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## Static and dynamic assessments of polysulfonamide and poly(amide-sulfonamide) acid-stable membranes

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## ABSTRACT

Polysulfonamide (PSA) and poly(amide-sulfonamide) (PASA) thin film composite (TFC) membranes as the novel acid-stable membranes have been prepared by two aromatic and cycloaliphatic diamines. The acid-stable membranes were synthesized by interfacial polymerization of the diamines with benzene-1,3-disulfonyl chloride (BDSC) and/or trimesoyl chloride (TMC) on PES support membrane and their structures and performance were compared with polyamide (PA) TFC membranes. The stability of the TFC membranes in acids were studied by static acid soaking tests in two strong acids of 2.5% (w/w) HNO<sub>3</sub> and 10% (w/w) H<sub>2</sub>SO<sub>4</sub> at high temperature of 55 °C for 24 h. The dynamic permeation experiments were also done by 500 ppm MgSO<sub>4</sub> at 0.5 MPa in deionized water and in 5% (w/w) H<sub>2</sub>SO<sub>4</sub> solution. The acid retention in all of the membranes was very low. In contrast, the salt rejection was high in both water and acid solutions. The salt rejection was enhanced in acid solution filtration test because of the positive surface charge of the membranes in very low acidic pHs. The PSA membranes showed very good stability in high temperature acids while the PA membranes were completely degraded after acid soaking tests. Despite of the MPD-PA membranes which showed higher salt rejections than PIP-PA, the MPD-PSA membranes had lower rejections of 32% compared to PIP-PSA one (46%). The percent changes of salt rejection in water were -54%, -71%, -9.6% and -22% in H<sub>2</sub>SO<sub>4</sub> and -29%, -54%, -2.1% and -13% in HNO<sub>3</sub> for PIP-PASA, MPD-PASA, PIP-PSA and MPD-PSA membranes, respectively. The high molecular weight PSA polymers with improved acid stability and salt rejection were obtained from aliphatic diamine of PIP compared to aromatic MPD.

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### 1. Introduction

Nanofiltration (NF) is the second largest membrane process in water and wastewater treatment which found many important applications such as cheese whey diafiltration, pharmaceutical preparations, removal of color, removal of TOC and trihalomethane precursors from the surface water and removal of hardness, radium and TDS from well waters [1–6]. Nanofiltration membranes are a class of membranes with the separation potential between RO and UF membranes [2,7]. There is an excessive demand for polymeric NF membranes with high resistance to the aggressive industrial streams and harsh acidic media. These streams include effluents from the metal industry, ferment industry, extraction process, rinse process, pulp and paper industry and textile dyeing process. They usually contain high amount of different acids such as HCl, H<sub>2</sub>SO<sub>4</sub>, and HNO<sub>3</sub> [8]. Acid recovery from industrial wastes to reuse it in

the main process is considered as a beneficial recycling technology [6]. However, strong acids can degrade membrane components by altering the morphology and/or the physico-chemical integrity of the membrane. Consequently, a decline in membrane performance can occur [9]. Polyamide (PA) membranes which are the most commercial NF membranes are not stable in harsh conditions, e.g. high temperatures and extremely low pH [1].

Polysulfonamide (PSA) is a kind of polymer in which the stable sulfonyl and phenyl units and the conjugation made them extremely chemical and thermal stable [10]. Comparing the chemical properties of amides and sulfonamides strongly suggests that polysulfonamide thin film membrane is preferred to polyamide ones in harsh conditions. For example, it was reported that the produced PSA membrane had a good CuSO<sub>4</sub> retention value and excellent resistance after soaking in 20% sulfuric acid aqueous solution at 90 °C for 24 h [9] and 4.9% sulfuric acid at ambient temperature for 60 days [8]. Furthermore, when sulfonamides react with 80% NaOH at 250 °C, they are much more resistant to hydrolysis than amides [11]. The interfacial polymerization (IP) reaction for fabrication of PSA membranes is slower and more complex than PAs.

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So, they are not as commonly studied as PAs. However, in general aliphatic diamines (such as triethylenetetramine) and aromatic sulfonyl chlorides have been polymerized to form PSAs [12,13] while it was ultimately shown that the most ideal RO and NF polyamide membranes with high flux and salt rejection were obtained from aromatic amine monomers such as MPD. There is lack of more information about why aliphatic amines are preferred to aromatic amines for PSAs fabrication while the best PA membranes are synthesized from aromatic amines.

M-phenylenediamine (MPD) and piperazine (PIP) are two kinds of different amine monomers which are the base of widely used commercial PA membranes. These diamines are based on dissimilar structure with different behaviors. M-phenylenediamine (MPD) is an aromatic amine and piperazine is a cycloaliphatic diamine. The commercial PA membranes such as FT-30, SW-30, NF90 and BW-30 (FilmTec), TFC-L (UOP Fluid Systems), CPA2 (Hydranautic), UTC-70 (Toray) and Permasep® A15 are formed from the reaction of MPD and acyl halides and the NS-300, NF-270 and NF-40 (FilmTec), NTR-7250 (Nitto Denko), UTC-20 and UTC-60 (Toray) are PIP-based PA membranes [1]. The extremely successful FT-30 membrane, developed by Cadotte at Filmtec in the 1970s, was produced from MPD as the aromatic amine and TMC as the acyl halide monomer [14].

In this study two main objectives that have been not considered extensively up to now were attended. The first, is the synthesis of novel fully aromatic and partially aromatic acid stable TFC membranes by MPD and PIP, respectively. The amines were interfacially polymerization with benzene-1,3-disulfonyl chloride (BDSC) and/or trimesoyl chloride (TMC) on porous polyethersulfone support membrane. The second is, comprehensive evaluation of the membranes in terms of physico-chemical characteristics, acid stability and membranes permeability *via* dead-end permeation tests. To increase the speed of the degradation process -which under actual conditions would take a long time- we exposed the membranes to 10% H<sub>2</sub>SO<sub>4</sub> and 2.5% HNO<sub>3</sub> at the high temperature of 55 °C. Membranes morphology including surface and cross-section was studied by atomic force microscopy (AFM) and scanning electron microscopy (SEM). The chemical structure of the thin film was characterized by attenuated reflectance infrared (ATR-IR), X-ray photoelectron spectroscopy (XPS) and contact angle measurements. Surface streaming potential was also measured to determine the membrane surface charge.

## 2. Experimental

### 2.1. Materials and reagents

To prepare the support membrane, polyethersulfone (PES ultra-son E6020P with MW = 58,000 g/mole) polymer was supplied by BASF Company. Dimethylformamide (DMF) as solvent, poly(vinyl pyrrolidone) (PVP, MW = 25,000 g/mole) as the hydrophile agent and sodium dodecyl sulfate (SDS) as an additive to aqueous phase solution was purchased from Merck. Diamine monomers such as piperazine (PIP) and m-phenylenediamine (MPD) to prepare TFC membranes were prepared from Merck. Organic solvents, Isopar G (Isoparaffin type hydrocarbon oil) and n-hexane, were supplied by Merck. Organic phase monomers such as trimesoyl chloride (TMC, 98%) as crosslinking agent and benzene-1,3-disulfonyl chloride (BDSC, 97%) were purchased from Sigma-Aldrich. In addition, magnesium sulfate (MgSO<sub>4</sub>) as a divalent salt was prepared from Merck. Distilled water was used throughout this study.

### 2.2. Preparation of polyethersulfone support layer

To prepare support layer, asymmetric polyethersulfone (PES) ultrafiltration membrane was fabricated through phase inversion

**Table 1**

The composition of the organic and aqueous solutions for preparation of TFC membrane.

Membrane	Aqueous-phase amines		Organic-phase reagents	
	MPD (w/w %)	PIP (w/w %)	BDSC (w/v %)	TMC (w/v %)
PIP-PA	0	2	0	0.1
MPD-PA	2	0	0	0.1
PIP-PASA	0	2	0.05	0.05
MPD-PASA	2	0	0.05	0.05
PIP-PSA	0	2	0.16	0
MPD-PSA	2	0	0.16	0

caused by immersion precipitation [15,16]. The casting solutions contained 18% (w/w) PES, 1% (w/w) polyvinylpyrrolidone (PVP) and 81% (w/w) DMF. PVP was added into the dope solution in order to increase the porosity. It was first dissolved in DMF solvent, followed by the addition of PES and was mixed by a mechanical stirrer for 8 h to obtain a homogeneous solution. The solution was casted using a casting knife with 100 μm knife gap on a commercial polypropylene non-woven fabric attached to a clean glass plate with laboratory tape. This was immediately immersed into the non-solvent bath for immersion precipitation at room temperature without any evaporation. The water along with 0.1% SDS was used as the non-solvent gelation media. After initial phase separation and membrane formation, the membranes were stored in water for 24 h to guarantee the complete phase separation. Finally, the membranes were dried between two sheets of filter papers for 24 h at room temperature.

### 2.3. Preparation of TFC acid-stable membranes

Six different kinds of thin film composite nanofiltration membranes were prepared by IP technique in a clean room; two polyamide, two poly (amide-sulfonamide) (PASA) and two polysulfonamide membranes. To prepare polyamide membranes, the PES support layer was immersed in an aqueous solution of 2.0% (w/w) PIP or MPD for 300 or 120 s, respectively. Then it was drawn out to remove excess solution and the surface was rolled with a soft rubber roller to eliminate any tiny bubbles from the membrane surface. Afterwards, the saturated membranes were immersed in organic solution containing 0.1% (w/v) TMC in n-hexane for about 40 s and 25.0 °C as listed in Table 1. To complete the thin film formation *via* IP, the produced composite membranes were cured at 80 °C for about 5 min.

To produce PASA membranes, the aqueous phase were comprised of 2.0% (w/w) PIP or MPD and 0.1% dimethylaminopyridine to shorten the time of IP reaction. The procedures in aqueous solutions and heat-curing were as above. The difference is that 0.05% (w/v) TMC and 0.05% (w/v) BDSC were dissolved simultaneously in Isopar G stirring for about 1 h. The reaction time in organic solution was 40 s. For PSA membranes preparation, the procedures in aqueous solutions and heat-curing were the same as the PA membranes. In this regards, 0.16% (w/v) BDSC was dissolved in Isopar G and the residence time in organic solution was 25 min. After washing the resultant composite membranes with de-ionized water, they were stored wetly until they were used.

### 2.4. Characterization of the acid-stable TFC membranes

#### 2.4.1. Scanning electron microscopy (SEM)

Philips XL 30 Scanning Electron Microscope was used in this study to provide the visual data of the cross-sectional and top surface morphology of the membrane. The membrane samples were cut into small pieces. After cleaning with filter paper, they were immersed in liquid nitrogen for a period of 60–90 s to freeze and

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