THE USE OF PVDF-BASED MEMBRANE FOR TREATING INDUSTRIAL WASTEWATER IN THE PERSPECTIVE OF FABRICATION TECHNIQUE AND FOULING MITIGATION VIA ADDITIVE BLENDING AND SURFACE COATING

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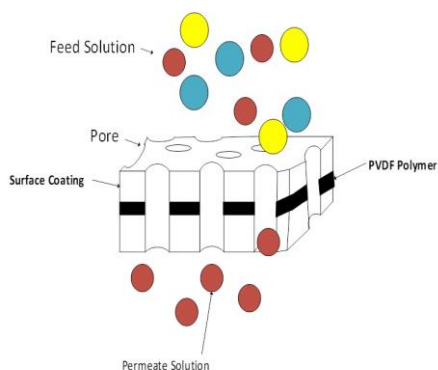[b]Department of Chemical Engineering and Petroleum Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

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Graphical abstract

Abstract

This review particularly discusses current development of PVDF (polyvinylidene fluoride)-based membrane technology for wastewater purification in terms of the potentiality, various fabrication techniques and specific fouling mitigation. Firstly, membrane technology for treating industrial wastewater and other polluted water is presented properly. In this section, essential aspects in membrane technology such as membrane usage in wastewater treatment field, fouling phenomena, fouling characteristics, and its mechanism would be explained. The second part then includes PVDF polymer, the utilization of conventional and green solvents used in membrane fabrication process as well as prominent methods available for fabricating PVDF-based membranes. Ultimately, the last section critically covers fouling mitigation efforts covering two prominent strategies namely additive blending and surface coating using novel substances as reported in current literature. Although some research related to the preparation of membrane materials has existed in the literature, there are still several challenging issues that need to be critically discussed deeper for establishing a reliable PVDF-based membrane and modifying the membrane for obtaining better properties of permeate flux, selectivity and anti-fouling leading to better membrane performance for purifying industrial wastewater containing high concentration of recalcitrant organic and inorganic pollutants. Overall, this review will considerably contribute to understand membrane fabrication and current surface modification as part of possible dependable loopholes for reducing fouling rate especially on PVDF-based membranes, and it will be a strong foundation for future research regarding the fabrication of polymeric membrane derived from PVDF having better durability and antifouling property.

Keywords: PVDF-based membrane, additive blending, surface coating, flux, fouling

1.0 INTRODUCTION

The increasing amount of polluted water due to massive development of industrial manufacturing sectors and increasing global population number has been a challenging issue for the sustainability of environment. Therefore, more efforts and interest in water recycling have been given to overcome this matter and avoid further damaging impacts [1, 2]. As there is a wide range of pollutants that can be discharged by various industrial and other human activities such as oil compounds, dyes and pigments, heavy metals, phenol, antibiotic compounds, and other organic and inorganic pollutants [3, 4], several wastewater treatment methods are then available to remove those harmful pollutants including advanced oxidation processes (AOPs), coagulation/flocculation, adsorption, biological techniques, and membrane separation [5].

While AOPs refer to the reduction of organic pollutants through mineralization process by utilizing hydroxyl radicals accountable for transforming the organic pollutants into other harmless substances, coagulation and flocculation link to the usage of chemical coagulant agents including aluminium and ferric chloride to separate pollutant particles from solution [6, 7]. Despite their effectiveness in the treatment, chemical cost and perilous by-product generation have been considered as the disadvantageous points of these methods [6, 8]. Furthermore, biological treatment that relates to the application of living microorganisms such as bacteria for breaking down the pollutants can be regarded as cost-effective and environmentally friendly choice. However, it tends to need longer reaction time and larger plant for treatment ponds [9]. Adsorption process is also prone to experience lower removal efficiency especially for treating industrial wastewaters that have high and complex organic loading along with the need of tackling saturated used adsorbent despite having simple application and lower energy consumption, [5, 10-12].

Therefore, membrane technology has gained an increasing interest due to its simplicity, faster time, and greater performance resulting in higher quality of treated water and wastewaters referring its ability to detect pollutant particles based on their size as seen in Figure 1 [2, 13, 14]. Other than that, membranes separation offers low carbon production and great pollutant rejection on various suspended impurities and pathogens through various mechanism namely size exclusion, adsorption and electrostatic repulsion [15-17]. Membranes act as selective barriers between two or more phases controlling particles or impurities transport.

In general, membrane materials can be categorised into four types namely (i) polymeric membrane; (ii) liquid membrane; (iii) ceramic membrane; and (iv) ion-exchange membrane [18]. In terms of polymeric membrane, several polymers such as polyethersulfone (PES), polyamide (PA), polysulfone (PSf), cellulose acetate (CA), and PVDF have been prominently used for fabricating different membrane types including membrane ultrafiltration (UF), microfiltration (MF), nanofiltration (NF), and reverse osmosis (RO) [19].
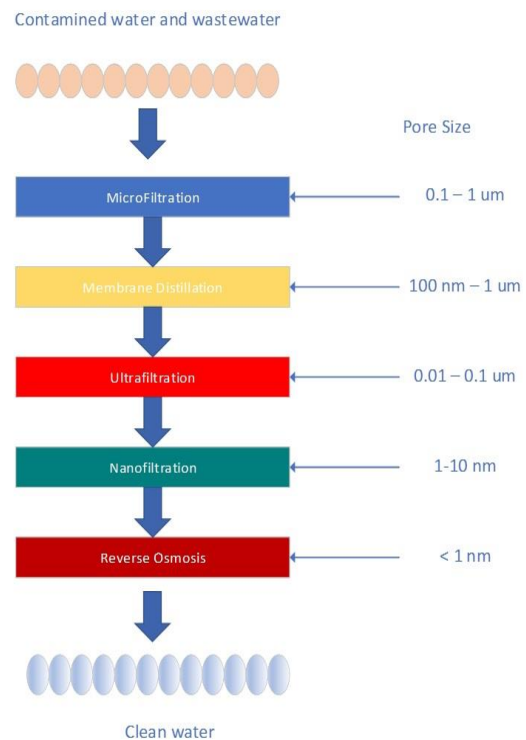
Figure 1 Membrane classification based on the pore size

Notwithstanding having excellent performance, membrane technology still has a complex issue named membrane fouling that reduces membrane capability in treating the feed and shortens membrane lifespan. Therefore, several fouling mitigations such the development of membrane module design, periodic maintenance, the application of pre-treatment process, and the modification of membrane characters have been proposed and investigated extensively [20, 21]. Among others, character modification on membrane through adding additives and coating the surface can be considered reliable to mitigate fouling and prevent severe irreversible fouling.

To the best of our knowledge, while there are some studies concerning the motigation of severe fouling and optimalization of membrane hydrodynamics via pre-treatment process and periodic cleaning, there is still limited review on chemical modifications strategies for overcoming membrane fouling on PVDF polymer-based membrane through additive blending and surface coating.

Chemical surface modification is believed to have significant benefit as it could alter membrane properties to obtain the desired behaviour by lowering the adsorption of organic and inorganic pollutants during filtration time. The coated membranes may also have better surface energy for water flux along with better selectivity on particle characteristic in the feed solution.

Therefore, this review focuses the discussion on the current breakthroughs of chemically modified membranes application on PVDF-based membrane

via additive blending and coating techniques. Additionally, other closely related aspects such as membrane fouling types, fouling mechanisms, PVDF polymer and solvents as well as prominent membrane fabrication methods would also be discussed critically for better understanding.

2.0 MEMBRANE

As explained above, despite having excellent performance, membrane technology, at some stages, still faces fouling phenomenon resulting in the reduction of its capacity in treating membrane feed along with shorter membrane lifespan. To get deep understanding related to membrane and fouling, this article then presents various fouling types, fouling mechanism, membrane materials and their fabrication techniques.

2.1 Membrane Fouling

Fouling on membrane is influenced by various parameters which connect to each other. The salient physical and chemical properties of membrane feed along with pollutants characteristics and their concentration have important roles in forming the severity and the patterns of membrane fouling [19, 22, 23]. Other than that, the specific properties of membrane itself also decide the nature of fouling speed as the feed has direct interaction with membrane surface that may be followed by some pollutants deposition.

The level of roughness on membrane surface could also directly impact fouling formation regarding hydrophobic behavior. In this case, membranes with high roughness tend to have more hydrophobic tendency due to higher trapped air particles on the pores. However, it is also considered that the presence of trapped air at the membrane/liquid interface as a result of high surface roughness could reduce the fouling tendency of the membrane. Increasing membrane surface roughness has been widely embraced in membrane distillation to improve the membranes' resistance towards fouling [24, 25].

Once there is fouling layer formed on membrane surface leading to flux decline, the coefficient of mass transfer should have higher resistance level of hydraulic and thermal points affected by the thickness and fouling film porosity. Different formed porous layers can solely react with thermal resistance where a fouling film with no or less porosity may provide well resistance reaction to thermal and hydraulic aspects. Moreover, fouled membrane surface will decrease the range of temperature values enabling more temperature-related polarization occurrence. This type of polarization happens when the bulk feed solution temperature differs from the membrane's interface temperature resulting in flux reduction [26, 27]. Furthermore, non-porous fouling film involving strong bond of hydrophobic sites of both pollutant particles and membrane pore/ surface has been considered as the most challenging fouling that need complex cleaning process due to hydrophobic contents like

oil compounds. As the main point affecting fouling severity is surface property, controlling membrane surface behavior then should be prioritized. Chemical modification on membrane properties including coating technique and additive blending affecting on the energy consumption, surface wettability, and membrane texture can be promising solutions to this matter [28, 29]. Some self-cleaning coatings, for example, can be applied to enhance antifouling feature of the membrane.

Other than that, in order to obtain better understanding of fouling mitigation, the types of predominant membrane fouling as well as their characters in nature should also be taken into account. The following section then discusses several well-known fouling classifications namely inorganic fouling, organic fouling, biological fouling, and colloidal fouling that can happen solely or simultaneously on membrane surface and pores. The fouling causing pollutants and their illustration were tabulated in Table 1 and displayed in Figure 2, respectively.

2.1.1 Inorganic Fouling (Scalling)

Inorganic fouling can be referred to inorganic compounds, such as calcium carbonate, silicate, aluminium oxide, calcium phosphate, and ferric oxide, in the form of solid particles accumulating on membrane pores or surface. They are part of membrane feed components undergoing scaling formation through particular mechanisms like crystallization and transport processes [24, 30]. Membrane scale deposit is triggered by the availability of some salt which has limited solubility in water. The change of temperature, solvent evaporation, and concentration polarization then can increase the amount of dissolved salt in membrane feed leading to super-saturation condition, nucleation, and crystallization mechanisms regarding crystalline solid formation. Crystallization process can be homogenous or heterogeneous. While heterogeneous type mainly happens at high operating pressure with lower feed rate, homogeneous crystallization is prone to occur at high pressure and average feed rate [30]. Several fouling layers generated on the membrane surface during crystallization mostly have relative tolerance on thermal change that influence temperature polarization giving negative impact on the driving force and permeate flux rate [30-32].

2.1.2 Organic Fouling

Organic fouling can be linked to the existence of natural organic matters (NOM) including bovine serum albumin (BSA), humic acid (HA), proteins, lipids, amino acids, and organic acids on membrane surface or inside membrane pores [33]. Membrane feed containing high concentration of NOM may degrade membrane hydrophobicity to some extent as the adhesion of organic matter on membrane surface can modify hydrophobic and electrostatic interactions. The adsorbed NOM on membrane pores will cause severe clogging on the pores and reducing permeate flux. This is because the

increasing NOM adsorption and other particulates can form a gel layer on membrane surface followed by the formation of cake layer containing particles with low permeability [34, 35].

2.1.3 Biological Fouling

Biological fouling happens due to the presence of living microorganisms on the membrane surface that accumulate on membrane surface forming biofilm. It then decreases membrane permeability and performance. Biofilm has specific structural component namely extracellular polymeric substances (EPS). This structures are molecular-weight natural polymers consisting of living, inactive, or decomposed microorganisms accumulated in multiple layers and relatively stubborn to remove. Consequently, this condition can partly or completely cause irreversible membrane blockage. A study related to biological fouling research on PVDF-based flat sheet MDBR reported that around 6% of permeate flux decline occurred during the first three days of wastewater treatment followed by another 51% of flux decline after 23 days. In this work, the biofilm thickness measured after operating for seven days and 20 days were reported between 2-8 mm and 20 mm, respectively [36]. Bacteria contained in membrane feed would thicken the biofilm by consuming EPS nutrients. The types of bacteria such as aerobic and anaerobic can also be influential for arranging the operating conditions. In this case, higher temperatures are unfavourable for the growth of aerobic bacteria, while some anaerobic bacteria and fungi can grow faster in such high temperatures.

2.1.4 Colloidal Fouling

Colloidal fouling is the effect of suspended colloids having nanometres or micrometres in size settled on membrane pores or surface leading to severe fouling level. Generally, colloidal particles can be linked to inorganic pollutants and organic macromolecules. While inorganic colloidal may consist of silica, clay, and aluminium silicate minerals, organic macromolecules can comprise proteins, polysaccharides, and other natural organic matters [37, 38]. There are some aspects affecting the formation of colloidal fouling including colloids characteristics, electrostatic interaction, and the frequency of particulate collisions along with membrane feed characters and operating condition. As other fouling types aforementioned, colloidal fouling layer will also enhance concentration polarization and mass transfer resistance resulting in lower permeate flux rate.
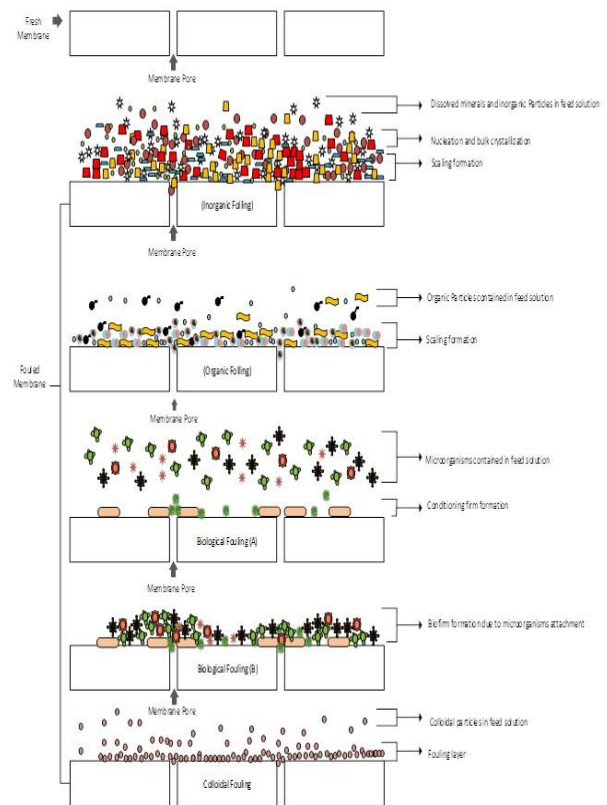

Figure 2 Membrane fouling types

Table 1 Four types of predominant fouling

Blocking type	Fouling-causing pollutants
Inorganic fouling	Inorganic particles such as dirt, dust, ice, crystal, $CaSO_4$, NaCl, $CaCO_3$, $MgSO_4$
Organic fouling	Organic particles such as oil and grease compounds, surfactants, organic solvents, organic dyes, protein, humic acid, carbohydrates, organic acids, alginate acid
Biological fouling	Biomolecules or microorganism such as fungi, aerobic and anaerobic bacteria, proteins, platelets, cells, viruses
Colloidal fouling	The combination of two or three fouling types (inorganic, organic and biological pollutants)

2.2 Fouling Mechanism

The rate profile of permeation flux during filtration time is the main indicator of fouling. By understanding its change or fluctuation, membrane operators and engineers can prepare future design or modification to both lengthen membrane lifespan and reduce fouling. Thus, the following formula is mostly applied for measuring permeate flux rate (Equation 1) [16]:

$$J = \frac{V}{A\,t} \qquad (1)$$

where J, V, A, and t are the permeate flux rate (L/m^2h), permeate volume (L) at certain time interval, active membrane area (m^2), and permeate collection time (h), respectively. Particular

application of general Hermia's model in each blocking type is stated in Table 2 tabulating Equations 2–5.

Table 2 Hermia's model equations fitted in blocking models

Blocking mechanism		n	Hermia's model	
Cake formation	layer	0	$\frac{1}{J^2} = \frac{1}{J_o^2} + K\,t$	(2)
Intermediate blocking	pore	1	$\frac{1}{J} = \frac{1}{J_o} + K\,A\,t$	(3)
Standard blocking	pore	1.5	$\frac{1}{J^{0.5}} = \frac{1}{J^{0.5}} + K\,t$	(4)
Complete blocking	pore	2	$ln\,(J) = ln\,(J_o) - K\,t$	(5)

Furthermore, the removal percentage of pollutant particles from contaminated solution is the next landmark of membrane performance that can be determined using Equation 6:

Removal efficiency = $(1 - C_p/C_f) \times 100$ (6)

Where C_p and C_f are the concentration of certain pollutant in permeate and feed solution, respectively (mg/L).

How the fouling can happen on membrane surface and pores has been an interesting matter to be further analysed. For this reason, Hermia's models covering four types of fouling mechanisms namely complete blocking, standard blocking, intermediate blocking, and cake filtration models then can be explored by following general Hermia's equation (Equation 7) [16, 32].

$$\frac{d^2t}{dV^2} = K \left(\frac{dt}{dV}\right)^n \qquad (7)$$

In Hermia's models, the cake formation type theorizes that pollutant particles may have a bigger size than the average membrane pore size. They will accumulate to build up cake layer on the surface by understanding that each particle could locate on other particles that already blocked the pores leading to no room available to directly obstruct some membrane area.

In contrast, the intermediate fouling will occur related to pollutant particles that have an equivalent size to the membrane pores. Pollutant particles may settle on previously existed particles that has blocked some pores or it will block some other membrane pores.

In terms of standard blocking, there is not uniform in particles adsorption on membrane surface or pores reducing membrane pores diameter and declining flux rate. In this model, each particle that arrives to the membrane would be deposited onto the internal pore walls reducing the pore volume. Moreover, complete blocking model claims that pollutant particle having a bigger size than the pores would settle on the surface of membrane and reduce permeate flux rate with time. In other words, the pollutant particle arrives to the membrane surface or pores participating to block the pore with no superposition of particles [16].

By involving Equation 1 for flux measurement, Hermia's model then can be rewritten as stated in Equation 8:

$$\frac{dJ}{dt} = -K\,(J - J_{ss})\,J^{2-n} \qquad (8)$$

Where K and J_{ss} are a constant and steady state permeation flux rate, respectively. The values of n for cake filtration, intermediate blocking, standard blocking, and complete blocking model are 0, 1, 1.5, and 2, respectively. More specific formulas of each model are tabulated in Table 2, while fouling mechanism illustrations were depicted in Figure 3.

Further, as part of membrane resilience and fouling reversibility indication, the analysis of membrane reusability is considerably important to measure. This can be evaluated by measuring the value of flux recovery ratio (FRR) that can be expressed as follows (Equation 9) [16]:

$$FRR = (J_{f,c} / J_{f,i}) \times 100 \qquad (9)$$

Where $J_{f,i}$ and $J_{f,c}$ are feed flux rate using a new membrane and a cleaned membrane, respectively.
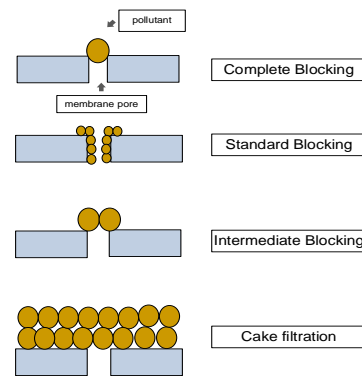
Figure 3 Membrane fouling mechanism based on Hermia's models

2.3 PVDF-Based Membrane

The PVDF, a multifunctional polymer comprising of around 59 wt. % of fluorine and 3 wt. % of hydrogen, is developed via polymerization process of monomer namely vinylidene fluoride ($C_2H_2F_2$). It has incredible features that resist creeping to some extent enabling it to be in polymerization level up to 2500 VDF monomers [39]. Other than that, it offers stable electrochemical and mechanical characters along with good degree of lightweight and dielectric points. Its durability to various chemicals can be linked to the release of hydrogen fluoride reacting with nucleophiles or the electron donor so it can adapt well to a wide range of chemicals, temperatures, and UV irradiation [39, 40].

The character of spherulitic structures in PVDF material will be eroded when it starts to solidify near the melting point. This phenomenon is influenced by complex morphological factors in the polymorphs form due to some crystalline-like structure indicating the existence of amorphous area. This thermoplastic fluoropolymer is odourless, tasteless, hydrophobic, and soluble in most of polar solvents. In terms of

water purification, PVDF has been used widely as main basic material for producing reliable porous membranes due to its particular characteristics aforementioned as well as its capability on the selection of diverse organic pollutants, excellent binding ability and versatile behaviour during fabrication process via phase inversion. Moreover, the usage of PVDF in membrane distillation, wastewater treatment, gas, and aqueous media separation processes has been extensively investigated even though its propensity of being fouled during membrane separation process was considerable especially for PVDF-based membrane with less or no internal and surface modification structure [41, 42].

2.4 Solvent

Solvents have an important function as they influence membrane morphological shape in conjunction with membrane property and practical outcome. There are several organic solvents such as N-methylpyrrolidone (NMP), N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetone, dimethyl phthalate (DMP), triethyl phosphate (TEP), and tetrahidrofuran (THF) that have less polarity than water along with water-like hydrogen bonding referring to the amphiphilic aggregation [19, 43]. Despite being used widely due to their ability to homogenously dilute a wide range of polymers, they are also known to be less environmentally friendly due to considerate level of flammability, irritability and toxicity. Therefore, their usage needs high level of precautionary to avoid health issues.

In accordance with the risk aforementioned, the use of safer solvents with lower toxic impact has gained more attention considering better human health and environmental sustainability. This phenomenon is supported by related membrane studies which have reported the performance of membranes fabricated using greener solvents such as organic carbonates, methyl lactate, triethylphosphate (TEP), polarClean, and γ-valerolactone.

Solvents derived from organic carbonate including propylene carbonate and butylene carbonate have been regarded as greener solvents referring their higher biodegradability value. Literature shows that combining this solvent type with ordinary polar solvent like NMP in NF membrane fabrication could reduce the amount of the NMP solvent used in the dope solution followed by a great rejection rate by more than 90% [44].

Other study produced PVDF based-membranes in the form of flat sheet and hollow fibre using TEP solvent in copolymer mixtures [45]. It reported some deferment occurred during phase separation process resulting in sponge-like membrane having lower flux than that of finger-like membrane. Other work confirmed that PVDF-based membrane made using TEP solvent could perform better in terms of permeate flux decline and pure water than membrane which were made using DMF, trimethylphosphate, and hexamethyl phosphoramide solvents despite lower protein rejection [46].

Furthermore, green solvent named rhodiasolv-polarclean which is derived from a by-product of nylon synthesis was claimed to have high biodegradability and water solubility when it was used to fabricate PVDF-based membrane [19]. The involvement of this solvent in the development of polymeric hollow fibre membrane resulted in a dense membrane with low water permeability. As this solvent can be easily miscible in water, thus varying temperature, and water-solvent diffusion can significantly affect phase separation process.

Green solvent named gamma valerolactone also has good solubility in water. It could be derived from lignocellulosic biomass like hemicellulose changed into furfural alcohol via acid hydrolysis process followed by esterification stage. A study proved that membrane using this solvent was effective to remove rhodamin B dye pollutant nearly 90 % implying its competitive performance as solvent [47].

2.5 Membrane Fabrication Techniques

2.5.1 Interfacial Polymerization

Interfacial polymerization technique is a widely applied option for fabricating RO, UF, and thin film composite NF membranes. The development of ultra-thin polyamide membrane via this technique has also been said as an excellent breakthrough for manufacturing desalination membranes.
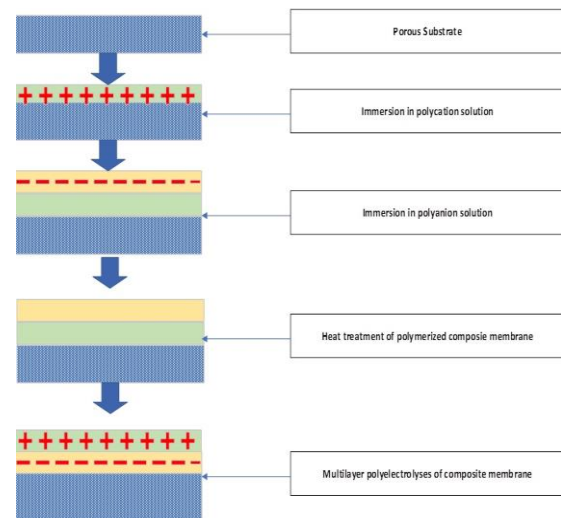

Figure 4 Interfacial polymerization process

In this method, amine diffusion stage into selected organic solution along with reactive monomers would result in compact polymer based-membrane having a very thin layer and less defects (Figure 4). It can strengthen membrane structure during pressure-based filtration [19]. Specifically, membrane layer will grow during the process until it confines the movement of amine diffusion yielding some restriction to the thickness of active membrane layer from 50 nm to 200 nm. Several reliable monomers that could be utilised in developing RO or NF membrane via interfacial polymerization technique are piperazine and trimesoyl chloride [19, 48].

2.5.2   Phase Separation Method

Polymer-based membranes have been highly considerable to be applied in wastewater treatment as they are notable for great selectivity degree, easy operational procedure, and the availability of various modification to improve their performance [2, 15]. For membrane production, phase separation techniques have been part of dependable methods applied extensively. These methods refer to some particular prominent classifications namely non-solvent induced phase separation (NIPS), temperature induced phase separation (TIPS), vapour induced phase separation (VIPS), and solvent evaporation induced phase separation (EIPS).

The non-Solvent induced phase separation (NIPS) is basically well known for fabricating porous polymeric membrane. In this process, a chosen polymer material or the mixture of two or more polymers needs to be dissolved in a solvent or a mixture of solvent and co-solvent in order to get a homogeneously uniform dope solution. Some additional pore formers, additive, or coating particles could be further added in the dope solution for obtaining better structure of membrane surface [49].
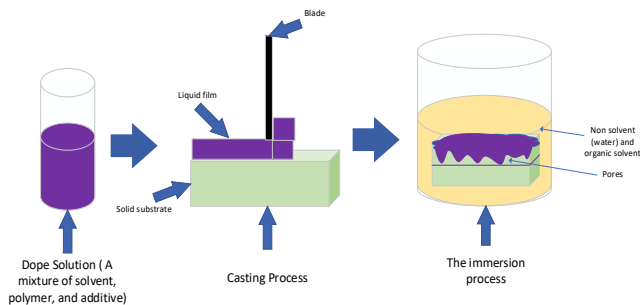
Figure 5 Non-solvent induced phase separation (NIPS)

The homogeneous dope solution has to be cast to form a liquid film on a prepared glass plate or the other polymeric substrate where it is further immersed in a coagulation non-solvent bath as seen in Figure 5. Subsequently, the process of phase inversion will happen when the solvent in the formed film could exchange with the non-solvent resulting in asymmetric membranes having dense selective layer with supportive sub-layer. While formed selective layer can provide rigorous selective separation for the membrane regarding the exception of size or charge, the porous supportive layer can strengthen membrane mechanical structure stabilizing the selective layer.

In the temperature induced phase separation (TIPS) method, a prepared dope solution comprising polymer and solvent is processed at decided temperature points near the chosen polymer melting point. It is followed by casting stage into a film for further cooling down step at lower or room temperature. Furthermore, the phenomena of phase separation will occur within the change of temperature points followed by the formation of a dense film. The TIPS mode could be applied for binary systems despite higher energy intensive needed due to required temperature limit [19].

In vapour induced phase separation (VIPS) method, a prepared dope solution cast in the liquid film is introduced to the non-solvent vapours atmosphere in the provided chamber [19]. Despite some particular similarities to NIPS method, the occurrence of phase separation happens along with the transfer mechanism of water vapour into the film as solvent diffusion into the vapour will create a compact membrane film. The development of PVDF-based porous membrane via VIPS technique was reported to exhibit the cellular structure at vapour temperature of 65°C. The cast liquid film exposing the vapour phase of non-solvent will delay the process of phase separation process leading to the formation of cellular contexture. This can be regarded to strengthened mechanical feature due to bi-continuous cellular structure of polymeric membrane [50].

For conducting evaporation induced phase separation (EIPS), a prepared solution film should be homogenous. It can be obtained by dissolving a chosen polymer into a mixture of solvent and non-solvent. In this case, selected non solvent should have lower volatility value than the solvent. Phase separation process will occur via solvent evaporation de-mixing of the mixture forming a high porous film. In this case, membrane pore structure could be conductible by modifying the mixture composition comprising polymer, solvent, and non-solvent [51]. It is worthy to understand the difference between VIPS and EIPS including their mechanisms. Specifically, in VIPS, a non solvent solution will diffuse into a polymer solution film in a vapour form, while for EIPS, a solution film would experience solvent evaporation promoting phase separation. On the other flip side, for VIPS mode, the non-solvent vapour diffusion into a solution film has been known to be the activator of phase separation process, while for EIPS, the diffusion of solvent and non-solvent from a liquid film hold the function of phase separation trigger [51, 52].

2.5.3   Electrospinning

Electrospinning process has been the emerging method for fabricating membrane due to its ability to prepare strong and smooth nanofibres having manageable morphological surface from a wide range of polymers. In this process, the involvement of high electric terrain application is a pivotal for generating expected nanofibres derived from the charged polymer solutions. The entangled fibres with three-dimensional porous network will lead to higher specific surface area and wettability. Various types of membrane fibre morphology and surface topography can be obtained by modifying parameters of electrospinning process along with the properties of polymer in the solution [53, 54]. A related study managed both the ramification and bending process of applied charged polymer jet via differing the voltage of electrical field during electrospinning in order to create columned tissue of the polymer nanofibres to form closed loops modes [55] (Figure 6).

In this technique, the formation of fibre in membrane structures is promoted by the repulsive electrostatic force given during electrospinning time. Some instabilities are possible to happen in relation to Coulomb interaction in charged fluid jet resulting in the jet instability dictating the end of fibres architecture leading to the formation of a Taylor cone in the tip of the needle by the polymer jet. This phenomena could make the jet exiting the needle causing jet thinning. Consequently, it would be followed by solvent evaporation that halts the polymer fibres depositing on the grounded collectors. Other than that, the instability of polymer jet could be followed by the breakage preventing continuous fibres formation as those nanofibres are generated when charged polymer jet bending to expand the loop. It then gathers on the substrates [56].

Additionally, the unstable condition may also occur at low polymer concentration prohibiting the formation of fibre due to low solution viscosity and less polymer entangled during fibre development. This occurrence is known as electrospraying that indicates particles or droplet formation. Literature has shown that the electrospun MD, RO, and NF membranes used for removing heavy metal ions and oil particles from the aqueous media were effective and efficient as they could give more supportive layer on membrane especially for desalination process of NF and MD membrane types [56, 57].
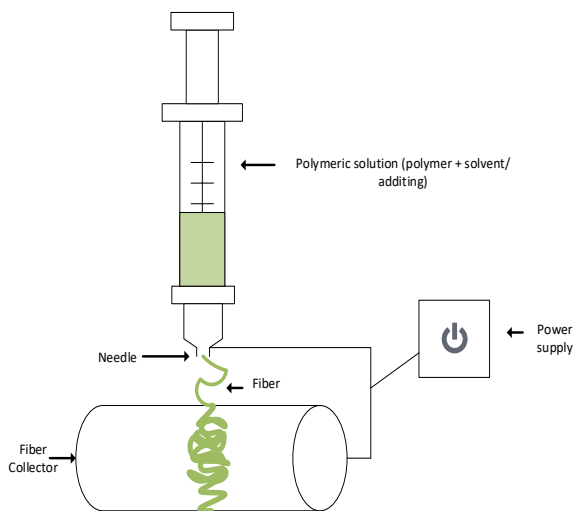

Figure 6 General electrospinning set-up

3.0 MEMBRANE SURFACE MODIFICATION

Preventing severe fouling and optimizing membrane hydrodynamics need reliable techniques such as conducting pre-treatment process, periodic cleaning, and chemical surface modification. Chemical surface modification including additive blending and surface coating for altering membrane properties to obtain the desired behaviour are considered effective to improve membrane performance internally and externally. They could reduce the adsorption of organic and inorganic pollutants during filtration time. Coated membranes may also experience better surface

energy that positively influenced water flux while having better selectivity on particle characteristic in the feed solution (Figure 7). Several studies then revealed various novel findings related to additives and coating compounds as seen in Table 3 and 4.

Complete pore blocking model assumes that every pollutant particle having a bigger size than membrane pores would settle on it. However, it is not superimposed upon other creating a single layer of pollutant particles blocking all pores, not the area within the pores. In this case, the function of additives previously predicted to have the capability of antifouling and self-cleaning has been proven by decreasing fouling rate.

3.1 Additive Blending

To begin with, Yuan *et al.*, (2021) developed an organic conductive PVDF-based membrane by applying polymerized additive named 3.4-ethylene dioxythiophene (EDOT) through chemical vapour deposition mechanism. They found an increasing hydrophilic behaviour on fabricated membrane which can be regarded to the existence of alkoxy group (-O-CH$_2$-CH$_2$-O-). This modified membrane showed better chemical stability during alkali cleaning even after the six cycles of short-term filtration where modified membrane given 1 V/cm of electric field showed more stable anti-fouling properties due to less filter cake formation on the membrane surface [58]. However, the adsorption ability of modified membrane in treating three different feed streams named bovine serum albumin (BSA), sodium humate and sodium alginate solutions reduced due to more blocked pores by PEDOT particle. In accordance with this blocked pore, modified membrane also showed smaller average pore diameter leading to lower pure flux from 848.52 ± 20.27 L/m^2/h to 338.93 ± 28.45 L/m^2/h. The PEDOT polymerization on the membrane surface has caused the increasing values of zeta potential, membrane roughness, and electrical resistance even after five cycles of cleaning process.

Furthermore, Mishra *et al.*, (2021) [59] tried to mitigate fouling by blending Ag@TiO$_2$ components with PVDF polymer along with the addition of (3-Aminopropyl) triethoxysilane (APTES) as a cross linker for holding nanoparticles through phase inversion technique. The synthesized membrane performed well by exhibiting a pure water flux up to three-fold of its blank version with BSA rejection by 96.3% or outperforming its virgin version by five-fold increase. The fabricated membrane also offered less nanoparticle wastage implying cost-effectiveness. Flux recovery ratio (FRR) also increased from 61.4% to 93.7% indicating better antifouling property, while SEM analysis showed uniformly dispersed nanoparticles within membrane matrix leading to higher membrane porosity.

Other work deployed a new combined polymer solution consisting of hexafluoropropylene (PcH) and polyethersulfone in NMP and DMF solvents mixture in the presence of lithium chloride additive which was claimed to be the novelty in hydrophilic membrane fabrication model [60]. This research arranged both electrospinning and phase inversion methods for

finding new structure on membrane surface and characteristics. The modified membrane was then found suitable for membrane distillation purpose as it has high porosity and considerable hydrophobic tendency of more than 84.4% and 136.39°±3.1, respectively. The values were comparable to the commercial membrane available at the same type. Additionally, the morphological analysis showed the appearance of micro porous structure packed with complete interconnected multi fibrous layer and interstices amongst those fibres. This structure can be linked to lithium chloride blended with polymers. The additive increased membrane electrical conductivity leading to higher polarity when producing superfine nanofibre during electro-spinning process.

Zhu et al., (2020) blended PVDF polymer with the Fe_3O_4–palygorskite nanocomposites (MPGS) via chemical coprecipitation followed by phase inversion technique for the first time. This work anchored Fe_3O_4 nanoparticles on the surface of the palygorskite nanofibers forming deformed rebar-like patterns [61]. Further analysis found that MPGS addition to the membrane casting solution brought visibly positive changes in terms of membrane viscosity, tensile strength, morphological structure, water flux and BSA rejection rate. Compared to pristine membrane, pure water flux and FRR values increased significantly from 123.57 L/m^2h to 356.16 L/m^2h and from 31.6% to 80%, respectively. On the other flip side, BSA flux also increased from 18.80 L/m^2h to 27.52 L/m^2h. These phenomena were caused by the changes of membrane pore size and surface roughness as the additives influenced membrane internal structures.

After comprehensive investigations, other novel copolymer named amphipathic pluronic® F127 can be found to be added into a dope solution to develop the distinct polymorph membrane surface [62]. Simulated surface water containing humic acid, bovine serum albumin and dextran was used as membrane feed. The newly proposed β-PVDF membrane was prepared by combining PVDF polymer and pluronic® F127 in NMP solvent using the non-solvent induced phase separation (NIPS) technique. It was further compared with a conventional a-PVDF membrane having no pluronic® F127 that utilised polyethylene glycol solution only. Ultimately, a series of filtration tests showed that modified β-PVDF membranes have better FRR than a-PVDF membranes even running under the same operating conditions. The study on amphiphilic PVDF membrane utilising block copolymer pluronic F127 was then continued by Zhao et al., (2021) [43]. They claimed that the element has both hydrophilic polyethylene oxide and hydrophobic polypropylene oxide groups mostly suitable for PES and other polymers, except for PVDF. Therefore, this study tried to find new approachable techniques to make it work well in PVDF polymer. Eventually, after some preliminary tests, they detected the efficacy of polytetrafluoroethylene (PTFE) particles as a binding agent. Through a combination step between non-solvent and thermally induced phase separation (N-TIPS) procedures, better stability of F127 in PVDF

membrane could be obtained. Moreover, when comparing with bare membranes, the modified membranes showed better porosity and tensile strength where lower water contact angle reduced from 102 ± 4° to 76 ± 3° along with higher pure water permeability by 869 ± 39 L/m^2hbar.

Further, graphene oxide-zinc sulfide (GO-ZnS) additive blended with PVDF polymer via phase inversion method has also been declared effective to reduce fouling [63]. This nanocomposite was synthesised via hydrothermal method by involving ultrasonication process. Both filtration and fouling tests indicated that the additive could reduce water contact angle by more than 20% implying higher hydrophilicity behaviour on membrane surface. these positive changes.

The invention of new additive named SnO_2-graphene oxide (SnO_2-GO) was also claimed by Chen et al., (2021) [64]. The nanocomposite was composed using a straightforward hydrothermal synthesis where fully sponge-like pores structure was created by the delay phase conversion. After a series of filtration tests, it was then found that valorised membrane has lower rate of flux reduction than that of primordial type. This outcome referred to some positive alteration regarding membrane resistance of flowing pollutant particles. On the other hand, membrane permeate elevated with water rinsing due to losing trapped protein on membrane surface indicating self-cleaning feature on membrane. This phenomenon was further seen after 30 min of UV irradiation in which the FRR of SnO_2-GO/PVDF membranes outperformed bare membrane, PVDF/GO and PVDF/SnO_2 membranes. Other than that, BSA rejection of SnO_2-GO/PVDF membrane was considered incredible with over 97.2% of rejection along with 363.2 L/m^2h of permeate flux. On the contrary, pristine PVDF could just attain 64% and 201.2 L/m^2h of the same parameters, respectively.

For membrane distillation, a study revealed the interesting finding on several additives namely SiO_2NPs made of functionalised silica (f-SiO_2) nanoparticles (NPs). In this work, silane reagents consisting of octadecyltrimethoxysilane (OTMS), N-octadecyltrichlorosilane (ODTS), and chlorodimethyl-octadecyl silane (Cl-DMOS) were utilised separately via in-situ electrospinning method [65]. The additives were produced via a green chemical reduction pathway involving the extract of apple and NaOH involving ultrasonication process. Firstly, the dope solution containing both PVDF polymer and one of SiO_2NPs was electrospun in situ. It then was coated with a layer comprising carboxylated multiwalled carbon nanotubes (f-MWCNTs) and silver nanoparticles (AgNPs). Sodium alginate, colloidal silica, and thermophilic bacteria effluent were used as representative solutions for organic, inorganic, and bio-foulant models, subsequently. Finally, the experimental tests showed that OTMS-SiO_2NPs membrane type averagely has the highest initial water flux and salt rejection of pristine and other modified membranes blended with ODTS or Cl-DMOS. They theorized that the formation of cake layer containing alginate grew a biofilm layer on membrane surface leading to lower pure water

fluxes. However, a coated membrane then indicated superhydrophobic behaviour referring its resistance to microbiological adhesion as well as avoiding the interaction between silanol-alginate substances, so it could maintain higher salt rejection and lower permeate flux decline for longer time.

Bian *et al.*, (2021) introduced a newly improved hollow fibre PVDF based-membrane for treating both BSA solution and dyeing effluent [66]. Polyvinylpyrrolidone (PVP), β-cyclodextrine (β-CD), polyethylene glycol (PEG), tween 80, PVP/β-CD, PEG/β-CD and Tween 80/β-CD were added separately in casting solutions containing 17% of PVDF and polymethyl methacrylate (PMMA) polymer dissolved in DMAc solvent. The membranes were prepared via dry-wet spinning technique. They concluded that the inclusion of 5wt.% PVP could enhance membrane porosity and pure water flux despite decreasing BSA rejection level. From another point of view, the same portion of β-CD could improve membrane tensile strength leading to stronger mechanical feature. However, this study pointed more to the addition of 5wt.% PVP and 1 wt.% β-CD which could show superior water flux and BSA rejection by more than 427 L/m^{2}h and 89.7%, respectively. When comparing to its pristine type, this modified membrane has more power to simultaneously eliminate COD, UV254, turbidity, and dye contents.

The fabrication of PVDF ultrafiltration membrane containing Cu_2S nanoparticles additive was also reported [67]. The additive was extracted from natural chalcocite involving ball-milling processes followed by non-solvent induced phase separation procedure. In general, initial hydrophilic tests denoted positive increment regarding the membrane performance. Around 0.2 wt% of additive addition was claimed enough to reinforce the values of pure water flux and FRR for up to 65% and 19%, respectively, compared with bare PVDF membrane under the same operating condition. Fouling assessment using BSA protein solution also showed the tendency of modified membranes to have better protein solution flux indicating better anti-fouling behaviour. In terms of treating dye solutions namely reactive blue 21, direct black 38, and direct yellow 12, the dyes rejection also increased within 1% to 30% as a result of the repulsion effect which was measured by comparing the zeta potential values between modified and pristine membrane.

Further, the effect of adding TiO_2 nanoparticles in flat sheet membranes for purifying humic acid solution via the in-situ colloidal precipitation technique was reported [68]. In this case, the effect of additive embedment, particle size on surface morphology, and anti-fouling characters were studied. Three different TiO_2 nanoparticles sizes; <8 nm (X500) and 20 nm (PC-20), and 21nm (P25) were deployed separately as additives in PVDF/DMAc casting solution having the ratio of 18:82. Ultimately, the study clearly stated that the P25 TiO_2 having 21 nm of particle size embedded membrane outperformed others in relation to the irreversible FRR, especially after getting UV irradiation for 6 h. However, the modified membrane containing X500 TiO_2 could exhibit others regarding anti-fouling and

de-fouling perspectives due to having smoother and higher reactive membrane surface area. The X500 TiO_2 nanoparticles also has the best water permeability encouraging the function of this fully anatase type on membrane hydrophilicity improvement.

Abba and colleagues then specifically assessed the effect of weight percentage of TiO_2 additive to learn the profile of permeate and water flux as well as pollutants rejection. They incorporated the nanoparticles within 0 to 2.0 wt% dosages to a mixture of PVDF/PVP via phase inversion method [69]. They reconfirmed that created membranes have better porosity degree and higher selectivity for removing copper contained in landfill leachate Specifically, laboratory tests showed that the addition of TiO_2 by 1.0 wt.% resulted in higher values of water flux, rejection rate, copper adsorption capacity by 223 L/m^{2}h, 98.18 %, and 69.68 mg/g, respectively, by obeying Freundlich isotherm model. Despite a little decline, permeate flux still remained stable after 340 min of filtration time. Deng *et al.*, [70] promoted other novel additive named bismuth oxychloride (BiOCl). They set the mass ratios of BiOCl/PVDF within the range of 3.5% to 17.4% through the deployment of both KCl and $Bi(NO_3)_3$ during PVDF membrane fabrication process. After conducting cross-flow filtration way, several points can be inferred as the results of comparative test between modified and control membranes. Firstly, fluxes of water and humic acid separation increased to two-fold and three-fold, respectively, along with three-fold enhancement of Cr (VI) adsorption. Secondly, the rate of BSA rejection was higher by reaching more than 90% for all three periods. On the contrary, control membranes faced massive fouling with less than 40% of BSA rejection. They argued that the interaction of protein-membrane and filtration hydrodynamics may have some correlation to hydrophilic property as the effect of surface-preferential and precipitation.

Finally, Lin *et al.*, (2021) [71] found a new additive invention namely 2-hydroxyethyl acrylate-terminated poly(styrene-alt-maleic anhydride) or (SMA-HEA). This compound consists of hydrophobic poly(styrene-alt-maleic anhydride) (SMA) and a hydrophilic 2-hydroxyethyl acrylate (HEA) made a ring-opening reaction. In this work, the performance of modified PVDF flat sheet membranes fabricated via nonsolvent-induced phase separation was compared to the primordial membrane. The dead-end filtration tests then gave promiscuous results where water contact angle could reduce significantly from 130° to 24.9° followed by decreasing protein absorption from 112.5 µg/cm^2 to 4.2 µg/cm^2, while the FRR value was levelled up from 42.5% to 100.0%. The Zwitterionic monomer influenced by SMA-HEA linker was believed having a big role behind this antifouling increment especially for protein based molecules like BSA and lysozyme.

3.2 Surface Coating

Efforts to reduce bio-fouling on PVDF-based membrane surface can also be conducted using coating process as done by some research groups

including Zheng and colleagues who firstly synthesised Cu-MOF-74 for coating membrane surface [73]. This compound was created by utilising chemicals named $Cu(OAc)_2$, MeOH, and 2,5-dihydroxyterphthalic acid within the range of 1.04 to 5.2 mg/cm^2. The commercially available PVDF membrane and simulated effluent containing Escherichia coli as bio-pollutants were used. Overall, they found the increase in roughness and hydrophilic properties on membrane surface leading to higher anti-bacterial rejection by above 97%. Through a dead-end membrane filtration set up, the decrease in initial pure water flux was recognised. However, an increasing amount of Cu-MOF-74 embedded on membrane surface has resulted in higher antibacterial tendency. The release of Cu^{2+} could also be overcome about one week in which Cu^{2+} production and hydroxyl radicals contributed to suppress E. coli generation by damaging their DNA.

Furthermore, Chen and colleagues discovered new coating substance comprising pyrogallol (PG) and N-[3--(Trimethoxysilyl)propyl]ethylenediamine (KH792) produced under alkaline atmosphere using tris buffer solution [74]. In this work, dodecane and soybean oil were prepared as membrane feeds which were then divided into different solutions named surfactant-free and surfactant-stabilized oil in water emulsions. Finally, the experimental data showed uncoated membrane has just about 377 ± 61 L/m^2h of pure water flux. In contrast, coated membrane using tris buffer solution, PG, and KH792 by 100 mL, 200 mg, and 100 mg, respectively, could unpredictably boost membrane water flux multiple times for up to 7166 ± 272 L/m^2h. However, at higher concentration of coating agents, negative outcomes impacted membrane thickness and pore blockage. This phenomenon can be linked to the increasing membrane surface wettability and decreasing water contact angle. Despite this issue, coated membrane was not prone to oil droplet contamination indicating its resistance along with incredible oil removal efficiency by more than 99% on average. Another impressed features of this coating agent was stable hydrophilic degree even in stronger acidity and higher salt condition making it versatile to be applied in industrial ways.

For the first time, the combination of AgNPs and cysteine (cys) flowers was used as coating agent for approaching an anti-adhesion system on membrane [75]. It was found that this synthesised material decreased the adsorption of organisms as well as their mechanism on the surface of coated PVDF membrane regarding trapped E. coli bacteria. To conclude, the existence of inorganic AgNPs and organic L-cysteine was believed effective to

preventing microorganisms growth derived from natural organic matter (NOM). Therefore, it would be dependable for further application in treating various raw NOM wastewaters.

In other case, the natural particle based-coating material named tannic acid (TA) has been reported potential by Wu *et al.,* (2021) [76]. They harnessed TA via combination process with titanium (IV) solution. A streamlined layer by layer self-assembly method was then implemented to prepare the coated membrane namely TA-Ti@PVDF composite membrane for separating oil/water emulsion. Through morphological analysis, the surface of unmodified membrane confirmed lower roughness than that of the TA-Ti@PVDF composite membrane which experiencing higher hydrophilicity and antifouling properties. With higher rates of oil emulsion permeation (689.6 L/m^2hbar) and foulant efficiency of 99.35%, the membrane performed stably even after immersion into acid and basic solutions or multiple filtration cycles.

Study reported by Yang *et al.* about the utilisation of different approach of natural tannic acid compounds by fabricating TA-Fe@PVDF nanocomposite via facile one-pot membrane surface coating is also interesting to be reviewed [77]. They deployed ferric nitrate and TA to completely separate oil/water emulsion stabilized by surfactant. This study then found that the new membrane composite having ratio of TA and Fe^{3+} by 1:3 has the best performance. It has low underwater oil contact angle and low oil adhesion despite higher separation efficiency of varying oil emulsions by more than 99.5%. Comparing with its pristine type, the coated membrane has significant enhancement in both separation and reusability rates leading to an assumption of its dependable application for treating assorted industrial oily wastewaters.
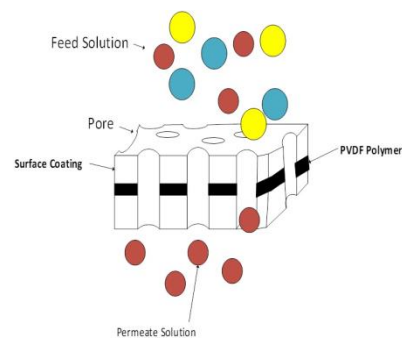

Figure 7 The illustration of coated PVDF-based membrane

Table 3 The PVDF-based membranes surface modification via additive blending

Membrane components	Solvent	Novel technique	Feed	Operating condition/ filtration experiment data	Cleaning process	In comparison with its unmodified version	Ref
PVDF, PVP, ethylene-dioxythiophene (EDOT), iron trichloride	DMAc	The combination of the immersion precipitation technique induced-phase inversion and polymerization of	BSA, sodium humate, sodium alginate	Anaerobic MBR, external pressure 200 mbar, membrane gap height 100 µm, continuous	HCl followed by NaOH/ NaClO mixed solution	Having lower pollutants adsorption, the increase in membrane resistance from	[58]

Membrane components	Solvent	Novel technique	Feed	Operating condition/ filtration experiment data	Cleaning process	In comparison with its unmodified version	Ref
		EDOT monomer in the vapour phase with co-polymer PVP		filtration for 8 h		$0.12 \times 10^{12} m^{-1}$ to $3.69 \times 10^{12} m^{-1}$, lower initial water flux by >50%	
PVDF, PVP, (3-Amino-propyl) triethoxysilan, silver nitrate (AgNO₃), TiO₂	NMP	Phase inversion technique followed by Ag@TiO₂ decoration, hydroxylation, and APTES addition	BSA protein solution	Room temperature, pressure 0.1 MPa, BSA solution 1 g/L, membrane active area 19.5 cm², rejection: 96.3% FRR: 93.7%	DI water and UV radiation	Having some increases in BSA rejection from 67.5% to 96.3%, and FRR from 61.4% to 93.7%	[59]
PVDF, amphipathic Pluronic® F127 additive	NMP	Non-solvent induced phase separation technique applied on the mixture of PVDF and amphipathic Pluronic® F127 in the solvent to create β-polymorph PVDF membranes	Simulated surface water containing humic acid, bovine serum albumin and dextran	The dead-end filtration test for 60 min, pressure 0.07 MPa, stirring 200 rpm, filtration time 1 h	DI water with stirring speed 600 rpm for 5 min	Having higher FRR, lower attractive bonding to pollutants and decrease in membrane-water interfacial interplays from 22.96 mN/m to 1.61 mN/m	[62]
PVDF, graphene oxide and ZnS nanoparticles	DMAc	PVDF polymer blended with synthesised graphene oxide-zinc sulfide (GO-ZnS) via the immersed phase inversion method	BSA protein solution	BSA solution 0.1 g/L, pressure 0.1 bar, filtration time 100 min, rejection: 87.1% FRR: 66.7 %	DI water followed by 30 min of UV radiation	Having self-cleaning, better antifouling characters, the increases in FRR and BSA rejection values from 56.5% to 66.7%, and from 86.2% to 87.7%, respectively	[63]
PVDF, octadecyltri methoxysilane, silica nanoparticles additive, carboxylated multiwalled carbon nanotubes and silver nanoparticles as coating agents	DMAc	PVDF-based membrane distillation prepared by in-situ electrospinning method was functionalized by SiO₂NPs derived from tetraethyl orthosilicate (TEOS), and was coated using functionalized MWCNTs and AgNPs	Sodium alginate, colloidal silica	Feed temperature 60 °C, Permeate temperature 20 °C, flow-rate 0.75 L/min, filtration time 50 h, surface area: $1.25 \times 10^{-2} m^2$	-	Having higher and stable flux profile. For colloidal fouling, rejection rate increased from 97.5% to 99.3%, while alginate fouling increased from 93.5% to >98 % at the end of filtration time.	[65]
PVDF, polymethyl methacrylate (PMMA). PVP, β-cyclodextrine	DMAc	Creating a novel hollow fibre PVDF/ polymethyl methacrylate (PMMA) based-membrane fabricated via dry-wet spinning by adding both PVP and β-cyclodextrine (β-CD) additives	BSA protein solution and dyeing effluent	Water flux measurement using single filament module at 0.1 MPa, BSA solution 0.1 g/L, pressure 0.1 MPa. Four hundred hollow fibers with effective length 60 cm installed in a module with 1 m² of effective surface area/ rejection: 89.7%	NaClO solution and oxalic acid solution	Adding 1 wt.% of β-CD and 5 wt.% PVP resulting in increasing pure water flux from 2.9 to 427.9 L/m²·h, lower contact angle from 83° to 25°, and higher BSA rejection into 89.7% with higher COD and dye removal	[66]

Membrane components	Solvent	Novel technique	Feed	Operating condition/ filtration experiment data	Cleaning process	In comparison with its unmodified version	Ref
PVDF, PVP, Cu$_2$S nanoparticles	DMAc	Preparing PVDF-based membrane containing PVP mixed matrix and Cu$_2$S nanoparticles (0.05 - 1 wt%) via non-solvent induced phase separation	BSA protein solution, reactive blue 21, direct black 38, and direct yellow 12	A dead-end system with four cells for water and dye filtration test. BSA solution 0.5 g/L, pressure 2 bar, filtration time 90 min/ BSA rejection:>98% Dyes rejection: 64.7%- 99.8% FRR: 92.4%	DI water	Having 65% and 19% higher water flux and FRR values, respectively, along with higher BSA and dyes rejection rate	[67]
PVDF, TiO$_2$	DMAc	Fabricating PVDF membrane containing 0.01 g/L of TiO$_2$ nanoparticle additive having different average crystalline size (<8, 20, and 21 nm) in separate membrane casting solution via in-situ colloidal precipitation technique	Simulated humic acid solution	Cross-flow membrane filtration test, membrane filtration area 72.0 cm^2, HA feed 2 mg/L, pH 7.1, FRR: 78.24 %	DI water followed by UV lamp irradiation	Membrane with TiO$_2$ crystalline size <8 nm outperformed others. Compared to the bare type, it reached increasing water permeability by 68.17%, lower fouling tendency from 24.24% to 14.69%, and decreasing FRR from 82% to 78.24%	[68]
PVDF, PVP, TiO$_2$	DMAc	Fabricating PVDF-based membrane blended with PVP and various amounts of TiO$_2$ nano-particles through phase inversion method	landfill leachate con-taining copper ions	A dead-end filtration mode, around 20 membrane pieces having uniform length of 35 cm each, pressure 0.3 MPa, total filtration time 200 min with 50 min for each evaluation interval/ rejection: 98.18%	Tap water	The increase in copper removal, and flux from 96.36% to 98.18 %, and from 89 to 157 L/m^{2}h, respectively, while contact angle reduced from 66.71° to 50.01°	[69]
PVDF, PVP, Bi(NO$_3$)$_3$, KCl, ethylene glycol	NMP	Phase inversion method used for fabricating PVDF-based membrane containing bismuth oxychloride nanocomposite particles derived from KCl and Bi(NO$_3$)$_3$ additives	HA, BSA, and Cr(VI) solutions	A Cross-flow filtration system, membrane effective area 2.5 cm^2, HA solution 0.1 g/L, BSA solution 1 g/L, pressure 0.32 bar/ rejection:> 90%/	HCl and DI water rinsing	The increase in the values of water flux, HA, BSA, and Cr(VI) removal from 377 to 854 L m^{-2} h^{-1} bar^{-1}, from 240 to 780 L m^{-2} h^{-1} bar^{-1}, from within the range of 10.5%-35.7% to > 90% in the three cycles, and from 0.25 mg/g to ~1.5 mg/g, respectively.	[70]
PVDF, polyethylene glycol (PEG), 2-hydroxyethyl acrylate, and	NMP	Grafting PVDF-based membrane through a branch-like structure of zwitterions using amphiphilic linker	BSA protein and lysozyme enzymes olution	A dead-end flow ultrafiltration test, pressure 1.66 bar, temperature 25 ± 1 °C, BSA solution 1 mg/mL,	Back-washing using pure water	Having double increase in FRR, lower water contact angle, and lower BSA and lysozyme	[71]

Membrane components	Solvent	Novel technique	Feed	Operating condition/ filtration experiment data	Cleaning process	In comparison with its unmodified version	Ref
polystyrene-*alt*-maleic anhydride (SMA-HEA)		made of 2-hydroxyethyl acrylate-terminated poly(styrene-*alt*-maleic anhydride) by the ring-opening reaction		filtration time 7h, active area 4 cm^2 / rejection: 90%, FRR 100%.		adsorption from 130° to 24.9°, from 112.5 to 4.2 µg/cm^2, and from 106.25 to 38.4 µg/cm^2 respectively.	
PVDF, Polytetrafluor oethylene (PTFE), Pluronic® F127	DMP and TEP	Developing immobilized pluronic F127 added in PVDF hollow fiber membrane dope solution along with a binding agent PTFE via combined non-solvent and thermally induced phase separation (N-TIPS) techniques.	BSA solution	Membrane modules having around 4 to 6 fibers, an effective length of 16.3 cm sealed on both ends were utilised, BSA solution 1 g/L, filtration time 120 min FRR 76.4%	DI water	Having higher porosity and pore size distribution. Water contact angle reduced from 102 ± 4° to 76 ± 3° while tensile strength increased from 6 MPa to 7 MPa. Decreasing flux from 74.4% to 62% and increasing FRR from 58.5% to 76.4%	[43]
PVDF, PVP, SnO$_2$ and graphene oxide (GO)	DMF	Developing SnO$_2$-GO/PVDF membrane having full sponge-like pores via delaying phase conversion technique	BSA protein solution	Filtration test at temperature 25 °C pressure 0.1 MPa, BSA solution 1 g/L, solution pH 7.4, rejection 97.2%, FRR 96.1%	DI water and UV radiation	Having higher pore size distribution and porosity, lower water contact angle and surface roughness where BSA rejection rate and FRR increased from 64% to 97.2%, and from 59.2% to 96.1%, respectively.	[64]
PVDF, halloysite n-notube	TEP	Introducing PVDF blended with halloysite (PHNT) through direct contact membrane distillation along with dissolution in TEP solution by immersion precipitation process	Simulated o hydroc hloride (OTC) solution	A cross-flow filtration test, membrane active area 47.5 cm^2, feed temperature 60 °C, permeate temperature 20 °C, OTC solutions 100 ppm and 10 ppm, filtration time 3 h, Rejection 100%	-	Having greater interfacial adhesion degree, better morphological uniformity, and near similar OTC removal	[72]
PVDF-co-hexafluoropr opylene (PcH), polyethersulf one (PES), lithium chloride	A mixture of NMP and DMF	A new PVDF membrane made of PcH and PES diluted in a solvent mixture containing NMP and DMF with additive lithium chloride via combining electrospinning and phase inversion methods simultaneously	Water	-	-	Modified membrane with 4 wt.% PcH has higher water vapor permeability than bare PcH polymer resulting in fabrication cost reduction over 50%, higher porosity value up to 84.4% ± 0.6.	[60]

Table 4 The PVDF-Based Membrane Surface Modification via Coating

Membrane components	Solvent	Novel technique	Feed	Operating condition/ filtration experiment data	Cleaning process	In comparison with its unmodified version	Ref
PVDF, polyethylene glycol, iron acetyl acetonate, Fe_3O_4-palygorskite nanoclay	TEP	Combining PVDF polymer with Fe_3O_4–palygorskite nanocomposites via chemical coprecipitation technique to produce PVDF-based ultrafiltration membrane	BSA solution	The dead-end filtration cell method, BSA solution 1 g/L, pressure 0.1 MPa, rejection 99.09%, FRR >80% %	Ultrasonically pure water	The increase in pure water flux, BSA rejection, and FRR from 123.57 to 356.16, from 90% to 99.09%, and from 31.6 to> 80%, respectively.	[61]

4.0 CONCLUSION

This review paper critically covers the research development of PVDF polymer-based membrane especially fouling mitigation efforts through chemical surface modifications. Other related aspects such as fouling mechanism, fouling types, solvents, and prominent membrane fabrication methods have also been selectively discussed. There has been increasing interest in finding novel substances or methods for reducing the chance of clogging or fouling on membrane surfaces. As the relationship of membrane surface and different pollutant particles is involving particular mechanisms, different types of membrane fouling namely organic fouling, bio-fouling, inorganic fouling, and colloidal fouling can occur solely or simultaneously. In this work, fouling mechanisms called Hermia's model consisting of cake layer formation, intermediate pore blocking, standard pore blocking, and complete pore blocking have been critically included. Eventually, chemical surface modifications comprising additive blending and membrane surface coating on PVDF-based membrane are then analyzed deeper. Surface modifications could encourage the existence of hydrophilic functional groups that positively influence membrane hydrophilicity and fouling severity. Newly developed additives such as ethylene dioxythiophene, aminopropyl triethoxysilane, and bismuth oxychloride along with novel coating compounds including Cu-MOF-74 and KH792 have brought massive improvements in terms of longer fouling formation and lower fouling severity on membrane during filtration time. Through those novelties, the use of PVDF-based membranes which have excellent pollutants removal efficiency, cost-effectiveness, longer life-span, simple procedure, and less fouling in the real industrial wastewater treatment can be more achieved in the near future.

Nomenclature

J	permeation flux ($Lm^{-2}h$)
V	volume of collected permeate (L)
A	active membrane area (m^2)
T	time taken in permeate collection (h)
Cp	permeate concentration (mg/L)
Cf	feed concentration (mg/L)
K	a constant
J_{ss}	permeate flux in steady condition ($Lm^{-2}h$)

Conflicts of Interest

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

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