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High stability and performance of organic pollutant removal using PVDF-TiO_2 fabricated by non-solvent induced phase separation process

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ABSTRACT

The present study aims to prepare, characterize, and evaluate the performance of polyvinylidene fluoride (PVDF) and PVDF-TiO_2 membranes prepared using the non-solvent induced phase separation technique. The influence of titanium dioxide (TiO_2) loading on membrane morphology, surface characteristics, and filtration behavior will systematically be examined. The membrane performance was assessed using both single-dye and binary-dye systems, using a single-based system of methylene blue as a cationic dye and acid yellow 17 as an anionic dye, and a binary-based system of mixed methylene blue-acid yellow 17. The results show that the pristine PVDF membrane has the morphology of an interconnected pore network due to the effect of the solvent-non-solvent exchange process. Further investigation also shows that the surface membrane has micropores where the incorporation of nanosized TiO_2 reduces the pore size by coating and filling the membrane under optimum conditions, while excessive TiO_2 leads to agglomeration, which negatively affects the mechanical stability, material hydrophilicity, and dye removal efficiency. The membrane containing a 10% ratio of TiO_2 (w/w) compared to PVDF weight exhibited the best overall performance, achieving removal efficiencies of 87.53% for methylene blue and 53.29% for acid yellow 17 in a single-dye filtration system. In the binary system, the rejection slightly decreased to 84.67% for methylene blue, whereas acid yellow 17 removal increased to 66.31%. These results suggest that separation in single-dye systems is primarily governed by electrostatic interactions between the dye molecules and the membrane surface, while binary systems involve a combination of size exclusion and charge-based interactions. These findings open the possibilities of the optimum condition to treat the complex wastewater, especially for those with large particle removal. The study also demonstrates that PVDF–TiO_2 membranes are a suitable option for membrane since they has good mechanical and physical properties, are easy to prepare, and provide a promising potential for complex wastewater treatment applications.

Keywords: titanium dioxide$_2$, polyvinylidene fluoride, filtration, dye rejection, wastewater.

INTRODUCTION

Over several decades, the massive development in the industrialization, agriculture sector, and urbanization has significantly intensified the global water crisis by exposing a wide array of pollutants to the water source worldwide, ranging from persistent organic pollutants, including synthetic dyes, antibiotics, pesticides, etc., which could also supply heavy metals to the water source (Salehi, 2022). The presence of organic pollutants not only threatens human health through cross-contamination transport, but also poses a serious effect on the ecosystem, which is not responsible for the presence and effects obtained from contamination. A reduction technique in the contamination movement seems not possible to be implemented in the environment due to massive water use and unstoppable anthropogenic activities, which lead to more contamination ending up in the water body. The conventional water treatment methods, such as clarification, direct oxidation, and filtration, often fail to adequately remove the contaminants due to the complex chemical properties and low concentration (Cevallos-Mendoza, J., 2022). Therefore, the implementation of more effective water treatment technology with a facile process and high efficiency is essential to ensure the sustainable, safe water supply for humans and biodiversity.

Membrane-based technology, including microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, has gained much attention in the last several decades, due to its rapid and efficient in removing most of the persistent organic pollutants (Nasir et al., 2022). Membrane-based technology has been reported to successfully remove a broad spectrum of contaminants, including heavy metals, pathogens, and most persistent chemicals, including the complex dyes and antibiotics, while also enabling integration with other treatment systems for enhanced performance (Nasir et al., 2022; Wang et al., 2014). Among all the polymeric raw materials to fabricate membranes, polyvinylidene fluoride (PVDF) has gained lots of attention due to its high mechanical strength, toughness, and durability, which offer long-term operation (Pramono et al., 2023). PVDF also has high stability toward chemical and thermal resistance, including acid, base, solvent, and chemical reaction, such as photocatalyst (Nieto-Sandoval et al., 2023), and thermal stability up to 400 °C (Chang-Yu, 2015). However, PVDF has several limitations, such as its hydrophobic properties, which could easily lead to fouling, especially when filtering the organic-based pollutants such as protein and dyes (Liu et al., 2025). The fouling that occurred in the PVDF membrane was reported as the irreversible fouling, because of layered dye on the membrane surface, which could decline its permeability and require a deep chemical cleaning for reactivation (Nawaz et al., 2021). Thus, changing the hydrophobic properties of PVDF could be the way to prevent the fouling process and enhance the water flux of membranes. Kan, (2023) reported that modifying the PVDF membranes to have hydrophilic properties could increase the pure water flux of the membrane about 18-fold, compared to hydrophobic or non-modified PVDF membranes (Kan et al., 2023).

To modify the hydrophobic properties of PVDF membrane, several techniques have been implemented, such as grafting for surface modification (Shen et al., 2017), surface coating using hydrophilic substances (Li et al., 2023), membrane functional group modification (Wang et al., 2023), and nanoparticle incorporation (Nawaz et al., 2021; Samree et al., 2020). Among all the techniques, nanoparticle incorporation is reported to have a high success in enhancing the hydrophilicity of PVDF membrane since most of the nanoparticles have hydrophilic properties, which could support the hydrophilic sites on the PVDF membrane. On the other hand, the nanoparticle incorporation was also easily implemented and provides additional advantages such as enhanced water permeability and pollutant rejection and can be easily combined with other process that provides superior antifouling properties (Sisay et al., 2022). However, several challenges were reported in incorporating PVDF with nanoparticles, such as the form of nanoparticle agglomeration, which reduces the membrane performance, membrane stability toward nanoparticle leaching, morphology control, and process scalability and reproducibility (Rafiei et al., 2021).

The blending modification technique is considered one of the most facile and effective methods for incorporating nanoparticles into a polymer matrix. However, the most challenging was how to completely blend the nanoparticle, which has hydrophilic properties, with the PVDF matrix, with hydrophobic properties. The poor blending between nanoparticles and PVDF matrix could form a non-uniform distribution of nanoparticles and agglomeration, which could not only reduce the performance and stability, but also cause the PVDF matrix to lose its performance as a membrane. Non-solvent-induced phase separation was reported as the most widely used technique for preparing membranes, including PVDF-based membranes, since it is versatile and produces asymmetric membranes with controllable pore structures (Da-Ming, 2013). However, the choice of solvent and the method of solvent removal determine the successful blending of nanoparticles in the polymer matrix due to the solvent-non-solvent exchange process and the dispersion of nanoparticles in the polymer matrix (Alyarnezhad et al., 2020).

The present study aims to prepare and examine PVDF and PVDF-TiO_2 membranes using the non-solvent induced phase separation (NIPS) technique, which is reported as the most suitable and rapid synthesis method for membrane preparation. The morphology and characteristics of the as-prepared membrane will be explored. Furthermore, the performance of PVDF and PVDF-TiO_2 will be assessed for removing single-dye and binary-dye removals using a vacuum filtration process. The effect of TiO_2 loading during the membrane preparation will be discussed in detail. The study is expected to provide information on the facile synthesis of a functional membrane with high rejection and flux performances, which could exhibit high stability for long-term use. The discussion on process scalability and reproducibility will also be discussed in detail at the end of the paper to provide an insight into the development of membrane technology in the future.

METHODS

Preparation of PVDF and PVDF-nanoTiO_2 thin film membrane

Approximately 0.4 gram of polyvinylidene fluoride powder (PVDF, Sigma Aldrich) is suspended in a 2:1 v/v mixture of N-Methyl-2-pyrrolidone (NMP, 99%) and acetone. The suspended solution is stirred for 30 minutes and then dropped with 0.5 mL of glycerol (Sigma Aldrich, 99% purity), followed by an additional 15 minutes of stirring at room temperature until a homogeneous solution is achieved. The mixture solution is poured into a 4 × 4 × 0.5 cm membrane cast glass for filming and air-dried for 5 minutes in room temperature. The membrane solution cast is immersed in a distilled coagulation bath and kept for 15 minutes. The obtained PVDF film is dried by air at room temperature for 30 minutes.

For PVDF-NanoTiO_2 thin film membrane preparation, the homogeneous solution of PVDF

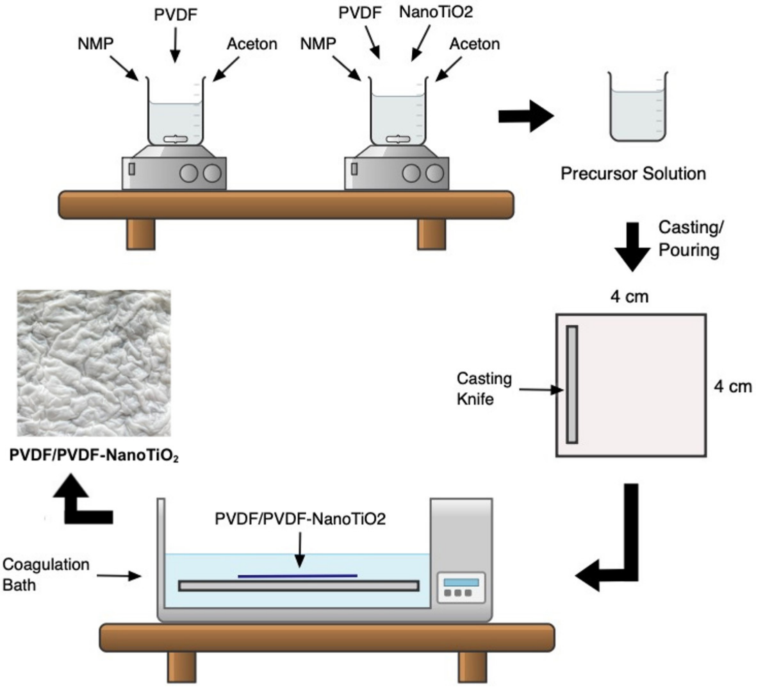

Figure 1. Schematic mechanism of PVDF and PVDF-TiO_2 thin film membrane preparation using the non-solvent induced phase separation (NIPS) method

in NMP and Acetone solution is suspended with 0.018 grams of TiO_2 as 5% TiO_2 ratio with PVDF (w/w) and stirred at 250 rpm for 60 minutes at 60 °C. The suspended solution is then cast and immersed in a coagulation bath as in the previous procedure. To investigate the effect of NanoTiO_2 addition on the PVDF-NanoTiO_2 properties, the same procedure of PVDF-NanoTiO_2 is repeated with the different loads of NanoTiO_2 of 10% (0.036 gram) and 15% (0.054 gram). Figure 1 shows the schematic mechanism of PVDF-NanoTiO_2 preparation.

Characterization

The PVDF and PVDF-NanoTiO_2 materials were characterized using a scanning electron microscope (SEM) integrated with energy dispersive x-ray spectroscopy (EDS) (Thermo Scientific, Axia ChemiSEM LoVac) to investigate the surface morphology, cross-section, and elemental composition of the as-prepared material, especially the elemental composition in the surface of the membrane and the distribution of NanoTiO_2 in the PVDF matrix. Furthermore, the mechanical testing of the membrane was also characterized using a Universal Testing Machine (UTM, WEW-300A) to assess the effect of NanoTiO_2 addition on PVDF mechanical strength. The effect of NanoTiO_2 on the hydrophilic improvement is also evaluated by assessing the membrane surface using a contact angle (CA) test with distilled water. A higher contact angle (CA) generally indicates greater resistance to wettability, which is a characteristic of hydrophobic surfaces. A CA of 90° is typically considered the threshold between hydrophilic and hydrophobic behavior, while a CA above 150° is classified as superhydrophobic (Baroud, 2023).

Dye reduction assessment of PVDF and PVDF-TiO_2 using vacuum filtration process

The as-prepared PVDF and PVDF-TiO_2 membranes were tested to remove three synthetic organic pollutants, which are methylene blue (MB), acid yellow 17 (AY17), and mixed methylene blue-acid yellow 17 (MB-AY17). All the organic pollutants were prepared in a 2.5 mg/L concentration, where the binary dye system of mixed MB-AY17 will have an equal concentration between the MB dye and the AY17 dye system. Each filtration process will use 50 mL of organic pollutants with a fixed vacuum pressure of 500 millibars. The filtration process was counted since the solution was poured into the Buchner Funnel until there is no solution was dropped in the Erlenmeyer flask. Furthermore, approximately 3 mL of permeate solution was taken to measure the concentration of dye solution after the filtration using a UV-Vis Spectrophotometer (Agilent Cary 60). The dye rejection rate (R) and the permeate flux (J_w) of the as-prepared material were calculated using the following Equations 1 and 2 (Arif, 2024):

$$R = \frac{C_0 - C_t}{C_0} \qquad (1)$$

$$J_w = \frac{V}{t \times A \times P} \qquad (2)$$

In Equation 1, R refers to dye rejection (%), C_0 and C_t are the initial dye concentration before the adsorption and permeate concentration in mg/L, respectively. In Equation 2, Jw is the permeate flux of the as-prepared material ($L.m^{-2}.h^{-1}.bar^{-1}$), V is the volume of dye solution (L); t is the filtration time (h), A is the surface area (m^2), and P is the vacuum pump pressure (bar).

RESULT AND DISCUSSION

The SEM analysis revealed the top images of PVDF and PVDF-TiO_2, shown in Figure 2. The top morphology of the PVDF membrane shows an interconnected network-type structure with a roughness on the surface of the membrane film. The interconnected structure formation is initiated by the solvent-in and solvent-out process during the non-solvent induced phase separation (NIPS) process, where PVDF is known as a hydrophobic polymer that only dissolves in NMP solution. The micropores were seen in the surface of the membrane, where the addition of TiO_2 reduces the micropores due to a compact structure of PVDF-NanoTiO_2 material. The inset image confirms that the PVDF membrane has a bigger hole compared to PVDF-TiO_2 5% (Figure 2B), where the addition of NanoTiO_2 starts to fill the pores on the PVDF matrix. Furthermore, the membrane of PVDF-NanoTiO_2 10% has a different pore on the top surface of the membrane, where TiO_2 fills the matrix of the PVDF membrane and closes all the micropores (Figure 2C), where there is no micropore formed in the top image of PVDF with 10% TiO_2. However, the addition of TiO_2 15% changes the top morphology, where micropore starts to form as part of the mechanical failure of the membrane due to the brittle characteristics of TiO_2. Furthermore, the ratio of 15% exhibits the excess ratio for making the composite membrane (Figure 2D).

Cross-sectional SEM images were taken to examine the dispersion of TiO_2 in the inner layer of the PVDF matrix, where PVDF and PVDF with a 10% ratio of TiO_2 were employed. The reason for examining PVDF-TiO_2 with a specific ratio of 10% was that it provides a significant effect on the top morphology of the PVDF membrane surface, as confirmed by top image analysis using SEM. Figure 2(A-B) shows the cross-sectional morphology of PVDF and PVDF-TiO_2, respectively. The result provides additional information, where the PVDF membrane has a layer-like micropore with micro-tunnel structures beneath the surface micropores. The size of the micropores is not uniform and relatively larger in size compared to the top-site micropores. The formation of large micro-tunnel areas between the membrane layers is attributed to the solvent–non-solvent exchange process during membrane fabrication, in which the bottom layer forms first, followed by the subsequent layers toward the top [22]. Furthermore, the effect of TiO_2 addition provides a different cross-section morphology, where the nanoparticles are distributed throughout the micropores, confirmed by EDS mapping shown in Figure 2C. EDX confirms that the PVDF membrane only consists of PVDF matrix, where PVDF-TiO_2 has a uniform distribution of TiO_2 (Figure 2D and 2E) all over the membrane layer. On the PVDF-TiO_2, the distribution of TiO_2 appears to reduce the micro-tunnel structures in the PVDF matrix, leading to a more compact

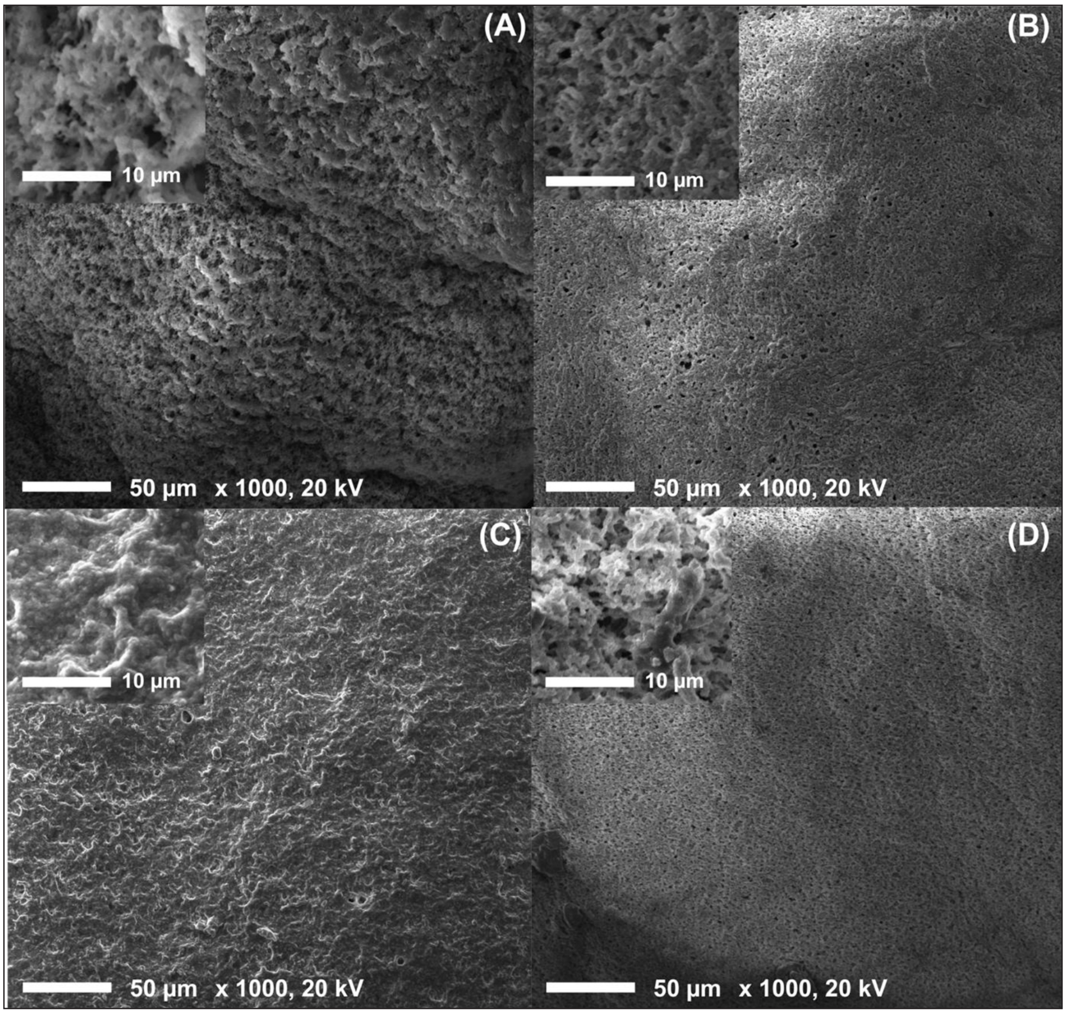

Figure 2. SEM images of (A) PVDF membrane and PVDF with (B) 5%, (C) 10%, and (D) 15% ratios of nanoTiO_2

morphology that may enhance the contact between water and the membrane surface. However, since PVDF is inherently a hydrophobic polymer, the compact structure could reduce the permeability of PVDF-TiO_2 films [23]. On the other hand, the presence of TiO_2 on the PVDF matrix could change the hydrophobicity of PVDF properties since TiO_2 is considered a hydrophilic substance, which could provide more permeability on the PVDF-TiO_2 material [24]. Furthermore, the addition of TiO_2 also slightly increases the thickness of PVDF-TiO_2 and modifies its structural morphology, which may enhance water-membrane contact and improve flux performance (Wang et al., 2014; Zhang et al., 2022). Figure 2F shows the physical form of the PVDF-TiO_2 membrane.

The CA measurement test was done to see the effect of the TiO_2 addition on the hydrophilicity of the as-prepared membrane. The CA was based on the solid's ability to repel or adsorb water, where a higher CA indicates greater resistance to wettability by water, which is a characteristic of hydrophobic surfaces. A CA of 90° is typically considered the threshold between hydrophilic and hydrophobic behavior, while a CA above 150° is classified as superhydrophobic (Baroud, 2023). Figure 3(A) shows that the as-prepared PVDF membranes are inherently hydrophobic, which is slightly lower compared to the literature (Lu, 2021). In general, PVDF should have a high CA, such as 120 (Hamad et al., 2022) and 118.76 (Kusuma et al., 2021), where the lower CA is attributed to a combination of surface

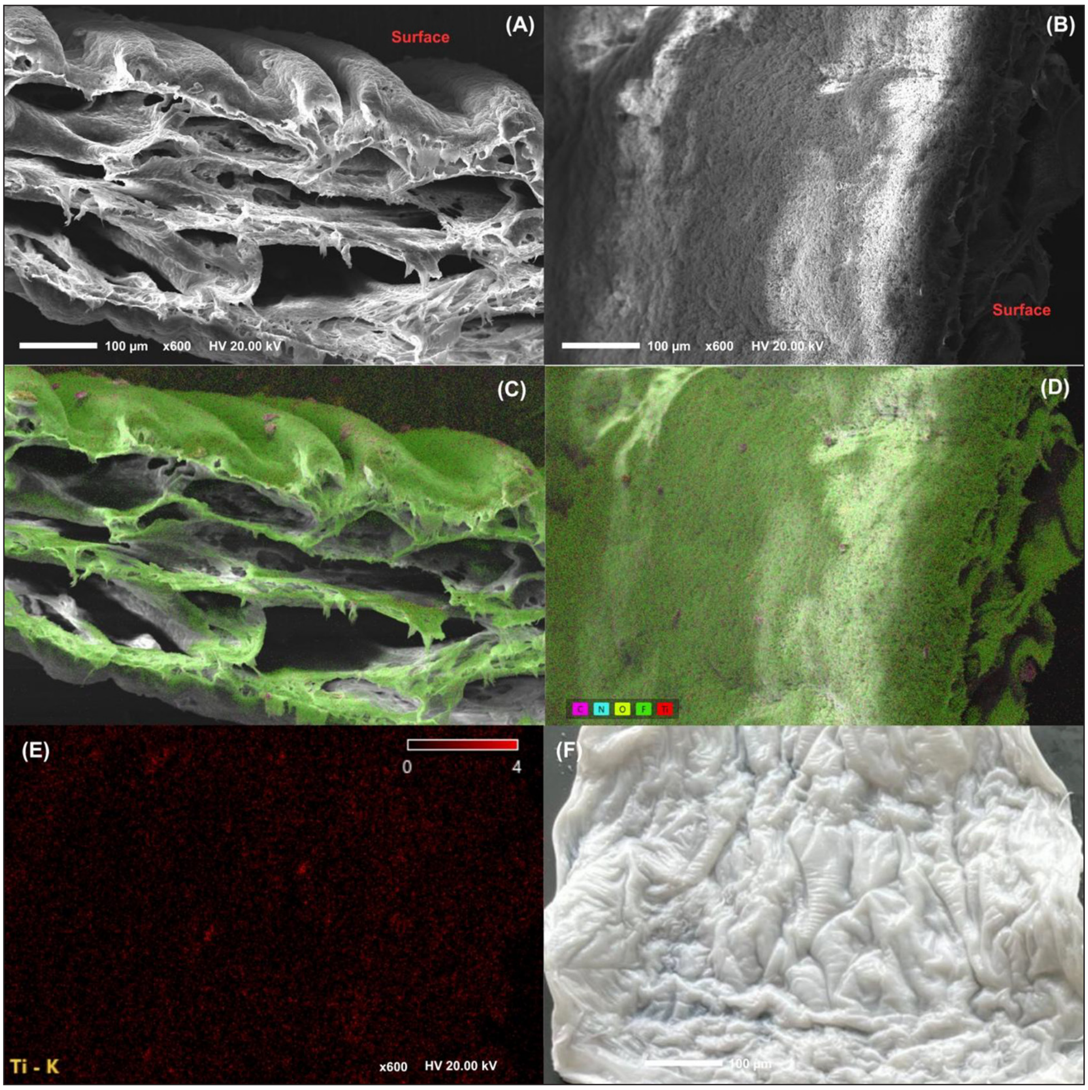

Figure 3. Cross-section SEM images of (A) PVDF membrane and (B) PVDF-nanoTiO_2 10%. Elemental analysis of (C) PVDF membrane and (D) PVDF-nanoTiO_2 10% for all elements and (E) titanium oxide; and (F) The sample of membrane PVDF-nanoTiO_2

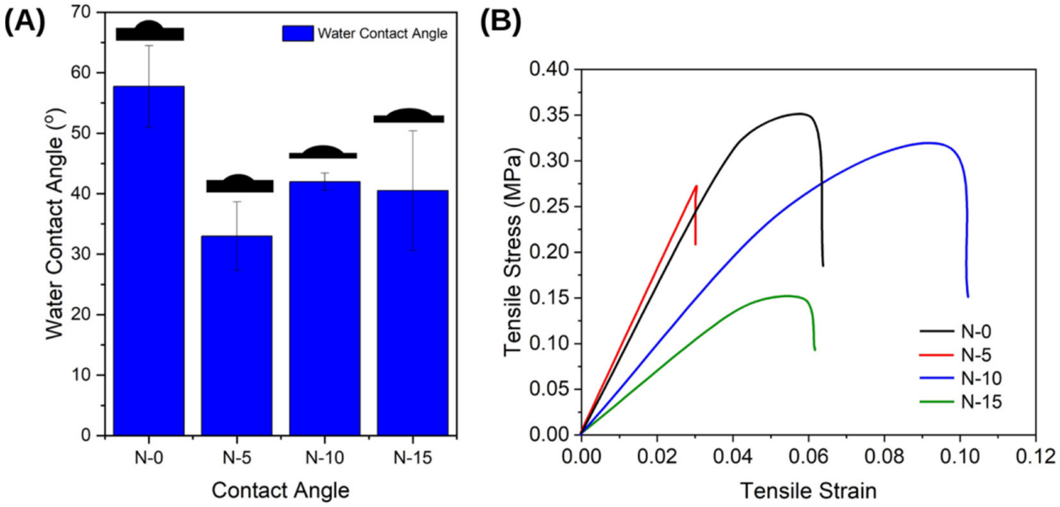

Figure 4. (A) Water contact angle and (B) mechanical strength of PVDF and PVDF-TiO_2

roughness and the addition of glycerol as a binding agent during membrane preparation, which has hydrophilic properties.

The reduction in the hydrophobic properties of the membrane surface was also attributed to the formation of an air pocket, which facilitates interaction between water and PVDF membrane (Zeng et al., 2022). The air pocket also physically forms a massive roughness on the surface of the membrane, which could be seen physically on the surface of the membrane (Figure 3F). The air pocket in the membrane surface could be formed as micro- and nano-scale air pockets that facilitate interactions between water molecules and the hydrophilic regions of the material surface, in accordance with the Wenzel and Cassie–Baxter wetting models (Zhou et al., 2022).

Furthermore, the other reason for the reduction of hydrophobic properties of the membrane was due to the addition of glycerol, which has several roles in the membrane formation. First, glycerol aims to modify the film's hydrophobicity by adding hydrophilic properties, as glycerol has high hydrophilic properties. Second, glycerol is reported as the preserved porous support, which stimulates the formation the porosity on the PVDF membrane and enhances the performance of the membrane (Zeng et al., 2022). Third, glycerol is used as a plasticizer, which supports the membrane flexibility that is important in the membrane fabrication. Thus, the use of glycerol could support the reduction of hydrophobic properties of PVDF membrane through the combination of its roles in the membrane fabrication.

On the PVDF-TiO_2 membranes, the addition of TiO_2 lowers the CA on the PVDF-TiO_2 membrane, as TiO_2 is reported as a hydrophilic material (Rudakova et al., 2021). However, the wettability test confirms that the PVDF with 5% of TiO_2 has the highest hydrophilic site, indicating as the most hydrophilic membrane from all the as-prepared PVDF and PVDF-TiO_2. The distribution of TiO_2 on the surface of the PVDF membrane provides the main effect on the boosting of hydrophilic properties of PVDF with 5% of TiO_2, where it can be seen from the SEM images that TiO_2 covers the micropores of the PVDF matrix. The presence of TiO_2 on the surface of the PVDF matrix provides more permeability in the PVDF-TiO_2 material (Zhang et al., 2022). Interestingly, the addition of a higher ratio could not support increasing membrane hydrophilic properties, where PVDF with a 10% ratio of TiO_2 has a higher CA, and it slightly lowers in the ratio of 15% TiO_2. From cross-section analysis, a higher ratio of TiO_2 fills the inner layer of the membrane film, which does not really affect the surface modification on the PVDF membrane. However, the addition of the inner layer of PVDF matrix could affect the membrane performance and mechanical properties. Figure 4B shows the mechanical properties of PVDF and PVDF-TiO_2.

Mechanical test data for PVDF and PVDF-TiO_2 membrane film were assessed, as shown in Figure 4B. The PVDF membrane has 0.35 MPa as a tensile strength, which is relatively low compared to the one reported (Sriyanti et al., 2024; Mu'izzah et al., 2023). The addition of glycerol is expected to reduce the mechanical strength due to the role of glycerol as a plasticizer and pore-forming agent (Yeow et al. 2024). In addition, the presence of TiO_2 on the PVDF matrix continuously reduces the mechanical strength of the PVDF membrane because of the effect of the inherently brittle material obtained from the natural properties of TiO_2 as a ceramic material (Razmjou et al., 2011). However, the addition of a 10% ratio of TiO_2 with a uniform distribution enhances the tensile stress and provides a higher strain on the membrane, confirming the high mechanical performance of PVDF membrane film. The high strain on the as-prepared membrane could provide high stability in the high-pressure filtration process. However, the addition of a 15% ratio of TiO_2 seems to be overpowered, where the agglomeration confirmed on SEM images (Figure 2D) decreases in tensile strength and flexibility due to the increased brittleness from TiO_2 on the PVDF matrix. From the result, the distribution of TiO_2 on the PVDF matrix plays the main role in determining the mechanical properties of PVDF, rather than the ratio of TiO_2. A similar finding was also reported by Li-Yun, (2009) and Cheng, (2020), which reports that the best mechanical properties of PVDF incorporated with TiO_2 are those with the best uniform dispersion on the PVDF matrix (Li-Yun et al., 2009; Cheng et al., 2020). The result shows that a ratio of 10% provides the best mechanical improvement on PVDF-based membranes. The well distribution of TiO_2 on PVDF with 10% TiO_2 could facilitate more contact during the filtration process and enhance the rejection performance of the membrane. On the other hand, the high mechanical properties of PVDF-TiO_2 10% could provide high durability on the as-prepared membrane toward long-term uses and a less brittle structure (Abu-Zurayk et al., 2025).

To confirm the performance of the as-prepared membrane, single and binary dyes are used as samples of synthetic organic pollutants. The reduction performance was tested using the vacuum filtration processes. For single-based dye filtration, single methylene blue (MB) and acid yellow 17 (AY17) dyes were used as the representatives of cationic and anionic dyes, respectively. For the binary dye, the mixed MB-AY17 was observed to investigate how the material reacts to a more complex wastewater system compared to a single-based filtration system. The UV-Vis absorption spectra for MB and AY17 were controlled at 665 nm and 405 nm, respectively, as the maximum absorption response of MB and AY17. Figure 5

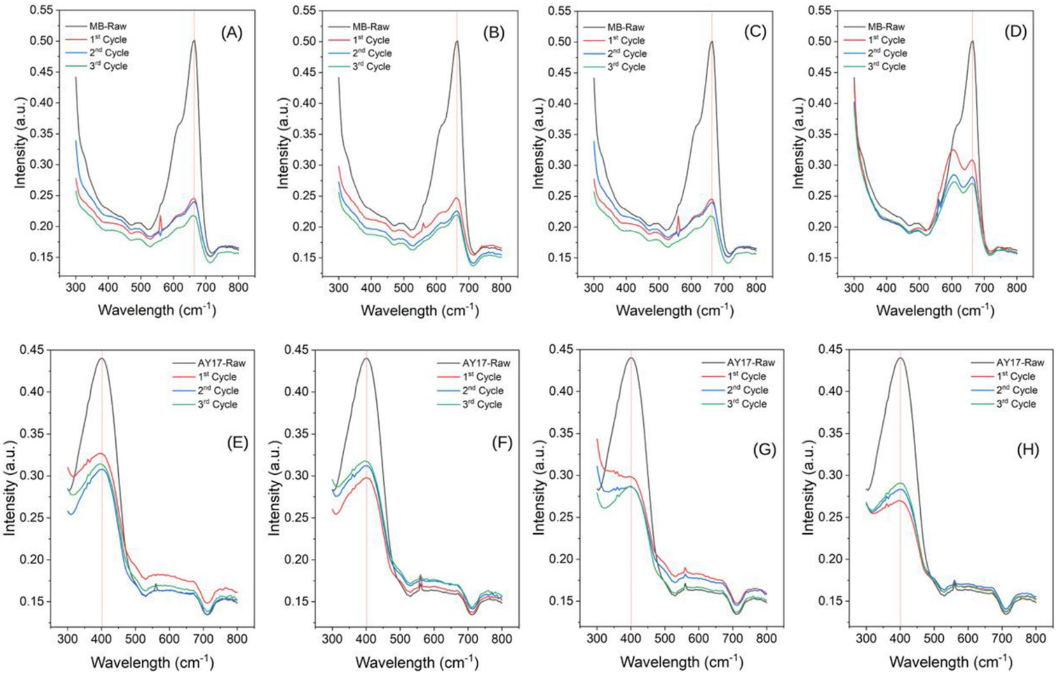

Figure 5. UV-vis adsorption spectrum of methylene blue (MB, top graph) and acid yellow 17 (AY17, bottom graph) before and after vacuum filtration process. (A) and (E) PVDF; (B) and (F) PVDF-TiO2 5%; (C) and (G) PVDF-TiO2 10%; and (D) and (H) PVDF-TiO2 15%

shows the result of single-dye rejection using the as-prepared PVDF and PVDF-TiO_2 membranes.

For the pristine PVDF membrane, both MB and AY17 reduction show a similar pattern, where the PVDF membrane could strongly remove the organic pollutant in the first cycle. The interconnected structure with an air pocket between layers does not reduce the efficiency of the organic pollutant reduction, where the PVDF membrane could effectively contact and adsorb the organic pollutant on the surface of the membrane. The type of dye differentiates the efficiency of membrane rejection, where the PVDF membrane has high adsorption toward MB, as the cationic dyes, whereas the rejection of anionic dye (AY17) provides lower rejection performance. On the PVDF-TiO_2, the addition of TiO_2 does not provide a significant difference in the rejection performance compared to the PVDF membrane, especially on the PVDF with ratios of 5% and 10%. The main difference was seen on the PVDF with a 15% TiO_2 ratio, where the performance is slightly low. The presence of TiO_2 on the surface of the membrane could initiate the electrostatic repulsion with MB molecules due to the same charge surfaces.

The filtration performance was slightly different on the AY17 reduction, where the ratio of TiO_2 differentiated the rejection performance of the membrane. On the first cycle, the PVDF with 15% of TiO_2 has the best rejection performance, followed by PVDF with 5% TiO_2, 10% TiO_2, and the pristine PVDF. The presence of TiO_2, even with agglomerated formation on the surface, could attract AY17 molecules through size exclusion, where incorporating TiO_2 reduces the pore size and attracts more AY17 on the membrane.

On the stability test, the pristine PVDF membrane has good stability on MB molecule, confirmed by the better rejection performance as the membrane is repeatedly used in the second and third cycles. The formation of a cake layer on the surface of the membrane facilitates better rejection on the PVDF membrane, where the type of dyes does not show any significant performance (Agrawal et al., 2025). On the PVDF-TiO_2, the stability test by using the same membrane used for the following second and third cycle is differentiated by the type of dyes, where PVDF-TiO_2 has a better stability toward MB and forms a rejection drop on PVDF with 5% and 15% of TiO_2. The study shows that the TiO_2 attached to the surface of PVDF has low stability toward long-term use as TiO_2 could leach during the second and third cycles (Herrmann et al., 2024). The performance of PVDF with a 10% ratio shows a different route, where both MB and AY17 rejection performance show a similar trend with high stability for the reusability test. The as-prepared membrane could maintain the performance on the second and third cycle, similar to the performance of the pristine PVDF membrane. The result confirms that the well distribution of TiO_2 on the PVDF matrix distributes the adsorption pathways toward the layered membrane, which prevents the formation of a cake layer on the surface of the membrane. The distribution of TiO_2 plays a role in determining the lifespan of the membrane for long-term processes (Damavandi et al., 2023).

The rejection and permeate flux of each filtration process are calculated and shown in Figure 6. The result shows PVDF-TiO_2 10% and PVDF-TiO_2 15% demonstrate the best membrane based on percentages of rejection by removing MB and AY17, approximately 78.89% and 64.31%, respectively, in the first cycle. The high performance of PVDF with a 10% ratio of TiO_2 on MB rejection was due to the well distribution of TiO_2, which lowers the pores on PVDF membranes and facilitates the contact between MB and PVDF active site. On the AY17 removal, the high concentration of TiO_2 in the surface of the membrane plays a role, where PVDF with a 15% ratio of TiO_2 has a high concentration of TiO_2 in the surface. TiO_2 on the surface could facilitate the first landing of AY17 molecules in the first contact during the filtration process. The high rejection of PVDF-TiO_2 10% on MB rejection is supported by the high permeate flux, where the well-distributed TiO_2 on the PVDF matrix does not lower the flux through the membranes, which normally affects the flux due to the hydraulic resistance (Sun et al., 2025). However, the result confirms that the presence of TiO_2 does not significantly improve the rejection performance of PVDF membrane toward MB molecules, where it only affects the permeate flux at the optimum ratio of TiO_2. The presence of TiO_2 only affects the AY17 rejection, since TiO_2 provides a positive charge, which attracts the adsorption process on AY17 on the membrane surface. On the other hand, the addition of TiO_2 lowers the permeate flux in general compared to the pristine PVDF. However, the ratio loading does not differentiate the permeate flux and only affects the rejection performance of the membrane. The result confirms that the

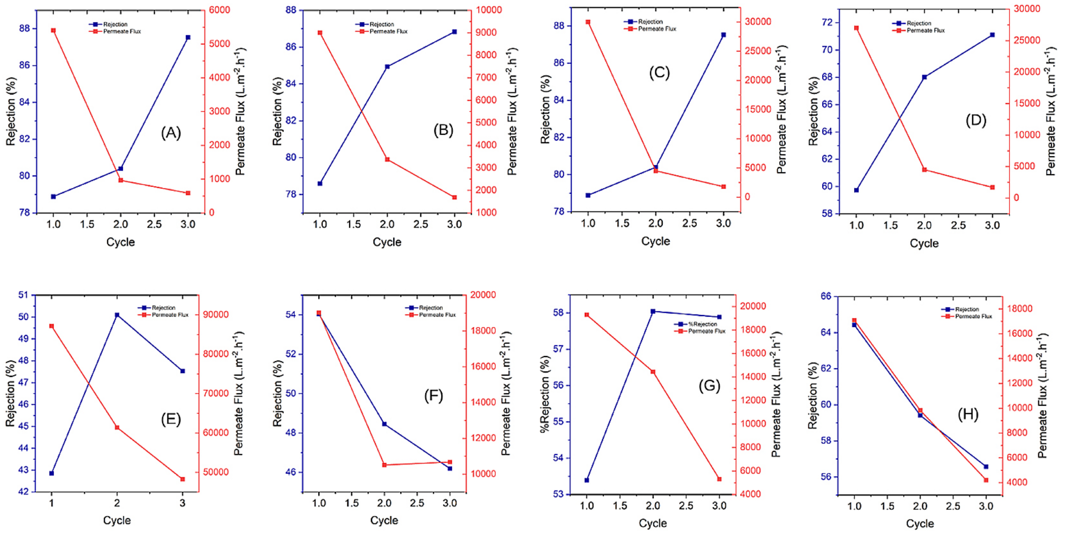

Figure 6. Rejection and permeate flux of PVDF and PVDF TiO_2 with different ratios of TiO_2 over a single-dye system of methylene blue (MB) and acid yellow 17 (AY17) solution on top and bottom graphs, respectively. PVDF (A-E); PVDF-TiO_2 5% (B-F); PVDF-TiO_2 10% (C-G); and PVDF-TiO_2 15% (D-H)

TiO_2 has the role as the hydrophilic agent, which could facilitate more contact between the membrane surface and organic pollutant, where it only provides a significant effect toward the anionic charge-based pollutant.

The stability towards the fouling process was also discussed. After the first filtration, a significant reduction in filtration performance was observed due to the lower membrane stability counters the fouling process. Most of the TiO_2, which plays the role in the electrostatic interaction with AY17, has been occupied in the PVDF matrix, leading to a weak electrostatic interaction between the PVDF surface and the AY17 solution. This confirms that the similar charge on PVDF and PVDF-TiO_2 provides a quick fouling process on the surface of the membrane film, which shows a lower affinity for negative charge pollutants like AY17 over positive charge pollutants like MB. The result confirms that PVDF has a lower stability towards the negative-charge-based pollutant, which provides electrostatic repulsion between the membrane film surface and dye pollutant. The result also confirms that the rejection mechanism on the as-prepared material is based on an adsorption process involves pollutant interacting with PVDF and PVDF-TiO_2, where the high rejection performance was based on the high adsorbed molecules on the material surface, and it was not based on Donnan exclusion, where the same charge as the material surface will be prevented to enter and passing through the pores of material.

To confirm the performance of the as-prepared membrane, the study was continued on the binary dye system using the mixture solution of MB and AY17. The adsorption spectra of the mixed dye are a combination of the individual spectra, with peaks corresponding to both MB and AY17 dyes appearing distinctly, where there is no shifting of the maximum absorption wavelength of each dye, confirming that both dyes do not react together to form the other substrate. After the filtration, the UV-Vis absorption spectra of MB and AY17, shown in Figure 7, exhibit a significant reduction in the mixed dyes solution, confirmed by a lowering of the intensity of the maximum absorption of MB and AY17. Compared to the single-dye filtration, the binary filtration system demonstrates a progressive decrease in rejection performance with successive filtration cycles, compared to the single-dye system, indicative of effective and better stability toward dye removal on complex molecules. Based on UV-Vis absorption, the membranes showed a slight decrease in rejection performance with increasing number of filtrations. It shows that the fouling was slower occurred using a complex dye solution compared to a single dye system. The result also exhibits that PVDF and PVDF-TiO_2 have a strong performance in removing a complex mixture of cationic and anionic dyes from solution, where the size exclusion role dominated in the rejection of pollutants, as expected in a single-dye system. The electrostatic interaction shows a weak effect on the binary

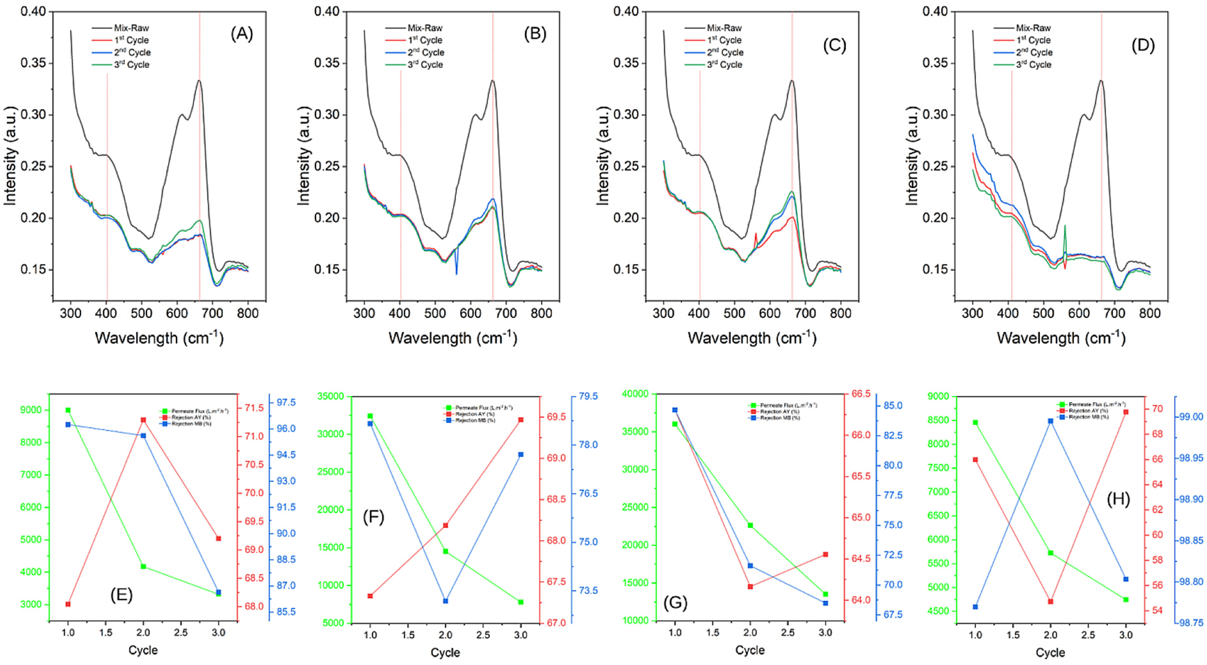

Figure 7. UV-vis adsorption spectrum of mixed dual MB-AY17 dye system on the top section and the rejection and permeate flux for as-prepared membranes on the bottom. (A and E) PVDF; (B and F) PVDF-TiO_2 5%; (C and G) PVDF-TiO_2 10%; and (D and H) PVDF-TiO2 15%

system, since both cationic and anionic dyes are present in the organic pollutant solution. The electrostatic interaction effect could still be seen in the dominance of material removing MB and AY17, where the membrane is more selective toward cationic dyes compared to anionic dyes. To be more specific, the rejection of AY17 in the binary system was relatively lower compared to the single-dye system on AY17, indicating the membrane is getting more selective towards cationic dye in the presence of anionic counterparts, as the dominance of negative charge from the PVDF matrix. Furthermore, the effect of TiO_2 loading affects the permeate flux, where adding the TiO_2 increases the water passed on the membrane. The high permeate flux was due to the change in porosity and hydrophilicity on the membranes.

The filtration test of the as-prepared membrane film exhibits several findings related to the filtration mechanism. The results confirm that the rejection of dyes in a single dye system is primarily governed by the electrostatic interaction between the dyes and the membrane surface charge, where the binary dye system offers a combination of size exclusion and electrostatic attraction. The high MB rejection was because PVDF provides a negative charge surface, which strongly attracts the positive charge on MB molecules. On the contrary, PVDF has a strong electrostatic repulsion towards AY17, which made the rejection efficiency of AY17 filtration low. The finding was consistent with the result reported by Liu, (2025), which performance of PVDF and PVDF-composite based membranes depends on the electrostatic attraction between the dye and the surface charge of the membrane (Liu et al., 2025). The electrostatic attraction will determine the adsorption mechanism of the dye molecule on the surface of the membrane, where the same charge on the membrane surface will pass further through the membranes without proper dye adsorption, resulting in lower rejection performance (Liu et al., 2025). Furthermore, the presence of TiO_2 could provide two main functions. First, the nanosized TiO_2 could fill the micropores on PVDF membranes, which could lower the pore size and enhance the rejection by blocking molecules. Second, the presence of TiO_2 also modifies the surface properties of PVDF, which are reported as naturally hydrophobic to hydrophilic. The hydrophilic properties of the PVDF could enhance the water flux, which could prevent the fouling process (Lu and Li, 2021). Finally, the study proposed that the incorporated TiO_2 on the PVDF matrix is suitable for complex wastewater treatment processes since it could lower the effect of electrostatic interaction and dominate the size exclusion process, which is suitable for real domestic wastewater treatment.

CONCLUSIONS

The fabrication of PVDF and PVDF-TiO2 membranes was successfully conducted in a simple and fast process through a non-solvent induced phase separation technique, where the ratio of TiO2 differentiates the membrane morphology, surface properties, mechanical properties, and membrane performance. In general, all prepared membrane offers a highly porous material which could be used to remove all the organic pollutants from the wastewater. To be more specific, the additional of TiO2 reduced micropore size through pore filling and surface coating, where the excessive amount of TiO2 resulted in agglomeration, which reduced in mechanical strength and performance for cationic dyes due to electrostatic repulsion. Furthermore, the incorporated TiO2 introduced additional positive surface charge, which enhances the attraction toward the negatively charged acid yellow 17, an interaction that is weak in the PVDF membrane. The combination of a reduction in micropore size, the optimum ratio of TiO2 could effectively remove the pollutant through both charge-dye interactions and size-exclusion effects. This combination is beneficial for wastewater treatment, which has more complex pollutants. The combined benefits of improved hydrophilicity, modified surface charge, and enhanced size exclusion create a more robust and efficient separation mechanism suitable for mixed organic pollutants.

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