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# Preparation and properties of polyamide/titania composite nanofiltration membrane by interfacial polymerization

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## HIGHLIGHTS

- We added $TiO_2$ sol instead of $TiO_2$ nano-particles to make $PSF/TiO_2$ hybrid membrane.
- The polymerization reaction happened on the surface of $PSF/TiO_2$ hybrid membrane.
- The addition of $TiO_2$ sol changed the salt rejection slightly.
- The water flux increased three times after adding proper $TiO_2$ sol.

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## ABSTRACT

The $TiO_2$ sol was added in the polysulfone (PSF) casting membrane solution to prepare polysulfone/titania hybrid membrane in this work. Then the polypiperazine–amide composite nanofiltration (NF) membranes were prepared on $PSF/TiO_2$ hybrid membranes by interfacial polymerization. Piperazine and trimesoyl chloride were used as monomers in aqueous phase and organic phase, respectively. Different preparation conditions affecting the separation performances of NF membrane were discussed, including $TiO_2$ sol concentration, piperazine concentration, trimesoyl chloride concentration, and reaction time. The chemical structure characterizations of polyamide composite membrane were tested by attenuated total reflectance infrared (ATR-IR). The surface images and cross sections were observed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The addition of $TiO_2$ sol changed the salt rejection slightly, but the water flux was three times than that of the polyamide membrane on the PSF support membrane. The polyamide NF membrane prepared under the optimum condition exhibited $Na_2SO_4$ rejection of 96.94% and water flux of 12.84 $L\,m^{-2}\,h^{-1}$. According to the intercepting experiments of polyethylene glycols, the molecular weight cut-off (MWCO) of the resulting membrane was under 600 Da.

## 1. Introduction

NF membrane is a kind of pressure driven membrane between reverse osmosis (RO) membrane and ultrafiltration (UF) membrane, which has got fast development in the world in recent years [1,2]. On account that the composite NF membrane has higher salt rejection and water flux, it has attracted considerable attention, and has become a research hotspot in membrane field in the domestic and overseas [3]. The composite NF membrane can be optimized separately according to the required performances of the composite layer or the support layer. The NaOH solution was used to modify the polyacrylonitrile (PAN) membrane before it was used as the support layer, so that the surface of the PAN membrane had hydrophilic groups on it and water flux was improved [4]. Yu et al. [5] adopted the surface modifying N-isopropyl acrylamide–acrylic copolymer on the surface of the composite membrane, so that the membrane surface hydrophilicity and borden of electric intensity were both improved, increasing the water flux and NaCl rejection. A thin surface layer could be fabricated in many different methods, between which the composite means is the mostly used and most efficient way at present. The thin film composite membrane (TFC) has been attracting considerable attention since it showed up. Since Cadotte et al. used interfacial polymerization method to prepare composite membranes [6], interfacial polymerization method has achieved a wide range of applications in membrane technology field owing to its simple operation and easy management [7]. Interfacial polymerization method stemmed from the interfacial polymerization theory by Morgan [8]: two kinds of monomers dissolve in two different

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non-dissolved solvents, then the monomers react at the interface between the solvents, producing an ultra-thin composite layer.

Water flux is an important index to evaluate membrane performance. Under the same conditions, higher flux can increase removal efficiency and decrease energy consumption, so as to decrease operation cost. There are many ways to improve water flux in the process of polymerization reaction, including pretreatment to improve the hydrophilicity of support membrane [4,9–11], adding hydrophilic materials in solution [12,13], increasing operation pressure, etc. Specifically, a novel research direction has been paid attention, which is by means of nano-particles, including $ZrO_2$ [14], $Al_2O_3$ [15], $TiO_2$ [16], $SiO_2$ [17], and $Fe_3O_4$ [18]. The $TiO_2$ nano-particles were added in the reaction of interfacial polymerization [16]. If $TiO_2$ particles were added in aqueous phase, they mainly existed in the dactylopores of the PSF support layer. If $TiO_2$ particles were added in organic phase, they primarily existed in the polyamide composite layer. The water flux and salt rejection were improved in both ways, while the latter was better. The $SiO_2$ nano-particles were added in aqueous phase and water flux increased 21.1% because of remarkable RMS increasement [17]. Besides, nano-Ag also could effectively improve the hydrophilicity of the composite membrane. However, the $TiO_2/SiO_2$ nano-particles were ultrasonic dispersed in aqueous or organic phase; there might be heterogeneity in the vertical direction when still standing. This phenomenon would result in membrane heterogeneity, leading to a variation on the mechanical properties of the membrane. In this study, the $TiO_2$ sol was added in the PSF casting membrane solution to prepare the PSF/$TiO_2$ hybrid membrane. Both the $TiO_2$ sol and PSF solution were colloidal, so they could be mixed uniformly after constant stirring, and could avoid the problems brought by nano-particles, which was mentioned before.

In this work, we prepared the polyamide/$TiO_2$ composite nanofiltration membrane using interfacial polymerization method and evaluated its properties through ATR-IR, SEM and AFM. The PSF/$TiO_2$ hybrid membrane was used as support membrane, and piperazine and trimesoyl chloride were used as monomers for polymerization reaction. The $TiO_2$ sol concentration, piperazine concentration, trimesoyl chloride concentration and reaction time were discussed. We aim to study out composite NF membranes with high water flux and $Na_2SO_4$ rejection under low pressure.

## 2. Experiment

### 2.1. Materials

Polysulfone (PSF) was bought from Dalian Polysulfone Plastic Manufacturing Co., Ltd. PIP (purity 99%) and TMC (purity 98%) were purchased from Shanghai Aladdin Reagent Co., Ltd. Dimethylacetamide (DMAc), N-methyl pyrrolidone (NMP), glacial acetic acid, butyl titanate (TBOT), concentrated hydrochloric acid, polyethylene glycol (PEG), n-hexane, sodium dodecyl sulfate (SDS), triethylamine (TEA), bull serum albumin (BSA), $Na_2SO_4$, NaCl, $NaHSO_3$, KI, $I_2$, and $BaCl_2$ were all analytical reagent and used without any further purification.

### 2.2. Fabrication of titanium dioxide sol

Sol–gel process [19] was applied to prepare the titanium dioxide sol. An amount of 10 mL of NMP was separately taken into two 100 mL beakers. The required 1 mL glacial acetic acid and 10 mL TBOT were put into beaker A when churning, which was liquor A. The required 2 mL deionized water and 0.3 mL concentrated hydrochloric acid was put into beaker B, mixing uniformly, which was liquor B. Liquor B was dropwise added into liquor A when it was churning. After the mixture of A and B was done, the pH of the mixed liquor was adjusted to 4 with concentrated hydrochloric acid. Then the stable, transparent and pale yellow $TiO_2$ sol was fabricated [20].

### 2.3. Preparation of the composite membrane

The resulting $TiO_2$ sol was dropwise added in the casting membrane solution when churning. The casting membrane solution was made with PSF as raw material, DMAc and NMP as solvent, and PEG as pore-foaming agent. The solution remained churning for 24 h, producing PSF/$TiO_2$ sol. L-S phase inversion method [21] was used to prepare the PSF/$TiO_2$ hybrid membranes, which were the support layer of interfacial polymerization reaction.

Piperazine and trimesoyl chloride were used as monomers respectively in aqueous phase and organic phase. TEA was used as acid absorber [22–24]. SDS was an anionic surfactant, which could enhance the interface bondability between composite and support layer, and prevent from the composite layer stripping, so as to improve the stability of the composite NF membrane [25,26]. And it is confirmed that TEA and SDS create no significant change in the chemical composition of the composite layer [27]. Deionized water was aqueous solvent, and n-hexane was organic solvent. At first, the support membrane was soaked in aqueous phase containing different PIP concentrations for 5 min. After it was surface dried vertically at room temperature, this membrane was immersed in the organic phase containing different TMC concentrations for a certain time. Then the membrane was put at 70 °C [9,28,29] oven for 15 min for further polymerization. At last, the resulting membrane was washed with deionized water and stored in 1.0 wt.% $NaHSO_3$ solution. For short time storage (less than one week), 1.0 wt.% $NaHSO_3$ solution was adequate for preventing biological growth [17].

### 2.4. Membrane characterization

The chemical structure characterizations of polyamide composite membrane were tested by attenuated total reflectance infrared (Spectrum One). The measured wavenumber range was 4000–500 $cm^{-1}$.

The surface images and cross sections of PSF/$TiO_2$ hybrid membrane and polyamide composite membrane were observed by scanning electron microscopy (FEI Sirion) and atomic force microscopy (Veeco, DI Bioscope).

The TFC NF membrane performance tests of the resulting membranes were performed with $Na_2SO_4$ rejection and water flux. The schematic diagram of experimental setup was exhibited in Fig. 1. The water flux was determined by direct measurement of permeate flow with cross-flow filtration way. The membranes were pressured at 0.5 MPa for 30 min with the $Na_2SO_4$ solution before the water flux and rejection were measured. The $Na_2SO_4$ solution was 2000 mg $L^{-1}$, when the temperature was 25 °C. The water flux ($J_w$) of membranes was calculated as follows:

$$J_w\left(L\cdot m^{-2}\cdot h^{-1}\right) = V_w\cdot A^{-1}\cdot t^{-1} \tag{1}$$

where $V_w$ is the volume of the obtained permeate during the experiment, A is the effective membrane area (17.71 $cm^2$ in this experiment), and t is the operation time. The salt rejection (R) was calculated as follows:

$$R = \left(1-C_p/C_0\right)\times 100\% \tag{2}$$

where $C_p$ and $C_0$ respectively represent permeate and feed concentrations. The salt concentrations in permeate and feed solutions were measured by conductivity meter.

Solutions of different molecular weight PEG flowed through the nanofiltration membrane according to the sequence from the high molecular weight to the low. When the PEG could be intercepted by the NF membrane, it means that the MWCO of the membrane is under its molecular weight. The concentrations of PEG were measured by iodine precipitation method [30,31].