



Review

Hybrid Organic–Inorganic Membranes for Photocatalytic Water Remediation

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Abstract: Mismanagement, pollution and excessive use have depleted the world's water resources, producing a shortage that in some territories is extreme. In this context, the need for potable water prompts the development of new and more efficient wastewater treatment systems to overcome shortages by recovering and reusing contaminated water. Among the water treatment methods, membrane technology is considered one of the most promising. Besides, photocatalytic degradation has become an attractive and efficient technology for water and wastewater treatment. However, the use of unsupported catalysts has as its main impediment their separation from the water once treated. With this, providing the membranes with this photocatalyzed degradation capacity can improve the application of photocatalysts, since in many cases their application improves their recovery and reuse. This review describes the general photocatalytic processes of the main inorganic nanoparticles used as fillers in hybrid polymeric membranes. In addition, the most recent hybrid organic–inorganic membranes are reviewed. Finally, the membranes formed by metal–organic frameworks that can be considered one of the newest and most versatile developments are described.



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1. Introduction

The never-ending growth of the world's population together with the major international problem of water contamination caused by industrial, domestic and environmental influences put global water resources at risk. During the last decades, the freshwater scarcity has become a wide world problem, estimating that around two-thirds of the global population live under severe water scarcity conditions [1–3]. In this context, seawater desalination, non-conventional water resources (rainfall-runoff) and the remediation of wastewaters or marginal-quality water have arisen as necessary alternative resources to fulfill the freshwater needs on a near future of the world population [4].

Wastewater treatment, sometimes called water remediation, is defined as “the application of known available technologies to treat wastewater to such an extent that the quality of the treated water meets the specifications of governmental environmental regulatory agencies” [5]. These processes are normally classified into five different treatments: preliminary, primary, secondary, tertiary and advanced. These transform wastewater to pure one by applying sieves, sedimentation and coagulation methods, biological treatments or disinfection, among others. Particularly, processes such as adsorption, ion exchange, membrane and advanced oxidation of wastewaters grab considerable attention of many researchers worldwide due to the increased number of contaminants detected in water [5,6].

Although the contaminants found in water are very varied, they could be easily divided based on their chemical composition into inorganic and organic pollutants. Inorganic pollutants, such as oxyanions/cations and metal ions, especially heavy and/or radioactive

metals, are considered more persistent than organic contaminants, being an important environmental problem. On the other hand, organic pollutants, due to their diversity, are more extended in the aquatic media than inorganic ones. These contaminants include oils, pesticides/insecticides/herbicides, detergents, pharmaceuticals, dyes or polyaromatic hydrocarbons. Even now, some compounds that were previously not considered contaminants or not known that have significantly increased their presence on the environment, in terms of distribution and/or concentration, are considered as emerging contaminants (EC) [7]. These ECs could potentially cause several known (or suspected) ecological or human health issues. The ECs include some pesticides (atrazine and imidacloprid) [8], metal ions (Fe, Pb and Ni) [9], dyes (methylene blue and rhodamine-B) [10,11] or personal care and veterinary drugs (tetracycline) [12], among others.

There are several methods in use for contaminants removal from water, the most commonly used being: coagulation-flocculation, ion exchange, digestion (aerobic and anaerobic), membrane filtration, chemical precipitation, and chemical oxidation, among others. The efficiency and the cost of these methods vary depending on the concentration, chemical nature pollutants and their requirements in means of infrastructure. Among all of them, membrane-based processes stand out, as they are considered an excellent technology in water and wastewater treatment. This technology has several advantages such as high efficiency, easy to use, no phase change, high selectivity, normal operating temperature condition and low power consumption [13,14]. However, many of the traditional methods, even if they are very effective in remediation of conventional pollutants, present many lacks when facing the removal of emerging contaminants [15]. In this way, numerous efforts have been made in the development of membranes for the remediation of polluted water, and the most challenging membranes must be capable to remediate not only traditional contaminants, but also to efficiently remediate emerging contaminants.

Membrane-based technologies are one of the most promising methods for emerging contaminants removal from water due to their cost-effectiveness and their capacity to be adapted to the contaminants because of the wide variety of compositions available. Considering the main material used on membranes, they could be classified as inorganic and polymeric membranes. However, there are specific limitations ascribed to each of them, so the use of hybrid membranes that could combine the properties of inorganic and polymeric materials, at the same time avoiding their weakness. In addition, even if their use is widely spread, hybrid membranes with inorganic fillers such as calcium carbonate, glass fibers or mica, among other inorganic fillers, present several disadvantages, such as the brittleness and poor mechanical properties, which have driven the search for alternative hybrid membranes [16]. On the other hand, polymeric membranes have excellent mechanical, physical and chemical properties, which, added to their inexpensiveness and ease of production, make them widely used. In the light of this, polymeric hybrid membranes with nanosized inorganic fillers are gaining great attention.

Hybrid organic–inorganic membranes, also called thin-film nanocomposite (TFN) membranes, are prepared by incorporating nanomaterials into solid polymers. While polymer provides mechanical and thermal properties, nanoparticles are chosen to enhance properties such as separation efficiency, hydrophilicity, chlorine resistance or anti-fouling properties, among others [17]. Polyethersulfone (PES), polyvinylidene fluoride (PVDF), polyethylene terephthalate (PET), polyacrylonitrile (PAN), or even natural-based polymers such as cellulose, chitosan or bio-polyurethanes, are some of the typical polymeric materials employed for membrane preparation [18,19]. Attending to the particles, TiO₂, silver, cerium, silica, and carbon-based materials (carbon nanotubes, graphene, etc.) are the most common used ones [17]. Nowadays, metal–organic frameworks or MOFs (explained in Section 4) are increasingly used because of their unique physio-chemical performances including ultra-high surface area or regular and highly controlled porosity [20,21].

The inorganic fillers capable to photodegrade pollutants are ones of the most interesting in water remediation. Photocatalysis is a great approach as an efficient and sustainable oxidation technology for application in wastewater treatment due to be considered a simple, green and rapid progress that consume short amounts of energy [22,23]. TiO_2 , graphite carbon nitride ($\text{g-C}_3\text{N}_4$), carbon gels-modified TiO_2 or graphene-based membranes are just some examples of materials employed in the photodegradation of pollutants [24–28], including under visible-light irradiation [29]. However, suspended photocatalysts present some drawbacks that increase the use of them supported in membranes. Even if the suspended photocatalysts show a higher surface area, leading to higher photocatalytic efficiency, their recovery from the reaction media is considered their main disadvantage. Moreover, the presence of the suspended photocatalyst could reduce the permeate flux of the membrane, reducing the efficiency of the flow reaction. In addition, the separation process required to recover the employed photocatalysts could increase the cost and the time in a potential treatment [30–32]. In this context, the immobilization of the photocatalysts onto a membrane support could be an effective way to ease the recovery of the catalyst and simultaneous filtrate the wastewater during its treatment.

A photocatalytic membrane reactor (PMR) is a device that could combine various treatment processes simultaneously such as photocatalytic degradation of contaminants and filtration/separation. In addition, in those systems in which suspended photocatalysts are employed, they could be recovered during the process. The main advances of PMR-based technologies are their high energy efficiency and the scalability [33–35].

PMRs can be divided into two main groups; on the one hand, the reactors with catalyst suspended in the feed solution (SPMR) and, on the other hand, the reactors with catalyst immobilized in/on the membrane (IPMR). Figure 1 shows examples of the different types of most common PMRs. The light source configuration will vary depending on the type of PMR being used [36–38]. Thus, in the case of supported membranes, the light source is placed above the PMR. While using suspended photocatalysts, the radiation source can be placed in the feed tank, in the membrane module or in another separate tank, as illustrated in Figure 1.

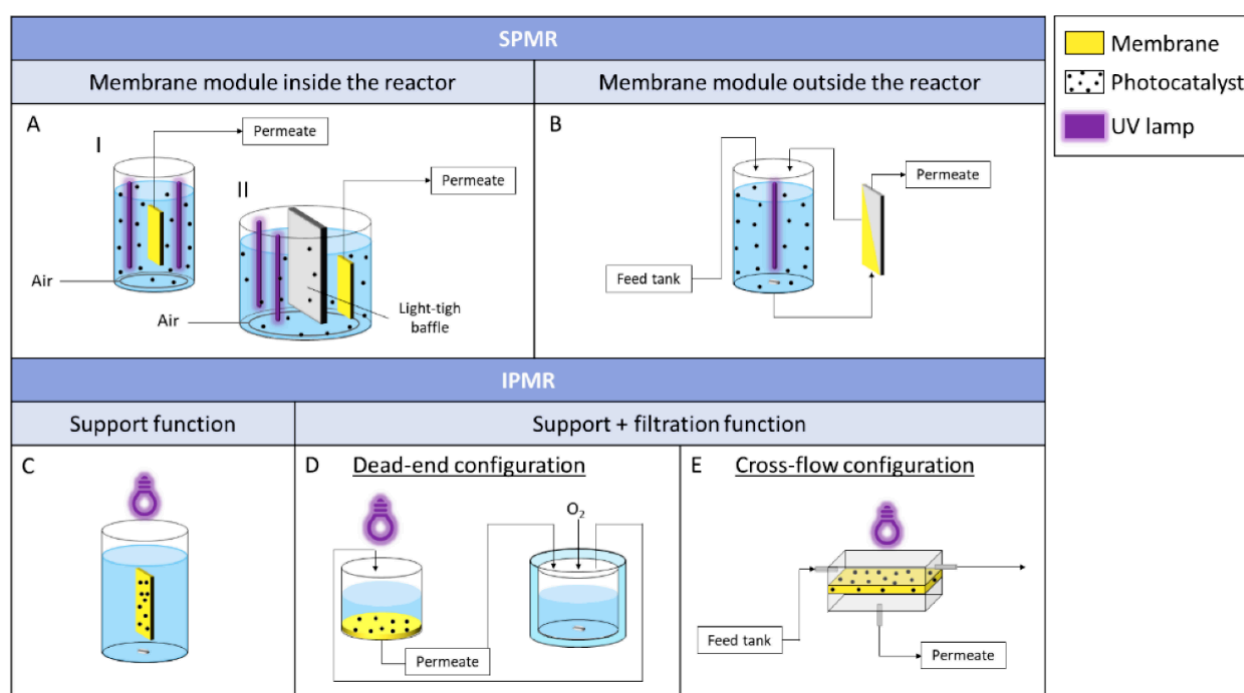


Figure 1. Scheme of different configurations of suspended photocatalyst membrane reactors (A,B) and immobilized photocatalytic membrane reactors (C–E). Reproduced from [39] (CC by 4.0).

This review describes the general photocatalytic processes of some of the main inorganic nanofillers used in the fabrication of hybrid membranes. Furthermore, the most recent hybrid polymeric inorganic membranes are reviewed, describing their remediation capacity and their main characteristics. Finally, the membranes formed by metal–organic frameworks that can be considered one of the newest and most versatile developments are described. Thus, as a novelty, present work groups the main hybrid inorganic–organic membranes prepared in the bibliography with the metal–organic frameworks-based membranes for water remediation.

2. Photocatalysis and Water Remediation

The catalytic degradation processes, and more specifically those of photocatalytic degradation, are gaining increasing acceptance by the scientific community owing to the advantages they present over other contaminant remediation methods. They present high water recovery rates, no residues are generated, could be considered cheap, and require moderate temperature and pressure conditions.

The heterogeneous photocatalysis is the most used process. In this method, the reagents and the catalyst are in different phases. The oxidation and reduction reactions occur on the surface of the catalyst, due to photoinduced molecular reactions or transformations. Among these photocatalysts, the most common are transition metal oxides (MO) and semiconductors. This is because they contain a void energy region where no energy levels are available to promote the recombination of the produced electron and hole by photoactivation in the solid. The void region, which extends from the top of the filled valence band (VB) to the bottom of the vacant conduction (VC) band, is called the band gap [40]. The photocatalytic process is described schematically in Figure 2.

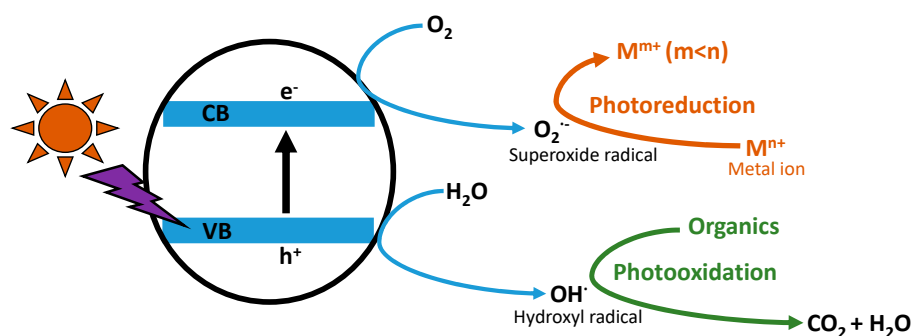
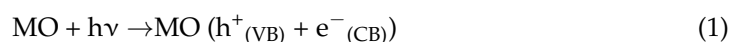


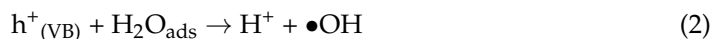
Figure 2. General mechanism of semiconductor-based photocatalyst in presence of UV radiation.

Starting the process requires ultraviolet or visible light in which a photon is absorbed by the semiconductor. The energy of the photon must be greater than or equal to semiconductor band gap (BG). In this way, it generates the holes (h^+) of the valence band (VB) and electrons (e^-) of the conduction band (CB) [41]. The generated electron-hole pair is called exciton and generally occurs on the surface of transition metal oxide (MO). In reaction (1) the generation of exciton is represented.



Both excited electron and hole can recombine and release the energy obtained from the electron excitation in heat form [42]. The generated exciton on the surface of semiconductors makes possible to start new reduction and oxidation reactions, which is the main objective of the photocatalyst.

On the one hand, the generated holes react with adsorbed reducer species to produce oxidized products, that is, in the specific case of water, the holes of the VB react with water on the surface generating hydroxyl radicals ($\bullet\text{OH}$) as it is shown in reaction (2).



These generated hydroxyl radicals are very oxidative with a redox potential of +3.06 V [43]. Moreover, their non-selectivity makes them responsible of the photooxidation process of adsorbed organic compounds, so thanks to those radicals that are very unselective, the degradation of organic molecules in water can be performed, and therefore the cleaning and disinfection of it occurs [44–48].

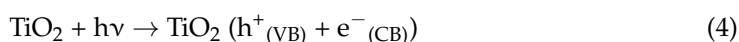
On the other hand, excited electrons react with oxidizers to produce reduced products, in the case studied in this work CB electrons react with gaseous diatomic oxygen in the medium and result in superoxide radicals ($\text{O}_2\bullet^-$), as it is shown in reaction (3).



These radicals react with another metal introduced into the system through a photoreduction process. Although they can react also with water to generate hydrogen peroxide and decompose to hydroxyl radicals.

In order to understand better the work performed by the semiconductor, that is, the photocatalyst, in the following paragraphs some examples are going to be presented using titanium oxide (TiO_2) and metal–organic frameworks (MOFs) for the degradation of methylene blue (MB) dye, which is one of the most used dye in the world.

Among the heterogeneous catalyst TiO_2 semiconductor is the most typical and used molecule. This molecule is a MO, so the photocatalyst reaction mechanism can start after light irradiation. This reaction is represented in general way in reaction (1) and can be expressed in specific mode for this system as reaction (4) [49].



After this reaction, the adsorbed water and oxygen molecules on the semiconductor reacts with as in reactions (2) and (3). During reaction (2) the $\bullet\text{OH}$ radicals are form, which are responsive of degradation of organic molecules. Recent studies combine TiO_2 molecule with another compounds in order to improve the degradation of pollutants. For example, Nikola Toshikj et al. [50] prepared by self-assembly method graphene platelets with manganese doped TiO_2 nanoparticles. In this study, they used the mentioned system in order to determine the degradation of MB in water after visible light irradiation. For this purpose, they used Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (MALDI-TOF MS). The high accuracy of this technique gives the opportunity to determine the complete degradation of MB and also the degradation products in smaller molecules. On another study, Junwei Hou et al. [51] compare the photocatalyst degradation of MB using two systems: TiO_2 and ZnO/TiO_2 heterojunction nanomeshes. They conclude that degradation efficiency of MB was higher with the second system.

More recently, MOFs and their derivatives are taking special attention as photocatalyst due to their good properties related to large specific surface area and high porosity. Moreover, there are plenty of possibilities based on their different composition and structure. However, the knowledge gap on the mechanism and the fate of heterogeneous catalyst species during organics degradation activities by MOFs presents considerable impediments, particularly for a wide application and scaling up the process [52,53]. Following to the degradation of MB by photocatalyst process Ming Zhang et al. [54] compared the degradation efficiency of two different MOFs under visible light with and without the addition of H_2O_2 . Without H_2O_2 the results were poor, but adding H_2O_2 the results were improved. These results are due to the nature of H_2O_2 , which is electron acceptor and suppress the recombination of the electron-hole pair.

As described above, a traditional semiconductor, a classical photocatalyst, TiO_2 , can be directly excited by incident light with energy greater than the bandgap and generate electron-hole pairs. Similarly, the photocatalytic mechanism of MOFs is based on the fact that electron transitions can also occur from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), leaving holes (h^+) in the HOMO. That is, the HOMO/LUMO could perform in similar way to the CB/VB in semiconductors, as illustrated in Figure 3. Thus, similar to semiconductors, photogenerated electrons in the LUMO can be transferred to O_2 , and form superoxide radical. On the other hand, holes in the HOMO can oxidize the hydroxyl group/surface water and generate ($\text{HO}\bullet$) by the presence of reactive species ($\text{O}_2\bullet^-$, $\text{HO}\bullet$ and h^+) [55,56].

Different band gaps ($E_{\text{HOMO-LUMO}}$) have been reported, varying with the studies' MOF. For example, UiO-66(Zr), and MIL-125(Ti) present $E_{\text{HOMO-LUMO}}$ of 3.4 eV, 3.9 eV, and 3.6 eV for MOF-5, respectively [55–58]. On the other hand, it should be noted that Fe-MOFs have a narrow band gap that makes them of great interest for the remediation of contaminants. These can be directly excited by visible light, with $E_{\text{HOMO-LUMO}}$ values ranging between 1.88 eV and 2.88 eV, leading to more efficient use of solar energy [59–61].

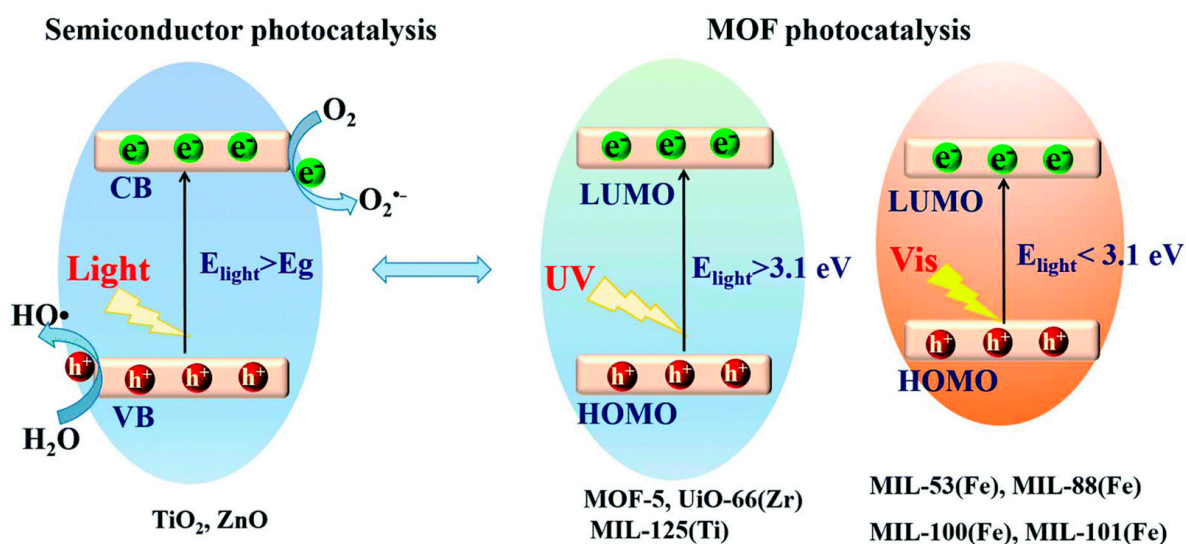


Figure 3. Schemes of photocatalytic mechanism for semiconductor (left) and MOFs (right). (Reproduced with permission from [56] Copyright (2020) Royal Society of Chemistry).

However, their main drawback is the lack of synthetic methods that could endow materials scientists with tools to precisely tailor their structures/pores, and consequently, possess an accurate control of the adsorption kinetics, capacity and selectivity of pollutants, which is of main relevance towards increasing the performances of adsorbents and implementing efficient water reclamation.

In this review, the water remediation based on the photocatalytic degradation is described, mainly focus on hybrid metal–organic frameworks polymer membranes capable to degrade different organic pollutants.

3. Inorganic-Polymer Hybrid Materials for Photocatalytic Applications

As it has been mentioned, photocatalysis is a very wide applied method for water and wastewater treatment. The use of a photocatalytic materials allows the oxidation of organic compounds and microorganisms from water. This, together with the need to have a water decontamination strategy with a sustainable approach that enables the access to safe drinking water, makes indispensable the research on new photocatalytic materials for water remediation [62,63].

Many years ago, inorganic materials such as TiO_2 were employed as photocatalysts for the oxidation of different organic compounds, microorganisms and other molecules

that are now considered as water pollutants [64]. ZnO, iron oxides, vanadates or other binary and ternary oxides are some of the inorganic materials employed as photocatalysts for environmental remediation [65]. Quickness and high efficiency degrading wide range of organics, chemical stability and strong mechanical properties are some characteristics of these inorganic materials, particularly for titania (TiO_2), that make them the most used photocatalytic materials [13]. TiO_2 highlights over the other inorganic photocatalysts and has been employed in several ways including itself, modified with other components, nanoassembled in a composite with carbon nanotubes, with a deposition of conjugated carbon materials or N-doped [65,66].

Despite inorganic materials still being the more used materials for photocatalysis, they present some disadvantages, such as the small amount of photons absorbed in the visible region (as a consequence, illumination by UV light is almost mandatory), high recombination rate for the photo-reduced electron-hole pairs, deactivation in the absence of water vapor or difficulty to support on some materials [65]. Particularly, attending to the global scale application in water remediation, the use of inorganic materials continues to be complex because it presents the limitation of final separation of the catalyst from the treated water [62].

In this way, one of the alternatives on which the most effort has been made is to embed or add these inorganic photocatalytic particles to polymeric films. Thus, materials named as photocatalytic membranes or photocatalysts immobilized membranes (PMs) have been created. In this way, the photocatalytic reaction takes place on the membrane surface and water could be in a continuous flux without the loss of photocatalyst particles and without powder filtration [13]. In addition, this system has advantages in terms of the easy and cheap manufacture of the polymeric materials [67]. The PMs degrade pollutants by the reactive oxygen species generated during the photocatalytic process and, therefore, prevents the formation of a cake layer on the membrane. Thus, the pore blocking is reduced and in consequence hindering membrane fouling and reducing the cleaning and replacing frequency of the PMs [68].

Attending to the polymeric matrix, polyvinylidene fluoride (PVDF) [69], polyethylene terephthalate (PET) [70], polyethersulfone (PES) [71], polyacrylonitrile (PAN) [72] and polyester [73] are some materials employed to the PMs synthesis. PVDF is one of the most used polymer materials in microporous membranes because of its high mechanical strength, thermal stability and variety of porous shapes allowed, while PET as a substrate for photocatalytic films offers flexibility, low weight and excellent impact resistance [69,70]. PES has characteristics such as heat resistant, thermal stability and high pH resistance, and PAN (in form of fibrous membrane), for its part, includes large specific surface area and low density, as well as has high mechanical strength with good chemical resistance [71,72].

There are many works done with PMs, and the great majority using TiO_2 as a photocatalyst. Among them, some are focused on the use of these PMs for water and wastewater treatment. H.P. Ngang et al. [69] obtained PVDF- TiO_2 mixed-matrix membranes via phase inversion technique and characterized their pore size distribution, porosity, absorption, photodegradation and ultrafiltration against methylene blue (MB) pollutant water solution. The addition of TiO_2 particles to the PVDF membrane increases the hydrophilicity of the PMs and mixed-matrix membranes showed excellent removal efficiency. The UV-cleaning properties of the mixed-matrix membrane were also proved by a complete flux recovery ratios indicating the photocatalytic effect of the TiO_2 particles and the ability of them to degrade the adsorbed MB in the membrane.

In a similar study, J.-P. Méricq et al. [74] prepared low-fouling PVDF membranes with TiO_2 nanoparticles entrapped, in this case, by non-solvent induced phase separation (NIPS) wet-process (Figure 4). Here, membrane structure or other properties such as hydrophilicity and permeability were improved by an optimum concentration of TiO_2 nanoparticles of 25 wt.%. Two phenomena are observed when membranes are UV illuminated: the super-hydrophilicity and the photocatalytic effect of TiO_2 . After UV illumination of PM membranes, an electron is photo-generated and it reacts with oxygen molecules of the

environment. Thus, the radical anion O_2^- is produced and the photo-generated hole reacts with water in the environment producing OH radical. Both compounds are able to decompose and remove organic compounds at the membrane surface, therefore cleaning it.

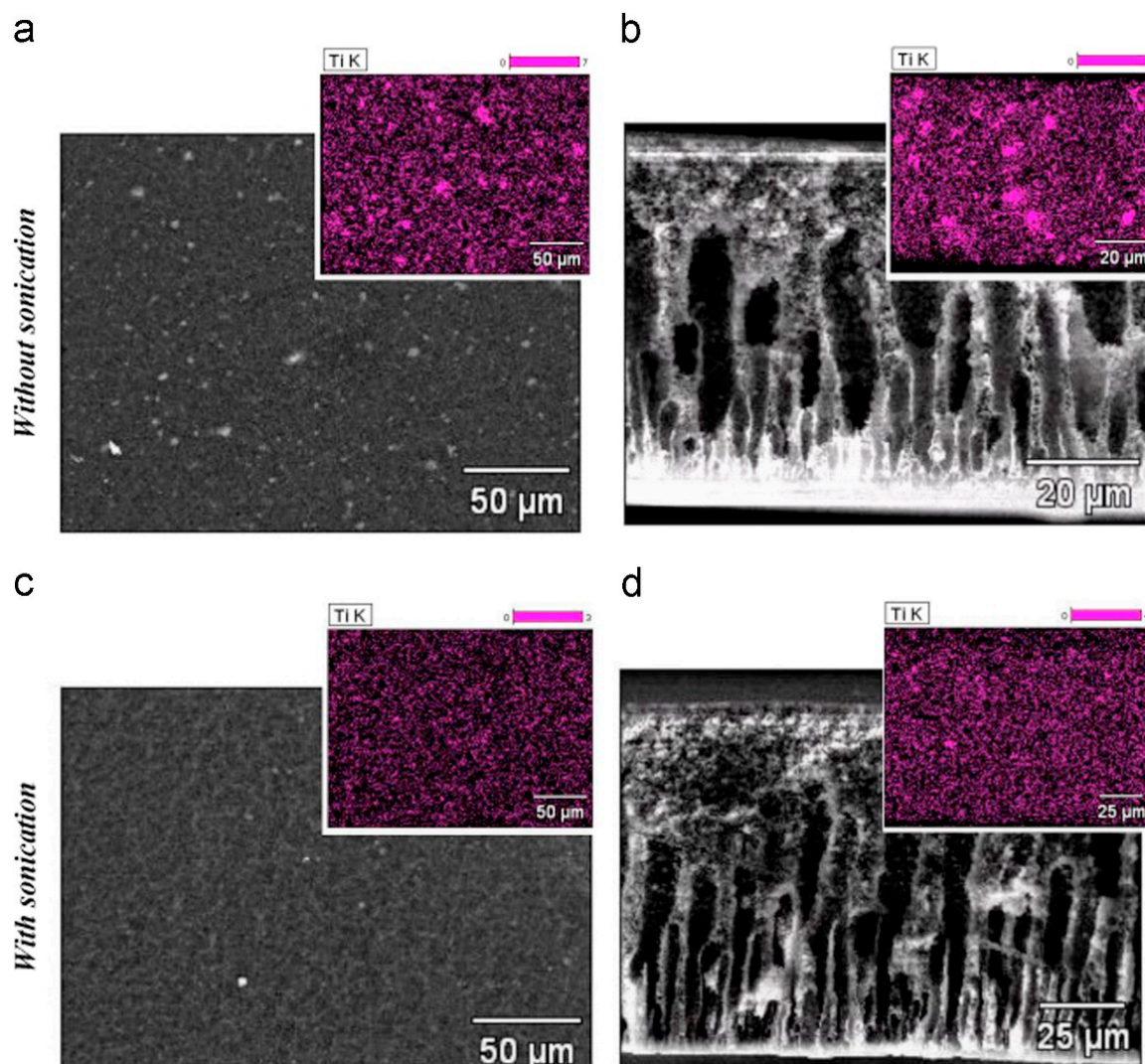


Figure 4. SEM images and EDS analysis of the PVDF/TiO₂ nanoparticles developed by J.-P. Méricq et al. [74]. Surface and cross-section of membranes without casting solution ultrasonic treatment (a,b) and with casting solution ultrasonic treatment (c,d). (Reproduced with permission from [74] Copyright (2015) Elsevier).

There are many studies focused on the use of PVDF and TiO₂ nanoparticles for photocatalytic applications. However, PVDF is not the only polymer proven for PMs synthesis. Polyethersulfone, polyacrylonitrile, polyethylene terephthalate and polyamide 6 (PA6) were also used. In some cases, the PMs were obtained by the electrospinning process of the polymers–nanoparticle composite solutions. Thus, PAN and its composites with TiO₂ nanoparticles were electrospun into nanofibers for photocatalysis and antifouling applications. These PAN fibers were linked to the nanoparticles by O–Ti–C bonds and presented superhydrophobicity. After the illumination with a visible light, the photocatalytic properties of prepared materials were investigated using MB as pollutant. Their studies demonstrated the ability of fiber electrospun TiO₂/PAN composites to degraded 90% of MB within 3 h and produced OH radicals in a higher extent than neat PAN fibers [75]. Furthermore, also using the electrospinning technique, M. Blanco et al. [76] prepared veils of PA6 with linked TiO₂ nanoparticles and characterized their photocatalysis for

the degradation of an organic contaminant, the Remazol Black B, and for the removal of *Escherichia coli* and other bacteria. Results indicated appropriate photocatalytic activity under UV light irradiation allowing a 70% reduction of the pollutant in 4 h (Figure 5) and successful antibacterial behavior removing studied compounds after 24 h of contact with them. Moreover, the stand-alone structure of the membranes allowed for the reusing of the immobilized catalyst.

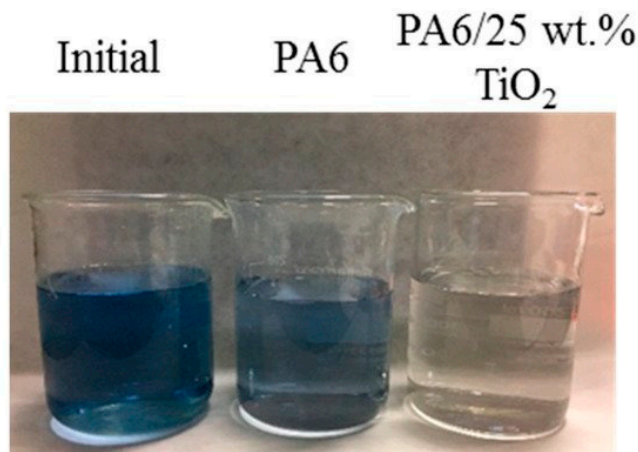


Figure 5. Images of Remazol Black B dye removal from the solution (initial) after 4 h and under UV-light for PA6 membrane and PA6/25 wt.% TiO₂ nanoparticles nanofiber membranes. Reproduced from M. Blanco et al. [76] (CC BY 4.0).

Besides the electrospinning technique, immersion precipitation is other technique employed to the synthesis of PMs. A. Rahimpour et al. [77] used this process to prepare three kind of membranes based on polyethersulfone: TiO₂-entrapped membranes, UV-irradiated TiO₂-entrapped membranes and UV-irradiated TiO₂-deposited membranes. The immersion of PES membrane into a TiO₂ colloidal suspension and a subsequent UV irradiation were determined as the optimum conditions for the higher flux and higher antifouling properties of the PMs. In addition, photocatalytically active filtration systems were prepared by M. Kutuzau et al. [78] based on PET membrane modified with TiO₂ nanoparticles. In this work, PMs are formed by two-step hydrolysis of TiO₂ on the surface of PET membranes including the hydrated TiO₂ precipitation from solutions of titanium tetrachloride and the peptization in a mixture of nitric and hydrochloric acids. Dimensions of TiO₂ nanoparticles were controlled by synthesis conditions and the designed systems are promising for filtration, antibacterial or self-cleaning applications. Further, photocatalytic activity of these materials represents the opportunity to oxidize pollutants (organic molecules) under soft natural conditions due to UV irradiation is not required and the photocatalysis could be carried out just by sunlight.

Following with this polymer membranes modified by coupling photocatalytic active materials such as TiO₂, other studies were focused on the modification of the shape of the photocatalytic particles to improve surface properties of PMs. In this sense, TiO₂ nanotubes were synthesized and then supported on polyurethane (PU) membrane to generate a PMs. Immobilized PU/TiO₂ membrane were characterized in terms of photocatalytic activity against the degradation of methyl orange (MO). The illumination with high pressure mercury lamp for 5 min demonstrated the degradation of around 90% of MO in 5 min for a several repeated times (up to 6), washing the catalyst with ethanol between the different assays [79].

Moreover, TiO₂ nanoparticles were also functionalized, modified or added together other components in order to improve the photocatalytic properties of PMs. H. Salazar et al. [80] functionalized TiO₂ nanoparticles surface with silver (Ag) nanoparticles and this hybrid material, Ag-TiO₂, as well as TiO₂ nanoparticles were added to the poly

(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) to create composite membranes by solvent cast and electrospun techniques with different particles concentrations. Thus, Ag-TiO₂/PVDF-HFP membranes presented improved photocatalytic activity with a degradation efficiency of 80.7% after 5 h of visible light illumination and 64.2% after 1.5 h under UV irradiation, both for the degradation of norfloxacin. Additionally, these PMs showed antimicrobial behavior and recyclability. Y. Peng et al. [81] used Ag-TiO₂-APTES photocatalyst together with PVDF to generate antibacterial, photocatalytic and self-cleaning membranes. The rejection rate of methylene blue (MB) was discussed, obtaining a 90.1% value with respect to 74.3% for pristine membrane when 0.5 wt.% of functional particles were added. Due to the presence of Ag, prepared membranes revealed an antibacterial behavior.

Similarly, graphene oxide (GO) was coupled to TiO₂ particles to generate a GO/TiO₂ nanocomposites that then were mixed with PVDF to develop GO/TiO₂-PVDF hybrid ultrafiltration membranes [82]. The degradation of bovine serum albumin demonstrated a significantly improved photodegradation efficiency (about 50–70%) and superior photodegradation kinetics (1.0–1.5 times faster) of the GO/TiO₂-PVDF PMs compared with PVDF membranes supplemented with TiO₂ and GO. In addition, the GO/TiO₂-PVDF membranes presented self-cleaning property under UV irradiation as well as two times higher water flux compared with PVDF pristine membrane. Furthermore, GO and TiO₂ nanoparticles were used together by T. D. Kusworo et al. [83] as fillers in the fabrication of polysulfone (PSf) membranes (Figure 6). The incorporation of both TiO₂ and GO allowed the obtaining of PMs with a permeate flux, organic and ammonia removals of 13.05 L m⁻² h⁻¹, 60.98% and 91.27%, respectively. In addition, PSf-TiO₂/GO membrane showed the fastest photodegradation after 2 h of UV light irradiation.

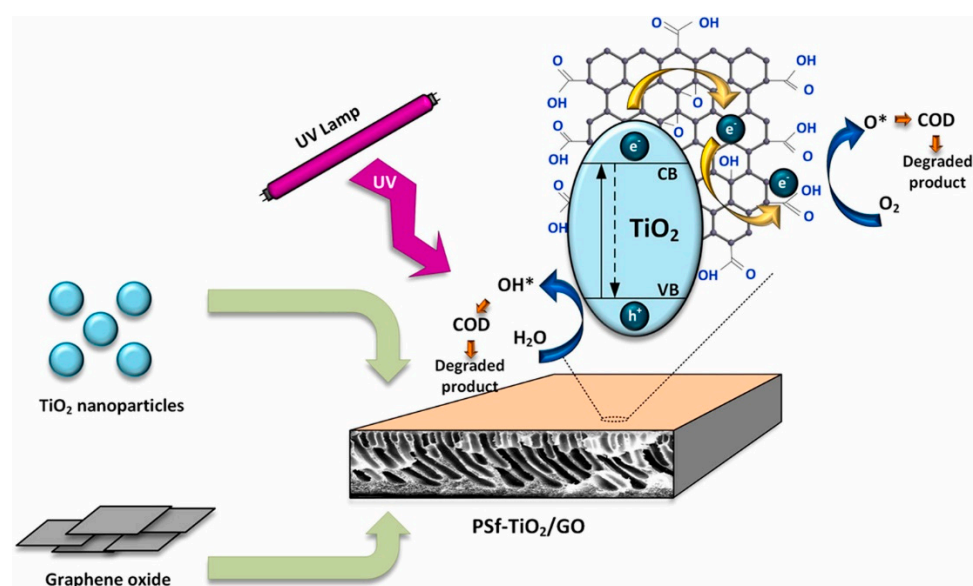


Figure 6. Scheme of the photocatalytic PSf TiO₂/GO membranes fabricated by T. D. Kusworo et al. [83]. Reproduced with permission from T. D. Kusworo et al. [83] Copyright (2021) Elsevier.

Another filler that is used with the TiO₂ nanoparticles in order to improve the photocatalytic activity is the LiCl [84]. PVDF-LiCl-TiO₂ membranes were prepared by adding 0.5 wt.% of LiCl and TiO₂ nanoparticles. The rejection of natural organic matter (NOM) and flux decline, together with the effect of photocatalytic degradation on PMs, were investigated. Results indicated that prepared PVDF-LiCl-TiO₂ membranes were effective for NOM rejection and reduction of membrane fouling at the same time, also showing good self-cleaning ability due to the photocatalytic activity of the membrane. Prepared membrane was cleaned with UV irradiation and the foulants' photocatalytic degradation was most effective in the first 30 min.

ZnO was also employed to dope TiO₂ nanoparticles and generate ZnO-TiO₂ nanospheres with a various percentage of ZnO ranging from 0 up to 10 wt.% [85]. These nanospheres were used to coat a filter paper (Fp) to generate the Fp-ZnO-TiO₂ membranes that were then used to photocatalytically oxidize MO dye and reduce harmful Cr(VI) to non-toxic Cr(III) of a wastewater. The results of the photocatalytic degradation study carried out with these membranes are depicted in Figure 7. The 1 wt.% ZnO-TiO₂ content membrane was observed as the most efficient material with reducing time taken to completely remove toxic Cr(VI) waste and MO of 33% and 11%, respectively, compared to conventional photocatalytic powder dispersion method. 1% Fp-ZnO-TiO₂ membrane reported complete MO and Cr(VI) photodegradation within 80 and 160 min, respectively.

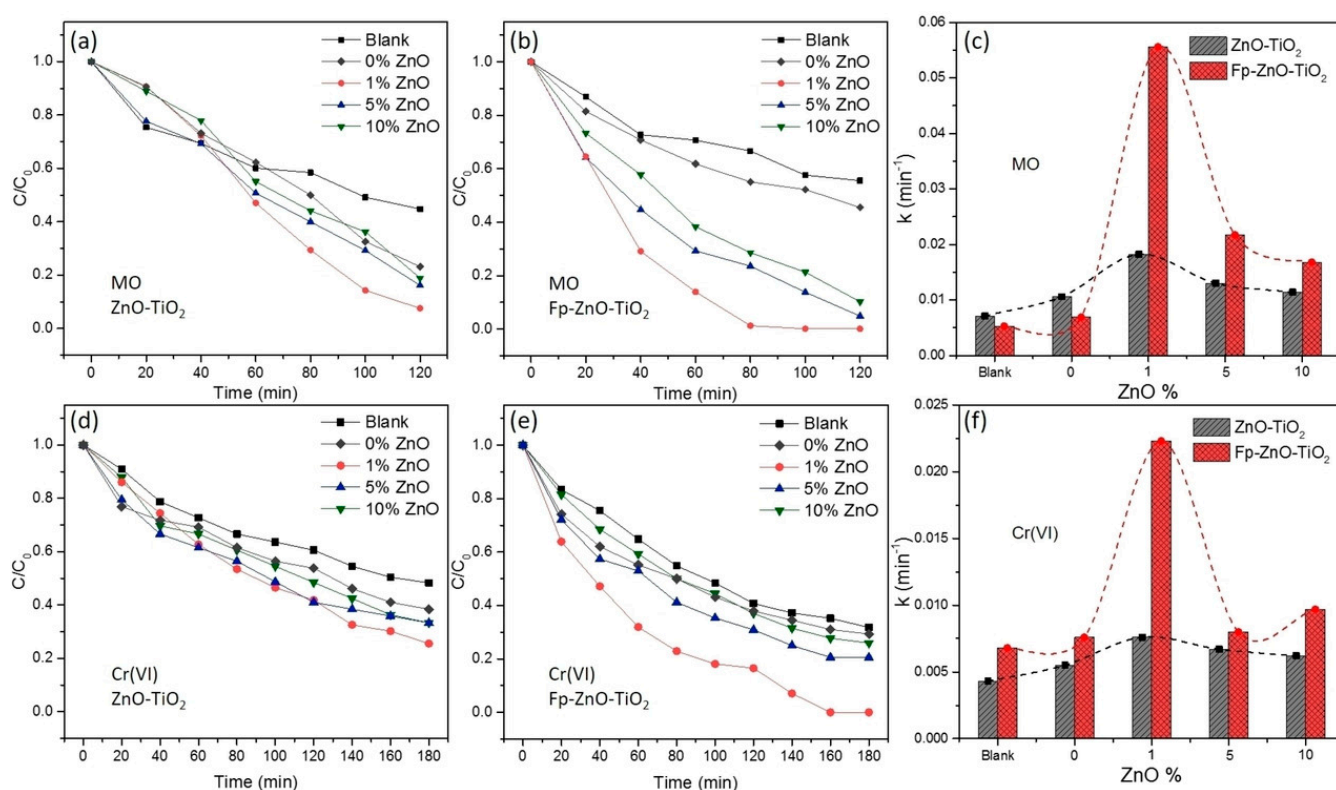


Figure 7. Photocatalytic degradation of methyl orange (MO) and Cr(VI) with ZnO-TiO₂ (a,d) and with Fp-ZnO-TiO₂ (b,e). Comparative of the MO and Cr(VI) photodegradation rate constants k of ZnO-TiO₂ and with Fp-ZnO-TiO₂ at different ZnO concentrations (c,f). Reproduced with permission from Shejale et al. [85] Copyright (2018) Wiley-VCH Verlag.

4. MOF-Based Membranes for Photocatalytic Water Remediation

The use of PMs for water and wastewater treatment has been extensively evaluated [86,87]. In this sense, the use of different polymers and polymer shapes has been studied. However, less investigation is focused on the evaluation of other inorganic materials as photocatalysts for PMs. Here, metal–organic frameworks (MOFs) appear as an alternative of traditional photocatalysts for water remediation such as TiO₂ or ZnO [88].

Metal–organic frameworks (MOFs) are defined as inorganic–organic hybrid porous materials constructed from inorganic clusters linked by organic ligands [89]. Attending to the metal, organic ligands and their combination possibilities, MOFs structures can be easily tailored and developed, making their applications in various fields possible, including separation membranes, gas storage and delivery, or sensing applications [90]. Some MOFs present semiconductivity when they are exposed to the light, denoting their applicability as photocatalysts [91]. In addition, advantages of MOFs such as high porosity, high surface area, controllable pore size or outstanding cycle lifetime has to be mentioned [92]. Thus,

MOFs can be synthesized to satisfied the requirements of light absorbance and be used in photocatalytic water remediation [93]. In this framework, MOFs are extensively used for remove pollutants of water [94–97], also embedded on polymer membranes [20].

The combination of the advantages of MOFs with the mentioned advantages of the inclusion of photocatalytic materials on polymer membranes to generate PMs (easy and cheap manufacture, reduce pore blocking, hinder membrane fouling and reduce the cleaning and replacing frequency), makes MOF-based membranes an interesting and possible high efficiency alternative for photocatalytic water remediation. In this way, different polymeric materials have been used for the generation of MOF-based PMs. PVDF, such as is mentioned before, is an excellent material for membrane preparation. The use of this polymer together with MIL-125(Ti) MOF allowed the obtain of PMs with a superb self-cleaning merit through a wet phase inversion method [98]. Hybrid membranes containing MIL-125(Ti) were able to effectively degrade the foulant rhodamine B (RhB) under natural light. A MIL-125(Ti) content up to 20 wt.% was added, showing an upward trend of the water permeance with the highest value without compromising the RhB rejection of $64.3 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$ for a sample with 10 wt.% of MOF (RhB dye retention of 99.7%). Furthermore, an excellent photocatalytic degradation of the pollutant was observed due to the initial flux recovery after three cycles. These MIL-125(Ti)/PVDF membranes also exhibited an ultra-high bacteriostatic rate of nearly 100%. PVDF was also employed together with another MIL MOF, the MIL-101 [99]. Here, CdS/MIL-101 nanoparticles were prepared and added in a 1 wt.% to PVDF polymer to synthesis CdS/MIL-101 modified membranes. Under visible light irradiation, PMs demonstrated an excellent antimicrobial ability characterized by inactivation rate against *E. coli* and *S. aureus* of 93% and 89%, respectively. Further, PMs presented antifouling behavior that was studied using bovine serum albumin (BSA), humic acid (HA) and sodium alginate (SA) foulants. Under visible light irradiation, the development of foulants layer on the membrane resulted in a water flux decline of 17.8, 68 and 16.1% for CdS/MIL-101 with 1 wt.% of MOF particles, compared with that of 39.2, 100 and 36% for a pristine membrane during 40 min filtration.

Polyacrylic acid (PAA)-poly (vinyl alcohol) (PVA) nanofibers or fibrous membranes is another polymeric material employed together with MOF for PMs synthesis. T. Li et al. [100] fabricated PMs by in situ growing $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (PW_{12}) @UiO-66 crystals onto a nanofiber membrane of PAA-PVA prepared through electrospinning. The PAA-PVA/ PW_{12} @UiO-66 membranes were used as a photocatalyst for simultaneous photocatalytic degradation of MO and formaldehyde (FA) in an aqueous solution under UV light illumination. Degradation of MO in the presence of FA was around 97.35% after 120 min of irradiation, and the degradation efficiency of MO for the fifth cycle was 92.58%, demonstrating the reusability of PAA-PVA/ PW_{12} @UiO-66 membranes (Figure 8).

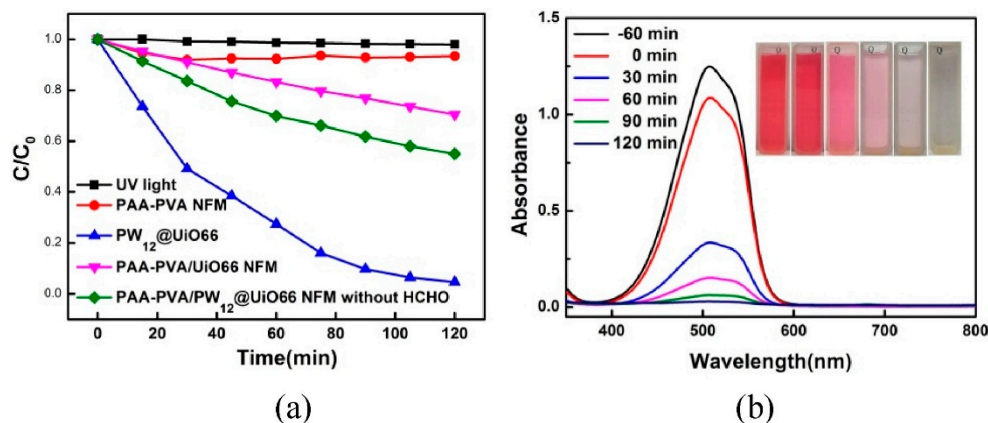


Figure 8. (a) The experiments used as control for different formulations and (b) MO photodegradation catalyzed over the time catalyzed by PAA-PVA/ PW_{12} @UiO-66 NFM. Reproduced with permission from T. Li et al. [100] Copyright (2021) Elsevier.

J. Huang et al. [101] also employ PAA-PVA fibrous membranes cyclic adsorption and degradation of dyes. In this case, NH_2 -MIL-125 MOF is used as photocatalyst and the obtained NH_2 -MIL-125 fibrous membranes were studied in terms of adsorption capacity to MB and sodium fluorescein. After irradiation for 180 min with visible light, the dyes could be degraded completely recovering the PMs. The use of H_2O_2 during the photocatalytic process allowed the reduction of irradiation time down to 60 min and membranes remained usable after three cycles of dye adsorption and degradation.

PAN was employed to embed hydrophilic Zr-porphyrin MOF with different dimensions (2D or 3D) and create a self-cleaning membrane with enhanced separation performance [102]. The addition of Zr-porphyrin MOF changed membrane morphology and improved its hydrophilicity and surface charge, thus greatly improving the separation and self-cleaning ability of the membrane. In addition, Zr-porphyrin MOF gave photoactivity response to the membrane. The Zr-porphyrin/PAN membrane with a 0.01 wt.% of MOF material presented a water flux ($110.4 \text{ L/m}^2\cdot\text{h}$) threefold higher than pristine film as well as almost 100% dye rejection for five dyes: Reactive Black 5, Direct red 23, Congo red, RhB and MB. These PMs also presented photocatalytic degradation self-cleaning ability under visible light illumination with a recovery of water flux that exceeded 97% after 4 cycles.

Recently, MOF materials have been used together with environmentally friendly biopolymers such as cellulose in the wastewater treatment of complex contamination, such as water simultaneously containing oils, dyes and heavy metal ion. W. Lu and co-workers [103] fabricated a photocatalytic membrane of carboxymethylated cotton fabric (CCF) as scaffold for the in situ synthesis of MIL-100(Fe) MOF and subsequent immobilization of Ag@AgCl NPs on MOF surface, Figure 9a. This Ag@AgCl@MIL-100(Fe)/CCF membrane presented improved hydrophilicity that further enabled the membrane with an efficient adsorption capacity of dyes and underwater oleophobicity against oils. The photocatalyst Ag@AgCl nanoparticles promoted the photocatalytic activity of prepared membrane, showing a simultaneous high removal efficiency towards dyes (97.3%) and oils (99.64%). This efficiency was maintained after five cycles and also, due this photocatalytic activity, the permeation flux is also maintained at $4927 \text{ L/m}^2\cdot\text{h}$. As an example, these membranes present excellent results for the photocatalytic degradation of methylene blue (MB), as could be observed in Figure 9b,c. In Figure 9b, the total degradation of MB by irradiation of the water in presence of Ag@AgCl@MIL-100(Fe)/CCF could be observed after 40 min.

Based on these promising results, W. Lu and co-workers [104] also studied the possibility of electrospun cellulose-based materials and generate PMs. Thus, an electrospun nanofiber membrane was prepared via electrospinning of deacetylated cellulose acetate/polyvinyl pyrrolidone (CeP) solution. Then, in situ synthesis of beta hydroxyl oxidize iron decorated iron-based MOF ($\beta\text{-FeOOH@MIL-100(Fe)}$) heterojunctions as photocatalysts was carried out. This MOF is in a 78 wt.% of the photocatalytic membrane denoting a large surface area of $1105 \text{ m}^2/\text{g}$. These interesting membranes showed outstanding performances with simultaneous high removal efficiency for oils (99.5%), dyes (99.4%) and chromium ion (Cr(VI)) (99.7%). Five different oils (petroleum ether, toluene, dichloroethane, cyclohexane and colza oil) and MB as the dye were used. Additionally, the photocatalytic activity of prepared membrane allowed the reuse of the material after five cycles (separation efficiency with visible light illumination is near 100% for oils, MB and Cr(VI) after 5 cycles).

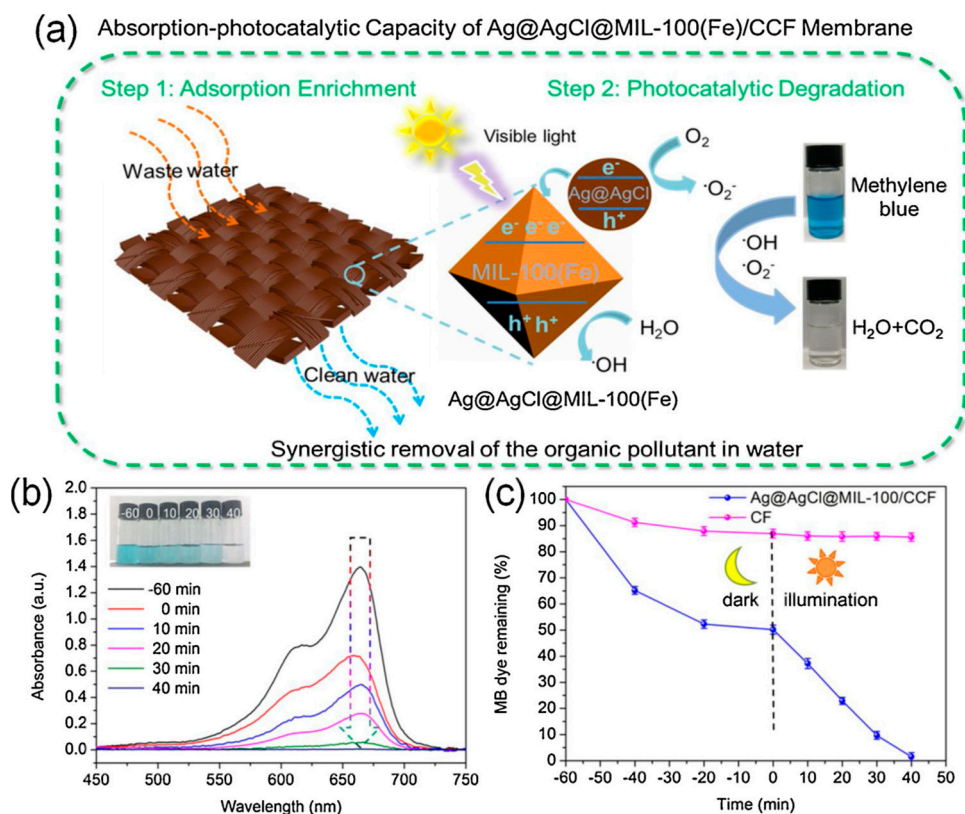


Figure 9. (a) Scheme of water remediation mechanism of Ag@AgCl@MIL-100(Fe)/CCF. Step 1: Contaminant adsorption and Step 2: photo-degradation of contaminants. (b) UV-vis spectra of Methylene blue reduction due to visible light irradiation in the presence of Ag@AgCl@MIL-100(Fe)/CCF. (c) Evolution of the percentage of MB dye at dark and with illumination for cotton fabric (reference substrate) and Ag@AgCl@MIL-100(Fe)/CCF. Reproduced with permission from [103] Copyright (2020) Elsevier.

5. Conclusions and Future Perspective

This review summarized the latest advances on hybrid inorganic/polymer membranes for photocatalytic degradation of pollutants and microbes. These membranes present many advantages compared to pure inorganic and polymeric membranes, giving these hybrid membranes noticeable properties. Among the properties that have been enhanced due to this hybridization, photocatalytic degradation capacity could be considered as a key property when it comes to the use of these membranes for wastewater remediation. In addition, it is important to notice that several of the inorganic fillers with photocatalytic properties could also present bactericidal capacity. However, even if during this review many promising hybrid membranes have been described, there is a lack of commercial membranes. The majority of these new materials have been tested at lab-scale, and only few at pilot or full scale.

Some issues should be resolved before the total application of this technique for water purification. The challenges faced in the use of photocatalytic membranes for wastewater treatment are still control of fouling and low permeate flux. In addition, the contact area between light, target pollutant and photocatalyst is lower than in the conventional slurry photocatalytic systems, issue that can be resolved via restructuring the morphology of the membranes from 2D to 3D. Further, although some photocatalytic membranes based on visible light induced photocatalysts have been reported in this review, there is a need on future investigate more membranes excited by visible light instead of UV light, gaining that a low energy consumption due to the utilization of renewable solar energy. Additionally, there is still a lack of durability data of photocatalytic membranes both in terms of the stabilization of photocatalyst inside the membrane and the photocatalytic

activity of the membranes. The reduction of the degradation rate of the polymeric matrix of these membranes and the variation of their degradation pathways in order to generate environmental friendly residues or even a potential reuse of the materials could be also one interesting challenge for this technology.

In the same way, future investigations will also be focused on the cost-effective synthesis of nanomaterials and the investigation on novel, innovative and ecofriendly photocatalytic materials with improved activity. This is the case of metal–organic frameworks that appear as good photocatalysts in photocatalytic membranes, but whose synthesis still has high cost, is difficult and dangerous. Thus, the use of membranes containing MOFs in water purification applications may be considered as a potential environmental and health hazard, and new synthesis techniques with mild conditions, utilizing nonhazardous compounds and the selection of a compatible MOF/polymer system should be well investigated.

Considering the environmental emergency and the scarcity of water resources in many territories, the development and implementation of this type of membrane will be of great importance in the near future.

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