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Green Synthesis of Polyvinylidene Fluoride using Xanthan Gum Biopolymer and Dimethyl Sulfoxide Green Solvent

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ABSTRACT

The usage of conventional solvent during the membrane fabrication could cause undesirable negative impact to the environment. Associated with this, greener alternative to membrane synthesis has grab the attention of researchers globally. Therefore, this study explored on the green synthesis of polyvinylidene fluoride (PVDF) membrane by adopting the natural ingredient Xanthan Gum (XG) biopolymer together with green solvent dimethyl sulfoxide (DMSO) to form a new generation PVDF membrane. The membrane was prepared by phase inversion method with different XG concentration ranging from 0 wt% to 1.5 wt% while maintaining the constant PVDF and DMSO concentration. Several membrane performance tests were done which included water flux test, Congo red (CR) rejection, and flux recovery ratio (FRR). In this study, the incorporation of XG in membrane shown enhancement in membrane hydrophilicity with a noticeably reduction of wettability from 48.57^{o} to 42.15^{o}. The results shown that membrane embedded with 0.5 wt% XG appeared as the optimum XG concentration. As for the membrane performance, it achieved the pure water flux and FRR of 182.87 L/m^2.h and 89.46%, respectively. According to the overall performance evaluation, the incorporation of XG promoted the performance of membrane.

Keywords: Xanthan gum, dimethyl sulfoxide, polyvinylidene fluoride, green synthesis, green solvent

1.0 INTRODUCTION

The direct discharge of wastewater effluents into the environment without any treatment procedure will put the whole biodiversity and aquatic ecosystems at risk. The hazardous and toxic water pollutants that are discharged everyday will affect the marine environments and cause fatality of the species. Hence, it is a huge obstacle towards environmental conservation. In order to protect the environment, aquatic life and humans from water diseases, these wastewater effluents should be treated adequately [1].

Membrane technology has progressively become a more advanced technology used in water treatment due to its environmental friendliness, cost effectiveness and ease of operation. This is a promising technology for water treatment process and will be used for a long time in the future. Membrane technology enables continuous water purification under moderate operating conditions with relatively low energy usage and no additives are needed. In addition, the

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technology can be used in conjunction with other separation processes to form a hybrid process. In today's world, many industries and researchers are working on the development of membrane technology in a variety of aspects [2, 3].

The preparation of membrane required the usage of polymer as the polymer matrix backbone, solvent to dissolve the polymer, and additional additives to improve membrane selectivity and permeation. Traditionally, conventional solvent such as N-methyl-2-pyrrolidone (NMP) and dimethylformamide (DMF) have been used to fabricate polymeric membrane. These conventional solvents are toxic and might generate secondary pollutant upon discharging. The discharging process may possibly create harm to the environment and human health. NMP is an irritant to human as it will cause redness, swelling, and painful when there is direct contact to skin. It also has low acute toxicity to the aquatic organisms [4]. As for DMF, it can cause acute effects including skin irritation, abdominal pain, constipation, and dizziness. When there is long-term exposure to DMF, birth defects may occur [5]. Due to the negative impacts stated, an alternative solvent should be identified to avoid the creation of harmful to environment and human health. Therefore, in line with the twelve pillars of green chemistry which is utilizing safer solvent, this research is designed to replace the conventional solvents with green solvents in membrane fabrication process.

There are several studies in recent years concerning the utilization of bioderived solvent in membrane fabrication, indicating the replacement of conventional solvents with bioderived solvent is the current researching interest [6]. Among many green solvents, Dimethyl sulfoxide (DMSO), a non-toxic, low VOC green solvent was identified as a great solution to replace the common toxic solvent used such as DMF in producing PVDF membranes. DMSO have similar solvent characteristic to conventional solvent in terms of the viscosity, polarity, and solvency power. It was reported that utilising DMSO as a solvent resulted in a thinner active surface layer than using DMF or N-Methylpyrrolidone (NMP) solvent and it able to obtain a superior performance in terms of water selectivity and permeability [7].

Apart from that, membrane fouling is the main drawback of membrane technology because it can lead to low efficiency on separating pollutant in the water resources and shorten the membrane lifetime. As the contaminants accumulated on membrane surface, it will form a foulant layer, blocking the fluids to pass through membrane. In this case, the permeation rate of fluid is decreased. Besides, when the fouling condition becomes severe, membrane replacement is required which increases the cost of a plant. With the presence of additives in polymeric membrane, the permeation and antifouling performance of membrane can be improved due to its properties and the existence of hydrophilic functional groups on the particle surface [8–10] Therefore, the addition of additives in membrane fabrication is used in this research to improve the membrane antifouling performance. Various green additive such as Gum Arabic (GA), Deep Eutectic Solvent (DES) and XG [9–11] were identified as the potential materials to be adopted in membrane fabrication as a practice for the preparation of sustainable membrane.

Therefore, in this study, preparation of new generation PVDF membrane is aimed to be achieved via green approaches by adopting XG as

biopolymer additive and DMSO as green solvent. To the best of the author knowledge, the adoption of XG additive in PVDF/DMSO membrane is scarce and worth to be investigate. Besides, this research is in accordance with several of the Sustainable Development Goals established by the World Health Organization (WHO), which are expected to be achieved by 2030.

2.0 METHODS

2.1 Materials

Polymer Polyvinylidene Fluoride (PVDF) pellets and Dimethyl Sulfoxide (DMSO) were supplied by Solvay and Friedemann Schmidt Chemical respectively while both the Congo Red (CR) and Xanthan Gum (XG) was provided by Sigma Aldrich. All the materials and chemicals used were analytical grade.

2.2 Preparation of PVDF Membrane Dope Solution

There was a total of five membrane samples studied where the dope solution was prepared by dissolving PVDF pellets and XG powder into DMSO solvent with the respective composition ratio as shown in Table 1. The PVDF pellets were dried in an oven for 2 hrs at 70℃ to remove the moisture content in them. Then, the dried PVDF pellets and XG powder were added into DMSO solvent separately according to the composition ratio. Both mixtures were stirred at 100 rpm at 65℃ until it achieved homogeneous mixing. After that, XG/DMSO mixture was mixed into PVDF/DMSO mixture and continue stirred until homogeneous dope solution was obtained. The mixed dope solution was then undergone degassing process. It was ready to be used when there is no air bubble presence [12].

2.3 Fabrication of New Generation PVDF Membrane

Phase inversion method was conducted to fabricate the composite membrane. The dope solution was poured on a glass plate and casted with a customized casting blade to obtain a uniform layer with the thickness of 0.2 mm. Then, the casted dope solution was immersed immediately into a coagulation bath filled with distilled water for five minutes until the dope solution was precipitated into membrane. After that, the fabricated membrane was immersed overnight in a different container filled with distilled water to ensure no residual solvent was remained [12]. Lastly, it was stored in container containing distilled water at room temperature for further usage.

2.4 Contact Angle Measurement

To determine membrane hydrophilicity, contact angle measurement was measured by contact angle goniometer. The water droplet was dropped on the membrane surface by using syringe and the contact angle was analyzed. Five sets of measurement were repeated for every membrane sample to obtain the average result. When the contact angle is smaller than 90° ($\theta < 90°$), the solid is known as ‘wetting’, where water can spread over the solid surface spontaneously. When the contact angle is larger than 90° ($\theta > 90°$), the solid is known as ‘repelling’, where water contacted to the solid does not spread much on the surface [13].

Table 1 Composition of membrane dope solution

Membrane Sample	Concentration of Material (wt.%)		
	PVDF	**XG**	**DMSO**
P1	15	0	85
P2	15	0.25	85
P3	15	0.50	85
P4	15	1.00	85
P5	15	1.50	85

2.5 Water Flux

To determine membrane permeability, water flux test was conducted. It is conducted by applying dead-end filtration system (Model: HP 4750, Sterlitech). Before the test, membrane pre-compaction was done by performing dead-end filtration for 30 mins with distilled water and continued for 30 mins with HA solution, at 1 bar, to stabilize the flux. To perform pure water flux, dead-end filtration was conducted with 300 mL of distilled water at 1 bar. The water passed through was weighed and recorded every five minutes until the result was constant. For permeate flux, 300 mL of HA solution was applied at the same pressure and the permeate passed through was weighed and recorded every five minutes for 30 minutes. The water flux was calculated with equation (2) as shown below [14].

$$J_w = \frac{Q_w}{A} \quad (2)$$

where,
J_w = pure water flux, L/m^2.h
Q_w = water volume flow rate, L/h
A = Area of the membrane, m^2

2.6 Congo Red Rejection

The rejection study was done by using 20 ppm of CR solution as foulant. The HA permeate collected in permeate flux was analyzed by UV-Vis spectroscopy with 497 wavelength (λ = 497 nm) to determine the absorbance of HA in permeate. Then, the absorbance was converted to concentration by referring to the HA calibration curve. The rejection was observed by using equation (3) [14].

$$R = \left[1 - \left(\frac{C_p}{C_f}\right)\right] \times 100\% \quad (3)$$

where,
R = Rejection, %
C_p = Permeate Concentration, ppm
C_f = Feed solution, ppm

2.7 Flux Recovery Ratio (FRR)

The FRR was determined to study the membrane antifouling performance. A second pure water flux was conducted by dead-end filtration system with 300 mL of distilled water at 1 bar to observe the water flux recovery after the permeate flux performed. In the second pure water flux, the water passed

through was weighed and recorded every five minutes until the result was constant. Along the flux tests, the same membrane sample was used. The FRR was calculated by equation (4) [15,16].

$$\text{FRR} = \frac{J_{w2}}{J_{w1}} \times 100\% \quad (4)$$

where,
FRR = flux recovery ratio, %
J_{w1} = water flux for first test, L/m^2.h
J_{w2} =water flux for second test, L/m^2.h

3.0 RESULTS AND DISCUSSION

3.1 Contact Angle Measurement

Figure 1 illustrates the average contact angle of each membrane samples. Contact angle measurement of a membrane can be attributed to membrane hydrophilicity. The smaller the contact angle, indicating the increasing of membrane wettability and hydrophilicity [14]. According to Figure 1, the average contact angle described a decreasing trend from membrane sample P1 to P5. Membrane sample P1 has the highest contact angle of 48.57°, followed by P2, P3 and P4 and with 45.99°, 42.15° and 41.52°, respectively, while P5 has the lowest contact angle of 38.73°. Membrane samples with XG addition shows a noticeable changed on contact angle which demonstrated lower contact angle than pure PSF membrane.

Based on the results shown, it can be concluded that the addition of XG can reduce the contact angle of membrane, and the higher the concentration of XG added, the lower the contact angle can be achieved. This can be explained by the presence of the hydrogen bonding between water molecules and XA molecules. Such interaction enables the membrane to facilitate the water permeation across the membrane associated to its improved hydrophilicity properties. Such behaviour also reported in available literature studies [10, 17].

3.2 Water Flux and Rejection

The pure water flux of membrane samples is conducted at 1 bar by dead-end filtration, and the results obtained indicate the permeability of membrane, where the higher the pure water flux, the better the membrane permeability. Referring to Figure 2, the pure water flux for all modified membrane was higher than the unmodified membrane with the enhancement in the range of 20 – 46%. Unmodified membrane, P1 has the lowest water flux of 143.67 L/m^2.h, membrane sample P2, P3, P4 and P5 has a higher water flux of 209.70 L/m^2.h, 182.87 L/m^2.h, 173.91 L/m^2.h and 173.57 L/m^2.h respectively. This shows that XG biopolymer addition has a positive impact to membrane performance. The pure water flux results obtained are directly proportional to water permeability [18, 19].

The incorporation of XG into membrane matrix promotes the hydrophilicity of membrane, increasing the pure water flux. This is because XG attracts the water molecules inside the membrane matrix and further facilitates the passage of the water molecules to pass through the membrane due to the presence of the hydrogen bond [17].

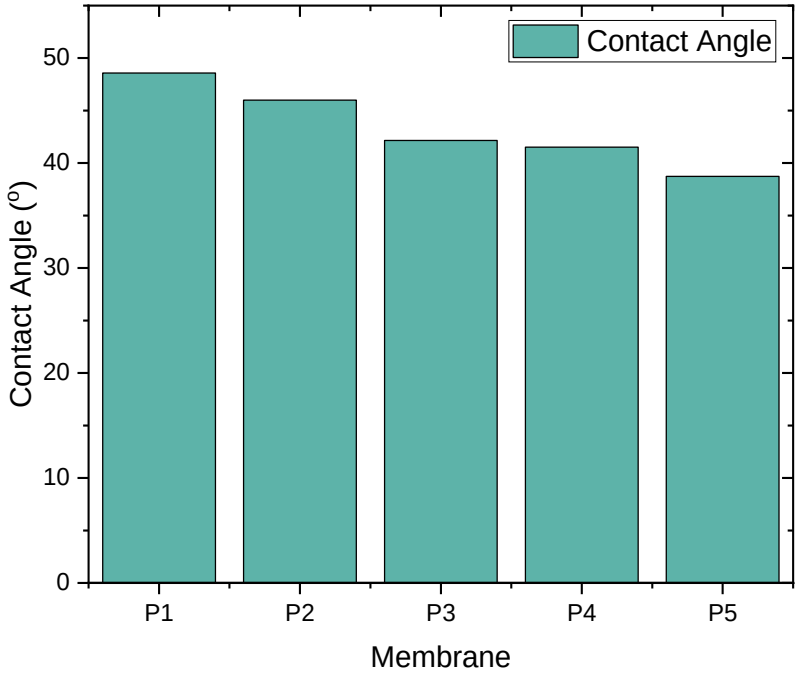

Figure 1 Membrane contact angle

As for CR rejection performance shown in Figure 2, it represents the ability of the membrane to block the pollutant from flowing through it, where the higher the rejection, the better the membrane performance. Based on Figure 2, membrane sample P1 has the highest CR rejection rate of 86.73%. However, the CR rejection rates of membranes with the addition of XG are slightly lower than the bare membrane, with percentage of 85.60%, 83.33%, 80.61% and 81.63% respectively. This could be explained by the higher water permeability of the membrane that reduces the CR rejection rate.

Besides, this study has yielded similar results to the study conducted by Kiani, Mousavi and Bidaki in 2021 [17]. They found that the permeate rejection of the membranes was slightly reduced when 0.25 wt.% and 0.5 wt.% concentration of XG were added, due to the larger pore formation on the membrane surface. However, when the concentration of XG was increased to 1 wt.%, the permeate rejection of the membrane improved as the membrane pore size was reduced. In light of these results, it can be concluded that the membrane rejection rate can be improved with higher loading of XG concentration.

On the safe side, the rejection still maintained above 80% for all the membrane and such weakness could be overcome by adopting higher percentage of PVDF concentration to form a denser membrane, thus tuning the membrane to reject effectively while at the same time allowing a higher water rate to pass through the membrane.

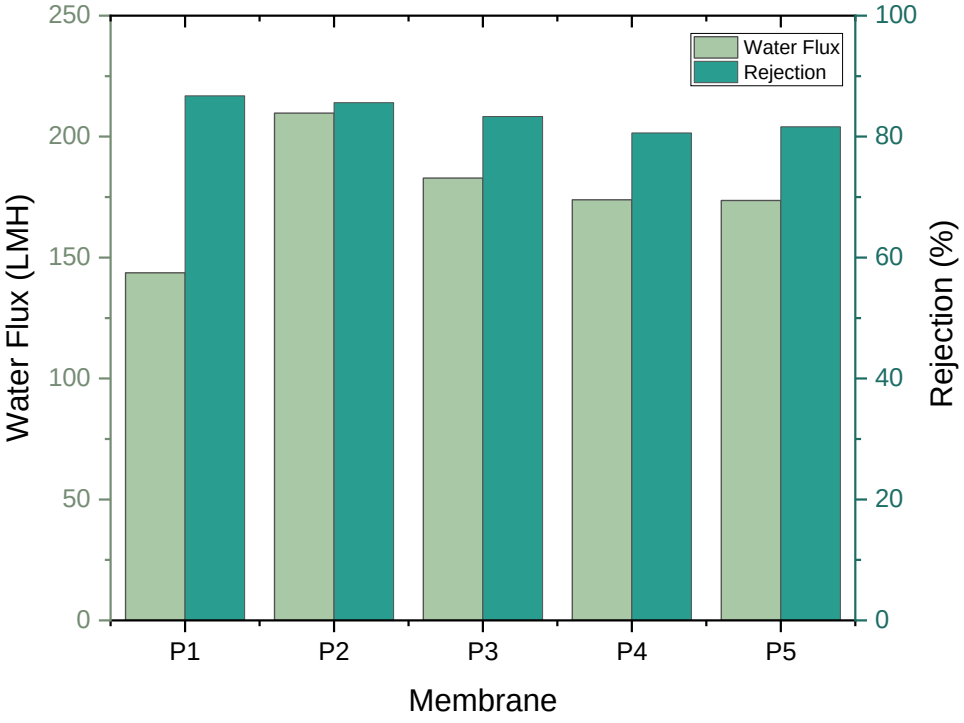

Figure 2 Membrane Water Flux and Rejection Performance

3.3 Membrane Antifouling Behaviour

FRR is applied to determine the antifouling performance of a membrane. It describes the ability of membrane to retrieve the water flux after a permeate flux. The higher the FRR, the better the membrane antifouling performance. If a membrane has a better antifouling performance, it indicates that the membrane has a longer lifetime, leading to reduction of operating cost in filtration process.

As illustrated in Figure 3, the FRR of membrane sample P1 is 81.71%, while membrane sample of P2 and P3 has an increasing FRR trend of 81.81% and 89.46%, respectively, whereas membrane sample P4 and P5 has reduction in the FRR to 74.50% and 64.83%. According to the results, P3 has the highest FRR which improved the ratio up to 9.5% as compared to unmodified PVDF membrane, while the FRR of P5 recorded the lowest FRR drops by 20.66% as compared to P1. The overall performance evaluation suggested that XG-embedded membranes with concentration of 0.25-0.5% are the better option for membrane synthesis, as both membrane able to show higher FRR than pure PVDF membrane, indicating XG can provide enhancement in membrane antifouling characteristics.

The FRR enhancement achieved by XG addition which indicated the hydrophilicity properties of XG does play an important role in designing the membrane. However, when the XG loading was increased further to 1.0wt% and 1.5wt%, the FRR showed a decreasing trend as shown in Figure 3. The decrease in FRR with high XG loading could be attributed to the high viscosity of the casting solution, which slows down the demixing process and

leads to the formation of small pore size [20]. Additionally, research by Hairom, Mohammad and Kadhum (2014) reported that the decrease in performance could also be related to the aggregation and adsorption of CR in the internal pore of the membrane, which can block the membrane pore and lead to irreversible fouling of membrane [21]. This ultimately results in a decrease in the FRR performance.

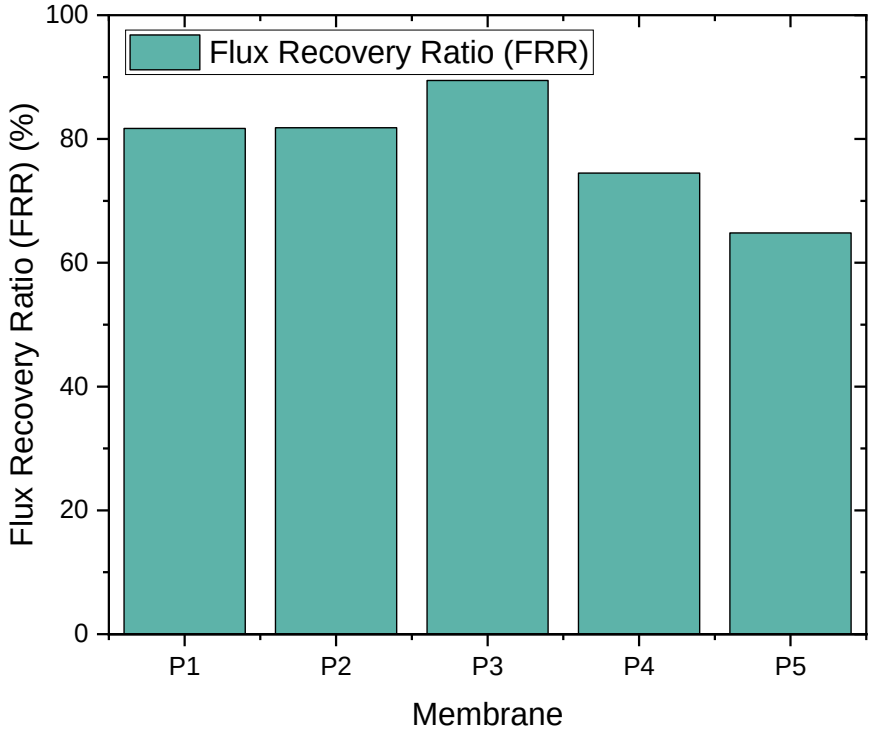

Figure 3 Flux recovery ratio of membrane

3.4 Recent Development of Green Membrane Synthesis

Currently, the study adopting green approaches in green membrane synthesis still at its development stages and the potential of the new generation green membrane is undeniable. The reported membrane fabrication using green solvents that was prepared by other literature studies were listed in Table 2.

Table 2 Reported membrane fabrication with green approaches

Year	Polymer	Green Approaches		Presence of Nanomaterial	Reference
		Green Solvent	Green Additive (Biopolymer or Natural)		
2015	PVDF	Rhodiasolv@Polarclean	NA	NA	[22]
2016	PVDF	Triethyl Phosphate (TEP)	NA	NA	[23]

Year	Polymer	Green Approaches		Presence of Nanomaterial	Reference
		Green Solvent	Green Additive (Biopolymer or Natural)		
2017	PVDF	Triethyl Phosphate (TEP)	NA	NA	[24]
2018	PES	Rhodiasolv@Polarclean	NA	NA	[25]
2018	PSF	Rhodiasolv@Polarclean	NA	NA	[26]
2018	PES	DESs	NA	NA	[11]
2019	PES	Dimethylsulfoxide (DMSO)	NA	NA	[27]
2019	PSF, PES, CA	Rhodiasolv@Polarclean	NA	NA	[28]
2019	PES	Cyrene	NA	NA	[29]
2020	CA	Methyl Lactate	NA	NA	[30]
2021	PSf	DMSO, Cyrene, TEP	Gum Arabic	NA	[9]
2021	PSf	NA	Gum Arabic	GO	[8]
2022	PSf	DMSO	NA	GO	[31]
2022	PVDF	DMSO	Xanthan Gum	NA	This study

4.0 CONCLUSION

Green synthesis for new generation PVDF membrane adopting XG biopolymer and DMSO as green solvent was successfully synthesized. It can be concluded that the presence of the XG able to tune membrane performance in terms of hydrophilicity, flux and FRR. The experimental results revealed that the optimum XG concentration was recorded at 0.5 wt% as the FRR is the highest with 89.46 while maintaining competitive performance in terms of water flux, rejection and hydrophilicity which recorded at 182.87 L/m^2.h, 83.33% and 42.15^o.

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REFERENCES

[1] S. P. Bera, M. Godhaniya, C. Kothari. 2022. Emerging and advanced membrane technology for wastewater treatment: A review, *J. Basic Microbiol.* 62: 245-259.

[2] T. A. Saleh, V. K. Gupta. 2016. An overview of membrane science and technology. *Nanomater. Polym. Membr.* 1-23.

[3] P. V. Chai, J. Y. Law, E. Mahmoudi, A.W. Mohammad. 2020. Development of iron oxide decorated graphene oxide (Fe_3O_4/GO) PSf mixed-matrix membrane for enhanced antifouling behavior. *J. Water Process Eng.* 38: 101673.

[4] B. Åkesson. 2001. Concise international chemical

assessment document 35: N-methyl-2-pyrrolidone. *IPCS Concise Int. Chem. Assess. Doc.*

[5] G. Long, M. E. Meek, M. Lewis. 2001. Concise international chemical assessment document 31: N,N-dimethylformamide. *IPCS Concise Int. Chem. Assess. Doc*. 1-56.

[6] T. Marino, F. Galiano, A. Molino, A. Figoli. 2019. New frontiers in sustainable membrane preparation: Cyrene^{TM} as green bioderived solvent. *J. Memb. Sci.* 580: 224-234.

[7] W. J. Lee, P. S. Goh, W. J. Lau, A. F. Ismail, N. Hilal. 2021. Green approaches for sustainable development of liquid separation membrane. *Membranes (Basel)*. 11: 1-35.

[8] P. V. Chai, P. Y. Choy, W. C. Teoh, E. Mahmoudi, W. L. Ang. 2021. Graphene oxide based mixed matrix membrane in the presence of eco-friendly natural additive gum Arabic. *J. Environ. Chem. Eng*. 9: 105638.

[9] Y. X. Foong, L. H. Yew, P. V. Chai. 2020. Green approaches to polysulfone based membrane preparation via dimethyl sulfoxide and eco-friendly natural additive gum Arabic. *Mater. Today Proc.* 46: 2092-2097.

[10] R. Sathish Kumar, G. Arthanareeswaran, D. Paul, J. H. Kweon. 2015. Effective removal of humic acid using xanthan gum incorporated polyethersulfone membranes. *Ecotoxicol. Environ. Saf.* 121: 223-228.

[11] B. Jiang, N. Zhang, B. Wang, N. Yang, Z. Huang, H. Yang, Z. Shu. 2018. Deep eutectic solvent as novel additive for PES membrane with improved performance. *Sep. Purif. Technol.* 194: 39-248.

[12] S. Zinadini, A. Akbar, M. Rahimi, V. Vatanpour. 2014. Preparation of a novel antifouling mixed matrix PES membrane by embedding graphene oxide nanoplates. *J. Memb. Sci.* 453: 292-301.

[13] B. Tylkowski, I. Tsibranska. 2015. Overview of main techniques used for membrane characterization. *J. Chem. Tech. and Metallurgy.* 50: 3-12.

[14] A. Najjar, S. Sabri, R. Al-Gaashani, M.A. Atieh, V. Kochkodan. 2019. Antibiofouling performance by polyethersulfone membranes cast with oxidized multiwalled carbon nanotubes and arabic gum. *Membranes (Basel).* 9.

[15] D. Ariono, P. T. P. Aryanti, S. Subagjo, I. G. Wenten. 2017. The effect of polymer concentration on flux stability of polysulfone membrane. *AIP Conf. Proc.* 1788.

[16] P. V. Chai, A. W. Mohammad, Y. H. Teow, M. Ebrahim. 2017. Evaluation of Iron oxide decorated on graphene oxide (Fe_3O_4/GO) nanohybrid incorporated in PSF membrane at different molar ratios for Congo red rejection. *J. Teknol.* 79: 73-81.

[17] S. Kiani, S.M. Mousavi, A. Bidaki. 2021. Preparation of polyethylene terephthalate/xanthan nanofiltration membranes using recycled bottles for removal of diltiazem from aqueous solution. *J. Clean. Prod.* 314: 128082.

[18] S. Vetrivel, M. S. A. Saraswathi, D. Rana, A. Nagendran. 2018. Fabrication of cellulose acetate nanocomposite membranes using 2D layered nanomaterials for macromolecular separation. *Int. J. Biol. Macromol.* 107: 1607-1612.

[19] P. V. Chai, E. Mahmoudi, Y. H. Teow, A. W. Mohammad. 2017.

Preparation of novel polysulfone-Fe3O4/GO mixed-matrix membrane for humic acid rejection. *J. Water Process Eng.* 15: 83-88.

[20] Y. Manawi, V. Kochkodan, E. Mahmoudi, D. J. Johnson, A. W. Mohammad, M. A. Atieh. 2017. Characterization and separation performance of a novel polyethersulfone membrane blended with acacia gum. *Sci. Rep.* 7: 1-12.

[21] N. H. H. Hairom, A. W. Mohammad, A. A. H. Kadhum. 2014. Nanofiltration of hazardous Congo red dye: Performance and flux decline analysis. *J. Water Process Eng.* 4: 99-106.

[22] N. T. Hassankiadeh, Z. Cui, J. H. Kim, D. W. Shin, S. Y. Lee, A. Sanguineti, V. Arcella, Y. M. Lee, E. Drioli. 2015. Microporous poly(vinylidene fluoride) hollow fiber membranes fabricated with PolarClean as water-soluble green diluent and additives. *J. Memb. Sci*. 479: 204-212.

[23] S. Fadhil, T. Marino, H. F. Makki, Q. F. Alsalhy, S. Blefari, F. Macedonio, E. Di Nicolò, L. Giorno, E. Drioli, A. Figoli. 2016. Novel PVDF-HFP flat sheet membranes prepared by triethyl phosphate (TEP) solvent for direct contact membrane distillation. *Chem. Eng. Process. Process Intensif.* 102: 16-26.

[24] J. Chang, J. Zuo, L. Zhang, G. S. O'Brien, T. S. Chung. 2017. Using green solvent, triethyl phosphate (TEP), to fabricate highly porous PVDF hollow fiber membranes for membrane distillation. *J. Memb. Sci.* 539: 295-304.

[25] T. Marino, E. Blasi, S. Tornaghi, E. Di Nicolò, A. Figoli. 2018. Polyethersulfone membranes prepared with Rhodiasolv®Polarclean as water soluble green solvent. *J. Memb. Sci*. 549: 192-204.

[26] X. Dong, A. Al-Jumaily, I.C. Escobar. 2018. Investigation of the use of a bio-derived solvent for non-solvent-induced phase separation (NIPS) fabrication of polysulfone membranes,. *Membranes (Basel).* 8.

[27] T. Marino, F. Galiano, S. Simone, A. Figoli. 2019. DMSO EVOL^{TM} as novel non-toxic solvent for polyethersulfone membrane preparation. *Environ. Sci. Pollut. Res.* 26: 14774-14785.

[28] H. H. Wang, J. T. Jung, J. F. Kim, S. Kim, E. Drioli, Y. M. Lee. 2019. A novel green solvent alternative for polymeric membrane preparation via nonsolvent-induced phase separation (NIPS). *J. Memb. Sci.* 574: 44-54.

[29] R. A. Milescu, C. R. McElroy, T. J. Farmer, P. M. Williams, M. J. Walters, J. H. Clark. 2019. Fabrication of PES/PVP water filtration membranes using cyrene®, a safer bio-based polar aprotic solvent. *Adv. Polym. Technol.*

[30] M. A. Rasool, C. Van Goethem, I. F. J. Vankelecom. 2020. Green preparation process using methyl lactate for cellulose-acetate-based nanofiltration membranes. *Sep. Purif. Technol.* 232: 115903.

[31] Y. F. Ong, Y. T. Wong, P. V Chai. 2020. Materials Today : Proceedings Green synthesis of graphene oxide polysulfone membrane using dimethyl sulfoxide as green solvent. *Mater. Today Proc.*