



THE EFFECT OF POLYVINYLPIRROLIDONE ON THE PERFORMANCE OF POLYVINYLIDENE FLUORIDE MEMBRANES

Mirna R. LUBIS*, Wahyu RINALDI, Suraiya KAMARUZZAMAN, Umi FATHANAH

Universitas Syiah Kuala, Department of Chemical Engineering, Banda Aceh, 23111, Indonesia

Received: 20 November 2021

Revised: 31 December 2021

Accepted: 17 January 2022

In this investigation, polyvinylidene fluoride membranes were resulted by a phase inversion technique with polyvinylpyrrolidone (PVP) as an agent to form pores, as well as n-methyl pyrrolidone as a solvent. In addition, the effect of PVP concentration (1–4%) was investigated to prepare membranes with better membrane antifouling performance and characteristics. Furthermore, functional groups, morphological structures, and membrane porosity were analysed by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and membrane porosity calculation. The surface SEM images revealed that the size of the modified membrane pores increased. The increase of the PVP concentration added, resulted in the number of modified membrane pores. FTIR spectra confirmed that PVP functional groups were dispersed in the PVDF membrane matrix. Optimum pure water permeability (PWP) of 60 L/(m²·h·bar) was achieved using 3% PVP, resulting in a humic acid rejection percentage of 80% and a water flux recovery ratio (FRR) of 85%. These findings indicate that the utilization of PVP as a pre-forming agent resulted in higher PWP, lower humic acid rejection, and good antifouling properties.

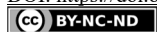
Keywords: antifouling, porosity, polyvinylidene fluoride, polyvinylpyrrolidone, pure water permeability.

INTRODUCTION

Currently, the increasing population demands the need for clean water. Usually, humans use sea water (1), well water, as well as other surface water sources to meet their water needs. However, the water quality still does not meet the health quality standards because of the presence of organic matter (e.g., humic acid) and other dissolved solids (2). So far, conventional methods (e.g., coagulation, sedimentation, and filtration) have been used for water treatment; however, the organic matter content of processed water is still above the quality standard required by the Ministry of Health. In addition, the use of large amounts of coagulant in conventional processes, apart from being expensive, also has a negative consequence on the environment. Membrane filtration is one of the clean water treatment technology that is superior in terms of the quality of the water produced. Membrane technology is a promising separation method to solve clean water problems because of the advantages of membrane technology, including low energy consumption, operation with the minimal use of chemicals, ease of use, and environmentally friendly and simple process methods (3).

Various polymeric materials have been utilized to manufacture membranes. Among them, polyvinylidene fluoride (PVDF) has been commonly utilized as an ultrafiltration membrane because of its advantages, such as good chemical resistance, good thermal quality, high organic selectivity, good membrane forming and mechanical characteristics (4).

* Corresponding author: Mirna Rahmah LUBIS, Universitas Syiah Kuala, Chemical Engineering Department, Banda Aceh, 23111, Indonesia, e-mail mirna@che.unsyiah.ac.id



There have been many applications of PVDF membranes for ultrafiltration and micro-filtration processes. Currently, exploration is being carried out for the contactor membrane and distillation membrane processes because of their hydrophobic nature. PVDF is soluble in polar compounds, such as dimethyl sulfoxide and *N*-methyl-pyrrolidone because of the polar nature of the arrangement of the CH₂ and CF₂ groups. These polar solvents are ideal for the manufacture of PVDF membranes through the phase inversion technique.

However, PVDF is limited because it easily gets dirty because of its hydrophobic nature and is difficult to clean (5). PVDF membrane is hydrophobic so it is not resistant to fouling in water treatment processes containing organic matter and protein. Proteins have a tendency to be very easily adsorbed on the membrane layer or clog the surface pores, reducing the permeability and performance of the separation process in general, reducing the service life of the membrane which will immediately lead to an increase in operating costs for membrane module replacement and maintenance. Fouling causes solutes accumulate on the membrane layer (6), thereby reducing the work performance (i.e., selectivity and flux) of the membrane. Thus, membrane modification is very significant to improve the hydrophilicity (7) of the PVDF membrane. Efforts have been focused on obtaining antifouling and hydrophilicity behaviour through membrane modification in the manufacturing process. Modifications can be done by mixing the polymer with a third compound, namely polymer blending (8), chemical grafting (9), and surface modification (10).

Polymers blending is often used for membrane modification. The mixing of additives into the polymer matrix during membrane formation can prevent fouling (11). The addition of additives can change the characteristics of the membrane top layer (12), pore size, hydrophilicity, thickness, and membrane structure, such as porosity (13), which is beneficial for modifying the membrane properties through the aid of pore formation and the hydrophilic properties of the membrane (14). Many materials can be used as additives, such as Mg(OH)₂, chitosan, Pluronic F127, Tetronic 1307, graphene oxide (GO), and polyvinylpyrrolidone (PVP). Mg(OH)₂ is able to increase the polyethersulfone (PES) membrane hydrophilicity by reducing the water contact angle of pure PES membranes from 84.2° to 68° after membrane modification (15). The membrane modified with Mg(OH)₂ gave a permeability coefficient of 8.236 L/m²·h·bar, while the membrane modified with chitosan yielded a value of 6.237 L/m²·h·bar (16). The PES membrane modified with the addition of 5% chitosan has the rejection percentage value of 73.84% and the largest permeability coefficient value of 37.02 L/m²·h·bar (17).

Ultra-filtration studies proved that PES-PVP membrane exhibited the most significant behaviour compared to the Pluronic F127 and Tetronic 1307 additives (18). GO and PVP enhance the antifouling characteristics of PVDF membranes because of their hydrophilicity (19). Graphene oxide nanoribbons and PVP showed a synergistic effect in controlling membrane properties (20). Usually, PVP is used as an additive, and it can serve as a pore-forming agent. PVP is a hydrophilic polymer, which can increase the membrane hydrophilicity. The use of PVP in the matrix of the membrane was reported to increase the permeation flux and prevent fouling (21). Figure 1 shows the structural formulas for PVDF and PVP.

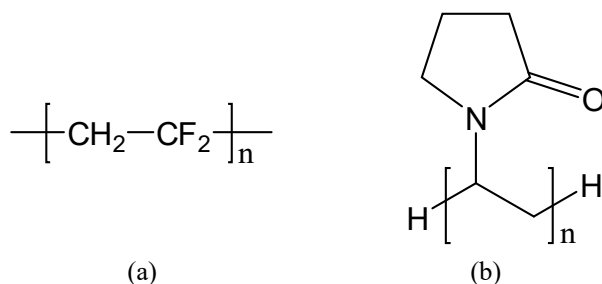
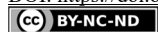


Figure 1. Chemical structure of (a) PVDF and (b) PVP

It was confirmed that various membrane solutions affect the morphology of the membrane, such as macrovoids, support layers, and skin layers (22). The incorporation of hydrophilic polymers in the polymer matrix exerts an important effect on the membrane properties. In the asymmetrical structure, PVP leaching during membrane operation can occur because of its relatively high solubility, especially in the phase inversion technique. This is the main disadvantage of using PVP as antifouling agent. Several methods, such as grafting or the use of PVP copolymers have been applied to overcome this problem. Industrial hollow membranes were fabricated using amphiphilic diblock copolymers, such as polymethyl-methacrylate, because they lasted longer than PVP under repeated washing (23). However, compared to PVP with small molecular weight (40 kg/mol), more PVP with large molecular weight (360 kg/mol) remained in the asymmetric structure because of their heavier weight as well as associated denser membrane morphology (24). Therefore, in this study, the utilization of PVP with a large molecular weight was carried out. Previous studies investigated membranes made of various combinations of polymers, additives, solvents, and non-solvents, such as PVDF-PVP-dimethylacetamide (DMAc)-deionized water (DI) (25), PVDF-PVP/TiO₂-DMAc-water (26), PVDF-TiO₂/PEG-DMAc-water (27), PVDF-PVP/GO-dimethyl-formamide-DI (20), and PVDF-PVP/GO-n-methyl-pyrrolidone (NMP)-DI (28).

In this investigation, the membrane was modified by mixing PVP with PVDF membrane utilizing NMP solvent and distilled water as non-solvent to improve antifouling characteristics and humic acid rejection behaviour. The combination of the PVDF-PVP-NMP-distilled water forming a planar membrane becomes the originality of the work. Morphological structures, functional groups, and membrane porosity were analysed by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and membrane porosity assays, respectively (29). The behaviour of the membrane was determined to obtain pure water permeability (PWP), antifouling properties by calculating the membrane water flux recovery ratio (FRR), and humic acid rejection. These results will be compared with the findings of the PES membrane filtration test with the similar treatment. The PES test results showed the permeability of the N-0.5 and D-0.5 membranes was 41.5 L/m²·h·atm and 47.5 L/m²·h·atm with higher antifouling performance in the modified membrane compared to unmodified membrane (30).



EXPERIMENTAL

MATERIALS

PVDF (Solvay Specialty Polymer, USA) with molecular weight 380 kg/mol was utilized as the main compound for the manufacture of membranes. PVP-K30 (Sigma, Germany) was used as an additive. NMP (Merck, Germany) was utilized as a solvent. Humic acid (Sigma Aldrich, Germany) was utilized as a water contaminant sample, and distilled water as a non-solvent was utilized in membrane filtration. A glass plate (support medium) and applicator were used to print the membrane, and the ultrafiltration module was used to check the membrane characteristic and other laboratory analyses.

FABRICATION

The PVDF polymer was dissolved at a concentration of 17% by weight in NMP solution at 60 °C and PVP in the amount of 1%, 2%, 3%, and 4% by weight of the total dope solution. Furthermore, the dope solution was stirred at room temperature (25 °C) using a magnetic stirrer until the solution dissolved homogeneously.

Table 1. Various dope solutions for PVDF membrane

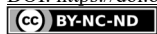
Membrane	PVDF wt. (%)	PVP wt. (%)	NMP wt. (%)
P-0	17	0	83
P-1	17	2	81
P-3	17	3	80
P-4	17	4	79

Homogeneous dope solution was printed by pouring it on a casting apparatus (glass plate), then it was allowed to cover the top surface of the flat plate at a temperature of 24 °C utilizing a casting knife until a thickness of 300 µm was obtained. These flat plates were soaked in a bath filled with distilled water. Furthermore, this membrane was allowed to stand at 60 °C distilled water before being used for membrane characterization and filtration tests. Table 1 displays the complete contents of the membrane dope solution.

MEMBRANE CHARACTERIZATION

The membrane was characterized by analysing the membrane morphology of cross section with SEM at a temperature of -100 °C, analysing the composition of the membrane functional group using FTIR, where the data was recorded in % transmittance in the spectral range of 500–4000 cm⁻¹. The membrane porosity measurement was carried out using the gravimetric method, namely by measuring the mass of the membrane in wet and dry conditions. Equation 1 could be used to determine the membrane porosity (31).

$$\varepsilon = (\omega_w - \omega_d) / (\rho \times A \times l) \times 100\% \quad [1]$$



ULTRAFILTRATION MEMBRANE PERFORMANCE

The membrane filtration performance was tested with an ultrafiltration module using a dead-end flow type (32). The membrane performance that was reviewed was the permeability and selectivity (rejection) of humic acid. Permeability indicated the ability of the membrane to filter pure water at room temperature (25 °C) and membrane operating pressure. The pure water permeability was calculated at room temperature by determining the tangent to the flux curve at operating pressure. Equation 2 was used to determine the membrane permeability coefficient (30).

$$L_p = J/\Delta p \quad [2]$$

where L_p was the coefficient of permeability of pure water ($L/(m^2 \cdot h \cdot bar)$), J was the flux ($L/(m^2 \cdot h)$), while Δp was the pressure drop (bar).

For the membrane selectivity test, humic acid rejection was examined using a 50 ppm humic acid solution at 25 °C. Equation 3 was utilized to determine the humic acid rejection coefficient (R) (30).

$$R (\%) = (1 - C_p/C_f) \times 100\% \quad [3]$$

where R was the rejection percentage, C_f and C_p were the humic acid concentrations in the feed as well as permeate, respectively.

Furthermore, the antifouling properties were analysed with a dead-end ultrafiltration module using distilled water feed as well as humic acid as a contaminant model for a natural organic compound. The experiment was carried out by flowing distilled water through the membrane to get stable flux data. The pure water flux (J_{w1}) was checked for one hour at a pressure of 1 bar. Furthermore, the study was resumed again by flowing 50 ppm humic acid solution. The humic acid flux (J_{HA}) was operated at the same conditions as the pure water flux measurement. The filtered humic acid was collected, then analysed for its concentration with a UV-Vis Spectrophotometer. Then, the membrane cleaning procedure is carried out with the backwash technique, where the dirty membrane is placed upside down on the membrane module, while distilled water is flowed at a pressure of 0.1 bar for 20 minutes. Then, the membrane is turned over again, and placed in its original place. The investigation of filtration with distilled water was repeated to result in pure water flux after backwashing (J_{w2}); all the investigations were carried out at 25 °C. The results from this whole series of investigation were utilized to test the total water flux recoverable after backwashing, which is known as FRR. FRR can be used as an indication that the membrane had resistance to fouling to be cleaned during backwash. FRR can be determined with Equation 4 (30).

$$FRR (\%) = (J_{w2}/J_{w1}) \times 100 \quad [4]$$

where J_{w1} and J_{w2} were pure water fluxes before as well as after backwash, respectively.

RESULTS AND DISCUSSION

FUNCTIONAL GROUP ANALYSIS

FTIR spectroscopy is an apparatus that is widely utilized to analyse the functional groups of sample surfaces as a result of molecular interactions observed as the transmittance or absorbance of infra-red (IR) rays accepted by the sample. The IR spectra of modified and unmodified PVDF membranes can be observed in Figure 2. FTIR investigation was utilized to explain the changes in membrane chemical group when PVP was used as an additive. In Figure 2, it can be seen that the FTIR spectrum of P0, P1, P2, P3, and P4 show the transformation of the chemical structure.

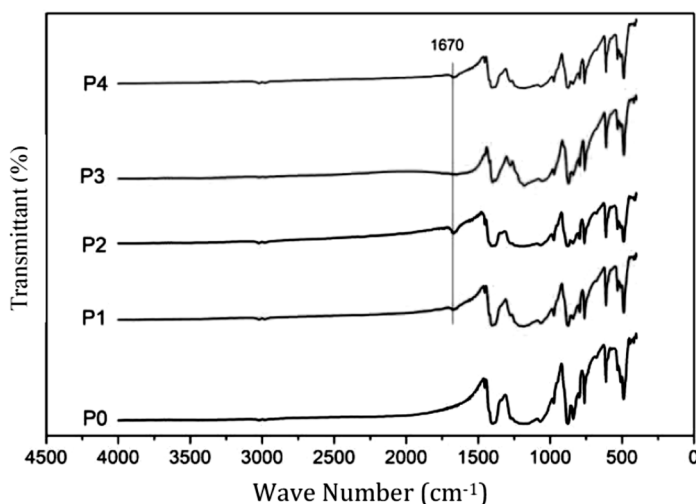


Figure 2. FTIR spectra for various membranes

For the PVDF transmission spectrum, the most specific peaks can be seen at wavelengths of 3030 cm^{-1} as well as 2980 cm^{-1} that show asymmetric and symmetrical vibrations for C-H bonds. Other specific PVDF peaks are indicated by the available peaks at wave numbers 841 , 879 , 1180 , and 1403 cm^{-1} to indicate the C-F stretching vibrations, C-C-C asymmetric stretching vibration, C-H band, and CH_2 wobble vibration (33).

The new absorption peak was more prominent in the infrared spectrum at 1678 cm^{-1} on the PVP-modified PVDF membrane, whereas the rest of the spectra remained the same. This spectrum represents the major amine group strain of PVP. The same finding has also been reported by previous researchers (34). This shows that PVP is trapped in the PVDF membrane matrix, and is integrated with the polymer structure. PVP provides more hydrophilicity to PVDF membrane layers, as in PES membranes (35). Furthermore, the literature findings report that interactions can occur between sulfone groups (PES) and pyrrolidone groups (PVP), or between PES aromatic ring and side cyclic groups (PVP) through the study of the viscoelastic behaviour of these polymer blends (36). The PVP molecules are trapped in the matrix thereby ensuring that the PVP remains on the matrix (37) and the



PVDF membrane surface, even after soaking the PVDF membrane with excess water. However, the leaching of PVP after immersion in water for eight hours needs to be further investigated by FTIR to identify the remaining PVP in the membrane related to the amount of PVP added or its molecular weight. High molecular weight PVP has stronger affinity and longer main chain, so it can remain in the membrane (24).

MORPHOLOGICAL STRUCTURE

The analysis of the morphological structure of the membrane was carried out using SEM with the aim of seeing the changes in the membrane morphology that occurred on the membrane surface before and after being modified with the addition of PVP additives (Figure 3). The P0 membrane looks dense, where the presence of pores looks smaller and denser than those of the P3 membrane. In this membrane, the appearance of the pores scattered on the surface of this membrane is clearly visible. This indicates that the PVP additive functions as an agent to form pores on the PVDF membrane. These pores are formed because the addition of PVP can accelerate the water penetration rate through this membrane. A similar finding was also reported (38) that at a low concentration of 2% PVP, an even distribution of pores was generated on the membrane surface.

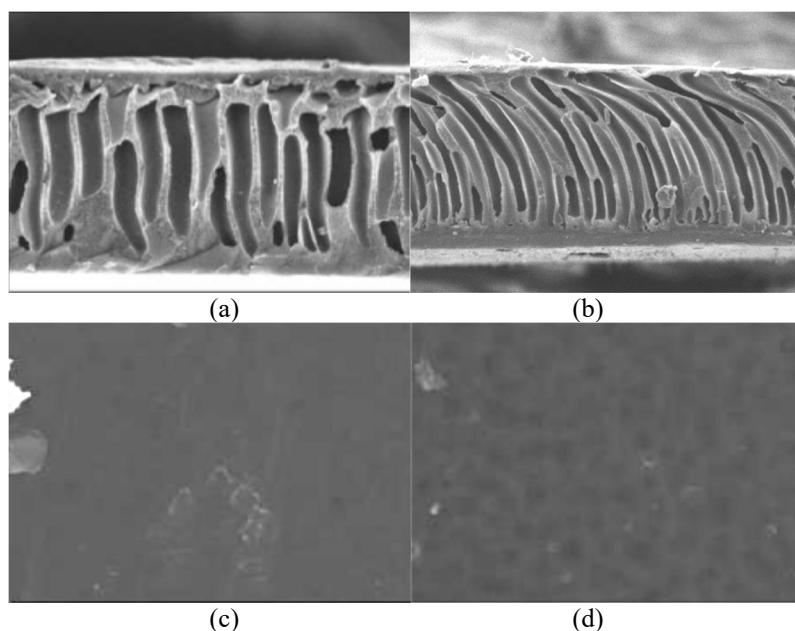


Figure 3. Morphology of cross-section: (a) P0 membrane; (b) P3 membrane; and surface morphology: (c) P0 membrane; (d) P3 membrane

MEMBRANE POROSITY

The effect of adding PVP on the membrane pores was also carried out by evaluating the porosity of the resulting membrane. All membrane porosities are displayed in Figure 4. In general, the membranes modified with the addition of PVP (P1, P2, P3, and P4) had higher porosity than the unmodified PVDF membrane (P0 membrane). Based on Figure 4, the rise of the concentration of PVP added to the PVDF membrane has an effect on increasing the membrane porosity. The P3 membrane has the highest porosity value, which is 35%.

This is also supported by the results of SEM photo analysis (Figure 3) that shows an increase of the number as well as the pore size of P3 membranes more than P0 membrane. Previous studies proved that increasing the PVP concentration was able to increase the porosity and macrovoids in the internal membrane. However, the presence of PVP additive at a concentration of 4% resulted in a decrease in porosity. This is because the addition of an additive concentration that is too high (4%) allows the viscosity of the solution to increase considerably, thereby delaying the phase separation process because it interferes with the formation of pores (39).

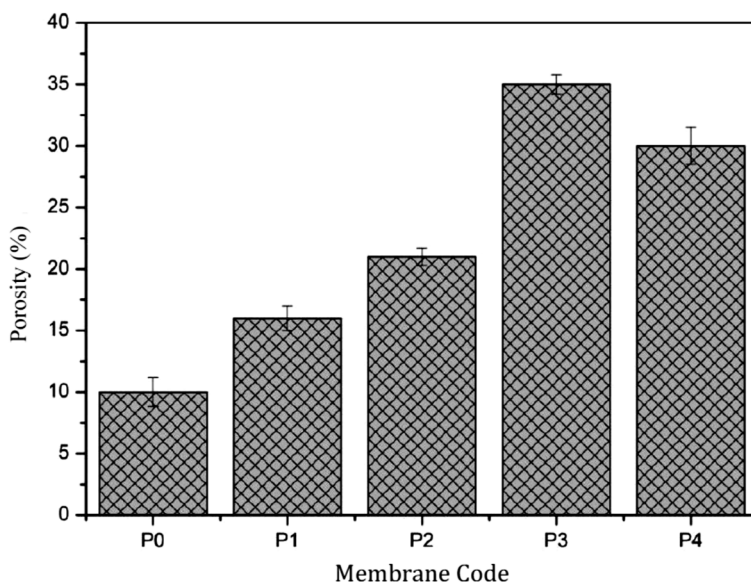


Figure 4. Porosity in various membranes

PURE WATER PERMEABILITY

Two important membrane performance parameters are water permeability and solute rejection or the ability to repel particles in a given compound. Water permeability indicates the volume of water (litres) filtered by the membrane surface per unit surface area (m^2) of the membrane, per filtration time (h), and operating pressure (bar).

Based on Figure 5, it can be ascertained that the modified membrane in the presence of PVP has a higher PWP value than the membrane without modification (P0). Because of its non-porous and hydrophobic morphology, the P0 membrane only produced a PWP of $3.1 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$, then with the addition of 3% PVP additive, the PWP increased up to 20 times to $60 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$. This phenomenon is relevant to changes in the membrane morphology structure that can be observed in SEM image.

The cross section in the membrane surface with the addition of 3% PVP (P3) has more pores than the pure membrane (P0) which is confirmed in Figure 3. The presence of membrane pores distributed in the membrane layer makes it easier for water to pass through the membrane, which results in increased water permeability. Furthermore, the presence of PVP in the membrane hydrophilic layer allows the membrane to interact better with water. The permeability of pure water is strongly influenced by the membrane morphology and characteristics, especially those related to the nature of the pores. However, the addition of PVP (P4) reduces the permeability of pure water because of the increase in polymer concentration making the structure denser (39).

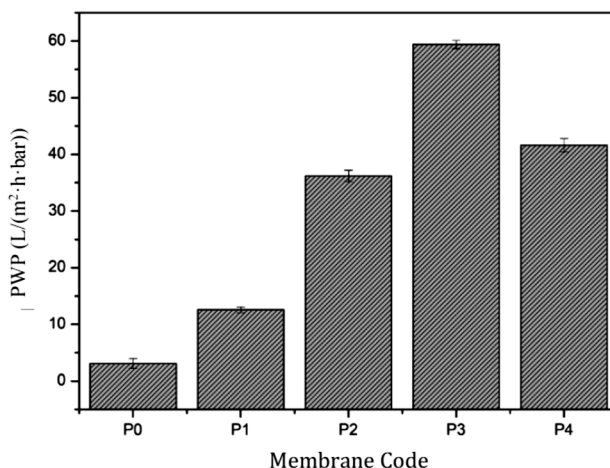


Figure 5. Pure water permeability (PWP) on various types of membranes

Although an increase in the number of pores have and size an effect on increasing the PWP of the membrane, it has a less favourable impact on the membrane selectivity or repulsion performance. As exhibited in Figure 6, the unmodified PVDF membrane had the highest rejection value, while all the modified membranes yielded a slightly lower rejection percentage than the pure PVDF membrane (P0).

This is because the pores in the membrane layer will allow some percent of the humic acid particles to enter the permeate (36). The rejection value for P0, P1, P2, and P3 were 83%, 82%, 81%, and 80%, respectively, with one exception being the last sample (81%) of P4 membrane. The trend is assumed to be the combined effect of hydrophobic interaction and size between the membrane and humic acid during filtration, which causes the repulsion of humic acid by the membrane. The P4 membrane had smaller pores on its active surface, which might trap humic acid significantly more than the other prepared P0–P3.

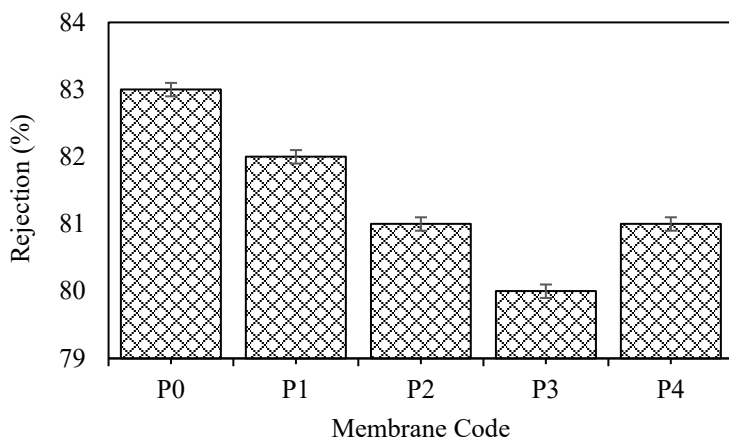


Figure 6. Rejection in different types of membranes

ANTIFOULING PERFORMANCE

The antifouling tendency of the fabricated membrane, as another important assessment of the resulting membrane, was analysed by permeating pure water again after back-flushing. The data are presented in the form of FRR that is a significant sign of the membrane's ability to restore permeation performance after backwashing (40).

Fouling treatment is generally carried out through membrane washing, and the effectiveness of this washing indicates the antifouling properties of the membrane, which is seen from the large amount of water flux that can be recovered from the initial flux after the washing process, which is known as water FRR. The high FRR percentage value indicates that the water flux value after washing is getting closer to the water flux value before washing, which means that not much water flux is lost because of fouling. This means that the formed fouling can be cleaned effectively by washing (the membrane has good antifouling) (41). The results of the antifouling evaluation for the modified membrane in this investigation are indicated in Figure 7.

Figure 7 displays the results of the FRR test on the resulting membrane. The results show an increase in the resulting FRR in the modified membrane. In Figure 7, it is able to be identified that the FRR value on the P0 membrane has the lowest FRR value compared to the modified membrane. The P0 membrane has a surface characteristic that is hydrophobic so that the hydrophobic humic acid particles easily bind to the membrane layer. As a result of this strong hydrophobic-hydrophobic interaction between the humic acid particles and the membrane surface, the formed impurities cannot be removed easily even after backwashing (42).

The FRR values of the P0, P1, P2, P3, and P4 membranes were 10%, 35%, 67%, 85%, and 75%, respectively. These data indicate that these modified membranes have a higher FRR values than that the unmodified membrane, where the highest FRR value is obtained on the P3 membrane. In general, higher FRR indicates the high antifouling characteristic of the membrane. These findings indicate that modification of PVDF membrane with PVP additives can improve the antifouling characteristic of the PVDF membrane.

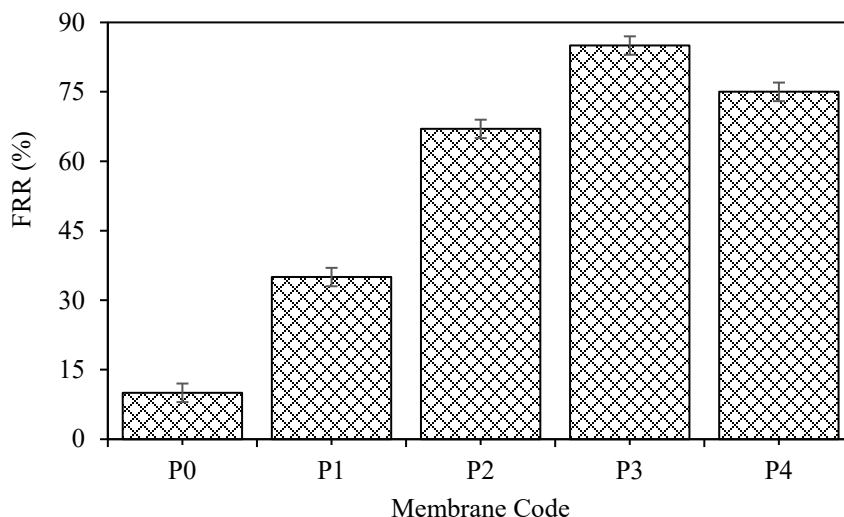


Figure 7. FRR of water on several types of membranes

CONCLUSION

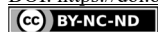
Modification of the PVDF membrane using PVP additives has been successfully carried out using the polymer blending method made with the phase inversion technique. The data showed that PVP modified the morphological structure of the membrane as displayed by the results of the SEM analysis. In addition, chemical interactions occur on the modified membrane as shown by FTIR analysis. Membranes with the addition of PVP additives can increase membrane permeability. The best performance was obtained on the modified membranes with the addition of 3% PVP with an increase in permeability of about 10 times compared to the unmodified PVDF membrane of 60 L/m²·h·bar, with humic acid rejection of 80%, and water FRR of 85%. These findings suggest that PVP acts as a pore-forming agent resulting in higher PWP, lower humic acid rejection, and good antifouling properties. However, greater modifications are needed to improve the behaviour of the resulting membranes, especially when chemical cleaning is used for PVDF/PVP ultrafiltration.

Acknowledgements

Thanks to the Ministry of Education, Culture, Research, and Technology of the Republic Indonesia and LPPM of Universitas Syiah Kuala through the Lecturer Research Scheme with contract No. 172/UN11.2/SPK/PNBP/2021.

REFERENCES

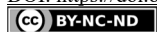
1. Mishaqa, E.I.; Radwan, E.K.; Dagher, T.M.; Ibrahim, M.B.M.; Hegazy, T.A.; Ibrahim, M.S. Occurrence of disinfectant by-products in desalinated drinking water in Egypt. *Water Environ. J.* **2019**, *34* (4), 1–8.



2. Martin, A.; Arsuaga, J.M.; Roldan, N.; Abajo, J.; Martinez, A.; Sotto, A. Enhanced ultrafiltration PES membranes doped with mesostructured functionalized silica particles. *Desalination*. **2015**, 357, 16–25.
3. Liang, S.; Kang, Y.; Tiraferri, A.; Giannelis, E.P.; Huang, X.; Elimelech, M. Highly hydrophilic polyvinylidene fluoride (PVDF) ultrafiltration membranes via postfabrication grafting of surface-tailored silica nanoparticles. *ACS Appl. Mater. Interfaces*. **2013**, 5, 6694–6703.
4. Cui, X.; Choo, K. Natural organic matter removal and fouling control in low-pressure membrane filtration for water treatment. *Environ. Eng. Res.* **2014**, 19 (1), 1–8.
5. Yang, S.; Yang, D.; Ren, W.; Liu, J.; Mou, J.; Wang, Y. Analysis of research status of modified PVDF ultrafiltration membrane. *IOP Conf. Ser. Earth Environ. Sci.* **2020**, 585, 012190.
6. Shi, X.; Tal, G.; Hankins, N.P.; Gitis, V. Fouling and cleaning ultrafiltration membranes: A review. *J. Water Process. Eng.* **2014**, 1, 121–138.
7. Fathanah, U.; Machdar, I.; Riza, M.; Arahman, N.; Lubis, M.R.; Yusuf, M. The improvement of hydrophilic property of polyethersulfone membrane with chitosan as additive, *J. Chem. Eng. Environ.* **2020**, 15 (1), 53–61.
8. Liu, L.; Chen, H.; Yang, Y. Enhancing membrane performance by blending ATRP grafted PMMA-TiO₂ or PMMA-PSBMA-TiO₂ in PVDF. *Sep. Purif. Technol.* **2014**, 133, 22–31.
9. Ashfaq, A.; Clochard, M.; Coqueret, X.; Dispenza, C.; Driscoll, M.S.; Ulanski, P.; Al-Sheikhly, M. *Polymerization reactions and modifications of polymers by ionizing radiation*. *Polymers*. **2020**, 12, 2877.
10. Zhao, G.; Chen, W. Enhanced PVDF membrane performance via surface modification by functional polymer poly(N-isopropylacrylamide) to control protein adsorption and bacterial adhesion. *React. Func. Polym.* **2015**, 97, 19–29.
11. Munnawar, I.; Iqbal, S.S.; Anwar, M.N.; Batool, M.; Tariq, S.; Faitma, M.; Khan, A.L.; Khan, A.U.; Nazar, U.; Jamil, T.; Ahmad, N.M. Synergistic effect of chitosan-zinc oxide hybrid nanoparticles on antibiofouling and water disinfection of mixed matrix polyethersulfone nanocomposite membranes. *Carbohydr. Polym.* **2017**, 175, 661–670.
12. Martins, D.B.; Nasario, F.D.; Silva-Goncalves, L.C.; Tiera, V.A.O.; Arcisio-Miranda, M.; Tiera, M.J.; Cabrera, M.P.D.S. Chitosan derivatives targeting lipid bilayers: synthesis, biological activity and interaction with model membranes. *Carbohydr. Polym.* **2018**, 181, 1213–1223.
13. Koromilas, N.D.; Anastasopoulos, C.; Oikonomou, E.K.; Kallitsis, J.K. Preparation of porous membranes based on pyridine containing aromatic polyether sulfone. *Polymers*. **2019**, 11 (1), 59.
14. Pereira, V.R.; Isloor, A.M.; Bhat, U.K.; Ismail, A.F. Preparation and antifouling properties of PVDF ultrafiltration membranes with polyaniline (PANI) nanofibers and hydrolysed PSMA (H-PSMA) as additives. *Desalination*. **2014**, 351, 220–227.
15. Fathanah, U.; Machdar, I.; Riza, M.; Arahman, N.; Lubis, M.R.; Nurfajrina, F.; Yolanda, A.; Wahab, M.Y. Effects of magnesium hydroxide (Mg(OH)₂) on the characteristic and performance of polyethersulfone membranes (PES) for water treatment. *IOP Conference Series: Materials Science and Engineering*. 845 (2020) 012024.
16. Fathanah, U.; Machdar, I.; Riza, M.; Arahman, N.; Lubis, M.R.; Mukramah. Modification of polyethersulfone membrane (PES) using solutions normal methyl pyrrolidone (NMP) by non-solvent induction phase separation (NIPS). *Prosiding Seminar Nasional Universitas Serambi Mekkah*. **2019**, 2, 274–285.
17. Fathanah, U.; Machdar, I.; Riza, M.; Arahman, N.; Lubis, M.R.; Qibtiyah, M. Manufacture and characterization of polyethersulfone (PES)-chitosan membrane by blending polymer. *Prosiding Seminar Nasional Politeknik Negeri Lhokseumawe*, **2019**, 3 (1), A62–A66.
18. Arahman, N.; Mulyati, S.; Lubis, M.R.; Razi, F.; Takagi, R.; Matsuyama, H. Modification of polyethersulfone hollow fiber membrane with different polymeric additives. *Membr. Water Treat.* **2016**, 7 (4), 355–365.



19. Beygmohammadi, F.; Kazerouni, H.N.; Jafarzadeh, Y.; Hazrati, H.; Yegani, R. Preparation and characterization of PVDF/PVP-GO membranes to be used in MBR system. *Chem. Eng. Res. Des.* **2020**, *154*, 232–240.
20. Tofighy, M.A.; Mohammadi, T.; Sadeghi, M.H. High-flux PVDF/PVP nanocomposite ultrafiltration membrane incorporated with graphene oxide nanoribbons with improved antifouling properties. *J. App. Polym. Sci.* **2020**, *138* (4), 49718.
21. Arahman, N., Fahrina, A.; Wahab, M.Y.; Fathanah, U. Morphology and performance of polyvinyl chloride membrane modified with pluronic F127. *F1000 Res.* **2018**, *7*, 726.
22. Fahrina, A.; Maimun, T.; Humaira, S.; Rosnelly, C.M.; Lubis, M.R.; Bahrina, I.; Sunarya, R.; Ghufuran, A.; Arahman, N. Morphology and filtration performances of poly(ether sulfone) membrane fabricated from different polymer solution. *MATEC Web of Conf.* **2018**, *197*, 09001.
23. Oikonomou, E.K.; Karpati, S.; Gassara, S.; Deratani, A.; Beaume, F.; Lorain, O.; Tence-Girault, S.; Norvez, S. Localization of antifouling surface additives in the pore structure of hollow fiber PVDF membranes. *Journal of Membrane Science*, **2017**, *538*, 77–85.
24. Wan, L.S.; Xu, Z.K.; Wang, Z.G. Leaching of PVP from polyacrylonitrile/PVP blending membranes: a comparative study of asymmetric and dense membranes. *J. Polym. Sci. B Polym. Phys.* **2006**, *44* (10), 1490–1498.
25. Mavukkandy, M.O.; Bilad, M.R.; Giwa, A. Leaching of PVP from PVDF/PVP blend membranes: impacts on membrane structure and fouling in membrane bioreactors. *J. Mater. Sci.* **2016**, *51*, 4328–4341.
26. Ong, C.S.; Lau, W.J.; Goh, P.S.; Ng, B.C.; Ismail, A.F. Preparation and characterization of PVDF-PVP-TiO₂ composite hollow fiber membranes for oily wastewater treatment using submerged membrane system. *Desalin. Water Treat.* **2013**, *53* (5), 1213–1223.
27. Humairo, F.Y.; Ong, C.S.; Widiastuti, N.; Ismail, A.F.; Putri, S.A.; Jafar, J. PVDF/TiO₂/PEG hollow fiber membrane for oily wastewater treatment at various concentration of oily wastewater. The 1st International Seminar on Science and Technology. **2015**, B208-57–B208-58.
28. Beygmohammadi, F.; Kazerouni, H.N.; Jafarzadeh, Y.; Hazrati, H.; Yegani, R. Preparation and characterization of PVDF/PVP-GO membranes to be used in MBR system. *Chem. Eng. Res. Des.* **2020**, *154*, 232–240.
29. He, M.; Zhang, S.; Su, Y.; Zhang, R.; Liu, Y.; Jiang, Z. Manipulating membrane surface porosity and pore size by in-situ assembly of pluronic F127 and tannin. *J. Membr. Sci.* **2018**, *556*, 282–292.
30. Fathanah, U.; Lubis, M.R.; Muchtar, S.; Yusuf, M.; Rosnelly, C.M.; Hazliani, R.; Rahmanda, D.; Kamaruzzaman, S.; Busthan, M. Synthesis, characterization and performance of hydrophobic membranes using polyvinyl pyrrolidone (PVP) as additive. *Alchemy Jurnal Penelitian Kimia.* **2021**, *17* (2), 140–150.
31. Elizalde, C.N.B.; Al-Gharabli, S.; Kujawa, J.; Mavukkandy, M.; Hasan, S.W.; Arafat, H.A. Fabrication of blend polyvinylidene fluoride/chitosan membranes for enhanced flux and fouling resistance. *Sep. Purif. Technol.* **2018**, *190*, 68–76.
32. Quezada, C.; Estay, H.; Cassano, A.; Troncoso, E.; Ruby-Figueroa, R. Prediction of permeate flux in ultrafiltration processes: A review of modelling approaches. *Membranes.* **2021**, *11*, 368.
33. Bai, H.; Wang, X.; Zhou, Y.; Zhang, L. Preparation and characterization of poly(vinylidene fluoride) composite membranes blended with nano-crystalline cellulose. *Prog. Nat. Sci. Materials International.* **2012**, *22* (3), 250–257.
34. Susanto, H.; Ulbricht, M. Characteristics, performance and stability of polyethersulfone ultrafiltration membranes prepared by phase separation method using different macromolecular additives. *J. Membr. Sci.* **2009**, *327* (1–2), 125–135.
35. Milesu, R.A.; McElroy, C.R.; Farmer, T.J.; Williams, P.M.; Walters, M.J.; Clark, J.H. Fabrication of PES/PVP water filtration membranes using cyrene^R, a safer bio-based polar aprotic solvent. *Adv. Polym. Technol.* **2019**, *2019*, 9692859.



36. Sun, M.; Su, Y.; Mu, C.; Jiang, Z. Improved antifouling property of PES ultrafiltration membranes using additive of silica-PVP nanocomposite. *Ind. Eng. Chem. Res.* **2010**, *49* (2), 790–796.
37. Vatsha, B.; Ngila, J.C.; Moutloali, R.M. Preparation of antifouling polyvinylpyrrolidone (PVP 40K) modified polyethersulfone (PES) ultrafiltration (UF) membrane for water purification. *Phys. Chem. Earth.* **2014**, *67–69*, 125–131.
38. Sadrzadeh, M.; Bhattacharjee, S. Rational design of phase inversion membranes by tailoring thermodynamics and kinetics of casting solution using polymer additives. *J. Membr. Sci.* **2013**, *441*, 31–44.
39. Son, M.; Kim, H.; Jung, J.; Jo, S.; Choi, H. Influence of extreme concentrations of hydrophilic pore-former on reinforced polyethersulfone ultrafiltration membranes for reduction of humic acid fouling. *Chemosphere.* **2017**, *179*, 194–201.
40. Saraswathi, M.S.A.; Kausalya, R.; Kaleekkal, N.J.; Rana, D.; Nagendran, A. BSA and humic acid separation from aqueous stream using polydopamine coated PVDF ultrafiltration membranes. *J. Environ. Chem. Eng.* **2017**, *5* (3), 2937–2943.
41. Zhao, X.; Zhang, R.; Liu, Y.; He, M.; Su, Y.; Gao, C.; Jiang, Z. Antifouling membrane surface construction: Chemistry plays a critical role. *J. Membr. Sci.* **2018**, *551*, 145–171.
42. Sun, W.; Liu, J.; Chu, H.; Dong, B. Pretreatment and membrane hydrophilic modification to reduce membrane fouling. *Membranes.* **2013**, *3* (3) 226–241.