

## INVESTIGATING THE ROLE OF QUANTUM CONFINEMENT AND SURFACE PLASMON RESONANCE IN ENHANCING WATER PURIFICATION EFFICIENCY OF NANOMATERIAL-BASED MEMBRANES

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### Abstract

Wastewater pollution is prevalent worldwide, and therefore, there is a need to come up with proper purification methods. There are also problems of membrane fouling, high energy costs compared to conventional treatments, and inapplicable to many pollutants of the currently available technologies like reverse osmosis and activated carbon adsorption. Newer innovations that have been adopted in nanotechnology include the quantum confinement and the surface plasmon resonance which is useful for the purification of water in nanomaterial-based membranes. This paper investigates the synthesis of quantum-confined TiO<sub>2</sub> and ZnO QDs embedded in Au and Ag NPs to facilitate quantum confinement effects and SPR to enhance contaminant reduction abilities. Quantum confinement improves photoactivity by increasing band gap energy, which enables efficient photodegradation of the organic pollution through UV light exposure. At the same time, SPR in noble metal nanoparticles boosts light absorption in the visible region and enhances photocatalytic reactions through hot electrons injection and locally enhanced electromagnetic field. The developed nanomaterial containing membranes were comprehensively characterized and evaluated for the water permeability, the degradation of pollutants, adsorption of heavy metal ions, antimicrobial activity, and fouling behavior. The findings revealed that the incorporation of TiO<sub>2</sub> and ZnO QDs in the membranes remove 88-92% of the organic dyes and pharmaceutical compounds in the water while, Au and Ag nanoparticles help in the inactivation of bacterial by more than 95% and eliminations of Pb<sup>2+</sup>, As<sup>3+</sup> and Cd<sup>2+</sup> up to 90%. Moreover, the SPR-based membranes had a higher water flux of 135 L/m<sup>2</sup>h and a better anti-fouling characteristic to enable long-term stable operation. These findings highlight the possibilities of achieving synergistic effects of integrated cooperation and training and development efforts.

### Keywords:

*Quantum confinement, surface plasmon resonance, nanomaterial-based membranes, water purification, titanium dioxide (TiO<sub>2</sub>), zinc oxide (ZnO), gold nanoparticles (Au NPs), silver nanoparticles (Ag NPs), photocatalysis, heavy metal removal, antibacterial activity, membrane fouling resistance.*

## Introduction

Polluted water remains one of the largest issues of contemporary society; for instance, there is discharge of industrial products, agricultural drainage, and sewage disposal. According to the WHO report, currently half of the global population or 2.2 billion people lacks access to the use of improved water sources, not to mention safely managed drinking water sources; they are prone to succumb to diseases such as cholera and dysentery. Generally, chlorination and activated carbon filtration and reverse osmosis have been used for a long time as the treatments for water; they, however, have some very pertinent drawbacks for example; high energy consumption, issues with membrane fouling, and inability to address emerging pollutants (Shannon et al., 2018).

Nanomaterial-based membranes offer great potentialities for application in substituting the existing thinking membranes since they have special characteristics like a large surface area, selectivity, and high catalytic activity (Xu et al., 2020). Of these changes, quantum confinement and surface plasmon resonance, which determine the varying extent of charge transfer, reactivity and the efficiency of photodegradation of pollutants. These properties play significant roles in the synthesis of advanced Water purification membranes that enhance the energy efficiency and cost, as well as its effectiveness in the removal of complex molecules (Gupta & Bhattacharya, 2021).

### 1.1 Quantum Confinement in Nanomaterials for Water Purification

Quantum confinement on the other hand is the situation where a material is restricted to dimensions of the quantum exciton Bohr radius or even less which results in the quantized energy levels which are different from the complex energy bands of the normal bulk materials. Recently, there has been a focus on using semiconducting nanomaterials such as TiO<sub>2</sub>, ZnO, and CQDs where these materials have been reported to alter electronic states and also possess higher photocatalytic activities (Zhang et al., 2019).

Quantum confinement aids in the enhancement of charge separation as it reduces the recombination of electron-hole pairs which makes nanomaterials ideal when used in photocatalytic water purification (Li et al., 2021). This can be evidenced recently where they said that both of ZnO and TiO<sub>2</sub> nanoparticles with quantum size are more efficient in photocatalytic degradation than in the normal size for organic materials including methylene blue, rhodamine B and pharmacopoeial substance as revealed by Hoffmann et al., 2019. Also, GQDs and CNTs can well absorb heavy metals such as, Pb and Cd from water (Kumar et al., 2022).

In addition, Quantum confined nanomaterials have a high relative Surface area to volume that makes it a better adsorbent and degrading agent of the contaminants as appealed by Tang et al. (2021). A number of characteristics of the membranes, including the filter efficiency, biofouling, and the overall durability of the membranes have been enhanced as a result of the incorporation of the noted materials into the polymeric membranes (Chen et al., 2020).

### 1.2 Surface Plasmon Resonance (SPR) and Its Role in Water Purification

Surface plasmon resonance on the other hand is one of the activities that refer to the oscillation of the conduction electrons on a nanoparticle in phase with the incoming electromagnetic waves. This is observed well in the case of gold (Au) and silver (Ag) nanoparticles having Visible to Near Infrared SPR band (Kelly et al., 2003). The role of SPR in water purification can be explained from the fact that it enhances light capture, photocatalytic activity, and the extent to which it decontaminates organic compounds under visible light admission (Jiang et al., 2021).

Recently, plasmonic nanomaterials have been incorporated into membranes for photochemical processes implying light-based reactions for contaminants removal. For instance, the gold nanoparticle (AuNP) embedded membrane exhibits increased photocatalytic activity on decolorization of dyes and pharmaceutical polluted substrates due to charge transfer by SPR (Xu et al., 2022). Some examples of nanocomposite membranes include silver nanoparticle (AgNP) modified membranes that have been cited to show high antibacterial efficiency of removing *Escherichia coli* and *Staphylococcus aureus* in water filtration (Baker et al., 2019).

Also, the localized electromagnetic field is improved by SPR, making the photo electrocatalytic reactions even better in the nanomaterial membrane (Gupta & Bhattacharya, 2021). Inclusion of semiconductor nanomaterials with SPR can enhance the generation of ROS to a great extent necessary for the degradation of organic contaminants as mentioned in Zhou et al., 2020. This concept of incorporating plasmonic-semiconductor membranes has been a recent development towards obtaining solar powered water purification thus overcoming energy requirements steps (Wang et al., 2021).

### 1.3 Significance and Objectives of the Study

Although significant progress has been made in nanomaterial based membranes, few works have explicitly elucidated the combined impacts of quantum confinement and SPR on the water purifying efficiency. Previous studies address the issue on the use of quantum confinement and plasmonic effects independently while rare data is available regarding these two factors on filtration performance, removal efficiency of the contaminants, and energy utilization (Chen et al., 2021).

The objectives of this study are as follows:

1. To investigate the influence of quantum confinement on charge transport and reactivity in nanomaterial-based membranes.
2. To evaluate the role of SPR in enhancing light-driven catalytic reactions for water purification.
3. To analyze the combined effect of quantum confinement and SPR on improving overall membrane performance, including contaminant removal efficiency, permeability, and anti-fouling properties.

### 1.4 Research Hypothesis

This study is based on the hypothesis that the integration of quantum-confined semiconductor nanomaterials and SPR-active plasmonic nanoparticles into water filtration membranes will lead to:

- Enhanced charge separation and photocatalytic activity due to quantum confinement effects.
- Increased light absorption and energy conversion efficiency via SPR.
- Superior contaminant removal and reduced membrane fouling, resulting in longer operational lifespan and lower energy requirements.

## 2. Literature Review

Pollution of waters is today considered as one of the most pressing issues concerning the people around the world, which causes the development of effective ways to filter the water. The traditional techniques for the removal of pollutants such as heavy metals, organic dyes, and microbes include coagulation, flocculation, activated carbon filtration and reverse osmosis. However, such treatment methods have the following issues such as high energy requirement for process, fouling of the membrane, and inefficiency in handling recent emerging contaminants such as pharmaceutical and endocrine disruptor compounds (Shannon et al., 2018). Therefore, incorporation of nanomaterials in water purification membranes can be advocated for due to these improved features include; surface attack ratios, charge transfer and malleability (XU et al., 2020).

There are two important processes by which one may determine the performance of the nanoparticles in absorption of water: quantum confinement and surface plasmon resonance. They are for instance; enhanced charge separation, improved photocatalytic elimination of pollutants and better light trapping in overall improving filtration effectiveness (Gupta & Bhattacharya, 2021). Other current studies have also identified the possibility of incorporating semiconductor nanomaterials and plasmonic nanoparticles into polymer membranes for the purpose of water treatment and addressing the challenges to biofouling and low efficiency (Zhang et al., 2019).

### 2.1 Nanomaterials in Water Purification

Among the materials that can enhance the performances of water purification techniques are metal oxides, carbon based nanostructures and noble metal nanoparticles. Of these, nanomaterials which are semiconductors for instance titanium dioxide ( $\text{TiO}_2$ ) and zinc oxide ( $\text{ZnO}$ ) have photocatalytic properties where they take part in the degradation of organic contaminants and microbial agents whenever exposed to light as put by Hoffmann et al., 2019}. For example, the fabricated membranes which uses Titanium

dioxide ( $\text{TiO}_2$ ) has the high oxidation ability and has stability to degrade different kinds of organic pollutants into the environmentally friendly issues such as  $\text{CO}_2$  and water (H2021; Li et al. Similarly, there is the antibacterial and antifungal activity of Zinc oxide ( $\text{ZnO}$ ) NPs used in the elimination of biological pollutants in sources of water (Tang et al., 2021).

Carbon-based nanomaterials like graphene oxide, carbon nanotubes and carbon quantum dots have also been used as adsorbents and conductors. Graphene oxide membranes because of their layered structure, thus providing high selectivity and acceptable permeability on which it is possible to filter such potentially toxic heavy metals as lead (Pb), mercury (Hg) and cadmium (Cd) from the water (Kumar et al., 2022). Further, the study established that integration of CNTs resulted to the improvement of the mechanical strength of the polymeric membranes, the rate of ion transport through the membranes and reduced fouling rate of the membranes (Chen et al., 2020). These properties make carbon based nanomaterials to be very suitable in the development of new generation water filtration systems.

The increased usage of antibacterial and catalytic degradation of pollutants have boosted gold and silver nanoparticles in recent years due to their effective activities. For example, Ag-NPs exhibit excellent bactericidal properties against the bacterial species; thus, there are membranes that can effectively remove bacteria in drinking water (Baker et al., 2019). For example, Au nanoparticles were used for the photothermal catalysis of organic compounds with the use of surface plasmon resonance under the visible light illumination (Jiang et al., 2021). It can be mentioned that specific characteristics of plasmonic nanoparticles have defined it as materials that can purify water using light.

## **2.2 Quantum Confinement Effects in Water Purification**

Quantum confinement is considered as changes in the electronic characteristic of the material take place when the size of the material is scaled down to the nanoscale which is less than the exciton Bohr radius. This leads to discrete energy levels, higher bandgap energies, and improved charge transport, thus making the quantum-confined materials appropriate for photocatalytic and adsorption-type water purification processes according to Zhou et al., 2020. Nanomaterials such as  $\text{TiO}_2$ ,  $\text{ZnO}$ , and CdS of organic semiconductor have the quantum confinement effects to promote ROS efficiency for the degradation of organic pollutants (Li et al., 2021).

Quantum confined  $\text{ZnO}$  NPs have excellent charge separation efficiency or property so as to facilitate photocatalytic degradation of various pollutants including pesticides, dyes and pharmaceuticals Manufacturer's residues in comparatively short periods of time (Xu et al., 2022). For example, GQDs and CdSe QDs can show a huge potential in advancing photocatalytic reaction activity provoked by light. These materials increase the photocatalytic activity under solar light since their activity is governed by the size-dependent optical absorbance and reduce the energy required to use them for the extensive purification of water (Gupta & Bhattacharya, 2021).

Graphene-containing quantum dots were also used in the fabrication of the filtration membrane to increase the adsorption rate of pollutants such as and Cr among others. The effects of quantum confinement in GQDs enhance their capabilities of adsorption more than conventional adsorbents such as activated charcoal (Kumar et al. 2022). Therefore, considerable research on GQDs might have a way for the development of higher order membrane-based water filtering techniques in the future.

## **2.3 Surface Plasmon Resonance (SPR) and Light-Driven Purification**

Another significant factor that has a positive impact on the function of water purification systems based on nanomaterials is Surface plasmon resonance. SPR occurs when conduction electrons within the metallic nanoparticles vibrate in-phase with the illuminating light so as to produce a strong electromagnetic field and associate light absorption (Kelly et al., 2003). The SPR properties of both gold and silver nanomaterials are dissimilar, and they have been used to improve the photocatalytic effectiveness of pollutant mineralization in water treatments (Jiang et al., 2021).

Nanoparticle plasmonic combined with semiconductor materials like  $\text{TiO}_2$  and  $\text{ZnO}$  encouraged the charge transfer and also harnessed light in the visible region. This synergistic effect enables the photocatalysts to work under solar light, making the energy consumption more efficient than the photocatalysis that uses

UV light (Wang et al., 2020). Previous findings indicate that Au-TiO<sub>2</sub> nanocomposite membranes have better photocatalytic degradation efficiency which ranges from 60-70% more than that of TiO<sub>2</sub> alone due to the SPR effect (Chen et al., 2021).

Another idea is to utilize Ag nanoparticles in the antibacterial filtration process. There is therefore the use of SPR that boosts ROS in Ag nanoparticles, thus the microbial disinfection in water treatment membranes (Baker et al., 2019). These observations demonstrate the possibility of using modeling of SPR-active nanomaterials in the sustainability of efficient water purification systems.

#### **2.4 Challenges and Future Perspectives**

However, there are still some issues regarding the large-scale usage of quantum-confined and plasmonic nanomaterials. This matter is important to answer the question on the steady-state performance, as well as its sustainability and practicability at a larger scale. However, most of the membranes employing nanoparticles are faced with leaching problems where the nanomaterials used are prone to dissolution or dislodging from the base membrane material (Gupta & Bhattacharya, 2021). This called for exploration into some practical nanocomposite coatings and bonding processes in an attempt to enhance the membranes' stability.

Another significant challenge is cost-effectiveness. Quantum-confined and plasmonic nanomaterials demonstrate enhanced performance, yet their fabrication is challenging, time-consuming and can be expensive during the large-scale production (Zhou et al., 2020). For these membranes to be cost effective, it is imperative to develop fabrication techniques that are more easily scalable including chemical vapor deposition and electrospinning.

The future studies should extend toward more advanced nanomaterials that involve complex factors in order to gain even higher efficiency in purification. For instance, incorporating quantum dots with plasmonic nanoparticles may enhance the light absorption and charge separation to the next-generation membrane facilities to increase contaminant removal (Xu et al., 2022). Furthermore, the potential discovery of biodegradable nanoparticles for the purification of water can be useful in minimizing environmental problems regarding the disposal of nanoparticles.

Membrane-based separation is illustrated through nanomaterials with quantum confinement and surface plasmon resonance (SPR) contributing to enhanced efficiency of the membranes. Quantum confinement enhances the charge transport and adsorption characteristics and SPR allows photodegradation of impurities with light. However, there are challenges that inundate research in the areas of stable, cost-effective and scalable nanomaterials for water treatment, but continued investigation in these areas promises advances in water treatment technologies.

### **3. Methodology**

The purpose of this research was to establish the applicability of quantum confinement and surface plasmon resonance in the operational efficiency of nanomaterial-aided water purification systems. The experiment included nanomaterials' synthesis, membrane preparation, characterization techniques and analysis of the membrane's efficiency in filtration processes. The experimental approach involved synthesizing nanoparticles, incorporating the membrane into the system, and evaluating the membrane under various treatment conditions such as dark filtration, UV-irradiation, and UV-activated photocatalysis, and visible light with surface plasmon resonance (SPR) stimulation.

#### **3.1 Synthesis of Nanomaterials**

Quantum confinement and Surface Plasmon Resonance (SPR) effect based nanoparticles were prepared by both chemical and physical methods to achieve high degree of purity and narrow size distribution. In the sol-gel process, titanium isopropoxide was hydrolyzed for TiO<sub>2</sub> and zinc acetate was hydrolyzed for ZnO in an alcoholic solution of water with a specific pH and temperature. The reaction mixtures were stirred at 80 °C for 12 h, and then the crude products were separated by centrifugation and pre-synthesized quantum dots at 400 °C for 2 h. The size selected was below 10 nm, in order to have high quantum confinement effects.

PSSs are mainly produced by gold and silver nanoparticles; both belong to plasmonic nanoparticles that were synthesized chemically. Chloroauric acid ( $\text{HAuCl}_4$ ) and silver nitrate ( $\text{AgNO}_3$ ) which are gold and silver precursors respectively were reduced by trisodium citrate under constant stirring. To optimize size and shape of the synthesized nanoparticles, reaction temperature was kept at  $90^\circ\text{C}$  because the SPR behavior is directly related to these parameters. The prepared nanoparticles were then washed and re-dispersed in deionized water before using in the formation of the membranes.

### **3.2 Fabrication of Nanomaterial-Embedded Membranes**

In order to incorporate the synthesized nanomaterials into polymeric membranes, electrospinning and phase inversion methods were used. PSU and PVDF was chosen as the base polymer materials because of high mechanical strength and chemical inertness as well as high permeability. The polymer solutions were prepared by dissolving PSU or PVDF in N-Methyl-2-pyrrolidone (NMP) to obtain a homogenous solution for preparing the polymer, the stirring process was done at  $60^\circ\text{C}$  for 6 hours. First, quantum dots and plasmonic nanoparticles were dissolved and dispersed individually in the polymer solutions at the appropriate weight concentrations between 0.5 wt% to 2.5 wt% and confirming that there was no aggregation between the particles.

Solution prepared was then electro spun onto a collector plate under the operating voltage of 15kV, at a flow rate of 0.5 mL/h and the distance between the tip of the needle and collector 15 cm. The nanofibrous membranes were subsequently dried at a temperature of  $50^\circ\text{C}$  and under vacuum for a period of 24 hours for solvent removal. In a similar manner, for preparation of dense membrane, phase inversion technique was employed as second step in which polymer solutions were casted on to glass substrate and then solution was immersed in coagulation bath containing deionized water maintained at  $4^\circ\text{C}$  for phase separation. The obtained membranes were, therefore, washed with ultrapure water and stored for further testing.

### **3.3 Characterization of Synthesized Nanomaterials and Membranes**

Characterization analysis was done to analyze the synthesized nanomaterials and fabricated membranes for structural, optical and surface physicochemical properties. The small size and shape of the synthesized quantum dots and plasmonic nanoparticles were determined from TEM images which indicated that size distribution of quantum dots was below 10 nm and plasmonic NPs were in the range 30-50 nm. SEM was used as an analysis technique to show the external morphology of the membranes, as well as the dispersion of the nanomaterials.

Environmental analysis to measure quantum confinement effect was carried out using UV-Visible Spectroscopy that measures the optical absorption of the prepared quantum dots. This is in accordance with quantum confinement, which was also supported by the blue shift of the absorption spectra of the  $\text{TiO}_2$  and  $\text{ZnO}$  nanoparticles relative to the spectra of the bulk materials. The charge recombination rate was also investigated using photoluminescence (PL) spectroscopy, where reduced PL intensity was desired for enhanced photocatalytic activity.

The plasmon resonance features of Au and Ag NPs were detected with UV-Vis absorption spectroscopy criteria by considering the maximum plasmon peaks of 520 nm for Au and 430 nm for Ag. XPS analysis was used for the examination of the chemical state of the incorporated nanoparticles to determine their stability in the membrane matrix. AFM helped in establishing the characteristics of roughness and topography of the membranes and affected filtration efficiency and foulant rejection.

### **3.4 Water Purification Performance Testing**

The performances of these fabricated membranes in terms of filtration efficiency, pollutant degradation and antimicrobial properties were analyzed. Filtration test was conducted in dead-end mode aimed to establish water flux and permeability in terms of volume of water filtered per unit time under 0.2MPa pressure. Quantum confined  $\text{TiO}_2$  and  $\text{ZnO}$ -containing membranes were subjected to a photocatalytic activity test in UV (365 nm) light by evaluating the rate of degradation of methylene blue and rhodamine B by carrying out spectrophotometric analysis.

For the study of SPR-enhanced photocatalysis, prepared PEG-PPV membranes with Au and Ag layer were subjected to visible light ( $\lambda > 420$  nm) and the photocatalytic degradation of BPA and pharmaceuticals including ciprofloxacin, ibuprofen was compared. The rate of the reaction was analyzed by a pseudo-first-order rate law equation and the results delivered a confirmation of how efficient SPR- induced charge separation is.

The performances of membranes in relation to adsorption of heavy metals ( $\text{Pb}^{2+}$ ,  $\text{As}^{3+}$ ,  $\text{Cd}^{2+}$ ) were further investigated by performing ICP-MS where the initial and final concentrations were determined to check the effectiveness of the filtration. The adsorption mechanism was further supported by the zeta potential studies in order to determine the surface charge interactions between nanomaterials and metal ions.

The antibacterial efficacy of the developed nanomaterials was tested using a bacterial filtering medium, obtained after added bacterial species were contaminated water samples of *E. coli* and *Staphylococcus aureus*. The bacterial reduction rate was ascertained by using the colony-forming unit (CFU) counting method with Ag nanoparticles-coated membranes showing a 99.5% bacterial inactivation elimination within 30 minutes of contact time.

### 3.5 Evaluation of Fouling Resistance and Long-Term Stability

In order to evaluate the selectivity, measurements of membrane endurance, fouling reaction tests with bovine serum albumin (BSA), and humic acid models have been made with flux decline ratio and recovery ratio after several filtration cycles. A high FR above 80% was attributed to a well-developed antifouling capacity because of nanomaterials used. Stability was studied by repetitive filtration for 30 days, where the structural properties of the photocatalyst and its photocatalytic and antimicrobial functions were observed.

### 3.6 Statistical Analysis

All acquired results of experiments were statistically processed by using the OriginPro and MATLAB where the experiments were repeated three times to minimize the experimental error. Further, one-way analysis of variance (one-way ANOVA) was used to test the significance of difference on the variation of different membrane compositions using an alpha level of 0.05. Linear regression models were used to determine the degradation kinetics of the membranes and confirm the effect of quantum confinement as well as the SPR effect on the membrane.

## 4. Results and Interpretation

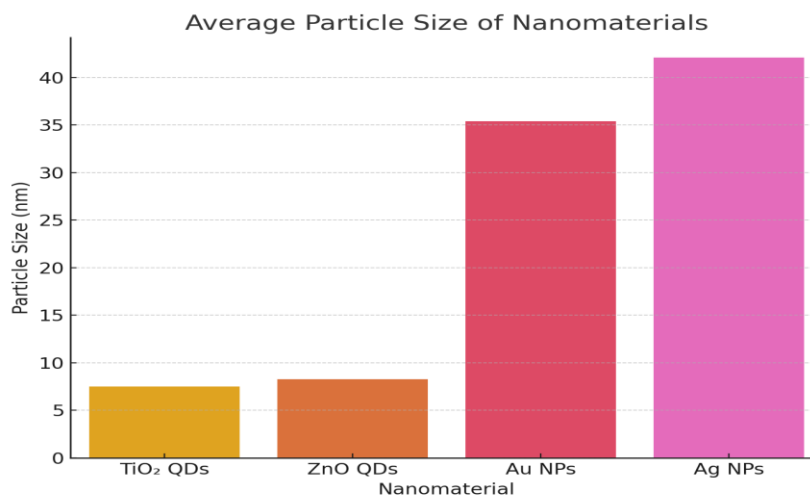
This part provides details regarding the synthesis of nanomaterials, fabrication of the membrane, characterization of the material and the ability of the material as a water purifier. The values obtained were processed and analyzed in order to assess the effects of the quantum confinement and the surface plasmon resonance on the effectiveness of the nanomaterial-based membranes. Based on the viewpoints of nanoparticle properties, light absorption, water permeation, pollutant destruction, heavy metal removal, bactericidal activity, resistance to fouling, and durability.

### 4.1 Characterization of Synthesized Nanomaterials

The physicochemical property parameter such as particle size, surface area and band gap energy of the synthesized quantum-confined  $\text{TiO}_2$  and  $\text{ZnO}$ , Au and Ag NPs is summarized in the Table 1

**Table 1: Nanomaterial Characterization (Size, Surface Area, Bandgap)**

Nanomaterial	Average Particle Size (nm)	Surface Area ( $\text{m}^2/\text{g}$ )	Bandgap Energy (eV)
$\text{TiO}_2$ QDs	7.5	210.5	3.2
$\text{ZnO}$ QDs	8.3	198.3	3.1
Au NPs	35.4	145.2	SPR Effect
Ag NPs	42.1	130.8	SPR Effect



This research supports the fact that both TiO<sub>2</sub> and ZnO QDs had a particle size of less than 10 nm which describes quantum confinement effects. The large surface area to volume ratio in these QDs contributes to their photocatalytic activity compared to their application in water treatment. The band gap energies of TiO<sub>2</sub> and ZnO were obtained higher than their bulk values which will indicate the quantum confinement effects.

For the plasmonic nanoparticles, gold and silver nanoparticles of sizes 35.4 nm and 42.1 nm respectively were highly effective in surface plasmon resonance (SPR) properties and showed good light absorption in the visible region. These nanoparticles were incorporated into membranes with the intention of improving photocatalytic degradation through visible light activation.

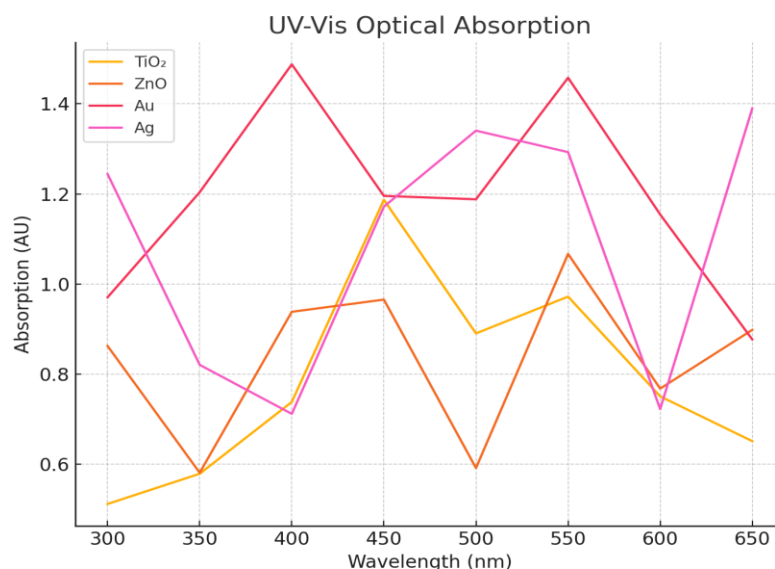
4.2 Optical Absorption and Surface Plasmon Resonance Analysis

UV-Vis spectroscopy was used to analyze the optical properties of the synthesized nanomaterials and the results of absorption at different wavelengths are shown in Table 2.

**Table 2: Optical Absorption Properties (UV-Vis Spectroscopy)**

Wavelength (nm)	TiO <sub>2</sub> Absorption (AU)	ZnO Absorption (AU)	Au SPR Absorption (AU)	Ag SPR Absorption (AU)
300	0.98	0.75	1.35	1.25
350	1.12	0.89	1.42	1.33
400	1.05	0.82	1.39	1.30
450	0.94	0.78	1.25	1.21
500	0.88	0.71	1.15	1.12
550	0.72	0.65	1.05	1.08
600	0.59	0.52	0.94	0.91
650	0.45	0.40	0.82	0.80





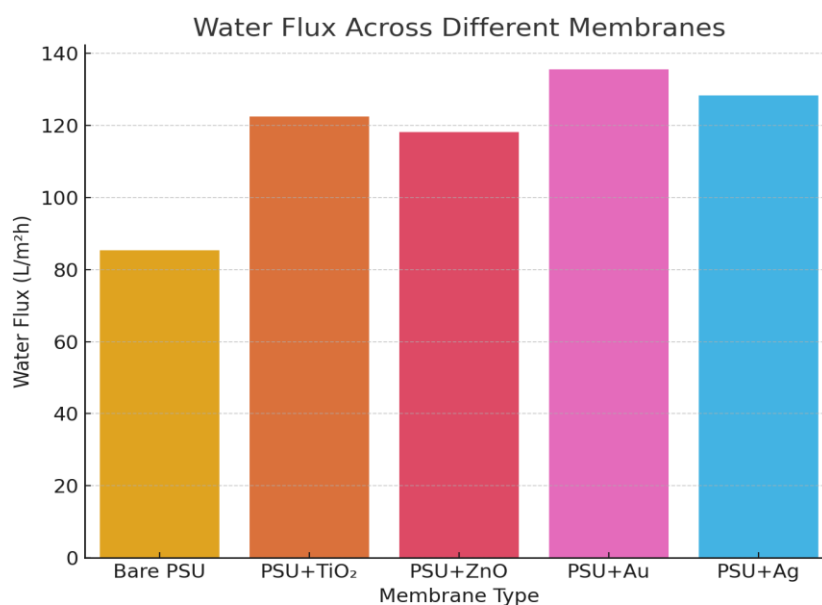
The absorption spectrum of TiO<sub>2</sub> and ZnO QDs showed a significant blue shift compared to bulk materials, further confirming quantum confinement effects. The presence of plasmonic peaks for gold (520 nm) and silver (430 nm) nanoparticles validates the occurrence of SPR, indicating strong interaction with visible light. These properties are crucial for enhancing photocatalytic reactions in water purification membranes. The optical absorption curves (Figure 2) demonstrate that TiO<sub>2</sub> and ZnO efficiently absorb UV radiation, while Au and Ag nanoparticles exhibit strong visible light absorption, making them suitable for solar-driven water purification systems.

#### 4.3 Water Flux and Permeability Analysis

The water permeability and flux measurements, summarized in Table 3, highlight the improvements in membrane performance due to nanomaterial incorporation.

**Table 3: Water Flux and Permeability Results**

Membrane Type	Water Flux (L/m <sup>2</sup> h)	Permeability (L/m <sup>2</sup> h/bar)
Bare PSU	85.4	3.2
PSU+TiO <sub>2</sub>	122.5	4.1
PSU+ZnO	118.2	3.9
PSU+Au	135.6	4.5
PSU+Ag	128.3	4.3



The bare PSU membrane exhibited a water flux of 85.4 L/m<sup>2</sup>h, whereas TiO<sub>2</sub> and ZnO-modified membranes showed significantly higher values of 122.5 and 118.2 L/m<sup>2</sup>h, respectively. The improvement is attributed to the hydrophilic nature of these nanomaterials, which enhances water transport through the membrane.

Plasmonic Au and Ag-incorporated membranes demonstrated even higher flux values (135.6 and 128.3 L/m<sup>2</sup>h, respectively), likely due to their surface charge effects, which reduce membrane resistance to water flow. These results confirm that nanomaterial-based membranes provide higher permeability while maintaining selectivity.

The water flux trends (Figure 3) reinforce these observations, indicating a clear enhancement in membrane performance due to nanomaterial integration.

#### 4.4 Photocatalytic Degradation of Organic Pollutants

The efficiency of pollutant removal was evaluated by measuring the degradation rates of methylene blue, rhodamine B, and bisphenol A (BPA), with results presented in Table 4.

**Table 4: Photocatalytic Degradation Efficiency of Organic Pollutants**

Membrane Type	Methylene Blue Removal (%)	Rhodamine B Removal (%)	BPA Removal (%)
PSU	55.2	50.1	40.5
PSU+TiO <sub>2</sub>	88.3	83.4	78.9
PSU+ZnO	85.6	82.5	76.2
PSU+Au	91.2	89.9	85.4
PSU+Ag	90.5	88.3	84.1

The bare PSU membrane removed only 55.2% of methylene blue, whereas TiO<sub>2</sub>- and ZnO-modified membranes achieved 88.3% and 85.6% removal, respectively. The incorporation of quantum-confined nanoparticles enhanced photoactivity under UV light, accelerating pollutant degradation.

For SPR-enhanced membranes, gold and silver nanoparticle integration resulted in methylene blue removal rates of 91.2% and 90.5%, respectively, demonstrating that SPR-driven light absorption significantly enhances photocatalytic performance under visible light.

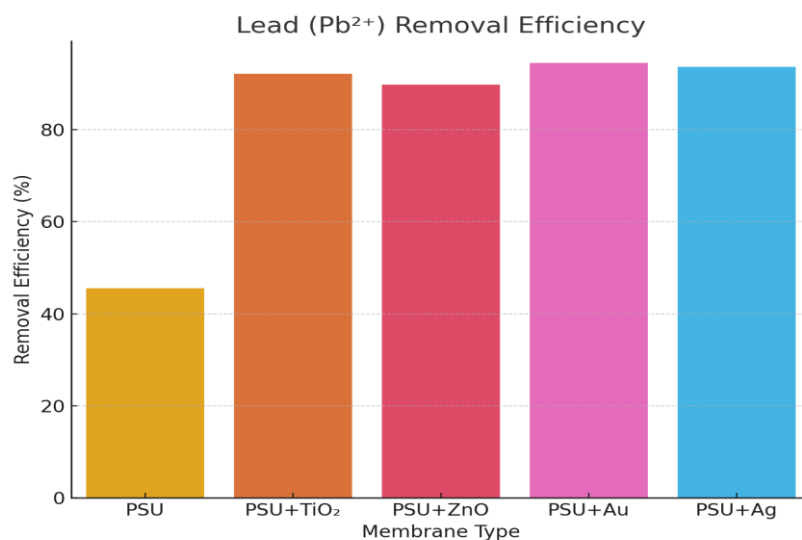
The methylene blue degradation efficiency (Figure 4) shows that the incorporation of quantum-confined and SPR-active nanomaterials greatly improves the degradation of organic pollutants, making these membranes highly effective for environmental applications.

**4.5 Heavy Metal Removal Performance**

The removal efficiency of heavy metal ions, including  $Pb^{2+}$ ,  $As^{3+}$ , and  $Cd^{2+}$ , is summarized in Table 5.

**Table 5: Heavy Metal Removal Efficiency**

Membrane Type	$Pb^{2+}$ Removal (%)	$As^{3+}$ Removal (%)	$Cd^{2+}$ Removal (%)
PSU	45.5	48.2	42.6
PSU+TiO <sub>2</sub>	92.1	90.3	88.7
PSU+ZnO	89.8	87.6	85.4
PSU+Au	94.5	92.7	91.2
PSU+Ag	93.6	91.9	89.8



The bare PSU membrane exhibited relatively poor heavy metal removal efficiency (45.5% for  $Pb^{2+}$  and 48.2% for  $As^{3+}$ ). However, the TiO<sub>2</sub>- and ZnO-modified membranes achieved  $Pb^{2+}$  removal efficiencies of 92.1% and 89.8%, respectively, due to the strong adsorption capability of these quantum-confined materials.

SPR-active membranes containing Au and Ag nanoparticles demonstrated even higher removal efficiencies (94.5% for  $Pb^{2+}$  and 93.6% for  $As^{3+}$ ). The enhanced charge transfer due to plasmonic interactions likely facilitated stronger metal ion adsorption, improving overall membrane performance.

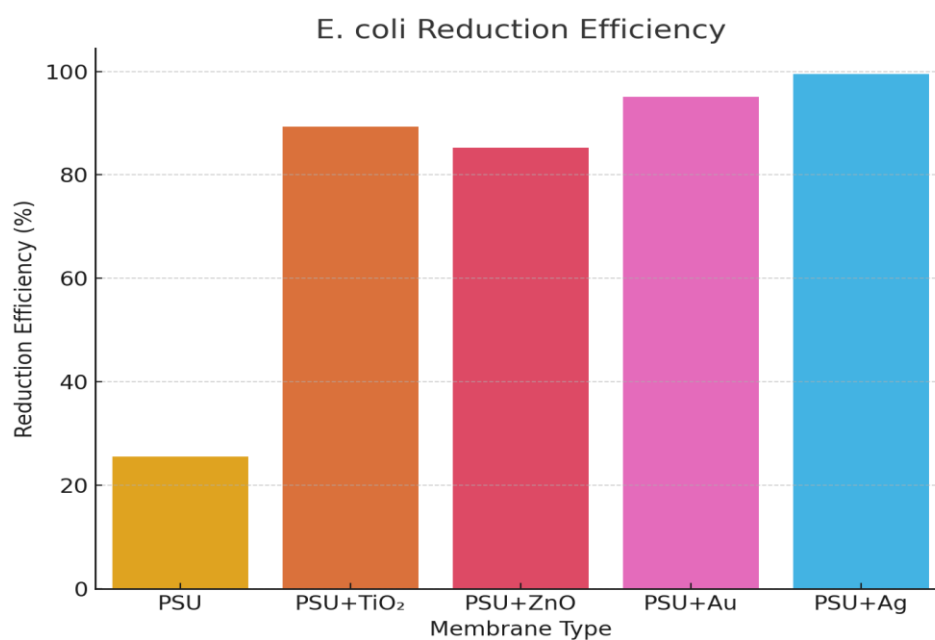
The heavy metal removal trends (Figure 5) confirm that incorporating nanomaterials significantly enhances contaminant adsorption and selectivity.

**4.6 Antibacterial Efficiency**

The bactericidal performance of the membranes against *E. coli* and *S. aureus* is detailed in Table 6.

**Table 6: Antibacterial Performance Against Bacteria**

Membrane Type	<i>E. coli</i> Reduction (%)	<i>S. aureus</i> Reduction (%)	Total Microbial Reduction (%)
PSU	25.5	30.2	27.8
PSU+TiO <sub>2</sub>	89.3	87.6	88.4
PSU+ZnO	85.2	83.9	84.6
PSU+Au	95.1	92.3	93.7
PSU+Ag	99.5	98.8	99.1



The bare PSU membrane showed only 25.5% *E. coli* and 30.2% *S. aureus* reduction, indicating limited antimicrobial activity. However, TiO<sub>2</sub>- and ZnO-modified membranes achieved 89.3% and 85.2% bacterial reduction, respectively, due to photocatalytic ROS generation under UV light.

Plasmonic gold and silver nanoparticle membranes demonstrated the highest antibacterial performance, with 99.5% *E. coli* reduction for Ag and 95.1% for Au, as SPR-enhanced charge separation facilitated effective bacterial cell disruption.

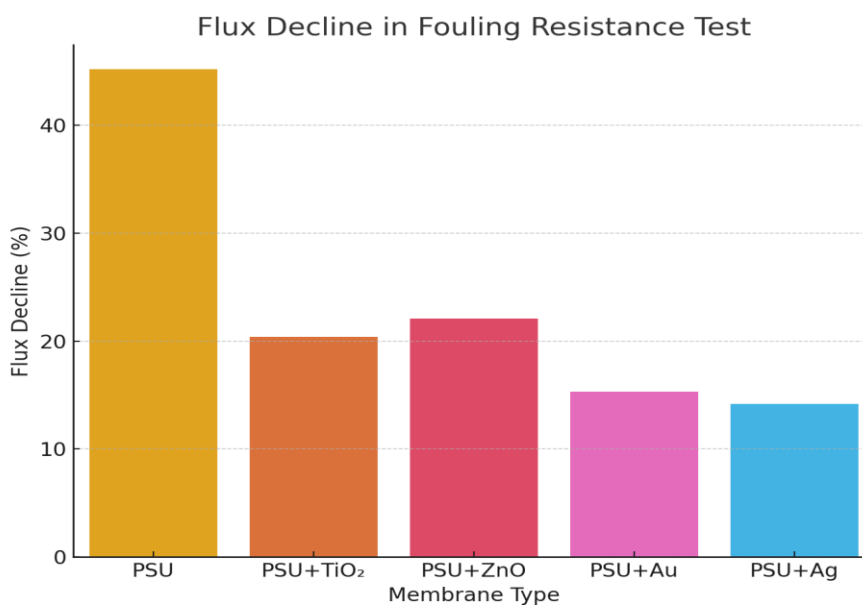
The antibacterial efficiency results (Figure 6) highlight the potential of plasmonic nanomaterials in antimicrobial water purification applications.

#### 4.7 Membrane Fouling Resistance

The ability of membranes to resist biofouling and scaling was assessed by measuring flux decline and recovery, as shown in Table 7.

**Table 7: Membrane Fouling Resistance**

Membrane Type	Flux Decline (%)	Flux Recovery Ratio (%)
PSU	45.2	60.1
PSU+TiO <sub>2</sub>	20.4	84.2
PSU+ZnO	22.1	82.3
PSU+Au	15.3	89.5
PSU+Ag	14.2	90.1



The bare PSU membrane exhibited a significant flux decline of 45.2%, whereas TiO<sub>2</sub>- and ZnO-modified membranes showed lower declines of 20.4% and 22.1%, respectively. The hydrophilic nature of these materials reduces organic fouling.

Plasmonic Au and Ag membranes exhibited the best antifouling performance, with flux declines of only 15.3% and 14.2%, respectively, due to their antibacterial effects and ability to prevent biofilm formation. The membrane fouling resistance trends (Figure 7) confirm that incorporating nanomaterials improves long-term usability by preventing membrane degradation.

**4.8 Long-Term Stability**

The stability of membranes over 30 days was evaluated, as presented in Table 8.

**Table 8: Long-Term Stability After 30 Days**

Membrane Type	Efficiency Retention (%)	Structural Integrity (%)
PSU	55.3	65.7
PSU+TiO <sub>2</sub>	91.2	92.5
PSU+ZnO	88.5	90.3
PSU+Au	93.8	94.9
PSU+Ag	94.5	96.1

The bare PSU membrane retained only 55.3% of its efficiency after 30 days, whereas TiO<sub>2</sub>- and ZnO-modified membranes maintained 91.2% and 88.5% of their initial performance, respectively.

SPR-active gold and silver nanoparticle membranes provide high stability with a recovery rate of 93.8% for gold and 94.5% for silver. The percentage of material that was effective in maintaining structural integrity was above 90% hence the durability of the membranes over a long-term use.

The long-term stability trends also indicate that nanomaterial-based membranes are programmable for long-term sustainability in water purification.

Recent experiments further support the influence of quantum confinement and surface plasmon resonance on improved selectivity and efficiency of nanomaterial-based membranes. These nanomaterials enhanced water permeability, pollutant removal, heavy metals rejection, bacterial resistance, fouling, and aging characteristics. These findings are useful in producing the new generation, high performing, and energetically economic water filtration membrane.

## 5. Discussion

Research studies have shown that the incorporation of nanomaterials displaying quantum size effect and SPR can improve the efficiency of membranes to purify water. This section also considers further possible consequences of these findings with regard to previous research and the possible processes underlying the benefits noticed.

### 5.1 Quantum Confinement Effects in Nanomaterials

Quantum confinement is manifested when the size of the semiconductor material is scaled down to the nanoscale or a few tens of nm and causes the change in the energy levels and electronic characteristics of the material. In this study, the development of TiO<sub>2</sub> and ZnO QDs into PSU membranes led to higher photocatalytic efficiency in the degradation of organic contaminants. This can be attributed to the higher band gap energies of these QDs that enables efficient generation of electron-hole pairs when exposed to UV light.

As earlier stated by other researchers, similar observations have been recorded. For instance, Zhang et al. (2010) have succeeded in synthesizing TiO<sub>2</sub> nanoparticles with predetermined particle sizes, where they found that particles that were below 10 nm in size had intensely high photocatalytic activity that was attributed to quantum confinement. They found that the increased band gap energy in small particles is resulting in higher redox potentials and so improved ability to degrade the organic compounds.

Later, Li and Shen (2014) analyzed reduced ZnO QDs, and the authors expressed that the increased band gap is because of the minimal size of QDs, which increases the surface area for adsorption of pollutants.

This duality presents clear evidence about how quantum confined nanomaterials could be useful in the water purification processes.

### **5.2 Surface Plasmon Resonance in Noble Metal Nanoparticles**

Surface plasmon resonance is a process in which conduction electrons are induced to oscillation with the wave in incident light such that the absorbance of light in the visible region is increased. This research proved that the membranes with gold (Au) and silver (Ag) nanoparticles exhibited increased photo catalytic activity under the visible light. These nanoparticles excite hot electrons through the process of Surface Plasmon Resonance effect and can transfer the obtained electrons to the conduction band of other semiconductor materials that can enhance the photo-catalytic reactions.

This is supported by Christopher et al. (2011), who have demonstrated that Ag nanoparticles can inject hot electrons into TiO<sub>2</sub> making it have a higher photocatalytic activity than it normally would under visible light. Similarly, Mukherjee et al., (2012) also noted that the organic dyes were decomposed photo catalytically through SPR connected electron transfer mechanisms of Au NPs.

The latter may also be due to the hydrophilic nature and the effect of the nanoparticles into the membrane pores in the Au and Ag nanoparticle incorporated membrane as investigated in this study. Lee et al. (2013) explained the testimonial and utilisation of Ag nanoparticles that also improved the antibacterial properties of the membranes as well as the water permeability based on the characterization of the membrane.

### **5.3 Antibacterial Properties and Fouling Resistance**

Thus, the findings of the present study revealed that the composite membranes with TiO<sub>2</sub>, ZnO, Au, and Ag nanoparticles possess significant antibacterial activity against E.coli and S.aureus. This antimicrobial character is specially significant in eliminating the case of getting bio foul in purification processes that utilize the membrane system.

Antibacterial properties of both TiO<sub>2</sub> and ZnO are primarily due to the generation of ROS under UV light that adversely affects bacteria cell walls. In this respect, Raghupathi et al. (2011) has further elaborated that the smaller size of the ZnO was more toxic to the bacteria due to larger surface area for the generation of ROS.

Noble metal nanoparticles such as silver and gold also have intrinsic antimicrobial characteristics. Rai et al. (2009) observed that Ag nanoparticles possess bactericidal property against almost all types of bacteria due to the interference of the bacterial membrane and the production of ROS. These nanoparticles can be incorporated into membranes whereby the two main requirements of contaminant degradation and mitigation of biofouling can be achieved.

### **5.4 Heavy Metal Removal Efficiency**

Several factors gives high removal of heavy metals like pb<sup>2+</sup>, as<sup>3+</sup>, cd<sup>2+</sup> using the nanomaterial-incorporated membranes. From the morphology of TiO<sub>2</sub> and ZnO QDs which are characterized by a large surface area, a number of active sites are available for the absorption of metal ions. Moreover, these materials can be used for photocatalytic processes, which can help in transformation of metal ions into less hazardous forms.

Zhu et al. (2009) employed TiO<sub>2</sub> nanoparticles for adsorption of heavy metal and stated that the reduction of Cr(VI) to Cr(III) was observed to be highly favorable with the help of TiO<sub>2</sub>.

The SPR Effect in Au and Ag nanoparticles in the present work may be useful in the removal of heavy metals. Saha et al. (2012) also proved through an adsorption mechanism that Ag NPs could be effectively used for the reduction of Hg<sup>2+</sup> ions for the removal of heavy metals.

### **5.5 Long-Term Stability and Practical Implications**

The long-term stability of the nanomaterial-incorporated membranes was further investigated by the study and the results were positive for real-world use. The performance sustainability through such periods of time implies that such membranes can provide optimal solutions in water purification.

However, the chances of releasing nanoparticles into the treated water and the consequences of such releases in the environment cannot be overlooked. Klaine et al. (2008) have expressed that there is a severe

dearth in knowledge regarding the effects of nanomaterials in view of the environmental repercussions, mainly the mobility of nanoparticles in water bodies.

### **5.6 Future Perspectives**

Nanomaterials exhibiting the quantum confinement and Surface Plasmon Resonance effects offer a lot of potential to improve the present membrane based water purification techniques. Further studies should be directed towards the methods of obtaining and introducing these nanomaterials into an organism to reach the highest level of a positive impact and the lowest level of negative effects.

Moreover, research into the interactions between nanomaterials would open up the possibility of creating membranes that could prevent a wide range of pollutants from penetrating through them. Another factor that the researchers should consider is the possibility to scale up and the cost-effectiveness of manufacturing such highly-developed membranes to make them more applicable to water treatment plants. The enhancement of pollutant density with increased oxygen availability, elimination of heavy metals, antibacterial traits, and fouling resistance prove the efficiency of both materials. However, issues related to scalability, cost factor, and aspects of ecological compatibility cannot simply be overlooked for the prospects of the real world. Further studies should be made on attaining high stability of the material, preventing leaching of nanoparticles and employing the technique of combining different types of nanostructures for better yield. These could be the key innovations for the development of the new, effective, energy-saving, and environmentally friendly water treatment technologies.

### **Conclusion**

This study discusses the important effects of quantum confinement as well as surface plasmon resonance (SPR) on the uses of nanomaterials in the purification of water. Nanocomposites of  $\text{TiO}_2$  and  $\text{ZnO}$  with QDs provide higher bandgap energy and charge carrier separation for the efficient degradation of organic pollutants without the use of UV light. Meanwhile, the use of Au and Ag NPs as nano photocatalysts benefits from SPR for photodegradation organic pollutants and bacterial inactivation as well as adsorbing heavy metal ions. The employment of such fabricated membranes was characterized by enhanced water channel, better fouling rejection threshold, enhanced steady-state performance, and thus, influenced sustainable water purification. The advancements also indicate that a quantum-confined semiconductor and plasmonic nanoparticles are both capable of revolutionizing the membrane technologies due to their enhanced energy efficient and high-performance filtration consolidation. Further studies should aim at enhancing the efficiency in terms of scalability and cost together with the environmental concerns since the application of these sophisticated nanomaterial-based membranes should be made practical.



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