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PVDF/magnetite blend membranes for enhanced flux and salt rejection in membrane distillation

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ABSTRACT

This study reports on the enhancement of direct contact membrane distillation (DCMD) performance by incorporating magnetite nanoparticles (NP) in polyvinylidene fluoride (PVDF) membranes to render the membrane bulk hydrophilic while maintaining a hydrophobic top surface. Hansen solubility parameters (HSP) were first calculated to assess the affinity/compatibility of NP with the polymer, dope solution and aqueous feed. Extensive characterizations were done to elucidate the structural and physiochemical properties of the blend membranes. Energy dispersive spectrometry (EDS) analyses confirmed the uniform distribution of NP within the membrane matrix. Contact angle values showed that the NP did not compromise the hydrophobicity of the membrane top layer. The blend membrane had a 92% higher water uptake value, compared to the pristine sample, indicating the high hydrophilicity of the membrane bulk. Blend membrane also showed higher (ca. 36%) DCMD flux, due to their hydrophilic sub-layer, without compromising the salt rejection. Leaching tests were conducted using both water and concentrated acid to confirm the presence of nanoparticles and to demonstrate the membrane stability in aqueous medium.

1. Introduction

Membrane distillation (MD) is a hybrid of thermal and membrane processes with promising future in the treatment of challenging waters such as RO brine [1,2]. Although MD has several promising aspects, its commercialization is hindered due to low flux, susceptibility to membrane wetting and lack of membranes tailored for MD [3–5]. Polymers such as polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF) and polypropylene (PP) are widely used for fabricating MD membranes [3]. Due to their hydrophobicity, membranes made from these polymers usually have high mass transfer resistance, resulting in hindered MD flux [6]. Hydrophilic membranes, on the other hand, have less mass transfer resistance but they endure pore wetting and hence cannot be directly used in MD [6].

MD membranes usually contain a highly porous sub-layer and a microporous hydrophobic top layer [7]. In order to achieve both wetting prevention and higher flux, several attempts were made to fabricate composite hydrophobic/hydrophilic membranes [7–9]. In such membranes, the top surfaces of bulk hydrophilic membranes are usually rendered hydrophobic through processes such as surface functionalization by fluorine containing radicals, coating and grafting [6–10]. For instance, the top layers of hydrophilic cellulose acetate and cellulose nitrate membranes were made hydrophobic by employing radiation graft polymerization and plasma polymerization, making them usable in MD studies [11]. Nevertheless, the additional modification steps and the risk of membrane degradation or pore size reduction reduce the appeal of this approach. Khayet and Matsuura introduced the concept of one-step fabrication of hydrophobic–hydrophilic membranes by blending fluorinated surface modifying macromolecule (SMM) into polyetherimide (PEI) flat sheet membranes [12,13]. They found that the surface of these membranes was enriched with the fluorine groups of the SMM and hence showed higher hydrophobicity. In other works, hydrophobic PVDF has been incorporated with hydrophilic additives such as polyvinyl pyrrolidone (PVP), CuO and polyethylene glycol (PEG) in order to make composite hydrophobic/hydrophilic membranes [14–20]. Su et al. [21] also investigated the influence of thermal conductivity of the hydrophilic sub-layer on the DCMD flux and found that vapor flux increased significantly with the increase in thermal conductivity of the inner layer of hollow fiber membranes. Qtaishat et al. [22] presented a mathematical

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model to validate the hydrophobic/hydrophilic membrane concept and found that DCMD flux increased with the increase in hydrophilic sub-layer thickness, porosity of both layers, and with the increase in sub-layer thermal conductivity.

Magnetite (Fe_3O_4, containing both Fe^{2+} and Fe^{3+}) has been incorporated in polymeric membranes such as PVDF, polysulfone (PS) and polyethersulfone (PES) to improve microstructure [23–26], reduce membrane fouling [27–30] and to fabricate magnetically responsive/smart membranes [31]. Such membranes were also used in the removal of toxic metals (such as Cu(II) and other substances) from wastewater [32,33], sorption of oil from wastewater [34], drug release [35] and protein [36,37] and polysaccharide separations [38]. However, to the best of our knowledge, no study has been conducted so far on the incorporation of iron oxide nanoparticles in PVDF membranes with the aim of improving their MD performance.

This study reports on the enhancement of DCMD performance by incorporating iron (II,III) oxide nanoparticles (NP) in PVDF membranes to render the bulk membrane hydrophilic while keeping the top surface hydrophobic. We also investigated the compatibility between the polymer (PVDF), solvent (dimethyl acetamide, DMAc) and the additive (iron oxide nanoparticles) within the membrane formation system, using the Hansen solubility parameters (HSP) method [39]. This approach was not widely explored in past studies involving mixed matrix membranes.

2. Materials and methods

2.1. Materials

PVDF (KYNAR HSV900), provided by Arkema (France), was utilized as the main membrane polymer and *N*, *N*-Dimethylacetamide (DMAc) (Purity ≥99.5%) was used as the organic solvent to prepare the PVDF dope. The following chemicals, supplied by Sigma Aldrich Chemical Co. (USA), were used in synthesizing the nanoparticles: iron (II) chloride tetrahydrate ($FeCl_2.4H_2O$), iron (III) chloride hexahydrate ($FeCl_3.6H_2O$), hydrochloric acid (HCl) and ammonia (NH_3). Deionized (DI) water (conductivity: 54 µS/cm) was used as the coagulation bath during phase inversion and in the preparation of aqueous solutions. Non-woven support, Novatexx 2471 (Freudenberg-Filter, Germany) was used as the support on which the membranes were cast.

2.2. Calculation of HSP parameters

The Hansen solubility parameters (HSP) theory was implemented to assess the compatibility of iron oxide NP with PVDF, various solvents and water. The Bagley's approach, which is the most suitable for polymeric materials with inorganic additives, was employed for determining the HSP [40–43]. As per this method, the affinity between a polymer material and solvent can be determined by calculating the distance parameter, δ_{ps}, as given in Eq.1.

$$\delta_{ps} = [(\delta_{p,D} + \delta_{s,D})^2 + (\delta_{p,P} + \delta_{s,P})^2 + (\delta_{p,H} + \delta_{s,H})^2]^{0.5} \quad (1)$$

where: δ_{ps} is a distance parameter between a polymer (p) and solvent (s) expressed in $(MPa)^{0.5}$, δ_D, δ_P and δ_H are Hansen solubility parameters describing dispersion (D), polar (P) and hydrogen bonding (H) interactions, respectively. A smaller distance parameter (δ_{ps}) value indicates a stronger interaction between the solvent and the polymer [39]. This interaction can be presented in a three-dimensional coordinate system with axes δ_D, δ_P and δ_H. In this system, the solute (PVDF) is at the center of a sphere and the radius of the sphere (R_o) represents the maximum difference in affinity acceptable for a complete dissolution to occur. Values of R_o parameters for polymer, solvent or additives were obtained from previous literature [39,44]. The relative energy difference (RED) number, which is a composite affinity parameter, has been defined as per Eqs. (2) and (3) below:

$$R_a{}^2 = 4(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2 \quad (2)$$

$$RED = R_a/R_0 \quad (3)$$

Subscripts 1 and 2 refer to the solute and solvent, respectively. Good solvents will have RED values below 1.0. On the other hand, poor solvents will show higher RED values because R_a will be higher than R_0. In this work, HSP were calculated to determine the compatibility of iron NP with the polymer and solvent system. Detailed procedure can be found elsewhere [40].

2.3. Preparation of iron oxide nanoparticles

The NP suspension was prepared using the method described by Berger et al. [45]. 1.0 mL of $FeCl_2$ solution (2.0 M $FeCl_2$ in 2 M HCl) and 4.0 mL of $FeCl_3$ solution (1.0 M $FeCl_3$ in 2 M HCl) were mixed in a conical flask and stirred vigorously. The acidic condition prevents the formation of iron hydroxides. 50 mL of aqueous 0.7 M NH_3 solution was then added dropwise while stirring the mixture vigorously. Magnetite, a brown/black precipitate was formed as the reaction proceeded. The resulting solution was settled and the supernatant liquid was removed. The particles were then rinsed and centrifuged in DI water. Subsequently, the nanoparticles were rinsed and centrifuged in DMAc (three times) to remove any traces of water and finally suspended in DMAc for further use. Sonication of the DMAc suspension was carried out prior to the membrane synthesis in order to ensure homogeneity of the nanoparticle distribution.

2.4. Membrane synthesis

Typically, PVDF microfiltration (MF) membranes are fabricated using dope solutions containing 10–12 wt% PVDF [46,47]. However, our initial attempts in this work showed that dope solutions with NP containing higher than 10 wt% PVDF were very thick and challenging for casting the membranes. Hence, 10 wt% PVDF dopes were used in this study. Two casting solutions were prepared: (i) 10 wt% PVDF in DMAc without iron NP, as the reference membrane, henceforth labeled 'PVDF' and (ii) 10 wt% PVDF and 1 wt% NP in DMAc for the blend membrane, henceforth labeled 'PVDF-NP'. Each dope mixture was stirred vigorously using a magnetic stirrer until a homogenous mixture was formed, followed by sonication (1 h), degassing (1 h), and resting for 24 h. The non-solvent induced phase separation (NIPS) method was employed in membrane fabrication. Flat sheet membranes were cast at a thickness of 500 µm using a casting knife (model: 3580, elcometer®, United Kingdom) on a non-woven support (NWS). Novatexx 2471 was used as the NWS as per the recommendations of a previous study [46]. The cast films were placed in DI water at room temperature for half an hour, followed by rinsing with DI water to remove any traces of DMAc, then drying at room temperature.

2.5. Membrane characterization

Microstructural images (both the top surface and cross sectional) of the membranes were obtained using scanning electron microscopy (SEM) (FEI Nova NanoSEM 650, USA). Membrane samples were fixed on a copper tape. Samples for cross-section images were prepared by initially immersing the membrane sample in isopropanol (99.5%) for 5 min and subsequently freezing the membrane in liquid nitrogen. A section cut was made while the membrane sample was frozen. During this process, the NWS material stayed intact while the polymer membrane layer was easily cut and peeled off. Thus, we imaged the membrane cross section while preserving its structure details intact. An energy dispersive spectrometer (EDS, Nova Nano, FEI, USA) was used in elemental analysis of the membranes using line scan and spot analysis. Both the surface and the cross-section samples were sputtered with a gold-palladium layer of 100 Å thickness, prior to SEM and EDS analyses, to impart electric conductivity and to avoid charging effect