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Optimizing Hybrid Membrane with Kappa-Carrageenan and Silver Graphene Oxide: A Sustainable Approach using Green Solvents

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ABSTRACT

The application of toxic solvents in membrane production poses significant risks to human health, environmental sustainability, workplace safety, and regulatory compliance. In response to the increasing demand for sustainable practices, recent research had shifted towards developing greener alternatives to achieve more sustainable membrane principle. Solvents such as ethylene carbonate (EC), dimethylacetamide (DMAc), and dimethyl sulfoxide (DMSO) have demonstrated potential due to their minimal environmental impact and effectiveness in maintaining the membrane performance. This study explores the fabrication of hybrid membranes polysulfone (PSf) with kappa-carrageenan (k-car) embedded with silver graphene oxide (Ag-GO) using less toxic solvents. The additives, k-car, serve as a pore-forming agent to enhance hydrophilicity, while Ag-GO NPs as an antibacterial agent and reduce the hydrophobicity of PSf. The membranes were fabricated by the wet phase inversion technique, with embedment of k-car and Ag-GO into a mixed-matrix of PSf casting solution. The inclusion of k-car and Ag-GO NPs significantly enhanced the hydrophilicity from 68.52 to 57.32 degree and porosity from 63 to 88%, respectively. Membrane performance analysis demonstrated that all membranes, except GS2, achieved Fe2+ and Mn2+ removal rates above 95%. Notably, the GS3 membrane exhibited the highest water flux at 213.12 L.m-2 h-1 and the highest iron and manganese removal rates, at 98.1 and 99.8%, respectively. The GS3 membrane demonstrates exceptional performance due to its optimized porosity, increased hydrophilicity, high permeate flux, and enhanced ionic solute removal efficiency. This performance is further intensified by using DMSO as a green solvent during fabrication which improves membrane structure and function while aligning with sustainable processing standards. This study underscores the potential of green solvents in producing high-performance, environmentally friendly membranes for water treatment applications.

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1. Introduction

The application of hazardous solvents in membrane production can have a detrimental effect on human health, environmental integrity, workplace safety, regulatory compliance and consumer well-being. As a result, there is a growing emphasis on developing greener and more sustainable alternatives that minimize or eliminate the reliance on harmful solvents while maintaining membrane performance and reliability [1,2]. As membrane technologies have potential of the widespread adoption across diverse sectors such as water purification, wastewater treatment, energy generation and chemical separation, there is a concurrent increase in sustainability challenges. The production of many conventional membranes typically relies on non-renewable, petroleum-derived polymers, and their synthesis often requires high energy input, leading to increased carbon emissions and resource depletion. Moreover, the use of organic solvents during fabrication raises concerns related to toxicity and hazardous waste generation [3]. Consequently, the adoption of sustainable solvents in membrane preparation had gained significant importance due to conventional method utilized highly volatile solvent in membrane fabrication.

In recent years, the focus on sustainability and environmental consciousness had led to significant advancements across various industrial sectors, including membrane technology. Development greener solvents for membrane fabrication had gained attention as researchers aim to minimize the environmental impact of solvent use in maintaining and improving membrane performance. Research done by GlaxoSmithKline (GSK) had initiated scomprehensive solvent evaluation in 2011, assessing up to 110 solvents [1]. This initiative was further expanded by Mehrabani *et al.*, [1], who evaluated 34 solvents and classified them into four categories: 17 solvents were deemed unsuitable for further study, while the remaining were categorized as recommended, problematic, hazardous, or highly hazardous [1]. Therefore, ethylene carbonate (EC), dimethyl sulfoxide (DMSO) and dimethylacetamide (DMAc) become the potential solvents for sustainable of membrane fabrication. These solvents offer potential to reduce environmental impacts, while simultaneously enhancing the effectiveness of membrane performance which comply the principles of green membrane compared to the conventional hazardous NMP solvent [4,5]. Some solvent had been considered 'green' however the production is in very toxic manners and lack of efforts in investing to sustainable membrane production which considered as wasteful since the term 'green' can be applied to solvents that shows the green upstream emissions and green recovery solvents rather than final product [6]. In membrane fabrication, the phase inversion technique remains widely used due to its ability to produce asymmetric, porous membranes. This technique, when combined with greener solvents, holds promise for the advancement of eco-friendly and high-performing membranes that meet both environmental and industrial needs [7].

As for today, the study of polymeric materials had become a major focus as alternatives to ceramic membranes in membrane production. However, synthetic polymeric membranes present several challenges for water treatment filtration, including fragility, low water flux, poor contaminant rejection, and high tendency for fouling [8]. In this study, polysulfone (PSf) was chosen due to its remarkable high mechanic structure, wide range of pH, high heat resistance and chemical resistance. However, it also exhibits limitations particularly in water treatment application [9]. Therefore, additives in PSf membrane fabrication were considered to overcome the low water flux, hydrophobicity and biofilm formation.

An environmentally friendly membrane should adhere to few principles which were included in using non-toxic solvents, reduce waste in membrane production using renewable or raw materials and minimize energy in membrane production [4]. Addressing sustainability concerns in membrane technology requires the development of greener approaches, such as bio-based polymers, recyclable materials, energy-efficient processing and eco-friendly solvents in membrane fabrication. In this study the innovation in preparing hybrid membranes is essential not only minimizing the environmental footprint of membrane technologies but also for ensuring their effectiveness of membrane performance.

Several researchers have focused on utilizing Hansen solubility parameters (HSP) to assess the ability of solvents to dissolve polymers effectively before initiating experimental or fabrication processes [1,7]. HSP theory suggests that a solvent efficacy in dissolving a polymer can be systematically predicted by analyzing the interactions within three main solubility parameters: dispersion forces (δ_d), polar interactions (δ_p) and hydrogen bonding interactions (δ_h). Dispersion forces (δ_d) also known as London dispersion forces or van der Waals forces. The δ_d parameter quantifies the strength of these forces indicates compatibility in terms of solubility. Polar interactions (δ_p) involve attractions between molecules with permanent dipoles. When the δ_p values of a polymer and solvent were closely match, it indicates a good potential for solubility due to the alignment of their polar characteristics and stabilize each other. Hydrogen bonding interactions (δ_h) is a strong type of dipole-dipole interaction between a hydrogen atom covalently bonded to a highly electronegative atom such as oxygen, nitrogen or fluorine. Matching δ_h values between a solvent and polymer indicates a the likelihood of hydrogen bonding interactions that enhance solubility [7].

The interaction between solvent and polymer is further quantified by calculating the Relative Energy Difference (RED) value, which provides a numerical measure of solvent suitability. The RED value is derived by comparing the Hansen solubility parameters of the solvent and polymer that allowing for a more precise understanding of their interactions[1]. A RED value below 1 indicates that the solvent is effectiveness in dissolving the polymer, signifying good compatibility between the two[1]. In their investigations, Mehrabani *et al.*, [1] and Karimi *et al.,* [7] have specifically explored the effects of various solvents on membrane fabrication using HSP and RED calculations. Their research aimed to identify solvents that not only effectively dissolve target polymers but also influence the structural properties of the resulting membranes. By employing HSP and RED, they assessed the compatibility of different solvents with the polymers, enabling a more informed selection process[1,7].

The choice of solvent is critical as it influence the characteristic of fabricated membrane such as pore size distribution, surface morphology, and mechanical strength. The study by Mehrabani *et al.,* [1] and Karimi *et al.,* [7] contributes to the advancement of membrane technology by providing valuable insights into how solvent selection can optimize membrane performance for specific applications [1,7]. This theoretical framework plays a crucial role in advancing sustainable membrane technologies, particularly in developing membranes with superior performance characteristics.

This study aims to develop composite hybrid membrane by incorporating kappa-carrageenan (ƙ-car) as pore-forming agent and silver graphene oxide nanoparticles (Ag-GO NPs) for their antibacterial properties. The inclusion of these additives is expected to enhance the characteristics of polysulfone (PSf) membranes resulting with higher water flux, increased hydrophilicity and improved porosity while using green solvents for fabrication [9,10]. Green solvents have shown potential in enhancing membrane performance while promoting sustainable production methods, aligning with the goal of creating eco-friendly membranes for water treatment industries [11].

The structural and functional of the membranes fabricated by wet phase inversion technique were characterized through a range of advanced techniques. These include attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) for chemical structure identification, a contact angle goniometer to evaluate the hydrophilicity of membrane surface, porosity of membrane, pore size classification, tensile strength testing to assess mechanical robustness and field emission scanning electron microscopy (FESEM) for morphological analysis. Lastly, the bench-scale dead-end stirred cell set-up for performance test in iron and manganese removal of membrane fabricated.

These comprehensive analyses were conducted to evaluate and correlate membrane properties with the solvents used during fabrication, ensuring high-performance functionality is maintained. The expected contributions of this study include the development of a high-performance, green membrane with enhanced water flux, improved porosity and increased resistance to fouling. The aim of this study is to develop a high-performance, environmentally sustainable hybrid membrane by incorporating ƙ-car and Ag-GO NPs into PSf matrix and fabricated using green solvents. This research evaluated the performance of green solvents compared to toxic solvent in focusing on their effectiveness in enhancing water flux, hydrophilicity, porosity and fouling resistance for advanced water treatment applications.

2. Methodology

2.1 Materials and Methods

PSf pellets sourced from Sigma (Darmstadt, Germany) serve as the primary polymer in this study. Silver graphene oxide nanoparticles (Ag-GO NPs) synthesized at the Membrane Research Laboratory at Universiti Kebangsaan, ƙappa-carrageenan (ƙ-car) powder with a molecular weight of 401.32 $g.mol^{-1}$ was used as a biopolymeric additive to enhance membrane hydrophilicity and biocompatibility. Various solvents are utilized during the fabrication process to effectively dissolve the polymeric solution and additives while controlling the membrane structure through the phase inversion technique. These include DMSO, EC, DMAc and NMP are all provided by R&M Chemicals (Kuala Lumpur, Malaysia). These solvents are chosen based on their solubility properties and diffusivity in relation to PSf and other additives.

2.2 Fabrication of Membrane

The phase inversion technique is widely used in membrane fabrication, especially for the commercial production of flat-sheet and hollow fiber membranes. The process begins with preparing of a homogeneous casting solution, where the polymer is dissolved in a selected solvent, as shown in Figure 1. In this study, 20 wt% PSf was dissolved in 80 wt% of a selected solvent mixture of EC, DMSO, DMAc or NMP. The solution is stirred and heated at 60°C for 6 hours, followed by 30 minutes of sonication to achieve a uniform and homogenous casting solution.

In the fabrication of these hybrid membranes, the polymer, additives, and antibacterial agents were prepared in separate flasks to ensure precise mixing and full dissolution of all additives for optimal performance. Specifically, Flask A contained of 20 wt% PSf dissolved in 40 wt% of the selected solvent. Flask B contained of 0.5 wt% silver-graphene oxide nanoparticles (Ag-GO NPs) dissolved in 20 wt% of the selected solvent. Flask C contained 0.25 wt% ƙ-carrageenan (ƙ-car) dissolved in 20 wt% of the solvent, which heated for 6 hours at 60°C.After heating period, the contents of Flask B and Flask C were carefully added to Flask A. The mixture was then subjected to additional heating at 60°C in silica oil bath for another 6 hours. This combined casting solution was subsequently sonicated for 30 minutes at 30°C to ensure homogeneity and rest at room temperature for 10 minutes. Following, the casting solution was cast onto clean surface of glass plates at a fixed thickness of 0.2 mm. The coated plates were swiftly immersed in deionized water bath for 15 seconds to facilitate phase inversion and membrane formation. The formed membranes were then detached from the glass plates and transferred to a container filled with deionized water to preserve the structural characteristics and morphology of the membranes in preparation for further procedures.

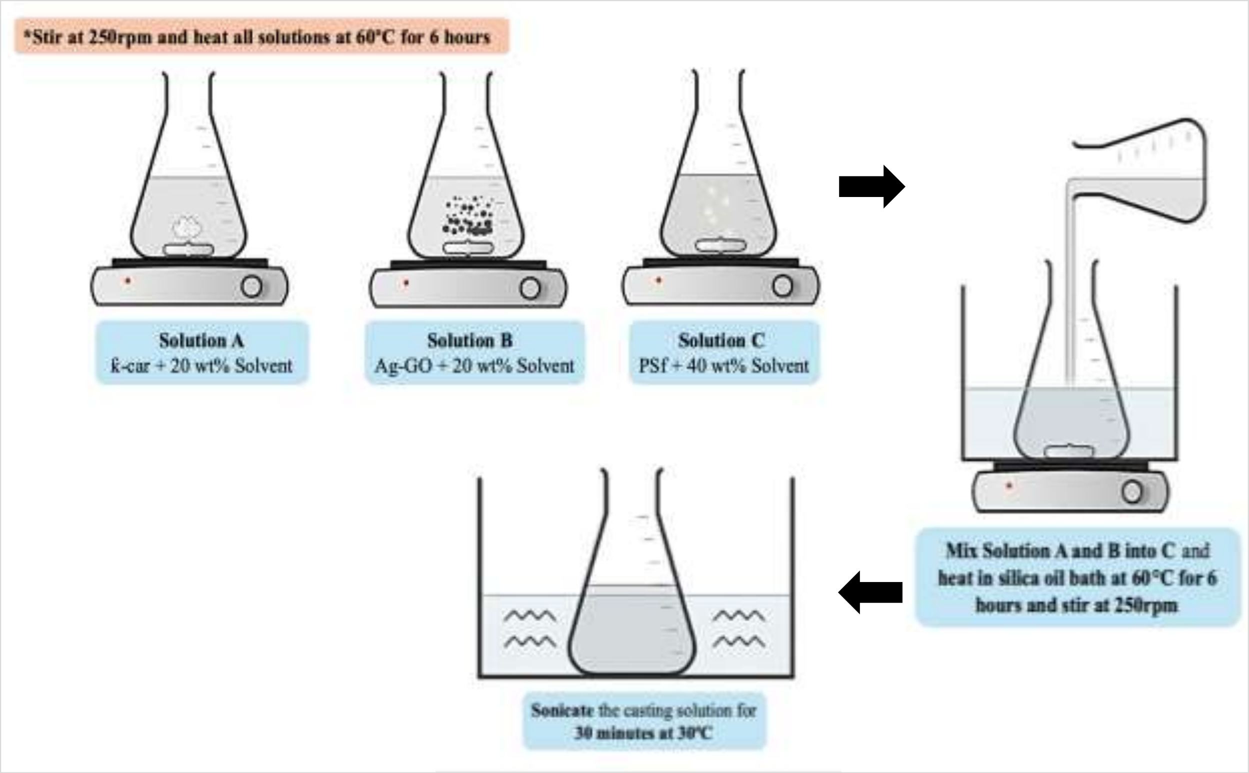


Fig. 1. Steps in preparing casting solution

A preliminary study was conducted to assess the solubility and interaction of PSf with the selected additives in various solvents. This step was crucial in determining the compatibility of the polymer and additives with the solvents, ensuring proper dissolution and homogeneous mixing. Various solvents such as EC, DMSO, DMAc, and NMP were tested to evaluate their effectiveness in dissolving PSf and incorporate additives without phase separation or precipitation. The solubility study encourages in optimizing solvent selection to improve membrane properties such as pore formation, mechanical strength, and overall performance in the subsequent membrane fabrication process.

The membrane compositions in Table 1 showcase various formulations, each with specific ratios of polymers, solvents, and additives. Most samples contain of 20% PSf as the base polymer, chosen for its mechanical strength and stability. The solvents vary across the samples, including NMP, EC, DMAc and DMSO with concentrations ranging from 20% to 80%. The resulting membranes were categorized into GS (fabricated with a single solvent) and GM (fabricated with a solvent mixture), while the prime notation (') refers to hybrid membranes that contain both ƙ-car and Ag-GO NPs. In this study, GS0 utilized the toxic solvent NMP as a pure PSf membrane, serving as the control membrane. In contrast, GS1 and GS2 employed green solvents, EC and DMAc, respectively. GS3 and GS3' incorporated DMSO as a green solvent while GS3' embedded with ƙ-car (0.25 wt%) and Ag-GO (0.5 wt%) designated as a hybrid membrane. GM4 and GM4' combined NMP and DMSO in a 60:20 ratio to minimize the use of the toxic solvent, with GM4' classified as a hybrid membrane with ƙ-car (0.25 wt%) and Ag-GO (0.5 wt%).

Table 1
Composition of membrane casting solution with varying ratios of different solvent, ƙ-carrageenan, Ag-GO NPs and PSf

Sample	Solvent	Additives	
		ƙ-car	Ag-GO NPs
GS0	NMP	No	No
GS1	EC	No	No
GS2	DMAc	No	No
GS3	DMSO	No	No
GS3’	DMSO	Yes	Yes
GM4	60 NMP:20 DMSO	No	No
GM4’	60 NMP:20 DMSO	Yes	Yes

2.3 Membrane Characterisation and Performance

Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) was employed to identify functional groups associated with hydrogen bonding within the spectral range of 3445 cm^{-1} and 1630 cm^{-1}. The membrane's hydrophilicity was assessed using a contact angle goniometer (model L2004A1, Ossila, The Netherlands). This assessment was conducted at room temperature, utilizing deionised water as the testing liquid. The contact angle measurement is a crucial parameter in understanding the wettability of a membrane. A lower contact angle indicates higher hydrophilicity, indicating that the membrane had greater affinity for water. Calculation of porosity and pore size of membrane as display in Equation (1) and (2), respectively.

The overall porosity (ε), as defined in Eq. (1):

$$\varepsilon = \frac{\omega_1 - \omega_2}{A \times l \times d_w} \tag{1}$$

Where, ω_1 is the mass of wet membrane, ω_2 is the mass of dried membrane, A (m^2) is the surface area of membrane, l is the thickness, and d_w is 998 $kg.m^{-3}$ the density of water.

Using the porosity data and Geurout-Elford-Ferry equation. The pore sizes of the fabricated membrane calculated using Eq. (2):

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon)\, 8nlQ}{\varepsilon \times A \times \Delta P}} \tag{2}$$

Where, n is the water viscosity (8.9×10^{-4} Pa s), Q is the volume of pure water permeated through the membrane per unit time ($m^3.s^{-1}$) and ΔP is the operational pressure (0.7 MPa).

The tensile strength of the membranes was analyzed using an Instron 5869 Universal Testing Machine (Canton, Massachusetts). Membrane samples (10 mm x 100 mm, thickness 0.20 mm) were placed in rubber-fitted grips to enhance contact adherence and tested at a speed range of 0.01 to 10 mm/s under ambient conditions, following ISO 527-1 (2012).

Tensile strength calculates using Eq. (3):

$$\sigma = \frac{F}{A} \tag{3}$$

Where, σ is tensile strength (MPa), F is the force exerted (N), A is the first specimen cross-sectional area, measured in square (mm^2).

In analysing the morphology of the cross-section of the fabricated membrane, field-emission scanning electron microscopy (FESEM) was used. The specific model used was the Gemini SEM 500 from Zeiss, located in Oberkochen, Germany. The FESEM was operated at a magnification of 2k, which allows for detailed examination of the membrane morphology such as pore size, distribution and overall cross section of the membrane. This study systematically investigated the performance of membranes in water permeability and the efficacy of contaminant removal.

A bench-scale dead-end stirred cell set-up, as depicted in Figure 2, was employed to facilitate the experiments. Before the performance assessments, the membrane underwent compaction process for 30 minutes at 10 bar using ultra-pure water. This step was crucial for eliminating any residual chemicals and ensuring a consistent and uniform water flux across the membrane surface. After compaction, water flux measurements and removal iron and manganese were conducted at a controlled pressure of 2 bars. This pressure level was selected to minimize energy consumption while still providing reliable data on membrane performance.

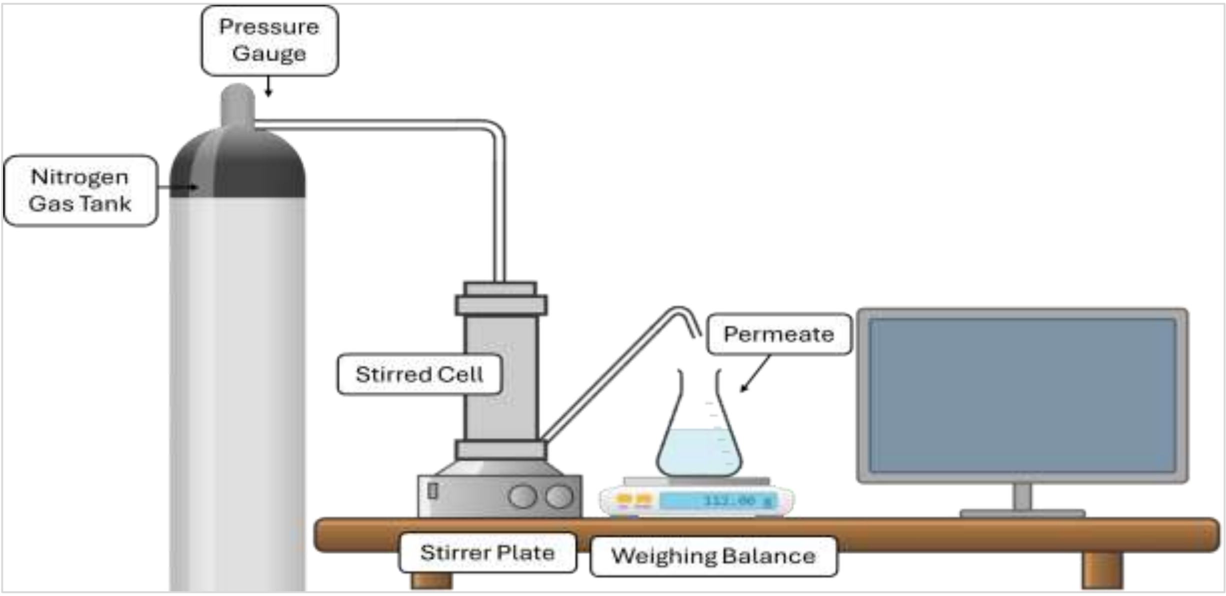


Fig. 2. A bench-scale dead-end stirred cell set-up for membrane performance study

Water flux and permeate flux calculated using Eq. (4):

$$J = \left(\frac{\Delta V}{A\Delta t}\right) \tag{4}$$

Where, J ($L/m^2.h$) is the permeate flux, ΔV is the permeate cumulative volume (L), A is the effective surface (m^2), and Δt is the filtration time (h).

Removal of iron and manganese is measured by Eq. (5):

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \tag{5}$$

Where, R is the rejection and C_p and C_f are the concentration of permeate and feed, respectively.

3. Results and Discussion

3.1 Membrane Properties

In this research, EC was selected as the primary green solvent due to its classification as a non-toxic alternative to traditional solvents. EC is recognized for its low environmental impact and its capacity to minimize hazardous waste, aligning with the principles of sustainable chemistry and green technology. However, this preliminary study had revealed significant challenges associated with EC as a solvent for thin film membrane fabrication.

One of the challenges is EC relatively high freezing point, which necessitates elevated temperatures specifically around 150°C for effective dissolution and casting of the membrane. As shown in Figure 3(a), the solvent achieves a homogeneous state only at this elevated temperature. However, in Figure 3(b) shows that at a lower temperature of 30°C, the solvent exhibits clumping which indicating poor solubility in the membrane mixture. This observation highlights EC limitation in green technology as high temperature and energy requirement conflics with the priinciples of sustainable membrane production [4]. The increased energy requirements not only rises production costs but also contribute to a larger carbon footprint, which contradict in developing eco-friendly membrane solutions [4].

On the other hand, DMAc is known for its solvent capabilities. However, it was not being further studied in the hybrid membrane formulation due to its inability to fully dissolve kappa-carrageenan (ꓘ-car) additive for enhancing the membrane properties. This limitation hindered the desired performance enhancements such as increased hydrophilicity and enhancing fouling resistance. Consequently, the lack of ꓘ-car not only restricted the intended functional improvements but also detracted from the overall objective of producing a high-performance green membrane. Therefore, EC and DMAc present specific limitation that must be addressed to improve sustainable and effective membrane technologies.

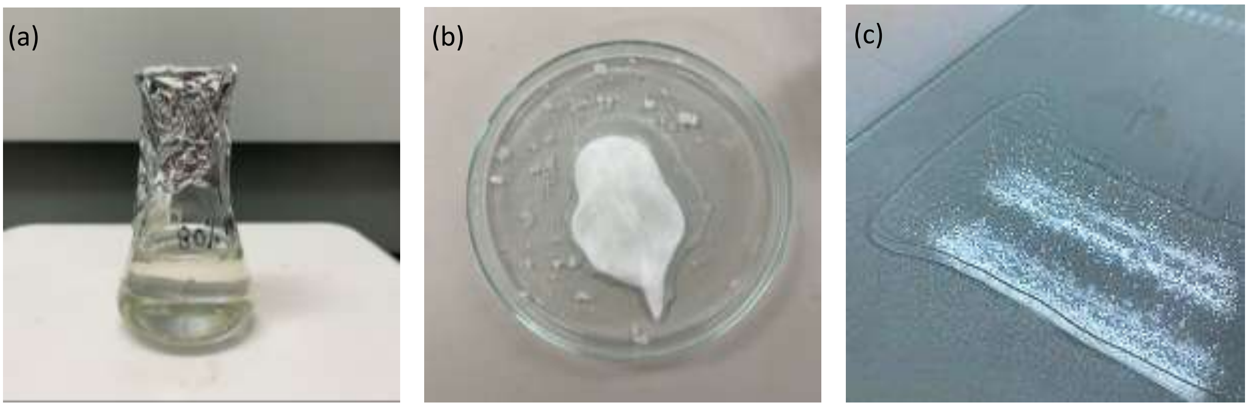


Fig. 3. (a) GS1 casting solution at 150°C, demonstrating homogeneity; (b) GS1 casting solution at 30°C, showing clumping; (c) ꓘ-car residue in the casting solvent with DMAc, indicating incomplete dissolution

3.1.1 Functional group analysis

In this study, chemical interactions of hydrogen bonding between functional groups play a crucial role in determining the performance of membrane materials in filtration and separation applications. Figure 4 shows a prominent spectrum of the O-H bond in the range of 3445 cm^{-1} and 1630 cm^{-1}, indicating of intermolecular hydrogen bonding, which favours good miscibility between the solvent and polymer interaction [12]. The characterization of the samples reveals distinct differences in the O-H peaks presence, suggesting the role of hydroxyl functional groups in enhancing hydrophilicity and membrane performance. The GS0 membrane was found lacked of detectable O-H stretching peak, indicating the absence of hydroxyl groups, which reduces its potential for hydrogen bonding and hydrophilicity. This deficiency could lead to decreased water permeability and a higher propensity for membrane fouling.

In contrast, the GS2, GS3, GS3', GS4, and GS4' membranes exhibit pronounced O-H peaks in the range of 3368.33 cm^{-1} to 3371.99 cm^{-1} indicating the presence of hydroxyl groups. Additionally, the transmittance values in Table 2 provide further insights into their characteristics. Result shows that GS2 membranes exhibits a transmittance of 72.25% which is slightly higher than GS3 and GS3' with transmittance values of 70.04% and 68.24%, respectively. This suggests that GS2 membranes could have a slightly more open structure allowing for greater water flow in compared to GS3 and GS3'membranes. Meanwhile, for GM4 and GM4' membranes that resulted transmittance values within a narrower range, from 69.06% to 69.26%. The membrane GS2 with highest value of transmittance indicated substantial hydrophilicity and enhanced surface properties compared to the GS0 membranes.

This analysis demonstrates that the use of DMSO and DMAc as solvents in preparing the GS2 and GS3 membrane have significantly enhanced the hydrophilicity of the membranes compared to the GS0 membrane, which was prepared with NMP. These findings revealed that NMP solvent is ineffective in improving membrane hydrophilicity. Additionally, the presence of O-H peaks in the modified membranes (GS2, GS3, GS3', GS4, and GS4') indicates an increase in hydrophilic functional groups.

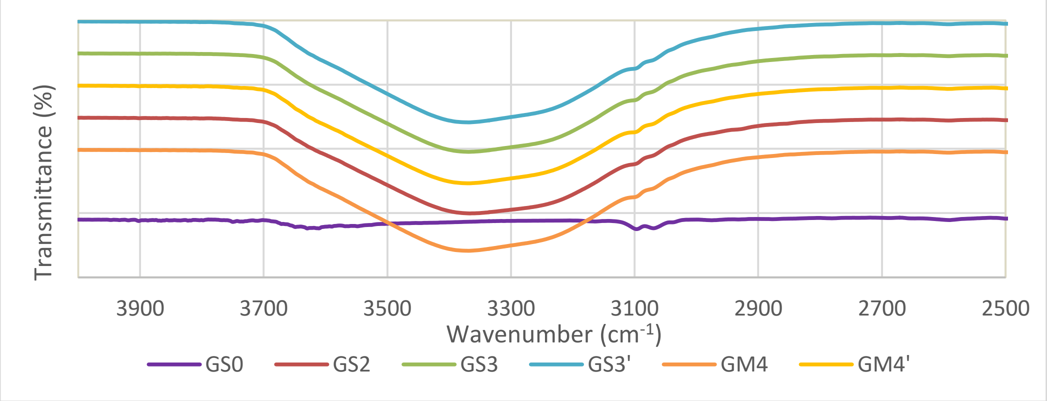


Fig. 4. FTIR spectra og GSO, GS2, GS3, GS3', GM4 and GM4' membranes

Based on Hansen solubility δ_h parameter analysis in Table 3, NMP had the lowest hydrogen bonding energy among the solvents tested, whereas EC, DMAc, and DMSO show higher hydrogen bonding parameter values. This higher value of δ_h directly contributes to the enhanced hydrophilicity observed in membranes fabricated with DMSO and DMAc [7,13]. A study by Suhalim *et al.*, (2023) had demonstrated that the incorporation of graphene oxide (GO) significantly enhances the hydrophilicity of PSf membranes by introducing oxygen-containing functional groups, which improve water affinity [13]. This finding indicates that GS0 membrane exhibits lower hydrophilicity is due to the absence of Ag-GO nanoparticles (NPs) in the membrane structure. The absence of these nanoparticles reduces the availability of hydrophilic functional groups, leading to a less hydrophilic surface. Moreover, the choice of solvent during membrane fabrication plays a pivotal role in determining the membrane hydrophilicity. Solvents with higher polar (δ_P) and hydrogen bonding (δ_h) components contribute to a membrane ability to interact with water molecules more effectively.

Table 2
FTIR Spectra of O-H stretching vibration of GS0, GS2, GS3, GS3’, GS4 and GM4’ membranes

Membrane Fabricated	Wavenumber (cm^{-1})	Transmittance (T%)	Group
GS0	3380.84	32.14	O-H stretching vibration
GS2	3371.99	72.25	
GS3	3368.33	70.04	
GS3’	3368.44	68.24	
GM4	3368.81	69.06	
GM4’	3369.11	69.26	

Solvents such as DMAc and DMSO, with relatively high δ_P and δ_h values able to promote stronger interactions with water molecules, thus enhancing the membrane hydrophilicity. This is particularly important in phase inversion and polymer-solvent interactions during membrane casting, as these interactions dictate the surface properties and porosity of the final membrane. Table 3 shows that NMP had lower polar and hydrogen bonding parameters compared to DMAc and DMSO. This difference explains the reason of membranes fabricated with NMP will exhibit lower hydrophilicity in comparison to those prepared with DMAc or DMSO.

While both DMAc and DMSO improve hydrophilicity, they exhibit distinct behavior. DMSO had a higher polar (δ_P) component whereby it interacts more readily with polar molecules which can enhance water uptake. On the other hand, DMAc had a higher hydrogen bonding (δ_h) capacity in which making it more effective in forming strong hydrogen bonds with water molecules. In summary, the presence of both Ag-GO nanoparticles and the choice of solvent particularly their polar and hydrogen bonding parameters have significant influenced the hydrophilicity of fabricated membranes. Solvents like DMAc and DMSO with strong polar and hydrogen bonding properties lead to improved water interactions, resulting membranes more hydrophilic than fabricated using NMP. The combination of these factors contributes to the overall performance and hydrophilicity of the membrane which is crucial for applications in water treatment and filtration.

Table 3
The solubility, diffusivity and relative energy different (RED) value

	δ_d ($MPa^{1/2}$)	δ_p ($MPa^{1/2}$)	δ_h ($MPa^{1/2}$)	δ_{p-s} ($MPa^{1/2}$)	D_m ($cm^2.s^{-1}$)	RED	Ref
Solvent							
DMSO	18.4	16.4	10.2	1.69	8.4	0.38	[1,7]
DMAc	17.8	14.1	11.8	3.61	11.8	0.34	[1,7]
EC	19.4	4.6	9.8	0.09	-	0.18	[14]
NMP	18.4	12.3	7.2	1.69	9.1	0.21	[1,7]
Polymer							
PSf	19.7	8.3	8.3			1	[1]

3.1.2 Hydrophilicity analysis

In membrane fabrication, characteristics such as hydrophilicity and water permeability need to be considered especially in the field of water treatment. In hydrophilicity analysis, the contact angle of a membrane surface is a key indicator of its hydrophilic or hydrophobic properties. A lower contact angle (less than 90 degrees) signifies that the membrane is hydrophilic, while a higher contact angle (greater than 90 degrees) indicates hydrophobicity [15,16]. PSf is widely used as a base polymer in membrane fabrication due to its exceptional thermal, mechanical, and chemical stability, which ensures durability under diverse operational conditions. However, PSf is its inherent hydrophobicity poses significant challenges in membrane performance. The hydrophobic nature of PSf membranes leads to low water permeability, resulting in poor water flux. Moreover, hydrophobic surfaces tend to attract foulants, such as organic matter and bio foulants which exacerbates membrane fouling [12].

In address this issue, the membrane was modification by incorporating the biopolymer ƙappa-carrageenan (ƙ-car) and silver graphene oxide nanoparticles (Ag-GO NPs) as pore former and antibacterial to boost the hydrophilicity of membrane. Figure 5 presents the contact angle measurements of the membranes, along with corresponding images, while Figure 6 presents the trend in water contact angle (WCA) of membranes fabricated. As shown in Figure 5, membrane GS0 exhibits the highest WCA at 68.52°, indicating its more hydrophobic nature compared to the others. In contrast, GS2 had the lowest WCA of 42.13°, suggesting a more hydrophilic surface. The WCAs of GS3 and GM4 were measured at 60.12° and 63.11°, respectively. Notably, the hybrid membranes, GS3’ and GM4’ exhibit a significant reduction in WCA to 57.32° and 60.77°, respectively. Thus, these results indicated the improvement of hydrophilicity in these modified membranes.

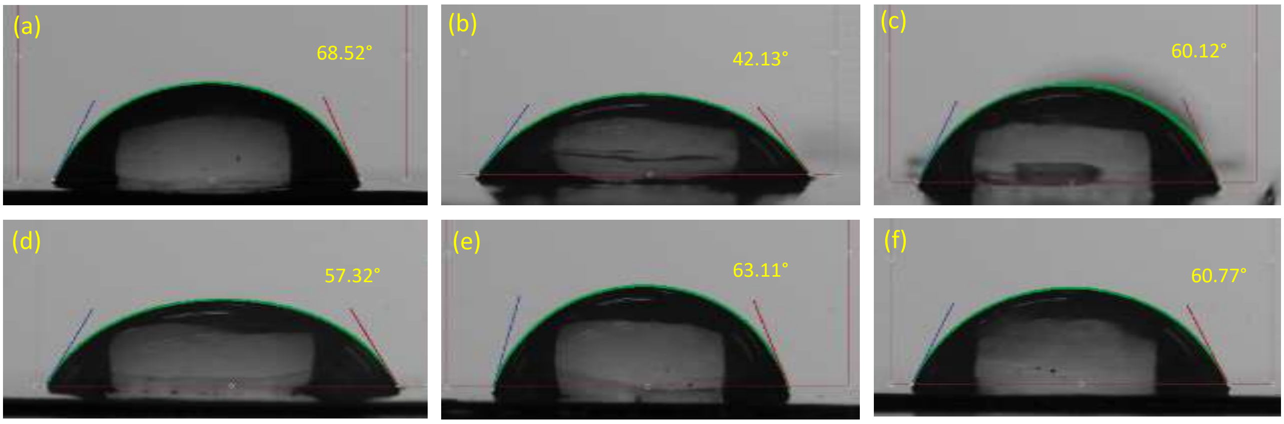


Fig. 6. Contact angle of fabricated membrane (a) GS0, (b) GS2 (c) GS3, (d) GS3’, (e) GM4 and (f) GM4’

This phenomenon can be explained by the reduce interfacial energy of the composite membranes which is influenced by the functional groups of Ag-GO NPs embedded on the membrane surfaces and the addition of ƙ-car resulting pore former [17,18]. The tendency of hydrophobic surfaces to attract foulants such as organic matter and bio foulants that leads to membrane fouling. Membrane fouling not only reduces its efficiency but also increases the need for frequent cleaning and maintenance, ultimately limiting the overall effectiveness of PSf-based membranes [15].

Moreover, the hydrophilic nature reduces pore blockage and surface helping to maintain a higher water flux over time. Since flux decline due to fouling is one of the most common challenges in membrane systems, the enhanced hydrophilicity of these membranes able to maintain a steady permeate flows and contribute to reducing the frequency of operational shutdowns for cleaning or replacement. Consequently, the operational stability of hydrophilic membranes contributes to more efficient process control, with lower energy consumption for cleaning cycles and reduced environmental impact from chemical usage [19,20]. It is reported by Wang and co-worker observed that DMSO-cast membrane resulting more negative chargers and enhance the permeability [21].

3.1.3 Porosity and pore size

The development of high-performance membranes for water treatment and separation processes increasingly focuses on optimizing pore structure and porosity, which directly influences water permeability. As presented in Figure 7, the porosity of various membranes differs depending on the solvent and the presence of additives in the fabrication process. The GS0 membrane which fabricated with PSf and NMP exhibits a porosity of 76% while the GS2 membrane, which uses DMAc as the solvent, shows a slightly higher porosity of 80%. In contrast, the GS3 membrane which uses DMSO as the solvent, had lower porosity of 63%. The GM4 membrane fabricated with a mixture of solvent of NMP and DMSO had achieved a porosity of 70%.

The incorporation of Ag-GO NPs and ƙ-car into GS3’ and GM4’ membranes lead to a significant enhancement in porosity. The GS3’ membrane hybrid version of GS3 showed an increase in porosity from 63 to 88%. Similarly, the GM4’ membrane demonstrate a 10% increase in porosity reaching 80% compared to its unmodified GM4. The incorporation of Ag-GO NPs is expected to contribute in the formation of highly porous structure which beneficial for membrane permeability [22]. The high surface area and layered architecture of graphene oxide sheets facilitate the development of interconnected pores, thereby improving the overall porosity of the membrane [23]. Hence, the finding of this study supported by Figure 7, indicate that the incorporation of Ag-GO NPs and ƙ-car not only improves hydrophilicity properties but also significantly enhances membrane porosity and pore distribution.

In membrane technology, ultrafiltration (UF) membranes, with pore sizes ranging from 1 to 100 nm, were ideal for removing macromolecules and small particles [24]. Nanofiltration (NF) membranes, characterized by pore sizes between 0.1 and 1 nm, effectively remove divalent ions and small organic molecules [24]. While, Reverse Osmosis (RO) membranes possessing pore sizes typically less than 0.1 nm were highly efficient in desalination and purification [25,26]. The main focus in this research is to produce NF membrane. Figure 8 presented the pore size measurements of each fabricated membrane, while Table 4 classified the membranes accordingly.

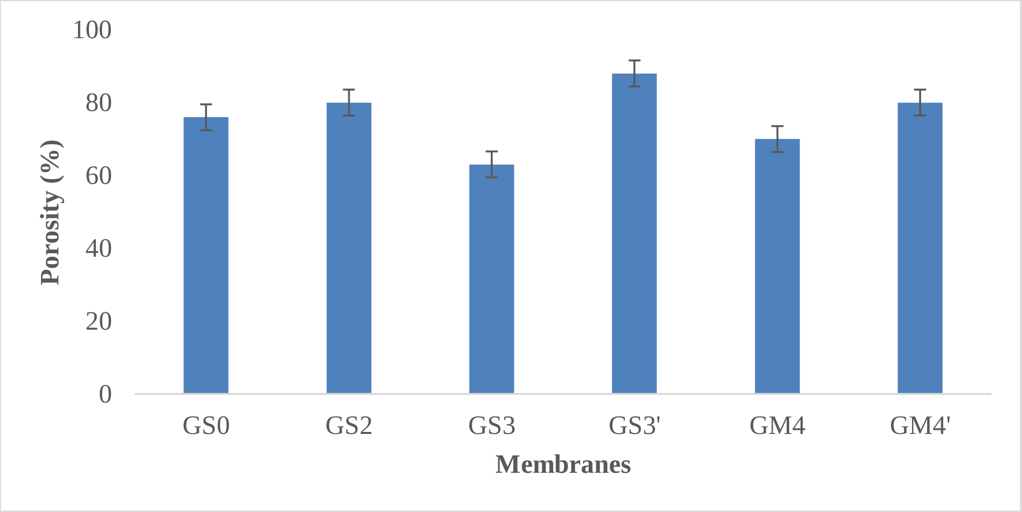


Fig. 7. Porosity of fabricated membrane

The pure PSf membrane GS0, with a pore size of 2.5 nm is classified as an NF membrane. In contrast, GS2 membrane with a pore size of 14.8 nm falls into the UF category, similar to GS3 and GM4 membranes, which have pore sizes of 14.8 nm and 11.2 nm, respectively. However, the hybrid membranes GS3’ and GM4’, which incorporate Ag-GO NPs and ƙ-car demonstrate a significant reduction in pore size, with measurements of 6.4 nm and 6.2 nm, respectively, classified them as NF membranes. The incorporation of Ag-GO NPs and ƙ-car not only improves the membranes' hydrophilic properties and porosity but also effectively reduces their pore size into the NF classification. NF membranes were favoured in applications which required selective removal of smaller solutes while maintaining high permeability and high performance.

Ag-GO NPs and ƙ-car as the additive had led to small pores formation due to the density of gel-like structure of ƙ-car and Ag-GO NPs act as nucleation sites which promotes in a more controlled and uniform phase separation, resulting in well-defined pores [27]. Based on Table 3, D_m value of DMAc (11.8 $cm^2.s^{-1}$) > NMP (9.1 $cm^2.s^{-1}$) > DMSO (8.4 $cm^2.s^{-1}$) indicating by having slow diffusion rate during membrane fabrication leads to the formation of larger pore sizes [28]. This pattern is observed in this study, whereby GS3 membrane (with DMSO) and GM4 membrane (mixture NMP and DMSO) exhibit larger pore sizes compared to GS2 membrane (with DMAc). In contrast, GS0 membrane (with NMP) had a smaller pore size due the low δ_h as shown in Table 3. Based on study done by Karimi *et al.,* [7], low value of δ_h will results in a denser top layer structure with reduced water flux. Meanwhile, the hybrid membranes GS3’ and GM4’, with pore sizes of 6.4 nm and 6.2 nm, respectively, demonstrate the impact of Ag-GO NPs and ƙ-car. The unique structure of Ag-GO NPs and the gel-like matrix of ƙ-car slow the diffusion rate during phase separation, promoting the controlled casting solution which leads to smaller and more uniform pores [7,29]. This controlled pore formation enhances membrane performance by balancing pore size reduction with improved permeability.

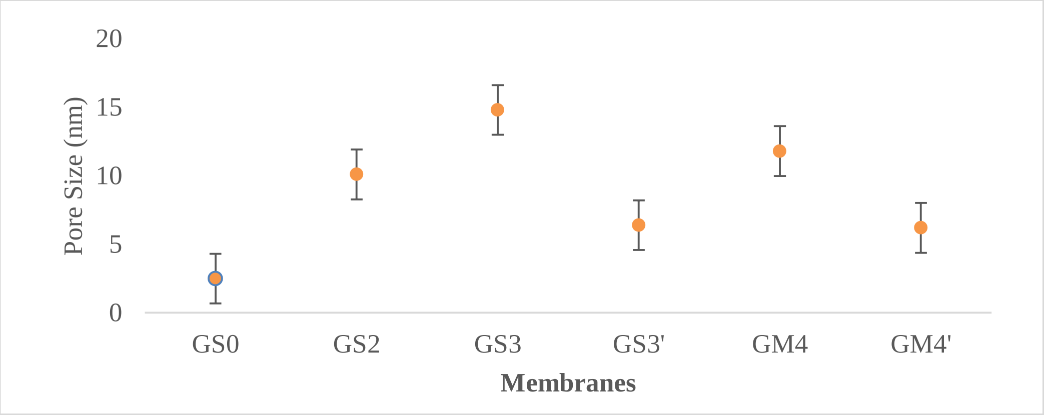


Fig. 8. Plot pore size of membrane fabricated

Table 4
Classification of membrane fabricated based on pore size measurement

Membrane Fabricated	Pore Size	Type of Membrane
GS0	2.5	Nanofiltration (NF)
GS2	10.1	Ultrafiltration (UF)
GS3	14.8	Ultrafiltration (UF)
GS3’	6.4	Nanofiltration (NF)
GM4	11.8	Ultrafiltration (UF)
GM4’	6.2	Nanofiltration (NF)

3.1.4 Mechanical strength

The development of sturdy and high-performance membranes is crucial for advanced filtration applications, particularly in demanding environments. One of the main challenges in membrane technology is balancing permeability with mechanical strength to ensure long-term durability. In Figure 9, GS0 membrane exhibits the highest mechanical strength with a tensile strength of 0.41 MPa. In comparison, GS2 membrane fabricated using DMAc as the solvent, significantly lower tensile strengths of 0.12 MPa. However, GS3 membrane with DMSO as the solvent exhibits a slightly higher tensile strength of 0.16 MPa compared to GS2 membrane. The GM4 membrane, fabricated with a mixture of NMP and DMSO, demonstrates the lowest tensile strength of 0.08 MPa. In contrast, the hybrid membranes GS3’ and GM4’ membranes which incorporate Ag-GO NPs and ƙ-car showed an improvements in mechanical endurance. The GS3’ membrane achieves a tensile strength of 0.31 MPa, while the GM4’ membrane reaches 0.25 MPa. This reflecting significant enhancements in structural integrity due to the reinforcing effect of Ag-GO NPs. These additives contribute to better dispersion of polymer chains and increased cross-linking, resulting in stronger, more durable membranes [30].

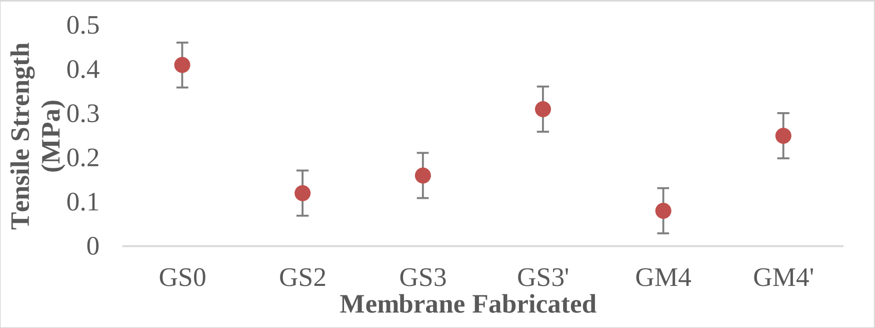


Fig. 9. Plot of tensile strength of membrane fabricated

Research by Nouri *et al.,* [31] highlights that the limited mechanical strength of kappa-carrageenan films had restricted their application, particularly in food packaging under humid conditions. To address this limitation, the mechanical properties of kappa-carrageenan biopolymers were often improved by blending with other biopolymers or incorporating nano-fillers [31]. Similarly, Kassab *et al.,* [32] encountered similar challenges with kappa-carrageenan films and addressed them by reinforcing the films with cellulose nanocrystals [32]. These nanocomposite films, strengthened by cellulose nanocrystals, demonstrated enhanced durability and structural integrity, making them more suitable for applications requiring both strength and resilience, particularly in demanding environments [32]. Therefore, in this study, Ag-GO NPs further reinforces the hydrogel matrix of ƙ-car and enhances cross-linking polymers of PSf, contributing significantly to the overall mechanical robustness of the membranes. This enhancement in mechanical properties underscores the potential of Ag-GO NPs as a valuable additive in membrane technology, providing both structural integrity and improved performance at harsh environment [33].

3.1.5 Membrane morphology

The cross-sectional morphology analysis is presented by FESEM images in Figure 10. In Figure 10 (a) GS0 membrane, which shows an open structure and less uniform structure. This is due to the slower evaporation rate and lower diffusivity of NMP [7]. In Figure 10(b), GS2 membrane had shown tighter pore at the surface due to DMAc high diffusion rate which promotes faster solvent exchange during phase inversion. This leads to more defined and tighter pore formation and more uniform pores in the membrane [21]. Figures 10(c) DMSO, display a well-uniformed, symmetrical structure with elongated, finger-like pores. This is due to DMSO had a low evaporation rate, high permeability and high viscosity that facilitates a more controlled phase inversion process, leading to well-defined pores [7,21,28]. Meanwhile, GM4 membrane fabricated with mixture ratio of NMP and DMSO solvent demonstrate mixed diffusion rate where NMP slows down the phase inversion. This results in less uniform pore size distribution and more complex pore structure.

In contrast, hybrid membranes GS3’ and GM4’ membranes that incorporate with Ag-GO NPs and ƙ-car membrane show a slight bending towards the bottom of the membrane. This is attributed to the high hydrophilicity of graphene oxide (GO), which increases water attraction during the phase inversion process. The strong interaction between GO and water influences the membrane structure formation which lead to this distinct morphological feature [10]. Moreover, ƙ-car had improved pore connectivity due to its gel-forming properties while Ag-GO NPs enhances intricate pore network [27].

A study by Karimi *et al.,* [7] on the effect of various solvents on the modification of PVDF ultrafiltration membranes were highlighted that the mutual diffusion rate between the solvent and non-solvent plays a pivotal role in determining the formation and structure of the membrane sub-layer [7]. This diffusion rate influences the phase separation process, which directly impacts the pore morphology, porosity, and overall membrane performance. Faster diffusion rates generally lead to tighter and more uniform pore structures, while slower diffusion rates can result in larger and less uniform pores. [7]. Similarly, Kahrs *et al.,* [34] found that a faster diffusion rate between the solvent and non-solvent promotes the rapid formation of smaller pores in the membrane [34]. In contrast, the diffusion rates of water with NMP and DMSO were slower than with DMAc resulting in a slower nucleation process. Nucleation sites were crucial for controlling the formation of a membrane pore structure during phase separation. Additives such as Ag-GO NPs act as nucleation sites by providing surfaces or points where the polymer matrix begins to solidify that lead to the formation of well-defined pores. These nucleation sites help regulate pore distribution and size by concentrating phase separation around the particles that resulting in a more uniform and controlled pore structure [35].

The generation of fewer nuclei led to the formation of larger finger-like pores in the membrane sub-layer, as shown in Figure 10 (a), (c)-(f) for membranes that were prepared with DMSO or NMP as the solvent. Conversely, the faster diffusivities of solvent or non-solvent pairs in DMAc have promoted quicker nucleation, leading to the formation of membranes with numerous, smaller finger-like pores, as depicted in Figure 10(b). As a result, the choice of solvent had a significant impact on the pore formation, which directly influences the overall morphology and performance of the membranes [7,34].

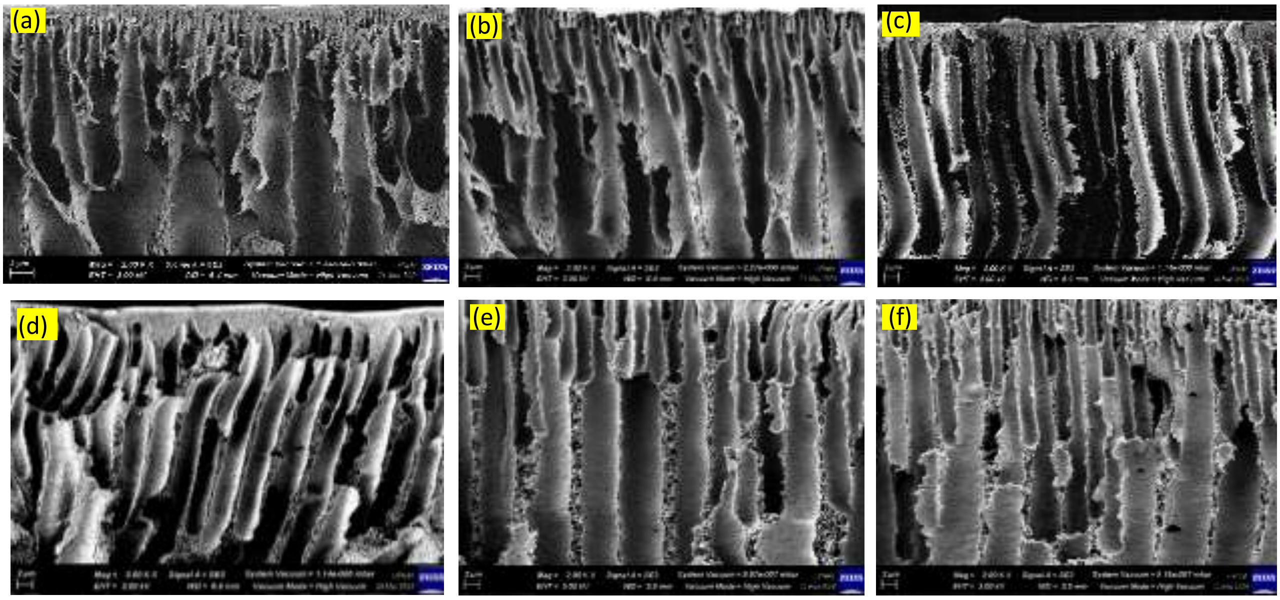


Fig. 4. FESEM images of (a) GS0 (b) GS2, (c) GS3, (d) GS3’, (e) GM4 and (f) GM4’ (magnification: 2KX)

3.2 Membrane Performance

3.2.1 Pure water flux of membrane

Pure water flux is a critical parameter used to evaluate a membrane permeability and its capacity for water uptake, both of which were essential indicators of its performance in filtration processes. In this study, the fabricated membranes will undergo water flux testing at a pressure of 2 bar, a condition selected to strike a balance between achieving optimal operational efficiency and minimizing energy consumption. This pressure setting aligns with the principles of green chemistry 'Design for Energy Efficiency' principle, which reduces energy input across industrial processes without sacrificing performance. By conducting filtration at a relatively low pressure, the membrane system operates with significantly reduced energy requirements. This simultaneously enhance the sustainability of the filtration process and contributes to overall environmental benefits such as lower carbon emissions and energy conservation, while maintaining effective membrane performance. Consequently, this approach supports the development of energy-efficient water treatment technologies, in line with the growing demand for sustainable and eco-friendly solutions in industrial applications.

In Figure 11 shows the water flux of membranes fabricated at 2 bar, the water flux of the membranes exhibits a progressive pattern. The water flux begins at 0.14 L·m^{-2}·h^{-1} for GS0, increases significantly to 56.12 L·m^{-2}·h^{-1} for GS2, and further rises to 69.28 L·m^{-2}·h^{-1} for GS3. The highest flux is achieved by GS3’, reaching 213.12 L·m^{-2}·h^{-1}. A decline is noted with GM4 at 28.55 L·m^{-2}·h^{-1}, followed by an increase to 71.60 L·m^{-2}·h^{-1} for GM4’. These variations in water flux are attributed to the choice of solvent during membrane fabrication, which significantly influences the membrane's hydrophilicity and overall water permeability. The membrane GS0, tested at 2 bar, exhibited extremely poor water flux (0.14 L.m^{-2}.h^{-1}), shows it inefficient under these conditions. This result indicates that the use of NMP as a solvent lead to a denser membrane structure, thereby increasing resistance to water flow. This highlights the importance of solvent choice in membrane fabrication, as it significantly affects membrane morphology, water flux and overall performance.

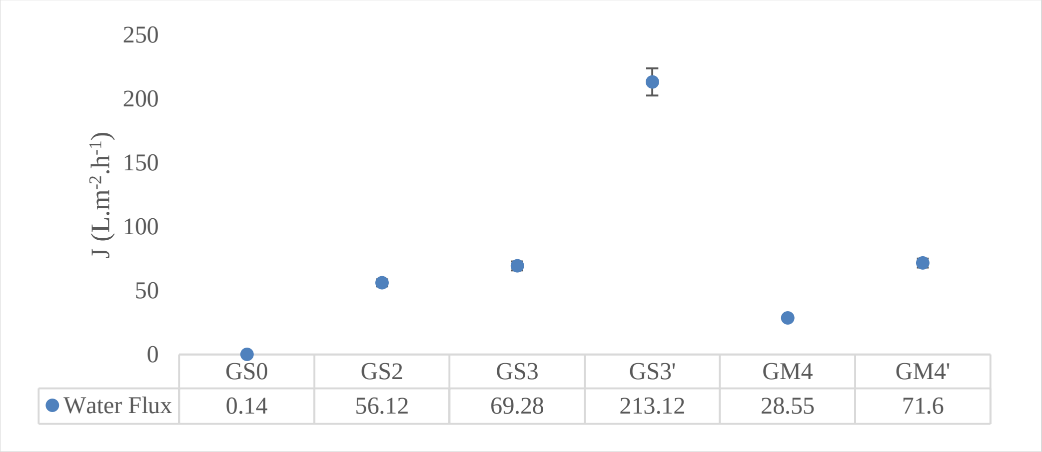


Fig. 11. Water flux of fabricated membranes at pressure 2 bar

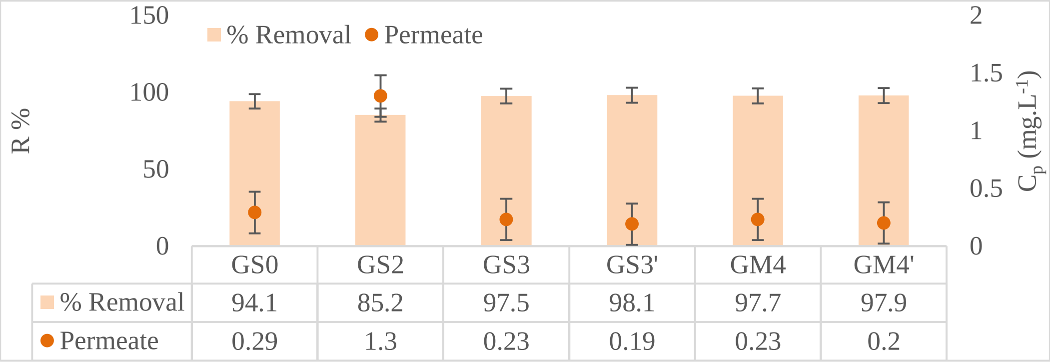
Increased membrane porosity is a critical factor in enhancing water flux, as demonstrated in previous studies and confirmed in this research. Farahani *et al.,* [36] showed that embedding carbon nanotubes in nanofiltration membranes significantly increases pure water flux. This improvement is attributed to the structural role of carbon nanotubes, which create more open channels within the membrane, enhancing permeability without sacrificing selectivity [36]. Similarly, Liu *et al.,* [37] observed that electrospun polyvinyl alcohol (PVA) membranes with high porosity achieved up to 7 times higher pure water flux and up to 6 times higher permeate flux compared to conventional Millipore GSWP 0.22 µm membranes [37]. This further validates the importance of porosity in achieving superior water flux.

In the current study, the high-performance GS3’ membrane, with a porosity of 88% (Figure 7), exemplifies the benefits of a porous structure. This increased porosity facilitates easier passage of water molecules through the membrane which resulting in significantly higher water flux. Thus, the findings in this study align with existing research, highlighting that increased membrane porosity not only enhances water flux but also supports the membrane effectiveness in water treatment applications. This makes high-porosity membranes particularly suitable for applications such as drinking water purification and industrial wastewater treatment, where efficient water transport is essential.

3.2.2 Iron removal of membrane

Natural groundwater often contains trace amounts of heavy metals such as iron (Fe) and manganese (Mn), as these elements were commonly found in soil and rock formations. At low concentrations, Fe and Mn were generally harmless and can even be beneficial in small amounts [38]. However, elevated levels of these metals in groundwater present serious health risks, particularly in regions where groundwater serves as a primary drinking water source. High concentrations of iron can lead to gastrointestinal issues and water discoloration whereas excessive manganese exposure is associated with neurological effects and can negatively impact cognitive development in children [39]. According to the Department of Mineral and Geoscience in Malaysia, the concentrations of iron and manganese in natural groundwater sources were recorded at 7.15 mg.L^{-1} and 0.87 mg.L^{-1}, respectively [40]. In this study, synthetic groundwater with 10 ppm of Fe^{2+} is implemented to replicate the common existence of divalent ion in natural groundwater.

In Figure 12, result shows that all membrane capable to removal Fe at above 95% except GS2 membrane with 85.2% removal percentage. Hence, GS3’ membrane shows the highest removal of 98.1% removal of Fe. Study of solvent DMAc in GS2 membrane had showing the incapability of dissolves ƙ-car as pore former in fact resulting the poor membrane performance and ineffective for Fe removal. Indeed, based on this results present GS0, GS3, GS3’, GM4 and GM4’ membrane show permeates concentrations of Fe comply to the comply the Ministry of Health (MOH) drinking water standards of 0.3 mgFe.L^{-1}, indicating their suitability for effective Fe removal in water treatment applications.



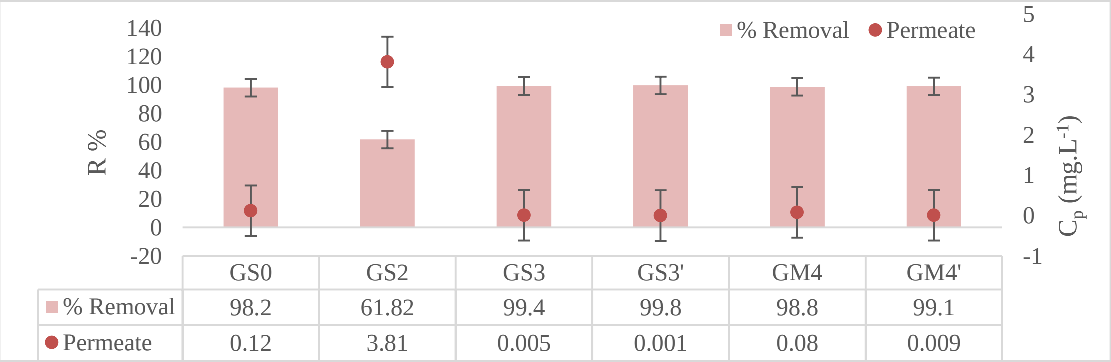
	GS0	GS2	GS3	GS3'	GM4	GM4'
% Removal	94.1	85.2	97.5	98.1	97.7	97.9
● Permeate	0.29	1.3	0.23	0.19	0.23	0.2

Fig. 12. Iron removal of the fabricated membranes with feed concentration 10 mg Fe.L^{-1}

In the study conducted by Lee *et al.,* [41], membrane performance was attributed to the synergistic effects of increased porosity, narrow pore size distribution, enhanced hydrophilicity and membrane surface charges [41]. Similarly, research on graphene-Ag nanofiltration membranes had demonstrated high efficiency in removing heavy metals from contaminated water [42]. Hence, membranes enhance its high surface area, high porosity and functionalized surfaces to enhance adsorption and contribute to highly effective at capturing heavy metal ions from wastewater streams. In this study, the GS3' membrane exhibited the best overall characteristics, including a small pore size, high water flux, and high porosity, along with notable hydrophilic properties. These features contributed to its superior performance in the removal. Nonetheless, both membranes performed well, showcasing the positive impact of incorporating Ag-GO NPs and ƙ-car into the membrane matrix for enhanced filtration efficiency.

3.2.3 Manganese removal of membrane

The removal of dissolved manganese (Mn^{2+}) from water poses significant challenges due to its small ionic size and inability to form precipitates, making it difficult for conventional membranes to effectively remove [43]. Advanced membrane technologies such as nanofiltration or reverse osmosis were typically required to address this issue [43]. Figure 13 shows the manganese (Mn) removal performance of the fabricated membranes. The study reveals that the GS0 membrane achieves a Mn removal of 98.2%, while the GS2 membrane shows a significantly lower efficiency of 61.82%. High Mn removal is observed in the GS3 and GM4 membranes, with efficiency of Mn removal at 99.4% and 98.8%, respectively. However, the hybrid membranes GS3' and GM4' outperform than the others, with Mn removal of 99.8% and 99.1%, respectively. These results indicate that GS3, GS3', GM4, and GM4' membranes permeate of concentration obtained comply the Ministry of Health (MOH) drinking water standards of 0.1 mgMn.L^{-1} based on their permeates quality.



	GS0	GS2	GS3	GS3'	GM4	GM4'
▨ % Removal	98.2	61.82	99.4	99.8	98.8	99.1
● Permeate	0.12	3.81	0.005	0.001	0.08	0.009

Fig. 13. Manganese removal of the fabricated membranes with feed concentration 5 mg Mn.L^{-1}

Research by Akalin *et al.,* [44] on the controlled release of manganese using ƙ-carrageenan (ƙ-car) highlights that the sulfonic acid groups in ƙ-car have create active binding sites for metal ions. When ƙ-car is dissolved and processed in a solvent, these functional groups remain accessible, significantly enhancing the membrane capacity to attract Mn ions [44]. Similarly, Vo *et al.,* [45] demonstrated that GO composites show excellent optical sensitivity to trace amounts of heavy metal ions, along with high adsorption affinity and catalytic efficiency for the removal of organic compounds [45]. This indicates that Ag-GO NPs provide excellent adsorption capacity for Mn due to the extensive surface area and functional groups present on graphene oxide (GO), as well as the antimicrobial properties of silver [42].

The choice of solvent is crucial in preparing and optimizing ƙ-car and Ag-GO NPs in membranes for Mn removal. Solvents assist in dissolving and casting ƙ-car evenly, facilitate in the dispersion and functionalization of Ag-GO NPs, and ultimately improve the filtration and adsorption performance of the membranes [7]. In this study, the GS3' and GM4' membranes demonstrate high Mn removal capabilities. However, GS3' membranes were the best hybrid membrane compared to GM4' due to its superior water flux and Mn removal efficiency and achieved at low pressure. This makes GS3' membrane a significant innovation in this study, highlighting its potential for efficient Mn removal in filtration applications.

4. Conclusion

The findings of this study highlight the significant impact of solvent selection and the incorporation of functional additives on membrane performance. The GS3' hybrid membrane fabricated using DMSO and modified with Ag-GO NPs and ƙ-car had demonstrated superior characteristics including high water flux with excellent removal efficiency and enhanced mechanical strength. These attributes make the membrane highly effective in removing ionic solute from water while maintaining high flux at a low operating pressure of 2 bar which significantly reduces energy consumption. Furthermore, the membranes comply the Ministry of Health Malaysia (MoH) drinking water standards for iron (Fe) at 0.3 mg.L^{-1} and manganese (Mn) at 0.1 mg.L^{-1}, respectively. These result, underscore their practical applicability in water treatment. The use of DMSO had influences the membrane performance and supports the growing demand for environmentally sustainable manufacturing practices in membrane technology. This study demonstrates that DMSO solvent is highly potential to facilitate an eco-friendly membrane fabrication paving the way for greener technologies in the water treatment industries. The result suggest that hybrid membranes fabricated with DMSO solvent and reinforced with Ag-GO NPs and ƙ-car present a promising solution to achieving high-performance water treatment while adhering with green membrane goals by substituting toxic solvent with green solvent alternatives.

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