



Research Paper

Fouling and Rejection Characteristic of Humic Substances in Polysulfone Ultrafiltration Membrane

P.T.P. Aryanti, S. Subagjo, D. Ariono, I.G. Wenten*

Department of Chemical Engineering, ITB, Jl. Ganesha 10, Bandung 40132, Indonesia

HIGHLIGHTS

- Low fouling polysulfone membrane was prepared for humic substances removal.
- Over than 80% humic substances rejection could be obtained.

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ABSTRACT

In this study, the ultrafiltration membrane for humic substance removal was prepared by blending polysulfone with a high concentration of PEG400 as additives. The influences of the additive to the fouling resistance capability and humic substances rejection of the polysulfone membrane were investigated. The addition of 35%wt of PEG400 concentration improved the pure water flux up to 200, but resulted in higher fouling resistance of humic substances. High concentration of PEG400 increased irreversible fouling and significantly reduced the flux recovery ratio of the membrane. More than 80% humic substances rejection is achieved when a high concentration of PEG400 was added into the membrane solution

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1. Introduction

In the recent water treatment field, high attention is given to the humic substances removal, due to their reactivity with water clarifying antiseptics (such as chlorine) that form carcinogenic substances known as disinfectant by-products (DBPs), such as tri-halomethanes (THMs) and haloacetics (HAAs) [1]. The reactivity of humic substances is contributed by both molecular weight and aromaticity, which depends on aliphatic, phenolic, and carboxylic functional groups in their structures [2,3]. Reverse osmosis (RO) and nanofiltration (NF) processes have been extensively used and considered as innovative solutions to remove humic substances, since they exhibit many advantages, such as high product quality, small footprint area, and less chemical and energy consumption compared to conventional processes. However, these membranes are operated in high pressure conditions that contribute to high water cost. In addition, another major issue to be considered during membrane operation is the adsorption of humic substances on the membrane surface, which leads to significant loss of productivity and a further increase of operational pressure. Therefore, a low pressure membrane for humic substances removal is continuously developed.

Several studies performed the humic substances removals using the

ultrafiltration (UF) membrane. This membrane is limited by low rejection of soluble humic substances and a continuous membrane flux decline by fouling [4-6]. Since humic substances tend to be hydrophobic and negatively charged in natural water, most of membrane modification methods are primarily focused on increasing membrane hydrophilicity and introducing negative charge into the membrane structure to avoid excessive fouling. Various methods have been reported, such as the blending method, chemical grafting, radiation treatment, plasma treatment, and physical adsorption [7-12]. Blending polymeric materials with hydrophilic or charged additives are considered an attractive and simple method. The common additives used are hydrophilic polymer, such as polyvinyl pyrrolidone (PVP) and polyethylene glycol (PEG), and charged polymer, such as sulfonated polyether ether ketone (SPEEK). Bowen et al. (2002) blended polysulfone with sulfonated poly(ether ether ketone) (SPEEK) to induce high negative charge into the membrane structure [13,14]. These membranes provided high rejection of humic acid and low fouling properties. Hwang et al. (2012) blended hydrophobic polyphenylsulfone (PSU) with polyetherimide (PEI) and PEG [15,16]. The blended polymeric membrane possessed weak negative charge and exhibited good resistance to humic substance fouling. Recently, super

* Corresponding author at: Tel/fax: +62 2511404.
 E-mail address: igw@che.itb.ac.id (I.G. Wenten).

hydrophilic and antimicrobial nanoparticles are commonly chosen as additives to produce a low fouling nanocomposite UF membrane, such as TiO₂, SiO₂, ZrO₂, or silver [17,18]. Hamid et al. (2011) prepared a hollow fiber membrane from dope solution containing polysulfone/DMAc/PVP/titanium dioxide (TiO₂) by the wet spinning method, which rejected humic substances above 91% [6]. To further improve the effectiveness of the photo catalytic activity, TiO₂ can also be combined with a non-metallic or metallic element, such as silver (Ag) [19]. Major problems in utilizing nanoparticles such as blending materials for the commercial membranes manufacture are the incorporation of nanoparticles into polymeric membranes and the expensive cost of nanoparticle materials. Further researches are still needed in order to improve membrane performance.

Besides hydrophilic and negatively charged polymers, several volatile solvents have also been used as additives in polysulfone membrane preparation to improve the membrane selectivity by reducing the skin layer pore size. Ismail and Lai (2003) introduced tetrahydrofuran (THF) into the polysulfone membrane solution that induced a defect-free and ultrathin skin layer [20]. These properties of the resulted membrane contribute to higher selectivity of the membrane. Aryanti et al. (2013) studied the effect of PEG400 and a low concentration of acetone additive on the hydrophilicity and selectivity of the polysulfone membrane [21]. They found that over 80% rejection of humic substances is achieved by the addition of 25%wt of PEG400 and 4%wt of acetone. However, the membrane solution showed the earlier phase separation when the PEG400 was increased up to 30%wt. It has been known that a high concentration of PEG400 improved membrane hydrophilicity, which also plays an important role in organic matter rejection. In the present work, the influence of PEG400 is investigated with regard to its fouling and rejection of humic substances during peat water, and then compared with the resulted membranes in the previous work [21]. The fouling resistance of the membrane is observed by calculating flux recovery ratio (FRR) and flux loss after two (2) hours of peat water filtration. The effect of both additives in the membrane solution provides a basis for the rational selection of the membrane composition for low molecular weight compounds in water, particularly humic substances.

2. Materials and Method

For the experimental procedure we refer to our previous research [21]. The flux of the membrane is measured by demineralized water, both before and after the filtration of peat water. The selectivity of the polysulfone membrane is estimated by humic substances rejection during peat water filtration for two (2) hours.

2.1. Materials

The type of polysulfone used in this experiment is UDEL-P3500 (MB7), which is supplied by Solvay Advanced Polymer. DMAc with 99.9% purity is used as solvent without further purification and supplied by Shanghai Jingsan Jingwei Chemical Co. Ltd. PEG400. Demineralized water is used as non-solvent in the coagulant bath to induce the formation of membrane structure. The peat water is obtained from Pekanbaru River – Riau, Indonesia, which has a measured pH of around 3.

2.2. Membrane preparation

The flat sheet membrane is prepared by the immersion precipitation method. Polysulfone is dissolved into DMAc at room temperature and then mixed with PEG400 as additive. The membrane solution is stirred for around 12 hours in a closed stirred tank until a homogenous solution is obtained and then left without stirring until no bubbles are observed. Afterwards, the solution is casted on a flat glass plate with 200µm thickness and immediately immersed into a demineralized water bath as coagulant for five (5) hours or until the solvent is completely evaporated. The variation of casting membrane solution used in this experiment is shown in Table 1.

2.3. Flux and selectivity measurement

The experimental setup used in the present work is the same as our previous work (Figure 1) [21]. Prior to the experiment, a circular flat sheet membrane is placed inside the membrane module and rinsed by demineralized water for 30 minutes at 1 bar. The active surface area of the flat sheet membrane is 45 cm².

Table 1
Composition of Membrane Solution.

| Membrane Code | Composition of membrane solution (%wt) | | | |
|---------------|--|--------|---------|------|
| | PSF | PEG400 | Acetone | DMAc |
| PSf-1a | 20 | 0 | 0 | 80 |
| PSf-2a | 20 | 20 | 0 | 60 |
| PSf-3a | 20 | 25 | 0 | 55 |
| PSf-4a | 20 | 30 | 0 | 50 |
| PSf-5a | 20 | 35 | 0 | 45 |
| PSf-6a | 20 | 40 | 0 | 40 |
| PSf 1b* | 20 | 0 | 4 | 76 |
| PSf 2b* | 20 | 5 | 4 | 71 |
| PSf 3b* | 20 | 10 | 4 | 66 |
| PSf 4b* | 20 | 15 | 4 | 61 |
| PSf 5b* | 20 | 20 | 4 | 56 |
| PSf 6b* | 20 | 25 | 4 | 51 |

2.3.1. Pure water flux (PWF) and peat water flux

Pure water flux is determined using demineralized water and measured in cross flow mode at constant pressure (15 psig or 1.02 bar), followed by peat water flux measurement during two (2) hours of filtration. Peat water flux is measured at 0, 1 and 2 hours of filtration. PWF and peat water flux is calculated by the following equation:

$$J_{w1} = \frac{V}{A \times \Delta t} \quad (1)$$

where J_{w1} is pure water flux (PWF) (Lm⁻²h⁻¹), V is volume of permeate (m³), t is permeation time (s), and A is membrane surface area (m²). Peat water flux is mentioned as J_t that is measured at the first time of filtration calculated by the same equation as Eq.(1).

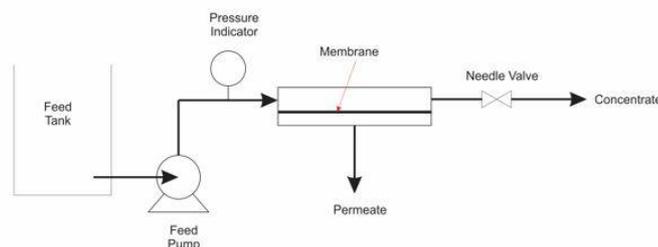


Fig. 1. General scheme of the applied experimental set-up.

2.3.2. Filtration performance and fouling analysis

After two (2) hours of peat water filtration, the flat sheet membrane is flushed by demineralized water for around 45 minutes. The pure water flux (PWF) of the cleaned membrane is measured and denoted as J_{w2} . Flux recovery ratio (FRR) is calculated by Eq. (2) to investigate the effect of organic matter on membrane fouling during peat water filtration.

$$FRR(\%) = \left(\frac{J_{w2}}{J_{w1}} \right) \times 100 \quad (2)$$

Flux loss due to reversible (r_r) and irreversible (r_{ir}) fouling in the polysulfone membrane are also calculated. Reversible fouling (r_r) is formed by gel formation on the membrane surface, which can be easily removed by flushing or the backwash method. Meanwhile, irreversible fouling (r_{ir}) is pore blocking fouling that shall be removed by chemical cleaning. In this research, both reversible and irreversible flux loss due to fouling are evaluated by the flushing method. The flux loss is calculated by the following equation:

$$r_r = \frac{J_{w2} - J_t}{J_{w1}} \quad (3)$$

$$r_{ir} = \frac{J_{W1} - J_{W2}}{J_{W1}} \quad (4)$$

Total flux loss (r) is the sum of r_r and r_{ir} . The total resistance in the polysulfone membrane is calculated by the resistance-in-series model, as shown in Eq. (5).

$$J = \frac{\Delta P}{\mu R_t} = \frac{\Delta P}{\mu (R_m + R_f)} \quad (5)$$

In Eq. (5), ΔP is transmembrane pressure (bar), μ is viscosity of solution (bar.h), R_t is total resistance (m^{-1}), R_m is membrane resistance (m^{-1}) and R_f is fouling resistance (m^{-1}). The membrane resistance (R_m) is determined by filtering demineralized water through the membrane, and then calculated by the following equation:

$$R_m = \frac{\Delta P}{\mu J_{W1}} \quad (6)$$

After two (2) hours of peat water filtration, the peat water flux is measured in order to calculate the total fouled membrane (R_{ft}). Then, R_f is determined by subtracting the membrane resistance (R_m) from the total fouling resistance (R_{ft}), as shown in Eq. 7.

$$R_f = R_{ft} - R_m \quad (7)$$

2.3.3. Rejection of humic substances

Humic substance content in raw and treated peat water after two (2) hours filtration is analyzed using UV/vis spectrophotometer with 254 nm wavelength ($\lambda=254$ nm) [22]. The humic substances rejection (R ,%) is calculated by the following equation [23]:

$$R(\%) = \left[1 - \left(\frac{C_p}{C_f} \right) \right] \times 100 \quad (8)$$

where C_p and C_f are concentration of humic substances in the permeate and feed solution.

3. Result and Discussion

In the following section, analysis of the relationship between PEG400 concentration on hydrophilicity, fouling resistant capability and selectivity is presented. Then, those membrane performances are compared with the previous obtained polysulfone membranes that were blended with 4%wt of acetone concentration [21].

3.1. Effect of PEG400 concentration on polysulfone membrane flux

It has been known that the addition of PEG into membrane solution improved the membrane hydrophilicity and permeability [24, 25]. The effect of PEG400 concentrations towards pure and peat water flux are shown in Table 2. It shows that the PWF of the polysulfone membrane can be improved about 200 times when the PEG400 concentration in the membrane solution is increased up to 35%wt. High concentration of entrapped PEG400 in the membrane matrix increases the rate of water through the membrane [24, 26]. Meanwhile, the presence of acetone in the membrane solution increases membrane hydrophobicity that is indicated by the low water flux. During the membrane structure formation, the rapid loss of acetone leads to higher polymer concentration in the membrane skin layer and produces a tight skin pore size [27].

As found in several researches, the presence of humic substances and other organic matters in peat water have extremely influenced the membrane flux. At low pH, humic substances tend to form a less charged compact configuration, which is attributed by the reduced electrostatic repulsion between the humic acid molecules in the solution [2]. In addition, low pH solution also reduces the electrostatic repulsion between the cleaned membrane and humic substance molecules. As a result, the deposition of

humic substances on the membrane surface is enhanced. The peat water flux decline on polysulfone membranes after two (2) hours of peat water filtration are compared in Figure 2. In the absence of acetone in the membrane solution, the obtained membrane is more susceptible to organic fouling as indicated by the sharp flux decline. The rapid flux decline occurs by the addition of 20%wt PEG400 concentration. It suggests that the formation of open pore due to high concentration of PEG400 allows the irreversible fouling in the membrane structure and reduces the peat water flux through the membrane [28]. Meanwhile, the stable flux decline could be achieved by the addition of acetone in the membrane solution [21]. The tight skin layer formation due to rapid loss of acetone during membrane structure formation improved the antifouling of the polysulfone membrane.

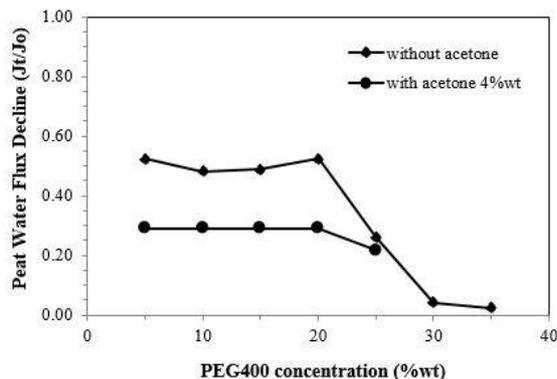


Fig. 2. The effect of PEG400 concentration to peat water flux decline after two (2) hours of peat water filtration.

The effects of PEG400 concentrations on the membrane fouling characteristics are also evaluated by measuring flux recovery ratio (FRR) and flux loss. The experimental results are shown in Figure 3. Flux recovery measurement is performed in order to determine the cleaning efficiency related to the fouling-resistant capability of the membrane. It is estimated by comparing the membrane flux between the used and cleaned membrane. Figure 3-A shows the polysulfone membrane performance resulted in the present work (without acetone). The FRR value of the membrane does not significantly decline by the addition of PEG400 up to 20%wt, which decreased from 92 to 79%. Within this range of PEG400 concentration, membrane fouling is still dominated by reversible fouling, which can be easily cleaned by the cross-flow method. However, a further increase of PEG400 concentration above 20%wt suppresses the FRR value up to 10% due to the dominance of irreversible fouling. This means that high PEG400 concentration in the membrane solution reduces membrane fouling resistance and enhances the solute-membrane interactions, although it produces high membrane permeability. The irreversible fouling in the membrane structure is attributed by the formation of open pore in the skin layer and substructure of the membrane [28]. Moreover, the irreversible fouling can also be attributed to the compact molecule configuration in low pH solution, which allows the humic substance molecules flowing into the membrane structure [2].

The above-mentioned irreversible fouling could be minimized by the addition of low concentration of acetone in the membrane solution indicated by higher FRR as presented in Figure 3-B [21]. Improvement in low fouling membrane performance is attributed to the tight skin layer formation due to immediate solvent loss that leads to high polymer concentration in the membrane's top layer. With the addition of 4%wt acetone in the membrane solution, the obtained membrane has irreversible resistance value and FRR of about 0.11 and 0.9, respectively, as the PEG concentration is maintained at 25 %wt. This result indicates that the used membrane can still retain its high water flux property after the cleaning mechanism through the flushing method. It then means that interaction between the membrane and humic substance molecules can be reduced as acetone is added to the membrane solution.

3.2. Effect of PEG400 concentration on total resistance of the fouled membrane

The effects of PEG400 concentration on total resistance of the fouled

Table 2
Effect of PEG400 concentration to permeability of polysulfone membrane.

| Membrane code | Composition of membrane solution (%wt) | | | | Permeability (PWF) ($\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$) | Peat Water Flux ($\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$) |
|---------------|--|--------|---------|------|---|--|
| | PSF | PEG400 | Acetone | DMAc | | |
| PSf-1a | 20 | 0 | 0 | 80 | 15 | 0 |
| PSf-2a | 20 | 5 | 0 | 75 | 27 | 14 |
| PSf-3a | 20 | 10 | 0 | 70 | 66 | 32 |
| PSf-4a | 20 | 15 | 0 | 65 | 92 | 45 |
| PSf-5a | 20 | 20 | 0 | 60 | 118 | 62 |
| PSf-6a | 20 | 25 | 0 | 55 | 273 | 72 |
| PSf-7a | 20 | 30 | 0 | 50 | 285 | 12 |
| PSf-8a | 20 | 35 | 0 | 45 | 301 | 7 |
| PSf-1b* | 20 | 0 | 4 | 76 | 0 | 0 |
| PSf-2b* | 20 | 5 | 4 | 71 | 20 | 6 |
| PSf-3b* | 20 | 10 | 4 | 66 | 40 | 12 |
| PSf-4b* | 20 | 15 | 4 | 61 | 60 | 19 |
| PSf-5b* | 20 | 20 | 4 | 56 | 80 | 23 |
| PSf-6b* | 20 | 25 | 4 | 51 | 126 | 28 |
| PSf-7b* | 20 | 30 | 4 | 46 | Demix | |
| PSf-8b* | 20 | 35 | 4 | 41 | Demix | |

All flux are measured at fixed pressure operation 1 bar (15 psig).

*Refer to the previous research result [49].

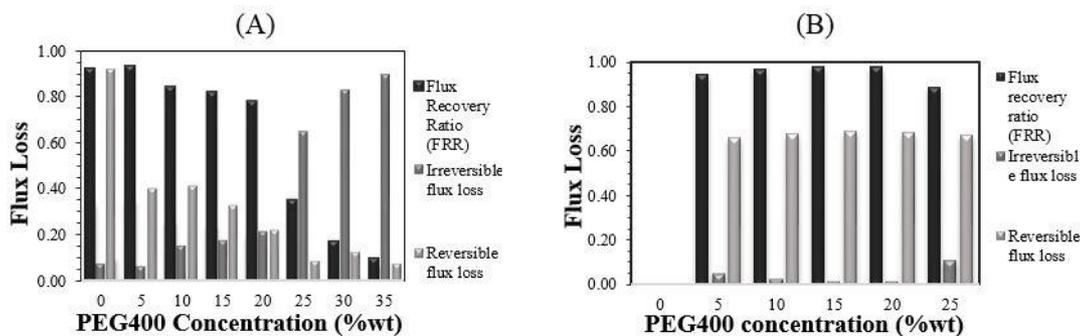


Fig. 3. Effect of PEG400 concentration to membrane flux loss of polysulfone membrane: (A) without and (B) with the addition of 4% wt acetone.

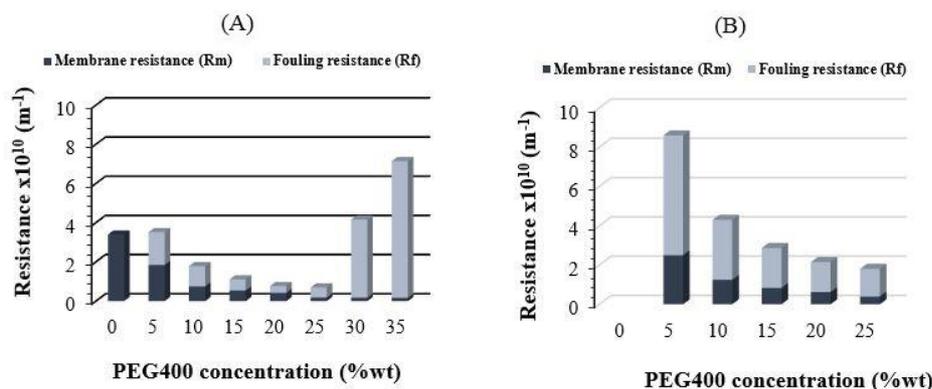


Fig. 4. The Effect of PEG400 concentration on total resistance of polysulfone membrane after 2 (two) hours of filtration: (A) without and (B) with the addition of 4% wt acetone.

membranes are presented in Figure 4. In both figures, the membrane resistance is continuously reduced by the addition of PEG400 in the membrane solution, which contributes to the enhancement of pure water flux as shown in Table 2. However, the decrease of membrane resistance is not always followed by the decrease of fouling resistance. As shown in Figure 4-A, the significant increase of fouling resistance is found when 30% wt of PEG400 is added into the membrane solution. It suggests that the formation of open pore in the membrane skin layer due to high concentration of additive leads to the irreversible fouling. As a result, a higher value of fouling

resistance is obtained. On the other hand, the addition of 4% wt acetone concentration in the membrane solution provides higher fouling resistance value, as displayed in Figure 4-B. The interaction between the membrane surface and humic substances is reduced due to the tight pore in the membrane skin layer. As a result, the irreversible fouling on the membrane surface could be prevented. Figure 5 presents the humic substances fouling after two (2) hours of peat water filtration. This figure shows that higher accumulation of humic substances on the polysulfone membrane is achieved without the addition of acetone in the membrane solution.



Fig. 5. Humic substances fouling on polysulfone membrane: (A) without and (B) with the addition of 4%wt acetone.

3.3. Effect of PEG400 concentration on humic substances rejection

Figure 6 demonstrates the effect of PEG400 concentration on average humic substances rejection during peat water filtration. The decrease in humic substances rejection is initially observed as PEG400 concentration is increased up to 20%. Then, it starts to rise as more PEG400 is added into the solution. Higher rejection at above 20%wt of PEG400 is associated with irreversible fouling in the membrane structure, which reduces the effective pore in the membrane structure and acts as an additional selective layer. On the contrary, the addition of 4% wt acetone improves the humic acid rejection over 85% regardless of the PEG400 concentration. This is attributed to the improvement in membrane skin structure that increases membrane selectivity.

4. Conclusion

The relationship between PEG400 concentration in polysulfone membrane solution to fouling and rejection characteristics of humic substances have been investigated. It is found that the addition of PEG400 improves the membrane hydrophilicity. The pure water flux is enhanced up to 200 times more than the unmodified membrane when 35%wt of PEG400 is added into the membrane solution. The increase of membrane hydrophilicity is not followed by the improvement of fouling resistance of the membranes. It is analyzed that the irreversible fouling is increased at a high concentration of PEG400. A high concentration of PEG400 induces the formation of an open pore in the membrane skin layer, which may contribute to the irreversible fouling. This leads to significant reduction in the flux recovery ratio. The humic substances rejection reduces from 76% to 20% when the PEG400 concentration is enriched up to 20%. The humic substances rejection starts to elevate more than 80% as PEG400 concentration is further increased up to 35%wt.

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