



# Preparation, evaluation and modification of PVDF-CTFE hydrophobic membrane for MD desalination application



Libing Zheng<sup>a,b,c</sup>, Jun Wang<sup>a,d,e,\*</sup>, Jie Li<sup>a,d</sup>, Yong Zhang<sup>a,d,e</sup>, Kun Li<sup>a,b</sup>, Yuansong Wei<sup>a,b,\*\*</sup>

<sup>a</sup> State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China

<sup>b</sup> Laboratory of Water Pollution Control Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China

<sup>c</sup> University of Chinese Academy of Sciences, Beijing, 100049, China

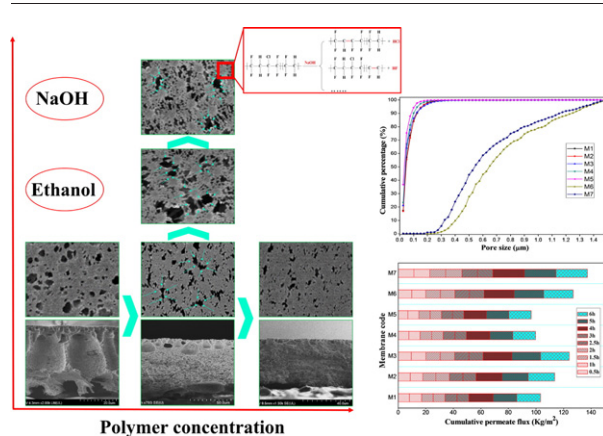
<sup>d</sup> Beijing Key Laboratory of Industrial Wastewater Treatment and Resource Recovery, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China

<sup>e</sup> The National Engineering Laboratory for High Concentration and Refractory Organic Wastewater Treatment Technology, Chinese Academy of Sciences, Beijing, 100085, China

## HIGHLIGHTS

- Effect of PVDF-CTFE content on phase inversion process was investigated.
- Hydrophobic membrane with excellent MD desalination performance was prepared.
- Effective pore passages were proposed for membrane permeability evaluation.
- Dehalogenation and membrane shrinkage obstruction were the mechanism for NaOH and ethanol solution.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 29 June 2016

Received in revised form 31 August 2016

Accepted 6 October 2016

Available online 19 October 2016

### Keywords:

PVDF-CTFE

MD desalination

Membrane modification

Interconnectivity

Dehalogenation

Membrane shrinkage

## ABSTRACT

Desalination by membrane distillation (MD) have found rapid growth and diversified applications in recent decade, associated with it was the demand for hydrophobic membranes. Poly (vinylidene fluoride-co-chlorotrifluoroethylene) (PVDF-CTFE) was used for hydrophobic membrane preparation with LiCl additive by non-solvent induced phase inversion (NIPS), the effect of polymer concentration was investigated in terms of membrane morphology, pore structure, hydrophobicity, thermal property, and membrane distillation (MD) performance to evaluation its potential in MD desalination. It was found that the solid-liquid demixing process showed more influence with increasing polymer content due to the delayed phase inversion process, which was responsible for the suppressed macrovoids, reduced pore size, higher hydrophobicity and pore interconnectivity. The melting temperature and crystallinity also increased due to the crystallization during membrane formation. M3 with 12% polymer content presents the best MD performance (permeate flux of 20.65 kg/m<sup>2</sup>·h with a salt rejection higher than 99.95%). Ethanol and sodium hydroxide (NaOH) solution were applied as the second immersion bath to post-treat the nascent membranes. Pore enlargement effect was found for both post-treated membranes. However, the dehalogenation process was the most important mechanism for NaOH, while the obstruction of partial shrinkage was the mechanism of ethanol solution. In a word, PVDF-CTFE hydrophobic

\* Correspondence to: J. Wang, 18 Shuangqing Road, Haidian District, Beijing 100085, PR China. Tel.: +86 10 62849198; fax: +86 10 62849198.

\*\* Correspondence to: Y. Wei, 18 Shuangqing Road, Haidian District, Beijing 100085, PR China. Tel.: +86 10 2849109; fax: +86 10 62849109.

E-mail addresses: [junwang@rcees.ac.cn](mailto:junwang@rcees.ac.cn) (J. Wang), [yswei@rcees.ac.cn](mailto:yswei@rcees.ac.cn) (Y. Wei).

membrane show potential in MD desalination, especially when a second solution bath is used for membrane modification as the flux enhancement without the sacrifice of salt rejection.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Hydrophobic membrane-based process like MD [1,2], membrane emulsification (ME) [3], osmotic distillation (OD) [4], pervaporation [5], and membrane crystallization (MCR) [6] have found various applications and shown proven advantages in desalination, wastewater treatment, gas separation, concentration and recovery of temperature sensitive materials [7,8]. The membrane applied in these process should presents hydrophobic nature firstly, along with the ideal pore structure with narrow pore distribution, low thermal conductivity, excellent chemical tolerance and mechanical strength [9,10]. The commercial ultrafiltration or microfiltration membranes which have been commonly applied can hardly meet all the criterions. Thus the commercial-scale hydrophobic membrane-based processes like MD remain challenging due to the constraint of commercially available high performance membranes and modules.

In recent decades, hydrophobic membrane preparation and membrane formation mechanism study have been a hotspot in membrane science. Most of these membranes are fabricated from polymeric materials due to the lower surface energy, lower cost and better processability, even hydrophobic-modified ceramic membranes also show potentials in hydrophobic membrane-based process [11–13]. Non-solvent induced phase inversion (NIPS), including immersion phase inversion, vapor-induced phase inversion (VIPS), and dry-wet phase inversion, is a versatile membrane preparation technology due to the mild operation conditions, easily controlling of membrane structure and performance [9,14]. Thus, poly(vinylidene fluoride) (PVDF) and PVDF-based copolymer got more attractions as compared to polytetrafluoroethylene (PTFE) and polypropylene (PP) [10,15,16], as they can dissolve in many common organic solvents.

NIPS process involves a heterogeneous casting solution including polymer, solvent, non-solvent, and/or additives, the phase inversion happened along with the exchange of solvent and non-solvent and the solidification of polymer-rich phase under specific ambient and operation conditions [14]. For semi-crystalline polymer like PVDF and its copolymers, the phase inversion was more complicated as both solid-liquid demixing (crystallization, vitrification, or gelation) and liquid-liquid demixing happened [17–19]. Membrane structure and performance was easily affected as the phase inversion process was vulnerable to various factors. Among them, polymer concentration and additive present tremendous influences due to their remarkable thermodynamic and kinetic effects. The effect of polymer concentration has been widely studied for PVDF, PVDF-HFP, PVDF-TFE hydrophobic membranes [19–22]. However, although PVDF-CTFE has been applied for membrane preparation in the recent decade by NIPS for water treatment or electrolyte separator [23–25], the effect of polymer concentration was hardly reported, especially for hydrophobic membrane preparation. LiCl is one of the most commonly used additives which had found widely applications during hydrophobic membrane preparation. The use of LiCl is characterized by the strong interaction between  $\text{Li}^+$  and solvent or polymer material. So the viscosity of casting solution increased significantly when LiCl was added, which may impede the exchange of solvent and non-solvent. The macrovoids was restricted and the crystalline structure showed in membrane surface and cross-section due to the lower phase inversion rate, i.e., the LiCl additive benefit the solid-liquid demixing process [19,25–27].

However, problems still exist for hydrophobic membrane in terms of additive residual, shrinkage, poor surface morphology and pore structure, which lead to poor performance and short membrane lifespan.

Even when a supporting material was applied to preventing membrane shrinkage, partial shrinkage still happened which tends to influence the pore structure [28]. The lower permeate flux, severe membrane wetting and fouling issue, and short lifespan impede the development of hydrophobic membrane application, especially for commercial expansion. Thus, membrane modification was a necessary prerequisite. Modification methods for hydrophobic membrane have been widely reported by state-of-art literatures, which mostly realized by doping, coating and grafting [29,30]. However, most of the modification method are complex and expensive. Post treatment by immersion with specific solution is a simple method which have been proved to improve membrane properties and performance [31–33]. The immersion of nascent membrane with a second solution especially liquid with low surface energy was proven to improve membrane structure and performance by preventing membrane shrinkage and further leaching out of additives or solvent. However, the effects of solution immersion on membrane morphology, pore structure, physico-chemical properties, and performance have been hardly reported. Meanwhile, as the PVDF hydrophobic membrane was commonly used under alkali or volatile organic solvent condition or cleaned by alkali, the stability is another most concerned issue. The effect of alkali immersion on membrane has also been studied to investigate the impact on membrane pore structure and their stability by simulating the condition of the membrane process under harsh condition [34–36]. Samsure et al. [37] also reported that the alkaline solution in mild condition had pore enlargement effect, which benefited the higher flux and improve the membrane properties.

In the present contribution, we prepared hydrophobic PVDF-CTFE flat-sheet membrane by NIPS (more precisely, dry-wet phase inversion) with the PVDF-CTFE/LiCl/DMAc/ $\text{H}_2\text{O}$  quaternary solution system. Effect of PVDF-CTFE concentration on membrane morphology, pore structure, thermal and crystalline properties, and hydrophobicity were carefully investigated. Ethanol and NaOH solutions were used as the second immersion bath to investigate their effects on membrane structure and properties, as well as the stability of membranes after post-treatment. The hydrophobic membrane performance was also assessed by a 6 h continuous DCMD operation to evaluate its potential in MD desalination.

## 2. Experimental

### 2.1. Materials

PVDF-CTFE copolymer (Solvay Solef® 32008,  $M_w = 280,000$ ) was obtained from Solvay Solexis for membrane preparation due to its hydrophobic nature. Dimethylacetamide (DMAc, >99.0%), purchased from Shanghai Jingwei Chemical Co., Ltd., was used as solvent. LiCl (AR, >97.0%), supplied by Tianjin Guangfu Research Institute of Fine Chemical Engineering, was applied as additive. 50% Ethanol (GR, >99.7%) and 5 g/L NaOH (AR, >96%) solutions were used as the second immersion bath to modify the membrane. 35% NaCl solution was used as the feed solution, deionized (DI) water was firstly used in the permeate side in DCMD test. Tap water was used as non-solvent in the coagulation bath.

### 2.2. Membrane preparation and post treatment

The PVDF-CTFE flat-sheet membranes were prepared by NIPS, which combined the solvent evaporation process and immersion phase inversion process induced by coagulation bath. At first, the copolymer was

Download English Version:

<https://daneshyari.com/en/article/4988009>

Download Persian Version:

<https://daneshyari.com/article/4988009>

[Daneshyari.com](https://daneshyari.com)