Modified Polysulfone Ultrafiltration Membrane for Humic Acid Removal During Peat Water Treatment

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Abstract. In this research, UF membrane was prepared by blending polysulfone (PSf) in DMAc with the addition of PEG400 and low concentration of acetone as additives. The effect of PSf/PEG400 and polymer/solvent ratio on the performance of PSf membrane was investigated during two hours of peat water filtration. The results showed that the increase of ratio PSf/PEG400 from 1:1 to 1:2.5 improved the membrane hydrophilicity. It was indicated by a decrease of water contact angle from 62° to 33° and increased water content in membrane structure from 65 to 74.5%. In addition, the pure water flux also increased up to 200 times. A stable flux is achieved when the ratio PSf/PEG is 1:2 and resulted in 84% rejection of humic acid. The increase of polymer concentration in the membrane solution reduced the pure water flux but increased the rejection of humic acid. Higher polymer concentration in membrane solution reduced fouling tendency towards the membrane surface. It showed that flux decline was reduced from 60% to 40% when the ratio of polymer/solvent concentration was changed from 40/60 to 50/50.

1. Introduction

Peat water is one of the water sources that commonly found in a tropical peatland ecosystem and characterized as yellow-brown colour water due to high concentration of humic acid and acidic. The humic acid endowed with aromatic and aliphatic characteristic which contribute to surface charge and reactivity mainly by the phenolic and the carboxyclic groups [1]. The reactions between water clarifying antiseptics and dissolved humic acid or phenolic molecules produce some carcinogen substances, which is known as disinfectant by-products (DBPs) that contribute negative effects to the human health in long term period [2]. Consequently, the peat water should be treated into clean water for daily use, particularly for drinking water supply.

Many methods have been proposed for peat water treatment, such as coagulation and flocculation [3, 4], photocatalytic degradation [5, 6], oxidation and ozonation [7], adsorption [8], and membrane filtration [9]. Among these methods, membrane technology has attracted most attention due to lower energy requirement while producing high quality of water product. Ultrafiltration (UF) membrane is one of membrane technologies, which has an excellent ability to remove a significant amount of macromolecule solute, colloids, bacteria, and viruses in water. In water treatment plant, the UF membrane can serve as disinfectant unit and significantly reduce chemical addition such as chlorine, coagulant, flocculant or other chemicals for PH adjustment [10]. However, the application of UF membrane in water treatment is limited by low rejection against humic acid (<50%) due to the smaller
molecular size of the substances (up to 200 Da) compared to the UF pore size [11-14]. Consequently, fouling by humic acid in the membrane structure becomes inevitable that resulted in increased pressure drop across the membrane and flux decline [15, 16]. For long term application, those problems may contribute to the operational troubles and membrane failure [17, 18]. Therefore, modification of UF membrane is required to improve selectivity while maintaining high productivity and has low-fouling properties [19, 20].

Most of commercial UF membrane is prepared by immersion precipitation method, which involves the transformation of liquid membrane phase into solid membrane matrix in immersion bath containing a non-solvent [21]. In immersion precipitation method, the final UF membrane structure is influenced by some parameters, i.e. the composition of membrane solution, non-solvent type, and operating conditions in the immersion bath [22]. Most studies in UF membrane manufacturing focus on variations in membrane solution composition to obtain desired membrane structure [23]. It has been reported that fouling of humic acid on the membrane structure can be minimized by improving the membrane hydrophilicity [24, 25]. Blending hydrophilic additives into the membrane solution is a simple method to improve the hydrophilicity of membrane. Polyethylene glycol (PEG) and polyvinylpyrrolidone (PVP) are widely used as additives due to their compatibility with polysulfone (PSf)-based polymer and their reasonable price [26, 27]. The effect of PEG on the resulted PSf membrane structure [28]. They found that the presence of PEG improved the membrane hydrophilicity significantly as well as the membrane porosity. The addition of PEG reduces the thermodynamic stability of the membrane solution, which further generates finger-like pore formation in the membrane structure [21].

PEG400 as additive to improve hydrophilicity of PSf membrane [16]. The increase of PEG400 concentration in the membrane structure induced open pore formation in the membrane surface layer that led to the reduction of humic acid rejection. The selectivity of the membrane is improved by the addition of acetone into the polymer solution, which resulted in higher rejection of humic acid [29]. In other research, The effect of PSf concentration on the UF membrane performances during peat water filtration at various operating pressure [30]. They blended PSf polymer with PEG400 (25%wt) and acetone (4%wt) in DMAC solvent. They found that the increase of PSf concentration (up to 24%wt) in polymer solution reduced the water flux significantly. Reversible fouling is formed on the resulted UF membrane and almost 90% of FRR was achieved when 18%wt of PSf is used in the polymer solution. Furthermore, the operating pressure during the filtration of peat water also played an important role to the fouling behavior of the UF membrane. High operating pressure, above 1 (one) bar, formed irreversible fouling in the membrane structure, which significantly reduced the water flux and reduced the humic acid rejection.

In the present work, the influence of membrane solution compositions consisting of PSf, PEG400, acetone, and DMAC is further investigated, where the polymer concentration (mixture of PSf and PEG400) is maintained constant (50% weight). The influence of PSf/PEG400 ratio is studied to the structure and characteristics of the resulted membrane. Furthermore, fouling on the membrane structure is also investigated during 2 (two) hours of peat water filtration.

2. Methods

2.1. Materials

The PSf used in this study was UDEL-P3500 (MB7) supplied by Solvay Advanced Polymer. DMAC was used as solvent with 99.9% purity, which supplied by Shanghai Jinsan Jingwei Chemical Co. Ltd. Demineralized water was used as non-solvent filled in a coagulation bath. Meanwhile, the peat water was obtained from Pekanbaru River-Riau, Indonesia, which has a measured pH of around 3.

2.2. Ultrafiltration membrane preparation

The flat-sheet UF-PSf membrane was prepared by dissolving 50% by weight of the polymer, consisting of PSf and PEG400, into a DMAC solvent (46% by weight) and acetone (4% by weight). The polymer solution was stirred in a closed stirred tank until a homogenous solution was obtained. Then, the
Homogenous solution was left until no bubbles are observed in the solution, and then casted on a flat glass with 150 μm thickness. The polymer film was immediately immersed into a demineralized water bath for 5 (five) hours or until the solvents was completely evaporated. The variation of casting polymer solution used in this experiment is shown in Table 1.

### Table 1. The composition of polysulfone (PSf) membrane solution

| Polymer/Solvent Ratio | Membrane Code | PSF: PEG400 Ratio | Composition of Membrane Solution (%) wt | Polymer (PSf+PEG400) | Acetone | DMAc |
|-----------------------|---------------|-------------------|-----------------------------------------|----------------------|---------|------|
| 50/50                | PSf-1         | 1:1               | 50                                      | 4                    | 46      |
|                      | PSf-2         | 1:1.5             |                                         |                      |         |      |
|                      | PSf-4         | 1:2               |                                         |                      |         |      |
|                      | PSf-4         | 1:2.5             |                                         |                      |         |      |
| 40/60                | PSf-5         | 1:1               |                                         |                      |         |      |
|                      | PSf-6         | 1:1.5             |                                         |                      |         |      |
|                      | PSf-7         | 1:2               |                                         |                      |         |      |
|                      | PSf-8         | 1:2.5             |                                         |                      |         |      |

2.3. Characterization of modified PSf membrane

The morphology of modified UF membrane was characterized by Scanning Electron Microscope (SEM) with 500x magnification. To view the cross section of the resulted membrane, the membrane sample was immersed in liquid nitrogen to preserve the pore structure and then cut using a metal clamp. Prior to imaging, the analysed part of sample was coated with a thin layer of gold.

Contact angle (CA) of demineralized water on the membrane surface was measured using sessile drop method. The CA values were measured at room temperature and taken as an average of six points with a droplet volume of 10 ± 1 μL [31]. Prior to CA measurement, the membranes were dried in vacuum desiccators for 48 hours.

Membrane porosity (ε) and equilibrium water content (EWC) were also studied to determine the hydrophilicity degree of the modified membranes. After immersion in demineralized water bath for 24 hours, the membrane was weighed in the wet state after carefully removing the surface water with a filter paper. Afterwards, the wet membrane was dried in vacuum desiccators for 48 hours and weighed until a constant weight was achieved [32]. Based on the weight of wet and dry membranes, the membrane porosity (ε, %) and EWC (%) were calculated by the following equations [33]:

\[
\varepsilon_p (%) = \frac{(W_w - W_d) / \rho_w}{\frac{W_w - W_d}{\rho_w} + \left(\frac{W_d}{\rho_p}\right)} \times 100
\]  

\[
\text{EWC} (%) = \frac{W_u - W_d}{W_u} \times 100
\]

where \(W_u\) is the weight of the wet membrane (g), \(W_d\) is the weight of the dry membrane (g), \(\rho_w\) is the density of pure water (g/cm\(^3\)), and \(\rho_p\) is density of the polymer (g/cm\(^3\)). EWC indicates the amount of water that fills the membrane pores.

2.4. Flux and selectivity measurement

The experimental procedures refer to our previous work, as shown in Figure 2 [29, 30]. A circular UF membrane module was used to measure water flux and rejection of humic acid during 2 (two) hours of peat water filtration. The active surface area of the circular flat-sheet membrane was 45 cm\(^2\). Prior to
the experiment, the flat-sheet membrane was rinsed with demineralized water for 30 minutes at 1 bar. The membrane system was operated in cross-flow mode at constant transmembrane pressure (15 psig or 1.02 bar).

![Figure 1](image-url)

**Figure 1.** Experimental set-up

The pure water flux (PWF) was calculated by the following equation [29]:

$$J_{W1} = \frac{V}{A \cdot \Delta t}$$  \hspace{1cm} (3)

$J_{W1}$ denotes pure water flux (Lm$^{-2}$h$^{-1}$), $V$ indicates volume of permeate (m$^3$), $t$ indicates permeation time (h), and $A$ indicates the membrane surface area (m$^2$). The peat water flux is measured by the same equation as Eq. (3) and mentioned as $J_t$.

Rejection of humic acid (R,%) after 2 (two) hour of peat water filtration was calculated by Eq. (4), as follows:

$$R(\%) = \left[1 - \frac{C_p}{C_f}\right] \times 100$$  \hspace{1cm} (4)

where $C_p$ and $C_f$ are concentration of humic acid in the permeate and feed solution. The concentration of humic acid was measured using UV/vis spectrophotometer with 254 nm wavelength [34].

3. Results and discussion

3.1. Morphology and characteristic of modified UF-PSf membranes.

Figure 2 shows SEM images of the modified membranes at polymer/solvent concentration ratio of 50/50 and various concentrations of PEG400. When the concentration of PEG400 in Psf solution increased, the membrane pore structure extended and approached the bottom of the membrane. The hydrophilic nature of PEG400 encouraged more water to diffuse into the Psf solution, which formed larger membrane pores. In addition, smooth finger-like membrane structures were formed at higher PEG400 concentrations. It is suggested that higher concentration of PEG400 enhanced the viscosity of Psf solution as well as the affinity of the solution to water. Consequently, the finger-like structures were formed without pore coalescence when high water concentrations entered the polymer solution.

Water contact angle measurements of the modified UF-PSf membrane are presented in Figure 3. The increase of Psf/PEG400 ratio in the polysulfone solution reduced the water contact angle, which indicated that the affinity of membrane to water was improved. By increasing Psf / PEG ratio of 1:1 (Psf-1) up to 1: 2.5 (Psf-4), water contact angle was reduced from 62° to 33°. The increasing affinity of water in the membrane at higher PEG400 concentration contributed to the increase water content in membrane structure. As shown in Table 2 that the EWC value of the membrane is increased from 65 to 74.5% when the Psf/PEG400 ratio is changed from 1:1 to 1:2.5. At Psf/PEG400 ratio of 1:1, the resulted membrane structure was very dense, which is indicated by the absence of water penetrating the membrane up to 30 psig. The presence of PEG400 in the polysulfone solution formed an open pore in the membrane skin structure, which can significantly improve the pure water flux. Membrane permeability increased up to 200 times when the ratio is increased from 1:1 to 1: 2.5.
Figure 2. SEM of UF-PSf membrane at a polymer/solvent ratio of 50/50 and various PSf/PEG400 ratios: (a) 1:1, (b) 1:1.5, (c) 1:2, and (d) 1:2.5 (magnitude of SEM: 500x)

Figure 3. Contact angle of UF-PSf membrane at various PSf/PEG400 ratios and polymer/solvent ratio of 50:50

Table 2. The influence of PSf/PEG400 ratio to the membrane hydrophilicity

| Polymer/Solvent Ratio | Membrane Code | EWC(%) | Porosity (%) | PWF (Lm⁻²h⁻¹) |
|-----------------------|---------------|--------|--------------|---------------|
| 50:50                 | PSf-1         | 65     | 0,33         | "             |
|                       | PSf-2         | 68     | 0,72         | 5,01          |
|                       | PSf-3         | 73,0   | 0,77         | 111,70        |
|                       | PSf-4         | 74,5   | 0,79         | 232,20        |

3.2. The influence of PSf/PEG400 ratio on the peat water flux

The influence of PSf/PEG400 ratio on peat water flux was observed at a fixed polymer/solvent ratio of 50:50. Since the membrane skin layer structure was very dense at PSf/PEG400 ratio of 1:1, the peat water was unable to penetrate the membrane. High viscosity of the membrane solution due to high concentration of PSf inhibited pore formation in the membrane surface structure and formed a dense layer. As the decrease of PSf concentration and further increase of PEG400 concentration, the viscosity of the membrane is lowered and open pore in the membrane skin layer is formed. At PSf/PEG ratio of 1:1.25, the resulted membrane was severly fouled by humic acid, which is indicated by the significant flux decline in the first 20 minutes of the filtration process. High concentration of PEG400 in the polysulfone solution enhanced the open pore size on membrane surface layer, therefore the humic acid molecules are easily dragged into the UF membrane structure and rapidly formed irreversible fouling.
In addition, fouling in the membrane structure increased the membrane hydrophobicity, which contributed to further adsorption of organic compounds on the membrane surface. A stable flux is obtained at a PSf/PEG400 ratio of 1:1.5.

![Figure 4](image_url)

**Figure 4.** The influence of PSf/PEG400 ratio in polymer solution on modified UF membrane at operating pressure of 15 psig.

3.3. The influence of polymer and solvent ratio on fouling and rejection of humic acid

The influence of polymer and solvent ratio on fouling of organic matter is presented in Figure 5, which is observed at a fixed PSF/PEG ratio of 1:2. It was found that a significant reduction in peat water flux was achieved for both membrane composition, which indicated the existence of fouling in the first moments of filtration. More severe irreversible fouling is formed on UF membranes prepared with lower polymer concentrations. It is suggested that low polymer concentrations allowed the larger open pore formation on the membrane surface, thus the resulted UF membrane is severed to irreversible fouling and reduced the peat water flux. Flux decline was reduced from 60% to 40% when the ratio of polymer/solvent concentration was changed from 40/60 to 50/50. The fouling in the membrane structure influenced the membrane selectivity. As shown in Table 3 that higher rejection of humic substances is achieved at lower concentration of polymer and higher concentration of PEG400. A decrease in effective pore size of the membrane due to irreversible fouling led to an increase in the membrane's ability to reject the humic substances.

![Figure 5](image_url)

**Figure 5.** The influence of polymer and solvent ratio on peat water flux at operating pressure of 15 psig and PSF/PEG ratio of 1:2.
Table 3. The influence of polymer and solvent ratio on the humic acid rejection

| Polymer/Solvent Ratio | Membrane Code | PSf:PEG400 Ratio | Composition of Membrane Solution (%wt) | Polymer (PSf+PEG400) | Acetone | DMAc |
|-----------------------|---------------|------------------|---------------------------------------|----------------------|--------|------|
| 50/50                 | PSf-1         | 1:1              |                                       | -                    |        |      |
|                       | PSf-2         | 1:1.5            | 50                                    | 4                    | 46     | 80   |
|                       | PSf-4         | 1:2              |                                       | 84                   |        |      |
|                       | PSf-4         | 1:2.5            |                                       | 85                   |        |      |
| 40/60                 | PSf-5         | 1:1              |                                       | 77                   |        |      |
|                       | PSf-6         | 1:1.5            | 40                                    | 4                    | 56     | 86   |
|                       | PSf-7         | 1:2              |                                       | 86                   |        |      |
|                       | PSf-8         | 1:2.5            |                                       | 88                   |        |      |

4. Conclusion
A modified ultrafiltration membrane has been prepared by dissolving acetone and PEG400 into a polysulfone solution in a DMAc solvent. The effect of polymer/solvent ratio and PSf/PEG400 on morphology and ultrafiltration membrane performance has been investigated in various concentrations of membrane solution. From the SEM photo observation, the membrane pore structure extended and approached the bottom of the membrane when the concentration of PEG400 is enhanced. Furthermore, the increase in PSf/PEG400 ratio from 1:1 to 1:2.5 in membrane solution improves the hydrophilicity. It is indicated by a decrease of water contact angle from 62° to 33° and increased water content in membrane structure from 65 to 74.5%. Meanwhile, the pure water flux increases up to 200 times.

The UF-PSf membrane with PSf/PEG400 ratio of 1:2 produces stable flux, produce a stable flux, either on polymer/solvent ratio of 40:40 or 50:50. More than 84% of humic acid rejection was achieved. Membranes with higher polymer ratios result in denser surface structures with smaller pores impacting on the higher rejection of humic acid. Higher polymer concentration in membrane solution reduced fouling tendency towards the membrane surface. Flux decline is reduced from 60% to 40% when the ratio of polymer/solvent concentration is changed from 40/60 to 50/50.

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