# Improved performance of composite nanofiltration membranes by adding calcium chloride in aqueous phase during interfacial polymerization process

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## ARTICLE INFO

## ABSTRACTS

The composite nanofiltration membranes were prepared via interfacial polymerization of tetraethyle-nepentamine (TEPA) and 1,3,5-benzenetricarbonyl trichloride (TMC). The improved performance of the composite nanofiltratiom membranes by adding calcium chloride in aqueous phase during the interfacial polymerization was verified in terms of pure water permeability, rejection of different solutes including dyes and inorganic salts and chlorine resistance. The results showed that the pure water permeability of composite nanofiltration membranes would acquire a remarkable increase with a slight decrease in solute rejections under the optimized addition of CaCl$_2$. The addition of CaCl$_2$ also dramatically enhanced the chloride resistance of composite nanofiltration membranes in comparison with the control membranes prepared without CaCl$_2$ added. Therefore, inorganic salts like CaCl$_2$ could be considered as a potential additive to enhance the performance of composite nanofiltration membranes.

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## 1. Introduction

Nanofiltration is a membrane separation process between reverse osmosis and ultrafiltration with a molecular weight cut-off (MWCO) range from about 100–1000 Da. The nanofiltration process takes place on a selective separation layer of a semipermeable membrane. The driving force of the nanofiltration is the pressure difference between the feed and permeate side. One or several components of a dissolved mixture with high molecular weight are retained by the nanofiltration membrane, while water and substances with low molecular weight below MWCO are able to permeate the semipermeable separation layer. Nanofiltration is considered as an attractive separation technique which has an extremely wide scope of application in sewage treatment, drinking water production, seawater desalination, food and paper industries [1–3].

The active separation layer of nanofiltration membrane is usually prepared by the interfacial polymerization technique. The interfacial polymerization technique is based on the polymerization reaction which takes place at the interface between two immiscible phases of aqueous and organic solution [3,4]. Traditional polyamide nanofiltration membrane is the reaction product forming a thin film from polyamine in aqueous phase and polyacyl chloride in organic phase upon porous support for obtaining the composite nanofiltration membranes. Therefore, the composite nanofiltration membranes contain two layers: a porous support which has good mechanical properties and a dense, ultra-thin active layer which has relatively high permeability and proper rejection [5].

The nature of solvents and monomers as well as monomer concentrations, monomer ratios, reaction temperature and time determine the porosity and pore size, the structural morphology and the composition of the thin layer of the composite nanofiltration membrane [6–8]. Additives in the aqueous phase are able to change monomer dissolution and diffusion rates, ever take part in cross-linking reaction, which play an important role in determining the performance of the nanofiltration membranes [9–12]. Polyvinylalcohol (PVA) dissolved in the aqueous solution for interfacial polymerization can generate high flux and antifouling nanofiltration membranes without sacrificing rejection or changing the nanofiltration membrane structures [9]. The introduction of silica sol, titanium dioxide or multiwalled carbon nanotubes (MWNTs) into aqueous solution during interfacial polymerization also have been demonstrated increased antifouling ability as well as improved water permeability or rejection [10–12]. However,

few researches have been performed upon using inorganic salt as the additives in the aqueous phase during interfacial polymerization. In fact, inorganic salts would probably enhance the performance of nanofiltration membranes for interacting with the groups of polymer [13,14]. Kraus et al. found that salts added to aromatic polyamide solutions exerted a pronounced effect on the structure and performance of reverse osmosis membranes [13]. Tang et al. demonstrated that the addition of LiBr in the aqueous phase could increase the reactivity of –OH groups and accelerate the hydrolysis of the acid chloride groups of TMC during interfacial polymerization [14].

Polyamide nanofiltration membranes or reverse osmosis membranes, suffer from significant performance degradation when exposed to the solution containing free chlorine, which is widely used as the disinfectant [15,16]. Since chemical cleaning processes are frequently used in the practical membrane processes, the chlorine resistance is considered as one of the most important factors for the polyamide membranes lifetime, The previous experiments reveal that electrophilic chlorine attack the alkaline nitrogen atoms of the amide bonds [17,18] as the first step and then induce the cleavage of the polyamide chain. Orton rearrangement will accelerate the cleavage of the polyamide chain if benzene ring exits [16].

In the present study, the composite nanofiltration membranes were prepared by interfacial polymerization with aqueous monomer tetrathylenepentamine (TEPA) and organic monomer 1,3,5-benzenetricarbonyl trichloride (TMC). Inorganic salt of calcium chloride dissolved in aqueous phase is introduced as the additive during the interfacial polymerization process. Calcium ions have the ability of complexation with carbonyl groups [19,20] to embed into the thin film, which could optimize the structure of the polyamide active layer and improve the performance of the composite nanofiltration membranes.

## 2. Experimental

### 2.1. Materials

Polyethersulfone (PES, Ultrason E 6020P) in flake form was purchased from BASF Co. (Germany) and dried at 110 °C for 12 h before used. 1,3,5-Benzenetricarbonyl trichloride (TMC) was obtained from Alfa Co. (USA). Tetraethylenepentamine (TEPA), N,N-dimethylformamide (DMF) and n-hexane were purchased from Kewei Chemical Reagent Co. (China) and used as received. PEO-PPO-PEO triblock copolymer Pluronic F127 with a molecular weight of 12,600 and a PEO content of 70 wt% was purchased from Sigma. Orange GII, Congo Red, and other inorganic salts were also purchased from Kewei Chemical Reagent Co. (Tianjin, China).

### 2.2. Preparation of composite nanofiltration membranes

PES was used as membrane bulk material and Pluronic F127 as pore forming agent. PES support membranes were fabricated via a non-solvent induced phase inversion process which was described in our previous works [21,22]. The polyamide active layer was synthesized upon the PES support membranes via interfacial polymerization of TEPA and TMC containing $CaCl_2$ in the aqueous phase. Aqueous solutions of TEPA (1.0 wt%) with $CaCl_2$ at varying concentrations from 0 wt% to 5.0 wt% and n-hexane solutions of TMC (0.5 wt%) were prepared, respectively. First, the PES membranes were immersed into the aqueous solution for 10 min to make TEPA and $CaCl_2$ adsorbed on the surface of PES membranes. Then, the excess solution was drained off with filter papers. The PES membranes were immersed into the n-hexane solution for 2 min to finish the interfacial polymerization reaction. The PES

membranes were taken out from n-hexane solution and dried in room temperature for 30 min for further polymerization, leading to the formation of a polyamide active layer. Finally, the prepared TEPA/TMC composite nanofiltration membranes were rinsed and stored in deionized water until used.

### 2.3. Characterization of composite nanofiltration membranes

The surface morphology of the TEPA/TMC composite nanofiltration membranes was investigated by field emission scanning electron microscope (FESEM, Nova Nanosem 430, FEI Co., USA). The nanofiltration membrane samples freeze-dried with a vacuum freeze dryer (FD-1C-50, Boyikang Co., China) were sputtered with gold before SEM measurement and the nanofiltration membrane samples were observed under 120,000 × magnification. The surface chemical compositions of the TEPA/TMC nanofiltration membranes were probed by Energy Dispersive X-Ray Spectroscopy (EDX) instruments during SEM observation.

Before Fourier Transform Infrared (FT-IR) measurement, the TEPA/TMC nanofiltration membranes were dried for 2 h via exposure to air. FT-IR spectra were obtained by the Fourier Transform infrared spectroscopy (VERTEX 70, Bruker Co., Germany) instrument equipped with both horizontal attenuated total reflectance accessories. The experiments were run with air as the background. Scans were accumulated with a resolution of $2\ cm^{-1}$ for each spectrum to analysis the functional groups on the composite nanofiltration membrane surfaces.

Water contact angle was employed to evaluate the hydrophilicity of the nanofiltration membrane surface. The static contact angles of water on the nanofiltration membrane surfaces were measured by a contact angle goniometer (JC-2000C Contact Angle Meter, Powereach Co., Shanghai, China). The average value of static contact angle on each nanofiltration membrane was calculated with at least five different locations on each nanofiltration membrane.

The membrane surface charge was also the important characterization of nanofiltration membranes. It was characterized via tangential flow streaming potential measurement [24]. The Zeta potential was determined from streaming potential measurements by an Electro Kinetic Analyzer (Anton Paar KG, Austria) equipped with a plated sample cell. The measurements were carried out at temperature $25 \pm 0.5$ °C in KCl solution (1.0 mM, pH 6.5). Prior to use, the samples were conditioned in 1.0 mM KCl solution for at least 24 h. The resultant Zeta potential was calculated using the Helmholtz–Smoluchowski equation.

### 2.4. Permeability and rejection of composite nanofiltration membranes

The measurement of permeability and rejection was carried out with a dead-end stirred cell filtration system connected with a nitrogen gas cylinder and a solution reservoir was designed to assess the permeation of the fabricated nanofiltration membranes. The system was composed of a filtration cell (model 8200, Millipore Co.) which had 200 mL volume capacity and an inner diameter of 62 mm. The effective area of the filtration cell was 28.7 $cm^2$. The feed side of the system was pressed by nitrogen gas. Before measurement, all the nanofiltration membranes were pretreated at a high pressure drop of 0.25 MPa for about 30 min. The pure water flux ($J_w$, L/$m^2$ h) of the nanofiltration membranes were measured at the operation pressure of 0.2 MPa and it was calculated by Eq. (1)

$$J_w = \frac{V}{A\Delta t} \tag{1}$$