Effects of incorporating ZnO on characteristic, performance, and antifouling potential of PSf membrane for PRW treatment

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Abstract. Numerous researchers around the world have developed the separation process by membrane technology. The application of membrane-based separation in industrial activity is limited due to its low production capacity due to the fouling formation on the surface of the membrane. The incorporating of nanomaterial has been developed to enhance membrane performance and productivity. In this study, we introduced the zinc oxide (ZnO) nanoparticles to process the petroleum refinery wastewater (PRW). The SEM result shows the presence of ZnO nanoparticles on the surface of the polysulfone (PSf) membrane, and it increased the porosity of the membrane. The addition of ZnO nanoparticles has been successfully increasing the hydrophilicity, increase the water uptake ability, and also increase the tensile strength and elongation break of the modified membrane. The investigation of the performance of the membranes shows that incorporating ZnO nanoparticles into the membrane has resulted in the higher of permeate flux and pollutant removal efficiency compared to the pristine membrane. The quantitative analysis of the fouling behavior by the model shows the addition of ZnO nanoparticles has been successfully reduced the resistances during filtration that mean the decreasing of the fouling tendency on the surface of the membrane. These also proved by the antifouling potential analysis at the addition of 1 %-wt ZnO nanoparticle decreased up to 39% of total resistance and increased the flux recovery ratio up to 72%.

1. Introduction

The effort to find water resources are becoming challenged in Indonesia and even in the world [1]. Number of challenges also is occurring because of climatic pattern changes, which is resulting in the reduction of precipitation or rain in key areas of the world, including Indonesia as a tropical country [2]. Also, global warming has raised a worldwide temperature of 1.5 °C around the world, and this condition has been caused another negative effect in terms of freshwater supply, which is rapidly deficit, especially in the tropical region [3]. Nowadays, those circumstances have made people, and almost all living things are suffering and dying. Moreover, in Indonesia, it has been a contra-productive action for the water conservation effort. For example, oil and gas industries generate drilling wastewater as known as produced water up to 12-million-barrels water per day and petroleum refinery wastewater (PRW) up to 30-50 cubic meters per ton of crude [4]. That huge of wastewater have not met the effective handling
and intentionally just disposed to environment that made worse effects. Produced water contains several hazardous substances there are; biochemical oxygen demand (BOD) and chemical oxygen demand (COD) at contents of about 150-250 mg/L, and 300-600 mg/L, respectively; phenolic substances at number of 20-200 mg/L; grease at number of 1-100 mg/L; heavy metals at 0.1-100 mg/L and others pollutants [5]. There is a long list of organic and inorganic pollutants associated with PRW.

Several articles about produced water treatment have been published, there are some method to overcome this wastewater problem such as reverse osmosis filtration [2], zeolite [6], surfactant [7], until membrane filtration [8]. However, far too little attention has been comprehensively studied to treat PRW in recent years. Considering the negative impacts of untreated PRW, a proper technique and management system are needed before it disposed or used for certain purpose [9]. On the other hand, one of many way to solve this water crisis, we have to treat PRW into usable water. However, conservation activity alone commonly do not sufficiently diminish water shortages, water reusing to counterbalance consumption should be a critical part of the studies. Improved wastewater treatment technologies can be a critical part of addressing future water crisis, notably, improved methods for purification to treat such as for PRW with high levels of dissolved solids, oil, heavy metals and others hazardous pollutants. General method from conventional technique are needed several stages that are physical, chemical and biological treatment by operating them in different equipment [10].

PRW can be utilized to another application of water after being through the proper treatment. Research conducted to develop techniques to demonstrate the PRW economic advantage of PRW utilization [11]. There are several method have been applied to utilize this wastewater. Physical, biochemical, until chemical treatment have been used to treat PRW. However, these several well-known methods didn’t meet the product standard. Particularly, the application of conventional membrane still needs high pressure to be operated [12]. The oil and grease consisting in the PRW have been occurred fouling formation on the surface of the membrane [13]. This condition has been driven researchers around the world to modify the membrane to have more superior ability in term of membrane performance. Membrane fouling is caused by the low surface hydrophilicity property [14]. Therefore, there are some methods to improve the hydrophilicity of the membrane have been studied. Several methods such as polymer blending [15], grafting chemical group [13], hydrophilic film deposition [16], and inorganic nanoparticle blending [17].

Zinc oxide (ZnO) nanoparticles has been raised attention in numerous industrial applications such as medic, optics, electronics, and recently in the modification of membrane science and application, owing to their good antimicrobial, anti-corrosive, excellent thermal and mechanically stable [18]. Several researches have been worked on the addition of ZnO nanoparticle into different membrane polymer such as polysulfone (PSf), polyether sulfone (PES) and polyvinylidene fluoride (PVDF). These studies reported on the formation of ultrafiltration (UF) and tight UF membranes with improved membrane performances such as higher permeability, rejection capability, porosity, hydrophilicity, and enhanced antifouling properties [19]. In addition, the ZnO embedded membranes also performed a significant heavy metal ions (Cu²⁺) adsorption [13], reduced oleic acid fouling, and improved dye rejection ability [20], collagen separation and excellent photo catalysis ability [21]. These attractive previous results indicated that ZnO has the potential to be a superb nanoparticle selection for better membrane characteristic and performance to proceed PRW.

However, in previous studies, investigations on the use of ZnO as an agent to increase the hydrophilicity of the membrane surface have only studied the characteristics and performance of flux and rejection [22], [20], [19]. Observations on other parameters such as water uptake ability and resistance analysis of the filtration process have not been widely studied. A study on the parameters of water uptake ability and antifouling potential is very important to understand how much influence the addition of a substance has to increase separation ability and susceptibility to fouling. Therefore, in this study, we investigated not only the effect of incorporating ZnO nanoparticles into PSf polymer membrane on its basic characteristics but also on its water uptake ability and antifouling potential. Moreover, ZnO as a surface modifying agent may be increased the mechanical strength to prolong the
durability of the modified membrane. Last but not least, the modified membrane can performed the less fouling tendency to treat the PRW into clean water.

2. Materials and methods

2.1. Materials
Polysulfone (PSf) as the membrane polymer was obtained from Solvay AM, USA. N methyl Pyrrolidone (NMP) as a solvent to the produced dope solution was supplied from Merck, Germany. Nano Center Indonesia provided for the zinc oxide (ZnO) nanoparticle powder (±350 nm). Sample of PRW was obtained from the effluent stream of the physicochemical wastewater treatment plant in Refinery Unit IV of PT. Pertamina, Central Java, Indonesia.

2.2. Fabrication of composite PSf-ZnO membrane
Composite PSf-ZnO membrane was prepared by dry-wet non-solvent induced phase inversion (NIPS) as reported by our previous study [23]. The concentrations of ZnO in total solids were 0.5, and 1.0 wt-\%.

2.3. Initial characterization of PRW
Initial characterization of PRW was done to determine the characteristics of this wastewater as shown in Table 1. Several parameters were measured such as, physical appearance and total dissolved solid (TDS) content using TDS meter A-013, China. We were determined the chemical oxygen demand (COD) using redox titration method and to measure pH using (pH meter Y98, China).

Table 1. Characteristics of PRW

| Parameter                    | Unit | Value          |
|------------------------------|------|----------------|
| Appearance                   | -    | Yellowish      |
| Odor                         | -    | Bad smell      |
| Total dissolved solid        | ppm  | 2897 ± 5.2     |
| Chemical oxygen demand       | ppm  | 104 ± 1.1      |
| pH                           | -    | 8.83 ± 0.09    |

2.4. Characterization of fabricated membrane
The surface morphology of the fabricated membranes were evaluated using a scanning electron microscopy (SEM) by (JEOL Series instrument, Japan), this method produced the surface morphology picture of the membrane for in-depth qualitatively analysis. The evidence of ZnO doped to PSf polymer was analyzed by X-ray diffraction (XRD) by (SHIMADZU, Japan). The mechanical strengths that are tensile strength and elongation break to evaluate their durability was calculated by using mechanical testing instrument by (UTSH001, China). The membrane hydrophilicity was investigated using contact angle meter by (RASE contact angle meter, Japan).
2.5. **Membrane’s thickness, porosity, and average pore radius evaluation**

Membrane thickness was evaluated using digital micrometer (Mitutoyo 293, Japan). Porosity of the membrane was investigated using scientific approximation. Firstly, the membrane was soaked in DI water for 24 h and weighing the film after mopping the water on the surface using proper filter paper. Then, it was placed in an oven at 60 °C for 24 h and then it was putted in desiccator before measuring the dry weight of the membrane. The porosity of membrane was calculated using Eq.1. [23]

\[
\varepsilon = \frac{W_f - W_i}{\rho_w \times A \times \delta} \times 100\%
\]

(1)

Where \(\varepsilon\) is the membrane porosity (%), \(w_f\) and \(w_i\) are the mass of the wet and dry membranes (gram) respectively. The density of DI water at room condition \(\rho_w\) (0.997 g.cm\(^{-3}\)), \(A\) is the effective membrane contact area (cm\(^2\)). \(\delta\) is the thickness of the membrane (cm).

We analyzed the average pore radius using the Guerout-Elford-Ferry approximation. The pore size \((r)\) could be calculated by Eq.2. [23]

\[
r = \sqrt{\frac{8 \eta \delta Q \times (2.9 - 1.75 \varepsilon)}{\varepsilon \times A \times \Delta P}}
\]

(2)

Where, \(\eta\) is the pure water viscosity at room condition \((8.9 \times 10^{-4} \text{ Pa.s})\), \(\delta\) is the thickness of the membrane (m), \(Q\) is the volumetric flow rate of the permeate (m\(^3\).s\(^{-1}\)), and \(\Delta P\) is the trans-membrane pressure (Pa).

2.6. **Water uptake ability of fabricated membrane**

The procedure of water uptake ability was adapted from [24]. Water uptake was measured using Eq.3.

\[
U = \frac{W_w - W_d}{W_d} \times 100\%
\]

(3)

Where, \(U\) is the water uptake ability (%), \(w_w\) is the weight of wet membrane (gram), and \(w_d\) is the weight of dry membrane (gram).

2.7. **Performance study of fabricated composite PSf-ZnO membrane**

The separation performance of membrane was evaluated using cross flow filtration module with a piece of flat sheet membrane with diameter of 4 cm shown in Fig. 1. This membrane filtration apparatus system has been used in previous research [8, 23]. The feed water used in this filtration experiment was the PRW without pre-treatment. The PRW from the plant was directly placed in the feed container before the filtration started.

2.7.1. **Permeate flux**

Permeate flux is the amount of water across through the membrane per unit of area per unit of time. We were evaluated pure water flux and PRW flux to understand the membrane performance. The permeate flux was calculated using Eq.4.

\[
J = \frac{V}{A \times t}
\]

(4)

Where, \(J\) is the permeate flux. \(V, A, t\) are the volume of permeate (L), effective membrane contact area (m\(^2\)), and filtration time (h), respectively.
2.7.2. Pollutant rejection
The pollutant rejection performance was determined by measuring the concentration before and after membrane filtration test. The pollutant parameters were total dissolved solids (TDS), chemical oxygen demand (COD), and pH. The pollutant rejection was determined by Eq. 5.

\[ R = \left(1 - \frac{C_f}{C_i}\right) \times 100\% \]  \hspace{1cm} (5)

Where, \( R \) is the pollutant rejection (%), \( C_i \) and \( C_f \) are the feed and permeate concentration/ value of pollutant parameter (ppm), respectively.

2.8. Antifouling potential study of composite PSf-ZnO membrane
The evaluation of antifouling potential was examined to obtain the total fouling ratio (\( R_t \), %), reversible fouling ratio (\( R_r \), %), irreversible fouling ratio (\( R_{ir} \), %), and the flux recovery ratio (\( F_{RR} \), %) by using these following formula [15].

\[ R_t = \left(\frac{J_{pw0} - J_{ww}}{J_{pw0}}\right) \times 100\% \]  \hspace{1cm} (6)

\[ R_r = \left(\frac{J_{pw1} - J_{ww}}{J_{pw0}}\right) \times 100\% \]  \hspace{1cm} (7)

\[ R_{ir} = \left(\frac{J_{pw0} - J_{pw1}}{J_{pw0}}\right) \times 100\% \]  \hspace{1cm} (8)

\[ F_{RR} = \left(\frac{J_{pw1}}{J_{pw0}}\right) \times 100\% \]  \hspace{1cm} (9)

Where, \( J_{pw0} \) is the initial pure water flux. \( J_{pw1} \) is the pure water flux after cleaning. \( J_{ww} \) is the permeate flux of wastewater.
3. Results and discussion

3.1. Characterization of fabricated membrane

3.1.1. Surface morphological study
The evaluations of the effect of ZnO nanoparticle with PSf polymer on membrane surface morphology was compared in Fig. 2. A smooth surface without any pores represented in Fig. 2A shows the surface of neat PSf membrane. On the other hand, Fig. 2B, which is composite membrane PSf/ZnO 1 %-wt depicts some white dots on the surface of the membrane, is the effect of ZnO nanoparticles mixing with PSf polymer. This condition agreed with the unsimultaneous solidification of the composite membrane in time with the coagulation process in the non-solvent bath [23].

![Fig.2. SEM images of membranes; A) Neat PSf and B) PSf/ZnO 1%.

However, this condition is still right related to the appearance of those spots on the membrane surface is quite rare. Therefore, it may be the more massive amount of ZnO nanoparticle are already embedded in the sublayer of the film of the membrane. This condition could be due to the high affinity between ZnO nanoparticles and PSf matrix. The embedded ZnO in the middle layer of the PSf membrane is helpful to increase the anti-compaction effect, thus obtaining in steady permeate flux [22]. ZnO nanoparticle has hydrophilic properties. The embedded ZnO nanoparticle in the PSf polymer, which is hydrophilic, could be gained more water through it and could be increased the permeate water flux.

3.1.2. Pore properties of fabricated membranes
The evaluation of membrane pore properties was conducted by investigating the membrane thickness, porosity, and average pore radius. Table 2 shown the thickness, porosity, and average pore radius of the membrane increased in line with increasing ZnO concentration. Incorporating ZnO to PSf slightly increase the thickness up to 54.3 ± 0.67 micrometer, this caused by the swelling effect due to the addition of nanoparticle to the membrane sublayer. The increasing of thickness will be raising the resistance of the membrane [18]. However, this thickness addition size is quite small and not significantly reduced membrane performance.

Similarly, the porosity of the membrane was increased with higher addition of ZnO nanoparticles. The addition of 1 %-wt ZnO nanoparticle was increased porosity from 52.2 ± 0.28 % to 59.3 ± 1.23 %. The blending of hydrophilic substance to the membrane increases the pore formation to the sublayer of the membrane. Consequently, the density of pores in the membrane increased by incorporating some amount of ZnO nanoparticles. This condition was contributed to an increase in the porosity of the membrane sharply. Also, a similar trend was in the average pore radius. The increasing concentration of ZnO nanoparticle was slightly increasing the pore radius on the membrane. The ultrafiltration membrane has pore radius between 10 – 100 nm [25]. The more significant pore would be reduced the selectivity of the membrane. The composite PSf/ZnO 1 %-wt has achieved the maximum average pore radius of 41.6 ± 0.56 nm, that still in the range of ultrafiltration membrane.
Table 2. Pore properties of the fabricated membranes

| Variables        | Thickness (micrometer) | Porosity (%) | Average pore radius (nm) |
|------------------|------------------------|--------------|--------------------------|
| Neat PSf         | 53.0 ± 0.58            | 52.2 ± 0.28  | 38.2 ± 1.01              |
| PSf-ZnO 0.5%     | 53.7 ± 0.88            | 55.1 ± 0.10  | 40.5 ± 0.60              |
| PSf-ZnO 1%       | 54.3 ± 0.67            | 59.3 ± 1.23  | 41.6 ± 0.56              |

3.1.3. XRD diffractogram study

The crystalline structure of composite membranes was investigated to analyze the change in the physical structures of the PSf membrane with the incorporation of ZnO nanoparticle. Fig 3 represents the results of XRD diffractogram of membranes. Study of XRD was to confirm the existence of ZnO nanoparticles in the sublayer of the membrane. The presence of a broad peak at around 20° is the central character of PSf membranes [26]. The sharp peaks that appeared in the diffractogram representing the crystalline structure. In neat PSf membrane, there is no sharp peaks appeared indicating the amorphous structure.

Fig.3. XRD diffractogram of membranes; A) Neat PSf, B) PSf/ZnO 1 %-wt, C) ZnO powder.

The ZnO powder diffractogram exhibits some typical sharp peaks at around 31°, 37°, 41°, 50°, and 62°. The PES/ZnO 1 %-wt membrane, represents a similar broad peak like the neat PSf and some sharp peaks like the ZnO diffractogram. The composite membrane diffractogram represents the existence of ZnO nanoparticle in the sublayer of the PSf membrane. It was the critical evidence that the ZnO nanoparticle wasn’t dissolving and leach out during the phase inversion process and soaking process. The embedded ZnO nanoparticle can enhance the properties and performance of the PSf membrane.

3.1.4. Hydrophilicity properties and water uptake ability

The surface characteristics of membrane play a significant role in water transport through the membrane during the filtration process. The membrane hydrophilicity was investigated by analyzing the contact angle and water uptake ability of the membrane shown in Fig. 4. The water contact angle of neat PSf membrane was 81° ± 1.15°, and that was reduced to 65° ± 0.88° with the incorporation of 0.5%-wt of ZnO nanoparticles. Further, reduce in contact angle was found in the addition of 1%-wt of ZnO nanoparticles. The combination of PSf/ZnO 1 %-wt provided the least contact angle value of 60° ± 0.57°.
The reduction of the contact angle by the addition of ZnO also reported in other research [19]. The incorporation of ZnO nanoparticle reduced the contact angle caused by induced dipole and dipole-dipole interaction between water molecules and membrane surface [27]. The surface characteristics of the membrane also play a significant effect at the boundary of water and membrane surface in term of sorption capability. Moreover, hydrophilicity is an important factor for enhancing the antifouling potential of the membrane [28]. Hydrophilicity is a parameter to measure the tendency for water to penetrate on the membrane, so a reduction in water contact angle means the higher tendency of membrane surface to gain the water uptake of the membrane [18].

One more method to explain the hydrophilicity of the membrane is water uptake ability. The water uptake of membrane strongly depend on the number of hydrophilic parts exist in the membrane surface, and the other one is the existence of macro voids in the polymer sublayer [29]. It can be seen from the water uptake results in Fig. 4 that the water uptake increases as the concentration of ZnO nanoparticle increased. This result is the clear indication of the hydrophilic sites in the PSf polymer was increased due to the addition of ZnO nanoparticles.

![Fig. 4. Results of A) water contact angle and, B) water uptake ability results of the membrane](image)

3.1.5. Mechanical strengths study

The evaluation of mechanical strength of the membrane is important to be known since it describes the membrane durability to the external pressure of filtration process [23]. The incorporating of ZnO nanoparticle was successfully embedded in the membrane based on SEM and XRD results previously. The ZnO nanoparticle caused changing in the structure of the membrane matrix. The structural pattern play a significant role of the mechanical strength of the membrane. Fig. 5 represents the results of mechanical strength and elongation break of membranes. The pristine PSf membrane shows the least value of tensile strength and elongation break measurement of 2.73 ± 0.12 MPa and 4.46 ± 0.08 %, respectively. By increasing the ZnO nanoparticle concentration showed the increase in tensile strength and elongation break measurement. The highest tensile strength and elongation break value was achieved by addition of 1 %-wt of ZnO nanoparticles. The highest measurement was 4.03 ± 0.03 MPa of tensile strength and 8.80 ± 0.03 % of elongation break. The addition of ZnO nanoparticle was help to absorb the pressure force applied to the membrane. It made the membrane doesn’t easily break with a higher external pressure force.
3.2. Performance study of composite PSf-ZnO membrane

3.2.1. Permeate flux performance study
Permeate flux is one of the critical methods to observe the performance of the membrane during the filtration process. Fig. 6 represents the pure water flux (PWF) of the prepared membrane. The PWF was experimented using DI water as the feed. All of three membranes composition shows the higher water flux compared with the same membrane when performed with PRW as the feed. This result is because the DI water has less amount of pollutant. The other finding was that the PWF increased by the increasing ZnO nanoparticle concentration in the membrane. The water uptake evaluation caused that the water uptake increases with ZnO adding, and a similar result has been found in the case of PWF. The addition of ZnO nanoparticle into membrane produces in higher availability of hydrophilic sites, which expedites the sorption ability of water.

Fig. 7A depicts the permeate flux of the membranes with PRW as the feed water in the filtration experiment. Based on Fig. 7A represents that the neat PSf membrane has the inferior permeate flux among the others with initial permeate flux was 11.14 L.m⁻².h⁻¹. The membranes with the incorporation of ZnO nanoparticles was showed better performance. The composite membrane achieved the superior performance in term of permeate flux with incorporating 1 %⁻⁻⁻⁻wt of ZnO nanoparticles, with the initial
The permeate flux of 11.29 L.m$^{-2}$h$^{-1}$. All of the membranes permeate flux was reduced with the time; the fouling probably caused it. The decline of permeate flux during filtration shows in Fig. 7B. It represents the normalized permeate flux curves. It can be used to explain the fouling indication on the surface of the membrane [30].

![Fig. 7. Permeate flux analysis results; A) Permeate flux and, B) Normalized permeate flux.](image)

The normalized curves also can explain the fouling resistance of the membrane. It was shown that the addition of ZnO nanoparticle into membrane has resulted in the least fouled. The PSf/ZnO 1 %-wt membrane shows about 40% of fouling at the end of the filtration process, and the neat PSf membrane shows the worst fouling, about 80%. The addition of ZnO nanoparticle is proved in order to increase the improvement of flux recovery ratio and fouling ratios (that will be further discussed in section 3.3). The improvement was indicated in the increase of porosity, surface hydrophilicity and water uptake ability. Notably, the increase of surface hydrophilicity is help in rejecting the hydrophobic pollutant particulates—consequently, the fouling tendency to the surface of the membrane was reduced with the addition of ZnO nanoparticles.

### 3.2.2. Pollutant rejection performance study

Pollutant rejection is another parameter to evaluate membrane performance. In this project, the pollutant parameter that measured to be removed by the membrane are total dissolved solids (TDS), chemical oxygen demand (COD), and pH. The pollutant rejection performances of the fabricated membrane are shown in Fig. 8. Based on Fig. 8 that the performance of pollutant rejection of the membrane increase with the ZnO nanoparticle increased. The neat PSf rejection performance was about 16% and 6% for TDS and COD, respectively. The superior rejection performance was achieved by the PSf/ZnO 1%-wt membrane with about 48% and 34% for TDS and COD, respectively. The surface hydrophilicity plays a critical action in this phenomena. The ZnO nanoparticle contributes to the positive electrostatic force to create the positively charged surface [17]. Therefore, the increasing ZnO nanoparticle to the membrane tends to have higher rejection performance. However, the uncontrolled addition of nanoparticle would cause a negative impact on the membrane. It is due to the agglomeration created by excessive nanoparticle and caused severe damage to membrane pores. It will worsen the membrane rejection performance.

Fig. 9A represents the pH of the permeate product of the membranes. The PRW characteristic has a pH of about 8.83 ± 0.09. This basic condition is due to the existence of ammonium ion (NH$_4^+$) [8]. The pH of the permeate product by using neat PSf membrane was 8.42 ± 0.02. It was the highest permeate product of filtration among the others. The PSf/ZnO 1%-wt membrane shows the excellent pH of permeate with pH about 8.11 ± 0.01. It was the closest value of pH to the pure water. The increasing composition of ZnO nanoparticle would be reduced the measured pH. Similar to the previous argument that the increasing ZnO nanoparticle to the membrane tends to have higher rejection performance.
Another finding that the reduced value of pH is caused by the declined value of the electrical conductivity. Fig. 9B shows the electrical conductivity of the permeate product of the membranes. Electrical conductivity is indicated the ionic substance contents in the water. The more ionic substances, the higher the electrical conductivity measured. The reduction of electrical conductivity by the ZnO nanoparticle increased is occurred by the positively charged surface of the membrane to repel the basic type ion in PRW, which was the ammonium ion (NH$_4^+$).

Fig. 9. pH and electrical conductivity of permeate water

3.3. Antifouling potential analysis of composite PSf-ZnO membrane

The antifouling potential analysis is conducted to explain the effect of adding ZnO nanoparticle to the membrane fouling tendency. The ratio of total fouling ($R_t$), reversible fouling ($R_r$), irreversible fouling ($R_{ir}$), and the flux recovery ratio ($F_{RR}$) have calculated by using Eq. 6, Eq. 7, Eq. 8, and Eq. 9, respectively [15]. These results can be seen in Fig 10. The total fouling ratio and irreversible fouling ratio were declined with increasing the ZnO nanoparticle content. These phenomena indicates that the incorporation of ZnO nanoparticle to the membrane have succeeded to improve the antifouling potential.
on the surface of the membrane [31]. The reversible fouling ratios of all membranes weren’t found any significant difference. It means the reversible type of pollutant amount in the PRW was not significant. The flux recovery ratios (FRR) increase significantly by increasing the ZnO nanoparticle into it. The maximum FRR was achieved by the composite membrane PSf/ZnO 1 %-wt with a value of about 72.4% ± 1.22%. The increase of FRR value indicates less effort to do the hydraulic cleaning of the membrane. The superior result exhibits by composite membrane PSf/ZnO 1 %-wt is the evidence of synergetic effects of improving hydrophilicity, porosity, and water uptake by ZnO addition.

![Fouling ratio graph](image)

**Fig. 10.** The results of fouling ratio of membranes

4. Conclusion
In this research, modification of the PSf membrane was fabricated via NIPS process with incorporating nanoparticle. ZnO nanoparticle was chosen and mixed with PSf polymer to increase the hydrophilicity of the fabricated membrane in order to overcome the fouling behavior. The addition of ZnO nanoparticle changed some characteristics of the membrane. Therefore, it was found that the incorporation of PSf and ZnO produced better than the neat PSf. Particularly, the composite membrane of PSf/ZnO 1%-wt was the most significant in membrane properties; porosity, hydrophilicity, water uptake ability, and antifouling characteristics. It was also the most significant in terms of performances; PWF, permeate flux, and pollutant rejection. The antifouling potential study was found that the composite membrane of PSf/ZnO 1%-wt has superb characteristics which have the highest flux recovery ratio about 72.4% ± 1.22%. This current research is a good contribution in term of enhancing membrane synthesis, modification, and application in the field of petrochemical wastewater treatment.

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