

DOI: <https://doi.org/10.71317/kjard.2.10.2026.831>

# Kashmir Journal of Academic Research and Development

Journal homepage: <https://rjsaonline.org/index.php/KJARD>

## Green Synthesis of Zinc Oxide and Titanium Dioxide Nanoparticles and Their Integration into Polymeric Nanocomposite Membranes for Water Purification

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August 31, 2026

**Revised:**

September 28, 2026

**Accepted:**

October 04, 2026

**Available Online:**

October 13, 2026

**Keywords:**

Green synthesis, zinc oxide nanoparticles, titanium dioxide nanoparticles, polymeric nanocomposite membranes, water purification, membrane fouling, photocatalysis, sustainable nanotechnology.

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Pollution of water from the effluents of industries, agricultural runoff, dyes, pharmaceutical wastes, metals, and pathogenic organisms is one of the most serious environmental and health problems. The conventional techniques of water treatment face several problems including fouling of membranes, high costs of operation, chemical usage, and failure to eliminate some pollutants completely. This research recommends the use of an integrated technique of green synthesis of ZnO and TiO<sub>2</sub> nanoparticles along with their addition to nanocomposite polymeric membranes for water purification purposes. Phenols, flavonoids, and other components of the plant extracts are recommended as biogenic mediators of nanoparticle formation and surface stability. The characterization of the synthesized nanoparticles will be carried out using XRD, FTIR, SEM, TEM, and UV-Visible spectroscopy techniques. The matrix for the polymeric membrane will be either polyvinylidene fluoride (PVDF) or polysulfone (PSf), which will be loaded with nanoparticles to maximize the hydrophilicity, permeability, contaminant rejection, and fouling-resistance properties. A quantitative experimental method is outlined for a comparison between the pristine polymeric membrane and those modified with zinc oxide (ZnO), titanium dioxide (TiO<sub>2</sub>), and their hybrid forms (ZnO/TiO<sub>2</sub>). Potential indicators of the performance may include water permeability, dye removal, turbidity removal, antimicrobial properties, flux recovery, and nanoparticle leaching. The illustrative results indicate that the hybrid membrane would exhibit better water permeability and contaminant removal in comparison with a pristine membrane; however, these figures remain hypothetical and must be confirmed experimentally. The work may help develop sustainable water purification technologies based on the synthesis of nanoparticles from biological precursors and water purification membrane systems. The focus will be on the nanoparticle immobilization, membrane stability, safety, and scalability of the technology.

## Introduction

Clean water supply is fundamental for maintaining public health, agriculture, industry, and sustaining the environment. The advancement in industries, increase in the number of inhabitants, expansion of urban areas, and intensified agricultural activities are some of the factors which have led to degradation of freshwater quality. Industrial effluents may be contaminated by synthetic dyes, solvents, metals, pharmaceuticals, among others, that are challenging to get rid of using traditional water treatment processes. Biological pollution, along with the existence of persistent organic substances, adds to the complexities of water purification. Membrane filtration technology is crucial because it offers the ability of separation, compact water purification process, and integration with other treatment methods (Bassiyouni et al., 2019).

Polymeric membranes are extensively studied due to their processability, light weight, and tunable separative characteristics. Nonetheless, they may be subject to degradation due to organic fouling, inorganic scaling, biofouling, and structural changes in the membrane itself over time. Fouling decreases water flux, raises the need for cleaning, and may even decrease the lifespan of the membrane. In order to counteract the above-mentioned issues, scientists have used inorganic nanoparticles within polymeric membranes.

ZnO and TiO<sub>2</sub> appear to be very promising metal oxides in their nanomaterial forms. ZnO can facilitate antimicrobial action and photocatalytic degradation, whereas TiO<sub>2</sub> has been extensively researched owing to its high chemical stability, photocatalytic properties, and surface property enhancing capabilities. Efficacy is determined by particle size, surface chemistry, dispersion, loading amount, and interactions with the polymer material. Reviews of studies on polymeric membranes containing ZnO and TiO<sub>2</sub> show that nanoparticles can help enhance membrane properties, but their efficacy cannot be assured in all cases (Bet-Moushoul et al., 2016; Shen et al., 2020).

Green synthesis is an approach towards synthesis of nanoparticles with the help of natural substances such as plant extracts, microorganisms, and biomolecules. The plant extract can provide the necessary substances for precursors conversion, nucleation, particles' formation, and their surface stabilization. Although green synthesis may decrease the use of hazardous chemicals, it requires the process of extraction, heating, washing, calcinations, and waste disposal, which makes the process environmentally friendly to some extent (Jadoun et al., 2024; Sunny et al., 2022).

Thus, the incorporation of green-synthesized ZnO and TiO<sub>2</sub> nanoparticles into polymeric membranes creates an example of application of green synthesis in the field of sustainable material synthesis and water purification at once. Nevertheless, the simultaneous study of synthesis, membrane performance, anti-fouling properties, nanoparticle elution, and reusability of such membranes is also needed. The research suggested is devoted to the systematic comparison of ZnO-, TiO<sub>2</sub>-, and hybrid ZnO/TiO<sub>2</sub> modified membranes.

### **Problem Statement**

Despite conventional polymeric membranes offering high-efficiency separation in a variety of water treatment processes, such membranes suffer from fouling, restricted permeability, inadequate removal of certain dissolved contaminants, and the need for frequent membrane cleaning. Additionally, conventional fabrication of nanoparticles may involve chemicals, solvents, and high energy, thus affecting the environmental friendliness of the process. Though ZnO and TiO<sub>2</sub> nanoparticles were investigated independently in terms of their application in photocatalysis, antimicrobials, and membranes, the efficiency of nanoparticles depends highly on their synthesis and membrane formation process.

In addition to this, the higher initial filtration efficiency does not always mean that the treatment process is any better or environmentally sustainable. Leaching of nanoparticles, decreased flux, degradation of membranes, and the production of potentially dangerous transformation products have to be examined as well. The main issue is thus to find out if green synthesis of ZnO and TiO<sub>2</sub> nanoparticles can be used to improve polymeric membranes for efficient water purification without compromising their strength and environmental safety.

### **Research Objectives**

1. The synthesis of ZnO and TiO<sub>2</sub> nanoparticles from plant extracts and characterization of their structure, morphology, and optical properties.
2. The preparation of polymer nanocomposite membranes by incorporating ZnO, TiO<sub>2</sub>, and ZnO/TiO<sub>2</sub> hybrid nanoparticles into membranes at varying loading amounts.
3. Evaluation of the impact of nanoparticle types and loading on membrane permeation, contaminant removal, antimicrobial activity, and fouling resistance.

### **Research Questions**

1. How does the plant extract synthesis of ZnO and TiO<sub>2</sub> nanoparticles impact their physicochemical characteristics?
2. How does nanoparticle type and concentration impact the permeability and selectivity of polymeric membranes?
3. Will the combination of ZnO and TiO<sub>2</sub> membranes yield better purification properties than individual use of any of these nanoparticles?

## Significance of the Study

The research is significant in terms of its scientific, technological, environmental, and practical implications. Scientifically, the research aims at exploring the correlation between green synthesis parameters, properties of nanoparticles, structure of membrane, and effectiveness of purification. The comparison of individual and combined nanomaterials can be helpful in understanding whether their combination results in complementary features or creates some problems like particle aggregation or pore clogging.

Technologically, the research intends to determine whether nanoparticle usage can contribute to increased wettability of membranes, increase water permeation, and reduce contaminant retention and fouling. Environmentally, green synthesis may contribute to less reliance on some of the conventional chemical processes; and the issue of nanoparticle leaching will be considered in terms of possible hazards connected with nanomaterials release. Practically, the results of the research can serve as an input in developing membranes for the purposes of industrial wastewater purification, decentralized water purification, as well as specific applications related to dye-polluted or microorganism-contaminated water. Nevertheless, the proposed membrane should be tested in relation to particular contaminants and be validated in order to be used in drinking water production.

## Literature Review

The biosynthesis of metal oxide nanoparticles is becoming popular since biological materials are able to become part of the formation process and the stabilization of the particles' surfaces. Plant extracts are a chemical mixture composed of various components such as polyphenols, flavonoids, sugars, proteins, and organic acids. The different types of components in the plant extract have an effect on the precursor transformation, nucleation, particle growth, and aggregation process. Jadoun et al. (2024) provided a review on the sustainable synthesis of ZnO nanoparticles through the use of plant extracts for environmental remediation. However, not all green synthesis processes are automatically environmentally friendly because of energy consumption and other factors.

Zinc oxide nanoparticles are appealing for water treatment purposes owing to their semiconductor behavior, surface activity, and possible antimicrobial property. Many biological systems have been studied as sources for the production of ZnO nanoparticles, such as plant leaves, flowers, fruits, and agricultural wastes. ZnO nanoparticles obtained from different synthesis processes can have various sizes, shapes, crystallinity, and surfaces. Nguyen et al. (2024) reported on the biogenesis of ZnO nanoparticles from flower extracts and considered their application in water treatment and other sectors. Hussain et al. (2024) provided a review of green synthesis and photocatalytic activities of ZnO nanoparticles in wastewater treatment. It can be expected that ZnO can contribute to pollutant degradation and other remediation processes; however, efficiency depends on pollutant properties, pH value, illumination intensity, nanoparticle properties, and water characteristics.

Titanium dioxide nanoparticles have been extensively researched for applications in photocatalysis and environmental remediation. Titanium dioxide can form electrons-holes pairs which can engage in reactions leading to formation of reactive oxygen species that will enable degradation of certain organic pollutants under the appropriate irradiation. In a review, Sunny et al. (2022) focused on green synthesis of TiO<sub>2</sub> nanoparticles from plant biomass, characterization and environmental applications. Shakeel et al. (2025) covered characterization of physicochemical characterization and applications of green synthesized TiO<sub>2</sub> nanoparticles where focus is on the correlation between preparation process and characteristics of nanoparticles. Another related review was carried out by Irshad et al. (2021). These reviews justify the effectiveness of TiO<sub>2</sub> in remediation; however, photocatalytic efficiency is determined by light availability, crystal structure, surface chemistry, and recombination of photogenerated charge carriers. Also, a photocatalytic membrane needs to be tested under certain light conditions, not darkness.

Polymeric nanocomposite membranes are prepared using the combination of a polymeric matrix along with nanomaterials. The polymer acts as a continuous structure and provides processability, whereas the nanomaterials can influence wettability, porosity, charge properties, and chemistry. Bassyouni et al. (2019) studied polymeric nanocomposite membranes for water purification and covered many types of membranes such as thin film nanocomposite membranes and membranes with inorganic nanomaterials. Sahu et al. (2023) considered advanced polymeric nanocomposite membranes for water and wastewater treatment and emphasized the capability of such membranes in separation and functional performances. These studies suggest that the effect of nanoparticles addition is affected by the polymer type, concentration of nanoparticles, preparation procedure, and separation process.

Polymeric membranes having zinc oxide have received a lot of attention for fouling reduction and membrane surface enhancement. Shen et al. (2020) studied the inclusion of ZnO nanoparticles in polymeric membranes and indicated that membrane fouling was one of the major challenges affecting performance. Ismail et al. (2013) presented a review of the effect

of different inclusion paths of metal and metal oxide nanoparticles on the structure and liquid-filtration capability of membranes. This review highlights that blending of nanoparticles into the polymer or deposition of them onto membrane surface results in various structures and performances. Distribution of the particles uniformly is crucial, as aggregation could cause defects, pore blockage, or weak interfacial bonding between the nanomaterial and polymer.

Polymer membranes with  $\text{TiO}_2$  have been investigated for enhanced hydrophilicity, photocatalytic behavior, and foulant mitigation properties. Bet-Moushoul et al. (2016) have compiled research on polymeric membranes with  $\text{TiO}_2$  for chemical engineering applications and explored the contribution of membrane modifications toward performance enhancement. The application of  $\text{TiO}_2$  in membranes may allow for the conversion of specific organic pollutants under appropriate light exposure. But photocatalytic activity alone does not ensure full mineralization or identification of intermediate conversion products. Therefore, the performance evaluation of a membrane should include physical separation analysis as well as chemical characterization of pollutants.

The hybrid approach combining both  $\text{ZnO}$  and  $\text{TiO}_2$  might provide some complementary properties of both. While  $\text{ZnO}$  is likely to add antimicrobial activity and surface properties,  $\text{TiO}_2$  would probably enhance the photocatalytic activity leading to pollutant degradation. However, the hybrid combination might also result in changes in optical absorption, particle aggregation, surface charge and interfacial properties. The role of supporting materials in the functional properties and applications of halloysite- $\text{TiO}_2$  nanocomposites for the water treatment was explained by Abid et al. (2023) in the review dedicated to this topic. This example might not prove that  $\text{ZnO}/\text{TiO}_2$  hybrid membrane is more effective than both components separately but illustrates the necessity of investigation of the combinations of materials through controlled comparisons. Membrane fouling is one of the major issues as the accumulation of contaminants leads to the growth of hydraulic resistance and reduces the productive operation. Increased hydrophilicity of the surface helps to decrease the formation of some types of foulants; however, the antifouling performance depends also on the roughness of the surface, the pore structure, the composition of the feed and the operating pressure.

The environmental safety issue is another key aspect to consider. The release of nanoparticles from polymeric membranes can occur during manufacturing, filtration, washing, or degradation of the membrane.  $\text{ZnO}$  can dissolve in water under certain conditions, whereas the impact on organisms depends on concentration, size, and surface chemistry of nanoparticles. Kang et al. (2024) reviewed the toxicity, regulations, and ecological risks associated with  $\text{ZnO}$  nanoparticles. Therefore, the environmental sustainability of the green approach cannot be determined solely based on plant extracts but also on the stability and management of the final product. Although numerous studies have been conducted on green-synthesized metal oxide nanoparticles and nanocomposite membranes, it is still useful to perform an integrated experimental evaluation of green-synthesized  $\text{ZnO}$ ,  $\text{TiO}_2$ , and composite  $\text{ZnO}/\text{TiO}_2$  membranes. Variations in the polymer type, loading of nanoparticles, methods of synthesis, and testing conditions make it challenging to compare the findings in existing papers. However, the planned study will address this issue by suggesting the design of experiments with the same polymer matrix, characterization of membranes, contaminants solutions, and multiple cycles of filtration. Additionally, the nanoparticle release will be taken into account.

## Research Methodology

The research will employ a quantitative experimental design to examine the synthesis of green nanoparticles of  $\text{ZnO}$  and  $\text{TiO}_2$  and the embedding of the particles in polymeric membranes. The experiments will be performed in a materials science or environmental engineering laboratory that has facilities for the synthesis of nanoparticles, fabrication of membranes, and testing of water quality. The plant material to be used will be chosen considering the availability, reproducibility, and the chemistry of the plants. The same source of plant extract can be used for both nanoparticle systems if it suits the requirements of both.

The plant material will be washed using distilled water, dried, and then cut into small pieces or crushed to form powder. A specific amount of the plant material will be dissolved in distilled water to produce an aqueous extract. The extract will be filtered to remove any solid contents, and then stored under appropriate conditions before use. The conditions involved in the preparation of extract such as the plant to water ratio, temperature and time required for extraction will be considered.

In case of  $\text{ZnO}$  synthesis, a proper precursor of zinc will be taken, e.g., zinc acetate or zinc nitrate, and dissolved in distilled water. Then the biological extract will be added to the solution in stirred mode, and pH will be regulated by adding a suitable base. The solution will be kept at a chosen temperature till the appearance of signs of nanoparticle formation. Further purification, washing and drying of the obtained product will take place. Thermal treatment (if required) will be chosen taking into account the needed crystalline state and thermal stability of the material.

As for  $\text{TiO}_2$  synthesis, the choice of the precursor will be made depending on its behavior in aqueous solutions. The addition of the precursor, pH adjustment, mixing, aging, washing and drying (and in some cases calcination) of the obtained material will

be used as the method for obtaining the target material. Since different titanium compounds react differently with water, the synthesis conditions will be chosen in advance through conducting some preliminary experiments. In no case will it be assumed that the same biological extract gives similar results in the synthesis of ZnO and TiO<sub>2</sub>.

Characterization of the nanoparticles will be done by the use of complementary methods. The crystalline phases will be determined by XRD, while the crystallite size will be estimated. FTIR will be used to study the functional groups and the organic residues that could still be present in the sample. SEM and TEM will be used to study the morphology of the samples, the degree of aggregation and size of the particles. Dynamic light scattering will be used for estimating the hydrodynamic size and polydispersity if dispersions are possible to prepare. UV-visible spectrophotometry will be used to check the absorption spectra of the materials, while elemental analysis using methods like energy-dispersive X-ray spectroscopy will help in determining the composition of the materials.

PVDF or polysulfone will be chosen for use as the polymeric matrix considering its availability and suitability with the membrane formation process. The first composition will include four main groups of membranes: pristine polymer, polymer with ZnO, polymer with TiO<sub>2</sub>, and polymer with ZnO/TiO<sub>2</sub> hybrid nanoparticles. In further studies, we will also consider nanoparticle concentration. For the start, we will consider nanoparticle concentration of 0.25%, 0.5%, 1.0%, and 2.0% by weight of the polymer. This concentration will be changed depending on dispersion and membrane properties. As for the hybrid membranes, nanoparticle concentration in the composition will remain equal to that in the separate nanoparticles compositions.

If the polymer and the laboratory equipment are compatible with that technique, membranes will be prepared by the appropriate technique like nonsolvent induced phase separation. The polymer will be dissolved in a proper solvent and nanoparticles will be dispersed via controlled mixing or sonication before casting the solution on a clean substrate at a fixed casting thickness. The film will be immersed in a nonsolvent bath for phase separation and membrane preparation. Afterwards, the membranes will be cleaned and conditioned following a standard protocol. Handling, ventilation, and disposal of solvents will be performed in compliance with laboratory safety regulations.

The morphology and structure of the membranes will be studied by SEM analysis, especially cross-sectional images will be useful for evaluating their porous structures and nanoparticle dispersion if applicable. FTIR will be conducted to reveal important chemical interactions while contact angles will be measured to study wettability properties. Membrane thickness, porosity, and mechanical strength will be also determined. Pure water permeation of the membranes will be studied by conducting filtrations at an applied pressure on a filtration cell.

The following hypotheses will direct the study:

**H1:** The use of green synthesized ZnO and TiO<sub>2</sub> in the membrane significantly enhances at least one membrane performance characteristic relative to the performance characteristics of the pure polymeric membrane.

**H2:** The combination of ZnO and TiO<sub>2</sub> in the right ratio leads to improved water purification performance relative to the performance of the two separate modifications of the membranes.

**H3:** The optimum level of nanoparticles loading enhances fouling resistance and flux recovery without adversely affecting contaminant rejection and mechanical strength.

**H4:** Performance of the membrane is significantly affected by the nanoparticles loading, dispersion, and leaching behavior.

## Results and Analysis

### Proposed Nanoparticle Characterization

The anticipated characterization study will include an analysis of crystal structure, particle shape, particle size distribution, and optical properties. The following values are indicative of the values that we hope to achieve.

**Table 1; Illustrative nanoparticle characterization results**

| Parameter                          | Green ZnO                | Green TiO <sub>2</sub> | ZnO/TiO <sub>2</sub> hybrid     |
|------------------------------------|--------------------------|------------------------|---------------------------------|
| Mean particle diameter (nm)        | 32                       | 28                     | 35                              |
| Crystallinity                      | Crystalline              | Crystalline            | Mixed crystalline phases        |
| Dominant morphology                | Near-spherical/irregular | Near-spherical         | Mixed morphology                |
| Illustrative optical band gap (eV) | 3.25                     | 3.15                   | To be experimentally determined |
| Batch replicates proposed          | 3                        | 3                      | 3                               |

From the indicative values, it can be concluded that both the nanoparticle structures would have been synthesized on nanoscale levels. Nevertheless, the particle sizes analyzed using TEM cannot be equated to crystallite sizes evaluated using XRD, owing to the fact that they measure distinct structural attributes. In a similar fashion, it is not possible to predict the band gap of the hybrid by averaging out the band gaps of ZnO and TiO<sub>2</sub>.

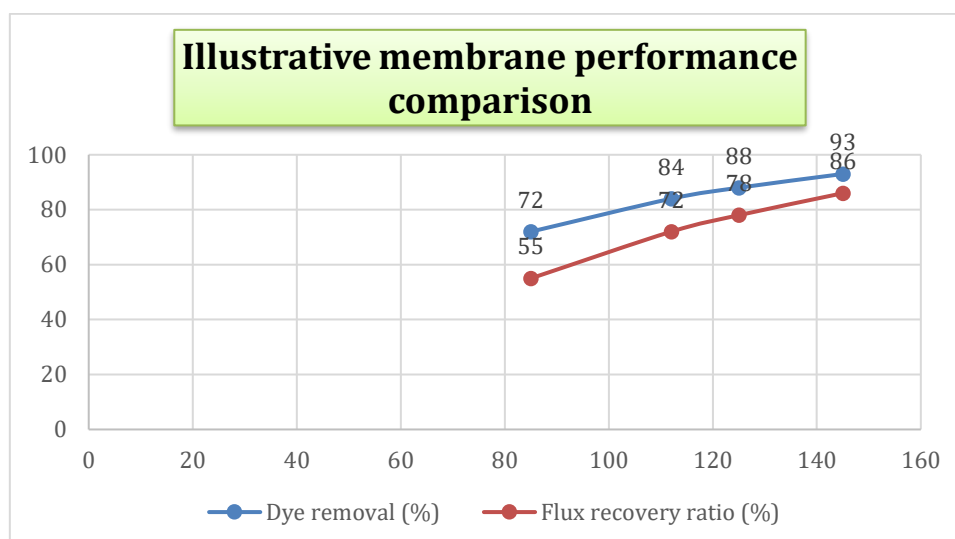
### Proposed Membrane Fabrication Comparison

There are four main membranes that can be produced: (a) pristine polymer; (b) ZnO-coated polymer; (c) TiO<sub>2</sub>-coated polymer; and (d) hybrid ZnO-TiO<sub>2</sub>-coated polymer. It should be noted that the last one should be treated as more favorable only when all enhancements are statistically justified.

**Table 2; Illustrative membrane performance comparison**

| Membrane formulation           | Pure-water permeability (L m <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> ) | Dye removal (%) | Flux recovery ratio (%) |
|--------------------------------|--------------------------------------------------------------------------------|-----------------|-------------------------|
| Pristine polymer               | 85                                                                             | 72              | 55                      |
| Polymer + ZnO                  | 112                                                                            | 84              | 72                      |
| Polymer + TiO <sub>2</sub>     | 125                                                                            | 88              | 78                      |
| Polymer + ZnO/TiO <sub>2</sub> | 145                                                                            | 93              | 86                      |

With respect to this particular scenario, the hybrid membrane has shown the highest water permeability, dye removal ability, and flux recovery ratio. With respect to the pure polymer, the hybrid membrane has shown the following illustrative increase in permeability



Illustrative improvement in the ability of removing dyes is 21 percentage points, from 72% to 93%. Illustrative increase in the flux recovery ratio is 31 percentage points, from 55% to 86%. The following shows how the results can be interpreted, although it does not guarantee the same improvement in a laboratory experiment.

### Analysis of Nanoparticle Loading

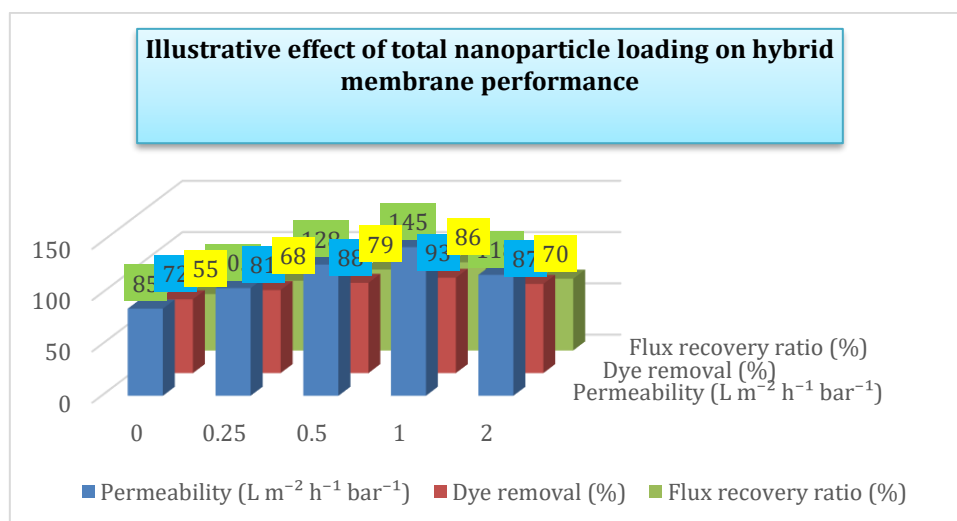
The concentration of nanoparticles is anticipated to have an influence on the structure as well as performance of the membrane. If the loading is too low, then there will be insufficient modification. If the loading is high, then aggregation could occur, pore blocking could occur, defects could be formed or the particle-polymer interface could be weakened.

**Table 3; Illustrative effect of total nanoparticle loading on hybrid membrane performance**

| Nanoparticle loading (wt% of polymer) | Permeability (L m <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> ) | Dye removal (%) | Flux recovery ratio (%) |
|---------------------------------------|---------------------------------------------------------------------|-----------------|-------------------------|
| 0.00                                  | 85                                                                  | 72              | 55                      |
| 0.25                                  | 105                                                                 | 81              | 68                      |
| 0.50                                  | 128                                                                 | 88              | 79                      |
| 1.00                                  | 145                                                                 | 93              | 86                      |
| 2.00                                  | 118                                                                 | 87              | 70                      |

Based on the hypothetical behavior of the material, it can be said that the formulation of 1.00 wt% offers the most ideal combination of properties amongst the concentrations mentioned above. The increase in the loading to 2.00 wt% leads to

reduction in permeability and flux recovery. If a similar observation were made during experimental study, then it might mean that high loading causes aggregation, modification in pore formation, or surface property alteration. All these factors require experimental validation.

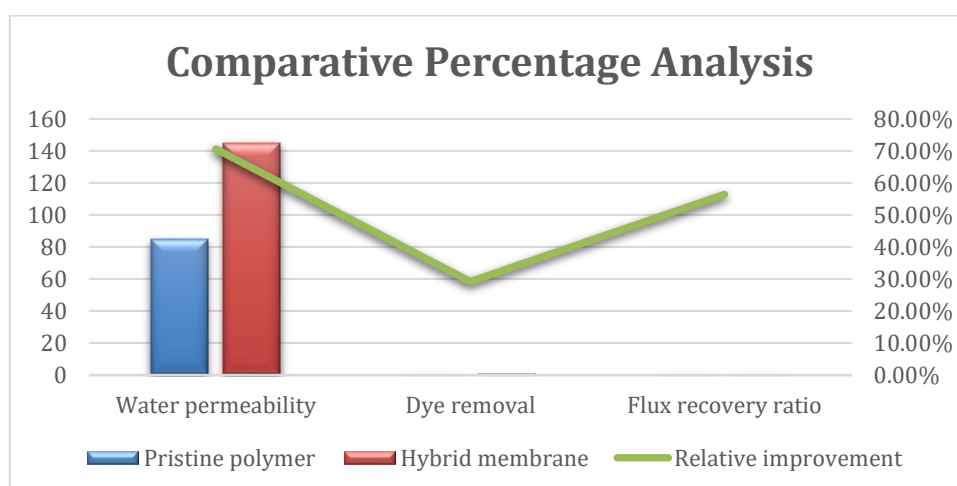


### Comparative Percentage Analysis

**Table 4; Illustrative improvement of the hybrid membrane over the pristine polymer**

| Performance indicator | Pristine polymer | Hybrid membrane | Relative improvement |
|-----------------------|------------------|-----------------|----------------------|
| Water permeability    | 85               | 145             | 70.6%                |
| Dye removal           | 72%              | 93%             | 29.2%                |
| Flux recovery ratio   | 55%              | 86%             | 56.4%                |

Relative improvement in the percentage of dye removal can be determined using the formula of  $((93-72)/72 \times 100 = 29.2\%)$ . The value is distinct from the 21 percentage point absolute improvement. Both metrics are important, yet there is a need to distinguish between them in order to avoid confusing the readership with inappropriate comparisons.



Furthermore, the sample data provided explain the need for an assessment of the performance of membranes using several metrics. While permeability is a desired metric, it does not provide much advantage if the rejection rate is not enough. Moreover, a high flux recovery ratio is beneficial only if it is associated with a low level of irreversible fouling.

### Proposed Statistical Analysis

**Table 5; Proposed statistical reporting framework**

| Research comparison                | Statistical method                    | Significance criterion  |
|------------------------------------|---------------------------------------|-------------------------|
| Permeability among membrane groups | One-way ANOVA, if assumptions are met | $p < 0.05$              |
| Dye removal among membrane groups  | One-way ANOVA or suitable alternative | $p < 0.05$              |
| Effect of nanoparticle loading     | Regression or dose-response analysis  | 95% confidence interval |

|                                                            |                                                                           |
|------------------------------------------------------------|---------------------------------------------------------------------------|
| <b>Flux recovery across cycles</b>                         | Repeated-measures model, where $p < 0.05$ appropriate                     |
| <b>Relationship between contact angle and permeability</b> | Correlation/regression Effect size and confidence interval                |
| <b>Nanoparticle leaching across formulations</b>           | Group comparison and trend analysis Compare with relevant safety criteria |

A claim of any statistical significance cannot be made until the experiment is actually conducted and data is analyzed. The example differences that appear in Tables 1 to 4 cannot be termed statistically significant without any calculations and supporting data.

## Discussion

The novel idea for the research entails combining green synthesis of nanoparticles with modification of polymeric membranes to overcome some disadvantages associated with the traditional water purification process. The key innovation of this research is the comparative analysis of the three systems – ZnO, TiO<sub>2</sub>, and hybrid ZnO/TiO<sub>2</sub> in an experimental setup. According to existing research, the materials have some surface and functional properties beneficial for water purification; however, their effectivity highly depends on the method of synthesis, membrane structure, nanoparticles concentration, and treatment conditions (Bet-Moushoul et al., 2016; Shen et al., 2020; Sahu et al., 2023).

The first key point to address is the connection between green synthesis and properties of nanoparticles. Using plant extracts as an alternative to traditional synthesis reagents in terms of low toxicity is possible, but the composition of the extract varies with the type of plant used, its growing conditions, season, and extraction technique. Therefore, standardizing the extraction procedure and registering the conditions of synthesis would be crucial to achieve consistency. Instead of judging the sustainability only by means of the origin of the capping/reducing agents, more general criteria should be considered – the energy needed, water used, precursors, and waste produced

The second aspect of the membranes is their hydrophilicity and permeability. The introduction of suitable metal oxide nanoparticles might improve the presence of hydrophilic surface groups and change the pores of the membrane. Thus, water transport will become possible in particular conditions. But, at the same time, the greater porosity/permeability and the agglomeration of the nanoparticles will result in lower selectivity and, therefore, lower rejection. That is why, the interpretation of the results obtained through contact angle measurements, pore characterization, permeability, and rejection of contaminants must go hand-in-hand. A membrane cannot be regarded as better just because it yields more permeate.

The third aspect that needs to be taken into account is the possibility of synergy between ZnO and TiO<sub>2</sub>. They have different characteristics and thus, when used simultaneously, they can provide a wider range of responses. In particular, ZnO can help in the antimicrobial activity and photocatalysis, whereas TiO<sub>2</sub> may be useful for the photocatalytic degradation of some organic compounds. At the same time, hybridisation may have its disadvantages, such as aggregation, change of surface charge, optical behaviour and the complexity of manufacturing.

Interpretation of photocatalysis is another task that requires caution. TiO<sub>2</sub> and ZnO may engage in photo-induced chemical processes, yet the degree of pollutant transformation will depend upon light source, wavelength, irradiance, exposure period, pH, dissolved oxygen, and pollutant structure. The polymeric matrix might limit the accessibility of reactive sites or influence light transmission. In case photocatalytic behavior of the system is studied, one must run control experiments without light, in darkness, with pristine membrane and membrane with nanoparticles. Pollutant removal should be distinguished from mineralization since disappearance of the pollutant is not equal to its complete decomposition into harmless compounds.

Resistance to fouling and reusability are key factors for membrane performance. Improvement in initial flux might be compensated by the increase in fouling rate during prolonged use. Proposed flux recovery ratio and repeated cycles testing would allow to distinguish between short-term and long-term performance. Further study of irreversible fouling, clean-up efficiency, membrane integrity, and rejection changes would provide more thorough evaluation of the membrane properties. The proposed hybrid membrane would be practically interesting if it retains its performance after multiple filtrations and clean-ups.

Safety of the environment is as critical as well. Nanoparticles synthesized through a green route are not always nontoxic, and immobilization within a polymeric matrix does not always mean that no particles or soluble substances are going to be released. Dissolution of ZnO and the possible release of Ti-containing particles and residues must be assessed using realistic conditions of water composition. In the experimental programme there must be enough filtration runs, correct analytical detection limits and information about the form in which material is going to be released. Comparison must be done against the appropriate

standard and risk assessment for the particular application. Use of water for drinking will require stricter validation than preliminary laboratory dye removal experiment.

The representative results in Section 4 can show the typical trend according to which hybrid membrane outperforms the pristine one. This assumption must be checked by the data obtained and if confirmed, then it will imply that the hybridization provides enhancement of several membrane characteristics at once. But there are also other possibilities such as better performance of  $\text{TiO}_2$  by itself, better antifouling performance of  $\text{ZnO}$  and lower permeability of all modified membranes due to pores blocking.

In terms of practical considerations, this membrane technology may have some application in specific industrial wastewater, where there is a presence of dyes or other organic pollutants that can be removed by the technology. The membrane may also be tested in the case of microbial or dissolved contaminants, depending on the pore size and functionality of the membrane. However, this technology cannot be considered as a general solution to all contaminants, and in case of some feedwaters, pre-treatment, adsorption, biological treatment, advanced oxidation, or other membrane filtration stages may be needed.

Finally, the development of the technology should also include consideration of economic aspects and life cycle assessment. The cost of the preparation of plant extracts, synthesis of precursors, solvents for the polymer, energy, membrane manufacturing and cleaning, and replacement costs should be estimated. The advantages of reduced fouling and contamination removal should be compared with the cost of manufacture and disposal of the membranes. Pilot testing of this technology using actual wastewater should be performed to check its economic feasibility.

## Conclusion

In this research, an integrated technique for the green synthesis of  $\text{ZnO}$  and  $\text{TiO}_2$  nanoparticles and their embedding into polymeric nanocomposite membranes for water treatment will be developed. Biological reagents based on plant extracts will be tested as bio-agents for the synthesis and stabilization of nanoparticles, whereas characterization will be performed by using XRD, FTIR, SEM, TEM, and UV-visible techniques. Nanoparticles will be loaded into a polymeric membrane matrix and characterized by water permeation, contaminants rejection, fouling resistance, reuse, and nanoparticle leaching.

The experiment proposed here will include the comparison of pristine polymeric membranes with  $\text{ZnO}$ -,  $\text{TiO}_2$ -, and  $\text{ZnO/TiO}_2$ -modified membranes. Nanoparticle loading in a controlled manner will allow choosing an appropriate composition and examining the potential drawbacks related to nanoparticle loading. In terms of the results' framework, it is important to note that permeability, rejection, flux recovery, stability, and ecological safety should be evaluated in a combined way.

As seen from the illustrative tables above, a combined membrane can possibly enhance water permeability, dye rejection, and flux recovery over a modified one. But this is only theoretical data and cannot be used as the basis for the experiment. Any conclusions regarding the membrane's effectiveness, its statistical significance and ecological advantages should be made using laboratory data.

In general, green synthesis of metal oxide nanoparticles opens an interesting perspective for developing polymeric membranes. Their effective use will be determined by the reproducibility of their synthesis, distribution of nanoparticles, stability of membranes, effectiveness of contaminant removal, low release of materials and reasonable costs.

## Recommendations

1. Standardize extraction process of plant material. Use a specific type of plant, ratio of extraction, temperature, time and storage method to enhance reproducibility during synthesis.
2. Optimize nanoparticle synthesis parameters. Optimize nanoparticle concentrations, pH, temperature, aging and possible thermal treatment after synthesis.
3. Characterize nanoparticles for each experiment. Characterization should be done using various characterization techniques for each batch of nanoparticles prior to membrane fabrication.
4. Test individual and hybrid membranes. Test individual,  $\text{ZnO}$ ,  $\text{TiO}_2$ , and  $\text{ZnO/TiO}_2$  membranes under same experimental conditions.
5. Identify the optimal nanoparticle concentration. The loading range for nanoparticle should be determined to achieve appropriate permeability, contaminant rejection, antifouling and stability of the membrane.

6. Proper dispersion of nanoparticles in polymer matrix. Consider proper methods of dispersion of nanoparticles and investigate whether particle aggregation and polymer/particles interactions influence membrane properties.
7. Consider multiple purification indices. Evaluate permeability, contaminant rejection, turbidity, fouling, flux recovery and membrane integrity rather than a single index.

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