



RPMME

Homepage: <http://publisher.uthm.edu.my/periodicals/index.php/rpmme>

e-ISSN : 2773-4765

Review on The Effect of Zinc Salt on Performance of Polysulfone Material

Ahmad Azfar Zuhri Abdul Ghafar¹, Muhamad Zaini Yunos¹

¹Nano Structure and Surface Modification (Nanosurf), Faculty of Mechanical and Manufacturing Engineering,
Universiti Tun Hussein Onn Malaysia, Batu Pahat, 86400, MALAYSIA

*Corresponding Author Designation

DOI: <https://doi.org/10.30880/rpmme.2022.03.01.068>

Received 15 Nov. 2021; Accepted 15 April 2022; Available online 30 July 2022

Abstract: This project was conducted to identify the reaction of additive material due to lack of performances of Polysulfone (PSF) and to improve the Polysulfone membrane and the reason used of this non-solvent additive because the low cost and dilute insolvent. This project aims to improve the Polysulfone membrane by using an additive's material and this study aims to investigate the effect of non-solvent additive on Polysulfone membrane and to characterize the mechanical behaviour, physical, and also membrane performance of prepared material. In this study, the experiments work to determine the Polysulfone membrane by using Zinc Chloride, Zinc Acetate, and Zinc Nitrate. The concentration will be varied from 0-5% and the result showed the mechanical properties will be enhance due to increases of zinc salt. The results for physical of the Polysulfone membrane showed decreases in contact angle and rose in porosity. This results for the performance of the membrane by its permeability and rejection also increases, and fouling will be minimize.

Keywords: Zinc Chloride, Zinc Nitrate, Zinc Acetate, Polysulfone, Membrane

1. Introduction

Polluted water-carrying oil produced from factories also wastes crude oil and water sources in addition to polluting the atmosphere. Furthermore, it is difficult to treat emulsified and soluble oil in wastewater using conventional methods. Membrane technology has been widely used in water treatment, especially for the treatment of oil-containing wastewater. This is because membrane separation technology was among the most successful operation units of chemical engineering, for it and have a lot of benefits such as simple operation, low price, no phase transfer, high performance, and capability of reducing pollutants [1].

A membrane is defined as a thin sheet, film, or layer, which works as a selective barrier between two phases that can be liquid, gas, or vapor. In other words, a membrane is an interface between two adjacent phases acting as a selective barrier, regulating the transport of species between the two compartments [2].

The mechanism of membrane separation is a procedure in which a membrane is used to isolate the elements in a solution by rejecting undesirable compounds and allowing others to move through the membrane [2]. In existing pressure-driven membrane processes such as MF, UF, NF, and RO, solvent and various solutes are permeated through the membrane, whereas other components are rejected only depending on the membrane structure and pore size [3].

*Corresponding author: mzaini@uthm.edu.my

2022 UTHM Publisher. All right reserved.

penerbit.uthm.edu.my/periodicals/index.php/rpmme

2. Materials and Methods

Polysulfone that been provided from University Tun Hussein Onn Malaysia (UTHM), N-methyl-2-pyrrolidone (NMP) supplied from University Tun Hussein Onn Malaysia (UTHM), Zinc chloride ($ZnCl_2$), Zinc nitrate ($(NO_3)_2$), Zinc acetate is a salt with the formula $(CH_3COO)_2$, were also supplied by University Tun Hussein Onn Malaysia (UTHM).

2.1 Methods

For the preparation of PSF/zinc salt composite membrane casting solutions, PSF (17 g) was completely dissolved in solvent (NMP) (82.75g, 82.50g, 82.0g) at 60°C and non-solvent Zinc Chloride (0.25, 0.50, and 1.0g) will be added to the PSF solution then the solution was stirred for 4 h 60 °C (solution 1). Next, the same step from solution1 that using Zinc Nitrate (0.25, 0.50, and 1.0 g) will be added to the PSF solution then the solution was stirred for 4 h 60°C (solution 2). The last solution, Zinc Acetate (0.25, 0.50, and 1.0g) will be added to the PSF solution then the solution was stirred for 4h, 60°C (solution 3). The phase inversion technique will be used for the preparation of membranes, as mentioned in our previous study. Casting solution compositions are given in the table below.

2.2 Experiment process

For the preparation of PSF/NMP/Zinc Salt membrane casting solutions, PSF completely dissolved in solvent (NMP) and zinc chloride concentration vary from 0-5% added to the PSF solution then the solution stirred (solution 1). PSF and zinc nitrate concentration 0-5% was dissolved in certain amounts of NMP (solution 2). Next PSF and zinc acetate concentration 0-5% was dissolved in certain amounts of NMP (solution 3). The phase inversion technique used for the preparation of membranes.

Table 2: Casting solution for Zinc Chloride, zinc nitrate and zinc acetate

Membrane	Casting solution (wt %)		
	PSF	NMP	Zinc salt
M1	17	82.75	0.25
M2	17	82.50	0.50
M3	17	82.0	1.0

The first phase is the combination of Polysulfone (PSF), N-Methyl-2-Pyrrolidone (NMP) with zinc salt which is Zinc Acetate. All of the material will combine in a beaker then make a mixture to form a membrane by its solution. The second step is the combination of Polysulfone (PSF), N-Methyl-2-Pyrrolidone (NMP) with zinc salt which is Zinc Nitrate. All of the material will combine in a beaker then make a mixture to form a membrane by its solution, and the third step is the combination of Polysulfone (PSF), N-Methyl-2-Pyrrolidone (NMP) with zinc salt which is Zinc Chloride. All of the material will combine in a beaker then make a mixture to form a membrane by its solution.



Figure 2.1: the solution of PSF/NMP/Zinc Acetate

After that each solution is mixed and heated using a magnetic stirrer for 4 hours. The finished solution is poured on a smooth surface or glass to be leveled to obtain a piece of membrane, the membrane that has been poured on glass will be soaked in a container filled with water.



Figure 2.2: Process the mixture will pour on the pieces of glass



Figure 2.3: Water bath process

2.3 Equation

The permeability tests were performed the pure water permeability ($L/m^2 \cdot h \cdot bar$) was calculated using the following expression:

$$\text{Pure Water Permeability} = \frac{\text{Pure Water Flux}}{\Delta P} \tag{3.1}$$

Equation: pure water permeability

The porosity of a membrane has a very important role in permeability and retention. The porosity of the membrane is determined by the equation:

$$\text{Porosity} = \frac{W_w - W_D}{P_w \times V} \tag{3.2}$$

Equation: porosity

3. Result and Discussion

Results, discussion Calculation, and measurement of the mechanical testing which is the results and determination of tensile strength, this experiment also involved measurement of physical test which is included contact angle and porosity. The performance of the membrane was also be testing which is included permeability, rejection, and fouling

3.1 Contact angle results

The contact angle results were obtained from previous studies and were analysed with several other studies and the results of the analysis found that the contact angle tend to decreases when the addition of zinc salt occur. The contact angle result get from droplet on the membrane and the angle value verified the result either the membrane were hydrophilic or hydrophobic properties. For this experiment results we can see the three zinc salt which is zinc chloride, zinc nitrate and zinc acetate cause the membrane became more hydrophilic state, but to many concentration of the zinc salt the membrane structure can be change due to the porosity.

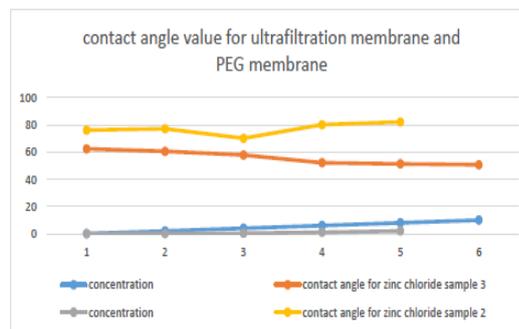


Figure 3.1: the value of contact angle for ultrafiltration and PEG membrane. [17] [18]

The results of contact angle for zinc acetate show on figure below the decreases of contact angle value when we added high concentration of zinc compound, the results also compared with three different type of experiment but still using the same zinc acetate as an additives material. The trend showed the similarity.

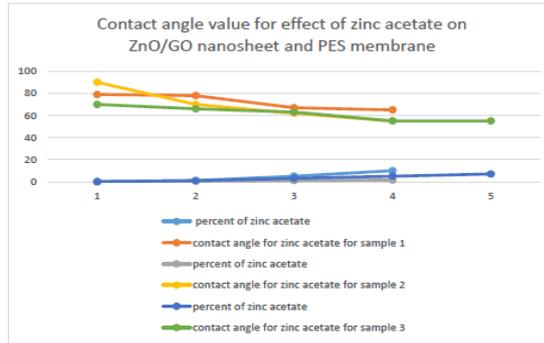


Figure 3.2: The value of contact angle for ZnO modified and the PES membrane. [20] [21]

The results of contact angle for zinc nitrate also show the same trend that decreases of contact angle value when we added high concentration of zinc compound, the results also compared with two different type of experiment but still using the same zinc salt as an additives material. The trend showed the also drop for contact angle value.

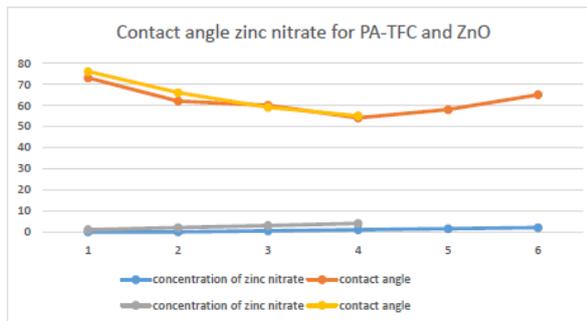


Figure 3.3: the graph of contact angle for PA-TFC membrane and ZnO membrane [23] [24]

The morphology of the membrane tend to be more hydrophilicity after adding the amount of zinc solution, this is because the reaction of zinc and the membrane showed the membrane be more porous and the pure water flux will be increases due to the srtructure.

3.2 Porosity results

Based on the observation of the analysis of the study found that the porosity will increase as soon as the concentration of zinc salt is added to the mixture, this proves the presence of zinc will cause the membrane structure to change. An increase in zinc concentration will change the membrane to be more porous and more finger-like macro void.

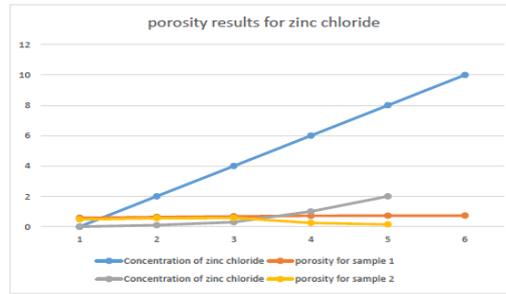


Figure 3.4: the graph of porosity results for zinc chloride [17] [18]

By increasing the weight percentage of ZnO in the ZnO modified GO nanocomposite, the porosity of the membrane is increased. This behavior is often observed in the construction of mixed matrix membranes, where an increase in the concentration of zinc acetate injected into the membrane matrix leads to an increase in membrane porosity and pore size.

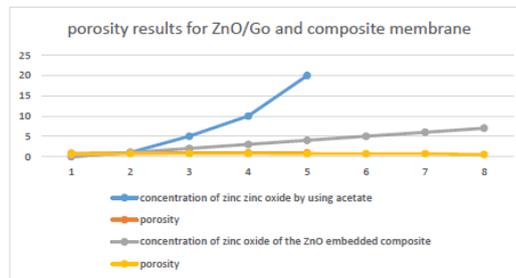


Figure 3.5: the graph of porosity results for ZnO/Go and composite membrane [20] [25]

Graph below showed the porosity result for zinc nitrate and the porosity on the membrane became largest as we added the amount of zinc material, so from data above we can conclude all this three zinc salt give the similar result which is porosity increases when the concentration zinc salt increases.

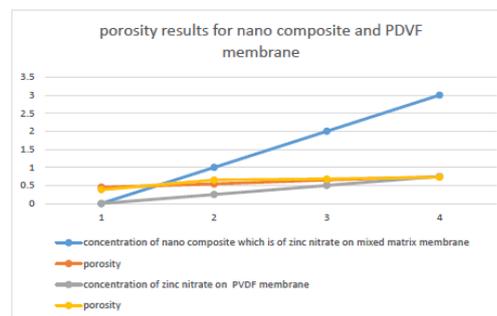


Figure 3.6: the graph of porosity results for nano composite and PDVF membrane. [24] [22]

Increases in zinc salt concentration also improved membrane permeability, and high zinc salt concentrations influenced the size of pores. We may deduce that when pore size increases, permeability increases as well, and the two have a very strong connection.

3.3 Permeability results

Membrane made with concentration of zinc salt has the largest porosity, resulting in the highest permeability. The permeability of the PSF membrane without any additives is less than the permeability value with additives material, in this result we can see the permeability for various membrane with the same zinc salt that used. But in some membrane the permeability show the instead of result due to different kind of mixture and also technique but overall we can conclude the the highest concentration of zinc salt tend the membrane became more permeability.

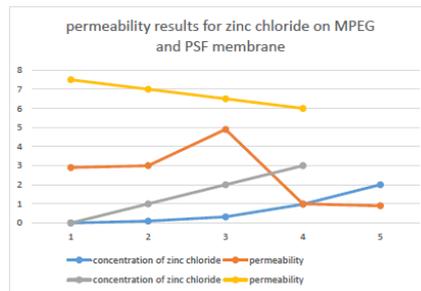


Figure 3.7: Permeability result for zinc chloride for MPEG and PSF membrane [18] [22]

The graph below showed the permeability result increased which related to the membrane contact angle result. The polar ZnO nanoparticles and functional groups on the surface of GO nanosheets have a strong attraction to water molecules, which can attract more water molecules through the membrane, as explained by the porosity and average pore radius of the membrane. Compared with clean PSF membranes, the increased permeability of MMM membranes is due to increased porosity and larger average pore size.

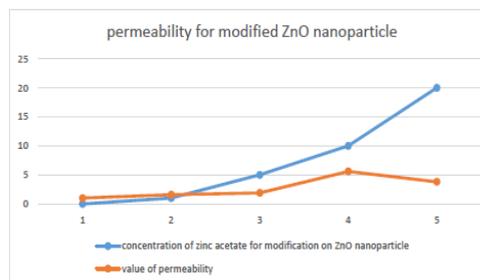


Figure 3.8: the value permeance for zinc nitrate, zinc chloride and zinc acetate membrane [19]

In this experiment the permeation of propylene and its separation performance from the binary gas mixture using the three membranes ZAc (zinc acetate) membrane produced the highest propylene permeation value followed by ZNi (zinc nitrate) membrane and then and ZCl (zinc chloride) membrane.

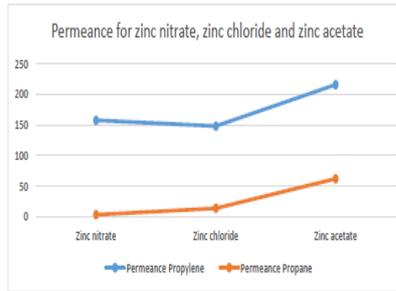


Figure 3.9: the graph of membrane permeability for modified on ZnO nanoparticle [20]

As a result, greater porosity will result in the largest growth of pores. When the permeability is improved, the pure water flux results improve as well.

3.4 Rejection results

The addition of zinc salt increases the water permeation and increased the rejection rate of the membrane, in some experiment, the permeability showed different value or results that obtain when the increases of concentration of zinc salt, as we can see on the figure below when the increases of concentration the value of rejection will drop. The membrane permeance of PVP, has been has said the different kind of permeance material will comeout with different result but in other experiment showed the rejection result can be improve or enhance due to high concentration in zinc salt.

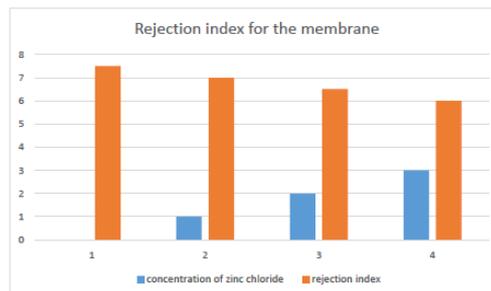
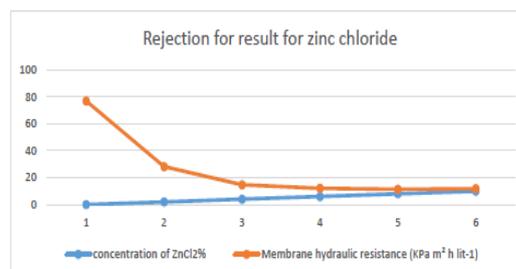


Figure 3.10: the rejection graph for the concentration of zinc chloride [22]

A mixed membrane is better than a pure water flow measurement. With the increase of the content of (ZnCl₂) in the mixed membrane, the flux is increased to six times at most. When the concentration of the modifier increases, the hydraulic resistance of the mixed membrane decreases



ZnCl₂ lead to denser solute rejection properties of were measured with lower solutes (glucose, PEG 200, 400, and 600), as shown in figure below. For the 2 wt. % (MPEGZ-2) membrane, all solutes have achieved a rejection rate of 100%.

Figure 3.11: Rejection Result for Zinc Chloride [17]

membranes, so the these two membranes molecular weight

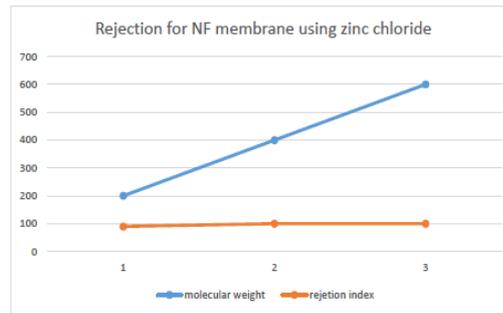


Figure 3.12: The rejection graph for NF membrane [18]

Graph below show the rejection for zinc acetate membrane and permeance with the two material which is arsenic and lead and the result showed as below, the trend of the graph show when the pressure increases and due to the excessive amount of nanoparticles, the retention efficiency is reduced, resulting in an increase in porosity.

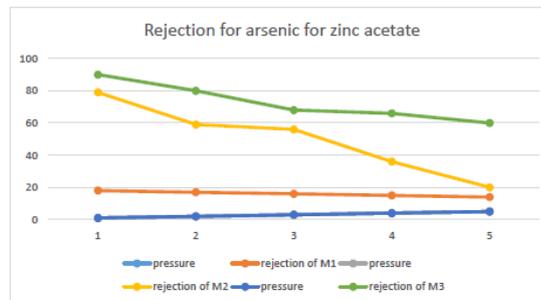


Figure 3.13: Arsenic Rejection. [24]

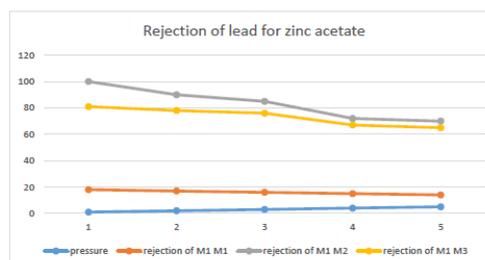


Figure 3.14: Lead Rejection. [24]

3.5 Fouling effect

The membrane fouling is the biggest obstacle to the application of membrane, research on the membrane fouling is of vital importance to this technology, used of additive and material can lead to control or can manage the membrane fouling. To determined solution for improvement of direct membrane filtration performances is to develop new membrane with increased anti-fouling properties. In view, the membrane fouling control technologies of the membrane filtration process, when the controlling the fouling effect so the energy consumption can be minimize, less chemical usage and easier the operation. Once membrane fouling occur, it will reduce permeate flux, increases system downtime, increases membrane maintenance and operation cost due to maintenance cleaning and decreases of membrane lifetime.

So from the result we can see the permeability, porosity and also rejection has improve. So the anti-fouling effect can be maximize and produce the quality of membrane. Beside the mechanical tensile strength also improved due to higher concentration of zinc salt on the membrane.

4. Conclusion

By the end of the results, the objectives of the study were achieved. The effect of zinc salt on the performance of polysulfone material was evaluated by using different types of zinc salts which are zinc chloride, zinc nitrate, and zinc acetate respectively. The membrane characterization has been determined according to its mechanical tensile strength, contact angle, porosity, permeability, rejection, and also fouling effect. Although the results were taken into the experiment based on previous experimental observations the results identically or close to the actual results because the material that been used was also the same.

From the results, we can conclude that when increases happen in zinc salts so hydrophilicity of the membrane also increases, it can be proved because the value of contact angle drops or decreased when can know the hydrophilicity and the contact angle have a very close relation. The value of the contact angle also will determine the hydrophilic or hydrophobic for the membrane. The increases in zinc salt also will enhance the permeability of the membrane, the high concentration of the zinc salts affected the development of pores size. We can conclude that when pore size rose and the permeability also will be enhanced. Therefore the greatest development of pores will come out with an increase in porosity. When the permeability was increased it also will enhance the pure water flux results.

The increase of zinc salts concentration also will give a big impact on mechanical tensile strength, when the high concentration of zinc salt the tensile strength results were also be improved. But too many concentration it cans started to reduce the tensile strength because viscosity effect, what can be said is still increased in tensile strength. Last but not least, the fouling effect also decreased due to its high rejection through the membrane. This can be related to enhanced permeability, porosity, pure water flux, hydrophilicity so the rejection also can be maximized and the fouling effect can be minimized. All the previous data showed the same trends for the results, so we can predict the actual results for the experiments

Acknowledgement

The authors wish to thank to the Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussein Onn Malaysia that has supported on the accomplishment of research activity.

References

- [1] Y. Zhang, Z. Jin, X. Shan, J. Sunarso, and P. Cui, "Preparation and characterization of phosphorylated Zr-doped hybrid silica/PSF composite membrane," *J. Hazard. Mater.*, vol. 186, no. 1, pp. 390–395, 2011, doi: 10.1016/j.jhazmat.2010.11.016.
- [2] T. A. Saleh and V. K. Gupta, "An Overview of Membrane Science and Technology," *Nanomater. Polym. Membr.*, pp. 1–23, 2016, doi: 10.1016/b978-0-12-804703-3.00001-2.
- [3] I. G. Wenten, K. Khoiruddin, A. N. Hakim, and N. F. Himma, *The Bubble Gas Transport Method*. Elsevier B.V., 2017.
- [4] Y. Liu, G. H. Koops, and H. Strathmann, "Characterization of morphology controlled polyethersulfone hollow fiber membranes by the addition of polyethylene glycol to the dope and bore liquid solution," *J. Memb. Sci.*, vol. 223, no. 1–2, pp. 187–199, 2003, doi: 10.1016/S0376-7388(03)00322-3.
- [5] J. Y. Lai, F. C. Lin, C. C. Wang, and D. M. Wang, "Effect of nonsolvent additives on the porosity and morphology of asymmetric TPX membranes," *J. Memb. Sci.*, vol. 118, no. 1, pp. 49–61, 1996, doi: 10.1016/0376-7388(96)00084-1.
- [6] S. Mondal and S. Kumar Majumder, "Fabrication of the polysulfone-based composite ultrafiltration membranes for the adsorptive removal of heavy metal ions from their contaminated aqueous solutions," *Chem. Eng. J.*, vol. 401, no. April, p. 126036, 2020, doi: 10.1016/j.cej.2020.126036.
- [7] M. Hu et al., "Pregelation of sulfonated polysulfone and water for tailoring the morphology and properties of polyethersulfone ultrafiltration membranes for dye/salt selective separation," *J. Memb. Sci.*, vol. 618, no. May 2020, p. 118746, 2021, doi: 10.1016/j.memsci.2020.118746.
- [8] B. Ladewig and M. N. Z. Al-Shaeli, "Membrane Characterization Techniques," pp. 131–150, 2017, doi: 10.1007/978-981-10-2014-8_5.
- [9] O. S. Serbanescu, S. I. Voicu, and V. K. Thakur, "Polysulfone functionalized membranes: Properties and challenges," *Mater. Today Chem.*, vol. 17, p. 100302, 2020, doi: 10.1016/j.mtchem.2020.100302.
- [10] M. K. Purkait, M. K. Sinha, P. Mondal, and R. Singh, *Introduction to Membranes*, vol. 25. 2018.
- [11] J. M. Gohil and R. R. Choudhury, *Introduction to Nanostructured and Nano-enhanced Polymeric Membranes: Preparation, Function, and Application for Water Purification*. Elsevier Inc., 2018.
- [12] N. Abdullah, M. A. Rahman, M. H. D. Othman, J. Jaafar, and A. F. Ismail, *Membranes and Membrane Processes: Fundamentals*. Elsevier Inc., 2018.
- [13] I. Membranes, "Chapter 8."
- [14] H. T. V. Nguyen et al., "Preparation and characterization of a hydrophilic polysulfone membrane using graphene oxide," *J. Chem.*, vol. 2019, pp. 15–20, 2019, doi: 10.1155/2019/3164373.
- [15] "W. Clegg, I. R. Little and B. P. Straughan," no. Ii, pp. 1701–1703, 1986.

- [16] H. Hongshan, "A new monoclinic polymorph of anhydrous zinc acetate," *Acta Crystallogr. Sect. E Struct. Reports Online*, vol. 62, no. 12, pp. 3291–3292, 2006, doi: 10.1107/S1600536806046678.
- [17] K. Rambabu and S. Velu, "Polyethersulfone - Zinc chloride blend ultrafiltration membranes for enhanced flux," *J. Chem. Pharm. Sci.*, vol. 2014-Decem, no. June 2015, pp. 48–49, 2014.
- [18] S. R. Panda and S. De, "Preparation, characterization and performance of ZnCl₂ incorporated polysulfone (PSF)/polyethylene glycol (PEG) blend low pressure nanofiltration membranes," *Desalination*, vol. 347, pp. 52–65, 2014, doi: 10.1016/j.desal.2014.05.030.
- [19] N. T. Tran, T. Yu, J. Kim, and M. R. Othman, "ZIF-8 tubular membrane for propylene purification: Effect of surface curvature and zinc salts on separation performance," *Sep. Purif. Technol.*, vol. 251, no. March, p. 117354, 2020, doi: 10.1016/j.seppur.2020.117354.
- [20] N. Adilah Rosnan, T. Y. Haan, and A. W. Mohammad, "The effect of ZnO loading for the enhancement of PSF/ZnO-GO mixed matrix membrane performance," *Sains Malaysiana*, vol. 47, no. 9, pp. 2035–2045, 2018, doi: 10.17576/jsm-2018-4709-11.
- [21] T. D. Dipheko, K. P. Matabola, K. Kotlhao, R. M. Moutloali, and M. Klink, "Fabrication and Assessment of ZnO Modified Polyethersulfone Membranes for Fouling Reduction of Bovine Serum Albumin," *Int. J. Polym. Sci.*, vol. 2017, 2017, doi: 10.1155/2017/3587019.
- [22] S. R. Kim, K. H. Lee, and M. S. Jhon, "The effect of ZnCl₂ on the formation of polysulfone membrane," *J. Memb. Sci.*, vol. 119, no. 1, pp. 59–64, 1996, doi: 10.1016/0376-7388(96)00113-5.
- [23] K. Kotlhao, I. A. Lawal, R. M. Moutloali, and M. J. Klink, "Antifouling properties of silver-zinc oxide polyamide thin film composite membrane and rejection of 2-chlorophenol and 2,4-dichlorophenol," *Membranes (Basel)*, vol. 9, no. 8, 2019, doi: 10.3390/membranes9080096.
- [24] P. Sherugar et al., "Fabrication of zinc doped aluminium oxide/polysulfone mixed matrix membranes for enhanced antifouling property and heavy metal removal," *Chemosphere*, vol. 275, 2021, doi: 10.1016/j.chemosphere.2021.130024.
- [25] A. Sarihan and E. Eren, "Novel high performance and fouling resistant PSf/ZnO membranes for water treatment," *Membr. Water Treat.*, vol. 8, no. 6, pp. 563–574, 2017, doi: 10.12989/mwt.2017.8.6.563.
- [26] S. By, "Separation of Zinc Chloride (ZnCl₂) Metal Using Membrane Process Universiti Teknologi PETRONAS," no. 8117, 2010.