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Solar-powered photocatalysis in water purification: applications and commercialization challenges

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ABSTRACT

Although heterogeneous photocatalysis has been recognized as a promising technology for decontaminating and disinfecting municipal and industrial wastewater over the last few decades, it has not yet successfully transitioned from laboratory-scale research to real-world applications. This limited progress is attributed to inherent physicochemical properties of most photocatalytic materials available, which exhibit reduced photoefficiency under visible light irradiation, along with multiple engineering considerations. This comprehensive review delves into the intricate dynamics of photocatalytic reactions kinetics, exploring several types of photocatalytic reactors and elucidating the significance of materials employed in photocatalytic wastewater treatment. This critical survey systematically examines the effectiveness of different materials such as titania, zinc oxide and graphitic carbon nitride which are commercially applied for different reactor systems. Understanding the role of these materials for photocatalytic reactions is essential to address the challenges associated with wastewater treatment. Furthermore, the discussion extends beyond the technical aspects to encompass the broader landscape of challenges hindering the commercialization and widespread adoption of photocatalytic technologies. By critically evaluating these challenges, the minireview aims to provide valuable insights for researchers, engineers, and policymakers seeking to advance and implement photocatalytic wastewater treatment on a broader scale. This synthesis of knowledge consolidates the current state of the field and outlines future prospects for overcoming barriers and optimizing the potential of photocatalytic processes in environmental remediation.

1. Introduction

Water covers 71% of the Earth's surface, with over 96% of it being saline and present in oceans. The remaining percentage is freshwater, of which 68% is locked away as glaciers and ice, and 30% exists in the form of groundwater [1,2]. This distribution leaves the ever-growing population of 7.88 billion (based on 2021 figures) humans and animals with a disproportionately limited proportion of water available for their livelihoods [3]. The need for sustainable solutions is ever increasing with the evident effects of climate change staring at our doorstep. The escalating global population and the rapid pace of urbanization have consequently heightened the demand for both safe drinking water and energy. Depletion of groundwater resources and unregulated disposal of sewage and industrial wastewater in numerous developing and underdeveloped countries have contributed significantly to the overall deterioration of water quality [4]. Therefore, the need for sustainable solutions for water treatment and disinfection cannot be more imperative than at any time of this century.

Various water treatment methods, encompassing a combination of physical, chemical, and biological approaches, have shown promise and currently play a crucial role in providing safe drinking water to millions of people worldwide [5]. Techniques such as sedimentation, filtration, chlorination, ozonation, aerobic and anaerobic treatments are employed individually or in multiple steps for comprehensive water treatment [6–8]. However, these methods have limitations, particularly in addressing newer forms of chemicals found in water, such as forever chemicals and microplastics[9]. Additionally, these traditional methods are often expensive and necessitate sludge management processes. The

Abbreviations: CPC, Compound Parabolic Collector; CSTR, Continuous Stirred Tank Reactor; Da, Damkohler number; FPR, Flat Plate Reactor; MWW, Wastewater.; OMTP, Offset Multi-Tubular solar Photoreactor; PFR, Plug Flow Reactor; PTR, Parabolic Trough Reactor; Re, Reynolds number; ROS, Reactive Oxygen Species; T, Optical thickness; Ω, Scattering albedo; TOC, Total Organic Carbon; WW, Wastewater.

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total cost of wastewater treatment plants is significantly dependent on the level of treatment, in line with the literature.

Advanced Oxidation Processes (AOPs) are recognized as promising techniques for eliminating emerging contaminants from wastewater effluents. Within the realm of AOPs, photocatalysis has been extensively explored for wastewater treatment. Over the past two decades, more than 32,500 scientific articles featuring " photocatalysis and water " have been published (as shown in Fig. 1), with an annual increase in publications. The growing number of photocatalytic wastewater treatment-based research articles is an interesting marker towards the persistent curiosity and equally the growth of novel sustainable strategies. This surge is unsurprising, given the extensive research on the physico-chemical, morphological, and structural properties of photoactive materials for applications such as wastewater treatment, outdoor and indoor air purification, self-cleaning surfaces, cancer therapy, etc. [10].

Photocatalysis has emerged due to the use of sunlight encompassing both the UV and visible light for activating a catalytic surface for light mediated reactions for degradation and disinfection of municipal and industrial aqueous effluents. Photocatalytic process can be operated at ambient room temperature and pressure with reduced operating costs, and usually does not require additional processes or secondary treatment steps to remove reaction byproducts [11]. These features make the process extremely viable and effective for large wastewater treatment plants.

However, despite being considered a promising technology for reducing chemical and microbiological pollutants in wastewater, heterogeneous photocatalysis has not progressed beyond the bench-scale to real practical applications. Several technical limitations confront the advancement of photocatalytic materials tailored to efficiently capture a wide spectrum of solar radiation. Studies such as those by Yang *et al.* and Kuspanov *et al.* emphasize the challenges associated with optimizing the bandgap structure and surface properties of photocatalysts to achieve enhanced solar energy conversion efficiency [12,13]. Furthermore, the cost implications of these materials, as highlighted in research by Mei *et al.* and Stoller *et al.*, underscore the economic barrier hindering widespread adoption, thereby intensifying the financial burden on large-scale wastewater treatment facilities [14,15]. Moreover, the intricate charge transfer dynamics inherent in novel photocatalysts pose a significant hurdle in accurately forecasting the overall efficiency of pollutant degradation pathways. Research conducted by Ye *et al.* and Chen *et al.* elucidates the complexities involved in elucidating charge transfer mechanisms, underscoring the need for advanced characterization techniques and theoretical modelling to unravel these intricacies effectively [16,17].

In addition to charge transfer dynamics, the challenge of catalyst recovery and recyclability, particularly for powdered samples, remains a pressing concern in the field. Studies have delved into strategies for enhancing catalyst recovery efficiency through immobilization techniques and tailored reactor designs[18,19]. These findings highlight the critical importance of catalyst selectivity, synthesis methodologies, and recovery strategies in optimizing photocatalytic processes for large-scale wastewater treatment applications. Furthermore, the holistic assessment of reaction pathways and charge transfer mechanisms, as emphasized, is paramount for designing robust photocatalytic reactors. Integrating insights from experimental investigations and computational modelling, researchers can gain deeper insights into reaction kinetics and identify key parameters influencing overall process efficiency. Ultimately, these factors collectively shape the narrative surrounding the feasibility and commercial viability of photocatalytic wastewater treatment projects. Addressing these technical challenges and leveraging advancements in materials science and process engineering, stakeholders can pave the way for the widespread implementation of photocatalytic technologies in both developed and developing regions, thereby mitigating water pollution and fostering sustainable environmental management practices.

Just considering the last few years (2020–2024), several review articles were published on the photocatalytic processes for wastewater treatment, with particular focus on the photocatalytic (nano)-materials engineering [20–26] and the reactor design and configurations [25, 27–30]. However, with the aim to implement these processes to the real wastewater treatment, it is imperative to thoroughly examine the principles governing pollutant degradation and disinfection.

In this context, this minireview aims at providing a summarized glance of different possible photocatalytic reactions kinetics, diverse types of photocatalytic reactors as well as a discussion on effective materials for photocatalytic wastewater treatment. A plethora of novel photocatalytic materials are continually being developed and reported across various applications every week. However, this study focuses on exploring conventional and widely used semiconductor materials, such as titania and ZnO. The integration of composite structures within these nanomaterials has shown considerable promise, and this article offers a concise overview of several reactors designed using these materials. Additionally, the emergence of graphene and graphene-based nanocomposites cannot be overlooked, despite facing challenges in achieving commercial scalability. Nevertheless, the cost of graphene has significantly gone below to €2 per cm^2, down from €1000 per cm^2, fostering widespread adoption across energy-related applications and driving research efforts towards large-scale production[31]. Projections suggest

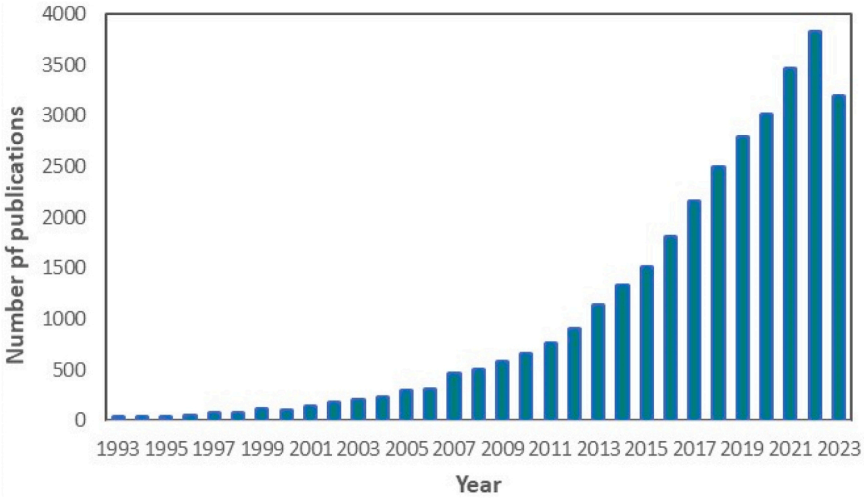

Fig. 1. Number of papers about photocatalytic water treatment published in the last 20 years (Data obtained from ISI Web of Science). Keywords: photocatalysis and water.

that graphene could achieve a comparable price point to lithium by 2031, underscoring its potential impact[32]. Hence, it is crucial to discuss the significance of graphene and its composite nanomaterials, despite not being novel, due to the optimistic outlook they offer for various technological advancements.

Moreover, unlike previous literature surveys, this study critically analyses the primary drawbacks of heterogeneous photocatalytic processes for wastewater decontamination and disinfection. The engineering factors limiting commercialization and the major roadblocks for the technology to be used widely are systematically discussed. Finally, potential approaches aimed at overcoming these shortcomings are examined.

2. Kinetics and modelling of photocatalytic wastewater treatment

In the realm of photocatalytic processes, closing the gap between promising experimental outcomes achieved at a bench-scale and the actual upgrade of these processes on a large utility scale poses a major challenge. Indeed, a more comprehensive understanding of the intrinsic kinetics involved in the photocatalytic removal of recalcitrant contaminants from WW is necessary for the advancement of novel effective reactors and advanced photocatalytic materials.

To mathematically model the kinetics of photocatalytic reactions, it is essential to have a thorough grasp of the dynamics of molecular processes occurring at the interface between the photocatalytic materials (*e.g.*, semiconductor photocatalysts) and the aqueous medium in which contaminants are dissolved.

Based on the knowledge of the radiation field and the reactor model, the focus of the modeling analysis should be the development of a kinetic pathway and a reaction mechanism made of a set of mass balance equations for the main species involved in the photocatalytic process (see Fig. 2 for the methodological procedure for modeling photocatalytic processes). Afterwards, the mathematical model developed should be employed for analyzing data collected at different experimental conditions. A reliable prediction of the pollutant removal during each photocatalytic experiment considered should be achieved. By using this procedure, the modeling investigation allows to estimate the kinetic parameters not available in the literature review to be employed for a reliable process scale-up.

The estimation of intrinsic kinetic parameters may help evaluate the treatment time needed for the specific oxidation process. Moreover, identifying reaction intermediates and products and evaluating their potential toxicity to ecosystems and human health may allow to develop more accurate reaction pathways and kinetics. It is noteworthy that reaction intermediates and products may exhibit higher toxicity than the original compounds [33]. Therefore, the estimation of proper residence times (RT) and space velocities (SV) within effective treatment facilities should guarantee the transformation of harmful substances in wastewater into species with lower ecotoxicity and environmental impact. In this regard, high values of RT (*i.e.*, between 30 and 100 minutes) have been reported in the literature survey for the complete and safe removal of both microbiological and organic pollutants, in contrast with the lower values (*i.e.*, below 10 minutes) required by established technologies in WW pilot plants, such as ozonation [34].

The high values of RT and SV reported for photocatalytic WW treatments could be related to the following aspects reducing the overall photonic efficiency [34]:

(i) The presence of photocatalytic slurry systems, causing issues in continuous mode operation.
(ii) Reduced diffusional and adsorption rates in heterogeneous photocatalytic systems.
(iii) The intermittent nature of sunlight irradiation decreasing the overall process photoefficiency in the case of solar reactors.
(iv) Limited visible-light absorption and wide band gap of most semiconductor photocatalyst available and commercially viable so far.
(v) Reduced rate of ROS generation for the degradation of organic contaminants and pathogen inactivation.
(vi) A closed contact between contaminant and photocatalyst required for hydroxyl radicals (*i.e.*, with an average lifetime of few nanoseconds) to exert their oxidation process, especially in the presence of pathogens (*e.g.*, bacteria). The contact is diminished in case of supported photocatalysts.

Nevertheless, only few literature data are reported for the required kinetic parameters. Hence, it becomes imperative to formulate thorough reaction mechanisms encompassing the influence of all reacting species, especially those interacting with ROS. Subsequently, rate laws for target contaminants should be derived from these mechanisms.

2.1. Photocatalytic oxidation of organic pollutants in wastewaters

Overall, photocatalytic processes for pollutant removal from wastewater encompass several key stages, which include:

1) Photocatalyst activation through light absorption with proper wavelength and actual use of the absorbed energy for generation of charge carriers (*i.e.,* electrons and holes), as reported in reaction r_1.

$$photocatalyst \longrightarrow^{h\nu} e^- + h^+ \quad (r1)$$

The knowledge of the photon absorption rate is crucial to estimate the reaction rate during the photocatalyst activation step. The photon absorption rate can be regarded as (*i*) a volumetric rate for oxidation processes involving photocatalyst particles in aqueous suspension or (*ii*) a surface rate in case of fixed photocatalysts

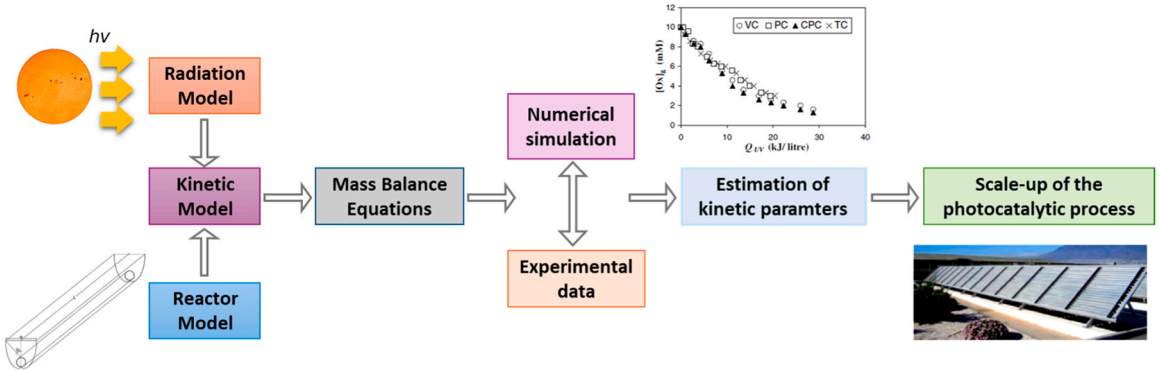

Fig. 2. Methodological procedure for modeling a photocatalytic process.

anchored on proper supports [35]. Estimating the radiation field is needed to evaluate the photon absorption rate, based on proper data on the optical parameters of the system (*i.e.*, actinometric and radiometric measurements for UV-Visible lamps, or measurements of solar radiation) and the incident radiation at the reactor walls (*i.e.*, boundary conditions of the radiation problem). With all this information, it necessary to implement a numerical method to calculate the volumetric or surface rate of photon absorption [35]. Depending on the photocatalytic system employed, the incorporation of the radiation field through the local volumetric or surface rate of photon absorption (*i.e.*, LVRPA or LSRPA) is a crucial modification enabling kinetic models to be universally applicable to reactors of any size and geometry [36,37].

According to a simplified kinetic model for photooxidation processes in batch photoreactors [38], the reaction rate r_1 (*i.e.,* a photochemical step) can be estimated as the sum of product between the quantum yield in the UV (Φ_{UV}) and/or the visible range (Φ_{VIS}) depending on the emission spectrum of the light source and the corresponding irradiation powers absorbed by the solid suspension ($I_{a,UV}, I_{a,VIS}$), divided by the irradiated volume (eq1).

$$\text{reaction rate} = \frac{\Phi_{UV}}{V} I_{a,UV} + \frac{\Phi_{VIS}}{V} I_{a,VIS} \quad \text{(eq1)}$$

2) Immediate separation and transfer of electrons and holes at the liquid-semiconductor junction, where they participate to redox reactions. Indeed, it is well known that photogenerated electrons and positive holes can recombine with release of heath or light:

$$e^- + h^+ \xrightarrow{k_r} \textit{heat and light} \quad \text{(r2)}$$

$$\text{reaction rate}: \quad k_r [h^+] \cdot [e^-] \quad \text{(eq2)}$$

As reported by others [38], reaction r_2 is regulated by a second-order kinetic law in which k_r is the electron/hole recombination reaction constant. The use of proper co-catalysts or proper species in the aqueous suspension capable of promoting electron-hole separation is needed to achieve remarkable process efficiencies.

3) Adsorption of contaminant molecules, reactive oxygen species (ROS), and water on the surface-active sites of the photocatalyst. The presence of surface-active sites with suited distribution allows the occurrence of redox reactions of interest.
4) Trapping of photogenerated charge carriers by proper acceptors. Photogenerated electrons are captured by oxygen (i.e., the primary electron acceptor) or different oxidizing species (i.e., metal ions). On the other hand, photogenerated positive holes are trapped by the adsorbed species, as reported in reactions r3-r4.

$$S + \quad \therefore^* \quad \rightleftarrows \quad S^* \quad \text{(r3)}$$

$$[S^*] = \frac{C_T \cdot K_{ads} \cdot [S]}{(1 + K_{ads} \cdot [S])} \quad \text{(eq3)}$$

$$S^* + h^+ \xrightarrow{k_{h^+}} S_{ox} + H^+ \quad \text{(r4)}$$

$$\text{reaction rate}: \quad k_{h^+} [h^+][S^*] \quad \text{(eq4)}$$

Where:

S is the substrate molecule

$\therefore^*$is an active site on the catalyst surface

S^* is the substrate molecule adsorbed on the catalyst surface

S_{ox} is the oxidation product

As previously reported [38,39], the direct oxidation of substrate molecules (S) by photogenerated positive holes may occur only if these species are strongly adsorbed on the catalyst surface (*i.e.*, reaction r_3). As described for the equilibrium related to r_3, a Langmuir-Hinshelwood (L-H) type adsorption model maybe employed to evaluate the adsorbed species concentration $[S^*]$ (eq_3). K_{ads} is the adsorption equilibrium constant. C_T is the total concentration of active sites on the photocatalyst surface for a certain catalyst load (*i.e.*, q). C_T can be evaluated as the product between q and N (*i.e.*, the total moles of active sites per unit mass of catalyst) [38,39].

According to reaction r_4, the formation of reaction intermediates/products with possible proton release in the aqueous medium occurs in the oxidation process (eq_4). Industrial pollutant levels are typically on the order of ppm, which are low enough for the rate of reaction r_4 to follow a pseudo first-order kinetics. Depending on the operating conditions, the mineralization of substrates to carbon dioxide and water proceeds [40].

5) Attack of ROS on substrate molecules through redox reactions.

The L-H model posits the occurrence of monolayer adsorption on the catalyst surface both in the dark phase before irradiation and during the irradiated phase. However, irradiation can significantly alter the catalyst surface, potentially leading to multilayer adsorption [41,42]. Moreover, multilayer adsorption may also occur for organic concentration higher than 1 mg/L [43]. Adaptations to the conventional L-H model have been suggested to address these limitations [41].

In the kinetic investigation of photocatalytic processes, complexities arise from a variety of factors including light absorption in solid suspensions, non-uniform light intensity, pH, degree of mixing of the fluid, and mass transfer limitations. Moreover, the adoption of volume-averaged quantities in traditional photocatalytic batch reactors for the sake of simplicity could influence the proper evaluation of intrinsic kinetic parameters, potentially compromising their suitability across diverse scales [33].

Another notable limitation of existing kinetic models of photocatalytic processes for wastewater treatment is lack of consideration for real water matrix compounds, despite numerous studies highlight their impact on the rate of photocatalytic contaminant degradation [44,45]. Indeed, components such as organic substances (e.g., humic acid, HA), natural organic matter (NOM), and inorganic ions (Fe^{3+}, Mg^{2+}, Ca^{2+}, SO_4^{2-}, Cl^-, NO_3^-, *etc.*) are also commonly found in real water matrices [46]. These components may exert beneficial or detrimental effects on the photocatalytic removal of contaminants depending on the intrinsic properties of both pollutants and components, making it challenging to estimate kinetic rate constants for contaminant degradation [44].

2.2. Photocatalytic disinfection of wastewaters

Among further kinetic models reported in the literature survey for heterogeneous photocatalytic water disinfection and removal of numerous organic pollutants (*e.g.*, phenolic compounds, dyes, pesticides, aliphatic alcohols, alkanes, carboxylic acids, *etc.*) the Hom (H) and the Chick–Watson (C–W) models, or their empirical modifications, are the most frequently employed [7,47].

Both the H and the C–W models operate on the assumption that the photodisinfection rate (*i.e.*, a linear function in the case of the C–W model) depends on the bacteria concentration and the catalyst load, as reported in equation eq_5.

$$\ln\frac{N}{N_0} = -k \times C^n \times t^m$$
$$n, m = 1 \ (C - W \ model)$$
$$n, m \neq 1 \ (H \ model) \quad \text{(eq5)}$$

with

N = microorganism concentration at generic time t

N_0 = starting microorganism concentration

C = photocatalyst load

n, m= empirical constants
t = treatment time

3. Major design and scale-up considerations for solar photocatalytic reactors

The design and scale-up of a photocatalytic reactor is crucial for successful implementation of photocatalytic technologies, as it enhances the process efficiency and reduces water treatment costs by maximizing solar energy conversion into chemical reactions and/or reducing the amount of electric energy needed to decompose contaminants. The degradation efficiency is dependent on the flow rate, contaminant concentration, solution pH, photocatalyst dosage, and radiation intensity.

Large-scale photocatalytic plant design requires thorough consideration of all these aspects before engineering calculations can be performed. According to Shaghaghi *et al.* [48], for an optimal reaction design, it is important to consider numerous factors, including *(i)* tools like mirrors and reflectors based on dimensions, materials, and cleaning method, *(ii)* photocatalyst, and *(iii)* radiation source-based reactor geometry. Due to reactor complexities such as fluid pumping energy, pressure drop, temperature, tubing materials, and water matrix species, the industry confronts obstacles in designing and building efficient photocatalytic water treatment units. The development of efficient photocatalytic reactors and models [49,50], which incorporate reaction kinetics, hydrodynamics, both mass and radiation transport, enables a prior prediction and optimization of performance [37,51]. In this sense, the mathematical model for solar driven thin-film slurry photocatalytic reactors for water purification developed by Li Puma *et al.* [52] presents a suitable methodology for optimal geometrical design of highly efficient configurations, serving as a tool for design, scale-up, and optimization.

For scaling-up objectives, dimensionless parameters (Re, Da, τ, ω) are hence highly recommended. Specifically, low scattering albedo (ω) values correspond to simpler scaling-up processes, whereas more complex mathematical models are required for more complex processes [53]. Advances in modelling have developed pilot-scale and full-scale photocatalytic reactor designs for water treatment.

In light of this, several reactor configurations can be obtained based on need and purpose, that can be classified in different ways, such as batch or continuous, the radiation source (UV or visible, solar, or artificial), catalyst form (suspended or immobilized), as well as the hydrodynamic regime (CSTR or PFR), as reported in different review articles [48,54–62].

Continuous reactors are the most suitable for large-scale industrial applications, due to the large volume involved, with CSTR and PFR reactors representing the two extremes of these systems. The perfect flow mixing and the possibility to control the feed concentration and the flow rate are the main advantages of the CSTR, while the choice of the length of the cylindrical tube in PFR is crucial to improve the efficiency of the process. When the number of CSTR in series is high enough, it can be assimilated to PFR system, in which a single CSTR represents a section of a PFR [63]. Hence, in the reaction design, the number of reactors placed in series, the volume/unit and the total volume utilized can significantly affect the performance. However, some challenges still restrict their utilization in industrial application (*i.e.,* photodegradation efficiency, reduction in active sites of a catalyst, economic feasibility, and catalyst recovery). Binjhade *et al.* [55] described the evolution of continuous photocatalytic reactors from the first examples to the most recent technologies, focusing the attention on the parameters affecting the cost and the efficiency of the processes. Among them, the critical evaluation of the mass transfer resistance and the assessment of the long-term performance of the coated photocatalysts resulted the most useful to study the reactor efficiency. Hence, mass transfer strongly affects the efficiency of the photocatalytic process and should be considered in the reactor design. These characteristics differs for suspended and immobilized photo-catalytic reactors. Despite suspended catalyst forms tend to be more reactive than immobilized catalyst, immobilized photocatalytic reactors are easier to use in industrial applications [64,65]. The limitations met in immobilized photocatalytic reactors can be overcame by the appropriately design, thus resulting in a similar efficiency to that obtained with the suspended photocatalytic reactor, as reported by Adams *et al.* [66]: they proposed a titania **immobilized thin film tubular photoreactor** in which the configuration was able to maintain the pollutant constantly in contact with a coated surface. When the reaction vessel volume was 250 mL, 92 tubes (260 mm length) were used, observing a degradation efficiency higher than 90% after 90 min of irradiation. In this context, some other authors [67] have proposed the use of micron-sized powder photocatalysts with sonication every 30 minutes to reduce the loss of the photocatalyst in the continuous reactor: the use of a CSTR system with dispersed catalyst resulted advantageous to develop a continuous operation photocatalytic reactor. Along with mass transfer, photon transfer should be critically evaluated during the reactor design. The light source hence represents another key point for the large-scale implementation: solar versus artificial light based-photoreactors remains a contentious issue in the context of large-scale implementation [68]. Solar collectors/concentrators represent the main component of a solar photocatalytic reactor, and for this reason they are the starting points in the design of the solar based reactors. Among the solar-driven reactors, common pilot-scale configurations include **parabolic trough reactor** (PTR), **flat plate reactor** (FPR) and **compound parabolic collector** (CPC), the latter representing most popular due to its efficient solar radiation capture, effective water treatment, reduced dependence on weather conditions, and negligible overheating [62,69].

To overcome some commercial limitations of CPCs, such as the low treatment volumes and difficulty scaling up to large bore diameters due to pipe fragility and larger-size end connections, some authors [70] proposed a new prototype, the **offset multi-tubular solar photoreactor** (OMTP). With a flowrate of 24 L/min, 4-chlorophenol (120 ppm) photodegradation efficiency was about 242% higher than the CPC after accumulating 8000 J/m^2 of solar energy, thus demonstrating the greater potential of this photocatalytic reactor design. The OMTP exhibits several advantages over the CPC, including an increased total treatment capacity, an extended residence time for wastewater and a simplified reactor scale-up process. The slow kinetics and light intensity variation associated to solar photoreactors, led to the development of lamp-based artificial illumination solutions to overcome these challenges [71]: the **classical annular reactor** is a typical example, despite its use is limited due to the lack of agitation, the difficult catalyst recovery, and the hard reaction media illumination. **Multi-tube photoreactors** or TiO_2-coated **optical fiber photoreactors** are useful to improve the light illumination but have high electricity costs and large area requirements [72]. Hence, due to their energy-efficient light--emission, **LED photocatalytic reactors** are proposed as an alternative to overcome the above-mentioned issues. Very recently some authors [73] proposed a novel photoreactor with luminous textile coupled to UV-A LED (5 W/m^2) for the photodegradation of Paracetamol under different operating conditions. Compared with an existing technology (i.e., immobilized TiO_2 with external UV irradiation), the photodegradation rate resulted about 40 times higher, with a mineralization efficiency per Watt about 80-fold higher. The impressive performances of luminous textiles make them an attractive alternative to conventional reactors. In recent years, **integrated membrane photocatalytic reactors** have been proposed as possible technologies to the specific surface area of the reaction medium under illumination, with both the immobilized and suspended photocatalyst [74–77]. These reactors offer good stability, controllability, and efficiency, and involve the separation of the photocatalyst from the reaction medium; this feature helps to reduce the energy consumption of the photocatalytic process, eliminating the additional operations necessary to remove and recover the photocatalyst from the system [75,78]. In Fig. 3, some of the

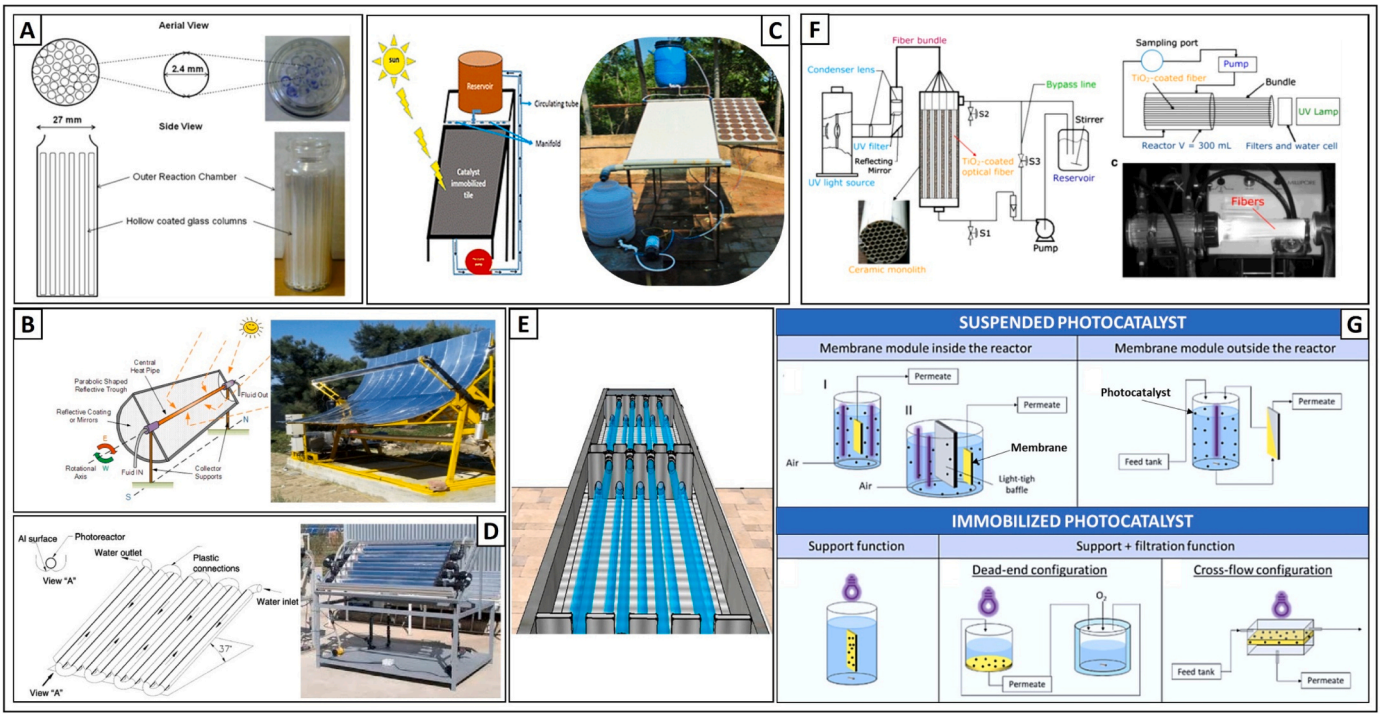

Fig. 3. (A) Immobilized thin film tubular photoreactor, reproduced with permission of ref [66]; (B) Parabolic trough reactor, reproduced with permission of ref [79]; (C) Flat plate reactor, reproduced with permission of ref [80]. (D) Compound parabolic collector, reproduced with permission of ref [81]. (E) Offset multi-tubular solar photoreactor, reproduced with permission of ref [70]. (F) Optical fiber photoreactors, reproduced with permission of ref [82]. (G) Membrane photocatalytic reactors, reproduced with permission of ref [76].

above-mentioned reactor configurations are reported.

4. Effective photocatalytic materials for solar-driven water purification

Designing effective photocatalytic materials presents its own set of challenges. The fabrication process requires the development of non-toxic, cost-effective semiconductor materials capable of absorbing a broad range of the solar spectrum. Fundamentally, the availability and production of ROS is key for the efficient photocatalytic reactions. Additionally, the kinetics of the reaction must remain unaffected by the overall recombination rate. While these characteristics seem reasonable, achieving a combination of all these features is a complex task. In this section we discuss some of the conventionally used semiconductor nanomaterials and their composites used for solar driven water purification. Semiconductor nanomaterials such as TiO_2 and ZnO are the commonly used wide band gap semiconductors used for several industrial applications for the last 50 years. However, when it comes to large scale photocatalytic reactor systems, it remains a challenge. Commercial scale production of these materials is not the restriction but efficiently driving the photocatalytic reaction pathways for the AOP has been the primary task. Photogenerated electron hole pairs in these wide gap semiconductors have two options; *i)* recombine and generate energy in form of heat (10^{-12} s) and *ii)* electron generated gets trapped on the surface and thus available for creation of ROS[83]. Hence, delaying the recombination and trapping the electrons for ROS creation exists as the primary task. Moreover, considering the kinetics point of view between these options, latter is an extremely slow process and hence overall limiting the overall efficiency of the photocatalytic reaction[84].

In the realm of photocatalytic water purification, understanding the intricate mechanisms governing reactive oxygen species (ROS) formation and utilization is paramount. These ROS, including superoxide radicals ($O_2^{\bullet-}$), holes (h^+), electrons (e^-), hydroxyl radicals ($^{\bullet}OH$), and hydrogen peroxide (H_2O_2), play pivotal roles in driving photocatalytic reactions towards efficient pollutant degradation. Superoxide radicals ($O_2^{\bullet-}$) are key intermediates in photocatalytic pathways, formed through the reduction of oxygen molecules by photogenerated electrons. Studies have shown that $O_2^{\bullet-}$ can further react with water to produce hydroperoxyl radicals ($HO_2^{\bullet}$), which are potent oxidants capable of degrading organic pollutants[85,86]. Additionally, the interaction of $O_2^{\bullet-}$ with hydroxyl radicals ($^{\bullet}OH$) can lead to the generation of more reactive species such as hydroperoxyl radicals ($^{\bullet}OOH$) and perhydroxyl radicals ($HO_3^{\bullet}$), amplifying the oxidation potential of the photocatalytic system [87]. Holes (h+) generated in semiconductor photocatalysts act as strong oxidizing agents, initiating oxidation reactions with water molecules to produce hydroxyl radicals ($^{\bullet}OH$)[88]. Hydroxyl radicals are highly reactive species known for their capability to oxidize a wide range of organic pollutants present in wastewater. Furthermore, the photogenerated electrons (e^-) can become trapped on the semiconductor surface, where they participate in redox reactions with adsorbed oxygen species to produce additional ROS, such as hydrogen peroxide (H_2O_2)[89].

Recent advancements in photocatalytic research have focused on enhancing ROS generation and utilization to improve the efficiency of pollutant degradation. Studies by Gao *et al.* [90]and Etacheri *et al.* [91] (2021) have demonstrated the effectiveness of surface modification techniques, such as doping and plasmonic nanoparticle deposition, in enhancing ROS generation and extending their lifetime. Additionally, research by Li *et al.* [92] and Zhao *et al.* [93] has explored the synergistic effects of combining semiconductor nanomaterials with cocatalysts to promote ROS-mediated photocatalytic reactions. Hence, the formation and utilization of reactive oxygen species play a crucial role in driving photocatalytic pathways for water purification. Understanding the mechanisms underlying ROS generation and optimizing photocatalyst properties to enhance ROS-mediated reactions are essential steps towards achieving efficient and sustainable wastewater treatment solutions.

4.1. TiO_2 based photocatalysts

TiO_2, commonly known as titania, is a widely recognized photocatalyst with applications in various degradation and disinfection reactions. It exists in two primary forms: anatase and rutile, with anatase being the photocatalytically active phase. The differences in the photocatalytic nature of these two phases are well-explained by Luttrell *et al.* [94]. The anatase phase of titania possesses a wide band gap absorption, allowing it to absorb the UV region of the solar spectrum. This characteristic leads to the generation of different types of ROS, which play a crucial role in various disinfection and water decontamination reactions. Some of the surface characteristics such as the presence of defects and availability of molecular coordination sites for binding as well as the indirect band gap of the anatase phase could be some of the factors favoring titania. Moreover, the ease of synthesis, cost-effectiveness, average surface area, and non-corrosive nature make anatase-phase titania an ideal material for incorporation into reactors for large-scale commercial applications.

There are several examples of the use of titania-based composite for air purification solutions, coatings for self-cleaning and antifogging applications as well. However, in this section we focus our attention on real world applications for water purification. In one of the early reports of membrane derived prototypes which integrated both ultrafiltration and light-based catalysis using titania coated membranes displayed promising results. A titania sol was used to prepare a coating on the membrane using a dip coating technique. The degradation and filtration of methylene blue and methyl orange were tested to evaluate the effectiveness of the prototype and it was found to be quite effective. The use of both UV and visible light source was efficient and found to be interesting as the inner coating on the surface of the membrane provides better degradation response because of the higher mass/volume value [95]. In another recent study, authors studied the influence of integrating photocatalytic nanomaterials into the membrane to evaluate the removal of humic acid in water. The TiO_2@MIL-88A (Fe) photocatalysts was integrated into polyacrylonitrile membrane (Fig. 4 **(d)**). As the loading of the catalyst increased from 0% to 6%, the hydrophilicity and anti-fouling properties of the membrane improved. The 6% sample of the photocatalytic membrane reactor displayed the best humic acid removal of 79% in 2 hours in slurry state. While the membrane of the same composition displayed a high rejection rate of humic acid when tested for a 10 hour long run at 2 bar pressure. The combined feature of hydrophilicity, visible light induced catalysis are the factors to promote anti-fouling properties and effective water remediation observed in this study [96]. Another report of membrane derived methylene blue degradation was reported by Zhang *et al.* A hollow glass fiber-based membrane was fabricated using TiO_2 coating to create asymmetric pore structure. The titania sol was used to dip coat on the surface of the glass hollow structure and further calcinated at 550 °C. The single layer coated membrane displayed 97.2% of methylene blue degradation and the coating was uniform all across with no evident cracks in the structure. The membrane was used for multiple rounds of cyclic study, and it displayed above 90% removal rate and thus demonstrating the extended stability and the effective removal of the dye pollutant [97].

A pilot scale novel photocatalytic nanofiltration reactor was designed for agricultural wastewater remediation. The pilot reactor unit has 12 ceramic membrane monoliths, seven channeled photocatalytic nanofiltration monoliths fabricated using wash coating method. The monoliths are embedded in titania nanoparticles in 240 PVDF hollow fibers. The filtration reactor had photocatalytic surface both the sides of the shells. The reactor was illuminated with a UV-LED high power chip module and UV sleeved lamps along with some optical fibers on the side of the reactor unit. Overall, the system displayed effective photocatalytic efficacy for the removal of organic effluents. The PVDF-titania hollow fibers effectively had a 1.2 m3/day water production capacity. Moreover, 41.5% removal of thiabendazole, a common fungicide was observed after 2 hours. Cyclic studies revealed about 95% efficacy after cyclic recycling and treatment [99]. Another attempt to fabricate a pilot scale reactor using titania nanoparticles was reported by Yu *et al.* [98]. The reactor consists of a pipe composed of a helical structured support which is initially dip coated with SiO2 nanoparticles. Later the helical structure is spray coated with titania (P25) nanoparticles. The helical structure is placed inside an annular reactor with a UV lamp in the middle (as shown in Fig. 4**(a, b, c)**). The photocatalytic efficacy of the system was measured by the disinfection trials of E. coli strains. The reactor was tested for a high number of bacterial colonies and in all the different levels, the light based photocatalyst driven water samples showed the best results. The colonies were also measured after 96 hrs of incubation to measure the reproducibility nature of the bacterial colonies. Photocatalytic disinfection is key along with cease their re-activation. In another attempt to fabricate a filter for water remediation, Horváth *et al.* fabricated a filter with a composite material of TiO2 and CNT. Immobilized titania nanoparticles as a form of coating often lead to cracks and thus integrating with CNT provides prevents from possible mechanical failure. The membrane is coated with the composite

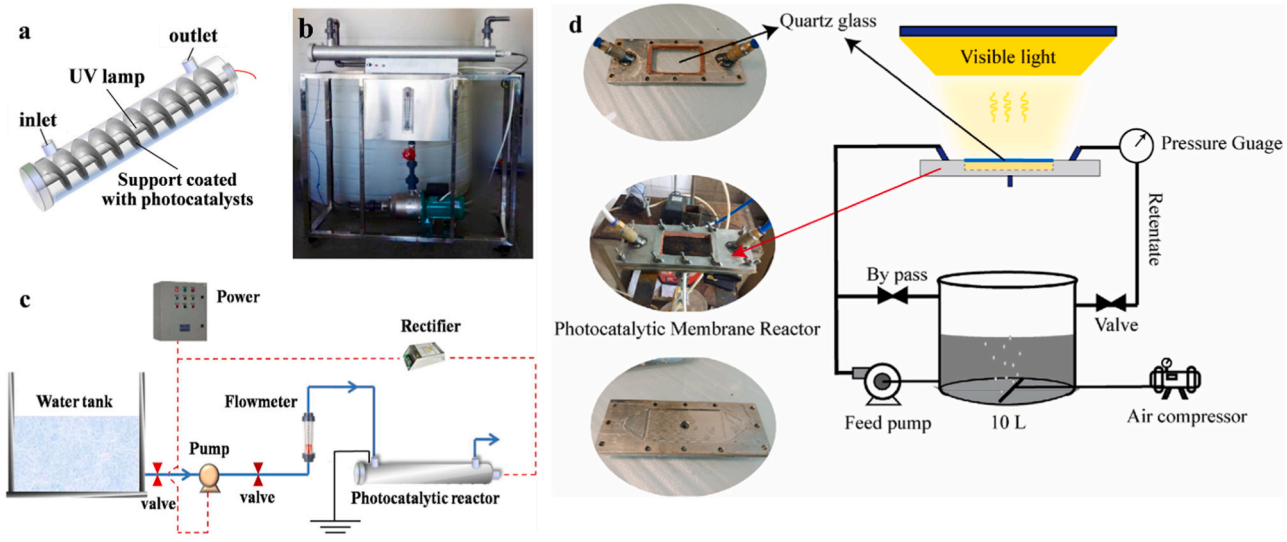

Fig. 4. (a) Picture displaying the helical support in photocatalytic reactor, (b) picture of the pilot-scale photocatalytic reactor, (c) Flow diagram elaborating on the process; reproduced with permission of ref [98] and (d) Schematic illustration of the photocatalytic reactor as explained in ref [96]. Reproduced with permission of ref [96].

structure using doctor blade. A mixture of 9 different effluents and bacterial strains were used to test the efficacy of the filter. The water was pumped in from one end and the nanoporous nature of the composite structure enabled to retain the microbial strains. On the other hand, the ROS generated within the system enables degrading the rest of the effluents. The CNT in the composite structure enables absorbing wide range of spectral region and aids in delaying the recombination. The effluent sample was pumped several times across the filter and the concentration of some such as gabapentin and metformin were observed to lower down by 25%. However, their concentration increased again because of thermal desorption and subsequently decreased later on. The shorter contact time is attributed to the alteration in the concentration values. The river water samples were also analyzed. The bacterial strains within these samples were mechanically held and inactivated completely by photocatalysis. The authors found that UV based degradation rate was higher compared to visible light induced activity and stressed upon the scale up process by increasing the area of the filter [100]. The aforementioned studies showcase the efficient utilization of titania-based composites in diverse reactor designs and setups. The facile commercial synthesis, coupled with the capacity to coat various structures and anneal samples at high temperatures (up to 650 °C), renders titania an exceptionally coveted photocatalytic material.

4.2. ZnO based photocatalysts

Zinc oxide, an *n*-type semiconductor with a wide band gap of 3.37 eV, has demonstrated excellent photocatalytic applications over the past two decades. However, the wide band gap presents certain constraints, including a low absorption of a narrow band of UV from the solar spectrum. Despite this, the low toxicity of the nanomaterial adds an advantage for various applications. ZnO can be synthesized using readily available precursor materials and can be easily scaled up for commercial applications.

ZnO is not the most obvious or common choice of material for commercial reactor units, unlike its counterpart titania with similar features. Photocorrosion and stability of the catalyst are some of the disadvantages to list. However, structural modifications and heterostructure development are some of the methods that have been opted by researchers to improve stability and photocatalytic efficiency. In an attempt to design photoreactors for commercial applications, there have been several studies highlighting the use of ZnO to develop small scale reactor units. In such study, the authors synthesized ZnO hydrothermally and later developed coating on surface of a stone. A pump with a flow rate of 1 mL/s and a rectangular prism are some of the basic units of the reactor. The light source for the reactor is three low pressure UV-C lamps (three, 6 W lamps) placed at the top of the reactor. The reactor

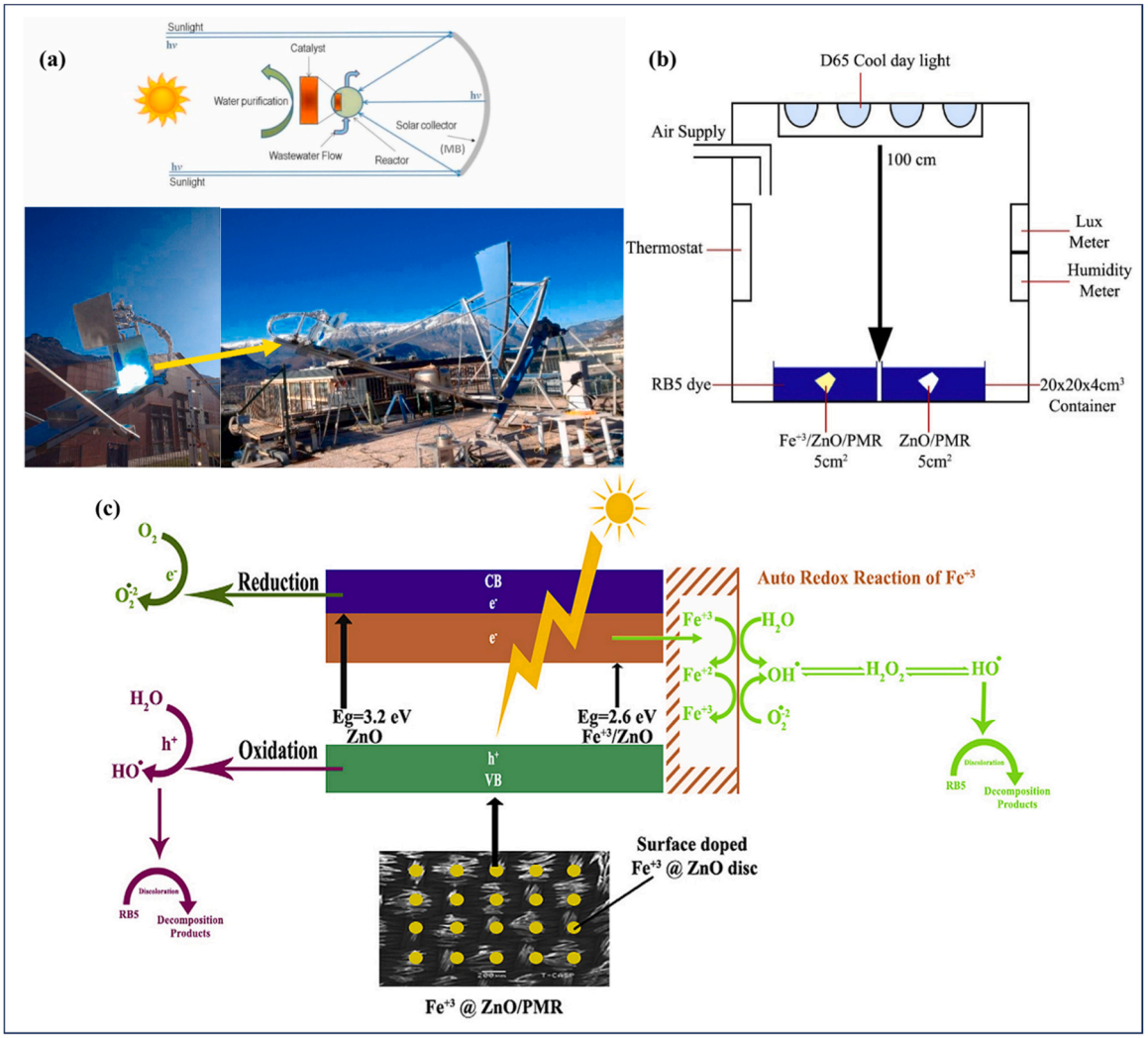

Fig. 5. (a) Schematic illustration of a working scheme of solar photoreactor and solar concentrator unit as shown in ref[103]; reproduced with permission of ref [103] (b) Schematic illustration of a working scheme of photoreactor integrated with Fe^{3+} doped ZnO photocatalytic polymer membrane (PMR) and (c) Schematic illustration displaying a photocatalytic degradation pathway as shown in [104]. Reproduced with permission of [104].

setup was used to analyze the degradation efficiency of *p*-nitroaniline. The catalyst loading was kept at 1 g/L and was observed to achieve 94% of degradation efficacy within less than 2 hours of exposure [101]. In a similar attempt, the researchers tried to use a hybrid process of UV based photocatalysis and catalytic ozonation based advanced oxidation process. A modal dye (Acid Red 18) was used to study the efficacy of the reactor unit. A catalyst dosage of 3 g/L and dye concentration of 25 mg/L was found to provide a degradation efficacy of 97% within 40 minutes of exposure. These hybrid methods are promising as they are some of the techniques that could be used for industrial applications [102]. In a separate investigation, researchers explored the concept of a reactor incorporating a parabolic dish solar collector to capture and utilize solar energy. The reactor featured an immobilized structure of ZnO coating applied to glass using two distinct techniques (see Fig. 5a). In one approach, ZnO nanorods were synthesized through a green synthesis technique, while the other method involved depositing a 135 nm thin film of ZnO using pulsed laser deposition. The effectiveness of these methods was assessed through the degradation of methylene blue dye. In just 2 hours of concentrated sunlight exposure, 55% of the dye degraded. However, this figure significantly increased to 94% when immobilized ZnO coatings were introduced. Additionally, a comprehensive economic analysis by the researchers revealed that the most cost-effective approach is the combined use of concentrated sunlight exposure and immobilized coatings of ZnO nanorods synthesized through a green route. This presents opportunities for large-scale applications [103].

Cost estimation plays a crucial role in the narrative of any commercialization process. Mirzaie *et al.* conducted a study on the degradation efficiency of fluoride doped ZnO for sulfamethoxazole degradation. In this research, the authors outlined key strategies to reduce overall energy consumption. Firstly, they emphasized the importance of reducing the rate of recombination of charge carriers by incorporating dopants and forming heterostructures. Secondly, enhancing the hydrophobicity of the photocatalyst surface was identified as a means to improve the rate of hydroxyl radical generation, which is essential for the oxidation reactions of pollutants. Thirdly, based on their study, the authors recommended a narrow cylindrical structure for the photoreactor design. This design facilitated the concentration of emitted radiation, thereby improving the overall quantum yield [105]. Considering these factors, the present review underscores similar studies in the previous section that demonstrated the effectiveness of photocatalysts, including doped and undoped, as well as mobilized or immobilized photocatalysts within a reactor. In a related context, Ashar *et al.* reported the fabrication of iron doped ZnO grown on polyester fabric. The hydrothermally grown photocatalyst on the fabric material was further employed in membrane reactors (Fig. 5**b**). The introduction of Fe^{3+} in ZnO decreased the wide band gap of the ZnO from 3.2 eV to 2.6 eV. The photocatalytic efficiency of the membrane reactor was studied for RB5 dye illuminated by artificial solar light. The doped sample exhibited increased efficacy from 88.9% to 98.34% compared to the undoped samples within 3 hours of exposure (Fig. 5**c**). The cyclic study of the doped samples was conducted using the same recycled catalyst sample, revealing a gradual decline in the degradation efficacy after the 8th cyclic run [104].

4.3. Graphene and graphene based photocatalysts

The revolution in graphene and graphene-like nanomaterials has shown significant potential. Graphene, one of the most interesting nanomaterials, has revolutionized various fields such as electronics, photonics, and biomedical engineering [106]. These nanomaterials, with their unique features like increased surface area, high thermal and electrical conductivity, and the ability to absorb a broad range of visible light, make them intriguing candidates for photocatalytic applications. However, their narrow band gap and high recombination rate present challenges that need to be addressed. Similarly, graphitic carbon nitride ($g\text{-}C_3N_4$), another graphene analogue with a mid-band gap level of 2.7 eV, has shown promising applications across different fields [107–109]. Its increased visible light absorption and ease of synthesis using cheaper precursors, such as melamine, make this semiconductor nanomaterial extremely desirable for various photocatalytic applications[8,110]. However, like other semiconductor nanomaterials, it also suffers from recombination and a poor charge transport rate.

Immobilization of photocatalytic membrane to improve the overall disinfection process has been discussed in previous sections. In this section, an overview of the different examples of integration of graphene and graphene based photocatalysts is discussed. Incorporation of photocatalyst embedded membrane aids in both filtration as well as in the photocatalytic disinfection process as well.

The use of cellulose based membranes has been tried out commonly as a greener alternative to other non-disposable polymeric substrates. A composite of graphitic carbon nitride and reduced graphene oxide ($g\text{-}C_3N_4$/rGO) was integrated in a cellulose membrane. The importance of heterostructure creation has been discussed thoroughly in multiple studies. Therefore, here the focus has been aimed towards the applications of such membranes. These membranes were used to eliminate Bisphenol-A (10 mg/L), Rhodamine B (5 mg/L), Methylene Blue (16 mg/L), Sudan orange (10.7 mg/L) and also studied for the inactivation of *E. coli* strains. The membrane displayed almost complete inactivation of the bacterial strains and 100% removal of the dye molecules with BPA removal of 22%. The membrane was also assessed for real water samples and was observed to remove turbidity (84%) and bacterial inactivation (97%) through a combination of filtration and photocatalytic treatment. This membrane displayed an effective removal of organic effluents as well [111]. In another study, the authors reported the fabrication of a phosphorus doped $g\text{-}C_3N_4$ on a hollow Al_2O_3 photocatalytic membrane reactor (as shown in Fig. 6a). The phosphorous gets doped at various carbon vacancies created across the graphitic sheet. Incorporation of these doped atoms lowers the overall band gap and improves the photocatalytic efficiency by reduced recombination rate. A mixture solution of phenol, methylene blue and rhodamine B was prepared and used as a modal pollutant solution to test the efficacy of the membrane reactor. The overall total organic carbon (TOC) content is removed up to 92% and methylene blue content displayed a reduction of 94%, even after 4 cyclic runs [112].

In another heterostructure creation titania nanoparticles were incorporated within 2D heterostructure of graphitic carbon nitride and graphene oxide membrane. The titanium nanoparticle and carbon nitride composite were introduced between GO nanosheets using vacuum assisted self-assembly method. The increased pore size between the sheets displayed and increased permeation flux for oil/water separation to 4536 $Lm^{-2}\ h^{-1}\ bar^{-1}$. This value is about 40-fold increase of GO membranes at 101 $Lm^{-2}\ h^{-1}\ bar^{-1}$. The adsorption of oil particles on the surface of the membrane results in fouling. To improve the efficacy of the membranes for multiple cycles, the self-cleaning ability of the photocatalytic membrane was exploited. This resulted in a flux recovery ratio of 95% even after 10 cyclic runs [113].

In another study, dopamine modified graphene oxide sheets were synthesized. The insertion of dopamine results in formation of Poly dopamine which results in formation of reduced graphene oxide sheets. The presence of Poly dopamine increases the rate of photo induced electron transfer. Further composite of graphitic carbon nitride was formed on the surface of cellulose acetate sheets. This membrane developed exhibited increased efficacy of continuous flow through of oil/water emulsion and simultaneous degradation of organic dye molecules. Fig. 6b displays the schematic representation of oil/water separation under photocatalytic degradation using the composite membrane. The increase in $g\text{-}C_3N_4$ within the composite resulted in enhanced filtration and degradation efficacy [114]. Another study Venkatesh *et al.* reported the fabrication of rGO/$g\text{-}C_3N_4$/TiO_2 nanofibers on PVDF membrane. Fabricated membranes were studied for the separation off motor oil, cooking oil, hydrocarbon oil toluene in water

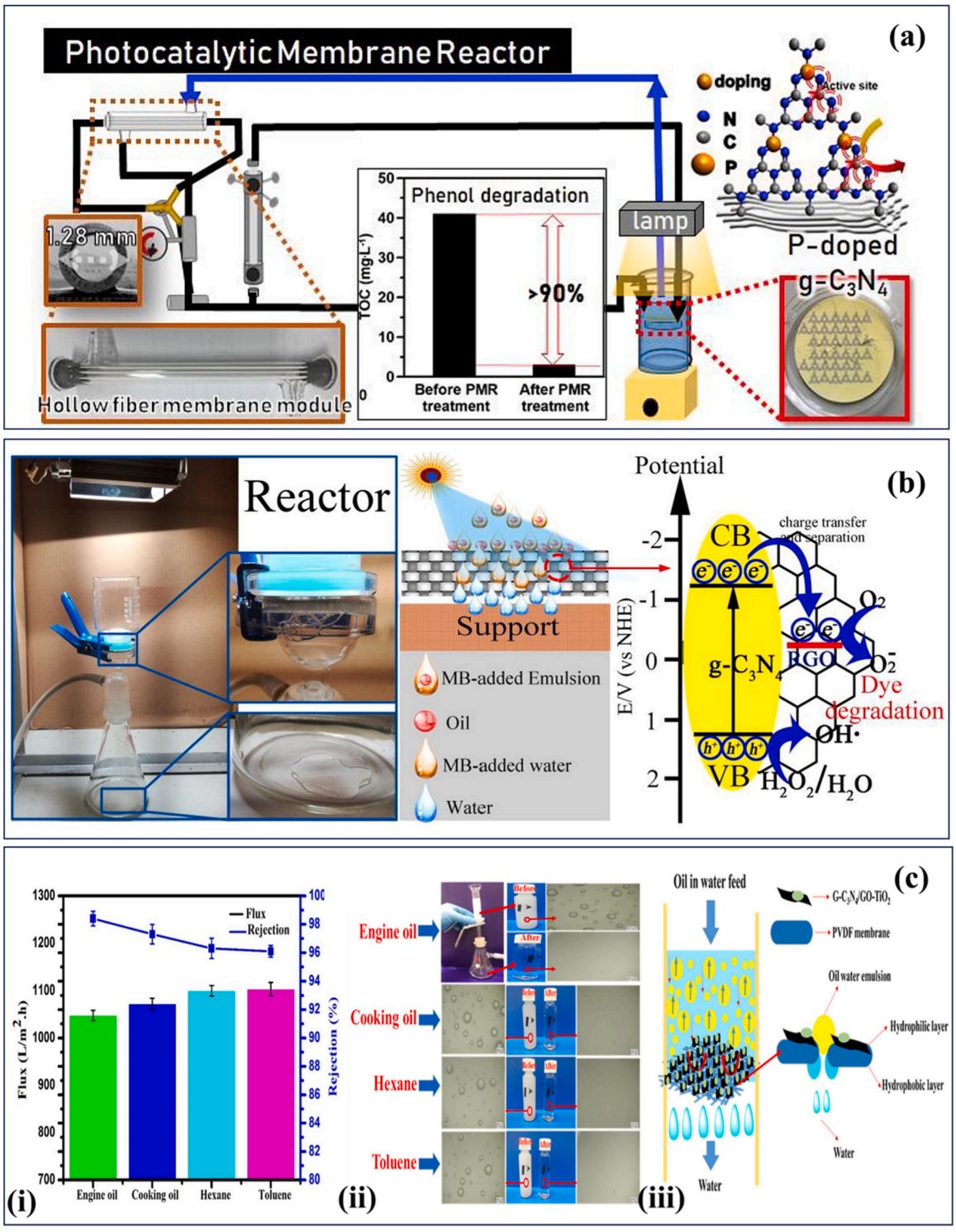

Fig. 6. (a) Graphic illustration of the photocatalytic membrane reactor system incorporating an inorganic Al_2O_3 hollow fiber membrane module and PCN@S. Reproduced with permission of [112]; (b) Visual representation of the process involving oil/water separation and photocatalytic degradation within the composite membrane. Reproduced with permission of [114]; (c) (i) Investigation of water flux and rejection using the 50 mg/L G rGO/g-C_3N_4/TiO_2 nanofibers on PVDF surface membrane for oil/water mixtures containing engine oil, cooking oil, hexane, and toluene. (ii) Optical microscopy images depicting the conditions before and after filtration of engine oil, cooking oil, hexane, and toluene. (iii) Schematic representation illustrating the filtration mechanism for oil-water separation in the hybrid membrane. Reproduced with permission of [115].

sample. As displayed in Fig. 6c, the hybrid membrane displayed increased permeability and improved rejection efficacy compared to pristine PVDF membrane[115].

5. Challenges to commercialization of photocatalytic wastewater treatment

5.1. Assessment of the Readiness Level

While using photocatalysis as an environmental cleanup approach for wastewater offers numerous inherent advantages over existing strategies, achieving viable commercialization and widespread adoption of this technology has proven elusive. Typically, researchers tend to highlight technical success of photocatalytic water treatment at bench scale without considering economic feasibility.

As previously reported[116], the readiness assessment of a technology comprises four dimensions: Technology Readiness Level (TRL), Manufacturing Readiness Level (MRL), Commercial Readiness Level (CRL), and Business Readiness Level (BRL). TRL assesses technology advancement across nine levels, from concept generation to real-world application (Fig. 8). Each level signifies different stages of technological development, from initial study to product delivery. The MRL was developed by the United States Department of Defense and evaluates manufacturing readiness and system risks. It complements TRL and ranges from prototype stability to ongoing improvement of the manufacturing process. The CRL gauges marketing efforts and product introduction to target markets. It involves the development of marketing strategies and assessing market opportunities. CRL is linked with MRL and ranges from hypothetical commercial propositions to business growth. The BRL evaluates management efforts, including business model development, capital acquisition, and team management. BRL aligns with CRL and spans from upscaling processes to sustainable growth and industry leadership.

The use of photocatalysis for wastewater treatment is stuck on a "technological research" level, that is a TRL between 2 and 6, as shown in Fig. 7. The major drawbacks still include (i) high costs of the process, (ii) technical issues limitations, (iii) missing regulation for the release of contaminants of emerging concern (CECs) into the environment, and (iv) reduced overall process efficiencies if compared with consolidated treatment technologies for municipal and industrial wastewater [117].

Fundamentally to advance photocatalytic reactor systems to commercially viable scale for water remediation there are several sets of challenges. Understanding the TRL is key to accessing the challenges across these levels and essentially progressing to higher levels. The existing reactor systems for water remediation have been developed up to TRL 6. Although there exist photocatalytic applications such as self-cleaning which is already deployed at industrial scale (TRL 9) as shown in Fig. 8. At lower TRL systems, the laboratory-scale prototypes face challenges under controlled conditions to validate their efficacy in treating wastewater. This involves assessing factors such as pollutant removal efficiency, reactor stability, and lifespan of photocatalytic materials. For instance, reviews by Mei *et al.* [15] and Skillen *et al.* [118] have summarized the importance of optimizing reactor parameters, such as flow rates and catalyst loading, to maximize treatment efficiency while minimizing energy consumption. Furthermore, investigations have emphasized the significance of reactor design modifications, such as enhancing light penetration and increasing surface area-to-volume ratios, to improve photocatalytic performance and reactor stability [119,120]. These studies highlight the importance of incorporating advanced materials and engineering techniques to enhance the functionality and reliability of photocatalytic reactor systems. Subsequently, scaling up the reactor design to pilot-scale units allows for testing under more realistic operating conditions, providing valuable insights into system performance and durability over extended periods. During this phase, optimization of reactor parameters, such as flow rates, residence times, and catalyst loading, is crucial to maximizing treatment efficiency while minimizing energy consumption and operational costs. Additionally, incorporating advanced monitoring and control systems enables real-time tracking of key performance indicators, facilitating adjustments to optimize system performance. Furthermore, collaboration with industry partners and stakeholders is essential to ensure the integration of photocatalytic wastewater treatment systems into existing infrastructure and regulatory frameworks. This involves conducting feasibility studies, cost-benefit analyses, and environmental impact assessments to demonstrate the viability and sustainability of the technology.

As above mentioned, the main technical challenge associated with using photocatalysis for water treatment is the slow kinetics, leading to large energy demand. In simpler terms, while it is frequently reported that photocatalysis effectively degrades a compound, it is crucial to note that a considerable amount of energy per molecule destroyed is often necessary. Furthermore, major technological limitations such as low quantum yields, slow overall reaction rates if the catalyst is supported, low-order dependence of reaction rates upon radiation intensity,

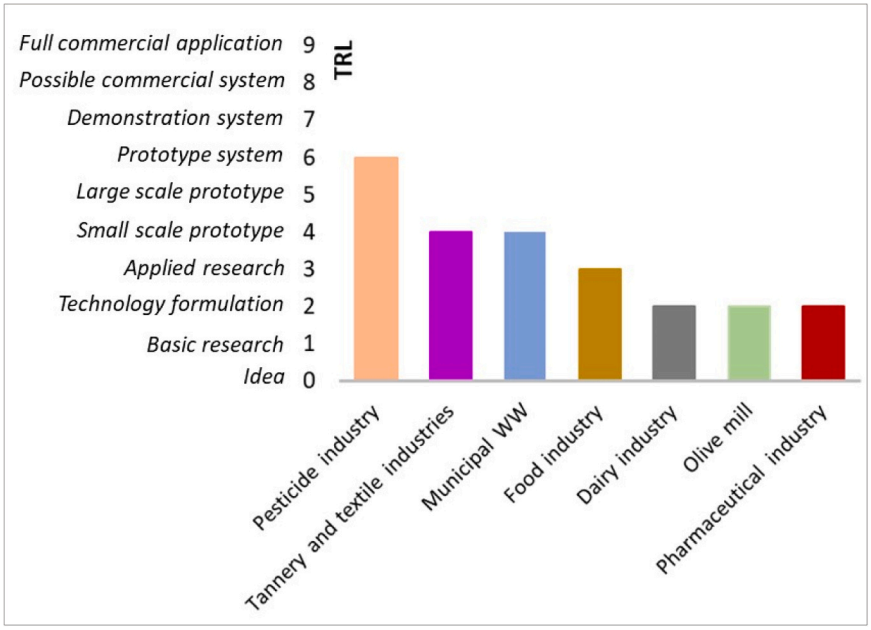

Fig. 7. TRL of photocatalytic processes applied to different industrial effluents and municipal wastewater.

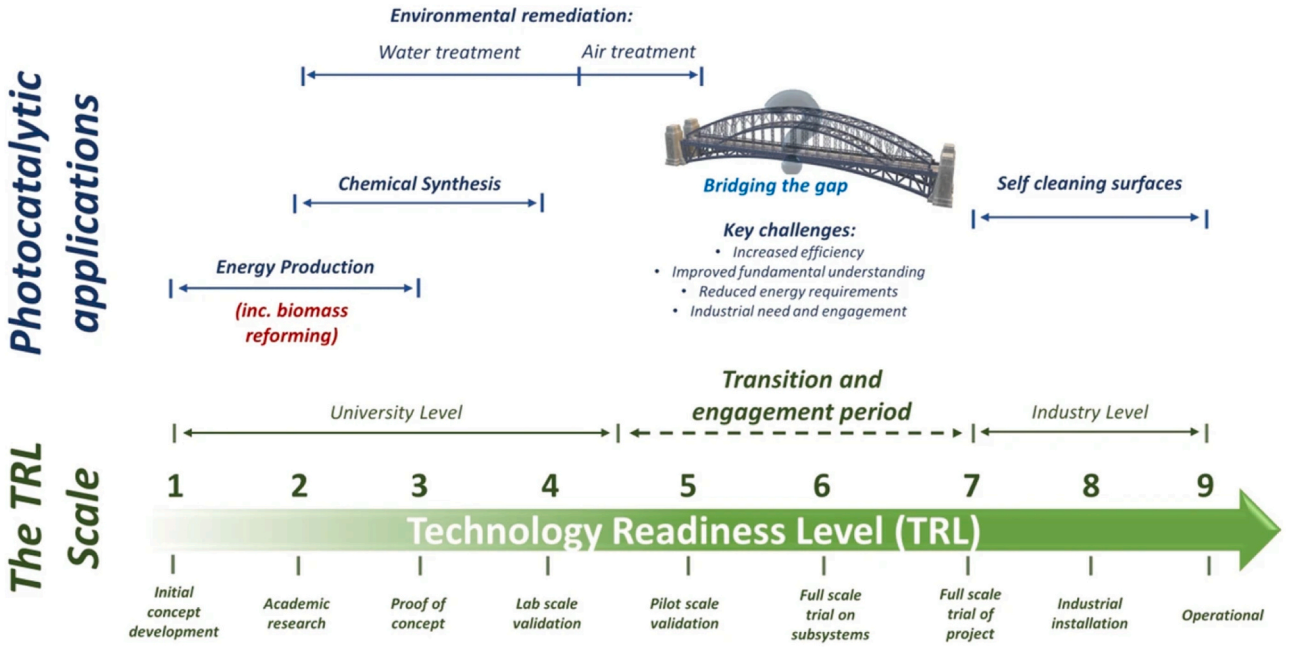

Fig. 8. Summarized glance of the TRL scale for photocatalytic applications. Reproduced with permission of [118].

photocatalyst fouling and poisoning, difficult photocatalyst reuse in slurries, possible photocatalyst toxicity in water, the intermittent nature of solar energy due to diurnal and annual cycles, are regarded as some of the possible drawbacks hindering the efficiency of photocatalytic wastewater treatment at large scale [34]. Additionally, the effectiveness of photocatalysis for wastewater treatment can be significantly influenced by the composition of the aqueous matrix, as above reported. The presence of total suspended solids (TSS) and various soluble substances in wastewater contributes to a decrease in light transmittance due to absorption, reflection, and scattering, thus requiring pre- or post-treatment measures [117].

According to exhaustive review papers recently appeared in the literature survey [10], nearly 40% of studies published in the field of photocatalytic wastewater treatment since 2010 focus on the purification and detoxification of municipal wastewater (MWW) effluents. Despite photocatalysis is reported to be effective for degrading CECs and inactivating pathogens in secondary treated MWW, it is not competitive with established technologies (*e.g.*, ozonation) due to the above reported technical disadvantages [121,122]. Thus, as reported in Fig. 7, photocatalytic treatment of MWW still exhibits a TRL of 4.

Even if future research advancements successfully overcome these technological limitations, the lack of specific regulations worldwide governing the release of CECs into the environment acts as a deterrent for to the substitution of conventional tertiary treatments (*i.e.,* disinfection through peracetic, chlorine, or UV radiation) with alternative expensive processes such as photocatalysis.

The remaining 60% of studies focusing on the photocatalytic treatment of real wastewaters since 2010 were performed on industrial wastewaters survey [10]. In this case, the concentration of TOC, BOD, and COD strongly varied depending on the type of industrial activity (*i.e.*, COD values may range between tens of milligrams to tens of grams per Liter). Photocatalytic treatment has been successfully applied as a pre-treatment step before the biological oxidation for raw industrial wastewater, thus increasing its biodegradability and reducing its ecotoxicity survey[10]. However, since high organic loads in wastewater are of concern, photocatalysis is less effective than established pre-oxidation treatments (*i.e.*, ozonation and Fenton) to improve wastewater biodegradability before the biological step. On the other hand, photocatalysis could be included as a post-treatment step (after the biological treatment) for industrial wastewater enabling to degrade toxic contaminants refractory to biological processes (e.g., phenols in olive oil wastewater treatment). However, it is crucial to point out that no studies on the photocatalytic treatment MWW and industrial effluents considered the possible reuse the treated effluents so far survey [10]. Table 1 reports the main advantages and persistent obstacles to commercialization of the photocatalytic treatment of wastewater from various industrial productions (*i.e.*, pesticides, textiles, leather, food, olive oil, pharmaceuticals) and urban environments.

It is also noteworthy that the reduced reaction rates of heterogeneous photocatalysis under sunlight irradiation allow to treat small volumes of water. The process is also limited by the daylight duration, casting doubts on the viability of this technology at large scale. Thus, solar photoreactors require a massive footprint in terms of land area [117]. For a quick estimate, as recently reported, a daily provision of 50 liters of safe water per person has been suggested by the World Health Organization (WHO) [123]. A CPC collector with an area of 4.5 square meters has the capacity to treat approximately 60 liters of water daily. Therefore, a series of CPC with a total surface of 500,000 square meters would be required for a city with a population of 2 million generating nearly 240,000 cubic meters of wastewater daily. This value of land area is roughly equivalent to the size of 65 soccer fields! Consequently, solar photocatalytic wastewater treatment employing CPC reactors (*i.e.*, currently the most efficient solar photocatalytic reactors) would demand an extensive area for an average city, rendering the process economically and technically unfeasible [34].

Solar photocatalytic treatments face also both geographical limitations, with reduced insolation and treatment potential at latitudes distant from the equator, and seasonal constraints due to reduced photoefficiency for pollutant removal during winter. These constraints may pose much smaller challenge for solar-based photocatalytic treatments of wastewater for agricultural reuse. Indeed, regions with intensive agricultural practices are generally placed in low value land far away from urban centers, enabling larger footprints. Furthermore, the demand for irrigation is more pronounced in latitudes and seasons characterized by higher insolation. However, also in the case of wastewater reuse for agricultural irrigation, proper health risk assessments should be performed due to possible presence of CECs or pathogens in the treated effluents [10,117].

Table 1
Benefits and drawbacks of photocatalysis for the treatment of different categories of industrial effluents and urban wastewater [117].

TRL of photocatalytic treatment

Type of wastewater	Benefits of photocatalytic treatment	Drawbacks of photocatalytic treatment
Pesticide industry	- In situ treatment - Remarkable decrease in dissolved organic carbon concentration	Large variability of wastewater components
Textile and tannery industries	- Increased biodegradability before biological oxidation step - COD abatement - Contaminant discoloration	Less competitive than Ozonation and Fenton treatments
Municipal WW	- Possibility of photocatalyst recovery and reuse - CECs degradation - Pathogen detoxification	High costs
Food industry	Hydrogen production through oxidation of carbohydrates	Only lab scale tests available
Dairy industry	No benefits found	Suspended solids and high organic concentration
Olive oil industry	- Decrease in organic concentration - Degradation of phenols	Suspended solids and high organic concentration
Pharmaceutical industry	- Decreased before biological oxidation step - COD abatement	High COD and TOC concentrations

Another potential factor that could underscore the necessity of photocatalytic wastewater treatment is the environmental aspect of antibiotic resistance. The prevalence of antibiotic-resistant bacteria has been reported in effluents coming from ozonation and established tertiary treatments. Whether photocatalysis will prove to be an effective technology for mitigating antibiotic resistance, the justification for its relatively high cost will lie in the absence of environmentally sustainable and viable alternative treatment methods [117].

Whether these possible needs will not be addressed soon by photocatalytic wastewater treatment, this technology should become at least one order of magnitude more efficient to compete with consolidated tertiary treatment technologies. The development of efficient visible-light active and commercially available photocatalysts with higher quantum yields for hydroxyl radical generation and proper engineering advances in solar reactor design could make photocatalytic wastewater treatment attractive for real applications.

Currently, there is no information available regarding the BRL, MRL, and CRL values for solar photocatalytic wastewater treatment processes. However, utilizing literature tools, data, and examples [116,124], these unknown dimensions should be estimated by comparing them with the available TRL value for a complete readiness assessment framework containing all four dimensions necessary for industrial implementation.

5.2. Cost analysis and process intensification

When considering a system for purifying urban or industrial wastewater, initially all processes appear theoretically competitive. three major analyses should be conducted to assess the optimal option [125]. First, the desired effluent quality must be evaluated. Subsequently, various factors that may limit the applicability of certain processes need to be examined. These factors include land availability and characteristics, as well as environmental, climatic, economic, institutional, and political aspects. Lastly, a cost-effectiveness analysis is essential to determine the economically viable solution. The cost of land, construction, operation, and maintenance are the three primary parameters of the total cost that require detailed consideration in an economic analysis. Table 2 reports a cost estimation example for a solar

Table 2
Estimated capital and operating costs of a 300 m^2 solar detoxification plant for the yearly treatment of 6000 m^3 of wastewater contaminated by pesticide through a TiO_2-persulfate photocatalytic system [126]. The reported costs have been herein updated according to the currency revaluation in the years 1999–2024 (source: Italian National Institute of Statistics).

COST ITEM	VALUE (k€, 2024)	CALCULATION
I) Facility	227	
I) Project contingency	34	15% of I
I) Spare parts	11,3	50% of I
I) Engineering and set-up	131,3	50% of I+II
V) **Total Installed Cost**	403,6	I+II+III+IV
V) Annual maintenance materials	5,2	2% of I+II
V) Annual electricity	2,4	
V) Annual labor cost	8,1	
I) Annual chemical supplies	90,7	
X) **Total Operating Cost**	106,4	VI+VII+VIII+IX

photocatalytic process.

Due to the footprint area required, capital costs represent the primary expenditure in a solar photocatalytic water treatment process. Therefore, small-sized solar photoreactors for water disinfection in rural areas with reduced land cost would be cost-effective. Further authors reported the economic feasibility of the photocatalytic processes, identifying in the photocatalytic items 40% of the total capital cost, with a payback period ranging between 2.5 and 6.5 years [127,128]. Specifically, photocatalytic reactors and UV lamps represent the most affecting factors, the latter influencing the operational cost as well due to their energy consumption and replacement. These costs are ten times lower in the solar installation, reagents and photocatalyst preparation representing the main expenses in this case [129].

As regards the optimum photocatalyst properties, despite several studies suggesting that immobilized catalysts could be more energy-efficient than slurry systems at bench scale, an accurate comparison of energy consumption at pilot scale is warranted. In slurry systems, photocatalyst particles allowing an easy catalyst recovery (i.e., particles with magnetic properties or of micrometric size) should also decrease the overall water treatment costs [130,131]. Nevertheless, it is noteworthy that catalysts with larger size (i.e., micrometric size) may exhibit lower photocatalytic performance due to reduced photon absorption efficiency and surface area. Therefore, particles with larger size necessitate a higher photon dose (and thus higher cost) to achieve equivalent treatment performance compared to smaller photocatalyst particles (i.e., nanometric photocatalysts). It is also essential to assess operating issues affecting water treatment costs such as long-term catalyst deactivation and leaching, co-catalyst dissolution[132], etc. Some authors compare from an economical point of view different photocatalytic materials for a real-time livestock photocatalytic wastewater treatment, noticing a total operational cost ranging between 0.68 USD/kg and 62.16 USD/kg based on the adopted photocatalyst [133]. Thus, to improve the economic feasibility of the process, the design of an optimal photocatalyst should be taken into account, along with the optimal utilization of the solar radiation and an appropriate reactor configuration.

It is also important to note that treatment costs may vary significantly with the target contaminant. An average cost of nearly 20 €/m^3 for treating pesticide-contaminated water with solar photocatalysis has been reported when considering all process costs [134](i.e., facility, labor, and maintenance). Significantly lower costs than pesticides have been reported for completely inactivating E. coli [135](i.e., around 0.3 €/m^3) or treating trichloroethylene-polluted wastewater [136](i.e., around 7 €/m^3) through solar photocatalysis. Further examples of capital and operating costs estimated in pilot-scale studies using solar photocatalysis for treatment of different types of wastewaters are reported in Table 3.

The “electrical energy per order" (EEO) figure of merit has been reported in the literature survey as an indicator of energy efficiency of water treatment processes[132]. The EEO is defined as the quantity of kWh required to reduce the concentration of pollutants by one order of in one cubic meter of solution (i.e., kWh•m^{-3}•$order^{-1}$) and serves as a basis for comparing different technologies for a given degradation reaction. Reported EEO values vary widely, ranging from 0.6 to over 300, depending on operating factors such as process type, pollutant, and its initial concentration[142]. Lower EEO values indicate greater efficiency in pollutant removal, although this value can also be influenced by the specific composition of the water matrix, as constituents within the water may either quench ROS or absorb light, consequently diminishing the energy efficiency of the water treatment process [143].

Significant variations in EEO values are reported across different categories of "conventional" AOPs [142]:

- O_3, O_3/H_2O_2, O_3/UV, UV/H_2O_2, UV/persulfate, and UV/chlorine typically exhibit median EEO values of less than 1 kWh•m^{-3}•$order^{-1}$.
- Photo-Fenton and electrolytic AOPs display considerably higher EEOs, ranging from 1 to 100 kWh•m^{-3}•$order^{-1}$.
- UV-based photocatalysis, ultrasound, and microwave AOPs tend to have median values exceeding 100 kWh•m^{-3}•$order^{-1}$.

Besides the type of water matrix, another major factor influencing EEO determination is the process scale (i.e., laboratory, pilot, and full-scale applications) and the specific equipment utilized. For instance, in processes involving UV, the type of lamp used has been found to significantly impact EEO determination. However, the proper application of an available renewable energy source (i.e., solar energy) makes this AOPs method promptly accessible and effective. For instance, Dehghani et al.[144] recently recorded a value of EEO figure of merit equal to 0.19 kWh•m^{-3}•$order^{-1}$ by adopting sunlight-driven photocatalysis to degrade per- and polyfluoroalkyl substances (PFAS) over ZnO/cellulose nanofibers in a continuous flow reactor. The PFAS oxidation has been achieved by the Authors using direct sunlight and real wastewater samples [144]. As above reported, the effectiveness and economic viability of TiO_2-based solar photocatalysis for pollutant degradation may be enhanced through synergistic association with other AOPs, such as [145] and non-thermal plasma [146]. Karoui et al. investigated the effect of various operating parameters on the degradation mechanism of ciprofloxacin using non-thermal plasma in different water matrices [146]. The Authors adopted a combined plasma-photocatalysis approach to achieve both lower energy costs and enhanced contaminant degradation, by introducing a novel TiO_2-luminous textile catalyst into the discharge system. To the same aim, Almansba [147] introduced a new photocatalytic material that integrates a luminous textile and optical fibers to remove the antibiotic Flumequine from wastewater. This composite photocatalytic material allows for a compact reactor setup supporting TiO_2 and ensuring effective light transmission. The Authors successfully evaluated reactor scalability and energy consumption through pilot-scale testing.

6. Conclusions and future perspectives

This comprehensive review is an attempt to provide an insightful examination of photocatalytic reaction kinetics, diverse reactor types, and the crucial role of materials in advancing wastewater treatment technologies. Nanomaterials play a pivotal role in achieving optimal outcomes for photocatalytic water remediation. This review places

Table 3
Selected pilot-scale reactors for the treatment of different types of wastewaters by TiO_2-based solar photocatalysis: operating and capital costs [132].

Wastewater type	Photocatalyst	Reactor type	Rector volume	Operating cost	Capital cost	Ref.
Bisphenol A, bisphenol B, diamylphthalate, butylbenzylphthalate, methylparaben, ethylparaben	TiO_2	CPC	100 L	55,3 €/m^3	32,7 k€	[137]
Pentoxifylline	Fe/TiO_2	Fixed-bed reactor	5 L	903,16 $/$m^3$	15,5 $	[138]
Power plant wastewater	TiO_2/H_2O_2	CPC	50 L	0,05 €/m^3	23,3 k€	[139]
Tannery wastewaters	TiO_2/Fe/H_2O_2	Annular	96 m^3/day	21,34 $/$m^3$	168,9 k$	[140]
Metoprolol	TiO_2	CPC	10 L	10,4 €/L	18,5 k€	[141]

focuses attention on both materials utilized in commercial reactors and those developed for prototype applications. The discussion extensively covers titania, the most commonly employed photocatalytic material, exploring its use in various reactor setups and detailing numerous heterostructure composites of TiO_2. Additionally, another significant wide-bandgap semiconductor, ZnO, is thoroughly examined in the context of several reactor configurations. The introduction of dopants, impurities, and the creation of heterostructure composites actively contribute to enhanced visible light absorption and effective management of the recombination rate of photocatalysts. Beyond traditional catalyst materials, emphasis is given to graphene, a noteworthy material of the past two decades. The review delves into the intriguing physical and chemical properties of graphene, with detailed discussions on its potential utilization as a photocatalytic reactor material. The design of reactor configurations results crucial for successful implementation of photocatalytic technologies, as they enhance process efficiency and reduce water treatment costs by maximizing solar energy conversion into chemical reactions. CPC reactor still represents the most popular configuration, despite other reactor types being proposed recently (*i.e.*, offset multi-tubular solar photoreactor or membrane photocatalytic reactors).

The reactor designs and materials are crucial components in designing an operational commercially scaled photocatalytic wastewater treatment center. However, it should be understandable that exposing real wastewater directly only to be treated with photocatalytic system might not be the efficient process as they can result in fouling in a small span of time. Therefore, pretreatment of the water using conventional techniques and further exposing the water flux through photocatalytic reactors can become an effective treatment strategy. With the existing reactor efficacy, the plant volume cannot be implemented at large scale as compared to conventional treatment structure. Therefore, it might seem an effective option to integrate such treatment plants within different commercial industries which will effectively reduce the cost of discarding wastewater into nearby water sources. However, this method of dumping untreated/partially treated water as industrial effluent is not conventional in developed countries. Such practices depend on national policies and based on EU and UK standards, high penalties could be issued to industries for discharging untreated water.

The exploration of effective materials underscores the importance of tailored solutions for optimizing photocatalytic processes, thereby enhancing the overall efficiency of wastewater treatment. In this context, a deep understanding of intrinsic kinetics is necessary both for the advancement of effective reactors and photocatalytic materials. Indeed, the mathematical modeling of photocatalytic water treatment should emphasize the scale-up of the process from laboratory to pilot-scale and eventually industrial-scale, addressing practical engineering challenges. Future modeling endeavors should include *(i)* simplified radiation models enabling the process simulation of diverse reactor geometries and *(ii)* a comprehensive assessment of the impact of water matrix species on the overall process efficiency.

Despite the promising advancements, the road to commercialization poses significant challenges. The discussion of these challenges highlights the need for collaborative efforts between researchers, engineers, and policymakers to overcome technical, economic, and regulatory hurdles. Solar-based photocatalytic treatments of wastewater for agricultural reuse appears to be an environmentally and economically viable real implementation on this technology. By addressing these challenges, the full potential of photocatalytic wastewater treatment can be realized, contributing to a sustainable and environmentally friendly approach to water purification. Looking ahead, this review sets the stage for future research and innovation in photocatalysis, encouraging the development of scalable and economically viable solutions. As the field progresses, overcoming the outlined challenges will be pivotal in fostering the widespread adoption of photocatalytic technologies and establishing them as integral components of sustainable wastewater treatment strategies.

CRediT authorship contribution statement

Marica Muscetta: Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation. **Laura Clarizia:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Methodology, Investigation, Data curation, Conceptualization. **Priyanka Ganguly:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

Data availability

No data was used for the research described in the article.

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