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Photocatalytic Membranes for Organic Pollutants Removal from Water and Wastewater: A Review

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ABSTRACT

The insufficient removal of organic pollutants obstacles the reclamation of wastewater and threatens water security. Photocatalytic membrane, a hybrid water treatment method by integrating photocatalysis with membrane filtration, has drawn considerable attention in the removal of organic pollutants from various sources of wastewater such as textile industries, palm oil mill effluent, sewage, and industrial wastewater. This review consolidates the recent advances in the application of photocatalytic membranes for the removal of organic pollutants from contaminated water. Various types of polymer-based photocatalytic membranes and TiO_2-based photocatalytic membranes have been reviewed. Strategies to enhance the photocatalytic activity by implementation of different immobilization methods for fabricating photocatalytic membranes are also addressed. Furthermore, the applications of typical TiO_2-based photocatalytic membranes and key factors affecting organic pollutants removal are discussed based on the literature database. Overall, utilization of the photocatalytic membrane presents a promising approach towards the development of an effective photocatalyst and membrane performance in simultaneous process.

Keywords: Photocatalyst, photocatalytic membrane, photodegradation, wastewater treatment

1.0 INTRODUCTION

Membrane process is a selective barrier which can achieve separation of solid particles from liquid effectively. Application of coupled membrane process with photocatalytic process has reported improvement the reusability of the photocatalyst in the photocatalytic systems. This process employed separation of photocatalyst and treated water and keeping the photocatalytic activity simultaneously [1]. The membrane provides a selective barrier to separate the pollutant, as well as the supporting substrate for the photocatalyst particles [2]. Pollutants feed water passes through the membrane in filtration process. The pollutant adhered on the membrane surface which may led to reduce the membrane permeability or membrane fouling [3]. The presence of the photocatalyst in the photocatalytic membrane system may perform photocatalytic degradation reaction of the pollutant which separated by the membrane, thus reduce the membrane fouling in the membrane surface [2-3]. There are two primary configurations

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for photocatalytic membrane reactors: suspended photocatalyst and immobilised photocatalyst. Due to the large total surface area photocatalyst per unit volume, the suspended photocatalyst or slurry reactor configuration was favoured [4]. The major parameter was the amount of photocatalysts supplied to the reactor, and nanoparticle TiO_2 has been frequently employed and found to have a better photocatalytic efficiency. Nevertheless, it is challenging to separate from treated water, and the opacity of the overconcentrated slurry suspension may reduce light irradiance [5]. Consequently, immobilised photocatalyst enables both physical separation via membrane filtering and photocatalytic decomposition of contaminants in a single unit [6].

2.0 POLYMER-BASED PHOTOCATALYTIC MEMBRANE

It is feasible to create immobilized photocatalytic membranes by depositing photocatalyst on the membrane surface or including it into membrane casting solutions. Nevertheless, the fabrication of immobilized photocatalytic membranes presents several obstacles, including limited photocatalytic activity in the visible light area and the possibility of membrane structural breakdown [7]. The method in which photocatalyst is placed on the membrane is one of the variables that contribute to the high effectiveness of photocatalytic membranes. Entrapped photocatalyst inside membranes reduces light irradiance and, thus, photocatalytic efficacy. In contrast, the well-dispersed photocatalyst on the surface of the coated photocatalytic membrane increases its photoactive performance [8]. In addition, it is important to prevent the supporting membrane material damaged from self-oxidizing in the photocatalytic reaction. Polymeric membranes offer inexpensive materials, also can be modified to enhance the stability and efficiency under light irradiation or oxidizer agents. It is better option for industrialization than the high-cost ceramic membranes [7]. Comparison of application of polymer-based photocatalytic membrane shown in Table 1.

Bhattacharyya *et al*., (2023) [9] reported the use of TiO_2 deposited on the commercial Polyethersulfone (PES) for methyl orange (MO) removal. Modification of membrane surface with 0.25% resulted in high photodegradation of MO 82.3% under UV light for four hours. They also reported reusability of the photocatalytic membrane with 79% MO removal after 3 cycles.

Another research on modification of polymeric membrane was reported by Feng *et al*., (2023) [10]. They mixed porous nano photocatalyst NH2-MIL-88B(Fe) with polyaryl ether nitrile (PEN) then grown Ag2S on the surface of the composite membrane. The composite photocatalytic membrane reported 99.97% removal of an antibiotic Sulfadiazine (SDZ). It also has high removal of SDZ as 91.76% after 8 cycles. Moreover, it also has good strength, toughness, and high temperature resistance. In another research of composite polymeric membrane, Wu *et al*., (2023) [11] studied MIL-53(Fe)/PVDF mixed matrix membrane. The composite membrane also showed high photodegradation of tetracycline, an antibiotic compound, until 93% under UV light irradiation.

Table 1 Comparison polymeric membrane materials

Polymer	Remarks	Ref.
Commercial membrane PES (NF)	• 0.25 wt.% TiO_2 layer on the surface • 82.3% degradation of Methyl Orange in four hours under UV lamp • 79% MO degradation after 3 cycles	[9]
PEN	• Double heterojunction photocatalyst Ag_2S/NH_2-MIL-88B(Fe) • Degradation of SDZ 99.97%, mineralization rate 85.41% • 91.76% removal rate of SDZ after 8 cycles	[10]
PVDF	• Immobilization of MIL-53(Fe) 1-5 wt.% • High rejection of 87% TC • 93% photodegradation of TC under UV light	[11]
PS, PTFE, PVDF (MF)	• Direct hydrolysis of TiO_2 on the membranes surface • Amount TiO_2: TiO_2/PS 11.0 wt%, TiO_2/PTFE 2.7 wt%, and TiO_2/PVDF 3.3 wt%. • Degradation DCF: TiO_2/PS 93%; TiO_2/PVDF 92%; TiO_2/PTFE 89% • Degradation EE2: TiO_2/PS 96%; TiO_2/PVDF 94%; TiO_2/PTFE 92% • TiO_2/PS highest photocatalytic activity, damaged after first photocatalysis cycle • TiO_2/PTFE significant increased permeate flux after first photocatalysis cycle • TiO_2/PVDF high photocatalytic activity, stable permeate flux	[8]
PES (NF)	• Incorporation metal-nonmetal doped (K-B-N-TiO_2) 0.5% • High permeation 27 kg/m^2, dye removal 98%, and COD removal 90%	[13]
PP, PS, PES (MF)	• Decreased membranes resistance within UV exposure for 24 h: PP 20%; PS 26%; PES 30% (all membranes breakdown within 3 days of UV exposure)	
PAN PTFE PVDF-hydrophobic PVDF-hydrophilic (MF)	• Structure stability within 30 days of UV exposure • TOC released after 30 days of UV exposure: PTFE 13.0; PVDF-hydrophilic 3.6 ppm; PVDF-hydrophobic 109.0 ppm; PAN 29.0 ppm • Breakdown within 10 days H_2O_2/UV exposure: PAN	[12]
PS (UF)	• N,Pd co-doped TiO_2 in PS membrane • 87-97% pollutant removal (dye) within 4 h under visible light • Slower initial rate of photoreaction in the first hour • No flux data	[14]

Research reported by Chin, Chiang and Anthony, (2006) [12] made a comparison of ten different types of polymeric membranes for photocatalytic use. They observed the oxidative effects of photocatalysis and UV exposure effects on the membranes structure. UV-screening test by 24 h of UV exposure on membranes made a change in resistance membranes indicated membranes damaged. Polypropylene (PP) which consist only methyl groups (-CH-) had 20% resistance change associated with the breaking of the chemical bonds of the methyl group by UV energy. This also happened to the membranes which contain sulphur like polyethersulfone (PES) and polysulfone (PSf) with 26 and 30% decreased membranes resistance, respectively. The other parameter which used for indicating membrane breakdowns was releasing total organic carbon (TOC). The released TOC amount from PS and PES was higher than other membranes. Furthermore, they set up longer UV exposure for the screening test. Polytetrafluoroethylene (PTFE), PVDF-Pall (hydrophilic), PVDF (hydrophobic), and polyacrylonitrile (PAN) membranes were shown its structure stability in 30 days of UV test and the amount TOC released were 13.0; 109.0; 3.6; 29.0 ppm, respectively. Oxidation test was conducted using H_2O_2 as powerful oxidizer and UV exposure for analysing effects of the oxidizer on the membrane surface. PAN membranes broke down after 10 days of H_2O_2/UV exposure. This indicated that weaker polymer chemical bonds tended to break down under UV exposure and presence of powerful oxidizer. PAN membrane contain the larger number of -CH- bonds which weaker than PTFE (-CF_2CF_2-)n and PVDF (-CH_2CF_2-)n [12]. Dekkouche *et al*., (2021) [8] published an investigation comparing different photocatalytic membranes employing direct hydrolysis of TiO_2 on hydrophilic PTFE, PVDF, and PS membranes. The polymeric membranes were first activated in alcoholic solutions and then immersed in ethanolic solutions containing titanium (IV) isopropoxide (TTIP) as titania precursors for in-situ hydrolysis directly on the membrane surface. TGA was used to determine the quantity of TiO_2 on the polymeric membranes, yielding TiO_2/PS 11.0 wt%, TiO_2/PTFE 2.7 wt%, and TiO_2/PVDF 3.3 wt%. Under UV irradiation, diclofenac (DCF) and 17- ethinylstraddiol (EE2) degradation was used to assess the photocatalytic activity of membranes. TiO_2/PS membranes were the most photoactive in removing model pollutants (93% and 96% for DCF and EE2, respectively), followed by TiO_2/PVDF membranes (92% and 94% for DCF and EE2, respectively) and TiO_2/PTFE membranes (89% and 92% for DCF and EE2, respectively). The results demonstrated that the membrane's TiO_2 content affected the photocatalytic activity. Nevertheless, photocatalytic performance of TiO_2/PS was comparable to that of TiO_2/PVDF despite substantial changes in TiO_2 concentration. This indicated that the way in which photocatalyst deposited on membranes also influenced photoactivity. In situ growth of TiO_2 clusters on the surface of a PS membrane reduces UV-led irradiation of TiO_2 particles. By estimating the permeate flow, membrane stability was investigated. Although TiO_2/PS had the highest photocatalytic activity, it was damaged after the first photocatalysis cycle. TiO_2/PTFE exhibited a significant decrease in membrane performance due to an increase in permeate flux after the first cycle of photocatalysis, whereas TiO_2/PVDF exhibited not only high photocatalytic activity but also excellent membrane

stability under UV exposure, as evidenced by the stable permeate flux. Other study by Kuvarega *et al*., (2018) [14] reported N,Pd co-doped TiO_2 in PSf membrane for degradation of eosin yellow as model pollutant by phase inversion method under visible light irradiation. Their objectives were fabricating efficient, low cost, and low energy consumption membrane for wastewater treatment. The fabricated membrane performed good photocatalytic activity by 87-97% pollutant removal (eosin yellow) within 4 h. The result can be achieved due to increasing porosity of the nanoparticles embedded membrane which led faster permeation of the aqueous solution into membrane. However, it shown a slower initial rate of photoreaction in the first hour of visible light irradiation and increased thereafter.

Overall, PVDF was promising material as a support membrane for photocatalytic membrane. It shown better stability performance under UV irradiation, resistance from oxidizing agents, and doped TiO_2 photocatalyst also provided high photocatalytic activity and stable permeate flux [6–8].

3.0 TiO_2-BASED PHOTOCATALYTIC MEMBRANE

TiO_2 is one of useful semiconductor materials for photocatalysis. It is inexpensive compared to other materials used for water treatment, less toxicity, and high chemical stability [1], [4], [15]. In comparison, ZnO is prone to photo-corrosion by UV light [7], SnO_2 and CdS may produce toxic product during photocatalysis [16-17]. TiO_2-based photocatalytic membrane can be fabricated as composite TiO_2 photocatalytic membrane reactor or pure TiO_2 as freestanding photocatalytic membrane reactor. Composite membrane reactor can be made from several materials such as ceramic, inorganic/organic material, and polymer [1]. TiO_2 polymer composite membranes mostly were applied for the treatment of wastewater and purification of water which polymer as support material. TiO_2 particle can be dispersed in the polymer matrix or coated on the polymer surface. Most studies of TiO_2-based composite membrane were employed support materials of polyvinylidene fluoride (PVDF), polysulfone (PSf), polyamine (PA), polyaniline (PANI). Fabrication of these composite membranes often used phase inversion method and phase separation method using pore-forming additive like polyethylene glycol (PEG), in which employed N-methyl-2-pyrrolidinone (NMP) or N,N-dimethylacetamide (DMAc) as solvent [1], [7]. Several fabrications of TiO_2-based polymer composite membranes were summarized in Table 2.

Kumaravel *et al*., (2023) [18] studied photocatalytic composite membrane from PVDF and Ru-TiO_2 photocatalyst. The photocatalytic membrane was tested for decolorization of methylene blue (MB) and crystal violet (CV). Immobilization of 1% Ru-TiO_2 showed significant photocatalytic degradation of the dyes with 84% and 83% for MB and CV, respectively. The mineralization of the dyes was 64% and 61% of MB and CV, respectively. The membrane also exhibited high stability in recyclability test. Another approached of PVDF-TiO_2 membrane was reported by Liu *et al*., (2023) [19]. They evaluated the photocatalytic membrane for degradation of a steroid hormone E2 under UV exposure. Loading 6.5% of Ti showed highest E2 (100 ng/L) removal up to 96% and flux of 60 L/m^2h.

Research by Damavandi *et al*., (2023) [20] utilized polyacrylic acid

(PAA) grafted on the PES membrane then coated by TiO_2 nanoparticles for phenol removal. The photocatalytic membrane showed 62% phenol removal after 3 hours under UV light irradiation. The membrane also indicated minimal leaching after 72 hours of cross-flow filtration test.

Table 2 Fabrication of TiO_2-based polymer composite membranes

Configuration & Membrane type	TiO_2 precursor (loading)	Fabrication method	Remarks	Ref.
• PVDF	TTIP Ru-TiO_2 (1%)	Phase inversion	• Ru-TiO_2/PVDF 1%/12%, casted on the glass plate • Decolorization of MB 84%, CV 83% under visible light irradiation	[18]
• PVDF	TTIP		• TiO_2 6.5%, E2 feed 100 ng/L • Removal 96% of E2, flux 60 L/m^2h, 25 mW/cm^2	[19]
• PES	TiO_2 P25	Phase inversion	• PES membrane: PES/TEG/DMF 15/20/65 wt.%, grafted PAA • Dip coating TiO_2 0.1% • Removal 62% of phenol after 3 h, under UV light irradiation	[20]
• PVDF	TiO_2 NPs (25 wt.%)	Phase separation	• Casting solutions: 25 wt% of TiO_2/PVDF, PEG200, DMAc solvent • Casting media: Teflon sheet covering a glass plate • Immersion: tap water coagulation bath, washed DI water • Max permeates flux 150 L/h/m^2 • Flux recovery ratio under UV: 77-112% • No data % degradation of pollutant	[21]
• PVDF/ SPES	TiO_2 NPs (4 wt.%)	Phase inversion	• Polyethersulfone sulfonation treatment (SPES) • Casting solutions: PVDF, SPES, 4%/76% TiO_2/DMAc solvent, polyvinyl pyrrolidone (PVP) additive • Casting media: polyester non-woven fabric • Immersion: Water • Photo-bactericidal properties • No data % degradation of pollutant	[22]

Configuration & Membrane type	TiO_2 precursor (loading)	Fabrication method	Remarks	Ref.
• TiO_2 coated membrane • PES	TiO_2 NPs (0.03 wt.%)	Phase inversion-dip coating	• Dip coating: 0.03 wt% of TiO_2, 15 min immersion, 15 min UV irradiation • Casting solutions: PES, TiO_2, additive PVP, DMAc solvent • Casting media: no data • Immersion: Water/isopropyl alcohol • Flux 63% after 4 h • Rejection: 99% protein	[23]
• PES • PVC-PAN	TiO_2 NPs TiO_2 Sol (0.1 wt.%)	TiO_2 spraying, vacuum coating, sol-gel coating	• Spray & vacuum coating: 0.1% w/v TiO_2/DI water • Spraying and vacuum coating: negligible permeability • Sol-gel coating: 65-80% pure water permeability; more than 30 and 40% degradation of MB and CHD, respectively	[24]
• PAN	Titanium butoxide (2 wt.%)	Electrospinning	• In situ polymerization of aniline • 16.6 mg/g adsorption of congo red • 91% regeneration capacity	[25]
• PES	Titanium foil (0.1 g)	Magnetron sputtering	• Degradation of MB after 120 min under visible light: vapor-crystallized TiO_2 nanotubes 50%; hydrothermal crystallized 40%	[26]
• PVDF	TTIP:PVP 2:3	Electrospinning-hot press	• photodegradation of BPA under visible light: 84.53%, 77,61%, and 62.54% for PVDF/TiO_2-100°C, PVDF/TiO_2-160°C, PVDF/TiO_2-180°C • Higher hot-press temp, lower water flux • Hot-pressed temp 60°C the membrane not adhered completely	[27]

Méricq *et al*., (2015) [21] reported fabrication of PVDF/TiO_2 membranes by non-solvent induced phase separation using DMAc solvent and PEG additive. Increasing TiO_2 content led to enhancement the membrane

permeability and flux performance. The presence of the photocatalyst also enhanced the photocatalytic performance by preventing pure water flux decline under UV irradiation. Deposition of the photocatalyst on the membrane surface also influenced the photocatalytic performance. Rahimpour *et al*., (2008) [23] compared the membranes performance and antifouling properties of TiO_2-entrapped and TiO_2-coated in the PES membranes. They reported that the coated TiO_2 membrane has better performance than the entrapped TiO_2 inside membrane matrix which proven by higher flux recovery. It was shown 99% of protein rejection from milk water permeation and the flux membrane was 63% after 4 h milk ultrafiltration, which higher than flux of the neat membrane (42%). This result proved that the presence of TiO_2 nanoparticles and UV irradiation enhanced the antifouling properties of the membrane. Chakraborty *et al*., (2017) [24] examined three immobilization techniques for depositing TiO_2 nanoparticles on polymeric hollow fibre membranes utilizing PES and PVC-PAN as catalytic supports. They evaluated the modified membrane for degradation of MB and chlorhexidine digluconate (CHD) under simulated solar radiation by spraying, vacuum coating, and sol-gel coating. Spray and vacuum procedures result in an additional layer on the membrane's surface, reducing its permeability. The pore-blocking deposition of TiO_2 shown by SEM examination to have low membrane permeability. The sol-gel technique was utilized using diluted sol as the coating solution, and the membrane was then dipped into the solution to deposit TiO_2 onto the membrane surface. Controlling the concentration of TiO_2 solution was used to determine the optimal coating procedure for maintaining membrane permeability. The flow of pure water through the coated membrane was 65-80% lower than that of the untreated membrane. In addition, the photodegradation experiment resulted in greater than 30 and 40 percent degradation of MB and CHD, respectively.

Sputtering photocatalyst onto membrane surface is another method for immobilizing on the membrane surface. Fischer, Gläser and Schulze, (2014) [26] synthesized a TiO_2/PES membrane by magnetron-sputtering a titanium film onto a PES membrane, followed by anodization and crystallization of the membrane using two distinct processes (vapor-thermal and hydrothermal). Photocatalytic testing with methylene blue resulted in 50% and 40% degradation after 120 minutes for vapor-crystallized and hydrothermally crystallized TiO_2 nanotubes, respectively. The improved surface area and light-harvesting capabilities of the anatase nanotubes structures had an influence on the membrane.

The immobilizing of photocatalyst by electrospinning has been explored. Nor *et al*., (2016) [27] prepared electrospun PVDF/TiO_2 nanofibers by hot pressing nanofibers photocatalyst on the surface of PVDF flat sheet membrane. The PVDF membrane was fabricated by phase inversion method and TiO_2 nanofiber was synthesized using electrospinning technique. Then, the elctrospun TiO_2 nanofibers were placed and hot pressed on the surface of PVDF membrane within constant pressure 80 bars and varied temperature (60°C, 100°C, 160°C and 180°C) for 30 min. photodegradation of BPA under visible light shown 84.53%, 77,61%, and 62.54% for PVDF/TiO_2-100°C, PVDF/TiO_2-160°C, PVDF/TiO_2-180°C, respectively. By using similar method, Xu *et al*., (2020) [25] developed a PAN/TiO_2/PANI for

removal of congo red as target pollutant and recovered the photocatalytic membrane employed visible light irradiation. the membrane was prepared by electrospun PAN/TiO_2 membrane then added aniline directly on the PAN/TiO_2 membrane for in situ polymerization. The membrane tested of the adsorption towards congo red shown 16.6 mg/g adsorption capacity which higher than PVA/PAA/GO-COOH fiber membrane (8.88 mg/g). Regeneration of the membrane evaluated using visible light irradiation. Overall, the regeneration capacity of the prepared membrane was 91%, three times higher than water-wash regeneration (31%).

4.0 CONCLUSION AND FUTURE DIRECTIONS

Despite the selection of photocatalyst and polymeric membrane, the selection of methods used also needs to be consider enhancing the photocatalytic activity of the photocatalytic membrane. Compared to the suspended photocatalytic membrane system, the embedded photocatalyst in the membrane system will reduce the membrane fouling significantly that may improve the water permeability. TiO_2 photocatalyst nanoparticles entrapped in the membrane system will not be released to the liquid pollutant stream during filtration process and will give higher pollutant removal efficiency because of the photocatalytic reaction that occurs on the membrane surface also in the membrane pores during filtration process when the pollutant is permeated through the membrane [28–32].

Moreover, there are several factors that reported affect the embedded photocatalytic membrane performances. In the photodegradation system, pH of the pollutant feed may be one factor that affect the photodegradation process [33–35]. This is connected to the charge repulsion between the pollutant and photocatalyst nanoparticles because the capacity of a pollutant to adsorb can be critical for a catalyst's high catalytic activity, as it can improve electron/hole transfer efficiency and interaction with photogenerated active species [36]. The photocatalyst loading in the membrane system give significant impact in the membrane properties. It may act as a pore forming agent in the fabrication process of symmetric membrane until the optimum composition achieved. At the higher amount of photocatalyst loading, it may agglomerate in the membrane pores which results defect membrane pore structure and decrease the permeability [37-38].

Utilization of the photocatalytic membrane has become an advanced option for wastewater treatment. Development toward solar-driven photocatalytic membrane as the greener energy has emerged recently. Also, optimization of photocatalytic membrane configuration may be explored like different photocatalytic membrane system designs and configurations to enhance the photodegradation efficiency. This could include exploring variations in the immobilization technique, catalyst loading, membrane properties, and light distribution to improve the contact between the immobilized photocatalyst and the target pollutant.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this paper.

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