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Studies on fouling by natural organic matter (NOM) on polysulfone membranes: Effect of polyethylene glycol (PEG)

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HIGHLIGHTS

- Fouling behaviour of PSf by NOM
- Different concentrations and molecular weights of PEG were used as additives in membrane.
- Detailed morphology and membrane performance were characterized and measured.
- Real river water which possesses hydrophobic and hydrophilic characteristics was used to evaluate membrane fouling.

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ABSTRACT

Polysulfone membranes were prepared via phase inversion technique by using polyethylene glycol with molecular weights of 400, 1500 and 6000 Da as pore forming agent in dope formulation. The performance of membrane was characterized using humic acid and water sample taken from Sembrong River, Johor, Malaysia was used as natural organic matter sources. Membrane properties were also characterized in terms of mean pore radius, pure water flux, humic acid rejection and fouling resistance. The results indicated that the pure water flux and mean pore radius of membranes increased with the increase of PEG content. Fourier transform infrared spectroscopy results revealed the presence of hydrophilic component in PSf/PEG blend with the significant appearance of O–H peak at 3418.78 cm^{-1}. Scanning electron microscopy analysis revealed the presence of finger-like structure for all membranes and the structure intensified as PEG content was increased. The results obtained from the fouling study indicated that the membrane with the lowest PEG content and molecular weight has an excellent performance in mitigating fouling.

1. Introduction

Natural organic matter (NOM) is one of the major pollutants in acidic and low turbidity water source. In Malaysia, most of the water sources are contaminated with NOM especially that from peat soil. Natural organic compounds such as humic acid and fulvic acid contributed to the natural colour of water (brown to black) which becomes more visible if the dissolved organic carbon (DOC) exceeds 5 mg/L. Therefore, the removal of NOM is usually known as colour removal. According to Thurman [1], surface water in average contains about 45% fulvic acid, 5% humic acid, 25% low molecular weight acid, and the remaining consists of neutral compounds, bases and contaminants. Although these compounds are relatively harmless, they are able to form carcinogenic disinfection byproducts such as trihalomethanes [2,3]. In order to remove these substances and render environmental remediation, ultrafiltration (UF) has been recognised as one of the attractive approaches that has been highlighted in many studies due to its compactness, easy automation, high removal rate of organic matter and also capability to remove virus [4].

Polysulfone (PSf) is the most commonly used polymer in the fabrication of UF membrane. PSf is known for its resistance in extreme pH condition and high thermal stability [5]. However, one of the major problems of polysulfone is its hydrophobic characteristic which often causes hydrophobic particle to adsorb on the surface of the PSf membrane. This phenomenon had led to membrane fouling and drastically decreased the membrane permeability.

Fouling is described as pore-blocking, solute aggregation or adsorption phenomenon. Irreversible membrane fouling by proteins, NOM and other biomolecules' adsorption reduces the flux of membrane and

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hinders the wide scale application of UF membranes [6,7]. The current technique to counter this problem is by cleaning the membrane with aggressive chemicals such as hypochlorite, nitric acid, sodium hydroxide and oxalic acid at extreme pH [8,9]. These chemicals can only remove the adsorbed foulants for some time and the membrane must be replaced when this cleaning method becomes ineffective. The mechanisms and causes of fouling that strongly depend on the membrane surface characteristic (hydrophilicity, charge and roughness), concentration polarization, cake layer formation, foulant properties and water chemistry have been well studied and reported [7,10–12]. Among all these causes, membrane surface seems to be the most crucial factor to be looked into since the properties of membrane surface could potentially affect the overall performance of the resultant membranes. Surface modifications of membrane to obtain high hydrophilicity, low surface roughness and positive charge have been progressively investigated in order to produce a membrane with high antifouling properties [13–15].

A membrane with good rejection and water permeability is usually prepared by incorporating suitable additive through an efficient fabrication method. Various types of additive such as mineral fillers, polymer, salts, non-solvent and solvent were incorporated using different approaches to improve the membrane properties [16–19]. Generally, inorganic and mineral fillers are used to enhance and create stability to the membrane performances. Hamid et al. reported that the addition of titanium dioxide nanoparticle in polysulfone has reduced the fouling resistance of the membrane [20]. They also found that the additive has increased rejection of humic acid up to 90%. Idris et al. studied the effect of lithium bromide salts on the performance of a polyethersulfone hollow fibre membrane and found that lithium bromide enhanced membrane hydrophilicity and water permeability [21]. The capability of a strong non-solvent such as water as an additive in the membrane performance was studied by Yunos et al. [22]. They discovered that by adding water in PSf dope formulation, pure water flux was greatly enhanced despite the deterioration in the strength of the membrane. Typically, a low molecular weight polymer is used as an additive to improve the pore forming of the membrane. Polyvinyl pyrrolidone (PVP) and polyethylene glycol (PEG) are the most common additives used in membrane formulation [23–26]. Investigation of PEG as an additive has attracted enormous attentions from many researchers due to the ease of preparation as PEG can dissolve in water and organic solvent, low toxicity and cost [26–29]. PEG has shown promising potential in increased membrane pore size and permeability. Ma et al. have studied the effect of PEG on the resultant PSf membrane and they found that the presence of PEG has greatly improved the membrane hydrophilicity, porosity and water permeability [27]. The addition of PEG has also reduced the thermodynamic stability of dope formulation which then led to finger-like formation in the membrane structure [26].

According to some previous reports [16,30,31], surface-bound long-chain hydrophilic molecules in PEG were sufficient to form steric repulsion which prevents adsorption of protein molecules onto membrane. Zhu et al. [32] found that the addition of PEG in membrane could reduce the total adsorption of bovine serum albumin (BSA) on the membrane surface. Kim et al. [33] prepared a surface-coated membrane using PEG hydrogel on reverse osmosis (RO) membrane and demonstrated fouling reduction of salt water as foulant. Grafting of PEG on membrane surface was also found effective to reduce at least 96% BSA adhesion as studied by McCloskey et al. [34]. They found that grafted PEG created hydration shell that renders surface resistant to BSA adsorption.

As far as we are concerned, the investigations in the effect of PEG concentration on the performance of membrane for NOM removal and fouling mitigation were rarely studied. Thus, in this work, the fouling behaviour of the PSf membrane with PEG as an additive was studied by using NOM source from real river water. The prepared membranes were characterized via scanning electron microscopy (SEM) and Fourier transform-infrared spectroscopy (FTIR) to provide further insights in the fouling mechanism of PSf membrane.

Table 1
Composition of casting solution.

	PSf	NMP	PEG 400[a]	PEG 1500[a]	PEG 6000[a]
P.4.400	18	82	4	-	-
P.8.400		82	8	-	-
P.10.400		82	10	-	-
P.12.400		82	12	-	-
P.16.400		82	16	-	-
P.10.1500		82	-	10	-
P.10.6000		82	-	-	10

[a] Represent molecular weight (Da).

2. Experimental

2.1. Materials

Polymer solutions were prepared using polysulfone (UDEL P1700) as polymeric material and N-methyl-2-pyrrolidone (NMP) (MERCK) as solvent. Meanwhile PEG 400, 1500 and 6000 (Qrec) were used as an additive. Distilled water was used as a non-solvent bath for the purposes of phase inversion. All chemicals purchased in this study were used without any further purification.

2.2. Membrane preparation

In this study, PSf/PEG flat sheet membranes were prepared by casting a polymer solution (18 wt.% of PSf) with different PEG contents and molecular weights on a glass plate. Table 1 shows the composition of various polymer solutions prepared in this study. Polymer solution was cast on the glass plate with casting knife gap setting at 150 μm with an appropriate casting shear. The cast solution was then immersed in water bath until the membrane thin film peels off naturally. The procedures were conducted at constant temperature and relative humidity (HR) (25 °C; HR 84%).

2.3. Scanning electron microscopy (SEM)

SEM JEOL GSM was used to examine the morphology of membrane. The membrane was immersed in liquid nitrogen and fractured

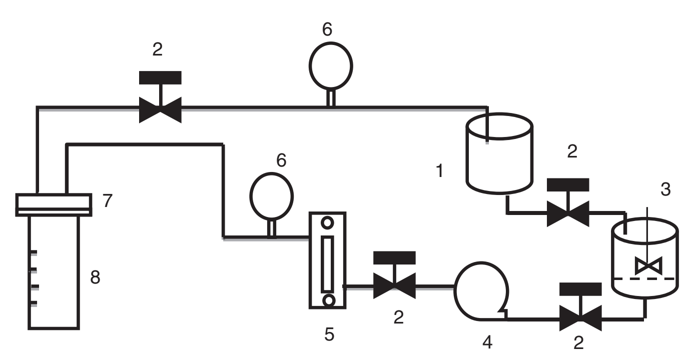

Fig. 1. Ultrafiltration permeation testing unit schematic diagram, (1) feed tank; (2) control valve;(3) pre-treatment tank; (4) osmotic pump; (5) flow meter; (6) pressure gauge; (7) filter holder; (8) beaker for collecting permeate.