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Formation of thin film composite nanofiltration membrane: Effect of polysulfone substrate characteristics

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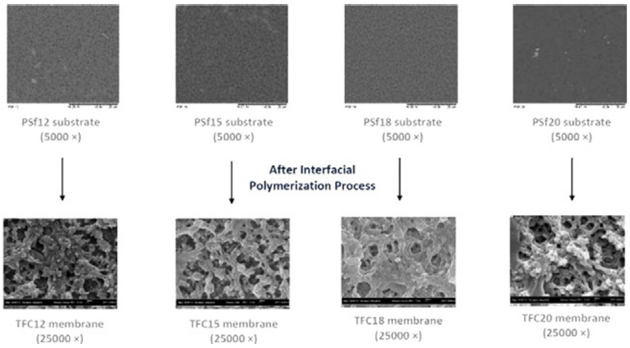
HIGHLIGHTS

- Properties of PSf substrate membranes were fundamentally investigated.
- Pore size and porosity of substrate portray major role in the changes of PA layer.
- TFC NF membrane made of PSf 15 wt.% substrate produced the best performance.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, polysulfone (PSf) substrates with different properties were made by varying the polymer concentration in the dope solution in the range 12–20 wt.%. Polyamide (PA) thin layers were then formed via interfacial polymerization between piperazine and trimethylchloride over the PSf substrates. Both top PA thin layers and bottom PSf substrates were characterized with respect to physicochemical properties, structural morphology, and water flux/salt rejection to investigate the influence of substrate properties on the characteristics of PA thin layers. Physical properties of the PA layers were reported to be altered using different PSf substrate properties and were in good agreement with the change in water flux. From the FESEM pictures, it is found that the thickness of PA layer increased as the surface pore size of support membrane decreased. The change in the membrane structural properties in particular pore size is found to portray significant contribution to the changes of formed PA layer. Interestingly, only slight changes on Na_2SO_4 and $MgSO_4$ salt rejection were reported on any TFC membranes. Considering both water permeability and salt rejection rate, the best performing TFC membrane produced in this work was the membrane made over substrate of 15 wt.% PSf concentration.

1. Introduction

Since the first introduction in the early 1980s, nanofiltration (NF) membranes have attracted considerable industrial interest as a promising cost-effective material to the growing needs of separation and purification technologies. Considering that a NF membrane has a microporous

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pore diameter (d_p) less than 2 nm, it is able to separate divalent and some monovalent ions, dissolved organic solutes (molecular weight M_w between 200 and 500 g/mol), hardness and heavy metals, effectively [1,2]. To date, thin film composite (TFC) membrane by far is the most commercially successful membrane for various industrial separation processes, particularly in the water treatment and purification applications [3–7]. The TFC membrane consists of an ultra-thin selective layer which is interfacially polymerized over a microporous substrate [8]. The main advantage of TFC membranes over asymmetric membranes is that each layer can be independently optimized to attain desired permeability and selectivity.

Up to now, various parametric studies have been conducted in an attempt to develop high performance TFC membranes by optimizing mainly the top thin selective layer. Physical and chemical properties of the substrate, however, are paid less attention during TFC membrane fabrication, probably because the substrate plays no significant role in the solute separation and fouling reduction as the top selective layer does [9]. The impact of substrate properties of the composite membrane formation is, therefore, less reported in the open literature during the preparation of TFC membranes. In view of the importance of a substrate to the formation of a composite membrane, several studies have been done in the past recent years to investigate the correlation between substrates made of different properties and the properties of ultrathin polyamide (PA) selective layer [10–12]. It is believed that the morphology (i.e. structure, thickness and surface charge) and the performance (i.e. permeability and selectivity) of a TFC membrane may be altered with the use of different substrate properties [6,12,13].

In 2006, Singh et al. [10] revealed that the change in pore size distribution of the polysulfone (PSf) substrate could affect the formation of a reverse osmosis TFC membrane and its performance as well. Smaller pores of PSf substrates (<70 nm) exhibited a tremendous salt rejection efficiency to that of bigger pores (>150 nm). This is mainly due to a notable increase in effective layer thickness caused by the smaller pores which restrict the penetration of PA into those pores. Years later, another extensive study was also conducted by Ghosh and Hoek [12] to investigate the impact of PSf support properties on the formation of composite membranes. It explained that the variance in the physical structure and chemistry of a PSf substrate apparently produced a PA with different characteristics and performance.

In particular, the polymer concentration in the substrate casting solution is believed to be one of the primary factors influencing the physical characteristics of the substrate. Moreover, the polymer concentrations in the casting solution are found to be above 12 and below 20 wt.%, and mostly in the range of 15 to 18 wt.% [6,12,14–17]. Therefore, it is our intention to investigate the relationship between the physical properties of substrate (i.e. surface pore size, pore size distribution and surface porosity), made of different polymer concentrations (in the range of 12–20 wt.%), and the characteristic of NF composite membrane. It is generally known that each substrate possesses its own characteristics. Therefore, the support layer itself has to form a good agreement between pore size and high flux to diminish the additional resistance for water transport. However, to what extent would the pore structure eventually influence the composite membrane fabrication still remains unclear. In order to gain further insights and to achieve the objective of the present study, topographical images of each substrate surface will be further recorded by SEM and AFM following quantitative measurements described by previous studies. Thus, the obtained values from both characterizations will be discussed in detail. It should be noted that optimized conditions of PA layers, including monomer concentration, reaction time, curing temperature and time, or the addition of additives, during the TFC membrane preparation is not conducted in this study. It is expected that the findings from this work would provide more insight in TFC membrane fabrication which can be generally optimized through the top PA active layer and bottom substrate layer.

2. Experimental

2.1. Materials

Polysulfone (Udel® P-1700) purchased from Solvay Specialty Polymers, USA was used to fabricate substrate for TFC membrane. PSf (in pellet form) was first dried at 100 °C overnight prior to use. Polyvinylpyrrolidone (PVP) K30 of M_w 40,000 used as a pore forming agent during substrate fabrication was purchased from Fluka Chemie GmbH, Switzerland. Trimethylchloride (TMC) and piperazine (PIP) were purchased from Sigma-Aldrich and Merck, respectively and were used to establish the PA layer on PSf substrate. 1-Methyl-2pyrrolidone (purity > 99.5%) and n-Hexane supplied from Merck were used without further purification. Na_2SO_4 and $MgSO_4$ supplied by GCE Laboratory Chemicals were used to prepare aqueous salt solution for membrane flux and rejection determination.

2.2. Membrane preparation

2.2.1. Preparation of PSf substrate

Asymmetric PSf substrates were prepared via phase inversion technique using the dope formulations as shown in Table 1. In order to increase the porosity of PSf substrates, 1 wt.% PVP was added into dope solution and acted as a pore forming agent. To prepare the dope solution, PVP was first dissolved in NMP solvent followed by PSf. The dope solution was stirred continuously until a homogeneous polymer solution was obtained. The substrate was then cast on a glass plate using the dope solution prepared. The cast substrate was kept for 30 s at ambient temperature before immersing into a water coagulation bath at room temperature. Obtained microporous PSf support was washed thoroughly with de-ionized water to remove residual solvent followed by keeping wet at 5 °C prior to use. The substrates prepared were denoted as PSf 12, PSf 15, PSf 18 and PSf 20, respectively, where the number corresponded to the PSf concentration used in the dope solution.

2.2.2. Preparation of thin-film composite (TFC) NF membrane

TFC NF membranes were prepared via in-situ interfacial polymerization process between PIP and TMC as shown in Scheme 1. PSf substrate was initially taped onto the glass plate followed by 120 s of immersion in an aqueous solution of 2% (w/v) PIP. The excess solution from the impregnated membrane surface was eliminated using a soft rubber roller. The membrane was then immediately immersed into the *n*-hexane solution of 0.2% (w/v) TMC for 60 s, which resulted in in-situ formation of an ultra-thin PA layer over the microporous PSf substrate. Subsequently, the resulting membrane was cured at 60 °C for 5 min and finally was thoroughly washed with de-ionized water before storage in de-ionized water at 5 °C prior to use. The composite NF membranes prepared were then denoted as TFC 12, TFC 15, TFC 18 and TFC 20, respectively, where the number corresponded to the PSf concentration used in preparing the substrate.

2.2.3. TFC NF membrane performance evaluation

The flux and rejection of fabricated TFC NF membranes were analyzed using a dead-end filtration system (Sterlitech™ HP4750 Stirred Cell) under a nitrogen atmosphere. TFC membranes were initially compacted at a trans-membrane pressure of 0.8 MPa with DI water

Table 1
Dope formulation used to prepare different types of substrates.

Substrate	Dope formulation (wt.%)		
	PSf	PVP	NMP
PSf 12	12	1	87
PSf 15	15	1	84
PSf 18	18	1	81
PSf 20	20	1	79