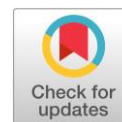


An overview of wastewater treatment using combined heterogeneous photocatalysis and membrane distillation

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Abstract

The need for efficient remediation solutions to wastewater has risen due to the concerning prevalence of toxic organic pollutants. It is possible for the linked photocatalysis-membrane separation system to concurrently achieve the photoreaction of pollutants and their removal from wastewater in order to accomplish the goal of completely purifying the wastewater. This investigation's objective is to provide analytical overview of the photocatalytic and membrane coupling process, photocatalytic membrane reactors, and the potential applications of these technologies in the treatment of wastewater for the persistent organic matter removal. In the review, an examination of photocatalytic and membrane processes to remove organic compounds from wastewater is presented. Based on the literature analysis, it was observed that the application of photocatalytic membrane reactors is significantly influenced by a wide variety of factors. Some of these factors include pollutant concentration, dissolved oxygen, aeration, pH, and hydraulic retention time. Light intensity is another factor that has a significant influence. It was also revealed how distillation membranes work when integrated with photocatalytic process. This brief overview will help researchers understand how successful coupled photocatalytic and membrane distillation are in the treatment of wastewater containing organic pollutants.

Keywords

heterogeneous photocatalysis
membrane
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Key findings

- The application of photocatalytic membrane reactors is significantly influenced by a wide variety of factors.
- Integration of distillation membrane with photocatalysis enhances the degradation of pollutant in wastewater.
- The recovery of membrane fluxes in membrane distillation after UV irradiation could be achieved using silver-based photocatalysts.

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1. Introduction

Rapid industrialization and processing of raw materials into different products has resulted into the introduction of various synthetic chemicals into the aqueous effluents [1–3]. These anthropogenic activities have contributed to environmental damage [4, 5]. To safeguard both human health and the environment, environmental rules and regulations have been made stricter. This is expected to continue for the foreseeable future. Green chemistry principles and clean technologies can be used in manufacturing

processes to safeguard the environment according to a variety of directions [6, 7]. As a result of their strong resistance (recalcitrant substances), organic contaminants typically remain in high quantities in treated effluents after conventional chemical (e.g. adsorption, chemical oxidation) and biological treatment methods are used to clean up water [8]. Hence, new technologies for the removal of developing hazardous chemicals from water and wastewater are required.

To avoid the creation of sludge and its disposal, photocatalytic reactions can be employed to degrade organic

contaminants in to tiny, non-toxic compound fragments completely without any chemicals being used at all [9]. Titanium dioxide (TiO_2) is the most common photocatalytic substance. TiO_2 can be suspended in a solution or anchored to a support [10, 11]. When compared to reactors with an immobilized catalyst, photocatalytic reactors with a suspended catalyst provide significantly greater interaction between the photocatalyst and dissolved contaminants [12]. Photocatalytic activity of TiO_2 is great, but its particles must be separated for practical usage. Using photocatalytic processes, a wide range of organic pollutants can be completely degraded (i.e., mineralized) in to very small and harmless substances, thereby minimizing the use of chemicals and avoiding sludge production and its disposal as a result of the highly unselective reactions involved [13, 14].

The active surface accessible for components of the solution is greatly decreased for the photocatalyst placed on a support, which typically leads to a loss of photoactivity [15]. Therefore, photocatalyst particles must be removed from the treated water after the detoxification if the catalyst is administered as a suspension. Photocatalytic membrane reactors (PMRs) which are hybrid reactors that combine photocatalysis and membrane processes are a possible solution to the challenge of separating the photocatalyst and the products and byproducts of photodecomposition from the reaction mixture [16]. The membrane would serve as both a simple barrier for the light catalyst and a selective barrier for the molecules that would be destroyed by the photocatalyst [17]. In PMRs, the catalyst can be immobilized on a membrane (photocatalytic membranes) or suspended in the reaction mixture, similar to traditional photoreactors [18]. Compared to traditional photoreactors, photocatalytic membrane reactors offer the advantages of: using a membrane that could serve as an intermediate in the process of containing the photocatalyst inside the reaction environment; regulating the amount of time that each molecule spends within the reactor; realizing a process that can run continuously while simultaneously isolating the catalyst and products from the reaction environment [16].

In the application of PMRs for wastewater treatment, it is also possible to avoid extra steps like coagulation–flocculation–sedimentation, which are required to remove the photocatalyst from the treated solution [19]. The first advantage of this is that it saves energy and reduces the installation size [20]. In addition, the photocatalyst may be reused in subsequent runs, which is almost impossible with the standard separation approach of coagulation–flocculation–sedimentation. Photocatalysis and pressure-driven membrane processes such as microfiltration (MF), ultrafiltration (UF), and nonfiltration are found in nearly all PMRs described in the literature [21]. Membrane fouling is observed when the catalyst in suspension is utilized, particularly in the case of MF and UF membranes [17]. Furthermore, even in the event of NF, tiny molecules can easily

pass through the applied membranes, resulting in a lower permeate level. New forms of photocatalytic membrane reactors that combine photocatalysis with dialysis, pervaporation, and direct contact membrane distillation were reported [22]. The advantage of this setup is that the membrane is not fouled by the photocatalyst. Molinari et al. [23], Molinari et al. [24], and Nasrollahi et al. [17] reviewed the hybrid photocatalysis-membrane processes. The authors presented and discussed a comparison of four hybrid photocatalysis-membrane processes, namely: photocatalysis + MF for catalytic recycling of slurry; photocatalysis + UF for recycle of catalyst slurry and (polymer) reactant; immobilized photocatalyst and UF/RO recycling of reactant; photocatalytic freezing UF/RO membrane for membrane self-cleaning. Considering the fact that various new PMR arrangements have been described in the literature over the last few years, and that there is a lack of publications outlining current advancements, it is necessary to explore fresh innovations and research development regarding the application of PMRs in wastewater treatment. This review, therefore, focuses on the advances in the application of PMRs for wastewater treatment, and also discusses the membrane photoreactors with immobilized and suspended photocatalysts in various arrangements.

2. Heterogeneous photocatalysis

Heterogeneous photocatalysis refers to the process of boosting or speeding up a photoreaction in the presence of a photocatalyst [25]. The photochemical splitting of water into hydrogen and oxygen by Fujishima and Honda in the presence of TiO_2 in 1972 was a hot issue in the history of heterogeneous photocatalysis [26]. In oxidation-reduction processes, a wide range of semiconductor catalyst materials have been employed. Recently, research has focused on the use of photocatalytic semiconductor materials to remove organic and inorganic species from aqueous or gas phase systems in environmental clean-up, drinking water treatment and industrial applications [27, 28]. In addition to oxygen and water, TiO_2 may remove both organic and inorganic chemicals from the atmosphere through redox processes. While TiO_2 has emerged as one of the most intriguing materials for photocatalysis, it has also managed to grab the attention of physicists, chemists, and engineers in a variety of other domains [29]. Chemical inertness and long-term photostability have made TiO_2 an important material in many practical applications and commercial products, ranging from pharmaceuticals to foods, cosmetics to catalyst, paint to medicines and sunblock or solar cells where TiO_2 is used as a desiccant, brightener, or reactive mediator [14]. The United States Federal Drug Agency permits the use of up 1% of TiO_2 as an inactive ingredient in food. No known health effects have been linked to TiO_2 ; nonetheless, children aged 3–6 were found to be at the greatest risk from the effects of TiO_2 particles in their meals. Numerous new TiO_2

properties have been found in the recent several years. TiO_2 has been thoroughly examined for its possible application in environmental cleanup and the manufacture of solar fuels [14, 30, 31]. The bandgap excitation of TiO_2 causes charge separation, and the surface-adsorbed species scavenge electrons and holes.

2.1. Mechanism of photocatalytic oxidation

When organic contaminants are exposed to a light source and an oxidizing agent like oxygen or air, they are eliminated via a photocatalytic oxidation process that utilizes semiconductor photocatalysts like TiO_2 and ZnO . As shown in Figure 1, electrons in the valence band (VB) can only be excited by photons with energies larger than the band-gap energy (E) [16]. Heat is often dissipated when photons with energy lower than E or longer wavelengths are absorbed. Creation of a hole in the valence band (h^+) and an electron in the conduction band (e^-) occurs when the photocatalytic surface is illuminated with enough energy (CB). Water pollutants are oxidized directly, while the electron in conduction band oxidizes any oxygen that was adsorbed on the photocatalyst (TiO_2).

The photocatalytic oxidation process generates hydroxyl radicals as described in the above phases [32]. Because oxygen inhibits the recombination of an electron-hole pair during the oxidation of adsorbed water to hydroxyl radicals (OH), the hydroxyl radical is a key oxidant in organic pollutant degradation. There is an increase in the recombination rate of e^- and h^+ if the reduction of oxygen and the oxidation of pollutants do not proceed at the same time in the photocatalytic degradation of pollutants [33]. Thus, it is critical to keep electrons from building up in photocatalytic oxidation processes. TiO_2 has been widely explored in photocatalysis because of its high activity, good physical and chemical features, low cost, and availability [18, 34, 35]. The anatase and rutile forms of TiO_2 have been widely studied as photocatalysts. The photocatalytic activity of anatase was shown to be higher than that of rutile. Previous studies on the photocatalysis of several pesticide and herbicide derivatives prevalent in storm water and wastewater effluent employed various light sources, such as UV lamps and solar radiation.

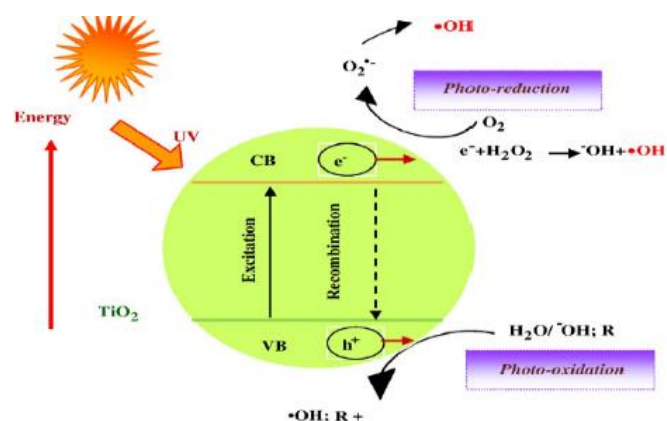
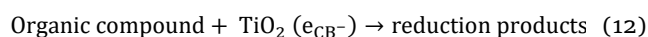
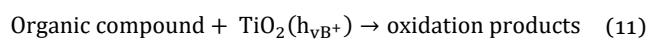
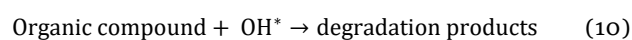
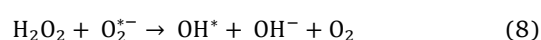
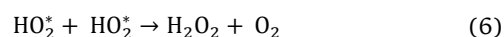
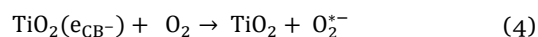
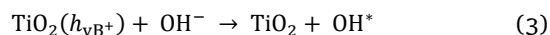
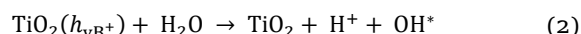
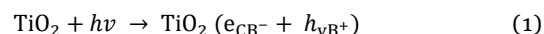


Figure 1 An illustration of the TiO_2 photocatalysis mechanism Ahmed et al. [12].

The photocatalytic oxidation of organic compounds under UV light can be represented by the mechanisms in Equations (1) to (12).



An electron (e^-) may be promoted from the valence band (VB) to the conduction band (CB) represented in Equation (1) if the photon energy is equal to or greater than the band gap width. This would result in an electron vacancy-hole (h^+) being created. As shown in Equations (2)–(12), when the electron and hole move to the catalyst surface, they can engage in redox reactions with various adsorbed substances. In Equations (2)–(3), there is combinations of holes with surface-bonds of water or hydroxyl to produce hydroxyl radicals (OH^*), but in Equation (4), electrons can combine with oxygen to produce superoxide radical anions ($\text{O}_2^{\bullet -}$). Hydroxyl radicals can also arise by going down the path shown in Equations (5)–(9). Hydroxyl radicals OH^* are listed as the main oxidizing species in Equation (10) for the photocatalytic oxidation processes. An illustration of how holes might oxidize organic molecules is the so-called photo-Kolbe reaction, in which holes directly react with carboxylic acids to produce CO_2 . In heterogeneous photocatalysis, the role of the reductive pathways in Equation (12) is less important than that of oxidation. When dyes are exposed to visible light, a separate photooxidation pathway is apparent. The process known as photosensitized oxidation (photo-assisted deterioration) occurs in this condition. The dye was in excitation stage when adsorbed visible light on the catalyst surface leads to appropriate singlet or triplet states. The electron is transferred to the conduction band of the semiconductor particles from the excited dye molecule and the dye is changed to the cationic dye radical ($\text{Dye}^{+\bullet}$). The $\text{Dye}^{+\bullet}$ radical reaction with hydroxyl ions or interaction with $\text{O}_2^{\bullet -}$, HO_2^* or OH^* species generates

intermediates. Eventually, CO₂, water and other degeneration products (e.g. nitrates, sulfates, etc.) are formed.

2.2. Photocatalysts

The surface and structural characteristics of the semiconductor, such as crystal composition, surface area, particle size distribution, porosity, band gap, and surface hydroxyl density, affect the photocatalytic activity of TiO₂ [36]. Because it directly affects catalyst's efficiency by defining its specific surface area, particle size is crucial in heterogeneous catalysis. In aqueous conditions, the photocatalytic degradation of phenolic compounds and dyes has been studied using a variety of commercially available catalysts [37]. Consideration must be given to the band gap value while choosing the best photocatalyst. Due to their typically low band gap, between 1.4 and 3.8 eV, semiconductors are preferred to serve as photocatalysts [31]. TiO₂ has a number of advantages that make it one of the best photocatalysts, including affordability, excellent chemical stability, commercial availability, non-toxicity, and environmental friendliness. The broad band gap of TiO₂ as a photocatalyst is its main flaw.

The strategies of doping semiconductor photocatalyst such as TiO₂ with metal or nonmetal elements and constructing a semiconductor heterojunction by mixing them with another semiconductor have been adopted in recent years to boost photocatalytic efficiency and overcome the obstacles faced by ordinary semiconductors [38]. Doping of semiconductors can boost the visible photo-response and the photocatalytic activity. A reduction in the energy required to excite an electron in the bandgap can be achieved using non-metal dopants such as carbon and nitrogen, which can form new electronic states close to the valance band. Metal elements such as Fe, Ag, Cu, Mg, Au, Pt, Cr, and W were used to control the bandgap and increase the photocatalyst performance by extending the lifespan of the photogenerated electron-hole pairs generated by the photovoltaic process [40, 41].

In order to get the best catalytic characteristics and performance, the procedures utilized to prepare the doped TiO₂ photocatalysts are critically important to understand and optimize their performance in degrading organic pollutants in wastewater. TiO₂ doped with a variety of elements may be prepared in different ways, including hydrothermal hydrolysis, co-precipitation, sol-gel impregnation, ligand-assisted reduction, chemical vapor deposition, hydrothermal-solvothermal, photodeposition, self-assembly, high temperature sulphuration, photochemical deposition, adsorption-calcination and so on (Table 1). Sol-gel method of doping TiO₂ photocatalyst is a standard technique. Preparation of nanomaterials is facilitated by the use of inexpensive materials and a straightforward approach. This technique has been utilized since the mid-1800s in a wide range of applications, including membranes and chemical sensors. Doped TiO₂ can also be produced via the hydrothermal technique. The hydrothermal

methods help to create crystals of uniform size with a smaller band gap, thereby increasing the photocatalytic activity under visible light irradiation.

2.3. Factors affecting the photocatalytic degradation of organic pollutants

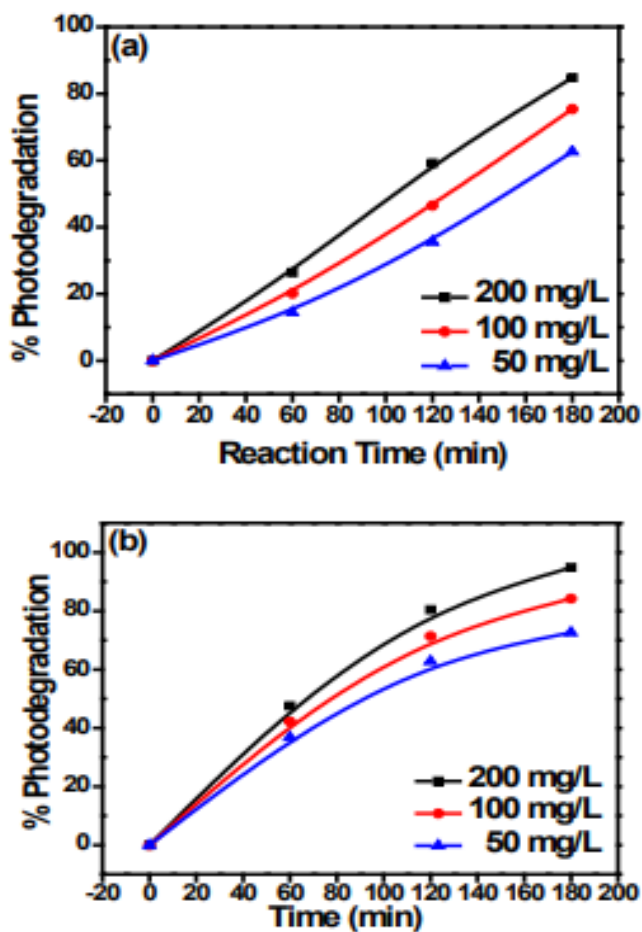
Several factors may have an impact on how organic pollutants are degraded by photocatalysis. The intensity of the light is one of these factors [41]. The intensity of the light source affects how much light of a specific wavelength is absorbed by the photocatalyst. Light intensity has a significant impact on photochemical electron-hole production during photocatalysis. The distribution of light intensity within the reactor determines the degree of pollutant conversion and degradation efficiency. The impact of light intensity on pollutant breakdown rates for various organic pollutants has been studied extensively [42]. While some research discovered a linear relationship between reaction time and light intensity, others discovered a square root relationship.

According to some studies, the photocatalyst loading in the photoreactor also affects how much organic pollutants are degraded (Figure 2) [43]. The photocatalytic rate initially rises with catalyst loading but then starts to fall as the catalyst loading increases [45]. The propensity for agglomeration (particle-particle contact) to grow at high solid concentrations results in a reduction in the surface area accessible for photocatalytic degradation [46]. Although, while the number of active sites in solution rises with catalyst loading, it appears that there is a limit beyond which light penetration is hindered by high particle concentration. By balancing these two opposing processes, catalyst loading for photocatalytic reactions can be made more efficient. If the catalyst loading is increased above the optimum, non-uniform light intensity distribution will happen, which will slow down the reaction rate [47].

The initial concentration of the organic pollutant is also a vital factor that influences their photocatalytic degradation [44]. For the photocatalytic oxidation system to work well, it must be determined if the rate of photocatalytic degradation depends on the initial concentration of the substrate. The influence of substrate initial concentration on the mineralization of 4-nitrophenol was studied by Parida et al. [46]. The study revealed that, as the initial substrate concentration rises, the amount of degradation decreases from 100 to 40.9%. This is as a result of the substrate absorbing light at high concentrations for the specified catalyst loading. At significant levels, the OH radicals available are insufficient for pollutant breakdown. Therefore, when the initial concentration rises, the degradation rate of the pollutant is reduced. As the substrate initial concentration rises, the catalyst's surface may adsorb intermediates that might contaminate the reaction. Deactivation of photocatalyst active sites can be slowed by the slow diffusion of intermediates from the catalytic surface. This results in a decrease in the degradation rate.

Table 1 Summary of selected TiO₂-based photocatalysts used for photodegradation of organic pollutants.

Photocatalyst	Preparation method	Dosage (mg)	References
Cu-TiO ₂	Sol-gel	100	[34]
Pt-Au/TiO ₂	Ligand-assisted reduction	10	[47]
MoS ₂ /TiO ₂	Chemical vapor deposition	10	[48]
MoS ₂ /TiO ₂	Hydrothermal	80	[49]
Pd@N-TiO ₂	Hydrothermal-Solvothermal	15	[50]
Ag@Ni/TiO ₂	Photodeposition	50	[51]
CMS/THS	Self-assembly	100	[52]
TiO ₂ -NiCoS-PC	High temperature sulphuration	20	[53]
N-TiO ₂ /g-C ₃ N ₄ @Ni _x P	Photochemical deposition	50	[54]
CdS@TiO ₂ /Ni ₂ P	Impregnation followed by Na ₂ H ₂ PO ₂ treatment	10	[55]
NiCoP(1 wt.%)/TiO ₂	Absorption followed by calcination	20	[56]
CoOx/TiO ₂ /Pt	Template-assisted atomic layer deposition	35	[57]
RuO ₂ /TiO ₂ /Pt-B	Chemical reduction	50	[58]
CuO/TiO ₂	Hydrothermal	20	[59]
Cu-TiO ₂ nanowire	Hydrothermal	50	[60]
Ti ₃ C ₂ T _x /TiO ₂	Impregnation	30	[61]
Ti ₃ C ₂ @TiO ₂ @MoS ₂	Hydrothermal	10	[62]
Ni(OH) ₂ /TiO ₂	Precipitation	50	[63]
Pt/black TiO ₂	Impregnation	100	[64]
Pt/Black TiO ₂ -xH _x	Photodeposition	100	[65]
Pt/TiO ₂ -001	Deposition-precipitation	15	[66]
Pt ₁ /def-TiO ₂	Adsorption followed by H ₂ treatment	20	[67]
ME-TiO ₂ @Ru	Adsorption-Calcination	50	[68]
Ni-a/TiO ₂	Molten salt synthesis	50	[69]

**Figure 2** Effect of TiO₂ loading(a) and effect of N-TiO₂ loading on the degradation of organic pollutant with irradiation time [70] (b).

The pH of the substrates is another factor that could affect the photodegradation of organic pollutants [71]. To understand the photocatalytic degradation of organic pollutants, it is important to understand how they interact with photocatalytic materials. If the solution pH is high enough, it can have significant effects on a photocatalyst surface charge and an organic pollutant's ionization or speciation (*pK_a*). The pH of the solution has a significant impact on the electrostatic interaction between the semiconductor surface, solvent molecules, substrate, and charged radicals produced during photocatalytic oxidation. The speciation behaviour, water solubility, and hydrophobicity of organic molecules in wastewater vary widely. In natural water and wastewater, certain chemicals are uncharged, whereas other compounds show a wide range of speciation (or charge) and physico-chemical characteristics. An organic compound is a neutral species with a pH lower than its *pK_a* value. An organic substance has a negative charge above this *pK_a* value. It is possible in aqueous solution for certain chemicals to exist in positive, neutral, and negative forms. The photocatalytic degradation behaviour of these materials can likewise be considerably influenced by this difference. Wastewater pH is subject to wide variation.

The oxygen content in the solution is also a crucial factor that influences the photodegradation of organic pollutant [72]. In photocatalysis reactions, oxygen dissolved in solution is usually utilised as an electron acceptor to make sure that there are enough electron scavengers available to catch the excited conduction band electron and prevent

recombination. The adsorption on the TiO_2 catalyst surface is unaffected by oxygen because the reduction and oxidation processes occur at different locations. Dissolved oxygen is involved in the stabilisation of radical intermediates, mineralization, and direct photocatalytic reactions. Furthermore, it was demonstrated that it can lead to the disintegration of aromatic rings in organic pollutants present in water matrices.

3. Membrane distillation

The membrane distillation process relies on the presence of the vapour phase in the pores of the membrane for the evaporation of volatile feed components [73]. A liquid mixture's vapour/liquid equilibrium serves as the basis for the separation process. Only water vapour is transported across the membrane for solutions containing non-volatile solutes, and the resulting distillate is made up of demineralized water [74]. The unique separation features of the MD method remove the colours from the water in textile wastewater treatment, allowing for their reuse [75]. MD may also be used to treat salty wastewater, yielding both clean water and a concentrated solution that contains the original solution's constituents [76]. Concentration may not be enough in some circumstances, and solutes must be separated in solid form. Salt crystallization occurs once solution concentration reaches a supersaturated condition via the MD process. In addition to concentration, the MD procedure provides for the removal of volatile acids from the acidic waste solutions [77]. Using the MD technique for liquid low-level radioactive waste treatment, all radionuclides were eliminated. Membrane wettability and fouling are the key impediments to the implementation of MD. There are a number of components in the wastewater that might precipitate on the membrane surface during MD operation. As a result, even with elaborate pretreatment systems, part of the effluent cannot be treated directly using membrane methods. Fouling was shown to have a significant impact on the performance of MD processes during the treatment of various types of wastewaters [78].

Low tortuosity and homogeneous pore size distribution are desirable properties for MD membranes [79]. Microporous membranes used in MD must have low mass transfer resistance and low thermal conductivity in order to prevent heat loss across the membrane. Also, MD membranes must be able to withstand high temperatures and chemicals (e.g., acids and bases) [80]. Pore size must be matched between high permeate flow and effective wetting resistance in order to achieve optimal membrane performance. The performance of high-porosity membranes with limited mechanical strength deteriorates even under modest operating pressures. Different MD membranes used in high-strength wastewater reclamation have porosity levels ranging from 70–85%, according to the testing. Polytetrafluoroethylene (PTFE), polypropylene (PP), and polyvinylidene fluoride (PVDF) are the most often used active layers

in commercial hydrophobic MD membranes. PP or polyester can also be used as a support layer [81].

3.1. Integrated photocatalytic and membrane distillation process for wastewater treatment

In order to completely purify wastewater, the combined photocatalysis-membrane distillation process can be employed to achieve the photoreaction of contaminants and their removal from wastewater at the same time. Integrated photocatalytic and membrane distillation process used for wastewater treatment is gradually gaining research interest [82]. Photocatalysis-membrane separation hybrid systems have been used to purify wastewater while also removing contaminants from it [82]. These systems have been demonstrated to be effective in recent years. Photocatalysis can simultaneously photodegrade organic pollutants using the strong oxidation properties of photo-generated species as well as photoreduce metal ions using photoinduced electrons in this synergistic photocatalysis-membrane separation system [83]. Both the oxidation and reduction processes can help each other. Moreover, the photoreaction could be carried out at a consistent pace and efficiently stimulated by the membrane separation process [84]. Previous research demonstrated great efficiency for the removal of organic pollutants and their inorganic products using a photocatalysis-membrane distillation reactor [85]. Synergistic effects of organic removal and metal recovery in PMR have not yet been thoroughly explored, notably the influence of recovered metal ions on pollutant removal. Several authors reported the application of coupling photocatalytic wastewater treatment with membrane distillation [60, 64, 65]. Zou et al. [84] reported the removal of metal ions and organic pollutants from wastewater using a photocatalysis-membrane distillation method. For the purpose of an effective treatment of wastewater, the authors designed a photocatalysis-membrane distillation reactor to concurrently remove aqueous organics and metal ions. Through the synergistic action of photocatalysis and direct contact membrane distillation, the simultaneous removal of the probing contaminants 4-chlorophenol (4-CP) and Ag^+ ion was effectively accomplished. Li et al. [87] reported the treatment and reuse of petrochemical effluent via treatment with membrane distillation combined with a unique two-stage pretreatment involving photocatalysis. By combining membrane distillation (MD) with a two-stage pretreatment procedure that included oil/water separation and photocatalytic organics degradation, the authors created a unique hybrid system for the treatment and reuse of petrochemical effluent. Oil emulsions were separated from water by the oil/water separation method, and dissolved oil and volatile organic contaminants were eliminated by the subsequent photocatalysis procedure. After that, the pretreated water was used in the membrane distillation procedure to create distilled water. For the elimination of oil emulsions, a customized stainless-steel mesh/glass microfiber filter was utilized, and it demonstrated good

performance and durability. TiO₂ P25 was used as the photocatalyst in the photocatalysis step to efficiently break down the residual organic compounds and render microorganisms inactive when exposed to UV light. The two-stage pretreatment achieved a total organic degradation rate of 99.5%. The hybrid system's benefits include preventing membrane fouling and generating high-quality distillate with low total dissolved solids and few volatile organics, which are challenging to extract by a traditional MD process.

For the removal of ketoprofen from diverse aqueous matrices, a novel submerged photocatalytic membrane reactor based on membrane distillation was developed by [86]. The developed process combines photocatalysis with direct contact membrane distillation applied for the removal of ketoprofen from simulated marine, brackish, and surface water as well as secondary effluent of a municipal wastewater treatment plant. The experiments showed that ketoprofen with starting concentration of 10 mg/L was nearly protoxidized after 5 h. The distillate did not contain any ketoprofen; however, the amount of total organic carbon and total inorganic carbon varied depending on the kind of feed. The distillate with the greatest total organic compound level was found in the secondary effluent. The kind of aqueous matrix had an impact on the amount of dissolved oxygen in feed, which reduced most noticeably in surface water.

Guo et al. [88], reported a self-cleaning membrane regeneration using a BiOBr/Ag photocatalytic membrane incorporated with visible light during membrane distillation. The authors effectively coated an electrospun membrane with BiOBr/Ag catalyst particles utilizing electrospray technique to obtain better hydrophobicity and repeatable properties. There were three membranes examined for comparison: an BiOBr/Ag membrane, a commercial PVDF membrane, and a PTFE membrane. Optical coherence tomography was used to monitor the fouling processes on all three membranes in real time. Through the electron holes' significant oxidation ability, the BiOBr/Ag particles on the BiOBr/Ag membrane surface accelerated dye foulant degradation. As a result, the photocatalyst's electron separation and transfer efficiency was increased as well as its ability to reduce electron recombination by using Ag nanoparticles coated on it via UV deposition. The findings revealed that BiOBr/Ag photocatalyst membrane showed a considerable improvement in the recovery efficiency of the water contact angle and water flow under UV irradiation compared to the two commercial membranes. As a cocatalyst, the addition of Ag to BiOBr increased the amount of visible light that could be harvested.

Ning et al. [41] manufactured a membrane in membrane distillation to remove semi-volatile organic molecules from wastewater. The authors developed a new AgCl/MIL-100(Fe)/PTFE photocatalytic membrane to remove nitrobenzene from wastewater. The photocatalytic membrane distillation system boosted the nitrobenzene removal when

compared to the using standalone membrane distillation method. The authors also revealed that there was a steady performance throughout five nitrobenzene removal cycles. The combination of membrane distillation and photocatalysis may be responsible for the improved removal of the nitrobenzene [89].

3.2. Effect of process parameters on hybrid photocatalytic-membrane distillation process for wastewater treatment

Several factors, such as photocatalytic loading, reaction temperature, and initial concentration of the pollutant was reported to influence the photodegradation rate of pollutants in hybrid photocatalytic-membrane distillation process.

The effect of different loadings of photocatalysts on the photodegradation of AY36 in wastewater using hybrid photocatalytic-membrane distillation process has been reported by Mozia et al. [83]. The degradation of an azo dye (AY36) was shown to be highly sensitive to photocatalyst concentration. As the photocatalyst loading was increased from 0.1 to 0.3 g/dm³, the AY36 concentration decreased marginally. A further increase in the photocatalytic loading to 0.5 g/dm³, the concentration of azo dye reduced the most. Study have shown that more surface area of the catalyst is available for adsorption and degradation as the catalytic loading rises. However, the photocatalytic degradation rate is reduced as the catalyst loading is increased because of the increased opacity of the solution, which reduces the penetration of the photon flux in the reactor [90].

When considering the photodegradation rate of organic pollutant in wastewater, the reaction temperature is also crucial. The studies revealed that the degradation of AY36 from wastewater is more effective with increasing reaction temperature. In a reaction temperature range of 20 °C to 60 °C, a linear relationship between the rate constant of photodegradation of the dye and the reaction temperature was reported by Mozia et al. [83]. According to Chen and Ray [45], the increased frequency of molecular collisions in solution is what causes the photodegradation rate to increase when temperature increases from 10 to 50 °C. Adsorption of the reactant, which is a spontaneous exothermic event, is made more likely by a drop in temperature. The final products of the process, whose desorption tends to hinder it, are likewise more readily absorbed when the temperature is lowered. On the other hand, exothermic adsorption of the reactant becomes unfavourable and tends to limit the reaction when temperature rises over 80 °C and moves to the boiling point of water.

The efficacy of a dye's photodegradation is greatly influenced by its concentration, which is a crucial factor. It is frequently stated that a dye's initial rate of degradation increases with an increase in concentration. Yet, additional growth over a particular value causes its degradation rate to decline. One explanation for this is the dye ion coating on the catalyst surface, which inhibits the production of

hydroxyl radicals. It is evident that a reduction in the initial azo dye concentration resulted in a notable enhancement of the efficiency in breakdown of the organic pollutant in wastewater.

4. Limitations

This review presents the advances in the application of photocatalytic membrane reactors for wastewater treatment incorporated with immobilized and suspended photocatalysts in various configurations. Even under low operational pressures, highly porous membranes are limited in operating ability in such a way that with weak mechanical properties it functions poorly. According to tests, the porosity levels of several membranes used in high-strength wastewater reclamation range from 70–85%. The most often utilized active layers in commercial hydrophobic membrane distillation are polytetrafluoroethylene (PTFE), polypropylene (PP), and polyvinylidene fluoride (PVDF). As a support layer, PP or polyester can also be employed.

5. Conclusion and future perspectives

Photocatalytic membranes utilized in the membrane distillation process have so far been mostly studied for their ability to self-clean and for direct solar distillation. In situ control strategies for pollutants in membrane distillation treatment procedures are not well studied. Although photocatalytic technology may theoretically and realistically be integrated with membrane distillation systems, it is typically disregarded. An effective way to prevent the shading effect is to combine the photocatalytic membrane with membrane distillation heat cycling technology to create an organic waste-removal photocatalytic system that operates in a continuous flow. The recovery of membrane fluxes in membrane distillation after UV irradiation has been achieved using silver-based nanomaterials with high photocatalytic capabilities. Also, by utilizing photocatalyst-coated membranes in place of chemical cleaning, it is possible to increase fouling resistance during the membrane distillation process as well as aid in the recovery of fouled membranes. Photocatalytic nanomaterials on the membrane surface have recently been presented as a strategy to improve fouling resistance during membrane distillation process used for wastewater treatment.

As an advantage of the hybrid photocatalysis–membrane distillation system, TiO₂ particles in feed did not foul the membrane. Even more importantly, the distillate was of the highest quality since only water vapour and other volatile components were allowed to enter the membrane distillation unit. Because photo degradation was more successful and the residence periods were longer, the membrane distillation process was thought to be a better choice than pressure-driven membrane approaches. The photocatalytic membrane reactors have various benefits over traditional photoreactors. There is still room for improvement in terms

of permeate flow and membrane fouling as well as product (permeate) quality when it comes to the hybrid photocatalysis–membrane processes performance. Furthermore, it is critical to look at actual treatment techniques for wastewaters. By taking into account the entire scope of the environmental challenge, optimised treatment settings for tiny amounts of wastewater in hybrid photocatalysis–membrane distillation system reactors are typically unrealistic and inapplicable. The development of engineering-designed reactors and treatment methods are thus identified as being truly competitive alternatives. In that regard, reactor design and techno-economic evaluation pose real challenges to putting research findings into action. To fully use promising photocatalytic treatments of organic pollutants, research efforts should focus on configuring benchmark reactors and contrasting passive treatment systems with active ones.

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• Conflict of interest

The authors declare no conflict of interest.

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