



Research Article

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Preparation and Characterization of PVDF/NCs/TiO₂ Photocatalytic Membrane for Rhodamine b Dye Degradation

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Abstract

This study focuses on the synthesis and characterization of polyvinylidene fluoride (PVDF) membranes enhanced with nanocellulose (NCs) and TiO₂ for the removal of rhodamine b (RhB) dye. PVDF/NCs/TiO₂ membranes were fabricated with varying TiO₂-P25 contents (0.18, 0.36 and 0.72wt%). Initially, PVDF and NCs were separately dissolved in dimethylacetamide (DMAc), followed by the addition of TiO₂-P25 nanoparticles. The resulting solutions were cast into membranes using the doctor blade technique and dried at room temperature. Fourier transform infrared spectroscopy (FTIR) confirmed the successful incorporation of both NCs and TiO₂ into the PVDF matrix. Water flow rate measurements were conducted to assess membrane permeability. Photocatalytic activity was evaluated using RhB dye solutions at pH 4, 7, and 10. The results indicated that membranes containing NCs and TiO₂ exhibited superior water permeability and dye removal efficiency compared to pure PVDF membranes. These findings suggest that PVDF/NCs/TiO₂ membranes are promising candidates for the treatment of dye-contaminated wastewater.

Keywords: PVDF/NCs/TiO₂, Photocatalytic Membrane

1. Introduction

Water pollution caused by synthetic dyes from textile and industrial effluents has become a serious environmental issue due to the high stability, toxicity, and resistance to biodegradation of these compounds. Among various treatment technologies, photocatalysis using semiconductor materials has emerged as an effective and environmentally friendly method for degrading organic pollutants (1). In particular, titanium dioxide (TiO₂) is one of the most widely studied photocatalysts due to its high oxidative power, chemical stability, low toxicity, and affordability (2-3). However, the practical application of TiO₂ nanoparticles in suspension systems often faces challenges such

as agglomeration and difficulty in separation and recovery. To overcome these limitations, TiO₂ has been incorporated into polymeric membranes to form photocatalytic membranes, which combine filtration and photocatalytic degradation in a single step (4). This hybrid approach allows for continuous treatment, improved surface contact between pollutants and photocatalyst, and easier recovery of the catalyst. Among various polymers, polyvinylidene fluoride (PVDF) is widely used for membrane fabrication due to its excellent chemical resistance, thermal stability, and mechanical strength (5-6). Nonetheless, the dispersion of TiO₂ particles within the PVDF matrix remains a challenge, often leading to reduced

photocatalytic activity. Recent research has explored the use of nanocellulose (NCs), a biodegradable, renewable nanomaterial with a high surface area and abundant hydroxyl groups, as a means to enhance TiO₂ dispersion and membrane performance (7-8). NCs can serve as a stabilizing scaffold for TiO₂ nanoparticles and improve membrane porosity and mechanical properties. Additionally, its surface functionality can facilitate interactions with both the polymer matrix and photocatalyst. Previous studies, such as the work by Yin et al. (2021) (9), demonstrated the fabrication of PVDF/TiO₂ coreshell fibrous membranes for the degradation of methyl orange. The results showed promising photocatalytic activity, but limitations in nanoparticle agglomeration and membrane structural integrity highlighted the need for further optimization, particularly with the incorporation of support materials like NCs. In this study, we aim to develop a PVDF/NCs/TiO₂-P25 photocatalytic membrane for the efficient removal of RhB, a model dye pollutant commonly found in wastewater. The TiO₂-P25 content is varied to investigate its influence on membrane performance. The membranes are characterized using Fourier transform infrared to examine surface functional groups, water flow rate analysis to evaluate permeability, and photocatalytic tests under different pH conditions to assess RhB degradation and filtration efficiency.

2. Materials and Experiment

2.1 Materials and Experiment

To prepare the membrane, 2.3 ml of PEG-600 were dissolved in DMAc using a magnetic stirrer at 120°C for 30 min until a homogeneous solution was obtained. Then 1 g of NCs was added under magnetic stirrer. After complete mixing, 0.18 g of TiO₂-P25 were added with magnetic stirrer until homogeneity was achieved. Then, the temperature was reduced to 60°C, and 7.5 g of PVDF were added under magnetic stirrer for 3h. The resulting solution was cast into molds in volumes of 2.5 ml, then cooled in water at room temperature until dried as shown in Figure 1. All films were stored in a refrigerator. The thickness of film was measured and the average thickness is ~0.75 mm. The same procedure was repeated with modified amounts of 0.36 and 0.72 wt% of TiO₂.

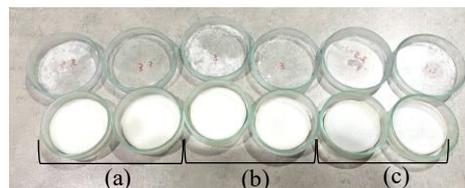


Figure 1 (a) PVDF/NCs/TiO₂ 0.18wt%
(b) PVDF/NCs/TiO₂ 0.36wt%
(c) PVDF/NCs/TiO₂ 0.72wt%

2.2 Characterization of prepared membrane

The functional groups present in the synthesized film were analyzed using a Fourier transform infrared (FTIR) spectrometer. The photocatalytic activity and dye adsorption efficiency of the film under UV and visible light were evaluated using RhB dye as a model contaminant.

2.3 Water flow rate test

Water flow rate test through different membrane thickness First, a film with a thickness of 0.75 ml was placed in the filter section of a filtration apparatus. Then, 100 ml of water were added, and a vacuum pump was activated to allow the water to pass through the film. The volume of water that flowed through the membrane within one minute was measured. The same procedure was repeated for all membranes.

2.4 Dye Degradation and adsorption test

The prepared membrane was placed in the filtration apparatus as shown in Figure 2. A 50 ml RhB solution at 4mg/L of concentration was added to the filtration unit, and a vacuum pump was used to allow the dye solution to pass through the film completely. RhB solution after filtration were then analyzed using a UV-Vis spectrophotometer to determine the remaining concentration of RhB in the solution. The dye degradation efficiency (%D: %Degradation & Absorption) was calculated using the following formula:

$$\%D = [(A_0 - A_t) / A_0] \times 100$$

where: A₀ = Initial concentration of RhB and A_t = Concentration of RhB at a given time.

3. Results and Discussion

3.1 Chemical composition of the membrane

The FTIR spectra of PVDF-based photocatalytic membranes reveal characteristic absorption bands corresponding to the functional groups of PVDF and the incorporated

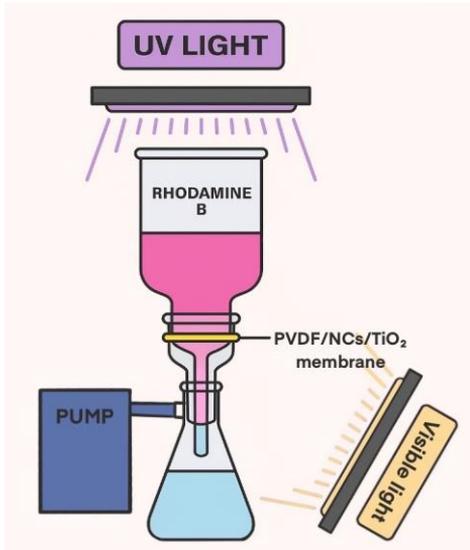


Figure 2 Schematic of RhB decomposition test.

nanomaterials and displayed in Figure 3. As seen in blue, red and black, strong absorption band observed at around $500\text{--}650\text{ cm}^{-1}$ corresponds to the Ti–O–Ti stretching vibration, confirming the presence of TiO_2 . The bands around 840 and 1170 cm^{-1} are attributed to the CF_2 stretching and bending vibrations, indicating the presence of the β -phase of PVDF. Upon the addition of TiO_2 , noticeable changes in the intensity and position of certain peaks are observed, especially in the $500\text{--}1500\text{ cm}^{-1}$ region, suggesting interactions between the PVDF matrix and the nanofillers. The broad band around 3400 cm^{-1} corresponds to O–H stretching, which becomes NCs, indicating enhanced hydrophilicity due to surface hydroxyl groups. These spectral changes confirm the successful incorporation of TiO_2 and NCs into the PVDF matrix and the potential modification of membrane surface properties relevant for photocatalytic activity.

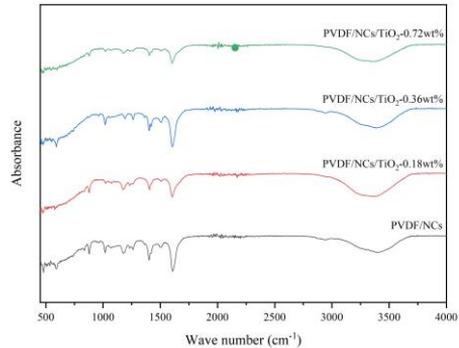


Figure 3 FTIR spectra of PVDF/NCs/ TiO_2 membrane at various TiO_2 contents.

3.2 Water flow rate analysis

The membrane thicknesses of 0.25 ml , 0.3 ml , and 0.35 ml were tested. The conclusion was that the 0.25 ml membrane had the fastest flow rate. Therefore, for other film ratios, the volume of 0.25 ml was chosen for testing.

The water flow rate of membrane at various TiO_2 ratios shows that the sample membrane without TiO_2 component has a water flow rate of 11.23 ml/min . The membrane with a TiO_2 ratio of $0.18\text{ wt}\%$ has a water flow rate of 12.94 ml/min . The membrane with a TiO_2 ratio of $0.36\text{ wt}\%$ has a water flow rate of 13.11 ml/min , and the membrane with a TiO_2 ratio of $0.72\text{ wt}\%$ has a water flow rate of 17.37 ml/min , as shown in the Table 1.

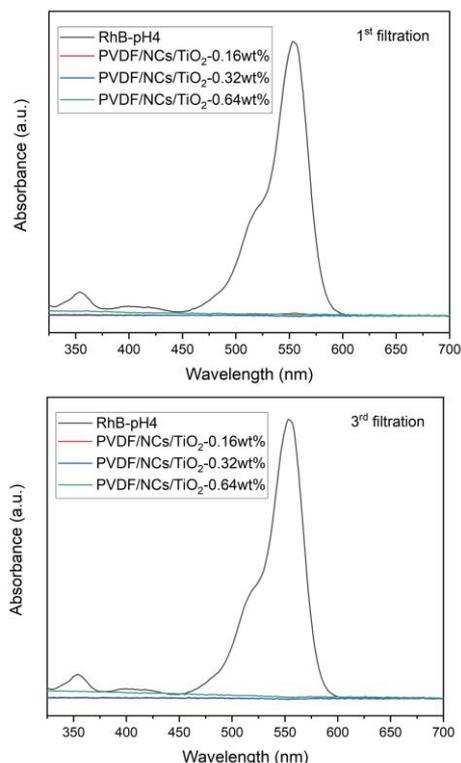
The sample membrane with the highest water permeability is the membrane with a TiO_2 ratio of $0.72\text{ wt}\%$, while the membrane with the lowest water permeability is the membrane without TiO_2 components. This means that the water permeability varies directly with the ratio of TiO_2 in the membrane. TiO_2 affects the film by creating more pores, as the addition of TiO_2 into the membrane matrix leads to the formation of crystalline structures that create pores in the membrane and increase the contact angle. Additionally, it enhances the hydrophilic properties. When used as a film for water treatment, it allows water to pass through more effectively than membranes with hydrophobic properties.

Table 1 Water flux rate of PVDF/NCs/TiO₂ membrane at various TiO₂ contents.

Sample	Membrane volume (ml)	Water flow rate (ml/min)
PVDF/NCs	2.5	11.23
PVDF/NCs/TiO ₂ -0.18wt%	2.5	12.94
PVDF/NCs/TiO ₂ 0.36wt%	2.5	13.11
PVDF/NCs/TiO ₂ 0.72wt%	2.5	17.37

3.3 Dye Degradation and adsorption testing

Figure 4 (a) shows RhB dye degradation and filtration test using PVDF/NCs/TiO₂-0.18wt%, PVDF/NCs/TiO₂-0.36wt%, and PVDF/NCs/TiO₂-0.72wt% membrane under uv-visible light irradiation. For the membrane without TiO₂, around 80% of RhB solution was decolorization and filtration. For all PVDF/NCs/TiO₂ membrane, they show that the complete disappearance of the RhB absorption peak at 554 nm after the first filtration strongly suggests that filtration and photocatalytic degradation played a major role in dye removal. Under simultaneous UV and visible light irradiation, the TiO₂ nanoparticles embedded within the PVDF/NCs membrane likely generated reactive oxygen species (ROS), such as hydroxyl radicals ($\bullet\text{OH}$) and superoxide anions ($\text{O}_2^{\bullet-}$), which can break down organic dye molecules. These photocatalytic reactions occur on or near the TiO₂ surface, leading to the mineralization or transformation of RhB into colorless intermediates or end-products. In addition to photocatalytic activity, physical filtration likely contributed to the observed RhB removal. The molecular size of RhB may exceed the average pore size of the PVDF/NCs/TiO₂ membrane, resulting in physical retention of dye molecules. This is supported by the visual observation of pink residues on the surface of the membrane post-filtration, suggesting that dye molecules or aggregates were unable to pass through the membrane pores. Therefore, the combined effects of photocatalytic degradation and size-exclusion-based filtration contributed synergistically to the highly efficient removal of RhB in a single filtration step.

**Figure 4** RhB decomposition test at pH4 using PVDF/NCs/TiO₂ membrane for (a) 1st filtration and (b) 3rd filtration.

Based on the results of duration of RhB degradation rate and the degradation-retention efficiency of RhB dye, the PVDF/NCs/TiO₂-0.18wt% membrane exhibit the highest overall performance. Although the dye removal efficiencies among the samples were comparable, this membrane demonstrated the highest water permeation rate. Therefore, it was selected for further investigation, including reusability testing and pH measurement of the treated wastewater after filtration. The reusability of the membrane was evaluated by performing a third filtration of RhB solution. As shown in Figure 4 (b) the UV-Vis spectra, the characteristic absorbance peak of RhB at approximately 554 nm was almost eliminated in all samples after the third use, indicating consistent photocatalytic and filtration

performance. The results suggest that the membrane's structure and photocatalytic activity remained stable and effective over multiple cycles. This confirms the membrane have strong reusability and highlights its potential for practical applications in dye-contaminated wastewater treatment.

The pH measurements before and after filtration of RhB solutions (initially adjusted to pH 4, 7, and 10) using the PVDF/NCs/TiO₂ membrane revealed a noticeable shift toward mildly acidic conditions (final pH ~5–6) as displayed in Table 2. This pH change suggests the occurrence of photocatalytic degradation and/or ion exchange processes during filtration. The decrease in pH under neutral and basic conditions (from 7 and 10 to 5 and 6, respectively) indicates the generation of acidic intermediate products, possibly due to oxidative breakdown of the RhB dye molecules catalyzed by TiO₂ under light irradiation. Additionally, the slight increase in pH in the initially acidic sample (from 4 to 5) may be attributed to partial neutralization by hydroxyl radicals or surface interactions with nanocellulose (10). Overall, these pH changes support the effective photocatalytic activity of the membrane and provide indirect evidence of dye degradation during the filtration process.

Table 2 pH value test before and after filtration.

sample	pH value of RhB after filtration			Duration of RhB degradation for pH4 (ml/min)
	pH4	pH7	pH10	
PVDF/NCs/TiO ₂ -0.18wt%	5	5	6	10.00
PVDF/NCs/TiO ₂ -0.36wt%	5	5	6	11.17
PVDF/NCs/TiO ₂ -0.72wt%	5	5	6	15.04

4. Conclusions

PVDF-based membranes incorporated with NCs and varying amounts of TiO₂-P25 (0.18, 0.36, and 0.72 wt%) were successfully synthesized and characterized for RhB dye removal. FTIR analysis confirmed the presence of both NCs and TiO₂ within the PVDF matrix. Water flow rate decreased with increasing TiO₂ content, with the highest value of 10.00, 11.17, 15.04 mL/min observed in 0.18, 0.36, 0.72wt% TiO₂, respectively. Under combined UV and visible light irradiation, solution was clear and

free from any detectable RhB dye contamination within a single filtration, the membranes achieved complete dye degradation through a synergistic effect of photocatalysis and physical filtration. The occurrence of photocatalytic degradation was further supported by post-filtration pH changes, indicating the formation of acidic intermediates. Notably, the PVDF/NCs/TiO₂-0.18% membrane maintained degradation and filtration efficiency even after three reuse cycles, confirming its durability and consistent photocatalytic performance. These findings demonstrate that membrane offers an optimal balance between high water flow and effective dye removal efficiency.

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Declaration of Conflicting Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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