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Organic phase addition of anionic/non-ionic surfactants to poly (paraphenyleneterephthalamide) thin film composite nanofiltration membranes

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ABSTRACT

Thin-film composite (TFC) nanofiltration (NF) membranes containing poly (paraphenylene terephthalamide) skin layer on polyethersulfone (PES) support layer were prepared by in situ interfacial polymerization using *p*-phenylenediamine (PPD) in water and terephthaloyl chloride (TPC) in *n*-hexane. The effects of sodium lauryl ether sulfate (SLES), triethanolamine lauryl ether sulfate (TEA-LES) and disodium laureth sulfosuccinate (DSLS) as anionic surfactants as well as cocamide-MEA, polysorbate 20 and nonylphenol as non-ionic surfactants, in the organic phase on the properties of TFC membrane were investigated. The performance of prepared TFC membranes was investigated for the rejection of NaCl, Na_2SO_4 and $MgSO_4$ ion solutions by dead-end filtration set-up. ATR-IR, SEM, AFM and zeta potential were applied to characterize the structure and morphology of the prepared TFC membranes. By addition of anionic surfactants in the organic phase, no significant change in the morphology and performance was observed; however, in the presence of non-ionic surfactants, the morphology and performance were changed and the salt rejections were increased. The structure of thin layer of membrane incorporated TEA-LES surfactant was not good and its surface had defect and micro crack. The highest salt rejections were obtained using nonylphenol in comparison with the other anionic/non-ionic surfactants.

1. Introduction

Nanofiltration (NF) was defined as a membrane process that exhibit separation characteristics in the intermediate between reverse osmosis and ultrafiltration and has advantages including high permeation flux, high retention of multivalent ion salts, low operation pressure, and low maintenance cost. NF has various applications such as water softening, waste water treatment, industrial water production as well as the textile, pharmaceutical and biochemical industries [1–7]. Most of recently developed NF membranes are thin-film composite (TFC) membranes which have important advantages in comparison with asymmetric membranes [5,8,9]. TFC membranes are fabricated by forming an ultra-thin skin layer as active layer on a porous support. There are several methods for the preparation of TFC nanofiltration membranes. Interfacial polymerization (IP) is a common method, which was first introduced by Morgan in 1965 [10]. In this method, the skin layer is generally obtained by the reaction between poly-functional amine and poly-functional acid chloride monomers in an aqueous and an organic phase, respectively. The polymerization reaction between two monomers takes place at the interface of two immiscible solutions. The commonly used monomers are aliphatic or aromatic diamine, such as piperazine (PIP), m-phenylenediamine (MPD) and *p*-phenylenediamine (PPD) [8,11]. In this technique a cross-linker, such as trimesoyl chloride (TMC), isophthaloyl chloride or terephthaloyl chloride [9,11–13] may be used.

In the TFC, the support layer gives the suitable mechanical strength with low resistance to permeate flow, while the skin layer is the important component, which mainly controls the solute rejection and permeability of the membrane.

Previous literatures reports the improvement of interfacial polymerization technique and subsequently the performance of membranes by optimizing preparation parameters such as type of monomer, monomer concentration in aqueous/organic solution, monomer ratios, reaction time and curing temperature [1,4,8,14]. However, the addition of surfactants in aqueous/organic solution is

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Nomenclature

A	Membrane area
AFM	Atomic force microscopy
ATR	Attenuated total reflectance
C_f	Concentrations of the feed solutions
C_p	Concentrations of the permeation
Cocamide-MEA	Cocamide mono ethanol amine
DMAc	Dimethylacetamide
DSLS	Disodium laureth sulfosuccinate
MWCO	Molecular weight cut off
NF	Nanofiltration
PEG	Polyethylene glycol
PES	Polyethersulfone
PPD	*P*-Phenylenediamine
PWF	Pure water flux
PVP	Polyvinylpyrrolidone
Q	Quantity of permeated pure water flux
R	Percent of salt rejection
SEM	Scanning electron microscopy
SLES	Sodium lauryl ether sulfate
T	Operation time
TEA-LES	Triethanolamine lauryl ether sulfate
TFC	Thin film composite

similar as important as aforementioned factors in improving the morphology and performance of the membranes. Surfactants are capable of changing the polymerization efficiency by assisting monomer moving from the water phase into the organic layer which results in significant improvement of the properties of the fabricated TFC membranes [4,11,15].

Various surfactants have been reported as additives in the aqueous/organic solution for modifying the thin layer membrane. Jegal et al. [16] had studied the effect of triethyl benzyl ammonium bromide (TEBAB), trimethyl benzyl ammonium bromide (TMBAB) as well as triethyl benzyl ammonium chloride (TEBAC) on the properties of TFC membranes. They found that only by addition of TEBAB, considerable change in the performance of membranes was observed. Sodium lauryl sulfate (SLS) as an anionic surfactant was used for synthesis of the PA layer by Saha and Joshi [17]. They saw that in the high SLS concentration, the NaCl rejection was decreased. Mansourpanah et al. [3,18] used sodium dodecyl sulfate (SDS), cetyltrimethyl ammonium bromide (CTAB) and Triton X-100 as anionic, cationic and non-ionic surfactants respectively. They found that, the properties of thin layer membranes were changed in the presence of SDS, CTAB and Triton X-100 during the IP. Recently, four types of amine salts, including tetraethylammonium chloride (TEAC), tetrabutylammonium bromide (TBAB), camphorsulfonic acid triethylamine salt (CAS-TEA), and 1-butyl-3-methylimidazolium chloride (BMMIC), were reported, that noticeably affect the membrane properties [15]. A recent literature review [11] indicated that there is no appreciable research about the application of surfactants for improvement in the efficiency of IP process and performance of thin layer membrane.

This study investigates the effect of addition of sodium lauryl ether sulfate (SLES), triethanolamine lauryl ether sulfate (TEA-LES) and disodium laureth sulfosuccinate (DSLS) as anionic surfactants as well as cocamide mono ethanol amine (cocamide-MEA), polysorbate 20 and nonylphenol as non-ionic surfactants for improving the performance and morphology of prepared membranes in the organic phase. The IP technique was employed using terephthaloyl chloride (TPC) and *p*-phenylenediamine (PPD) as reactant monomers to prepare the thin-film layer. The performance of TFC nanofiltration membranes was characterized by the rejection of NaCl, $MgSO_4$ and Na_2SO_4 salt solutions. Furthermore, the properties of TFC membranes including the chemical composition and the structure were discussed.

2. Experimental

2.1. Materials

Polyethersulfone (PES Ultrason E6020 P with MW = 58,000 g/mol) was purchased from BASF company, Germany. Polyvinylpyrrolidone (PVP, 25,000 g/mol) as pore former in the support membrane, polyethylene glycols (PEG) with different molecular weights (200–6000 Da) for measurement of the membrane molecular weight cut-off (MWCO), dimethylacetamide (DMAc) as organic solvent, *p*-phenylenediamine (PPD) and terephthaloylchloride (TPC) as monomers were obtained from Merck company. Sodium lauryl ether sulfate (SLES), triethanolamine lauryl ether sulfate (TEA-LES) and disodium laureth sulfosuccinate (DSLS) as anionic surfactants as well as cocamide-MEA, polysorbate 20 and nonylphenol as non-ionic surfactants were supplied from Sigma-Aldrich. The rejection performance was investigated using NaCl, $MgSO_4$ and Na_2SO_4 (all salts from Merck). Deionized water was used in the current study. Chemical structures of anionic/non-ionic surfactants are shown in Table 1.

2.2. Preparation of PES support layer

The support membrane was fabricated using the PES polymer with the concentration 17 wt.% (this a common concentration for preparation of a support membrane) and the PVP with a variety concentrations changed from 2 to 8 wt.% in DMAc. By testing with the PWF at different total operating pressures (2, 4 and 6 bar), results (not presented here) showed that the PWF was maximum at 2 wt%. Therefore, the concentration of PVP was selected 2 wt.%.

The casting solution was mechanically mixed consistently for 8 h. The homogeneous solution was kept at the room temperature for the elimination of air bubbles for approximately 12 h. Afterwards, a film applicator with the thickness size of 150 μm was used for casting the homogenous solution on the glass plate at ambient condition. Immediately, the glass plate was immersed into the distilled water bath at 10 °C without for around 24 h for the polymer precipitate and forming the membrane. Finally, the support membranes were dried between two filter paper sheets for 24 h in room temperature.

2.3. Preparation of TFC membranes

The TFC membrane was prepared via the IP technique. For obtaining the optimum condition, the IP was performed using different monomer concentration (from 0.1 to 0.3 wt.%.), reaction time (from 1 to 6 min) and curing temperature (from 50 to 90 °C). The fabricated TFC membranes were used for the PWF test and salt rejection (results not presented here) and the optimum condition was selected for the preparation of TFC membranes containing different surfactants.

The PES support membrane was fixed on a glass plate. The aqueous phase containing PPD 0.3 wt.% were poured on the top of the support membrane and allowed to immerse for 10 min to ensure PPD diffuse into the porous support at the ambit temperature. A soft rubber roller was applied to remove tiny bubbles and remove the excess solution from the soaked membrane surface. Then, terephthaloyl chloride (0.3 wt.%) as organic solution and the surfactant 0.3 w/v.% in *n*-hexane was poured over the membrane to accomplish the IP reaction for 4 min. The excess organic solution was drained off and for better