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Full Length Article

A novel polyester composite nanofiltration membrane formed by interfacial polymerization of pentaerythritol (PE) and trimesoyl chloride (TMC)

Jun Cheng [a], Wenxin Shi [b,*], Lanhe Zhang [a,*], Ruijun Zhang [b]

[a] School of Chemical Engineering, Northeast Electric Power University, Jilin 132012, PR China
[b] State Key Laboratory of Urban Water Resource and Environment, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, PR China

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ABSTRACT

A novel polyester thin film composite nanofiltration (NF) membrane was prepared by interfacial polymerization of pentaerythritol (PE) and trimesoyl chloride (TMC) on polyethersulfone (PES) supporting membrane. The performance of the polyester composite NF membrane was optimized by regulating the preparation parameters, including reaction time, pH of the aqueous phase solution, pentaerythritol concentration and TMC concentration. A series of characterization, including permeation experiments, attenuated total reflectance-fourier transform infrared spectroscopy (ATR-FTIR), scanning electron microscope (SEM), atomic force microscopy (AFM), zeta potential analyzer and chlorine resistance experiments, were employed to study the properties of the optimized membrane. The results showed that the optimized polyester composite NF membrane exhibited very high rejection of Na_2SO_4 (98.1%), but the water flux is relatively low (6.1 L/m^2 h, 0.5 MPa, 25 °C). The order of salt rejections is $Na_2SO_4 > MgSO_4 > MgCl_2 > NaCl$, which indicated the membrane was negatively charged, just consistent with the membrane zeta potential results. After treating by NaClO solutions with different concentrations (100 ppm, 500 ppm, 1000 ppm, 2000 ppm, 3000 ppm) for 48 h, the results demonstrated that the polyester NF membrane had good chlorine resistance. Additionally, the polyester TFC NF membrane exhibits good long-term stability.

1. Introduction

Nanofiltration (NF) is a kind of pressure driven membrane separation process between reverse osmosis (RO) and ultrafiltration (UF) [1,2]. Compared with RO and UF, NF membrane can offer high rejection of multivalent ions and organic molecules due to its charged property and nano-scale pore size [3]. As a technological process, NF has been widely used in water softening, organic matter removal, biochemistry, pharmacy, food and dyeing [4–20]. In NF technology, the thin film composite (TFC) NF membranes have become dominant in market due to its high flux and effective separation performance [21,22]. Many methods have been proposed to fabricate TFC NF membrane with an ultrathin active layer on the substrate, such as interfacial polymerization, grafting, dip coating, electron beam irradiation and plasma-initiated polymerization [23]. Among all the technologies, interfacial polymerization was a common technique which has been widely used in laboratory and commercial scale. In interfacial polymerization process, an ultrathin active layer was generated on the substrate which was the key factor for determining performance of the TFC NF membranes [24,25]. The ultrathin active layer can be controlled and optimized for particular function by choosing different monomers either in aqueous phase or organic phase.

In the past several decades, most of TFC NF membranes were prepared by selecting or synthesizing new monomers as aqueous phase in interfacial polymerization process. Many researchers used multifunctional amine monomers as aqueous phase in interfacial polymerization to form polyamide TFC NF membranes. Piperazine (PIP) and M-phenylenediamine (MPD) were the common multifunctional amine monomers utilize for preparing TFC NF membrane. Other multifunctional amine monomers were also

* Corresponding authors.
E-mail addresses: swx@hit.edu.cn, shiwenxin2@yahoo.com (W. Shi), zhanglanhe@163.com (L. Zhang).

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used for producing polyamide TFC NF membranes [26–29]. For instance, Yu et al. used m-phenylenediamine-4-methyl (MMPD) as multifunctional amine monomer to synthesize polyamide TFC RO membranes [30]. Compared with polyamide TFC NF membranes, only a few researchers used interfacial polymerization technique to prepare polyester composite membranes. For example, M.N. Abu Seman et al. [31] produced polyester NF membrane and studied irreversible fouling of TFC membranes using humic acid model solutions at different pH values. Tang et al. [32] synthesized a novel polyester thin film composite membrane by the interfacial polymerization of triethanolamine (TEOA) and trimesoyl chloride (TMC) on the polysulfone (PSF) supporting membrane. The order of the membrane rejections was Na_2SO_4 (82.2%) > $MgSO_4$ (76.5%) > NaCl (42.2%) > $MgCl_2$ (23%) (salt concentration in feed solutions were 5 mmol/L). Wu et al. [33] used β-cyclodextrin (β-CD) and TEOA as aqueous monomer in interfacial polymerization to form a novel polyester TFC membrane. Yan et al. [34] selected natural material tannic acid as aqueous monomer to fabricate the novel polyester composite NF membranes. The inorganic salt rejection ratios of all prepared NF membranes followed the order: NaCl < $CaCl_2$ < Na_2SO_4 < $MgSO_4$ < 60% (salt concentration in feed solutions was 0.01 mol/L).

In general, previously prepared polyester membranes have low rejection of salts. The rejection of salts was a very important performance of NF membrane. Thus, it is natural to seek a novel active monomer for interfacial polymerization in order to improve salt rejection of polyester NF membranes. Pentaerythrotol (PE) was an active monomer which has numerous applications in flame retardants, surfactants, antioxidants, crosslinking agents, polyoxometalate derivatives, metalcontaining catalysts, lubricant and resin [35–41]. PE is expected to react with multifunctional acid chloride to form cross-linked network structure which attribute to the existence of multi-hydroxyl in its molecule [42]. However, in our knowledge, PE has never been used to prepare TFC NF membranes. Therefore, PE was used as aqueous phase monomer to synthesize TFC NF membranes in this work.

Herein, a novel polyester thin film composite NF membrane which has high rejection of salts was synthesized by interfacial polymerization of PE and TMC on the polyethersulfone (PES) supporting membrane. The performance of the polyester TFC NF membrane was optimized by studying the preparation parameters, such as the reaction time of polymerization, the pH of aqueous phase, the concentration of PE and TMC. The structure morphology of the membranes was characterized by ATR-FTIR, SEM and AFM. The membrane properties of the polyester TFC NF membrane were measured by testing separating performance of various salts (including Na_2SO_4, $MgSO_4$, NaCl and $MgCl_2$) and organic molecules (including PEG400, PEG600, PEG800 and PEG1000). The surface charging was measured by an electrokinetic analyzer. Additionally, chlorine resistance and long-term performance stability of optimized membrane were also studied.

2. Experimental materials and methods

2.1. Materials

The PES UF membranes (MWCO 30,000) were purchased from SUN (USA). Pentaerythritol (PE), Na_2SO_4, $MgSO_4$, NaCl, $MgCl_2$, Na_3PO_4 and N-hexane were purchased from Sinopharm Chemical Reagent Co., Ltd (China). 1, 3, 5-benzene-tricarbonyltri chloride (TMC) was purchased from TCI (Shanghai, China). PEG400, PEG600, PEG800 and PEG1000 were purchased from Aladdin Industrial Corporation (Shanghai, China). NF270 were purchased from DOW (USA). All reagents and chemicals were analytical grade and used without further purification. Ultrapure water was used in this study.

2.2. Membrane preparation and preparation condition optimization

2.2.1. Membrane preparation

The PES supporting membranes were washed in 1% (v/v) ethanol solution for 8 h on an orbital shaker at 130 rpm under 30 °C and subsequently stored in water until the application. The washed PES supporting membrane was rolled with a rubber roller to dry the water on its surface and subsequently immersed in PE aqueous solution for 10 min then was taken out (the aqueous solution of pH was adjusted by Na_3PO_4 and camphorsulfonic acid). Afterwards, the wet membrane was rolled with a rubber roller to remove the excess aqueous solution remaining on its surface and immersed into the *n*-hexane solution of TMC for certain time to interfacial polymerization, resulting in the formation of polyester on the surface of PES supporting membrane. The reaction equation of PE and TMC was outlined in Fig. 1. The above experiment was conducted under 30 °C.The composite membranes were subsequently cured in an oven at 60 °C for 40 min for further polymerization. The membranes were washed thoroughly with ultrapure water and stored in ultrapure water overnight before test.

2.2.2. Preparation condition optimization

In this study, the performance of the polyester thin film composite NF membrane were optimized by studying the preparation parameters, including the concentration of reactive monomer, the reaction time of polymerization and the pH of aqueous phase.

(1) In order to investigate the influence of the concentration of aqueous phase monomer in interfacial polymerization process, different concentration of PE was selected as aqueous phase and solution pH was adjusted to 12. Meanwhile, the concentration of TMC was 0.2 (w/v) and the reaction time was 20 min
(2) In order to investigate the influence of the concentration of organic phase monomer in interfacial polymerization process, different concentration of TMC was selected as organic phase.

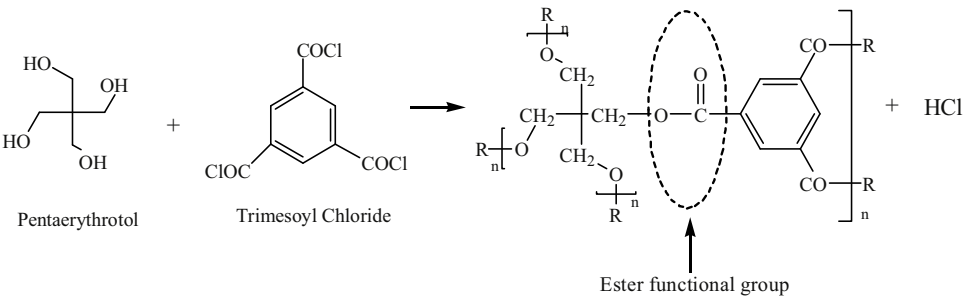

Fig. 1. The interfacial polymerization mechanism of PE and TMC.