



Photocatalytic membranes: a new perspective for persistent organic pollutants removal

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Abstract

The presence of conventional and emerging pollutants infiltrating into our water bodies is a cause of concern as they have seriously threatened water security. Established techniques such as photocatalysis and membrane technology have proven to be promising in removing various persistent organic pollutants (POP) from wastewaters. The emergence of hybrid photocatalytic membrane which incorporates both photocatalysis and membrane technology has shown greater potential in treating POP laden wastewater based on their synergistic effects. This article provides an in-depth review on the roles of both photocatalysis and membrane technology in hybrid photocatalytic membranes for the treatment of POP containing wastewaters. A concise introduction on POP's in terms of examples, their origins and their effect on a multitude of organisms are critically reviewed. The fundamentals of photocatalytic mechanism, current directions in photocatalyst design and their employment to treat POP's are also discussed. Finally, the challenges and future direction in this field are presented.

Keywords Photocatalytic membrane · Photocatalysis · Persistent organic pollutant · Wastewater · Mixed matrix membrane · Submerged membrane photoreactors

Introduction

As many countries across the world are experiencing rapid development, industrialization and growth in populations, water consumption and demands are also increasing exponentially. Countries such as Malaysia (Ali Hassan 2013), Greece (Shan et al. 2015), Poland (Shan et al. 2015), South Africa, Malta (Annalise Grech 2012) and Iran (Ashouri 2014) have shown increment in water consumption in the past 10 years

due to various reasons including growth in population and industrialization. Clean water sources become very limited as many of the existing water bodies are severely polluted by industrial discharges from textile, pharmaceutical, petrochemical and agricultural industries. Such wastewater intrusion affects the quality of water bodies thus increasing the cost of water treatment for domestic consumption. The emergence of various types of micropollutants that can harm human health as well as the increasingly stringent environmental laws have pushed researchers to look for efficient and sustainable water treatment techniques. Water treatments are necessary to ensure wastewater effluent pollution level is reduced to an acceptable level before they are discharged into natural water bodies. Currently applied wastewater techniques such as coagulation and flocculation (Verma et al. 2012) require additional chemicals to work effectively, while separation techniques such as gravitational settling and filtration (Yu et al. 2017) only contain the pollutants and transfer them into different phase/media. Secondary treatment is normally required to complete the treatment process.

Heterogeneous photocatalysis has shown great promise in treating wastewater effluents via advanced oxidation process (AOP), where a semiconductor catalyst is activated upon light

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irradiation to produce highly reactive oxidative species (ROS) that can non-selectively degrade pollutants (Ibhadon and Fitzpatrick 2013). Hydroxyl radicals which can be efficiently created by efficient photocatalysts are known to be the strongest oxidants in aqueous solution after fluorine. These hydroxyl radicals are capable to degrade harmful pollutants and organic pollutants into harmless inorganic molecules without creating secondary waste (Leong et al. 2014). AOP has been further utilized by employing various forms of oxidant sources. Some of the sources include the utilization of hydrogen peroxide (H_2O_2) and ozonation, energy sources in the form of lights (ultraviolet (UV) light) and the employment of catalysts such as Fenton oxidants like ferrous iron (Galvão et al. 2006), zeolite (Arimi 2017) and semiconductors like TiO_2 (Molinari et al. 2006). The primary goal is similar regardless of the sources, which is to induce oxidation reaction and subsequently producing large quantities of hydroxyl radicals.

One very popular photocatalyst that has been extensively studied is TiO_2 , particularly the P25 Degussa variant, as it has shown very good photocatalytic activity with a low band gap energy (3.2 eV), good recombination stability, low cost and photocatalytic friendly crystallinity (90% anatase) (Gomes et al. 2019). The excellent characteristics of TiO_2 allow it to mineralize pollutants of wide variety. TiO_2 has shown remarkable performance for degradation of synthetic dye (Muruganandham and Swaminathan 2006), oily wastewater (Kang et al. 2011), endocrine disrupting chemicals (EDC) (Laoufi et al. 2008) and other organic pollutants (Chen et al. 2020). Even though they exhibit remarkable photodegradation performance, they do come with some inherent limitations. Firstly, common semiconducting photocatalysts such as TiO_2 are only able to respond towards UV light source, which limits its usability. Hence, an independent source of UV light is consistently required to sustain photocatalytic activity. In addition, photocatalyst recovery after treatment is tedious, as a secondary filtration method is required to recover the photocatalyst. These limitations are the major stumbling blocks that hinder the practical application of photocatalyst as a feasible water treatment solution in industry.

To solve these pertaining issues, researchers have consistently explored photocatalyst doping, which refers to the incorporation of a foreign metallic or non-metallic atom into its lattice structure. Doping distorts the lattice and electronic structure of semiconductors (Byrne et al. 2021), and allows access towards the forbidden band, an energy band that is activated by visible light photons. Successful doping has shown two improvements, which are responsiveness towards visible light and lower band gaps which requires less energy for photocatalytic activation. Several successful researches have been conducted on doping TiO_2 with metals such as Fe (Vargas et al. 2012), Mn (Liu et al. 2012), Co (Siddiqi et al. 2015), Cu (Byrne et al. 2019), Ni (Sharma et al. 2006) and

non-metals such as N (Morikawa et al. 2005), S (Lisovski et al. 2012), BN (Byrne et al. 2020), F (Barndök et al. 2013) and C (Park et al. 2009). Research also shows that doped TiO_2 can respond towards visible light, which enables the utilization of solar light as an activation energy source. To improve photocatalyst recovery, deposition of photocatalyst onto different substrates has been explored extensively. Substrates such as thin films (Lin et al. 2013), glass plates (Mozia et al. 2012) and sand and clay (Azrague et al. 2007) are choices of substrates explored. Researchers have also incorporated photocatalyst into membrane matrices, immobilizing it inside the membrane structure. Such membranes can exhibit photocatalytic activity while enhancing membrane performance. The performance of such membranes has been illustrated well when employed to treat various pollutants such as aerobically treated palm oil mill effluent (AT-POME) (Subramaniam et al. 2018) and oily wastewater (Ong et al. 2015). However, a reduction in photocatalytic activity is also noticeable due to the loss of surface area of photocatalyst due to immobilization in polymeric membrane matrix.

With the advancement made in the design of highly functional photocatalysts, the development of photocatalytic membranes presents an interesting topic that also deserves great attentions in wastewater treatment. Topics related to photocatalytic membranes have been reviewed in the last few years. Nasrollahi et al. reviewed the fouling mitigation potentials of photocatalytic membranes (Nasrollahi et al. 2021). Focus was placed upon the parameters of submerged membrane reactors which govern membrane fouling, including influence of pH, oxidizing agents and photocatalyst loading. A similar review discussing the parameters involved in the setting up of a submerged membrane reactor has also been published by Argurio et al. (2018). The design of reactors and parameters that could affect the performance of such photocatalytic membranes were summarized. Another review summarized conventional oil separation methods and their limitations, with emphasis placed on membrane separation technologies (Nascimbén Santos et al. 2020). The recent reviews have placed more emphasis on using photocatalytic membranes as means for a fouling-free membrane and the parameters which influence the performance of such membranes when coupled into a submerged membrane reactor. However, these reviews did not provide further insights into the fundamental understanding in regard to the major components of photocatalytic membranes, i.e. the photocatalysts and the polymeric hosts. Furthermore, there is a lack of review on the fabrication and performance of photocatalytic membranes of different configurations, which has their own advantages and disadvantages.

In view of the current gaps in the review of photocatalytic membranes, the major aim of this review paper is to provide insights into the potentials of photocatalytic membranes for the removal of organic pollutants from wastewaters. The fundamentals of photocatalysis and emerging pollutants that can

be treated by photocatalysis are first discussed. The development of photocatalyst membranes in terms of preparations, configurations and performance evaluations is presented in the following sections. Finally, the review is wrapped up with the challenges and future research direction in the development of photocatalytic membrane as a promising candidate for organic pollutants removal from wastewater.

Persistent organic pollutant

Water sources across the globe are constantly under stress, especially with natural and anthropogenic organic substances repeatedly released into them. Adding to this, the practice of landfilling also deposits large quantities of POPs into the soil, which leach into groundwater sources and into rivers, polluting water bodies. POPs are classified as long lasting compounds that are difficult to be degraded naturally, enabling it to travel great distances (Weber et al. 2011). The infiltration of POPs into water bodies increases its biochemical oxygen demand (BOD) and chemical oxygen demand (COD). In addition, bioaccumulation of these POPs in aquatic life occurs, which builds up across the food chain as these POPs cannot be metabolized by aquatic life nor humans. With humans being at the top of the food chain, these POPs can find their way into human bodies and cause health problems, leading to irreversible changes on both wildlife and human health (Aydin and Talinli 2013). Figure 1 a–c show various information on POPs.

Figure 1 details the sources of different types of POPs and the detection of POPs in breast milk using different determinants such as consumption of fatty fish and fish oil supplements. Fish is known to be a common bioaccumulator of various POPs and heavy metals. The figure also shows the levels of bioaccumulation in aquatic animals. There are several methods which have been greatly discussed in literature to remove EDCs from wastewaters. Some of the methods described include adsorption, electrocoagulation (EC), polymeric membrane separation, thermal degradation and photocatalysis (Sun et al. 2020a; Titchou et al. 2021; Waheed et al. 2021). All the above-mentioned methods have shown promising performance in removing POPs from different water sources. However, each method being mentioned exhibits inherent disadvantages which make their application in the difficult. Some of the disadvantages faced by the existing treatment methods include the difficulty in recovering spent materials (adsorption/photocatalysis), membrane fouling phenomena, require special electrodes to feed current into the solution, limited temperature range and energy intensive. There are many kinds of POPs present in the environment, but for the purpose of this review, only two types of POPs are focused, namely EDCs and dyes, due to their increasing appearance in the existing water sources.

Endocrine disrupting chemicals (EDCs)

The term “endocrine disruptors” was coined in the early 1990s, signalling the identification of a new type of pollutants which is present in our waterways. However, it was not until in the early 2000s that extensive research was conducted on these EDCs and their debilitating effects toward human beings. In 2013, the WHO and USEPA urged researchers to place more emphasis to better understand the health risk posed by EDCs towards both human and animals (Darbre 2019). Extensive research has shown that the ever-growing presence of various types of EDCs in our waterways has detrimental effects toward the human health. EDCs are understood to be a form of pollution that is faced by waterways, which can interfere with the human endocrine system at various thresholds. There are three possible ways on how EDC would severely impact the human endocrine system. Firstly, they are able to mimic a natural hormone and bind onto a hormone receptor within the cell. The EDC would either provide a weaker or stronger signal as compared with hormone, and this would lead to incorrect response by the cell. Additionally, the EDC may also trigger a response when not necessary. Secondly, EDCs can bind with a receptor and prevent the correct hormone to bind and provide the required signal. Hence, the cell would not respond as required by the human endocrine system due to incorrect signal. Thirdly, these EDCs can interfere and block the function of the hormone and the receptors. Interferences and blockages at high doses of EDCs may lead to organ failures.

Another potential problem related to the ever-increasing presence of EDCs in waterways is the bioaccumulation of such compounds in animals. EDCs that are persistent and resist degradation can bioaccumulate in the fatty tissue of organisms and this would increase in concentration as they move up through the food web. Windsor et al. (2018) provided a detailed list of aquatic animals ranging from various types of fishes and mussels which could bioaccumulate EDCs. On the other hand, evidences have also suggested that vegetables uptake various types of EDCs which are present in artificial fertilizers and pesticides (Ribeiro et al. 2017). Natural endocrine-active substance such as phytoestrogens can disrupt with endogenous estragon signalling pathways are also found in vegetables (Cederroth et al. 2012).

Dyes

It is estimated that 700,000 tonnes of various colouring from about 100,000 commercially accessible dyes are manufactured each year (Rafatullah et al. 2010; Abdi et al. 2017). Dyes are used to colour a variety of products, but majority of its usage is by the textile industry. The majority of dyes used in the textile industry are synthetic dyes, which include sulphur dyes, solvent dyes and reactive dyes. Most

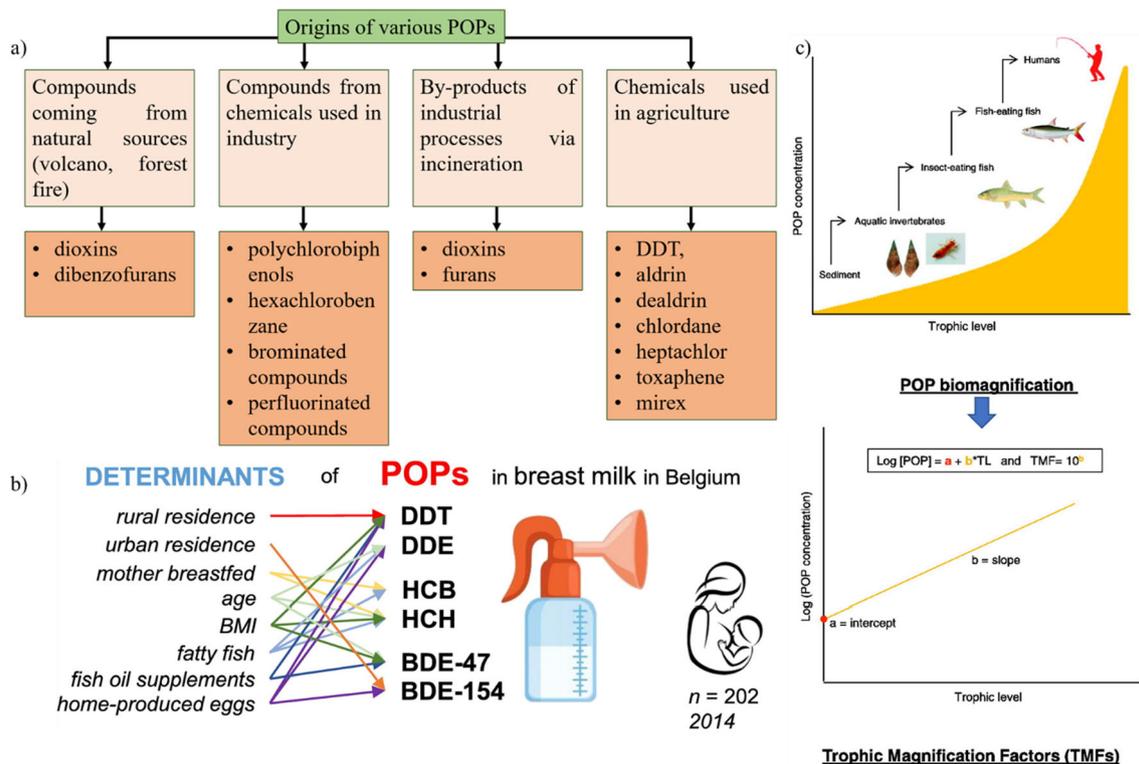


Fig. 1 **a** Origins of various types of POPs present in the environment (Fitzgerald and Wikoff 2014), **b** matrices to determine the presence of various POPs (dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethylene (DDE), hexachlorobenzene (HCB), hexachlorocyclohexane (HCH), polybrominated diphenyl ethers (BDE

47, BDE 154)) in human breast milk in Belgium (Aerts et al. 2019) and **c** the concentration of POP in various aquatic organism which are consumed by humans and the biomagnification of such accumulation (Choo et al. 2020)

synthetic dyes contain chemicals which can either alter the chemistry of water or introduce harmful chemicals into the resultant wastewater. For instance, dyes such as reactive, direct, basic and acids are soluble in water. When dissociate in water, they alter the water pH, turbidity and its aesthetics. The presence of molecules with chromophoric groups would impart colouration onto the receiving water bodies (Berradi et al. 2019). Such drastic changes of water characteristics would lead to many detrimental phenomena including algal bloom and drastic increase of COD and BOD levels in water (Lellis et al. 2019). The increase in colouration also disturbs light penetration into water bodies. This adversely affects photosynthesis in the receiving water bodies, which leads to a reduction in dissolved oxygen levels, affecting the entire aquatic biota (Hassan and Carr 2018; Lellis et al. 2019).

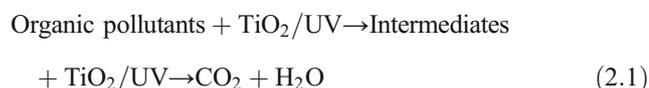
Similar to other pollutants that cannot be metabolized by living organisms, the threat of bioaccumulation is also present in dye molecules. Such pollutants remain persistent in the environment and can cross through an entire food chain which leads to bioaccumulation in organisms higher the food chain pyramid (Gita et al. 2017). These textile dyes can be toxic, mutagenic and carcinogenic to living organisms. Hence, they pose a significant problem to the environment, organisms, and humans who are at the top of the food chain. For instance,

dioxins, formaldehyde and azo dye groups are known to be carcinogen agents and hormone disruptors. On the other hand, most dyes also contain traces of heavy metals. Bioaccumulation of heavy metal in the human body can pose a wide array of medical-related conditions. Long-term exposure can lead to conditions like Parkinson’s disease, multiple sclerosis, muscular dystrophy, Alzheimer’s disease and cancer (Shen et al. 2019).

Fundamentals of photocatalysis

Heterogeneous photocatalysis have been extensively studied using with various types of semiconductors, but the one which has consistently shown exceptional photocatalyst activity and stability is TiO₂ nanoparticles. Photocatalysis is a form of AOP, which is defined as an oxidation of organic pollutants via hydroxyl radical in aqueous solution (Quiroz et al. 2011). The elevation of electrons from valence to conduction band leaves behind a positive election hole that oxidizes molecules in contact, such as adsorbed molecules or water to oxidize or produce hydroxyl radicals that in turn non-selectively degrade organic pollutants.

Water is an important medium in photocatalysis, as it is used as the sacrificial molecule to generate hydroxyl radicals. H_2O_2 can also be used as a sacrificial molecule, as it is able to dissociate to produce hydroxyl radicals upon UV irradiation or concurrently used with Fenton catalyst such as ferrous iron (Bensalah et al. 2017). Without the presence of water molecules, the highly reactive hydroxyl radicals could not be formed and obstruct the photodegradation of liquid phase organics. Photocatalysis can degrade a wide variety of organic pollutants, including tannic acid, oil molecules, EDCs such as phenol, chlorophenol and bisphenol A (BPA) and synthetic dyes such as methylene blue (MB) and reactive red. Commonly, heterogeneous photocatalysis occurs in aqueous solutions due to the importance of water in hydroxyl radical production, and the subsequent mineralization of pollutants will end in the formation of carbon dioxide and water. Equation 2.1 shows the overall photocatalytic reaction.



Photocatalyst performance, especially TiO_2 , hinges on a few factors, such as the crystallinity, surface area and band gap value. TiO_2 generally exists in three different crystallinity forms, which are anatase, rutile and brookite. Both anatase and rutile are tetragonal in structure, while brookite is commonly found in orthorhombic structure (Di Paola et al., 2013). Rutile is known to be stable, while anatase and brookite are metastable in nature, thereby easily being converted into rutile upon heat treatment. Pure crystalline TiO_2 is rarely found, as there will always be small traces of rutile phase in all nanoparticles synthesized due to the instability of anatase and brookite (Zhu and Gao 2014). This is important as studies conducted by Cong and Xu (2011) showed that a mixed polymorphs of anatase and rutile TiO_2 exhibited efficient photocatalyst efficiency in degrading phenol as compared with pure phase TiO_2 . The larger particle size exhibited by rutile plus superior O_2 sorption by anatase is cited as reasons behind its superior photocatalytic activity. Moriai et al. (2008) also suggested that the mixed anatase-rutile crystallinity demonstrated superior photoefficiency for degradation of methylene blue (MB).

A theoretical study done by Landmann et al. (2012) concluded that the band gap of brookite, rutile and anatase were 3.30 eV, 3.39 eV and 3.60 eV, respectively. Even though brookite or rutile can exhibit superior photocatalyst activity due to its lower band gap, anatase consistently exhibits superior photocatalytic activity as compared with the former. This is because anatase provides higher photocatalytic activity owing to the higher density of localized states, consequent surface-adsorbed hydroxyl radicals and slower charge carrier recombination rate relative to rutile compared to anatase

crystallinity (Lin et al. 2013). Owing to their superior crystallinity, electronic structure and availability of localized electrons, anatase-rutile TiO_2 has consistently exhibited efficient photocatalytic activity compared to other forms. However, their restricted band gap only allows UV light absorption, as TiO_2 is not able to absorb visible light source to initiate photocatalytic activity. A constant UV light source is required to sustain photocatalytic activity. Sunlight has been touted as an alternative source of photon. However, sunlight only contains 5% UV irradiation, which is not sufficient. To rectify this matter, researchers have delved into photocatalyst doping to induce a red wavelength shift, allowing the photocatalyst to be responsive under visible light source (Ylhäinen et al. 2012; Komaraiah et al. 2019).

Photocatalyst doping

The apparent limitation exhibited by semiconducting photocatalyst of only being responsive towards UV light sources pushed researchers to improve its responsiveness towards visible light. Responsiveness towards visible light would improve the application potential of photocatalysts in the real world. In the past decade, extensive research on photocatalyst doping with various materials, metallic and non-metallic in nature has been accomplished. Doping refers to the incorporation of foreign atoms into the lattice structure of a semiconductor (Liu et al. 2012; Shi et al. 2012), to create a new band gap that is lower in value as compared to the band gap of undoped semiconductors like TiO_2 . When irradiated with a light source with the energy equivalent or more than the new band gap, electron can be excited from the defect state to the conduction band. Additionally, the incorporation of foreign atoms also provides a sink for electron to be trapped before recombining back in the valence band, hence prolonging photocatalytic activity. The new energy levels of metal and non-metal doping is illustrated in Fig. 2a–c.

Photocatalyst doping has consistently shown to affect the characteristics of the photocatalyst in three different parts, which are the wavelength absorption, band gap and oxygen vacancies. These characteristic changes are due to the presence of foreign atoms, altering the lattice and electronic structures of TiO_2 . The most important change incurred in semiconductor photocatalysts when incorporated with foreign atoms is its responsiveness towards visible light. This is closely related to the change in band gap, as doping narrows the band gap of semiconductors, allowing them to be responsive towards visible light. Studies have shown that doping reduces band gap up to 2.1 eV, compared to 3.2 eV of pristine TiO_2 (Kang et al. 2019). Most doped TiO_2 consistently exhibits lower band gap compared to pristine TiO_2 , with cobalt doping via hydrothermal method exhibiting a band gap value of 2.14 eV (Cao et al. 2012). This can also be seen in Fig. 3b,

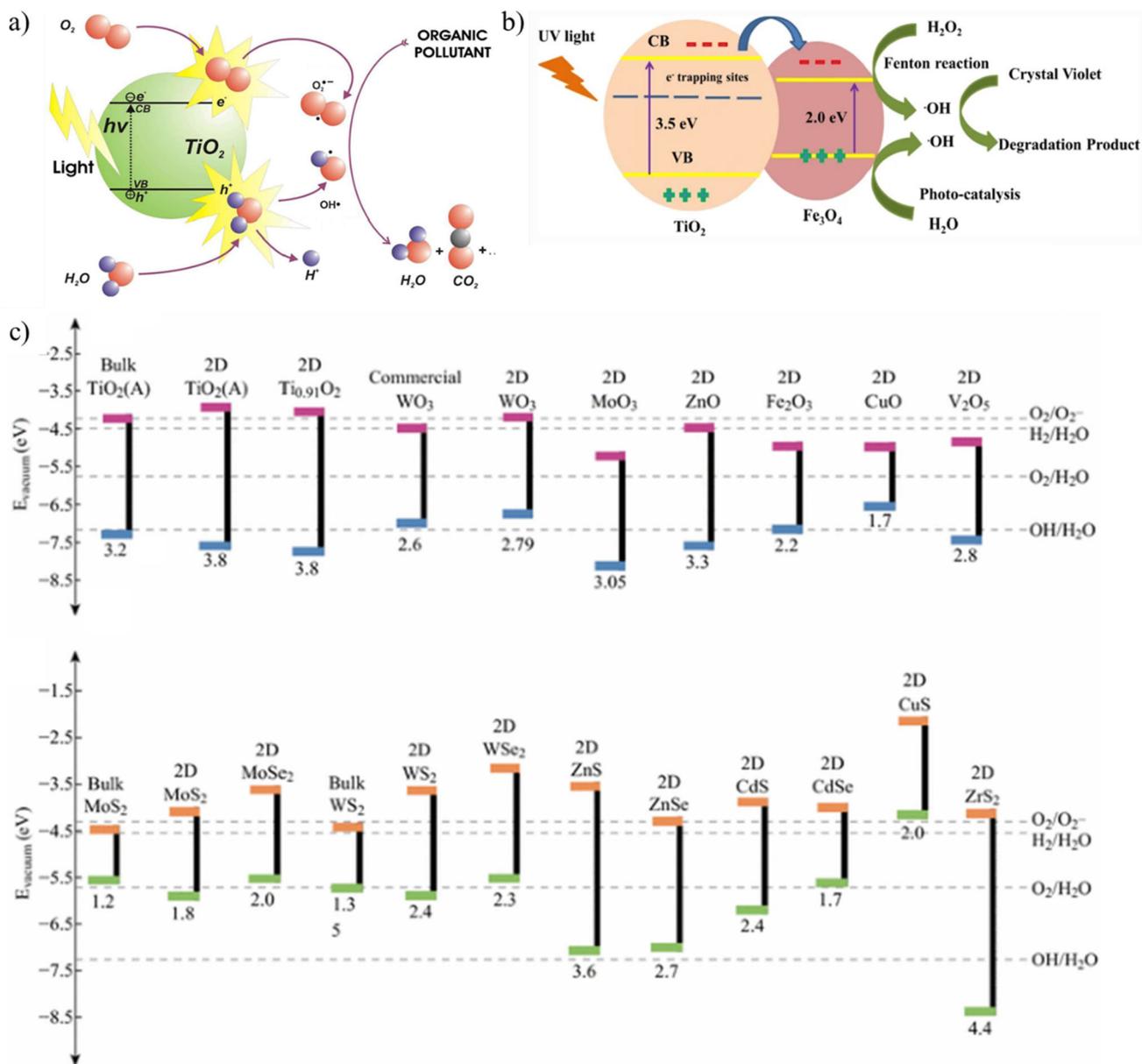


Fig. 2 Band gap of **a** pure TiO₂, **b** metal doped TiO₂ and **c** conduction band, valence band potentials and band gap energies of various semiconductor photocatalyst (Tu et al. 2014)

where doping TiO₂ with Fe₃O₄ led to the reduction of the band gap, while Fe₃O₄ also functions as an electron sink to prolong the lifespan of the valence hole which further accelerates the formation of radical species for effective photodegradation. Non-metallic doping such as nitrogen is able to lower the band gap to 2.3 eV (Ansari et al. 2016). The incorporation of foreign atoms induces a red wavelength shift in the band-gap transition possibly because metal doping introduces new energy levels in the band gap of TiO₂, hence decreasing the band gap. Raza et al. (2015) postulated that the reduction in band gap of TiO₂ may be led by the overlapping of *d*-orbital (dopant ions) with the conduction band of TiO₂. This resulted in the absorption of light in visible region. It was

further explained that the presence of Ce in the lattice structure allowed a 4*f* electron transition, permitting it to act as an efficient electron trapping site for sustained photocatalytic activity. The phenomena of electron trapping by foreign atom for sustained photocatalytic activity were also reported by Goei and Lim (2014) and Etacheri et al. (2015). Another study done by Ng et al. (2016) discussed about replacement of Ti⁴⁺ ions and O²⁻ ions by Ag⁺ ions in TiO₂ which forms a lower energy level of valence band. The specific 3*d* electronic configuration of Ag plays a crucial role in generating electron–hole pairs to improve visible light response. The replacement of Ti⁴⁺ ions by metallic ions such as Cu ions (Etacheri et al. 2015) and Fe ions (Ahmed et al. 2013) was reported due to the fact that both

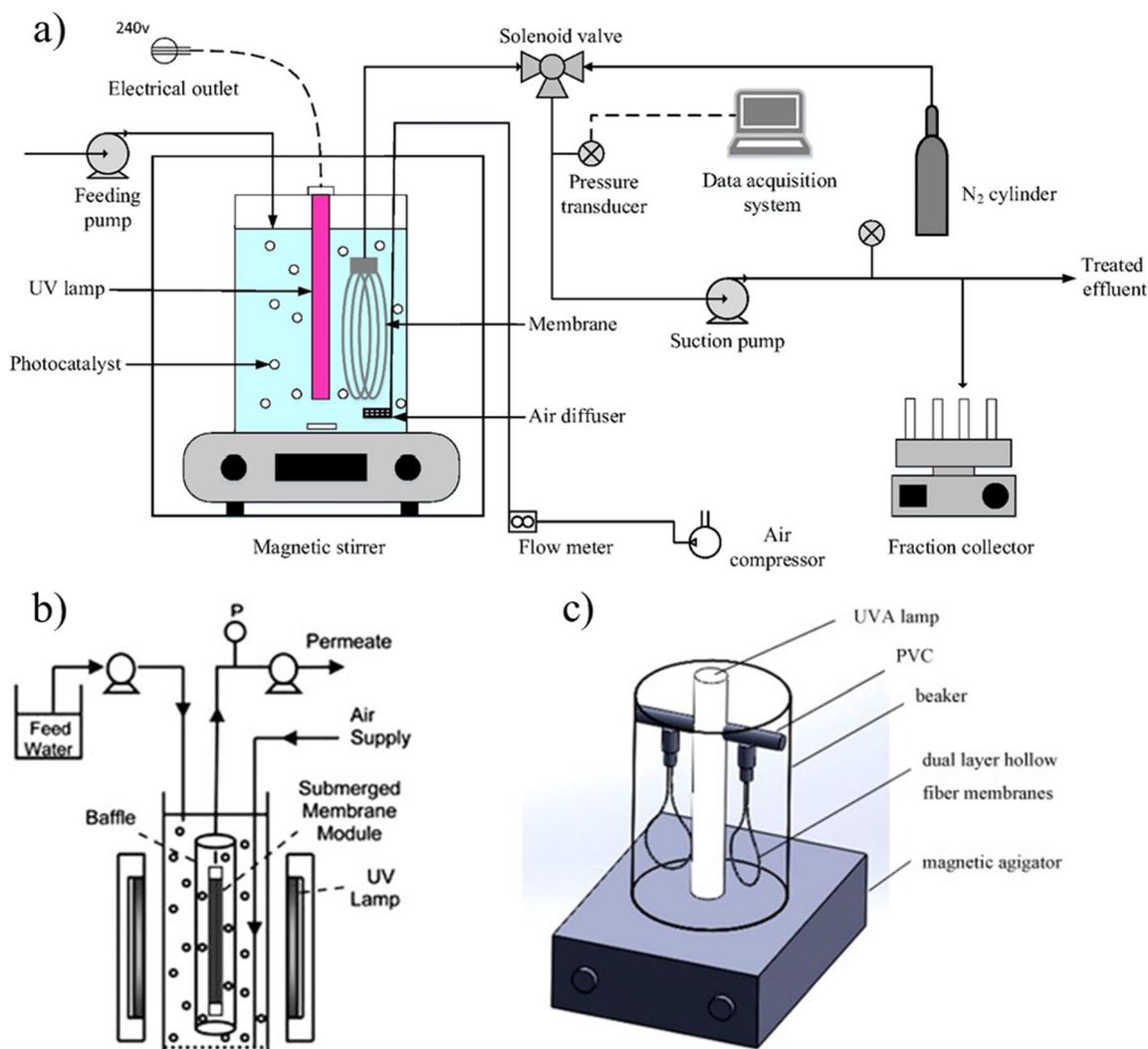


Fig. 3 Schematic diagram of **a** photocatalytic reactor with membrane and suspended photocatalyst for the treatment of wastewater (Jiang and Choo 2016), **b** submerged membrane module with suspended photocatalyst

(Fernández et al. 2014) and **c** dual-layered membranes with photocatalyst immobilized on membrane outer layer (Dzinun et al. 2016)

have similar ionic radii, which is also an important determinant factor of dopant for suitability analysis.

On the other hand, there are other methods which can be used to expand the visible light spectrum of traditional photocatalyst. Recently, researchers have explored the potential of dye sensitization, where dyes are used as photosensitizers (PS) to allow semiconductor photocatalysts to be responsive towards visible light sources. Some of the dyes which are commonly used as PS for semiconductors in literature include xanthene dyes, transition metal-based dyes, organic dyes and naturally occurring dyes (Youssef et al. 2018). Goulart et al. (2020) developed a TiO_2 photocatalyst which was sensitized using natural dyes, anthocyanins and carotenoids. The PS TiO_2 photocatalyst degraded up to 70% of MB while the unsensitized TiO_2 only managed to degrade 11% of Mb under sunlight. Another popular method which has shown promise in literature is the formation of

heterojunction photocatalyst. Heterojunction photocatalysts form different facets of a single semiconductor due to different atomic arrangements and structures that have shown great promise to spatially separate photogenerated charge carriers and improve photoactivity (Goktas and Goktas 2021). The coupling of traditional photocatalyst such as TiO_2 and ZnO with other metals is illustrated in Fig. 2c, where the band gap of each photocatalyst can be modified based on the differences in the energies of both the valence band and the conduction band. This is similar to photocatalyst doping, where heterojunction supported photocatalyst can lead to the exploitation of a larger portion of the solar spectrum with effective charge carrier separation, concurrently (Das et al. 2021). Doping has synergistically improved photocatalysis by virtue of enabling it to be responsive towards visible light and also lowering the band gap, which also reduces the energy required for activation.

Photocatalytic membranes

Photocatalyst is capable of eliminating a variety of pollutants that are present in the environment. The ability to absorb UV or visible light to degrade pollutants into less harmful compounds has spurred a strong interest among researchers to utilize them as means to reduce environmental pollution. Albeit photocatalyst has shown tremendous potential in treating wastewaters of different sources, they still do have certain limitations that reduce their usability and practicality. Several researchers had indicated that the process of photocatalyst recovery was tedious, and additional recovery steps were often required to recover the used catalyst, such as via centrifugation or separation using membranes (Patchaiyappan et al. 2016). Additionally, the loss of catalyst during treatment also happens, which reduces catalyst efficiency. To counter this, researchers explored the feasibility of photocatalyst immobilization, where the catalyst is deposited onto a substrate to assist catalyst recovery process while maintaining efficiency and averting loss of photocatalyst.

Parallel to photocatalysis, membrane technology has been employed to treat a wide array of wastewater laden with pollutants as a pathway to produce clean water for various usage. Its effectiveness in separating almost all types of pollutants from water sources makes membrane technology a promising prospect. Advantages such as ease of fabrication, ease of use, simplicity and flexibility to fabricate specialized membranes have made membrane technology a popular choice among researchers and industrialists (Ezugbe and Rathilal 2020). While membrane technology has exhibited immense potential, it has its own shortcomings. Some problems faced by membrane technology include requirement of pre-treatments, membrane fouling and frequent membrane replacement. Such problems may lead to issues like long operation downtime and higher cost incurred for maintenance (Gkotsis et al. 2014; Ang et al. 2017).

In light with the hindrances faced by standalone photocatalysis and membrane technology, researchers have explored several possibilities to merge both treatment methods into one hybrid technology. This is where photocatalytic membranes come into the fore. Photocatalytic membranes are separation units which are incorporated with photocatalyst. These membranes are able to play a dual-role in water treatment, which are degradation of pollutants and effectively separate the pollutants to produce clean water.

Photocatalytic degradation of organic pollutants

The absorption of visible or UV light by a photocatalyst would lead to the creation of different ROS that are responsible for degradation. Table 1 shows the employment of various types of photocatalysts for the remediation of POPs.

Table 1 shows that in recent years, many researchers have focused on the development of more novel, intricate photocatalysts which consist of different facets in search of materials which could remedy pollutants of varying types. It is worth noting that most photocatalysts are designed using TiO_2 as an integral part due to its superior catalytic activity (Balabanič et al. 2012). Jiang et al. developed a $\text{TiO}_2@SiO_2$ composite microsphere via the deposition of TiO_2 on the raspberry-like $SiO_2@polystyrene$ microspheres (Jiang et al. 2020). The photocatalyst was used for the treatment of methyl orange (MO), a common azoic dye. The experimental results indicated that a mineralization of 99.7% was achieved within 180 min. The design of the photocatalyst played a major role, as the raspberry-like silica microspheres was able to enhance the number of active sites available for the reaction, thus increasing photoactivity. Furthermore, the presence of Si allowed Ti to absorb visible light for photoactivation and reducing the band gap, further enhancing the photoactivity. Similarly, other research work had shown that the employment of carefully designed photocatalyst was able to completely mineralize dyes in wastewater within a short period of time. Tavker and Sharma (2020) focused on the photodegradation of both dyes and pharmaceutical waste, which were Rhodamine B (RhB) and real pharmaceutical waste which consisted of different variants of organic aromatic cyclic compounds. To achieve this, a tin sulphide (SnS) photocatalyst using pure cellulose as a template was developed. The results elucidated that up to 91% of RhB was degraded within 25 min. Additionally, 77% of pharmaceutical waste which consisted of various organic aromatic cyclic compounds were degraded effectively. Rivero et al. developed a $\text{TiO}_2\text{-rGO}$ photocatalyst for the remediation of dichloroacetic and perfluorooctanoic acids which are classified as carcinogen agents (Rivero et al. 2020). Similar to the degradation of both dyes and pharmaceutical waste, the developed photocatalyst was able to mineralize 87% of dichloroacetic (268 ppm) and 86% of perfluorooctanoic acids (268 ppm) within a reaction time of 8 h. The degradation steps included radical reactions and then dehalogenation of both carcinogens, leading to complete mineralization of both compounds. The photodegradation of perfluorooctanoic acids was also highlighted in a different work conducted by Bacha et al. (2019). Here, the development of a novel bismuth-based photocatalyst was explained in detail. The bismuth-based photocatalysts (BiOCl) removed 99.9% of perfluorooctanoic acids (20ppm) within a reaction time of 45 min. The faster degradation time attained in this study compared to the one reported by Rivero et al. (2020) was due to the initial concentration of perfluorooctanoic acids which was 13 times lower. These results highlighted the effectiveness and the versatility of various photocatalysts to achieve one goal, which is the remediation of a wide array of POPs that are present in waterways.

Table 1 Employment of various types of photocatalyst for the remediation of POPs

Photocatalyst	Pollutant	Type	Removal Efficiency (%)	Reference
(CuC ₁₀ H ₂₆ N ₆) ₃ (PW ₁₂ O ₄₀) ₂ /AgCl@Ag	2,4-Dinitrophenol	POP	65.0	(Chen et al. 2019)
H ₃ PW ₁₂ O ₄₀ /Ag ₃ PO ₄	4-fluorophenol	EDC	99.9	(Li et al. 2020a)
Bi ₂ WO ₆ /In ₂ O ₃	RhB	Dye	97.3	(Qin et al. 2020)
AgIO ₃ /BiVO ₄	Tetracycline hydrochloride	EDC	99.9	(Si et al. 2020)
BiOPO ₄ /BiOCl	Perfluorooctanoic acid	Carcinogen	99.9	(Bacha et al. 2019)
Cu doped ZnO/g-C ₃ N ₄	Eriochrome Black T	Dye	99.9	(Ahmad 2020)
TiO ₂ /TNTs	BPA	EDC	91.2	(Zhao et al. 2018)
H ₂ O ₂ -assisted TiO ₂	Terbutylazine	EDC	100.0	(Tang et al. 2019)
Cellulose-SnS	RhB	Dye	91.0	(Tavker and Sharma 2020)
Graphitized carbon/TiO ₂	Acetaminophen	EDC	94.0	(Liu et al. 2020b)
g-C ₃ N ₄ /NiO/ZnO/Fe ₃ O ₄	Esomeprazole	EDC	95.1	(Raha and Ahmaruzza-man 2020)
TiO ₂ -rGO	Dichloroacetic and perfluorooctanoic acids	Carcinogen	86.0	(Rivero et al. 2020)
BiOI-on-SiO ₂	Diesel oil	POP	73.0	(Qiu et al. 2020)

Treatment of organic pollutants using membrane technology

Membrane is defined as a barrier that allows certain substances to pass through while blocking others. In the case for water remediation, membranes can be used to allow water molecules to pass through while retaining unwanted particles and pollutants, including POPs of various forms and sizes. Membranes commonly work via size exclusion method (microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO)), where membranes can be tailored by designing the pore size, allowing molecules of specific sizes only to pass through. Membranes can be prepared using a variety of materials from polymers such as polyether sulfone (PES), polyvinylidene fluoride (PVDF) and polysulfone (PSf) to clay materials such as silica, alumina and bentonite to produce ceramic membranes.

In recent years, the drive to prepare membranes tailored for specific wastewater treatment rose into prominence rather than the “one size fits all” styled membranes developed before. Here, researchers explored the possibility of incorporating novel nanomaterials into the matrix of membranes for two reasons. The addition of such nanomaterials can alter the

physical properties of membranes for improved permeation, separation performance and impart specific chemical characteristics which are absent in traditional polymeric or ceramic membranes. The incorporation of metal oxides such as TiO₂, ZnO, CuO and metal organic frameworks (MOF) and non-metal nanoparticles such as graphene oxide (GO), carbon nanotubes (CNT), zirconia and silica oxides as nanofillers in membrane matrices is prominent. Many specific functions were imparted into membranes with the addition of such nanofillers, including improved membrane flux and rejection, anti-fouling capabilities, surface charge modification and increased adsorption capacity. Table 2 summarizes the development of membranes incorporated with various nanofillers and their specific improvements.

In general, there are two important improvements that are brought about with the incorporation of nanomaterials, which are improvement in membrane flux and rejection capabilities. Thuyavan et al. (2020) developed a hybrid filtration-adsorption membrane for the removal of dye from wastewater using PES as polymer of choice (Thuyavan et al. 2020). Fetician nanotube (TNT) and Ag-TNT were incorporated into the membrane matrix to improve membrane flux and rejection. Additionally, the addition of such nanomaterials could

Table 2 Various membranes incorporated with different nanofillers and the specific characteristics imparted for improvement in membrane performances

Membrane material	Nanofiller	Characteristics Imparted	Removal mechanism	Wastewater	Removal efficiency without nanomaterial (%)	Removal efficiency with nanomaterial (%)	Reference
Polyphenylsulfone (PPSU)	Al-MOF	Antifouling, improved flux and rejection	Filtration	Dye	74.0	98.3	(Xiao et al. 2020)
PES	GO, activated carbon (AC)	Improved adsorption	Adsorption and filtration	<i>p</i> -cresol and creatinine	7.4	80.0	(Fu et al. 2020)
PVDF	Fe ₃ O ₄ -palygorskite	Improved membrane strength, flux and rejection, antifouling	Filtration	Protein (bovine serum albumin (BSA))	31.6	80.0	(Zhu et al. 2020)
Cellulose acetate (CA)	Fe-Al-Mn@chitosan	Antifouling, antibacterial, improved defluorination	Filtration	Seawater	-	-	(Chaudhary and Maiti 2020)
PSf	Acid functionalized GO	Enhanced hydrophilicity, antifouling, improved permeation and rejection	Filtration	Oily wastewater	89%	99%	(Abdalla et al. 2020)
PES-fGO	PES	Improved flux and rejection, high tensile strength, surface repulsion	Filtration	Heavy metal removal	-	-	(Giwa and Hasan 2020)
PVDF	Ag-Si nanopollens	Antibacterial, antibiofouling	Filtration	Municipal wastewater	-	-	(Zhang et al. 2020)

impart another means of pollutant removal, which is adsorption. The membrane loaded with nanomaterial was able to remove up to 97% of textile dye from the wastewater. The removal was also enhanced by the fact that binding of oxygen groups in dye molecules with the metal ions (Fe and TiO₂) occurred. The addition of novel nanofillers in an attempt to reduce membrane contact angle and improve membrane hydrophilicity for water treatment was prevalent, as seen in the work performed by Xiao et al. (2020). The Al-based MOF membrane exhibited higher surface hydrophilicity than that of pristine membrane; hence, demonstrating increased water flux as the higher hydrophilicity would promote the transfer of water molecule across the membrane with enhanced antifouling capability when treating wastewater laden with methyl violet dye.

The employment of novel nanofillers into polymeric membranes was also attempted by Zhang et al., where silver@silica nanopollens were developed and incorporated into PES membranes to treat municipal wastewater (Zhang et al. 2020). The incorporation of the antibacterial nanopollens significantly reduced the occurrence of biofouling experienced by pristine PES membranes. The incorporated silver@silica nanopollens also inhibited colonization of bacteria which are capable of

causing membrane biofouling. Recent literature had clearly elucidated the role played by nanofillers in enhancing membrane performance for separation of pollutants from various waterways (Campbell et al. 2015; Mahmoudi et al. 2019).

Shortcomings rising from photocatalysis and membrane technology

It has been evidenced that both photocatalysis and membrane separation offer promising solution for the remediation of water pollution as both methods are efficient. However, they do face certain limitations which could hinder their application in a larger scale for wastewater treatment.

One of the major limitations in using photocatalysis for treatment of pollutants in wastewater originates from the technique the catalyst is employed itself. Photocatalysts are commonly dispersed in feed solution and stirred to ensure maximum contact with pollutant for improved photocatalytic efficiency. This would create a solution with high turbidity which may lead to two different problems. First, the increased turbidity may scatter the light source illumination towards the feed tank to initiate and sustain photocatalytic degradation, which may hinder photocatalysis sustainability. Another issue

that crops out is the reclamation of used or spent photocatalysts. Previous research had shown that photocatalyst can work effectively up to 10 cycles (Jiang et al. 2020; Pal et al. 2020; Uthirakumar et al. 2020). This implies that the reclamation of the catalyst after the wastewater is treated would be economically viable as less catalyst would be used for remediation per volume of wastewater treated. Several attempts have been made to incorporate membrane into such systems as means of separation between treated effluent and photocatalyst. However, the photocatalyst tends to accumulate onto the surface of membrane and eventually form a layer, hindering water transport through the membrane. Such phenomenon can be seen in Fig. 3a, where the photocatalyst is dispersed in the feed solution while the membrane module effectively serves as a separation mechanism. The photocatalyst can foul the membranes used to separate them from treated effluent. Figure 3 shows the schematic diagram of a photocatalytic reactor coupled with membrane.

The work conducted by Jiang and Choo (2016) detailed on the development of a photocatalytic reactor which utilize a polyethylene (PE) MF hollow fiber membrane as a separation unit while TiO_2 was used as the photocatalyst. The work noted that even though the membrane assisted in the separation of photocatalyst from the treated effluent, the set up could impede the overall performance of the system. As the photocatalyst was dispersed into the feed solution, the flow of the feed through the membrane to produce permeate had forced the photocatalyst onto the membrane surface, facilitating attachment and deposition. Fouling happened quickly because of the formation of a cake layer with a mixture of photocatalysts and colloids. This not only hindered membrane permeation, it also inhibited photocatalytic activity. Photocatalyst deposited on the membrane would lose surface area due to formation of colloids, reducing their efficiency since photocatalysis is a surface-related phenomenon. A similar observation was as well reported by the work carried out by Li et al. (2019) where a $\text{TiO}_2\text{-GO-Fe}_3\text{O}_4$ composite photocatalyst was used for the remediation of amoxicillin. The photocatalyst was circulated in the tank via aeration as means to reduce the tendency for photocatalyst deposition of membrane surface. As the treated wastewater permeated through the membrane, the surface of the ceramic membrane was totally covered by the $\text{TiO}_2\text{-GO-Fe}_3\text{O}_4$ composite photocatalyst particles, forming the dense cake layer. Even though this highlights the efficiency of membrane to separate the photocatalyst from the effluent, it also highlighted the drawback of the method, which was the severe fouling experienced by membranes used for separation. This could be alleviated by frequent back pulsing and backwash to mitigate photocatalyst deposition on membrane surface. In addition, the provision of strong bubbling which creates a water flow in the feed tank can also help to mitigate this problem, as reported by Fernández et al. (2014), as illustrated in Fig. 3b.

Without such mitigation steps, it was reported that the transmembrane pressure (TMP) increased dramatically during the subsequent runs.

In the context of exploiting membrane technology for the remediation of POPs, extensive research had shown that it was highly efficient and versatile as they could be tuned to meet the demands of different pollutant characteristics. Recent research had shown that other problems faced by membrane technology including fouling and low permeation rates could be well mitigated with the incorporation of nanomaterials (Khan et al. 2016). However, one overlooked issue on the use of membrane technology is the fact that it only separates the pollutant from the wastewater, producing a concentrated form of pollutant. This leads to the formation of a secondary form of waste which still requires additional remediation to eliminate it. Furthermore, membranes may also require some form of antifouling mechanisms incorporated into the treatment system, such as backwashing and back pulsing to ensure long term efficiency and performance. Hence, a solution to retain the qualities exhibited by both photocatalysis and membrane technology while eliminating their individual inherent limitations is necessary to combat wastewater remediation. Figure 3 c shows the set up for a SMPR for a membrane which has been immobilized with TiO_2 photocatalyst. As observed in Fig. 3c, the authors placed two membrane modules beside a submerged UV lamp to increase photodegradation rate, as two membrane modules would effectively double the degradation rate as compared to a single module only. Similarly, Fernández et al. (2014) placed two UV light sources on each side of the reactor to increase the efficiency of the reactor in a whole. These works suggest that the configuration of membranes and the placement of UV light sources can also be studied upon to enhance the efficacy of the photocatalytic membrane reactors.

Development of photocatalytic hybrid membranes

In an effort to incorporate the functions of both photocatalysis and membrane separation into a unified treatment method, researchers have explored on the possibility of incorporating photocatalytic materials into membranes to counter the limitations faced by both technologies, individually. One of the earliest works in incorporating photocatalysts into membranes as a substrate was developed by Yamashita et al. (Yamashita et al. 2003). In this work, TiO_2 was coated on a superhydrophobic porous Teflon membrane via ion-assisted deposition method. The employment of the photocatalyst was focused on the self-cleaning ability of TiO_2 without compromising the superhydrophobic feature of the Teflon membrane. The combined effect of antifouling and photocatalysis also contributed to the membrane's antifouling and self-cleaning ability. Earlier works in incorporating photocatalysts into membrane were focused on the antifouling and self-cleaning

ability imparted onto the membrane surface, evidenced in other works (Bae and Tak 2005; You et al. 2012). However, with time, researchers realized that the incorporation of photocatalyst into membrane structures could not only impart self-cleaning ability, but can directly involve in the remediation of treated effluent by degrading the pollutants present. Initial work on photocatalytic membrane for degradation of pollutant was done by incorporating the photocatalyst into the membrane matrix by blending it with the polymer solution. However, in recent times, more focus had been placed on the immobilization of such photocatalyst on the membrane surface to improve efficacy. Table 3 tabulates the preparation of different types of photocatalytic membranes for the remediation of various effluents.

Literature review shows that there are different methods used for the preparation of photocatalytic membranes (Nasrollahi et al. 2021). Generally, photocatalyst particles are either embedded into the membrane matrix or they can be deposited on the membrane surface for controlled incorporation which leads to better photocatalytic performance. Blending technique is commonly used as it is an easy and hassle-free method to prepare photocatalytic membranes. Here, the photocatalyst is blended with the polymeric dope solution before they were used for membrane casting or spinning (Argurio et al. 2018). Secondly, the photocatalyst can be deposited in a controlled manner to enhance its permeation and photocatalytic activity by employing different methods,

including dual-layer spinning (Yaacob et al. 2020), thin film nanocomposites (Mutharasi et al. 2020) or deposition on membrane surface (Berger et al. 2020). Some novel methods such as magnetically induced freeze casting method have also been reported for the fabrication of photocatalytic membranes (Li et al. 2019). Overall, the design of photocatalytic membranes plays a huge role in maximizing the efficiency of pollutant removal. Hence, a fundamental understanding on the benefits and deficiency of each preparation technique needs to be understood. With this, promising photocatalytic membranes can be developed for the remediation of various pollutant laden wastewaters.

Polymer selection

There have been plenty of polymers used in the development of membrane, which include PES, PVDF, polyphenylsulfone (PPSU), polyetherimide (PEI) and cellulose acetate (CA). Different polymers bring about different characteristics which would suit certain applications. For instance, PES is very much prominent in the field of membrane development because of its high mechanical strength and durability, coupled with its high chemical stability (Arahman et al. 2015), while CA is a common polymer used when researches are keen to develop environmentally friendly and sustainable polymers by extracting cellulose from plant materials for membrane fabrication. Based on the literature review conducted, it had

Table 3 Preparation of different types of photocatalytic membranes for the remediation of various effluents

Membrane	Photocatalyst	Optimum Loading	Immobilization technique	Membrane type	Pollutant	Removal Efficiency (%)	Irradiation	References
PVDF	ZnIn ₂ S ₄	3.9 mg/cm ²	Pressure deposition	Single-layer flat sheet	Fluvastatin and RhB	97.19 and 53.29	Visible light	(Liu et al. 2020a)
Aluminium oxide	TiO ₂	-	Atomic layer deposition	Ceramic single-layer flat sheet	MB	80	UV	(Berger et al. 2020)
PES	iron@TiO ₂	-	Layer by layer assembly	Single-layered flat sheet	Hexavalent chromium	100	UV	(Kazemi et al. 2020)
PVDF	TiO ₂	15%	Blending	Dual-layer hollow fiber	Nonylphenol (NP)	100	UV	(Dzinun et al. 2016)
PVDF	TiO ₂ -N	10.5%	Blending	Dual-layer hollow fiber	Reactive Black 5 (RB5)	100	UV	(Kamaludin et al., 2019)
Cellulose-cotton fabric	Ag@AgCl@MOF	38.6%	In situ immobilization on membrane surface	Single-layered flat sheet	Oily wastewater	99.64	Visible light	(Lu et al. 2020)
PVDF	TNT	1%	Blending	Single-layered hollow fiber	(AT-POME)	67.3	UV	(Subramaniam et al. 2018)
PVDF	Fe ₃ O ₄ /g-C ₃ N ₄	1%	Magnetically induced freeze casting	Single-layered flat sheet	RhB	100	Visible light	(Li et al. 2019)
PES	C, N-doped TiO ₂ -CdS)	1%	Blending	Single-layered flat sheet	Municipal wastewater	77.2	Visible light	

been evidenced that PVDF was predominantly used as the polymer of choice when developing a photocatalytic membrane, while some researchers had also used PES and alumina membrane (Ong et al. 2014; Nor et al. 2017; Paredes et al. 2019; Zhang et al. 2019). The polymer of choice is very important due to the fact that many works still employ UV light source for irradiation of photocatalyst, while it is well known that long-term UV exposure would lead to the degradation of polymer chain. This would eventually lead to the deterioration of membrane separation efficiency. Exposure to UV radiation will lead to polymers experiencing rapid photooxidative degradation which results in fracture in polymer chain (Yousif and Haddad 2013). This also leads to the production of free radicals and reduce its molecular weight, causing loss in mechanical strength.

PES, a prominent polymer used during membrane preparation, is known to have weak resistance towards UV light exposure (Ng et al. 2017). It had also been elucidated in research work that most sulfonated polymers such as PES, PSU and PPSU could be susceptible to rapid degradation when exposed to continuous UV light exposure. When UV light is irradiated towards sulfonated polymers, two phenomena happens (Lawrence and Yamaguchi 2008): firstly, detachment of the sulfonic acid groups due to oxidative attack, followed by rapid polymer chain scission. Such events will greatly harm the durability and stability of membranes prepared. However, PVDF, a type of fluoropolymer, is known to exhibit better resistance towards UV radiation as opposed to sulfonated polymers (Katan et al. 1998; Teng 2012). Hence, PVDF has become a popular polymer choice owing to its stability. Some researchers also employed alumina- or ceramic-based membranes; both are very durable and UV-resistant materials. Previous research had pointed out this fact, where the outer surface layer of PVDF membranes experience significant fractures after a direct exposure to 120 h UV light (Ong et al. 2017). Another study highlighted that similar phenomenon happened when PVDF hollow fiber membranes experienced cracks on the membrane surface when exposed to continuous UV light irradiation (Dzinun et al. 2017). Such observations conclude that despite the potential of PVDF to be used as a photocatalyst host, efforts are required to further improve the thermal and chemical stability of this polymer for long-term usages. The exploration of new types of UV light-resistant polymers is another interesting topic to be explored in this field.

Membrane preparation techniques

In terms of incorporating the photocatalyst into membranes, two different modes have been explored, namely (i) blending prepared photocatalyst with polymeric dope solution before membrane fabrication and (ii) deposition/growth of photocatalyst onto membrane structure. Membranes blended

with photocatalyst can be commonly found in the literature as a facile way to produce photocatalytic membrane since it requires less preparation steps (Rajeswari et al. 2017). The prepared photocatalyst were blended with the polymeric dope solution via sonication and mechanical stirring before they are used for membranes preparation. This method had been elucidated clearly elsewhere (Kamaludin et al. 2017; Subramaniam et al. 2018; Wu et al. 2020). The dispersion of photocatalyst across the membrane matrix allows immobilization of photocatalyst onto the membrane. This can also improve the membrane permeation and rejection capabilities as addition of nanomaterials into membrane has shown to improve such features. This dope solution preparation is applicable for the fabrication of both flat sheet and hollow fiber membranes.

Flat sheet and hollow fiber mixed matrix membrane These dope solutions can be casted on glass plates to produce flat sheet membranes. Casting knives where its height can be adjusted are frequently used to manipulate the thickness of membrane prepared. For hollow fiber MMMs, dry/wet spinning technique is commonly used to extrude the membranes using dual orifice spinnerets. Both the fabrication method of flat sheet and hollow fiber MMM can be found elsewhere (Kamaludin et al., 2019; Rosman et al. 2020; Wu et al. 2020). However, photocatalytic mixed matrix membrane (MMM) displays one major flaw. When the photocatalyst is dispersed across the membrane matrix, particles which are embedded deep into the matrix may not be activated as they would not come in contact with photons emitted from light source. Such incidence would reduce the rate of photoactivity exhibited by membranes, thus reducing its efficacy. Albeit this deficiency, blending of photocatalyst into polymeric membranes still brings about significant improvement, such as improved water permeation and membrane rejection (Peyravi et al. 2020). Such phenomenon applies for both flat sheet and hollow fiber MMMs. Membranes also exhibit better antifouling propensity and are able to treat a wide variety of pollutant non-selectively.

Flat sheet thin film membrane To overcome this particular deficiency while maintaining the immobilization of photocatalyst and improvement it brings about for membrane permeation and separation, researchers began exploring on a new membrane configuration, known as dual-layered membranes. In this configuration, the photocatalyst is concentrated on the membrane surface for improved contact with pollutants. There are several ways where a dual-layered membrane can be developed. They include thin films, deposition, surface coating and the employment of triple orifice spinnerets. The growth of thin films on flat sheet membranes has garnered significant interest among researchers as it provides a means to control the structure and selectivity of flat sheet membranes.

This method is frequently used in flat sheet membrane configuration as the growth of the film can be controlled easily. Such method is rarely used for hollow fiber membranes due to difficulty in controlling thin film growth and uniformity of nanomaterial dispersion. Thin film flat sheet membranes are typically developed by first preparing a polymer substrate layer which works as a support for the thin film. Thin films of flat sheet membranes are developed using combination interfacial polymerization of piperazine (PIP) and trimesoyl chloride (TMC). During the fabrication of such thin films, nanofillers such as photocatalysts can be added into the solution, ensuring that they are trapped on the surface of the membrane within the matrix of the thin film (Lai et al. 2016). Such photocatalytic thin film membranes were demonstrated in the work done by Ramezani Darabi et al., where a $\text{Fe}_3\text{O}_4/\text{ZnO}$ photocatalyst was incorporated in the thin film nanocomposite membrane (Ramezani Darabi et al. 2018). Similar membranes have also been reported for various types of photocatalyst, including ZnO (Krishnaswamy et al., 2020), TiO_2 (Ramezani Darabi et al. 2018; Syahida et al. 2019) and nitrogen-doped TiO_2 (Horovitz et al. 2016). More discussion on the performance of thin film photocatalytic membranes is presented in the following section.

Dual-layered hollow fiber membrane For polymeric hollow fiber membranes, the spinneret is modified to allow two different dope solutions to flow together uniformly to produce dual-layered hollow fiber membranes (DLHFM). To maximize their concentration on the surface of the membrane, the photocatalysts are dispersed on the outer layer dope solution while the inner layer dope solution works as a support membrane. Hence, researchers were able to fabricate a membrane which holds the photocatalysts on its surface for better photoactivity. Figure 4 a shows the cross-section dimensions of a three orifice spinneret and the schematics of a spinning system.

The modification of spinneret has allowed further tailoring of the inner and outer layer of hollow fiber membranes to meet the specification and needs. In the case of photocatalytic membrane, this allowed researchers to concentrate the photocatalyst onto the surface of the membrane in an effort to improve photoactivity while reducing loss of catalyst due to deep embedment. For the preparation of DLHFM, two different dope solutions are prepared, where the outer dope solution is incorporated with the photocatalyst of choice while the inner dope solution is added with pore formers to provide a porous and strong support layer. As seen in Fig. 4b, the introduction of two dope solutions during the fabrication of the membrane allows different phase inversion rates between both inner and outer layer of membrane. This leads to the formation of a porous inner structure and a dense outer layer where both structures promote better permeation and rejection properties.

Another method that has been used by researchers to concentrate photocatalyst onto hollow fiber membrane surface is via deposition on inorganic hollow fiber membranes, produced from ceramic. Ceramic-based membranes are mechanically stronger, and they are able to withstand high temperatures. Owing to its strength, they can be used in high temperature processes to either deposit or grow photocatalysts on its surface without changing the membrane's structure. The thermally fragile nature of polymeric membranes restricts such modifications. Berger et al. successfully deposited TiO_2 on the surface of aluminium oxide ceramic membranes with pore sizes of 20 nm and 200 nm via atomic layer deposition (Berger et al. 2020). The interaction between aluminium in the membrane and photocatalyst allowed the latter to be visible light responsive. Similar work was also undertaken by Golshenas et al. (2020), where a disk supported ceramic membrane was coated with $\gamma\text{-Al}_2\text{O}_3$ thin film via sol-gel technique. Similarly, the membrane was effective in photocatalytic degradation under visible light irradiation, while improving the membrane permeation and rejection properties due to the surface coating. Table 4 summarizes the preparation parameters of photocatalytic membranes present in literature.

Performance of photocatalytic membranes for POP removal

The performance of photocatalytic membranes are assessed by looking into several important parameters. The membrane filtration properties like permeation and rejection are two major parameters to be evaluated. Additionally, other performances which are relatable to the enhancement photocatalysts that bring onto the membrane like photodegradation rate, antifouling properties and recovery ratio are also important. Figure 5 shows the coating of a photocatalyst on the surface of a polymeric membrane. The SEM images (Fig. 5b) of a photocatalytic membrane with EDX analysis clearly show the presence of photocatalyst on the membrane surface and the performance of such membrane for the removal of various POPs.

In current literature, photocatalytic membranes are either prepared as single layered or dual layered for both flat sheet and hollow fiber membrane configurations. Blending remains as a popular choice for membrane preparation due to its simplicity. Rosman et al. prepared a blended photocatalytic PVDF- $\text{ZnO}/\text{Ag}_2\text{CO}_3/\text{Ag}_2\text{O}$ flat sheet nanocomposite membrane to remove ibuprofen (IBU) from aqueous wastewater (Rosman et al. 2020). The incorporation of $\text{ZnO}/\text{Ag}_2\text{CO}_3/\text{Ag}_2\text{O}$ into the matrix of PVDF enhanced the flux from 37.98 $\text{L}/\text{m}^2\text{h}$ to 45.30 $\text{L}/\text{m}^2\text{h}$ and rejection improvement from 20.05 to 27.37%. The addition of the photocatalyst improved membrane hydrophilicity and reduced its pore size, which enhanced both permeation and rejection. When light is introduced to the membrane, the flux improved further to 49.67 $\text{L}/\text{m}^2\text{h}$, while the IBU rejection improved to 35.27% due to

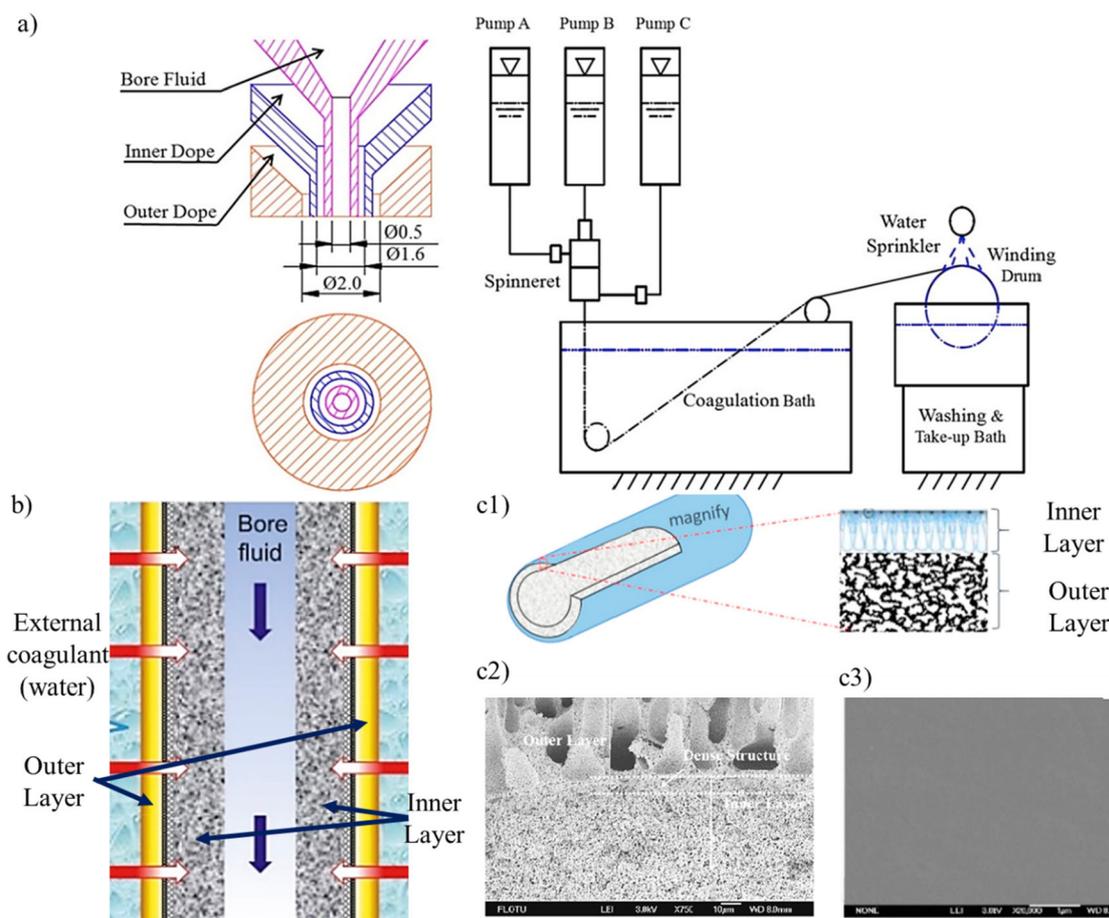


Fig. 4 **a** Design of a triple orifice spinneret and the spinning system, **b** formation of dual-layered membranes during phase inversion process, **c1** Illustration of DLHFM membrane structure, **c2** cross section and **c3**

surface scanning electron microscopy (SEM) image of DLHFM membrane (Xia et al. 2018)

photocatalytic degradation. A similar blending technique was adopted by Tran et al. (2020), where a PVDF/TiO₂ hybrid flat sheet membrane was successfully developed. Energy dispersive X-ray (EDX) spectroscopy showed that the photocatalyst was evenly dispersed through the membrane matrix. In this regard, the PVDF/TiO₂ hybrid membrane exhibited a tenfold increase in flux as compared with neat membrane, as the photocatalyst enhanced the membrane water transport properties. Additionally, with the presence of UV light, the flux increased by 30% due to the photoactivity on the membrane surface. The membranes also exhibited only 5% of flux drop with the presence of UV light as opposed to a 75% drop in the absence of UV light.

Improvements in membrane performance and photoactivity were also evident in thin film flat sheet membranes, as elucidated in the work presented by Ramezani Darabi et al. (2018). The incorporation of Fe₃O₄/ZnO into the thin film layer of membrane improved membrane surface hydrophilicity and imparted upon the antifouling propensity towards the membrane, which were both absent in the control membrane. It was proved that the hydrogen bonding between

the nanocomposite photocatalyst and the amine monomer led to improved water attracting properties. Furthermore, the photocatalyst played an active role in improving both membrane permeation capabilities. Without UV light irradiation, membrane PES 0.2% exhibited a flux of 208.4 L/m²h, while the introduction of UV light led to improved flux at 222.6 L/m²h. However, in another work reported by Grilli et al. (2015) where sol-gel was used to coat an alumina membrane to prepare a photocatalytic thin layer onto its surface, a loss of flux was observed. This was expected due to the highly porous nature of alumina membranes which was subsequently blocked due to the deposition of a thin layer on its surface which reduced its pore size. However, the presence of photocatalyst on the membrane surface led to the photodegradation of carbamazepine (CBZ) under a solar simulator, as up to 60% of the pollutants were degraded within 14 h. Similarly, Starr et al. coated the surface of flat sheet alumina membrane with TiO₂ via layer by layer (LbL) assembly method for the remediation of MB laden wastewater (Starr et al. 2016). While there was a loss in membrane permeation properties due to the coating which may have reduced the

Table 4 Dope composition and spinning parameters of photocatalytic membranes

Type of membrane	Inner layer polymer composition (wt%)	Outer layer polymer composition (wt%)	Photocatalyst	Preparation parameters (ml/min)	Treated effluent	References
Polymeric single layer	-	PVDF/TiO ₂ /DMAc (15/9/77)	TiO ₂	DSFR/BFFR (1.5/1.5)	MB	(Abdullah et al. 2018)
Polymeric single layer	-	PES/PEG/CaCu ₃ Ti ₄ O ₁₂ /NMP (17.25/1.75/4/75)	CaCu ₃ Ti ₄ O ₁₂	DSFR/BFFR (5.4/1.8)	RhB	(Ayode Otitoju et al. 2019)
Polymeric single layer	-	PVDF/PVP/TNT/NMP (18/5/1/76)	Titania nanotubes (TNT)	DSFR/BFFR (3/3)	AT-POME	(Subramaniam et al. 2018)
Ceramic single layer	-	Kaolin/PES/Arlacel/NMP (40/5/1/54)	TiO ₂	DSFR/BFFR (9/10)	RB5	(Mohtor et al. 2018)
Ceramic single layer	-	Al ₂ O ₃ /TiO ₂ /PSf/PVP/DMAc (41.25/2/6.5/0.5/49.75)	CuO	-	BPA	(Wang et al. 2019)
Polymeric single layer	-	PSf/PEG/TiO ₂ /DMF (20/2/4/74)	TiO ₂	DSFR/BFFR (3/20)	Steel Industry Effluent	(Mukherjee and De 2016)
Polymeric single layer	-	PVDF/H ₂ O/PVP/Ag-Zeolite/DMAc/TEP (15/3/3/1/54.6/23.4)	Ag-loaded zeolites	DSFR/BFFR (8/1.7)	Bacteria	(Shi et al. 2013)
Polymeric single layer	-	PVDF/PVP/TiO ₂ /NMP (18/5/4/73)	TiO ₂	DSFR/BFFR (3.5/1.17)	Oily Wastewater	(Ong et al. 2014)
Polymeric dual layer	PVDF/PEG/DMAc (18/5/77)	PVDF/N-TiO ₂ /DMAc (15/7.5/77.5)	N-TiO ₂	Inner DSFR/outer DLFR/BFFR (8/2/8)	-	(Kamaludin et al. 2020)
Polymeric dual layer	PVDF/PEG/DMAc (18/5/77)	PVDF/TiO ₂ /DMAc (15/3/82)	TiO ₂	Inner DSFR/outer DLFR/BFFR (8/2/8)	-	(Kamaludin et al. 2017)
Polymeric dual layer	PVDF/DMAc (18/82)	PVDF/TiO ₂ /DMAc (15/10.5/74.5)	TiO ₂	Inner DSFR/outer DLFR/BFFR (8/1/8)	NP	(Dzinun et al. 2015)
Polymeric dual layer	PVDF/PVP/NMP (18/5/77)	PVDF/ZrO ₂ -TiO ₂ /PVP/NMP (15/1/5/80)	ZrO ₂ -TiO ₂	Inner DSFR/outer DLFR/BFFR (1.2/2.48/0.73)	Oily Wastewater	(Yaacob et al. 2020)
Polymeric dual layer	PVDF/PVP/DMAc (18/5/77)	PVDF/TiO ₂ -clinoptilolite/DMAc (15/3/82)	TiO ₂ -clinoptilolite	Inner DSFR/outer DLFR/BFFR (8/1/8)	-	(Dzinun et al. 2019)

membrane pore availability, the membranes were able to continuously degrade MB.

The advantages of dual-layered membranes over single-layered MMMs was clearly demonstrated by Mutharasi et al. (2020). A 2D Zn/Al layered double hydroxide tailored low-pressure membrane was prepared and its performance was compared with MMM with similar nanomaterial incorporated. Whereas the MMM exhibited a MB dye flux of 77 L/m²h, its degradation properties were hindered, evidenced by the low MB removal rate of 90%. The thin film membrane exhibited a flux of around 26.4 L/m²h, and also an increase in degradation of MB (95%). Furthermore, the thin film membrane exhibited 2.5 times better flux and rejection recovery ratio, meaning that the membrane was able to maintain an excellent performance in repetitive cycles as compared with

MMM. The outstanding permeation and rejection recovery were attributed to the improved surface hydrophilicity and the hydration layer formed at the membrane interface.

Even though flat sheet membranes have shown good permeation and photoactivity, hollow fiber configuration is favourable simply due to its large surface area. The low operating conditions for photocatalytic membranes also ensure that hollow fiber membranes can work without compromising its integrity. Higher surface area is imperative to ensure photocatalyst can work effectively as better contact with pollutant molecules is attained. Similar results in terms of improved permeation and rejection have also been seen when photocatalyst is blended in dope solutions for the preparation of photocatalytic hollow fiber membranes. Subramaniam et al. developed a PVDF hollow fiber membrane with TNT blended

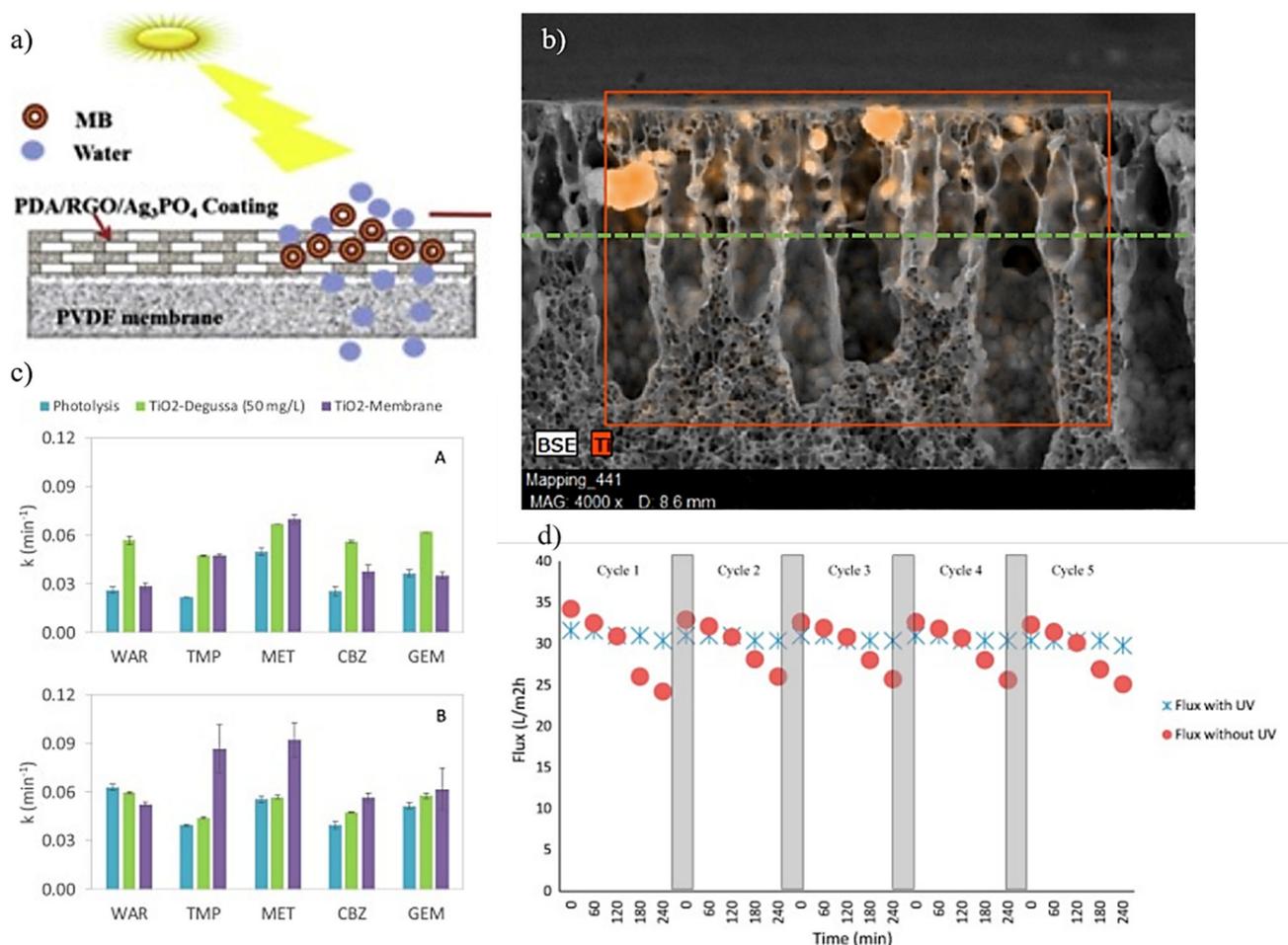


Fig. 5 **a** Schematic diagram of the deposition of PDA/RGO/Ag₃PO₄ coated on the membrane host (Zhang et al. 2019), **b** cross-section SEM image of dual-layer hollow fiber membrane (Paredes et al. 2019), **c** photocatalytic performance of TiO₂-membrane catalyst compared to photolysis and conventional photocatalysis for the removal of various pollutants

(warafin (WAR), trimethoprim (TMP), metoprolol (MET), carbamazepine (CBZ) and gemfibrozil (GEM)) (Paredes et al. 2019) and **d** flux change of photocatalytic membrane for 5 cycle of filtration (Subramaniam et al. 2018)

in the dope solution (Subramaniam et al. 2018). The membranes exhibited better flux and rejection with the presence of light than in the dark conditions. This was due to the photocatalytic activity on the surface of the membrane. Additionally, the membrane also experienced flux and rejection drop of lesser than 5% in the presence of light. A 20% decrease in flux was observed without irradiation, which highlights the importance of photoactivity in improving membrane properties and capabilities. In addition to this, the incorporation of photocatalyst into the membrane also enhanced the membrane antifouling properties, as seen in Fig. 5d. The photocatalytic activity on the membrane surface averted permanent adhesion of pollutants present in AT-POME, which can lead to permanent membrane fouling. In the work developed by Sakarkar et al. (2020), a photocatalytic PVDF membrane with TiO₂ entrapped in its matrix was prepared for dye wastewater treatment. The membrane incorporated with TiO₂

exhibited a pure water flux of 14.2 L/m²h, while pristine membrane only exhibited a flux of 3.3 L/m²h. The addition of nanomaterial helped to enhance both membrane porosity and membrane hydrophilicity, which helped to increase the flux. In addition, the addition of nanomaterial allowed the formation of a thin layer on membrane surface with smaller pores which improved membrane permeation. The addition of TiO₂ also imparted photoactivity on the membrane. When illuminated with UV-C, the membrane was also able to degrade the dye molecules (remazol turquoise blue) in the wastewater. Similar improvements on membrane filtration performance were also seen elsewhere (Rahimpour et al. 2008; Rawindran et al. 2019). In another work done by Galiano et al. the blending method was used to disperse TiO₂ nanoparticles into PVDF to fabricate photocatalytic hollow fiber membranes (Galiano et al. 2018). The incorporation of TiO₂ increased membrane permeation rate and improved the

membrane's mechanical stability. Furthermore, the membrane exhibited superior photocatalytic activity, capable of removing 97% of MB.

Even though the design allows good separation and adequate photocatalytic activity, it led to the loss of photoactivity as the photocatalyst embedded deep in the structure cannot be activated. Similar phenomenon was experienced in other works where the catalyst is directly blended in the dope solution (Wang et al. 2016; Zhang et al. 2017; Benhabiles et al. 2019). Many researchers had shown that the incorporation of photocatalyst into membranes could bring about such rudimentary improvement due to several factors including the hydrophilicity of photocatalyst and the influence of such nanomaterials in the formation of the intrinsic structure behind membrane with performance (Yang et al. 2010; Putri et al. 2015). Utilizing a different method, Yu et al. had successfully created an Au-TiO₂ surface coated cellulose membrane via suction filtration method that was able to filter and photodegrade up to 99% of RhB solution (Yu et al. 2019). In this work, the cellulose membrane does not only worked as a substrate to host the photocatalyst, but it also actively improved photodegradation as exhibited by the membrane performance. The interaction between the Au-TiO₂ photocatalyst and cellulose led to the improvement of the conductivity, instantaneous charge separation and migration rate which might have enhanced the overall photocatalytic activity.

Paredes et al., (2019) utilized a triple orifice spinneret to prepare a DLHFM with TiO₂ utilized as the photocatalyst of choice. The study focused on the determination of intermediate compound and the energy consumption of the system of effectively treat pharmaceutical wastewater. The configuration allowed the photocatalyst to be concentrated on the membrane surface, while the inner layer acted as a porous support. Coupled in a submerged membrane photo reactor (SMPR), the membrane was able to effectively remove more than 80% of a mixture of pharmaceutical compound, including CB, diclofenac (DCF), iopromide (IOP), gemfibrozil (GEM), metoprolol (MET), sulfamethoxazole (SMX), trimethoprim (TMP) and warfarin (WAR), as seen in Fig. 5c. In addition to this, the use of DLHFM to treat secondary effluent reduced the energy consumption by an average of 50% as compared with current means practiced in the industry. The same fabrication technique was used in another work which was carried out by Dzinun et al. (2016), where a DLHFM with TiO₂ immobilized on its outer layer was used to treat NP. The dual-layer configuration improved the dispersion of TiO₂ nanoparticles on its surface, which improved membrane strength. Furthermore, removal of 85% in NP was attained for DLHFM within 4 h of UVA irradiation when coupled in an SMPR, as compared with 70% for the single-layered membrane. The kinetic rate of dual-layer membranes was calculated to be 0.0092 min⁻¹ against 0.0062 min⁻¹ for its single-layer counterpart. The kinetic studies suggested that the

photodegradation rate exhibited by DLHFM was faster than single-layered membrane. Two plausible reasons had been identified, i.e. the improved contact between pollutant and photocatalyst and the high number of photocatalysts activated in DLHFM as compared with single-layered membrane. These findings were in conformity with another research work which used the same technique to prepare DLHFM using nitrogen-doped TiO₂ as the model photocatalyst. The DLHFM developed in the research work carried out by Kamaludin et al., (2019) was able to photodegrade up to 70% and 100% of RB5 under both visible and UV light, respectively. The tested feed samples also did not show any trace of titania, which indicated that the photocatalyst was well entrapped in the matrix of the outer layer, ensuring no leaching of photocatalysts.

Some approaches have been employed to ensure the concentration of photocatalysts is confined on the surface of the membrane. Mohtor et al. (2018) deposited a layer of TiO₂ on the structure of a ceramic hollow fiber membrane for the photodegradation of industrial dyes via hydrothermal technique. In this work, a pre-fabricated ceramic membrane was placed inside a hydrothermal autoclave together with titanium tetrabutoxide (TBOT), a common precursor for TiO₂. Surface imaging evidenced the growth of a TiO₂ layer on the surface of ceramic membrane, while performance testing showed that there was an increase in permeation capability as compared to uncoated ceramic membrane. Enhanced liquid surface tension, lower membrane surface charge and lower membrane surface roughness were governing factors towards improved permeation. Furthermore, the membrane was able to photodegrade up to 95% of MB within 9 h of treatment time. A similar approach was also taken by Wang et al. (2019), where CuO photocatalyst was deposited on the surface of ceramic hollow fiber membranes via dip coating technique. The optimum CuO coated ceramic hollow fiber membranes exhibited excellent catalytic activity for degradation of BPA in the presence of humic acid (HA), chloride ions (Cl⁻) and bicarbonate (HCO³⁻). Top surface imaging also showed intrinsic growth of CuO nanoparticles on membrane surface, while an increase in membrane surface roughness also confirmed the growth was successful. The dip coating also reduced the pore size of ceramic membrane, which enabled higher rejection performance as compared with uncoated ceramic membrane. The thermal resistance of ceramic hollow fiber membranes are an integral part in employing coating techniques which require high heat, as exhibited by another work done by Li et al. (2020b), where a ceramic membrane was coated with a layer of TiO₂ using sol-gel technique. However, the fragile nature of ceramic membranes and their large pore size may render them incompatible when preparing photocatalytic membranes which are employed to treat small-sized pollutants. This is the advantage of polymeric membranes, as they can achieve UF range, while ceramic

membranes are commonly placed in the microfiltration range. Nonetheless, both types of membrane structures show great potential for further development of efficient photocatalytic membrane for various wastewater treatment applications. Figure 6 shows the performances of various photocatalytic membranes for the removal of POPs. Figure 6 a shows the importance of UV light to activate the photocatalyst which assists in the removal of MB while Fig. 6 b and d show the antifouling properties of photocatalytic membranes. Almost complete flux recovery of photocatalytic membrane can be observed due to the continuous photodegradation of POPs adhered on membrane surface. The photocatalytic activity also improves membrane permeation, as observed in Fig. 6c.

Future directions and conclusion

The employment of photocatalytic membrane as means to separate and degrade various POPs has significant potential in combating water pollution. Photocatalytic membrane can overcome the limitations that both photocatalysis and

membrane technology faced when employed individually while maintaining excellent efficiency. Even though research on photocatalytic membrane has been conducted extensively by researchers, there are still rooms for improvement. One significant progress that needs to be done is the development of photocatalytic membrane which can directly treat raw effluents produced by industry. As mentioned earlier, most works are conducted in lab scale using model effluent which can be very mild as compared to the real effluent produced. In lab scale, such controlled conditions may exhibit promising results. However, studies where such lab scale reactors are scaled up to tackle real effluent are scarce. More studies are required to study the feasibility of upscaling such photocatalytic reactors to further understand its capabilities to treat various types of industrial effluent. Another direction where researchers can focus on is the problems faced by polymeric membranes when exposed to UV light, which is degradation of the polymer chains. Such phenomena may compromise membrane structure, which would lead to deterioration in rejection capabilities. Here, more research can be conducted on the incorporation of UV inhibitors such as hindered amine

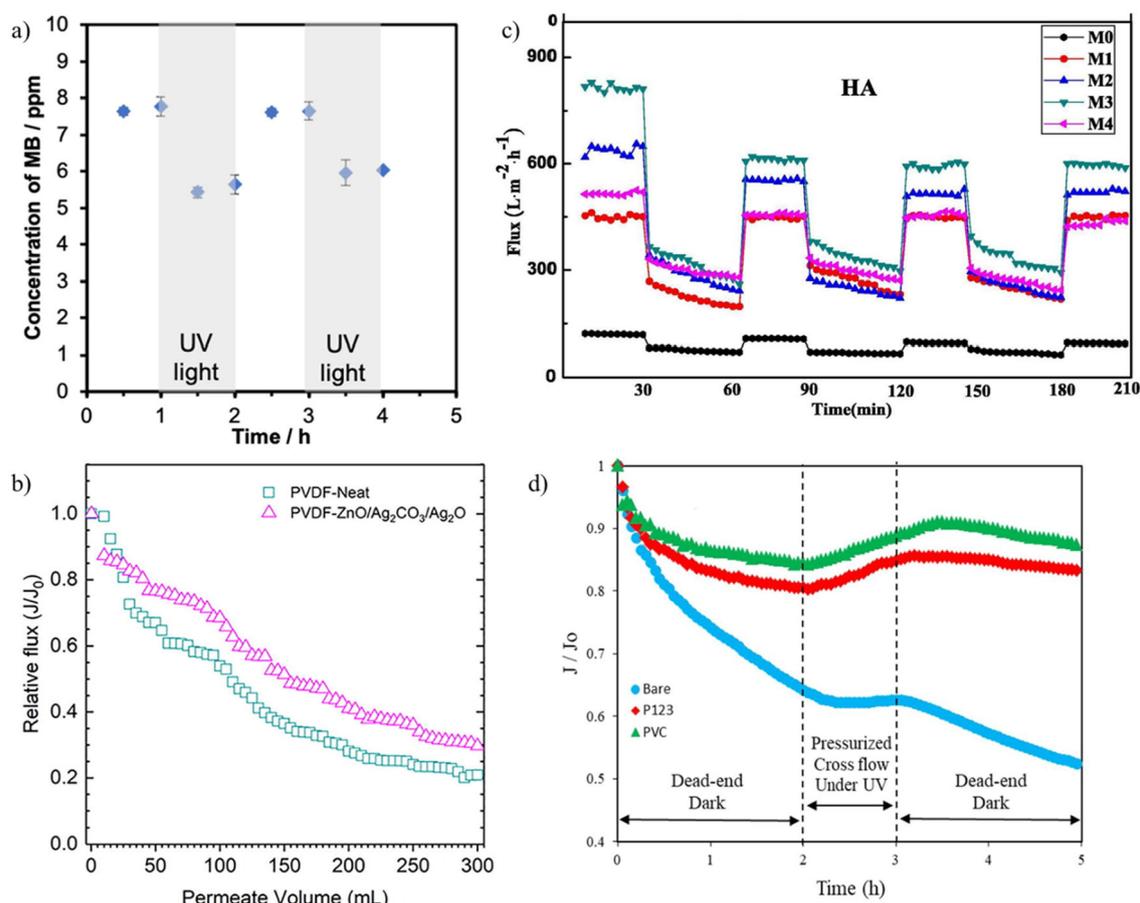


Fig. 6 Performance of various photocatalytic membrane where **a** the photodegradation of MB in the presence and absence of UV light by a TiO₂ coated membrane (Deepracha et al. 2021), **b** difference in the flux of a antifouling PVDF-ZnO/Ag₂CO₃/Ag₂O nanocomposite membrane

(Rosman et al. 2020), **c** flux and rejection recovery of self-cleaning photocatalytic membrane (Sun et al. 2020b) and **d** comparison of anti-fouling properties of a partially coated TiO₂/Al₂O₃ membrane (Ahmad et al. 2020)

light stabilizers (HALS) into polymeric membrane to reduce the decay of polymeric membranes without compromising membrane effectiveness. In addition to this, research on visible light active photocatalyst incorporated into membranes is already being conducted. However, all work that is conducted uses simulated light source as activation source. Less work was done to explore the feasibility of using direct sunlight as photon source for activation of photocatalyst embedded in the membranes. In addition to this, researchers can look into different photocatalytic deposition methods with better adhesion to avert photocatalyst leaching during operation. Photocatalytic membranes prepared via deposition methods such as physical vapour deposition (PVD) and dip coating may experience leaching over operation time due to deterioration. Photocatalytic membrane has shown immense potential as means to separate and destroy various types of POPs simultaneously and intensified research is necessary to ensure that this potential can be translated into a wastewater treatment technology at an industrial scale.

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Data availability All data generated or analyzed during this study are included in this published article.

Declarations

Conflict of interests The authors declare that they have no conflict of interest.

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

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