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PVDF membranes prepared via thermally induced (liquid–liquid) phase separation and their application in municipal sewage and industry wastewater for water recycling

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ABSTRACT

To date, remarkable progress has been achieved in the fabrication of poly(vinylidene fluoride) (PVDF) membranes with high performance for applications in wastewater treatment. After a comprehensive overview of recent progress on the preparation of PVDF membranes via thermally induced phase separation (TIPS) method, this paper provided historical information about the plenty of work focused on the preparation and advanced industrialization of PVDF membranes that was carried out by Beijing Key Laboratory of Membrane Materials and Engineering of Tsinghua University (Beijing, China). The work followed the line of formula design, advanced production, and membrane module development. Firstly, an innovative PVDF membrane with good performance was prepared via TIPS (liquid–liquid, L–L) method based on exhaustive thermodynamic and dynamic researches on the membrane formation process. Secondly, advanced production of the PVDF hollow fiber membrane was achieved by an effective combination of material processing and unit operation. Additionally, different ultrafiltration (UF) modules were fabricated according to various application situations. The final step explored the possibility of using an integrated membrane solution that adopted the modules where wastewater treatment was intended for water recycling, as shown in four application cases. The application results have shown that PVDF membranes prepared via TIPS (L–L) method break through the traditional phase separation limitation and exceed performance expectation. This paper can be a useful reference for the preparation and development of polymeric membranes and modules.

Keywords: Thermally induced phase separation; Poly(vinylidene fluoride); Membrane preparation; Membrane module; Wastewater treatment

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1. Introduction

Until now, worldwide, an estimated 768 million people remain without access to an improved source of water and demands for freshwater will continue to increase significantly over the coming decades to meet the needs of growing populations and economies, which will greatly amplify existing pressures on limited natural water resources [1]. Water reclamation is the most effective and economical solution to the water shortage problem. Membrane technology for liquid separation that takes membranes as the core component, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and electrodialysis (ED) plays an important role in water reclamation [2,3]. It is noted by Lux research center that the international membrane market, inclusive of MF, UF, NF, and RO, will rise from $1.5 to $2.8 billion accompanying a faster growth in MF/UF which has been considered as a key part of the integrated membrane technology for wastewater treatment [4–8].

1.1. Poly(vinylidene fluoride)

Poly(vinylidene fluoride) (PVDF) has received considerable attention as an important membrane material with regard to its outstanding properties such as high mechanical strength, thermal stability, chemical resistance, and high hydrophobicity, in comparison to other membrane materials, and these properties make it suitable for wastewater treatment [9–12]. Commercial PVDF is generally produced by polymerization of vinylidene fluoride (VDF) in emulsion or suspension using free radical initiators, leading to the formation of repeat units of $–CH_2–CF_2–$ [10]. In recent years, more and more efforts have been invested in the preparation of PVDF membranes which can be extensively applied in MF/UF processes [13,14].

The preparation of PVDF membranes can be traced back to the early 1980s, when a large amount of fundamental work on membrane formation had been carried out on cellulose acetate membranes [15,16]. Since then, several methods that include phase inversion, stretching, and sintering were employed in the fabrication of PVDF membranes. At present, most of the commercial membranes are produced via phase inversion methods mainly because of its simplicity and flexible production scales. According to the manner of a liquid transforming to a solid state, phase inversion can be separated into several techniques, namely (a) thermally induced phase separation (TIPS); (b) immersion precipitation (IP); (c) precipitation from the vapor phase; (d) controlled evaporation of solvent from three-component system [17]. However, among these techniques, TIPS and IP are the two most commonly used methods in the fabrication of PVDF membranes.

1.2. Thermally induced phase separation

TIPS method that was invented by Castro in 1980s can be applied to a wide range of amorphous or semicrystalline polymers [18]. It is a technique that a polymer is firstly mixed at an elevated temperature with a diluent of a high boiling point to form a homogeneous solution, then the induced phase separation and solidification can occur by quenching (or heating) the polymer solution with an upper critical solution temperature (or lower critical solution temperature) on the desired shape surface. In the last period, the diluent which is trapped in the polymer matrix during phase separation and solidification is removed to obtain a microporous structure. Compared to IP, TIPS has several advantages: firstly, it is a process with strong controllability which can be easily extended to industrial scales; secondly, membranes of the same polymer prepared by TIPS always possess higher mechanical strength and fewer defects than those prepared by IP; Finally, TIPS process has less controlling parameters thereby allowing shortening of the time spent on the development period.

The membrane formation process via TIPS is a complex and multiscale process that can be separated into phase separation and solidification. Until now, the phase diagram of a PVDF–diluent system that is based on Flory–Huggins polymer solution theory is still the basic thermodynamic method to understand the mechanism of the membrane formation via TIPS. According to the polymer solution theory, it can be known that for a polymer–diluent system, the interaction between the polymer and the diluent plays a key role in determining the phase separation process and the resulting membrane morphology; hence affecting the membrane properties, such as pore size and distribution, mechanical strength, and flux. A PVDF–diluent system can undergo a liquid–liquid (L–L) phase separation process or a solid–liquid (S–L) phase separation process due to different compatibilities between PVDF and the diluent [19,20].

However, the phase separation is too quick to depend on the thermodynamic knowledge to study the membrane formation. Thereby, many dynamic researches including experimental and theoretical studies have been carried out to analyze the membrane formation and to optimize the membrane performance. Experimental studies include both indirect and direct methods. Indirect methods are usually speculating the membrane formation mechanism through characterization of the resultant membranes by experimental instruments, such as scanning electron microscope (SEM), X-ray powder diffraction (XRD), differential scanning calorimetry (DSC). These methods can provide some information about effects of process factors on the membrane structure and properties with only a few details about the TIPS process itself. In contrast, direct methods are more intuitive because they are using optical microscope, hot stage, light scattering, or self-made apparatus to view the phase separation process [21–24]. Some information about the growth of the phase separation morphology and crystallization is easily acquired via the indirect methods. Nevertheless, these studies generally remain in macroscopic scale, and are not so explicit and flexible attribute to the complexity and instantaneity of the polymer solution systems that is a multiscale issue.

In consequence, theoretical studies that covered macroscopic, mesoscopic, and microscopic scales were also developed for a better fundamental understanding of TIPS membrane formation mechanisms. For the macroscopic scale, several models were built to explain transport phenomena since 1990s. One-dimensional models that are based on Fick's law have been proposed to simulate the concentration and temperature profiles in thin films under different evaporation conditions. Consequently, the membrane structure can be predicted to some extent by the results of those models [25–29]. Nevertheless, these model results can only reflect the temperature and concentration changes without the evolution of the phase separation process. For the mesoscopic scale, much attention has been paid to study the phase separation dynamics by the method of mathematical modeling incorporating Cahn–Hilliard theory and Flory–Huggins theory. The researches demonstrated that the droplet morphology changed with the gradient by imposing an external force [30–34]. Whereas the results are unintuitive and the microscopic information can hardly be included. For the microscopic scale, Monte Carlo [35] and molecular dynamics simulation were introduced to describe droplet growth and spinodal decomposition, but it is difficult and even beyond computational capacity to describe these systems at the microscopic level due to the short time scale and the large number of microscopic particles.

1.3. PVDF membranes prepared via TIPS (S–L) or TIPS (L–L)

There are more than 10,000 literatures retrieved by taking "TIPS Paper & Patent" as the keywords from 1970 to 2015 and the amount presents a remarkable increase after 2000, which demonstrates that this field has become a hot topic of membrane science in these years. Preparation of PVDF membranes via TIPS has been recognized since the late 1980s, however, the emergence of the fabrication of PVDF membranes via TIPS method is observed to be more significant in the recent years [36–39].

With regard to the microporous PVDF membrane preparation via TIPS, most effort has been paid on the selection of the diluent rather than the thermodynamic and dynamic researches on the membrane formation via TIPS as mentioned above, since the diluent determines the essential thermodynamic and dynamic properties of the polymer–diluent system. Table 1 summarizes the study history of the diluent selection of the PVDF membrane preparation during these years.

Reviewing the researches on the PVDF membrane preparation for water treatment shown in Table 1, it has been found that most alcohol solvents cannot dissolve PVDF even at a high temperature due to its strong polarity. Only some ester or sulfone compounds can be used as diluents, such as glyceryl triacetate (GTA), propylene carbonate (PC), phthalate solvents, especially dibutyl phthalate (DBP) that have good compatibility with PVDF and then have been applied in many studies to prepare PVDF membranes. Whereas most of the systems only undergo TIPS (S–L) process and membranes obtained always present spherulitic structures that are like structures shown in Fig. 1(a). Nevertheless, permeability and mechanical strength of this kind of membranes are unsatisfactory. Thus, attempts have been made to add some nonsolvents of PVDF (for example, di 2-ethyl hexyl phthalate (DEHP) or ethanol) to increase the porosity, but the results are not good enough [49,63]. Besides, nanoparticles such as SiO_2, $CaCO_3$, and TiO_2 have been adopted to obtain a three-dimensional network structure shown in Fig. 1(b), which could take the membranes prepared by Asahi Kasei Group as an example [64–66]. Until recently, much attention has been paid to finding some sustainable single solvents or mixed solvents to prepare PVDF membranes with good properties, and membranes with spherulitic structures are obtained from these systems. Over the past few years, TIPS has been widely applied in many fields, such as combining with IP method to prepare membrane with high strength and rejection, using polymer blend to produce a microporous membrane with special property, and preparing particles or scaffolds [67–70].

Besides the selection of diluent, some attention also has been paid to study effects of different preparation conditions (such as PVDF concentration, polymer

Table 1
A brief study history of diluent selection for membrane preparation of PVDF via TIPS

Date	Author	Institution	Diluent system	Results
1985	Hiatt et al. [40,41]	Akzona company	Diluent : cyclohexanone; γ-butyrolactone (γ-BL); propylene carbonate (PC); ethylene glycol monoethyl ether acetate (CABA)	Membranes prepared almost presented spherulitic structures, but leafy structure could be obtained when CABA was used as the diluent
1987	Josefiak and Wechs [42,43]	AKZO NV company	Diluent: glyceryl triacetate(GTA); glycerol diacetate; additive diluent: castor oil; dioctyl adipate (DOA)	The existence of nonsolvent was crucial for the existence of the cellular structures
1990	Lloyd et al. [36]	University of Texas Austin, USA	Diluent: dibutyl phthalate (DBP)	Membranes prepared presented spherulitic structure
1991 2000	Doi and Matsumura [44–46]	Asahi Kasei Group, Japan	Diluent: DBP; Additive: SiO_2 nanoparticles	Three-dimensional network structure was obtained by adding SiO_2 nanoparticles which were dissolved by NaOH solution into PVDF-DBP system
1996	Beck et al. [45]	Memtec Ltd.	Diluent: GTA Additive diluent: diglycol	Membranes with microporous structure were obtained after stretching the precursor of PVDF–diluent mixture system
2005	Smith et al. [47]	Minnesota Mining and Manufacturing Company	Diluent: GTA	A network structure was gained only by correlating TIPS with stretching method
2006	Lu and Li [48,49]	Tianjin Polytechnic University, China	Diluent: DBP; additive diluent: DOP	For the system with less DOP, a large spherulitic morphology was obvious,, whereas no large spherulitic structure existed in the membrane as the DOP content increased to 20%
2006 2007	Gu et al. [50,51]	Nanjing University of Technology, China	Diluent: dimethyl phthalate (DMP); additive diluent: DOA, dibenzylidene sorbitol (DOS)	Membranes with interconnected spherulitic structure were obtained and the addition of the second diluent made the spherulites becoming more discernable
2007 2008	Chen et al. [52,53]	Tsinghua University, China	Diluent: PC; γ-Butyrolactone (γ-BA), dibutyl sebacate (KD); additive diluent: cyclohexanone(CO)	membranes with spherulitic structure were prepared
2007 2008	Xu et al. [54–56]	Zhejiang University, China	Diluent: DBP; Sulfolane; additive diluent: di 2-ethyl hexyl phthalate (DEHP)	Membranes prepared presented spherulitic structure
2007	Cha et al. [57]	Myongji University, Korea	Diluent: γ-BL	Hollow fiber membranes with spherulitic structures were obtained via a modified TIPS process
2008	Matsuyama et al. [58]	Kobe University, Japan	Diluent: GTA; Additive diluent: glycerol; ethanol	Hollow fiber membranes presented spherulitic structures
2013	Lee et al. [59–61]	Hanyang University, Korea	Diluent: ci-trate-based solvents: acetyl tributyl citrate (ATBC); acetyl triethyl citrate (ATEC); triethyl citrate(TEC)	At a low PVDF concentration, the membranes showed more bicontinuous structure, while the structures of the PVDF membranes produced with high polymer concentrations were more spherical

(*Continued*)

Table 1 (*Continued*)

Date	Author	Institution	Diluent system	Results
2015	Lee et al. [62]	Hanyang University, Korea	Diluent: Methyl-5-(dimethylamino)-2-methyl−5-oxopentanoate (PolarClean)	Due to the solubility of PolarClean in water, the membranes were produced by a combination of TIPS and IP mechanisms Fingerlike structures with very thin skin layers formed at the outer surface of the hollow fibers, while in the middle and inner parts, spherical structures were formed,

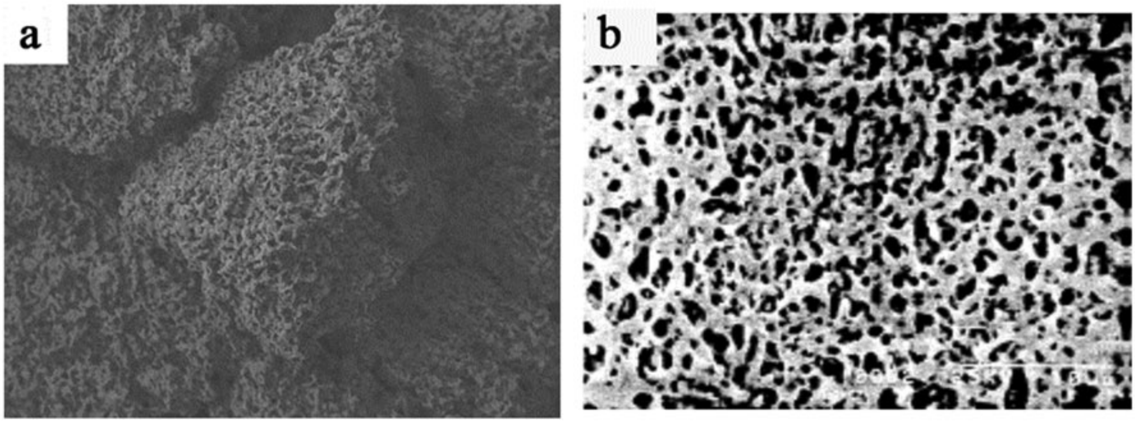

Fig. 1. Different cross-section morphologies of membranes: (a) a spherulitic structure obtained by diluent DBP [36] and (b) a three-dimensional network structure prepared by Asahi Kasei Group [44].

molecular weight, and quenching temperature) and process optimization, nevertheless these results depend much on the property of the target PVDF–diluent system [71–78]. For a specific PVDF–diluent system, certain experimental researches are necessary to realize the optimization of the membrane preparation. For example, the interaction between PVDF and the diluents can be flexibly controlled by changing polymer concentration or polymer molecular weight. In addition, increasing the polymer concentration or polymer molecular weight usually enhances the mechanical properties and reduces porosity of the resultant membranes [76,77].

As mentioned in section poly(vinylidene fluoride) and thermally induced phase separation, PVDF microporous membranes prepared via TIPS can be very suitable for wastewater treatment, whereas most of the polymer–diluent systems listed in Table 1 only undergo the TIPS (S–L) process and membranes with spherulitic structures are mostly obtained. Until now, only Asahi Kasei Group has developed and commercialized PVDF membrane modules with good performance via TIPS and researches of most groups are still limited to the development period, which means the PVDF membranes that they prepared may be not suitable in practical use and thus little information is available about the manufacture and development of PVDF membranes and modules.

On the contrary, since 2008, researchers from Beijing Key Laboratory of Membrane Materials and Engineering of Tsinghua University have paid much effort to solve this problem and found several diluent systems that with PVDF can undergo the TIPS (L–L) process. The research work follows the line of preparation of formula design, advanced production, module development, and application. Firstly, innovative PVDF membranes with good performance were prepared via TIPS (L–L) method based on the thermodynamic and dynamic researches on the membrane formation process via different methods. Then advanced production of PVDF hollow fiber membrane was realized by effectively combining material processing and unit operation. Also, according to various application situations, different UF modules were fabricated. The final step explored the possibility of using an integrated membrane solution that adopted the PVDF modules where wastewater treatment was intended for water recycling, as shown in four application cases. During the last decade, more than 50 related research articles and patents have been published, which rank forefront of all relevant research groups around the world. The following part of this paper presents complete historical information about these researches that include preparation of a PVDF membrane, advanced production of a PVDF hollow fiber membrane, applications of modules for wastewater treatment and recycling. Recalling this series of research works can help improve the understanding about the design and development of membranes and modules for the purpose of application. We hope that this paper would be a useful reference for researchers who are working on the development of polymeric membranes and modules.

2. Preparation of a PVDF membrane via TIPS (L–L) method

2.1. Thermodynamic aspect

2.1.1. From solubility parameter to dielectric constant

It is found by our group that differences in molecular structure between polymer and diluent decide the interaction of a polymer–diluent system that directly determines the phase separation behavior and the corresponding membrane structure. So, the interaction of a polymer–diluent system can be controlled by selecting diluents. Solubility parameter that includes two different systems (Hildebrand and Hansen) is the most common method to evaluate and predict the interaction of a system. However, since the polarity of PVDF is a little high, it is not proper to use Hildebrand solubility parameter to evaluate the interaction between PVDF and diluents. Besides, different references or calculation methods always return different Hansen solubility parameters for a polymer–diluent system. Therefore, a new method should be developed for better representing the interaction between PVDF and diluents. In 2008, it is firstly found that the dielectric constant should be regarded as one of the important parameters measuring interaction among molecules, after studying the effect of difference of dielectric constants between PVDF and different diluents, including 1,4-butyrrolactone, dimethyl phthalate (DMP), methyl salicylate, GTA, PC, and di-n-butyl phthalate on morphology of PVDF membranes [79–82]. Qualitatively speaking, the attractive interaction among PVDF molecules leads to the aggregation of PVDF and crystallization when the dielectric constant of PVDF is larger than that of the diluent, accompanying membranes with incompact particle structure. When PVDF and diluents have similar dielectric constants, attraction and repulsion exist in a state of equilibrium, thus accompanying a channel-like structure. If the dielectric constant of PVDF is smaller than that of diluent, PVDF molecules crystallize difficultly in the diluent due to the repulsive interaction. Based on these, a novel diluent diphenyl ketone (DPK) which could undergo the liquid–liquid phase separation with PVDF was selected for the preparation of PVDF membranes, and PVDF membranes with bicontinuous structure were obtained without necessity to add nonsolvents or a stretching process further.

2.1.2. Phase diagram

The compatibility of polymer and diluent directly affects the thermodynamic properties of the system such as the binodal temperature and crystallization temperature. As the compatibility becomes lower, the binodal curve is shifted to a higher temperature, whereas the crystallization temperature is less influenced by the compatibility. As a subsequent work, Lin et al. compared the molecular structures of different diluents that are shown in Fig. 2 [83]. It is easy to find that these three diluents have a homologous symmetrical diphenyl structure, but differ in functional groups between diphenyl structures. Basically, the polarity of DPK almost results from the stronger electron-withdrawing ability of the oxygen atom in carbonyl group. In DPC, because of the existence of two oxygen atoms

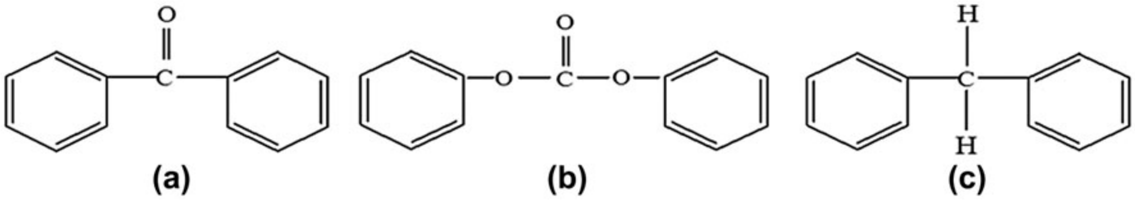

Fig. 2. Molecular structures of diluents: (a) DPK, (b) DPC, and (c) DPM [76].

on the two sides of carbonyl group, the electron clouds move away from the oxygen atom of the carbonyl group in contrast to DPK. Therefore, the polarity of DPC is a little weaker than DPK leading to the lower compatibility between PVDF and DPC. With regard to DPM, the polarity of which is much weaker than DPK and DPC because of its whole symmetrical structure and the methylene group, thus PVDF cannot be compatible with DPM like DPK- and DPC- diluted systems. It is found that both DPK and DPC are able to undergo the TIPS (L–L) process with PVDF and the lower polarity of DPC results in the higher value of the cloud point curve in comparison with that of DPK–diluent system (as shown in Fig. 3) [83]. However, the crystallization temperature is less influenced by the compatibility, so that the monotectic point of PVDF–DPC system is successfully extended to higher polymer concentration than PVDF–DPK system. Therefore, the interaction of the system can be not only controlled by the dielectric constant, but also by modifying the diluent molecular structure. In PVDF–DPC system, the L–L phase separation could be induced when PVDF concentration is more than 30 wt.% to make sure that the resulting microporous polymer membrane presents both good structure and excellent mechanical properties. It should be noted that DPC does not dissolve in water but dissolve in ethanol, which makes it easy to scale-up production of PVDF membranes.

Nevertheless, reviewing the researches on the preparation of PVDF membrane via TIPS method, it can be figured out that by finding a proper single diluent to control the interaction of the system is very hard. In consideration of this, much effort has been paid to investigate the effect of mixed diluents on the membrane formation. Firstly, Tang et al. conducted several researches on the L–L phase separation region of PVDF–DPK system which showed that the region can be extended to a higher polymer concentration by adding 1,2-propylene glycol (PG) that is a nonsolvent of PVDF into PVDF–DPK system. The phase diagram of PVDF–DPK/PG system is shown in Fig. 3(c) which illustrates that as the mass ratio of DPK/PG increases, the L–L phase separation region is getting larger and a bicontinuous cross-sectional structure with good mechanical strength can be obtained simultaneously when PVDF concentration is higher than 30 wt.% [84]. Secondly, Tang et al. constructed a methodology that is based on Dissipative Particle Dynamics (DPD) simulation method to investigate how a second diluent influences the TIPS (L–L) process of polymer–diluent systems [85,86]. It is found that adding a second diluent to a polymer–diluent system will change the membrane formation process from a TIPS (S–L) process to a TIPS (L–L) process, which results in the membrane structure changing from spherulitic to bicontinuous. In addition, factors including molecular structure and solubility parameters should be both taken into consideration in order to select a proper second diluent that has good compatibility with the primary diluent but poor compatibility with the polymer.

2.2. Dynamic respects

The actual membrane formation process is very fast, so combining dynamics and thermodynamics is sufficient to understand the membrane structure formation process and prepare a membrane with good properties.

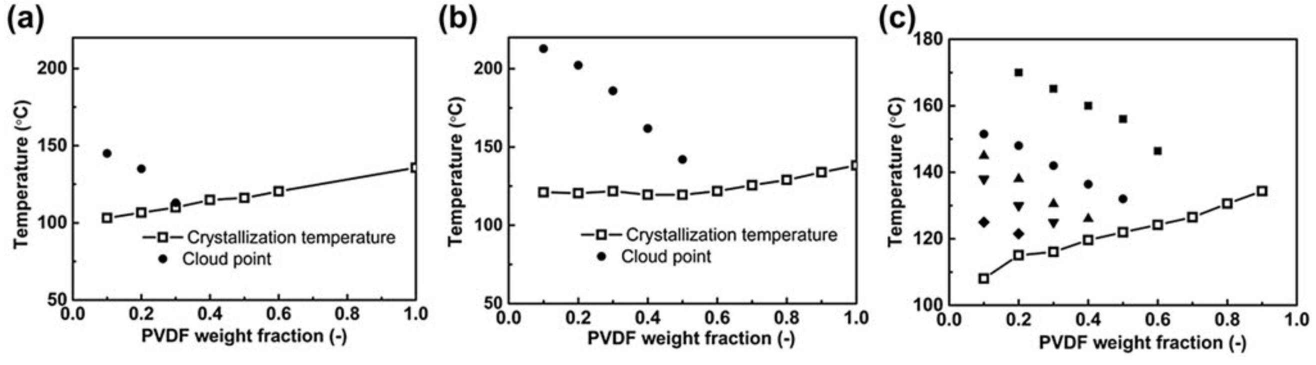

Fig. 3. Phase diagrams of different systems: (a) PVDF–DPK [79], (b) PVDF–DPC [83] and (c) PVDF–binary diluent (DPK/PG) system. It should be note that in (c) solid symbols present cloud points: ■, ●, ▲, ▼, and ◆ represent the PG/DPK mass ratio are 2/3, 3/7, 1/4, 1/9, 0, respectively; Hollow symbols show the crystallization temperatures. As the difference in the crystallization temperatures were not more than 5% when the PG/DPK mass ratio changing from 0/10 to 2/3 at a fixed PVDF concentration. The temperatures here were averaged temperatures in the five PG/DPK mass ratios at a fixed PVDF concentration [84].

2.2.1. Experimental dynamic research

In the first place, several experimental researches have been conducted to investigate the effects of PVDF concentration, cooling rate, quenching depth, and evaporation time on the membrane structure prepared by TIPS (L–L) method. These studies found that as PVDF concentration increases, membrane structure gradually changes from bicontinuous to cellular, until spherulitic. Additionally, a lower polymer concentration and higher quenching temperature leads to a large pore size membrane as well as the tensile strength of the membrane rises with an increase in the polymer concentration, but the porosity of the membrane reduces [79–82].

2.2.2. PVDF crystallization dynamics

PVDF chains can crystallize into at least four distinct phases that are α, β, γ, and δ. Many studies have found that the most common polymorph of PVDF membranes prepared via TIPS is α-phase and the degree of the crystallinity of PVDF can range between 30 and 70%. Also, the crystallization and polymorphism that determine the ultimate membrane structure during the phase separation are controlled by several variables including polymer molecular weight, molecular weight distribution, polymerization method, thermal history and cooling rates [87–93]. Commonly, It has been known from the literatures that adding some additives or altering the temperature and the property of the coagulation bath are effective to adjust the interaction between the polymer and the diluents to raise the crystallization and form β-phase polymorphism more easily, which are helpful to improve the mechanical strength and other properties of the resultant PVDF membranes.

Consequently, our group discussed the interplay between the L–L phase separation and its arrest due to the crystallization of PVDF [94,95]. It is found that the crystallization of PVDF affects the two-phase structure of PVDF crystals and diluent droplet in the TIPS process significantly [96]. Subsequently, effects of four types of nanoparticles (including montmorillonite (MMT), SiO_2, $CaCO_3$, and polytetrafluoroethylene (PTFE)) on the crystallization of PVDF as well as the nonisothermal crystallization behaviors of PVDF/nanoparticles composites were investigated. The results show that the enhancement of nucleation and the growth rate of the spherulites decrease in the order of $SiO_2 > CaCO_3 >$ PTFE > MMT [97]. Moreover, the crystallization of PVDF is favored by the addition of these nanoparticles with less than 1.0 wt.%. When 5.0 wt.% nanoparticle is added into PVDF, the crystallization of PVDF would be hindered to some extent. Based on the results, it can be found that MMT has a better interaction with PVDF molecules and should be chosen for improving the property of the resultant membranes. Whereas, poly(methylmethacrylate) (PMMA) was taken as a compatibilizer agent to improve the dispersibility of MMT. Depending on the dispersion of MMT nanoparticles in the systems, a supramolecular organization of PVDF lamellae is formed from the PVDF/MMT/DPK diluted system with PMMA additions via TIPS process, which is shown in Fig. 4 [98–101].

2.2.3. DPD simulation

On the other hand, a methodology based on the DPD simulation method in two and three dimensions was developed to gain more fundamental understanding about the dynamics of TIPS (L–L) process [85,102]. The simulation results have shown that TIPS (L–L) process can be influenced and regulated by thermodynamic properties including polymer molecular weight, polymer molecular weight distribution and diluent molecular structure (shown in Fig. 5). In addition, TIPS (L–L) process can also be affected by the external conditions such as quenching depth, and the mass transfer across the polymer solution—coagulation bath interface. The simulation methodology has been acknowledged as a supplementary method on the mesoscale between the microscopic theories and the experiments [103–106]. The results obtained by the

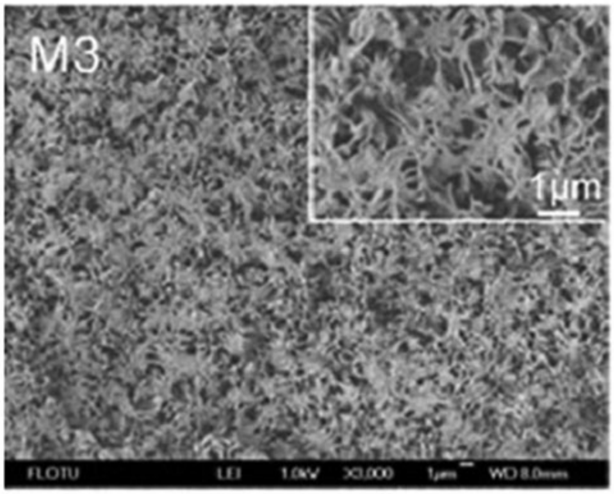

Fig. 4. A cross section of the mixture derived from PVDF/MMT/PMMA/DPK system with the composition of the PVDF/MMT//PMMA/DPK mixture is 29.4/0.3/0.3/70 [86].

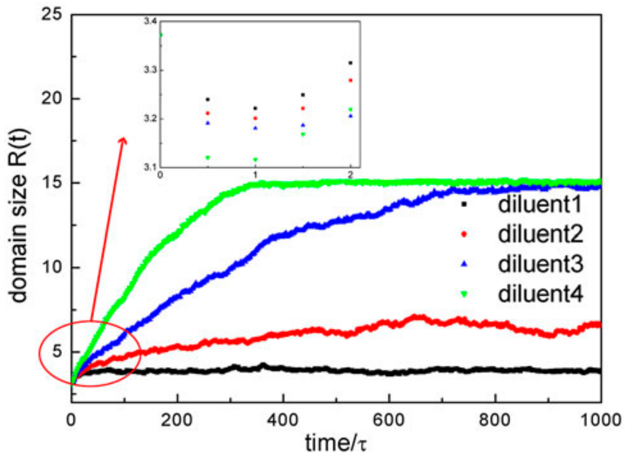

Fig. 5. Time evolution of the structure factor as a function of wave number for different diluents [89].

methodology are beneficial for the membrane fabrication via TIPS (L–L) process.

3. Advanced manufacture of PVDF hollow fiber membranes and membrane modules

3.1. PVDF hollow membranes

The hollow fiber membranes present high potential for the commercial application in UF/MF process, since the productivity and the efficiency of the separation process can be largely improved due to the large surface area per unit volume of the fiber module [107]. On the basis of the previous researches on the TIPS (L–L) process, a PVDF hollow fiber membrane fabrication procedure which includes extraction and rectification for diluent recovery was designed and assembled by an effective combination of material processing and unit operation, by which continuous production of PVDF hollow-fiber membranes was successfully realized. Fig. 6 shows an abstracted schematic of the PVDF hollow fiber membrane preparation apparatus: PVDF, hydrophilic polymer and diluent with known amounts are blended in the vessel heated to a high temperature (~200℃). The homogenous polymer solution is fed to a spinneret by extruding. Bore liquid is used to make a lumen of the hollow fiber. The hollow fiber is extruded from the spinneret and wound on a take-up winder after entering into a water bath to induce the phase separation and polymer solidification. The diluent remaining in the hollow fiber membrane precursor is extracted by immersing the precursor in ethanol; after removing the diluent, PVDF membrane is obtained. The diluent and the ethanol both can be recovered through the diluent recycle process (shown as the part in the dot dash box), which firstly water is added to the extract liquid for stratification, then the ethanol is received by distilling the aqueous phase and the diluent can be obtained from the oil phase after spray drying. The whole technical processing is convenient, highly efficient, and reliable, and the membrane production cost can be greatly reduced. In addition, since both 99% of ethanol and diluent are able to be recovered as well as water is adopted, the membrane fabrication process commits to zero discharge for environment.

Fig. 7 shows the structures of the PVDF hollow fiber membranes fabricated by the above process. As described in the investigation of diluent selection, a bicontinuous structure is observed as shown in Fig. 7(b). The pore and the porosity of at or near the inner surface are bigger than those of outer surface with the comparison between Fig. 7(c–f), as well as there are no skin layers at the surfaces, which ensures

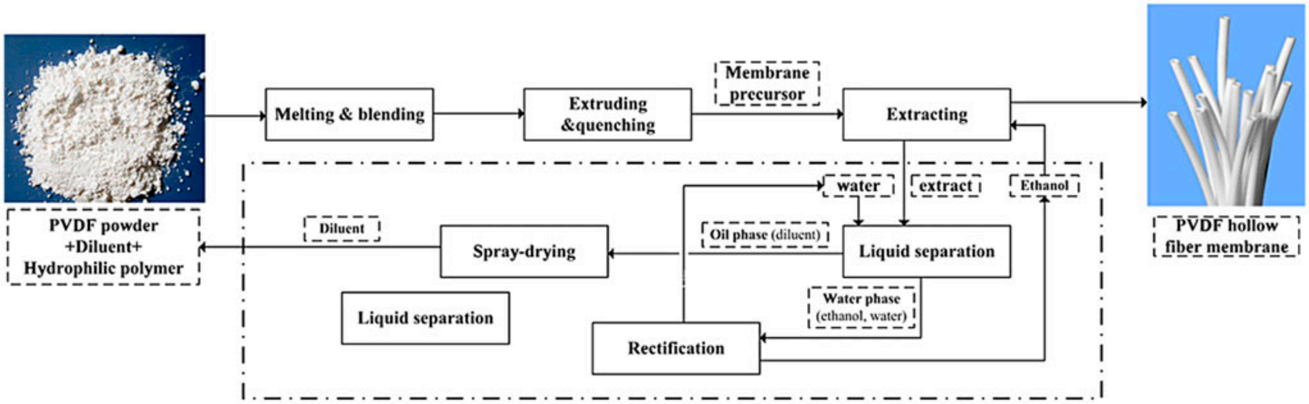

Fig. 6. A schematic of the advanced production for PVDF hollow fiber membrane via TIPS (L–L) method.

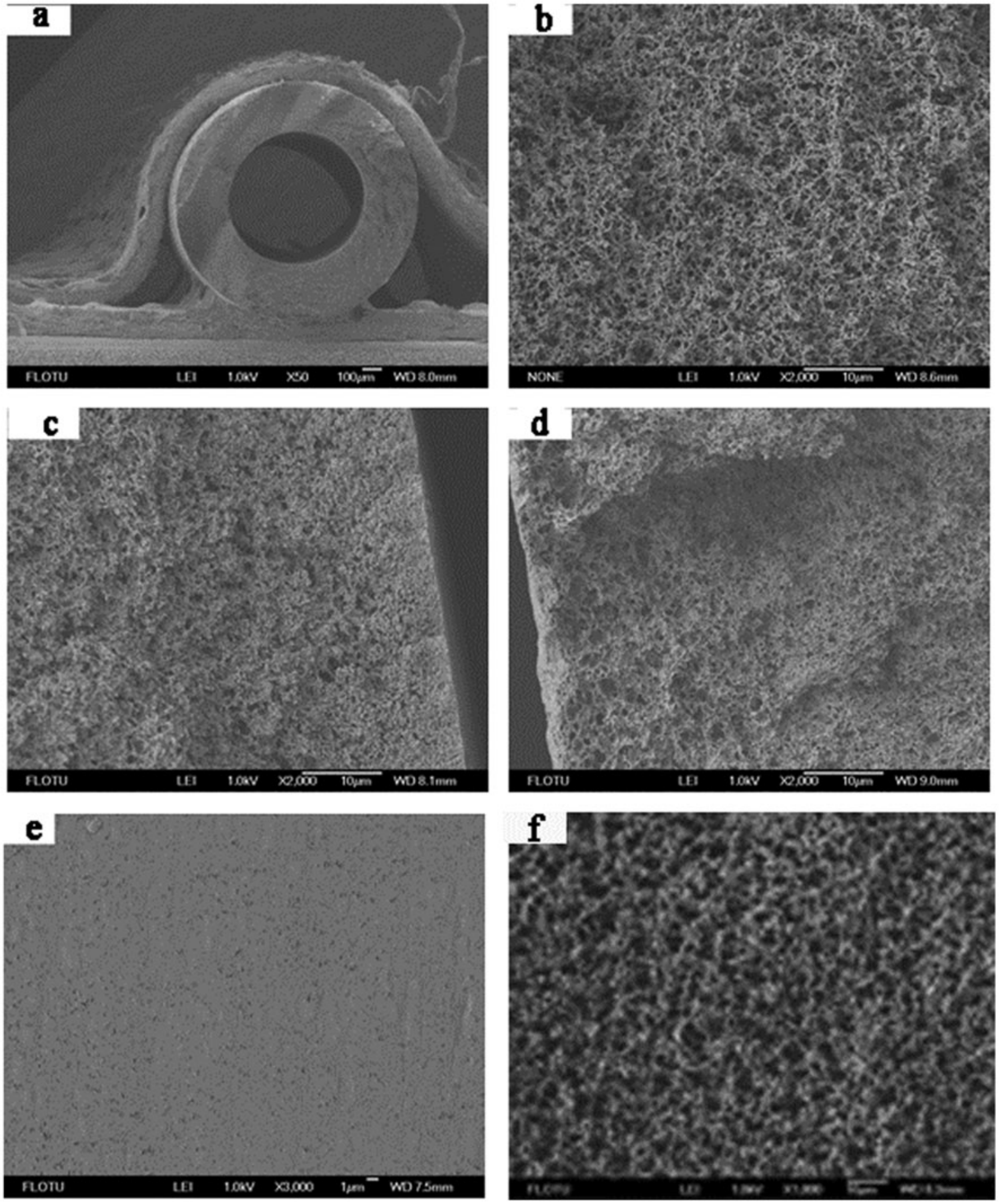

Fig. 7. SEM photographs of PVDF hollow fiber membrane prepared via TIPS (L–L) process: (a) whole cross section, (b) enlarged cross section, (c) cross section near the outer surface, (d) cross section near the inner surface, (e) outer surface, and (f) inner surface.

that the membrane has a high flux. What's more, the pore size distribution at the outer surface is narrow, which guarantees the water quality. Table 2 summarizes specifications of the PVDF hollow fiber membrane products.

3.2. PVDF hollow membrane modules

On the basis of the unique adhesive formula and innovative technology of encapsulating, different membrane modules, including Pressurized UF modules, Submerged UF modules, and Membrane

Table 2
Specifications of the PVDF hollow fiber membrane products via TIPS (L–L) method

Membrane fiber type	HF1800	HF1300
Inner/outer (I/O) diameter (mm)	1.2/1.8	0.7/1.3
Average pore size (μm)	0.1	0.1
Tensile strength (MPa)	>6.0	>6.0
Tensile elongation (%)	>120%	>120%
Pure water permeability L $(m^2\ h\ 100\ kPa)^{-1}$	>1,200	>1,200
Chemical resistance (ppm NaClO)	5,000	5,000
Cleaning pH	1–13	1–13

Bio-Reactor (MBR) modules, have been designed and assembled according to the characteristics of the prepared PVDF membrane and different application situations. These modules are currently provided by a membrane company called Beijing Scinor Membrane Technology Co., Ltd.

The properties of the different modules are overviewed in Table 3 and Fig. 8 illustrates schematic diagrams of them. The pressurized module products exhibit excellent features of high flux, good mechanical strength, and chemical resistance to be suitable for portable water treatment, wastewater treatment, seawater pretreatment and recycling and desalination field, especially the superior advantage in actual application of high turbidity and seriously contaminated water. Outside-in configuration of the pressurized module ensures that the modules are available for every operating mode including dead-end, cross, and internal recycle flow, resulting in less susceptible to plugging or fouling, which allows the corresponding wastewater treatment system is easy to operate and run stable only via regular backwash and chemical involved-in cleaning.

Submerged UF process (also called immersed UF) is an innovative UF application for sewage treatment in recent several years. In general, submerged UF elements are packed inside the modules without housing to immerse into a basin or a tank, and then water containing solids and other high weight particles passes through membranes with 10–100 nm micropores on the surfaces to remove impurities. The submerged modules own excellent features of high flux, good mechanical strength, and chemical resistance. The appropriate open structure benefits to lower fouling on fiber surface and wider turbidity for feed water. The module with integrated air and hydraulic piping system possesses patented design, by which the biggest capacity is highlighted compared with similar products: simple installation, less maintenance requirement, and lower cost.

Table 3
Overview of properties of the different membrane modules

Module type Membrane fiber type	Pressurized module HF1300	Submerged module HF1300	MBR Module HF1800
Operating condition			
Temperature (℃)	1–40	1–40	5–40
pH range	1–11	1–11	1–11
Maximum NaClO (ppm)	5,000	5,000	5,000
Operating TMP[a] (MPa)	0.02–0.15	≤0.04	0–0.03
Maximum TMP (MPa)	0.3	0.075	0.055
Operating flux $(L\ m^{-2}\ h^{-1})$	40–120	25–70	15–25
Backwash flux $(L\ m^{-2}\ h^{-1})$	50–120	30–70	–
Aeration capacity $(Nm^3\ h^{-1}$ per element)	5–12	3–6	6–12
Cleaning pH range	1–13	1–13	1–13
Filtered water performance			
Turbidity (NTU)	≤0.1	≤0.2	≤0.3
Silt density index (SDI_{15})	≤3	≤3	≤3
Bacteria removal	No detected per 100 ml sampling		–

[a] TMP is an abbreviation of transmembrane pressure.

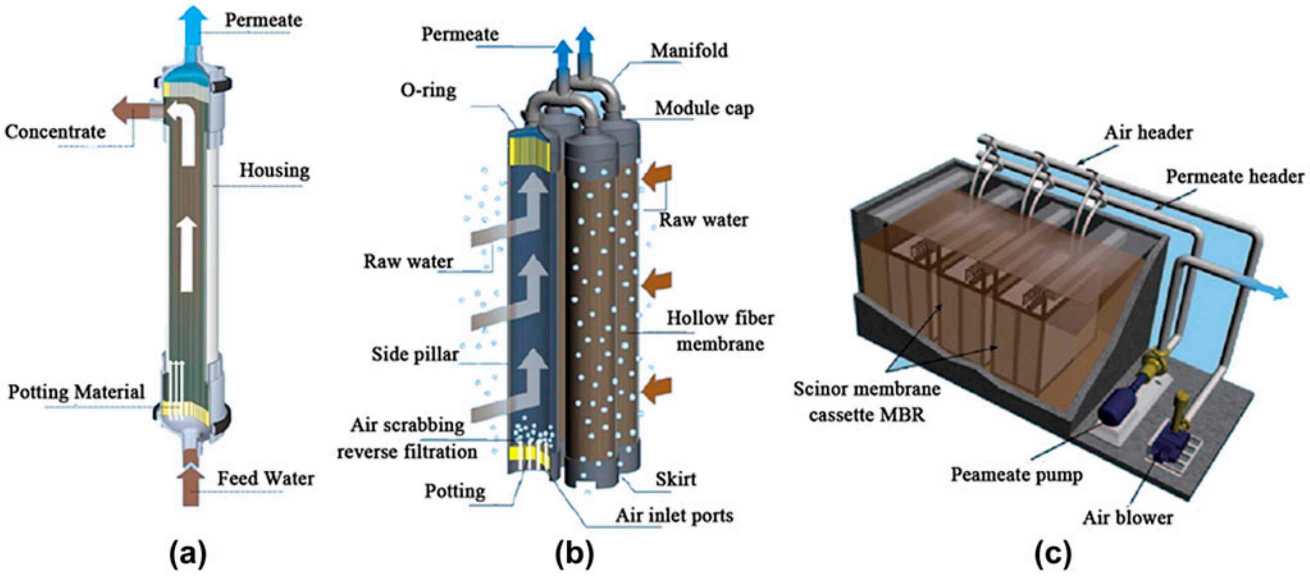

Fig. 8. Schematic diagrams of different membrane modules, including: (a) the pressurized module, (b) the submerged module, and (c) the MBR module.

Fig. 9. Scinor SMT600-P50 modules (the pressurized module) used in the water purification project in Taiyuan iron and steel Co., Ltd. of China.

The MBR modules present excellent features of high flux and enhanced mechanical strength. Through well-balance fiber distribution and optimum engineering rack design for integration of air and hydraulic piping system, they benefit to low energy consumption, minimization of installation and maintenance compared with other conventional MBR modules. Intermittent vacuum suctions are used to draw water from outside of the membrane to in. In order to keep stable operation, regular backwash and chemical involved-in cleaning have to be carried out for fouling removal.

Table 4
Analysis of water samples from the UF/RO desalination plant

Analysis item	UF feed	Filtered water
SDI_{15}	–	1.3
Turbidity (NTU)	<5	<0.03

4. Application of PVDF hollow fiber membrane module

4.1. Application of the pressurized membrane modules

The pressurized modules have the widest application that covers treatment of both industry wastewater and municipal sewage for water reuse [108]. A classic

Fig. 10. A simple flowchart of the reclamation water plant in Beijing Future Science and Technology Park, China.

example for the industry wastewater reuse can be the water purification project in Taiyuan Iron & Steel Co., Ltd. of China. The daily handling capacity of the project is 55,000 $m^3 d^{-1}$. The raw water that is cold rolling wastewater is put into the UF and RO system after multimedia filter and initial treatment to become make-up desalted water. There are twelve UF systems in this project and five of them adopt Retrofit Replacement Series membrane modules (as shown in Fig. 9) while the rest adopt modules from another famous band. Since 2011, Scinor UF systems keep running stably with normalized TMP of 20–70 kPa while there is only one need for NaClO cleaning every 6 months during the continuous running. Excellent filtered water quality and quantity can be both arrived to reduce the operation cost. It is worth to mention that the results in Table 4 indicate that total organic carbon (TOC) removal of the UF unit is more than 80%, which is beneficial ensuring long-term stable and effective operation of the subsequent RO unit. These results have proved that Scinor UF systems have better performance than modules from the other famous brand.

A classic application case of the pressurized modules in municipal sewage reuse can be the reclamation water plant of Beijing Future Science and Technology Park, China. The plant is the only reclamation water plant equipped with ozone system in Beijing, and provides water for landscaping and rivers. In the plant, the municipal sewage is introduced to the primary sedimentation tank and the AAO tank for biochemical treatment and then goes to the biofilter, the cloth filter and the UF system, which is shown in Fig. 10. There are 160 Scinor SMT600-P50 modules (shown in Fig. 11) adopted in each UF system plant and the capacity of each UF system is about 10,000 $m^3 d^{-1}$. Since the plant began running in 2,004.4, the operating flux keeps around 58.4 $L m^{-2} h^{-1}$ with dead-end flow and zero concentration discharge. The plant has reduced water consumption of Beijing by 80,000 $m^3 d^{-1}$ and it has made great contribution to surface water pollution control and local environmental protection.

Fig. 11. Scinor SMT600-P50 modules (the pressurized module) used in the reclamation water plant in Beijing Future Science and Technology Park, China.

4.2. *Application of the submerged membrane modules*

Submerged UF process has been proved to be a new and low-cost membrane technology, which can be applied widely in municipal sewage treatment, such as the application of Scinor submerged PVDF modules in Shahe Water Reclamation Plant of Changping District, Beijing, China. The water plant is built up to treat the water from municipal sewage as source and produce clean water to satisfy the reuse criteria for urban non-potable household, scenic and environmental uses. The plant has employed reform A/A/0 plus sedimentation and submerged UF, which is shown in Fig. 12. The water from the secondary

Fig. 12. The process schematic of municipal sewage in Shahe Water Reclamation Plant of Changping District, Beijing, China.

Fig. 13. Scinor submerged modules in Shahe Water Reclamation Plant of Changping District, Beijing, China.

sedimentation tank is directly introduced to the UF system that performs further solid–liquid separation of water, thus saving coarse filtration and sterilization steps. In the UF system, 300 Scinor submerged membrane modules (as shown in Fig. 13) are adopted and the water production is 10,000 $m^3 d^{-1}$ with 27.78 L $m^{-2} h^1$ water flux, while the submerged modules Asahi UNS-620A are also adopted and the water production is 20,000 $m^3 d^{-1}$. The results have shown that two kinds of modules generate similar TMP and permeate water quality under the same operation conditions.

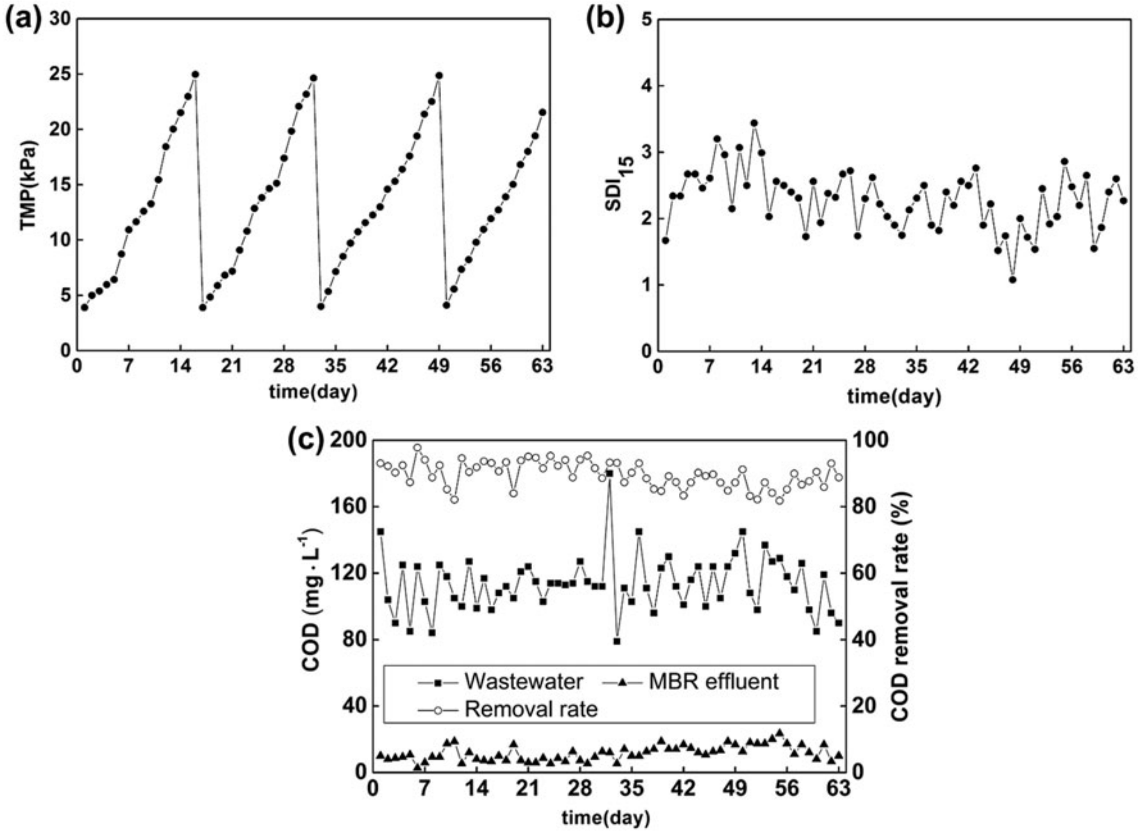

Fig. 14. Performances of the MBR modules used in the semiconductor industry, (a) the TMP evolution, (b) the SDI15 evolution and (c) evolutions of the COD and COD removal rate as functions of time.

Table 5
Characteristics of wastewater, MBR effluent and removal rates [109]

	Wastewater	MBR effluent	Removal rate
pH	6.0–7.5	5.8–7.8	–
SS (mg L^{-1})	16–104	below detection limit (<0.5)	–
CODCr (mg L^{-1})	63–180	2.6–18.8	82.1–97.8%
BOD_{15} (mg L^{-1})	30–60	0–0.8	>98.67%
TOC (mg L^{-1})	25–45	1.0–3.6	91–92%
Conductivity (μS cm^{-1})	1810–2,970	1,650–2,790	6.06–8.83%
NH_4^+-N (mg L^{-1})	1–26	0–3	>88.46%
TP (mg L^{-1})	0.63–1.50	0.28–0.64	55.55–57.33%
HCO_3^- (mg L^{-1})	28–100	19.9–24.8	28.80–75.20%
F^- (mg L^{-1})	2.2–7.3	0.6–5.7	21.92–72.72%
Cl^- (mg L^{-1})	550–1,450	404–670	26.54–53.79%
SO_4^{2-} (mg L^{-1})	138–265	107–209	21.13–22.46%
Na^+ (mg L^{-1})	310–542	237–357	23.55–34.13%
K^+ (mg L^{-1})	2.0–11.5	2.0–6.7	13.35–41.73%
Ca^{2+} (mg L^{-1})	145–291	143–245	1.38–15.81%
Mg^{2+} (mg L^{-1})	6.6–50.7	6.0–22.2	9.09–56.21%
Cu^{2+} (mg L^{-1})	0.27–0.35	0.20–0.23	25.92–34.28%
Zn^{2+} (mg L^{-1})	0.11–0.40	0.00–0.19	>52.50%
Ba^{2+} (mg L^{-1})	0.01–0.38	0.00–0.27	>28.95%
Sr^{2+} (mg L^{-1})	0.95–6.80	0.90–5.67	5.26–16.62%
Total Al (mg L^{-1})	0.02–3.76	0.00–3.22	>14.36%
Total Fe (mg L^{-1})	0.01–0.99	0.00–0.12	>87.88%
Total Si (mg L^{-1})	17.4–20.2	4.9–12.5	38.12–71.84%

4.3. Application of the MBR membrane modules

The combination of MBR and RO (MBR–RO) is becoming an attractive technology for industry wastewater reclamation and reuse. For example, the combined MBR–RO technology is applied to treat wastewater in a semiconductor industry with complex and fluctuating water quality [109]. The semiconductor wastewater mainly consisted of acid and alkaline wastewater, fluoride-containing wastewater, ammonia-containing wastewater, and chemical mechanical polishing wastewater as well as the complex compositions of the semiconductor wastewater always lead to RO membrane fouling. Fig. 14 shows the operational performance of MBR under the optimized aeration flow rate of 7 $Nm^3 h^{-1}$ and permeate flux of 18.5 $L m^{-2} h^{-1}$ (recovery of 95%) with the mixed liquor suspended solids around 4.5 g L^{-1} and temperature of 20–35℃. As shown in Fig. 14(a), the transmembrane pressure (TMP) increased gradually (about 1.32 kPa d^{-1}) due to the membrane fouling. The results in Fig. 14 indicate that a good stability of the MBR module is achieved under the strong fluctuations of the wastewater quality. As shown in Table 5, the MBR effluent quality is stable with SS below detection limit, SDI15 of 2.3, COD of 10.6 mg L^{-1}, TOC of 2.2 mg L^{-1}, NH_4^+-N of 1.6 mg L^{-1} and conductivity of 2,388μS cm^{-1} on average, although the wastewater quality changes widely with SS of 41.5 mg L^{-1}, COD of 113.8 mg L^{-1}, NH_4^+-N of 17.7 mg L^{-1} and conductivity of 2,705 μS cm^{-1} on average. Thus, the pretreatment of MBR prior to RO can alleviate the possible particulate/colloidal fouling and organic fouling on RO membrane surface. The main pollutants on the RO membrane that is fouled by MBR effluent are inorganic precipitations. The application results show that this MBR system with good fouling load capability can effectively remove the suspended solids, organics, microorganisms and even inorganics to reduce the fouling possibility of RO unit. The complementary of the MBR and RO in this integrated system is therefore effective.

5. Conclusion

After a brief but comprehensive overview of recent progress on the preparation of PVDF membranes via TIPS method, the paper reviews the historical information on the researches implemented by the group from Beijing Key Laboratory of Membrane Materials and Engineering of Tsinghua University during the past few years. These works are an effort to prepare and industrialize PVDF membranes with excellent performances. In the first stage, much researches conducted in the lab were carried out to prepare PVDF microporous membrane with good performance, including the thermodynamic and dynamic researches on the TIPS (L–L) process. Then advanced production of PVDF hollow-fiber membranes was achieved by an effective combination of material processing and unit operation. Subsequently different modules were designed and fabricated according to the characteristics of the PVDF membrane and different application situations. Finally, typical application cases of PVDF hollow fiber membrane modules for industrial and municipal wastewater treatment are demonstrated, which explore the possibility of using an integrated membrane solution that adopted the modules where wastewater treatment is intended for water recycling. It is believed that reviewing the series of researches can improve the understanding about the design and development of membranes and modules for the purpose of application. This paper would be a useful reference for researchers who are focusing on the manufacture and development of polymeric membrane modules.

Acknowledgments

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