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Tailoring structures and performance of polyamide thin film composite (PA-TFC) desalination membranes via sublayers adjustment-a review

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A B S T R A C T

Polyamide thin film composite (PA-TFC) membranes are finding more and more popularity in desalination via both reverse osmosis (RO) and forward osmosis (FO) process, which can effectively alleviate worldwide freshwater crisis through translating seawater into potable water. Despite of huge progresses, great challenges still exist in trade-off between water flux and salt rejections, surface fouling, chlorination, and concentration polarization. This has encouraged tremendous research in tailoring structures and properties of virgin PA-TFC membranes. Nevertheless, it seems that major research has focused on the surface polyamide layer. It should be noticed that sublayer also significantly affect the PA-TFC membranes. Fortunately, researchers have realized this fact in recent years and have done some important and meaningful work. From this point of view, this paper reviews and discusses the state-of-the-art developments on achievements of sublayers adjustment for tailoring PA-TFC membranes used in RO and FO desalination. Traditional sublayers adjustment and novel electrospun nanofibrous membranes (ENMs) sublayers are highlighted. It also provides an insight for future research directions combined with comments and perspectives. It is sincerely expected that this review paper can provide some clues for further in-depth evaluation and research in exploring more advanced PA-TFC membranes by adjusting sublayers.

1. Introduction

1.1. Role of polyamide thin film composite (PA-TFC) membranes in reverse osmosis (RO) and forward osmosis (FO) desalination

Fresh water shortage is an emergent issue with increasing attention all around the world [1]. Currently, 1 billion people are facing the threat of potable water crisis and this number will be 3 billion up to the year 2025 [2,3]. It has been well known that seawater constitutes 97.5% of total water resource on the earth [4]. As a result, desalination which can acquire freshwater from seawater provides an intriguing and effective strategy to meet this emergency and has been widely adopted. Presently, > 17 thousands desalination plants distributed over 150 countries have been built with a total daily capacity of > 90 million cubic meters freshwater and 300 million people are benefited [5]. The major desalination technologies currently in use are based on membrane separation via reverse osmosis (RO) and thermal distillation (multistage flash (MSF) and multi-effect distillation (MED)). Particularly, RO is finding an increasing role in desalination and accounts for over 50% of the installed capacity, especially with the fact that the specific energy of desalination by RO has been reduced from over 10 kWh/m^3 in the 1980s to below 4 kWh/m^3 [6]. In addition, it is worthwhile to note that forward osmosis (FO) is an emerging technology which are grasping the attention of human beings. FO, which can gain fresh water from feed solution (low-osmotic-pressure) to draw solution (high-osmotic-pressure) by osmotic driving force through semi-permeable membranes, requires no applied hydraulic pressure and provides an effective and energy-saving method for desalination with lower membrane fouling propensity than RO [7]. Although the industrialization is still far from satisfaction, FO has attracted tremendous attention in desalination due to its great potential in energy-saving effectiveness especially after the introduction of ammonia-carbon dioxide solution in 2005 [8].

Since its invention in 1970s, the superior separation performance has enable polyamide thin film composite (PA-TFC) membranes overwhelmingly dominate the RO desalination area [9]. Typical PA-TFC RO membranes exhibit a three-layer structure in terms of non-woven fibrous mechanical support, polysulfone (PS) or polyethersulfone (PES) sublayer, and surface polyamide layer [10]. In spite of their excellent performance, PA-TFC RO membranes are still faced with three obstacles of trade-off between water flux and salt rejections [11], surface fouling [12], and chlorination [13], which hinder their fulfilled

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efficiency. Therefore, it is reasonable to expect that future RO desalination will ideally have high water flux per unit of pressure applied, near-complete rejection of dissolved species, low fouling propensity, and tolerance to oxidants used in pretreatment for biofouling control. Thus PA-TFC RO membranes related research in recent years is mostly emphasized on these issues. Various strategies such as interfacial polymerization (IP) process controlling [14], monomers substitution [15,16],surface modifications [17–22], and hydrophilic additives and/or functional nanoparticles incorporation [23–28], have been explored and adopted to solve these problems and further improve the performance of PA-TFC RO membranes.

In FO desalination, the most widely used reference FO membrane in reported research is the asymmetric cellulose triacetate (CTA) membrane which is from Hydration Technology Innovations (HTI, Albany, OR) first and now the product of Fluid Technology Solutions (FTS) [29]. Although the hydrophilic nature of CTA favors osmotic transport, its susceptibility to hydrolysis, relatively low water permeations, and low salt rejection have limited their wider applications [30]. Recent reports indicated that the growing interest in FO desalination has inspired the exploration and application of PA-TFC FO membranes [31]. Likewise, PA-TFC FO membranes also exhibit great flexibility in tailoring because both surface selective layer and support sublayer can be individually adjusted. However, a critical point that hinders the performance of PA-TFC FO membranes is internal concentration polarization (ICP), which could severely reduce the water permeations during the operations. ICP occurs in two ways [32]. In active layer facing feed solution (AL-FS) mode, permeate would dilute the draw solutions filled in the porous support layer. This will lower the concentration of the solute on active layer compared with that on the membrane surface and lead to dilutive ICP. In active layer facing draw solution (AL-DS) mode, solute of the feed would filled the porous support layer and accumulate on the surface of active layer. Under this condition, water chemical potential difference between two sides of the active would be lower than that of membrane surface and lead to concentrative ICP. In case of these two modes, the net osmotic driving force are reduced, which decrease the water flux dramatically. Tailoring in PA-TFC FO membranes are mainly focused on ICP decreasing.

1.2. Potential of sublayer in tailoring PA-TFC membranes

It is always believed that the salt rejections and water permeability of the PA-TFC membranes are mainly dependent on the surface polyamide layer and the support layer mainly provide mechanical endurance during the operations. As a result, most currently used strategies in tailoring PA-TFC membranes (e.g., membrane modifications and optimization of synthetic materials) are applied on the surface selective layer. Many reviews emphasizing on the adjustment of surface active layer have also been reported [10,31,33]. Nevertheless, it is worthwhile to notice that the structures and properties of the sublayers (e.g., polysulfone (PSf) and polyethersulfone (PES)) which have their own characters are also in close relation to the performance of PA-TFC membranes.

First of all, the characters of PA-TFC membrane are significantly different based on the structures underneath [34]. For instance, the physical mechanical durability, porous structure and hydrophilicity of the sublayers could affect the compaction during the high-pressure operations, the water flux and salt rejections of the membranes, respectively [35]. The mechanical strength of the sublayer is directly related to the endurability of PA-TFC membranes. The permeability of sublayer could also affect the total water flux of PA-TFC membranes. Specially, the sublayer plays more important roles in FO than that in RO because it can directly affect ICP.

In addition, the sublayers provide the platform for the IP and their surface has direct effect on IP reactions. The mechanism for IP has been extensively researched and confirmed. In the fabrication of PA-TFC membranes, immiscible amines and acyl chlorides are used as IP monomers. Due to the rapid hydrolysis of acyl chloride in aqueous phase and the asymmetric solubility, the mechanism is diffusion-controlled and comprises three stages [36]. Initially, the polymers precipitate at the interface between two immiscible solvents and then the polymerization and the film formation simultaneously occur at this interface [37,38]. Followingly, amines in the aqueous phase diffuse to the organic phase and the film grows perpendicularly towards the organic phase [39]. Finally, increase in the thickness and density of the film inhibits the diffusion of the monomers and the IP [38]. The diffusion-controlled mechanism determines the dual structures and the depth heterogeneity of polyamide layer consisting a dense layer atop by a looser layer, which has been evidenced by both simulations [40–43] and experimental approaches [44–47]. The mechanism indicates the determined roles of amines diffusion. Thus, the sublayer on which amines spread would definitely affect IP process and thereby the structures of polyamide layer. It was reported that the thickness of the free-standing polyamide membranes is ten times higher than that formed on the porous support, which is ascribed to the impregnation of amines into the support [38]. It is believed that the impregnation of amines during IP reactions closely relates to the surface properties of support layer. In addition, occasionally, it is observed that the dense polyamide layer could penetrate into the porous support layer. This phenomenon can be determined by the pore structures of the support layer to some extent. Therefore, it can be confirmed that the sublayers structure has critical influences on the formation of polyamide layer and further affect the separation performances of PA-TFC membranes. Thereby it could be feasible method to tailor PA-TFC membranes by adjusting sublayers.

Taking the aspects discussed above into account, one can expect that sublayers adjustment shows great potential in tailoring PA-TFC membranes. Moreover, the flexibility in PA-TFC membranes structure provides favorability for sublayers adjustment because both the surface active and support layers can be individually tailored for specific purpose (Fig. 1) Regrettably, compared with that in surface active layer, studies in sublayers are comparatively fewer. Rare review paper has involved research achievements for the sublayer investigations [48]. To the best of our knowledge, no dedicated review has been reported in elaborating the importance of sublayers adjustment in tailoring PA-TFC membranes and the corresponding research progress. At the same time, it is inspiring that researchers are beginning to focus on this issue and many interesting and important studies have been reported. Therefore, in this review, state-of-the-art research developments in this area was presented and commented with perspectives. The contents of this paper mainly focus on the adjustment of traditional sublayers (i.e., PSf and PES) and the most promising substitution of electrospun nanofibrous membranes (ENMs) that being used in PA-TFC membranes for both RO and FO desalinations. It is expected that this review paper can provide an insight and some useful clues for further in-depth research in exploring more advanced PA-TFC membranes via adjusting sublayers.

2. Sublayer materials for PA-TFC membranes

2.1. Traditional sublayer materials for PA-TFC membranes

Porous materials are commonly explored as sublayers for the TFC membranes in pressure-driven processes because of their advantages in terms of water flux enhancement [49]. In addition, the polymeric materials used for sublayer making should exhibit high pH/thermal tolerance as well as solvent resistance. For PA-TFC RO membranes, PSf and PES are the mostly widely used sublayer materials because their pore sizes obtained by phase inversion synthesis methods are in the range of ultrafiltration-nanofiltration membranes [50]. PSf is used widely as sublayers for the commercial PA-TFC RO membranes. Meanwhile, high mechanical strength and chemical resistance, high structural polarity and flexibility, high heat-distortion temperature, strong