



# Preparation of thin-film composite nanofiltration membranes with improved antifouling property and flux using 2,2'-oxybis-ethylamine



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## HIGHLIGHTS

- 2,2'-Oxybis-ethylamine was used to improve surface hydrophilicity of TFC membrane.
- Enhanced hydrophilicity of composite membranes was confirmed.
- Small amount of 2,2'-oxybis-ethylamine can keep high Na<sub>2</sub>SO<sub>4</sub> rejection and water flux.
- Flux recovery ratio exceeds 98% for composite membrane.

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## ABSTRACT

Thin-film composite (TFC) nanofiltration membranes were fabricated via interfacial polymerization using 2,2'-oxybis-ethylamine (2,2'-OEL) as an aqueous monomer. The chemical composition and morphology of the membrane surface were confirmed by X-ray photoelectron spectroscopy (XPS), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and scanning electronic microscopy (SEM). The results showed that interfacial polymerization successfully occurred and pore size of the resultant membranes was in the range of nanofiltration. Hydrophilicity of the membranes was investigated through water contact angle measurement. Water flux and salt rejection measurement showed that the prepared TFC membranes had a high flux at 35.6 L/m<sup>2</sup>h despite the salt rejection slightly decreased. The prepared TFC membranes showed good antifouling performance (best flux recovery ratio was 98.5%) and fouling resistant capacity increased with the concentration of 2,2'-OEL. Compared with the PIP-TMC membranes, low concentration of 2,2'-OEL could maintain as high Na<sub>2</sub>SO<sub>4</sub> rejection of membrane as PIP-TMC membranes and show better fouling resistance performance.

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## 1. Introduction

Membrane separation technology has been widely used in wastewater treatment, water purification, seawater desalination, food, medicine and other fields due to advantages of simplify, high efficiency, low cost and eco-friendly. Especially, process based on nanofiltration (NF) technology has been extensively applied in wastewater treatment and seawater desalination [1]. The molecular weight cutoff (MWCO) of NF membrane generally ranges from 200 to 1000 Da, and the pore sizes are 1–3 nm [2]. The main driving force of NF membrane is pressure difference between the feed and the permeate sides. Thin-film composite (TFC) nanofiltration membrane, coated with a thin barrier layer on the surface of the porous support, has proven to be an effective separation technology for NF. The skin layer of TFC membrane is looser than that of reverse osmosis membrane, but denser than ultrafiltration membrane due to various preparing techniques. Currently, there are several

methods to prepare TFC membranes like phase transformation, surface grafting, and interfacial polymerization [3–6]. Among these methods, interfacial polymerization is a common and effective approach to prepare TFC membrane, which is the maximum yield among commercial products currently.

Nowadays, with the development of industrial activities and environmental pollution, seawater desalination has become the main trend to solve the scarcity of fresh water. However, NF technology is greatly limited by membrane contamination from solute, colloidal or organic particles by physical or chemical interactions with membranes [7]. Generally, pore size, the charge density, and the surface hydrophilicity of NF membranes are critical factors for rejection behavior of NF membrane and application fields [8–11]. However, the pores are small enough and prone to be polluted by microorganism or protein. Contaminated pores were blocked up and diminished by deposition and adsorption of pollutants [12]. Consequently, adsorption of particles will damage the membrane properties and significantly affect the membrane permeability [13,14]. It is difficult to fully restore to the original level once the membrane was fouled. So the researchers did lots of research in the direction of

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resistance to pollution. Coating hydrophilic functional layer on the membrane surface is an effective method to reduce membrane fouling [15]. But post-surface treatment could increase the penetration resistance leading to flux decrease. Covalent bonding of hydrophilic groups is another attempt to improve fouling resistant performance [16–19]. Addition of monofunctional structure (o-Aminobenzoic acid-triethylamine salt) into the ingredient of interfacial polymerization, then coating of cross-linked PEG can improve the flux and antifouling performance of membranes according to Ho's work [20].

Ethyloxy groups have been widely applied to improve hydrophilicity of materials, such as nonion surfactant, owing to their amphiphilic property. Gol and Jewrajka [21] reported a novel approach for in-situ PEGylation on TFC membranes, which could effectively enhance antifouling capability of membranes. Meanwhile, salt rejection and water flux were almost unaffected. Hydrophilic surface modifying macromolecules, such as combination of active diisocyanate and PEG, were reported to enhance antifouling property of membranes when added into trimesoyl chloride (TMC) solution before interfacial polymerization [22]. Prince et al. [23] grafted PEG onto surface of PES membrane and then immobilized silver nanoparticles (Ag) through thermal grafting. As a result, the modified surface was more hydrophilic than the original PES membrane. Elimelech et al. [24] reported a forward osmosis (FO) TFC membrane functionalized using PEG derivatives which showed improved antifouling performance. Zhang et al. [25] introduced poly(ethylene oxide) segments into polyamide layer to enhance the hydrophilicity of composite film. An amino terminated poly(propylene oxide)/poly(ethylene oxide) block copolymer (PEG-amine) was used to attach PEG chains onto the surface of an asymmetric poly(etherimide) (PEI) ultrafiltration membrane, which improved resistance to protein fouling for the modified PEI membrane [26].

In recent years, many diamines had been screened to obtain suitable monomers for interfacial polymerization to prepare pollution resistance membranes. In this paper, we use 2,2'-oxybis-ethylamine(2,2'-OEL) as a hydrophilic ingredient mixed with piperazine (PIP) in aqueous solution, and then polycondensed with TMC in *n*-hexane to prepare TFC nanofiltration membranes. This diamine possesses an ethyloxy group in the structure, which is more hydrophilic and flexible than hydrocarbon diamines, therefore is an important intermediate for organic synthesis, such as crown ethers. Owing to short molecular chain, swelling of polymer would be limited comparing with long-chain PEG derivatives, which could improve the combine strength of base membrane and skin layer. Nanofiltration performance and fouling resistance property of the membranes were investigated to evaluate the effect of 2,2'-OEL in fabrication of TFC nanofiltration films. Water flux and salt rejection of the membranes were investigated to test separation performance of the TFC membranes. SEM, FTIR-ATR and XPS were used to characterize surface chemical features of the resultant membranes. Hydrophilicity of the membranes was investigated through water contact angle (WCA) measurement. Protein fouling resistance of the membranes was evaluated by water recovery rate after treatment in the presence of bovine serum albumin.

## 2. Materials and methods

### 2.1. Materials

Trimesoyl chloride (TMC, >99%), piperazine (PIP, >99.5%) and *n*-hexane were obtained from Sinopharm Chemical Reagent. 2,2'-Oxybis-ethylamine(2,2'-OEL > 95.0%) was purchased from J&K Chemical. NaCl, MgSO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> were purchased from Kermel Chemical Reagent Co., Ltd. (Tianjin, China) and used without any further purification. Bovine serum albumin (BSA) was purchased from Shanghai Aladdin Reagent Company. Phosphate-buffered saline was purchased from Sigma. Polysulfone ultrafiltration (PSF-UF) sheet membrane (MWCO = 20,000) with nonwoven fabric supporting was supplied by GE company. Deionized water was used throughout the study.

### 2.2. Preparation of the TFC membranes

Interfacial polymerization was operated on the surface of PSF-UF sheet membrane to fabricate nanofiltration composite membrane. Firstly, blend aqueous solution of PIP and 2,2'-OEL in different ratios was poured on the top of the PSF-UF sheet membrane for 10 min, then the membrane was taken out and excess solution was drained off with filter papers. Organic phase was prepared by dissolving TMC in *n*-hexane (0.1 wt.%). Then, the membrane was dipped in the organic phase for 30 s to obtain polyamide layer through interfacial polymerization between diamines or PIP and TMC. Afterward, the resultant composite membrane was air dried for 30 min to allow the *n*-hexane to evaporate and subsequently post-treated for attaining the desired stability of the formed structure. Finally, the membrane was washed with deionized water and stored in deionized water for further investigation. The total aqueous monomer concentration was set at 2 wt.% and the concentration of PIP was varied at 2, 1.33, 0.9 and 0 wt.% (Table 1) and the concentration of 2,2'-OEL at 0, 0.67, 1.1 and 2 wt.% correspondingly. The prepared TFC membranes were named as N1, N2, N3 and N4, respectively.

### 2.3. Characterizations

Chemical structure of membranes was characterized with a Vector-22 FTIR spectrometer (Bruker Company, Germany). All the samples were dried thoroughly in vacuum at 60 °C for 24 h prior to characterization. The XPS data were obtained on an AXIS-Ultra instrument Kratos Analytical (SHIMADZU, Japan).

Field emission scanning electron microscopy (FE-SEM) (S-4800, Hitachi, Japan) was used to analyze the surface and cross-sectional morphologies of the composite nanofiltration membranes. The samples frozen in liquid nitrogen were broken and sputtered with gold before SEM observation.

Water contact angle measurements were performed with the sessile drop method using a contact angle meter (Drop Shape Analysis 100, KRUSS GmbH Co., Germany). A syringe was used to place a water droplet of 3 μL on the membrane surface. Tangent lines to both sides of the droplet static image were generated and averaged by the software Drop Shape Analysis. At least three readings at different locations on one surface were measured to get a reliable value.

### 2.4. Nanofiltration performance tests

Performance of the composite membranes was investigated using a cross-flow module at 25 °C (unless otherwise specified, the following chapter performance tests were carried out at 25 °C) and 0.7 MPa. The membranes were pre-filtrated with deionized water at 0.7 MPa to reach a steady state before testing. Water flux and salt rejection of the membranes were investigated by 2 g/L Na<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub> and NaCl aqueous solution, respectively. The solution conductivity was tested at appropriate intervals with permeated liquid collected by a small beaker. The conductivity meter was DDS-11A (Shanghai Honggai Instrument Plant, China).

**Table 1**  
Chemical composition of the PSF, N1, N2, N3 and N4 membrane surfaces.

Membranes	2,2'-OEL:PIP (m%:m%)	Atomic Conc. (mol%)				N/O
		C <sub>1s</sub>	N <sub>1s</sub>	O <sub>1s</sub>	S <sub>2s</sub>	
PSF		77.35	2.93	14.94	2.49	0.19
N1	0:2	73.89	10.11	14.17	0	0.71
N2	0.67:1.33	71.99	7.43	16.09	0	0.46
N3	1.1:0.9	74.37	6.46	15.73	0	0.41
N4	2:0	73.9	7.91	15.75	0	0.50

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