Enhanced oil–water separation using polysulfone membranes modified with polymeric additives

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HIGHLIGHTS

- Facile fabrication of fouling resistant UF membranes using polymeric additives
- High fouling recovery rate and lesser decay rate are observed in Psf/PVP combination.
- PVP helped to enhance oil–water emulsion flux.

ARTICLE INFO

ABSTRACT

For separation of oil and water mixture using ultrafiltration (UF), polysulfone (Psf) membranes were synthesized by phase inversion method using N-methyl-2-pyrrolidone (NMP). In order to achieve both higher permeation flux and fouling resistance, modification of Psf has been done by adding polymeric additives such as polyvinyl-pyrrolidone (PVP), polyetherimide (PEI), polyethylene glycol (PEG) and polyethersulfone (PES). Pure Psf membrane showed a lower flux of about $0.26 \, \mathrm{L \, m^{-2} \, h^{-1}}$ which on PVP addition helped to enhance flux to the highest value of $33.66 \, \mathrm{L \, m^{-2} \, h^{-1}}$. The performance in oil and water separation in terms of rejection efficiency with respect to the concentration polarisation phenomenon was measured for each modified Psf membrane. The morphology and hydrophilicity of the modified membranes were investigated by a scanning electron microscopy (SEM) and contact angle analysis respectively. The UF experimental results using synthetic vegetable oil–water mixture showed that retention of oil over the membrane was nearly 99.8% for Psf/PVP membrane and also have excellent oil-fouling resistance ability even during dead-end batch UF under higher operation pressure.

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1. Introduction

The reliable key factor for decreasing the water scarcity would be the purification of non-conventional sources like seawater and oil contaminated wastewater [1–3]. Every year large volume of oily wastewater is produced by petrochemical, metallurgical, pharmaceutical and food industries resulting in terrible environmental pollution and resource utilisation problems. Conventional oily wastewater treatment methods namely gravity separation and skimming, air flotation, coagulation, de-emulsification and flocculation have the intrinsic disadvantages such as low efficiency, high operating cost, corrosion and recontamination problems [4] that subsequently lead to inefficient removal of emulsified oil droplets in micron and sub-micron sizes [5]. Additionally, emulsified oily wastewater containing surfactants as the third component is highly difficult to remediate due to the efforts required to break down the interfacial films formed between oil and water [6,7].

In consideration of these limitations in conventional treatment methods and to promulgate ecological consideration, several kinds of membrane processes including ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) have been recently employed for oil–water separation [8,9]. Because of its suitable pore sizes (usually in the range of 2–50 nm) and the capability of removing emulsified oil droplets without any de-emulsification processes, UF has been demonstrated as an efficient method or a pre-treatment step before NF and RO in the treatment of oil–water mixtures [10,11]. However, fouling is a serious problem inherent in UF membranes that can be caused either by deposition of an oil layer on the membrane surface or by membrane pore blocking by oil droplets that ends up in a substantial flux decline [12]. This can be due to a number of factors, such as adsorption inside the membrane, deposition on the membrane surface forming a cake layer and blocking of the membrane pores [13]. The membrane pore structure, the surface characteristics, as well as operating and process conditions are some of the other factors affecting membrane fouling. Hence, the proper tailoring of desired membrane material is the convenient method to reduce fouling and its adverse effects like flux and retention decline.

The hydrophilic membranes are found to have a lower fouling tendency but usually have limited chemical and thermal stabilities. Therefore, exhibiting anti-fouling properties on hydrophobic membranes are preferred by means of modifiers containing hydrophilic rich additives. Polysulfone (Psf) membranes with their hydrophobic nature make them more prone to fouling which is a major hurdle to their performance [14] in spite of their advantageous physico-chemical, mechanical and hydraulic stability. The highly hydrophobic nature of Psf tends to slow down the diffusion of the non-solvent (water) and retards coagulation during the phase inversion process, causing the formation of a denser skin layer, which will further result in an extremely lower flux [15]. Hydrophilic rich moieties like polyethylene glycol (PEG) have been found to impart fouling resistant to cellulose [16] and Psf [17] by means of surface modification. It has been also inferred from modification studies that more hydrophilic surface enables doubling of the flux and exhibits antifouling properties to the membrane compared with the unmodified one [18]. There had also been reports on adding polyvinylpyrrolidone (PVP) [19] and polydopamine (PD) [20] on polyethersulfone (PES) UF membranes for making it anti-fouling. PVP has been known for its pore formation in the hydrophobic PES membranes, which subsequently affects the polymeric pore size distribution [21, 22]. There are also surface modifying macromolecules (SMM) that have been extensively studied for improving the anti-fouling properties of hydrophilic polymers. However, all these are related to surface treatment and modification which possess complexity along with all of the UF process parameters like temperature, pH, flow velocity, and transmembrane pressure (TMP) to be controlled and monitored to possibly curb the fouling phenomenon.

The bulk modification of hydrophobic Psf is attempted in this study by means of various polymeric additives to achieve remarkable changes in the hydrophilicity and pore morphology. The objective is mainly focused to develop a facile and effective route for fabricating UF membranes with high permeability, excellent antifouling property and high rejection coefficient for oil–water mixture separation. Four different polymeric additives such as PVP, PEI, PEG and PES were chosen for the possible comparison of anti-fouling and oil retention efficiency. The separation performance of the prepared membranes was evaluated by treatment with pure water as well as synthetically made oil–water mixture. The membrane surface morphology and hydrophilicity have been characterised by a scanning electron microscopy (SEM) and contact angle studies respectively. The oil–water mixture separation performance in terms of anti-fouling property and rejection coefficient of modified Psf membranes were investigated under different operating conditions like dead-end batch and cross-flow continuous UF.

2. Experimental

2.1. Materials

The commercial Psf with molecular weight (M_w) of 35,000 kDa was provided by Sigma-Aldrich (MO, USA), N-methyl-2-pyrrolidene (NMP) was purchased from Loba Chemie Pvt Ltd., sodium dodecyl sulphate (SDS) and PEG (M_w: 600 Da) were purchased from Merck (India) Ltd., pore former PVP (M_w: 10 kDa) was purchased from Central Drug House (India) Ltd., PES (Veradale 3000) was procured from Solvay Chemicals (India) Ltd and PEI (M_w: 50 kDa) was purchased from Sigma Aldrich (MO, USA).

2.2. Membrane preparation

The Psf beads were dried in an oven at 80 °C for 1 h before use. Modified flat sheet Psf UF membranes were synthesized by phase inversion method using water as non-solvent. Modified Psf membranes were prepared using different polymeric additives namely PVP, PEG, PES, and PEI in the composition of 8.75 wt.% each along with Psf of 8.75 wt.%. Casting solutions were prepared by dissolving Psf and the respective additive in

82.5 vol.% of NMP as solvent at room temperature. There is no separate pore forming solvent in the membrane synthesis process. The detailed composition of each prepared membrane is given in Table 1. The casting solutions were stirred continuously for 4 h until clear homogenous solutions were obtained. Afterwards, the solution was de-aerated by a vacuum process until the bubbles were eliminated completely. The bubble-free solution was then cast onto the glass plate for the thickness of about 400 μm with the help of a thin film applicator (Elicometer). Then, the glass plate was immediately immersed into a distilled water bath maintained at 20 °C. The as-formed pure and modified Psf membranes are cut into the required area corresponding to dead-end and cross-flow UF experiments employed in this study.

2.3. Oil–water mixture preparation

The stable concentration of 2000 ppm of oil–water mixture was prepared in the laboratory with the help of deionised water and commercial grade vegetable oil. 2 g of vegetable oil was agitated with 500 ml of deionized water and 1 g of anionic surfactant SDS was also added to the mixture as the emulsifying agent. The final solution was diluted to 1000 ml in a volumetric flask and mixed by high-shear emulsifying dispersion for 30 min to delay the flocculation and coalescence of oil in water. The milky white oily water was formed after 2 h which was found to be stable without any flocculation. The stable oil–water mixture was then stored at room temperature and ensured the stability of particle size of oil in water for each run of UF experiment.

2.4. Characterisation of modified Psf membranes

The contact angle analysis for prepared membranes was performed to examine the degree of hydrophilicity by a contact angle goniometer (Model 250-F1, Rame-hart instruments, USA) interfaced with the camera. The equilibrium water contact angle was measured by determining the incident and receding angles using water droplet placed in five different locations. The average of the five readings was taken as the water contact angle of each membrane.

The top surface and cross-section morphology of each additive added Psf membranes was visualised using FESEM (TESCAN, FESEM-5600). The membrane samples were initially pre-treated with gold ion sputtering for making the surface conductive. The scanning has been done at the voltage of 20 kV to ensure proper electron beam focus.

Infra-red spectra have been recorded using Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer-Is5) built with attenuated total reflectance (ATR) measurements. The spectrum of each membrane was observed in the wavenumber range from 400 to 4000 cm^{-1} with the step up range of 500 cm^{-1} wavenumber. The spectral measurements were used to confirm the changes in the functional groups corresponding to each of the additive/polymer present in the membrane.

2.5. Performance of modified Psf membranes

2.5.1. Dead-end ultrafiltration

A dead-end stirred cell filtration system connected with air cylinder was used to characterise the rejection performance of pure and

Table 1
Description of modified Psf membranes and their contact angle values.

Casting solution composition				
Polymer	Modifiers (8.75 wt.%)	Solvent	Membrane description	Contact angle (°)
Psf (8.75 wt.%)	–	DMF (82.5 vol.%)	Pure Psf	75.0 (0.78)
	PES		Psf/PES	73.6 (0.32)
	PEI		Psf/PEI	72.0 (0.22)
	PVP		Psf/PVP	53.6 (0.42)
	PEG		Psf/PEG	66.0 (0.32)

Values given in parentheses denote the standard deviation errors.