiber was believed to be superior to all FO membranes reported in the open literature	[34]
PA-PES (PRO)	Water treatment	First time reported the fabrication of thin-film composite hollow fiber membranes which could be used in PRO process. water permeability (A) of $9.22 \times 10^{-12} \text{ m/(s Pa)}$, salt permeability (B) of $3.86 \times 10^{-8} \text{ m s}^{-1}$ and structural parameter (S) of $4.6 \times 10^{-4} \text{ m}$.	[37]
PDA-PES (PRO)	Water treatment	very high flux, excellent power density performance and good stability. Can be used in all engineered osmosis applications including pressure retarded osmosis.	[38]
PA-CaCl ₂ + PES	Saline water treatment	Highest pure water permeability and smallest salt permeability. Power density of 38 Wm^2 at 30 bar using 1.2 M NaCl solution and DI water as the draw and feed solutions.	[39]

4. Pervaporation

4.1 Alcohol Dehydration

Alcohols are widely used as good solvents, cleaning agents, raw materials or chemical intermediates for organic synthesis and in medical field. In the production and recycle of alcohols, dehydration of alcohol/water mixture is a critical issue. An azeotropic mixture is formed by alcohol (ethanol, isopropanol, or butanol) and water, which makes purification of alcohols by conventional methods such as distillation inefficient and uneconomic. Pervaporation process for purification of alcohols is energy saving, able to break azeotropes with high separation efficiency and friendly to environment. Thus, industries are showing

considerable interest in pervaporation process for dehydration/recycling of alcohol mixtures. Mostly it is the separation of isopropanol-water mixture.

The novel organic-inorganic TFC membranes exhibit pervaporation separation performance surpassing most polymeric membranes and inorganic ceramic membranes previously developed for isopropanol dehydration [40].

Chung and his coworkers [40, 41] reported the fabrication and characterization of TFC hollow fiber membranes for the pervaporation dehydration of isopropanol via proper monomer selection and optimal IP reaction.

Sukitpaneent and Chung [42] fabricated novel membranes with a thin selective polyamide layer, which was formed by interfacial polymerization onto a porous polyethersulfone (PES) hollow fiber support (free of macrovoids). The PES support was fabricated via dual-layer co-extrusion technology. A thin film of polyamide layer on the inner surface of PES hollow fiber was formed by an interfacial polymerization (IP) between the MPD monomer in the aqueous phase and the TMC monomer in the organic phase. The surface of the TFC was modified by coating with either polydopamine or silicone rubber. The polydopamine or silicone rubber coated membranes exhibited water separation factors of up to 51 and 60, with substantial high fluxes of 6.6 and 7.5 kg m⁻² h⁻¹, respectively, when used in pervaporation separation of ethanol /water mixture. These developed membranes possess reasonably good selectivity/separation factors and superior permeation fluxes in comparison with most polymeric membranes.

Zuo et al. [41] developed a novel TFC hollow fiber membrane comprising a polyamide selective layer on a porous polyamide-imide substrate. Four different amines (m-phenylenediamine (MPD), and three different molecular weight hyper-branched polyethyleneimine (HPEI)) were used for IP for the formation of the thin film on the outer surface of hollow fiber. It was reported that the TFC membrane fabricated from HPEI with a molecular weight 2 kg/mol showed best separation factor of 624 with a flux of 1282 g m⁻² h⁻¹ and a permeate water concentration of 99.1 wt.% using a feed composition of 85/15 wt.% IPA/water at 50 °C under the optimal IP conditions.

In another article Zuo et al. [40] described a novel organic–inorganic thin film composite (TFC) HF membranes with an introduction of an inorganic component 3-glycidyloxypropyltrimethoxy-silane (GOTMS) in the chemical structure of the in situ synthesized polyamide layer. The performance testing of these membranes revealed that the separation factor surpassed most of prior polymeric membranes and

inorganic ceramic membranes for isopropanol dehydration. Their TFC membrane exhibited an optimized flux of $3.5 \text{ kg m}^{-2}\text{h}^{-1}$ with a separation factor of 278 for a feed composition of 85/15 wt.% isopropanol (IPA)/water at 50 °C.

Tsai et al. [43] fabricated dual layer PA/PAN composite hollow fiber membrane via a fabrication technique involving simultaneous extrusion of two different dope solutions by using a triple orifice spinneret. SiO_2 was added into the dope to increase the hydrophilicity of the dope. It was found that PA layer was adhered to the lumen surface of the PAN hollow fiber membrane. The membrane performance was studied for the separation of 90 wt.% aqueous isopropanol solution at 25°C by pervaporation. A $419 \text{ g m}^{-2}\text{h}^{-1}$ of permeation flux and 96.6 wt.% of water content in permeate was obtained.

Hua et al. [44] described the fabrication of a thin-film composite tri-bore hollow fiber (TFC TbHF) membranes for the application of IPA dehydration. By conducting interfacial polymerization on the HF substrates, TFC HF membranes were prepared using monomer MPD and another monomer TMC. The membrane was tested for the dehydration of IPA. It was reported by authors that the molecularly designed TFC TbHF membranes exhibited excellent pervaporation performance for IPA dehydration. The optimal TFC TbHF membrane showed a flux of $2.65 \text{ kg m}^{-2}\text{h}^{-1}$ with a separation factor of 246 for water/IPA separation at 50 °C using 85/15 wt.% IPA/water as the feed.

Hua et al. [45] designed the Teflon AF2400/Ultem composite HF membrane with good vapor permeation separation performance together with excellent thermal stability for alcohol dehydration. The composite HF membranes were fabricated by dip coating a Teflon AF2400 layer on the outer surface of Ultem HF. Developed composite HF showed a promising and stable separation performance with a flux of $4265 \text{ g m}^{-2}\text{h}^{-1}$ and a separation factor of 383 for 95% isopropanol dehydration at 125 °C.

Table 2 summarizes TFC hollow fiber membranes for the separation and dehydration of alcohols via pervaporation.

Table 2 TFC hollow fiber membrane for separation and dehydration of alcohols via pervaporation.

Membrane Pervaporation	Use	Result	Ref
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PA (4 different MPD and 3 different HPEI)-PA + imide	Isopropanol dehydration	Separation factor of 624 with a flux of $1282 \text{ g m}^{-2} \text{ h}^{-1}$ and a permeate water concentration of 99.1 wt.% using a feed composition of 85/15 wt.% IPA/water at 50°C . under the optimal IP conditions	[41]
GOTMS+PA-Poly ether imide (Ultem [®])	Isopropanol dehydration	IPA/water at 50°C . Separation performance surpassing ceramic membranes.	[40]
PA-PES (dual layer) Surface modified polydopamine or silicone rubber.	Ethanol dehydration	Water separation factors of up to 51 and 60, high fluxes of 6.6 and $7.5 \text{ kg m}^{-2} \text{ h}^{-1}$. Good selectivity/separation factors and superior permeation fluxes in comparison with most polymeric membranes	[42]
PA-PAN + Si (dual layer, triple orifice spinneret)	Separation of 90 wt.% aqueous isopropanol solution	$419 \text{ g/m}^2\text{h}$ of permeation flux and 96.6 wt.% of water content in permeate	[43]
Poly (ether imide) Ultem [®] 1010 (tri-bore hollow fiber)	Isopropanol dehydration	Flux $2.65 \text{ kg m}^{-2} \text{ h}^{-1}$ with a separation factor of 246 for water/IPA separation at 50°C using 85/15 wt.% IPA/water as the feed.	[44]
Teflon AF2400 layer on the outer surface of Ultem HFs. (dip coating)	Isopropanol dehydration	Flux $4265 \text{ gm}^{-2}\text{h}^{-1}$ separation factor of 383 for 95% isopropanol dehydration at 125°C	[45]

5. Gas Separation

Thin film composite HF membranes for gas separations are usually prepared by coating the membrane surfaces via dip coating technique. The other technique i.e. IP is not successful and common.

5.1 Dip Coating Membranes

A porous HF, which can not separate gases to a significant extent, can be made achievable its intrinsic separation properties by coating with an appropriate material

[46]. Henis and Tripodi suggested that the separation properties of coated composite membranes are governed by the porous support material rather than by the coating material, and presented a resistance model to explain the behavior of composite gas separation membranes. Thus, Henis and Tripodi [47, 48] developed composite membranes with acceptable permeability and very high permselectivity [49, 50]. The membrane consists of a porous asymmetric substrate of one polymer with a dense layer and a coating of another polymer - a second layer that is made by a non-selective and highly permeable material. On coating, there could be two possibilities.

- i) If the pores of the substrate membrane are very large, its gas flow resistance is very low. In this case the thin layer coated on top of the substrate will govern both flux and selectivity.
- ii) In the other case, substrate membrane is considered as solution diffusion membrane with some defective pores. The substrate governs the membrane performance. The coated layer is only to stop the gas leakage by filling the defective pores.

It is difficult to know which mechanism is working. But normally PEBAX coating is thought to be in the first category and PDMS the second category.

5.2 IP Membranes

Only few membranes were successfully made by this method for gas separation. Dip coating can also be applied when there are defects in the membrane prepared by IP.

5.3 CO₂/methane and CO₂/nitrogen Separation

Climate change and global warming is the environmental issue and it is caused mainly due to the rise in CO₂ level in atmosphere. Carbon capture and storage (CCS) technologies and improvements on energy utility efficiency are important strategies to lower the atmospheric CO₂ concentration. Flue gas refers to the combustion exhaust gas produced at power plants. Its composition depends on what is being burned, but it usually consists of mostly nitrogen (typically more than two-thirds), carbon dioxide (CO₂), and water vapor. Gas separation membranes have been commercialized for this purpose for more than 3 decades and are continuously growing [51].

Liang et al. [52] fabricated defect-free PDMS/PAN composite hollow fiber membrane with high performance for flue gas and air separations. PDMS/PAN

composite membranes were made by a direct dip coating process. PDMS selective layer on PAN HF was 230 nm thick. From the permeance test it was found that the CO₂ permeance was > 5000 GPU and a CO₂/N₂ selectivity was about 11. Further, it was also found that the newly developed composite membrane could be used for various gas separations such as the production of oxygen-enriched air and the separation of CO₂ from flue gas. The defect-free composite membrane showed excellent O₂ and CO₂ permeances higher than 1000 and 5000 GPU, respectively; while the corresponding selectivity's of O₂/N₂ and CO₂/N₂ were about 2 and 11, respectively.

Liu et al. [53] fabricated a membrane by coating a thin layer of poly(ether block amide (PEBA) onto microporous PEI hollow fiber substrate membranes. The membrane was prepared by coating a thin layer of PEBA onto microporous PEI hollow fiber substrate membranes. Membrane was tested for CO₂/N₂ separation and it was revealed that at 790 kPa a permeate stream containing 62 mol % CO₂ was obtained, corresponding to 20% CO₂ recovery. On the other hand, 99.4 mol% N₂ can be obtained in the residue (nitrogen recovery 72%).

Fam et al. [54] prepared defect free Pebax®1657/[emim][BF₄] gel membranes in the form of thin film composite hollow-fiber membranes. On investigation, TFC gel membranes showed excellent mechanical durability including separation of CO₂ mixed-gas feed containing traces of water vapor and NO_x. It was suggested that the TFC gel membranes have the potential application for CO₂ capture with real gas feed.

Lasseuguette et al. [55] used four kinds of composite hollow fibers membranes for gas separation. TFC membranes were prepared using two different porous supports (MicroPES and Oxyphan) and two different permeable polymers (PTMSP and Teflon AF2400) for coating. These membranes exhibited high CO₂ and N₂ permeability's with CO₂/N₂ selectivity's between 3.4 and 2.5.

Borisov et al. [56] modified polysulfone (PSF) hollow fiber membranes by air plasma and the Piranha etch (H₂O₂ + H₂SO₄) for the development of high efficiency support for composite membrane preparation. For composite membrane formation polymer solution (poly[1-(trimethylsilyl)-1-propyne], (PTMSP) in hexane) was forced in HF's lumen. The TFC HF fabricated on air plasma treated surface showed high CO₂ permeance (3.3×10⁵ GPU) in comparison with unmodified membranes including highest surface energy (more phobic to hydrocarbons).

Zulhairun et al. [57] coated PDMS containing $\text{Cu}_3(\text{BTC})_2$ MOF layer onto PSF hollow fiber and investigated gas permeation properties. It was reported that the pure gas permeation experiment with CO_2 , N_2 and CH_4 corroborated the contribution of $\text{Cu}_3(\text{BTC})_2$ particle to the overall composite/hybrid membrane performance. The gas permeation rates were increased with increasing number of PDMS- $\text{Cu}_3(\text{BTC})_2$ coatings. CO_2 permeance increased from 69.7 to $109.2 \times 10^{-6} \text{ cm}^3 (\text{STP})/\text{cm}^2 \text{ s cmHg}$ after 5 consecutive coatings. In addition, the CO_2/CH_4 and CO_2/N_2 selectivity's were found to be increased as well. $\text{Cu}_3(\text{BTC})_2$ contributed to higher affinity toward CO_2 .

5.4 SO_2 Removal

To capture CO_2 from the combustion of fossil fuel plants, CO_2 capture and separation (CCS) technologies, which are often based on chemical absorption process, are used. The SO_2 in the emission gas affected the sorbents in the CCS process. Flue gas from coal-power plants contains 6–196 ppm of SO_2 after CCS process. To remove remaining SO_2 another CCS process is necessary. Some studies have been made to apply polymeric membranes for flue gas applications.

Kim et al. [58] prepared a PEBAX/PEI hollow fiber composite membrane via coating poly(ether-b-amide) (PEBAX) onto PEI hollow fiber and used to remove SO_2 from mixed gases. It was observed that the permeance of SO_2 and CO_2 increased with operating pressure. However, the permeance of N_2 was negligibly changed. With the increase in temperature, the permeation of SO_2 sharply decreased. Similar phenomenon was also observed for the selectivity of SO_2/CO_2 .

Kim et al. [59] prepared hollow fiber composite membrane was by coating a poly(vinyl chloride)-graft-poly(oxyethylenemethacrylate) (PVC-g-POEM) layer on a PEI substrate. The inner and outer diameters of the HFM was 261 and 429 μm , respectively and selective coating layer on the outer surface was around 0.1 μm . The membrane was tested for the permeance of pure gases (SO_2 , CO_2 and N_2) at different operating conditions. It was reported that permeance of SO_2 was 105–2705 GPU and the selectivity of SO_2/CO_2 was 3.9–175.6. From the mixed gas separation experiment, the maximum SO_2 removal efficiency reached up to 84.5%.

5.5 O_2/N_2 Separation

Liang et al. [52] reported that selectivity of O_2/N_2 was 2 and permeances of O_2 was higher than 1000 GPU with defect free PDMS/PAN composite hollow fiber membrane. Chong et al. [60] coated polysulfone (PSF) hollow fiber membranes by

a layer of polydimethylsiloxane (PDMS) or poly(ether block amide) (PEBAX) at different concentrations. Table 3 shows coating layer thickness of PDMS- and PEBAX-coated membranes with increasing the coating solution concentration from 1 to 5 wt. %. Fig. 8 shows the Effect of PDMS and PEBAX coating on the PSF membrane with respect to gas permeance.

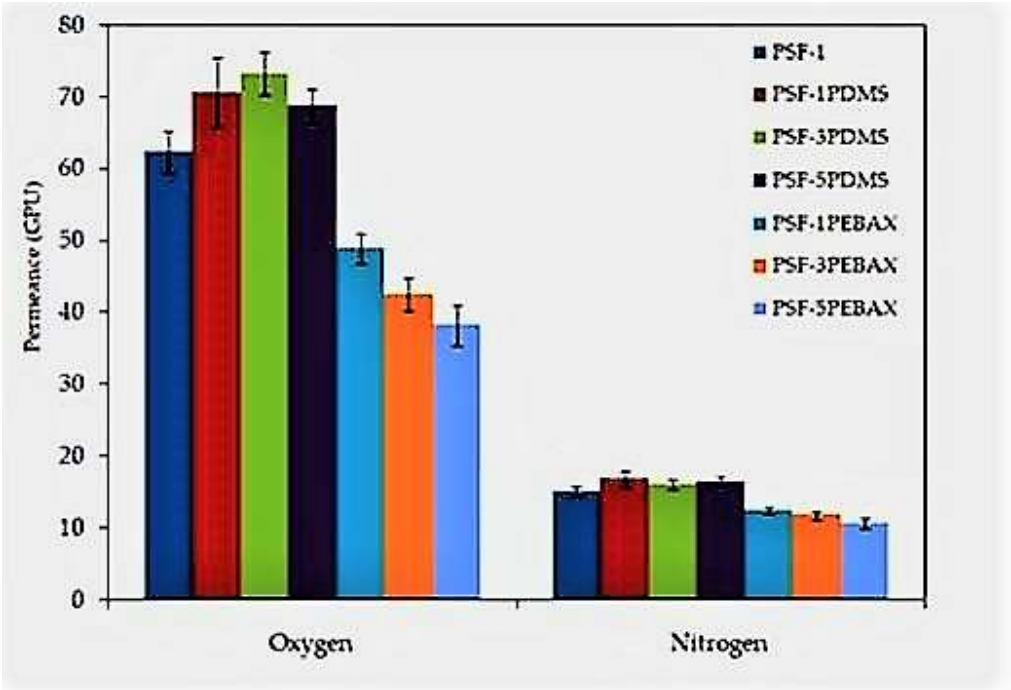


Fig. 8 Effect of PDMS and PEBAX coating on the PSF membrane with respect to gas permeance [60]

Table 3	
Coating thickness for the as spun hollow fiber membranes	
Membrane	Thickness (μm)
PSF-1PDMS	0.7 ± 0.07
PSF-3PDMS	1.1 ± 0.05

Coating thickness for the as spun hollow fiber membranes	
Membrane	Thickness (μm)
PSF-5PDMS	1.7 ± 0.06
PSF-1PEBAX	0.3 ± 0.10
PSF-3PEBAX	0.8 ± 0.09
PSF-5PEBAX	1.2 ± 0.14

These membranes were evaluated for the oxygen separation from the gas mixture.

Table 4 shows effect of PDMS and PEBAX coating on the PSF membrane with respect to gas selectivity.

Table 4

Effect of PDMS and PEBAX coating on the PSF membrane with respect to gas selectivity.

Membrane	Selectivity (α)
PSF	4.13 ± 0.14
PSF-1PDMS	4.20 ± 0.23
PSF-3PDMS	4.56 ± 0.15
PSF-5PDMS	4.17 ± 0.12
PSF-1PEBAX	3.94 ± 0.09
PSF-3PEBAX	3.62 ± 0.10
PSF-5PEBAX	3.60 ± 0.12

From the Fig. 5 it seems that the gas permeances of the membranes were in the range of 38–73 GPU for oxygen gas and 10–17 GPU for nitrogen gas. The uncoated membrane shows 62.35 and 15.11 GPU for the oxygen and nitrogen gas, respectively. As a comparison, the PDMS-coated membranes generally show higher

gas permeance for both oxygen and nitrogen gas. The membrane coated with 1 and 3 wt. % PDMS solution demonstrates 70.64 and 73.25 GPU, respectively for oxygen gas and 16.82 and 16.05 GPU, respectively for nitrogen gas.

Meng et al. [61] used polyvinylidene fluoride (PVDF) hollow fibre membranes uniformly coated via dip coating technique with dimethylsiloxane (PDMS) (thickness of around 5-12 μm) to study gas permeation. The separation properties of PDMS-PVDF composite hollow fiber membranes were also evaluated experimentally by using N_2/O_2 as the medium. The experimental data of both permeability and selectivity were in good agreement with the theoretical results predicted by the presented pore-distribution model.

Liang et al. [62] described a defect-free thin film composite (TFC) polydimethylsiloxane (PDMS)/polyacrylonitrile (PAN) hollow fiber membrane with an ultrathin PDMS selective layer of about 260 nm. From the study of the performances of the membrane it was observed that the composite membrane showed a N_2 permeance of about 280 GPU, an O_2/N_2 selectivity of 2.2 and a water vapor permeance ranging from about 800 to 3700 GPU depending on operation conditions.

Pian et al. [63] fabricated ceramic hollow fiber-supported polydimethylsiloxane (PDMS) composite membranes and used for oxygen enrichment from air and achieved oxygen permeance of 104 GPU with O_2/N_2 ideal selectivity of 2.0 under experimental conditions. The results obtained by Pian et al. suggested that the ceramic hollow fiber-supported PDMS composite membrane could be a competitive oxygen enrichment membrane for industrial application.

5.6 Water Vapor Transport

The removal of water vapor from specific gas streams is important for various applications, such as dehydration of natural gas, air conditioning, storage of foodstuffs, aviation and spaceflights. A number of techniques have been applied to remove water vapor from the gas stream. Conventional methods for water vapor removal include condensation and adsorption which are uneconomic. Membrane technology is better and economical and environmental friendly.

Ingole et al. [64] used a highly selective thin film composite hollow fiber membrane for mixed vapor/gas (of water vapor/ N_2 mixtures) separation. The membrane was prepared first by coating a polydopamine (PDA) layer using different concentrations of PDA solution on polyethersulfone (PES) hollow fiber supports. Then, TFC membrane was prepared with 3,5-diaminobenzoic acid (3,5-DABA) as an aqueous phase monomer and trimesoyl chloride (TMC) as an organic phase monomer to

synthesize a hydrophilic polyamide layer. The newly prepared TFC hollow fiber membranes acquired reasonably high selectivity and superior permeation fluxes. For example, the membrane coated with 2.0% PDA TFC prepared using 5 wt.% of 3,5-DABA with 0.2 wt.% of TMC and 60 s of reaction time revealed the best permeance and selectivity as 3185 GPU and 195, respectively,

In another article Ingole et al. [65] studied the performance of the metal organic framework (MOF) incorporated thin film nanocomposite (TFN) membrane for water vapor transport from the gas mixture and reported that it drastically enhances the water vapor transport. Ingole et al. used polysulfone (PSf) hollow fiber membranes as substrate material for the coating of thin nanocomposite layer by IP of MPD and TMC. The MOF particles NH₂-MIL-125 (Ti) (amine-functionalized titanium metal organic framework) were prepared from Ti(iPrO)₄ and Ti(BuO)₄ using reflux and solvothermal reactions [66]. It was revealed that a small quantity loading of MOF particles plays a vital role for water vapor transport through the TFN membranes. The water vapor permeance was increased from 785 GPU, for thin film composite (TFC) membrane, to 2244 GPU (MOF@TFN3) with the selectivity being enhanced from 116 to 542, when the NH₂-MIL-125(Ti) MOF nanoparticles content was 0.1 w/w% with respect to monomer solution.

Baig et al. [67] studied the water vapor removal using TFN hollow fiber polyamide membrane, decorating the surface with carboxylated TiO₂ nanoparticles. Surfaces of pure TiO₂ were modified by introducing functional groups to increase the hydrophilicity. After that, modified nanoparticles were homogeneously dispersed in the aqueous phase monomer (3, 5-diaminobenzoic acid) and reacted with trimesoyl chloride (TMC) to form a thin film nanocomposite membrane (TFN) on top of the polysulfone hollow fiber membrane (HFM) substrate. The presence of modified TiO₂ nanoparticles on the membrane surface increased the hydrophilicity of the TFN membrane due to excess carboxylic groups. From the water vapor permeation tests, it was revealed that water vapor permeance and selectivity drastically increased in comparison with the data obtained for unmodified membrane. At optimum conditions, the water vapor permeance and selectivity of 1340 GPU and 486 respectively were obtained.

Ingole et al. [68] fabricated polyethersulfone (PES) hollow fiber membranes via phase inversion technique. Composite layers were deposited on the surface by interfacial polymerization using four different aqueous phase monomers: 1,3-benzenedithiol (BDT), m-phenylenediamine (MPD), 1,3,5-benzenetrithiol (BTT), and piperazine (PIP). Trimesoyl chloride (TMC), was used to produce the covalent organic polymers. Mixed gas, water vapor and N₂, was used to investigate the gas

permeation activity of TFC membranes. Vapor permeation takes place through the membrane by the solution-diffusion mechanism. The TFC membrane with BDT exhibited superior results as water vapor permeance 2054 GPU, and the water vapor/N₂ selectivity 119. Table 5 shows the permeance of water vapor and N₂ in the mixed gas.

Table 5

Comparison of water vapor permeance and selectivity for various polymeric membranes.

Polymer	Temperature (°C)	Water vapor permeance (GPU)	Selectivity
PES-TFC-HF-1 ¹	30	2054	119 [H ₂ O/N ₂]
PES-TFC-HF-2 ²	30	452	41 [H ₂ O/N ₂]
PES-TFC-HF-3 [#]	30	1799	89 [H ₂ O/N ₂]
PES-TFC-HF-4 ⁴	30	903	66 [H ₂ O/N ₂]

- ¹. Polyethersulfone (PES)-TFC-HF-1 prepared by using 1,3-benzenedithiol and TMC.
- ². Polyethersulfone (PES)-TFC-HF-2 prepared by using MPD and TMC.
- ³. Polyethersulfone (PES)-TFC-HF-3 prepared by using piperazine and TMC.
- ⁴. Polyethersulfone (PES)-TFC-HF-4 prepared by using 1,3,5-benzene-trithiol and TMC.

From the above table, it was observed that the selectivity was comparatively higher than previously published work [69].

Ingole et al. [70] synthesized a novel thin film nanocomposite (TFN) membrane hybridized with amino functionalized acid-activated bentonite (ABn-NH) clay. The membrane was characterized by using physicochemical techniques including X-ray diffraction, BET surface analysis, thermal gravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM) and contact angle analysis. The concentration effect of ABn-NH clay (0–1.0 wt.%) on the permeation of water vapor and N₂ was investigated. It was observed that on incorporation of ABn-NH particles into the polyamide membrane, the permeance increases enormously. The best performance of ABn-NH-TFN-3 membrane (vapor permeance of 2809 GPU and water vapor/N₂ selectivity of 913) was achieved when additive loading was 0.5 wt.%.

Table 6 shows the performance of TFC hollow fiber membrane for the separation of gas or gas/water vapor mixtures.

Table 6

TFC hollow fiber membrane for separation of gases and water vapor transport.

Membrane	Use	Result	Ref.
CO₂/methane and CO₂/nitrogen separation			
PEBA - PEI	CO ₂ /N ₂	Permeate stream containing 62 mol % CO ₂ was obtained at a CO ₂ recovery of 20%. 99.4 mol % N ₂ in the residue with a nitrogen recovery of 36%.	[53]
Four kinds of TFC composite HFM. (TFC(MicroPES and Oxyphan) and two different permeable polymers (PTMSP and Teflon AF2400) for coating.	Gas separation	Exhibited high CO ₂ and N ₂ permeability with CO ₂ /N ₂ selectivity's between 3.4 and 2.5.	[55]
Pebax®1657/[emim][BF ₄] gel membranes in the form of thin film composite hollow-fiber membranes.	Separation of CO ₂ mixed-gas containing traces of water vapor and NO _x	Excellent mechanical durability. have the potential application for CO ₂ capture with real gas feed.	[54]
Modified air plasma and the Piranha etch PTMSP-PSF	CO ₂ permeance	High permeance (3.3×10 ⁵ GPU) in comparison with unmodified membranes including highest surface energy.	[56]

PDMS containing Cu ₃ (BTC) ₂ MOF-PSF	Gas permeation properties	<u>Permeation rates</u> increased. CO ₂ permeance increased from 69.7 to 109.2 × 10 ⁻⁶ cm ³ (STP)/cm ² s cmHg. CO ₂ /CH ₄ and CO ₂ /N ₂ selectivity's increased as well.	[57]
SO₂ Removal			
PEBAX/PEI	Removal SO ₂ from mixed gases	Permeance of SO ₂ and CO ₂ increased	[58]
PVC-g-POEM- PEI	Separation of gases. (SO ₂ , CO ₂ , N ₂)	Permeation of SO ₂ 105– 2705 GPU, selectivity of SO ₂ /CO ₂ was 3.9– 175.6. Mixed gas separation SO ₂ removal efficiency reached up to 84.5%.	[59]
O₂/N₂ separation			
PDMS or PEBAX-PSF (DCo))	Oxygen Enhancement Process	Higher gas permeance performance for both oxygen and nitrogen gas.	[60]
PDMS-PAN (DCo)	Gas separation	N ₂ permeance 280 GPU, O ₂ /N ₂ selectivity of 2.2, water vapor permeance ranging 800 to 3700 GPU	[62]
PVDMS-PVDF (DCo)	Gas separation (N ₂ /O ₂ separation)	Permeability and selectivity were in good agreement with the theoretical results predicted by the presented pore- distribution model.	[61]

PDMS-ceramic (DCo)	Oxygen enrichment from air	Permeance of 104 GPU with O ₂ /N ₂ ideal selectivity of 2.0	[63]
Water vapor transport			
PDA-PES (DCo)	Water vapor/N ₂ mixtures	Excellent selectivity. Permeance and selectivity as 3185 GPU and 195, respectively,	[64]
MOF incorporated TFN NH ₂ -MIL-125 (Ti)-PSF	Water vapor separation from flue gas.	The water vapor permeance was increased from 785 GPU, for thin film composite (TFC) membrane, to 2244 GPU (MOF@TFN3). Selectivity enhanced 116 to 542 with NH ₂ -MIL-125(Ti) MOF	[65]
ABn-NH-TFN –PSf	Water vapor/N ₂	Vapor permeance of 2809 GPU and water vapor/N ₂ selectivity of 913.	[68]
Carboxylated TiO ₂ +PA-HF	Flue gas dehydration	Permeance and selectivity of 1340 GPU and 486 respectively were obtained.	[67]
BDT, MPD, BTT), PIP – PES (4 monomers used for IP)	Water vapor/N ₂	BDT exhibited superior results as water vapor permeance 2054 GPU. and the water vapor/N ₂ selectivity 119.	[70]

6. Summary

Nowadays asymmetric thin film composite (TFC) polymeric hollow fiber (HF) membranes are extensively used in industrial gas/vapor separations and water

treatment. Many attempts have been made during the past decade to develop high flux TFC HFs, but those in the following areas seem particularly remarkable.

- 1) Among various methods to coat the thin selective layer on the porous sublayer, dip coating and IP are the most popular for practical applications.
- 2) The thin selective layer is developed mostly on the lumen side of HF.
- 3) As for gas/vapor separation, coating of the thin surface layer is done mostly by dip coating. There are only few examples of IP.
- 4) As for water treatment, applications of TFC HFs in FO and PRO are newly investigated for desalination purpose.
- 5) In pervaporation, applications of TFC HFs are most encouraging for alcohol dehydration.
- 6) Very little work has been done so far for the development of ceramic TFC HFs.

At present TFC HFs are still in early stage and need more R & D, especially to find the most desirable fabrication conditions. As the membrane technologies are economical, environmentally friendly, and easy to use, they are the leading choice for water purification, gas separation, dehydration of alcohols, separation of liquids etc. They will continue to be so for many years to come. TFC HF membranes will play a major role for the future advancement of the membrane technology.

7 References

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Abbreviation

ABn-NH	functionalized acid-activated bentonite clay
BDT	1,3 benzenedithiol
BTT	1,3,5-benzenetrithiol
CMCNa	sodium carboxymethyl cellulose
3,5-DABA	3,5-diaminobenzoic acid
DCo	Dip coating
DMS	dimethylsiloxane
FS	functional selective
GOTMS	3-glycidyloxypropyltrimethoxy-silane
HFM	Hollow fiber membrane
HPEI	hyper branched polyethyleneimine
IP	interfacial polymerization
IPC	isophthaloyl chloride
MPD	m-phenylenediamine
MWCO	molecular weight cut off
NF	nanofiltration
NPTs	nanoparticles
PAN	polyacrylonitrile
PAI	polyamide-imide
PDA	polydopamine
PDMS	polydimethylsiloxane
PEBAX	poly(ether block amide)
PES	polyethersulfone
Mpda	m-phenylenediamine

PIP	piperazine
PK	polyketone
PP	polypropylene
PQ-10	polyquaternium-10
PRO	Pressure retarded osmosis
PSF	polysulfone
PTMSP	poly[1-(trimethylsilyl)-1-propyne
PVA	polyvinyl alcohol
PVP	poly (4-vinyl pyridine)
PWF	pure water flux
RO	reverse osmosis
SIR	Silicon rubber
TDS	total dissolved solids
TEOS	tetraethylorthosilicate
TEPA	Tetraethylenepentamine)
TETA	triethylenetetramine
TFC	thin film composite
TFM	thin film membrane
TFN	thin film nanocomposite
TMC	trimesoyl chloride
TOC	total organic carbon