Effect of Polyvinyl Pyrrolidone Additive on the Characteristics and Performance of Polyether Sulfone Membrane for Reducement of Fe in Water

Sofyana*, Y Syamsuddin, S Mulyati, F Razi
Departement of Chemical Engineering, Universitas Syiah Kuala, Darussalam, Banda Aceh-23111, Indonesia

*Email: sofyana71@unsyiah.ac.id

Abstract. Decreasing the iron (Fe) content in raw water until it reaches the permitted threshold value can be done with filtration using membranes. In this study, the fabrication of membrane for Fe removal was done by using polyethersulfone (PES) as polymer and Polyvinyl Pyrrolidone (PVP) as additive. The addition of PVP aims to increase membrane swelling degree. The asymmetric membrane was prepared by phase inversion method with composition 18 wt% of PES and PVP with a concentration variation of 1; 1.5, and 2 wt%. Variations in the concentration of PVP added to the membrane influence the resulting membrane. Increasing the concentration of PVP shows an increase in the value of permeability, SEM results from modification membranes also show the different morphological structures. The results of the FTIR analysis show that the fabricated membranes have different functional groups. The swelling degree of PES, PES/PVP1, PES/PVP1.5, and PES/PVP2 membranes are increased with a value of 153 to 323%, while the overall porosity value is 62 to 142%. Membrane performance on iron content with 30 ppm feed concentration gives an optimum rejection value of 98.5%.

1. Introduction
Metal is a natural substance found in water sources. Metals enter the source of water naturally when rainwater seeps through the mountains where a number of metals will be dissolved into the water. This water will enter large water sources and will be used by the community for various purposes. Iron (Fe) is a metal that is naturally present in water [1]. Water source receive iron either through geogenic sources or through industrial waste deposits or through mining and metal corrosion [2]. The sources of iron in surface water are mainly pollution from iron and steel industries, mining and metal corrosion [3]. Aside from surface water, iron is also found in groundwater. Some countries have high iron content in groundwater sources, such as Indonesia, which in some regions has water sources with iron levels above the maximum threshold. Iron content in surface and groundwater varies from 3 to 4 mg/L to 15 mg/L [4]. Limits allowed for drinking water is 0.3 mg/L [5,6]. Water containing iron is generally brownish yellow and stinking, high iron content in the water can be felt when the water is drunk or can be seen from the onset of rust on equipment and clothing [7].

Removal of iron metals from water can be done by various methods both conventional methods such as filtration-precipitation-oxidation, zeolite softening/ion exchange, filter media separation, removal through supercritical fluid, wetland treatment, electrocoagulation/flotation, aeration, and with...
Membrane technology is a process that continues to develop and is widely applied in water treatment containing metals. Membrane separation technology is an applicable technology that is preferred because it does not produce harmful by-products, easy to operate, low energy consumption and does not use significant chemical additives.

Polymeric membranes are often used in the process of Reverse Osmosis, Nanofiltration, Microfiltration Ultrafiltration and Gas Separation. Organic membranes are usually made from synthetic polymers such as polysulfone, polyethersulfone, cellulose acetate, or polyamide. Recently polyethersulfone is often used because of some interesting properties, this is indicated by thermal stability, thermal resistance, chemical resistance to acids, petrol, oils and oxidizing agents such as flour and hydrogen peroxide in addition to mechanical strength, tolerance to a wide temperature range, pH, physiological neutrality, low sensitivity to UV.

The development of materials used in the manufacture of membranes continues to be done to obtain the best membrane in accordance with the application of the membrane. Membrane with a mixed matrix is one membrane that is widely used in the manufacturing process by combining several specific materials with significant characteristics into membrane structures such as titania, alumina, zinc oxide, silica, zirconia, iron oxide, polyvinyl alcohol and polyvinylpyrrolidone. In this study, membranes based on Polyethersulfone polymer are modified with polyvinylpyrrolidone (PVP) as a pore forming agent which is expected to be able to remove iron metal.

2. Methodology

2.1 Materials
Materials used in this research included Polyethersulfone was purchased from BASF, Polyvinil Pirolelydine and Dymethyl Acetamide was supplied by EMSURE, FeCl₂ solution as an artificial feed solution represents the condition of water contaminated with Fe metal, aqua distilled deionized. All chemicals used are analytical grade, except for distilled water.

2.2. Preparation of Membrane
The membrane is prepared using the Phase Inversion technique. Membrane solution is made by mixing PES, PVP, and DMAc, the mixture is stirred for 24 hours with a magnetic stirrer at a suitable speed, the homogeneous solution formed is called a dope solution. The dope solution is left at room temperature for debubbling and then cast on a glass plate with a thickness of 175 µm, after casting it is immersed in a coagulation bath containing water as non-solvent until the membrane is separated from the glass plate. The membrane formed is placed in distilled water for 24 hours and then the membrane is dried by placing it between two filter paper.

The membrane is made based on the composition as shown in Table 1, where the PES concentration remains 18% and the PVP concentration is varied, whereas the concentration of the DMAc solvent follows the percentage of PVP. One is a pure PES membrane without the addition of PVP which serves as a comparison. The prepared membrane is then stored for analysis.

2.3. Characterization
The characteristics of the membrane are performed before the membrane is tested for performance, including permeability test, swelling degree, and overall porosity, and also functional groups using Fourier Transform-Infrared (FTIR) (Shimadzu FTIR-Prestige 21 Series). Meanwhile, surface and cross-section morphology are analyzed with Scanning Electron Microscopy (SEM) (Jeol. Jsm - 6510 LA).

2.3.1 Permeability test.
Permeability testing is carried out using a distilled deionized water feed, by flowing pressure from nitrogen gas as a driving force to drain a distilled deionized water feed through the membrane. Permeate volume is held at certain intervals until steady conditions are achieved. Permeability testing is carried out at pressures 2, 3, 4, 5 and 6 bar.
| No | PES (wt%) | PVP (wt%) | DMAc (wt%) | Membrane ID |
|----|-----------|-----------|------------|-------------|
| 1  | 18        | 0         | 82         | PES         |
| 2  | 18        | 1         | 81         | PES/PVP1    |
| 3  | 18        | 1.5       | 80.5       | PES/PVP1.5  |
| 4  | 18        | 2         | 80         | PES/PVP2    |

2.3.2 Swelling degree and overall porosity.

To measure the degree of swelling, membrane samples of a certain size are immersed in water for 24 hours. Then dried by placing between filter paper and then weighed. After that the membrane is dried in an oven at 50 °C for 24 hours and after that the weight is weighed again.

\[
\text{Swelling Degree} \, (\%) = \frac{(W_w - W_d)}{W_d} \times 100
\]

Where \( W_d \) = dry weight (gram), \( W_w \) = wet weight (gram)

\[
\text{Overall Porosity} \, (\%) = \frac{W_w - W_d}{A \times l \times d_w} \times 100
\]

Where \( A \) is effective membrane area (cm\(^2\)), \( l \) is membrane thickness (cm), \( d_w \) is water density (g/cm\(^3\)).

To reduce errors, the test was repeated and the average value is shown as the data reported (Ghaemi, 2016).

2.3.3 Scanning Electron Microscopy

Cross-section morphology of the prepared membranes was examined by scanning electron microscopy (SEM). Samples were tested using electron beams with kinetic energy of 10 kV. Magnification of the pictures taken is 1000 times for the surface and 800 times for the cross-section.

2.4 Membrane performance testing

Membrane performance testing using FeCl\(_2\) feed solution was carried out in a stainless steel cell, holding the effective area of 10.2 cm\(^2\). The experiments were carried out using compressed nitrogen gas and solutions of different concentrations (10, 20 and 30 mg/L) and all measurements were made at 6 bars. The permeate obtained was collected and the flux value was calculated using equation (3) and the permeate obtained was analyzed by Fe content using a spectrophotometer UV-VIS, Shimadzu, 1700.

\[
J_w = \frac{V}{A \times \Delta t}
\]

Where \( J_w \) (L/m\(^2\).h) is the flux of water, \( V \) (L) is the volume of permeate

\[
\% \text{Removal} = 1 - \frac{C_f}{C_p} \times 100\%
\]

Where \( C_f \) and \( C_p \) are feed and permeate Fe concentrations, respectively.

The permeate obtained was analyzed for Fe concentration using Spectrophotometer UV-VIS equipment.

3. Results and Discussion

3.1. Permeability, swelling degree and overall porosity of membrane

A large porosity of the membrane will make the membrane have pores evenly distributed so that this membrane has the ability to filter unnecessary element in water [14]. It is due to when the water filtration
process takes place, the membrane cavity will be filled with Fe molecules, with a large number of membrane pores, so many Fe molecules can be absorbed. And it will be able to reduce Fe content optimally in groundwater.

![Figure 1. The schematic diagram of the membrane equipment](image)

**Table 2. Permeability of Membrane**

| Membrane ID | Lp (L/m².h.bar) | Swelling degree (%) | Overall porosity (%) |
|-------------|-----------------|---------------------|---------------------|
| PES         | 0.4219          | 153,547             | 62,361              |
| PES/PVP1    | 2.8678          | 221,234             | 120,432             |
| PES/PVP1.5  | 18,817          | 271,102             | 133,680             |
| PES/PVP2    | 19,822          | 342,801             | 148,351             |

From Table 2 it can be seen that the permeability value of pure water (Lp) on the PES membrane is increasing with an increase in PVP concentration. That is because the membrane with the addition of PVP additives has more pore structure and is evenly distributed in the support layer and in the top layer or active layer, so that the feed will easily pass through the membrane compared to the membrane without the addition of PVP [15]. The membrane classified as nanofiltration is a PES/PVP1 membrane with a permeability coefficient value obtained at 2.8678 L/m².h.bar [16].

3.2 Functional groups
As seen in Figure 2, shows that all three membranes have similar functional groups where there are sulfone and ether groups. Sulfon group (SO₂) is shown at wavenumber of 1265 - 1289 cm⁻¹, ether group (COC) at wavenumber of 1320 - 1137 cm⁻¹, CH group at absorption wavenumber of 1465 cm⁻¹, and group C = C at group wavenumber of 1600 cm⁻¹.

3.3 Membrane Morphology
Surface morphology analysis with SEM exhibits the difference between PES membrane and PES membrane with the addition of PVP at various variations of PVP concentration. Figure 3 (a) and (b) are the results of SEM on the surface of the PES membrane and PES with the addition of PVP, PES / PVP1 membranes have a more flat surface area, this shows a better pore distribution. The appearance of the cross-section structure shows that all membranes have asymmetric membrane characteristics that are
fabricated by the phase inversion method, which has a dense top layer structure supported by fine-finger like and macrovoid sub layers. Membranes with the addition of PVP show a different structure, a better pore formation is clearly seen on the support layer (Figure 3(b) to 3(f)). The addition of PVP concentration increases the value of swelling degree and overall porosity. This is in consistent with the cross-sectional structure seen in the results of Scanning Electron Microscopy, which is more pore formed and spread. Pore formation increases membrane permeability.

![Figure 2. FT-IR spectrum of PES/PVP1, PES/PVP1.5 and PES/PVP2](image)

The pure PES membrane has an active layer that is thicker than the PES/PVP membrane, so that the pure PES membrane Lp value is very low at 0.412 L/m².h.bar, different from the Lp value of the PES/PVP2 membrane which is 19.822 L/m².h.bar, where the active layer becomes thinner and the support layer forms a larger pore so that the permeability value increases.

3.3. The performance of the membrane in Fe removal

Flux is one of the most important parameters performed to determine the performance or ability of the membrane in the separation process, the measurement of flux in this study was carried out using FeCl₂ solution. FeCl₂ solution with a concentration variation of 10; 20 and 30 Mg/L are used as feed conditions in measuring flux values using the optimum pressure from permeability testing which is 6 bar. The flux value is obtained by using equation (4).

Figure 4 shows the difference in flux values between pure PES membrane and membrane after the addition of PVP additives at various concentrations of feed. The results of the flux values obtained indicate that the addition of PVP additives can increase the flux value of the modified membrane compared to the pure PES membrane, where the flux value at the 30 mg/L feed concentration of increased from 5.5 L/m².h.bar (pure membrane) to 35.1; 49.9 and 60.9 L/m².h.bar for PES/PVP1, PES/PVP1.5, and PES/PVP2 membranes, respectively. Similarly, in a feed concentration of 20 and 10 mg/L, the flux obtained also increased from 24.1 L/m².h.bar (pure membrane) into 51.1; 63.2; 69.4 L/m².h.bar for PES/PVP1, PES/PVP1.5, and PES/PVP2 membranes, respectively and from 8.3 L/m².h.bar (pure membrane) to 37.1; 59.4; and 82.3 L/m².h for PES/PVP1, PES/PVP1.5, and PES/PVP2 membranes, respectively. This is because the addition of PVP can increase the pore size and hydrophilicity of the membrane, a larger pore size will make the feed solution easier to pass through the membrane and cause an increase in the flux value.
Figure 3. SEM image of the surface of membrane: (a) PES and (b) PES / PVP1, cross section of membrane: (c) PES, (d) PES / PVP1, (e) PES / PVP1.5 and (f) PES / PVP2
Figure 4. Membrane flux to the FeCl$_2$ feed solution

Figure 5 shows the rejection value obtained after the feed solution is passed on the membrane using pressure as the driving force, the rejection obtained tends to fluctuate but is not very significant at various feed concentrations given. At a feed concentration of 10 mg/L the rejection value obtained reached 99% for the PES membrane with the addition of PVP, here the effect on the percentage of the addition of PVP did not have a significant effect. At a feed concentration of 20 mg/L the percent rejection value obtained reached 98.20% for the PES/PVP2 membrane, as well as 96.8; 94.9; 95.8 and 96.7% at a feed concentration of 30 mg/L respectively for membrane PES, PES/PVP1, PES/PVP1.5 and PES/PVP2. The greater the concentration of feed given, the smaller the rejection value obtained. This occurs because during the testing of different feeds there has been fouling or concentration build-up in the pores of the membrane, causing the value of the percentage of rejection obtained decreases (Liu et al., 2017).

4. Conclusion

The addition of Polyvinyl Pyrrolidone as a pore forming agent influences the structure of the Polyether Sulfone membrane by increasing the degree of swelling and porosity of the membrane thereby increasing the permeability value. As the PVP concentration increases, the permeability and flux values of the FeCl$_2$ feed solution increase, the PES membrane has a permeability value of 0.4219 L/m$^2$.h.bar different from the PES/PVP2 membrane that is 19.822 L/m$^2$.h.bar. The PES membrane with the addition of PVP has a morphological structure with a greater number of pores and the support part has a well-distributed finger-like pore. The ability of PES/PVP membranes in Fe metal recovery is quite good, which is in the range of 96 to 98%. The addition of PVP concentration did not have a major effect on
the ability to recover Fe metal. Increasing the concentration of the feed solution decreases the rejection value by ± 2% for each increase in the concentration of 10 mg/L.

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6. References

[1] Khatri N, Tyagi S and Rawtani D 2017 J. Water Process Eng. 19 291.
[2] Khatri N and Tyagi S 2015 Front. Life Sci. 8 23.
[3] Jusoh A, Cheng W H, Low W M, Nora’aini A, Megat Mohd Noor M J 2005 Desalination 182, 347.
[4] Ellis D, Bouchard C and Lantagne G 2000 Desalination 130 255.
[5] World Health Organization 1996 Iron in drinking water In: Guidelines for drinking-water quality, 2nd ed. Vol 2. Health criteria and other supporting information. Geneva.
[6] Khatri N, Tyagi S and Rawtani D 2016 Environ. Claims J. 28 1.
[7] Febrina L and Ayuna A 2015 Jurnal Teknologi 7 35.
[8] Arahman N, Mulyati S, Lubis M R, Takagi R, Matsuyama H. 2017 J Water. Proc. Eng. 20 173.
[9] Li N N, Fane A G, Winston Ho W S and Matsuura T 2008 Advance membrane technology and applications (New Jersey: Wiley & Sons).
[10] Pabby A K, Rizvi S S H and Sastre A M 2009 Membrane separations – chemical, pharmaceutical food and biotechnological applications (New York: CRC Press Taylor & Francis Group LLC).
[11] Barth C, Goncalves M C, Pires A T N, Roeder J and Wolf B A 2000 J. Membr. Sci. 169 287.
[12] Zhao W, Huang J, Fang B, Nie S, Yi N, Su B, Li H and Zhao C 2011 J. Membr. Sci. 369 258.
[13] Ghaemi N, Daraei P and Akhlaghi F S 2018 Carbohydr Polym. 191 142
[14] Arahman N, J. 2012 J Rekayasa Kimia & Lingkungan 9 (2) 68.
[15] Ghaemi N 2016 Appl. Surf. Sci. 364 221.
[16] Muchtar S, Wahab M Y, Fang L F, Jeon S, Rajabzadeh S, Takagi R, Mulyati S, Arahman N, Riza M, Matsuyama H. 2019 J. Appl. Polym. Sci. 136 47312.