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Recent Advances for Wastewater Treatment on Polyvinylidene Fluoride-Based Membrane: A Review

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Abstract

The development of scalable membrane-based separation processes has attracted considerable interest on laboratory and industrial scales. Polyvinylidene fluoride (PVDF) is one of the most widely used fluoropolymer materials for membrane fabrication due to its excellent mechanical strength, good thermal stability and chemical resistance as well as aging resistance. However, the hydrophobic nature of PVDF has resulted in serious membrane fouling during the filtration process. From the past decade, the embedment of hydrophilic materials in/on PVDF-based membranes can significantly alter the membrane's morphology and surface properties. Therefore, based on most articles retrieved from Web of Science, Scopus, Google Scholar, etc., this article provides the overview of the recent development of PVDF-based membranes during the recent several decades. The detailed information regarding PVDF as a polymer material as well as the main challenge in the development of PVDF-based membranes with better performance was summarised. Moreover, the factors influencing membrane fouling including surface hydrophilicity, roughness and

charge are also addressed. Then, the PVDF-based membrane preparation and its recent modification via the blending method were discussed. Finally, the overview and future perspective of PVDF-based membrane development are reviewed. Overall, it can be concluded that PVDF-based membranes have great potential for further advances towards the development of membrane technologies for the future.

1. Introduction

Water is the world's most precious and renewable resource and is a critical aspect of life. In the past few decades, the increasing world population and rapid industrial development intensify the clean water demand because of clean water resources shortage and massive pollution in fresh water. It has been reported that beyond 100,000 commercial dye products were discharged by the textile, paint, paper, leather and printing industries to the environment [1]-[3]. This pollutant will significantly affect human health, leaving victims with skin diseases, digestive disorders and a potential risk of cancer. Therefore, current wastewater treatment and safe water production technologies are necessary to remove these kinds of pollutants for a better future effectively.

Membrane technology application for augmenting freshwater supply is one of the fast-developing research fields. It has been widely used to treat all kinds of wastewater, including dye contamination, salt rejection, oil-in-water emulsions, etc [4]-[12]. The membrane-based process offers several advantages, such as no phase change requirement, low energy consumption, high efficiency, great selectivity, low chemical sludge effluent and excellent barrier to particles and pathogens, further representing an attractive solution to water pollution. The basic principle of any separation process is the minimum energy required to accomplish the process [13]. Therefore, the membrane itself is a key to successful separation. A membrane can be considered a physical “wall” that can separate two phases and only allows particular molecules to pass through it [14]-[16]. Membranes can be fabricated from a variety of different materials and can be classified as inorganic and polymeric membranes.

In recent years, inorganic and polymeric membranes have been extensively used due to their extraordinary properties, such as good mechanical and structural strength. Nonetheless, inorganic membranes commonly suffer lower permeability, making them less attractive to explore than polymeric membranes [16]. Hydrophobic polymers such as polyvinylidene fluoride (PVDF), polyethersulfone (PES), polydimethylsiloxane (PDMS), polyethylene (PE), polysulfone (PSU), etc., are typically used to prepare polymeric membrane. Among these polymers, PVDF has attracted much attention and become one of the most widely used membrane materials in wastewater treatment owing to their outstanding chemical and thermal stability as well as mechanical strength. To date, numerous studies have been reported on the development and application of PVDF membranes. However, fabricating PVDF membranes with excellent properties and performance remains challenging and hard to achieve. Deposition of some substances on PVDF-based membrane surfaces or inside their structure could result in poor membrane performance.

The remarkable accomplished progress of PVDF membrane leads to the present article which will focus on recent progress in the research and development of membrane separation technology with PVDF as a polymer material. Based on 169 articles published from 1991 to 2021, retrieved from Web of Science, Scopus, Google Scholar, etc., this article presents the theories and the advancement of PVDF-based membranes through the years. This article will also give an overview of PVDF characteristics and special emphasis on the emerging PVDF membrane challenge to treat wastewater efficiently. This work will also highlight the recent advances of PVDF membranes to overcome the challenge as well as enhance their separation performance. This article will also give an overview of PVDF characteristics and special emphasis on the emerging PVDF membrane challenge to treat wastewater efficiently. This work will also highlight the recent advances of PVDF membranes to overcome the challenge and enhance their separation performance. This article will be limited to the discussion for flat-sheet PVDF-based membrane performance incorporating hydrophilic materials such as metal oxide, carbon-based materials and hydrophilic polymer. It is believed that this review will provide important facts about the advancement of PVDF membranes, concurrently assisting researchers and the industrial sector in gaining a better understanding of PVDF-based membranes for future research and development.

2. Characteristics of PVDF Polymer

PVDF, from the family of fluoropolymers, is known to exhibit excellent chemical resistance, high mechanical strength and better thermal stability [17]-[19]. It also has been recognised as poly (1, 1-difluoroethylene) with a molecular formula of $-(CH_2CF_2)_{n-}$. Generally, PVDF is a semi-crystalline polymer with a typical crystallinity of 35 to 70% [17], [20], [21]. Its crystalline part is responsible for its mechanical strength and resistance, while its amorphous part is important for membrane flexibility [5], [22]. The melting temperature (Tm) and glass transition temperature (Tg) of PVDF are in the range of 155 to 192°C and -40 to -30°C, respectively, while its thermal

decomposition temperature is around 316°C. With these physical properties, PVDF has gained trust as a promising material for membrane fabrication.

Depending on their preparation method, PVDF can promote five different polymorphs (α-, β-, γ-, δ-, and ε-phases) [23]-[26]. Considering of crystallisation method, four polymorphs are well established, which are α-, β-, γ- and δ-phases [21], [27] with two types of dipoles: polar (β-, γ- and δ-phases) and non-polar (α-phase). Out of these polymorphs form, α-phase is easily found since it is developed from a molten PVDF over a broad crystallisation temperature range. Meanwhile, the β-phase can be formed either by mechanical stretching of PVDF or by adding nanofillers such as metal oxides, metal, carbon-based materials, etc. [25], [26]. Furthermore, the fact that the polymorph forms of PVDF can be converted to another form makes them an interesting material to explore. With the appropriate crystallisation condition and material utilisation with better piezo response, Peri et al. [26] successfully enhanced the β-phase content from 66.59 to 84.48 %. This was in good agreement with another study where 84 to 86% of β-phase content could be achieved with proper mechanical stretching and inclusion of graphene oxide (GO) or reduced GO (rGO) [28]. Nonetheless, it is important to have a stable α-phase of PVDF for membrane fabrication since it is a kinetically favourable phase compared to other phases, resulting in a membrane with better antifouling properties [20].

In addition, due to its polar property, PVDF is easily dissolved in some polar/organic solvents such as N-methyl-2-pyyrolidone (NMP), N, N-dimethylacetamide (DMAc), tetrahydrofuran (THF), N, N-dimethylformamide (DMF), triethyl phosphate (TEP), acetone, dimethyl sulfoxide (DMSO), etc. [5] and make them as an ideal material for membrane fabrication via phase inversion and electrospinning method. Furthermore, PVDF is also reported to exhibit better thermodynamic compatibility with other polymer such as poly (methyl methacrylate) (PMMA), polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP), etc., all over concentration range [29]-[33]. Despite its advantages, PVDF is highly hydrophobic due to its lower surface tension, which makes the fabricated PVDF membrane prone to fouling, further resulting in poor membrane performance.

3. Challenges in PVDF-Based Membrane Performance: Membrane Fouling and Trade-Off Effect

Although PVDF possesses excellent properties, they inevitably suffer from severe fouling as well as a trade-off effect between permeability and selectivity due to their hydrophobic nature. Since the beginning of membrane separation technology, membrane fouling and trade-off effect have become the bottleneck of the separation process, affecting the membrane's capability to perform well during filtration. Generally, fouling can be described as a detrimental deposition and accumulation of undesirable material (foulants) on the membrane surface or its pore due to the dye or contaminant adsorption [34]-[37].

The type of contaminant (foulant) presence on the membrane surface can be classified as organic, inorganic, colloidal and biofouling. Commonly, organic fouling is caused by non-biological organic contaminants deposition, such as cationic surfactants, hydrocarbons and humic acid (HA). In contrast, inorganic fouling occurs due to precipitation of dissolved ions and salts, including sulphates, hydroxides, metal chlorides and carbonates. Next, colloidal particles (silica, clay, iron and natural organic matter (NOM)) and high molecular weight organic substances (polysaccharides and proteins) are responsible for colloidal fouling. Meanwhile, biofouling occurs due to the deposition of biologically active organisms (extra-cellular polymeric substances, fungi, bacteria microbial cells and eukaryotic microorganisms) on the membrane surface.

Membrane fouling is a thoughtful and complex phenomenon to be understood in all pressure-driven membrane separation processes since, in most cases, it involves more than one type of foulant. It can occur when a cake layer forms on the membrane surface and/or the blockage of contaminants in the membrane pores [38]. The consequence of this situation is a rapid flux declined. At the same time as fouling is built-up, higher operation pressure and energy must be utilised to attain the desired throughput. It will indirectly affect the separation factor for targeted species in the feed, unstable product quality and poor recovery [37]. If this issue is not properly addressed, it could lead to early membrane replacement and damage further increase in operating cost [38], [39].

On the other hand, a trade-off between permeability and selectivity remains a major limitation in PVDF-based membrane fabrication and has been studied for a long time [40], [41]. The reported studies revealed that permeable PVDF-based membranes often presented less selectivity and vice versa. The trade-off behaviour was also detected in all PVDF-based membrane processes, including desalination, forward osmosis, ultrafiltration (UF) and pervaporation [42]-[47]. The changes in PVDF polymer structure for better permeation could sacrifice the selectivity due to the lack of ability to enhance free-element size and narrowing free-volume element size distribution [48]. The trade-off effect mainly relies upon the pore structure and skin layer thickness. Therefore, three strategies have been proposed to overcome the trade-off effect: (i) choosing the membrane materials with high rigidity to restrict the chain motions that further suppress pore collapse during the formation, (ii) blending the polymer with functionalised nanoparticles or cross-linking the co-polymer to tune the free volume in the membrane and (iii) improving the membrane hydrophilicity [49], [50].

Interestingly, the decrement of permeability properties is related to foulant adhesion and/or pore blocking. Therefore, applying extra force to repel the foulant adhesion and/or blocking can hinder poor permeability performance. The repulsive force could also retain foulants and improve selectivity [51]. Once again, it was clear that the trade-off effect is also related to the membrane fouling. The proper membrane modification will not only enhance the antifouling properties of the membrane, but it also can break through the limitation of the trade-off effect. A better understanding of membrane properties and performance relationship could solve these issues and be deployed for large-scale practical challenges.

3.1 Main Factor Influencing Membrane Fouling

Substantial research has been conducted to study the main factors influencing membrane fouling: surface features, feed properties and operating conditions [52], [53]. These factors can occur alone or simultaneously and directly or indirectly contribute to membrane fouling. However, membrane surface features are the most prominent factor in membrane fouling. In general, membrane surface features include pore size, porosity, surface charge, surface roughness, hydrophilicity and membrane structure. Nonetheless, surface hydrophilicity, roughness and charge are the prominent characteristics that dominate the fouling and antifouling properties of the fabricated membrane. In addition, the relationship of these three factors is complex and related. Foulants are commonly attracted to any material with lower hydrophilicity than water, while the surface charge presence could affect the interaction of the membrane surface and the liquid droplet. Based on this situation, it is believed that by improving surface hydrophilicity, the adhesion force between the contaminants and the membrane surface is weakened, further causing the foulant to drive away from the membrane surface [38], [54], [55]. Thereupon, membrane development that is highly bound to water molecules than other components to the membrane surface is highly required.

The contact angle is a parameter that represents surface hydrophilicity. Contact angle value always correlates reverse with membrane hydrophilicity, where a lower contact angle value indicates higher hydrophilicity. It means that a highly hydrophilic membrane can easily attract water molecules toward the membrane surface by forming hydrogen bonds with the membrane surface. As a consequence, membranes with high hydrophilicity always represent better membrane permeability than that of hydrophobic membranes. As discussed by other researchers, contact angle of hybrid membranes significantly decreases with the introduction of hydrophilic material as an additive, resulting in higher pure water flux with better antifouling properties [7], [29], [56], [57].

Vatanpour et al. [58] demonstrated that pure water flux and antifouling performance were enhanced due to the increment of hydrophilicity, porosity and mean pore sizes of the PVDF hybrid membrane. Similar observations have been previously reported by Ahmad et al. [59] and Gao et al. [60]. Next, membrane surface charge is also able to tune membrane performance. Membrane surface charge can affect both interfacial tension and the interaction between the liquid and solid phases [61]. A particle with opposite electrostatic charge would captivate each other and vice versa. Foulants with high negative zeta potential usually have lower fouling potential [62]. Abd-Razak et al. [63] studied the effect of membrane surface charge and porosity using UF membrane. Initially, the surface charge could control membrane surface performance compared to the molecular weight cut-off (MWCO) of the membrane. This study reported that a membrane with a negative surface charge has a greater fouling rate due to negatively charged species deposited on the membrane surface.

Nonetheless, the porosity of the fabricated membrane was highly restored, close to its original level after the cleaning process. It can be related to the better wettability of the membrane surface. This suggests that the fabricated membrane exhibits superior antifouling properties.

The relationship between hydrophilicity and surface charge can be confirmed through the study by Zhao et al. [54]. They reported that the contact angle value of the fabricated PVDF/GO reduced from 73° (pristine PVDF) to 56° as the zeta potential of the fabricated membrane showed a decrement in value (from -23.4 to -46.8 mV). It can be explained that the abundance of negative charge and hydrophilic functional groups of GO layers is capable of increasing the hydrophilicity and negative charge of the fabricated PVDF membrane surface. They also reported that improved hydrophilicity and negative charge on the PVDF membrane surface resulted in a lower irreversible fouling ratio and a better antifouling property, although more foulant accumulated on the PVDF membrane surface. This result was consistent with the study conducted by Tran et al. [33]. They found that the combination of GO and PVP demonstrated a highly hydrophilic PVDF membrane with better electronegativity, further resulting in better rejection efficiency (up to 87.5%) with better antifouling property as indicated by lower flux decline (< 27%) after 16 hours continuous filtration without membrane cleaning.

On the other hand, membrane surface roughness can also tune the fouling behaviour of the fabricated membrane. Surface roughness is the membrane surface topography deviation from an ideal atomically smooth surface [64]. Statistical information, including mean roughness, average roughness, root-mean-square roughness, peak count per unit area, etc., are keys to determining surface roughness, and it can be obtained through atomic force microscopy (AFM) analysis [64], [65]. Based on the literature, it is worth noting that a smoother membrane surface remarkably resulted in a membrane with excellent antifouling properties [19], [66]. It might be caused by

the fact that smoother hydrophilic membrane surfaces can easily allow the water layer to form over the membrane surface, further reducing the foulant and membrane surface interaction [67]. Moslehyani et al. [68] reported that membrane roughness of PVDF/MWCNTs membrane was decreased to 13.1 nm with a contact angle value of 42.9° compared to pristine PVDF (membrane roughness and contact angle value was 22.5 nm and 67.2°, respectively). A similar observation was reported in the previous works by Chang et al. [69] and Liu et al. [70].

It is worth noting that rougher membrane surface does not always result in poor antifouling properties. Some researchers have successfully proved that the opposite trend of membrane roughness could greatly enhance membrane performance [71]-[73]. In the case of hydrophilic material incorporation into PVDF polymer matrix, some of them might induce a rougher surface and increase membrane surface area, further enhancing the permeability and selectivity as well as their antifouling properties [74]. As reported by Meenakshi et al. [75], incorporating sulfonated GO (SGO) as an additive for PVDF membrane fabrication resulted in a highly hydrophilic membrane with a rougher surface. This situation further resulted in rougher cavities formation in PVDF-based membranes and increased the membrane's active surface area for water permeation. In addition, the highly hydrophilic properties of PVDF-based membrane can also minimize the foulant adhesion on the membrane surface, resulting in better antifouling properties. With the hydrophilic additive presence on the membrane surface, easier foulants detachment is obtained on the membrane surface.

3.2 Overview of Techniques for Fouling Control

Membrane fouling is related to the low-pressure or low-flux mode of operating condition that leads to very little or no cleaning required after filtration [76]. Although it is implausible to discard membrane fouling completely, it still can be minimised through additional techniques or methods [55]. It is well-established that fouling can be controlled in two manners, which are (i) involving strategies and procedures during or prior to the membrane separation process and (ii) developing antifouling membrane fabrication to minimise any foulants attachment on the membrane surface. Pre-treatment of feedwater is one of the efficient methods to reduce membrane fouling and improve membrane permeation. Proper pre-treatment before the membrane process can reduce membrane cleaning frequency, improve the whole system treatment efficiency, and prolong the membrane life span. It is worth noting that pre-treatment technique (coagulation, adsorption, oxidation and bio-filtration), mode of dosing, dosage, mixing method, NOM properties, temperature, solution properties and membrane characteristics strongly played a pivotal role in membrane fouling abatement via pre-treatment technique [77]-[79].

The proposed techniques have been proven to effectively reduce the pollutants accumulation on the membrane surface and modify their interaction, further reducing membrane fouling during separation. However, some shortcomings of feedwater pre-treatment have drawn attention, such as irreversible fouling, inefficient removal towards small molecules of toxic compounds and high energy requirements. These factors could lead to higher operation costs since they involve separate processes [80]. On the other hand, operation condition optimisation (trans membrane pressure (TMP), temperature and pH) also played a crucial role in membrane fouling mitigation. Concentration polarisation could lead to declining flux and severe fouling. However, these effects can be controlled by adapting suitable operation conditions [81]. The previous study showed that TMP was the key to the membrane fouling phenomenon, where an increment of TMP caused more foulant accumulation on the membrane surface. Therefore, adjustment of proper operation conditions may lead to better fouling control.

Meanwhile, either physical or chemical cleaning, membrane cleaning can maintain the selectivity and permeability of the membrane [34], [55], [82]. Membrane cleaning capability can be evaluated based on (i) how much membrane permeability can be restored and (ii) how fast the restoration of membrane permeability can occur. Various variables that contribute to the membrane cleaning capability must be considered. These variables include cleaning frequency, cleaning operation duration, cleaning reagents type and concentration, clean solution temperature and ironic strength, cleaning steps sequence and hydrodynamic condition during the cleaning process. The limitation of this technique is that frequent membrane cleaning reduces membrane performance and affects the operation efficiency and cost [77].

Physical cleaning mostly depends on mechanical treatment to mitigate the foulants from membrane surfaces. Physical cleaning has the attention of researchers due to its advantages, such as low frequency of chemical cleaning, effective small portion removal, lower practical cost, and greener and longer membrane lifetime [55], [82]. Regardless of its beneficial, physical cleaning is inefficient in removing irreversible fouling. The common physical cleaning methods include backwashing, air sparging, vibration and sponge ball cleaning. Backwashing is a common method for membrane fouling control in dead-end filtration mode. Backwashing is generally done by reversing the water permeation direction after a certain filtration time [36], [82]. This action lifted deposited foulant from the membrane surface, resulting in lower concentration polarisation near the membrane surface.

Next, chemical cleaning depends on the chemical reactions to remove foulants from the membrane surface by weakening the adhesion force between the foulants and the membrane [34]. This technique has been reported as the most effective method to recover membrane permeability and simultaneously remove the irreversible fouling and large foulants portion [52]. Nonetheless, the limitation of this method is the harsh chemical condition

requirement; a very high or low pH, thus shortening membrane lifetime due to the repeated cleaning procedure and long-time exposure to harsh chemicals. This method utilised strong oxidising and reducing agents such as acid (nitric and phosphoric), alkali (hydroxide, phosphate and carbonates) and surfactants (non-ionic, anionic and cationic) during the membrane cleaning. The oxidising and reducing agents are chosen based on the feed water characteristics such as ionic strength, temperature and pH, and membrane materials. The essential chemical characteristic that should be considered during membrane cleaning is their ability to (i) keep the foulant in the dispersion and solution, (ii) protect the membrane or other system part, (iii) loosen and dissolve the fouling and (iv) avoiding any new fouling formation.

Modifying the membrane to tailor its properties might become the best route to reduce membrane fouling. This strategy could minimise the membrane post- and pre-treatment frequency, cleaning cycle, and replacement. It can be done via additive blending and surface modification of pre-formed membranes. Most researchers choose this route to pronounce membrane fouling study [5], [70], [83], [84] than the other strategy since it is more convenient and easier to implement on a large scale. The modification of PVDF-based membranes will be discussed further in the next section.

4. Preparation of PVDF-Based Membrane

The membrane can be fabricated via phase inversion, stretching, sintering, electrospinning and template leaching techniques. These fabrication approaches played a vital role in the membrane's intrinsic properties development [85]. The advantages and drawbacks of these techniques are tabulated in Table 1. Among these techniques, phase inversion is the most versatile method for preparing flat sheet membranes. A homogenous membrane solution is prepared by dissolving membrane-forming polymer with organic solvent under controlled conditions. The prepared membrane solution is then cast on a support. The casted membrane is transferred into a coagulation bath to induce phase separation (exchange of solvent and non-solvent), resulting in membrane formation.

Table 1 *Advantages and drawbacks of various membrane fabrication methods [13], [20], [62], [86]*

Membrane Fabrication Method	Advantages	Drawbacks
Phase inversion	i. Applicable to various types of polymers ii. Easy to produce either flat-sheet or tubular membranes iii. Simple preparation and easy to scale up iv. Fast yield speed v. Convenient method in optimising pore size and membrane thickness vi. Resulted high porosity membrane (around 80%)	i. The polymer must be soluble in a solvent or solvent mixture
Stretching	i. This resulted in a highly porous membrane. ii. Easy to control the fabricated membrane quality by selecting the initial polymer material's physical properties	i. Involves multistage processes and numbers of processing parameter ii. Only suitable for membrane distillation (MD) membrane fabrication
Electrospinning	i. Easy to control nanofibre arrangement, diameter and microstructure ii. Large-scale selection of materials iii. Easy to incorporate various additive materials iv. Resulted high porosity and surface-to-volume ratio membrane	i. Difficult to acquire nanofibres with a diameter lower than 100 nm ii. Slow membrane fabrication
Sintering	i. Resulted in symmetric membranes with mean pore sizes of 0.1–10 μm ii. Suitable for chemically stable materials: polytetrafluoroethylene, polyethylene, metals and ceramics	i. Requires narrow-size particle distribution ii. Hard to achieve pores with sizes below 100 nm
Template leaching	i. Resulted symmetric membrane with pore size between 0.5-10 m ii. Extremely narrow pore size distribution	i. Hard to achieve nanopores ii. High cost and complex procedure

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Generally, there are four basic techniques to fabricate membranes via the phase inversion method, which are non-solvent induced phase separation (NIPS), thermally induced phase separation (TIPS), vapour-induced phase separation (VIPS) and precipitation by controlled evaporation. To date, the NIPS method is commonly applied for fabricating PVDF membranes. In this method, membrane morphologies mostly depend on the solvent and non-solvent exchange rate during the precipitation step. Instantaneous liquid-liquid demixing rate led to a membrane with a thin skin layer and finger-like structure, while delayed liquid-liquid demixing rate commonly produced a membrane with a sponge-like structure. Various membrane morphologies can be fabricated by adjusting the polymer solution and coagulation bath composition, solvent and non-solvent selection, and additive incorporation [87]-[90].

As discussed by other researchers [91]-[93], with a proper ratio of polymer concentration, membrane with a thin and dense skin layer with a finger-like structure was formed. Theoretically, the dope solution viscosity increased linearly with the polymer concentration and hydraulic resistance. Consequently, the liquid-liquid demixing rate will be delayed, forming a less porous membrane due to the slower phase inversion process. Higher polymer concentration could also be partly responsible for the trade-off occurrence, as shown in a previous study by Chung & Mohammad [92]. They reported that as the polymer concentration increased from 16 to 20 wt%, the membrane permeability trend decreased from 6.9 to 3.9 L/m^{2}hMPa, but interestingly, the humic acid (HA) rejection increased from 78 to 95 %.

Meanwhile, Ismail et al. [91] found that the tensile strength of the fabricated membrane became stronger as the polymer concentration increased from 20 to 30 wt%. However, the elongation at break (%) value of the fabricated membrane depicted a different trend as the polymer concentration increased up to 30%. Initially, the elongation at break increased significantly as the polymer concentration increased from 20 to 25 wt%, but it decreased as the polymer concentration was 30 wt%. These situations revealed that the macrovoid structure could be reduced as the polymer concentration increased. However, it then leads to a higher rigidity of membrane structure. Therefore, the proper amount of polymer concentration could affect the membrane performance and lead to proper morphological and mechanical properties.

The combination of solvent and non-solvent also becomes a pivotal factor in determining membrane morphology as they play a part during membrane precipitation [94]. The solubility difference between solvent and non-solvent will assist the exchange rate of solvent and non-solvent when the casted membrane is immersed into the non-solvent. In brief, higher solubility of solvent and non-solvent leads to the rapid precipitation rate of the polymer. As a result, a membrane with a thin and dense skin layer will successfully be formed. Various solvents, such as DMAC, DMF, NMP, TEP, etc., have been utilised during membrane preparation [66], [95]-[98]. Yeow and co-workers [99] prepared a membrane with varying solvent types (DMAC, DMF, NMP and TEP) with a water bath as non-solvent. The results demonstrated that DMAC showed the strongest solvent power, forming a finger-like structure with a spongy bottom beneath the skin layer. TEP and NMP exhibited symmetry sponge and irregular macrovoid structures, respectively.

This study was in line with Nasib et al. [93] and Karimi et al. [100] as they demonstrated that the utilisation of DMAC as solvent resulted in a membrane with a higher number of finger-like structures compared to other solvents (DMSO, NMP and DMF). However, in some cases, it is worth highlighting that utilising NMP could result in a membrane with higher porosity than that of DMAC and DMF [88], [96]. Arefi-Oskoui et al. [102] also showed the same pattern as the nanolayered double hydroxide/PVDF membrane utilising NMP as solvent presented better performance than that of membrane prepared using other solvents. Indeed, different solvents can cause different interactions, especially with additive inclusion, since they all exhibit different chemical and physical properties [102]. Consequently, it will influence the phase inversion process and further produce membrane with various characteristics.

The composition of the coagulation bath also influences the membrane's final morphology. Water is the common non-solvent that caused a rapid demixing process, thus resulting in an asymmetric membrane structure with finger-like pores structure [103]. Some researchers used non-solvent additives to the coagulation bath to control the exchange rate between solvent and non-solvent during precipitation, further resulting in the desired membrane's properties. However, it is worth noting that the incorporation of a non-solvent additive to the coagulation bath leads to a delayed liquid-liquid phase demixing, as discussed by previous researchers [97], [98], [103]-[107]. Therefore, this parameter can only be modified in MD fabrication.

5. Recent Modifications for Techniques and The Trends in Antifouling Properties

Blending with additives is the most popular strategy for tailoring membrane properties [55]. Blending is a process where two or more polymers or additives are physically mixed to fabricate a membrane with desired properties. It is also practical to be employed in an industrial-scale production. In recent years, the blending technique has attracted greater attention due to its simplicity, versatility and mild conditions that leave the polymer integrity intact [108], [109]. In addition, the desired membrane can be easily prepared with additives without any pre- or post-treatment [21], [110]. To date, the common additives incorporated into PVDF membrane dope solution are

inorganic nanomaterials, hydrophilic polymers and amphiphilic co-polymers. It is believed that the incorporation of these hydrophilic materials into the membrane matrix not only improves the membrane properties but also enhances membrane performance [57], [62].

5.1 Inorganic Nanomaterial

In recent times, nanomaterials have gained attention to be blended into the PVDF membrane matrix to obtain a 'special effect' toward its properties and performance. Recently, metal oxides have been widely used as additives to fabricate mixed matrix membranes for wastewater treatment. These metal oxides impart properties of nanosized pores and improved membrane performance. By incorporating metal oxides into membrane material, membrane passage can be constructed, modified and optimised so it will be able to present good permeability and antifouling performance [111]. Many nanomaterials have excellent performance in membrane modification technology, including graphene, TiO_2, SiO_2, ZnO and so on. These metal oxides are commonly employed in wastewater treatment due to their attractive properties such as superior hydrophilicity, permeability improvement capability, commercially available and high thermal resilience.

Metal oxides can be deposited onto the membrane surface or dispersed into the polymer solution for membrane casting preparation [15]. Kim & Lee [23] used hydrophilic TiO2 to enhance PVDF membrane performance. The result revealed improvement in terms of hydrophilicity, membrane porosity and permeability. The composite membrane's water flux was higher (7.80 L/m^2h) than the pristine membrane (1.54 L/m^2h). Wang et al. [112] prepared NF thin film by introducing GO and TiO_2 as additives and studied its effect on the physicochemical properties and performance of the fabricated membrane. They found that 0.2 wt% TiO_2/GO showed superior performance with a water flux of 22.43 L/m2h and 98.8% Na2SO4 rejection. Meanwhile, Wang & Sun [113] prepared PVDF/ZnO via the TIPS method and found that ZnO was also capable of tuning membrane properties and performance.

On the other hand, graphene, the thinnest two-dimensional atomic material, has seized the platform of nanotechnology by storm since 2014 with rapid application growth. Since then, the outstanding properties possessed by graphene have made it a "magic bullet" for the composite world. Graphene, a two-dimensional material (2-D), is the basic form of all other carbon allotropes, including CNT and graphite, with a hexagonal crystalline structure [114], [115]. It is noted that graphene owns a strong van der Waals force resulting from π-bonds, which makes them a crucial material to be utilised directly in any application [116]. In addition, most of the studies did not employ graphene in its pure form since the limited yield from the preparation point of view [115]. Nevertheless, graphene remained at the scientific research core because of its valuable properties, which have been transformed into practical applications.

Graphene and its derivatives (GO and rGO) are popular materials to be explored since they are well-known for their excellent potential to be applied for various applications, such as fuel cells, capacitive deionisation, desalination, supercapacitor, membrane separation and so on. In fact, the biggest shortcomings of pure GO membrane utilisation are real. The pure water flux of pristine GO membranes is lower than that of the conventional polymer membrane since the channels between the GO sheets are narrow [117], [119], [124]. In addition, interaction between the oxygen-containing functional groups with water molecules could easily damage during the long-term separation process [120], [121]. Therefore, to deal with this kind of problem, other materials can be intercalated into the GO nanosheets to alleviate the GO sheets restacking concurrently expand the channel structure for water transport.

As reported, graphene derivatives can be integrated with various materials, including inorganic nanostructure, metal or metal oxides, carbon-based material (CNTs or activated carbon), organic framework, organic crystals and polymers [111], [122]. CNT has a high aspect ratio as a dimensional (1-D) material. Integrating 1-D and 2-D materials forms a three-dimensional network structure [123]. Further, it could lead to different membrane performances since it is depended on the interaction of polymeric membrane, graphene derivative and other materials. In membrane separation technology, a membrane with high strength, non-toxic, smooth surfaces, and trap ability toward other substances and channels is highly demanded [111]. It is found that graphene and its composite materials perfectly satisfy these basic demands of membrane separation technology since it can provide a stronger support force and adjustable sheet spacing.

These basic requirements can be perfectly satisfied by graphene and its composite materials. As mentioned, GO contains abundant oxygen-functional groups in the carbon lattice across the basal and edge planes. These functional groups play an important role since they will support the interaction between GO and water [96]. In addition, water permeation through the membrane was attributed to the swelling of GO structures, which enables a penetration path of water between the individual GO layers. GO film is super thin since it is made of one single atom, so the water can simply penetrate the very small holes of the GO-based hybrid membrane and leave the salts or bigger size of molecules behind. However, various rGO composites have recently gained attention and have been extensively studied since it was believed to possess better membrane performance.

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Peng et al. [121] prepared SiO_2-intercalated rGO-based ultrathin laminar films using PVDF as a support layer via a facile vacuum filtration approach. To further enhance rGO-based membrane stability, poly-dopamine (PDA) has been introduced to prepare PVDF/rGO-SiO_2/PDA composite membranes. They found that more nanochannels could be established by increasing SiO_2 mass fraction, thus resulting in high permeation flux. However, the rejection ratio of methylene blue (MB) was not visibly changed with more SiO_2 content. They also reported that by utilising a 2: 0.67 mg mass ratio of GO: SiO_2 (immersed into PDA for 24 hours) (M1-PDA), pure water flux instantly decreased from 1389.1 L/m^{2}h (pure PVDF) to 133.2 L/m^{2}h. Despite the lower pure water flux, it is worth noticing that M1-PDA presented high MB and diesel removal, which is 99.8 and 99.2%, respectively. Therefore, based on this study, it was found that rGO-based composite membrane exhibited high water flux and great retention ratio. In addition, this composite membrane owns superior stability and recyclability in water treatment.

On the other hand, Zhang et al. [8] designed a composite membrane (s-GO/prGO-PVDF membrane) by applying a 'two-step' modification technique, which is (i) mixing the SGO, partial rGO (prGO) suspension and deposited on the substrate (PVDF membrane), and (ii) the thermal deoxygenation of the composite membrane. The water permeation of the composite membrane was found to be ~3.78 L/m^{2}h. This value showed an increment in the water permeation compared to a pure membrane (~0.98 L/m^{2}h), which was believed to be due to the enlarged 'gateway' for water molecules transport. Meanwhile, the organic dyes rejection of MB, methyl orange (MO), congo red (CR) and rhodamine B (RB) was reported to be 99.5, 99.9, 97.3 and 98.6 %, respectively. Ultimately, the fabricated s-GO/prGO-PVDF membrane is believed to have an efficient removal ability since it can provide a wider transport pathway for molecules and allow the mass of water to permeate through composite laminated layers.

Abdel-Karim et al. [124] incorporated PVDF membrane with rGO for MD application. They studied the oxygen content effect of the fillers in the MD performance by employing rGO nanoplatelets with different reductions. The membrane with 15.5 % oxygen content (C-O atomic ratio of 5.45) performed best. They also reported that the water flux of the membrane containing 0.5 wt% rGO showed a higher value (7.0 L/m^{2}h) than the pure PVDF (2.6 L/m^{2}h). Meanwhile, Huang et al. [125] found that rGO (treated for 2 hours) with a small amount of unreduced GO exhibited the highest water flow rate but the lowest Na^+/Cl^- ion permeation.

During membrane formation, these hydrophilic materials in the dope solution migrate to the membrane top layer due to their good affinity with non-solvent. They could accelerate coagulation exchange, enhancing pore formation and interconnectivity, increasing hydrophilicity, and suppressing macrovoid formation [75]. In addition, the polar functional group presence from hydrophilic additives commonly formed hydrogen bonds with the water molecules, which then leads to the hydration later formation onto the PVDF membrane surface. Better interaction between the PVDF membrane hydration layer and water molecules is very helpful in enhancing water permeability. This hydration layer also resulted in better foulant rejection due to the electrostatic repulsion between the membrane surface and the foulants [126]. Overall, the common inorganic materials usually used for PVDF blending modification are presented in Table 2.

Table 2 *The common inorganic materials that are usually used for PVDF blending modification*

PVDF-based composite	Flux (L/m^{2}h)	Rejection (%)	Contact angle (°)	Fouling (FRR) (%)	The obtained properties	Reference
PVDF/SGO	155.5	BSA: 99.2; HA: 98.9	59.5	> 95	Membrane surface becomes rougher Hydrophilicity improvement	[75]
PVDF/GO-ZnO	170.73	-	49.8	92.79	Membrane surface becomes rougher Hydrophilicity improvement Pore size enlargement	[127]
PVDF/GO-zinc sulfide (ZnS)	431.9	BSA: 87.1	61.7	66.7	Membrane surface becomes smoother. Hydrophilicity improvement Pore size enlargement	[128]
PVDF/catechol-functionalised poly (ethylene glycol) (cate-PEG)	194.0	-	55.0	95.5	Well-distributed finger-like structure Membrane surface becomes rougher	[129]

					Hydrophilicity improvement Pore size enlargement	
PVDF/flower-like molybdenum disulfide (HF-MoS_2)	21.5	Na_2SO_4: 98.6 $MgSO_4$: 97.75	-	-	Membrane surface becomes rougher Pore size enlargement Overcome the trade-off effect	[130]
PVDF/Fe_3O_4	175.8	MB: 97.6	48.2	-	Hydrophilicity improvement	[131]
PVDF/CNT	47.59	NaCl: 35	88	-	Enlargement of pore size Hydrophilicity improvement	[5]
PVDF/functionalised CNT	-	HA: 94.6	19.9	-	Hydrophilicity improvement	[132]
PVDF/conductive CNT	-	-	120	-	Electrical conductivity and antifouling properties improvement	[133]
PVDF/GO-oxidised MWCNTs	125.6	-	62.1	60.57	Membrane surface becomes rougher	[123]
PVDF/rGO	29.94	Boron: 98.16; Salt rejection: 99.72	124.5	-	Membrane surface becomes rougher	[134]
PVDF/GO-rGO	~1690	MB: ~97; RB: ~98	-	-	Hydrophilicity improvement	[135]
PVDF/GO-TiO_2	199.97	BSA: 91.38	-	89.22	Hydrophilicity improvement	[136]
PVDF/quaternities GO	1285	Dextran-500: 81	55	85.60	Pore size enlargement Membrane surface becomes rougher	[137]
PVDF/Ag-GO	177.5	-	63.4	-	Hydrophilicity improvement Anti-bacteria adhesion properties improvement	[138]
PVDF/TiO_2-GO	487.8	BSA: 92.5	61.08	82.1	Hydrophilicity improvement Membrane surface becomes smoother	[139]
PVDF/Ag-GO	491	-	60.13	-	Hydrophilicity improvement Tensile strength improvement	[140]
PVDF/TiO_2-GO	9.269	MB: 92.76	64	-	Hydrophilicity improvement Hydrophilicity improvement	[6]
PVDF/TiO_2-GO	-	MB: 92.61	65.4	119	Pore size enlargement Hydrophilicity improvement Pore size enlargement	[7]

5.2 Hydrophilic Polymer

Due to their remarkable properties, PVP, PVA and PMMA are versatile polymers used as additives in PVDF membrane fabrication over the past years. The membrane properties such as morphology, pore size and pore size distribution are easily tuned by incorporating these additives in the membrane matrix since the thermodynamics and kinetics in the casting solution could be easily adjusted. Consequently, a membrane with outstanding

performance and fouling resistance was obtained. PVP is a synthetic polymer that consists of linear 1-vinyl-2-yrrolidone groups [141]. It is water-soluble, hydrophilic in nature, non-toxic, pH-stable, temperature-resistant and chemically inert. It is also important as a surface modifier to enhance the stabilisation and dispersion of nanoparticles and pore former agents [56]. Concerning their excellent properties, PVP presence in membrane matrix is proven to enhance the exchange rate of solvent/non-solvent during the precipitation of membrane solution, further leading to large finger-like macrovoid formation.

As reported in many studies, incorporating PVP with various materials into a PVDF membrane matrix has shown positive membrane properties. The influence of PVP incorporation and its synergetic effect on GO in the PVDF membrane has been investigated by Chang et al. [69]. This work demonstrated that incorporating PVP and GO resulted in a typical asymmetric porous structure with a thin skin layer and finger-like porous structure. Further increment in PVP content resulted in a wider and larger finger-like structure. It is worth noting that PVDF/PVP presented larger pores than that of PVDF/GO/PVP, confirming that hydrogen bonds formation between GO and PVP affects the demixing process. Overall, the water flux measurement could reach up to 104.3 L/m^2h with a BSA rejection of 85% when PVP and GO content were fixed to 0.25 and 0.50 wt%, respectively. Antifouling properties of the fabricated membrane were also significantly enhanced with optimal GO to PVP ratio.

Similar results were obtained by Tofighy et al. [74] in their study, where the GO nanoribbons (GONRs) and PVP exhibited excellent synergetic effects, further enhancing the hydrophilicity, pure water flux and membrane properties. By incorporating 0.1:3 wt% GONRs: PVP, the optimum pure water flux and BSA rejection of 532.21 L/m^2h and 95%, respectively, were obtained. Apart from this, a higher FRR value of the fabricated membrane was obtained (86%) compared to a pristine membrane (around ~30 %). A higher FRR ratio demonstrated that the fabricated PVDF/GONRs/PVP membrane exhibits better antifouling properties. Su et al. [73] agreed that a proper ratio between GO and PVP could result membrane without cracks and outstanding properties with higher permeability and fouling-resistant performance. As discussed in their study, GO can interact with PVP through three interactions: (i) hydrogen-bonding interaction, (ii) protonation of the PVP nitrogen by the weakly acidic sites of the GO and (iii) nucleophilic substitution reaction. Therefore, the appropriate arrangement of GO nanosheet is vital to optimise the PVP – GO interaction [73].

Meanwhile, Van Tran et al. [33] have successfully prepared four types of PVDF-based membranes incorporating PVP and GO and are further used to study the individual and simultaneous effects of these additives. Incorporating PVP alone in the PVDF membrane matrix led to finger-like macrovoid formation with higher pore interconnectedness. This result agreed with other reported studies of PVDF/PVP [142]. Further incorporation of GO induced more changes in the membrane cross-section morphology, where the connectivity holes and voids in the sponge-like region increased in size. Additionally, the membrane permeability of PVDF/PVP/GO was 953.0 – 1353.0 $L/m^2h.MPa$ was higher than that of pristine PVDF (in the range of 48.7- 55.1 $L/m^2h.MPa$) and PVDF/PVP (in the range of 856.0- 1271.7 $L/m^2h.MPa$). In order to improve the antifouling properties of PVDF membranes, Du et al. [143] prepared PVDF nanofiber membranes by blending PVP and TiO_2 as additives. The obtained membrane has excellent antifouling properties, as indicated by its higher FRR value of 95.68%. For many years, a similar conclusion was also drawn by most of the researchers. They reported that PVP leaches during phase inversion or physical/chemical cleaning. Nonetheless, a small portion of PVP remains in the polymer matrix. It is important to highlight that the small amount of PVP is sufficient to render the membrane hydrophilicity [69], [144]-[149].

PVA is also gaining attention due to their good cohesion, biodegradability, biocompatibility, hydrophilic material, and good membrane forming properties [150]-[152]. Nonetheless, PVA possesses poor water resistance and tends to swell in aqueous solution extremely. These characteristics further lead to poor separation performance, lower mechanical strength, and thermal stability [152]. Zhang et al. [32] prepared the casting solution by blending the PVDF membrane with different dosages of PVA (concentrations were set to 0, 0.1, 0.3 and 0.5 wt%). The membrane was then fabricated via the phase inversion method. They have very well portrayed the nexus between the stability and compatibility with membrane properties. Overall, 0.1 wt% of PVA dosage showed the blended polymer's excellent compatibility and stability. The fabricated membrane also demonstrated better properties and antifouling characteristics. This was in good agreement with other researchers where PVDF/PVA maintained higher pure water flux recovery (over 95%) in eight cycling tests. Interestingly, the membrane presented neither crack or shedding which confirmed the PVDF/PVA stability [153].

Another common hydrophilic polymer that could be directly blended with PVDF membrane is PMMA. It is highly rigid, transparent, and chemical resistant [31]. Additionally, PMMA has good compatibility with PVDF membranes. With the experimental and thermodynamic analysis, the miscibility of the PVDF/PMMA dope solution has been sorted out by Aid et al. [31]. PMMA amount to be blended with the membrane played a major role in determining the membrane properties. It has been reported that higher PMMA content could increase and decrease the glass transition temperature and melting temperature of PVDF [154]. Previously, asymmetric PVDF/PMMA membranes fabricated via the phase inversion method exhibited larger finger-like cavities when the PMMA content was increased [155]. However, it is not recommended to incorporate a higher amount of PMMA since larger cavities formation will make the membrane easily collapse under pressure.

The ability of PMMA to enhance the antifouling properties of the fabricated membrane has been proved by Ochoa et al. [156] by using the cake model to analyse the reduction of membrane flux. As the hydrophilicity of the fabricated membrane enhanced with the inclusion of PMMA, the antifouling ability also improved, leading to a decrement in the apparent cake resistance. However, different trends have been highlighted by Meng et al. [157]. They found that the PMMA ability to enhance antifouling properties is deficient compared with PVP and PVA. This phenomenon was reported to be caused by the foulants that easily accumulate on/in membrane surfaces or internal pores, further increasing the fouling resistance.

5.3 Amphiphilic Polymer

Much research has previously reported on incorporating amphiphilic copolymer as a membrane additive. As mentioned above, the hydrophilic homopolymer tends to diffuse out from the polymer matrix, leading to poor membrane performance. This problem often occurs because of no specific interaction between PVDF and additives since they are blended [158]. Therefore, blending amphiphilic copolymers with polymer matrix has been reported as an alternative to enhance membrane hydrophilicity. Various synthesis routes of amphiphilic copolymer have been introduced, including thermal graft copolymerisation, radical polymerisation, reversible addition-fragmentation chain transfer polymerisation (RAFT) and atom transfer radical polymerisation (ATRP). The amphiphilic copolymer can enhance PVDF membrane surface hydrophilicity and improve antifouling properties [159].

The excellent antifouling properties presented by membrane blended with amphiphilic copolymer were related to its physicochemical properties, which involve the hydration layer strength presence on or near the membrane surface. In addition, they possess self-assembly ability that can lead to narrow pore size distribution, reliable pore size and higher pore density. It was believed that the hydrophilic segments of amphiphilic copolymer would minimise the interface-free energy by segregating and enriching at the interface of membrane matrix and water. At the same time, its hydrophobic chains will be immobilised with the membrane material via hydrophobic interaction [21], [83], [160]. Additionally, the strong interaction of bulk polymer and hydrophobic chains of amphiphilic copolymer increased the compatibility and stability between these two polymeric materials. There are various amphiphilic copolymers, such as branched copolymers, blocks and comb. Commonly, a copolymer with a poly(methyl methacrylate) as a backbone demonstrated excellent miscibility and long-term stability with PVDF. This further could result in better resistance for protein adsorption. Table 3 represents previous studies of PVDF blended amphiphilic copolymer.

Table 3 *Previous studies of PVDF blended amphiphilic copolymer*

Amphiphilic copolymer	Contact angle (°)	Pure water flux (L/m2h)	FRR (%)	Reference
Poly(ethylene glycol) methyl ether methacrylate (POEM)	-	567.8	98.1	[159]
Polyacryloylmorpholine-b-poly (methyl methacrylate)-b- Polyacryloylmorpholine (PACMO-b-PMMA-b-PACMO)	69.3	236	98.1	[83]
Poly(2-N-morpholino)ethyl methacrylate (PMEMA)	49.6	191.96	96	[161]
Poly(dimethylsiloxane)-poly(ethylene glycol) (PDMS-PEG)	67	285	>99	[162]
Poly{4-[11-(acryloyloxy)undecoxy] benzoic acid}-b-polystyrene-b-poly{4-[11-(acryloyloxy)undecoxy] benzoic acid} (PAUBA-b-PS-b-PAUBA)	71	47	78	[163]
PMMA-co-P (2-hydroxyethyl methacrylate-co-2-methoxyethyl acrylate) [PMMA-co-P (HEMA-co-MEA)]	-	3950	-	[164]
PVDF-b-PEG-b-PVDF	39	1400	-	[158]
Poly(poly(ethylene glycol) methyl ether methacrylate- methyl methacrylate) [P(PEGMA-MMA)]	145	322	-	[160]
PMMA-co-poly(dimethylaminoethyl methacrylate) (PDMA)	62-72	-	72-99	[165]
PMMA-co-poly(acrylic acid) (PAA)		375		
PMMA-co-poly(N-isopropyl acrylamide) (PNIPAM)		264		

PMMA-co-poly(N,N-dimethyl acrylamide) (PDMAA)		71		
PMMA-co-PVP		-		
PMMA-co-PDMA-co-PNIPAM		-		
PMMA-co-PAA-co-PNIPAM		361		
PMMA-co-PDMA-co-PDMAA		236		
4-methacrylamidobenzenesulfonic acid (MABS)	67.4	136.34	98.60	[166]
PS-r-PEGMA-r-PSBMA	95	425-611	91	[167]
P(MMA-co-2-ethyl methacrylate (DMAEMA))	132	-	-	[168]
PMMA-r-sulfobetaine methacrylate (SBMA)	-	165	-	[169]
PMMA-r-sulfobetaine-2-vinyl-pyvidine (SB2VP)		148		
Poly(tetrafluoroethylene-co-vinylpyrrolidone [P(TFE-VP)]	-	241	-	[129]

6. Overview and Future Perspective

As in many other fields, polymeric-based membranes have been widely developed in recent years owing to their excellent outcomes. The advances in this technology, especially in wastewater treatment, are exciting and have seen dramatic progress. However, the challenges are also enormous; membrane fouling and trade-off effects should be taken care of carefully. Therefore, a systematic study is highly required to address the advantages and drawbacks of this technology since such knowledge certainly would help to develop better and more efficient membrane technology for the separation process. Based on previous reported studies, PVDF-based membrane has a great potential to be applied for wastewater treatment. It is known that PVDF-based membrane properties can affect the overall performance including membrane rejection ability and antifouling properties.

In summary, various hydrophilic modification methods have been introduced to enhance membrane properties and increase their membrane efficiency in terms of selectivity, permeability and antifouling properties. Through blending modification, PVDF-based membrane properties can be tuned with hydrophilic additives presence. Improving membrane properties, especially hydrophilicity could further affect the ability of hydrogen bond formation between the water molecules. Membrane hydrophilicity endowment could lead to better water permeation, which leads to high flux. However, it is worth noting that many recent studies overlooked the importance of fabricating membranes with high permeability, better selectivity and antifouling performance. Some of them focussed more on enhancing the hydrophilicity rather than producing a membrane with better antifouling performance for a long time and vice versa. This limitation should be addressed in future research.

7. Conclusion

From the previous works, it can be concluded that PVDF-based membrane has proved its applicability in separation processes and has offered many more advantages. In addition, it has been found that incorporating hydrophilic materials such as metal oxides, carbon-based materials and hydrophilic polymers to alter the membrane morphology and surface properties will lead to better optimisation of PVDF-based membranes. It is worth noting that a small amount of these hydrophilic materials possesses better potential to overcome the limitation of PVDF-based membranes related to membrane fouling and trade-off effect. Hence, these hydrophilic materials are capable of inducing highly hydrophilic properties of PVDF-based membranes, further providing better improvement in the interaction between the membrane surface with water molecules via hydrogen bonding, thus contributing to excellent PVDF-based membrane performance in terms of separation and antifouling properties. With all these improvements, a breakthrough will overcome the limitation of the current existing membrane, further contributing to the better development of PVDF-based membranes in the future.

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Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

Author Contribution

The authors confirm contribution to the paper as follows: ***study conception and design:*** *R. Mohamat, A. B. Suriani, A. Mohamed;* ***data collection:*** *R. Mohamat, A. B. Suriani;* ***analysis and interpretation of results:*** *R. Mohamat, A. B. Suriani, A. Mohamed, Muqoyyanah, M. H. D. Othman, R. Rohani, M. H. Mamat, M. K. Ahmad, M. F. Malek, H. P. S. Abdul*

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