

Fluoropolymer Membranes for Membrane Distillation and Membrane Crystallization

Subjects: Polymer Science

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Fluoropolymer membranes are applied in membrane operations such as membrane distillation and membrane crystallization where hydrophobic porous membranes act as a physical barrier separating two phases. Due to their hydrophobic nature, only gaseous molecules are allowed to pass through the membrane and are collected on the permeate side, while the aqueous solution cannot penetrate. However, these two processes suffer problems such as membrane wetting, fouling or scaling. Membrane wetting is a common and undesired phenomenon, which is caused by the loss of hydrophobicity of the porous membrane employed. This greatly affects the mass transfer efficiency and separation efficiency. Simultaneously, membrane fouling occurs, along with membrane wetting and scaling, which greatly reduces the lifespan of the membranes. Therefore, strategies to improve the hydrophobicity of membranes have been widely investigated by researchers. In this direction, hydrophobic fluoropolymer membrane materials are employed more and more for membrane distillation and membrane crystallization thanks to their high chemical and thermal resistance.

Keywords: membrane distillation ; membrane crystallization ; fluoropolymer membranes

1. Introduction

In recent years, membrane technologies have been predominantly applied in many fields, such as food, pharmaceutical, printing, papermaking, aerospace, etc. This is due to their strong separation ability and many other advantages such as low cost, energy-saving and environmental impact compared to conventional technologies. Popular membrane operations include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), membrane distillation (MD), electrodialysis (ED), membrane contactors, etc. Among all these membrane technologies, MD and MCr are two membrane processes belonging to the membrane contactors family which need the use of microporous hydrophobic membranes. In these two processes, the microporous hydrophobic membrane acts as the interface to separate two phases, and the membrane pores provide the transport channels to realize mass transfer between the two phases. Different from the selective separation function of other general membrane processes, in the membrane contactors (as MD and MCr) the membrane does not have any selectivity for each component, but only acts as a barrier between two phases: the liquid phase is in contact with the feed side of the membrane, and the vapor phase is in contact with the permeate side of the membrane. Only volatile components can transfer from one phase to another through the membrane pores and are finally collected in the permeate side. The hydrophobic nature of the membrane prevents the feed liquid from penetrating into the membrane pores. Therefore, all non-volatile components are rejected in the feed side. In principle, the rejection of MD and MCr can reach 100%. The driving force of MD and MCr is the vapor pressure difference caused by the temperature difference and/or pressure difference (i.e., temperature difference for direct contact membrane distillation (DCMD) or pressure difference for vacuum membrane distillation (VMD)).

2. Membrane Distillation and Membrane Crystallization

2.1. Membrane Distillation (MD)

As mentioned above, MD is a thermally driven membrane separation process with a porous hydrophobic membrane as the separation medium, and the vapor pressure difference on both sides of the membrane as the driving force. One side of the hydrophobic membrane is in contact with the hot feed solution. As the volatile components in feed solution pass through the membrane pores, they are condensed and collected by the cooling medium on the permeate side. The main configurations of MD are direct contact membrane distillation (DCMD), vacuum membrane distillation (VMD), air gap membrane distillation (AGMD) and sweeping gas membrane distillation (SGMD). They differ according to the cooling medium on the permeate side.

DCMD is normally defined as the simplest design; here, the cooling liquid and the hot feed are directly in contact with both sides of the membrane, so the driving force is the vapor pressure difference caused by the temperature difference. Most DCMD configurations adopt counter-current configurations due to the maximum heat transfer efficiency and thus leading to the maximum mass transfer [1]. The flow rate of the hot side is normally higher than that in the cooling side. If the permeate side is changed into a vacuum, the configuration becomes VMD. The driving force is caused by the pressure difference between two sides of the membrane. Due to the constant vacuuming, the pressure for the permeate side is regarded as extremely low, so the driving force is higher compared with other types of configurations. For AGMD, there is an air gap in the permeate side and the vapor passes through the membrane as well as the air gap, and finally condenses on the cold surface of the permeate side. The transfer resistance for this type of configuration is high due to the existence of the air gap. Another configuration is SGMD, where an inert gas is normally selected as the cold sweep gas (such as nitrogen (N_2), carbon dioxide (CO_2), etc.). There are also other classifications of MD, such as osmosis membrane distillation (OMD), which is similar to DCMD but the permeate side contains a stripping solution, such as NaCl, $MgCl_2$, or $CaCl_2$ solution. The concentration of the stripping solution acts as the partial pressure contribution for the driving force. Liquid gap membrane distillation (LGMD) is one of the most recent configurations where a cold liquid (usually pure water) is normally maintained between a membrane and a cold surface. This configuration is rarely mentioned and applied in the literature, so it is not classified as a common configuration. Similarly, thermostatic sweeping gas membrane distillation (TSGMD) is a combination of SGMD and AGMD, of which a cold inert gas is circulated through the permeate side, carrying out the vapor permeate and condensing outside the membrane module in a condenser [2]. Other configurations such as vacuum-air gap membrane distillation (V-AGMD), vacuum-multi-effect membrane distillation (V-MEMD), permeate gap membrane distillation (PGMD) and material gap membrane distillation (MGMD) are also used as MD configurations.

The characteristics of these MD configurations are different in terms of energy efficiency, vapor flux, condensation method and thermal energy recovery. DCMD configuration is the simplest configuration and the one with the most choices in the experiments. DCMD configuration is characterized by high trans-membrane flux but lower thermal energy efficiency, while AGMD configuration presents high thermal energy efficiency but low flux [3]. AGMD configuration is more considered than SGMD configuration, but the problem of AGMD is that it is more complex to build up and the air gap is controlled with difficulty, which may induce the permeate accumulation in the air gap side [4]. Membranes for VMD configuration suffer the most severe fouling problem and have the highest wetting potential due to its higher pressure difference. In addition, the energy recovering of the SGMD and VMD configurations is more difficult than DCMD and AGMD configurations since the latter two configurations can recover the energy from the cooling plate and the permeate, respectively [5].

Electrical energy consumption in MD process is low because the pressure used is very low (around one bar) compared with pressure-driven processes such as RO. The recovery factor of MD is also high and it suffers the lowest concentration polarization phenomenon with respect to RO. The temperature used for the feed solution is relatively low and does not need to reach boiling temperature. So, it can be compatible with low-grade heat (such as waste heat) or sustainable heat (such as solar resources). It is independent with salinity; therefore, it can be used to treat highly concentrated solutions such as highly concentrated RO brine or high-salinity wastewater [6]. For what concerns the MD plant, it can be more compact and takes up less space compared to conventional distillation designs.

Although MD has many advantages, it also has disadvantages, such as temperature polarization (TP) and wetting. TP is the combined effect of fluid dynamics, low trans-membrane flux and heat necessary for the evaporation of the feed that reduces the temperature on the membrane surface [7].

The most significant problem of MD is that it still has limited applications at the industrial level due to the lack of available membranes. The membrane should have characteristics that meet the MD requirements. It should normally be hydrophobic and micro-porous to ensure the liquid retention and the transport of vapor. It also needs to possess high liquid entry pressure (LEP), high permeability, good thermal and chemical stability, low thermal conductivity and strong mechanical strength, narrow pore size distribution, proper thickness, etc. [8].

Over the years, efforts have been made to understand membrane characteristics and to develop novel membrane materials and modified membranes for MD. Both organic polymeric membranes and ceramic membranes are all desired membrane materials for MD. Ceramic membranes can be operated under harsh conditions, but its manufacturing cost is much higher so it is less favorable in commercial applications. Polymeric membranes are cheaper and are easier to be modified for MD applications, although they have many disadvantages, such as poor thermal and chemical stability.

2.2. Membrane Crystallization (MCr)

Similar to MD, MCr technology is also a promising separation technology which combines membrane separation and the crystallization process. In fact, MCr process can be regarded as an extension of MD process. The feed solution is firstly concentrated by MD process, and then further concentrated until supersaturation for obtaining crystals. The MCr process can promote crystal nucleation and growth in a well-controlled way, thus adjusting the final properties of crystals, including its structure (polymorph) and morphology (crystal shape, crystal size and crystal size distribution) ^[9]. Furthermore, the integrated technology of MD and crystallization further improves the possibility of treating some concentrated solutions. In this way, a high-quality water can be obtained, as well as crystal products with controllable properties, so as to avoid the pollution of water resources caused by the discharge of these wastewaters to the surface or underground ^[10].

MCr adopts microporous membranes as the media to transfer solvents. The total porosity of the membrane dominates the transmembrane flux, and the transfer characteristics are related to the membrane pore characteristics. It includes pore size, pore size distribution and channel curvature ^[11]. Therefore, the membrane used in MCr not only serves as the interface for vapor transport, but also as the role for controlling the supersaturation, nucleation and crystal growth.

Concentration polarization effect is also present in MCr process. There is a boundary layer in the feed side near the membrane surface where the concentration of the nonvolatile component is higher than that in the bulk solution. The microporous structure of the membrane can also embed the solute molecules which lead to a reinforced supersaturation. When the supersaturation occurs in the boundary layer, the interaction between the membrane surface and the solutes initiates the nucleation. After the nuclei growing for a period of time, they gradually aggregate into clusters and then into crystals. Then the gradually moving solvents promote crystallization in the bulk solution. Therefore, the membrane surface serves as a physical barrier and promotes heterogeneous nucleation ^[12].

Configurations for MCr are actually the same as that of MD, since MCr can be seen as the further concentration of feed based on MD. That is, DCMCr, VMCr, AGMCr and SGMCr (as indicated before). Among which, the DCMCr is the mostly utilized configuration for MCr because of its simple equipment design; SGMCr is usually used for removing volatile compounds from the feed solution such as in the food industries.

Other unconventional configurations include solvent/anti-solvent crystallization. These configurations adopt a mixture of solvents and anti-solvents in a solution as the original feed solution ^[13]. The chemical potential gradient between the two sides of the membrane generates a driving force (such as a temperature difference or a vapor pressure difference caused by the solvent and anti-solvent concentration difference, since the vapor pressure is higher for the solution with higher concentrations of solvent). The solution with a higher amount of anti-solvent has lower solubility for the solutes, so it is easier to precipitate them from the solution. This is also related to the anti-solvent addition configuration. In this type of configuration, the solute also dissolves in the mixture of solvent and anti-solvent solution, with the other side of the membrane gradually adding anti-solvent by generating a chemical potential difference. The addition of the anti-solvent enhances the supersaturation homogeneity of the solute in the solvent and therefore the solute crystallizes ^[14]. Another configuration related to membrane-assisted crystallization is solid hollow fiber cooling crystallization (SHFC). The feed solution is fed into the lumen side of the membrane and the cooling solution circulates in the shell side. When the temperature of the cooling solution is lower than the feed saturation temperature, the crystallization occurs ^[15].

As the driving force of MCr is the trans-membrane vapor pressure difference, increasing the feed temperature can improve the mass transfer by increasing the saturated vapor pressure on the feed side. However, higher temperatures may cause a high risk of membrane fouling for those solutes with low solubility at high temperatures. Therefore, it is necessary to find the appropriate operating temperature on the feed side for the different solutes. Since the crystals' nucleation could be formed on the membrane surface, it is easier for the membrane suffering from fouling. For the application of MCr in desalination of seawater, calcium is the common chemicals precipitated on the membrane surface. Several methods have been used in MCr to avoid this type of fouling, such as the chemical pretreatment of the feed to be concentrated via MCr, for example by adding $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ for removing 98% of Ca^{2+} ^[16]. Pretreatment process is often chosen to reduce organic matter in the bulk solution to avoid wetting, because the presence of organic matter can influence crystal structure. MCr process can also be combined with other technologies to fulfill long-term operation ^[17].

3. Preparation of Fluoropolymer Porous Membrane for MD/MCr

3.1. Preparation of PVDF Membrane

3.1.1. Non-Solvent-Induced Phase Separation Method (NIPS)

The NIPS method is the most commonly used method to prepare porous UF/MF membrane at an industry level. The basic principle is that the polymer solution is scraped onto the support or extruded and then immersed in a non-solvent bath (NIPS technique). In the bath, when the solvent in the polymer solution is dispersed into the non-solvent, the non-solvent also diffuses into the polymer solution, and therefore the phase separation is formed under the bi-directional dynamic diffusion. Finally, the polymer gels and precipitates in solid form [18]. For NIPS method, the phase composition of the system changes during phase separation, which ultimately determines the membrane pore structure. Phase separation is the basis of pore formation.

The mixed system outside the binodal curve (region 1) is in the thermodynamically stable region that forms a stable starting polymer solution, then there is a thermodynamic metastable region between the binodal curve and the spinodal curve (region 3). According to whether the system passes through the critical point or not, the liquid–liquid phase separation process can be divided into: the spinodal phase separation (passing through the critical point) and the nucleation phase separation (without passing through the critical point). Generally, if the composition of the system moves from below the critical point into the region 3, the system obtains a spherical structure with low mechanical properties; if the system enters the region 3 from above the critical point, the bi-continuous structure is obtained.

For PVDF membranes utilized in MD, the NIPS method is the most used one. There are many factors influencing the NIPS membrane preparation process. For example, the types of PVDF polymer and their initial concentration [8], the type of solvent and non-solvent [19], the composition and temperature of casting solution [20], the composition and temperature of coagulation bath [21], the characteristics of PVDF gelation and crystallization, and evaporation time [22][23] have been investigated for affecting the final structure and properties of the PVDF membrane. These properties also affect the membrane performance in MD. It is reported that the molecular weight of the PVDF polymer also affects the viscosity of the dope solution, which will finally affect the membrane surface energy and roughness. Chen et al. [24] compared three types of PVDF polymers with different molecular weight and applied them in VMD. Results show that the membrane surface roughness, surface energy and porosity all increased with increasing molecular weight, while the contact angle decreased with increasing molecular weight.

3.1.2. Thermally-Induced Phase Separation Method (TIPS)

Thermally-induced phase separation (TIPS) is a method for preparation of microporous polymeric membranes proposed by Castro [25] in 1981. The polymer is mixed with a specific diluent at high temperature to make a homogeneous casting solution, and then phase separation occurs during the cooling process. After preparation of the membrane, the corresponding extractant is selected to extract the diluent, and finally the microporous polymeric membrane is prepared. In short, it is “Dissolution under high temperature, and phase separation under low temperature”. The preparation of polymeric membrane by TIPS is mainly affected by the concentration, cooling rate, quenching temperature, diluent and additives. Temperature is the driving force of the whole phase separation process. The quenching temperature and cooling rate determine the pore size and the spherulite size, and ultimately affect the overall separation performance and mechanical properties. Membranes prepared by TIPS method usually have narrow pore size distribution, high porosity and the easy controlled microstructure [26]. The TIPS method was originally used to solve the problem of polymer materials (such as polyethylene, polypropylene, etc.) that is not suitable for the NIPS process, but it is widely used also for PVDF. Compared with the PVDF membrane prepared by NIPS, the strength of PVDF membrane prepared by TIPS has been greatly improved, thanks to the possibility of using a higher concentration of polymer in the starting dope solution, and the tensile strength can reach more than 10 MPa [27].

The liquid–liquid phase separation region and the solid–liquid phase separation region are separated by the dynamic crystallization line. The intersection point of the binodal curve and dynamic crystallization line is called the monotectic point, of which the corresponding polymer concentration is the critical concentration to distinguish the liquid–liquid phase separation and the solid–liquid phase separation in the system. For cooling paths 1, 2 and 3, the corresponding polymer concentration is lower than the monotectic point concentration, therefore resulting in liquid–liquid phase separation, and the obtained membrane is with bi-continuous structure. However, for path 4, the polymer concentration is higher than the monotectic point, thus resulting in solid–liquid phase separation, and the solidified membrane shows obvious spherical accumulation structure, indicating that liquid–liquid phase separation does not occur [28]. Generally speaking, when the polymer content in the casting liquid system increases gradually, the structure of the prepared membrane becomes more compact, and the porosity and pore size of the membrane will be smaller [29].

For the membrane preparation process of TIPS, solutions with good solubility and suitable interaction with polymers are generally selected as diluents, among which phthalic diluents such as dimethyl phthalate (DMP), diethyl phthalate (DEP), dioctyl phthalate (DOP) and dibutyl phthalate (DBP) [30] are representative, but these diluents are volatile at high temperature, therefore more and more researchers have begun to study environmentally-friendly diluents and multi-

diluents. PVDF, ECTFE flat sheet membranes and hollow fiber membranes have then been prepared by using environmentally-friendly diluent tri-n-butyl acetyl citrate (ATBC) [31][32]. The experimental results show that the increase of polymer concentration and quenching temperature is conducive to the densification of membrane structure, improving the mechanical properties, and reducing the pore size and porosity of the membrane. The contact angle of ECTFE membrane can reach 140°, the flux can reach a value of 22.3 L/(m²·h), and VMD process has a salt rejection of 99.9%. ECTFE flat sheet membrane by TIPS method was also prepared with trioctyl trimellitate (TOTM) as green diluent. The prepared membranes also presented high hydrophobic properties, excellent permeability and high salt rejection in VMD process [33].

3.1.3. Vapor-Induced Phase Separation Method (VIPS)

Vapor-induced phase separation (VIPS) was first proposed in 1918. It is a kind of membrane preparation method that first put the original membrane in the non-solvent vapor environment for a period of time, and then immerses it in the non-solvent coagulation bath to solidify the polymer into a membrane. For the membrane preparation process of VIPS, the main reason for phase separation is the inflow of non-solvent, not the outflow of solvent. Compared with NIPS method, the phase separation in VIPS process is more stable, and the mass transfer rate (non-solvent absorption and solvent extraction) is greatly reduced, which can effectively avoid large pore defects. During the membrane preparation process, the non-solvent phase is a gas; for the technical problems of controlling the gas state, at present, only a few gases are reported to be used in VIPS process. The most common one is humid air, and in addition, there are water vapor, acetone vapor and ammonia vapor. Because the phase separation of VIPS mainly occurs at the environment via a non-solvent, the requirement for environmental conditions is high; the temperature and humidity all have a crucial influence on the final membrane morphology. Therefore, the membrane preparation process of VIPS is generally completed in glove boxes or closed thermostatic glass chambers to control ambient temperature and humidity conditions [34][35].

VIPS method can be used to prepare polymeric membrane with a rough surface, so that it has high hydrophobic properties. Xie [36] and Mao [37] prepared porous and highly hydrophobic PVDF membranes with micro and nano-graded roughness by the VIPS method. Fan [38] used 100 RH% high humidity gas to prepare a hydrophobic PVDF membrane by the VIPS method. With the increase of vapor induction time, the membrane pores changed from asymmetric finger-like pores to symmetric sponge-like pores, and the membrane surface became rough and porous. The contact angle of hydrophobic membrane prepared by long time vapor induction could reach 145°. The membrane prepared under higher vapor-induced time also present higher flux in VMD. The best membrane showed a flux of 22.4 LMH at the feed temperature of 73 °C and NaCl rejection of 99.9% for 3.5 wt% concentration feed solution. The VIPS method can also be combined with NIPS for fabricating PVDF membranes. Russo et al. [39] prepared a PVDF membrane by V/NIPS method using TEP as a non-toxic solvent. The obtained membrane showed the asymmetric structure and the pore size in the range of UF membrane when a low concentration of PEG additive was used. The membrane showed bi-continuous structure and the humidity exposure time plays, and the important role of pore structure. The membrane showed thicker, higher porosity and more hydrophobicity when exposure time increased. The best membrane was prepared when the dope solution containing 15% PEG had an exposure time of 2.5 min before entering into a coagulation bath. The membrane presented 82.8% porosity, 0.43 µm pore size, and PWP at around 7900 L/m²·h·bar, which has the potential to be used for MF application. They also prepared the membrane in the range of UF that has potential to be used for MD [40].

3.1.4. Evaporation-Induced Phase Separation Method (EIPS)

For evaporation induced phase separation method (EIPS), a homogeneous solution is prepared by dissolving a polymer in the mixture of a solvent and a non-solvent, where the solvent has higher volatility than the non-solvent. By the evaporation of the solvent, phase separation phenomenon occurs from the solvent-non-solvent solution, forming a porous membrane. The pore structures can be controlled by adjusting the constitution of solvent-non-solvent solution. The major difference of EIPS method with VIPS method is that EIPS method is the outflow of solvent, not the inflow of non-solvent.

In general, the membrane prepared by VIPS or EIPS method has packed interconnected structure due to the liquid-solid mixing by crystallization and polymer gelation [41].

3.1.5. Electrospinning

Zeleny conducted the electrospinning technique in 1914 [42]. From 1934 to 1944, a series of patents were proposed by Anton of electrospun polymer filaments [43][44]. Due to the increasing interest of nanomaterials and nanotechnologies in recent years, electrospinning is attracting more and more attention. It can fabricate nanofiber membranes with the diameters from micron to nanoscale. These membranes have the characteristics of high porosity, excellent pore interconnectivity, low density, large surface area, micron interstitial space and tailorable membrane thickness. Traditional electrospinning is composited of a high degree of voltage, one or more grounded collectors and a spinneret. It can be

classified into vertical and horizontal apparatus at ambient temperature according to its position and direction. According to the solution status, it can be classified into solution electrospinning and melt electrospinning [45]. Firstly, the polymer solution is introduced into the syringe, a high voltage is applied between the spinneret and the collector. When the voltage overcomes the surface tension of the polymer fluid, the electric field causes the droplet to deform into a conical structure. This charged polymer solution is therefore ejected into the collector, and in the meantime, most of the solvents evaporate due to the unstable whipping motion and the continuous elongation of electrostatic repulsion between the nozzle and the collector. Finally, solution solidification makes the electrospun membranes [46][47][48].

Liao et al. [49] utilized the electrospinning method for preparing PVDF nanofiber membranes. Polymer concentration and the spinning parameters were investigated; the prepared membranes were characterized and applied in the DCMD process. Results show that the optimized membrane exhibits a rough surface of high hydrophobicity with the contact angle higher than 135° and a stable flux of 21 kg/m²h with the 3.5 wt% NaCl feed solution. This result was better than a commercial PVDF membrane and nanofiber PVDF-clay membranes for DCMD applications. Yao et al. [50] investigated the effect of heat-press temperature, pressure and duration on the morphology and mechanical characteristics of PVDF-co-HFP membrane and the application in DCMD. The final optimal conditions were heat-press temperature at 150 °C, pressure of 6.5 kPa, and a duration for 8 h. The DCMD flux of 29 LMH and 99.99% salt rejection were achieved at feed and permeate temperature of 60 and 20 °C.

3.2. Preparation of PVDF-co-HFP Membrane

3.2.1. NIPS

The NIPS method could also be used for fabricating PVDF-co-HFP membranes. Fadhil et al. [51] fabricated a flat sheet PVDF-co-HFP membrane by dissolving the polymer into a green solvent TEP via NIPS method. The membrane showed a sponge-like pore structure. A series of polymer concentrations were investigated, and the lithium chloride was added as an additive to increase the pore size and porosity of the membrane. An isopropanol–water mixture was used as a coagulation bath and the membrane produced at a concentration of 12 wt.% showed good performance in a DCMD test. A flux of 16.1 kg/m²h was achieved under the feed temperature of 60 °C and a rejection of 99.3% was obtained.

4.2.2. TIPS

Yadav et al. [52] prepared PVDF-co-HFP flat sheet membranes by incorporating CNT@MOF5 as additives by TIPS method. The composite membranes were characterized by SEM, thermogravimetric analysis (TGA), X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) analysis. The membranes with incorporation of the nanoparticles show rougher surface and higher porosity than the original membrane. The application in MD process also shows higher flux, with 14.40 kg/m²h for the hybrid membrane. It was also used in recovering CaSO₄ and NaCl from sub-soil brine by VMCR. The recovered salts show higher purity with the confirmation from SEM and XRD. Khayet et al. [53] also prepared the PVDF-co-HFP flat sheet membranes by TIPS method. Optimized preparation conditions for preparing the hybrid membranes were investigated, such as the polymer and additive concentrations, solvent evaporation time and temperature of the coagulation bath. They were also optimized for the DCMD test. The results show that under the optimized conditions of 19.1 wt.% PVDF-co-HFP concentration with 4.99 wt.% PEG, at the temperature of 35 °C coagulation bath and 102 s solvent evaporation time, that the membranes show the best performance in DCMD with the 99.95% salt rejection and 4.41 L/m²h flux.

3.2.3. Electrospinning

Hou et al. [41] prepared superhydrophobic PVDF-co-HFP/SiNPs hybrid flat sheet membranes by electrospinning method. A polyester non-woven fabric was used as the support layer. All membranes present interconnected open morphology. The addition of the nanoparticles SiNPs enhanced the hydrophobicity of the membrane surface and the water contact angle reached more than 150°. The membrane surface presented the hierarchical structure due to the beads-on-string in the nanofibers. The membrane was tested in DCMD with 35 g/L NaCl as feed. The test was run for 240 h and the NaCl rejection remained 99.99%. The highest flux obtained was 48.6 kg/m²h. All these performances show great potential of the electrospinning hybrid membrane for MD. Su et al. [54] also prepared the PVDF-co-HFP membrane by electrospinning method and employed it in DCMD. The membrane showed a contact angle of 128° and a flux of 4.28 kg/m². A total of 99.99% salt rejection was obtained when operating in MD for 12 h.

3.3. Preparation of PVDF-co-CTFE Membrane

3.3.1. NIPS

The NIPS method is known as the dry-wet phase inversion method. Wang et al. [55] prepared a PVDF-co-CTFE flat sheet and hollow fiber membranes by the NIPS method. LiCl and PEG were utilized as pore formers and their effect on the membrane properties were also investigated. DMAc was used as a solvent and the membranes were characterized by SEM, XRD and FTIR, etc. The optimization of the membrane preparation conditions was investigated and applied in MD experiments. The final membranes showed the flux of 62.09 kg/m²h and the conductivity of the permeate side remained below 5 μ S/cm.

3.3.2. EIPS

Zheng et al. [56] prepared PVDF-co-CTFE membranes by EIPS and NIPS method. The polymer was mixed with additive and non-solvent to prepare the casting solution at the temperature of 30 °C. The solution was then stirred for 24 h to achieve the homogeneous transparent solution. After degassing under a vacuum oven for 24 h, the casting solution was spread uniformly on the support at the temperature of 50 °C in the oven. Then the solution was maintained in the oven for 15 s for evaporation. The membrane was then immersed in the non-solvent coagulation bath to form the membrane. Then the membrane was taken out from the coagulation bath for washing solvent and additives. The membrane was finally dried in the air. The effect of the LiCl additive was investigated on the membrane morphology and pore structure. The membrane preparation during phase inversion was also investigated for the membrane structure. The additive with 5% LiCl was tested in DCMD with a flux of 21.85 kg/m² and salt rejection of more than 99.99%, and the conductivity was lower than 15 μ S/cm. The membrane showed no wetting for about 6 h in MD.

3.4. Preparation of PVDF-co-TFE Membrane

NIPS + EIPS

Feng et al. [57] prepared PVDF-co-TFE membranes by the phase inversion method. The method used for phase inversion can be seen as a combination of the NIPS and EIPS methods. The polymer and additives were dissolved in the DMAc at the temperature of 50 °C. After the homogenous dope solution was prepared, the solution was degassed for 24 h at the temperature of 30 °C. The solution was poured on a glass and remained at this state for 30 s and then put into the distilled water for 10 min for forming of the membrane. Then the membrane was immersed into ethanol for 2 days to remove the remaining solvent and additives. Finally, the asymmetric porous hydrophobic membranes were obtained. The membranes were tested in MD and compared with the performance of a PVDF membrane. The mechanical strength and contact angle of the PVDF-co-TFE membranes were better than that of the PVDF membranes, indicating the potential as membrane materials for the MD process.

3.5. Preparation of PTFE Membrane

3.5.1. Stretching and Sintering

Stretching and sintering is normally suitable for those polymer materials that cannot be fabricated by phase separation methods. Particularly PTFE, which is a typical crystalline polymer that has negligible solubility in all common solvents, and it has extremely high melting viscosity. A method involving mixing and aging, billet preforming, paste extrusion, stretching and sintering has been developed to fabricate a porous PTFE membrane.

Li et al. [58] investigated and optimized the stretching conditions of the PTFE membrane preparation and its performance in MD. The result shows the highest peak in pore size distribution, when the stretching rate is 30%/s. At low stretching temperature and high stretching ratio, salt rejections were excellent up to 99.99%. Xiong et al. [59] also investigated PTFE ultrafine fibrous membranes by sintering before being electrospun with different PTFE/PVA mass ratios.

3.5.2. EIPS

Khumalo et al. [60] prepared PVDF/PTFE flat sheet membranes by the EIPS method; the polymer was dissolved in NMP solvent and stirred to obtain the casting solution. After degassing, the membranes were casted on a glass with the thickness of 0.2 mm. Then the solution containing nanoparticles were casted on the membrane. The membranes were exposed to the air for evaporating the solvent by EIPS method. The membranes were formed at 40 °C and dried at 60 °C to remove the solvent completely. The membranes were tested in DCMD for removing urine components such as ammonia nitrogen, K⁺, Na⁺, TOC, etc. This shows that the MD technology could be used for water regeneration.

3.5.3. Electrospinning

Xu et al. [61] prepared nanofiber PTFE membranes by the electrospinning method. The PTFE membrane was co-electrospun by polyacrylonitrile (PAN) on the PTFE precursor membrane. The Stöber method was chosen to grow SiO₂ nanoparticles on the membrane surface and fix them on the PAN surface through chemical bonds by sintering. The SiO₂

nanoparticles were then fluorinated by trimethoxy (1H, 1H, 2H, 2H-heptafluorodecyl) silane (17-FAS). The results show that the membrane had a water contact angle of 166.9° and oil contact angle of 134.5°. This amphiphobic membrane showed a stable flux of 17.09 L/m²h and high salt rejection of 99.96% in MD for a hypersaline solution containing oily saline and surfactant. It was endowed with high anti-scaling and anti-fouling properties and showed great potential in MD for wastewater treatment.

3.6. Preparation of FEP Membrane

Melt Spinning

Chen et al. [62] prepared FEP membranes by using melt spinning method. A mixture of FEP, DOP, KCl and SiO₂ were spun into the hollow fibers in a certain weight ratio by a twin-screw spinning machine. Under certain conditions, the FEP hollow fiber membranes were prepared. The membranes were then applied in VMD and obtained the rejections of 99.9%. Huang et al. [63] also prepared FEP hollow fiber membrane by melt-spinning method and characterized them by porosity, LEP, hydrophobicity, pore size for MD.

3.7. Preparation of ECTFE Membrane

3.7.1. TIPS Method

As indicated above, a group [31] prepared ECTFE flat sheet membranes by TIPS method by using a green solvent ATBC. The ECTFE particles were dissolved in ATBC solvent at 250 °C for 5 h to form a homogeneous solution and degassed for 4 h. The dope solution was poured into a preheated mould with a thickness of 250 µm for 20 min. Then the mould was put into a water bath for quenching at a certain temperature. Then the membrane was immersed into ethanol for 24 h to wash the remaining ATBC. The membrane was finally dried at 25 °C for 2 days. The effects of polymer concentration and quenching temperature on the membrane structure and performance were investigated. The membrane was finally applied in MD and achieved a flux of 22.3 L/m²h and a salt rejection rate of 99.9%.

3.7.2. Dip-Coating Method

A group prepared flat sheet ECTFE membranes on a non-woven support by dip-coating method [64]. Low point ECTFE particles were immersed in the first diluent DEA. DEG was chosen as the second diluent. The transparent homogeneous dope solution was obtained after stirring at 160 °C for around 1 h. Then after about 3 h of degassing, the non-woven support was immersed in this dope solution at the same temperature. The immersion time was investigated. After the immersion, the membrane was taken out and cooled in a DEG coagulation bath at 5 °C. The residue solvent was extracted by washing the membrane in 2-propanol and finally drying in the air. The membrane was applied in DCMD at 40–60 °C feed temperature, and a highest flux of 22 L/m²h was obtained and a highest 99.8% salt rejection was achieved, which shows the good performance of this type of non-woven supported membrane in MD.

3.7.3. Low Temperature TIPS Method

The low temperature TIPS method is to prepare the membrane by TIPS method but at a lower temperature than its melting point. Polymer used in this method is a low melting point ECTFE polymer, which is also called Halar® 901, supplied from Solvay Co., Ltd. Pan et al. [65] prepared ECTFE hollow fiber membranes using the L-TIPS method. The ECTFE particles were dried in a vacuum oven to remove moisture before usage. The particles and solvent were mixed at a certain proportion and then spun in the twin-screw machine to get the pristine hollow fiber membrane. N₂ was used to form the lumen of the hollow fiber, and the membrane was entering into a quenching bath to form the membrane. The residue solvent was extracted by immersing the membrane into the ethanol and the ethanol was washed with pure water. The membrane was finally dried in the air. Effects of the additive on the membrane structure and morphology were investigated. For this type of preparation method, NIPS and TIPS methods are simultaneously used. The membrane exterior surface becomes thinner with the concentration of composite powder and shows a bicontinuous structure. The membrane was applied in a submerged vacuum membrane distillation (SVMD), and a flux of 10.8 L/m²h and a salt rejection of 98.9% was achieved.

Since most of the preparation methods of ECTFE membrane lie in using the TIPS method, the selection of solvent is an important issue for the TIPS method. The research direction of ECTFE is in developing new green solvents and modifying membranes with high characteristics including hydrophobicity, mechanical strength and fouling resistance [66][67]. Green solvents are not only suitable for preparing ECTFE membranes but can also be used for replacing toxic solvents of other membranes, which will be discussed further in the next [Section 4.8](#).

3.8. Green Production of Fluoropolymer Membranes for MD/MCr

3.8.1. Triethyl Phosphate (TEP)

TEP is a much safer solvent, and it is only harmful when swallowed. Researchers using TEP to fabricate PVDF flat sheet and hollow fiber membranes for MD. Nejati et al. [68] produced PVDF flat sheet membranes with porosity below 75% and has a flux of 40 L/m²h (LMH). Chang et al. [69] also produced PVDF flat sheet membranes using TEP as the green solvent with the highest flux of 13 LMH in DCMD. Chang et al. compared TEP/PVDF dope solutions with NMP/PVDF system and proved that when both the coagulant solution and the bore fluid contained 30 wt.% TEP, the prepared hollow fiber membranes presented a promising flux of 20 kg/m²h and LEP of 1.8 bar. Fadhil et al. [51] prepared novel PVDF–HFP flat sheet membranes with TEP as the green solvent and LiCl as the additive. By adding IPA in the coagulation bath, the prepared membranes have higher membrane porosity, larger pore size, higher contact angle and higher DCMD permeation at the temperature of 60 °C (16 kg/m²h) and the salt rejection at 99.3%.

3.8.2. Ionic Liquids (ILs)

Ionic liquids (ILs) are a group of organic salts (containing anions and cations) that exist as liquids at a low temperature (below 100 °C). Because of its immeasurably low vapor pressure, it is called a green solvent. ILs has many superior characteristics, such as chemical and thermal stability, recyclability, non-volatility and high ionic conductivity [70][71]. It is attractive to researchers because it can dissolve some materials that are hardly soluble in other solvents and show different performance [72]. Typical ILs including [BMIM]Tf₂N [73], [EMIM]Tf₂N [74], [C₂MIM]OAc [75], [EMIM]OAc [76], [MMIM]DMP, [EMIM]DEP, [EMIM]SCN [77], [BMIM]SCN [78], etc., were used as green solvents to prepare membranes, but most of them are used for gas separation and blended with CA membranes. For more applications in MD and the preparation of hydrophobic MF and UF membranes need to be further explored in the future. Jun et al. [79] prepared PVDF–PTFE membranes with the incorporation of ionic liquid [BMIM]PF₆ as solvent. The incorporation of the ionic liquid decreased the pore size to about 0.58 μm and increased the LEP to 83 kPa. Additionally, the operation of the composite membrane in DCMD showed a longer lifespan, of about 26 h.

3.8.3. PolarClean

PolarClean is an environmentally friendly solvent due to biodegradable properties [80]. It derives from 2-methylglutaronitrile (MGN), and it does not pose risks for human health and the environment. It has a high boiling point and is miscible with water. Hassankiadeh et al. [81] used PolarClean as a solvent to prepare PVDF hollow fiber membranes for the first time. The effects of PVP concentration, poly(methylmethacrylate)(PMMA) concentration, glycerol concentration, coagulation bath temperature on the membrane structures were investigated. The results show that PVDF/PolarClean membranes led to α- and β-phase polymorphisms and the PVP additives formed the β-phase on the membrane surface. Jung et al. [82] fabricated a PVDF hollow fiber membrane with PolarClean as solvent by NIPS–TIPS methods. The effects of polymer concentration, coagulation bath temperature and composition, and additives on the membrane morphologies were investigated. The results show that the membrane prepared with Pluronic as an additive achieved narrow pore size distribution and water permeability to 2800 L/m²hbar. Zou et al. [83] prepared a PVDF membrane with Polar Clean as a green solvent via the co-casting method; the prepared membrane had a salt rejection of 99.9% and a contact angle over 120°. The highest flux reached 37 kgm⁻²h⁻¹. Saidi et al. [84] also prepared a PVDF–HFP flat sheet membrane by the NIPS method with Tamisolve® NxG as the green solvent. The prepared membranes were utilized in DCMD and MCr tests. The membrane showed good performance compared to the commercial PVDF membranes. The rejection rates were higher than 99.9% with good trans-membrane flux.

3.8.4. Organic Carbonates

Organic carbonates are also the sustainable solvent alternatives in membrane preparation. As an ester of carbonic acid, it consists of a carbonyl functional group attached to two alkoxy groups. General structures are R₁-O(C=O)O-R₂. It is biodegradable and has low eco-toxicity. It includes propylene carbonates (PC), ethylene carbonates (EC), glycerol 1,2-carbonate, dimethyl carbonates (DMC), diethyl carbonate (DEC), 1,2-Hexylene carbonate, and butylene carbonates (BC), etc. [85]. Ismail et al. [86] utilized EC, PC and BC as green solvents to fabricate PVDF membranes. Experimental and simulation tests were both investigated towards the phase inversion mechanism, crystalline structure, polymorphisms and morphologies, etc. The prepared PVDF membrane with EC as a green solvent showed the highest porosity and pure water permeability and therefore was applied in DCMD (with water flux at 25.6 kg·m⁻²·h⁻¹). The membranes prepared from EC or PC were β-phase and the membranes fabricated from BC were the mixture of α-phase and β-phase. The results indicate that the cyclic organic carbonates are attractive green solvents.

3.8.5. Other Non-Toxic Solvents

Other less toxic solvents such as γ -Valerolactone [87], diethylene glycol monoethyl ether acetate (DCAC) [88], glycerol triacetate (TRIACETIN) [28], triethylene glycol diacetate (TEGDA) [89], N,N-dimethyl lactamide [90], acetyl tributyl citrate (ATBC) [91], acetyl triethyl citrate (ATEC), triethyl citrate (TEC), diethyl adipate (DEA) [92], methyl lactate [93], maleic acid dibutyl ester (DBM) [94], dibutyl sebacate, γ -butyrolactone (γ BL) [95], and dihydrolevoglucosenone (Cyrene™) [96] have potential to be used as green solvents for MD.

Solvents including acetone, ethyl acetate, 2-methyltetrahydrofuran (2-MeTHF) were selected as prospective greener alternatives for tetrahydrofuran (THF) and dichloromethane (DCM) to dissolve polymer inclusion membrane (PIM) components. THF is commonly used to dissolve the base polymers PVC and PVDF-HFP, while DCM is used to dissolve cellulose triacetate (CTA). Carner et al. applied these greener solvents to fabricate PVDF-HFP-, PVC- and CTA-based PIMs and the results demonstrate that these PIMs can be performed in bio-based solvents instead of the conventional toxic solvents [97]. Russo et al. [40] used dimethyl isosorbide (DMI) as a green solvent to dissolve PVDF and PES to prepare UF and MF membranes by NIPS–VIPS method. Water permeability indicates that this membrane is suitable for water treatment. All these greener solvents have potential applications in MD and MCr processes, which could be used for future new membrane preparation.

References

- Li, B.; Sirkar, K.K. Novel Membrane and Device for Direct Contact Membrane Distillation-Based Desalination Process. *Ind. Eng. Chem. Res.* 2004, 43, 5300–5309.
- Laqbaqbi, M.; Sanmartino, J.A.; Khayet, M.; García-Payo, C.; Chaouch, M. Fouling in Membrane Distillation, Osmotic Distillation and Osmotic Membrane Distillation. *Appl. Sci.* 2017, 7, 334.
- Lei, Z.; Dai, C.; Chen, B.; Ding, Z. *Special Distillation Processes*; Elsevier: Amsterdam, The Netherlands, 2021; ISBN 0128205113.
- Qin, W.; Xie, Z.; Ng, D.; Ye, Y.; Ji, X.; Gray, S.; Zhang, J. Comparison of Colloidal Silica Involved Fouling Behavior in Three Membrane Distillation Configurations Using PTFE Membrane. *Water Res.* 2018, 130, 343–352.
- Karanikola, V.; Moore, S.E.; Deshmukh, A.; Arnold, R.G.; Elimelech, M.; Sáez, A.E. Economic Performance of Membrane Distillation Configurations in Optimal Solar Thermal Desalination Systems. *Desalination* 2019, 472, 114164.
- Rice, D.; Ghadimi, S.J.; Barrios, A.C.; Henry, S.; Walker, W.S.; Li, Q.; Perreault, F. Scaling Resistance in Nanophotonics-Enabled Solar Membrane Distillation. *Env. Sci. Technol.* 2020, 54, 2548–2555.
- Qasim, M.; Samad, I.U.; Darwish, N.A.; Hilal, N. Comprehensive Review of Membrane Design and Synthesis for Membrane Distillation. *Desalination* 2021, 518, 115168.
- Pagliero, M.; Bottino, A.; Comite, A.; Costa, C. Novel Hydrophobic PVDF Membranes Prepared by Nonsolvent Induced Phase Separation for Membrane Distillation. *J. Memb. Sci.* 2020, 596, 117575.
- Di Profio, G.; Curcio, E.; Drioli, E. Supersaturation Control and Heterogeneous Nucleation in Membrane Crystallizers: Facts and Perspectives. *Ind. Eng. Chem. Res.* 2010, 49, 11878–11889.
- Drioli, E.; di Profio, G.; Curcio, E. Progress in Membrane Crystallization. *Curr. Opin. Chem. Eng.* 2012, 1, 178–182.
- Wu, M.; Yuan, Z.; Niu, Y.; Meng, Y.; He, G.; Jiang, X. Interfacial Induction and Regulation for Microscale Crystallization Process: A Critical Review. *Front. Chem. Sci. Eng.* 2022, 16, 838–853.
- Jiang, X.; Shao, Y.; Sheng, L.; Li, P.; He, G. Membrane Crystallization for Process Intensification and Control: A Review. *Engineering* 2020, 7, 50–62.
- Di Profio, G.; Stabile, C.; Caridi, A.; Curcio, E.; Drioli, E. Antisolvent Membrane Crystallization of Pharmaceutical Compounds. *J. Pharm. Sci.* 2009, 98, 4902–4913.
- Hussain, M.N.; Jordens, J.; John, J.J.; Braeken, L.; van Gerven, T. Enhancing Pharmaceutical Crystallization in a Flow Crystallizer with Ultrasound: Anti-Solvent Crystallization. *Ultrason. Sonochem.* 2019, 59, 104743.
- Cui, Z.; Li, X.; Zhang, Y.; Wang, Z.; Gugliuzza, A.; Militano, F.; Drioli, E.; Macedonio, F. Testing of Three Different PVDF Membranes in Membrane Assisted-Crystallization Process: Influence of Membrane Structural-Properties on Process Performance. *Desalination* 2018, 440, 68–77.
- Macedonio, F.; Drioli, E. Hydrophobic Membranes for Salts Recovery from Desalination Plants. *Desalination Water Treat* 2010, 18, 224–234.
- Tibi, F.; Charfi, A.; Cho, J.; Kim, J. Fabrication of Polymeric Membranes for Membrane Distillation Process and Application for Wastewater Treatment: Critical Review. *Process Saf. Environ. Prot.* 2020, 141, 190–201.

18. Teng, H. Overview of the Development of the Fluoropolymer Industry. *Appl. Sci.* 2012, 2, 496–512.
19. Yeow, M.L.; Liu, Y.T.; Li, K. Morphological Study of Poly (Vinylidene Fluoride) Asymmetric Membranes: Effects of the Solvent, Additive, and Dope Temperature. *J. Appl. Polym. Sci.* 2004, 92, 1782–1789.
20. Lai, C.Y.; Groth, A.; Gray, S.; Duke, M. Impact of Casting Conditions on PVDF/Nanoclay Nanocomposite Membrane Properties. *Chem. Eng. J.* 2015, 267, 73–85.
21. Wang, X.; Zhang, L.; Sun, D.; An, Q.; Chen, H. Effect of Coagulation Bath Temperature on Formation Mechanism of Poly(Vinylidene Fluoride) Membrane. *J. Appl. Polym. Sci.* 2008, 110, 1656–1663.
22. Kong, X.; Lu, X.; Ren, K. Towards High-Performance Polysulfone Membranes: A Controllable Membrane Formation Process Using Surfactant in NIPS. *J. Taiwan Inst. Chem. Eng.* 2021, 129, 171–179.
23. Loh, C.H.; Wang, R. Effects of Additives and Coagulant Temperature on Fabrication of High Performance PVDF/Pluronic F127 Blend Hollow Fiber Membranes via Nonsolvent Induced Phase Separation. *Chin. J. Chem. Eng.* 2012, 20, 71–79.
24. Chen, Z.; Rana, D.; Matsuura, T.; Meng, D.; Lan, C.Q. Study on Structure and Vacuum Membrane Distillation Performance of PVDF Membranes: II. Influence of Molecular Weight. *Chem. Eng. J.* 2015, 276, 174–184.
25. Castro, A. Methods for Making Microporous Products. U.S. Patent 4,247,498, 27 January 1981.
26. Hassankiadeh, N.T.; Cui, Z.; Kim, J.H.; Shin, D.W.; Sanguineti, A.; Arcella, V.; Lee, Y.M.; Drioli, E. PVDF Hollow Fiber Membranes Prepared from Green Diluent via Thermally Induced Phase Separation: Effect of PVDF Molecular Weight. *J. Memb. Sci.* 2014, 471, 237–246.
27. Li, X.; Xu, G.; Lu, X.; Xiao, C. Effects of Mixed Diluent Compositions on Poly(Vinylidene Fluoride) Membrane Morphology in a Thermally Induced Phase-Separation Process. *J. Appl. Polym. Sci.* 2008, 107, 3630–3637.
28. Rajabzadeh, S.; Maruyama, T.; Sotani, T.; Matsuyama, H. Preparation of PVDF Hollow Fiber Membrane from a Ternary Polymer/Solvent/Nonsolvent System via Thermally Induced Phase Separation (TIPS) Method. *Sep. Purif. Technol.* 2008, 63, 415–423.
29. Cui, Z.; Hassankiadeh, N.T.; Zhuang, Y.; Drioli, E.; Lee, Y.M. Crystalline Polymorphism in Poly(Vinylidenefluoride) Membranes. *Prog. Polym. Sci.* 2015, 51, 94–126.
30. Gu, M.; Zhang, J.; Wang, X.; Tao, H.; Ge, L. Formation of Poly(Vinylidene Fluoride) (PVDF) Membranes via Thermally Induced Phase Separation. *Desalination* 2006, 191, 160–167.
31. Xu, K.; Cai, Y.; Hassankiadeh, N.T.; Cheng, Y.; Li, X.; Wang, X.; Wang, Z.; Drioli, E.; Cui, Z. ECTFE Membrane Fabrication via TIPS Method Using ATBC Diluent for Vacuum Membrane Distillation. *Desalination* 2019, 456, 13–22.
32. Cui, Z.; Hassankiadeh, N.T.; Lee, S.Y.; Lee, J.M.; Woo, K.T.; Sanguineti, A.; Arcella, V.; Lee, Y.M.; Drioli, E. Poly(Vinylidene Fluoride) Membrane Preparation with an Environmental Diluent via Thermally Induced Phase Separation. *J. Memb. Sci.* 2013, 444, 223–236.
33. Liu, G.; Pan, J.; Xu, X.; Wang, Z.; Cui, Z. Preparation of ECTFE Porous Membrane with a Green Diluent TOTM and Performance in VMD Process. *J. Memb. Sci.* 2020, 612, 118375.
34. Caqueneau, H.; Menut, P.; Deratani, A.; Dupuy, C. Influence of the Relative Humidity on Film Formation by Vapor Induced Phase Separation. *Polym. Eng. Sci.* 2003, 43, 798–808.
35. Bouyer, D.; Vachoud, L.; Chakrabandhu, Y.; Pochat-Bohatier, C. Influence of Mass Transfer on Gelation Time Using VIPS-Gelation Process for Chitin Dissolved in LiCl/NMP Solvent-Modelling and Experimental Study. *Chem. Eng. J.* 2010, 157, 605–619.
36. Xie, Q.; Xu, J.; Feng, L.; Jiang, L.; Tang, W.; Luo, X.; Han, C.C. Facile Creation of a Super-Amphiphobic Coating Surface with Bionic Microstructure. *Adv. Mater.* 2004, 16, 302–305.
37. Peng, M.; Li, H.; Wu, L.; Zheng, Q.; Chen, Y.; Gu, W. Porous Poly(Vinylidene Fluoride) Membrane with Highly Hydrophobic Surface. *J. Appl. Polym. Sci.* 2005, 98, 1358–1363.
38. Fan, H.; Peng, Y.; Li, Z.; Chen, P.; Jiang, Q.; Wang, S. Preparation and Characterization of Hydrophobic PVDF Membranes by Vapor-Induced Phase Separation and Application in Vacuum Membrane Distillation. *J. Polym. Res.* 2013, 20, 134.
39. Marino, T.; Russo, F.; Figoli, A. The Formation of Polyvinylidene Fluoride Membranes with Tailored Properties via Vapour/Non-Solvent Induced Phase Separation. *Membranes* 2018, 8, 71.
40. Russo, F.; Galiano, F.; Pedace, F.; Aricò, F.; Figoli, A. Dimethyl Isosorbide As a Green Solvent for Sustainable Ultrafiltration and Microfiltration Membrane Preparation. *ACS Sustain. Chem. Eng.* 2020, 8, 659–668.

41. Hou, D.; Lin, D.; Ding, C.; Wang, D.; Wang, J. Fabrication and Characterization of Electrospun Superhydrophobic PVDF-HFP/SiNPs Hybrid Membrane for Membrane Distillation. *Sep. Purif. Technol.* 2017, 189, 82–89.
42. Zeleny, J. The Electrical Discharge from Liquid Points, and a Hydrostatic Method of Measuring the Electric Intensity at Their Surfaces. *Phys. Rev.* 1914, 3, 69.
43. Formhals, A. Method and Apparatus for the Production of Fibers. U.S. Patent 2,123,992, 10 May 1938.
44. Mestral, G. De Velvet Type Fabric and Method of Producing Same. U.S. Patent 2,717,437, 13 September 1955.
45. Demir, M.M.; Yilgor, I.; Yilgor, E.; Erman, B. Electrospinning of Polyurethane Fibers. *Polymer* 2002, 43, 3303–3309.
46. Raghavan, P.; Lim, D.H.; Ahn, J.H.; Nah, C.; Sherrington, D.C.; Ryu, H.S.; Ahn, H.J. Electrospun Polymer Nanofibers: The Booming Cutting Edge Technology. *React. Funct. Polym.* 2012, 72, 915–930.
47. Bhardwaj, N.; Kundu, S.C. Electrospinning: A Fascinating Fiber Fabrication Technique. *Biotechnol. Adv.* 2010, 28, 325–347.
48. Al-Qadhi, M.; Merah, N.; Matin, A.; Abu-Dheir, N.; Khaled, M.; Youcef-Toumi, K. Preparation of Superhydrophobic and Self-Cleaning Polysulfone Non-Wovens by Electrospinning: Influence of Process Parameters on Morphology and Hydrophobicity. *J. Polym. Res.* 2015, 22, 207.
49. Liao, Y.; Wang, R.; Tian, M.; Qiu, C.; Fane, A.G. Fabrication of Polyvinylidene Fluoride (PVDF) Nanofiber Membranes by Electro-Spinning for Direct Contact Membrane Distillation. *J. Memb. Sci.* 2013, 425, 30–39.
50. Yao, M.; Woo, Y.C.; Tijing, L.D.; Shim, W.G.; Choi, J.S.; Kim, S.H.; Shon, H.K. Effect of Heat-Press Conditions on Electrospun Membranes for Desalination by Direct Contact Membrane Distillation. *Desalination* 2016, 378, 80–91.
51. Fadhil, S.; Marino, T.; Makki, H.F.; Alsahy, Q.F.; Blefari, S.; Macedonio, F.; Di Nicolò, E.; Giorno, L.; Drioli, E.; Figoli, A. Novel PVDF-HFP Flat Sheet Membranes Prepared by Triethyl Phosphate (TEP) Solvent for Direct Contact Membrane Distillation. *Chem. Eng. Process. Process Intensif.* 2016, 102, 16–26.
52. Yadav, A.; Patel, R.V.; Vyas, B.G.; Labhasetwar, P.K.; Shahi, V.K. Recovery of CaSO₄ and NaCl from Sub-Soil Brine Using Incorporated Poly(Vinylidene Fluoride-Hexafluoropropylene) Membranes via Vacuum-Assisted Distillation. *Colloids Surf. A Phys. Eng. Asp.* 2022, 645, 128918.
53. Khayet, M.; Cojocar, C.; García-Payo, M.C. Experimental Design and Optimization of Asymmetric Flat-Sheet Membranes Prepared for Direct Contact Membrane Distillation. *J. Memb. Sci.* 2010, 351, 234–245.
54. Su, C.-I.; Shih, J.-H.; Huang, M.-S.; Wang, C.-M.; Shih, W.-C.; Liu, Y. A Study of Hydrophobic Electrospun Membrane Applied in Seawater Desalination by Membrane Distillation. *Fibers Polym.* 2012, 13, 698–702.
55. Wang, J.; Zheng, L.; Wu, Z.; Zhang, Y.; Zhang, X. Fabrication of Hydrophobic Flat Sheet and Hollow Fiber Membranes from PVDF and PVDF-CTFE for Membrane Distillation. *J. Memb. Sci.* 2016, 497, 183–193.
56. Zheng, L.; Wu, Z.; Wei, Y.; Zhang, Y.; Yuan, Y.; Wang, J. Preparation of PVDF-CTFE Hydrophobic Membranes for MD Application: Effect of LiCl-Based Mixed Additives. *J. Memb. Sci.* 2016, 506, 71–85.
57. Feng, C.; Shi, B.; Li, G.; Wu, Y. Preparation and Properties of Microporous Membrane from Poly(Vinylidene Fluoride-Co-Tetrafluoroethylene) (F2.4) for Membrane Distillation. *J. Memb. Sci.* 2004, 237, 15–24.
58. Li, K.; Zhang, Y.; Xu, L.; Zeng, F.; Hou, D.; Wang, J. Optimizing Stretching Conditions in Fabrication of PTFE Hollow Fiber Membrane for Performance Improvement in Membrane Distillation. *J. Memb. Sci.* 2018, 550, 126–135.
59. Xiong, J.; Huo, P.; Ko, F.K. Fabrication of Ultrafine Fibrous Polytetrafluoroethylene Porous Membranes by Electrospinning. *J. Mater. Res.* 2009, 24, 2755–2761.
60. Khumalo, N.; Nthunya, L.; Derese, S.; Motsa, M.; Verliefe, A.; Kuvarega, A.; Mamba, B.B.; Mhlanga, S.; Dlamini, D.S. Water Recovery from Hydrolysed Human Urine Samples via Direct Contact Membrane Distillation Using PVDF/PTFE Membrane. *Sep. Purif. Technol.* 2019, 211, 610–617.
61. Xu, M.; Cheng, J.; Du, X.; Guo, Q.; Huang, Y.; Huang, Q. Amphiphobic Electrospun PTFE Nanofibrous Membranes for Robust Membrane Distillation Process. *J. Memb. Sci.* 2022, 641, 119876.
62. Chen, K.; Xiao, C.; Huang, Q.; Liu, H.; Liu, H.; Wu, Y.; Liu, Z. Study on Vacuum Membrane Distillation (VMD) Using FEP Hollow Fiber Membrane. *Desalination* 2015, 375, 24–32.
63. Huang, Q.-L.; Xiao, C.; Miao, Z.-Q.; Feng, X.; Hu, X.-Y. Preparation and Characterization of Poly(Tetrafluoroethylene–Cohexafluoropropylene) (FEP) Hollow Fiber Membranes for Desalination. *Desalination Water Treat.* 2013, 51, 3948–3953.
64. Ursino, C.; Ounifi, I.; Di Nicolò, E.; Cheng, X.Q.; Shao, L.; Zhang, Y.; Drioli, E.; Criscuoli, A.; Figoli, A. Development of Non-Woven Fabric-Based ECTFE Membranes for Direct Contact Membrane Distillation Application. *Desalination* 2021, 500, 114879.

65. Pan, J.; Ma, W.; Huang, L.; Li, R.; Huang, Q.; Xiao, C.; Jiang, Z. Fabrication and Characterization of ECTFE Hollow Fiber Membranes via Low-Temperature Thermally Induced Phase Separation (L-TIPS). *J. Memb. Sci.* 2021, 634, 119429.
66. Falbo, F.; Santoro, S.; Galiano, F.; Simone, S.; Davoli, M.; Drioli, E.; Figoli, A. Organic/Organic Mixture Separation by Using Novel ECTFE Polymeric Pervaporation Membranes. *Polymer* 2016, 98, 110–117.
67. Müller, H.J. A New Solvent Resistant Membrane Based on ECTFE. *Desalination* 2006, 199, 191–192.
68. Nejati, S.; Boo, C.; Osuji, C.O.; Elimelech, M. Engineering Flat Sheet Microporous PVDF Films for Membrane Distillation. *J. Memb. Sci.* 2015, 492, 355–363.
69. Chang, J.; Zuo, J.; Zhang, L.; O'Brien, G.S.; Chung, T.S. Using Green Solvent, Triethyl Phosphate (TEP), to Fabricate Highly Porous PVDF Hollow Fiber Membranes for Membrane Distillation. *J. Memb. Sci.* 2017, 539, 295–304.
70. Zhao, H.; Xia, S.; Ma, P. Use of Ionic Liquids as “green” Solvents for Extractions. *J. Chem. Technol. Biotechnol.* 2005, 80, 1089–1096.
71. Xing, D.Y. Use Ionic Liquids for Hollow Fiber Spinning. In *Hollow Fiber Membranes*; Elsevier: Amsterdam, The Netherlands, 2021.
72. Kim, D.; Nunes, S.P. Green Solvents for Membrane Manufacture: Recent Trends and Perspectives. *Curr. Opin. Green Sustain. Chem.* 2021, 28, 100427.
73. Mariën, H.; Vankelecom, I.F.J. Optimization of the Ionic Liquid-Based Interfacial Polymerization System for the Preparation of High-Performance, Low-Fouling RO Membranes. *J. Memb. Sci.* 2018, 556, 342–351.
74. Dunn, C.A.; Shi, Z.; Zhou, R.; Gin, D.L.; Noble, R.D. (Cross-Linked Poly(Ionic Liquid)-Ionic Liquid-Zeolite) Mixed-Matrix Membranes for CO₂/CH₄ Gas Separations Based on Curable Ionic Liquid Prepolymers. *Ind. Eng. Chem. Res.* 2019, 58, 4704–4708.
75. Livazovic, S.; Li, Z.; Behzad, A.R.; Peinemann, K.V.; Nunes, S.P. Cellulose Multilayer Membranes Manufacture with Ionic Liquid. *J. Memb. Sci.* 2015, 490, 282–293.
76. Xing, D.Y.; Chan, S.Y.; Chung, T.S. Fabrication of Porous and Interconnected PBI/P84 Ultrafiltration Membranes Using OAc as the Green Solvent. *Chem. Eng. Sci.* 2013, 87, 194–203.
77. Xing, D.Y.; Peng, N.; Chung, T.S. Investigation of Unique Interactions between Cellulose Acetate and Ionic Liquid SCN, and Their Influences on Hollow Fiber Ultrafiltration Membranes. *J. Memb. Sci.* 2011, 380, 87–97.
78. Xing, D.Y.; Peng, N.; Chung, T.S. Formation of Cellulose Acetate Membranes via Phase Inversion Using Ionic Liquid, SCN, As the Solvent. *Ind. Eng. Chem. Res.* 2010, 49, 8761–8769.
79. Li, J.; Ren, L.; Shao, J.; Adeel, M.; Tu, Y.; Ma, Z.; He, Y. Effect of Ionic Liquid on the Structure and Desalination Performance of PVDF-PTFE Electrospun Membrane. *J. Appl. Polym. Sci.* 2020, 137, 48467.
80. Marino, T.; Blasi, E.; Tornaghi, S.; Di Nicolò, E.; Figoli, A. Polyethersulfone Membranes Prepared with Rhodiasolv® Polarclean as Water Soluble Green Solvent. *J. Memb. Sci.* 2018, 549, 192–204.
81. Hassankiadeh, N.T.; Cui, Z.; Kim, J.H.; Shin, D.W.; Lee, S.Y.; Sanguineti, A.; Arcella, V.; Lee, Y.M.; Drioli, E. Microporous Poly(Vinylidene Fluoride) Hollow Fiber Membranes Fabricated with PolarClean as Water-Soluble Green Diluent and Additives. *J. Memb. Sci.* 2015, 479, 204–212.
82. Jung, J.T.; Kim, J.F.; Wang, H.H.; di Nicolo, E.; Drioli, E.; Lee, Y.M. Understanding the Non-Solvent Induced Phase Separation (NIPS) Effect during the Fabrication of Microporous PVDF Membranes via Thermally Induced Phase Separation (TIPS). *J. Memb. Sci.* 2016, 514, 250–263.
83. Zou, D.; Hu, C.; Drioli, E.; Zhong, Z. Engineering Green and High-Flux Poly(Vinylidene Fluoride) Membranes for Membrane Distillation via a Facile Co-Casting Process. *J. Memb. Sci.* 2022, 655, 120577.
84. Saïdi, S.; Macedonio, F.; Russo, F.; Hannachi, C.; Hamrouni, B.; Drioli, E.; Figoli, A. Preparation and Characterization of Hydrophobic P(VDF-HFP) Flat Sheet Membranes Using Tamsolve® NxG Solvent for the Treatment of Saline Water by Direct Contact Membrane Distillation and Membrane Crystallization. *Sep. Purif. Technol.* 2021, 275, 119144.
85. Rasool, M.A.; Pescarmona, P.P.; Vankelecom, I.F.J. Applicability of Organic Carbonates as Green Solvents for Membrane Preparation. *ACS Sustain. Chem. Eng.* 2019, 71, 13774–13785.
86. Ismail, N.; Essalhi, M.; Rahmati, M.; Cui, Z.; Khayet, M.; Tavajohi, N. Experimental and Theoretical Studies on the Formation of Pure β -Phase Polymorphs during Fabrication of Polyvinylidene Fluoride Membranes by Cyclic Carbonate Solvents. *Green Chem.* 2021, 23, 2130–2147.
87. Rasool, M.A.; Vankelecom, I.F.J. Use of γ -Valerolactone and Glycerol Derivatives as Bio-Based Renewable Solvents for Membrane Preparation. *Green Chem.* 2019, 21, 1054–1064.

88. Wu, L.; Sun, J. An Improved Process for Polyvinylidene Fluoride Membrane Preparation by Using a Water Soluble Diluent via Thermally Induced Phase Separation Technique. *Mater. Des.* 2015, 86, 204–214.
89. Cui, Z.; Hassankiadeh, N.T.; Lee, S.Y.; Woo, K.T.; Lee, J.M.; Sanguineti, A.; Arcella, V.; Lee, Y.M.; Drioli, E. Tailoring Novel Fibrillar Morphologies in Poly(Vinylidene Fluoride) Membranes Using a Low Toxic Triethylene Glycol Diacetate (TEGDA) Diluent. *J. Memb. Sci.* 2015, 473, 128–136.
90. Gronwald, O.; Weber, M. AGNIQUE AMD 3L as Green Solvent for Polyethersulfone Ultrafiltration Membrane Preparation. *J. Appl. Polym. Sci.* 2020, 137, 48419.
91. Kim, D.; Salazar, O.R.; Nunes, S.P. Membrane Manufacture for Peptide Separation. *Green Chem.* 2016, 18, 5151–5159.
92. Ursino, C.; Simone, S.; Donato, L.; Santoro, S.; De Santo, M.P.; Drioli, E.; Di Nicolò, E.; Figoli, A. ECTFE Membranes Produced by Non-Toxic Diluents for Organic Solvent Filtration Separation. *RSC Adv.* 2016, 6, 81001–81012.
93. Rasool, M.A.; Van Goethem, C.; Vankelecom, I.F.J. Green Preparation Process Using Methyl Lactate for Cellulose-Acetate-Based Nanofiltration Membranes. *Sep. Purif. Technol.* 2020, 232, 115903.
94. Cui, Y.; Liu, X.Y.; Chung, T.S.; Weber, M.; Staudt, C.; Maletzko, C. Removal of Organic Micro-Pollutants (Phenol, Aniline and Nitrobenzene) via Forward Osmosis (FO) Process: Evaluation of FO as an Alternative Method to Reverse Osmosis (RO). *Water Res* 2016, 91, 104–114.
95. Su, Y.; Chen, C.; Li, Y.; Li, J. Preparation of PVDF Membranes via TIPS Method: The Effect of Mixed Diluents on Membrane Structure and Mechanical Property. *J. Macromol. Sci. Ence Part A Pure Appl. Chem.* 2007, 44, 305–313.
96. Marino, T.; Galiano, F.; Molino, A.; Figoli, A. New Frontiers in Sustainable Membrane Preparation: Cyrene™ as Green Bioderived Solvent. *J. Memb. Sci.* 2019, 580, 224–234.
97. Carner, C.A.; Croft, C.F.; Kolev, S.D.; Almeida, M.I.G. Green Solvents for the Fabrication of Polymer Inclusion Membranes (PIMs). *Sep. Purif. Technol.* 2020, 239, 116486.

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