Analysis of Fouling Mechanism in Polysulfone based Ultrafiltration Membrane during Peat Water Filtration

Danu Ariono* and Anita Kusuma Wardani
Department of Chemical Engineering, ITB, Jl. Ganesha 10, Bandung 40132, Indonesia

* Email: danu@che.itb.ac.id

Abstract. Polysulfone (PSf) has been widely used as ultrafiltration (UF) membrane material due to its thermal and chemical stability. However, membrane fouling becomes a severe problem limiting the potential of PSf membrane. This fouling is mainly formed by deposition of organic onto membrane surface which resulting the decrease of permeate flux. There are four fouling mechanisms proposed by Hermia (1982), namely cake formation, standard blocking, intermediate blocking, and complete blocking. In this work, the types of fouling mechanism that occurred in PSf based UF membrane during peat water filtration were investigated. In addition, the effect of trans-membrane pressure was also studied. The determination of fouling mechanism was conducted by optimization of the fouling parameters, including Kcf (cake formation), Ksb (standard blocking), Kib (intermediate blocking), and Kcb (complete blocking). The results showed that complete blocking became the dominant fouling mechanism in this work. Meanwhile, the trans-membrane pressure did not affect fouling mechanism.

1. Introduction
The stringent regulations of drinking water lead to increased attention in developing ultrafiltration (UF) membrane for water treatment. UF membrane offers several advantages such as high product quality, a small footprint area, and low energy consumption [1-6]. Furthermore, UF is able to remove viruses, bacteria, colloids, and larger particulate matter from suspensions [7-12]. One of the polymers commonly used as UF membrane material is polysulfone (PSf) since it has good chemical and thermal stability [13, 14]. However, PSf membrane is naturally hydrophobic and susceptible to natural organic matter (NOM) fouling during surface water treatment. This fouling not only leads to productivity decline, but also requires additional energy supply to keep the membrane performance constant [15-21].

Membrane fouling is a result of interaction between the membrane material and the components in the feed water. Regarding NOM fouling mechanisms, it is generally recognized that there are four main fouling mechanisms for UF membrane, as proposed by Hermia [22]. They are complete blocking, intermediate blocking, standard blocking or pore constriction, and cake formation. In complete blocking and intermediate blocking, the particles have the same size with membrane pores, thus the particles seal off pore entrances and prevent flow. However, for intermediate blocking, there is an accumulation of some particles on top of other deposited particles. This accumulation does not occur in complete blocking. Meanwhile, standard blocking results in a decrease of the membrane porosity and increase of membrane resistance since the bulk phase particles are small enough to enter the membrane pores [23]. The particles are accumulated inside membranes on the walls of cylindrical
pores, thus the pores become constricted and the permeability of the membrane is reduced. Furthermore, cake formation occurs when bigger particles accumulate on the surface of a membrane in a permeable cake of increasing thickness that increases membrane resistance.

In this work, PSf based UF membrane was prepared by inversion phase method. Peat water filtration was used to characterize the organic fouling on the membrane. The types of fouling mechanism that occurred in PSf based UF membrane during peat water filtration were investigated by optimization of the fouling parameters, $K_{cf}$ (cake formation), $K_{sb}$ (standard blocking), $K_{ib}$ (intermediate blocking), and $K_{cb}$ (complete blocking). In addition, the effect of trans-membrane pressure was also evaluated.

2. Materials and Method

2.1 Materials

The PSf (UDEL-P3500 MB7) from Solvay Advanced polymer was used as the main material. Meanwhile, Polyethylene glycol (PEG400) was chosen as an additives, Dimethylacetamide (DMAc) with a purity of 99.9% (Shanghai Jingsan Jingwei Chemical Co. Ltd) was used as a solvent, and demineralized water was used as a coagulant to induce the formation of membrane structure. Flux analysis was conducted using peat water from Dumai river-Riau, Indonesia.

2.2 UF membrane preparation

The UF membrane was prepared by blending 20%wt of PSf with 20%wt of PEG400 and 60%wt of DMAc. The membrane solution was stirred for about 8 hours in a closed stirred tank and then left without stirring until no bubbles appeared. Then, the membrane solution was casted on the flat glass plate and immediately immersed in demineralized water. The peat water filtration was conducted in TMP of 10 and 30 psi.

2.3 Simulation of fouling mechanism

Determination of fouling mechanism based on the experimental data was conducted by considering the flux expressions relative to the fouling mechanisms, which was established by Hermia [22]. Hermia proposed a mathematical model describing fouling mechanisms, as the following equation:

$$\frac{d^2t}{dV^2} = k (\frac{dt}{dV})^m$$  \hspace{1cm} (1)

Here $t$ is the filtration time and $V$ is the total filtered volume. $m$ denotes a parameter of cake filtration, standard blocking, intermediate blocking, and complete blocking respectively, each of which has values of 0, 3/2, 1, and 2. Meanwhile, the value of $k$ represents fouling parameter, which varied for each UF processes.

The Flux of UF membrane could be defined by equation (2) [1].

$$J = \frac{1}{A} \frac{dV}{dt}$$  \hspace{1cm} (2)

where $A$ is membrane area and $J$ is permeate flux. By combining Hermia’s mathematical model with flux expression, the flux decline could be expressed by equation (3).

$$\frac{dJ}{dt} = -kJ(A)^{2-m}$$  \hspace{1cm} (3)

Furthermore, the equation characterizing of flow decline due to fouling is detailed in table 1.
Table 1 Flux equation for each fouling mechanism

| Fouling mechanism     | Flux equation                      | Equation number |
|----------------------|-----------------------------------|-----------------|
| Cake formation       | \( J_v = \frac{J_{v,0}}{(2K_{cf}J_{v,0}^2t + 1)^{1/2}} \) \( K_{cf} = kA^2 \) | (4)             |
| Standard blocking    | \( J_v = \frac{4J_{v,0}}{(2K_{sb}J_{v,0}^{1/2}t + 2)^2} \) \( K_{sb} = kA^{1/2} \) | (5)             |
| Intermediate blocking| \( J_v = \frac{J_{v,0}}{K_{ib}J_{v,0}t + 1} \) \( K_{ib} = kA \) | (6)             |
| Complete blocking    | \( J_v = J_{v,0} \exp(-K_{cb}t) \) \( K_{cb} = k \) | (7)             |

3. Results and Discussion

3.1 Flux Characteristic of Polysulfone based Ultrafiltration Membrane

Figure 1 presents the peat water flux profile as a function of peat filtration time at a constant feed velocity. It shows that the peat water flux was sharply declined in the earlier of filtration process due to rapid accumulation of organic matter on the membrane surface. The rapid accumulation of organic matter on the membrane surface was led by the addition of PEG400 that contributes to the formation of an open pore in skin layer and also in sub-structure of the membrane [24].

![Effect of TMP on peat water flux](image)

Figure 1 Effect of TMP on peat water flux

Furthermore, the flux of higher TMP (30 psi) was declined sharper than lower TMP (10 psi). At higher pressure, severe fouling of membranes occurred under higher initial flux since the organic
substances were transported faster to the membrane and accumulates near the membrane surface. The organic fouling layer then became more compressed that led to an increase in hydraulic resistance [25].

3.2 Determination of Fouling Mechanism
To determine the fouling mechanism of ultrafiltration process in this work, the optimization of fouling parameters ($K_{cf}$, $K_{sb}$, $K_{ib}$, and $K_{cb}$) was conducted by the least squares method programmed with Matlab R2015b. The values of fouling parameters are presented in Table 2.

Table 2 Fouling parameter for each mechanism

| TMP (psi) | $K_{cf}$   | $K_{sb}$   | $K_{ib}$   | $K_{cb}$   |
|-----------|------------|------------|------------|------------|
| 10        | 2.10E-07   | 4.08E-04   | 3.85E-05   | 4.30E-03   |
| 30        | 5.40E-07   | 6.10E-04   | 7.40E-05   | 4.90E-03   |

Figure 2 shows that the flux decline was well described by the complete blocking mechanism. In complete blocking, the particles had the same size with membrane pores, thus particles deposited on the membrane surface and block the entrances of membrane pores completely with no overlapping particles. Since the number of membrane pores was decreased by deposited particles, the filtration resistance increased and the flux decreased as a function of time [26]. This model applied to both trans-membrane pressures of 10 and 30 psi. It indicated that TMP had no effect to the fouling mechanism in PSf based UF membrane during peat water filtration.
4. Conclusion
In this work, PSf based UF membrane was prepared by phase inversion method. Peat water filtration was used to determine membrane performance. Furthermore, the types of fouling mechanism that occurred in PSf based UF membrane during peat water filtration were investigated. The results showed that complete blocking became the dominant fouling mechanism in this work. Meanwhile, fouling mechanism was not affected by the trans-membrane pressure.

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