

# Fouling characteristics of humic substances on tight polysulfone-based ultrafiltration membrane

Danu Ariono<sup>1a</sup>, Putu T.P. Aryanti<sup>2b</sup>, Anita K. Wardani<sup>1c</sup> and I.G. Wenten<sup>1\*</sup>

<sup>1</sup>Chemical Engineering Department, Institut Teknologi Bandung, Jl. Ganesa 10, Bandung, Indonesia 40132

<sup>2</sup>Chemical Engineering Department, Universitas Jenderal Achmad Yani, Jl. Terusan Jendral Sudirman, Cimahi, Indonesia 40285

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**Abstract.** Fouling characteristics of humic substances on tight ultrafiltration (UF) membrane have been investigated. The tight UF membrane was prepared by blending polysulfone (PSf) in N,N-dimethylacetamide (DMAc) with 25%wt of Polyethylene glycol (PEG400) and 4%wt of acetone. Fouling characteristic of the modified PSf membrane was observed during peat water filtration in different trans-membrane pressure (TMP). It was found that the acetone modified membrane provided 13% increase in TMP during five hours of peat water filtration, where a stable flux was reached within 150 minutes. Meanwhile, the increase of TMP from 10 psig to 30 psig resulted in a fouling resistance enhancement of 60%. Furthermore, based on the fouling analysis, fouling mechanism at the first phase of filtration was attributed to intermediate blocking while the second phase was cake formation.

**Keywords:** fouling mechanism; humic substances; polysulfone membrane; peat water filtration; tight ultrafiltration

## 1. Introduction

Ultrafiltration (UF) is a pressure-driven membrane which have been widely used in water treatment due to its excellent performance in removing microorganisms, suspended solids, and colloids while maintaining the mineral contents of the treated water (Peter-Varbanets *et al.* 2009, Aryanti *et al.* 2017, Wardani *et al.* 2017). However, further application of UF membranes in water treatment have been restricted by fouling of natural organic matter (NOM), which deteriorate membrane performance and result in high energy consumption (Aryanti *et al.* 2015, Mansouri *et al.* 2016, Ariono *et al.* 2017a). Humic substances, which contain aromatic and aliphatic functional groups in their molecules, are the major constituent of NOM and foulant in UF membrane structure (Fan *et al.* 2001, Aryanti *et al.* 2016). Due to its small molecular size (up to 200 Da), humic substances can easily enter the membrane structure and form irreversible fouling (Filloux *et al.* 2016, Chu *et al.* 2017). Consequently, fouling control should be performed during the water treatment processes for maintaining UF performances, especially when used to treat water containing high concentration of humic substances, such as peat water (Aryanti *et al.* 2016, Chang

*et al.* 2016, Li *et al.* 2016).

There are several strategies which have been proposed to control fouling phenomena in membrane operation such as using appropriate pre-treatment, controlling membrane operating conditions, and preparing membrane with anti or low fouling characteristics (Himma *et al.*, Wenten 1995, Chen *et al.* 1997, Rana and Matsuura 2010, Yang *et al.* 2013, Himma *et al.* 2016, Wenten and Khoiruddin 2016, Himma *et al.* 2017, Sianipar *et al.* 2017). A large pore size of membrane allows pore constriction in addition to cake formation, while smaller pore is more likely to form a cake layer. It has been found that the retention of humic acid solutions on 1-10 kDa membrane are around 80-90% (Küchler and Miekeley 1994). In addition, smooth, low surface charge, and higher hydrophilic membrane are required to reduce initial fouling tendencies on membrane surface (Nghiem and Hawkes 2007, Cheng *et al.* 2013).

Several modifications of UF membranes to obtain low-fouling characteristic have been performed by adding hydrophilic polymers, such as polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG). The presence of hydrophilic polymer reduces the hydrophobicity of membrane, which weakens the hydrophobic interaction between membrane and organic molecules (Matsuyama *et al.* 2003, Chou *et al.* 2007, Chakrabarty *et al.* 2008, Aryanti *et al.* 2014, Aryanti *et al.* 2015, Ariono *et al.* 2017a). In our previous work (Aryanti *et al.* 2013), PSf membrane was modified by blending acetone and PEG400 as additives into membrane solution. The addition of acetone produced a tight membrane skin structure due to rapid loss of acetone during the membrane preparation. More than 80% rejection of humic substances was achieved when 4%wt of acetone and 25%wt of PEG400 were (Rana and Matsuura 2010) blended into 20%wt of PSf in DMAc. Furthermore, UF membrane

\*Corresponding author, Professor

E-mail: [igw@che.itb.ac.id](mailto:igw@che.itb.ac.id)

<sup>a</sup>Ph.D.

E-mail: [danu@che.itb.ac.id](mailto:danu@che.itb.ac.id)

<sup>b</sup>Ph.D.

E-mail: [p.teta@lecture.unjani.ac.id](mailto:p.teta@lecture.unjani.ac.id)

<sup>c</sup>Ph.D. Student

E-mail: [anita\\_kusumawardani@yahoo.co.id](mailto:anita_kusumawardani@yahoo.co.id)

with a tight structure showed a reduced irreversible fouling and an improved flux stability in water filtration process (Aryanti *et al.* 2015).

The choice of hydrodynamic condition during the membrane processes also plays an important role to the membrane performance (Wardani *et al.* 2017, Wenten *et al.* 2016, 2017). It has been noted that fouling in the ultrafiltration membrane influences the relationship between flux and trans-membrane pressure (TMP) (Chen *et al.* 1997). Howell (1995) reported that long term of membrane processes can be operated at a constant flux below the critical value, which was defined as the threshold value between concentration polarization (reversible) and fouling (irreversible), both in direct flow or cross-flow system (Howell 1995). The membrane filtration process can be operated in a clean regime below the critical flux, without chemical cleaning. Meanwhile above it, a deposit layer of foulant can be formed on the membrane surface and created an additional resistance to the permeate flow. Kwon *et al.* (Kwon *et al.* 2000) found that the critical flux is increased with the increase particle size, which means that membrane was severe to the deposition of smaller particle.

Fouling in UF membrane can also be controlled by adjusting the TMP in a constant flux operation. The elevation of TMP generates a growing polarization layer and cake formation or fouling (Crozes *et al.* 1997, Guo *et al.* 2012). At low pressure (low flux), the polarized layer have a low concentration of particles and more labile with little opportunity for consolidation due to solute-solute interaction (Chen *et al.* 1997). This polarized layer is reversible and could be easily removed by simple cleaning method. Fouling of the membrane could be estimated for any changes in TMP by resistance-in-series model to analyze and predict the flux decline behavior during filtration process (Tracey and Davis 1994, Cho *et al.* 2000, Taniguchi *et al.* 2003, Zularisam *et al.* 2007, Lee and Kim 2014). In this model, flux of the membrane is considered as a function of TMP and various resistances that consist of membrane ( $R_m$ ) and total fouling ( $R_f$ ) resistance. Up to this time, understanding the fouling characteristics remains a major challenge in UF membrane applications for water treatment.

Regarding NOM fouling mechanisms, it is generally recognized that there are four main mechanisms for UF membrane, namely standard blocking, intermediate blocking, complete blocking and cake formation (Fig. 1). Pore constriction (standard blocking) and pore blocking (both intermediate and complete blocking) are generated as a result of adsorption of filtered species within the membrane pores. Meanwhile, cake formation is formed by the species rejected by the membrane. Several mathematical expressions have been developed for better understanding of fouling mechanism and to predict the fouling on the membrane structure (Katsoufidou *et al.* 2005, Duclos-Orsello *et al.* 2006). Theoretical models can partially contribute to the understanding of fouling phenomena during filtration processes.

In this paper, fouling characteristics of tight UF membrane were studied at various operating pressure condition (TMP) during peat water filtration. The tight UF

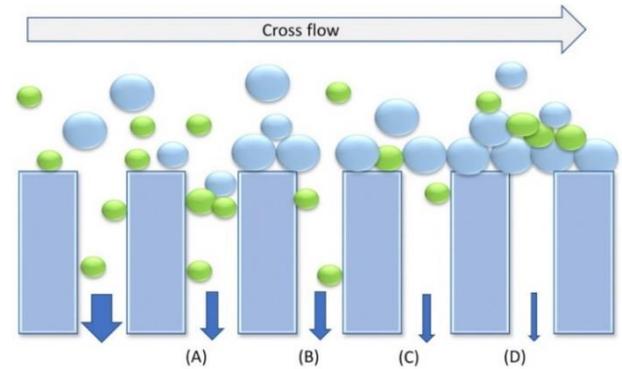


Fig. 1 Mechanism of pore blocking by humic acid: (A) standard blocking, (B) intermediate blocking, (C) complete blocking, and (D) cake formation

membrane was prepared by blending 20%wt of PSf and 25% of PEG400 in DMAc with 4%wt of acetone, which refer to our previous studies (Aryanti *et al.* 2015, Aryanti *et al.* 2016). Since the peat water contains high concentration of humic substances compared to other surface water sources, the peat water is used as feed solution to the membrane system. Experimental data for the flux decline during peat water filtration was analyzed using a simple fouling model, which has been proposed by Hermia (Hermia 1982).

## 2. Materials and methods

### 2.1 Numerical simulation procedure

The PSf (UDEL-P3500 MB7) was purchased from Solvay Advanced polymer. DMAc with a purity of 99.9% was supplied by Shangshai Jingsan Jingwei Chemical Co. Ltd., without further purification and used as a solvent. PEG with molecular weight of 400 Da (PEG400) and acetone were chosen as additives to improve the PSf membrane performances. Meanwhile, demineralized water was used as coagulant to induce the formation of membrane structure. For UF performance test, peat water, with a pH less than 4, was obtained from Dumai river-Riau, Indonesia.

### 2.2 Tight UF membrane preparation and analysis

The tight UF membrane was prepared by blending 20%wt of PSf with 25%wt of PEG400 and 4%wt of acetone in DMAc. This membrane formulation refers to our previous study (Aryanti *et al.* 2013). The membrane solution was stirred for about 14 hours in closed stirred tank and then left without stirring until no bubbles appeared. Afterwards, the membrane solution was casted on a flat glass plate with 200  $\mu\text{m}$  thickness and immediately immersed into coagulation bath filled with demineralized water. The peat water filtration was operated in different TMP, i.e., 10, 15 and 30 Psig.

The chemical compositions of modified UF membrane were analyzed by an ATR-FTIR spectrophotometer (Model 752, Nicolet, Madison, USA) at 2  $\text{cm}^{-1}$  resolution.

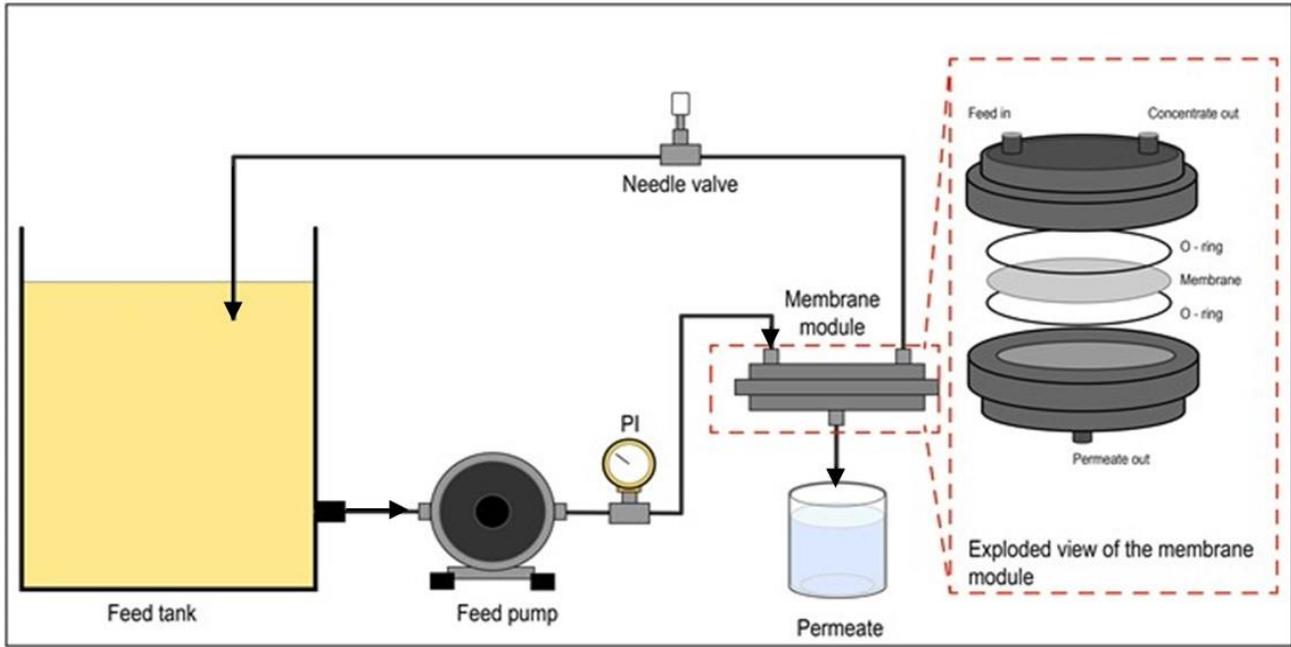


Fig. 2 Experimental setup

### 2.3 Flux and rejection measurement

The experimental setup was arranged as shown in Fig. 2 and performed in cross-flow mode. The circular flat sheet membrane, with an effective surface area of 45 cm<sup>2</sup>, was placed inside a membrane module. The membrane was rinsed by demineralized water for 30 minutes at 1 atm to remove the remaining solvent in membrane structure and obtain a stable flux. Then, demineralized water was flown to the membrane module in cross-flow mode to measure the pure water flux (PWF) of membrane before being used for experiments using peat water.

The peat water filtration was operated for two (2) hours. The peat water flux was measured periodically every 20 minutes, while the rejection of humic substances is measured at the end of filtration. Humic substances content in raw water and permeate solution were analyzed using UV/vis spectrophotometer with 254 wavelength ( $\lambda = 254$  m) (Beckett *et al.* 1987, Traina *et al.* 1990). The PWF and peat water flux were calculated by the following equation:

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

where  $J_{w1}$  is pure water flux (PWF) (Lm<sup>2</sup>h<sup>-1</sup>),  $V$  is volume of permeated water (L),  $\Delta t$  is permeation time (hour), and  $A$  is effective membrane surface area (m<sup>2</sup>). Peat water flux is mentioned as  $J_t$  that was measured at the first period of filtration calculated by the same equation in Eq. (1). Meanwhile, the humic substances rejection ( $R, \%$ ) was calculated by Eq. (2) (Baker 2004):

$$R(\%) = \left[ 1 - \left( \frac{C_p}{C_f} \right) \right] \times 100 \quad (2)$$

where  $C_p$  and  $C_f$  represent of humic substances content in permeate and feed solution respectively, as measured by UV/vis spectrophotometer.

### 2.4 Determination of flux recovery ratio (FRR) and total resistance

After two (2) hours of experiment, the flat sheet membrane was cleaned by flushing method using demineralized water for around 30 minutes. After the flushing process, PWF of the cleaned membrane was measured and denoted as  $J_{w2}$ . Flux recovery ratio (FRR) was calculated by Eq. (3) to investigate the effect of organic matter on membrane fouling during peat water filtration.

$$FRR(\%) = \left( \frac{J_{w2}}{J_{w1}} \right) \times 100 \quad (3)$$

Flux loss due to reversible ( $r_r$ ) and irreversible ( $r_{ir}$ ) fouling in PSf membrane were also calculated. Reversible fouling ( $r_r$ ) is attributed by concentration polarization of solute on membrane surface, which can be easily removed by flushing or backwash method. Meanwhile, irreversible fouling ( $r_{ir}$ ) is caused by strong attachment of solute that shall be removed by chemical cleaning. In this research, both reversible and irreversible flux loss were evaluated after cleaning method. The flux loss was calculated by the following equation:

$$r_r = \frac{J_{w2} - J_t}{J_{w1}} \quad (4)$$

$$r_{ir} = \frac{J_{w1} - J_{w2}}{J_{w1}} \quad (5)$$

where  $J_t$  is the peat water flux after two (2) hours of ultrafiltration process. The total flux loss ( $r_t$ ) is the sum of  $r_r$  and  $r_{ir}$ .

Fouling mechanism of the UF membrane was evaluated from the following resistance-in-series model (Dal-Cin *et al.* 1996):

$$J = \frac{\Delta P}{\mu R_t} = \frac{\Delta P}{\mu (R_m + R_f)} \quad (6)$$

where  $\Delta P$  is TMP (bar),  $\mu$  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 ( $R_m$ ) was calculated by filtering demineralized water through the UF membrane, then calculated by the following equation (Tracey and Davis 1994):

$$R_m = \frac{\Delta P}{\mu J_{w1}} \quad (7)$$

Total fouling resistance ( $R_{ft}$ ) was calculated using equation (7) based on the measured peat water flux after the membrane was used for two (2) hours of filtration. Then,  $R_f$  was determined by subtracting the membrane resistance ( $R_m$ ) from the total fouling resistance ( $R_{ft}$ ), as shown in Eq. (8).

$$R_f = R_{ft} - R_m \quad (8)$$

## 2.5 Simulation of fouling mechanism

Theoretical models can partially contribute to the understanding of fouling phenomena during filtration processes. In most cases, the fouling mechanism during peat water filtration was analyzed by considering the flux expressions relative to the fouling mechanisms, which was established by Hermia (Hermia 1982). He proposed a mathematical model describing fouling mechanisms that based on classical constant-pressure of dead-end filtration (Bowen *et al.* 1995). However, many researchers used Hermia's models derived for dead-end UF for cross-flow UF (Mohammadi *et al.* 2003, Mahesh Kumar *et al.* 2007, Hwang *et al.* 2008, Vela *et al.* 2008, Susanto *et al.* 2009). They compared the models' predictions with their experimental data. The results showed that the models well predict the membrane fouling at different experimental conditions. Theoretically, the steady-state condition in cross-flow filtration is not a rigorous steady-state condition but a quasi-steady state condition in actual applications. This is due to the fact that although permeate flux is nearly constant for long time filtration, it is actually decreased very slowly until a permeate flux of zero is obtained for very long time filtration (Salahi *et al.* 2010). Therefore, Hermia's model still can be considered as an appropriate model to describe dominant fouling mechanism in cross-flow filtration.

At a constant TMP, the change of flux in a certain filtrate period can be identified by the following equation (Zhang and Ding 2015):

$$\frac{d^2 t}{dV^2} = k \left( \frac{dt}{dV} \right)^m \quad (9)$$

Here  $t$  is the filtration time and  $V$  is the total filtered volume. The values of  $m$  have been established for each mechanism, while the value of  $k$  represents a constant fouling parameter, which varied for each UF processes. Meanwhile, flux of UF membrane can be defined by equation (10) (Cho *et al.* 2000).

$$J = \frac{1}{A} \frac{dV}{dt} \quad (10a)$$

Or

$$\frac{dt}{dV} = \frac{1}{AJ} \quad (10b)$$

where  $A$  is membrane area and  $J$  is permeate flux. The second derivative of the above equation with respect to  $t$  is as follows:

$$\frac{d^2 t}{dV^2} = - \left( \frac{1}{A^2 J^3} \right) \frac{dJ}{dt} \quad (11)$$

By substituting Eqs. (10)-(11) to the equation (9), the flux decline can be expressed by the following equation:

$$\frac{dJ}{dt} = -kJ(AJ)^{2-m} \quad (12)$$

where  $m$  denotes a parameter of standard blocking, intermediate blocking, complete blocking, and cake formation respectively, each of which has values of 3/2, 1, 2, and 0 (Razi *et al.* 2012). The standard blocking (pore constriction) determines fouling in the internal structure of the membrane, where the membrane pores are assumed to be capillary structures. During the filtration, the membrane pore is reduced due to the foulant adsorption on the membrane surface, thus constricting the membrane pore. The intermediate blocking model predicts the possibility of foulant bridging a pore by obstructing the entrance without complete blocking (Todisco *et al.* 1996, Wang and Tarabara 2008). The complete pore blocking is similar to the intermediate pore blocking, in which the membrane flux is restricted by foulant that are larger than the UF membrane pore size. The water can only pass through the unblocked pore area. Meanwhile in cake fouling model, the fouling occurs over the entire membrane surface. The equation characterizing of flow decline due to fouling is detailed in Table 1.

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 solved by the least squares method programmed with Matlab R2015b. The objective function used to optimize the above fouling parameters is as follows (Goldrick *et al.* 2017):

$$f(x) = \sum (J_{v,exp} - J_{v,pred})^2 \quad (13)$$

subject to:  $k_{cf}, k_{sb}, k_{ib}, k_{cb} \geq 0$ .

Table 1 Flux equation for each fouling mechanism

Fouling mechanism	Flux equation	Equation number
Standard blocking $m = 3/2$	$J_v = \frac{4J_{v,0}}{(2K_{sb}J_{v,0}^{1/2}t + 2)^2}$ $K_{sb} = k_{sb}A^{1/2}$	(14)
Intermediate blocking $m = 1$	$J_v = \frac{J_{v,0}}{K_{ib}J_{v,0}t + 1}$ $K_{ib} = k_{ib}A$	(15)
Complete blocking $m = 2$	$J_v = J_{v,0} \exp(-K_{cb}t)$ $K_{cb} = k_{cb}$	(16)
Cake formation $m = 0$	$J_v = \frac{J_{v,0}}{(2K_{cf}J_{v,0}^2t + 1)^{1/2}}$ $K_{cf} = k_{cf}A^2$	(17)

Note:  $K_{sb}$  = fouling coefficient for standard blocking,  $K_{ib}$  = fouling coefficient for intermediate blocking,  $K_{cb}$  = fouling coefficient for complete blocking,  $K_{cf}$  = fouling coefficient for cake formation

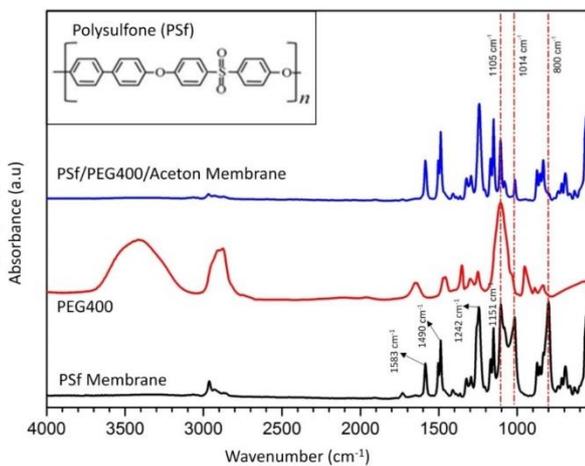


Fig. 1 ATR-FTIR spectrum of modified polysulfone membrane

### 3. Results and Discussion

#### 3.1 FTIR analysis of tight PSf-UF membrane

ATR-FTIR spectrum of modified PSf-UF membrane is shown in Fig. 3, which was compared to the unmodified PSf-UF membrane. At the unmodified membrane line, the peaks formed at wave numbers 1151 and 1242  $\text{cm}^{-1}$  denotes the symmetric and asymmetric vibrations of the dioxide ( $\text{O}=\text{S}=\text{O}$ ) groups (Kumar *et al.* 2015). Absorbance at wavelengths of 1490 and 1583  $\text{cm}^{-1}$  attributed to the presence of stretch aromatic hydrocarbon groups. Meanwhile, the peak at wave numbers below 1015  $\text{cm}^{-1}$  indicates the presence of stretching of C-O groups.

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groups.

The presence of -OH group in PEG400 structure is acknowledged by a wide peak at 3400-3300  $\text{cm}^{-1}$ . This peak was disappeared when PEG400 was blended into PSf solution along with acetone (PSf / PEG400 /acetone line). The disappearance of -OH peak on the acetone modified membrane is attributed by interaction between the -OH group and the rich polysulfone aromatic ring, which is further trapped inside the polysulfone chain structure. The increase of polysulfone concentration on the membrane surface as the rapid evaporation of acetone induces the increase of hydrophobicity of membrane. It has been found that the contact angle of the addition of acetone increased the membrane contact angle from 50,5 to 56,2 (Aryanti *et al.* 2016, Ariono *et al.* 2017b).

#### 3.2 Fouling and rejection characteristic of tight UF-PSf membrane

Fig. 4 presents the peat water flux profile and TMP as a function of peat filtration time at a constant feed velocity (50 L/h). The TMP was slightly elevated (from 15 to 17 psig), while the peat water flux was declined up to 57% after 5 (five) hours of filtration. The water flux was sharply declined in the earlier of filtration process due to rapid accumulation of organic matter on the membrane surface. The stable flux was achieved after 50 minutes of filtration. It has been discussed in previous research that high concentration of PEG400 contributed to the formation of an open pore in skin layer and also in sub-structure of the membrane, which led the rapid accumulation of organic matter on the membrane surface (Aryanti *et al.* 2013). The addition of acetone in membrane solution exhibited the formation of larger pore and formed a tight structure in membrane skin layer. As a result, flux stability of the membrane could be improved.

Meanwhile, Fig. 5 shows the effect of TMP on total resistances of the fouled PSf membranes, which evaluated using simple resistance-in-series model at various operating conditions. It shows that the increase of TMP led to the increase of the intrinsic resistance of the membrane and significantly enhanced fouling resistance. The increase of membrane resistance is attributed to hydrodynamic compaction of the membrane structure at higher pressure (Teow 2016). Fouling resistance also appeared to be increased with the increase of TMP. At low TMP, interaction of humic substance and the membrane surface is dominantly attributed to hydrophobic interaction and reversible. Further increase of TMP, higher concentration of organic matters is accumulated on the membrane surface, which leads to the increase of fouling resistance as well as the compaction of foulant on the membrane surface. It suggested that cake fouling was formed when the TMP was raised to 30 psig. This was indicated by a 60% increase in fouling resistance when the pressure was increased from 10 to 30 psig. In addition, low pH of peat water also plays an important role in the formation of fouling in the membrane. It has been reported that charge repulsion of humic substance was decreased at low pH of solution (Aryanti *et al.* 2015). Consequently, the humic substances tend to curl-up and formed smaller molecule size, which can easily

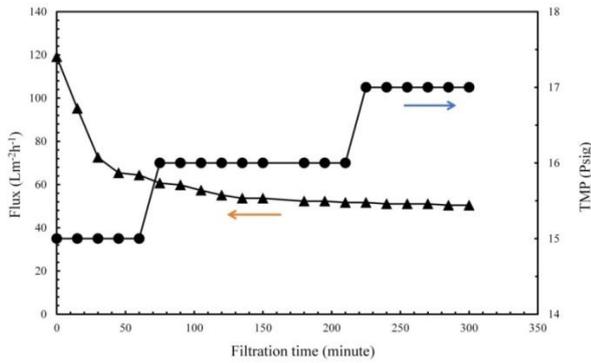


Fig. 2 Profile of flux and TMP during peat water filtration at constant feed velocity, 50 L/h

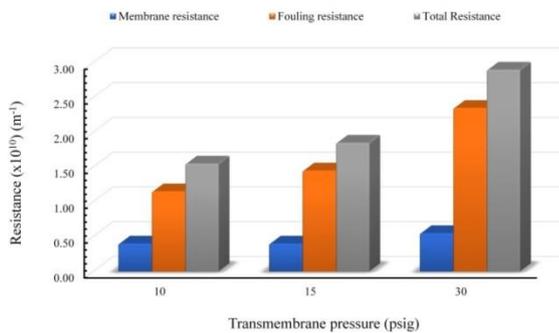


Fig. 3 Effect of TMP on total resistance after two (2) hours of peat water filtration

penetrate the membrane pores. Besides of low pH of solution, the charge repulsion of humic substances is decreased by the increase of ionic strength of solution, concentration of humic substances, and the presence of divalent ion in the solution

The effect of TMP on the flux loss of the tight PSf-UF membrane after 2 hours of peat water filtration is shown in Fig. 6. A low irreversible fouling resistance capability was achieved by the tight UF membrane. Tight skin layer of the membrane weakens the interaction between organic matters and the membrane surface that results in reversible fouling on the membrane surface. This reversible fouling can be easily cleaned by flushing method and contributes to higher flux recovery ratio (FRR). Greater reversible fouling was found when the TMP was raised to 15 psig. Higher pressure leads to the increase of concentration polarization on membrane surface, due to the increase of membrane exposure to organic matter and accumulation of the rejected component taking place on membrane surface. However low interaction between the membrane surface and the organic matter in peat water generates reversible fouling, which can be easily removed by flushing (cross-flow) method and results in more stable flux during peat water filtration. For further increase of TMP over 15psig, the irreversible fouling was started to severe, which contributed to the significant decrease of FRR.

Fig. 7 presents the effect of different TMP on humic substances rejection, which shows that higher TMP resulted in lower rejection of humic substances. When the operating pressure was increased, the humic substances were rapidly

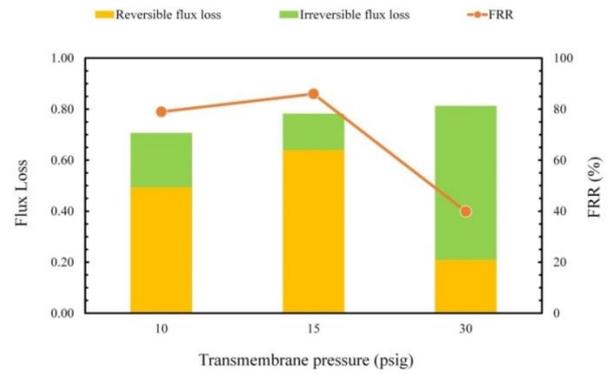


Fig. 4 The effect of trans-membrane pressure on total flux loss of modified PSf UF membrane during peat water filtration

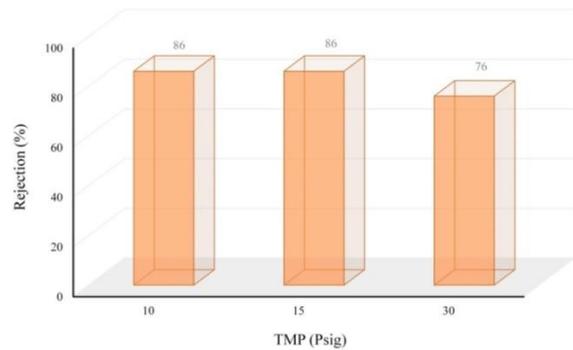


Fig. 5 The effect of TMP on humic substances rejection in PSf membrane

Table 2 Fouling parameter for each mechanism

	Kcf (s.m <sup>-2</sup> )	Ksb (s.m <sup>-5</sup> )	Kib (s.m <sup>-4</sup> )	Kcb (s.m <sup>-6</sup> )
Tight UF membrane	5.40E-07	6.10E-04	7.40E-05	4.90E-03

accumulated on the membrane surface. High concentration gradient of solutes on the membrane surface enhanced the transfer of solute to the permeate side (Noble and Stern 1995). Consequently, lower rejection of humic substances was resulted. In acetone modified membrane, high rejection of humic substances is not only affected by the tight pore size of the membrane skin layer. The high rejection of humic substances is also associated with reversible fouling on the membrane surface that acts as additional selective layer of the membrane.

### 3.3 Determination of fouling mechanism

The fouling parameters (*K*) were determined using Eqs. (14)-(17) with least square method based on the peat water filtration data in Fig. 4. The calculation was performed at a constant pressure of 15 psig. The calculated *K* values are presented in Table 2 and used to predict the fouling mechanism formed on the tight-UF membrane surface. The comparison between the theoretical flux and experimental data is shown in Fig. 8. Based on Figure 8, a single fouling

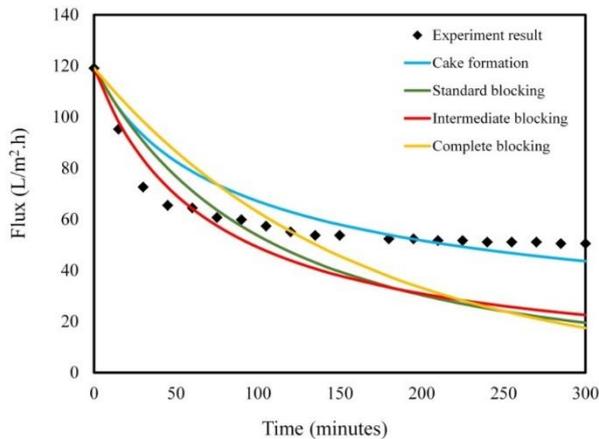


Fig. 6 Comparison of experiment and theoretical flux as a function of filtration time

mechanism was not able to describe dominant fouling mechanism during 300 minutes of filtration. Therefore, two steps of calculations were required to find the overall fouling mechanisms on the UF-membrane. For the first-time period or the first phase,  $J_0$  was fixed to the first experimental flux data corresponding to initial time  $t_0$ . Meanwhile, for the second phase, the value of  $J_0$  was considered as the last flux value of the previous fouling phase.

Figure 9 shows the two phase of fouling mechanism on tight UF membrane. In the first 80 minutes of the peat water filtration, the organic matters were attached on the UF membrane surface and cause intermediate pore blocking. It assumed that some of the membrane pores were covered by a fraction of foulant. The foulant deposited on the membrane surface not only contributes to pore blocking but also attaches to other foulant on the membrane surface. Further increase of filtration time, a cake layer is formed and lead the increase of TMP (Grenier *et al.* 2008). As shown in Fig. 9, membrane was relatively clean at the first phase. Up to the first 80 minutes of filtration, the foulant were deposited to the membrane surface, which indicated by the brown layer on the surface. After several times, the deposited particles blocked the membrane and formed a cake layer with a darker brown color. On the tight UF membrane, low-irreversible fouling and a limited thickness of cake layer is formed. It was found that 50% of flux decline was occurred in the first stage of filtration time (1-80 minute), while the flux decline was around 16% in the second stage (80-300 minute).

#### 4. Conclusions

Performance of tight polysulfone (PSf) ultrafiltration (UF) membrane has been investigated during peat water filtration at different trans-membrane pressure (TMP). The acetone modified membrane resulted in stable flux, in which 13% increase in TMP was achieved during five (5) hours of peat water filtration. Tight skin layer formation due to the addition of acetone in membrane preparation

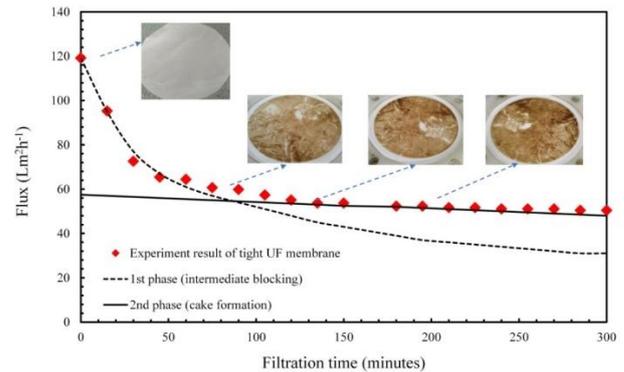


Fig. 7 Prediction of fouling mechanism on tight UF membrane (assuming more than one phase)

generated reversible fouling that could be easily removed by flushing and resulted in high selectivity of the membrane.

It has been found that fouling resistance was increased by 60% when the TMP increased from 10 to 30 psig. When the membrane was operated at TMP up to 15 psig, the fouling was reversible and could be easily cleaned by flushing method. It was indicated by a higher FRR (80%). When the TMP was increased to 30 psig, irreversible fouling was significantly increased and resulted in 80% flux loss. Generally, a higher rejection was obtained under a lower TMP. The maximum rejection of 85% was achieved at TMP of 15 psig and slightly decreased to 75% at TMP of 30 psig. It may be implied that the rejection of humic substances was associated with the tight structure of the membrane skin layer and also the formation of fouling layer (reversible fouling) on the membrane surface. In addition, from the fouling analysis, fouling mechanism at the first phase of filtration was attributed by intermediate blocking while the second phase was in agreement with the cake formation. The cake formed was of a limited thickness, thus at the second phase, the flux was only slightly declined.

#### References

- Ariono, D., Aryanti, P.T.P., Hakim, A.N., Subagjo, S. and Wenten, I.G. (2017a), "Determination of thermodynamic properties of polysulfone/PEG membrane solutions based on Flory-Huggins model", *AIP Conf. Proceed.*, **1840**(1), 090008.
- Ariono, D., Aryanti, P.T.P., Subagjo, S. and Wenten, I.G. (2017b), "The effect of polymer concentration on flux stability of polysulfone membrane", *AIP Conf. Proceed.*, **1788**(1), 030048.
- Aryanti, P., Sianipar, M., Zunita, M. and Wenten, I.G. (2017), "Modified membrane with antibacterial properties", *Membr. Water Treat.*, **8**(5), 463-481.
- Aryanti, P.T.P., Joscariita, S.R., Wardani, A.K., Subagjo, S., Ariono, D. and Wenten, I.G. (2016), "The influence of PEG400 and acetone on polysulfone membrane morphology and fouling behavior", *J. Eng. Technol. Sci.*, **48**(2), 135-149.
- Aryanti, P.T.P., Khoiruddin, K. and Wenten, I.G. (2013), "Influence of additives on polysulfone-based ultrafiltration membrane performance during peat water filtration", *J. Water Sustain.*, **3**(2), 85-96.
- Aryanti, P.T.P., Subagjo, S., Ariono, D. and Wenten, I.G. (2014), "Fouling and rejection characteristic of humic substances in polysulfone ultrafiltration membrane", *J. Membr. Sci. Res.*, **1**,

- 41-45.
- Aryanti, P.T.P., Yustiana, R., Purnama, R.E.D. and Wenten, I.G. (2015), "Performance and characterization of PEG400 modified PVC ultrafiltration membrane", *Membr. Water Treat.*, **6**(5), 379-392.
- Baker, R.W. (2004), *Membrane Technology and Applications*, John Wiley and Sons, Ltd., West Sussex, United Kingdom.
- Beckett, R., Jue, Z. and Giddings, J.C. (1987), "Determination of molecular weight distributions of fulvic and humic acids using flow field-flow fractionation", *Environ. Sci. Technol.*, **21**(3), 289-295.
- Bowen, W.R., Calvo, J.I. and Hernández, A. (1995), "Steps of membrane blocking in flux decline during protein microfiltration", *J. Membr. Sci.*, **101**(1), 153-165.
- Chakrabarty, B., Ghoshal, A.K. and Purkait, M.K. (2008), "Effect of molecular weight of PEG on membrane morphology and transport properties", *J. Membr. Sci.*, **309**(1), 209-221.
- Chang, H., Liang, H., Qu, F., Ma, J., Ren, N. and Li, G. (2016), "Towards a better hydraulic cleaning strategy for ultrafiltration membrane fouling by humic acid: Effect of backwash water composition", *J. Environ. Sci.*, **43**, 177-186.
- Chen, V., Fane, A.G., Madaeni, S. and Wenten, I.G. (1997), "Particle deposition during membrane filtration of colloids: Transition between concentration polarization and cake formation", *J. Membr. Sci.*, **125**(1), 109-122.
- Cheng, Q., Zheng, Y., Yu, S., Zhu, H., Peng, X., Liu, J., Liu, J., Liu, M. and Gao, C. (2013), "Surface modification of a commercial thin-film composite polyamide reverse osmosis membrane through graft polymerization of N-isopropylacrylamide followed by acrylic acid", *J. Membr. Sci.*, **447**, 236-245.
- Cho, J., Amy, G. and Pellegrino, J. (2000), "Membrane filtration of natural organic matter: Factors and mechanisms affecting rejection and flux decline with charged ultrafiltration (UF) membrane", *J. Membr. Sci.*, **164**(1-2), 89-110.
- Chou, W.L., Yu, D.G., Yang, M.C. and Jou, C.H. (2007), "Effect of molecular weight and concentration of PEG additives on morphology and permeation performance of cellulose acetate hollow fibers", *Sep. Purif. Technol.*, **57**(2), 209-219.
- Chu, K.H., Shankar, V., Park, C.M., Sohn, J., Jang, A. and Yoon, Y. (2017), "Evaluation of fouling mechanisms for humic acid molecules in an activated biochar-ultrafiltration hybrid system", *Chem. Eng. J.*, **326**, 240-248.
- Crozes, G.F., Jacangelo, J.G., Anselme, C. and Laine, J.M. (1997), "Impact of ultrafiltration operating conditions on membrane irreversible fouling", *J. Membr. Sci.*, **124**(1), 63-76.
- Dal-Cin, M.M., McLellan, F., Striez, C.N., Tam, C.M., Tweddle, T.A. and Kumar, A. (1996), "Membrane performance with a pulp mill effluent: Relative contributions of fouling mechanisms", *J. Membr. Sci.*, **120**(2), 273-285.
- Duclos-Orsello, C., Li, W. and Ho, C.C. (2006), "A three mechanism model to describe fouling of microfiltration membranes", *J. Membr. Sci.*, **280**(1-2), 856-866.
- Fan, L., Harris, J.L., Roddick, F.A. and Booker, N.A. (2001), "Influence of the characteristics of natural organic matter on the fouling of microfiltration membranes", *Water Res.*, **35**(18), 4455-4463.
- Filloux, E., Gernjak, W., Gallard, H. and Croue, J.P. (2016), "Investigating the relative contribution of colloidal and soluble fractions of secondary effluent organic matter to the irreversible fouling of MF and UF hollow fibre membranes", *Sep. Purif. Technol.*, **170**, 109-115.
- Goldrick, S., Joseph, A., Mollet, M., Turner, R., Gruber, D., Farid, S.S. and Titchener-Hooker, N.J. (2017), "Predicting performance of constant flow depth filtration using constant pressure filtration data", *J. Membr. Sci.*, **531**, 138-147.
- Grenier, A., Meireles, M., Aimar, P. and Carvin, P. (2008), "Analysing flux decline in dead-end filtration", *Chem. Eng. Res. Des.*, **86**(11), 1281-1293.
- Guo, W., Ngo, H.H. and Li, J. (2012), "A mini-review on membrane fouling", *Bioresour. Technol.*, **122**, 27-34.
- Hermia, J. (1982), "Constant pressure blocking filtration law application to powder-law non-newtonian fluid", *Trans. Inst. Chem. Eng.*, **60**, 183-187.
- Himma, N.F., Anisah, S., Prasetya, N. and Wenten, I.G. (2016), "Advances in preparation, modification, and application of polypropylene membrane", *J. Polym. Eng.*, **36**(4), 329-362.
- Himma, N.F., Prasetya, N., Anisah, S. and Wenten, I.G. (2018), "Superhydrophobic membrane: Progress in preparation and its separation properties", *Rev. Chem. Eng.*, <https://doi.org/10.1515/revce-2017-0030>.
- Himma, N.F., Wardani, A.K. and Wenten, I.G. (2017), "Preparation of Superhydrophobic polypropylene membrane using dip-coating method: The effects of solution and process parameters", *Polym. Plast. Technol. Eng.*, **56**(2), 184-194.
- Howell, J.A. (1995), "Sub-critical flux operation of microfiltration", *J. Membr. Sci.*, **107**(1-2), 165-171.
- Hwang, K.J., Liao, C.Y. and Tung, K.L. (2008), "Effect of membrane pore size on the particle fouling in membrane filtration", *Desalination*, **234**(1), 16-23.
- Katsoufidou, K., Yiantsios, S.G. and Karabelas, A.J. (2005), "A study of ultrafiltration membrane fouling by humic acids and flux recovery by backwashing: Experiments and modeling", *J. Membr. Sci.*, **266**(1-2), 40-50.
- Küchler, I.L. and Miekeley, N. (1994), "Ultrafiltration of humic compounds through low molecular mass cut-off level membranes", *Sci. Total Environ.*, **154**(1), 23-28.
- Kumar, M., McGlade, D., Ulbricht, M. and Lawler, J. (2015), "Quaternized polysulfone and graphene oxide nanosheet derived low fouling novel positively charged hybrid ultrafiltration membranes for protein separation", *RSC Adv.*, **5**(63), 51208-51219.
- Kwon, D.Y., Vigneswaran, S., Fane, A.G. and Aim, R.B. (2000), "Experimental determination of critical flux in cross-flow microfiltration", *Sep. Purif. Technol.*, **19**(3), 169-181.
- Lee, S.J. and Kim, J.H. (2014), "Differential natural organic matter fouling of ceramic versus polymeric ultrafiltration membranes", *Water Res.*, **48**, 43-51.
- Li, K., Huang, T., Qu, F., Du, X., Ding, A., Li, G. and Liang, H. (2016), "Performance of adsorption pretreatment in mitigating humic acid fouling of ultrafiltration membrane under environmentally relevant ionic conditions", *Desalination*, **377**, 91-98.
- Kumar, M.S., Madhu, G.M. and Roy, S. (2007), "Fouling behaviour, regeneration options and on-line control of biomass-based power plant effluents using microporous ceramic membranes", *Sep. Purif. Technol.*, **57**(1), 25-36.
- Mansouri, J., Charlton, T., Chen, V. and Weiss, T. (2016), "Biofouling performance of silver-based PES ultrafiltration membranes", *Desalination Water Treat.*, **57**(58), 28100-28114.
- Matsuyama, H., Maki, T., Teramoto, M. and Kobayashi, K. (2003), "Effect of PVP additive on porous polysulfone membrane formation by immersion precipitation method", *Sep. Sci. Technol.*, **38**(14), 3449-34458.
- Mohammadi, T., Kazemimoghadam, M. and Saadabadi, M. (2003), "Modeling of membrane fouling and flux decline in reverse osmosis during separation of oil in water emulsions", *Desalination*, **157**(1), 369-375.
- Nghiem, L.D. and Hawkes, S. (2007), "Effects of membrane fouling on the nanofiltration of pharmaceutically active compounds (PhACs): Mechanisms and role of membrane pore size", *Sep. Purif. Technol.*, **57**(1), 176-184.
- Noble, R.D. and Stern, S.A. (1995), *Membrane Separations Technology: Principles and Applications*, Elsevier, New York,

U.S.A.

- Peter-Varbanets, M., Zurbrügg, C., Swartz, C. and Pronk, W. (2009), "Decentralized systems for potable water and the potential of membrane technology", *Water Res.*, **43**(2), 245-265. CC
- Rana, D. and Matsuura, T. (2010), "Surface modifications for antifouling membranes", *Chem. Reviews*, **110**(4), 2448-2471.
- Razi, B., Aroujalian, A. and Fathizadeh, M. (2012), "Modeling of fouling layer deposition in cross-flow microfiltration during tomato juice clarification", *Food Bioprod. Process.*, **90**(4), 841-848.
- Salahi, A., Abbasi, M. and Mohammadi, T. (2010), "Permeate flux decline during UF of oily wastewater: Experimental and modeling", *Desalination*, **251**(1), 153-160.
- Sianipar, M., Kim, S.H., Khoiruddin, K., Iskandar, F. and Wenten, I.G. (2017), "Functionalized carbon nanotube (CNT) membrane: Progress and challenges", *RSC Adv.*, **7**(81), 51175-51198.
- Susanto, H., Feng, Y. and Ulbricht, M. (2009), "Fouling behavior of aqueous solutions of polyphenolic compounds during ultrafiltration", *J. Food Eng.*, **91**(2), 333-340.
- Taniguchi, M., Kilduff, J.E. and Belfort, G. (2003), "Modes of natural organic matter fouling during ultrafiltration", *Environ. Sci. Technol.*, **37**(8), 1676-1683.
- Teow, Y.H. (2016), "Characterization and performance evaluation of ultrafiltration membrane for humic acid removal", *Indian J. Sci. Technol.*, **9**(22).
- Todisco, S., Pena, L., Drioli, E. and Tallarico, P. (1996), "Analysis of the fouling mechanism in microfiltration of orange juice", *J. Food Process. Preservation*, **20**(6), 453-466.
- Tracey, E.M. and Davis, R.H. (1994), "Protein fouling of track-etched polycarbonate microfiltration membranes", *J. Colloid Interface Sci.*, **167**(1), 104-116.
- Traina, S.J., Novak, J. and Smeck, N.E. (1990), "An ultraviolet absorbance method of estimating the percent aromatic carbon content of humic acids", *J. Environ. Qual.*, **19**(1), 151-153.
- Vela, M.C.V., Blanco, S.Á., García, J.L. and Rodríguez, E.B. (2008), "Analysis of membrane pore blocking models applied to the ultrafiltration of PEG", *Sep. Purif. Technol.*, **62**(3), 489-498.
- Wang, F. and Tarabara, V.V. (2008), "Pore blocking mechanisms during early stages of membrane fouling by colloids", *J. Colloid Interface Sci.*, **328**(2), 464-469.
- Wardani, A.K., Hakim, A.N., Khoiruddin, K. and Wenten, I.G. (2017), "Combined ultrafiltration-electrodeionization technique for production of high purity water", *Water Sci. Technol.*, **75**(12), 2891-2899.
- Wenten, I.G. (1995), "Mechanisms and control of fouling in crossflow microfiltration", *Filtr. Sep.*, **32**(3), 252-253.
- Wenten, I.G. and Khoiruddin, K. (2016), "Recent developments in heterogeneous ion-exchange membrane: Preparation, modification, characterization and performance evaluation", *J. Eng. Sci. Technol.*, **11**(7), 916-934.
- Wenten, I.G., Khoiruddin, K., Aryanti, P.T.P. and Hakim, A.N. (2016), "Scale-up strategies for membrane-based desalination processes: A review", *J. Membr. Sci. Res.*, **2**(2), 42-58.
- Wenten, I.G., Steven, S., Dwiputra, A., Khoiruddin, K. and Hakim, A.N. (2017), "From lab to full-scale ultrafiltration in microalgae harvesting", *J. Physics: Conf. Series*, **877**(1), 012002.
- Yang, X., Wang, R., Fane, A.G., Tang, C.Y. and Wenten, I.G. (2013), "Membrane module design and dynamic shear-induced techniques to enhance liquid separation by hollow fiber modules: A review", *Desalination Water Treat.*, **51**(16-18), 3604-3627.
- Zhang, W. and Ding, L. (2015), "Investigation of membrane fouling mechanisms using blocking models in the case of shear-enhanced ultrafiltration", *Sep. Purif. Technol.*, **141**, 160-169.
- Zularisam, A.W., Ismail, A.F., Salim, M.R., Sakinah, M. and Ozaki, H. (2007), "The effects of natural organic matter (NOM) fractions on fouling characteristics and flux recovery of ultrafiltration membranes", *Desalination*, **212**(1), 191-208.