Fabrication, Characterization of Modified Polyvinylpyrrolidone/Polysulfone Blend Membrane for Ultrafiltration Application

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Abstract

The present study in the current work novel derivative of water insoluble polyvinyl pyrrolidone (PVP) polymer was synthesized and characterized by NMR and FTIR analysis. New derivative of hydrophilic PVP polymer was synthesized by condensation of hydrazine hydrate followed by hydrazone formation using polar aldehyde (2-hydroxybenzaldehyde and 2-nitrobenzaldehyde). The modified polysulfone (PSf) membranes were fabricated by blending with different concentration of PVP derivative (PVPD) via immersion precipitation method. The morphological change and surface topological properties of PSf/PVPD blend membranes were studied by SEM and AFM. All the prepared membranes exhibited symmetric morphological structure with improved macrovoids in sublayer. AFM analysis result showed that the blending of PVPD in to PSf membrane has synergetic effect on the surface properties and morphological features. Addition of PVPD into the casting solution showed decreasing trend of surface roughness compared to pristine PSf membrane. The membrane with 30 wt.% of PVPD-(hydroxy functional group) membrane showed decrease in mean roughness around 48 percentage with the maximum feature heights (Rmax) of 67.3 nm compared to other membranes. The ultrafiltration performance study of blend membranes was investigated using Sterlitech dead end, cross flow filtration units and Arabian Gulf seawater, reverse osmosis brine was used as feed. In terms of water flux, the membrane with 30 wt.% PVPD composition achieved steady water flux of 172 L/m^{2}h and 138 L/m^{2}h against Arabian Gulf seawater and reverse osmosis brine respectively. From our study it was concluded that, PVPD has strong impact on membrane morphology, hydrophilicity, permeation and antifouling nature of resultant membrane.

Keywords: Ultrafiltration, polyvinyl pyrrolidone derivative, water flux, antifouling.

1. Introduction

In the recent year's membrane technology is well known technology for seawater desalination and received considerable attention due to their low energy consumption compared with thermal desalinations which are multi-stage flash distillation (MSF), multiple-effect distillation (MED) (Ahmadvand et al. 2019; Ghalavand et al, 2014). In

membrane and thermal desalination process microfiltration, ultrafiltration and nanofiltration membranes are used as pre-treatment membranes to reduce the fouling in membrane desalination and scaling in thermal desalination (Hashlamon et al. 2015; Valavala et al. 2011). Pre-treatment membrane performance is depending on pore size, hydrophilicity, surface and cross-sectional morphology. Hydrophilicity and surface topological features of the membranes play a major role to show good antifouling behaviour of membranes (Badruzzaman et al. 2019). The literature study has proved that the incorporation of hydrophilic polymer additive enhances the hydrophilicity, pore size and morphology of membranes (Sun et al. 2013; Jung 2004; Liang et al. 2016). In chemical and food industries polyvinyl pyrrolidone (PVP) was used as additive, binder and as encapsulating agent due to its nontoxic behaviour. PVP is highly water-soluble polymer and it was used in the membrane technology as a pore forming agent in hydrophilic membrane fabrication process by diffusion induced phase separation (DIPS) technique (Liu et al. 2013; Wang eta al. 2012; Jiang et al. 2013). Due high-water solubility behaviour of PVP polymer, this polymer will leach out during the membrane fabrication process. Therefore, PVP polymer use as a blending polymer with PSf or any other polymer is difficult in the membrane fabrication process. The water solubility of PVP polymer can be easily varied by chemical modification method. In our study, water insoluble PVP polymer was designed and synthesized. The structure of PVP derivative (PVPD) was characterized using advanced analytical technique and fabricated blend membrane with PSf for the ultrafiltration application.

2. Material and Methods

Polyvinylpyrrolidone (PVP: 40000 Da) and polysulfone (PSf: 35,000 Da) were purchased from Sigma Aldrich Co, Germany. The solvent N-methyl pyrrolidone (NMP), pore former poly(ethylene glycol) (PEG) 400, hydrazine hydrate and 2-nitro benzaldehyde were obtained from Merck- Germany. The feed seawater and RO brine was collected from Desalination Research Plant (DRP) Doha, Kuwait, the total dissolved solids (TDS) of seawater feed is 45,377 ppm and rejected brine is 54,900 ppm.

The structure of PVP derivative was confirmed by FTIR (ALPHA-FT-IR: Bruker Company, Germany) and NMR (Bruker 400 MHz; solvent: DMSO-d_6). The blend membrane of PVPD and PSf was fabricated using DIPS method. The fabricated membrane morphology was analysed using EVO MA18 with Oxford EDS(X-act) instrument and topology features were analyzed using Concept Scientific Instrument (Nano-Observer), France. The ultrafiltration tests were conducted using Sterlitech dead-end and cross-flow filtration unit. The water flux and antifouling performance of the membranes were calculated using following equations:

$$J_w = \frac{Q}{\Delta t\, A} \qquad (1)$$

Where $J_w$is expressed in L/m^{2}h and 'Q' is the amount of water collected for Δt (h) time duration using a membrane of area 'A' (m^2).

$$FRR(\%) = \left(\frac{J_{w2}}{J_{w1}}\right) X\ 100 \qquad (2)$$

Where FRR is flux recovery ratio, J_{w1} (L/m^{2}h) is the water flux of membrane without Bovine Serum Albumin (BSA) in feed water and J_{w2} (L/m^{2}h) is water flux of membrane after BSA filtration and membrane washing.

The quantitative and qualitative analysis of feed and reject from the tests were analysed using plasma optical emission spectrometry (ICP-OES, iCAP 6000, Thermo Scientific, USA), conductivity meter (ORION STARA222), spectrophotometer (LANGE DR 2800), and pH meter (ORION STAR A221) in standard analytical conditions.

3. Case Study

The PVPD polymer was synthesized in two step process. First PVP polymer was converted into its hydrazine derivative (PVP-NHNH$_2$) using hydrazine hydrate in ethanol solvent. PVP-hydrazine derivative was isolated then in second step, hydrazine derivative was converted into hydrazone by treating 2-nitrobenzaldehyde. The schematic representation of chemical reactions was shown in Fig 1.

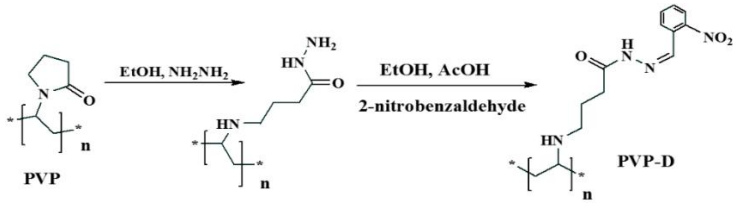

Fig 1. The schematic representation of the synthesis of PVP-D polymer.

The final PVPD polymer formation was confirmed by identifying FTIR spectral peaks and chemical shift values from the NMR spectrum. The disappearance of FTIR peak at 3610 cm^{-1}, 3639 cm^{-1} (Due to NH-NH$_2$ in hydrazine derivative) and shift of the FTIR peak from 1677 cm^{-1} to 1521 cm^{-1} shows the formation of hydrazine PVP derivative. ^{1}HNMR aromatic protons appeared at δ 7.76 to δ 8.21 corresponds to four aromatic protons of 2-nitrobenzaldhyde, δ 8.99 singlet C-NH (amide) Peak and aliphatic protons at δ 1.38 to δ 3.80 further conforms the formation of hydrazone in the polymer backbone (Vijesh et al. 2018).

All the newly fabricated membranes showed asymmetric membrane structure which is comprised by a dense layer at the top followed by a porous sublayer. The increase of PVPD polymer concentration in blend membranes increased the finger-like pores (or macrovoid) in the sub layer as shown in the Fig 2. This may be due to hydrophilic nature of the PVPD there is possibility for the formation of hydrogen bonds with solvent (NMP) molecule which resulted in delayed demixing in the coagulation bath.

From the AFM results it was found that, with addition of PVPD into the casting solution showed decreasing trend of surface roughness compared to PVPD 01 membrane as shown in Fig 2. This observation is particularly important since

smoother surface shows less adsorption of organic molecules to reduce the organic fouling.

The ultrafiltration experiments were conducted for all newly fabricated blend membranes using dead-end and crossflow filtration unit. The water flux results show that, the water flux was in the order of PVPD 04 > PVPD 03 > PVPD 02 > PVPD 01 for seawater and RO brine feed at 3 bar pressure as shown in the Fig. 3. The increase of water flux with increase of PVPD concentration in the blend membrane may be due to hydrophilic property of PVPD polymer. This may be due to the presence of $–NO_2$, -NH and -OH polar functional groups in the PVP polymer backbone. The PSf with 30% PVPD polymer blend membrane showed steady water flux of 172 L/m^{2}h and 138 L/m^{2}h against Arabian Gulf seawater and reverse osmosis brine respectively. The antifouling property of the membrane PVPD 04 was tested by mixing BSA in seawater feed. The membrane with 30% of PVPD showed maximum FRR of 85 %, this may be due to presence of negative charge polar functional groups in the PVPD polymer.

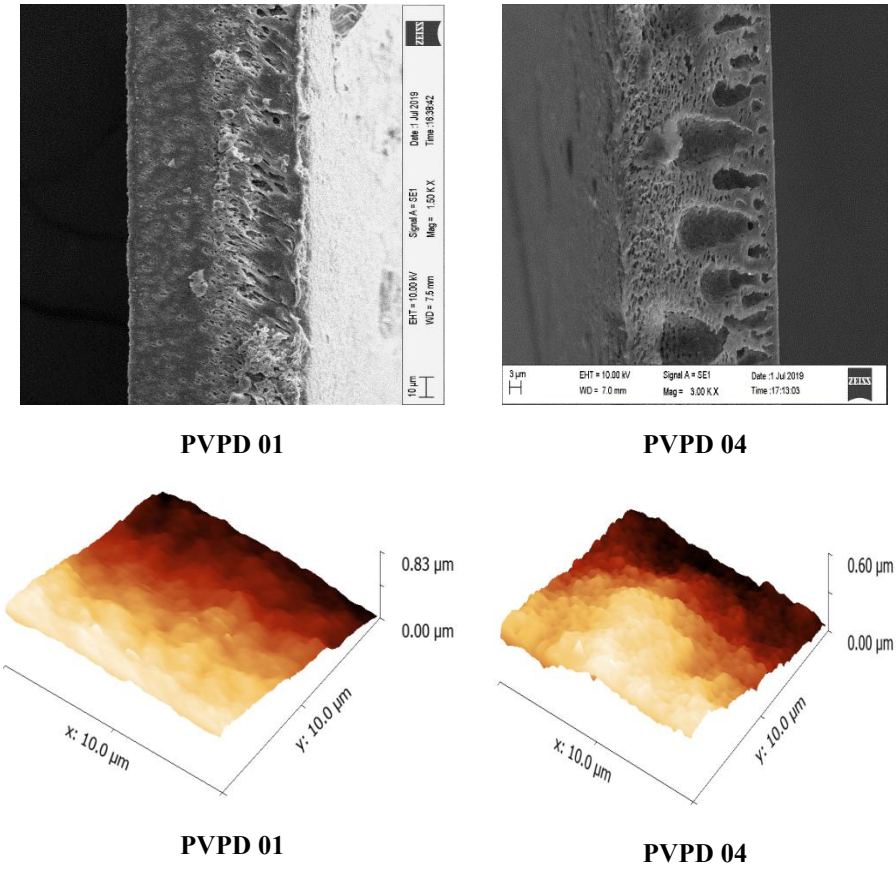

Fig. 2 The cross-sectional magnified SEM images and three-dimensional AFM images of a) PVPD 01, and d) PVPD 04 membranes.

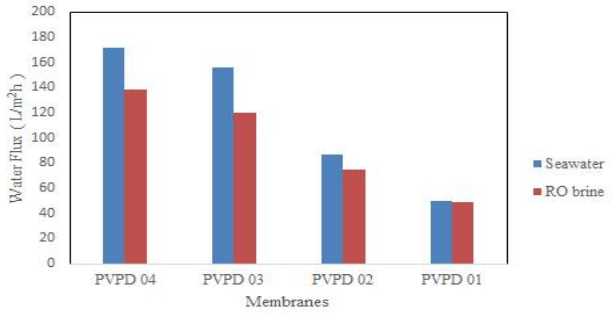

Fig. 3 The water flux of the membranes

4. Conclusions

The water insoluble PVP polymer was synthesized and its structure was confirmed by FTIR and NMR spectroscopy. The PVPD and PSf blend membranes were fabricated by varying PVPD concentration 10, 20 and 30 weight percent in the polymer dope solution. Newly fabricated membranes showed asymmetric structure and pore size was in the range of ultrafiltration. The three-dimensional AFM image showed the decreasing trend of surface roughness with increase of PVPD concentration in the blend membrane. Water flux and flux recovery ratio increases with increase in PVPD polymer concentration compared with pristine PSf membrane. Therefore, polar functional groups at the side chain of PVP polymer may play a major role in water flux and antifouling property.

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