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Comparison between dual-layer (superhydrophobic–hydrophobic) and single superhydrophobic layer electrospun membranes for heavy metal recovery by air-gap membrane distillation

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ABSTRACT

A novel approach to enhance membrane performance using electrospinning fabrication technique for recovery of heavy metals using air-gap membrane distillation is described. Accordingly, a comprehensive study was accomplished to fabricate a unique electrospun dual-layer membrane (ESD) with an upper superhydrophobic layer and hydrophobic electrospun support layer and compare with a superhydrophobic electrospun single layer membrane (ESS). Superhydrophobic alumina nanoparticles (Al_2O_3) were embedded in a low polymer concentration of polyvinylidene fluoride (PVDF) to produce superhydrophobic ESS and top layer of ESD using electrospinning technique, while a mat with different concentrations of PVDF were used as hydrophobic electrospun support layer. In this study, dual layer membranes were fabricated in two sets. In the first set, layer thickness was varied by changing the spinning volume of the top and support layer with maintain total spinning volume, while in the second set the fibre diameter of the support layer was varied by changing the polymer concentration. Moreover, the electrospun membranes were characterized in terms of membrane performance such as: permeate flux, heavy metal rejection and energy consumption; wettability performance such as liquid entry pressure (LEP), and water contact angle (WCA); membrane structure such as mean with maximum pore size and porosity; membrane integrity such as mechanical and thermal integrity. The heavy metal rejection was > 99% for all single and dual layer membranes when filtering artificial wastewater (Pb, Cd, Cr, Cu, Ni). When compared with single layer electrospun membrane made from spinning 16 ml PVDF, dual layer membrane made from the same spinning volume exhibited some improvement, such as higher permeate flux above 23 l/m^2·h (LMH) when filtering 2500 ppm concentration heavy metal feed water. Additionally, both sets of dual layer membrane demonstrated better mechanical performance and slight reduction of LEP compared with single layer electrospun membrane.

1. Introduction

Industrial wastewater contaminated with toxic materials, such as heavy metals, is a major environmental issue. Heavy metals, such as lead, cadmium, zinc, copper, and nickel, are highly poisonous, especially when discharged in high concentration to the water body. These heavy metals are discharged from several industrial sectors in significant concentrations, such as mining, electroplating, printing, wood processing, pulp and paper, petrochemicals, steel and battery industries and many more [1,2]. According to the U.S. Environmental Protection Agency (USEPA), the maximum level of heavy metals which can be discharged after adequate treatment to the surface water is 0.006, 0.01, 0.25, 0.8, 0.2 mg/l for lead, cadmium, copper, zinc, and nickel respectively [3]. Therefore, many attempts have been made to remove or recover these materials from discharged wastewater, for instance by absorption, chemical precipitation, ion exchange, coagulation with flocculation, and electrodialysis [1,4]. In addition to these treatment methods, membrane technology is a promising alternative. Membrane distillation has many advantages for heavy metal removal over other membrane techniques, including reverse osmosis (RO) or nanofiltration (NF), such as low operation pressure, high rejection percentage for non-volatile components, high water recovery, small footprint and lower membrane fouling [5,6]. Furthermore, many studies have successfully tested MD for removal of inorganic material, such as heavy metals

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[7–15]. Hydrophobic membranes, which are crucial in MD applications, can be used to prevent liquid water from crossing the membrane while encouraging the vapour to transfer from a hot feed stream to a cold permeate stream, can be found in four different configurations. These are: direct contact membrane distillation (DCMD), in which both the feed and the permeate side are in direct contact with the membrane; air gap membrane distillation (AGMD), which uses an air gap between the permeate side and the membrane; vacuum membrane distillation (VMD) and sweep gas membrane distillation (SGMD) which both use an external condenser to condensate the vapour flux by using vacuum pump and inert gas, respectively [16]. AGMD demonstrates high thermal efficiency and reduction of heat lost by conduction due to the presence of the air gap between the membrane and condensate plate [16].

Key factors which can hamper commercialization of membrane distillation (MD) is membrane wettability and low permeate flux, which are related to the membrane fabrication technique and surface chemistry. The most common methods to fabricate commercial membranes are phase inversion, stretching, and thermally induced phase separation, with the membranes commonly made from hydrophobic materials such as polytetrafluoroethylene (PTFE), polypropylene (PP), and polyvinylidene fluoride (PVDF) [5]. However, these methods do not fulfil the requirements of the membranes used in MD applications, such as high porosity, narrow pore size distribution, high surface area, low surface energy, high surface roughness and high LEP. Therefore, the electrospinning technique has gained considerable attention recently as it can be used as an alternative method to fabricate hydrophobic membranes and enhance MD membrane performance. This technique uses a high voltage between a spinneret and a static or movable collector to fabricate a non-woven mat with nanofibrous structure which can be used as a membrane for microfiltration [17]. The electrospun membrane can enhance membrane flux in MD applications due to high porosity, adjustable pore size, high surface area-to-volume ratio and high hydrophobicity due to the surface roughness compared with other fabrication methods [18].

Several electrospun membrane configurations (single, dual and triple layers) have been reported in the literature to improve membrane performance by controlling heat and mass transfer resistance for MD application. Apart from single layer, dual layer membrane has gained much attention recently to enhance membrane productivity. Electrospun dual layer membranes for DCMD application have been fabricated from several different polymer layers such as PVDF/PES [19], polyvinylidene fluoride–polytetrafluoroethylene (PVDF-PTFE)/polyacrylonitrile (PAN) [20], PVDF-SiO_2/PVDF [21], PVDF-PTFE/PVDF-PTFE [22]. However, in terms of AGMD, very few studies have been reported using dual and triple layer membrane configurations, while single layer membranes dominate the published research. Single layer electrospun hydrophobic membranes have been mainly fabricated by using PVDF [23] and polyvinylidene fluoride–polytetrafluoroethylene (PVDF-PTFE) [24]. On the other hand, single composite superhydrophobic layer membrane have been fabricated using embedded functionalized nanoparticles (NPs) in a polymer dope solution, such as PVDF-PTFE-CNT [25], PVDF-PTFE-GO [26], PVDF-Al_2O_3 [14]. In terms of dual layer membranes, the performance of the membrane is governed by the top layer through control of hydrophobicity, LEP and porosity, while the supporting layer provides mechanical support as well as reducing heat loss through conduction. Woo et al. [27] investigated the effects of three different supporting layers made from PVA, Nylon-6, and PAN with a top hydrophobic layer fabricated from PVDF-PTFE on membrane performance and mechanical properties using AGMD. Triple layers consisting of a top thin layer of electrospun PVDF deposited on a micro-porous PVDF layer fabricated by phase inversion on a support layer made from polyethylene terephthalate was reported by Prince et al. for AGMD application [28].

In the present study, comparison between a single layer superhydrophobic and a dual layer (superhydrophobic–hydrophobic) electrospun membranes were accomplished in terms of membrane performance (flux and rejection), membrane characteristics (porosity, pore size, LEP), membrane integrity (mechanical and thermal properties) and energy consumption for AGMD applications. For single layer membranes, membrane thickness was varied by changing the electrospinning volume over a constant collected area, while the dual-layer membrane was fabricated in two sets. For the first set, top and bottom layer thickness were altered by changing the spinning volume while maintain the total spinning volume at 16 ml. The second set, fibre diameter of the support layer (4 ml spinning volume) was altered by varying the dope polymer concentration while the top layer maintained the same polymer concentration and spinning volume (16 ml). To our knowledge, this is the first attempt to optimize dual-layer membrane in terms of membrane thickness made from superhydrophobic electrospun top layer for AGMD application.

2. Experimental

2.1. Materials

Polyvinylidene fluoride pellets (Mw = 275,000 g/mol), Dimethylformamide (DMF), Acetone (Ac), cationic surfactant hexadecyl trimethyl ammonium bromide (HTAB), ethanol, isopropanol, toluene, Alumina (Al_2O_3) NPs (Mw = 101.96 g/mol, particle size = 13 nm) were supplied by Sigma-Aldrich. Lead (II) nitrate, nickel nitrate hexahydrate, copper nitrate trihydrate, cadmium nitrate tetrahydrate and zinc nitrate hexahydrate were purchased from Fisher Scientific. Isostearyl acids were provided by Nissan Chemical Industries. A Milli-Q plus system (Millipore, USA) was used to provide DI water with high quality to prepare synthetic wastewater. All chemicals were used without further purification.

2.2. Preparation of dope solution

Polymer solution with three different polymer concentration (15, 17.5, 20 wt%) was used to fabricate base layer for dual layer electrospun membrane in which pre-weighed PVDF pellets were dissolved in a mixture of DMF and acetone with a weight ratio 3:2 (60/40 wt%). A small amount of cationic surfactant (HTAB) was added to enhance electro-spin ability by reducing the surface tension of the dope solution, as shown in Table 1. The dope solution was heated to 50 °C for 12 h with a stirring speed of 200 rpm using an incubator shaker (Innova 44R, New Jersey, USA). Next, a vacuum oven (Salvis, Swissland) was used for 30 min to remove the bubbles after cooling the polymer solution to room temperature. In terms of superhydrophobic layer for ESS and top layer of ESD, superhydrophobic Al_2O_3 NPs were sonicated first for

Table 1
Polymer dope compositions and electrospinning parameters used in the present study.

Polymer solution code	PVDF (g)	DMF (g)	Acetone (g)	HTAB (g)	Al_2O_3 NP (g)	Voltage (Kv)	Needle (1 &4), each (ml/h)	Needles (2&3), each (ml/h)	Viscosity (cp)
11 wt%	2.473	12	8	0.01	0.494	17.0 ± 1	0.3 ± 0.05	0.15 ± 0.02	91 ± 0.4
15 wt%	3.532	12	8	0.01	–	15.0 ± 1	0.35 ± 0.03	0.20 ± 0.02	179 ± 0.7
17.5 wt%	4.245	12	8	0.01	–	14.3 ± 0.2	0.50 ± 0.07	0.25 ± 0.04	296 ± 0.5
20 wt%	5.003	12	8	0.01	–	14.2 ± 0.3	0.70 ± 0.11	0.30 ± 0.07	540 ± 0.9