The Separation of Oily Water Mixture Using Membrane

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Abstract. The increment of oil discharge in the water system gives a great impact to the environments. Membrane separation has been widely used to treat the oily water mixture due to its environmentally process, low operating cost and has better efficiency. Polysulfone (PSF) is widely used in the membrane fabrication due to its good physico-chemical, mechanical and hydraulic stability, but its hydrophobicity limits its application in the separation of oily mixture due to the fouling. The blend of PSF with poly (vinyl alcohol) (PVA) could compensate this limitation where the covalent bonding between PSF/PVA could form a protective layer to prevent the deposition of organic foulants on the membrane surface. Furthermore, PVA has been studied intensively for membrane applications because of its good chemical stability, film-forming ability and high hydrophilicity. To ensure the compatibility and high stability of the resultant membrane, the cross linking of the polymer blend (PSF/PVA) with tetraethylorthosilicate as silica nano precursor through sol-gel reaction was conducted in this study. Polyethylene glycol 400 was added as an additive to improve the properties of the integral membrane. The concentration of tetraethylorthosilicate was varied at 0wt.%, 0.5wt.%, and 1wt.% while the concentrations of other polymers are remained constant. Performance testing on the fabricated membrane through pure water flux and rejection of oil particles were conducted. The results exhibited that higher concentration of tetraethylorthosilicate led to higher water flux and higher rejection of oil particles respectively for the fabricated membrane. The crosslinked membranes achieved 100% of oil rejection after 45 minutes filtration time, meanwhile membrane from pure polymer blend only achieved 60.2% of oil rejection. This finding shows the potential of the fabricated membrane to be further explored in the area of oily water mixture treatment process.

1. Introduction

Population growth and rapid industrial developments such as petrochemical, metallurgy, coal tar, and metal-finishing initiating an increment of oil discharge in the water system which leads to water pollution. Oily wastewater that is not treated properly will give negative impact to the environment like affecting the clean water resources, endangering aquatic ecosystem, endangering human health, causing atmospheric pollution, and affecting crop production [1]. Due to different properties, oil is immiscible in water. Oil water treatment can be classified into six aspects, which includes flotation, coagulation, biological treatment, membrane separation technology, combined technology, and advanced oxidation process.

Membrane separation is one of the most popular processes and has been proven successful in separating oil from water. The membrane acts as semi-permeable layer between the two phases of oil and water and the membrane selectively filter from the two phases [2]. In addition, membrane
technology shows more advantages compared to traditional methods such as better efficiency, relatively low operating costs, chemical stability, and environmentally friendly process. Different membrane separation process required different pore sizes and driving forces. The filtration process such as ultrafiltration (UF), microfiltration (MF), reverse osmosis (RO), and nanofiltration (NF) are depending on the membrane pore sizes.

The materials used to produce membranes include polymer, ceramic, and inorganic compounds. In many applications, polymer membranes have been widely used compared to ceramic based membrane because of their high efficiency in separating mixtures. The blended polymer will form the interaction between hydrophobic side chain combination with intramolecular and intermolecular hydrogen bonds and this interaction improved the membrane’s filtration [3].

The example of polymer materials that are widely used for membrane preparation include polysulfone (PSF), polyethersulfone (PES), polypropylene (PP), cellulose acetate (CA), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), and polyethylene (PE) [4]. One of the problems that commonly occurred in the membrane separation is fouling where it reduces the performance of membrane. Polysulfone is widely used due to its good physico-chemical, mechanical and hydraulic stability. Besides high tendency of fouling, the hydrophobic nature of polysulfone slows down the diffusion of non-solvent and retards coagulation during the phase inversion process, which will subsequently form a dense skin layer. Therefore, it causes a flux declining situation. Blending it with hydrophilic polymers could lessen these phenomenon [5]. Poly (vinyl alcohol) (PVA) has been studied intensively for membrane applications because of its good chemical stability, film-forming ability and high hydrophilicity. However, due to PVA is extremely hydrophilic material and polysulfone is a hydrophobic material, the cross linking of the polymer blend (Polysulfone/PVA) with silica nano precursor (tetraethylorthosilicate) was conducted in this study to ensure high stability for the resultant membrane. It has been proven that the combination of organic and inorganic polymers yields membrane with better mechanical and thermal properties due to the introduction of hydrogen and covalent bonds in the polymer matrix during the cross-linking reaction [6][7]. Furthermore, polyethylene glycol (PEG) was added in the formulation to overcome and reduce fouling by increasing pore size, developing a large pore structure, and enhancing antibacterial properties. The fabricated membrane was evaluated in term of rejection performance of oil particles from oily water mixture by incorporating different loadings of tetraethyl orthosilicate.

2. Methodology

2.1. Chemicals
Polyvinyl alcohol (PVA) with hydrolysis degree of 87-90% (MW: 85,000 – 124,000), polysulfone (PSF) with molecular weight (Mn) 22,000, and polyethylene glycol (molecular weight: 400 g/mol) used as additives. Tetraethylorthosilicate with 99% purity was used as a crosslinking agent and hydrochloric acid with 37% purity as the catalyst. All the chemicals above were obtained from Sigma Aldrich, Malaysia. In addition, 1-methyl-2- pyrrolidone (NMP) (purity 99%) and dimethyl sulfoxide (DMSO) used as solvents were obtained from Merck, Malaysia.

2.2. Membrane preparation
The integral membranes were prepared in 3 types of variations by using phase inversion method. Table 1 showed the formulations of each membrane (M1, M2, and M3).
Table 1. Integral membranes formulations.

| Membrane | PSF Solution | PVA Solution |
|----------|--------------|--------------|
|          | PSF (g)      | PEG 400 (g)  | NMP (g) | PVA (g) | TEOS (g) | DMSO (g) |
| M1       | 13           | 5            | 82      | 1       | 0        | 99       |
| M2       | 13           | 5            | 82      | 1       | 0.5      | 99       |
| M3       | 13           | 5            | 82      | 1       | 1        | 99       |

2.2.1 Preparation of PSF Solution. The PSF solution was prepared by dissolved 13 g of polysulfone pellet and 5 g of polyethylene glycol (PEG400) into 1-methyl-2-pyrrolidone (NMP) to prepare 13 wt.% of polysulfone. The mixture was heated and stirred continuously with 300 rpm at 80°C for 6 hours until it became homogeneous [8][9].

2.2.2 Preparation of PVA Solution. The polyvinyl alcohol (PVA) solution was prepared by adding 1 g of PVA in 99 g of dimethyl sulfoxide (DMSO) which was heated and stirred with 400 rpm at 80°C for 2 hours. Through a sol-gel method, 0.5 g of tetraethylorthosilicate (TEOS) was added as the crosslinker followed by 1 ml of HCl with 37wt.% as the catalyst. The mixture was stirred with 400 rpm for another 6 hours at 40°C. The same method was repeated for different TEOS concentrations; 0 wt.% and 1 wt.% [3][8].

2.2.3 Preparation of PSF/PVA Blend Membrane. The PSF / PVA solution was prepared by adding the 0.5 g of PVA solution into 100 g of PSF solution. The mixture was heated at 80°C and stirred for 1 hour with 750 rpm. Then, the mixture was left to cool at room temperature, 25°C [3].

2.2.4 Preparation of Integral Membrane. The blend membrane solution was poured onto a glass plate and spread using Baker Film Applicator at thickness 100 μm. Next, it was immersed in a coagulation bath for 24 hours for solidification. Then, the integral membrane was dried at room temperature for 24 hours. After that, the dried integral membrane was heat-cured at 45°C in an oven for 1 hour [3][10].

2.3 Oil Water Emulsion Preparation. Emulsifiers are the surfactants used to develop high surface pressure at emulsion surface. The oil water emulsion with 1000 mg/L oil concentration was prepared by mixing 1 L of distilled water with 30 mg of cetrimonium bromide (CTAB) surfactant and stirred for 5 minutes. Next, 1 g of vegetable oil was added into the distilled water for 10 minutes to ensure complete mixing of the mixture. The emulsion was stirred at 1250 rpm and heated at 30°C [11].

2.4 Permeation Performance of The Membranes. All the experiments were conducted at room temperature (~25°C). The permeation experiment of an ultrafiltration membrane was characterized by two different types of feed which are the pure water and oil water emulsion. The permeate flux was calculated by using Equation 1 and 2. The flux of pure water and oil water emulsion were measured by using Dead End filtration equipment, which was connected to a gas cylinder of compressed nitrogen that applied pressure to the feed. The filtration tests were carried out at 8 bar for 45 minutes, with 15 minutes interval each. The flux was measured gravimetrically with a digital electronic balance by weighing the permeate solution.

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J_p = \frac{Q_p}{A \Delta t} \quad (1)
\]

\[
Q_p = \frac{W_p}{\rho} \quad (2)
\]
Where $J_p$ is the permeate flux (L/m²h), $Q_p$ the volume of permeate (L), $A$ the effective membrane area (m²), $\Delta t$ is the sampling time (h), $W_p$ the weight of permeate (g), and $\rho$ the density of permeate (g/cm³) [12][13].

### 2.5 Oil Removal Efficiency

The same method in 2.4 was used while using oil water emulsion as feed. The oil concentration was 1000 mg/L. High oil concentration in feed increased the oil adsorption and caused great resistance for permeating water [14]. Equation 3 was used to calculate the percentage oil rejection.

$$R(\%) = \left(1 - \frac{C_p}{C_F}\right) \times 100$$

Where $C_p$ is the concentration of oil in the permeate (mg/L) and $C_F$ is the concentration of oil in the feed (mg/L). The oil concentrations in permeate and feed were determined using a UV–vis spectrophotometer. The oil-in-water emulsion was initially calibrated for different known oil concentrations in terms of absorbance recorded at a wavelength of 235 nm which is the wavelength at which maximum absorption occurs [15]. The figure 1 showed the schematic diagram of the experimental set-up.

![Figure 1. The schematic diagram of the experimental set-up [14]](image)

### 3. Results and Discussions

#### 3.1 Permeation Performance of The Membrane

Figure 2 shows the result of pure water flux for different type of membrane for filtration of 45 minutes. Based on Figure 2, the pure water flux of all membranes decreases as time increase. The increase in TEOS concentration resulted in higher water flux as observed from the figure where M3 recorded the highest water flux, M1 recorded the lowest water flux of water over time. The water flux related is with the size of pores and hydrophilicity of the membrane surface [12]. The flux declines as time increase during membrane filtration process is attributed to the concentration polarization on the membrane’s surface. M3 had higher pure water flux because of enhanced hydrophilicity of the membrane with the presence of silica from TEOS [16]. Similar results found by [17] where hydrophilicity and permeability of the membrane increase with the increase in TEOS content from 0wt.% to 2wt.% [18].

Figure 3 illustrates oil water emulsion flux against time. Similar results were recorded with pure water flux where the fluxes of oil water emulsion also decrease with time increase. However, the oil water flux decreases with the increase in TEOS concentration in membrane. M1 recorded the highest oil water flux, followed by M2 and M3. The reduction of oil water flux on M3 was due to the crosslinking reaction occurred which had resulted in greater combining forces between SiO₂ and PVA and the formation structure of the membrane possibly more compact [19]. Therefore, it allowed more oil particles to deposit on the surface of the membrane thus, creates the concentration polarization.
phenomenon. As a result, M3 had the lowest flux of oil in water compared to M2 and M1. The use of 1000mg/L of oil concentration also contributes towards this situation because the concentration of oil in the feeds directly affect the oil adsorption (fouling). Fouling is mainly caused by adsorption of oil on the membrane structure, which modifies the critical surface tension and the wettability, as well as the effectiveness of pore diameter, resulting in reducing the membrane permeability [20].

3.2 Oil Removal Efficiency
Figure 4 shows the percent rejection of oil for each membrane. As time increase, the percentage of oil rejection increase. After 45 minutes, the M3 and M2 achieved maximum rejection of 100%. In contrast M1 only achieved 60.2% of rejection. This situation could be explained through the dense structure of M2 and M3 as a result of crosslinking blend of PSF/PVA with TEOS, where pore size of the membrane is smaller than the diameter of the oil molecule. Different pattern for M1 could be related to situation where longer retention time of oily mixture in the filtration rig leads to gravity settling of water and oil particles, where oily mixture started to demulsify so that the separation of the oily water mixture finally occurs [21][22].

Apart from observation on the performance of the fabricated membrane, the visual observation on the membrane solution was also conducted. The opposite characteristic of polysulfone and polyvinyl alcohol will create a different compatibility degree with solvent such as N-methyl 2-pyrrolidone, which will be resulted in inhomogeneous blend and results to low structural stability of the integral membrane [23]. Therefore, a good selection of solvents is important during the blending. Low structural stability is due to significant differences in surface tension between these two materials that results in the segregation of the two layers of the integral membrane under swollen condition. Based on the obtained result, a homogeneous blend was obtained from good selection of solvents and through the sol-gel
method during crosslinking process respectively, which ensures the dispersion of the organic and inorganic components are at the molecular level in the membranes so that the resultant membrane solution is homogeneous [24].

4. Conclusion

Removing oil particles from oily water mixture by using the fabricated integral membrane was successful, where membrane M3 with 1 wt.% of TEOS had achieved the highest rejection of oil particles followed by M2 and M1. The presence of TEOS in the membrane had enhanced hydrophilicity of the membrane, that was reflected through the increase in pure water flux. The homogeneous blend of the membrane solution depicts the good selection of the solvents for both hydrophilic and hydrophobic polymers respectively, and as a result of crosslinking process. The finding shows the potential of the fabricated membrane to be further explored in the area of oily water mixture treatment process. Further study will be conducted by investigating on the effect of pressure during the separation process and the influence of different types of surfactants.

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