



Preparation of novel carboxylated thin-film composite polyamide-polyester nanofiltration membranes with enhanced antifouling property and water flux



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ABSTRACT

A new carboxylated aromatic diamine-diol (CDADO) monomer was synthesized and employed to fabricate polyamide-polyester thin-film composite (TFC) nanofiltration (NF) membranes, which showed better antifouling and performance properties. The interfacial polymerization (IP) procedure was utilized to prepare carboxylated TFC nanofiltration membranes by reaction of trimesoyl chloride (TMC) in the organic phase with amine and hydroxyl groups in the aqueous phase. By varying the amount of CDADO, it was possible to improve both salt rejection and flux of the membranes. The prepared membranes were characterized using SEM, FTIR, AFM, and contact angle and zeta potential analyses. The outcomes of antifouling and contact angle experiments showed that in presence of the synthesized monomer membrane performance and hydrophilicity improved. The high permeability and antifouling characteristic was due to the presence of suitable hydrophilic carboxylic acid groups and also, terminal hydroxyls and amines at the created polyamide layer. The results showed that the optimum concentration for the CDADO diamine was 2 wt%. The salt retention order for the 2 wt% membrane was Na₂SO₄ (91%) > NaCl (70%) > CaCl₂ (17%). Moreover, the influence of varying pH on rejection of the fabricated membrane with optimized CDADO concentration was investigated, interestingly the membrane showed a pH-responsive gating property. The satisfactory performance of the novel high flux NF membrane compared to pipirazine (PIP) based membranes revealed its valuable potential for the applied purpose.

1. Introduction

Nowadays, the nanofiltration (NF) owing to distinctive benefits of high rejection for organic molecules (200–1000 Da) and multivalent ions accompanied by low operation pressure with high permeate flux has fascinated great attention among the pressure-driven membrane separation technologies [1]. Moreover, the growing interest in reusing wastewater, the lower prices of enhanced membranes, the rising demand for high quality water, the better consistency membranes and supplementary strict standards in the drinking water industry are the main reasons to guarantee rapid growth of the NF membranes [2]. Nevertheless, every technology has merits and demerits and NF technology is not exempt.

Fouling is considered as a major limitation of NF technique by membrane experts which it considerably restricts the use of NF membrane in wastewater treatment and water industries [3]. Physico-chemical properties of membrane surface such as electrostatic charge,

roughness and hydrophilicity strongly affect the membrane fouling property [4]. The membrane experts put their best effort to optimizing membrane features to have maximum solute rejection, maximum permeate flow and minimum operating expenses [5]. Since protein and most of other foulants have a hydrophobic characteristic, it has been proved that the fouling resistance improves by an increment of membrane hydrophilicity [5]. Many researches have been conducted to increase water flux by (1) the choice and adjustment of the membrane support [6–9] and (2) synthesis of a new monomer to form the active TFC membrane skin layer and the improvement of the active top layer properties [10–12]. Since the performances of the TFC membrane are principally specified by the chemical and structural properties of the active top layer, consequently novel monomers have turned out to be the subject of different surveys on TFC membranes in present decade [13–15].

Chemical properties of monomers play the significant role in controlling the chemical resistance, pore dimension, hydrophilicity,

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thickness of the active layer and roughness. Hence, it is not astonishing that IP procedure has been performed with various active monomers [16, 17]. Recently many scholars with the purpose of preparing better TFC-NF membranes have tried to select monomers containing different functional groups such as polyols [18], polyamines [19], polyphenols [20], charged monomer [21], melamine [22] as well as zwitterion amine [23], which have been employed as hydrophilic monomers to fabricate TFC membranes.

TFC membranes properties have much dependency on the charge density, which is very crucial in the rejection of charged particles, particularly for NF membranes [24]. In TFC membranes, two prominent mechanisms that play a major role in the rejection of charged materials are steric hindrance and electrostatic interactions. Considering that the NF membranes are less tightly meshed than the reverse osmosis [25], solute retention by steric hindrance is less important. As a result, the electrostatic interactions play the chief role in ion rejection. The source of TFC membrane charge is usually from the $-\text{CO}_2\text{H}$ group, which increasing carboxyl charge density improve the relative rejection of salt [26]. Regarding this point, 3,5-diaminobenzoic acid (DBA), which embraces both $-\text{CO}_2\text{H}$ and $-\text{NH}_2$ groups, has been lately employed as a diamine to react with trimesoyl chloride (TMC) to prepare a polyamide (PA) layer with enhanced hydrophilicity in which the obtained TFC hollow fiber membranes have also shown higher permeation fluxes and excellent selectivity [27].

Moreover, another polymer that can form TFCs is polyester, that its TFC is prepared by reaction of polyphenols or polyols in the aqueous phase with TMC in the organic phase [28]. Kwak et al. [29] prepared polyester based TFC membranes, which had water flux more than ten times higher than the PA membrane. Moreover, ester linkages due to lack of amidic hydrogens is less prone to chlorine attack which could lead to improve the oxidation resistance of the membrane.

Totally, the PAs TFC have better salt rejections due to their ability to establish high cross-linked structures, whereas the polyesters TFC due to their terminal hydroxyl groups have higher antifouling ability against hydrophobic foulants. Consequently, preparing TFC-NF membranes that embrace the advantages of both polyester membrane and PA membrane is a fascinating area of research [11]. Recently, Yu et al. has prepared a novel polyesteramide TFC-NF membrane by IP method of serinol (having aliphatic structure) and TMC. The result showed that membrane properties such as antifouling, water flux and salt rejection improved [30]. Moreover, bulky diamines, because of their low diffusion rate in organic phase and high free volume will form a very thin selective layer with more pores of the active skin layer and loose cross-linking cause good permeability of the NF membrane, while its salt rejection also will decrease. But by placing carboxylic acid groups on large diamines, the charge amount of the surface membrane increases, which it prevents the reduction of rejection.

Inspired by the above literature, herein synthesis of a novel diamine-diol containing carboxylic acid and preparation of a novel TFC-NF membrane was reported. The synthesized monomer and the prepared NF membranes were fully characterized by Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR) spectroscopy, atomic force microscopy (AFM) and scanning electron microscopy (SEM). The hydrophilicity, pH response and fouling resistance of the NF membranes were also thoroughly evaluated. The separation performance of the obtained membranes was studied by 2000 ppm NaCl, Na_2SO_4 and CaCl_2 solutions.

2. Experimental

2.1. Materials

The support of TFC membranes was prepared using polysulfone (Ultrason S6010 with MW = 58,000 $\text{g}\cdot\text{mol}^{-1}$, BASF, Germany) and *N,N*-dimethylformamide (DMF, Merck, Germany) on a polyester non-woven fabric (Hollytex 3329). Trimesoyl chloride (TMC), sodium

dodecyl sulfate (SDS), NaCl, Na_2SO_4 and CaCl_2 were obtained from Merck Co., Germany. The n-hexane as the organic phase of IP was provided from Mahshahr Petrochemical Co., Iran. Other materials like piperazine (PIP) monomer, 4-formylbenzoic acid, 4'-hydroxyacetophenone, hydrochloric acid, thiourea, bovine serum albumin (BSA- MW = 67,000 $\text{g}\cdot\text{mol}^{-1}$) and diiodine were purchased from Sigma-Aldrich Co., Germany.

2.2. Synthesis of diamine monomer

Monoamine (MA) was synthesized according to the reported procedure [31, 32]. Briefly, a mixture of 1.36 g (10 mmol) of 4'-hydroxyacetophenone, 1.53 g (20 mmol) of thiourea, and 2.53 g (10 mmol) of diiodine was heated and stirred at 110 °C for 12 h. Then, the solid reaction mixture was solved into 200 mL water and neutralized with sodium hydroxide solution (1 M) to precipitate. The product was filtered, washed with water, and recrystallized from $\text{H}_2\text{O}/\text{EtOH}$ (1:1) to afford 4-(2-amino-thiazol-4yl)-phenol (MA) as a pale yellow solid.

To prepare carboxylated aromatic diamine-diol (CDADO) monomer, a 100-mL round-bottom flask was charged with a mixture of the MA (3.84 g, 20 mmol), 4-formylbenzoic acid (1.51 g, 10 mmol), and hydrochloric acid (50 mL) and refluxed for 12 h at 100 °C. Then, it was cooled to the room temperature. The reaction mixture was poured into 200 mL of water and neutralized with NaOH. The obtained precipitate was collected by filtration and recrystallized from the mixture of (DMF/water) (v/v = 1:5) to afford a light yellow solid, the isolated yield was about 60%. To prepare carboxylated diamine without hydroxyl groups (CDA), the same procedure was followed; the only difference was that acetophenone was used as the starting material (Fig. 1).

2.3. Procedure of membrane preparation

Polysulfone asymmetric supports were fabricated by the water induced phase inversion of a solution containing 19 wt% PSf dissolved in DMF. The degassed and homogeneous solution was cast on a non-woven polyester support; the film applicator thickness was adjusted at 170 μm . The casted polymeric films were instantly immersed in a distilled water bath at ambient condition.

The IP procedure was used to prepare TFC membranes with different weight ratios of CDADO, CDA and TMC monomers on the PSf substrate (Table 1). To dissolve diamine completely and increase the rate of polymerization by eliminating of the formed hydrogen chloride through amide and ester bond formation (as acid acceptor), the pH of the aqueous solution was set at 10 by sodium hydroxide [13]. Basic pH also is beneficial to converting the $-\text{OH}$ group to a better nucleophilic group.

The TFCs were prepared by the immersion of the wet PSf supports in an aqueous solution containing a specific concentrations of the synthesized diamine and 0.1 wt% dodecyl sulfonic acid sodium (SDS) as a surfactant to help monomers homogeneity which was coated on the PSf-UF membrane. After 8 min, the membranes were removed from the aqueous solution and the excess water droplets on the surface were removed from the surface by a rubber roller. The diamine absorbed membranes were contacted with TMC in n-hexane solutions for 2 mins. The reaction of diamine and TMC proceeded and a thin PA-polyester layer was formed above the PSf-UF supports. Finally, the obtained TFC membranes were washed with n-hexane and cured at 80 °C for 10 min to vaporize the organic solvent and further polymerization. Lastly, the obtained membranes were stored wetly until they were tested.

2.4. Diamine characterization

The FTIR spectra of diamines were verified with Perkin-Elmer FTIR (240-C) spectrometer. Proton and carbon nuclear resonance spectroscopies (^1H NMR and ^{13}C NMR) were carried out on a Bruker DRX 300 MHz AVANCE spectrometer (Germany). Tetramethylsilane (TMS)

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