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Fluorographite modified PVDF membranes for seawater desalination via direct contact membrane distillation

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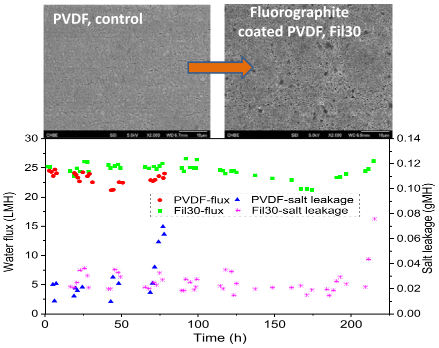
HIGHLIGHTS

- A fluorographite modified PVDF membrane was developed for membrane distillation.
- It exhibited high surface hydrophobicity and good anti-wetting properties.
- It showed better performance sustainability in continuous DCMD tests.
- It sustained >200 h using a 10 wt% NaCl solution as the feed.

GRAPHICAL ABSTRACT



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ABSTRACT

Membranes with high hydrophobicity are essential for membrane distillation of seawater desalination. A facile surface modification method has been developed to obtain hydrophobic PVDF membranes by depositing fluorographite particles on the membrane surface. The surface hydrophobicity increases with an increase in the number of fluorographite particles on the membrane surface. After the fluorographite modification, the resultant membranes exhibit good wetting resistance and better performance sustainability in direct contact membrane distillation (DCMD) tests using a highly concentrated (10 wt%) sodium chloride solution. The modified PVDF membrane can last about 200 h while the pristine PVDF membrane can only sustain about 70 h. A variety of techniques including field emission scanning electron microscopy (FESEM), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) were applied to examine the effects of the fluorographite modification on surface chemistry and morphology of the derived membranes. This work may provide a facile and useful approach for the hydrophobic modification of MD membranes for seawater desalination.

1. Introduction

Clean water supply plays a crucial role in multiple aspects of our life, such as public health, agricultural and industrial production. However, clean water scarcity has long been a serious concern for many countries. To solve this worldwide problem, people have been looking for effective and low-cost methods to decontaminate and disinfect water. In addition to recycle wastewater, searching for other water supply to effectively alleviate the stress of water shortage is urgently needed [1]. Since seawater constitutes >97% of the total water on earth, desalination of even a tiny fraction could have a huge impact on water supply. Among newly developed desalination technologies, membrane distillation (MD) has

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received increasing attention, especially after the rapid advances in MD membranes and solar energy [2–12]. In addition, researches have been carried out to integrate the MD process with other membrane processes for different applications [13–16].

MD is a mass transfer process driven by the vapor pressure difference across a hydrophobic porous membrane because of a temperature gradient. During MD, water in the hot feed solution evaporates, diffuses across the membrane, and then condenses at the permeate side. Comparing to conventional thermal and membrane separation processes, MD offers some unique advantages; namely, 1) theoretically 100% salt rejection, 2) low operating temperature, 3) low operating pressure, and 4) less sensitive to the feed concentration [3–12]. Direct contact membrane distillation (DCMD) is a type of MD configurations where an aqueous solution at a lower temperature in direct contact with the permeate side of the membranes. It is widely studied in literatures and laboratories because of its simplicity [17].

An efficient MD process must be able to continuously produce potable water with a consistently low conductivity. However, there is a risk of pore wetting and liquid penetration during the continuous MD operation and results in the loss of membrane selectivity. A series of studies showed that an increase in surface hydrophobicity of MD membranes can effectively increase the wetting resistance [18–21]. As such, membrane scientists have placed a special focus on the development of hydrophobic surface such as (1) creating a rough surface or (2) employing hydrophobic materials [22–28].

Li et al. increased the surface hydrophobicity by coating a variety of microporous plasmapolymerized silicon-fluoropolymer [29]. Kuo et al. fabricated novel polyvinylidene fluoride (PVDF) membranes with a contact angle as high as 130° by using alcohol as the coagulant to induce a high roughness and porous surface [30]. Ma et al. developed hydrophobic glass membranes which showed better performance than the polymeric membrane due to the formations of ordered arrays of spiked nanostructures [31]. Hydrophobic SiO_2 or TiO_2 nanoparticles have been coated on PVDF membrane surfaces to increase the hydrophobicity by creating a rough surface using various methods such as dip coating, filtration and spray-deposition [23–35]. Yan et al. added nano-$CaCO_3$ into the PVDF matrix to make a highly porous and rough surface with a high contact angle [36], while Lu et al. created a superhydrophobic surface by coating Teflon on the surface of PVDF hollow fiber membranes [27].

In this paper, for the first time, we employed fluorographite to modify the PVDF membrane surface for the DCMD process. Fluorographite, which is a highly hydrophobic microcrystalline powder, has received rising interests in the applications as lubricants and cathode materials in primary lithium batteries [37]. Fluorographite is a commercialized product by means of direct reaction between fluorine gas and graphite at a temperature between 300 and 600 °C [37]. The hydrophobicity grows with increasing fluorine content in fluorographite. By dispersing fluorographite particles on the PVDF membrane surface using the filtration method, we have successfully enhanced the surface hydrophobicity of PVDF membranes. The fluorographite particles irregularly adhere to the PVDF surface via hydrophobic-hydrophobic forces and results in the membrane surface with a greater roughness.

Table 1
Spinning conditions for the pristine PVDF hollow fiber membranes [27].

Dope composition (wt%)	PVDF/NMP/EG/PTFE = 10/75/12/3
External coagulant (v/v)	IPA/Water = 60/40
Spinneret dimension (mm)	Single bore
Dope fluid temperature (°c)	50
Bore fluid temperature (°c)	26 ± 1
External coagulant temperature (°c)	26 ± 1
Bore fluid composition	Water
Dope flow rate (ml/min)	4
Bore flow rate (ml/min)	4
Air gap (cm)	4
Take up speed (r/min)	6

Therefore, the objectives of this work were to study the fundamentals of this surface modification and explore the feasibility of using fluorographite modified PVDF membranes for seawater desalination via DCMD. In addition to examine the hierarchical structure and the rise of surface hydrophobicity after the modification, a variety of techniques such as field emission scanning electron microscopy (FESEM), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and contact angle measurements were employed to investigate the membrane properties before and after the modification. The membrane performance in DCMD was studied using both pure water and model seawater as feeds. The sustainability of the modified membrane in a high salinity feed solution containing 10 wt% NaCl was also evaluated for 200 h. This work may open up the exploration of using fluorographite for the development of next-generation hydrophobic MD membranes for seawater desalination.

2. Materials and methods

2.1. Materials

The polymer PVDF, Kynar HSV900, was kindly supplied by Arkema Inc. *N*-methyl-2-pyrrolidone (NMP, >99.5%), ethylene glycol (EG, > 99.5%), isopropanol (>99.5%) and sodium chloride (NaCl, 99.5%) were obtained from Merck. PTFE particles (<1 μm), fluorographite (>61 wt% F) and hexane (>99.5%) were purchased from Sigma-Aldrich. Deionized (DI) water was produced by a Milli-Q unit (MilliPore) with the resistivity of 18 MΩ cm.

2.2. Preparation of fluorographite coated PVDF membranes

The single-bore PVDF hollow fiber membranes were fabricated by a dry-jet wet-spinning process. Table 1 lists the dope formulation and spinning conditions because membranes spun from these conditions had a high water flux under DCMD tests [27]. After spinning, the fibers were soaked in water for 3 days to remove the residual solvents. Then the fibers were freeze-dried overnight for further modifications and tests. Before conducting the filtration coating of fluorographite particles, three pieces of hollow fiber membranes with an effective length of about 15 cm were assembled into a plastic module holder.

The coating solution was prepared by dissolving fluorographite powders in hexane with a concentration of 0.01 mg/ml. Hexane was employed as the solvent because (1) it dispersed fluorographite well and (2) it would not dissolve PVDF and change the membrane morphology. However, due to its hydrophobic nature, the fluorographite particle

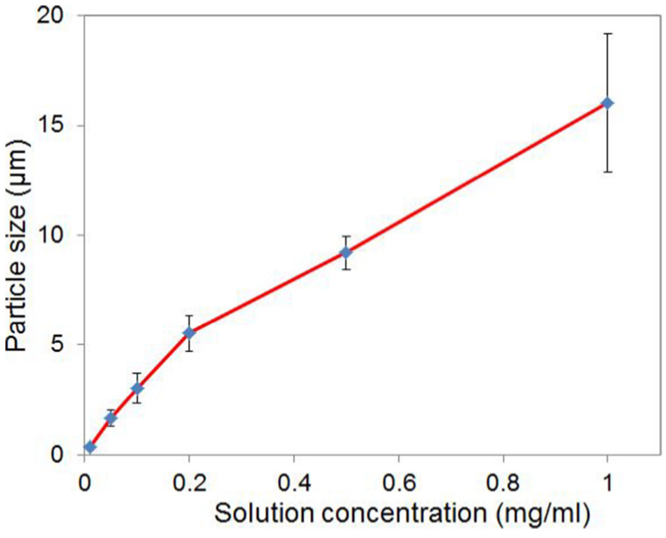

Fig. 1. Particle size of fluorographite in hexane with different concentrations.