FABRICATION AND CHARACTERIZATION OF PVDF POLY (VINYLIDENE FLUORIDE)-MEMBRANES USING DIMETHYL SULFOXIDE (DMSO): OPTIMIZING POLYMER CONCENTRATIONS FOR METHYLENE BLUE REMOVAL AND WASTEWATER TREATMENT

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ABSTRACT: Fabrication and characterization of poly(vinylidene fluoride) (PVDF) membranes using dimethyl sulfoxide (DMSO) as a solvent, focusing on optimizing polymer concentrations (14%, 16%, 18%, and 20% w/w) for enhanced methylene blue (MB) dye removal and wastewater treatment. The concentration of MB was studied using UV-Vis spectrophotometry, demonstrating significant dye adsorption. Additionally, wastewater samples were treated to assess reductions in total dissolved solids (TDS), total suspended solids (TSS), turbidity, chemical oxygen demand (COD), and biochemical oxygen demand (BOD). 14% PVDF membranes exhibited large pores and poor mechanical integrity, while 20% PVDF membranes were overly dense, leading to rapid fouling. Conversely, 16% and 18% PVDF membranes demonstrated optimal performance, balancing porosity and mechanical stability. Fourier transform infrared spectroscopy (FTIR) technique was used to identify different functional groups, while Differential Scanning calorimetry (DSC) was also used to assess thermal stability and behavior of membranes. Dead-end filtration tests evaluated flux performance. Contact angle measurements using a goniometer revealed moderate hydrophobicity. These studies contribute to the development of optimized PVDF membranes for industrial-scale dye removal and wastewater treatment applications, highlighting the importance of polymer concentration in membrane performance. By optimizing membrane properties, this research paves the way for sustainable and efficient water treatment solutions.

Keywords: Poly (vinylidene fluoride, Dimethyl Sulfoxide, Biochemical Oxygen Demand Chemical Oxygen Demand, Differential Scanning Calorimeter, Methylene Blue.

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INTRODUCTION

Poly (vinylidene fluoride) (PVDF) membranes are renowned for their exceptional chemical resistance, thermal stability, and mechanical and structural strength, making them highly suitable for applications in wastewater treatment and dye removal processes. These membranes have been extensively utilized to remove organic pollutants such as methylene blue (MB), a common dye found in industrial effluents(Zhang, Dai *et al*. 2019). However, the inherent hydrophobicity of PVDF membranes poses challenges in achieving high adsorption efficiency and fouling resistance during filtration processes, limiting their overall performance in wastewater treatment applications. Researchers have explored various fabrication techniques to overcome these limitations to modify PVDF membranes and optimize their structural and functional properties(Abriyanto 2021). Dimethyl sulfoxide (DMSO), a low-toxicity solvent, has emerged as a promising choice for PVDF membrane fabrication due to its ability to influence crystallization and pore morphology during the fabrication of membrane by phase inversion process(André, Teixeira *et al*. 2024).The use of DMSO enables controlled pore formation, which is critical for enhancing membrane performance in terms of permeability, dye adsorption, and fouling resistance (Wang, Li *et al*. 2025). Furthermore, variations in polymer concentration during fabrication significantly impact key membrane characteristics such as porosity, mechanical strength, and hydrophilicity (Abriyanto 2021). Higher polymer concentrations typically result in denser membranes with improved mechanical properties but reduced porosity, while lower concentrations favor increased porosity and flux at the expense of structural stability (Kusworo, Kumoro *et al*. 2023). This research focused on the fabrication and characterization of PVDF membranes using DMSO as a solvent at two polymer concentrations—16% and 18%—to evaluate their suitability for methylene blue removal and wastewater treatment. Comprehensive characterization and analytical techniques such as differential scanning calorimetry (DSC), Fourier-transform infrared spectroscopy (FTIR), Contact angle measurements, and dead-end filtration tests are employed to analyze the chemical structure, thermal stability, surface morphology, hydrophilicity, and filtration efficiency of the membranes. By comparing the performance of membranes fabricated at these concentrations, this research aims to determine the optimal polymer concentration for achieving high dye removal efficiency while maintaining robust mechanical and structural properties. The result of this research will contribute to advancing PVDF membrane technology by providing insights into the interplay between polymer concentration, membrane structure, and functional performance. This work highlights the potential of DMSO-based PVDF membranes as a sustainable solution for wastewater treatment applications. By addressing critical challenges such as fouling resistance and adsorption capacity optimization, this research will pave the way for developing high-performance membranes tailored for industrial effluent treatment

METHODOLOGY

Material required: Poly (vinylidene fluoride) (PVDF) pellets (Sigma Aldrich Germany) were used as the polymer matrix. Dimethyl sulfoxide (DMSO, ≥99.9% purity, *d*=1.1g/mL was brought from RCI-Labscan Limited Thailand.served as the solvent for dissolving PVDF. Methylene blue (MB, $C_{16}H_{18}ClN_3S$, ≥98%) was employed as the model dye pollutant for adsorption and filtration studies. Distilled water was utilized for coagulation baths during membrane fabrication and for preparing MB solutions. Cleaned glass substrates were used as casting surfaces for membrane formation. Optional hydrophilic additives (e.g., polyethylene glycol and isopropyl alcohol) may be included if specified in the experimental design.

Preparation of Dope Solution: Poly (vinylidene fluoride) (PVDF) dope solutions were prepared at polymer concentrations of 16 wt% and 18 wt% using dimethyl sulfoxide (DMSO) as the solvent. Before preparation, PVDF pellets were dried in oven at 80°C for 4 hours to remove the moisture. The polymer gradually added to DMSO under continuous mechanical stirring at 60°C to ensure complete dissolution. Stirring was maintained for 24 hours at a constant speed until a homogeneous and bubble-free solution was achieved. The prepared solutions were subsequently degassed at room temperature for 2 hours to eliminate air bubbles prior to membrane casting. This procedure ensured uniform polymer distribution and consistent viscosity, which are critical for achieving reproducible membrane morphology and performance.

Membrane Fabrication via NIPS Method: The prepared PVDF-DMSO dope solutions were cast into membranes using a (NIPS) technique Non-solvent induced phase separation. A TMAXCN Automatic Film Coater equipped with a precision casting knife (gap thickness: 250 µm) was employed for uniform membrane deposition onto a tempered glass substrate. The casting speed was maintained at 50 mm/s to ensure consistent thickness and surface homogeneity. Immediately after casting, the glass plate was immersed in a water bath which act as coagulation bath at 25°C and immersed in it for 24 hours to complete phase separation. The resulted membranes were then carefully peeled off from glass and rinsed thoroughly to remove residual solvent. In last, the membrane was dried through air at 25°C for 48 hours prior to characterization. This method ensures controlled phase inversion kinetics, critical for achieving tailored pore structures and reproducible performance**.**

Table 1 shows the composition of the membrane.

Membrane	Solution conc. (w/w%)	Solvent	PVDF Mass (g)	Solvent Mass (g)
M1	14	DMSO	4.2	25.8
M2	16	DMSO	4.8	25.2
M3	18	DMSO	5.4	24.6
M4	20	DMSO	6	24

Membrane Characterization

Contact angle measurement: To determine the hydrophobicity of membranes, contact angle measurements were performed using water. The contact angle measurement was performed by Goniometer. The 0.50 µL of water drop was taken on the membrane's surface by using a syringe(Liao, Wang *et al*. 2013). Software verifies these angles and takes three different surface angles of the membrane. Then, take the average of all measurement(Wang, Li *et al*. 2011). Table 2 shows the contact angle of membranes.

Porosity and Average pore size: The porosity of membrane was determined by using the dry-weight method. In this method, first cut the membrane and soak it in water for around 60 minutes. Then dry the surface of membrane and immediately weight. The porosity was calculated from following equation, W_1= weight of the soaked membrane. W_2= weight of dry membrane. V = volume of cutting membrane(Moslehyani, Nasser *et al*. 2013). ρw = is the density of water at 25°C which is (d = 1.0 g/cm^3)

$$\varepsilon = \frac{W1 - W2}{V\rho w} \quad (1)$$

With the membrane's porosity, we calculate its average pore radius. Therefore, we used the velocity filtration method and Guerout-Elford-Ferry.

$$r = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8\eta lQ}{\varepsilon \times A \times \Delta P}} \quad (2)$$

In equation (2) "η" is the water-viscosity at 25°C, while"l" is the membrane-thickness which was taken in (mm), Q is the volume of the water per second (m^{3}s^{-1}), A is the effective area of the cutting membrane (cm^2) and ΔP is the applied pressure (Pa) (Kusuma, Purwanto *et al*. 2021). By multiplying the "r" with 2 we get pore size. The porosity and pore size of membrane are shown in Table 4.

Water flux study of membranes. Pure water flux (PWF) was determined by testing the membrane with Dead-End filtration setup (Sterlitech-HP4750-Stirred). The distilled water passed through the membrane having a diameter of 2 cm and the effective surface area of the membrane was 19.63cm^2. Water flux was calculated by following equation(Sukitpaneenit and Chung 2011)

$$J = \frac{W}{A \times \Delta t} \quad (3)$$

where J in above equation represents the pure water flux (gcm^{-2} h^{-1}), W is the weight of permeate (L), A is the effective surface area(cm^2) of membrane and Δt is the permeation time (h).

Permeability and Rejection Rate: The Dead-End (Sterlitech-HP4750-Stirred) filtration setup system was used for all membranes to check their permeability and rejection rates. High-pressure nitrogen gas helps to pass the feed solution through the membranes(Wang, Zhang *et al*. 2021). The permeate and retentate were both collected. Their filtration pressure, time, and mass of permeate were noted during the experiment. Industrial wastewater, methylene blue, and salt samples were also filtered through a dead-end filtration setup(Zhao, Qian *et al*. 2021).

Fourier transform infrared (FT-IR): Structural and functional group confirmation was confirmed by FT-IR (Agilent Cary-630). The sharp peaks at around 760 cm-1 to 872cm^{-1} and 1170cm^{-1} to 1401cm^{-1} indicate the presence of PVDF structure in the membranes. It is also used to determine the crystallinity phase of PVDF membranes.

Differential Scanning Calorimeter (DSC):The thermal behavior of pristine PVDF was studied using a Differential Scanning Calorimeter DSC (Mettler Toledo, SDTA851). The melting point of membrane was indicated by peak on graph. It also helps to determine the alpha or beta phase of the membranes

Membrane performance

Separation of TSS and Turbidity of Wastewater: The efficiency of membranes in treating industrial wastewater was investigated. Experimental results demonstrated a substantial reduction in TSS and turbidity levels post-filtration. This water quality improvement highlights membrane technology's potential for industrial wastewater treatment.(Muhamad, Mokhtar *et al*. 2022)

Removal of Methylene Blue dye: The dye removal performance of the membranes was investigated through filtration experiments, where the initial and final concentrations of methylene blue were determined using UV-visible spectroscopy. The results indicated that it exhibited the highest removal efficiency of PVDF membrane (Rianjanu, Marpaung *et al*. 2024).

BOD and COD reduction: PVDF (Polyvinylidene Fluoride) membranes are highly effective in reducing the Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) from wastewater. These membranes are known for their chemical resistance, thermal stability, and mechanical strength(Ibrahim, Wirzal *et al*. 2018).Initially we measured the BOD and COD of waste water then this polluted water pass through the membrane via dead end filtration and collect the permeate and again check the BOD and COD.

RESULT AND DISCUSSION

Effect of Concentration of PVDF: This research explores the effect of PVDF polymer concentration on membrane fabrication and performance. Membranes were fabricated with concentrations ranging from 14% to 20%. The results indicate that membranes with 16% and 18% PVDF concentration exhibited superior filtration efficiency, tensile strength, dye and salt removal efficiency, and fouling resistance. The 14% concentration resulted in thin, mechanically weak membranes with large pore sizes, leading to poor filtration performance. Conversely, the 20% concentration resulted in membranes with negligible porosity and low tensile strength, hindering filtration and separation processes. Based on these findings, the 16% and 18% PVDF concentrations were identified as optimal for fabricating high-performance membranes. So, all the other membranes having concentrations 14% and 20% were eliminated from further experiments.

Hydrophobicity nature of PVDF-membranes: Hydrophobicity of PVDF-membrane determined by water contact angles on PVDF membranes prepared using DMSO. Membranes fabricated with DMSO exhibit the highest contact angles, indicating the most hydrophobic nature.. While the specific concentrations are not explicitly shown, there appears to be a slight trend towards increasing contact angle with increasing solute concentration within each group. These variations in hydrophilicity are likely attributed to differences in solvent-polymer interactions during membrane formation, influencing factors like polymer chain orientation and crystallinity, as well as the potential retention of residual solvent within the membrane matrix. The contact angle of membrane show in below.

Fourier transform infrared (FT-IR): The presence of prominent peaks around 1400 cm^{-1} and 840 cm^{-1} confirmed the identification of the PVDF polymer(Kim, Kim *et al*. 2009). The peak at 1400 cm^{-1} is associated with CH_2 bending vibrations, while the peak at 840 cm^{-1} is attributed to CF_2 symmetric stretching vibrations(Arshad, Wahid *et al*. 2019). It shows PVDF structure almost remain same in all membranes.

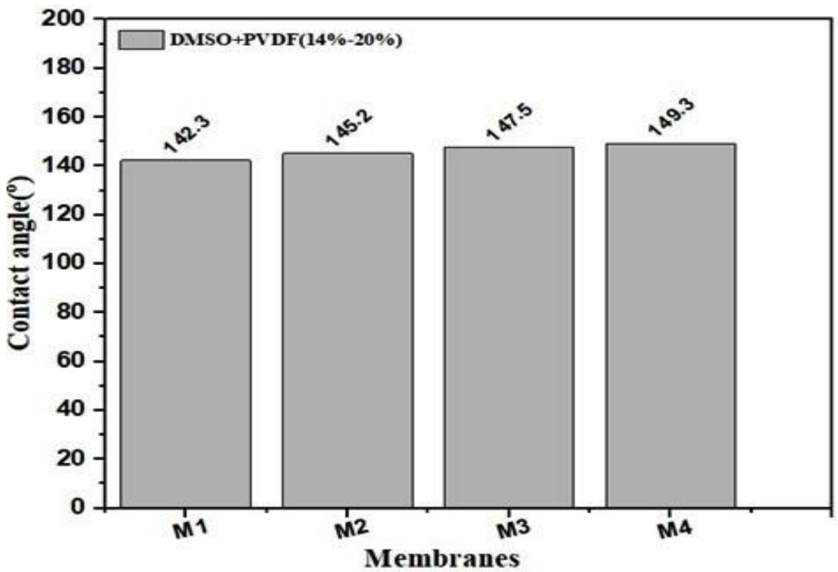

Fig. 1.show the contact angle of different membranes

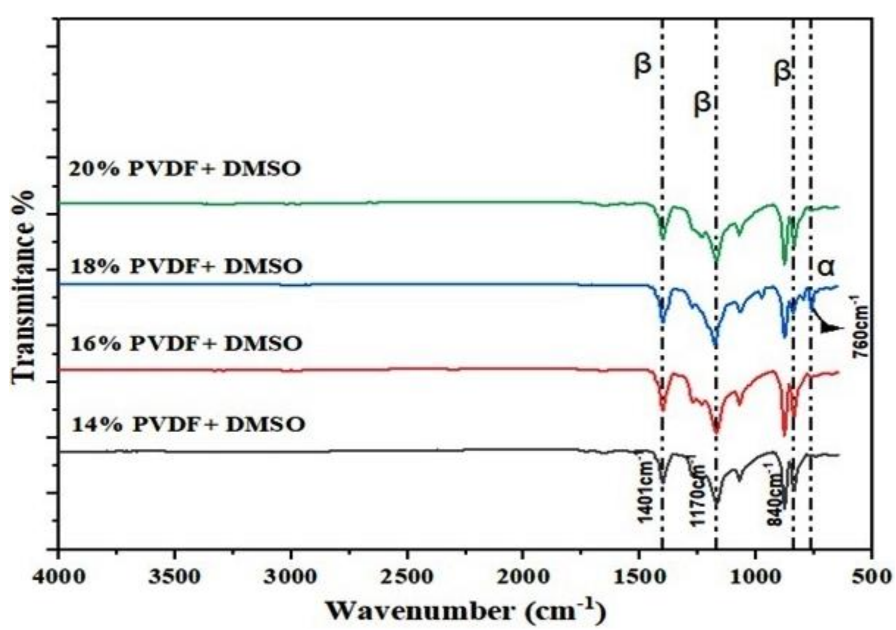

Fig. 2.show the FT-IR spectra of different membranes

Differential Scanning Calorimeter: The graph shows the heat flow as a function of temperature for PVDF membranes prepared using different concentrations (14%,16%,18%, and 20%) at 16% and 18% PVDF concentrations. DSC is a technique used to measure materials' heat flow associated with thermal transitions, such as melting and crystallization. The most prominent feature in the graph is a sharp endothermic peak. This peak corresponds to the PVDF polymer's crystalline phase(s) melting. The temperature at the peak of the endotherm represents the melting temperature (Tm) of the PVDF in the membrane. All membranes is melt at 168^{o}C while concentration 18% PVDF show 166^{o}C.

Membrane thickness, porosity and pore radius: Four PVDF membranes (M1-M4) were fabricated with varying PVDF concentrations (14-20 wt.%) in DMSO. Increasing PVDF content resulted in thicker membranes and a concomitant decrease in pore radius, attributed to increased polymer chain entanglement within the matrix (Akbari, Hamadanian *et al*. 2012). Water flux exhibited an inverse correlation with pore radius, with membranes prepared at lower PVDF concentrations and in DMSO demonstrating higher flux.

Methylene blue removal efficiency: The table presents the dye rejection performance of different PVDF membranes prepared with varying PVDF concentrations (14% and 20%) in (DMSO). Dye rejection was evaluated by measuring the absorbance of a dye solution before and after filtration through each membrane. The results demonstrate significant dye rejection capabilities for all membranes, with percentage reductions ranging from 82.47% to 93.99%. Table 4 show the absorption of before and after filtration through membrane.

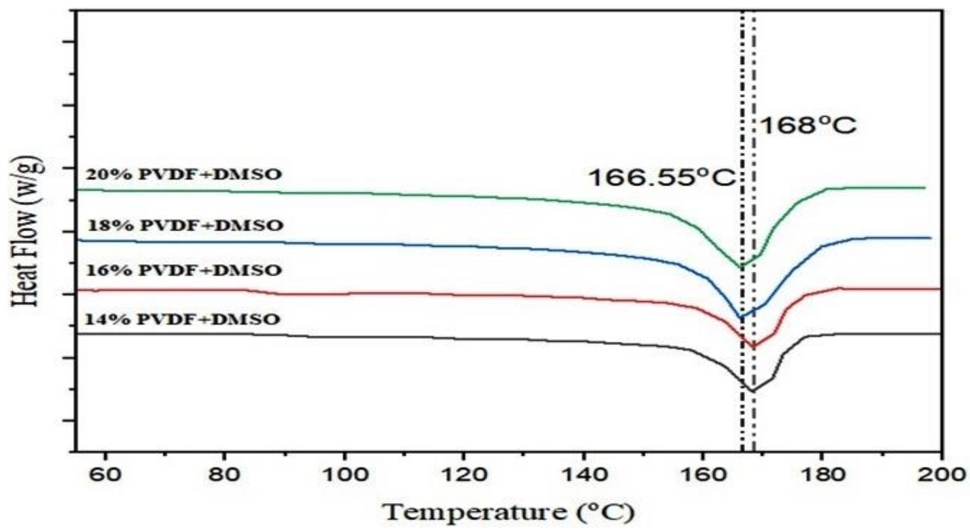

Fig 3 show the contact angle of different membranes

Table: 2 Membrane Structural properties

Membrane	Membranes (formulation)	Thickness (mm)	Pore radius (mm)	Water-flux (ml/h/cm2)
M1	14% PVDF in DMSO	0.157	1.9	129
M2	16% PVDF in DMSO	0.174	0.51	4.2
M3	18% PVDF in DMSO	0.177	0.45	3.0
M4	20% PVDF in DMSO	0.194	0.20	1.2

Table: 3 Membrane Efficiency to remove M.B dye.

Different PVDF membranes	Membrane Mark	Dyesample Absorbance	Absorbance after filtration	percentage reduction
	M	ε_o	ε_o	%
PVDF 14%+DMSO	M1	3.613	0.217	93.99
PVDF 16%+DMSO	M2	3.613	0.282	92.18
PVDF 18%+DMSO	M3	3.613	0.334	90.75
PVDF 20%+DMSO	M4	3.613	0.633	82.47

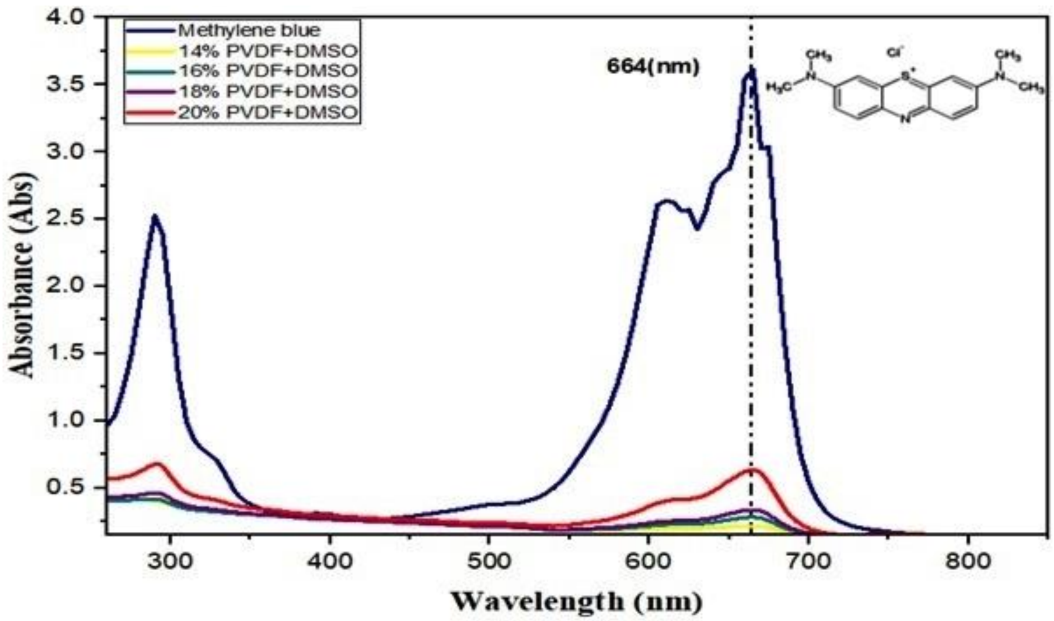

Fig: 4 UV-Visible Absorbance show reduction in M.B concentration

Rejection of total suspended solids TSS: The table presents the total suspended solids (TSS) rejection performance of four different PVDF membranes (prepared with 14% to 20% PVDF in DMSO) in a filtration process. All membranes demonstrated high TSS rejection, with percentage reductions ranging from 83.61% to 86.63%.

Reduction in BOD and COD: All membrane formulations demonstrated significant COD and BOD removal efficiencies, with percentage reductions generally exceeding 95%. Notably, membranes fabricated with 18% PVDF exhibited consistently higher removal efficiencies compared to their 16% counterparts across all solvent systems. Among the solvents, DMSO consistently yielded lower post-filtration COD values compared to DMAC and DMF, suggesting its potential as a more effective solvent for enhancing membrane performance in terms of COD removal.

Table:4 Difference in TSS in Fee and Permeate.

Different PVDF-Membrans	TSS Feed	TSS Permeate	TSS Difference	percentage reduction
Membranes	**mg/L**	**mg/L**	**mg/L**	**%**
PVDF 14%+DMSO	6547	963	5584	85.29
PVDF 16%+DMSO	6547	844	5663	86.49
PVDF 18%+DMSO	6547	1073	5474	83.61
PVDF 20%+DMSO	6547	993	5554	84.83

Table: 5 show the percentage reduction in BOD and COD

Different PVDF-Membrans	Waste Water COD	COD after filtration	Percentage reduction	Waste Water BOD	BOD after filtration	percentage reduction
M	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**mg/L**	**%**
M2	3300	148	95.51	2600	78	97.63
M3	3300	87	97.36	2600	52	98.42
M6	3300	139	95.78	2600	80	97.57
M7	3300	73	97.78	2600	47	98.57

Conclusion: This study investigated the fabrication and characterization of PVDF membranes using solvent DMSO and concentrations (14%, 16%, 18%, 20%). The results demonstrate that 16% and 18% concentrations yielded optimal membranes with a good balance of mechanical strength, permeability, and filtration performance. These membranes exhibited high tensile strength and a reasonable water flux. Furthermore, they demonstrated excellent removal efficiencies for dyes, TSS, salts, and organic pollutants (COD and BOD). Membranes prepared with DMF showed mixed results, with some exhibiting high elongation but lower water flux. 14% concentrations generally resulted in thin membranes, while 20% concentrations led to thicker, more brittle membranes with reduced permeability. Overall, this study provides valuable insights into the influence of solvent and concentration on the properties and performance of PVDF membranes, paving the way for further optimization and potential applications in various filtration process

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