Fouling resistant nanofiltration membranes for the separation of oil–water emulsion and micropollutants from water

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ABSTRACT

Fouling resistant nanofiltration membranes containing penta-block copolymer (PBC) as the active layer on top of polysulphone ultrafiltration membrane were prepared by self-assembly of PBC from acetone–ethanol solution followed by alkali treatment. Upon alkali treatment of the membrane, contact angle was decreased from 115° to 93°, molecular weight cut off values were increased from about 950 to 1350 Da and the pure water flux was increased from $0.5 \, \text{L m}^{-2} \, \text{h}^{-1} \, \text{bar}^{-1}$ to $1 \, \text{L m}^{-2} \, \text{h}^{-1} \, \text{bar}^{-1}$. The membranes showed the rejections in the range of 22–37% for NaCl, 33–44% for $MgSO_4$, 20–36% for $MgCl_2$ and 45–61% for Na_2SO_4 when tested using 500–4000 ppm feed solution at $3.5–28 \, \text{kg/cm}^2$ applied pressure. Rejection of organic micropollutants was decreased according to the increase in their hydrophobicity (log K_{OW} value) as follows: PEG-200 > benzoic acid > 2-chlorophenol > 2,4-dimethyl phenol > bisphenol-A. The composite membranes exhibited 95.5–99.5% oil rejection when tested using 500–1000 ppm engine oil in water emulsion as the feed at $3.5 \, \text{kg/cm}^2$ applied pressure. After 8 h of permeation of oil–water emulsion, the flux recovery values were 35% for polysulphone membrane and 89–95% for composite membranes, which indicate the superior antifouling nature of the composite membranes.

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1. Introduction

Many industries such as petrochemical, food, leather, and textile, generate large quantities of oily wastewaters and the direct discharge of these waters may have detrimental impacts on marine and terrestrial eco-systems. Hence, considerable attention has been focused in recent years on the treatment of oily wastewaters. The conventional separation processes such as mechanical separation, filtration, air flotation, coagulation, and chemical de-emulsification, used for the treatment of oily wastewaters have several disadvantages in terms of low efficiency, operational difficulties and high operational costs [1,2]. Recently, there have been intense research efforts to replace the conventional separation methods with membrane based processes. Compared to the conventional separation methods, membrane filtration processes such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis offer many advantages for the treatment of oil–water emulsions. The major advantages of membrane based separations are low energy costs, small space requirements and no necessity for chemical

additives and hence reduction in environmental pollution. A number of investigators have reported the use of different types of membranes such as microfiltration, ultrafiltration and nanofiltration membranes for the treatment of oil–water emulsions [3–8]. Efforts have been focused on the enhancement of membrane performance and antifouling properties through the blending of different types of polymers and surface modifications. Recent reviews report the application of different types of membranes for the treatment of oily-waste waters [9,10].

Nanofiltration membranes are used for a variety of separation applications such as water treatment (water softening, removal of natural organic matter, heavy metals, viruses and bacteria from water), dairy production, and concentration of organic dyes [11–12]. NF membrane is usually consists of an ultrathin (0.1–0.20 μm thickness) amorphous polymeric active layer with pores of 2–5 nm diameter on top of a porous support membrane [13]. The active layer is usually contains either a negative charge or a positive charge, depending on the type of monomers used for its preparation. Separation of solutes by nanofiltration membranes occurs primarily due to size exclusion and electrostatic repulsion between the membrane surface and solute molecules [14–16]. Sieving or size exclusion is the most responsible mechanism for the separation of uncharged molecules whereas, both

sieving and electrostatic interactions are responsible for the separation of ionic species. The active layer of the NF membranes is usually prepared by interfacial polymerization or free radical polymerization process of suitable monomers on top of a microfiltration/ultrafiltration membrane. Membranes based on di- and tri-block copolymer (BCPs) have been recently reported for water purification and for various other separation applications [17–20]. Block copolymers are able to exhibit more complex morphologies due to the tendency for phase separation of thermoplastic and elastomeric blocks, which greatly affects the transport properties of the membrane. The low surface energy polymers have a tendency to form excellent oleophobic micro-domains on the membrane surface, which would endow the membrane with excellent antifouling property for different separation applications. The present paper reports the preparation of nanofiltration membranes containing penta-block copolymer as the active layer on top of a polysulphone ultrafiltration membrane by self assembly process. The performances of the membranes were evaluated for the separation of various inorganic and organic solutes from aqueous solutions and oil–water emulsion mixture.

2. Experimental

2.1. Materials

Polysulphone (PSF, Udel P-3500) from Solvay Polymers was dried at about 110 °C for 2 h prior to the preparation of casting solution. Nordlys-TS100 non-woven polyester fabric (from Polymer Group Inc., France) was used as the reinforcement for PSF ultrafiltration membrane. Polyethyleneglycol (PEG), polyethylene oxide (PEO) and dextran samples of different molecular weights were purchased from Aldrich, USA. Dimethylformamide (DMF), tetrahydrofuran (THF) and the other chemicals were of analytical grade samples and used without further purification. Benzoic acid (BA), 2,4-dimethyl phenol (DMP), 2-chlorophenol (CP) and bisphenol-A (BPA) were procured from local suppliers and were used as received.

The synthesis and characterization of penta-block copolymer (PBC) such as poly(methyl methacrylate)-b-poly(n-butyl acrylate)-b-poly(dimethyl siloxane)-b-poly(n-butyl acrylate)-b-poly(methyl methacrylate) was reported elsewhere [21]. The chemical structure of the PBC used in the preparation of composite membranes is shown in Structure 1.

2.2. Preparation of composite nanofiltration membranes

Composite nanofiltration membranes were prepared in three steps. In the first step, polysulphone ultrafiltration membrane was prepared on Nodlys TS100 non-woven fabric according to the wet phase inversion process using a semi-automated membrane casting unit as reported elsewhere [22]. Molecular weight cut off (MWCO) value of the ultrafiltration membrane was determined by the permeation of aqueous solutions of different molecular weight polyethyleneglycols and dextrans and was found to be around 1.10 kDa.

For the preparation of PSF-PBC composite membrane, water wet polysulphone support membrane (18 × 22 cm size) was fixed in a glass tray along the edges. Then, 20 mL solution containing specific amount of PBC (0.07 wt.%) in acetone–ethanol (25:75) mixture was prepared and poured on top of polysulphone membrane. Solvent was then allowed to evaporate at room temperature for 1 h and then the membrane was cured at 50 °C for 2 h. This was resulted in the lamination of PBC layer on top of polysulphone support and thus produced PSF-PBC composite membrane.

In the next step, the PBC active layer of the composite membrane was exposed to aqueous NaOH solutions of different concentrations (0.5, 1.0 and 2.0 M) separately at 30 °C for 8 h. Then, the membrane was washed with water thoroughly for further characterization. Each modification was repeated a minimum three times and the average values were reported in the paper. The standard deviations were found to be ±5% for flux and ±1% for solute rejections.

2.3. Membrane performance

The performance of the membranes was determined using cross-flow RO test kit consisting of four stainless steel cells with an effective area of 14.5 cm^2 for each membrane coupon. After fixing the membrane coupons in test cells, initially pure water flux was determined at different pressures (7 bar). Then, the performance of the membranes was determined using aqueous feed solutions of different inorganic solutes (500–4000 ppm solutions of NaCl, Na$_2$SO$_4$, MgCl$_2$ and MgSO$_4$) separately at different operating pressures. The separation of low molecular weight organic compounds (benzoic acid, 2,4-dimethyl phenol, 2-chlorophenol, salicylic acid and bisphenol-A) and polyethyleneglycols were determined using separate membrane samples. The concentrations of feed and product water were determined by different techniques such as conductivity measurement for inorganic solutes, GPC for polyethyleneglycols and UV–Visible spectrophotometer for low molecular weight organic compounds. All the experiments were repeated twice and the average values were reported in the paper. Membrane permeate flux and rejection were determined according to Eqs. (1) and (2) respectively.

$$\text{Flux } (J_w, \text{ L/m}^2 \text{ h}) = V/At \tag{1}$$

where V is volume of permeated water (L), A is the membrane area (m^2) and t is the permeate sampling time (h).

$$\text{Rejection } (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{2}$$

where C_p and C_f are the concentrations of the solute in permeate and feed, respectively.

2.4. Membrane molecular weight cut off (MWCO) values

The MWCO values of the composite membranes were determined by the permeation of aqueous solutions of different molecular weight PEGs and measuring their rejection coefficient. The MWCO values of the membranes were determined from the plot
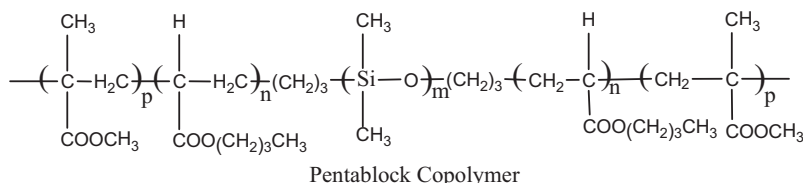
Structure 1. Chemical structure of penta-block copolymer used in the preparation of composite membranes.