© Universiti Tun Hussein Onn Malaysia Publisher's Office

IJIE

Journal homepage: http://penerbit.uthm.edu.my/ojs/index.php/ijie
ISSN : 2229-838X e-ISSN : 2600-7916

The International Journal of Integrated Engineering

In-Situ Synthesis of Silver Nitrate Incorporated with Polysulfone Membrane Characterization: Effect of Ag Precursor

Azlinnorazia Ahmad[1], Muhamad Zaini Yunos[1*]

[1]Faculty of Mechanical and Manufacturing Engineering,
Universiti Tun Hussein Onn Malaysia, Parit Raja, 86400 Batu Pahat, Johor

*Corresponding Author

DOI: https://doi.org/10.30880/ijie.2019.11.05.020
Received 5 March 2019; Accepted 26 March 2019; Available online 10 August 2019

Abstract:
Water treatment using membrane filtration is one of the common methods that can generate higher amount of quality water in future. However, polymer blending method via ex-situ synthesis method shows some weaknesses on membrane modification such as membrane prone to fouling and hydrophobic. In this present work, the characterization of in-situ synthesis of silver nitrate ($AgNO_3$)/polysulfone (PSf) membrane was carried out for water separation purposes. The characterization of in-situ synthesis of $AgNO_3$ in PSf membrane has been investigated with the present of silver (Ag) precursor. The Ag/precursor dope solution thermodynamic stability was evaluated via ternary phase diagram. The membrane was characterized in term of morphology, existence of element and membrane surface roughness. The performance of $AgNO_3$ was highly influences by PSf/alkali characterization. The interaction of PSf/$AgNO_3$/precursor reduced thermodynamic stability of the dope solution and increased the phase inversion rate between polymer and solvent and led to more porous sub layer with larger irregular finger like pores. In addition, high molecular weight of alkali reacts with $AgNO_3$ effectively and resulted on higher membrane surface roughness where it is increased up to 58 % causing higher surface area of the membrane. The amorphous peak is due to the presence of alkali in the membrane during the XRD analysis. The intensity of these peaks tended to decrease upon addition of silver in PSf membrane, as compared to regular polymer blending method of Ag on PSf membrane. Thus, in-situ synthesis of silver has potential to be used as a method in membrane fabrication as it enhances membrane performance for water separation.

Keywords: in-situ, $AgNO_3$, polysulfone membrane, amorphous, silver precursor

1. Introduction

Water is not only a personal demand. However, it is the most significant for human need throughout everyday life. To fulfill the need for water in the year of 2050, we can see the situation of the world water benchmark uncovers roughly 5500 km^3 of freshwater withdrawals will be required. All these requirements are including manufacturing, electricity production, and domestic use. The current global demand for this increase of about 55%, where the demanding of drinking water will be about 130% for households than volumes nowadays [1&2]. However, having some issue in the misuse of water resources and water contamination because of the quick advancement of the populace, there is a radically expanding issue in water shortage [3]. Subsequently, cost-effective innovations must be created to broaden water resources and solve water contamination issues.

The membrane is one of the physical barriers that allow only water to pass through and prevent humic substances to infiltrate the barrier [4]. Membrane filtration is one of the advanced methods which is reported to be able

*Corresponding author: mzaini@uthm.edu.my

to separate humic substance efficiently. Gao [5] stated that water treatment using membrane filtration generally have more advantages as compared to the normal water treatment process to separate wastewater. This is due to it is only required small spaces and less energy consumption. To achieve an excellent separation performance, a suitable membrane is of paramount importance in the separation process. It is reported that different types of silver resulted in different characterization properties. Thus, it is crucial to investigate the effect of different types of silver in the membrane dope solution. Rao et al., state that ex-situ synthesis of membrane modification causes phase splitting and property isotropy in the composite membrane [6]. In-situ synthesis method allows the controllable formation of nanoparticles and uniform dispersion within the composite membrane. They also discovered that in-situ synthesis resulted in higher antibacterial properties of membrane as compared to ex-situ process [7]. In the process of in-situ synthesis of silver in membrane dope solution, the precursor of silver such as silver salt and bases are the primary material that will form silver particle in the membrane. Ag has excellent mechanical properties and stable in both oxidizing and reduction atmospheres [8]. Most of the silver salt dissolve in dope solution. However, most of the bases do not dissolve in the dope solution as bases enhance instability of thermodynamic properties of the dope solution and result in phase separation between solvent and polymer [9]. Therefore, investigation on the effect of the precursor is important to produce a dope solution which has a homogeneous liquid phase.

2. Material and Method

2.1 Material

Three different types of strong alkali were used as Ag precursors. The thermodynamic stability of PSf/NMP solution was observed via mixing the solution with three different types of alkali which are Lithium Hydroxide (LiOH), Sodium Hydroxide (NaOH) and Potassium Hydroxide (KOH). The concentration of each Ag precursor was fixed to 5 mmol for each dope solution.

Table **Error! No text of specified style in document.**.1: Materials used in this study

Material	Molecular Formula	Manufacturer	Molecular Weight (g/mol)
Silver Nitrate	$AgNO_3$	Sigma Aldrich	169.87
Lithium Hydroxide	LiOH	Sigma Aldrich	41.96
Sodium Hydroxide	NaOH	Sigma Aldrich	40.00
Potassium Hydroxide	KOH	Sigma Aldrich	56.11

2.2 Solution Characterization via Ternary Phase Diagram

Solution characterization is one of the methods to ensure the best parameter to prepare a dope solution before membrane development. One of the best methods that have been used in this research was finding the cloud point for the system. The phase behavior of clouding and various methods adopted for the determination of cloud point of prepared PSf solution systems have been elucidated. In this study, the ternary phase diagram was used to predict the morphology of the membranes prepared via the phase inversion process. The precipitation rate of the PSf solution in the non-solvent was obtained by titration method using LiOH, NaOH, and KOH. To measure the cloud point data, the polymer dopes were prepared using a constant 5 mmol of the additives in additive solvent mixture with different polymer concentrations. The cloud point data were obtained using the titration method by adding non-solvent (distilled water mixed with alkali concentration) slowly into the polymer dope solution under constantly stirring at 25 °C. In cases when the agglomeration of the dope occurred, especially at higher polymer concentration, the stirring process was continued until the solution became homogeneous again. Then further addition of non-solvent was performed until the solution became permanently turbid at low polymer concentration and showed signs of cloudiness at high polymer concentration (the titration endpoint). Consequently, the compositions at the cloud point were calculated by weight.

2.2 Membrane morphology

Scanning Electron Microscopy (SEM) had been used to observe images morphology of the cross-section on the membrane. SEM/EDS model Hitachi SU1510 VP-SEM was used, and it provides a guaranteed secondary electron resolution of 3.0 nm (high vacuum mode) at 30 kV and a guaranteed backscattered electron resolution of 4.0 nm (variable pressure mode) at 6 Pa. Firstly, the samples size of 3 cm x 1 cm for each membrane were prepared. To get the view for the cross-section part, the sample was immersed in liquid nitrogen so that it is easy to break and split into two parts [10]. The observations were carried out to see the morphology structure in the cross-section of the membrane. The cross-section part that was scanned is in the fracture area. Then, the samples were attached on the plate and coated with gold to make the membrane conductive during analysis.

2.3 X-Ray Diffraction

XRD is one in the categories of a non-destructive analytical technique for identification and quantitative determination of various crystalline forms. In other word, it was known as a phase. The primary purpose of XRD analysis is to prove the presence of an element or compound in the fabricated membrane. XRD Bruker D8 machine was used to run the element identification process. Then, EVA Software XRD was used to analyze the presence of each element on the membrane. The membrane was compressed to a solid cube shape with a volume of 0.5 cm^3. It was put on the sample holder before entering the analysis chamber. The membrane was measured using the parameter at 2θ with a specific angle (20°-80°). The membrane will show its crystallinity for each Ag/precursor presence.

2.4 Surface Roughness of Membrane

Membrane surface roughness was measured by using the E-100 Park system of AFM machine. Membrane sample size 1cm x 1 cm was prepared and has been placed on the scanner tube. Membrane surface was scanned by 5 µm x 5µm size [11]. The value of average surface roughness then was recorded. The result shows the 3D images for every membrane surface roughness where the dark color in the image represent valley, and bright color represent the peak of the membrane surface.

3. Result and discussion

3.1. Isothermal Ternary Phase Diagram of PSf/NMP/AgNO3/Precursor System

The effect of precursor continued in this phase to investigate the membrane properties towards alkali solution in the presence of $AgNO_3$. The precipitation rate of the PSf/$AgNO_3$ solution in the non-solvent was obtained by titration method using LiOH, NaOH, and KOH. The result is shown in Figure 3.1. It can be seen from the figure that the cloud point diagrams shifted towards the polymer-solvent axis when the alkali was introduced to the polymer dopes. From the cloud point diagrams, the enhancement in precipitation of the polymer dopes can be given as the trend of LiOH > NaOH > KOH. This indicates that LiOH has the most substantial non-solvent influence, whereas KOH was the weakest among the additives. Less water is required to induce phase-inversion at the isothermal thermodynamic equilibrium for the addition of LiOH. The result indicates that the reaction between silver salt and alkali precursor reduced the thermodynamic stability of the dope solution. This might be due to the low amount of molecular weight of alkali precursor (refer Table 3.1) needed to interact with $AgNO_3$ as compared to the highest molecular weight of alkali precursor. The interaction reduced thermodynamic stability of the dope solution and increased the phase inversion rate between polymer and solvent. Thus, the addition of low concentration of $AgNO_3$ could be in favor of enhancing the casting solution thermodynamics and delaying the phase separation [12].

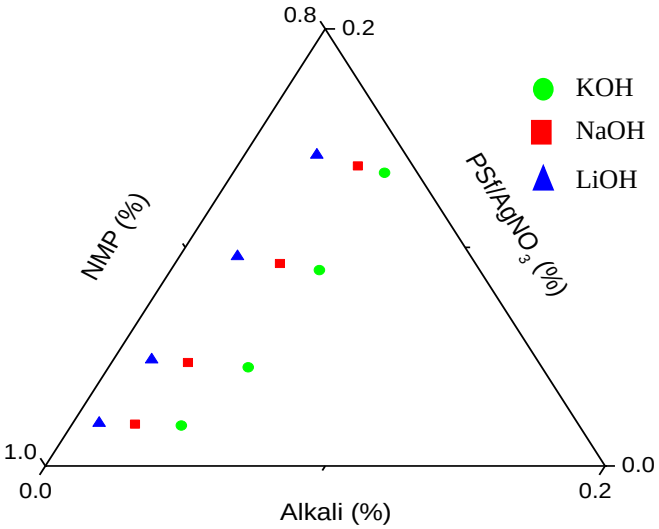
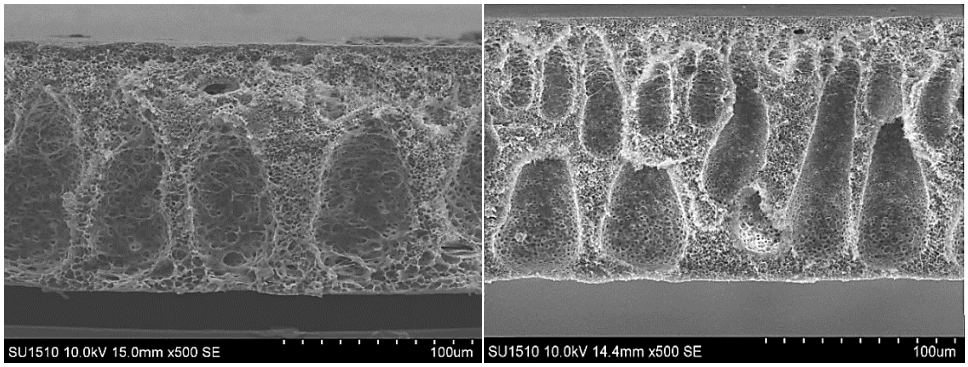


Figure 3.1: Ternary graph of PSf/NMP/$AgNO_3$/Alkali

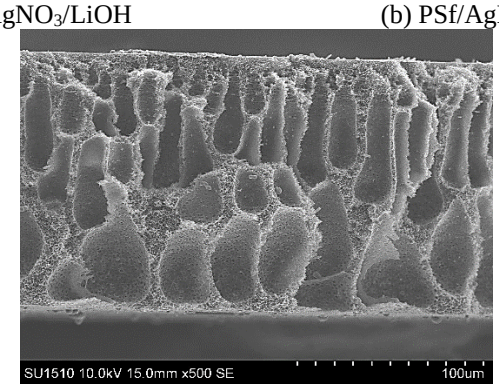
3.2. Membrane morphology analysis

Figure 3.2 shows the influence of different types of alkali precursors in the PSf/$AgNO_3$ membrane. It can be observed that the membrane structure was altered when $AgNO_3$ was introduced into the dope solution. The addition of alkali precursor in the PSf/$AgNO_3$ dope solution led to more porous sublayer with larger irregular finger-like pores. The skin layer acts as a separation layer and the support layer provides the mechanical strength of the membrane [13]. Then, the thickness of a dense skin layer drastically decreased with the addition of alkali precursor. In the figure, the sample with the presence of LiOH and NaOH shows that there is no continuous phase in the membrane sub layer. It can be observed that LiOH and NaOH increased membrane pores, and the membrane became porous. This result might be due to the

reduction of thermodynamic stability of membrane, as proved in Figure 3.1 via ternary diagram results. Besides, the rapid phase inversion process creates large pore and sponge-like structure in the membrane, as reported by Razali *et al.*,[14]. This behavior might increase permeability properties of the membrane.



(a) PSf/$AgNO_3$/LiOH (b) PSf/$AgNO_3$/NaOH



(c) PSf/$AgNO_3$/KOH

Figure 3.2: Membrane cross-section for PSf/$AgNO_3$ with alkali precursor

3.3. X-Ray Diffraction

Figure 3.3 shows the XRD pattern for silver nitrate and alkali content in the PSf membrane. XRD result revealed the purity of the silver oxide obtained in this study and matched with pattern number 00-043-0649. The PSf/$AgNO_3$/alkali peak corresponding to the $2\theta = 29.65°$ (111), 39.08° (200), of the sample respects the JCPDS 652871, and it was confirmed. The amorphous peak is due to the presence of alkali in the membrane. The result was supported by the similar amorphous peak gained by Sklute *et. al.,* where XRD patterns of the multicomponent amorphous salts show changes in position, shape, and magnitude of the characteristic diffuse scattering observed in all amorphous materials that could be used to help constrain the composition of the amorphous salt [15]. The intensity of these peaks tended to decrease upon addition of silver in the PSf membrane. The presence of these peaks confirmed the existence of Ag in the membrane with pattern number 00-043-0997. It can be concluded that the formation of Ag_2O with the addition of precursor following the chemical reaction below:

$$2Ag^+ + 2OH^- \rightarrow Ag_2O + H_2O \quad (4.1)$$

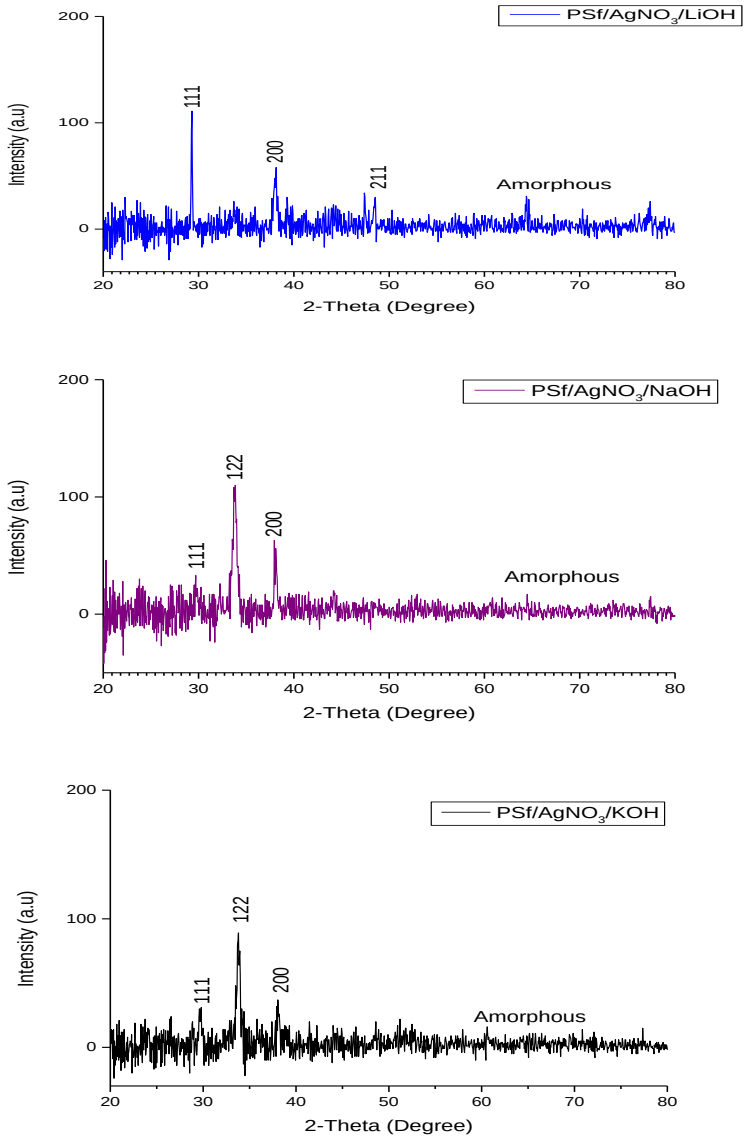


Figure 3.3: XRD analysis for PSf/$AgNO_3$/precursor membrane

3.4. Surface Roughness of Membrane

The effect from the presence of different alkali precursors on PSf/$AgNO_3$ membrane roughness is depicted in Figure 3.4. As shown, PSf/$AgNO_3$/LiOH illustrated the highest membrane surface roughness with the value ≥ 60 nm, followed by PSf/$AgNO_3$/NaOH (37.83 nm) and PSf/$AgNO_3$/KOH (34.93 nm). This result showed that in-situ synthesis of silver resulted in rougher surface of the membrane. Mollahosseini et. al., reported that the surface roughness of PSf membrane was increased by the addition of silver nanoparticles which is probably due to the effect of silver nanoparticles by disturbing the homogeneity of polymeric chains on the surface roughness[16]. The similar result agreed by Ahmad *et al* where the surface roughness was increased with the increasing of the peak current [17]. The addition of $AgNO_3$ affected the LiOH behavior that can cause the membrane to reduce fouling performance. Figure 3.5 shows the 3D AFM images for every membrane surface. The silver particles might aggregate and form roughness surface of the membrane. This high roughness might increase membrane fouling.

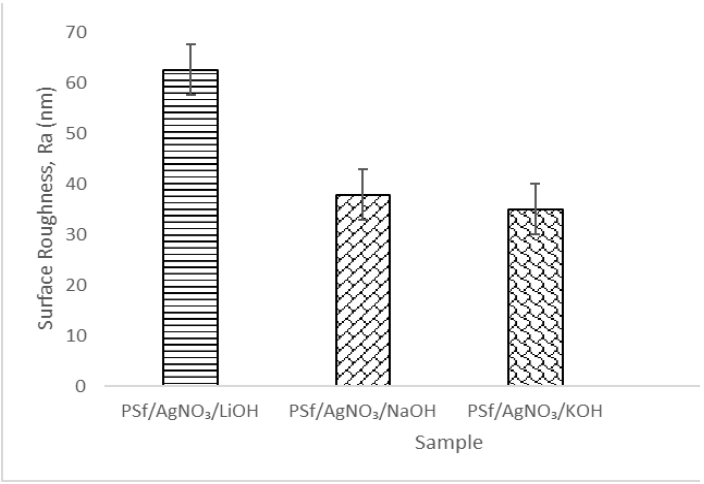
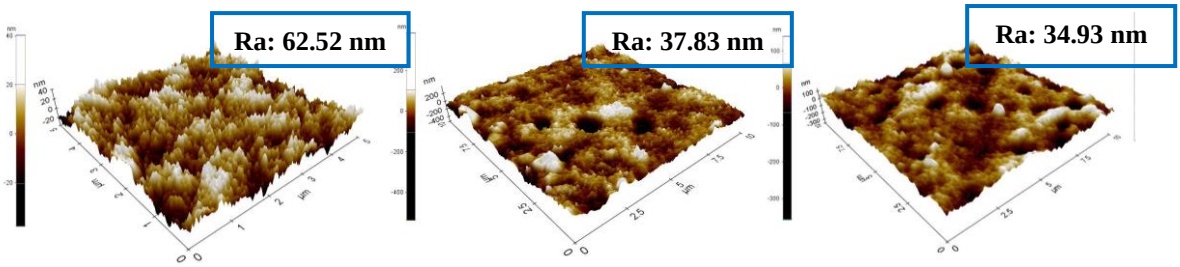


Figure 3.4: Membrane surface roughness for PSf/$AgNO_3$/alkali membrane



(a) PSf/$AgNO_3$/LiOH (b) PSf/$AgNO_3$/NaOH (c) PSf/$AgNO_3$/KOH

Figure 3.5: 3D AFM images for PSf/$AgNO_3$ made of alkali precursor

4. Conclusion

The development of PSf/$AgNO_3$ membrane has been successfully carried out via in-situ synthesis method. The effect of silver precursor and the effect of in-situ synthesis of silver in the PSf membrane have been investigated. Different silver precursor did affect the properties of the PSf/Ag membrane behavior. PSf reacts with $AgNO_3$ causes an increased in membrane characterization where the formation of membrane morphology led to more porous sublayer with larger irregular finger-like pores. It might improve water separation performance. It is supported by higher membrane surface roughness, causing the larger surface area of the membrane pore. It is essential to know the membrane behavior before membrane modification. PSf membrane performance towards Ag precursors was carried out to improve existing performance. The silver stability on the membrane surface also has been significantly enhanced. Thus, the in-situ synthesis of silver has the potential to be used as a method in membrane fabrication.

Acknowledgment

Authors would like to thank the financial support by Universiti Tun Hussein Onn Malaysia for GPPS financial support grant no H362 and H320 and also the Ministry of Higher Education Malaysia (KPT) for Fundamental Research Grant (FRGS) grant no. 1631.

References

[1] R. Connor, *The United Nations world water development report 2015: water for a sustainable world*. United Nations Educational, Scientific and Cultural Organization, 2015.

[2] M. Fitri, M. Akhir, N. A. Saad, N. A. Zakaria, L. Xin, and A. A. Athirah, "Desalination of Groundwater Using Marble Filter," *Int. J. Integr. Eng.*, vol. 1, pp. 92–100, 2019.

[3] S. Zhu *et al.*, "Improved performance of polyamide thin-film composite nanofiltration membrane by using polyetersulfone/polyaniline membrane as the substrate," *J. Memb. Sci.*, vol. 493, pp. 263–274, 2015.

[4] M. Z. Yunos *et al.*, "Influence of inorganic additives on the performance of polysulfone ultrafiltration membrane," *J. Teknol. (Sciences Eng.*, vol. 65, no. 4, pp. 111–115, 2013.

[5] J. Gao, "Membrane Separation Technology for Wastewater Treatment and its Study Progress and Development Trend," *Proc. 2016 4th Int. Conf. Mech. Mater. Manuf. Eng. (MMME 2016)*, vol. 79, no. Mmme, pp. 630–633,

2016.
[6] S. Rao, R. Xiu, J. Si, S. Lu, M. Yang, and Y. Xiang, "In situ synthesis of Nanocomposite Membranes: Comprehensive Improvement Strategy for Direct Methanol Fuel Cells," *ChemSusChem*, vol. 7, no. 3, pp. 822–828, 2014.
[7] L. Huang, S. Zhao, Z. Wang, J. Wu, J. Wang, and S. Wang, "In situ immobilization of silver nanoparticles for improving permeability, antifouling and anti-bacterial properties of ultrafiltration membrane," *J. Memb. Sci.*, vol. 499, pp. 269–281, 2016.
[8] N. K. Hoa, H. A. Rahman, and M. R. Somalu, "Influence of Silver Addition on the Morphological and Thermal Characteristics of Nickel Oxide-Samarium Doped Ceria Carbonate (NiO-SDCC) Composite Anode," *Int. J. Integr. Eng.*, vol. 10, no. 1, pp. 196–201, 2018.
[9] A. Mansourizadeh and A. F. Ismail, "Preparation and characterization of porous PVDF hollow fiber membranes for CO 2 absorption: Effect of different non-solvent additives in the polymer dope," *Int. J. Greenh. Gas Control*, vol. 5, no. 4, pp. 640–648, 2011.
[10] A. Ahmad *et al.*, "Effect of polyaniline on surface properties of polysulfone membrane," *Chem. Eng. Trans.*, vol. 56, pp. 691–696, 2017.
[11] M. Zaini, Z. Harun, H. Basri, M. Fikri, M. Riduan, and S. Hassan, "Effect of Zinc Oxide on Performance of Ultrafiltration Membrane for Humic Acid Separation," *J. Teknol. (Sciences Eng.*, vol. 65, no. 4, pp. 117–120, 2013.
[12] R. Singh and N. Hankins, *Emerging Membrane Technology for Sustainable Water Treatment*. Elsevier Science, 2016.
[13] M. R. Jamalludin, Z. Harun, H. Basri, M. Z. Yunos, and M. F. Shohur, *Performance studies of polysulfone-based membrane: Effect of silica morphology*, vol. 372. 2013.
[14] N. F. Razali, A. W. Mohammad, and N. Hilal, "Effects of polyaniline nanoparticles in polyethersulfone ultrafiltration membranes: Fouling behaviours by different types of foulant," *J. Ind. Eng. Chem.*, vol. 20, no. 5, pp. 3134–3140, 2014.
[15] E. C. Sklute, A. D. Rogers, J. C. Gregerson, H. B. Jensen, R. J. Reeder, and M. D. Dyar, "Amorphous salts formed from rapid dehydration of multicomponent chloride and ferric sulfate brines : Implications for Mars," *Icarus*, vol. 302, pp. 285–295, 2018.
[16] A. Mollahosseini, A. Rahimpour, M. Jahamshahi, M. Peyravi, and M. Khavarpour, "The effect of silver nanoparticle size on performance and antibacteriality of polysulfone ultrafiltration membrane," *Desalination*, vol. 306, pp. 41–50, 2012.
[17] S. Ahmad *et al.*, "Surface Roughness and Surface Topography of Inconel 718 in Powder Mixed Dielectric Electrical Discharge Machining," *Int. J. Integr. Eng.*, vol. 10, pp. 181–186, 2018.