Tropical Aquatic and Soil Pollution

Research Article
Volume 5(1), 2025, 1–17
https://doi.org/10.53623/tasp.v5i1.586

Fabrication and Characterization of Modified PVDF Membrane Using TiO_2 for Wastewater Containing Paracetamol

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SUBMITTED: 14 January 2025; REVISED: 2 February 2025; ACCEPTED: 4 February 2025

ABSTRACT: Modified membranes have gained significant attention due to their ability to enhance performance. Although membranes modified with TiO_2 nanoparticles have been studied, no research has specifically addressed their effectiveness in removing paracetamol contaminants, despite the widespread use of paracetamol and its potential contribution to increased waste production. Therefore, in this study, polyvinylidene fluoride (PVDF) membranes were modified with TiO_2 nanoparticles, providing new insights into the use of PVDF-TiO_2 specifically for paracetamol wastewater treatment. The results showed that TiO_2 nanoparticle-modified membranes exhibited better performance than unmodified membranes. The unmodified membrane had a lower performance rate (69.18%) compared to membranes modified with titanium isopropoxide (TTIP) at concentrations of 1 M (93.35%) and 0.5 M (90.05%). These results were supported by Scanning Electron Microscopy (SEM) analysis, which revealed that the unmodified membrane had an average pore size of 0.998 µm, whereas the membranes modified with TTIP at 1 M and 0.5 M had average pore sizes of 0.615 µm and 0.791 µm, respectively. The larger pores in the unmodified membrane allowed larger particles to pass through, reducing its filtration efficiency. These findings underscore the potential of TiO_2 nanoparticle-modified membranes for significantly enhancing water purification processes, particularly in the removal of pharmaceutical contaminants like paracetamol. Ultimately, this research could contribute to the development of more effective strategies for managing pharmaceutical waste in water sources, leading to improved environmental protection and public health.

KEYWORDS: Polyvinylidene fluoride membrane (PVDF); titanium dioxide (TiO_2); membrane modification; immersion; pharmaceutical wastewater.

1. Introduction

Pharmaceuticals have grown significantly over the past few decades to enhance the quality of life [1]. Nevertheless, the presence of pharmaceutical components in the environment may pose problems and threats [2, 3]. A wide range of pharmaceutical contaminants (PCs) can reach surface water, marine environments, and estuaries, contaminating freshwater ecosystems and drinking water [4]. Studies have shown that paracetamol, even at a low concentration of 0.063 ng/g in maize grain and root, negatively affects consumers. Another study found that an accumulation of 5 mg/l in *Lactuca sativa* L. led to oxidative stress [5]. Additionally, exposure to paracetamol can cause water contamination and interfere with aquatic life. Paracetamol has been shown to negatively affect the survival rates of *Danio rerio* [6], disrupt redox homeostasis in *Daphnia magna* [7], and induce oxidative stress in *Oncorhynchus mykiss* [8]. There is a potential risk of non-target humans consuming paracetamol through plants and fish, representing a global threat of pharmaceutical resistance. This makes the removal of paracetamol from the environment a critical issue.

The development of membranes over the past few decades has led to significant advantages and widespread industrial applications. Membranes have emerged as one of the most effective technologies due to their efficiency, rapid processing, lower energy requirements, small footprint, and ease of operation [9, 10]. They have been widely used in water and wastewater treatment, biotechnology, food and beverage industries, brine management, desalination, and pharmaceutical wastewater treatment [11–14]. Paracetamol can be removed using several techniques, including adsorption on porous carbon material derived from argan paste cake (up to 84%) [15], degradation by a 100% visible-light-irradiated Pd-BiVO4 catalyst [16], and adsorption on activated carbon (AC) followed by catalytic wet air oxidation (up to 98%) [17]. These techniques could be applied to paracetamol elimination. Nonetheless, they have certain limitations, such as adsorption percentages lower than 80% and high energy requirements for the photocatalytic process. In addition, these techniques are not simple procedures for paracetamol removal. Therefore, membrane application is promising, as it offers simple preparation procedures and effectively removes paracetamol from water [3].

Common materials used for nanomembranes include cellulose [18], chitosan [19], polyethylene (PE) [20], polyether sulfone (PES) [21], polyethylene terephthalate (PET) [22], polypropylene (PP) [23], polysulfone (PS) [24], polytetrafluoroethylene (PTFE) [25], and polyvinylidene difluoride (PVDF) [26]. Some materials, such as cellulose and chitosan, are often used due to their low cost and biodegradable properties. However, PVDF offers a combination of advantages. A PVDF-based membrane was researched and developed in this study. Compared to cellulose, which degrades easily and swells in water, and chitosan, which is prone to mechanical failure, PVDF exhibits low surface energy, high mechanical strength, chemical resistance, and stability under various conditions. PVDF is a highly versatile and robust material, making it an excellent choice for ultrafiltration membranes. Several industrial applications have been explored and implemented using this material due to its simplicity and thermal resistance [27–30]. However, membrane applications are limited by antifouling properties, which reduce membrane performance and lifespan in different industries [31]. Fouling occurs when membrane pores become blocked during filtration. Various approaches have been employed to minimize and control fouling due to its impact on the performance and cost-effectiveness of polymeric membrane filtration. Optimization of operating conditions, chemical treatments, and hydraulic techniques can be used to remove or eliminate fouling.

Despite these efforts, there is still potential for further development and modification. Several studies have shown that surface modification may be an effective fouling control strategy.

Surface modification of membranes with potential materials can enhance the surface area, improve performance, and prevent membrane fouling [32]. Surface modification is generally regarded as a mechanical approach with several advantages, including enhanced hydrophobicity, antifouling properties, ease of operation, improved membrane wetting, and cost-effective implementation [33]. Increasing hydrophobicity in membrane synthesis is essential for effectively reducing paracetamol in pharmaceutical wastewater. Additionally, surface modification does not alter the membrane's mechanical properties. Various inorganic additive materials have been used for polymeric membrane modification and coating, including carbon nanotubes (CNTs) [34, 35], graphene oxide (GO) [36, 37], nanodiamond (ND) [38], silica (SiO_2) [39, 40], silver (Ag) nanoparticles [41, 42], titanium dioxide (TiO_2) [43, 44], and zinc oxide (ZnO) [45, 46]. Among these, TiO_2 nanoparticles have been widely studied due to their availability, chemical stability, high physical properties, non-toxicity, affordability, antifouling capabilities, and biocompatibility [49]. TiO_2 also has a large surface area and acts as an effective oxidizer. Incorporating TiO_2 nanoparticles into membranes enhances thermal stability, mechanical strength, and overall performance [50].

In membrane manufacturing, these strategies can be achieved by depositing inorganic materials onto the membrane surface through coating and grafting or dispersing them in the polymer solution via blending [51-53]. The blending approach is simple but limits inorganic particulate loading. A widely used method for fabricating membrane surfaces is immersion, which involves submerging the material in a coating solution. This technique is relatively simple and can be scaled from laboratory experiments to industrial production. It allows for uniform coating or modification of membrane surfaces at an affordable cost. However, membrane properties, morphology, and performance are significantly influenced by the conditions under which they are formed [54]. Recent advancements in nanotechnology have led to increased interest in incorporating modified nanoparticles into membranes. This study aimed to present a simple and reliable technique for removing paracetamol from water using a membrane enhanced with TiO_2 nanoparticles. TiO_2 was synthesized using TTIP as a precursor agent and Pluronic F127 as a templating agent. The TiO_2 was then coated onto polyvinylidene difluoride to modify its surface through immersion. The modified membrane was characterized using SEM, Atomic Force Microscopy (AFM), Fourier-Transform Infrared Spectroscopy (FTIR), and a contact angle test. A UV-visible spectrophotometer was used to measure paracetamol removal.

2. Materials and Methods

2.1. Materials.

The materials used in this study, including the commercial 0.45 μm PVDF flat-sheet membrane, were purchased from Membrane Solution. The chemicals, such as TTIP (98%), Pluronic F127, 2,4-pentanedione, and perchloric acid (70%), were supplied by Sigma–Aldrich. Ethanol was obtained from the marketplace.

2.2. Synthesize process of TiO_2 nanoparticles.

Chemical compounds were calculated based on their molarity to determine their volume. The molar ratio of each component was as follows: TTIP: 2,4-pentanedione: $HClO_4$: H_2O: ethanol = 1: 0.5: 0.5: 0.45: 4.76. The synthesis of TiO_2 nanoparticles was carried out by mixing ethanol, 2,4-pentanedione, perchloric acid, TTIP, and ultrapure water. The solution was stirred at room temperature for one hour at 650 rpm to ensure homogeneity, thereby accelerating the chemical reaction and mass transfer. After stirring, the solution turned orange-yellow due to the reaction between TTIP and 2,4-pentanedione.

2.3. Preparation for a templating agent.

The templating agent, Pluronic F127, was dissolved in anhydrous ethanol at 50°C to prepare a separate solution. In solvents, Pluronic F127 dissolves more quickly, allowing surfactants to disperse more easily. A uniform distribution of the material in the solution was achieved after stirring the mixture at 650 rpm for one hour. The purpose of the templating agent was to maintain the final material's structure during mixing.

2.4. Preparation of TiO_2 precursor sol.

TiO_2 precursor sol was prepared by mixing the templating agent solution with the TiO_2 sol-gel solution. The two solutions were mixed separately for one hour, then combined and stirred again for another hour at 650 rpm. This process facilitated the formation of the nanoparticles' morphological structure. The final mixed solution was referred to as the TiO_2 precursor sol solution.

2.5. Membrane surface modification.

Following the preparation of the TiO_2 precursor sol, PVDF membranes were modified using the immersion method. Two different TTIP solutions (1M and 0.5M) were prepared in a beaker glass placed on a magnetic stirrer and stirred for five minutes to ensure homogeneity and uniform particle distribution throughout the membrane coating process. The membranes were then dipped and immersed in the solution for one hour with the modifying agent, allowing TiO_2 to form a new layer on the membrane surface. Afterward, the modified membranes were placed in Petri dishes and dried at 150°C for 16 hours, facilitating solvent evaporation and enhancing the bond strength between the nanoparticles and the membrane. These membranes were labeled as M01 for solution 1 and M02 for solution 2, while M00 referred to the pristine membrane.

2.6. Membrane characterization.

2.6.1. Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX).

A SEM was used to examine the surface and cross-sectional morphology of the membranes. The JSM-6510 LA was employed to analyze the surface structure of both the pristine and modified membranes with TiO_2 coatings. Software was used to evaluate the SEM images and estimate pore size distributions. Additionally, energy dispersive X-ray (EDX) analysis was conducted to assess the presence and dispersion quality of TiO_2 nanoparticles on the modified membrane surface.

2.6.2. FTIR.

A Perkin-Elmer UATR Spectrum Two was used to characterize the chemical groups present in the TiO_2 nanoparticles and the crystal structure of the prepared membranes through FTIR.

2.6.3. Contact angle.

Each membrane's surface properties were evaluated using contact angle (CA) measurements. The optical contact angle (OCA 25) was employed to measure the water contact angle on each membrane surface. The contact angle measurement determined whether the membrane was hydrophobic or hydrophilic by assessing the interaction between the membrane surface and the water meniscus.

2.7. Membrane performance.

Membrane filtration performance was evaluated using a dead-end filtration system at a constant flow rate. As the membrane surface compacted, fluxes gradually decreased during filtration before stabilizing. A solution containing 1 g/L of paracetamol was used to assess paracetamol rejection by each membrane. The concentrations of both feed and permeate solutions were determined using a UV-visible spectrophotometer at a wavelength of 243 nm. The effective membrane area used in this study was 0.00173 m². Membrane rejection was calculated using the following equation:

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

Where C_{final} is the permeate concentration (g/l), $C_{initial}$ is the feed concentration (g/l), and R is the paracetamol rejection rate (%).

3. Results and Discussion

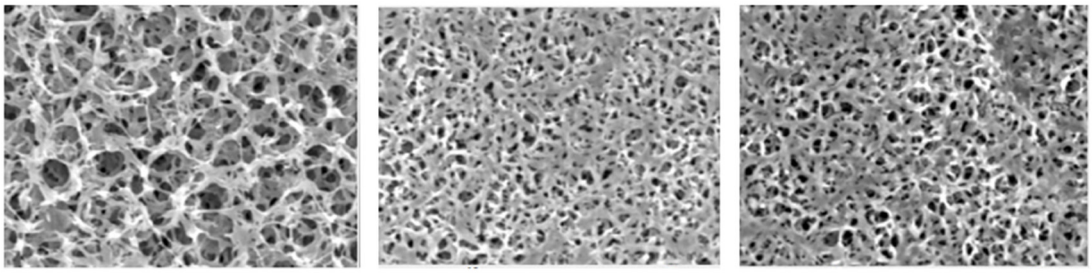
3.1. Membrane characterization.

3.1.1. SEM analysis.

SEM was used to characterize pristine and modified membranes, providing detailed information on membrane surface structure and morphology, including pore size. SEM analysis was conducted before and after membrane modification to observe changes in surface characteristics. The results of SEM imaging at a magnification of 3,000x are shown in Figure 1, where (a) represents the pristine membrane (M00), and (b) and (c) depict modified membranes (M01 and M02), respectively.

As observed in Figure 1, modification with TiO_2 resulted in noticeable changes in membrane surface morphology compared to the pristine membrane (M00). The PVDF-TiO_2 membranes (M01 and M02) exhibited larger pore sizes, whereas the pristine membrane had smaller pores. The average pore size of the pristine PVDF membrane was approximately 0.998 µm, while the modified membranes showed reduced pore sizes: M01 at 0.615 µm and M02 at 0.791 µm. These findings indicate that incorporating TiO_2 nanoparticles into the PVDF membrane influences pore size distribution. Larger pores, such as those in M00, allow greater

flux and permeate flow but also increase susceptibility to fouling. Surface roughness is another critical factor, as membranes with fewer pores tend to be smoother, reducing the likelihood of particle accumulation and fouling. A smoother membrane surface enhances long-term stability by minimizing performance degradation over time. Additionally, SEM observations provide insight into membrane wetting properties. Smaller pore sizes correlate with increased hydrophobicity, as denser membrane surfaces exhibit reduced wettability.



(a) (b) (c)

Figure 1. SEM images of the pristine and modified membrane **(a)** M00, **(b)** M01, **(c)** M02 with magnification 3.000x.

Figure 2 presents the pore size distribution of PVDF membranes, confirming that TiO_2 incorporation significantly alters pore structure. Experimental results indicate that using a 1M TTIP solution yields optimal modification results for PVDF membranes. This concentration has been widely used in prior studies [56–58], allowing for the formation of uniform layers and pores without undesirable structural changes.

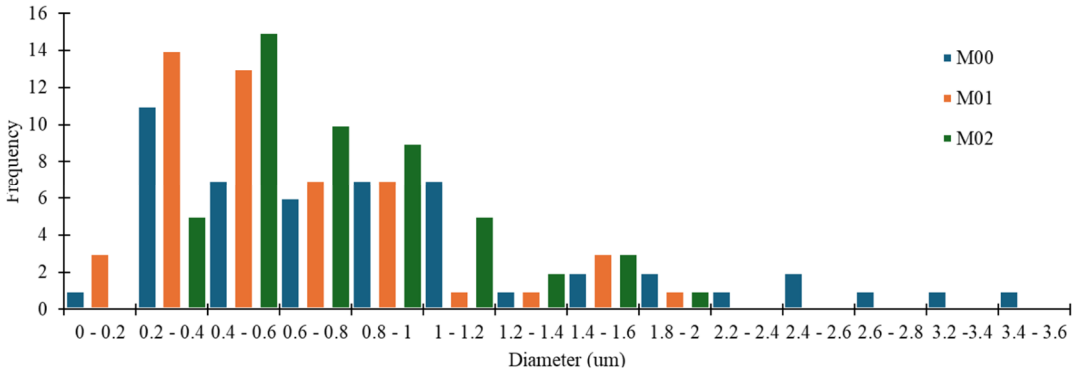


Figure 2. Pore size distribution of PVDF Membranes.

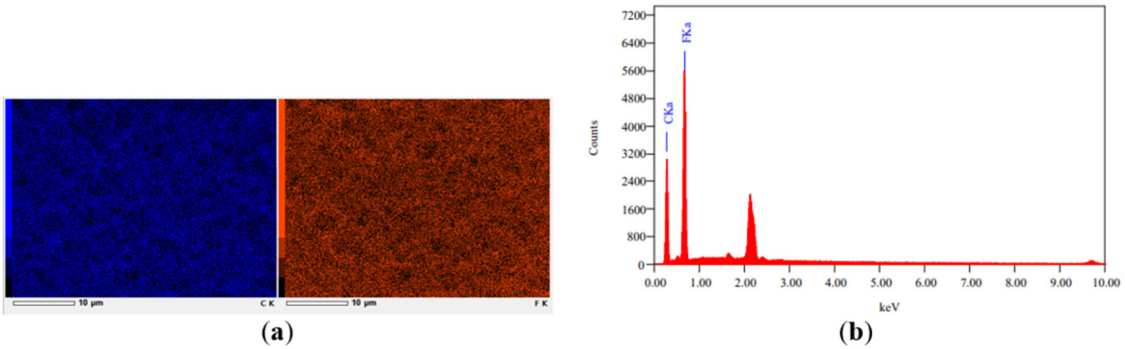
3.1.2. EDX-Mapping analysis.

The characterization and mapping using the EDX technique showed the elemental components of a material in the pristine and modified membranes. This analysis can perform qualitative analysis. Figures 3-5 show the EDX spectra of the membrane, the distribution of material and its changes in elemental composition. The material has a homogeneous distribution of the fluorine (F), oxygen (O), carbon (C), and titanium (Ti) elements. The results of the pristine PVDF membrane, as represented in Figure 3, consist mainly of carbon and fluorine. The bond between the carbon and fluorine atoms is strong. As of M00, neither O nor Ti appear on the membrane. The presence of new Ti-element bonds from TiO_2 nanoparticles on the membrane surface decreases the C and F content in the pristine PVDF membrane. The Ti elements also

bind to the F element to form a new Ti–F bond, reducing the F content on the PVDF membrane surface [59]. As shown in Table 1, the modification decreases the carbon content from 46.68% (M00) to 38.15% (M01) and 32.67% (M02) in mass ratio, with a sharp reduction in fluorine content from 53.52% to 6.73% (M01) and 10.03% (M02). Meanwhile, after modification with TiO_2 nanoparticles, analysis confirmed the presence of titanium (Ti) and oxygen (O), suggesting that the PVDF-TiO_2 material was successfully modified. M01, prepared using a 1M TTIP solution, has a titanium and oxygen mass ratio of 49.53% and 5.59%, respectively. In contrast, for M02, which was prepared using a 0.5M TTIP solution, the oxygen content decreased to 46.36%, while the titanium mass ratio increased to 10.94%. A higher Ti mass ratio results in stronger bonding between F and Ti elements. The O element from TiO_2 nanoparticles contributes to membrane stability and bond strength.

Table 1. Elemental analysis of EDX

Membrane	Carbon (C)	Fluor (F)	Oxygen (O)	Titanium (Ti)
M00	46.68%	53.52%	-	-
M01	38.15%	6.73%	49.53%	5.59%
M02	32.67%	10.03%	46.36%	10.94%



(a) **(b)**

Figure 3. Mapping (**a**) and EDX Spectra (**b**) of Pristine PVDF Membrane (M00).

EDX analysis revealed a difference in Ti content between the M01 and M02 membranes, which is related to the filtration process. A peak observed at an energy of 4.5 keV corresponds to titanium (Ti) and was not detected in the pristine membrane [57]. Since M02 contains a higher Ti content, it is more stable, more resistant to fouling, and performs better as a membrane. Titanium, particularly in the form of titanium dioxide (TiO_2), is known for its hydrophobic properties, which can aid in rejecting polar contaminants. However, the filtration results show that M01 exhibits a higher rejection rate, reaching 93%, compared to 90% for M02. While TiO_2 enhances membrane stability and fouling resistance, pore size also plays a crucial role in filtration. According to SEM results, M01 has a smaller pore size, making it more effective at retaining contaminants and improving paracetamol rejection. Although M02 has a higher Ti content, its larger pores make it less effective at retaining paracetamol contaminants.

The distribution of C, F, O, and Ti elements on the M01 and M02 membranes varies significantly. Figure 4a shows that in the M01 membrane, these four elements (C, F, O, and Ti) are more homogeneously distributed. Differences in nanoparticle concentration affect the homogeneity of element distribution in the membranes. As shown in Figure 5a, the M02 membrane exhibits a more heterogeneous element distribution, with uneven concentrations in certain areas. The graphs in Figures 4b and 5b illustrate the variation in Ti element height.

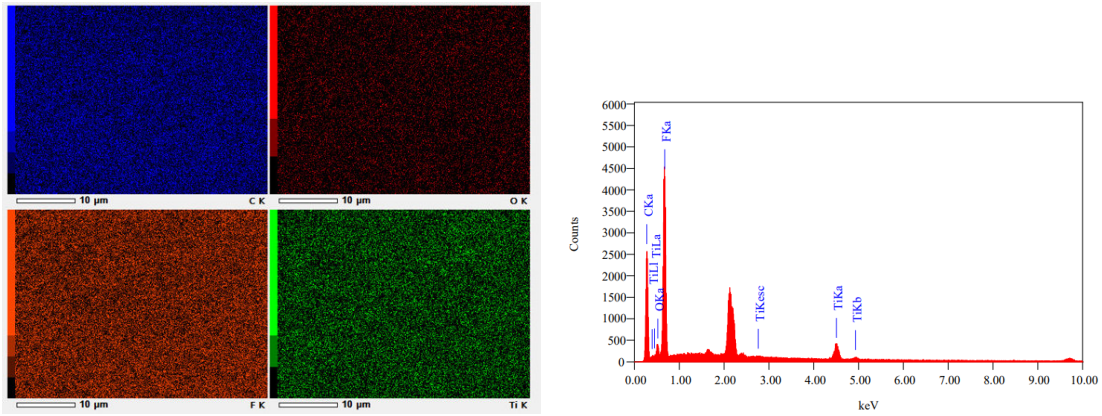


Figure 4. Mapping (**a**) and EDX Spectra (**b**) of Modified PVDF Membrane (M01)

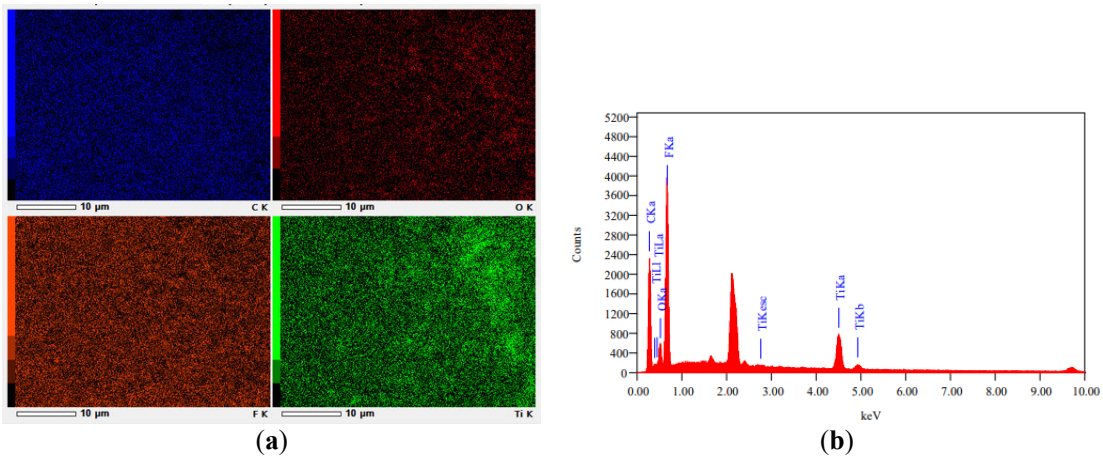


Figure 5. Mapping (**a**) and EDX Spectra (**b**) of Modified PVDF Membrane (M02)

3.1.3. FTIR Analysis.

FTIR analysis was used to characterize the membranes, determining their surface functional groups and changes during modification. PVDF exhibits different crystal phases: alpha (α), beta (β), and gamma (γ), with the α and β phases influencing its behavior. PVDF is known for its stable physical, chemical, and mechanical properties. The α-phase of the PVDF membrane is identified in the spectrum at 975.18 cm^{-1} [60], while the β-phase, which has strong polarity, appears at 1289.28 cm^{-1} [61]. The functional groups of TiO_2 are represented in Figure 6. In the pristine PVDF membrane, a strong absorption peak at 3415.19 cm^{-1} corresponds to the vibration of the hydroxyl (O-H) functional group [61]. High transmission (%) values indicate low O-H bond intensity in M00. In contrast, M01 and M02 exhibit lower transmission, suggesting a higher O-H bond presence. After surface modification, changes in the intensity of these peaks indicate that TiO_2 nanoparticles were successfully incorporated into the pristine membrane. The absorption peaks of the O-H functional groups in modified membranes M01

and M02 show decreased intensity compared to M00, indicating that the TiO_2 nanoparticle coating reduces water adsorption on the membrane surface. This reduction in O-H functional groups makes the membrane surface more hydrophobic, which influences contaminant rejection during filtration. Hydrophobic membranes tend to repel hydrophilic or polar contaminants, such as paracetamol, improving filtration performance.

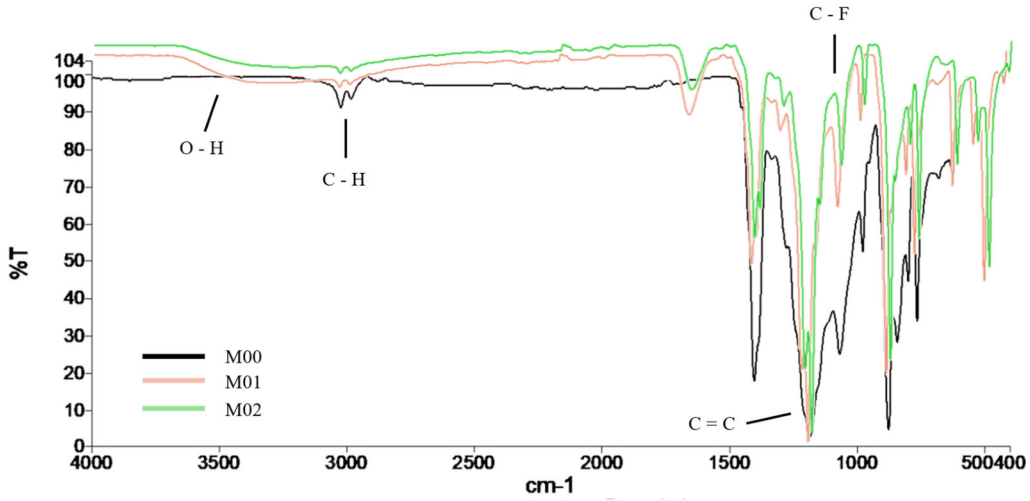


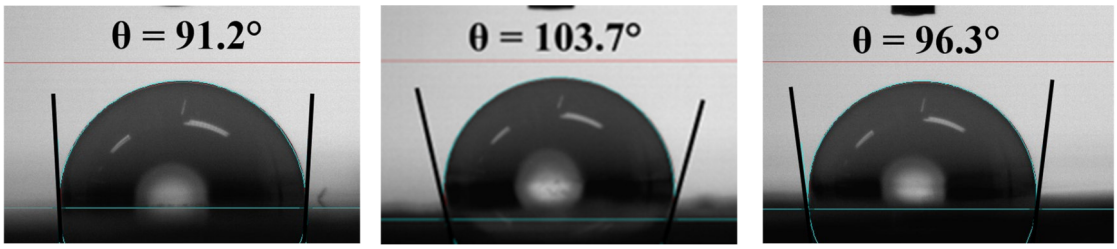
Figure 6. FTIR characterization results for membranes M00, M01, and M02.

In M00, the absorption peak at 2984.80 cm^{-1} is attributed to the C-H functional group with an aliphatic component. The C-H functional group is typically observed in the spectrum range of 2988–3000 cm^{-1}. In M01 and M02, the C-H functional group appears at 2985.88 cm^{-1} and 3025 cm^{-1}, respectively. The stronger C-F functional group, with an absorption peak at 1064.92 cm^{-1} in M00, exhibits lower intensity than in M01 and M02. In both modified membranes, this peak shifts slightly to 1065 cm^{-1} with higher transmission. Stretching in the C-F functional group influences membrane characteristics such as pore size distribution and surface roughness, as indicated by SEM analysis. The FTIR spectrum of the PVDF membrane highlights the interaction between polymer molecules and nanoparticles by analyzing the absorption bands of each functional group and the PVDF crystal phases. Pure PVDF membranes consist of strong carbon-fluorine (C-F) polymer bonds, resulting in low transmission values. Increasing the TTIP concentration strengthens the bond between carbon and fluorine elements in the membrane. M01 exhibits a lower C-F transmission value than M02, indicating stronger bonding, which also affects membrane roughness.

3.1.4. Contact angle analysis.

Membrane hydrophobicity can be determined by measuring the contact angle. Figure 7 compares the contact angles of pristine and modified membranes. All three membranes exhibit hydrophobic characteristics, as their contact angle values exceed 90°. As shown in Figure 7a, the pristine membrane, before modification with TiO_2, had a contact angle of 91.2°. Meanwhile, Figures 7b and 7c display the contact angles of the modified membranes, which increased after TiO_2 incorporation. Among them, the M01 membrane exhibited the highest hydrophobicity, with a contact angle of 103.7°, while the M02 membrane had a contact angle of 96.3°. Previous research has also reported an increase in membrane hydrophobicity with the addition of TiO_2 [62]. The increase in membrane hydrophobicity after modification is attributed

to the interfacial bonding between TiO_2 and PVDF. TiO_2 interacts with the fluorine groups on the PVDF surface, which are non-polar, reinforcing the membrane's hydrophobic structure. Additionally, TiO_2 alters the electron distribution on the PVDF surface, modifying its polarity and reducing its attraction to air molecules. This further enhances the membrane's hydrophobic properties. Membrane surface hydrophobicity significantly influences filtration performance. Polar compounds such as paracetamol form hydrogen bonds with water, making them more likely to interact with hydrophilic surfaces. However, more hydrophobic membranes, such as the modified M01 and M02 membranes, reduce the attraction between the membrane and polar compounds. As a result, polar molecules like paracetamol have greater difficulty adsorbing onto or permeating through the membranes. Hydrophobic membrane surfaces not only enhance contaminant rejection but also help reduce membrane fouling.



(a) (b) (c)

Figure 7. Contact angle results of PVDF membrane **(a)** M00, **(b)** M01, and **(c)** M02.

3.1.5. Water uptake analysis.

A membrane's water uptake characteristic is a key factor in determining its performance, particularly in filtration applications. Higher water uptake allows for faster and more efficient water flow during filtration. The water uptake measurement results indicate that the modified membranes differ significantly from the pristine membrane. Both M01 (271%) and M02 (262.7%) exhibit higher water uptake values compared to M00 (171.3%), suggesting an enhanced capacity for water absorption. Water uptake also influences the rejection rate; membranes with higher water uptake tend to achieve better rejection of polar compounds such as paracetamol. By absorbing more water, these membranes accumulate fewer contaminants on their surface, reducing fouling and improving rejection efficiency.

3.2. The performance of the membranes with artificial feed waters.

The flux and rejection performance of the membranes was evaluated using a dead-end filtration system. Experiments were conducted with artificial wastewater at a concentration of 1g/L, a commonly used standard in laboratory-scale studies and pharmaceutical waste simulations. This concentration is frequently cited in the literature as a benchmark for testing filtration efficiency and compound removal in wastewater, allowing for the evaluation of membrane performance under controlled conditions.

3.2.1. Analysis of membranes flux.

Figure 8 presents the water flux of both pristine and modified membranes. As the filtration time increases, the formation of a cake layer on the membrane surface reduces the difference in flux values. Over time, particles from wastewater accumulate on the membrane, leading to

a decline in flux. The modified membrane, M01, demonstrates the highest flux, reaching 7707 L/m²h. The graph indicates that membrane modification alters surface morphology and properties, contributing to variations in flux values. Notably, the flux of the pristine M00 membrane is higher than that of M02, which SEM analysis attributes to M00's larger pore size. Another critical factor affecting membrane flux is operating pressure. The three membranes exhibit different permeate fluxes due to variations in pressure. The difference in pressure between the two sides of the membrane generates the driving force required for filtration. The pristine M00 membrane operates at a high pressure of -175 kPa, whereas M01 and M02 require significantly lower pressures of -55 kPa and -24 kPa, respectively, during the rejection process. The filtration of pristine PVDF membranes thus demands more energy to pump the feed solution compared to modified membranes.

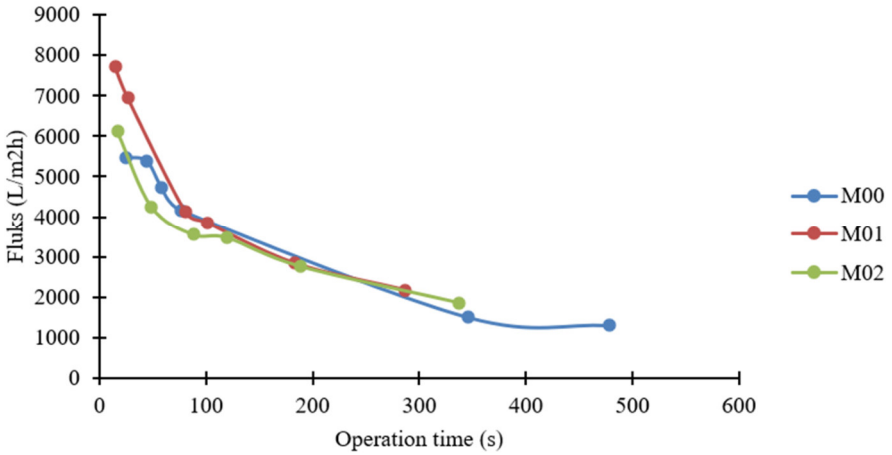


Figure 8. Permeate flux.

3.2.2. Analysis of membrane rejection.

All membranes were tested using dead-end filtration. The highest rejection percentage (%R) was recorded as follows: M00 at 69.18%, M01 at 93.35%, and M02 at 90.05%. The increase in rejection efficiency over time is illustrated in Figure 9. Several factors contribute to this improvement, including pressure, wastewater concentration, and membrane properties. Activating or conditioning the membrane surface at the beginning of the filtration process can enhance its performance over time. During the initial stages of filtration, the rejection rate gradually stabilizes, leading to increased efficiency. However, this improvement is temporary, as fouling eventually becomes more significant and may reduce membrane performance over extended filtration durations. The UV-Vis spectrophotometer was used to measure the absorbance of the resulting permeate. Paracetamol has a maximum absorption wavelength of 243 nm, which was used in this study to calculate its concentration.

M01 demonstrated good performance, including high flux and high paracetamol rejection. This high flux indicates the membrane's ability to transmit large volumes of permeate in a short period, which is crucial for high-capacity applications. Additionally, the strong rejection suggests that the membrane can effectively retain paracetamol contaminants. M01's high flux and efficient rejection make it a promising membrane for paracetamol removal in pharmaceutical wastewater. After the membrane was coated with TiO_2 nanoparticles, characterization tests and previous studies showed that the coated membrane's pore size affects both its selectivity and the efficiency of the filtration process. Paracetamol forms a bond with

the PVDF monomer (-CH_2-CF_2) at the hydroxyl group, which has polar properties that interact with the PVDF membrane's hydrophobic surface. Several strategies can be used to optimize PVDF-TiO_2 membranes for industrial-scale wastewater treatment, particularly for removing pharmaceutical contaminants. Combining PVDF-TiO_2 membranes with other technologies can help reduce contamination and increase efficiency in industrial applications. To be suitable for industrial-scale use, membranes must be durable, efficient, and cost-effective. It is essential to ensure that PVDF-TiO_2 membranes are stable and facilitate large-scale production. Testing membrane performance under actual wastewater conditions will provide a better understanding of their effectiveness in treating pharmaceutical contaminants.

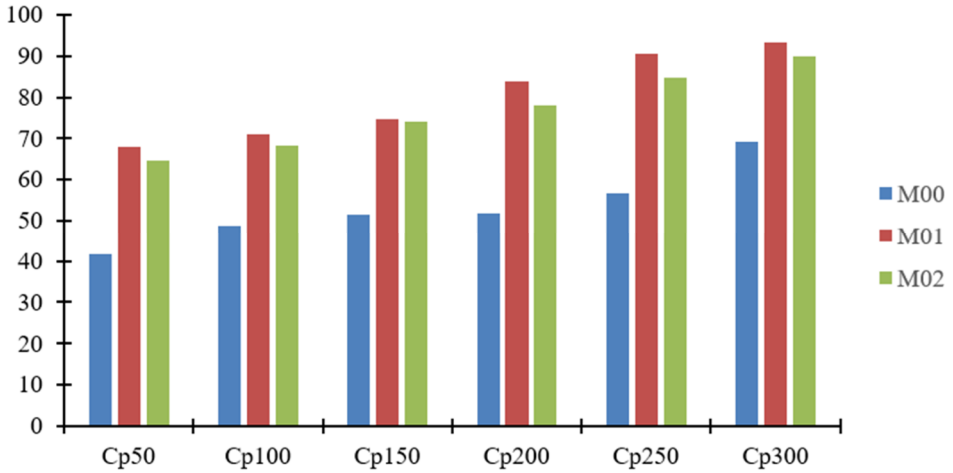


Figure 9. Removal efficiency of M00, M01 and M02.

4. Conclusions

This study presents the fabrication and characterization of PVDF membranes with TiO_2 nanoparticles via the immersion method. SEM, FTIR, and contact angle data confirmed the successful modification of TiO_2 nanoparticles onto the membrane surface. The PVDF-TiO_2 membrane demonstrated excellent paracetamol rejection and antifouling performance compared to the pristine membrane. The integration of PVDF and TiO_2 resulted in more effective and durable polymer membranes. Based on these findings, TiO_2 nanoparticle-modified membranes represent an effective strategy for managing pharmaceutical waste in water sources. Notably, while previous studies have discussed membrane modification using TiO_2, its applications have been limited to general purposes and have not been explicitly studied for paracetamol contamination.

Acknowledgments

The authors desire to appreciate the research funding granted by the Ministry of Education, Culture, Research and Technology Republic of Indonesia, for the financial support for this research through the postgraduate research scheme 2023 with contract no: 1975/PKS/ITS/2023.

Author Contribution

Conceptualization: Adhi Yuniarto, Isti Faizati Zainiyah; Methodology: Adhi Yuniarto; Data Collection: Isti Faizati Zainiyah, Intania Ika Fairuzi; Data Analysis: Isti Faizati Zainiyah,

Intania Ika Fairuzi, Bowo Djoko Marsono, Ipung Fitri Purwanti; Writing: Isti Faizati Zainiyah, Bowo Djoko Marsono, Ipung Fitri Purwanti; Supervision and Funding: Adhi Yuniarto.

Competing Interest

All authors should disclose any financial, personal, or professional relationships that might influence or appear to influence their research.

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