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Review

Poly(vinylidene fluoride) (PVDF) membranes for fluid separation

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ABSTRACT

The importance of poly(vinylidene fluoride) (PVDF) as a membrane material has long been recognised in many membrane processes. Compared to other types of polymeric membranes, the PVDF membranes have received great attention because of its outstanding properties including high hydrophobicity, thermal stability, chemical resistance and excellent mechanical strength. This article provides an overview of recent development in PVDF membrane processes, focussing on the commercial PVDF membrane products for water and wastewater treatment and possible applications of PVDF membranes in areas such as membrane based gas absorption and membrane distillation where no substantial commercial PVDF membrane processes are available so far.

Contents

1. Introduction

Poly(vinylidene fluoride) (PVDF) is one of the popular membrane materials due to its outstanding properties including thermal stability, chemical resistance and excellent mechanical strength. It is a semi-crystalline polymer, for which the crystalline phase provides mechanical strength and impact resistance whilst

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the amorphous phase offers flexibility. PVDF is also stable when attacked by corrosive chemicals and organic compounds including acids and oxidants. Due to the easy dissolution of PVDF in common organic solvents such N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP), porous PVDF membranes can be produced via a simple phase inversion method, which is one of the common industrial processes in large scale membrane production. These properties coupled with its intrinsic hydrophobicity have made PVDF popular as a membrane material in many membrane processes such as membrane based gas absorption, membrane distillation and other types of membrane contactor applications. Moreover, the relatively high mechanical strength of PVDF compared to other materials is another advantageous property that makes PVDF membranes useful in water and wastewater treatment applications.

In our previous article [1], the fundamental issues in the preparation and modification of PVDF membranes were addressed and discussed in details. Therefore, in this article, only important and promising applications of PVDF membranes will be focused, which include water and wastewater treatment such as drinking water production, pre-treatment for reverse osmosis (RO) systems and wastewater treatment, membrane contactors such as gas–liquid absorption and membrane distillation as well as some other applications.

2. Water and wastewater treatment

Water and wastewater treatment have always been an integral part in the environmental pollution control system. The world demand for water treatment equipment is expected to grow nearly 7% per year through 2017 [2] and the world demand for membranes is projected to increase 9% annually to $19.3 billion in 2015 [3]. This is because the membrane technology has become an essential treatment alternative for water and wastewater management due to its various advantages over conventional water/wastewater treatment technologies as illustrated in Table 1 [4]. As can be seen from Table 1, the higher safety and better control on bacterial/virus removal are the main advantages for the membrane technologies. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), which are the common examples of membrane processes, are increasingly being employed for the above-mentioned applications because of these benefits. This section provides a comprehensive review on the commercial PVDF membranes for water and wastewater treatment only, as the research progress in the preparation and modification of PVDF membranes in this field is already available in literature [1].

2.1. Commercial PVDF membrane products

Nowadays, PVDF membranes have occupied a large percentage market of commercial microfiltration (MF) and ultrafiltration (UF) membranes. PVDF MF membranes are normally used as a part of membrane bioreactors (MBR) or in the upstream of water treatment processes. On the other hand, commercial PVDF membranes are almost dominating the market in ultrafiltration. The PVDF UF membranes have three key applications, i.e. water purification in potable water plants, pre-treatment in desalination plants and wastewater recovery for industrial applications. As summarised in Table 2, numerous commercial PVDF membrane products have been developed by various manufacturers, such as Pentair X-Flow, General Electric (GE) Water & Process Technologies, Evoqua Water Technologies (previously Siemens Memcor), Asahi Kasei Chemicals Corporation (AKCC), Hyflux, Toray Membrane, and Koch Membrane Systems (KMS).

The ZeeWeed™ hollow fibre membranes produced by GE have been utilised in numerous applications of municipal, industrial and commercial water treatment all over the world [5]. The ZeeWeed™ series consist of three kinds of PVDF UF hollow fibre membranes, i.e. ZeeWeed™ 500, ZeeWeed™ 1000 and ZeeWeed™ 1500, and are designed to meet various application requirements. The ZeeWeed™ 500 membrane is immersed hollow fibre made of reinforced PVDF material and has the highest solid tolerance for the treatment of high turbidity water [6]. As a result, it can be applied in the treatments of virtually any wastewater and is the best choice for MBRs. ZeeWeed™ 500 membranes have also been employed to build up the ZeeWeed™ Mobile Water Treatment System [7], which can be applied in the reverse osmosis pre-treatment, industrial process water treatment, production of potable water and secondary effluent treatment. The unit production capacity of this system is up to 123 m^3/h at up to 69 kPa. The capacity of ZeeWeed™ 500 Cassette for high solids applications is 750–1000 m^3/d in MBR and 2500–3500 m^3/d in water filtration. Similar to ZeeWeed™ 500, ZeeWeed™ 1000 is immersed PVDF ultrafiltration hollow fibre membranes with smaller diameter and is designed for retrofits and larger plants [8]. The high efficiency in design with specific membrane geometry, high packing density and simplified operation reduces the capital, operating and lifecycle costs.

In addition, superior quality water which meets EPA drinking water standards can be produced using ZeeWeed™ 1000 membranes with less chemical, reduced physical footprint and less residual waste. The capacity of ZeeWeed™ 1000 Cassette for lower solids applications is 1500–2000 m^3/d. Therefore, the membrane is ideal for tertiary, drinking water, brackish, and seawater pre-treatment applications. ZeeWeed™ 1000 is the best choice for large scale membrane filtration system and filter expansion. Generally, the ZeeWeed™ immersed ultrafiltration membranes have advantages including low energy consumption and lifecycle cost, low fouling, increased membrane durability and lifetime, small footprint and superior water quality. Different from ZeeWeed™ 500 and 1000, ZeeWeed™ 1500 is pressurised UF hollow fibre membrane with low fouling membrane chemistry, high bacteria and solids rejection [9]. Due to the specific properties of the ZeeWeed™ 1500 membrane, less frequent and less aggressive cleaning with less chemical is needed. ZeeWeed™ 1500 also has high solids tolerance, which makes it capable of handling high turbidity water and large amount of flocculants. Furthermore, the membrane is available as packaged and custom designs for green field or retrofit solutions. It is ideal for drinking water treatment, tertiary filtration, and pre-treatment applications for brackish and seawater desalination. For example, simple ZeeWeed™ 1500 model has the flow range between 45 and 180 m^3/d.

Apart from hollow fibre membranes, GE also has PVDF tubular membrane products with a non-ionic and hydrophilic surface. The Tubular Membrane Permaflow-8XS [10] series include the MF membranes and the UF membrane with the molecular weight cut-off (MWCO) of 75 kDa. The tubular membrane series can handle tough wastewater containing total suspended solids (TSS) up to 30,000 mg/L, oil & grease up to 400,000 mg/L and mixed liquor volatile suspended solids (MLVSS) up to 30,000 mg/L. The permeate produced from the membrane module contains TSS < 1 mg/L, total fats, oils and grease (TFOG) < 100 mg/L, total petroleum hydrocarbons (TPH) < 5 mg/L and MLVSS < 1 mg/L. Therefore, such tubular membranes have been utilised in various applications such as MBR treatment, general oily wastewater concentration, drawing oil emulsion separation and concentration, water soluble coolants/cutting oils separation and concentration, flexographic ink wastewater treatment, sizing chemical and starch emulsions wastewater treatment.

With a history over 25 years, Memcor® membrane systems from Evoqua water Technologies (previously Siemens Water Technologies) process billions gallons of water per day in drinking water, wastewater treatment and pre-treatment for RO [11]. Memcor's

Table 1
Comparison of the properties of advanced disinfection technologies [4].

Characteristics/criteria	Chlorination/dechlorination	UV	Ozone	MF	UF
Safety	+	+++	++	+++	+++
Bacterial removal	++	++	++	+++	+++
Virus removal	+	+	++	+	+++
Protozoa removal[a]	–	–	++	+++	–
Bacterial growth	+	+	+	–	–
Residual toxicity	+++	–	+	–	–
By-products	+++	–	+	–	–
Operating costs	+	+	++	+++	+++
Investment costs	++	++	+++	+++	+++

"–" none; "+" low; "++" middle; "+++" high.
[a] In vitro analysis of Cryptosporidium.

membrane technologies have been used in more than 1500 plants all over the world. In a Memcor® membrane process, the membrane is a physical barrier capable of removing Cryptosporidium, Giardia, bacteria, turbidity and suspended solids without chemical pre-treatment [12]. Generally, filtration is conducted in an outside-in mode for a set interval (normally 15–60 min), followed by automated backwash with air-scouring for 90 s. Since Memcor® membranes are now prepared with oxidant–tolerant PVDF material, periodical chemical cleaning using chlorine and a low-strength acid is applied in order to completely remove the fouling on the membrane surface. In addition, a specially designed membrane integrity testing, named as Air Hold Test, is applied and it is able to detect a 3 μm break in a membrane fibre, seal or O-ring. The simple, automated operation of the Memcor® membrane systems guarantees the system integrity and provides advanced notice of potential maintenance.

Memcor® membranes have both pressurised and submerged configurations to meet multiple needs and they can work as stand-alone, pre-packaged units or as components for large projects. Memcor® pressurised membrane systems include Memcor® XP packaged plant and Memcor® CP component system; whereas Memcor® submerged membrane systems contain Memcor® XS packaged plant and Memcor® CS component system. Memcor® XP pressurised packaged plant is a self-contained, factory-tested, pre-packaged unit with capacities ranging from 25 gallons per minute (GPM) to 200 GPM in six different sizes [13]. Memcor® XP is ideally suited for small communities and industrial applications where suspended solids removal is critical. It is also the best choice for remote systems, schools, developments and disaster relief applications.

Memcor® CP system has a modular "building block" configuration with up to 960 L20V modules in one unit and can be applied in drinking water and wastewater reuse treatments, pre-treatment for RO systems, desalination or industrial water treatment processes and disinfection by-product treatments for organic reduction [14]. By using Memcor® CP systems, large production capacity (10 million gallons per day (MGD) on one skid) of high quality water effluent can be obtained with bacteria and protozoa removal > 6-log (99.9999%), silt density index (SDI) < 3.0 and turbidity < 0.01 Nephelometric Turbidity Unit (NTU). In addition, the Memcor® CP systems increase the water flow up to 30% and reduce the pumping energy up to 30% compared with other pressurised MF/UF systems. Nowadays, Memcor® CP systems produce more than 450 million gallons of water worldwide. Memcor® CP II ultrafiltration system is the next evolution of the Memcor® products [15]. The II system has an ultra-compact membrane array footprint, which is up to 50% less than previous Memcor® products. Meantime, the innovative MemRACK system consisting of Memcor® CP II modules has superior separation performance, more than 35% reduced backwash duration and consequently reduced operational costs. Therefore, Memcor® CP II is ideal for new installations and major upgrades applications.

On the other hand, within a compact footprint of 2.4 m * 4.4 m, Memcor® XS submerged membrane system is a fully skid-mounted, self-contained membrane system including ancillary equipment required for operation [16]. The Memcor® XS system has a capacity ranging from 120 to 400 GPM per unit and can produce over 2 MGD by connecting up to five parallel units. The Memcor® CS membrane system with a capacity over 3.0 MGD provides an economical solution to large scale treatment systems with reduced plant footprint, chemicals and power consumption [17]. Besides, 6-log removal of Giardia and Cryptosporidium can be achieved by using this system. Therefore, the economical Memcor® CS systems are ideal for high solids applications, large capacity systems and retrofitting conventional treatment plants.

Asahi Kasei Chemicals Corporation (AKCC) has several Microza™ membrane modules made from PVDF material for various applications. For example, the MF modules of UNA-620A and UNA-600A are composed of PVDF hollow fibre membranes with sharp and uniform pore size distribution and can be used in water clarification to produce high quality water without coagulants (turbidity < 0.01 NTU) [18]. AKCC also has immersion type microfilter UHS-620A with the advantages including high water recovery, small footprint and ability to treat highly turbid raw water [18]. In addition, AKCC's MUNC-620A module with a unique cylindrical design of highly crystalline PVDF hollow fibre membrane bundles is utilised in the treatment of high BOD and/or suspended solids containing water from sewage, food industry, electronic industry, chemical industry and livestock breeding [19]. The accumulation of sludge on the membrane surface can be eliminated even at reduced aeration rates due to the specific design of the module. The AKCC Microza™ pressurised membrane modules have been installed at over 600 water treatment facilities worldwide, whereas the Microza™ submerged membrane modules (UHS-620A) are applied in some Asian regions including China, Japan and Korea to treat high turbidity feed water and to recover backwash water from sand filters [20]. In particular, Microza™ systems have been installed at more than 100 sites in China, with a total combined water treatment capacity of over 150,000,000 m^3/d [21].

Hyflux, a relatively new player in PVDF membranes, has Hyflux's Kristal® polymer hollow fibre membranes which are certified by the National Sanitation Foundation (NSF) Standard 61 and have been widely applied in the treatment of aqua-based industrial waste streams, water purification, wastewater recycling and seawater desalination pre-treatment [22]. Kristal® UF membranes are employed in over 40% of pre-treatment systems for seawater RO desalination in the world. Kristal® K2000T hollow fibre membrane and Kristal® K2000T3 tri-bore hollow fibre membrane are two members of the Kristal® family and are made from Kynar® PVDF. Due to the excellent properties of PVDF material, the K2000T and K2000T3 membrane modules are widely applied in tough operating conditions such as feed water with high TSS or high concentration of chlorine. In the test conducted by Peng et al. [23], no

Table 2
Commercial PVDF membrane products.

Company	Product	Specifications	Operating conditions	Typical permeate quality	Typical applications	Reference
PENTAIR X-Flow	Compact 27	Tubular; Area: 27 m^2; Diameter: 8.0 mm	⩽25 g/L MLSS biomass	SDI < 3; Turbidity < 0.1 NTU	Leachate from landfill sites; Food industry wastewater with high COD loads	[38]
PENTAIR X-Flow	Compact 33V	Tubular; Area: 33 m^2; Diameter: 5.2 mm	Inside-out flow; ⩽15 g/L MLSS biomass	SDI < 3; Turbidity < 0.1 NTU	Municipal wastewater treatment	[37,39]
GE	ZeeWeed™ 500	Hollow fibre; Area: 31.6 or 40.9 m^2; Inner diameter (ID): 0.8 mm; Outer diameter (OD): 1.9 mm; Nominal pore size: 0.04 μm; Surface: non-ionic & hydrophilic	Outside-in flow; TMP: −55 to 55 kPa or −90 to 90 kPa; Max temperature: 40 °C; pH: 5.0–9.5	TSS ⩽ 1 mg/L; Turbidity ⩽ 0.1 NTU; SDI ⩽ 3	Drinking water treatment; Wastewater treatment (MBR); Water reuse; Industrial applications	[6,28,181]
GE	ZeeWeed™ 1000	Hollow fibre; Area: 41.8 or 51.1 m^2; ID/OD: 0.47 mm/ 0.95 mm; Nominal pore size: 0.02 μm; Surface: non-ionic & hydrophilic	Outside-in flow; TMP: −90 to 90 kPa; Max temperature: 40 °C; pH: 5.0–10.0	TSS ⩽ 1 mg/L; Turbidity ⩽ 0.1 NTU; SDI ⩽ 3	Direct filtration; Coagulation; Tertiary filtration; Multi-media filter retrofits; Pre-treatment for RO	[8,28,182]
GE	ZeeWeed™ 1500	Hollow fibre; Area: 55.7 m^2; ID/OD: 0.66 mm/ 1.1 mm; Nominal pore size: 0.02 μm	Outside-in flow; TMP: 0–276 kPa; Max temperature: 40 °C; pH: 5.0–10.0	Flow: 45–180 m^3/d; TSS ⩽ 1 mg/L; Turbidity ⩽ 0.1 NTU; SDI ⩽ 3	Drinking water treatment; Tertiary filtration; RO pre-treatment for brackish and seawater	[9,28,183]
Evoqua	Memcor® L10V & L20V & S10V	Hollow fibre; Area: 23.4 m^2, 28.9 m^2 or 38.1 m^2; Nominal pore size: 0.04 μm	Outside-in flow; Max temperature: 45 °C; pH: 2–10	Flow:30.3–89.5 m^3/d; Recovery: 93–96%; Turbidity < 0.02 NTU; SDI < 2.0	Chlorinated secondary effluent; Clear surface water; Turbid surface water; Sea water; Chlorinated municipal water	[184]
Evoqua	Memcor® L10U & S10U	Hollow fibre; Area: 18.7 m^2 or 22.1 m^2; Nominal pore size: 0.04 μm	Outside-in flow; Max temperature: 45 °C; pH: 2–10	Flow:24.2–28.7 m^3/d; Recovery: 93–94%; Turbidity < 0.02 NTU; SDI < 2.0	Turbid surface water; Surface water with Algae or coagulant	[184]
Asahi Kasei	Microza® UNA-620A & UNA-600A	Hollow fibre; Area: 50 m^2 or 23 m^2; Nominal pore size: 0.1 μm	Outside-in flow	Turbidity < 0.01 NTU	Water clarification; Potable water treatment	[18]
Asahi Kasei	Microza® UHS-620A	Hollow fibre; Area: 50 m^2; Nominal pore size: 0.1 μm	Immersion mode	Recovery: 95–99%	Highly turbid surface waters; Backwash discharge from sand filters and membrane filters	[18]
Hyflux	Kristal® K2000T	Hollow fibre; Area: 60 m^2; ID/OD: 0.6 mm/ 1.2 mm; Wall thickness: 0.3 mm; Nominal MWCO: 150 kDa Tensile force: 3 N	Outside-in flow; TMP: 0.2–1.5 bar Temperature: 5–40 °C; pH: 2–10	Turbidity < 0.2 NTU; SDI < 3; Bacteria rejection > 6-log	Water treatment/purification; Pre-treatment filtration; Wastewater recycling; Industrial process/waste fluid treatment	[22]
Hyflux	Kristal® K2000T3	Tri-bore hollow fibre; Area: 50 m^2; ID/OD: 0.6 mm/ 2.1 mm; Wall thickness: 0.3 mm; Nominal MWCO: 200 kDa	Outside-in flow; TMP: 0.2–1.5 bar Temperature: 5–40 °C; pH: 2–10	Turbidity < 0.2 NTU; SDI < 3; Bacteria rejection > 6-log	Water treatment/purification; Pre-treatment filtration; Wastewater recycling; Industrial process/waste fluid treatment	[22]

(*continued on next page*)

Table 2 (*continued*)

Company	Product	Specifications	Operating conditions	Typical permeate quality	Typical applications	Reference
Toray	Torayfil® HFU-2020N & HFU-1020N	Tensile force > 5 N Hollow fibre; Area: 72 m^2 or 29 m^2; Nominal MWCO: 150 kDa; Nominal pore size: 0.01 μm	Outside-in & dead-end filtration; Max pressure: 300 kPa; Temperature: 0–40 °C; pH: 1–10	Flux: 1.1–8.0 m^3/h	Drinking water production; Industrial water treatment; Pre-treatment for RO; Waste tertiary treatment	[24,185,186]
Toray	Torayfil® HFS-2020N & HFS-1020N	Hollow fibre; Area: 72 m^2 or 29 m^2; Nominal pore size: 0.02 μm	Outside-in & dead-end filtration; Max pressure: 300 kPa; Temperature: 0–40 °C; pH: 1–10	Flux: 1.0–11.0 m^3/h	Drinking water production; Industrial water treatment; Pre-treatment for RO; Waste tertiary treatment	[24,187,188]
Toray	Torayfil® HSU-1515	Hollow fibre; Area: 20 m^2; Nominal MWCO: 150 kDa; Nominal pore size: 0.01 μm	Outside-in flow; Max pressure: 300 kPa; Temperature: 0–40 °C; pH: 1–10	Not available	Tertiary treatment of sewage water; Industrial water production; Industrial wastewater reuse	[26,189]
Koch	HFM 100 & HFM 116	Spiral wound; Nominal MWCO: 50 kDa	Not available	Not available	Clarification; Concentration	[190]
Koch	HFM 180	Spiral wound; Nominal MWCO: 100 kDa	Not available	Not available	Juice clarification	[190]
Koch	HFM 300	Spiral wound; Nominal MWCO: 100 kDa	Not available	Not available	Electrocoat paint recovery	[190]
Koch	HFM 183	Spiral wound; Nominal MWCO: 100 kDa; Surface: positively charged	Not available	Not available	Electrocoat paint recovery	[190]
Koch	SUPER-COR™ HFM 180 & SUPER-G™ HFM 500	Tubular; Nominal MWCO: 100 kDa	Not available	Not available	Light juice clarification	[190]
Koch	SUPER-COR™ HFM 513 & SUPER-G™ HFM 513	Tubular; Nominal MWCO: 500 kDa	Not available	Not available	Juice clarification	[190]
Koch	ULTRA-COR™ HFM 183	Tubular; Nominal MWCO: 100 kDa; Surface: positively charged	Not available	Not available	Electrocoat paint recovery	[190]
Koch	HFP-707	Spiral wound; Nominal MWCO: 120 kDa	Not available	Not available	Oily wastewater treatment	[191]
Koch	PURON®	Hollow fibre; Nominal pore size: 0.03 μm	Not available	Not available	MBRs	[191]
Koch	FEG PLUS™ HFM-251	Tubular; Nominal MWCO: 100 kDa	Not available	Not available	Oily wastewater; External MBR; White water treatment; Metal hydroxide wastes; Other industrial wastewater	[191]

Table 2 (*continued*)

Company	Product	Specifications	Operating conditions	Typical permeate quality	Typical applications	Reference
Koch	FEG PLUS™ HFM-276	Tubular; Nominal MWCO: 120 kDa; Surface: negatively charged	Not available	Not available	Oily wastewater; External MBR; White water treatment; Metal hydroxide wastes; Other industrial wastewater	[191]
Koch	ULTRA-COR™ HFM-251	Tubular; Nominal MWCO: 100 kDa	Not available	Not available	Oily wastewater; Metal hydroxide wastes	[191]

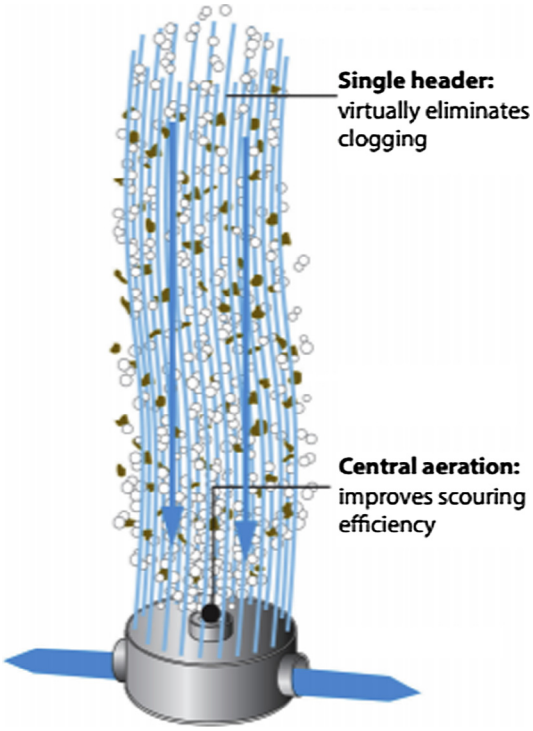

Fig. 1. PURON® single header design [42].

obvious impact on rejection and membrane tensile strength were observed after soaking Kristal® 2000 in 2000 ppm NaOCl for 1000 h. Furthermore, Kristal® 2000 has the least fibre breakage after 81.150 cycles of backwash and air scouring stimulation.

Toray Membrane has two series of pressurised PVDF hollow fibre membrane modules [24]. One is the HFU series with a nominal MWCO of 150 kDa and a special feature of low fouling layer. The other is the HFS series having a nominal pore size of 0.02 μm. Both membrane modules can be applied in drinking water production, tertiary treatment of sewage water, RO pre-treatment in seawater desalination, industrial water production and reuse of industrial wastewater. For example, there are two plants in Tokyo (Japan) and each can produce 44,000 m^3/d of drinking water using the Toray pressurised membrane modules [25]. Apart from pressurised membrane modules, Toray also produces submerged-type UF membrane modules, HSU series [26]. The HSU series have a nominal MWCO of 150 kDa and are able to treat high turbidity feed water with a continuous max turbidity of 200 NTU and an intermittent peak turbidity of 1000 NTU. Therefore, the submerged modules are applicable in tertiary treatment of sewage water, industrial water production and reuse of industrial wastewater. Toray's MEMBRAY® MBR Membranes are composed of PVDF flat sheet membrane as the functional layer on top of a polyethylene terephthalate (PET) non-woven support layer [27]. The nominal pore size is 0.08 μm with a narrow pore size distribution. Toray membrane elements with a 1.4 m^2 or a 0.9 m^2 membrane area are installed in the membrane modules. These modules are composed of 50–200 membrane elements and are classified into two series, i.e. TMR140 series and TMR090 series. The TMR140 series are large-sized modules, which are suitable for large-sized sewage treatment plant. On the other hand, the small-sized TMR090 series are widely applied in containerised package plants, cruise ships and domestic wastewater reuse in hotels and commercial buildings.

As shown in Table 2, various PVDF membrane modules with different configurations and separation ranges are available from Koch Membrane Systems to be applied in a wide range of aqua-based separation processes. The most famous product of KMS is the PURON® submerged membrane module, which has a specially designed single header and central aeration structure as shown in Fig. 1. In this patented module, reinforced PVDF hollow fibre membranes are fixed only at the bottom, which avoids the build-up of hair and fibrous material that normally clog the upper ends of normal modules with both top and bottom headers. In addition, the aeration nozzle is placed in the centre of the hollow fibre bundle in order to scour the entire fibre length with reduced power consumptions. In the filtration process, water molecules pass through the membrane from outside to the inside of the fibres, whereas solids and particulates are rejected by the membrane and remain on the outside. Due to the specific design of the PURON® module, PURON® MBRs have been widely utilised all over the world for the wastewater treatment.

As mentioned above, commercial PVDF membrane modules applied in water treatment generally have two configurations, i.e. pressurised membrane module and submerged membrane module. The pressurised membrane modules work in a closed environment, where feed water is pressurised to pass through the membrane. Pressurised membrane systems are suitable for the treatment of low-turbidity feed water to produce superior-quality water at high flux and can be operated easily. On the other hand, the submerged membrane modules are operated in an open tank, where water passes through the membrane by gravity and vacuum pressure applied in the permeate side. Submerged membrane systems are able to provide stable performance in the treatment of feed water with high turbidity and variable quality since the sludge can be drained and removed effectively. In addition, they are ideal for large-scale water treatment plants because construction costs can be reduced due to no pressure casing, less piping and few valves and a smaller footprint required due to the compact design of submerged membrane systems. The various commercial PVDF membrane products will be discussed in details regarding different applications in the following sections.

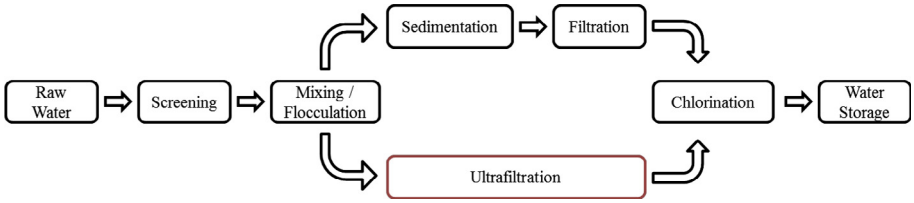

Fig. 2. Flow chart of drinking water process.

2.2. Drinking water production

The worldwide water demands have been increasing due to the growing populations, decreased available fresh water supplies and more stringent regulations. Fig. 2 shows the flow chart of the drinking water production process. By using UF membrane modules instead of the conventional sedimentation and filtration treatments, the plant footprint is reduced and hence, the production capacity is increased. Furthermore, the permeate water produced has high quality and meet or exceed the stringent drinking water requirements. At the same time, high level of public health protection from water borne pathogens is achieved due to UF membranes being a physical and verifiable barrier. As a result, the global market of potable water membrane production systems is growing nearly 10% annually and various commercial PVDF UF membrane products have been utilised in the drinking water production [21].

For example, in combination with other technologies such as ozone and activated carbon treatments, GE's ZeeWeed™ UF membranes are able to produce high quality water with turbidity < 0.1 NTU, TSS < 1 mg/L, bacteria removal > 99.99%, virus removal > 99%, Fe < 0.05 mg/L, Mn < 0.02 mg/L and As < 0.005 mg/L [28]. In addition, the compact design of GE modules offers a solution to the increased water needs within small plant footprint. For example, the CommunityTAP mobile drinking water unit combines the low-fouling ZeeWeed™ 1500 membrane and integrated post-chlorination treatment [29]. It has two models with capacities of 50,000 L/d and 100,000 L/d and it is applicable in remote locations with compromised water supply, humanitarian and aid relief, emergency response. On the other hand, GE's ZeeWeed™ membranes have been adopted by numerous water treatment plants. Among the current large drinking water treatment plants with capacities of over 100,000 m^3/d, 60% of the plants were installed with ZeeWeed™ UF membranes. Lorne Park Water Treatment Plant, which is the largest water treatment plant using ultrafiltration membrane technology in the world, was installed with GE's ZeeWeed™ membrane systems and has the daily production capacity of 382,285 m^3.

In 2004, Memcor® CS submerged membrane system was selected by the Sunrise Water Authority (Oregon City, USA) in the expansion of their existing municipal water plant [30]. The system was installed within 18 months in the original plant footprint (3962 m^2) and produces high quality water consistently and efficiently despite changing the conditions of the feed water. The installed Memcor® CS submerged membrane system has the production capacity of 37,900 m^3/d to serve 130,000 people in suburban and rural central Oregon. In 2013, the original filtration plant in the City of Highland Park was replaced by a Memcor® CS system with no change in the building footprint, and the treatment capacity was increased from 21 MGD to 30 MGD to serve around 60,000 people [31]. Furthermore, the Homestead Water Company in the Homestead was equipped with the Memcor® XS submerged membrane system containing three Memcor® XS units, each of which consists of 48 membrane modules [32]. The total plant capacity is 1.3 MGD of high quality water which meets the requirements of the Surface Water Treatment Rule. In addition, the operation cost is reduced since the new membrane system treats the resort's water without any chemical or mechanical pre-treatment applied.

In 2010, AKCC's Microza™ MF PVDF hollow fibre filtration system was installed in Manila to treat the brackish water for an RO system, which serves 100,000 m^3/d of high-quality drinking water to the Manila residents [33]. This plant is the first large-scale water treatment facility using membrane filtration technology in Philippines and one of the largest in Asia. In a United Nations Children's Fund (UNICEF) supported project, Microza™ MF membrane system was installed for drinking water production in Sri Lanka [33]. It was the first time that membrane filtration was used in this country. The system started to work in 2009 and has a production capacity of 6500 m^3/d. Another Microza™ system was installed in Asia's largest membrane-process water clarification plant in Hangzhou (China) [21]. After coagulation and sedimentation treatments, the feed water from Qian Tang Jiang River is treated with the Microza™ membrane system to serve the city with high quality tap water with a capacity of 300,000 m^3/d. With a daily production capacity of 27,000 m^3, Microza™ was also selected for a large-scale water treatment plant of K-water, which is the largest drinking water supplier in Korea [21].

2.3. Pre-treatment for reverse osmosis

Fig. 3 shows the flow chart of the seawater desalination process, in which ultrafiltration membrane plays a role of pre-treatment for the subsequent reverse osmosis process. The use of the UF membrane system provides high-quality feed water for RO, which enables RO to work at peak performance and also protects the RO system with reduced fouling and less cleaning.

Hyflux's Kristal® UF membrane modules have been widely applied in the seawater desalination plants all over the world. The Kristal® 2000 PVDF hollow fibre membrane has been tested as pre-treatment for RO in a pilot study at the SingSpring Desalination Plant (Singapore) for more than 1 year under different conditions [23]. The results suggested that Kristal® 2000 PVDF membrane could produce stable and reliable permeate water quality despite tough operating conditions or changes in raw seawater quality, and consequently, Kristal® 2000 is eligible for an effective RO pre-treatment system.

GE's SeaPAK systems combine the ZeeWeed™ UF membrane together with RO process and they are designed for packaged seawater desalination [34]. The ZeeWeed™ UF membrane is used to produce high quality feed water (turbidity $\leqslant$ 0.1 NTU, TSS $\leqslant$ 1 mg/L, SDI $\leqslant$ 3) for the RO system. The SeaPAK Models have UF production rates ranging from 2857 m^3/d to 7143 m^3/d. In

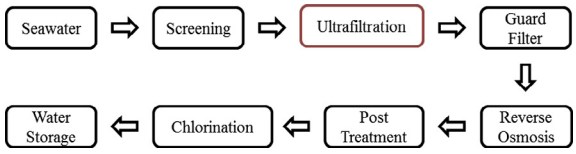

Fig. 3. Flow chart of seawater desalination process.

particular, GE's ZeeWeed™ 1500 UF membrane has been used in combination with reverse osmosis systems in order to deal with difficult-to-treat water and wastewater [35]. This integrated UF and RO platform is called either PROPAK system or RePAK system. It has more than 100 different configurations to meet the customers' specific requirements. From 2008 to 2013, more than 500 PROPAK systems had been installed with the global production of over 1.4 billion gallons of high quality water.

To solve the problem of water shortage in Western Australia caused by reduced freshwater supply together with expanding population, Memcor® CP960 ultrafiltration units were adopted as the pre-treatment for RO system in Perth's second largest seawater desalination plant in the Southern Seawater Desalination Project [36]. The ultrafiltration pre-treatment plant with a production capacity of 360,000 m^3/d has two independent banks, each of which contains five Memcor® CP960 filtration units composed of Memcor® L20V modules. In addition, the validation test over six months showed a stable filtration performance of 99% feed water recovery and flux of 65 L/m^2 h without addition of any coagulant to the feed.

2.4. Wastewater treatment

Apart from potable water production and seawater desalination, recovery of wastewater is another source of clean water production and is very important for environmental protection and water conservation. Wastewater treatment is the process of purifying used water from industries and municipality including residences and businesses. In the wastewater treatment process, membrane technology can be utilised in two ways. One is in the membrane bioreactor systems, in which the secondary effluent is obtained. The secondary effluent is treated wastewater which can be discharged directly. The other is in the treatment of secondary effluent to get tertiary effluent or high-grade recycled water.

2.4.1. Membrane bioreactor

As illustrated in Fig. 4, the conventional wastewater treatment process is a multi-step process involving more space, facilities and chemicals and longer operating time, whereas the MBR technology simplifies the process dramatically by combining the activated sludge with the membrane filtration process in one membrane bioreactor. The combination offers several advantages over the conventional activated sludge wastewater treatment system, such as higher biomass concentration and less sludge carry-over [37]. The increase in the biomass concentration leads to a more compacted system with smaller footprint, whereas the decrease in sludge carry-over results in less post-treatment and hence protection of ecologically sensitive areas. Therefore, the global market for MBR systems is growing by over 10% annually and MBRs have been widely applied in the treatment of industrial wastewater and municipal wastewater [21].

X-Flow's Compact 27 UF membrane module has a membrane diameter of 8 mm and area of 27 m^2 and can be installed with up to 8 modules in series. This module can tolerate up to 25 g/L mixed liquor suspended solids (MLSS) of biomass when equipped in MBRs and produce clear water which can be either used directly or fed to a RO system for further purification. The Compact 27 module has many advantages such as low energy cost, simple layout, high flux, and fully automatic operation. As a result, the MBRs installed with X-Flow's Compact 27 modules are applicable in the treatment of landfill leachate or in food industry with the need to remove high loads of COD [38]. On the other hand, X-Flow's Compact 33V membrane module with membrane area of 33 m^2 and membrane diameter of 5.2 mm is developed and installed in the Airlift™ MBR system [37,39]. In this MBR system, the membrane modules are placed vertically outside the bioreactor and the wastewater flows inside the membranes. Compared to conventional submerged MBRs, air in this system is injected from the bottom in order to facilitate the recycling flow of the activated sludge, to control membrane fouling in the lumen of the hollow fibres and to create turbulence which enables high flux rate at low transmembrane pressure (TMP) (0.05–0.3 bar) and a lower energy consumption (~0.3 kW h/m^3). In this system, a high quality of UF permeate can be obtained. Furthermore, the MBR has a fully enclosed system with fully automatic operation within a small footprint and no fumes or aerosols are exposed to operators. Therefore, the Airlift™ MBR is an ideal small footprint solution for the treatment of municipal wastewater. For example, there are two Airlift™ MBR systems installed in Netherlands applied in the treatment of municipal wastewater. One has the capacity of 3600 m^3/d, whereas the other can produce 14,000 m^3 of water per day. Apart from the treatment of municipal wastewater, the Airlift™ MBR is also applicable in the treatment of wastewater from specific industries including breweries, dairy plants, malt houses, refineries, etc. For instance, the Airlift™ MBR system installed in Venezuela is able to treat 2000 m^3 of brewery wastewater per day.

GE's ZeeWeed™ MBR technology combining activated sludge and ZeeWeed™ UF membrane is GE' patent technology. It can remove nitrogen and phosphors in order to meet the stringent water standards. For example, GE's Z-MOD L packaged plant has a very compacted system installed with ZeeWeed™ 500 reinforced PVDF hollow fibre membranes and is the smallest footprint MBR available on the market today [40]. The Z-MOD MBR series have the production capacities of 10–1120 GPM and the produced water has low turbidity (<1 NTU) and low TSS (<3 mg/L). Nowadays, GE has MBRs with total capacity of 3,500,000 m^3/d in operation or installation all over the world [28]. In particular, 7 out of 10 largest MBRs worldwide are ZeeWeed™ MBRs, out of which 4 have the highest capacities. The largest one is in the wastewater treatment plant in Jumeriah Gulf Estates (UAE) and it has the average production capacity of 227,100 m^3/d.

As part of the MBR process, Microza™ MF was employed in the largest membrane-filtration plant dealing with petrochemical plant effluent in Korea and the entire MBR system has a production capacity of 15,000 m^3/d [33]. In 2010, the Microza™ MBR system was adopted in a large wastewater treatment plant of a global major LCD manufacturer in Korea [21]. The MBR system is composed of two phases, each of which has a production capacity of 4200 m^3/d.

As mentioned in Section 2.1, Koch Membrane Systems is famous for the PURON® submerged membrane module because of its energy-efficient and cost-effective single header design.

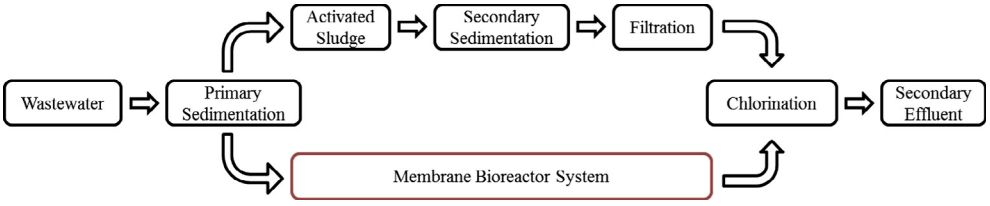

Fig. 4. Flow chart of wastewater treatment process: (up) conventional and (down) MBR technology.

PURON® MBR is ideal for wastewater treatment plants looking to reduce energy, minimise downtime and increase flux within a small footprint [41,42]. It can be applied in the treatment of municipal wastewater, food and beverage water, metal finishing, oil and gas water reuse, pulp and paper, semiconductor wastewater, etc. For example, the first large PURON® MBR of 1500 m^2 was installed in the City of Santa Paula (USA) in 2010 [43]. It is used to treat municipal wastewater and has capacities of 3.4 MGD average day flow, 7.2 MGD peak day flow and 10.4 MGD peak hour flow. Another member in the KMS family of PURON® products, PURON® HF (High Flow) submerged membrane module, has 44% more membrane area than PURON® MBR with the same dimensions [42,44]. The PURON® HF module with improved fibre chemistry has high solids tolerance and high packing density with water recovery of more than 96%. It is ideal for tertiary treatment, surface water treatment and RO pre-treatment. Furthermore, the PURON® PLUS Packaged Systems incorporate the MBR technology in a skid-mounted packaged plant [42,45]. The pre-engineered MBR plants have the production capacities of up to 760 m^3/d and meet most environmental discharge regulations. The PURON® PLUS Modular System provides filtration and ancillary equipment for capacities ranging from 760 m^3/d to 6840 m^3/d per train [42].

2.4.2. Water recycling/tertiary filtration

As shown in Fig. 5, water recycling, also named as tertiary filtration, is the process of treating the secondary effluent from wastewater treatment plants by removing impurities in order to re-use the water.

GE's Z-BOX series of packaged plants [28] with capacities of 9–525 m^3/h and the Z-PAK series [46] with capacities of 400–4000 GPM are both equipped with ZeeWeed™ UF membranes and are ideal for water treatment and tertiary systems. For example, the water plant equipped with Z-BOX in Foshan (China) has a production capacity of 5000 m^3/d, whereas Z-PAK installed in AEP Gavin (USA) can produce 3000 m^3 high quality water per day.

The AKCC Microza™ MF microfilter has been adopted for the Ulu Pandan Project plant in Singapore, which is the largest plant in the Singapore's national NEWater Project plant series [47]. The Microza™ MF system consists of PVDF hollow fibre membranes with a nominal pore size of 0.1 μm and is used for the recovery of wastewater secondary effluent. Low filtrate turbidity ($\leqslant$0.1 NTU) and complete removal of bacteria and pathogenic microorganisms such as Cryptosporidium can be obtained and the capacity of microfiltration-processed water is 191,000 m^3/d.

2.5. Other applications

Apart from the three basic applications of membrane technology in water and wastewater treatments, PVDF membranes have also been employed in some other aqua-based separation processes.

For example, GE has products of PVDF MF hollow fibre membranes, which are installed in the Mobile Membrane Microfiltration System [48]. The system can produce up to 180 m^3/h water flow with effluent turbidity < 0.05 NTU, SDI < 2 and non-detectable bacteria or particles larger than 3 μm. Therefore, the system is ideal for the pre-treatment for ion exchange or RO systems, removal of iron and magnesium from groundwater sources, removal of TSS and organics for reuse of process and wastewaters, removal of colour, odour and taste for municipal and industrial processes and replacement of clarifiers with no sludge generation. Besides, GE's Vinoclear model is made of J-Series PVDF MF membranes with a nominal pore size of 0.3 μm and it is mainly applied is wine and vinegar clarification [49].

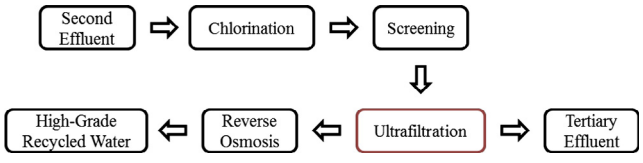

Fig. 5. Flow chart of water recycling/tertiary filtration process.

In the bioprocesses of virus removal, AKCC's Planova™ BioEX filters incorporate a durable hydrophilic PVDF hollow fibre membrane into cellulose hollow fibre filters, and they are used to deal with the harsh processing conditions in biopharmaceutical manufacturing and to filter large volumes of high protein concentration solutions safely and efficiently [50,51].

Automobiles, appliances, and many other metal products are coated with water-soluble paint in the electrocoating process. The SPIRAPAK™ elements are designed by Koch Membrane Systems and based on PVDF spiral membrane modules [52]. The SPIRAPAK™ systems are able to recover 96–98% of the paint and consequently reduce the waste significantly. Neutral or negatively-charged PVDF tubular membranes are also available in Koch's FEG PLUS™ series, which can resist plugging by changing pH and temperature [53]. This series of PVDF membranes are ideal for industrial-duty UF processes targeting at high-solid wastewater treatment and in-process membrane separation applications such as metal fabrication and finishing, food processing, pulp and paper, chemical processing and oily wastewater. Similar with FEG PLUS™ series, the ULTRA-COR™ series of UF membranes are applicable in the high-solid wastewater treatment and in-process membrane separation processes [54]. Both series of PVDF UF tubular membranes can be incorporated into KONSOLIDATOR™ systems for the treatment of wastewater with a high concentration of solids or fibrous material. The KONSOLIDATOR™ systems are plugging resistant and corrosion resistant and have capacities of 5000–500,000 gallons per day (GPD) per system [55]. Besides, both SUPER-COR™ and SUPER-G™ series ultrafiltration modules from KMS are ideal for juice clarification, in which the modules can enhance colour, flavour and stability without diatomaceous earth [56,57]. High flux and high recovery can be obtained for all types of juices by using these two series. In particular, the SUPER-G™ series can achieve three times higher solids levels than the SUPER-COR™ series.

To sum up, PVDF microfiltration and ultrafiltration membranes in various configurations have been commercialised and produced by various manufacturers such as GE, Siemens Memcor, and Koch. Combined with pre- and post-treatments, the commercial PVDF membrane products have been widely utilised in industrial and municipal water/wastewater treatment processes all over the world. On the other hand, PVDF membranes targeting at water/wastewater treatments have also been extensively investigated in laboratories. Due to the membrane fouling problem caused by the hydrophobic nature of PVDF material, most of the researchers in this field focus their work on the hydrophilic modifications of PVDF membranes. Detailed review in this aspect of PVDF can be found elsewhere [1].

3. Membrane contactors

As an alternative technology for gas–liquid and liquid–liquid contacting operations, the applications of membrane contactors have attracted increasing attention among researchers in recent years. Compared to the conventional packed columns and other traditional fluid–fluid contactors, porous membranes could overcome disadvantages such as emulsion, foaming, unloading and flooding, and could provide substantially higher interfacial area than the conventional methods [58]. The mass transfer of gas–liquid or liquid–liquid can be achieved in membrane contactors without

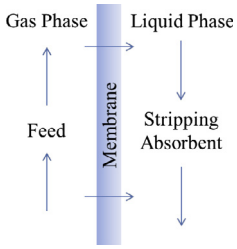

Fig. 6. Schematic diagram of a membrane contactor for gas absorption.

dispersing one phase within another. For example, in a gas–liquid membrane contactor as shown in Fig. 6, an aqueous absorbent passes over one side of the membrane, while the feed gas flows on the other side of the membrane. During the gas–liquid contacting process, the gas molecules diffuse through the membrane and then are absorbed into the absorbent. Since the aqueous solution is used as an absorbent, the membrane should be hydrophobic in order to prevent the liquid from passing through the membrane. In addition, the porous membranes are preferable in order to reduce the gaseous mass transfer resistance.

Among the various hydrophobic polymer materials including polypropylene (PP) and polytetrafluoroethylene (PTFE), PVDF is one of them that has been recognised as a suitable membrane material for membrane contactor applications such as membrane based gas absorption and membrane distillation. Unlike PP and PTFE membranes usually produced via stretching or thermal methods, the PVDF membrane can be produced via the phase inversion method, which is widely employed in large scale production due its process simplicity. In addition, the structure and morphology of PVDF membranes could be tailored to a specific membrane application by adjusting the parameters involved during the membrane fabrication process. Furthermore, the excellent thermal and chemical resistance properties of PVDF polymer have made it popular in the field of membrane contactors applications, since it possesses ability to withstand chemical attack by the absorbents. Currently, much effort is being devoted in the preparation of PVDF membranes with improved morphology and properties for various membrane contactor applications [59,60] including membrane distillation [61], and absorption or removal of gases such as CO_2 [62] and H_2S [63] from its flow streams. This section reviews the recent research progress in these areas.

3.1. Membrane based gas absorption

One important application of membrane contactors is the membrane based gas absorption, which involves the transfer of certain gases through a non-selective flat sheet or hollow fibre membrane before it is physically or chemically absorbed into a solvent. Owing to high surface area per unit volume, use of hollow fibre membranes in gas absorption has attracted considerable attention since 1980s [64,65]. This section describes various types of gas absorptions, removals or captures using hydrophobic PVDF membrane contactors.

3.1.1. CO_2 absorption

Because of the current global warming problem, the greenhouse gas emission has become a major concern worldwide. CO_2 has been proven to count for 80% of the greenhouse gas emission, which increases the temperature of earth's surface. A report has stated that half of the CO_2 emissions are originated by power plants and industries using fossil fuels [66]. Membrane based gas absorption is a relatively new technology that is currently explored by many researchers as a potential solution to remove CO_2.

PVDF has excellent thermal stability and good chemical resistance against most of the chemicals, including a wide range of harsh chemicals such as halogens and oxidants. By exploiting these properties coupled with its intrinsic hydrophobicity, the application of PVDF membrane module as the membrane contactor device for CO_2 absorption has been extensively explored in the recent years [62,67–70]. The performance of PVDF hollow fibre module for CO_2 absorption has also been compared with the conventional packed column [71]. CO_2 absorption rate per unit volume of the PVDF membrane contactor was found to be 2.7 times higher than that of the packed column through a chemical absorption process using monoethanolamine (MEA) and triethanolamine (TEA) solution as the absorbent.

A number of studies have been conducted in comparing the mass transfer rates of CO_2 absorption flux between different hydrophobic membrane materials such as PTFE, PP and PVDF in membrane gas absorption process. Yeon et al. compared the mass transfer rates of CO_2 absorption process using PVDF and PTFE hollow fibre modules as membrane contactors and aqueous MEA solution as the absorbent [72]. The mass transfer rate was found to be higher in the PVDF membrane due to the non-wetted condition of the PVDF membrane pores. A similar comparison of three different hydrophobic PTFE, PP and PVDF membrane has also been made for the CO_2 absorption using MEA solution as the absorbent, the highest CO_2 absorption flux was achieved by the PVDF membrane [73]. This is because in PP and PTFE modules, 60–80% of the total resistance was the membrane resistance caused by partial membrane wetting. However, in the PVDF module, 62% of the total resistance was the resistance in the liquid phase, which made the PVDF module have the most stable gas–liquid interface and the highest CO_2 removal efficiency. By using a membrane contactor-stripper hybrid process to recover CO_2 from flue gas, the PVDF hollow fibre demonstrated two and three times higher absorption flux than that of PP and PTFE hollow fibres, respectively. The comparison of the CO_2 absorption performance between these polymeric membranes is illustrated in Fig. 7. However, this may not be a fair comparison due to the differences in the pore sizes of these membranes, as the PTFE membrane used in the study exhibited a larger pore size than that of the PVDF membrane.

On the contrary, another comparison study of CO_2 absorption flux between PTFE, PP and PVDF hollow fibres using MEA as the absorbent showed that PTFE had the highest absorption flux, followed by PP and then PVDF [74]. Similarly, Wang et al. evaluated the long-term application of PVDF and PP membranes for CO_2 removal from flue gas and found that the membrane situation was worse for PVDF membrane compared with PP membrane after

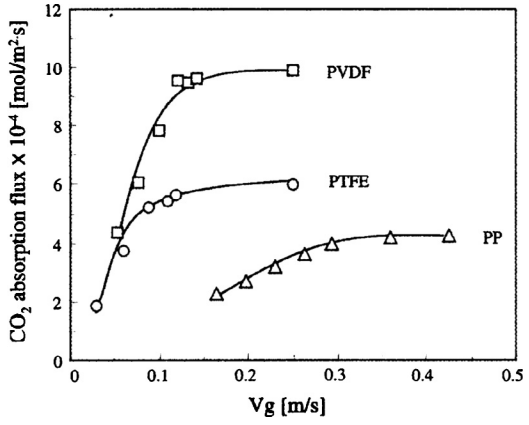

Fig. 7. CO_2 absorption flux for hollow fibre membrane contactors (Vg: superficial liquid velocity) [73].

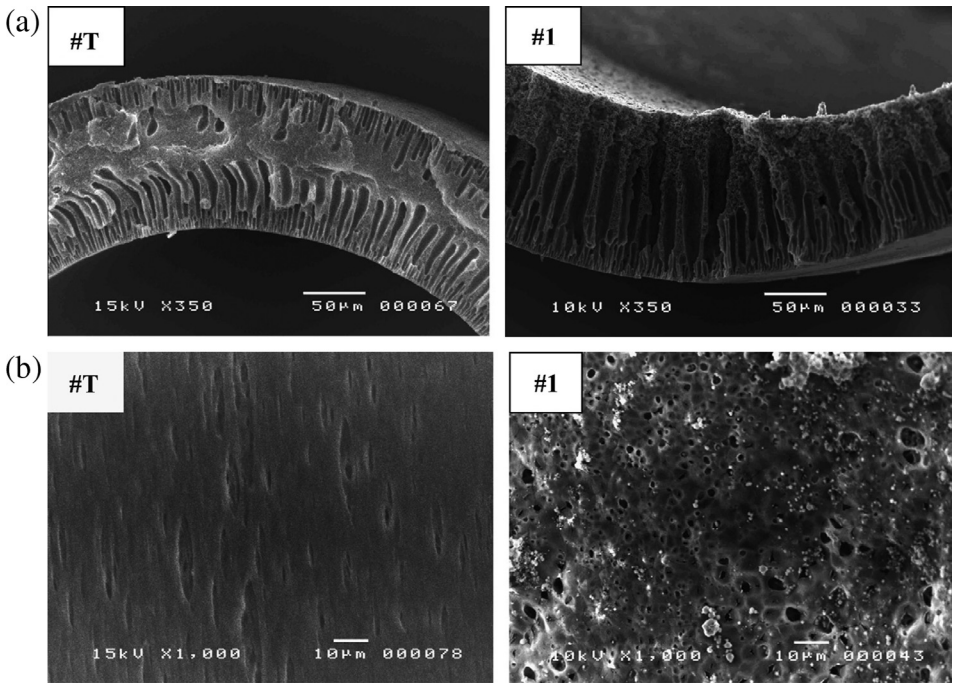

Fig. 8. (a) Cross-section and (b) inner surface images of PVDF hollow fibre membranes (membrane #T: a commercial membrane and membrane #1: in-house made membrane prepared from phosphoric acid as non-solvent additive [80].

30 days' operation [75]. In addition, both of the mass transfer resistances were increased dramatically due to membrane wetting caused by physical or chemical dissolving of membrane surfaces, which led to a decreased membrane hydrophobicity and deformation of membrane pore structure. Khaisri et al. also observed that PTFE hollow fibre exhibited the highest CO_2 absorption flux through physical and chemical absorption processes, although the in-house made PVDF membrane demonstrated superior performance than PP membrane in their study [76]. The authors observed that CO_2 flux of PVDF membrane was lower than that of PTFE by roughly 20%. Nevertheless, due to the much lower fabrication cost of PVDF membrane compared to PTFE membrane, the use of PVDF membrane as a membrane contactor in CO_2 absorption is anticipated to lead to a realistic path towards the industrial implementation.

The effect of different operating conditions on the CO_2 absorption efficiency has also been investigated by Mansourizadeh et al. [77]. In case of physical absorption using distilled water as the absorbent, the CO_2 flux could be increased by improving the amount of CO_2 dissolved in water, such as increasing the gas pressure or reducing the absorbent temperature. In chemical absorption processes, however, the mass transfer rate was controlled by the reaction between CO_2 and the absorbent such as MEA solution.

As has been discussed previously, the preparation condition can greatly affect the morphology and structure of PVDF membrane, as well as its performance [1]. As much work has been focused on the fabrication of PVDF membranes with improved membrane contactor properties for CO_2 absorption [67,78,79], the relationships between the preparation conditions and the resultant membrane structure, CO_2 absorption performance, membrane resistance as well as long-term operation are among the attractive issues which are further discussed below.

The effect of PVDF membrane structure on the mass transfer of CO_2 absorption in water has been investigated by Atchariyawut et al. [80]. Different PVDF membrane structures were obtained in their work. The results of the performance test indicated that the sample with skin-free inner structure had better performance compared to the commercial samples. Fig. 8 demonstrated the cross section and inner surface micrographs of the commercial and the fabricated PVDF hollow fibre membranes by Atchariyawut et al. [80] who suggested that the skin-free inner structure was favourable for gas transfer due to the reduction in the mass transfer resistance. Rajabzadeh et al. also reported similar finding, where their in-house fabricated PVDF hollow fibres had completely porous inner surface and demonstrated a comparable performance with the commercial PTFE hollow fibres [79]. Other researchers including Young et al. [81] and Feng et al. [82] also agreed with this finding and suggested that such a structure could be obtained by controlling preparation parameters such as dope composition, use of non-solvent additives, temperature of the coagulation bath, spinning temperature, air gap and shear rate during spinning, which will be discussed below.

3.1.1.1. Effect of dope preparation. Hollow fibres spun from a dope solution of lower polymer concentration may possess a wider pore size distribution. This feature could cause the membrane wetting problem during the long term operation, due to the existence of some large pores. However, another investigation on the effect of polymer concentration on the prepared membrane indicated that increased PVDF concentration in the dope resulted in the formation of a thicker and denser surface layer, which led to a decreased CO_2 flux in the contactor application with NaOH solution as absorbent [83].

The addition of non-solvent additives in spinning dopes has been recognised as one of the methods to modify the structure, increase the porosity of the hollow fibre membranes and enhance their separation performance. Ismail and co-workers have performed much work associated with the effect of additives employed in the spinning dope on the structure of the resultant PVDF hollow fibre membranes, and eventually on the CO_2 absorption performance in membrane contactor processes [67,77,84–88]. Several types of additives have been employed in the fabrication of PVDF hollow fibre membranes for CO_2 absorption, and different kinds of membrane structures were obtained through their studies.

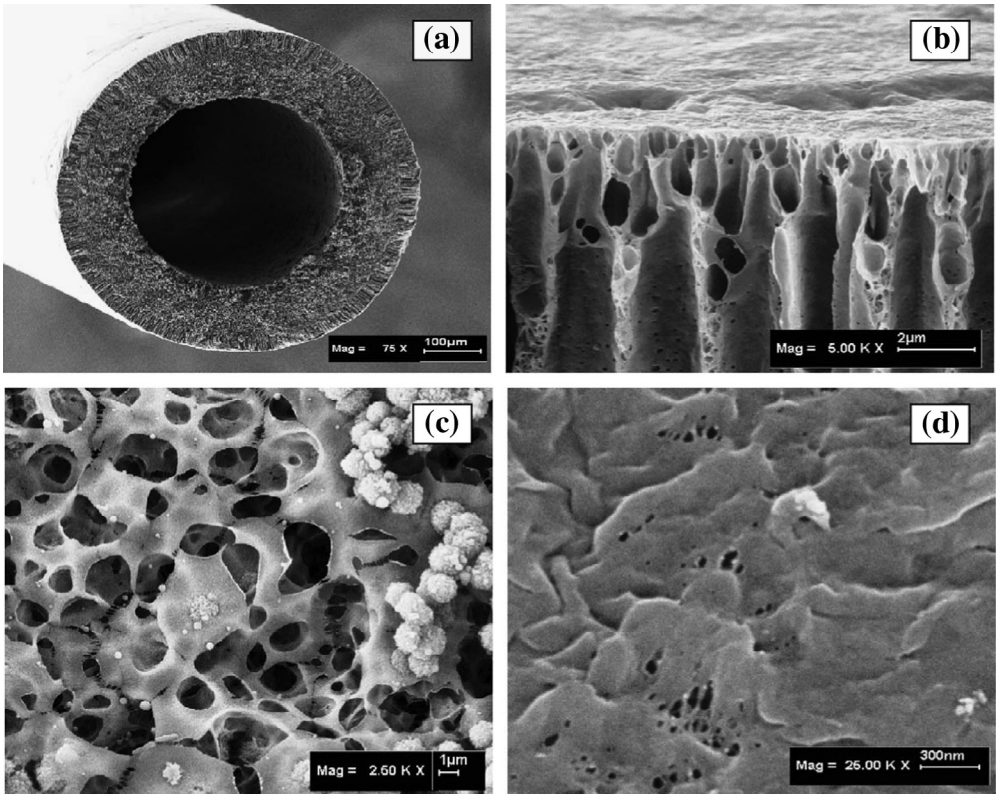

Fig. 9. FESEM image of asymmetric PVDF hollow fibre membrane for CO_2 absorption (a) cross section; (b) skin layer; (c) inner surface; and (d) outer surface [67].

For example, $LiCl{\cdot}H_2O$ has been employed as a non-solvent additive during the preparation of PVDF hollow fibre spinning solution, and the membranes with high surface porosity and small pore sizes were produced and were desirable for gas–liquid contacting application [77]. As a result of the small pore size, the critical water entry pressure of the prepared membrane was also higher than those of the commercial PP and PTFE membranes. During the long term operations, however, a 30% decrease in the CO_2 flux was observed after 23 h of physical absorption and 80 h of chemical absorption. The authors attributed the reasons for the partial wetting taken place during physical and chemical absorptions to capillary condensation and pore enlargement, respectively. The use of inorganic salt, LiCl as a pore forming additive in spinning solutions resulted in PVDF hollow fibre membrane with an improved asymmetric structure, higher effective surface porosity and significantly enhanced CO_2 absorption flux through physical absorption [67,84]. Compared to a commercial porous PTFE hollow fibre membrane, the prepared PVDF membrane demonstrated 68% higher CO_2 flux than that of the former [67]. Mansourizadeh and Ismail also provided the field emission scanning electron microscopy (FESEM) image of the prepared asymmetric PVDF membrane for CO_2 absorption, as shown in Fig. 9.

Glycerol, phosphoric acid, ethanol and polyethylene glycol with the average molecular weight of 400 (PEG-400) have also been employed as additives in the preparation of PVDF hollow fibre membranes by Ismail and Mansourizadeh [85,86]. The results showed that membranes prepared with PEG-400, glycerol and phosphoric acid as additives possessed sponge-like structure and high wetting resistance. Addition of glycerol led to larger mean pore size compared with PEG-400 and phosphoric acid. However, the PVDF membrane prepared with glycerol as a low molecular weight additive demonstrated the highest CO_2 absorption among all the tested membranes. Similar results have also been obtained by Ghasem and Al-Marzouqi [89]. They suggested that membranes prepared with 7% glycerol in the dope solution could remove CO_2 completely with NaOH solution as absorbent when gas and liquid volumetric flow rates were the same. In addition, the porous PVDF hollow fibre membranes with 4% glycerol in the dope solution was prepared by Mansourizadeh and Mousavian [90] and the membrane with almost sponge-like structure and ultrathin outer skin layer was produced and then tested in the membrane contactor for CO_2 absorption with diethanolamine solution as the absorbent. The results revealed that by varying the operating conditions, CO_2 absorption flux of 0.02 mol/m^2 s was obtained and it decreased by 26% in the first 10 h and then reached the steady state till the end of the long-term test for over 160 h.

In addition, Ismail and co-workers modified PVDF hollow fibre membranes by blending the dope solution with a surface modifying macromolecule, which self-enriched on the membrane surface during the phase separation process [87]. The membranes with improved hydrophobicity, pore size and surface effective porosity were obtained and showed better performance in the contactor for CO_2 absorption with reduced mass transfer resistance, higher flux and smaller flux reduction caused by partial pore wetting. Furthermore, the CO_2 absorption flux was increased considerably with increase of surface modifying macromolecule in the dope solution [88].

3.1.1.2. Effect of spinning parameters. The effect of spinning temperature on membrane morphology and gas absorption performance was also studied [91]. The results suggested that membrane porosity, strength and CO_2 removal efficiency could be improved by increasing the dope extrusion temperature. In addition, the formation of a dense skin layer caused by the high air gap during spinning was found helpful to avoid membrane wetting. Increasing shear rate during the spinning process could result in larger membrane pore size and higher CO_2 absorption rate during physical absorption using water as the absorbent [78].

Table 3
Comparison of the performance of PVDF hollow fibre membranes in membrane contact applications for CO_2 removal or capture.

Membrane material	Fibre OD (μm)	Fibre ID (μm)	Pore size (μm)	Membrane porosity	Separation component	Stripping absorbent	Absorption/permeate flux (mol/m^2 s)	Reference
PVDF Kynar 740	788	471	0.005	–	CO_2	Distilled water	$2.4 * 10^{-3}$	[78]
PVDF Kynar 740	828	514	0.02	0.76	CO_2	Distilled water	$1.35 * 10^{-3}$	[80]
PVDF Kynar 760	1000–1100	750–850	–	–	CO_2	Distilled water	$3.4 * 10^{-4}$	[81]
PVDF (Memcor)	1000	650	0.2	0.75	CO_2 from CH_4	NaOH	$3.2 * 10^{-3}$	[68]
PVDF (Memcor)	1300	800	0.2	0.60	CO_2	MEA	$4.0 * 10^{-4}$	[69]
PVDF (Solef)	1080	660	–	–	CO_2	MEA	$2.0 * 10^{-2}$	[79]
PVDF (Krict)	1070	830	0.03	–	CO_2 from flue gas	MEA and TEA	–	[71]
PVDF UMP-0047R	2200	1400	0.2	0.5	CO_2	PZ[a] and AMP	–	[62]

[a] PZ: piperazine.

3.1.1.3. Effect of coagulation conditions. The coagulation bath is another important factor that has influence on the ultimate membrane structure since the phase inversion process of the PVDF polymer takes place in the coagulation bath. Young and co-workers studied the effect of internal coagulants on the membrane performance of CO_2 absorption [81]. The PVDF membranes with a skinless inner surface were found to possess a comparable performance with the PTFE membrane, and considered as a less costly alternative for the separation or absorption of CO_2. A similar conclusion was drawn by Feng et al., who suggested that the inner skin could be eliminated by using NMP aqueous solution as a bore fluid, and this eventually increased the flux and reduced the membrane resistance [82]. The study on the effect of ethanol concentration in the coagulation bath on the PVDF membrane pore geometry was conducted by Ahmad et al. [92]. The results indicated that the existence of low concentration ethanol in the water bath resulted in membranes with higher hydrophobicity, smaller pore size and more uniform pore size distribution and hence, improved performance in the absorption of CO_2 using 2-amino-2-methyl-1-propanol (AMP) as absorbent. Ahmad and co-workers also improved PVDF membrane properties by adopting two-stage coagulation bath system composed of ethanol and NMP/water, respectively [93]. The prepared membrane has higher hydrophobicity with larger water contact angle of 127° and higher porosity of roughly 89% with narrower pore size distribution. As a result, the prepared membrane showed higher efficiency of CO_2 removal in the membrane gas absorption test. Furthermore, Ghasem et al. investigated the effect of quenching temperature on the porosity and pore size of PVDF membranes prepared by thermally induced phase separation technique [94]. In their study, porous membranes composed of spherical clusters were obtained. In addition, increasing quenching temperature resulted in larger pore size, effective surface porosity and hence, more CO_2 removed from natural gas.

As mentioned above, one major problem with PVDF membrane contactor for CO_2 absorption is membrane wetting, which is inevitable. It changes the overall mass transfer coefficient and leads to a reduction in CO_2 flux. Therefore, membranes with high hydrophobicity are desirable for membrane contactor applications.

Copolymer poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) is found to be more hydrophobic than the PVDF homopolymer due to the increase of fluorine content from hexafluoropropylene group, which makes it beneficial for the membrane contactor application. Shi et al. reported that PVDF-HFP hollow fibre membranes spun at the higher shear rate exhibited reasonable performances, as the CO_2 flux obtained was higher than the plain PVDF hollow fibre membranes [95]. Wongchitphimon et al. modified the outer surface of PVDF-HFP hollow fibre membranes with mixture of α, ω-triethoxysilane terminated perfluoropolyether or Fluorolink®S 10 and tetraethoxysilane (TEOS) [96]. Compared with plain PVDF-HFP membranes, the modified membranes possessed higher hydrophobicity with increased water contact angle from 95.5° to 127.8° and a decreased mean pore size from 32.7 nm to 25.2 nm. As a result, the CO_2 absorption performance was improved. Recently, Sairiam et al. treated commercial PVDF hollow fibre membranes with aqueous NaOH solutions and helium plasma, followed by surface grafting of organosilane [97]. All the modified membranes possessed much higher water contact angles and better mechanical strength compared with the unmodified membrane while other physical properties including porosity and pore size were not changed considerably. In addition, the modified membranes showed more stable performance in the long term test of CO_2 absorption with Taurine sodium solution as the absorbent for 15 days.

To sum up, considerable amount of research has been conducted on the application of PVDF hollow fibre membranes in the membrane based gas absorption for CO_2 removal. The membrane structure and performance could be controlled by adjusting the preparation conditions and employing additives. However, the problem of membrane wetting still remains challenging in this field, especially for the stability of long-term operation. The performance data of several PVDF membranes for CO_2 removal using the membrane contactor technique are summarised in Table 3. Meanwhile, the feasibility studies on commercially available PVDF membranes for CO_2 based absorption were also conducted for separation of CO_2 from CH_4 in natural gas processing [68], separation of CO_2 using different absorbents [62,69], and in a pilot-scale membrane hybrid system for the removal of CO_2 from flue gas [71].

3.1.2. Odour control by H_2S removal

Odour emission is one of the major environmental issues and is increasingly getting attention worldwide. It is often associated with the emission of H_2S gas from industrial and domestic processes, such as domestic wastewater treatment. H_2S does not only cause nuisance, but also has serious health effects and adverse environmental consequences such as acid rain when it is discharged. A short time exposure of several ppm H_2S can cause dramatic health effect, while long time exposure at very low levels of less than 1 ppm can also affect human health [63]. Therefore, the removal of H_2S to ultra-low concentrations, less than 5 ppb, is needed. The research on PVDF hollow fibre as a membrane contactor applied in removing H_2S is currently posing great challenges than other types of membranes.

In membrane based gas absorption, the efficiency of the absorption process depends on the membrane properties as well as the operating parameters. Li and co-workers extensively investigated the H_2S removal from gas streams through their in-house fabricated PVDF hollow fibre membranes [98–101]. They considered that the higher membrane's coefficient is the desirable characteristics of the membrane for mass transfer of H_2S at it low concentration. The PVDF hollow fibres with a reduced membrane resistance could be produced through the proper selection of preparation conditions and fabrication techniques. Wang et al. studied the effect of various operating conditions on the H_2S removal efficiency

Table 4
Summary of PVDF membranes in membrane contactor applications for other gas removal.

Membrane material	Fibre OD (μm)	Fibre ID (μm)	Separation component	Stripping absorbent	Membrane's coefficient (m/s)	Overall mass transfer coefficient (cm/s)	Reference
PVDF Kynar 760	907	607	H_2S	Na_2CO_3	–	1.9	[63]
PVDF Kynar 720	1063	625	H_2S from gas mixture	NaOH	0.072	0.036–0.051	[98]
PVDF Kynar [redacted]	[redacted]	380–630	H_2S or CO_2	NaOH	$4.09 * 10^2$	–	[99]
PVDF Kynar 760	907	607	H_2S from CO_2 gas stream	Na_2CO_3	–	1.6	[101]
PVDF Kynar 761	986	765	SO_2 from flue gas	NaOH	$2.3 * 10^{-3}$	–	[104]
PVDF Kynar 760	730	490	NH_3 from water	H_2SO_4	$1.52 * 10^{-5}$	–	[106]

and found that H_2S could be completely removed at a relatively short residence time when the feed concentrations of 17.9–1159 ppm H_2S was used [63]. They also found that the mass transfer coefficient strongly depends on the pressure and flow rate of the feed gas. Following that, an investigation was performed on the selective removal of H_2S from gas streams containing high concentration of CO_2 through a PVDF hollow fibre membrane module. The experimental results revealed that the selectivity of H_2S was one order of magnitude higher than that of packed towers [101]. Besides, the PVDF hollow fibre membrane modules have also been tested and applied in the purification of indoor air by attaching to air conditioners, where the condensed water produced during refrigeration was used as the stripping solution [100].

3.1.3. Absorption of other gases

Porous PVDF hollow fibre membranes have also been employed as membrane contactors in the absorption of other types of gases such as SO_2, NO_2 and NH_3. SO_2 emission is one of the major environmental concerns since SO_2 is the most pervasive air pollutant and can cause acid rain. SO_2 gas is commonly produced by the combustion of fossil fuels in power plants, incinerators and boilers sulphuric acid industry.

Li and co-workers experimentally and theoretically studied the removal of soluble acid gases such as SO_2 and H_2S from gas streams using asymmetric PVDF hollow fibres as membrane contactor modules with NaOH as the liquid absorbent [99]. Their results suggested that all the employed PVDF membranes remain non-wetted under the experimental operating conditions. This anti-wetting performance is one of the desirable characteristics for gas–liquid contacting modules, as discussed in previous sections. Following that, Li evaluated and compared the capabilities of the fabricated asymmetric PVDF hollow fibre membranes with the conventional symmetric PP hydrophobic hollow fibre membranes through an experimental study of mass transfer of SO_2 and H_2S [102]. The membrane's coefficient of the fabricated PVDF hollow fibre membrane was observed to be considerably higher than that of PP. PVDF hollow fibre membranes have also been prepared and tested in gas–liquid contactor application for the absorption of SO_2 from flue gas [103,104]. Compared to a conventional wetted wall column, the absorption rate of SO_2 in hollow fibre membrane contactor was found to be much higher, when only SO_2 was supplied as the feed inlet [103]. The SO_2 removal efficiency of ~85% could be achieved when NaOH solution as the absorbent [104].

Park et al. tested the absorption of NO_2 using a membrane contactor module constructed from PVDF hollow fibre membranes [105]. The highest NO_2 removal efficiency was obtained when Na_2SO_3 was used as an absorbent. On the other hand, Tan et al. applied the fabricated PVDF hollow fibre membranes for NH_3 removal from water through the membrane contactor; the removal of ammonia was effective with increasing pH up to 10 [106]. A summary of PVDF membranes for the separation of H_2S and other gases are given in Table 4.

3.2. Membrane distillation

Membrane distillation is one of the emerging membrane contactor technologies that have found a place in the field of separation, as a potential route to the low cost and energy saving technique over conventional processes such as distillation and reverse osmosis. The most commonly used membrane distillation technologies include direct contact membrane distillation (DCMD), vacuum membrane distillation (VMD), air gap membrane distillation (AGMD), sweeping gas membrane distillation (SWGMD), etc. Fig. 10 shows the schematic diagrams of the DCMD and VMD processes. Similar with the membrane contactor, in the membrane distillation process, a hot feed solution flows in one side of the membrane, whereas a cooled permeate flows in the other side of the membrane. In DCMD process, the vapour passes through the membrane and condensate directly, whereas in VMD process the vapour is sucked out of the permeate side and condensates outside the membrane module.

Advantages of membrane distillation over other separation processes have been reported by Lawson and Lloyd in their comprehensive review [107]. Lower operating temperatures and pressures compared to conventional distillation and pressure-based membrane separation process are among the numerous advantages of the membrane distillation. Although the commercial membranes are currently available, the efficient separation performance could not still be achieved due to the effects of membrane properties such as surface property, pore size and pore size distributions of the membranes [108–110]. It is well known that one of the criteria for the membranes to be used in membrane distillation processes in aqueous medium is that the polymeric membrane material must be hydrophobic. As PVDF is hydrophobic in nature, much effort has been devoted to the preparation and fabrication of PVDF membranes to meet the required properties for membrane distillation [110–113]. Potential applications of PVDF membranes for membrane distillation include desalination, concentration and

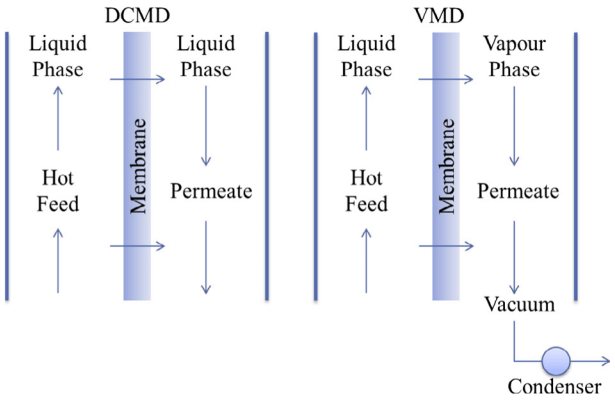

Fig. 10. Schematic diagrams of DCMD and VMD.

Table 5
Comparison of the maximum flux obtained in DCMD using PVDF membranes for desalination purpose.

Membrane	Maximum flux (kg/m^2 h)	Feed	Feed inlet temperature (°C)	Permeate inlet temperature (°C)	Reference
Dual layer PVDF hollow fibre	55	3.5 wt.% NaCl	90	16.5	[114]
Dual layer PVDF hollow fibre	70.08	3.5 wt.% NaCl	86	20.5	[112]
PVDF-PTFE hollow fibre	46.1	3.5 wt.% NaCl	79.5	17.5	[130]
PVDF hollow fibre	67	3.5 wt.% NaCl	80	16–18	[113]
PVDF flat sheet	9.8[a]	1–2 wt.% NaCl	60	20	[115]
PVDF hollow fibre	41.5	3.5 wt.% NaCl	79.3	17.5	[61]
Mixed matrix PVDF hollow fibre	79.2	3.5 wt.% NaCl	81.5	17.5	[192]
PVDF flat sheet	9.29	3.0 wt.% NaCl	50	20	[117]
PVDF hollow fibre	40.5	3.5 wt.% NaCl	81.8	20.0	[124]
Commercial PVDF flat sheet	32.4	Distilled water	79.3	17.5	[193]

[a] The original data reported are based on dm^3/m^2 d, but the data has been converted to kg/m^2 h.

crystallisation of aqueous solutions and removal of volatile organic compound (VOC) from wastewater, which are presented below.

3.2.1. Desalination of water and wastewater

Besides global warming, fresh water shortage has been considered as one of the most serious problems for human beings, as reported by United Nations in 1991. Because of this, desalination has become one of the important processes for producing fresh water in the world. Membrane distillation is an alternative technology in desalination, which offers several advantages over other conventional methods [112,113]. A high performance membrane for membrane distillation process should exhibit (1) low membrane resistance to the water vapour mass transfer, (2) low thermal conductivity, (3) good thermal stability and chemical resistance, and (4) high liquid entry pressure to prevent wetting [114]. The fabrication of high performance PVDF membrane with desirable properties for this particular application remains challenging. Table 5 summarises the PVDF membrane performances for desalination through the membrane distillation technique. In the following section, studies on PVDF membranes prepared for membrane distillation with respect to its geometry, preparation conditions, additives, etc. are discussed below.

3.2.1.1. Membrane geometry. Tomaszewka prepared PVDF flat sheet membranes with various polymer concentrations via the phase inversion process and employed them for the removal of NaCl from water through membrane distillation [115]. Elimination of chloride in the permeate was found to be higher than 99%. Bottino et al. casted PVDF membranes on a braid support and the obtained membranes exhibited a slightly higher flux than those of the commercial ones with high salt retention [116]. Furthermore, Kuo et al. investigated the effect of dual-bath coagulation method during the membrane casting process on the separation efficiency of direct contact membrane distillation process [117]. The permeation flux and rejection coefficient of the prepared membranes were found to be close to the commercial ones. Fan and Peng prepared hydrophobic PVDF flat sheet membranes and compared their performance in DCMD and VMD processes [118]. The results suggested that the prepared thin flat sheet membranes had high surface hydrophobicity and sponge-like structure, and showed a better performance with a permeate flux of 22.4 kg/m^2 h and NaCl rejection of 99.9% in the VMD application. Also, Fan et al. prepared symmetric PVDF flat sheet membranes by vapour induced phase separation technique and applied the membrane in VMD with 3.5 wt.% NaCl solution as the feed [119]. The preparation process was investigated and optimised. The best-produced membrane with water contact angle of 145° had a permeate flux of 22.4 kg/m^2 h and a salt rejection of 99.9% in the VMD test.

While flat sheet is the dominant geometry so far studied, researchers also continue to explore alternative format such as tubular membranes and hollow fibres. Moreover, PVDF membranes with other geometries, such as multichannel rectangular structure with grooved outer selective surface [120] and lotus-root-like multi-bore structure [121,122], were prepared with specially designed spinnerets by Chung and co-workers. The characterisation results of these membranes showed that the former performed a relatively high permeation flux whereas the latter had great mechanical durability. Further studies indicated that the multi-bore hollow fibre membranes exhibited excellent wetting resistance and salt rejection of over 99.99% in the VMD test with synthetic seawater feed [122].

3.2.1.2. Effect of additives for improved permeability and structure. High membrane permeability is always one of the important criterions for a membrane separation process. As a result, considerable investigations have been conducted to improve the flux of PVDF membranes applied in membrane distillation processes. For instance, Song and Jiang investigated the relationship between preparation conditions and the membrane performance [123]. They suggested that the addition of non-solvent additive had the most effect on the membrane distillation coefficient and thermal efficiency, whereas the coagulation medium had the least effect. Consequently, different additives including inorganic nanoparticles, pore forming agents and small organic molecules were employed to improve the hydrophobicity and membrane distillation performance of PVDF membranes. Hou et al. explored the preparation of hydrophobic PVDF hollow fibre membrane using LiCl and PEG as non-solvent additives for desalination purpose. The PVDF hollow fibre membrane with good hydrophobicity and high porosity was formed and the membrane exhibited a good permeation flux of 40.5 kg/m^2 h and NaCl rejection of 99.99% [124]. In addition to LiCl/PEG mixture, hydrophobic modified $CaCO_3$ nanoparticle was also dispersed in the PVDF dope solution to optimise the morphology of the produced membrane [125]. As a result, an improved permeation flux of 46.3 kg/m^2 h with satisfying stability for 30 days was achieved. On the other hand, polyvinylpyrrolidone (PVP) was first used as pore forming additive by Simone et al. in the preparation of porous PVDF hollow fibres designed for seawater desalination with VMD [126]. Their work suggested that the addition of PVP at high concentration led to the formation of sponge-like-structure membranes with improved mechanical strength. These membranes showed salt rejection around 99.98% in VMD tests on synthetic seawater. A mixture of acetone and H_3PO_4 was also used as non-solvent additive to prepare PVDF flat sheet membrane on the support of non-woven polyester fabrics [127]. In the DCMD test with 35 g/L NaCl solution, a maximum permeate flux of 47.6 kg/m^2 h was achieved. In the subsequent test with natural seawater containing 4.65 mg/L boron, salt rejection over 99.99% and boron rejection over 99.56% were achieved [128].

3.2.1.3. Dual layer membranes. Another strategy is by fabricating dual layer hydrophobic–hydrophilic hollow fibres to enhance the

flux in membrane distillation processes [114]. This is because membrane thickness has a significant influence on the permeate flux in membrane distillation processes, as they are controlled by both mass transfer and heat transfer. Thinner membranes increase the flux, but the driving force for the separation process is reduced due to the greater heat loss. Membrane thickness, being one of the important parameters, can be optimised by fabricating dual-layer membranes with a thin hydrophobic functional layer on top of a hydrophilic support layer. Hydrophobic PVDF membranes with three-dimensional porous structure could be produced by using a proper non-solvent. However, the prepared membrane had rather weak mechanical strength, which could be improved by incorporating hydrophilic and hydrophobic clay particles into the dope solutions. As a result, the membrane thickness was optimised whilst maintaining its mechanical strength, and consequently the permeation flux of the DCMD process was also enhanced. For example, methanol was adopted as a non-solvent additive and self-synthesised fluorinated silica particles were employed as a hydrophobic modifier to prepare dual-layer hydrophobic–hydrophilic PVDF hollow fibres with a dense interconnected globule structure [129]. The produced membranes demonstrated high permeation flux of 83.40 ± 3.66 kg/m^2 h in the DCMD test. However, delamination often occurs in dual-layer membranes, which is a problem limiting the application of such membranes.

One of the major issues, that limits the application of PVDF membranes in the membrane distillation, is the presence of macrovoids in the membrane structures. The formation of macrovoids in membranes is undesirable because the macrovoids can reduce the membrane mechanical strength, especially when operated at high pressures. Several attempts have been made by Chung and co-workers to prepare macrovoids-free PVDF hollow fibre membranes [112,113,130–132]. For example, highly porous and macrovoid-free PVDF hollow fibre membranes with reasonable mechanical strengths has been fabricated through a solvent-dope solution co-extrusion approach, while maintaining the permeation flux in the membrane distillation process [113]. The dope solution and NMP solvent were co-discharged from the middle and outer surface channels of a triple orifice spinneret, respectively shown schematically in Fig. 11. In addition, the fabrication of dual layer hydrophobic–hydrophilic hollow fibres was also found capable of reducing the macrovoids as well as enhancing the flux in the membrane distillation process. Chung and co-workers added 30 wt.% of PTFE particles in the outer-layer dope and resulted in dual-layer hollow fibres with macrovoid-free structure and a relatively thin outer-layer [131]. The produced membrane had high permeation flux of 50.9 kg/m^2 h and 100% NaCl rejection for 100 h operation. A dual-layer PVDF hollow fibre membrane composed of a finger-like inner-layer and a sponge-like outer-layer was obtained in their later work by adjusting the inner- and outer-dope and coagulation bath compositions [132]. The sponge-like contributed to a relatively high membrane wetting resistance. Membranes with such structures possessed a permeation flux of 98.6 L/m^2 h with a high energy efficiency of 94%. In addition, the mass transfer modelling suggested that the dual-layer configuration had a lower membrane resistance compared to the single-layer configuration.

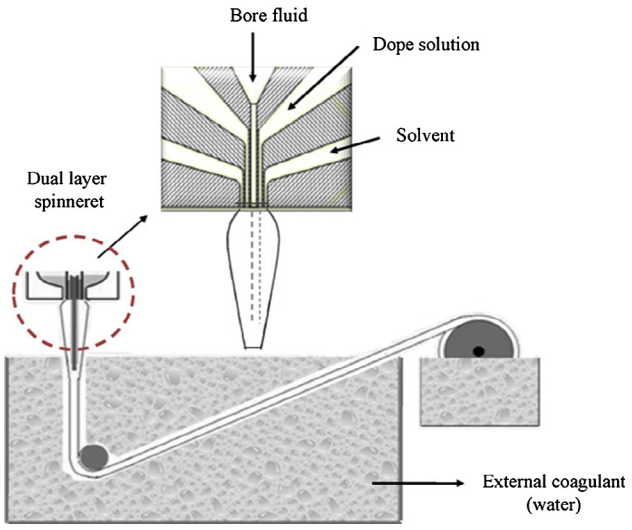

Fig. 11. Schematic diagram of hollow fibre spinning process using solvent-dope solution co-extrusion approach [113].

3.2.1.4. Membrane modification and optimisation. Yang et al. investigated the performance of unmodified, plasma modified and chemically modified PVDF hollow fibre membranes in DCMD [133]. The chemically modified membranes exhibited the narrowest pore size distribution and the best overall performance in terms of flux stability and permeation quality. Furthermore, Razmjou et al. coated TiO_2 nanoparticles onto the surface of porous PVDF membranes, followed with fluorosilanization [134]. The latter treatment of TiO_2 nanoparticles resulted in the formation of a robust uniform repellent film, which reduced the scale fouling and improved the long-term membrane stability. As mentioned above, one of the criteria for the membranes used in the membrane distillation process is that the polymer material must be hydrophobic in order to reduce the membrane wetting problem. Therefore, efforts can be found in preparing superhydrophobic PVDF membranes. For instance, Zhang et al. prepared superhydrophobic PVDF membranes by spray-deposition of a mixture of polydimethylsiloxane (PDMS) and hydrophobic SiO_2 nanoparticles on top of PVDF flat sheet membranes [135]. The modified PVDF membrane achieved NaCl rejection of over 99.99% in the long-term DCMD test of 180 h with 25 wt.% NaCl solution. Liao et al. prepared surface-modified PVDF nanofibous membranes by dopamine surface activation, silver nanoparticle deposition and hydrophobic treatment [136,137]. The produced superhydrophobic membranes showed excellent anti-wetting property and had a stable vacuum membrane distillation flux of 31.6 kg/m^2 h. On the other hand, Feng et al. prepared a modified PVDF membrane from poly(vinylidene fluoride-co-tetrafluoroethylene) [138]. Their results revealed that the modified PVDF membrane exhibits higher hydrophobicity and permeation flux than that of the unmodified PVDF membrane under the same operating conditions. Similarly, Su et al. prepared PVDF and PVDF-co-HFP nanofibrous membranes by electrospinning [139]. The testing results in a DCMD system indicated that the PVDF-HFP composite membrane had a higher salt rejection (99.9901%) compared to the PVDF membrane (99.9888%).

Some studies were also conducted in enhancing the performance of membrane distillation by optimising the operating conditions. For example, Chen et al. incorporated gas bubbling into DCMD and found that the gas bubbling could increase the permeation flux by 26% and slow down the deposition of scale fouling [140]. In addition, PVDF membranes have also been investigated to combine membrane distillation with other applications, such as NaCl crystallisation [141].

3.2.2. Removal of VOCs

Many countries are facing a major problem on the water supply due to the contamination of VOCs [142]. Some of the VOCs commonly found in water or wastewater are benzene, toluene, acetone, chloroform, etc. They can cause detrimental effects to the environment and are dangerous to the human health. Hence, the removal of VOCs from water or wastewater through an efficient method is important to human health and environment.

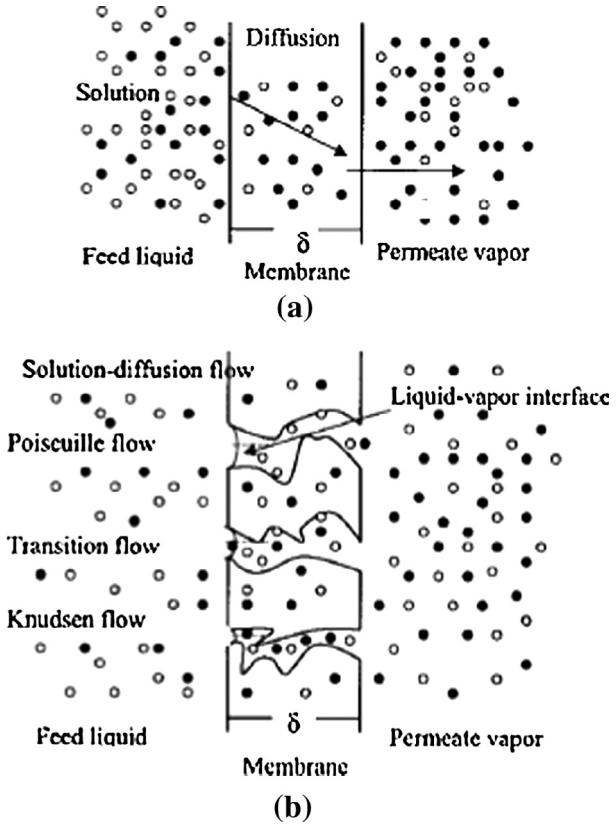

Fig. 12. Mechanisms of mass transfer in (a) pervaporation and (b) vacuum membrane distillation [146].

Recently, the removal of VOCs through the membrane distillation technology has become an interesting topic among the researchers. There have been a number of publications related to the preparation of PVDF membranes for the purpose of VOCs removal through membrane distillation from water or wastewater [111,142,143]. Pintauro and co-workers were among the pioneers who explored the preparation of asymmetric PVDF membranes for the removal of VOCs from water using VMD [144,145]. Although they had expressed the porous PVDF membranes for the separation of VOCs from water as the "pervaporation membranes", membrane characteristics and the mechanism of mass transfer involved in the separation process were identical and close to the VMD process. This is because pervaporation employs dense and selective membranes, for which the separation is based on the relative solubility and diffusivity of each component in the membrane material, whereas the VMD requires porous and hydrophobic membranes which act only as a support for the vapour–liquid interface, and do not contribute to the separation performance [146]. Fig. 12 shows the schematic diagram illustrating the fundamental differences between the two processes.

According to Pintauro and co-workers' study, the fabricated PVDF flat sheet membranes were highly efficient in removing low and high boiling non-polar organic components such as benzene, toluene and chloroform from water, and also performed as good as or better than composite-coated PDMS membranes [145]. The hydrophobic nature of PVDF was successfully utilised, as to promote the selective absorption and transport of the organics in feed solutions, where the separation factors as high as 4900 and high organic trans-membrane fluxes were obtained.

As a challenge to improve the separation performance, Jian and Pintauro prepared hollow fibres configuration of PVDF membranes due to the fact that hollow fibre membranes possess much higher surface area per volume compared to flat sheet membranes [147]. The produced hollow fibre membrane was then tested for the removal of ppm concentrations of organics from water. Although the performance of the hollow fibres was not as good as the flat sheets, they managed to fabricate membranes with remarkable separation factor and relatively good mechanical strength.

On the other hand, Khayet and Matsuura investigated the removal of chloroform from water using the fabricated PVDF flat sheet membranes via the VMD process [143]. By adding water into the casting solution as the non-solvent additive, the membrane porosity was increased and thus resulted in higher chloroform flux during the membrane distillation process. Wu et al. explored the removal of benzene and toluene from water using the in-house prepared PVDF hollow fibre membranes through a VMD technique [142]. They reported that the obtained membranes had high hydrophobicity and good performance since high separation efficiency of over 99% was achieved during the simultaneous removal of benzene and toluene from water. Subsequently, 1,1,1-trichloroethane (TCA) was removed from water using the similarly fabricated PVDF hollow fibre membranes through the VMD process [111]. The experimental results revealed that high TCA flux and separation factor were obtained from the prepared membranes. Furthermore, Feng et al. prepared highly porous and hydrophobic PVDF nanofibre membrane by electro-spinning method and then evaluated the membrane by the removal of chloroform in membrane air-stripping process [148]. The results suggested that VOC could be removed effectively because of the high hydrophobicity and pore size of the nanofibre membrane.

4. Other applications

Despite its broad commercial application in water and wastewater treatments and the extensive study in the application of membrane contactors, PVDF membranes have also been investigated for other applications such as support material, bioseparation and biotechnological applications. This section provides a brief review on these additional applications of PVDF membranes in both commercial and academic contexts.

PVDF is a popular support material due to its various outstanding properties such as thermal stability, chemical resistance and excellent mechanical strength. As a result, numerous studies have been conducted to coat a functional layer on top of PVDF membranes for the application of VOC removal. For example, Li and co-workers developed a composite hollow fibre membrane by coating divinyl-PDMS on the PVDF support layer and tested the prepared membrane for the recovery of benzene, toluene and xylene (BTX) through vapour permeation [149]. The results showed that BTX was selectively removed from nitrogen with a recovery of more than 95% and indicated that the developed composite membrane had a potential in substituting the conventional silicone rubber. Subsequently, modified silicone-PVDF composite hollow fibre membranes composed of PDMS^{vi}-PVDF were also fabricated and tested for the removal of a wide variety of VOCs including benzene, toluene, chloroform, ethyl acetate and acetone by the vapour permeation method [150]. The study revealed that the developed membranes exhibited very high removal efficiency of more than 96% for all the VOCs examined under favourable operating conditions. In addition, Liu et al. reported the preparation of hollow fibre composite membrane comprised of PVDF as a support, coated with poly(ether block amide) for the separation and recovery of gasoline vapour from nitrogen for emission control [151]. The composite membrane was found to be stable for gasoline vapour recovery. Ramaiah et al. prepared a novel thin film composite membrane by casting TEOS crosslinked zeolite filled PDMS on PVDF substrate [152]. The produced membrane was then tested

with volatile chlorinated hydrocarbons and showed remarkably high flux and selectivity due to the hydrophobic nature of the filler PDMS and PVDF. On the other hand, Zhao et al. developed a PVDF based MBR by immobilising microorganisms on the outer surface of the PVDF hollow fibre membranes [153]. The developed MBR was then tested with a mixture of air, toluene and trichloroethylene (TCE) as the feed passing through the fibres and liquid phase consist of synthetic nutrients circulating in the shell. As a result, toluene and TCE in the air feed were biologically removed by the biofilm on top of the membrane with the removal efficiency of 95% and 22.1%, respectively.

PVDF has also received much attention in biotechnological and bioseparations applications, because PVDF membranes possess strong mechanical properties, high hydrophobicity and remain chemically inert to many solvents. Moreover, these membranes can be heat sterilised without change of the membrane porosity and generally more durable than other polymeric membranes [154]. Because of these advantageous properties, PVDF membranes are well recognised in bio-applications. For instance, considerable studies have been carried out using PVDF membranes for protein analysis. There are three different types of Immobilon® PVDF membranes available from Millipore and each membrane targets at different protein blotting applications. For example, Immobilon Transfer has been used as supports in the sequence analysis of picomole quantities of proteins purification using gel electrophoresis [155]; Immobilon-P^{SQ} was applied in the detection of ubiquitin-conjugated proteins in human colorectal cancer tissue [156]; and Immobilon was employed in the amino acid sequencing of proteins associated with sensitisation in Aplysia [157]. Furthermore, Kawasaki et al. utilised a PVDF membrane for the multiplex analysis of proteins that were phosphorylated at tyrosine in the phosphoproteome of rice callus or human ovarian cancer cells [158]. Similarly, Shimazaki and co-workers prepared immunoaffinity membranes by modifying PVDF membranes with anti-transferrin antibody to study the primary structure and the less stable and highly accessible regions of antigens [159]. Later on, the researchers also employed PVDF membranes to build up a 3D-map for the qualitative and quantitative investigation of trypsin inhibition activity in human plasma proteins [160]. Behrouz et al. used PVDF membranes to investigate the placental proteins for auto-antibodies in pre-eclampsia patients [161]. Furthermore, electrospun PVDF nanofibre membrane was prepared and then attached with PET sheet to produce an economical Western blot membrane, which was capable of detecting proteins with high sensitivity [162,163].

In terms of PVDF membranes employed in the bioseparation processes, Walsh et al. used PVDF membranes for the separation of proteins from intact ribosomes and ribosomal subunits of the extreme Halobacterium Marismortui, through high resolution two-dimensional electrophoresis technique [164]. Li et al. carried out fractionation of human serum albumin (HSA)/immunoglobulin G (IgG) mixture by gas sparked ultrafiltration with a tubular PVDF membrane [165]. Huang et al. modified commercial PVDF membrane to form an environment-responsive hydrogel-based ultrafiltration membrane for separating binary model protein mixture of equine ferritin and human IgG (HIgG) by sequential transmission [166]. Besides, hydrophobic PVDF membranes were exploited in obtaining peptide fragments from electroblotted proteins for internal amino acid sequence analysis [167].

Membrane chromatography is another important application of PVDF membranes in the field of bioseparation of proteins, virus, etc. Ghosh employed porous PVDF membranes in the hydrophobic interaction membrane chromatographic separation of plasma proteins: HSA and HIgG [168]. PVDF membranes were also found useful in the removal of viral particles by size exclusion mode [169], and in the separation of monoclonal antibody IgG2b, which is used to prevent rejection in bone marrow transplants [170,171]. Yu et al. fractionated site-specific PEGylated therapeutic proteins by hydrophobic interaction chromatography using a stack of hydrophilic-modified PVDF membrane [172]. Wang et al. developed a microfabricated membrane chromatography containing PVDF membranes and used them for chiral separation with high-resolution [173]. Ghosh reported the purification of lysozyme from chicken egg white using PVDF membrane-based chromatographic process [174]. The results obtained from the study showed that the PVDF membrane employed could bind lysozyme by cation exchange mechanism. Tsai et al. developed PVDF-based affinity membranes with immobilised copper ions [175]. Wang et al. studied the purification of equine IgG from horse serum using enhanced hybrid separation technique, which combines precipitation–microfiltration and hydrophobic interaction based membrane adsorption [176]. Xu et al. conducted hydrophilic modification on PVDF ultrafiltration membranes in order to separate of flavonoids from Ginkgo Biloba extraction crude products [177]. Chang et al. reported the preparation of hydrophilic PVDF microfiltration membranes, and the membranes were observed to exhibit improved antifouling properties [178]. Thus, the results suggest that the prepared membranes have good performance of blood compatibility, and hence, have potential uses in biomedical applications.

Apart from the applications described above, the significance of PVDF membranes has also been found in the field of sterilising filtration [179] and immobilisation of yeast [180]. Rajniak et al. employed commercial hydrophilic PVDF sterilizing filters in the process of removing microorganisms from a fluid stream in the filtration of pharmaceutical products [179]. While Yang et al. fabricated annular hollow fibres consisting of PVDF as an inner layer and polyethersulfone (PES)/PVP as an outer layer [180]. Yeasts were grown in the annular passage of the prepared hollow fibre and the membrane was anticipated to have great potential in the immobilisation or entrapment of biocatalyst for biochemical reactions.

5. Conclusions

In this article, applications of PVDF membranes were comprehensively reviewed. Commercial PVDF MF and UF membranes have been broadly applied in drinking water production, wastewater treatment, pre-treatment for RO and other aqua-based separation processes.

Also, hydrophobic PVDF membranes have been extensively studied with possible applications as membrane contactors for gas absorption/stripping, membrane distillation for desalination and VOC removal. In the membrane contactor applications, the high hydrophobicity, low resistance to gas transfer and high liquid entry pressure are the desirable properties of the membranes. The gradual wetting of the membrane during the operation is one of the major problems affecting the long-term use of the PVDF membranes as it increases the membrane resistance and decreases the fluid flux. Although various modifications have been made to improve the membrane hydrophobicity and control the membrane structure during the preparation process, the problem of the membrane wetting is inevitable and remains a challenge in these applications.

Because of PVDF membranes possessing strong mechanical properties, high hydrophobicity and chemically inert to many solvents, they have also been utilised to analyse proteins, to separate bioparticles by membrane chromatography, etc.

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