



## Characterization of a positively charged composite nanofiltration hollow fiber membrane prepared by a simplified process



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### HIGHLIGHTS

- Positively charged composite NF hollow fiber membranes were fabricated.
- Preparation conditions of the NF hollow fiber membrane were optimized.
- Preparation process of the NF hollow fiber membrane was simplified.
- Different salts and dyes were used to evaluate properties of NF membranes.

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### ABSTRACT

A positively charged composite nanofiltration (NF) hollow fiber membrane was prepared by interfacial polymerization with polyethyleneimine (PEI) and trimesoyl chloride (TMC) as the reactive monomers. The preparation conditions were optimized, and a relatively simple preparation process was developed. In the optimized preparation process,  $\text{Na}_3\text{PO}_4$  is not needed and the heat-treatment process can be omitted, which saves operation time and reduces cost. The surface morphology and chemical structure of the resulting composite NF membrane were characterized by scanning electron microscopy (SEM), attenuated total reflectance-Fourier transform infrared (ATR-FTIR), and X-ray photoelectron spectroscopy (XPS). Pure water flux, contact angle, molecular weight cut-off (MWCO) and surface zeta potential of the composite NF membrane were also evaluated. The rejection of the NF membrane for  $\text{MgCl}_2$  (1 g/L aqueous solution at 0.4 MPa) was above 97.0%, and the permeate flux was approximately 35.3 L/m<sup>2</sup> h. Furthermore, the NF membrane also showed excellent rejection performance for different dye molecules. The rejections of the NF membrane to brilliant blue KN-R, cationic red X-GTL, acid red B, rhodamine B and cationic gold yellow X-GL were 99.9%, 99.8%, 98.8%, 97.5% and 96.7%, respectively.

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### 1. Introduction

Nanofiltration (NF) is a pressure-driven membrane separation process with characteristics that are intermediate to ultrafiltration (UF) and reverse osmosis (RO) [1]. The nominal molecular weight cut-off (MWCO) of a NF membrane ranges from 200 to 1000 Da. NF membranes generally have a less dense structure than RO membranes [2,3], and NF membranes can be used as an alternative to RO membranes in many applications such as water softening, the removal of pharmaceuticals and endocrine active compounds and wastewater treatment [4–8]. In addition, one of the biggest potential applications

for NF is dye desalination and the concentration of dye solutions [9]. With the increasing industrial demand, new economical advanced NF membranes prepared by a simple process are urgently required.

NF membranes are typically composed of a thin active layer and a porous sublayer [10]. The performance of NF membranes is determined by the structure of the active layer [11]. Various approaches are used to fabricate the active layer, such as interfacial polymerization, chemical cross-linking and UV grafting [12]. Interfacial polymerization is one of the most effective techniques for fabricating the active layer of NF membranes [13,14]. In this method, the active separating barrier layer is composited onto the porous support layer, and the performance of the active layer can be controlled by the preparation conditions [15–20].

Interfacial polymerized composite NF membranes are generally synthesized by condensing water-soluble monomers and water-insoluble acyl chlorides at a water-organic interface [19,21]. The composite NF membranes produced usually have thin, highly cross-linked

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structures [22]. However, at present, most commercially available composite NF membranes fabricated by interfacial polymerization are negatively charged. Positively charged NF membranes have more market applications than negatively charged NF membranes, such as the filtration of heavy metal ions in wastewater recycling [23,24] and the separation and purification of positively charged drugs [25]. With the field of membrane separation technology expanding, the market for positively charged NF membrane underscores the significant need for the development of new membrane materials and preparation methods. Polyethyleneimine (PEI) is generally chosen as the monomer in the aqueous phase to form the thin-film layer on top of the support. As a polyelectrolyte, PEI has attracted much interest for functionalizing polyimide membranes by cross-linking the carbonyl groups of imide rings in the polymer chains with amines [26,27]. The resultant membranes have shown excellent solvent resistance and positive charges. Several studies have reported the fabrication of positively charged NF membrane using PEI as a reactive monomer. For example, Chiang et al. prepared positively charged composite NF membranes with PEI and two acyl chlorides, trimesoyl chloride (TMC) and terephthaloyl chloride (TPC) [28]. Sun et al. fabricated a novel positively charged composite NF membrane via interfacial polymerization of hyperbranched PEI and isophthaloyl chloride (IPC) on a dual-layer hollow fiber membrane surface [29]. These positively charged composite NF membranes showed good performance in tests for salt rejection and dye removal. However, the preparation processes were complex and time consuming, making them an impractical solution for the increasing industrial demand. Therefore, it is crucial to develop a simple process for the preparation of NF membranes. Moreover, current NF modules are generally made in a spiral-wound configuration using composite flat-sheet membranes fabricated by interfacial polymerization. Compared with flat-sheet membranes, hollow fiber membranes exhibit a higher packing density, a higher surface area to volume ratio and self-support capability and are more cost-effective large-scale production and operation [30]. Thus, hollow fiber membranes are attracting an increasing amount of attention.

This study attempts to investigate the possibility of obtaining an economical and practical positively charged NF hollow fiber membrane from a simple preparation process. A positively charged composite NF hollow fiber membrane was fabricated through interfacial polymerization on the inner surface of a polyethersulfone (PES) UF hollow fiber membrane. PEI was selected as the monomer of the aqueous phase, and TMC was chosen as the monomer of the organic phase. The preparation conditions of the NF hollow fiber membrane were investigated, including the concentration of monomers and additives, the reaction time and the temperature of heat-treatment. The separation characteristics of the acquired composite NF hollow fiber membranes were evaluated in terms of permeate flux and rejections for salt solutions under different operating conditions. Furthermore, the positively charged composite NF hollow fiber membrane showed excellent performance for dye removal.

## 2. Experimental

### 2.1. Materials and chemicals

The polyethersulfone (PES) UF hollow fiber membranes with a MWCO of approximately 50,000 Da and a pure water flux of approximately 340 L/m<sup>2</sup> h at 0.1 MPa, were provided by the Development Center of Water Treatment Technology, State Oceanic Administration, Hangzhou, China.

All chemicals used were AR grade. Polyethyleneimine (PEI) with a molecular weight of 70,000 Da, which was used as the active monomer in the aqueous phase, was purchased from Aladdin Reagent Co., LLC, Shanghai, China. Anhydrous sodium phosphate (Na<sub>3</sub>PO<sub>4</sub>) (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was used as the additives. Trimesoyl chloride (TMC, purity > 99.0%) (Qingdao Benzo Chemical

Company, China) was used as the active monomer in the organic phase, and n-hexane (Shanghai Lingfeng Chemical Reagent Company, China) was used as the organic solvent. Sodium chloride (NaCl), magnesium chloride (MgCl<sub>2</sub>), magnesium sulfate (MgSO<sub>4</sub>) and sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) were supplied by Shanghai Sihewei Chemical Reagent Company, China. The dyes, including reactive brilliant blue KN-R, acid red B, cationic red X-GTL, rhodamine B and cationic gold yellow X-GL, were obtained from a local chemical factory. The molecular structures of PES, PEI, TMC and dyes are presented in Fig. 1. All chemicals were used as received.

### 2.2. Membrane preparation

The active skin layer of the composite NF hollow fiber membrane was prepared by interfacial polymerization on the inner surface of the PES UF hollow fiber substrate. The membrane modules were fabricated by sealing 6 pieces of PES UF hollow fibers in a polyethylene terephthalate (PET) tube with an effective length of 18 cm. An aqueous solution containing PEI and Na<sub>3</sub>PO<sub>4</sub> was extruded into the lumen side of the PES UF hollow fibers, the excess solution was drained from the soaked surface and the fibers were dried with pure nitrogen gas. Next, a TMC/n-hexane solution was extruded in the same manner. After removing the residual solution, the membrane module was heat-treated in an oven for 10 min. Finally, the fabricated composite NF hollow fiber membranes were washed with deionized (DI) water and stored wetly.

### 2.3. Membrane characterization

Surface and cross-section morphologies of the fabricated composite NF hollow fiber membrane were observed by a field emission scanning electron microscopy (FE-SEM, JEOL, JSM-5510LV, Japan). These samples were fractured in liquid nitrogen and sputtered with gold using an ion sputter JFC-1100 prior to FESEM observations. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) (Vector 22 FTIR, Bruker Optics, Switzerland) and X-ray photoelectron spectroscopy (XPS) (AXIS-Ultra DLD, Kratos, U.K.) were used to investigate the chemical composition of the selective layer. Hydrophobic/hydrophilic properties of the membranes were characterized by a water contact angle goniometer (OCA20, Dataphysics, Germany) at room temperature. Surface charge properties were studied by measuring streaming potentials of the membranes at various pH values using a SurPASS electrokinetic analyzer (Anton Paar GmbH, Austria). Measurements were performed at 25.0 °C with 0.001 mol/L aqueous KCl solutions and pH ranging from 5 to 12. The surface zeta potential was determined according to the Helmholtz–Smoluchowski equation with the Fairbrother and Mastin substitution [31].

### 2.4. Measurement of membrane separation properties

Membrane permeation experiments were performed using a laboratory scale cross-flow filtration apparatus. Before testing, the hollow fiber NF membranes were pre-pressurized under 0.4 MPa for 1 h with DI water to reach a stable state. The pure water flux of the NF hollow fiber membrane was measured by employing DI water as the feed, which was calculated using the following equation:

$$F = \frac{V}{A \cdot \Delta t} \quad (1)$$

where F is the permeate flux (L/m<sup>2</sup> h), V is the volume of the water or solution that permeated the filter during the experiment (L), A is the effective permeation area (m<sup>2</sup>), and Δt is the operation time (h).

Subsequently, the permeation tests were conducted with polyethylene glycol (PEG) of different molecular weights to determine the MWCO of the NF hollow fiber membranes, and the rejections and

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