

Research paper

Interfacial Engineering of PES Mixed Matrix Membranes Using Green-Synthesized ZnO Nanoparticles for Enhanced Water Transport, Selectivity, and Antifouling Performance

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Abstract: The incorporation of functional nanofillers into polymeric membranes offers a powerful pathway to overcome the inherent permeability–selectivity trade-off and fouling limitations of conventional mixed matrix membranes (MMMs). However, achieving uniform nanofiller dispersion while preserving membrane structural integrity and transport selectivity remains a critical challenge. In this study, green-synthesized zinc oxide nanoparticles (ZnONPs), produced using *Calotropis gigantea* leaf extract, were incorporated into polyethersulfone (PES) membranes via phase inversion to systematically engineer membrane interfacial properties and transport pathways. Structural and physicochemical characterization confirmed successful nanoparticle incorporation and revealed that ZnONPs significantly modified membrane hydrophilicity, pore architecture, and surface charge characteristics. The improved performance is attributed to nanoparticle induced acceleration of solvent–non-solvent exchange during phase inversion, resulting in enhanced pore connectivity, increased surface hydrophilicity, and optimized selective layer formation. Furthermore, the modified membranes demonstrated substantially improved antifouling behavior due to the formation of stable hydration layers and reduced foulant adhesion. These results demonstrate that green-synthesized ZnONPs can serve as effective interfacial modifiers to simultaneously enhance membrane permeability, selectivity, and fouling resistance, providing a sustainable and scalable strategy for advancing high-performance polymeric membranes for water purification.

Keywords: Green Synthesized ZnO nanoparticles; Mixed matrix membrane; Polyethersulfone; Water purification; Sustainable membrane technology

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1. Introduction

The availability of clean water plays a crucial role in protecting public health, supporting economic development, and preserving the environment. Yet, increasing industrialization, agricultural runoff, and urban expansion have severely compromised freshwater quality. Pollutants in wastewater pose long-term environmental and health risks owing to their toxicity, persistence, and tendency to bioaccumulate in living organisms [1, 2]. Traditional treatment approaches like coagulation, adsorption, and distillation are often insufficient for effectively removing such low concentration or persistent contaminants [3]. This challenge results in creating a growing demand to achieve water purification technologies that are more efficient, sustainable, and economically viable [4].

Among emerging solutions, membrane based separations has gained attraction due to its modular design, energy efficiency, and ability to selectively remove a wide range of pollutants [5]. In particular, mixed matrix membranes (MMMs) comprising of polymer matrix embedded with inorganic nanofillers, have shown enhanced performance in permeability, mechanical strength, and fouling resistance [6]. In the past two decades, researchers have explored the potential of wide range of fillers in MMMs to enhance performance characteristics. Nanofillers such as titanium dioxide (TiO₂), graphene oxide (GO), carbon nanotubes (CNTs), and metal organic frameworks (MOFs) impart functionalities like antimicrobial activity, photocatalytic degradation, and improved surface hydrophilicity [7-11].

Despite these benefits, membrane fouling remains a major operational challenge, as biological, organic, or inorganic matter accumulates on the membrane surface. This reduces performance and increases cleaning frequency and maintenance costs. To mitigate this, functional nanomaterials such as TiO₂ and ZnO are employed for their self-cleaning properties, while GO and CNTs reduce fouling via surface charge repulsion. Incorporation of AgNPs in MMMs imparts pronounced antimicrobial activity [12, 13]. However, the majority of these nanomaterials are produced through conventional chemical synthesis routes that involve toxic reagents, high energy inputs, and environmentally hazardous by-products thereby raising concerns about sustainability and cost effectiveness [14].

To address these issues, green synthesis methods using plant extracts have emerged as eco-friendly alternatives. These approaches eliminate the use of harmful chemicals and produce nanoparticles that retain bioactive properties such as antimicrobial and antioxidant activity [15]. Nanoparticles synthesized through green methods have been effectively applied in various fields, such as catalysis, drug delivery, and environmental remediation [16]. Among green nanomaterials, ZnO nanoparticles (ZnONPs) have gained particular attention due to their favorable characteristics: low toxicity, photocatalytic activity, environmental compatibility, and cost-efficiency [17]. When synthesized through plant mediated methods, ZnONPs exhibit multifunctional properties such as antimicrobial, antioxidant, and anti-inflammatory effects. Various plant based sources have been extensively applied in nanoparticle synthesis, where phytochemicals serve as natural reducing and stabilizing agents. These include leaves, peels, roots, and flowers from numerous medicinal and agricultural plants. Green nanoparticles are increasingly integrated into polymeric membranes, where they serve as functional nanofillers to improve hydrophilicity, permeability, antifouling behavior, and pollutant rejection [18]. Several studies have reported promising results using green synthesized ZnONPs for environmental applications. For example, ZnONPs synthesized from *Moringa oleifera* leaf extracts achieved over 90% degradation of dyes and demonstrated strong antibacterial activity suitable for industrial wastewater treatment [19]. A ZnO-CNFs nanocomposite synthesized using *Thymus daenensis* and *Stachys pilifera* Benth extracts showed high tetracycline removal and strong antimicrobial activity [20]. ZnONPs synthesized with jujube extract showed high removal of methylene blue and eriochrome black-T under sunlight in 5 hours [21].

In membrane specific applications, ZnONPs derived from *Arthrospira platensis* were incorporated into cellulose acetate membranes, achieving 94.77% Cr (VI) removal and enhanced water flux, with adsorption following Langmuir and pseudo-second-order kinetic models [22]. Similarly, rGO/ZnO nanocomposites synthesized with *Saraca asoca* extract improved dye rejection and flux recovery in PVDF membranes [23]. Studies using pomegranate and tangerine based green synthesized ZnO and TiO₂ NPs also demonstrated enhanced hydrophilicity, flux, and up to 98.7% rejection in PVC membranes [24]. ZnONPs from *Aloe vera* added to PSf membranes improved mechanical strength, porosity, and humic acid rejection (up to 99.9%), with 0.3–0.5 wt% loadings providing optimal antifouling and permeability [25]. Although many plant sources have been explored,

their application in membrane technology especially those from underutilized or invasive plants remains limited. Among these, *Calotropis gigantea* is notable for its phytochemical richness and wide availability, often classified as agricultural or roadside waste. As an invasive species, it contributes to land degradation by displacing native vegetation, yet its use in nanoparticle synthesis can provide environmental value by converting waste into functional material. While ZnO incorporation into polymeric membranes is by now a well-established strategy for improving hydrophilicity, permeability, and antifouling behavior, the specific novelty of the present work lies in (i) the use of an underutilized, invasive plant biomass as the ZnO precursor, converting an ecological liability into a functional nanomaterial feedstock, and (ii) the systematic interfacial-engineering framework linking *Calotropis gigantea*-derived phytochemical capping chemistry to phase inversion kinetics leading to enhanced pollutants rejection.

Despite extensive research on nanoparticle-incorporated MMMs, achieving simultaneous enhancement in permeability, selectivity, and fouling resistance remains fundamentally constrained by challenges associated with nanofiller dispersion, interfacial compatibility, and structural control during membrane formation. In particular, the role of green-synthesized nanoparticles as active interfacial modifiers influencing phase inversion kinetics, pore architecture evolution, and transport pathway formation remains insufficiently understood. Addressing this gap requires a systematic investigation of how bio-derived nanomaterials interact with polymer matrices to regulate membrane structure–property–performance relationships. In this study, ZnONPs synthesized via a plant-mediated route using *Calotropis gigantea* leaf extract were incorporated into PES membranes to engineer interfacial properties and modulate membrane formation dynamics. We hypothesize that the hydrophilic surface chemistry and interfacial activity of green-synthesized ZnONPs can accelerate solvent–non-solvent exchange during phase inversion, resulting in enhanced pore connectivity, improved surface wettability, and optimized selective layer formation. This interfacial engineering strategy is expected to simultaneously improve water transport, solute rejection, and antifouling resistance. By evaluating the structure–transport relationships arising from nanoparticle-mediated interfacial modification, this work provides fundamental insight into the design of high performance MMMs and establishes a scalable approach for engineering advanced polymeric membranes using environmentally benign nanomaterials.

2. Materials and methods

2.1 Materials

Fresh and healthy leaves of *Calotropis gigantea* were collected from the Defense Housing Authority (DHA), Lahore, Pakistan. The plant material was taxonomically identified as *Calotropis gigantea* (L.) W.T. Aiton by Dr. Tasleem Rasool, Assistant Professor, Department of Botany, Government College University Lahore, Pakistan. A voucher specimen has been deposited in the herbarium of Government College University Lahore under voucher specimen number GCUSAH-5188. Polyethersulfone (PES, MW $\approx$ 75,000 g/mol) was purchased from BASF (Germany). N-Methyl-2-pyrrolidone (NMP, ACS grade, 99%) and zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, MW = 297.49 g/mol] were obtained from Sigma-Aldrich (Germany). Tetrahydrofuran (THF) and aluminum chloride (AlCl_3 , MW = 133.34 g/mol) were procured from Carlo Erba Reagents (France). Magnesium sulfate (MgSO_4 , MW = 120.37 g/mol) and Congo red (CR, MW = 696.6 g/mol) were sourced from Daejung (Korea) and Applichem Panreac (Germany). Additional reagents included sodium arsenite (NaAsO_2 , MW = 129.91 g/mol), copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, MW = 249.69 g/mol), chromium(III) chloride hexahydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, MW = 266.45 g/mol), and aluminum nitrate nonahydrate [$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, MW = 375.13 g/mol], all obtained from Sigma-Aldrich (Germany). Unless otherwise specified, all chemicals were of analytical or reagent grade.

2.2 Methods

2.2.1 Preparation of the *Calotropis gigantea* leaves extract

Fresh leaves of *Calotropis gigantea* were thoroughly rinsed with deionized water to remove surface impurities, dust, and soluble contaminants, followed by shade drying at ambient temperature for 48 h to eliminate residual moisture while preserving thermally sensitive phytochemical constituents. The dried leaves were then finely ground into powder using a mechanical grinder to increase surface area and enhance extraction efficiency. Subsequently, 60 g of the powdered biomass was immersed in DI water to form a homogeneous suspension. The mixture was heated at 80 °C under continuous magnetic stirring for 1 h to promote the

efficient extraction of bioactive phytochemicals, such as polyphenols, flavonoids, and organic acids, which act as natural reducing and stabilizing agents during nanoparticle synthesis. The gradual development of a pale yellow coloration confirmed the successful release of these phytochemical species into the aqueous medium. Following extraction, the suspension was allowed to cool naturally to room temperature to prevent thermal degradation of the extracted compounds. The mixture was then filtered to remove insoluble plant residues and obtain a clear aqueous extract. The filtrate was collected in airtight glass containers and stored at 4 °C to preserve its chemical stability and prevent microbial degradation prior to use in nanoparticle synthesis. The extraction procedure was adapted with minor modifications from previously reported plant mediated nanoparticle synthesis protocols [26].

2.2.2 Synthesis of ZnONPs

Green-synthesized ZnONPs were prepared using *Calotropis gigantea* aqueous leaf extract as a phytochemical mediated complexing and stabilizing medium. A volume of 50 mL of freshly prepared plant extract was transferred into a reaction flask and heated to 70 °C under continuous magnetic stirring to activate phytochemical functional groups and promote interaction with the metal precursor. 5g Zinc nitrate hexahydrate was then gradually introduced into the heated extract under constant stirring to ensure uniform precursor dispersion and controlled nucleation. The reaction mixture was maintained at 70 °C for 2 h to promote homogeneous precursor complex formation, followed by continued stirring at ambient temperature for 72 h to allow complete precursor maturation. The obtained precursor was subsequently calcined at 400 °C for 2 h in a furnace under ambient atmosphere. The material was gently ground using a mortar and pestle to obtain a uniform particle distribution and stored in airtight glass vials under dry conditions at room temperature prior to characterization and membrane fabrication. The synthesis protocol was adapted with minor modifications from established plant-mediated ZnO nanoparticle synthesis methods [27].

2.2.3 Fabrication of Mixed Matrix Membranes

ZnONPs were incorporated as functional inorganic nanofillers to engineer the interfacial and structural properties of PES MMMs. Membranes were fabricated via the non-solvent induced phase inversion (NIPS) method, which enables precise control over pore structure, selective layer formation, and overall membrane morphology through thermodynamically driven solvent–non-solvent exchange processes [28]. The reference PES membrane was prepared using a polymer casting solution containing 22 wt% PES dissolved in a binary solvent system of NMP and THF at a volumetric ratio of 3:1. For MMM fabrication, ZnONPs were added to the solvent mixture at loadings of 0.25, 0.5, 0.75, and 1 wt% relative to the polymer mass. The polymer casting solution (PES/NMP/THF) was kept the same for all membranes to ensure fair comparison. The dispersion was stirred continuously for 1 h to ensure homogeneous suspension and minimize particle aggregation. PES powder was subsequently introduced into the nanoparticle dispersion in a stepwise manner to facilitate uniform polymer dissolution and promote effective nanoparticle distribution within the polymer matrix. The casting solution was stirred continuously for 24 h at ambient temperature to ensure complete polymer dissolution and stable nanoparticle dispersion. The prepared dope solution was then degassed by leaving it overnight to eliminate entrapped air bubbles. Membrane casting was performed on a nonwoven polypropylene/polyethylene (PP/PE) support (Novatexx-2471) mounted on a clean glass plate. Prior to casting, the support surface was lightly wetted with NMP to improve adhesion and prevent premature solvent extraction into the support pores. The polymer solution was cast using an automatic film applicator (Elcometer, UK) under controlled conditions. Following casting, the liquid film was exposed to ambient air for 30 s to allow partial solvent evaporation. The cast film was then immediately immersed in a deionized water coagulation bath at room temperature to initiate solvent–non-solvent exchange and complete the phase inversion process. The membranes were rinsed thoroughly with fresh deionized water to remove residual solvent and stored in deionized water prior to characterization and performance testing. Membranes were designated according to ZnONP loading, as summarized in Table 1.

Table 1. Details of the membrane formulations

Membrane	PES wt. %	NMP wt. %	THF wt. %	ZnONPs wt. % w.r.t PES
Neat	22.0	58.5	19.5	0
0.25wt%	22.0	58.5	19.5	0.25
0.5wt%	22.0	58.5	19.5	0.5
0.75wt%	22.0	58.5	19.5	0.75
1wt%	22.0	58.5	19.5	1

2.3 Characterizations Techniques

The formation of the *Calotropis gigantea* extract as well as the biosynthesis of ZnONPs was initially confirmed through UV–Visible spectroscopy. Absorbance spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Functional group identification and evaluation of potential chemical interactions in both the ZnONPs and the prepared MMMs were performed using Fourier transform infrared (FTIR) spectroscopy. Measurements were collected with a Thermo Nicolet 6700 instrument (USA) within the 500–4000 cm^{-1} range. The crystalline structure of the nanoparticles and membranes was assessed by X-ray diffraction (XRD) using a PANalytical X'Pert Pro PW3050/60 diffractometer (Philips, Malvern, UK). To examine surface wettability, static water contact angles were determined. A droplet of deionized water was carefully placed on a smooth, dry section of each membrane, and the angle was measured once equilibrium was attained. Morphological analysis was carried out by scanning electron microscopy (SEM). The membrane surface and cross-sectional morphologies were observed using a Hitachi S-4800 system (Japan). For membrane imaging, samples were cryo-fractured in liquid nitrogen and sputter-coated with a thin gold film to improve conductivity and reduce beam charging effects.

Membrane porosity was determined using the gravimetric wet–dry method. Membrane samples were first immersed in deionized water for 24 h at room temperature to ensure complete saturation of all accessible pores. After immersion, excess surface water was carefully removed using filter paper, and the wet membrane mass (W_w) was immediately recorded using an analytical balance. The membrane was then dried in an oven at 60 °C for 24 h to remove all absorbed water, followed by cooling in a desiccator prior to measuring the dry mass (W_d).

The membrane porosity (ε) was calculated using:

$$\varepsilon = \frac{W_w - W_d}{\rho_w A l} \quad (1)$$

Where W_w is the wet membrane mass (kg), W_d is the dry membrane mass (kg). ρ_w is the density of water, A is the effective membrane area (m^2), and l is the membrane thickness (m)

2.4 Membrane Performance

The separation performance of the prepared membranes was examined using a dead end filtration setup (HP4750 stirred cell, Sterlitech, USA), as shown in the schematic Figure 1. Prior to testing, membranes underwent compaction under nitrogen. Subsequently, pure water permeability (PWP) was measured using the following equation:

$$\text{PWP} = \frac{V}{t \cdot A \cdot \Delta P} \quad (2)$$

where V represents the collected permeate volume (L), A is the effective membrane surface area, t denotes the filtration time (h), and ΔP is the applied transmembrane pressure.

Salt rejection experiments were conducted using separate aqueous solutions (1000 ppm each) of NaCl, MgSO_4 , and CaCl_2 to evaluate membrane performance. Permeate conductivity was measured with a conductivity meter (Hanna Instruments, USA) and subsequently used to calculate salt rejection.

Salt rejection was evaluated using the equation given below:

$$R (\%) = \left(1 - \frac{C_p}{C_f} \right) \times 100 \quad (3)$$

where C_f and C_p are salts concentrations in feed and permeate, respectively.

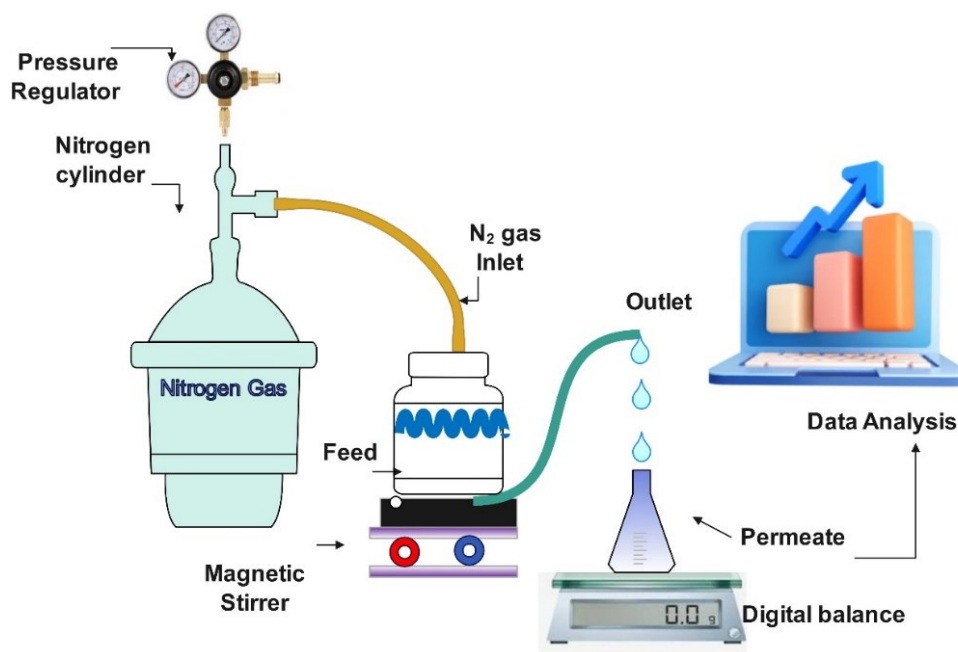


Figure 1. Schematic representation of the dead-end filtration setup

Long-term filtration experiments were conducted for up to 36 h to evaluate the stability of membrane separation performance under sustained operating conditions. The metal ion rejection of the membranes was also investigated using synthetic feed waters containing arsenic (As), copper (Cu), chromium (Cr), and aluminum (Al). Permeate samples were subsequently analyzed by atomic absorption spectroscopy (Agilent Technologies, USA).

Fouling resistance of the membranes was evaluated using sodium alginate as a model foulant at 1000 ppm. The test protocol consisted of three sequential phases. In the first stage, cycles of pure water filtration were conducted (J_1). In the second stage, fouling experiments were performed using the sodium alginate solution (J_p) under identical operating conditions, followed by membrane rinsing with deionized water for 30 min to facilitate foulant removal. The third stage involved repeating cycles of pure water filtration (J_2) to assess the degree of flux recovery.

Antifouling behavior was quantified through standard metrics, including the flux recovery ratio (FRR), total fouling ratio (R_t), reversible fouling ratio (R_r), and irreversible fouling ratio (R_{ir}), calculated according to established equations.

$$FRR (\%) = \left(\frac{J_2}{J_1} \right) \times 100 \quad (4)$$

$$R_t = \left(1 - \frac{J_p}{J_1} \right) \times 100 \quad (5)$$

$$R_r = \left(\frac{J_2 - J_p}{J_1} \right) \times 100 \quad (6)$$

$$R_{ir} = \left(\frac{J_1 - J_2}{J_1} \right) \times 100 \quad (7)$$

Where J_1 and J_2 are PWP before and after cleaning. R_t is the total fouling, R_r is reversible fouling and R_{ir} is the irreversible fouling.

3. Results and Discussion

3.1 Characterizations of zinc oxide nanoparticles

Figure 2(a) presents the UV-Visible absorption spectra of the *Calotropis gigantea* leaf extract, exhibiting a prominent absorption peak at ~400 nm. This peak is attributed to $\pi \rightarrow \pi^*$ transitions of conjugated aromatic systems (e.g., polyphenols and flavonoids) and $n \rightarrow \pi^*$ transitions of carbonyl-containing compounds present in the extract [29]. As shown in Figure 2(b), the synthesized ZnONPs display a sharp absorption band centered at ~367 nm, which is characteristic of the band-gap absorption of ZnO, corresponding to electron excitation from the valence band to the conduction band. This confirms the successful formation of ZnO nanoparticles [30].

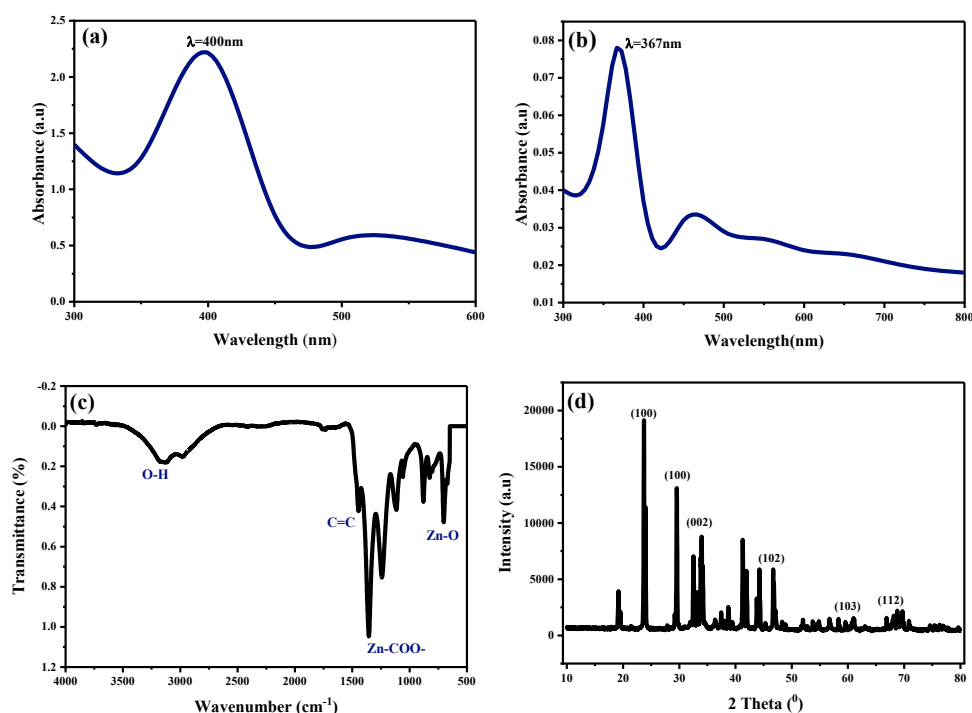


Figure 2. (a) UV-visible absorption Spectra of *Calotropis Gigantea* leaf Extract (b) UV-Visible Spectra of green synthesized ZnONPs (c) FTIR spectra of ZnONPs. (d) XRD pattern of ZnONPs

The FT-IR spectrum of the synthesized ZnONPs presented in Figure 2(c) exhibited a strong band at 704 cm^{-1} , attributed to the metal–oxygen (Zn–O) stretching vibration. Peaks observed at 1450 cm^{-1} correspond to the asymmetric stretching of carboxylate groups and possible C=C or C=O vibrations, respectively. The notable peak at 1358 cm^{-1} is attributed to the presence of Zn-COO. Additionally, a wide band appearing around 3150 cm^{-1} was attributed to O-H stretching, suggesting the existence of hydroxyl functionalities. These findings suggest the successful capping of ZnONPs by phytochemicals containing -OH and -COOH functional groups derived from *Calotropis gigantea* extract. These functional groups can facilitate electrostatic interactions with cationic molecules, enhancing the nanoparticles' potential for targeted applications [31].

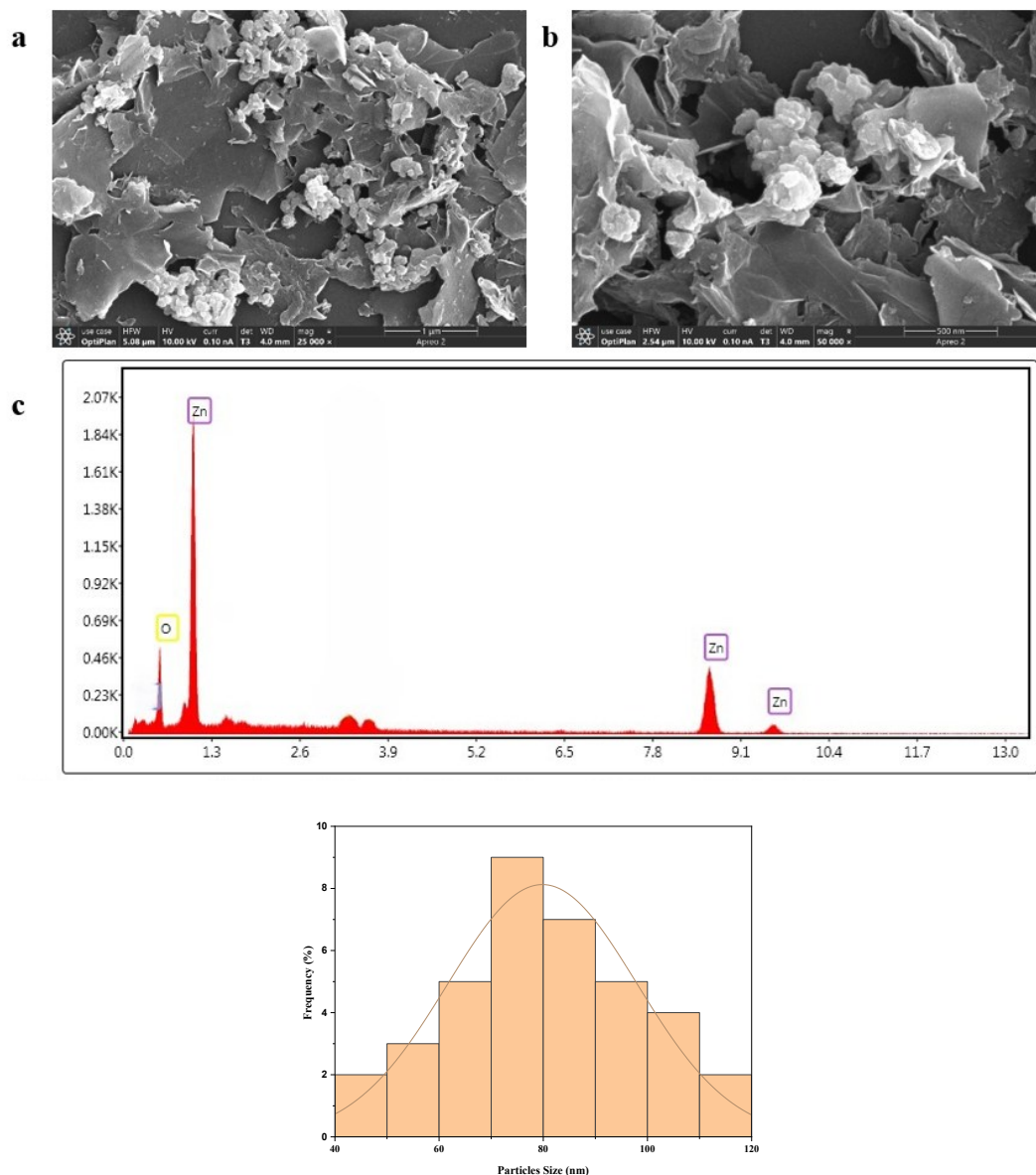


Figure 3. (a & b) SEM images of green synthesized ZnONPs at multiple resolution, **(c)** Energy dispersive X-ray spectroscopy EDX of ZnONPs **(d)** Particles size distribution of ZnONPs

The XRD results (Figure 2d) of ZnONPs showed characteristic peaks highlighting the high crystallinity of the material, in agreement with previous reports [27]. These results confirm the purity and successful synthesis of ZnONPs. The SEM micrographs (Figure 3a and 3b) demonstrate an irregular morphology at different resolutions. In Figure 3a, a broad view of the surface morphology reveals ZnONPs dispersed as fine clusters across a rugged and irregular substrate. This substrate likely comprises residual phytochemicals or organic compounds from the plant extract, serving as both reducing and capping agents during the synthesis. The particles appear relatively well-dispersed despite occasional agglomerates, a phenomenon commonly attributed to the high surface energy and inherent instability of particles formed via green routes [32].

EDX analysis provided confirmation of the elemental constituents present in the synthesized ZnONPs, with the spectrum (Figure 3c) showing distinct peaks only for Zn and O. The lack of extra peaks suggests excellent chemical purity, with no contamination from other elements. This purity is attributed to the post-synthesis calcination process, which effectively removes residual organic matter and stabilizes the ZnONPs structure. These results validate the formation of stoichiometric ZnONPs and confirm the

material's suitability for applications requiring high purity and structural integrity. Figure 3(d) shows that the ZnONPs exhibit a narrow and near-Gaussian profile, indicating uniform nanoparticle formation. The particle sizes range from ~40 to 120 nm, with a dominant peak around ~80 nm, representing the average particle size. The symmetric profile reflects controlled nucleation and growth, while the limited spread indicates minimal aggregation and good dispersion of nanoparticles.

3.2 Characterizations of MMMs

FT-IR analysis serves as an effective method to reveal the interactions between PES and ZnONPs. As illustrated in Figure 4(a), the FT-IR spectra of the MMMs were recorded for different loadings. The bands appeared at 2880 cm^{-1} and 2950 cm^{-1} demonstrated the asymmetrical and symmetrical stretching vibration of C-H bond. In the case of MMMs, vibrational bands observed at 1450 cm^{-1} and 650 cm^{-1} were attributed to Zn-carboxylate bond and Zn-O stretching respectively. This observation indicates that the surface hydroxyl (Zn-OH) groups of ZnO, together with residual O-H/C-H-bearing phytochemical capping agents from the extract, underwent partial deprotonation during its interaction with PES. Figure 4(b) illustrates the water contact angle of the MMMs, showing a clear dependence of surface hydrophilicity on ZnONPs loading. A gradual reduction in contact angle was observed with increasing ZnONPs concentration, indicating enhanced hydrophilicity of the membrane surface. The neat PES membrane exhibited a contact angle of 83° , which decreased to 63° at 0.75 wt.% ZnONPs, confirming that the incorporation of ZnONPs significantly improves the membrane's hydrophilic character due to the introduction of polar functional groups and improved surface wettability. This enhanced hydrophilicity facilitates the formation of a stable hydration layer on the membrane surface, which reduces interfacial resistance to water transport, leading to improved permeation flux, while also minimizing foulant adsorption through reduced hydrophobic interactions, thereby enhancing antifouling performance. However, at higher loading (1 wt.%), the contact angle increased to 80° , indicating a decline in hydrophilicity, which is likely attributed to nanoparticle agglomeration. Such aggregation results in non-uniform dispersion, reduced effective surface area, and partial masking of hydrophilic functional groups, thereby disrupting surface uniformity, hindering effective pore formation, and slightly diminishing membrane performance compared to membranes with well-dispersed nanoparticles.

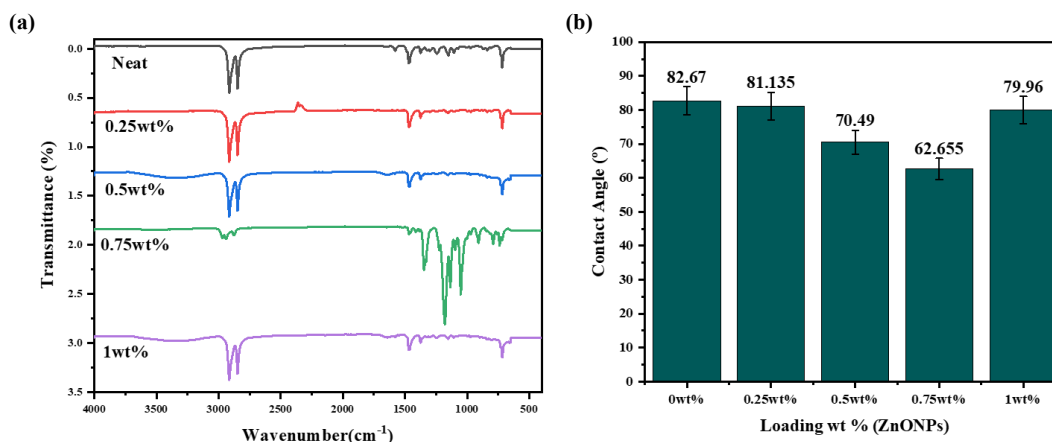


Figure 4. (a) FT-IR spectrums of neat PES and MMMs, (b) Contact angle measurement of Neat PES and MMMs

To examine the surface and cross-sectional morphology of the membranes, SEM images were captured and are presented in Figure 5 (a–h). The neat membrane (Fig. 5 a & b) shows a smooth surface and an asymmetric cross-section supported by finger-like voids in the substructure, which is characteristic of asymmetric membranes. This neat membrane serves as the baseline to assess how the addition of ZnONPs affects the membrane's morphology. At 0.75 wt% (Fig. 5 e, f and g), the cross-sectional view shows larger, well-defined finger-like voids, which indicates a balance between nanoparticle distribution and structural reinforcement. However, at 1 wt% ZnONPs (Fig. 5h), the cross-section still shows slightly lower porosity which may lead to decrease in water flux. The structural disruptions may occur due to the excessive nanoparticle loading which could compromise the membrane's functionality.

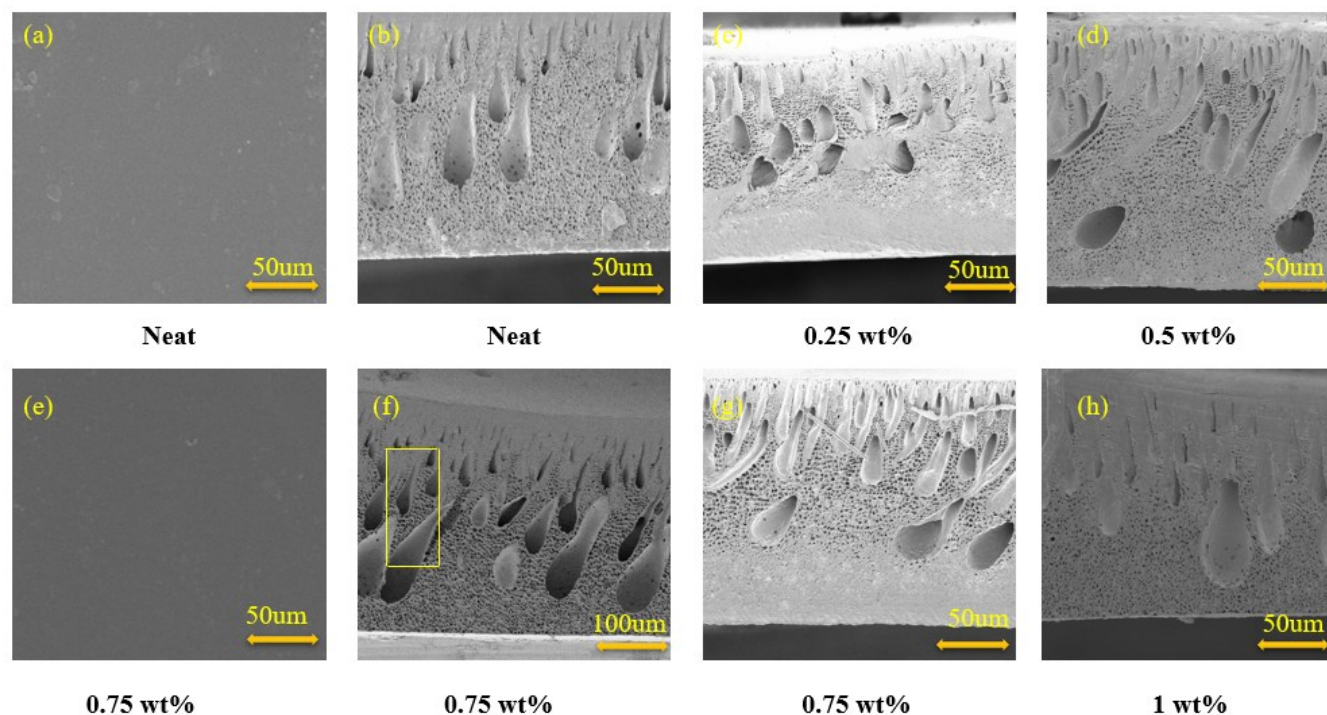


Figure 5. Surface and cross-sectional SEM images of the fabricated membrane: (a) surface of the neat membrane, (e) surface of 0.75 wt%, and (b, c, d, f, g, h) cross-sectional images from neat to 1 wt%. Images (f) and (g) correspond to 0.75 wt. %.

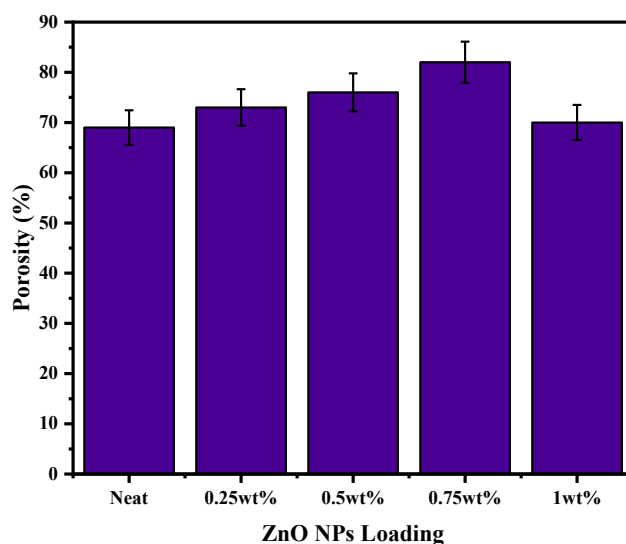


Figure 6. Effect of ZnONPs loading on membrane porosity (%).

Figure 6 shows the variation in membrane porosity as a function of ZnONP loading in the PES matrix. The incorporation of green-synthesized ZnONPs resulted in a clear increase in membrane porosity from approximately 69% for the pristine PES membrane to a maximum of approximately 82% at an optimal loading of 0.75 wt%. This increase in porosity can be attributed to the influence of ZnONPs on phase inversion kinetics during membrane formation. The presence of hydrophilic ZnONPs enhances thermodynamic instability in the polymer casting solution and accelerates solvent–non-solvent exchange during immersion in the coagulation bath. This rapid demixing promotes the formation of a more porous substructure and improved

pore connectivity, leading to increased overall membrane porosity [33, 34]. The enhanced porosity observed at intermediate nanoparticle loadings indicates effective dispersion of ZnONPs within the polymer matrix, which facilitates uniform nucleation sites for pore formation and promotes efficient phase separation. This structural modification is consistent with the observed increase in water permeance, as higher porosity reduces hydraulic resistance and enables more efficient water transport through the membrane. However, a slight reduction in porosity was observed at higher nanoparticle loading (1 wt%), suggesting the onset of nanoparticle aggregation and increased solution viscosity. Excessive nanoparticle concentration can hinder solvent–non-solvent exchange and restrict polymer chain mobility during phase inversion, resulting in partial pore blockage or reduced pore formation efficiency. This behavior highlights the existence of an optimal nanoparticle concentration, beyond which structural benefits are diminished due to unfavourable nanoparticle–polymer interactions and transport resistance effects.

3.3 Membrane Performance

3.3.1 Pure water permeability

The pure water permeability (PWP) of the fabricated MMMs was evaluated to assess the influence of ZnONPs incorporation on water transport, as illustrated in Figure 7 (a). The PWP progressively increased with ZnONPs addition, reaching a maximum at 0.75 wt%. The recorded values were 9, 32, 53, 73, and 38 $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ for the pristine PES membrane and those containing 0.25 wt%, 0.5 wt%, 0.75 wt%, and 1 wt% ZnONPs, respectively. This trend reflects a consistent enhancement in permeability up to 0.75 wt% loading, after which a decline is observed at 1 wt%. The improvement up to 0.75 wt% is ascribed to the hydrophilic character of ZnONPs, which enhances water affinity and facilitates transport through the membrane. Additionally, the presence of well-dispersed ZnONPs at lower concentrations increases membrane porosity and surface roughness, both of which facilitate water transport. When well-dispersed ZnONPs are incorporated into the polymer matrix, their hydroxylated surfaces and phytochemical capping groups attract water molecules during phase inversion. This accelerates the solvent–non-solvent exchange and promotes the formation of interconnected water channels within the membrane substructure. As a result, the membrane exhibits a lower contact angle (higher wettability), greater effective porosity, and faster initial water uptake, all of which contribute to higher PWP [35]. In addition, the hydrophilic surface forms a stable hydration layer that reduces foulant adsorption through hydrophobic interactions, thereby supporting improved flux recovery during filtration cycles. However, at higher nanoparticle concentrations (1 wt. %), the PWP dropped. This decrease is most likely due to nanoparticle agglomeration within the membrane matrix. When ZnONPs cluster together instead of dispersing uniformly, they can block pores or disrupt the membrane structure, reducing the number of effective channels for water passage. While ZnONPs significantly enhance water permeability at optimal concentrations, excessive loading compromises these benefits. These results demonstrate that maintaining a balanced nanoparticle concentration specifically around 0.75 wt% is crucial for achieving optimal membrane performance.

3.3.2 Rejection Performance

Figure 7(b) compares the salt rejection performance of the neat PES membrane and ZnONPs incorporated MMMs. All modified membranes showed significantly higher rejection for NaCl, CaCl_2 , and MgSO_4 than the neat PES membrane, which exhibited poor rejection (29.7%, 16.6%, and 21%, respectively). Incorporation of ZnONPs progressively enhanced salt rejection, reaching optimal values of 55.0% (NaCl), 62.5% (CaCl_2), and 67.0% (MgSO_4) at 0.75 wt% loading. This improvement is primarily attributed to increased membrane hydrophilicity, and formation of a denser selective layer. The compact structure and tortuous transport pathways induced by ZnONPs promote size and charge-based selectivity, leading to higher rejection of divalent salts compared to monovalent ones.

The addition of ZnONPs enhances heavy metal removal by increasing surface hydrophilicity, providing more active sites for ion removal, and reinforcing the selective layer. ZnONPs can influence surface charge and reactive sites, further promoting electrostatic repulsion. Figure 7(c) shows that the rejection performance of MMMs is in the order of $\text{As}^{3-} > \text{Cu}^{2+} > \text{Cr}^{3+} > \text{Al}^{3+}$. The corresponding hydrated ionic radii are As^{3-} (222 pm) $>$ Cu^{2+} (72 pm) $>$ Cr^{3+} (62 pm) $>$ Al^{3+} (53.5 pm), indicating that both size exclusion and electrostatic repulsion dominate the separation mechanism. Consistent with the salt rejection findings, the

highest heavy metal ion removal efficiency was obtained with the membrane containing 0.75 wt% ZnONPs, attributed to the optimal balance of pore size, surface roughness, and zeta potential-driven surface charge, which together maximize repulsion of heavy metal ions.

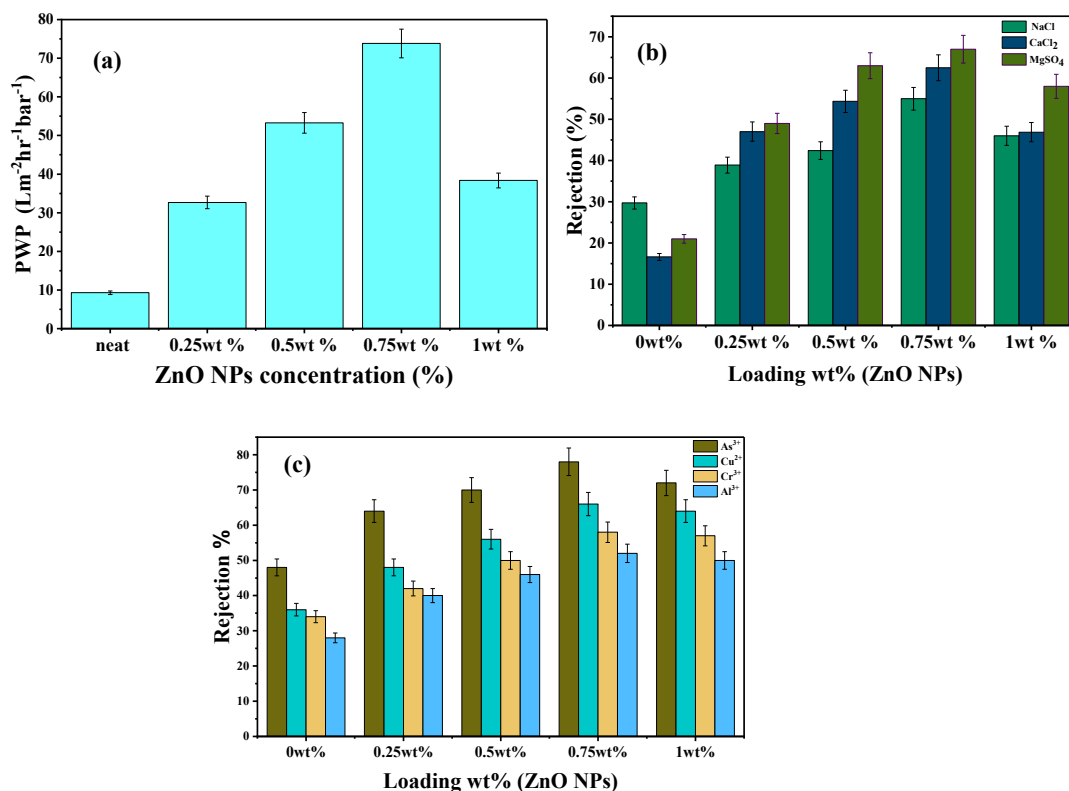


Figure 7. (a) Pure water flux, (b) Salts Rejection, (c) Heavy Metals ions (As^{3+} , Cu^{2+} , Cr^{3+} and Al^{3+}) rejection.

3.3.3 Membranes antifouling study

Membrane fouling remains a major challenge in filtration systems. This results in a decrease in permeation flux, shortens the lifespan of membranes, and increases maintenance costs. A widely adopted approach to address this problem involves adding hydrophilic nanofillers to the membrane structure. The incorporation of these fillers enhances both the hydrophilic nature and the overall permeability of the membrane. For this study, antifouling performance tests were conducted using a 1000 ppm solution of sodium alginate. Figure 8(a) shows the fouling cleaning behavior of the membranes. A pronounced decline in permeation flux was observed during sodium alginate filtration for all samples, which can be attributed to the formation of a gel-like fouling layer and pore blocking. However, the extent of flux reduction was significantly lower for the ZnONP-incorporated membranes, indicating enhanced resistance to foulant deposition. Following hydraulic cleaning, the modified membranes exhibited substantially higher flux recovery compared to the pristine PES membrane, confirming that the deposited foulants were predominantly weakly bound and readily removable. This observation is consistent with the fouling resistance analysis presented in Figure 8(b), where a significant reduction in irreversible fouling resistance (R_{ir}) and a corresponding dominance of reversible fouling (R_r) are observed. Although the total fouling resistance (R_t) showed a slight increase at 0.75 wt%, this increase is mainly associated with reversible foulant accumulation rather than permanent adsorption. The superior antifouling performance at 0.75 wt% can be attributed to the optimal dispersion of ZnONPs and enhanced surface hydrophilicity, which promote the formation of a stable hydration layer and minimize foulant–membrane interactions.

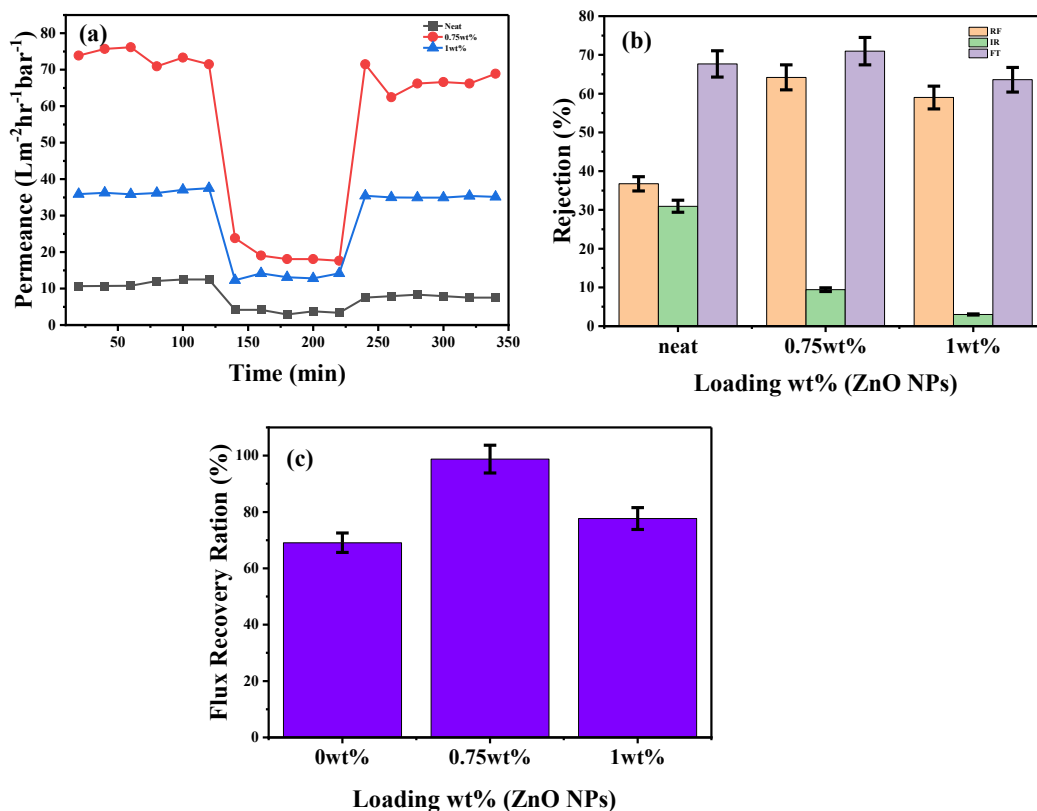


Figure 8. (a) Antifouling capacity of prepared membranes, (b) Fouling resistance ratio, (c) Flux recovery ratio

3.3.5 Long term stability studies

The long-term operational stability of the pristine PES membrane and the optimized PES/0.75 wt% ZnONPs MMMs was evaluated shown in the Fig 9. The pristine PES membrane exhibited a near stable pure water permeability and dye rejection throughout the testing period. In contrast, the PES/0.75 wt% ZnONPs MMM demonstrated significantly enhanced transport and separation performance, with permeance decreasing only slightly from 73 to 70 $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ over 36 h, corresponding to a flux decline of less than 4%. The minor reduction in permeance observed during extended operation can be attributed primarily to concentration polarization and gradual accumulation of pollutant near the membrane surface, which increases mass transfer resistance. Importantly, the absence of significant rejection loss indicates that the selective layer and internal pore structure remained intact, demonstrating strong resistance to structural degradation and pore enlargement. The enhanced long-term stability of the ZnONP-incorporated membrane is attributed to improved surface hydrophilicity and the formation of a stable hydration layer, which reduces irreversible adsorption of dye molecules and mitigates fouling. These results confirm that ZnONP incorporation effectively enhances both membrane transport performance and operational durability under continuous filtration conditions.

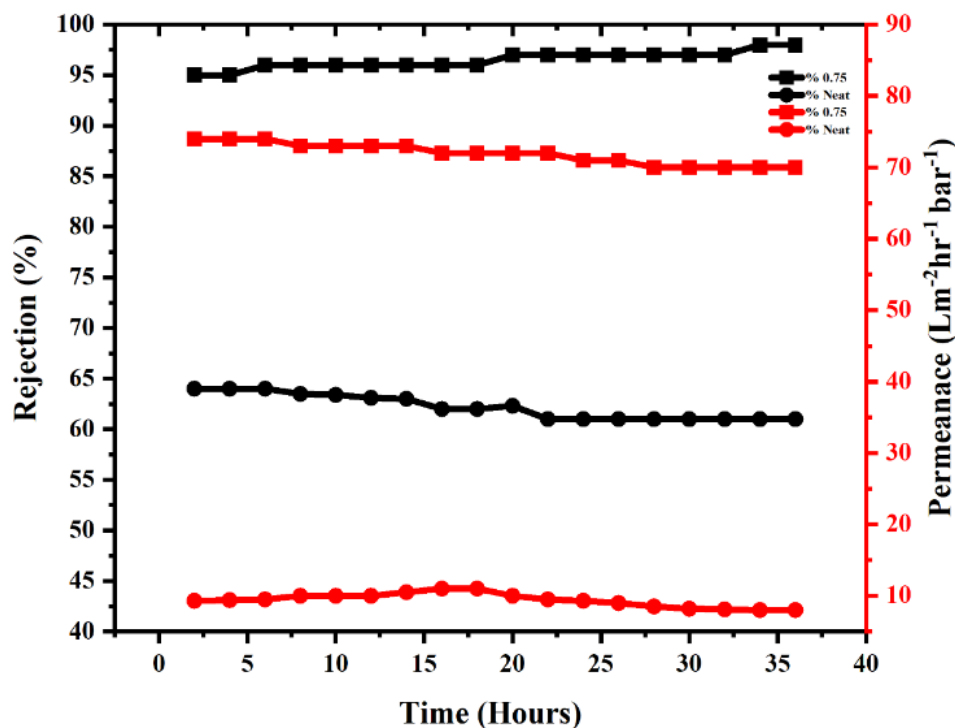


Figure 9. Long-term permeance and rejection performance of pristine PES and PES/0.75 wt% ZnONPs MMMs during continuous filtration of Congo red solution over 36 h.

3.3.6 Comparison with literature membranes

Table 2 presents a comparative overview of the transport and separation performance of ZnO-incorporated polymeric membranes reported in the literature. The developed PES/ZnONPs MMMs exhibited a pressure-normalized pure water flux of $73 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{bar}^{-1}$ while maintaining appreciable rejection of both monovalent and divalent salts, including NaCl (55%), CaCl_2 (62%), and MgSO_4 (67%). In addition, the membrane demonstrated promising removal efficiencies toward heavy metal ions and arsenic species, including As^{3+} , Cu^{2+} , Cr^{3+} , and Al^{3+} , indicating its potential applicability for complex wastewater treatment and water purification processes. Compared with previously reported ZnO-based membranes, the present membrane demonstrates a favorable balance between permeability and selectivity. Several earlier ZnO-incorporated systems exhibited either high rejection with relatively low flux or high permeability under substantially elevated operating pressures, making direct comparison difficult. In contrast, the membrane developed in this study achieved comparatively high pressure-normalized flux while maintaining competitive contaminant rejection performance under moderate operating conditions.

Furthermore, many previously reported membranes focused primarily on dye removal or selective ion rejection, whereas the current membrane demonstrated simultaneous removal capability for salts and multiple ionic contaminants, highlighting broader separation functionality. The enhanced membrane performance can be attributed to the effective incorporation of green-synthesized ZnONPs within the PES matrix, which likely improved membrane hydrophilicity, pore connectivity, and phase inversion behavior. These modifications contributed to enhanced water transport while preserving selective solute rejection characteristics. Importantly, the findings demonstrate that green-synthesized ZnONPs can serve as efficient functional nanofillers for high-performance mixed matrix membranes, offering an environmentally sustainable approach for membrane fabrication without compromising separation efficiency. It should be noted, however, that the sustainability benefits demonstrated here apply specifically to the nanoparticle synthesis route; the membrane casting process itself still relies on NMP and THF, both of which are hazardous, petroleum-derived solvents subject to increasing regulatory restriction (e.g., NMP's inclusion under the EU REACH regulation as a substance of very high concern). A fully sustainable membrane fabrication process would additionally

require transitioning to greener solvent systems (e.g., PolarClean, Rhodiasolv, dimethyl sulfoxide, or ionic liquids) or implementing solvent recovery/recycling during fabrication. The present work should therefore be positioned as improving the sustainability of the nanofiller synthesis step specifically, rather than the overall membrane fabrication process.

Table 2. Comparison with relevant literature results

Membrane Material	PWF ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\text{ bar}^{-1}$)	Pressure (bar)	Contaminants	Rejection (%)	References
PEES/n-ZnO	26.7	200 psi	Humic acid	98	[36]
			MgCl ₂	98	
			NaCl	92	
			MgSO ₄	68	
			Na ₂ (SO ₄)	60	
TFN-2 (ZnO–GO/PSf)	17.85	4	Cd(II)	99.82	[37]
			NaCl	73.21	
			MgSO ₄	81.23	
TFN (etched ZnO/PSF)	8.1	4	Cu ²⁺	>96	[38]
				>96	
			Zn ²⁺	>96	
			Ni ²⁺	>96	
PSF/ZnO	6.24	5	Na ₂ SO ₄	93	[39]
PES/ZnO	13	5	As(III)	27	[40]
			As(V)	71	
PEI/Glycidyl POSS-functionalized (ZnO)	8.48	5	Na ₂ SO ₄	83	[41]
			Pb(NO ₃) ₂	59	
			Cu(NO ₃) ₂	67	
PES/ZnONPs (green synthesis)	73	9	NaCl	55	Current study
			CaCl ₂	62	
			MgSO ₄	67	
			As ³⁺	78	
			Cu ²⁺	66	
			Cr ³⁺	58	
			Al ³⁺	52	

4. Conclusions

Green-synthesized ZnONPs, prepared using *Calotropis gigantea* leaf extract, were successfully incorporated into PES membranes via the phase inversion method to engineer membrane structure and interfacial properties. The incorporation of ZnONPs significantly influenced membrane formation dynamics, resulting in improved surface hydrophilicity, enhanced pore connectivity, and optimized transport pathways. These structural modifications translated directly into improved membrane performance, including substantially higher water permeance, enhanced solute rejection, and improved resistance to fouling. Among the fabricated membranes, the PES/0.75 wt% ZnONPs MMMs demonstrated the most favorable balance between permeability and selectivity, achieving a permeance of 73 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ along with high rejection for NaCl, CaCl₂, and MgSO₄, respectively. The membrane also exhibited a high flux recovery ratio, confirming its strong antifouling characteristics. The improved performance is attributed to the effective interfacial integration of ZnONPs within the polymer matrix, which enhanced membrane wettability and stabilized the selective structure without introducing transport defects. Long-term filtration experiments using Congo red confirmed the operational stability of the ZnONP-incorporated membrane, with minimal permeance decline and consistently high rejection over 36 h of continuous operation. This demonstrates the structural robustness

of the mixed matrix architecture and its resistance to performance degradation under sustained filtration conditions. Overall, this study demonstrates that green-synthesized ZnONPs can serve as effective interfacial modifiers for engineering high-performance mixed matrix membranes.

Conflict of Interest: The authors declare no conflict of interest related to the publication of this research.

Data Availability Statement: The datasets generated and/or analyzed during the current study are available from the corresponding author upon reasonable request. All relevant experimental data supporting the findings of this study are included within this article.

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Author Contributions

For research articles with several authors, a short paragraph specifying their individual contributions must be provided. The following statements should be used "Conceptualization, A. L. K; Methodology, G.M., N.B. and M.T.; Validation, A.A.K and W.A.; Formal Analysis, A.A.K and W.A., E.R.I.M, and H.A.; Investigation, A.A.K and W.A.; Resources, A.L.K and H.A.; Data Curation, E.R.I.M., A.L.K and H.A.; Writing – Original Draft Preparation, G.M. and N.B.; Writing – Review & Editing, A.L.K., M.H., M.T., M. A., A.A.K., W.A., E.R.I.M., and H.A; Supervision, M.H, M.A., and A.L.K.

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