Contents lists available at ScienceDirect

Process Safety and Environmental Protection

journal homepage: www.elsevier.com/locate/psep

Synthesis, characterization and performance studies of polysulfone and polysulfone/polymer-grafted bentonite based ultrafiltration membranes for the efficient separation of oil field oily wastewater

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ARTICLE INFO

Article history:
Received 4 November 2015
Received in revised form 9 March 2016
Accepted 15 March 2016
Available online 21 March 2016

Keywords:
Polysulfone
Ultrafiltration
Bentonite nanoparticles
Grafting
Oil field oily wastewater
Membrane fouling

ABSTRACT

In this study, polysulfone based mixed-matrix ultrafiltration membranes were prepared by blending polysulfone with different polymer-grafted bentonite additives. Formation of polymer-grafted bentonite was confirmed by Fourier transformed infra-red spectroscopy, energy-dispersive X-ray and thermal gravimetric analysis. Membranes were fabricated via wet phase inversion process with varying additive concentration. Hydrophilicity and structural changes of grafted polysulfone membranes were investigated by scanning electron microscope, water contact angle, molecular weight cut-off and pure water flux measurement. Prepared polysulfone/polymer grafted bentonite membrane was used for the separation of oil from oil-field oily wastewater and the membrane performance was evaluated in terms of permeate flux, oil rejection and fouling characteristics. Finally, results were compared with plain polysulfone and polysulfone/bentonite ultrafiltration membranes.

1. Introduction

Polysulfone (PSf) is a widely used membrane material for ultrafiltration (UF) operation and it has excellent mechanical strength and thermal stability (Harris et al., 1988). The phase inversion technique is commonly employed to fabricate PSf based UF membranes (Mulder, 1996; Suk and Matsuura, 2006). UF membranes prepared via phase inversion technique exhibits a characteristic morphology of asymmetric membrane having thin dense layer on top which plays a role of selective barrier film for solute transport while porous sub-layer offers an excellent mechanical strength to the membrane. The thickness and integrity of the dense top layer determine the transport characteristics of the asymmetric UF membrane, whereas the figure like porous sub-layer has very little or no effect on the transport characteristics. Phase inversion by introducing a third component (non-solvent, typically water) into a homogeneous polymer solution (referred as a wet phase inversion) followed by evaporation has a strong influence on the transport properties of the UF membrane (Kesting, 1985; Tsay and McHugh, 1991). However, the principal structure-forming processes of these membranes occur during quenching step when non-solvent, solvent exchange takes place during various phase transformations in polymer film through the complex interactions of thermodynamic and mass transfer processes. Therefore, various combinations of polymer, solvent, non-solvent and processing conditions affect the morphology of UF membranes and hence,

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http://dx.doi.org/10.1016/j.psep.2016.03.011

different transport characteristics (Han and Bhattacharyya, 1994, 1995; Lee et al., 2003). In addition, PSf based membranes never achieve full density in contrast to reverse osmosis membranes during the process of phase inversion (Lee et al., 2011). However, due to the hydrophobic nature, PSf membrane exhibits strong adsorption and deposition toward foulants on the membrane surface as well as inside membrane pores. This leads to a lowering of permeate flux and deterioration of membrane performances (Asatekin and Mayes, 2009; Shivanand et al., 2013). Therefore, modification of PSf membrane by adding hydrophilic additives has been attracting a great attention in the recent years (Deriszadeh et al., 2010; Song et al., 2012; Marchese et al., 2000). In this regard, several studies have been reported to improve the hydrophilicity of PSf membrane via surface coating, blending and grafting techniques. Thin film coating on the membrane surface with a hydrophilic polymer is the simplest way to increase the hydrophilicity of the membranes (Kim et al., 2012). However, the coated layer on the membrane surface imparts more resistance toward permeation resulting reduced water flux, and in addition, it is frequently delaminated during operation due to poor adhesion at the membrane surface. On the other hand, blending method is frequently used to enhance membrane hydrophilicity. In this method, several additives like polymers [e.g., polyethylene glycol (PEG), poly(1-vinylpyrrolidone) (PVP), etc.] and nanoparticles (e.g., $ZnCl_2$, TiO_2, Al_2O_3, SiO_2, ZnO_2, bentonite, etc.) have been used to improve the hydrophilic characteristics of PSf membranes (Shivanand et al., 2013; Dongwei et al., 2015; Song et al., 2012; Arthanareeswaran et al., 2010; Li et al., 2014; Sung et al., 2013; Panda and De, 2014; Yang et al., 2007; Kumar et al., 2015). More recently, Kumar et al. (2015) studied the performance of PSf/bentonite and PSf/silica nanoparticle blended mixed-matrix UF membrane and an enhanced performance of PSf/bentonite was reported over PSf/silica UF membranes. It was also observed that the significant amount of silica and bentonite was leached out during phase inversion process of membrane synthesis. It was known that most of the additives form an immiscible blend with PSf, resulting poor UF performance (Kim et al., 2002). To prepare nanoparticles blended mixed matrix PSf membrane, it is very difficult to disperse nanoparticles homogeneously in membrane matrix resulting additive aggregation and declined membrane performance. In addition, water soluble polymer additives (e.g., PVP and PEG) may also be washed out during membrane formation and UF operation. To alleviate above problems of the blended membranes, the variation in the molecular structure was incorporated into nanoparticle via polymerization which may cause to increase the miscibility of nanoparticle in the membrane matrix and decrease the leach-out phenomena of nanoparticles during UF (Song et al., 2014; Meagan et al., 2011; Wu et al., 2014; Eren et al., 2015; Michael et al., 2011; Yue et al., 2013; Zhu et al., 2014; Xiaokai et al., 2011; Du et al., 2015).

In this regard, several researchers prepared membranes by adopting graft copolymerization technique. Song et al. (2014) prepared composite PSf based UF membranes using PVP, P(VP-AN) and PVA polymers grafted silica additives and found that the water flux was twice as well as enhanced anti-fouling properties than that of plain PSf membranes. Meagan et al. (2011) synthesized silver nanoparticle grafted polyethyleneimine additive and prepared nanocomposite PSf UF membranes to enhance antimicrobial activity on the membrane surface. Wu et al. (2014) prepared PSf hybrid membranes by blending SiO_2–graphene oxide nanohybrid and found that water flux enhanced nearly twice while maintaining egg albumin rejection (>98.0%) than that of PSf/SiO_2 membranes. It was also reported that PSf/SiO_2-graphene oxide membrane improved anti-fouling properties for long term performance. Eren et al. (2015) prepared PSf composite membrane by blending PSf with poly[2,2′-(m-phenylene)-5,5′-dibenzimidazole] and found that blended membranes have more hydrophilicity and higher porosity but smaller pore size compared to the plain PSf membrane. Michael et al. (2011) fabricated composite asymmetric UF membranes using coated silica and titanium nanoparticle to increase membrane surface hydrophilicity. Yue et al. (2013) synthesized PSf membrane using grafted zwitterionic polymer of poly(sulfobetaine methacrylate) via free radical polymerization and found that protein anti-fouling property of grafted membrane was improved without affecting the rejection ratio. Zhu et al. (2014) synthesized poly(2-hydroxyethyl methacrylate) grafted silica based polyethersulfone membranes for enhanced hydrophilic and anti-fouling characteristics, and it were reported that surface hydrophilicity, water permeability, brovine serum albumin rejection and anti-fouling ability of polyethersulfone membranes were improved significantly. Xiaokai et al. (2011) synthesized poly(vinylidene difluoride)-g-maleic anhydride and poly(vinylidene difluoride)-g-acryl amide hybrid membranes to improve pure water flux. Du et al. (2015) synthesized PSf membrane using a polyol grafted polymers and found that surface grafting leads to an increase in surface hydrophilicity with declined water flux.

Bentonite (montmorillonite) was frequently used as an additive to improve the viscosity of drilling fluid. It consists of several close-packed platelets and each platelet has tetrahedral–octahedral–tetrahedral layered structure. The inter-sheet layers include exchangeable metal ions (e.g., Na^+, K^+, Ca^{2+}, etc.) to neutralize the net negative charges in the platelets which are generated by partial substitution of Al^{3+} with Mg^{2+} at the octahedral sites. Above characteristics of bentonite explain its stronger affinity toward water through the crystalline and osmotic swelling (Darley and Gray, 1998). Therefore, the swelling property of bentonite may help to enhance the performance of PSf based ultrafiltration by improving the membrane pore structure and permeability.

In the present study, polymerization of the various monomers like 1-vinylpyrrolidone (VP), vinyl acetate (VAc) and acrylonitrile (AN) were carried out in the presence of bentonite nanoparticles and 3-(trimethoxysilane)propyl methacrylate (MPS) coupling agent using azobisisobutyronitrile (AIBN) initiator to make polymer grafted bentonite hybrid materials. Polymer grafted bentonite blends were characterized by Fourier transformed infra-red (FTIR), X-ray defractometer (XRD) analysis, thermo gravimetric analysis (TGA), thermal differential analysis (DTA) and energy-dispersive X-ray (EDX) spectroscopic analysis. Considering these hybrid materials as an additive, several PSf based UF membranes were synthesized by a phase inversion technique using N-methyl-2-pyrrolidone (NMP) solvent, which were then used for the purification of oil field oily produced wastewater. PSf based polyvinylpyrrolidone-grafted-bentonite (PVP-g-bentonite), polyvinylacetate-grafted-bentonite (PVAc-g-bentonite) and poly(1-vinylpyrrolidone-co-acrylonitrile)-grafted-bentonite [P(VP-AN)-g-bentonite] UF membranes were also characterized using FTIR, TGA, DTA, field emission scanning electron microscope (FE-SEM) and EDX analyzer. The effect of polymer grafted-bentonite additives in PSf membranes were determined by water contact angle, pure water flux, MWCO and