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Effect of OH-treatment of PDMS on rejection in hybrid nanofiltration membranes for desalination

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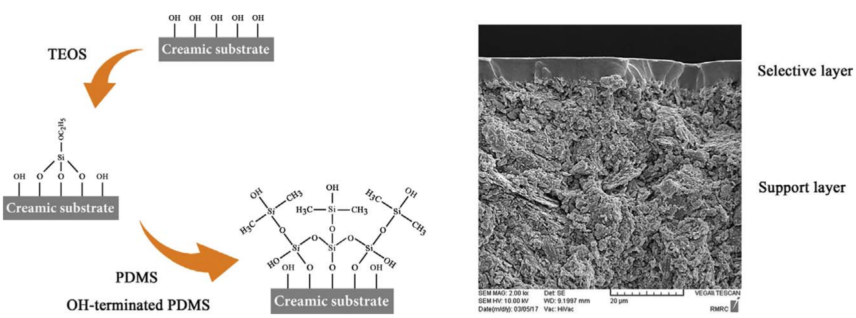
GRAPHICAL ABSTRACT



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ABSTRACT

In this study, Alumina-PDMS nanofiltration membranes are fabricated and the effect of PDMS OH-treatment and molecular weight is investigated on salt rejection. Pressing is used to prepare the alumina substrate and PDMS layers with various M_ws are coated on the substrate through dip-coating. Also, characterization is performed using FE-SEM, X-ray diffraction, ATR-FTIR and MWCO techniques. Results show that higher M_w PDMS shows enhanced efficiency due to better coverage on the substrate. Membrane rejection with the 5000 cSt PDMS plus 750 cSt OH-terminated PDMS was obtained as 75%, 67% and 35% for Na_2SO_4, $MgSO_4$ and NaCl, respectively. The average pore size is also calculated as~ 1.75 nm using MWCO technique. Based on the results, PDMS can be proposed as a proper option for development in desalination processes.

1. Introduction

Desalination is provoking interest due to the increasing depletion of sweet water resources using membrane-based alternatives. However, shortcomings regarding cost, low performance at high concentrations, swelling, fouling etc., have supplied the driving force for endeavors for the selection of new membrane materials. Low thermal, mechanical and chemical resistance of polymeric membranes has led to hybridization strategy in order to combine the advantages of ceramics and polymers.

Only around 0.5% of the overall global water is available as fresh, while seawater accounts for~ 97%. Also, 41% of the world population dwells in parched areas leading to fresh water supply rising as a worldwide problem. As a result, seawater desalination is an important alternative as a secure freshwater source [1]. Membrane-based desalination is also a technology with low energy requirements and operating costs compared with evaporation and distillation [2]. Current research activities are mainly focused on the development of advanced membranes and improvement of existing membrane processes through design alteration and integration [3]. Most membranes are composed of multilayers with the active top-layer playing the main separation role while others acting as mechanical support [4]. Among various pressure-driven filtration processes, the performance of nanofiltration (NF) is

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between reverse osmosis and ultrafiltration with higher water flux, lower operation cost and acceptable rejection of salt or low M_w organic compounds (< 1000 $gmol^{-1}$) [5–7].

Membrane materials are categorized into organic and inorganic [8]. Polymers are the most prevalent materials in membrane fabrication due to thermal stability over a wide range of temperatures and mechanical stability over a wide range of PH and high mechanical strength. PVDF, PAN, PES and PA are among the polymers for membrane fabrication [9].

Ceramics are thermally and chemically more stable with higher mechanical strength and structural stability fitting them for harsh environments [10]. However, less commercial attraction is experienced due to fragility and relative high expenses [11]. Alumina [12], silica [13], titania [11], zirconia [14] and nano-clay [15] are considered as the main materials in ceramic membrane fabrication. Dry and hot isostatics pressing [12,16], extrusion [17], gel-casting [18] and slip casting [19] are implemented for fabrication of porous ceramic membranes, while pore structure is mainly controlled by the variation of sintering temperature and heating rate. For example, Wey et al. (2014) showed that the pore size of α-Al_2O_3 supports sintered at various temperatures (1100 °C–1500 °C) is in the 5–11 nm range. Physical properties, such as pore size distribution (PSD), total pore volume and surface roughness of α-Al_2O_3 substrates, were altered by sintering temperature. The pore structure was squeezed and surface roughness enhanced resulting in a dense pore structure at 1500 °C [20].

Hybrid membranes are composed of thin dense top-layers supported by porous substrates enabling flux enhancement while maintaining selectivity [21], helping in the development of improved membranes, i.e. chemical and mechanical stability, reduced swelling and enhanced solvent affinity [8]. Cuiming et al. (2003) prepared hybrid membranes via sol-gel with average pore diameters ranging from hundreds to several nanometers depending on the coating period, sol composition and precursor concentration [22].

Polysiloxane-based polymers, like cross-linked polydimethylsiloxane (PDMS), are a very versatile group with a variety of applications due to unique properties including high free volume, nontoxic nature, thermal-chemical stability and solubility in non-polar solvents [8,23]. Cross-linked PDMS is flexible due to Si-O-Si bonds in the main chain. Several attempts are made to use PDMS in various membrane applications. For examples, Pinheiro et al. (2014) developed a new solvent resistant NF (SRNF) membrane by grafting PDMS into the 5 nm pores of an alumina substrate. A two-step synthesis route was applied grafting a linking agent on the ceramic membrane via vapor-phase or solution-phase method followed by grafting an epoxy-terminated PDMS [8]. Hillerstrom et al. (2008) prepared a hydrophilic PDMS surface by synthesis of an interpenetrating polymer network during a two-step process. PDMS was loaded with a cross-linker and initiator, then being submerged into a solution of hydrophilic monomers followed by UV-polymerization [23]. Wei et al. (2011) used three different PDMS M_ws to prepare PDMS/ceramic composite membranes for ethanol-water separation by pervaporation, improving membrane stability especially for high M_w PDMS [24]. Tanardi et al. (2014) grafted meso-porous alumina with monovinyl-terminated PDMS, using MPTES as a linking agent for NF of organic solvents, resulting in the reduction of toluene permeability upon grafting [25].

Hydrophobicity may have hindered the application of PDMS in desalination but just as other polymers, attempts can be performed toward hydrophilization. Attempts are made to improve the permeability of PA membranes by incorporating hydrophilic nanoparticles like zeolite [26]. Identical processes can be applied to PDMS. Functionalization is another strategy which is used in this study using OH treatment.

Various techniques are developed to fabricate thin layers upon membrane substrates. Electro-spinning requires high voltages to melt the coating material [27]. Spin-coating can prepare uniform coatings with different thicknesses by changing the spinning speed and time, while the substrate size is restricted to the limitations of the device [28]. Spray-coating and dip-coating provide simplicity, scalability, speed, low cost and compatibility with many substrates [29]. Dip-coating is a useful preparation technique widely used in ceramic membrane preparation [30] with a high efficiency for industrial applications for the preparation of highly uniform coatings [29]. Various dip-coating strategies have been employed to create polymer-based

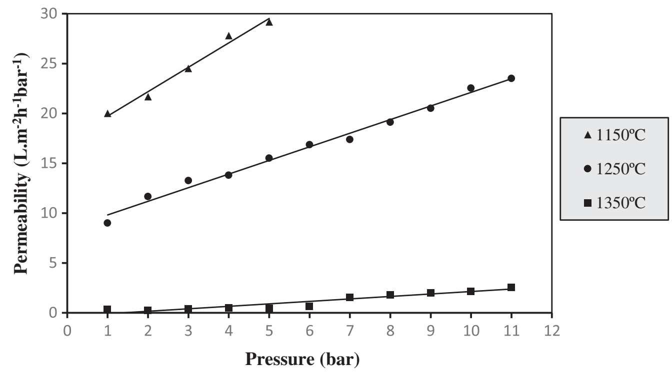

Fig. 1. The substrate permeability prepared at various sintering temperatures.

Table 1
The results of three substrates prepared at various sintering temperatures.

Substrate	Porosity (%)	Pore size (µm)
1150 °C	43	0.32
1250 °C	34	0.38
1350 °C	22	0.45

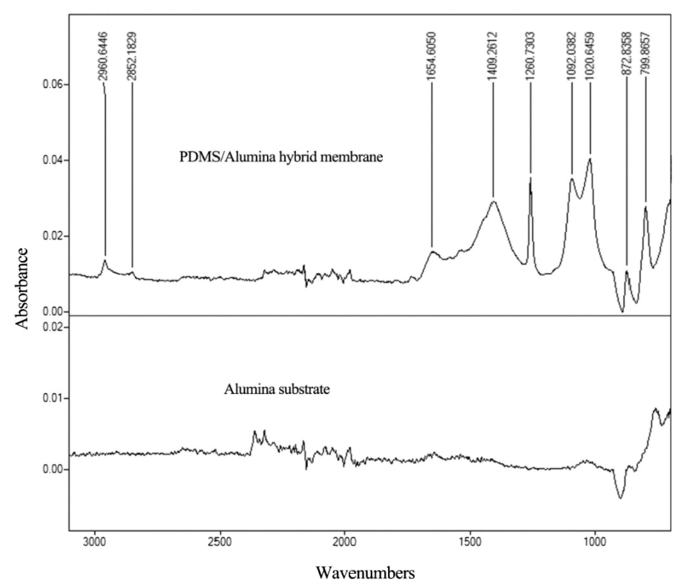

Fig. 2. The ATR-FTIR of substrate and PDMS/alumina hybrid membrane.

Table 2
Contact angle of hybrid membranes prepared by dip-coating of PDMS solution with three different viscosities.

Membrane	PDMS viscosity (cSt)	Dipping time (s)	Withdrawal speed (mm/s)	Contact Angel (°)
P1	150	120	5	92 ± 3
P10	1500	120	5	73 ± 2
P20	5000	120	5	51 ± 2
P30	5000 + 750	120	5	102 ± 3