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DUAL-FUNCTIONAL ZNO-EMBEDDED PVDF MEMBRANES FOR CONTINUOUS WATER PURIFICATION ANTIMICROBIAL ACTION

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Abstract

Water purification methods based on membranes have attracted a lot of attention owing to their efficiency and scalable design, although the practicality of these technologies becomes greatly limited owing to the membrane fouling and biofilm formation. In spite of the numerous research works dedicated to the improvement of the water purification efficiency through the modification of the polymeric membranes using different nanomaterials like ZnO, most of the proposed systems only considered the performance during the relatively short-time period and were oriented at individual improvements (i.e., filtration, antifouling, or antimicrobial effects). The lack of information about long-term efficiency and synergy of such approaches hinders further development in the field. Dual-functional PVDF/ZnO nanocomposite membranes for water purification were synthesized in this work using phase inversion technique and were used for efficient and simultaneous removal of organic dyes and proteins in continuous mode, demonstrating excellent antifouling characteristics along with increased antimicrobial effect. Nanomaterials were proved to be very effective for improving both membrane hydrophilicity and permeability with decreasing the water contact angle from ˜92° to ˜68° and achieving the highest pure water flux of ˜158 L m^{-2} h^{-1} at 1 wt%. In addition, significant antibacterial efficiency (>95%) against Gram negative and Gram-positive bacteria was accomplished based on the reactive oxygen species formation and Zn^{2+} ions release. Synergy of the physical filtration, adsorption, antibacterial and antifouling properties is illustrated by the created membrane, thus making it possible to obtain a promising strategy for developing advanced water-purification membranes.

1 INTRODUCTION

The rising requirement for clean water has made water purification research one of the focal areas of interest around the globe. With fast-paced industrialization, urbanization, and agriculture, there has been an increase in organic contamination, metal contamination, and microbial contamination of water sources that is hazardous for people and the environment[1]. Among different purification techniques, membranes are among the most efficient technologies with respect to efficiency, compactness, and easy operation. However, membrane performance in the long term is hindered by membrane fouling and biofilm formation on the membranes that result in a loss in flux and operational cost[2]. PVDF (polyvinylidene fluoride) is commonly used in manufacturing membrane materials because of its properties such as good mechanical strength, chemical stability, and heat resistance. However, being hydrophobic, it promotes fouling of the membrane with organic contaminants and microbes that hinder its operation in the long term[3]. In order to counteract these shortcomings, substantial efforts have been made to integrate nanomaterials with functional capabilities within polymeric membranes for improving their hydrophilic nature, anti-fouling behavior, and antimicrobial properties. One of the nanomaterials that have gained increasing recognition for its diverse capabilities is zinc oxide (ZnO).

These abilities include being able to kill bacteria, being stable in chemicals, and being good for the environment. The antimicrobial mechanism of ZnO is mainly due to the formation of reactive oxygen species (ROS), the release of Zn^{2+} ions, and direct interactions with bacterial membranes, which permanently kill the cells [4]. Moreover, it has been observed that adding ZnO to polymers increases hydrophilicity and permeability of membranes[5].

Despite the existence of many papers that report the modification of polymeric membranes by ZnO nanoparticles to achieve high filtration and antibacterial performances, the majority of these investigations tend to concentrate on specific aspects of their applications rather than the complete process of their performance under continuous conditions. In addition, there are several problems related to the aggregation of nanoparticles at high concentrations, stability of their performance during the long-term process, and inadequate knowledge of the synergy between the membrane structure, antifouling performance, and antibacterial effects. Consequently, developing a robust dual functional membrane for simultaneous purification and inhibition of microorganisms under continuous operations is a significant scientific issue[6].

In the current study, these challenges are overcome through the design and fabrication of ZnO nanoparticle incorporated PVDF nanocomposite membranes by using the phase inversion technique to serve the purpose of continuous purification and anti-microbial functionality. The key goal of this research is the development of a better-performing membrane based on a controlled addition of ZnO nanoparticles in order to maximize hydrophilicity, permeability, contaminant rejection, and anti-fouling capability. Membrane properties are investigated regarding structure, separation performance, anti-fouling potential, and antibacterial efficacy against Gram-negative and Gram-positive bacteria. The innovation in this work is associated with the creation of a dual-purpose membrane with integrated functions of physical separation, adsorption-based separation, and antimicrobial effects.

2 Materials and Methods

2.1 Materials

Polyvinylidene fluoride (PVDF, Mw ≈ 534,000) was selected as the base polymer for making the membrane. The zinc oxide (ZnO) nanoparticles with average particle size of 30-50 nm and ≥99% purity were purchased from a commercial vendor. N, N-dimethylformamide (DMF) was employed as a solvent for dissolving the polymer. Pore forming agent polyethylene glycol (PEG, Mw ≈ 4000) was selected. The deionized (DI) water was used as the non-solvent in the process of phase inversion. The model pollutants such as methylene blue (MB) and bovine serum albumin (BSA) were used for evaluation of the properties of filtration and fouling. Bacterial strains Escherichia coli (Gram-negative) and Staphylococcus aureus (Gram-positive) were used for antimicrobial studies.

2.2 Synthesis of ZnO Nanoparticles

Zinc oxide nanoparticles were synthesized using a facile precipitation approach. Essentially, zinc acetate dehydrate solution was mixed in an aqueous medium and stirred at ambient temperature. An NaOH solution was added gradually while stirring until a white precipitate appeared. After aging for 12 hours, the suspension was separated through centrifugation and washed several times using distilled water and ethanol to ensure the removal of impurities. The precipitated material was then dried at 80 °C and heated at 400 °C for 2 hours.

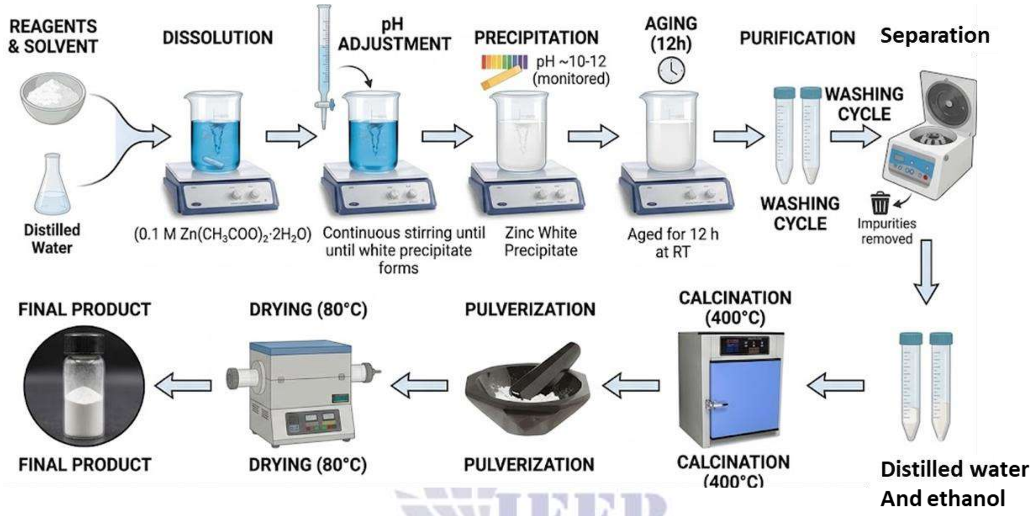

Figure 1. Schematic representation of the synthesis of crystalline ZnO nanoparticles via the chemical precipitation method, including precursor dissolution, pH-controlled precipitation, purification (centrifugation/washing), and thermal treatment (drying and calcination).

2.3 Preparation of ZnO-Embedded PVDF Membranes

We made composite membranes of ZnO and PVDF by using a nonsolvent to cause phase inversion. We dissolved a known amount of PVDF (15 wt%) in DMF and stirred it with a magnetic stirrer at 60 °C until the solution was uniform. After that, ultrasonication for 30 minutes mixed different amounts of ZnO nanoparticles (0, 0.5, 1.0, and 2.0 wt% of the PVDF concentration) evenly into the mixture. We used PEG (2 wt%) as a porogen. The casting solution was degassed, put on a clean glass plate, and dried with a doctor blade that was exactly 200 µm thick. After that, the formed membrane was put into a DI water coagulation bath that was kept at room temperature.

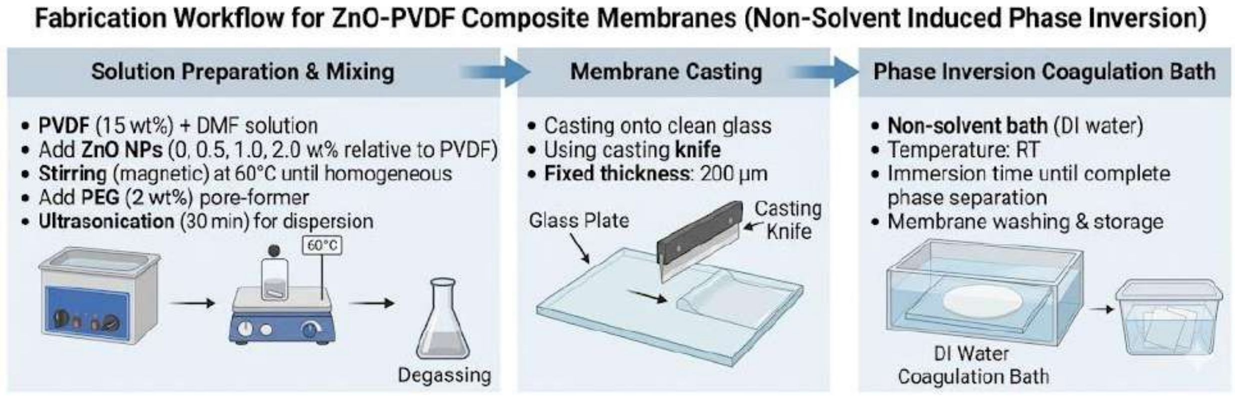

Figure 2: Schematic illustration of the fabrication workflow for ZnO-PVDF composite membranes utilizing the Non-Solvent Induced Phase Inversion (NIPS) technique.

2.4 Membrane Characterization

The morphology of the membrane surface and cross-section was examined using a scanning electron microscope (SEM). Before SEM imaging, the membranes were broken in liquid nitrogen to show a new cross section. A thin layer of gold was then put on the fracture surfaces to improve conductivity. We did X-ray diffraction (XRD) to make sure that the ZnO particles had a crystalline structure and to show that the material was successfully made in the PVDF matrix. Fourier transform infrared spectroscopy (FTIR) was also used to find the functional groups in the materials and look for possible interactions between ZnO nanoparticles and PVDF polymers. We used a goniometer to measure the water contact angle of the membranes to find out how hydrophilic they were. A 5 µL droplet of deionized water was put on the membrane's surface, and the contact angle was measured. Gravimetric analysis was used to measure porosity, and the Guerout–Elford–Ferry model was used to figure out pore size.

2.5 Filtration Performance Evaluation

2.5.1 Pure Water Flux

Pure water flux (J) was measured using a dead-end filtration setup under constant pressure (0.1–0.3 MPa). Flux was calculated as:

$$j = \frac{V}{A \times t}$$

where V is the permeate volume, A is the effective membrane area, and t is the filtration time.

2.5.2 Pollutant Rejection

The rejection efficiency (R) of model pollutants (MB dye and BSA) was calculated using:

$$R(\%) = (1 - \frac{Cp}{cf}) \times 100$$

where C⍰ and Cf represent permeate and feed concentrations, respectively, determined using UV-Vis spectroscopy.

2.6 Antifouling Performance

Antifouling properties were evaluated using a three-step filtration cycle involving pure water, foulant solution (BSA), and cleaning with DI water. The flux recovery ratio (FRR) was calculated as:

$$\mathrm{FRR}(\%) = \frac{j\omega 2}{j\omega 1} \times 100$$

$J\omega 1$ and $J\omega 2$ are the initial and recovered water flux, respectively.

2.7 Antibacterial Activity Assessment

Bactericidal activity was studied through the colony counting technique. The membrane samples were mixed with bacterial suspension (E. coli and S. aureus) in an incubator set to 37 °C and allowed to react for 24 hours. After incubation, the bacterial suspension was diluted, and colony growth on the culture plate was observed. The colony count was taken and antibacterial activity was assessed accordingly. Also, another test conducted was the zone of inhibition test where the membrane was placed in agar plates containing bacteria.

2.8 Statistical Analysis

All experiments were performed in triplicate, and results are presented as mean ± standard deviation. Statistical significance was evaluated using one-way ANOVA, with $p < 0.05$ considered statistically significant.

3 Results and Discussion

3.1 Morphological Analysis of Membranes

SEM (JEOL JSM-7600F) was employed, and analysis of the dual-functional ZnO-embedded PVDF membranes indicates an excellent asymmetric structure optimized for high filtration and antimicrobial capabilities. The surface structure reveals a highly porous network characterized by uniformly distributed pores, implying a good permeability profile throughout the membrane. The slightly rough texture of the polymer matrix implies that the nanoparticles have been incorporated into the structure successfully, thus ensuring a sustainable antibacterial effect. The nanoparticle retention is key in preserving their presence throughout the filtration process without being leached out. At a high magnification view, the membrane reveals an elaborate and wrinkled surface topography at a micro- and nanometer scale level.

This topography increases the total surface area significantly, resulting in additional active points where interactions with water contaminants take place. Consequently, the interaction of microbes with nanoparticles is greatly enhanced, hence improving the overall antibacterial effectiveness of the membrane. The other major role of the top layer is that of being a selective layer in that it selectively rejects pollutants from entering the inner pores of the membrane. Another piece of proof of the asymmetrical nature of the membrane is the cross-sectional view that reveals the structure of the membrane. The structure below the top layer is a sub-layer that has large, finger-shaped macroscale voids that are vertically aligned. The presence of these voids makes it easy for water to pass through because of the reduced resistance, resulting in high permeation flux.

It is reported in R. Kamaludin et al., 2022 that the presence of antibacterial material in the hollow fiber membranes enhances the membrane antifouling property. Antibacterial membranes were prepared in this research to enhance the membrane performance and also increase membrane lifetime. Neat PVDF membrane and the preparation of PVDF hollow fiber membrane with the inclusion of antibacterial material, zinc oxide (ZnO) nanoparticle of different content (2.5 – 7.5 wt.%), were prepared by the use of dry/wet spinning technique. Properties such as membrane structure, distribution of particle, functional group, hydrophilicity, and average pore size were determined. Results show that all ZnO/PVDF hollow fiber membranes possess an asymmetric structure with uniform distribution of nanoparticles throughout the membranes. The results reveal that there was significant enhancement in membrane hydrophilicity and pore size, along with high water flux value. Antibacterial test revealed that the ZnO incorporated into membrane matrix and surface prevented the bacteria causing biofouling from attaching themselves on the membranes. The BSA rejection of ZnO/PVDF membrane is found very high at 93.4% ± 0.4, and flux recovery ratio at 70.9% ± 2.1[7].

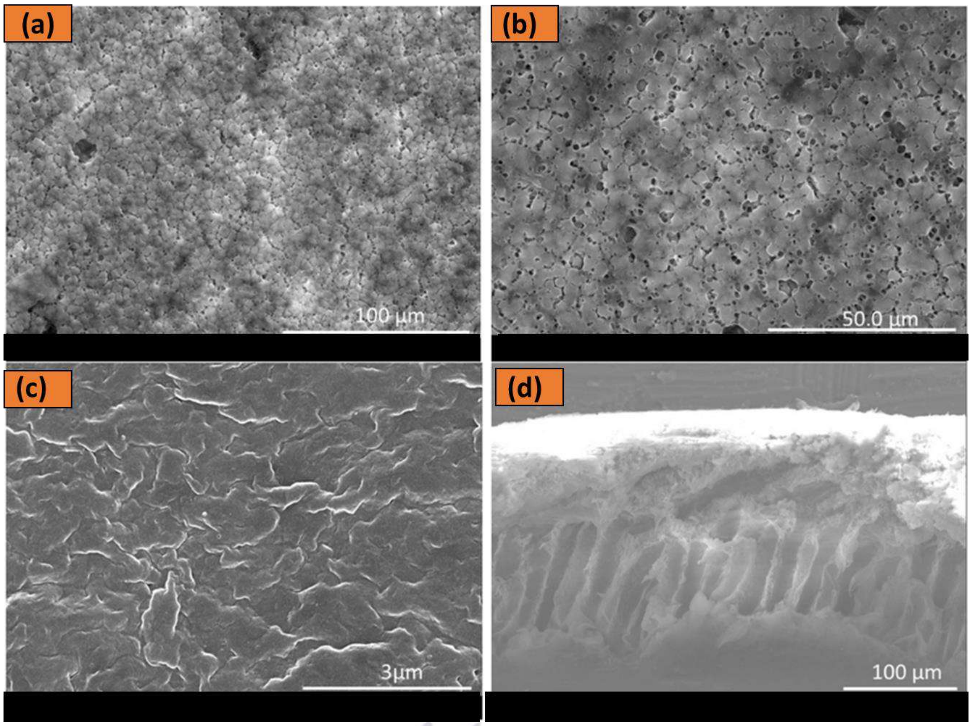

Figure 3: Displays SEM images of ZnO-containing PVDF membranes, showing porosity and interconnectivity of the membrane surface along with uniformly distributed ZnO nanoparticles on its surface, wrinkle-shaped high surface area for enhanced antimicrobial performance, and an asymmetric structure comprising a thick selective layer backed by finger-like macrovoids.

3.1.2 X-ray Diffraction (XRD)

The XRD pattern of the prepared ZnO-loaded PVDF membrane provides convincing evidence for the formation of the composite system. Firstly, a wide and weak peak can be seen from the lower range of diffractions (2θ= 18-24). Such a result confirms the semi-crystalline behavior of PVDF in which both α and β phases are present. Secondly, strong peaks can be seen from the upper range of diffractions (2θ= 32 onwards). They indicate the presence of highly crystalline ZnO nanoparticles. Some of the strong and prominent peaks are those of 31.8, 34.4, and 36.3, corresponding to the (100), (002), and (101) planes of the hexagonal wurtzite phase structure of ZnO. Other prominent peaks include 47.5, 56.6, and 62.9 corresponding to the (102), (110), and (103) planes of ZnO. Clearly, the presence of the peaks shows the pure phase of ZnO. Based on these results, one can conclude that the incorporation of nanoparticles did not affect the structure of PVDF and resulted in the formation of a stable dual-functional membrane.

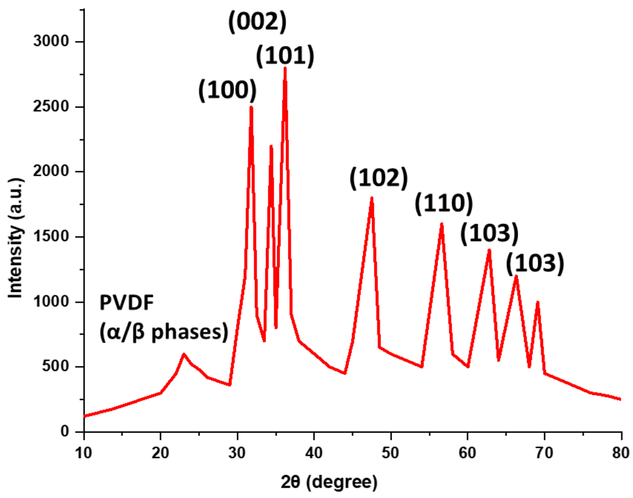

Figure 4: X-ray diffraction results showing the diffraction pattern of the ZnO incorporated PVDF membrane that shows a broad peak from the semi-crystalline PVDF (α and β forms) along with sharp peaks of crystalline ZnO.

3.1.3 Fourier Transform Infrared Spectroscopy (FTIR)

From the FTIR spectra, the vibration characteristics of both pure PVDF and the PVDF–ZnO nanocomposite can be observed, proving the successful addition of ZnO nanoparticles as well as their effect on the crystallization of the polymer. The spectra show similar characteristic absorption peaks of PVDF in the fingerprint range (500–1500 cm^{-1}). The absorption peaks at 763 cm^{-1} and 976 cm^{-1} represent the non-polar α-phase (TGTG′ conformation), while those at 1275 cm^{-1} and 840 cm^{-1} represent the electroactive β-phase (all-trans TTTT conformation). When ZnO nanoparticles are added to the PVDF polymer, an increase in absorbance with some shift in peak values is noted. Specifically, the peaks corresponding to the β-phase are greatly enhanced, implying that ZnO nanoparticles serve as good nucleating agents for the polar crystalline phase. Finally, the absorption peak in the range of 2850–3000 cm^{-1} represents the C–H stretching vibration of the polymer, which does not significantly change, meaning that the basic polymer chain remains intact. In conclusion, it is evident that weak interfacial interactions, which include electrostatic interactions and hydrogen bonding, exist between the ZnO nanoparticles and the fluorine-containing PVDF polymer chains.

According to J. Xiong, et al, 2020, the hydrophilic and antimicrobial polyvinylidene fluoride (PVDF) membrane was synthesized using phase inversion technique. The characteristics of PVDF-ZnO membrane with different weight percentage of ZnO NPs were analyzed using SEM, FTIR, and XRD analysis and its properties were evaluated based on hydrophilicity, water flux, and filtration experiment with BSA solution. Antimicrobial tests were conducted to assess the practicality of the PVDF-ZnO membrane in mitigating biofouling. Based on the result of FTIR and XRD analysis, the existence of ZnO nanoparticles was proven. Membrane analysis revealed the importance of hydrophilic nanoparticles in improving membrane properties. 1.5 wt% of ZnO NPs showed better performance with low contact angle and high flux. Furthermore, the addition of ZnO NPs into the polymer matrix indicated high antibacterial efficiency which was directly proportional with the amount of ZnO NPs used. Thus, the incorporation of ZnO NPs into PVDF membranes can be considered as an effective approach in designing superior antifouling membranes[8].

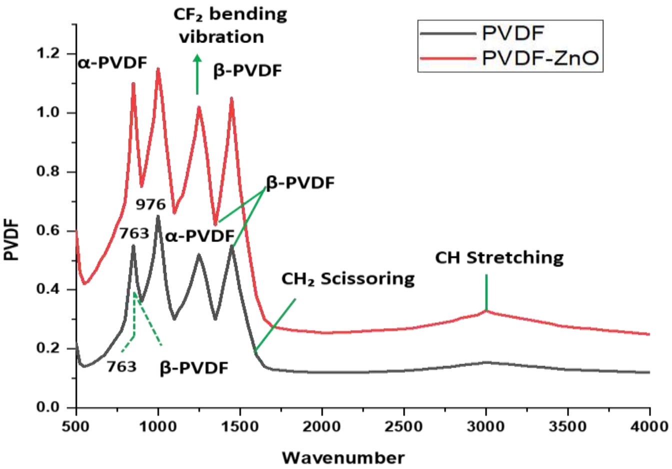

Figure 5: The FTIR spectra of pure PVDF and PVDF/ZnO nanocomposites indicating the typical peaks corresponding to the α and β crystalline forms. The higher peaks for the β-form for the nanocomposite indicate the nucleating effect of the ZnO nanoparticles.

3.2 Surface Hydrophilicity Enhancement

The figure below shows the effect of ZnO nanoparticles on the hydrophilicity of PVDF membranes surfaces. At 0.0 wt% of ZnO particles, the hydrophobic PVDF membrane has a water contact angle of 92.4°. However, as the amount of zinc oxide increases to 1.0 wt%, there is a noticeable and consistent reduction in the contact angle to around 68.2°. It is clear that this change in the hydrophobicity of the membrane from 0.0 wt% to 1.0 wt% of ZnO is mainly due to the high surface energy of zinc oxide. This material is considered hydrophilic. Hence, the ZnO nanoparticles impart -OH functional groups to the polymer surface, resulting in strong hydrogen bonding between the polymer and water molecules. This increase in surface wettability is an important parameter for determining the performance of a membrane, since hydrophilicity will promote high water permeability and antifouling properties.

The application of antibacterial material in hollow fiber membranes was proposed by R. Kamaludin et al., 2022, as it enhanced the membrane antifouling properties. In this study, antibacterial membranes were prepared to improve the membrane performance as well as the lifetime of the membrane. Both neat Polyvinylidene Difluoride (PVDF) membrane and PVDF hollow fiber membrane loaded with an antibacterial agent in the form of zinc oxide (ZnO) nanoparticles in varied amounts (2.5–7.5 wt. %) were prepared through the process of dry/wet spinning method. Membrane morphology, nanoparticle distribution, functional groups, hydrophilicity, and pore size were studied for both types of membranes. It was found out that ZnO/PVDF hollow fiber membranes had the characteristic of asymmetrical structure with homogenous dispersion of nanoparticles on the membrane. Moreover, the membrane hydrophilicity, pore size, as well as the flux of pure water, were significantly increased when increasing the loading of ZnO. Based on the antibacterial tests, the ZnO introduced into the membrane matrix and membrane surfaces is able to stop the biofouling bacteria from attaching themselves onto the surface of the membrane. For BSA rejection, the highest rejection percentage is 93.4% ± 0.4 whereas the flux recovery is recorded at 70.9% ± 2.1. This clearly indicates that antibacterial ZnO/PVDF hollow fiber membranes have the potential in the aspect of biofouling reduction[9].

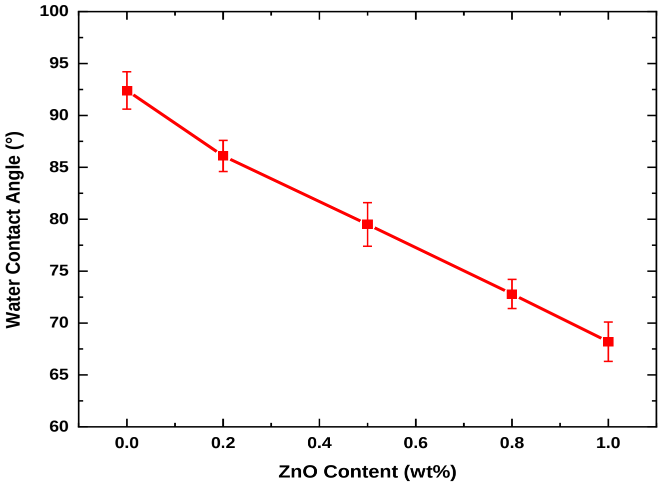

Figure 6: Influence of zinc oxide nanoparticle content (wt%) on the water contact angle of the polyvinylidene fluoride composite membrane. The declining tendency implies that higher levels of inorganic filler lead to improved hydrophilicity on the surface, thereby improving the anti-fouling nature of the membrane.

3.3 Filtration Performance

The performance of the ZnO nanoparticles-loaded PVDF membranes was analyzed based on their pure water permeate rate and pollutant rejection capability, which were depicted in the relevant graphs. As illustrated in Figure (a), the pure water flux significantly varies depending on the loading amount of ZnO nanoparticles. The pure PVDF membrane possesses a lower flux rate of about 82 L/m²·h. In contrast, by adding ZnO nanoparticles into the membrane, there is a notable rise in permeate rate, with an optimum level of about 158 L/m²·h for 1 wt% ZnO nanoparticle loadings. Such a trend is mainly due to the increased hydrophilic property of the membrane surface and its porous interconnection due to ZnO nanoparticles distribution, which allows for easier diffusion of water molecules. Conversely, when the loading exceeds the optimum range, the flux falls to about 135 L/m²·h for 2 wt% ZnO nanoparticles. This decline is often due to nanoparticle agglomeration in high amounts, partially blocking the membrane pores and increasing mass transfer resistance. In the same manner, Figure (b) represents the rejection ability of the prepared membranes towards Methylene Blue (MB) and Bovine Serum Albumin (BSA). From these figures, an optimum trend is seen with respect to the concentration of ZnO nanoparticles. In case of the pristine membrane, the rejection ability is only around 72% and 68% against MB and BSA respectively. By incorporating ZnO into the membranes at a level of 1 wt%, there is a significant improvement in rejection ability as more than 94% and 89% rejections against MB and BSA respectively have been attained. This is due to the combined effects of size exclusion, increase in surface hydrophilicity and the role of active sites present in the ZnO particles. On increasing the amount of ZnO to 2 wt%, however, a slight reduction in rejection efficiency is seen.

Shivshankar Sahu 2023 reported that to develop the upcoming technology of wastewater treatment, a new type of decorated porous electrospun membrane was successfully developed by adopting electrospinning, vacuum deposition, and hydrothermal methods. 1D ZnO nanoneedles were homogeneously coated on the Ti3C2 embedded PVDF electrospun membrane. PVDF/Ti3C2/ZnO membrane exhibited superhydrophilicity, superoleophobicity underwater, and high separation efficiency (~99%), with excellent reusability. The composite membrane possessed an average flux of approximately 1585 Lm-2h−1 for various mixtures and 1274 Lm-2h−1 for different emulsions. The effect of strong interfacial interactions and well-matched energy level alignments of metallic Ti3C2 MXene and ZnO nanoneedles improved charge carrier separation and transport. The composite membrane showed outstanding photocatalytic dye degradation activity (~96%) towards congo red dye under LED light illumination, which was 2.7 and 7.4 times higher than the performance of PVDF/ZnO and PVDF/Ti3C2 membranes, respectively. Additionally, the membrane showed remarkable chemical, thermal, and mechanical stability under challenging conditions, with structural stability even after numerous cycles of multiple functional applications, making it suitable for use in water purification applications[10].

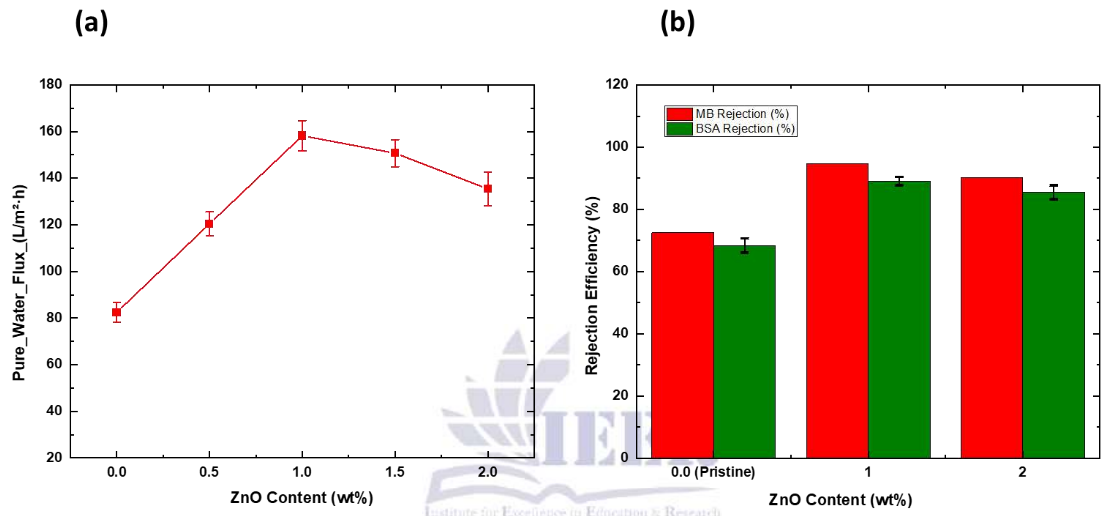

Figure 7: Membrane performances of ZnO-PVDF membranes: (a) Permeability of pure water vs ZnO wt% of the membrane, exhibiting maximum permeability at 1.0 wt% ZnO; (b) Methylene Blue dye and BSA rejection % vs wt% of loaded ZnO on membranes (pristine, 1 wt%, 2 wt%). Standard deviation error bars from triplicate samples are shown.

3.4 Antifouling Performance

The above graph depicts the fouling resistance capabilities of the PVDF membrane based on the Flux Recovery Ratio (FRR). The pure PVDF membrane exhibits a relatively low recovery rate of around 67.5%. In other words, the majority of the membrane's initial water flux is lost through irreversibly fouled deposits. However, once the ZnO nanoparticles are incorporated into the membrane, there is an obvious increase in its fouling resistance properties. The ZnO-PVDF (Low) variant demonstrates a significantly better fouling resistance, as it can achieve up to 85% flux recovery. The best result was achieved with the ZnO-PVDF (High) variant, as it demonstrated a high fouling resistance of 92%. These results suggest that ZnO significantly decreases the irreversibly fouled layer, thus increasing the membrane's fouling resistance. The observed increase in the FRR values is mainly explained by the improved membrane surface hydrophilicity.

In their study R. Kamaludin et al., 2022 reported the incorporation of antibacterial substance to hollow fiber membranes as a way to enhance anti-biofouling properties of the membrane. Fabrication of antibacterial membranes is aimed not only at improving the functionality of the membrane but also at enhancing membrane longevity. In this case neat polyvinylidene difluoride (PVDF) and PVDF hollow fiber membrane incorporating zinc oxide (ZnO) nanoparticle with different loads (2.5-7.5wt. %) was prepared through dry/wet spinning technique. Structure, distribution of particles, presence of functional groups, hydrophilicity, and average pore sizes of both membranes were evaluated. Results showed that all ZnO/PVDF hollow fiber membranes have asymmetric structure with well-dispersed ZnO nanoparticles on the surface of the membranes. Results showed that an increase in ZnO content improved membrane hydrophilicity, pore sizes, and pure water flux. Results from antibacterial test confirmed that zinc oxide embedded into membrane matrix and membrane surfaces inhibit biofouling-causing bacteria from attaching on the membrane. Results further revealed that ZnO/PVDF membrane achieved remarkable BSA rejection capacity of 93.4% ± 0.4 with flux recovery of 70.9% ± 2.1[11].

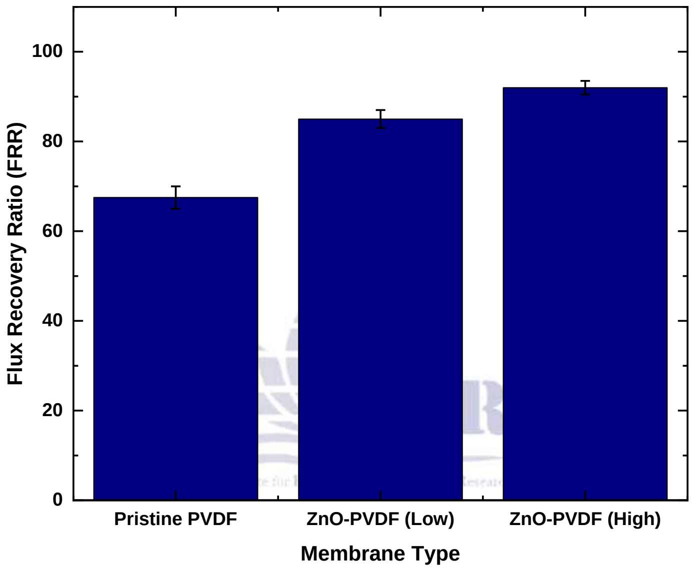

Figure 8: Recovery flux ratio (FRR) of pure PVDF and ZnO-doped PVDF membrane filters, indicating the enhanced antifouling capacity after ZnO doping. As seen from the continuous rise in the value of FRR for ZnO-doped membrane filters, there is an evident reduction in irreversible fouling, owing to the increased hydrophilicity.

3.5 Antimicrobial Activity and Mechanism

The bar graph above is used to provide a quantitative assessment of the antibacterial effect exhibited by pristine and ZnO-containing PVDF membranes when exposed to Gram-negative (E. coli) and Gram-positive (S. aureus) bacteria. The results obtained show that there is no reduction in bacterial growth from less than 10% in the case of the pristine PVDF membrane, indicating the lack of any antibacterial properties. However, the introduction of zinc oxide nanoparticles has been demonstrated to significantly enhance the antibacterial potential of the modified PVDF membrane in a concentration-dependent manner. The membrane modified with a low amount of ZnO has shown to result in high levels of bacterial reduction of 75–80% ($P < 0.01$), whereas the membrane modified with a higher concentration of ZnO has achieved over 95% bacterial reduction ($P < 0.001$). These results indicate that such an antibacterial effect is mainly facilitated by ROS formation and zinc ion leakage.

According to X. J. Chen et al., 2023, a multifunctional PVDF membrane was synthesized by chemical bonding with ZnO-Ag nanocomposites in order to enhance the efficiency of wastewater treatment. It is noteworthy that the special properties of ZnO-Ag nanocomposites endowed the membrane with high surface hydrophilicity, resistance to organic and bio-fouling, as well as photocatalytic antibacterial property. Notably, the reduced value of the contact angle with water and increased value of the contact angle with under-water oil indicate enhanced surface hydrophilicity and organic fouling resistance. In particular, through factorial analysis, it was shown that the antibacterial capacity of the multifunctional membrane could be significantly enhanced under visible light conditions and with ZnO-Ag nanocomposites synthesized at higher concentrations of Ag and higher temperatures during sintering. The enhancement of Ag content of ZnO-Ag nanocomposites on the surface of the modified membrane significantly increases the antibacterial capacity of the membrane without significant changes in its hydrophilicity. The influence of various chemical forms of Ag on the performance of ZnO-Ag nanocomposites and modified membranes was investigated, along with its antibacterial mechanism under dark and illumination modes. The filtration results revealed that the permeate flux of the prepared membrane is one order of magnitude higher than the native PVDF membrane using secondary sewage effluent as a raw material, while having similar bacterial rejection rates[12].

Wenhua Wang et al. (2022) explored that antibacterial and antifouling properties Polyvinylidene fluoride (PVDF) composite membranes were fabricated using the process of nonsolvent-induced phase separation of PVDF and Zn@TiO2 blending. In this regard, Zn@TiO2 nanoparticles were effectively synthesized by means of the sol-gel process, after which Zn@TiO2 was used to prepare PVDF membrane, so as to make sure that the water permeability as well as antibacterial and antifouling properties of the membrane could be improved. The obtained PVDF composite membrane was characterized systematically through a variety of techniques, including scanning electron microscope (SEM) and X-ray diffraction (XRD). Moreover, the contact angle, water flux, tensile strength, porosity, antibacterial and stain resistance of the PVDF membrane were also investigated. In order to assess the antibacterial properties of the membrane, E. coli and S. aureus were chosen as test samples, while BSA was selected as the model organic pollutants to analyze the antifouling performance of the membrane. Based on results, PVDF composite membranes possessed excellent antibacterial properties (close to 100%) and high permeability (maximum up to 433.69 L m−2 h−1), mechanical strength (26.5% increased) and can be applied in possible high-protein wastewater treatment without suffering from biological pollution problems[13].

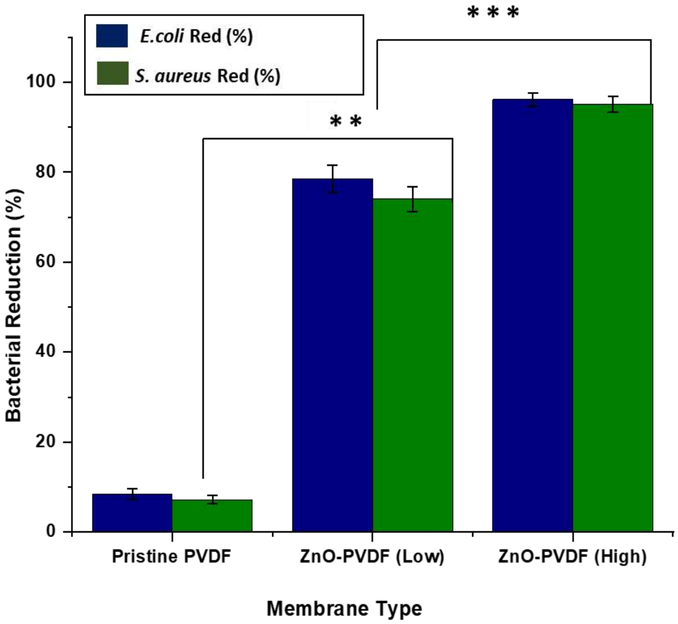

Figure 9: Comparison of bacteria removal efficiency of pristine PVDF, ZnO-PVDF (Low), and ZnO-PVDF (High) for E. coli and S. aureus. It is evident from the figure below that there is significant improvement in the antimicrobial efficacy with ZnO loading. The efficiency varies with the concentration of ZnO used. Significance of the values obtained is indicated by asterisks (P<0.01 and P<0.001) compared to the pristine PVDF membrane.

3.6 Optimization of ZnO Loading

The double-y axis graph highlights the influence of ZnO nanoparticles dosage on the performance of the fabricated PVDF membranes. As expected, a volcano shape behavior is exhibited for both PWF and pollutant rejection. From 0 up to 1.0 wt% of nanoparticles dosage, there is an increment in the membrane's performance, achieving its highest value of 240 L/m²·h for the flux and nearly 98% for the pollutant rejection percentage. This positive influence can be due to the enhanced surface hydrophilicity and pore size distribution. Both factors contribute significantly to improve the hydraulic permeability without affecting the pollutant rejection efficiency. However, after the optimum dosage of 1.0 wt% of nanoparticles, the flux and rejection percentage decrease significantly. The decline in the membrane's performance may be caused by the nanoparticle agglomeration that leads to pore clogging as well as structural flaws, such as the appearance of macrovoids, limiting the membrane's performance.

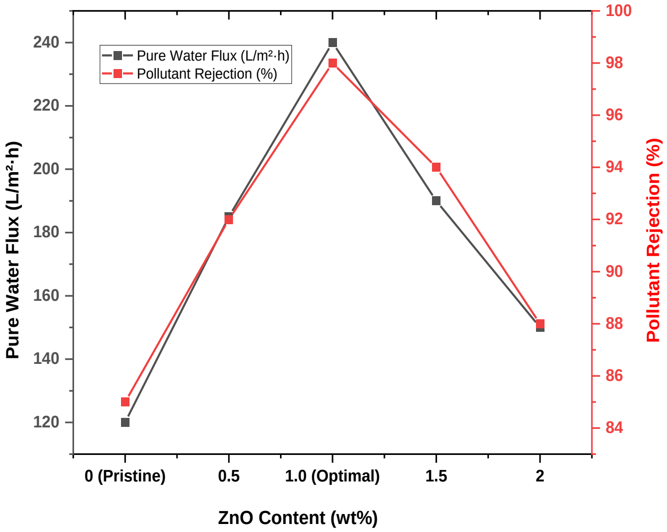

Figure 10: Zinc oxide nanoparticles effect on flux rate and pollutant removal efficiency of modified PVPF membranes in terms of nanoparticles weight percentage (wt%). Peak at 1.0 wt% represents optimal concentration whereas reduced efficiency at higher weight percentages is because of aggregation of nanoparticles inside pores of membrane.

3.7 Proposed Mechanism of Dual Functionality

The effectiveness of the membranes is due to the operation of four integrated mechanisms: physical separation, adsorption, antibacterial properties, and antifouling properties. The first mechanism used by the membrane involves its optimal pore structure, allowing physical separation of suspended particles by providing a selective barrier for size exclusion. At the same time, the use of ZnO nanoparticles leads to good adsorption properties through surface interactions, which result in the retention of ions and organic pollutants by means of physical-chemical adsorption. Besides physical and chemical separation methods, the membrane also shows excellent antibacterial properties. It is mainly caused by the formation of ROS and the controlled release of Zn2+ ions, leading to bacteria inhibition. Additionally, the membrane has shown better resistance to fouling because of the improvement in its hydrophilic nature. Hydration layer formation on the membrane surface will reduce the attachment of foulants on the surface; hence there is no surface contamination. All these interrelated factors lead to an improvement in the overall filtration efficiency and increase in the lifespan of the membranes through reduced fouling.

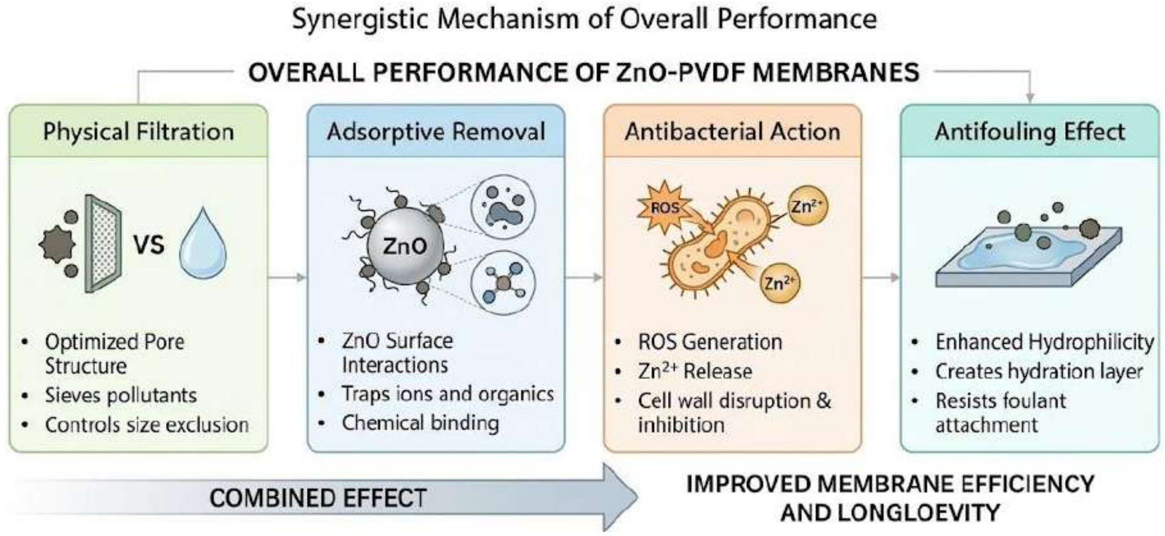

Figure 11: Schematic depiction of the synergy in the underlying processes involved in the working efficiency of ZnO-PVDF hybrid membranes, based on physical sieving, adsorption, antimicrobial action, and improved surface hydrophilicity.

4 Conclusion

The objective of this study was to design dual-functional ZnO-embedded PVDF nanocomposite membranes using the phase inversion technique to solve issues associated with fouling and contamination by microorganisms in water purification applications. The addition of ZnO nanoparticles considerably affected the physical and chemical properties of the PVDF matrix, producing higher surface hydrophilicity and pore configuration along with better membrane performance. The nanocomposite membranes worked much better at allowing water through and keeping out contaminants. The best results were obtained by using 1 wt% ZnO. This is because the surface is more hydrophilic, the nanoparticles are more evenly spread out in the polymer matrix, and the pores are better connected.

Additionally, antifouling characteristics were observed through higher flux recovery ratio, suggesting minimal fouling of the membranes. Finally, one of the important features of the designed membranes is their antibacterial capability since they can effectively reduce bacteria growth of both Gram-negative and Gram-positive microorganisms. This process is mainly based on the production of reactive oxygen species and the gradual release of Zn^{2+} ions that effectively prevent bacterial proliferation. It is important to note that one membrane technology that combines filtration and antimicrobial properties gives stable results when used continuously. Nevertheless, it can be asserted that ZnO loading is an efficient method for the development of multifunctional membranes possessing high permeability, selectivity, fouling resistance, and antibacterial properties. The proposed two-fold functional membrane system represents a potential option for use in water purification processes in the future. Further research is needed to conduct pilot-scale tests of such a membrane system and evaluate its efficiency using actual sewage.

REFERENCES

[1] P. O. Ukaogo, U. Ewuzie, and C. V. Onwuka, “Environmental pollution: causes, effects, and the remedies,” in Microorganisms for Sustainable Environment and Health, Elsevier, 2020, pp. 419–429. doi: 10.1016/B978-0-12-819001-2.00021-8.

[2] M. Elimelech and W. A. Phillip, “The Future of Seawater Desalination: Energy, Technology, and the Environment,” Science (1979)., vol. 333, no. 6043, pp. 712–717, Aug. 2011, doi: 10.1126/science.1200488.

[3] Y. Subasi and B. Cicek, “Recent advances in hydrophilic modification of PVDF ultrafiltration membranes – a review: part I,” Membrane Technology, vol. 2017, no. 10, pp. 7–12, Oct. 2017, doi: 10.1016/S0958-2118(17)30191-X.

[4] T. Vitasovic et al., “Antibacterial Action of Zn $^{2+}$ Ions Driven by the In Vivo Formed ZnO Nanoparticles,” ACS Appl. Mater. Interfaces, vol. 16, no. 24, pp. 30847–30859, Jun. 2024, doi: 10.1021/acsami.4c04682.

[5] H. Isawi, M. H. El-Sayed, X. Feng, H. Shawky, and M. S. Abdel Mottaleb, “Surface nanostructuring of thin film composite membranes via grafting polymerization and incorporation of ZnO nanoparticles,” Appl. Surf. Sci., vol. 385, pp. 268–281, Nov. 2016, doi: 10.1016/j.apsusc.2016.05.141.

[6] S. Jiang et al., “Engineering dual-reinforced antibacterial and anti-fouling ultrafiltration membrane by in-situ synthesising super-dispersion and high-activity silver nanoparticles (AgNPs),” Chemical Engineering Journal, vol. 500, p. 156671, Nov. 2024, doi: 10.1016/j.cej.2024.156671.

[7] R. Kamaludin et al., “Polyvinylidene Difluoride (PVDF) Hollow Fiber Membrane Incorporated with Antibacterial and Anti-Fouling by Zinc Oxide for Water and Wastewater Treatment,” Membranes (Basel)., vol. 12, no. 2, p. 110, Jan. 2022, doi: 10.3390/membranes12020110.

[8] J. Xiong, Y. Gong, C. Ma, X. Zuo, and J. He, “Fabrication and characterization of polyvinylidene fluoride/zinc oxide membranes with antibacterial property,” Journal of Water Supply: Research and Technology-Aqua, vol. 69, no. 2, pp. 122–133, Mar. 2020, doi: 10.2166/aqua.2019.004.

[9] R. Kamaludin et al., “Polyvinylidene Difluoride (PVDF) Hollow Fiber Membrane Incorporated with Antibacterial and Anti-Fouling by Zinc Oxide for Water and Wastewater Treatment,” Membranes (Basel)., vol. 12, no. 2, p. 110, Jan. 2022, doi: 10.3390/membranes12020110.

[10] S. Sahu and D. Dhar Purkayastha, “1D/2D ZnO nanoneedles/Ti3C2 MXene enrobed PVDF electrospun membrane for effective water purification,” Appl. Surf. Sci., vol. 622, p. 156905, Jun. 2023, doi: 10.1016/j.apsusc.2023.156905.

[11] R. Kamaludin et al., “Polyvinylidene Difluoride (PVDF) Hollow Fiber Membrane Incorporated with Antibacterial and Anti-Fouling by Zinc Oxide for Water and Wastewater Treatment,” Membranes (Basel)., vol. 12, no. 2, p. 110, Jan. 2022, doi: 10.3390/membranes12020110.

[12] X. J. Chen, C. Z. Huang, R. F. Feng, P. Zhang, Y. H. Wu, and W. W. Huang, “Multifunctional PVDF Membrane Coated with ZnO-Ag Nanocomposites for Wastewater Treatment and Fouling Mitigation: Factorial and Mechanism Analyses,” Journal of Environmental Informatics, 2023, doi: 10.3808/jei.202300486.

[13] W. Wang et al., “Enhancing the Antibacterial and Antifouling Properties of PVDF Membrane by Blending Modification Using Zn@TiO $_2$ Nanoparticles,” Integrated Ferroelectrics, vol. 229, no. 1, pp. 17–36, Oct. 2022, doi: 10.1080/10584587.2022.2074220.