



# Improving the water permeability and antifouling property of thin-film composite polyamide nanofiltration membrane by modifying the active layer with triethanolamine



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## ABSTRACT

Interfacially synthesized polyamide (PA) thin-film composite (TFC) membranes, as the state-of-the-art polymeric membranes for nanofiltration (NF), are prone to fouling in processing wastewaters and industrial fluids due to the inherent surface physicochemical properties of polyamide active layer. Here, we report the facile and effective modification of PA-TFC nanofiltration membranes for improved water permeability and antifouling property by surface grafting. Triethanolamine (TEOA) molecules were bonded onto the surface of PA-TFC NF membrane through esterification reaction between the hydroxyl groups of TEOA and the residual acyl chloride groups on the nascent PA-TFC membrane by pouring the TEOA aqueous solution on membrane surface. The covalent attachment of TEOA molecules was shown to tailor the surface chemistry of the composite membrane without altering the morphology of active layer. The PA-TFC membrane became more hydrophilic after modification and thus more permeable to water and antifouling against hydrophobic foulants, while maintaining its molecular weight cut-off. The results of tertiary treatment of industrial effluent also demonstrated that the modification performed in our study could effectively improve the water permeability and antifouling property of the PA-TFC NF membrane in processing wastewater.

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## 1. Introduction

Interfacially synthesized polyamide (PA) thin-film composite (TFC) membranes are the state-of-the-art polymeric membranes for the process of nanofiltration because of their high perm-selectivity and excellent chemical, thermal, and mechanical stability [1,2]. However, the major hindrance to the effective application of the PA-TFC nanofiltration membrane in reclamation of wastewaters and treatment of industrial fluids is membrane fouling, which usually decreases membrane productivity, deteriorates membrane perm-selectivity, increases operation cost and shortens membrane lifespan [3–5]. Therefore, it is of great importance to design and develop novel nanofiltration membranes with special surface properties that are less prone to fouling.

Surface modification has been proved to be a promising route

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to modulate membrane surface properties [6–8], which are known to be strongly related to membrane performance including anti-fouling property [9,10]. Many efforts have been devoted to improve the antifouling property of the PA-TFC nanofiltration membranes through appropriate surface modifications including physical and chemical treatments that can alleviate the deposition of foulants on membrane surface [11–14]. Of the modification approaches developed, covalent grafting methods are preferred for the long-term stability of the modified membranes. Considering the fact that the carboxylic acid groups on the active layer of the interfacially synthesized PA-TFC nanofiltration membranes are from the eventual hydrolysis of the unreacted acyl chloride groups, surface modifications have also been performed through using these unreacted acyl chloride groups before their hydrolysis.

For example, Zhu et al. [15] studied the graft of poly (amidoamine) dendrimer (PAMAM) on the interfacially polymerized PA-TFC hollow fiber nanofiltration membrane through using the unreacted acyl chloride groups. The graft of PAMAM was shown to improve membrane hydrophilicity and water permeability without compromising rejection. Mi et al. [16] investigated the

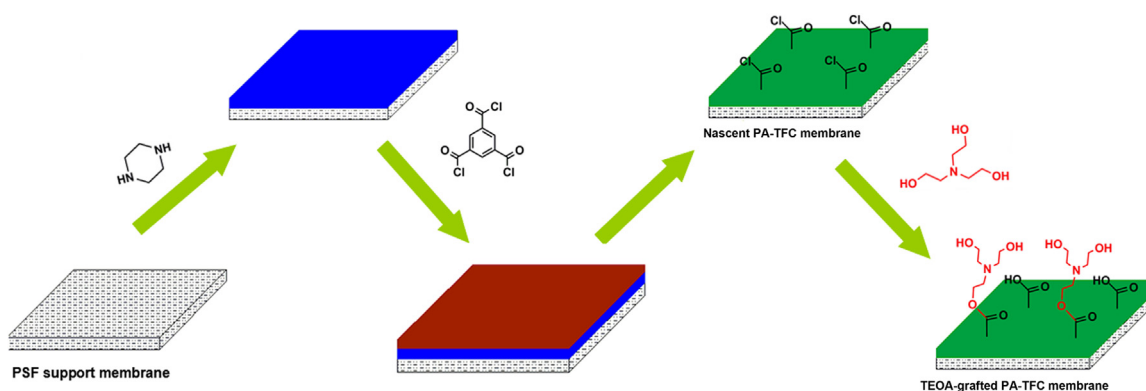


Fig. 1. Schematic diagram of the fabrication of TEOA-grafted PA-TFC nanofiltration membrane.

incorporation of a zwitterion monomer N-aminoethyl piperazine propane sulfonate (AEPPS) onto the surface of traditional polyamide NF membrane via chemical reaction between amine groups of AEPPS and acyl chloride groups on the surface of nascent membrane. The zwitterionic moieties on membrane surface were demonstrated to be benefit for both membrane flux and antifouling property. More recently, Biogenic and chemical AgNPs were grafted onto the surface of PA-TFC nanofiltration membrane with cysteamine as the bridging agent that has been covalently grafted on membrane surface through the reaction with the unreacted acyl chloride on the nascent membrane [17]. It was reported that both of the TFC-S-BioAg and TFC-S-ChemAg membranes showed enhanced surface hydrophilicity and water flux.

The aforementioned examples illustrate that PA-TFC nanofiltration membranes with special surface properties can be tailored through the post amidation reaction between the residual acyl chloride groups and the amino groups of the grafting monomer. However, the formed amide linkage (CONH) is of poor chlorine stability [18,19]. Therefore, in this study, the hydrophilic monomer triethanolamine (TEOA), an multi-hydroxyl monomer that is environment-friendly, economical, and easy to be obtained and has been successfully used to prepare TFC nanofiltration membrane through the interfacial polymerization with trimesoyl chloride [20], for the first time, was explored as a grafting monomer to modify the PA-TFC membrane for improved water permeability and antifouling property. Nascent PA-TFC nanofiltration membrane was prepared through the interfacial polymerization of piperazine and trimesoyl chloride on the polysulfone support membrane, TEOA molecules were then grafted on membrane surface through esterification reaction between the hydroxyl groups of TEOA and the residual acyl chloride groups on the surface of the nascent PA-TFC membrane. Membrane surface property and performance were tuned by varying the TEOA content and rigorously characterized in terms of physicochemical property, permeation property, antifouling behaviors to model foulants of bovine serum albumin, sodium alginate and cationic polyacrylamide, as well as separation performance in tertiary treatment of industrial wastewater.

## 2. Experimental

### 2.1. Materials

Flat-sheet nonwoven-reinforced polysulfone (PSF) support membrane with a molecular weight cut-off (MWCO) of around 80,000 g/mol and a pure water permeability of approximately 140 l/m<sup>2</sup> h bar was supplied by Hangzhou Tianchuang

Environmental Technology Co. LTD., China. Monomers trimesoyl chloride (TMC, > 99.0%) and piperazine (PIP, > 99.5%) for interfacial polymerization and triethanolamine (TEOA, > 99.5%) for grafting were purchased from Sigma–Aldrich and used as received. Isopar G (Isoparaffin type hydrocarbon oil) used as the solvent to prepare the organic phase solution was purchased from Guangdong Jesan Chemical Ltd. China. Glucose, saccharose, raffinose and  $\alpha$ -cyclodextrin used as the neutral solutes to evaluate membrane molecular weight cut-off were purchased from Sigma–Aldrich. Analytical standard bovine serum albumin (BSA), sodium alginate (SA) and cationic polyacrylamide (CPAM,  $M_w=5 \times 10^6$  g/mol, charge density=20.0%) were purchased from Shanghai Aladdin Reagent Company and used as model foulants. De-ionized (DI) water with a resistance of 18 M $\Omega$  was used in all experiments. All other chemicals were analytical reagents and used without further purification.

### 2.2. Preparation of TEOA-grafted PA-TFC Membrane

The preparation of TEOA-grafted PA-TFC nanofiltration membrane was schematically illustrated in Fig. 1. Nascent PA-TFC membrane was fabricated through depositing a PA selective layer on a porous support via interfacial polymerization of PIP and TMC [21]. The surface of the porous PSF support membrane clamped in a polyfluortetraethylene frame was first coated with 0.2 wt% PIP aqueous solution with a pH of 11.5 adjusted using Na<sub>3</sub>PO<sub>4</sub> · 12H<sub>2</sub>O for 2 min. Excess PIP solution was removed from membrane surface by rolling with a soft rubber. Subsequently, the surface of the PIP-saturated support membrane was contacted with 0.15 wt% TMC organic solution for 50 s to carry out the polymerization reaction and rinsed thoroughly with the clean organic solvent of Isopar G, followed by drying at 50.0 °C for 15 min for evaporation of organic solvent and further polymerization. Afterwards, the surface of the prepared nascent PA-TFC membrane was coated again with TEOA aqueous solution of pH 11.5 adjusted with triethylamine for 2 min and washed thoroughly with DI water. Membranes prepared with TEOA contents of 0, 0.25, 0.5, 1.0 and 2.0 wt% hereinafter are referred to as membranes NFM0, NFM1, NFM2, NFM3 and NFM4, respectively.

### 2.3. Characterization of membrane physicochemical properties

Membrane surface chemical structures and compositions were analyzed using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet Aratar 370 FTIR spectrometer) and X-ray photoelectron spectroscopy (XPS, PerkinElmer PHI 5000C ESCA System with Mg/Al Dual Anode Hel/Hell ultraviolet source, USA). Membrane morphologies in terms of cross-section and surface structure were observed using a field emission

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