

Engineering and Modeling Perspectives on Photocatalytic Reactors for Water Treatment

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Abstract

The debate on whether photocatalysis can reach full maturity at commercial level as an effective and economical process for treatment and purification of water and wastewater has recently intensified. Despite a bloom of scientific investigations in the last 30 years, particularly with regards to innovative photocatalytic materials, photocatalysis has so far seen a few industrial applications. Regardless of the points of view, it has been realized that research on reactor design and modeling are now equally urgent to match the extensive research carried out on innovative photocatalytic materials. In reality, the development of photocatalytic reactors has advanced steadily in terms of modeling and reactor design over the last two decades, though this topic has captured a smaller specialized audience. In this critical review, we introduce the latest developments on photocatalytic reactors for water treatment from an engineering perspective. The focus is on the modeling and design of photocatalytic reactors for water treatment at pilot- or at greater scale. Photocatalytic reactors utilizing both natural sunlight and UV irradiation sources are comprehensively discussed. The most promising photoreactor designs and models are examined giving key design guidelines. Other engineering considerations, such as operation, cost analysis, patents, and several industrial applications of photocatalytic reactors for water treatment are also presented. The dissemination of key photocatalytic reactor design principles among the scientific community and the water industry is currently one of the greatest obstacles in translating PWT research into widespread real-world application.

Keywords: Design; Modelling, Radiation transport; Reaction kinetics; Pilot plant; Process economics

1. Introduction

Photocatalytic water treatment (PWT) has been proposed as a green water treatment process to treat and purify water and wastewater contaminated with hazardous species to humans and the environment, such as heavy metals, pharmaceuticals, pesticides, estrogens, chlorinated hydrocarbons, dioxins, viruses and bacteria (Chong et al., 2010; Hoffmann et al., 1995). It has been labeled as a chemical-free and energy-saving process, thus cost-effective, compared to other conventional advanced oxidation processes (AOPs) to remove contaminants of emerging concern. With the sole input of solar energy, semiconductor photocatalysts can produce valence band holes (h_{vb}^+) and conduction band electrons (e_{cb}^-), which can initiate oxidation/reduction reactions to abate environmental contaminants. By judicious engineering of the photocatalysts bandgaps, it can also achieve the destruction of contaminants which are recalcitrant to other AOPs, such as per- and polyfluoroalkyl substances (PFAS) (Huang et al., 2016; Sahu et al., 2018b). Significant efforts have been made on catalysts modifications, e.g., improving the efficiency of the process under visible light irradiation and the separation lifetime between electrons and holes (Wang et al., 2018). More recently, biomimicry based design of photocatalysts, including immobilized photocatalysts which can act as omnidirectional trackers or mimic natural hierarchical architectures, and mobilized photocatalysts which are derived from algae and bacteria, have also attracted attention due to their improve light absorption capacity (Brillas et al., 2021; Serrà et al., 2021).

However, the connection to the treatment of real domestic, urban or industrial wastewater has been less successful (Loeb et al., 2018). Materials development is certainly important for the successful transfer of PWT into the water treatment and reuse industry. However, as it is often the case, these newly engineered photocatalytic

materials may not always meet the requirements for practical industrial application. Cost-effectiveness, photocatalyst stability, ecological safety, ease of recovery and reuse, and scalable production are some examples in which more work is needed, even though many photocatalysts have demonstrated high performance in laboratory scale studies. Though the advances in photocatalytic material development is fast developing (Loeb et al., 2019; von Gunten, 2018), it has been realized that process and photoreactor design are equally urgent to fill the gap between scientific efforts and industrial applications (Cates, 2017; Mauter et al., 2018; Nelson et al., 2018).

Photocatalytic reactor development is crucial for PWT process design, as innovative reactor designs can not only improve the performance of photocatalysts, but it can also help mapping the roadblocks impeding the technology transfer from R&D to actual practice. For example, photocatalytic particles with small sizes can increase the cost for recovery and reuse, while immobilized system can suffer from lower irradiated area of catalyst, mass transfer of reacting species and high rate of back-scattering of photons (Loeb et al., 2019). However, the opportunity of process improvement offered by reactor design has been greatly omitted, as only about ten percent of publications in PWT are relevant to this topic according to a recent review (Leblebici et al., 2015; Loeb et al., 2019). On the other hand, research and development on pilot- or even greater scale applications can also help point out the industrial applicability areas of PWT. Taking the pioneer projects in the European Union that have applied solar-light photoreactors for water treatment, as an example (Galvez and Rodriguez, 2003), it has been reported that PWT may not be applicable for universal water treatment purposes and that can only be considered under specific circumstances, such as those in which the concentrations of organic pollutants in water are below 1 g/L (e.g., microcontaminants removal) and in cases in which the

target contaminants are recalcitrant or not completely removed by conventional water treatment processes. Numerous types of photocatalytic reactors have been categorized on the basis of key design features such as the nature of the light source (artificial light and solar powered reactors), the geometry (annular, tubular and planar reactors) or the way the photocatalyst is loaded in the reactor (suspended or immobilized systems) (Leblebici et al., 2015). Nevertheless, only a few of them have been developed for full-scale industrial application, mainly because of inefficient catalysts and/or reactor design. Besides the reactor complexities, a variety of other engineering factors comes into play, such as fluid pumping energy, pressure drop, temperature, tubing materials, and the interfering effect of water matrix species. All together these factors make it challenging or uncertain to the industry to assemble an efficient PWT unit. Nevertheless, several pilot-scale and industrial scale PWT units have been developed over the last two decades. Selected examples include the solar light-based photocatalytic water treatment unit installed at Plataforma Solar de Almería (PSA) (Malato et al., 2002), solar light-based and portable water purification system by Panasonic, (2013) the UV-LED and solar light-based photocatalytic systems by APRIA Systems (Spain), the Photo-cat water purification system developed by Purifics (Benotti et al., 2009) and the industrial scale solar PWT plant (Figure 1) operated since 2009 by BICO International in Cali, Colombia (Colina-Márquez and Machuca-Martínez, 2012). To connect the industrial needs and scientific research in this field, it is necessary to overview the PWT reactor design and the relevant considerations on the engineering factors affecting their performance.

Inspired by the above needs, this critical review summarizes the recent development of photocatalytic reactors design and discusses the key barriers that need to be overcome for the further development of PWT. The focus of this review is

on pilot-scale and full-scale PWT systems that have demonstrated advancements in this field. The relevant mathematical models for the design of efficient PWT reactors are reviewed, and typical reactors designed following those models are presented. The engineering factors, the effects of water constituents, coupling with pre- or post-treatment, and cost comparison with other conventional AOPs are also reviewed. Moreover, relevant patents are summarized and analyzed. Several industrial applications are also presented. Overall, this review emphasizes that reactor design is currently one of the greatest obstacles in translating PWT research to widespread real-world application.



Figure 1. Full-scale solar PWT plant operating in Cali, Colombia.

2. Efficient reactors for PWT

It is common that in a typical PWT research study, several parameters are investigated, including the concentration of the photocatalyst and reacting species, the power and the wavelength of the incident light source, the separation space between

the light source and the reactor, the geometry of the reactor, the fluid-dynamics regime and the macromixing/micromixing conditions in the reactor. A full understanding of the impact of these parameters are key to allow a comparison among the performance of different photocatalytic reactor systems. However, it is unfortunate that most of the literature studies simply measure apparent kinetic rate constants (usually arbitrarily reported as first-order) or the percent degradation of a reacting species, making comparisons among studies difficult or impossible. It is also reasonable to believe that in some cases the reported apparent kinetics rate data in these studies can be further increased, by simply optimizing the operational conditions of the reactor. A typical example is the lack of a scientific methodology for the selection of the optimal catalyst loading in slurry photoreactors, which is too often left to semi-empirical considerations, although this can be easily determined using the well-known concept of “optimal optical thickness”, which is a dimensionless parameter used to scale-up photocatalytic reactors (Table 1 and Section 3.1) (Colina-Márquez et al., 2009). In other words, what is unwisely referred to as the “opacity” of a slurry photoreactor can be precisely determined using a simple mathematical formula (Colina-Márquez et al., 2015).

Table 1. Optimal range of optical thickness of some common photocatalytic reactor geometries.

Reactor geometry (light source)	Optimal optical thickness (dimensionless)	Catalyst	References
Annular/Flat (UV)	1.8-3.4	TiO ₂ -P25	(Li Puma, 2005)
Annular (multiple UV)	0.96-2.1	TiO ₂ -nano	(Santoro et al., 2017)
Flat (solar)	4.17 4.37	TiO ₂ -P25 Goethite	(Acosta-Herazo et al., 2019)
Flat (solar)	3.77 4.08 4.39 4.15 3.99 4.10	TiO ₂ -Hombikat TiO ₂ -P25 TiO ₂ -Aldrich TiO ₂ -Merck TiO ₂ -Fischer TiO ₂ -Fluka	(Otalvaro-Marín et al., 2014)
CPC (solar)	5.6 5.6 5.7 5.4	TiO ₂ -Hombikat TiO ₂ -P25 TiO ₂ -Aldrich TiO ₂ -Merck	(Otálvaro-Marín et al., 2017)

	5.4	TiO ₂ -Fischer	
	5.5	TiO ₂ -Fluka	
CPC (solar)	3.6	TiO ₂ -P25	Acosta-Herazo et al., 2020

The optimal design of photocatalytic reactors can also significantly decrease the water treatment costs. For example, the electrical energy per order (EE/O), which is defined as the electric energy (or the area of solar irradiation) needed to decompose a target contaminant by one order of magnitude in a unit volume of contaminated water. The EE/O value (kWh/m³ per order) can be calculated as follows (Serrà et al., 2021): $EE/O = \frac{Pt}{-\log(C/C_0)V}$ for batch systems and $EE/O = \frac{P}{-\log(C/C_0)Q}$ for continuous flow systems, where P is the power of the system, t is the treatment time, C and C_0 are the concentration of target contaminant at time t and time 0, respectively, V is the volume of batch system, Q is the flow rate of continuous flow system.

The EE/O for bisphenol A degradation in a pilot-scale Photocat unit using TiO₂ as photocatalyst has been reported to be 0.16 kWh/m³ per order (Benotti et al., 2009), while in a typical bench scale reactor was calculated to be higher than 5×10^4 kWh/m³ per order (Ohko et al., 2001). Thus, how to develop a photocatalytic reactor for efficient degradation of targeted water contaminants?

It has been estimated that the overall energy efficiency for converting photons (solar) or electricity (artificial light) to hydroxyl radicals ($\bullet$ OH) for pollutant destruction, is only about 0.0005%-0.4% for solar light photocatalysis and 0.0002%-2% for UV-light photocatalysis (Loeb et al., 2019). This low efficiency is attributed to a few factors, such as (1) the low conversion efficiency from electricity to photons (wall-plug efficiency), (2) photon losses in the reactors due to radiation scattering, (3) the fraction of the absorbed photons that results in the production of e^-/h^+ pairs, and (4) the high rate of e^-/h^+ recombination in the catalyst. The low conversion efficiency from electricity to photons may be improved by advances in electrical engineering (Garrod et al.,

2014), such as the development of highly efficient LED light sources, while the reduction of the rate of recombination of electrons and holes is one of the primary goals of material scientists working on new photocatalysts (e.g., Z-scheme heterojunctions, plasmonic, defects engineering, element doping etc.) (Wang et al., 2018). On the other hand, the appropriate design of photocatalytic reactors seems to be an attractive and feasible option to increase the conversion efficiency of photon energy to hydroxyl radicals. Indeed, over the past several decades, numerous studies have focused on reducing and minimizing reactor photons losses due to the light scattering (Li Puma and Brucato, 2007; Mueses et al., 2015; Spadoni et al., 1978), the inefficient management of the incident light (Portela et al., 2011; O'Neal et al., 2018), and light absorption by the interfering water matrix by developing efficient photocatalytic reactors and relevant models (Li Puma, 2003; Li Puma and Brucato, 2007; Puma and Yue, 1998a). Moreover, integration of reaction kinetics models and hydrodynamics with radiation transfer models has enabled the *a priori* prediction of the performance of photocatalytic reactors and thus their further optimization (Grčić and Li Puma, 2017; Wang et al., 2013b).

2.1 Modeling of PWT reactors

The radiation field, hydrodynamics and transport of the chemical species throughout the reactor are fundamental aspects that have a significant impact on the efficiency of PWT reactors, as they directly influence the local rate of generation of electron-hole pairs at the catalyst surface and the local rate of degradation of water pollutants. Figure 2 shows a methodological approach to modeling of PWT reactors, which essentially involves the following components: *i*) Reaction kinetics, wherein the quantum yield and mass balances are considered; *ii*) Hydrodynamics; and *iii*) Radiation transport, which must be computed from the light source, such as solar

radiation and atmospheric conditions or artificial light sources, to the reactor, including the absorption-scattering phenomena of the photocatalyst, non-catalytic particles, the reactor walls and the dissolved species (Mueses et al., 2013).

The integrated model leads to challenging numerical computations, owing to the multiphysics nature of the problem, which yields coupled partial differential equations for the hydrodynamics and for the transport of the chemical species, and an integro-differential equation for the Radiation Transport (Li Puma, 2005). The mathematical modeling of the reaction kinetics mechanism may also increase the complexity of the model depending on the number of elementary reactions and chemical species tracked.

The modeling approach can sometime be simplified, as showed in Figure 2, in which the radiation transport and hydrodynamics are solved separately from the material balance of the chemical species. This assumption is valid when there is a negligible variation of the catalyst concentration in the reactor (for instance, due to sedimentation), when the flow physical properties (density and viscosity) are not altered by the progression of the chemical reactions and when the reactor is assumed isothermal. These equations, either coupled or uncoupled, can be solved using computational fluid dynamics (CFD), although the coupled solution might be impractical without High Processing Computing (HPC). The use of CFD applied for PWT reactors has increased due to the possibility to combine the different phenomena and due to continuous improvements on computational resources and on efficiency of the codes.

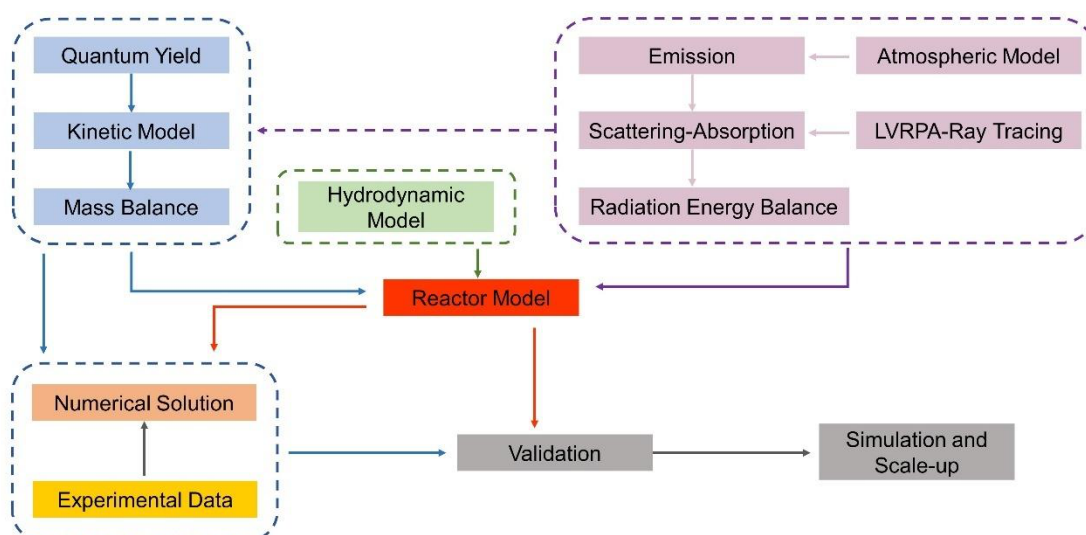


Figure 2. Methodological approach to modeling of a photocatalytic reactor. Adapted from (Ochoa-Gutiérrez et al., 2018).

2.1.1 Radiation transport

Radiation field modeling is key to the modeling of PWT reactors as it determines the local volumetric rate of photon absorption (LVRPA) which is the number of photons absorbed per unit reactor volume and unit time at each location within the reaction space (Brandi et al., 1996). This directly influence the local photocatalytic reaction rate of chemical species. It combines the radiation emission model for the light source and the radiation absorption and scattering model for the reaction space (the slurry suspension of catalyst or the immobilized catalyst film) in which the reacting species are transformed.

The incident radiation in reactors irradiated by solar light, is usually determined using semi-empirical atmospheric models or Global Solar Atlas (e.g., GSA 2.4, Dec 2020) that can be validated and readjusted to the specific geographical location using the meteorological local data for solar light irradiation and weather conditions (Colina-Márquez et al., 2009). In contrast, the incident radiation in reactors irradiated by artificial light sources is determined by radiation emission models, the simpler of which

is the linear source spherical emission (LSSE) model usually applied to long cylindrical UV lamps. The LSSE model considers the lamp as a line source and each point of the line emits radiation isotopically (Li Puma and Yue, 2003). Other models such as the linear source with diffuse emission (LSDE), extended source with voluminal emission (ESVE), extended source with superficial emission (ESSE) and extended source with superficial diffuse emission (ESDE) may better represent artificial light sources with diffuse emission or with volumetric emission (Machuca-Martinez et al., 2016). By calculating the radiation field in the reactor, the effect of reactor size and geometrical configuration on the rate of photon absorption can be evaluated, and areas with poor photon absorption can be identified. For example, more than 95% of the photon energy emitted by a long cylindrical lamp can be absorbed in a falling film annular reactor, if the reactor is operated under optimal optical thicknesses, the ratio between reactor length to radius is larger than 20 and the ratio of reactor height to lamp length equals 1.33 (Li Puma, 2003).

The light emission models described above represents the boundary conditions to solve the radiative transfer equation (RTE), which in turn yields the distribution of the local volumetric rate of photon absorption (LVRPA) for slurry photocatalytic reactors, or the local surface rate of photon absorption (LSRPA) when the catalyst is immobilized on the reactor walls. In the most complex case, it requires solving the radiative transfer equation (RTE) using the discrete ordinates method (DOM) (Figure 3a) which is computationally demanding (Casado et al., 2019; Casado et al., 2017a; Imoberdorf et al., 2007; Martín-Sómer et al., 2017; Moreno et al., 2019). An alternative approach is the Monte Carlo method which allows the solution of complex radiation transport problems without making significant simplifications (Figure 3b). However, this method is also computationally demanding (Acosta-Herazo et al., 2016). Due to

the inherent computational complexities of DOM and Monte Carlo methods in solving the RTE, particularly in reactor systems with fluctuating incident light such as solar light, other simplified approaches, such as the Two-Flux Model (TFM, Figure 3c) (Brucato and Rizzuti, 1997) and the Six-Flux Model (SFM, Figure 3d) (Brucato et al., 2006), have been proposed to compute the radiation field and therefore the LVRPA in the reactor. Compared to the TFM, which only consider two directions of travel for the photon (forward and backward) and that only performed well to model reactors with large lateral dimensions (Ramírez-Cabrera et al., 2017), the SFM is more widely used, as it considers that the trajectory of the incident photons has precise probabilities of dispersing along the six directions of the Cartesian coordinates. In its original formulation the SFM described the dispersion of radiation by scattering as a diffuse phase-function (Brucato et al., 2006), however, in further versions the dispersion of radiation in the SFM has been described by the isotropic or the Henyey-Greenstein (HG) scattering phase-function (Acosta-Herazo et al., 2016). The main advantage for using the SFM-HG is that it covers the entire range from back to forward photon scattering.

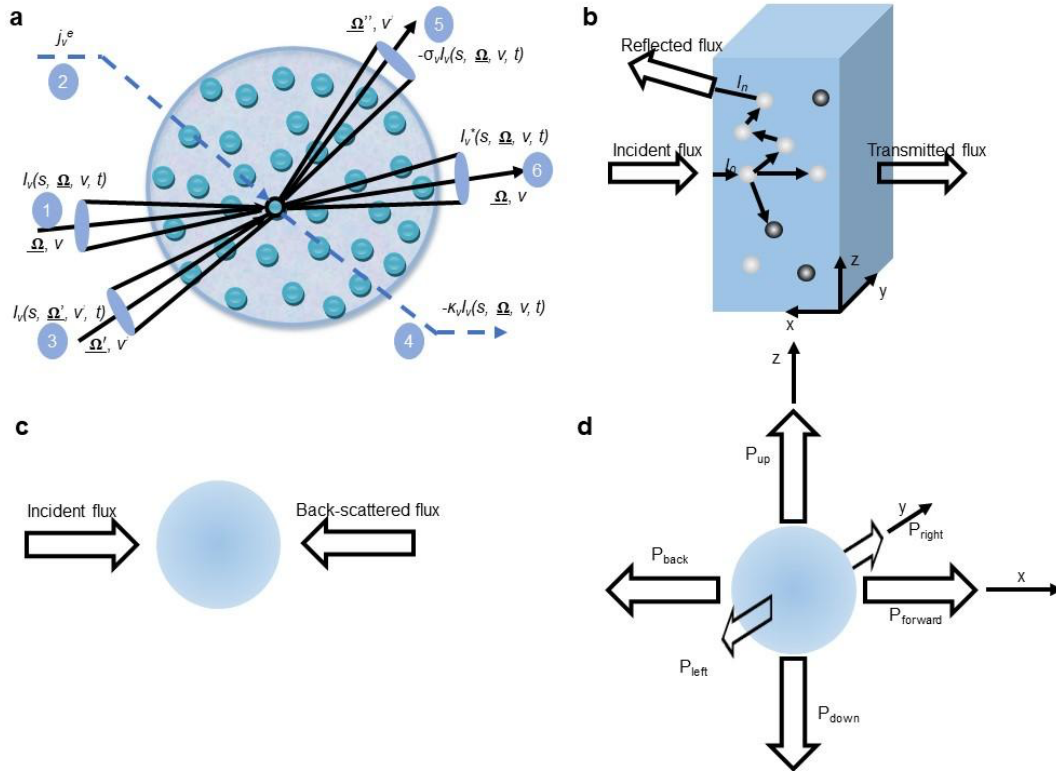


Figure 3. Illustrations of main radiation transfer modeling approaches of photocatalytic reactors: (a) RTE (b) Monte Carlo. (c) TFM. (d) SFM. (Cassano et al., 1995) Symbols: (1) Incident intensity along s with direction Ω and frequency ν , (2) emission of radiation in the direction Ω and frequency ν (gain radiation in the direction Ω and frequency ν), (3) intensity in a representative, arbitrary direction Ω' and frequency ν' to be scattered in the direction Ω and frequency ν (gain of radiation in the direction Ω and frequency ν), (4) absorbed intensity (loss of radiation in the direction Ω and frequency ν), (5) scattered intensity in a representative, arbitrary direction Ω'' and frequency ν' out of the direction Ω and frequency ν (loss of radiation in the direction Ω and frequency ν), and (6) emerging intensity along s in the direction Ω and frequency ν (after losses by absorption and out-scattering and gains by emission and in-scattering). l the free path of photons in Monte Carlo approach.

Despite its inherent limitations, the SFM model in its different versions has been applied to simulate PWT reactors with different geometries, including annular (Grčić and Li Puma, 2017; Peralta Muniz Moreira and Li Puma, 2020), flat plate (Brucato et al., 2006; Li Puma and Brucato, 2007) and solar compound parabolic collectors (CPCs) (Colina-Márquez et al., 2009; Colina-Márquez et al., 2015; Gora et al., 2006;

313 Otálvaro-Marín et al., 2019; Rodriguez-Acosta et al., 2014). Some important results
314 for practical applications have been obtained through these approaches. For example,
315 the LVRPA decreases pseudo-exponentially along the radiant flux direction in the
316 liquid depth (Brucato et al., 2006) and that an optimal range of catalyst concentration
317 can be calculated for any specific PWT reactor (Li Puma and Brucato, 2007). It should
318 be noted, however, that SFM has some limitations regarding its formulation and
319 extension to cylindrical geometries. One of its main limitations is the adjusted values
320 of the probabilities of photon direction because these values were obtained using inert
321 particles with a diffuse anisotropic behavior in their phase function and were not
322 corrected for experimental systems that are isotropic or specular. As a result, different
323 scattering phase functions have been investigated, and more precised values for the
324 SFM scattering probabilities have been determined that can be applied to different
325 materials with isotropic and anisotropic performances (Acosta-Herazo et al., 2016).
326 Some studies have questioned the validity of the SFM (Ramírez-Cabrera et al., 2017),
327 however, it should be noted the inadequate choice of reactor geometry in this study
328 (cubical reactor) which violates the lateral symmetry requirement of the SFM. It is
329 generally accepted that small differences could be found between SFM and exact
330 solution of the RTE due to its approximate nature. A recent study comparing the full
331 solution of the RTE and the approximation by the SFM using computational fluid
332 dynamics has determined that the SFM solved with irradiance boundary conditions
333 rather than fluence rate provides close approximation of the radiation field in an
334 annular photoreactor (Peralta Muniz Moreira and Li Puma, 2020). Table 2 shows the
335 different phase functions and its modeling applications. The models presented are
336 mathematical functions that describe the nature of the radiation scattering inside the
337 reactor. These are so-called phase functions and depend on the way the incident

photons scatter in space (backward, forward, or isotropic). Mathematically, the expressions reported in Table 2 represent the most important phase functions that are applied in radiant field modeling.

Table 2. Main Scattering-Absorption Phase Function in Photocatalytic Reactor Modeling.

Phase Function	Equation	Applications	References
Diffuse Reflectance (DR)	$p(\varphi) = \frac{3}{8\pi}(\sin\varphi - \varphi\cos\varphi)$	Determination of optical properties by spectrophotometry and DOM. Modeling photocatalytic degradation of water contaminants by SFM. Methods for kinetics, optimization and scale-up of annular tubular and CPC photoreactors	Cabrera et al., 1996; Toepfer, et al., 2006; Li Puma, et al., 2010.
Isotropic	$p(\varphi) = 1$	Modeling photocatalytic degradation of water contaminants. Approach for kinetics independent of the reactor conditions.	Brandi, et al., 1996; Grčić and Li Puma, 2013; Mueses, et al., 2015.
Specular Reflection (SR)	$p(\varphi) = \frac{1}{\rho}\rho'(\varphi)$	The phase function is strongly dependent of anisotropic direction. The specular directional reflectivity is overlaps on hemispherical reflectivity	Alfano and Cassano, 2000.
Henyeey-Greenstein (HG)	$(\varphi) = \frac{1}{2} \left[\frac{1 - g^2}{(1 + g^2 - 2g\cos\varphi)^{1.5}} \right]$	Determination of optical properties by spectrophotometry and DOM. Modeling photocatalytic degradation of organic compounds by DOM and MC method. Radiation field and evaluation of scattering for TiO ₂ suspensions in annular photoreactor by MC method. Optical properties by goniometry and CFD. HG phase function is proposed as an improvement. Optical properties reported for TiO ₂ with a tendency to forward scattering $g > 0.4$ Kinetics and scale-up methods for annular photoreactors. Phase functions found crucial on radiation field. HG parameter $0.6 < g < 0.8$ is reported as suitable for TiO ₂ . Experimental and numerical method for optical properties. The HG found as better for scattering characterization than the DR. A preferential forward scattering is reported for TiO ₂ , $g > 0.5$.	Satuf, et al., 2005; Marugan, et al., 2006; Satuf, et al., 2007; Marugan, et al., 2008; Marugan, et al., 2013; Valdés-Pelayo, et al., 2014; Valdés-Pelayo, et al., 2015; Turolla, et al., 2016; Ochoa, et al., 2018; Acosta-Herazo, et al., 2019; Acosta-Herazo, et al., 2020.

After that the LVRPA is computed from the solution of the radiation transport model, this is substituted into the algebraic reaction kinetics rate laws, and in the material balances for the target reacting species, which in turn incorporate the reaction kinetics and the fluid dynamic model. The concentration of the target pollutant species at the reactor outlet can then be determined by solving the coupled differential model equations with the appropriate boundary conditions (Li Puma, 2005).

2.1.2 Modeling of photocatalytic reaction kinetics

Mathematical modeling of photocatalytic reaction kinetics requires a fundamental understanding on the dynamics of the molecular processes occurring at the semiconductor/solution interface, e.g., the mechanisms for the photocatalytic processes. In general, photocatalytic processes involve several common steps, including 1) photocatalytic activation of catalyst by light absorption and formation of e^-/h^+ pairs, 2) adsorption of water, pollutant molecules, and reactive oxygen species (ROS) on the catalyst surface, 3) recombination of electrons and holes, (4) hole trapping by the adsorbed species, (5) electron trapping by oxygen as the main electron acceptor, (6) ROS attack on the substrate molecules (R_i) by redox reactions. (Brandi et al., 2003) Based on the above assumptions, the photocatalytic reaction kinetics of a given target species has often been represented by an apparent Langmuir-Hinshelwood (L-H) contaminant rate law (Turchi and Ollis, 1990). It should be noted that this model is based on the major assumption that the hydroxyl radical is the predominant ROS that attack the water contaminant. This assumption has been largely evidenced by isotopic experiments (Cunningham and Srijaranai, 1988) and electron spinning resonance (ESR) experiments in TiO_2 photocatalytic systems (Jaeger and Bard, 1979). However, other studies have shown that other species, such as holes, may also serve as primary oxidative species (Li et al., 2012; Sahu et al., 2018b). The L-H model assumes that a monolayer adsorption occurs on the catalyst surface during the dark phase, before irradiation, and that this continues during the irradiated phase. Nevertheless, the catalyst surface can be dramatically altered by irradiation, and thus multilayer adsorption can also take place (Gora et al., 2006; Imoberdorf et al., 2007). When the concentration of the organic substances is high (e.g., $> 1 \text{ mg/L}$) multilayer adsorption can also take place (Toepfer et al., 2006;

Marugán et al., 2006). As a result, modifications on the classic L-H kinetics model have been proposed to address these limitations (Gora et al., 2006; Rodriguez-Acosta et al., 2014). Among them, the incorporation of the radiation field through the LVRPA is the most important, as this modification makes the kinetic modeling generally applicable to reactors of any size and geometry. Table 3 presents a review of the studies that modeled the kinetics of photocatalysis, including the rate law adopted, the water pollutant treated, the photocatalyst and the reactor configuration.

Table 3. Review of studies that modeled the kinetics in PWT: Rate law used, the water pollutant treated, the photocatalyst and the reactor configuration.

Rate law	Water pollutants	Catalyst	Reactor configuration	Reference
$r_i = -\alpha_1 \sqrt{\hat{E}_{g(\lambda \rightarrow \lambda')}^a} \theta_i^{L-H}$	Trichloroethylene	TiO ₂	Flat plate photoreactor	Brandi et al., 2002
$r_i = -\alpha_1 \sqrt{\hat{E}_{g(\lambda \rightarrow \lambda')}^a} \theta_i^{L-H}$	Isoproturon, Simazine and Propazine	TiO ₂	Annular photoreactor	Toepfer et al., 2006)
$r_i = -\alpha_1 \left[-1 + \sqrt{1 + \alpha_2 \hat{E}_{g(\lambda \rightarrow \lambda')}^a} \right] \theta_i^{L-H}$	4-chlorophenol	TiO ₂ and TiO ₂ /SiO ₂	Annular photoreactor	Satuf et al., 2008
$r_i = -\alpha_1 \left[-1 + \sqrt{1 + \alpha_2 \hat{E}_{g(\lambda \rightarrow \lambda')}^a} \right] \theta_i^{L-H}$	Cyanide	TiO ₂	Cylindrical photoreactor	Marugán et al., 2008
$r_i = -\alpha_1 \left[-1 + \sqrt{1 + \frac{\alpha_2}{C_i} \hat{E}_{g(\lambda \rightarrow \lambda')}^a} \right] C_i$	Dichloroacetic acid	TiO ₂	Parallelepiped photoreactor	Ballari et al., 2008
$r_i = \{ \alpha_1 \phi C_i + \alpha_2 [1 - \phi \sqrt{C_i}] \} \sqrt{\hat{E}_{g(\lambda \rightarrow \lambda')}^a}$ where $\phi = \alpha_3 C_{i,0} [1 - \alpha_4 \hat{E}_{g(\lambda \rightarrow \lambda')}^a t]$	Oxalic acid	TiO ₂	Fluidized bed photoreactor	Pozzo et al., 2010
$r_i = -\alpha_1 \left[-1 + \sqrt{1 + \alpha_2 \hat{E}_{g(\lambda \rightarrow \lambda')}^a} \right] \theta_i^{L-H}$	1,4-dioxane, hormone disrupting estrogens (E1, E2, EE2, E3), propanal, dichloroacetic acid, phenol, chlorophenols, methylphenols,	TiO ₂	Tubular reactor with compound parabolic collector (CPC)	Mueses et al., 2013

	2,4-dichlorophenoxy-acetic acid (2,4-D), diuron and ametrine				
$r_i = \{\alpha_1 \phi C_i + \alpha_2 [1 - \phi \sqrt{C_i}] \sqrt{\hat{E}_{g(\lambda \rightarrow \lambda')}^a} \}$ where $\phi = \alpha_3 C_{i,0} [1 - \alpha_4 \hat{E}_{g(\lambda \rightarrow \lambda')}^a t]$	Oxalic acid	TiO ₂	Annular photoreactor	Grčić and Li Puma, 2013)	
$r_i = -\alpha_1 \sqrt{\hat{E}_{g(\lambda \rightarrow \lambda')}^a} \theta_i^{L-H}$	herbicides mixture (2,4-D, diuron, and ametrine)	TiO ₂	Tubular reactor with compound parabolic collector (CPC)	Colina-Márquez et al., 2015)	
$r_i = -\alpha_1 \sqrt{\hat{E}_{g(\lambda \rightarrow \lambda')}^a} \theta_i^{L-H}$	4-Nitrophenol	TiO ₂	Cylindrical photoreactor	Palmisano et al., 2015	
$r_i = \alpha_1 \left(-1 + \sqrt{1 + \alpha_2 \hat{E}_{g(\lambda \rightarrow \lambda')}^a} \right) C_i$	Formic acid	TiO ₂	Parallelepiped photoreactor	Camera-Roda et al., 2016	
$r_i = -\alpha_1 \left(-1 + \sqrt{1 + \alpha_2 \hat{E}_{g(\lambda \rightarrow \lambda')}^a} \right) C_i$	Clofibric acid	TiO ₂	Cylindrical photoreactor with two circular flat windows	Manassero et al., 2015)	
$r_i = \{\alpha_1 \phi C_i + \alpha_2 [1 - \phi \sqrt{C_i}] \sqrt{\hat{E}_{g(\lambda \rightarrow \lambda')}^a} \}$ where $\phi = \alpha_3 C_{i,0} [1 - \alpha_4 \hat{E}_{g(\lambda \rightarrow \lambda')}^a t]$	oxalic acid	TiO ₂	Annular photoreactor	Turolla et al., 2016	
$r_i = -\alpha_1 \sqrt{\hat{E}_{g(\lambda \rightarrow \lambda')}^a} \theta_i^{L-H}$	2-hydroxybenzoic acid	TiO ₂ and Ag@TiO ₂	Annular and channel photoreactors	Grčić and Li Puma, 2017	
$r_i = -\alpha_1 \left[-1 + \sqrt{1 + \alpha_2 \hat{E}_{g(\lambda \rightarrow \lambda')}^a} \right] \theta_i^{L-H}$	Phenol	TiO ₂	Cylindrical photoreactor	Tolosana-Moranchel et al., 2017	
$r_i = -\alpha_1 \left(-1 + \sqrt{1 + \alpha_2 \hat{E}_{g(\lambda \rightarrow \lambda')}^a} \right)$	Methanol	TiO ₂	Annular photoreactor	Casado et al., 2017	
$r_i = -\alpha_1 \sqrt{\hat{E}_{g(\lambda \rightarrow \lambda')}^a} C_i$	Clofibric acid	TiO ₂	Planar microreactor with immobilized catalyst	Satuf et al., 2019	
$r_i = -\alpha_1 \left[-1 + \sqrt{1 + \alpha_2 \hat{E}_{g(\lambda \rightarrow \lambda')}^a} \right] \theta_i^{L-H}$	Clofibric acid	TiO ₂ -rGO	Cylindrical photoreactor	Tolosana-Moranchel et al., 2019	
$r_i = \theta_i^{L-H} \frac{q_{inc}}{1 + \alpha_1 q_{inc}}$	Arsenite	TiO ₂	NETmix reactor with immobilized catalyst (BSI and FSI)	Santos et al., 2021	

Note: $\alpha_{i=1,...,N}$ are the rate law constants, $\hat{E}_{g(\lambda \rightarrow \lambda')}^a$ is the overall volumetric rate of photon absorption (OVRPA, Einstein/m³s), θ_i^{L-H} is Langmuir-Hinshelwood function (dimensionless), C_i is the concentration, $C_{i,0}$ is the initial reactant concentration and q_{inc} is the incident radiation.

389

390 The kinetic expressions shown in Table 3 have been derived from more or less
391 complex reaction mechanisms considering the competition of selected by-products for
392 the oxidant species.

393 Other semi-empirical kinetic models such as pseudo zero, first, and second order
394 reactions, which ignores the phenomenological aspects of the reaction mechanisms
395 have often been reported (e.g., Monllor-Satoca et al., 2007; Villarreal et al., 2004). The
396 impact of photon absorption is usually excluded in these semi-empirical kinetic
397 models, making the model and resulting rate constants closely related to the reactor
398 system under consideration and strongly dependent on the intensity of the incident
399 radiation. As a result, these mathematical models are not valuable for design and scale
400 up of photocatalytic processes.

401 Another major limitation of current PWT kinetic models is that the impact of the water
402 matrix components is usually excluded, though many studies have demonstrated that
403 these may have a significant impact on the rate of photocatalytic degradation of
404 organic pollutants (Lado Ribeiro et al., 2019; Wang et al., 2015b; Wang et al., 2013b;
405 Zhang et al., 2013). Common water components such as bicarbonate, sulfate and
406 chloride, may react with ROS following highly complex reaction pathways and natural
407 organic matter (NOM) may also scavenge ROS (Lado Ribeiro et al., 2019), making it
408 highly complex to determine the contaminants' kinetic reaction rates. (Wang et al.,
409 2013b). Instead, a sequential relative rate technique based on laser pulse photolysis
410 has been proposed to quantify the effects of individual water components on the
411 generation rate of hydroxyl radicals in a system in which multiple water components
412 coexisted (Wang et al., 2013a). It is therefore necessary to develop comprehensive
413 reaction mechanisms that account for the impact of all dissolved species and

particularly those that reacts with ROS. Then, target contaminants rate laws should be developed based on such mechanisms.

The kinetic models discussed have been extended and applied for the description of pollutants degradation as a function of TOC in complex and in multicomponent systems (Colina-Márquez et al., 2009, Colina-Márquez et al., 2015, Colina-Márquez et al., 2018, Mueses et al., 2013, Rodriguez-Acosta et al., 2014).

2.1.3 Hydrodynamics modeling

PWT reactors require accurate solutions of the hydrodynamics, since this impact the local catalyst concentration, the transport of the chemical species and, consequently, the local rate of reactions. The multiphase flow of slurry photocatalyst suspensions can be solved by the Eulerian-Eulerian (E-E) approach (Ishi and Hibiki, 2011), by the Eulerian-Lagrangian approach (E-L) (Boyjoo et al., 2013) or by assuming a pseudo-homogeneous catalyst/water mixture. The E-E approach assumes the phases as interpenetrating continua, and the phases are solved through the Eulerian frame of reference. The E-E mass and momentum conservation equations are given by:

$$\frac{\partial}{\partial t}(\alpha_q \rho_q) + \nabla \cdot (\alpha_q \rho_q \vec{u}_q) = 0 \quad (1)$$

$$\frac{\partial}{\partial t}(\alpha_q \rho_q \vec{u}_q) + \nabla \cdot (\alpha_q \rho_q \vec{u}_q \vec{u}_q) \quad (2)$$

$$= -\alpha_q \nabla p + \nabla \cdot \bar{\tau}_q + \alpha_q \rho_q \vec{g} + \vec{R}_{pq} + \vec{F}_M$$

where α_q , ρ_q and $\vec{u}_q$ are volume fraction, density and velocity of phase q , p is the pressure field, $\bar{\tau}_q$ is the q phase stress tensor and $\vec{g}$ is gravity acceleration vector. $\vec{R}_{pq}$ is the momentum exchange between phases p and q due to drag forces and $\vec{F}_M$ is the momentum exchange due to other interphase forces (e.g. due to particles collision).

In contrast, the E-L approach considers the dispersed phase as independent trajectories solved by ordinary differential equations in the Lagrangean frame of

reference, while the continuous phase is modeled by the conventional Eulerian framework. The continuous phase is solved by the mass and momentum equations:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{u}) = 0 \quad (3)$$

$$\frac{\partial}{\partial t}(\rho \vec{u}) + \nabla \cdot (\rho \vec{u} \vec{u}) = -\nabla p + \nabla \cdot \bar{\bar{\tau}} + \rho \vec{g} \quad (4)$$

where ρ and $\vec{u}$ are the continuous phase density and velocity. and $\bar{\bar{\tau}}$ is the continuous phase stress tensor. The Lagrangian particles trajectories are solved by:

$$\frac{d\vec{x}_p}{dt} = \vec{u}_p \quad (5)$$

$$m_p \frac{d\vec{u}_p}{dt} = m_p \vec{g} \frac{(\rho_p - \rho)}{\rho_p} + \vec{F}_{drag} + \vec{F} \quad (6)$$

where m_p is the particle mass, $\vec{x}_p$ is particle position, $\vec{u}_p$ is the particle velocity, ρ_p is the density of the particle, $\vec{F}_{drag}$ is the drag force and $\vec{F}$ accounts for additional forces.

Nevertheless, small, suspended particles in PWT reactors have usually low inertia, thus, quickly respond to fluid velocity fluctuations. In addition, the volume fraction of the slurry suspensions is low (<0.01% in volume). Hence, in these cases the slurry flow can be treated as a pseudo-homogeneous single-phase flow. Using this approach, the mixture phase mass and momentum conservation equations are solved (Eq. 3 and 4) using volume-weighted mixture properties, usually approximated by the properties of the continuous phase due to the low volume fraction of the dispersed phase.

This pseudo-homogeneous approach has been widely assumed to model photocatalytic reactors (Casado et al., 2017a; Colina-Márquez et al., 2009; García-Gil et al., 2019; Li Puma et al., 2004; Toepfer et al., 2006; Turolla et al., 2016) while few studies adopted the multiphase approach thus far (Boyjoo et al., 2014; Wang et al., 2019). Large photocatalytic particles with high inertia and settling properties quite certainly need this latter modeling approach.

The impact of hydrodynamics on PWT reactors efficiency has been investigated considering idealized flow models: laminar flow, slit flow and plug flow (Li Puma, 2003). Many experimental and numerical studies in photocatalytic reactors have been conducted in the laminar flow regime (Casado et al., 2017a; Li Puma et al., 2007; Turolla et al., 2016), particularly due to the laboratory-scale size of the photoreactors. However, mass transfer limitations may arise under laminar flow since the molecular diffusion is the driving force for the mixing process, and the pollutants mass diffusivities in water are very low. While in micro-reactors the mixing can be intensified by shortening the molecular diffusion distance (Marinho et al., 2018), reactors with larger dimensions exhibit mixing limitations up to a complete absence of mixing, in which material balances of the chemical species can be computed by independent streamlines (Grčić and Li Puma, 2013; 2017). The streamline flow pattern can be prejudicial to the reactor operation as the regions with very low irradiance (under darkness condition) behave as dead zones.

On the other hand, the mixing in the photoreactor is intensified under turbulent flows. The impact of turbulent flow has been investigated in PWT tubular reactors coupled with a compound parabolic collector (Colina-Márquez et al., 2009; García-Gil et al., 2019; Otálvaro-Marín et al., 2019; Otálvaro-Marín et al., 2017). The results have shown that the reactor efficiency can increase not only due to the higher velocity near the walls (where the light irradiance is higher) (Otálvaro-Marín et al., 2017), but also due to the turbulent diffusion, that is several orders of magnitude higher than the molecular diffusion. This can enhance the reactor efficiency making it closer to the behavior observed in plug flow reactors, thus minimizing the impact of the regions under darkness conditions. However, non-homogeneous concentrations of water pollutants might still be observed as a result of the highly non-homogeneous

irradiances in the reactor (García-Gil et al., 2019).

The most widely used approach for the modeling of turbulent flows in PWT reactors is the Reynolds-Averaged Navier-Stokes (RANS), in which the solution variables in the Navier-Stokes equations are decomposed into the mean (ensemble-averaged or time-averaged) and fluctuating components. In this approach, the nonlinearities in the Navier-Stokes equation lead to an additional term arisen from the fluctuating components, which is known as the Reynolds stress tensor. The modeling of this term is known as the closure problem, and the flow most industrial applications it is modeled by the Boussinesq hypothesis (Hinze, 1975) wherein two additional transport equations are solved to compute the turbulence quantities (the turbulence kinetic energy, k , and either the turbulence kinetic energy dissipation, ε , or the specific dissipation energy, ω). Among the most widely used turbulence models one can cite the Standard $k - \varepsilon$ model (Launder and Spalding, 1972), the Realizable $k - \varepsilon$ model (Shih et al., 1995) and the $k - \omega$ Shear Stress Transport (SST) (Menter, 1994). The latter has the advantage of solving the viscous sublayer (provided that the near-wall mesh resolution is fine enough), which is necessary for the modeling of turbulent flows with photocatalysts supported on walls (Duran et al., 2010). Moreover, the hydrodynamics boundary layer coincides with the region of the highest gradient of light irradiance, supporting the resolution of the viscous sublayer also for slurry flows. An alternative to the solution of the viscous sublayer is the use of wall functions, which demand lesser mesh resolutions and are reasonably accurate for the near-wall treatments for industrial flow simulations. To date, Standard $k - \varepsilon$ model with wall functions has been used as the modeling strategy for the modeling of hydrodynamics in PWT reactors (Boyjoo et al., 2013; García-Gil et al., 2019).

A summary of the numerical studies of PWT reactors in a CFD environment that

coupled hydrodynamics, species transport, chemical reactions and radiation transport is shown in Table 4. Among these only a few studies have focused on the effect of the slurry flow on the radiation field and on the transport of the chemical species in PWT reactors (Boyjoo et al., 2014; Qi et al., 2011). Indeed, the turbulent fluctuations of the photocatalyst particles within the reacting fluid may have an effect beyond the mixing of the species transport, for example, by varying photon scattering. Furthermore, formation of photocatalyst aggregates may increase the particle hydrodynamic diameter, that can lead to sedimentation of the catalyst (Mena et al., 2018), therefore affecting the concentration of catalyst the flow field, and may also vary the optical properties (Tolosana-Moranchel et al., 2017).

Table 4. Review of numerical studies coupling hydrodynamics, radiation transport and degradation of water pollutants in a CFD environment.

Reactor type and catalyst	Water pollutant	Hydrodynamics modeling strategy	Solution of the Radiation transport	Reference
Annular reactor with TiO ₂ P25 in suspension	Mineralization of organic pollutants	Euler-Euler multiphase flow model; Turbulent flow modeled by the Standard $k - \varepsilon$ model with Standard Wall Treatment	Discrete Transfer Radiation Model	Qi et al., 2011
Annular reactor with an immobilized TiO ₂ surface	Degradation of Toluene	Laminar flow	Applied constant irradiance over the surface (RTE not solved)	Jović et al., 2012
Annular reactor with an immobilized TiO ₂ surface	Degradation of Rhodamine B	Laminar flow	Applied constant irradiance over the surface (RTE not solved)	Kumar and Bansal, 2013
Annular reactor with 2 or 4 artificial UV lamps with TiO ₂ P25 in suspension	Mineralization of organic pollutants	Euler-Euler multiphase flow model; Turbulent flow modeled by the Standard $k - \varepsilon$ model with Standard Wall Treatment	Discrete Ordinates Model (3 bands);	Boyjoo et al., 2014
Annular reactor with an immobilized TiO ₂ surface	Degradation of benzoic acid and 2,4-Dichlorophenoxyacetic acid	Laminar flow and turbulent flow (modeled by the Standard $k - \varepsilon$, the Realizable $k - \varepsilon$, the Reynolds Stress Model (RSM) and the low-Re $k - \varepsilon$) with Enhanced-Wall Treatment (solution of the viscous sublayer).	Discrete Ordinates Model	Duran et al., 2010
Annular reactor with TiO ₂ P25 in suspension	Degradation of oxalic acid	Pseudo-homogeneous; Laminar flow	Spectral solution of the Discrete Ordinates Model coupled with the Henyey-Greenstein	Turolla et al., 2016

			Phase function (2 bands)	
Annular reactor with TiO ₂ P25 in suspension	Photocatalytic oxidation of methanol to formaldehyde	Pseudo-homogeneous; Laminar flow	Discrete Ordinates Model;	Casado et al., 2017a
Solar reactor based on a tubular reactor coupled to a compound parabolic collector (CPC) using TiO ₂ P25 in suspension	Photocatalytic oxidation of methanol to formaldehyde	Pseudo-homogeneous; Turbulent flow modeled by the $k - \varepsilon$ model with the Standard Wall Function	Spectral solution of the Discrete Ordinates model (3 bands);	Casado et al., 2019
Planar microreactor with immobilized TiO ₂ surface	Degradation of Clofibric acid	Laminar flow	Net-Radiation method (Siegel and Howell, 2002)	Satuf et al., 2019
Annular reactor with TiO ₂ in suspension	Degradation of 2-hydroxybenzoic acid	Pseudo-homogeneous; Laminar flow	Either the Spectral solution of Discrete Ordinates (2 bands) and the Six-Flux Model (2 bands)	Peralta Muniz Moreira and Li Puma, 2020

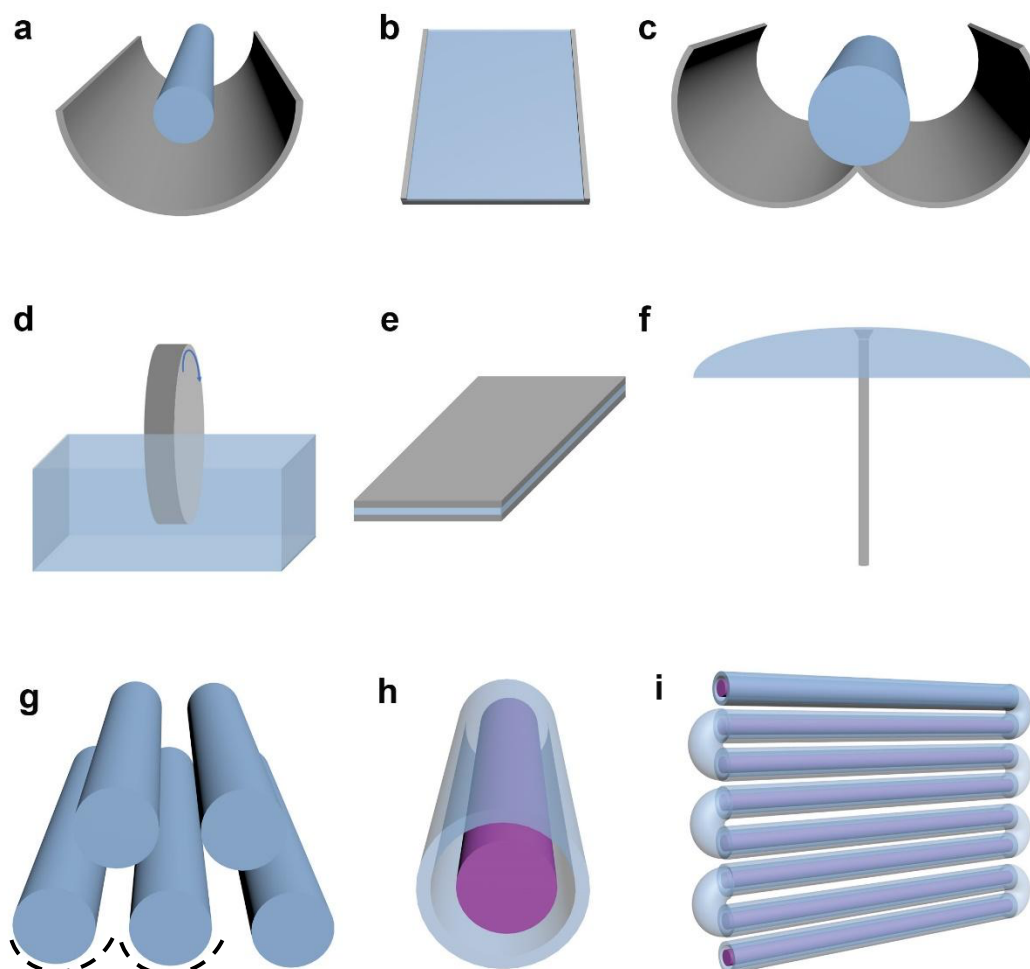
519

520 2.2 PWT configurations and their commercialization

521 The advances in modeling discussed have yielded several basic designs of pilot-
522 scale and full-scale photocatalytic reactors for water treatment (Figure 4 and 5). The
523 nature of the light source (solar or artificial light) strongly impacts the design of a PWT
524 unit. Solar PWT units typically have large, exposed surface areas due to the relatively
525 low intensity of solar light, unless a solar concentrator system (e.g., parabolic
526 reflectors, Fresnel lens and possibly optical fibers) is employed. Moreover, since some
527 solar PWT designs are open to air, the engineering of such systems should also
528 consider the impact of unfavorable weather conditions, in addition to maximizing the
529 absorption of solar light. In contrast, the engineering of PWT units powered by artificial
530 light mainly focus on decreasing the total rate of energy consumption through
531 improving the conversion of the electrical energy to useful photons and thought the
532 transport of these throughout the entire reactor volume in the most efficient way.
533 Several typical PWT configurations are discussed in the following section.

534 One of the earliest pilot-scale solar PWT unit was built by Sandia National

535 Laboratories (USA) where parabolic trough reactors (PTRs, Figure 4a) with width of
 536 2.1 m, length of 218 m, and a total aperture area of 465 m² was demonstrated to treat
 537 hazardous wastewater containing trichloroethylene (Alpert et al., 1991). Almost at the
 538 same time, a similar system with an aperture area of 384 m² was installed in PSA
 539 (Minero et al., 1993). The flow rate of these two units can be up to several m³/h.



540
 541 **Figure 4.** Geometry of several typical PWT pilot-scale reactors: (a) Parabolic Trough
 542 Reactor, (b) Free Falling Thin Film Slurry Reactor, (c) Compound Parabolic Collector,
 543 (d) Rotating Disk or Drum, (e) Double Skin Sheet Reactor, (f) Water Bell Fountain (g)
 544 Offset Multi Tubular Photoreactor, dash line is to show the reactors are placed in a
 545 parabolic way, (h) Annular Thin Film Slurry Reactor mounted vertically, and (i)
 546 Serpentine Assembly of Annular Thin Film Slurry Reactors.

547
 548 These installations were equipped with motorized systems that controlled the

orientation of parabolic troughs tracking the sun position for maximum light absorption. A variety of contaminants including chromium (VI), 4-chlorophenol, dichlorophenol, atrazine, and dichloroacetic acid were effectively degraded in PTRs (Malato et al., 2002). However, PTRs only collect the direct component of solar light, while the diffuse component is not absorbed, albeit direct and diffuse solar light reach the Earth's surface at almost equal intensities (Bockelmann et al., 1995). As a result, PTRs were soon judged as intrinsically flawed design since they become ineffective on cloudy days when only diffuse solar light was available. Another operational problem for this concentrating system, was the over-heating of the water, which required special engineering processes thus making PTRs relatively expensive to run (Braham and Harris, 2009).

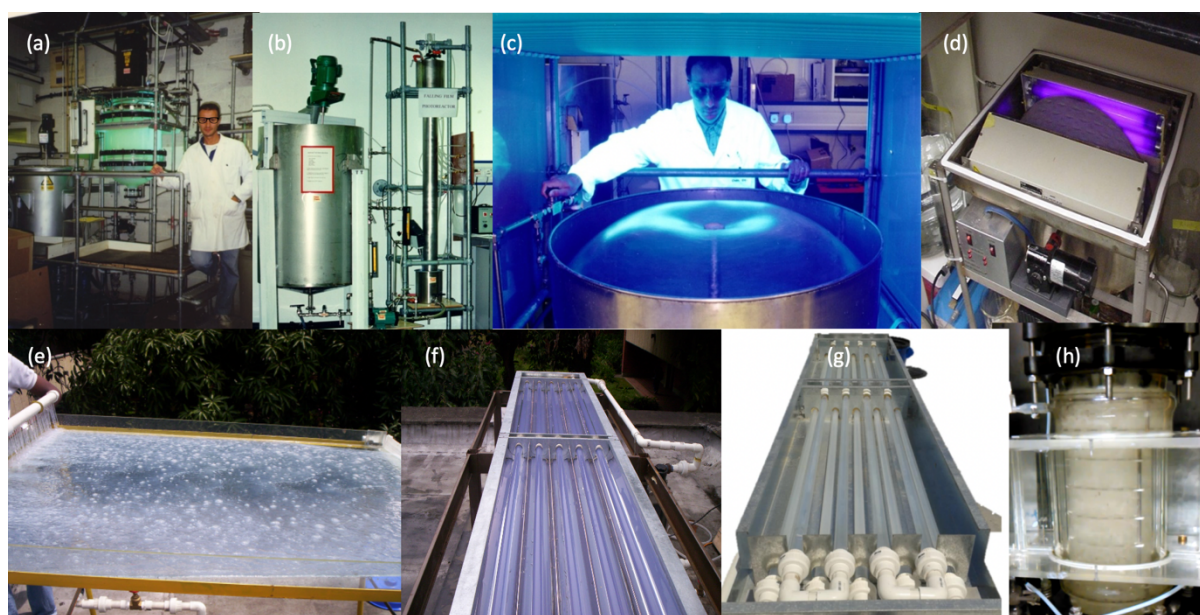


Figure 5. PWT pilot-scale reactors: (a) Draft-Tube Baffled Reactor (Bath University, UK; G. Li Puma and P.L Yue), (b) Annular Falling Film Slurry Reactor (The Hong Kong University of Science and Technology; Li Puma, and Yue, 1999a and 1999b), (c) Water Bell Fountain Reactor irradiated with simulated UVA solar light provided by commercial blacklights (The Hong Kong University of Science and Technology; Li Puma and Yue, 2001), (d) Rotating Disk Reactor (courtesy of Prof. Dionysiou, University of Cincinnati, USA; Dionysiou et al, 2000), (e) Flat Plate Falling Film Slurry

Reactor (Universidad del Valle, Colombia; Colina-Márquez et al., 2016), (f) CPC photoreactor module (Universidad de Cartagena, Colombia; Colina-Márquez et al., 2009), (g) Offset Multi Tubular Photoreactor (Universidad de Cartagena, Colombia; Ochoa-Gutiérrez et al., 2018), (f) Oscillatory Flow Reactor (Loughborough University, UK; Li Puma and Reis, 2016).

One of the earliest pilot-scale, UV powered reactor in Europe was constructed in 1991 at the University of Bath (UK). The 200 L draft-tube baffled photocatalytic reactor made with QVF (Figure 5a), was powered by six medium pressure mercury lamps immersed in the reactor and comprised two regions: a turbulent region including a mixing unit and a draft tube promoting the circulation of the suspended photocatalyst around the UV lamps; and a laminar region separated by a circular skirt in which catalyst retention in the reactor was taking place. The reactor could be operated in both batch and continuous flow.

Following these early studies, other non-concentrating reactor configurations such as solar ponds (Gernjak et al., 2004; Giménez et al., 1999), and falling film reactors (Malato Rodríguez et al., 2004), or partial concentrating systems, such as CPCs (Giménez et al., 1999; Malato et al., 2001), were developed. Free falling film reactors and solar ponds are in principle based on a thin film of water flowing as a catalyst slurry or over an immobilized catalyst (Figure 4b, and 5e). A 50 m² solar falling film photocatalytic reactor designed to treat 1 m³/h of textile wastewater has been demonstrated in Tunisia (Bousselmi et al., 2004; Zayani et al., 2009). Compared to the solar concentrating counterparts, these non-concentrating systems can collect both direct and diffuse solar light and in general do not require a sunlight tracking system, thus making these designs cost-effective if land space and land cost are not limiting factors. In addition, since the water may be in direct contact with air, it allows for a fully saturated aerobic environment, which is usually favorable for the degradation

of organic contaminants (Bockelmann et al., 1995). However, the performance of these two types of reactors can be affected by wind and unfavorable weather conditions. Additionally, the laminar flow hydrodynamic regime, which is typical of falling films, effectively limits the mass transfer rate of contaminants to the catalyst surface and may also induce catalyst sedimentation in slurry photocatalytic systems. The effect of mass transfer controlling the rate of reaction in immobilized photocatalytic films has been clearly demonstrated with a rotating disk configuration (Figure 4e and 5d) (Dionysiou et al., 2002). One important aspect is that optimal design of slurry falling film reactors can be easily achieved using appropriate values of catalyst loading to give optical thicknesses around 2-3. Under these conditions, the radiation field and the fluid residence time in these reactors are complementary (that is, the region with lower residence time receives the highest photon flux and vice-versa) making these in principle highly efficient photoreactor systems (Li Puma and Yue, 2003).

CPCs (Figure 1, 4c, and 5f) have demonstrated the advantages of both concentrating and non-concentrating systems including, the ability of capturing both the direct and the diffuse components of solar light, turbulent flow regime operation, a lesser dependence on weather conditions, no overheating of the water, and relatively small footprint (Colina –Márquez et al., 2009; Malato Rodríguez et al., 2004; Malato et al., 2007). As a result, several pilot-scale CPC units have been installed and used to investigate the removal of common micropollutants (Aguas et al., 2017; Miralles-Cuevas et al., 2017; Moreira et al., 2018). For example, a CPC plant with a total volume of 4000 L, a recirculation flow rate of 11 m³/h, and a solar collector field area of 100 m² has been operated by a Spanish pharmaceutical company for pretreatment of saline industrial wastewater since 2007 (Oller et al., 2007; Spasiano et al., 2015). Another CPC plant with a solar collector field area of 150 m² for removal of pesticides

has also been installed in Spain (Blanco-Galvez et al., 2006). Other non-concentrating reactors such as rotating disk (Dionysiou et al., 2000) (Figure 4d and 5d) or drum (Zhang et al., 2001), double skin sheet reactor (Figure 4e) (van Well et al., 1997) and water bell fountains (Figure 4f and 5c) (Li Puma and Yue, 2001) can be considered as the design extension of the above-mentioned reactors. Multiple rotating disks mounted on a single shaft with lamps/LEDs in between the disks provides a compact solution using artificial light sources, conversely the rotating drum and water bell configurations should be best suited for outdoor solar applications in open ponds. An interesting extension of CPC is the solar/UV lamp-irradiated tubular photocatalytic reactor (Portela et al., 2011). Differently from conventional CPC which can only be operated during daytime, with UV lamps inserted in the annular tube, this reactor can also be operational during night (Portela et al., 2011) with UV lamp powered by renewable energy (e.g., photovoltaics). A similar commercial system combining UV-LED photoreactors and CPCs has been developed by APRIA Systems (Spain). Despite the favorable properties of CPC, its low operating volumes of treatment compared to the large solar footprint is a major drawback. Thus, the Offset Multi Tubular Photoreactor (OMTP) was developed (Ochoa-Gutiérrez et al., 2018). This configuration increases the reactor volume by removing the parabolic reflectors of CPCs and introducing a further set of offset parallel tubes with their axes located at the contact points of the CPC involutes, in the space occupied by the involutes (Figure 4g and 5g). A summary of pilot-scale demonstrations of PWT using solar light is shown in Table 4.

The design of solar PWT reactors appears to follow a logical extension of solar thermal collectors (Malato et al., 2016), while that using artificial light sources is basically guided by the shape of the light sources, which in the early days were mainly

645 long cylindrical UV lamps. Early studies on solar photocatalysis reactors showed that
646 thin film slurries provide the most favorable geometry for the optimum utilization of the
647 incident photons (Puma and Yue, 1998a; b). As a result, one of the first configuration
648 of a UV PWT unit was an annular thin film reactor, where slurry suspensions of TiO_2
649 were pumped to a liquid distribution system and falling freely along a vertically
650 mounted hollow column (Puma and Yue, 1998b; Li Puma and Yue, 1999b; 2003)
651 (Figure 4h and 5b). The UV lamp was suspended in the middle of the hollow column
652 through a quartz or a borosilicate protecting sleeve. The optimized geometry of this
653 configuration is able to capture almost all photons emitted by the light source, if
654 operated under optimal value of the optical thickness (Li Puma, 2003; Li Puma and
655 Brucato, 2007), while the footprint is greatly reduced making this a highly efficient
656 photoreactor geometry. Meanwhile, the lessons learnt from solar PWT reactors have
657 suggested that the non-correspondence between the radiation field and fluid
658 residence time usually made PWT reactor inefficient (Li Puma and Yue, 1999a). This
659 is because photocatalytic processes are usually kinetically slow, thus the reactors
660 need to be operated with a sufficiently long residence time or with a recycle in order
661 to achieve complete degradation of the water contaminants. Thus, UV PWT reactors
662 with a serpentine-like geometry have been developed (Ray and Beenackers, 1998;
663 Wang et al., 2013b) and commercialized (Figure 4f) (Benotti et al., 2009) such as the
664 Purifics Photo-cat unit which is the only UV-PWT packaged unit that has seen
665 legitimate commercialization for small-scale applications (Cates, 2017). Photo-cat
666 units with a treatment capacity of 0.5 million gallons per day have been developed and
667 used for *ex-situ* groundwater treatment (Purifics). During the same period, various
668 reactors with immobilized catalysts on substrates, including glass fibers (Hofstadler et
669 al., 1994), optical fibers (Ling et al., 2017; O'Neal et al., 2018), membranes (Mozia,

2010), have been developed, though the concerns on their mechanical strength under strong turbulent conditions have not been addressed (Pozzo et al., 1997). It is also exciting to note that the advances on artificial light sources (e.g., LED) have enabled the design of compact UV reactors (Casado et al., 2017b; Martín-Sómer et al., 2017; O'Neal et al., 2018). However, full-scale reactors with LED are still at the early development stage of commercialization, as LED-activated photocatalysis faces some design challenges. For example, UVC LED with appropriate central wavelength ranging from 240 to 280 nm are suffering from overheating, high cost, reducing durability and very low wall-plug efficiencies (> 5% for UVC LEDs and > 22% for UVA LEDs) (Matafonova and Batoev, 2018). These efficiencies are significantly lower than that of low-pressure mercury UV lamps (typically 30-40% for both UVC and UVA) which have significantly lower costs. Thus, the current hype on the use of UV LEDs power sources should be carefully considered in terms of process economics, particularly if UVC LEDs are used. On the other hand, UVA LEDs with high power have been made available and these have generally higher transmittance through real water matrices. Moreover, as research continue to advance in the development of visible-light and plasmonic photocatalysts, the use of highly efficient and inexpensive visible LEDs powered with renewables and matching the plasmonic resonance wavelength of the photocatalyst may provide the awaited breakthrough in PWT efficiency. Several pilot-demonstrations of PWT using UV light are shown in Table 5.

Table 5. A list of pilot-scale demonstrations of PWT.

Light source	Reactor design	Flow rate/Treating capacity	Catalyst (conc.)/Oxidating	Contaminants treated (initial conc.)	Efficiency	Reference
Solar	PTR	4000 L/h, 838 L	P25 0.14 g/L	Sodium pentachlorophenolate (7mg/L)	20 min of operation time, ~ 100% degradation	(Minero et al., 1993)

	PTR	80 L	P25, 0.02 g/L	Diethylamine (5×10^{-4} M)	20 min, ~ 100% degradation	(Klare et al., 2000)
	PTR	269 L	P25 (0.2 g/L)	2,4-dichlorophenol (50 mg/L)	~ 47 min of residence time, concentration decreased to 2.5 mg/L	(Malato et al., 1997)
	CPC	10 L/min, 20 L	P25 (0.2 g/L)/H ₂ O ₂ (20 mg/L)	sulfamethoxazole, carbamazepine, and diclofenac (100 ug/L)	4h operation time, ~ 100% degradation	(Moreira et al., 2018)
	CPC	220 L	P25 (0.2 g/L)	Atrazine (10 mg/L)	Less than 1% left in about 20 min of residence time	(Minero et al., 1996)
	CPC	As high as 100 L/min, 12,000 L	P25 (0.1 wt%)	Trichloroethylene (120-5000 ppb)	~ 100 % of removal in about 4 min of residence time.	(Alpert et al., 1991)
	CPC	14 L	P25, supported on substrate (20 g/m ²)	<i>Escherichia coli</i> (10 ⁶ CFU/mL)	Decreased to 10 ² CFU/mL after 90 min of operation	(Sichel et al., 2007)
	CPC	20 L	TiO ₂ (35 mg/L)/H ₂ O ₂ (50 mg/L)	<i>Curvularia sp.</i> (10 ³ CFU/mL)	Decreased to 2 CFU/mL after 2h of treatment	(Aguas et al., 2017)
	CPC	35 L	TiO ₂ /reduced graphene oxide composite (200 mg/L)/H ₂ O ₂	200 ug/L of methomyl, pyrimethanil, isoproturon, and alachlor	Complete removal in 25 min	(Luna-Sanguino et al., 2020)
	Double-skin sheet reactor	30 L	TiO ₂	Dichloroacetic acid (77 ppm)	~ 100% of removal in 240 min of operation time	(van Well et al., 1997)
	Double-skin sheet reactor	143 L	P25 (5 g/L)	Dichloroacetic acid (56.8 mg/L)	19.2 mg/L after 4 h of operation	(Dillert et al., 1999)
	Free falling film	3 L/min, 200 L	TiO ₂ deposited on substrate (5 g/m ²)	Phenol (2.3 mg/L)	After 3.3 h of operation, the residual concentration was 1.25 mg/L	(Feitz et al., 2000)
	Free falling film	50mL/s, 100 L	TiO ₂ deposited on substrate (25 g/m ²)	Triadimenol (15,600 µg/L)	After 8 days of operation, the concentration decreased to 6050 µg/L	(Pichat et al., 2004)
	Free falling film	5 L/h	TiO ₂ deposited on substrate (-)	Municipal wastewater	COD decreased from 11 mg/L to ~ 1 mg/L after 4 h of operation	(Freudenh hammer et al., 1997)
	Free falling film	3 m ³ /h, 700 L	P25 deposited on substrate (10 g/m ²)	Azo dye (70 mg/L, prepared with well water)	Azo dye was removed in 300 min	(Zayani et al., 2009)
	Free	1 m ³ /h	Suspended or	Dichloroacetic acid	Treatment efficiency	(Bousseli

	falling film		deposited P25	(5 mM, in pre-treated textile wastewater)	was highly dependent on flow rate	et al., 2004)
UV	Annular Thin Film Slurry Reactor (Photo-cat)	24 L/min, ~11000 L	P25 (~ 50 mg/L)	Pharmaceuticals and endocrine disrupting compounds (16-1,300 ng/L)	Eleven of the 32 compounds were easily removed, with concentrations below or approaching detection limits with 0.53 kWh/m ³ of treatment: estrone, estradiol, ethinylestradiol, bisphenol A, octylphenol, butylated hydroxyanisole, atorvastatin, triclosan, diclofenac, sulfamethoxazole, and naproxen. Conversely, PFOS, tris(2-chloroethyl) phosphate, and tris(1-chloro-2-propyl) phosphate were largely resistant to the photocatalytic reactor membrane experiment, exhibiting concentrations following the maximum treatment (4.24 kWh/m ³) that were greater than 50% of their starting concentration.	(Benotti et al., 2009)
	Spinning disk	10 L, 50 cm ³ /s	P25 deposited on disk	4-chlorophenol (90 µM)	~ 100% degradation after 4h of operation	(Yatmaz et al., 2001)
	TiO ₂ coated optical fibers	41 L/h, 2 L	TiO ₂ coated optical fibers/H ₂ O ₂ (3.1 mM)	4-chlorophenol (1 mM)	~ 50% degradation after 25 h of operation	(Hofstadler et al., 1994)
	Annular Thin Film Slurry Reactor	24 L/h, 480 L	P25 (2.75 g/L)	salicylic acid (60 ppm)	TOC removal rate = 700 mg of carbon/h	(Puma and Yue, 1998b)

3. PWT system design

3.1. Conceptual design of PWT: Operating regime

Engineering and design considerations are as important as catalyst activity and reactor geometry in the development of an efficient PWT process. These include reactor tubing diameter, material of construction, water flow rate, pressure drop through the system, optimal catalyst loading, pH and dissolved oxygen concentration.

3.1.1 Catalyst concentration and optical thickness

As discussed in section 2, the optical efficiency of a slurry reactor strongly depends on the catalyst concentration. In real applications, it is usually found that the overall photocatalytic water treatment performance is linearly dependent on the catalyst concentration (C_{cat} , kg/m³) at low catalyst concentrations, then an optimum C_{cat} value is reached, beyond which the catalyst optical turbidity starts to screen light absorption darkening the regions of the reactor volume further away from the light source.

Two dimensionless design parameters determine optimal catalyst loading in slurry catalyst suspensions: These are the optical thickness (τ) (Eq. 1) which can be easily evaluated for any reactor, and the apparent optical thickness (τ_{app}) (Eq. 2) which is directly derived from the SFM (Colina-Márquez et al., 2015).

$$\tau = \kappa_{average} C_{cat} L \quad (7)$$

$$\tau_{app} = a\tau\sqrt{1 - \omega_{corr}^2} \quad (8)$$

where, $\kappa_{average}$ (m²/kg) (Eq. 9) is the spectral specific absorption coefficient of the catalyst suspension averaged across the wavelength spectrum I_λ of the incident radiation (thus light source dependent) that is able to photoactivate the catalyst (e.g., for TiO₂ anatase this is up to the band-gap edge at 384 nm);

$$\kappa_{average} = \frac{\int_\lambda \kappa_\lambda I_\lambda d\lambda}{\int_\lambda I_\lambda d\lambda} \quad (9)$$

L (m) is a characteristic reactor length (e.g., the radius of the reactor tube, the average thickness of a falling film or flat plate or the thickness of the reactor annulus) and a and ω_{corr} are dimensionless model parameters that can be easily derived with simple calculations from the SFM (see for example, Colina-Márquez et al., 2015). The concept of corrected scattering albedo (ω_{corr}) is closely linked to the SFM and has been discussed in the following studies: Brucato et al., 2006; Li Puma and Brucato, 2007. The procedure to obtain the average thickness of the falling film was discussed in the following works: Li Puma and Yue, 1998; Li Puma and Yue, 2003; Li Puma and Brucato, 2007; Colina-Márquez et al., 2016; Otálvaro-Marín et al., 2014). Although the optimum design values of τ rely heavily on of the catalyst scattering albedo, τ_{app} does not vary with the scattering albedo (Li Puma and Brucato, 2007). Thus, optimal values have been reported in literature for TiO_2 P25: τ_{app} equal to 7.8 for CPC, 13.0 for tubular reactors irradiated from above (Colina-Márquez et al., 2010) and 1.8 to 4.4 for flat plate reactors (Li Puma and Brucato, 2007), see also Table 1.

3.1.2 Dissolved oxygen

A high dissolved oxygen (DO) level is favorable for some photocatalytic oxidation reactions (Liang et al., 2008), while a low DO level, which can be achieved by purging with nitrogen, should be used for photocatalytic reduction reactions such as heavy metal remediation (Lee et al., 2003; Zheng et al., 2017) photocatalytic reforming (Nomikos et al., 2014) and photocatalytic CO_2 reduction to chemicals (Wang et al., 2019). Thus, reactors with an open design to the atmosphere are unsuitable for reduction reactions.

3.1.3 pH

pH is an important operational parameter as it affects the surface charge of catalysts and thus the adsorption or reacting species and the size of catalyst

aggregates in suspension (Chong et al., 2010). For example, at $\text{pH} \approx 7$, the mean size of TiO_2 (P-25) aggregates in water is close to 3 μm , while becomes less than 500 nm at pH lower than 6 or higher than 8.5 (Galvez and Rodriguez, 2003). Crucially, catalyst aggregate size also impacts the optical properties of the catalyst (i.e., specific absorption κ_{average} and scattering σ_{average} spectral-averaged coefficients) in the slurry and thus the transport of radiation in the reactor and the overall rate of photon absorption. This adds another layer of complexity to the design of photocatalytic reactors since optimal catalyst loading is a function of optical thickness (τ or τ_{app}). Thus, preliminary laboratory experiments may be necessary to determine the range of pH expected in a photocatalytic water treatment system to achieve optimal system design. The bandgaps of semiconductor particles are also slightly dependent on pH (Wang et al., 2017), which in turns affects the optical properties of the catalyst and in turn the rate of photon absorption. Moreover, pH determines the ionic composition of contaminants. Both factors affect the quantum yield of the photocatalyst towards the removal of the targeted contaminants. All these aspects add on the complexity of photocatalytic reactor modeling, and a pretreatment step may be necessary to adjust the pH to improve the performance of PWT.

3.1.4 Mixing and flow regime

A high water turbulence level (usually but not exclusively obtained at high flow rates) results in a high mass transfer rate of the reacting species to the catalyst surface in both immobilized and suspended catalyst systems, and this is usually reflected with an increase of the apparent photocatalytic activity as flow rate increases. These operational parameters vary with the constituents of the water to be treated and with the configuration of the photocatalytic reactor, and thus these aspects should be investigated during the design of the photocatalytic reactor. CFD simulations often

allow the appraisal of the impact of water flow rate and turbulence on reactor performance (Alpert et al., 2010; Ghafoori et al., 2014). On the other hand, pilot-scale photocatalytic reactors are usually operated in the turbulent flow regime ($Re > 2100$) to avoid the sedimentation of the suspended catalyst (Colina-Márquez et al., 2009). However, high flow rates imply short residence times in the light-irradiation zones in flow-through reactors, thus a long light-irradiated reactor zone often complemented by a certain degree of external recirculation of the reactor effluents is usually required to achieve complete removal of contaminants. It should be noted that in specific reactor designs, turbulence may be controlled independently of reaction time via mechanical mixing using impellers, baffles under oscillatory flow (Yue et al., 2000; Gao et al., 2003; Lucas et al., 2016; Li Puma and Reis, 2016; Figure 5h) or via static mixers (Li et al., 2011; Wang et al., 2013b; Díez et al., 2018).

For commercial scale applications, modular designs operated in the flow-through operational mode are preferred because they can deliver a customizable equipment, easy process control, and large water treatment rates. The use of inserts as static mixers, which can also serve as support for immobilized photocatalyst, has been recently reported following the process intensification principles (Díez et al., 2018). This design is intended to obtain more compact and efficient unit operations.

3.1.5 Mass transport and Damköhler number

Another useful dimensionless number for the design of PWT reactors is the Damköhler number (Da) as mass transport limitations may become significant in large reactor volumes. Da is determined by the ratio of the overall reaction rate, calculated at reactor inlet reactants concentration and at maximum photon flux, to the maximum convective/diffusive mass flow rate of reactants (Li Puma, 2005). It determines whether chemical reaction or convective/diffusive mass transport rates are controlling

the removal of water contaminants. Since Da is independent of reactor type and size, it has been computed for pilot-scale falling film (Puma and Yue, 1998a; Puma and Yue, 1998b), fountain reactor (Li Puma and Yue, 2001), rotating disk (Dionysiou et al., 2002), annular (Li Puma and Brucato, 2007), membrane (Camera-Roda et al., 2017) or tubular photoreactors (Otálvaro-Marín et al., 2019). In contrast to conventional chemical reactors, the Damköhler number in PWT should also account for the local rate of photon absorption since this influence the maximum reaction rate and therefore the scale-up of the photoreactor.

Recently, a new interpretation of Da as a local property was introduced to provide scale-up and design tools in unidirectional flow-through solar photoreactors (Otálvaro-Marín and Machuca-Martínez, 2021). By this approach, Da groups the effects of the optical and surface characteristics of the catalyst, catalyst load, fluctuating radiant flux, the rate of absorption of photons, the rate of reactions of different stages, and the design and operational variables. By keeping Da constant, the photoreactor can be scaled-up by varying the volumetric flow rate to estimate the required reactor volume and irradiance considering that $Da \propto V_{design} \sqrt{I_{source}} / Q$, where V_{design} is the reactor volume, I_{source} is the incident irradiance and Q is the volumetric flow rate. However, scaling up by keeping Da constant may be limited by the available incident irradiance, as a significant increase of I_{source} , either by natural or artificial light, may become unfeasible.

3.2. Pre-treatment, post-treatment and process intensification

An important aspect of PWT design is the coupling with a pre-treatment processes to improve overall efficiency, since the performance and lifetime of photocatalysts can be affected by the water matrix constituents. An efficient pre-treatment step may also help reduce the overall investment of a PWT unit. Filtration to decrease turbidity when

significant may be necessary, as high turbidity affects the penetration of light especially in pilot-scale solar applications (Khan et al., 2012). A high water alkalinity can induce the aggregation of catalyst particles since some common photocatalysts have points of zero charge at pH below 7 (~6 for TiO_2 and ~4 for BiPO_4) (Chou and Liao, 2005; Daskalaki et al., 2010). The photocatalytic reactor design guide should therefore start from an accurate evaluation of the optical properties of the catalyst particles (absorption and scattering coefficients and scattering albedo) in suspension or in an immobilized film, under the prevalent operational conditions (hydrodynamics and pH), which then guide the design and operation of the reactor under optimal optical thicknesses (Table 1). Pretreatment may also be needed to remove dissolved sulfate and chloride ions as these species can adversely affect the photocatalytic process, either by scavenging ROS or by causing the aggregation of catalysts. Specifically, natural organic matters (NOM) can consume ROS and thus negatively impact the treatment efficiency of PWT, (Wang et al., 2015b) while anions with high concentrations can easily compete with target contaminants for adsorption sites and neutralize the catalyst particles, if the photocatalysts are positively charged (Chang et al., 2015; Farner Budarz et al., 2017). However, the aggregation or adsorption issues could be mitigated if strong turbulence exists in the photocatalyst reactor. Overall, high water alkalinity is not recommended as carbonate species can scavenge hydroxyl radicals (Zhang et al., 2015).

A few studies have also suggested that PWT is not feasible to treat water with an overall pollutant load higher than (0.1 - 1.0) g/L (Kiriakidou et al., 1999). The main limitation here resides on the available surface area for contaminant adsorption, which effectively limits the rate of contaminant removal. In general, it may be concluded that, high pollutants loads (> 0.1 g/L) requires high catalyst concentrations, which in turn

results in the use of thin-film reactor geometries (e.g., falling films) to achieve optimal optical thicknesses (Table 1). Conversely, low pollutants loads (< 1 ppm) can be run with low catalyst concentrations, which in turn results in the use of thick-bore diameter reactor geometries (e.g., CPC). Wastewaters with dark color, such from the dying industry or landfill leachates, can reduce the UV irradiance and inhibit the PWT performance, thus pre-treatment may be needed to decrease the opacity of the water (Wiszniewski et al., 2006; Reza et al., 2017).

Although PWT is not feasible as a universal water treatment technique (Loeb et al., 2019), it can be considered as an alternative and sustainable, back-up or polishing solution when conventional treatment processes cannot achieve the intended treatment goals. PWT are most likely to be coupled with biological processes to provide an economical water treatment process. For this coupled system, the BOD/COD ratio is an appropriate indicator to determine the conditions in which PWT should be applied. Specifically, for wastewater containing high concentrations of recalcitrant compounds (i.e., a low BOD/COD ratio), photocatalysis as a pretreatment should be more appropriate. Conversely, if the BOD/COD ratio is high (> 0.4), PWT should only be used as a polishing treatment process (Colina-Márquez et al., 2013; Muñoz et al., 2006). Although the concept of coupling biological systems with photocatalysis is not entirely novel (Pulgarín et al., 1999; Sarria et al., 2002), this alternative has been gaining relevance because of the recent interest on applying process intensification and sustainability principles on advanced oxidation processes (AOPs) (Biard et al., 2018; Rodríguez-Chueca et al., 2018). Other water treatment processes, such as electrocoagulation (Boroski et al., 2009) and constructed wetland (Chen et al., 2011), have also been coupled with PWT.

In fact, the requirements for treated water can vary according to its final use. For

example, the most recent photocatalysis studies have focused on the removal of contaminants of emerging concern (e.g., pharmaceuticals and personal care products (PPCPs), X-ray contrast media, and PFAS) (Arce-Sarria et al., 2018; Rivas et al., 2012; Sahu et al., 2018b; Zurita et al., 2009), which are mostly non-biodegradable and refractory to many conventional water treatments. Nonetheless, the wastewater polluted with these contaminants may also carry a large load of biodegradable contaminants, thus a biological system should be used as pretreatment to remove the biodegradable organic matter, while the elimination of the refractory contaminants would be carried out by PWT (Hassan et al., 2016; Thiam et al., 2015).

A post-treatment process may also be necessary before release of the PWT effluent. An ultrafiltration unit is usually used to separate the catalysts from the treated water in slurry reactors. The catalysts can be reused into the treatment process again after the membrane unit is backwashed. This strategy of catalyst recovery has been used in two commercialized PWT units (Gerrity et al., 2008). Electron donors (e.g., methanol and citric acid) are sometimes added for efficient photocatalytic reduction (Zhang et al., 2012), though it may be unnecessary when the water contains organic contaminants that can play the same role (Galvez and Rodriguez, 2003). A filtration step to remove the product from electron donors (e.g., formate can be produced using methanol as electron donor), (Chen et al., 2003) or an alkaline addition step to neutralize the pH (e. g. formation of formate decreases the pH significantly) may be required under such circumstances. Temperature control is also required for batch systems, as high temperature can volatilize compounds with low boiling point in the wastewater. For example, hydrofluoric acid, which is harmful and volatilized, can be produced during the degradation of PFAS (Sahu et al., 2018a). To maintain a stable temperature in a pilot-scale Photo-cat system, a cooling jacket is equipped around the

UV reactor through which tap water is flowed through during operation (Benotti et al., 2009) although such system appears to be self-defeating.

3.3. PWT process economics

An example of cost estimation for a solar PWT process is shown in Table 6. Capital cost accounts for the major expense of a typical solar PWT process, mainly because of the footprint area that would be needed to achieve satisfactory treatment performance and capacity. It is thus reasonable to believe that small-sized solar photoreactor, which can be used for water disinfection in rural areas with low land cost, should be cost effective. On the contrary, very few studies estimated the treatment cost for UV PWT process at pilot or greater scale. However, since electricity accounts for the primary cost of a typical UV PWT process, the treatment cost can be decreased by developing more energy-efficient pumps and membranes and by powering all electrical components with renewables (e.g., photovoltaics).

Table 6. Cost estimation of a solar PWT plant and a UV PWT unit.

Item	Estimation ^c	Solar ^a
		Cost (thousand €, 1999)
A Facility cost		140
B Project contingency	15% of A	21
C Engineering and set-up	50% of A+B	81
D Spare parts	0.5% of A	7
E Capital Cost	A+B+C+D	249
F Annual Labor cost		5
G Annual Maintenance materials	2% of A+B	3.24
H Annual Chemical supplies		553.5
I Annual Electricity		1.5
K Annual Maintenance and Operation	F+G+H+I	65.7
M Annual treatment cost		18.0 €/m ³

Note: ^a a solar PWT process (300 m² solar PWT plant with TiO₂ as catalyst for annual treatment of 6,000 m³ of pesticide-contaminated water) (Galvez and Rodriguez, 2003).

The use of photocatalysts particles that facilitates catalyst recovery such as with

magnetic properties (Yao et al., 2015) or of micrometer size (Sahu et al., 2018b) should also reduce the water treatment cost. However, it should be noted that catalysts with larger size may demonstrate lower photocatalytic performance due to their lower surface area and lower photon absorption efficiency (Salaices et al., 2002), thus requiring a higher photon dose (thus higher cost) to achieve the equivalent treatment performance compared to their smaller size counterparts.

Even though several studies suggested that PWT employing immobilized catalysts could be more energy-efficient than slurry systems at bench scale (Lee et al., 2018; O'Neal et al., 2018), an accurate comparison on energy consumption at pilot- or greater scale is needed. It is also necessary to make an appraisal of the long-term catalyst deactivation, dissolution of co-catalysts or detachment from the supporting substrates (Hofstadler et al., 1994; Lee et al., 2018; Ling et al., 2017) since these aspects affects the water treatment cost. The use of low doses of supplementary oxidants in PWT, such as H_2O_2 can also make the technology more cost-competitive (Li Puma and Yue, 1999a).

When all process costs, such as facility, labor, and maintenance, were considered, the cost of treating pesticide-contaminated water with solar photocatalysis was estimated to be 18 €/m³ (~21.7 \$/m³ in 1999), whereas that of treating azo dye-contaminated water with UV photocatalysis was 3.84 \$/m³ (in 2010, Table 6). However, it should be noted that treatment cost may vary with the target contaminant significantly. For example, the cost of treating trichloroethylene-contaminated water with solar photocatalysis has been estimated to be only 7.9 \$/m³ (Mahamuni and Adewuyi, 2010), and the cost for *E. Coli*. Inactivation was only (0.06 - 0.4) \$/m³, significantly lower than that of pesticides. Table 7 summarizes the capital and operating costs estimated by pilot-scale studies.

937

938 **Table 7.** Review of pilot-scale studies that estimated the operation and capital cost.

Contaminants	Photocatalyst	Irradiation Source	Reactor Volume	Treatment Cost	Capital cost	Reference
Wastewater from a power plant	TiO ₂ /H ₂ O ₂	UV	CPC 28 L	0.3 €/m ³ (4.5 g TOC)	17,600 €	Durán et al., 2012
	TiO ₂ /H ₂ O ₂	Solar	CPC 50 L	0.05 €/m ³ (4.5 g TOC)	23,300 €	
<i>E. Coli.</i>	TiO ₂	Solar	CPC 25 L	0.4 \$/m ³	20,068 \$	Vidal et al., 1999
Volatile organic compounds	TiO ₂ /O ₃	UV	Annular 15 L	25.67 \$/m ³	12,789\$	Fernandes et al., 2019
Tannery wastewaters	TiO ₂ /Fe ²⁺ /H ₂ O ₂	Solar	Annular 96 m ³ /day	21.34 \$/m ³	168,906 \$	Selvabharathi et al., 2016
Polycyclic aromatic hydrocarbons ^a	TiO ₂	UV	235,000 L	7.1 \$/m ³	5,967,532 \$	Nirmala Rani et al., 2021
Diclofenac	ZnO	UV	Beaker 100 mL	77.14 \$/g diclofenac removal	N.A. ^b	Novakovic et al., 2020
2,4-dichlorophenoxyacetic acid	TiO ₂	UV	Annular 2 L	11.71 \$/m ³	N.A.	Balakrishnan et al., 2021
As (III)	Fe ₂ O ₃ /Mn ₂ O ₃	UV	Annular 1 L	5.1 €/g of As (III) removal	N.A.	Eslami et al., 2018
Acid blue 113	ZnO-Ag	UV	Annular 408 mL	0.92 \$/m ³	N.A.	Mohammadzadeh et al., 2015
Pharmaceutical and agrochemical chemicals	Carbon nanotubes/M OF-808 on substrate	Visible light	Thin film 200 mL	2.5 \$/m ³	N.A.	Samy, et al., 2021
Hospital wastewater	TiO ₂ CeO ₂	UV	Beaker 1 L	8.7 €/m ³ 2.28 €/m ³	N.A.	Sponza et al., 2017
Metalworking wastewater	ZnO/H ₂ O ₂	UV	Annular 5.3 L	5.3 \$/m ³	N.A.	Mofrad, et al., 2020
Acetaminophen, antipyrine, bisphenol A, caffeine, metoprolol and testosterone	TiO ₂	Solar	CPC 1.8 L	2.1 - 4.3 €/m ³	N.A.	Quiñones, et al., 2015
	TiO ₂ /O ₃	Solar	CPC 1.8 L	1.5 - 3.2 €/m ³	N.A.	
Aniline	TiO ₂ /H ₂ O ₂	UV	Rotating drum reactor 6L, coated Surface 1.13m ²	0.67 €/m ³	N.A.	Durán, et al., 2018
Diphenyldramine	TiO ₂	Solar	CPC 0.95 L	0.26 €/m ³	N.A.	López, et al., 2018
Pentoxifylline	Fe-TiO ₂	Solar	Fixed-bed reactor 5L	903.16 \$/m ³	15.5 \$	Bansal, et al., 2018
Valproic acid sodium salt	TiO ₂	Solar	CPC	0.48 €/m ³	N.A.	Haranaka-Funai, et al., 2017
	TiO ₂	UV	Vessel 2L	0.57 €/m ³	N.A.	
Metoprolol	TiO ₂	UV	Tubular reactor 1L	89.9 €/L	19460 €	Giménez, et al., 2015
	TiO ₂	Solar	CPC 10 L	10.4 €/L	18540 €	
Bisphenol A, bisphenol B, diamyl phthalate, butyl benzylphthalate, methylparaben and ethylparaben ^a	ZnO	Solar	CPC 100 L	34.7 €/m ³	32,694 €	Vela, et al., 2018
	TiO ₂ P25			55.3 €/m ³		
	TiO ₂ vlp 7000			98.6 €/m ³		

Note: ^aThe cost was estimated by scaling up a laboratory scale reactor. ^b N.A. represents the information is not available.

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941 “Figure of merit” has been proposed (e.g., electrical energy per unit order (EE/O))

942 (Bolton James et al., 2001) to allow the comparison among the efficiency of different

943 water treatment processes. It should be noted that EE/O can be greatly affected by

the water matrix composition (Bolton and Cater, 1994), as the water constituents may absorb light or quench ROS, thus reducing the energy efficiency of the water treatment process. For example, in a bench-scale UV/TiO₂ process using an annual photoreactor to remove metaldehyde, the EE/O increased from 6.4 to 41.1 kWh/m³ per order when the alkalinity, as CaCO₃ increased from 0 to 120 mg/L, due to the formation of TiO₂ aggregates which lowered the active irradiated surface area of the catalyst (Autin et al., 2013). The EE/O of PWT is usually reported to be higher than other AOPs such as UV/H₂O₂ and UV/O₃ (Figure 6) which also produce ROS to remove recalcitrant contaminants. However, comparison of EE/O values from different studies can be skewed by a variety of factors, such as influent quality, and treatment goal significantly impacts the EE/O. A more rational comparison should be conducted under similar operational conditions. For example, the EE/O of TiO₂/UV and UV/H₂O₂ processes compared using a Purifics Photo-cat unit with a TiO₂ membrane recovery system, showed that EE/O of TiO₂/UV was nearly one order of magnitude higher than in the treatment with the UV/H₂O₂ (Benotti et al., 2009; Cates, 2017). Though this comparison is highly insightful for practical applications, as all the operation parameters were maintained the same except the unit was operated with TiO₂ (UV/TiO₂ process) and without catalyst but with H₂O₂ (UV/H₂O₂ process), it should be noted that river water with high UV transmittance (92%) was used in this study. Further studies are, however, needed to evaluate the EE/O with waters that have lower UV transparency. The generally higher EE/O values of UV/TiO₂ than that of other AOPs may be ascribed to the lower quantum yield of photocatalysis (Loeb et al., 2019), and higher energy requirements for the catalyst recovery (Benotti et al., 2009). Another pilot-scale study which compared the efficiency of solar Fenton and solar TiO₂ photocatalysis also reported similar conclusions (Malato et al., 2001).

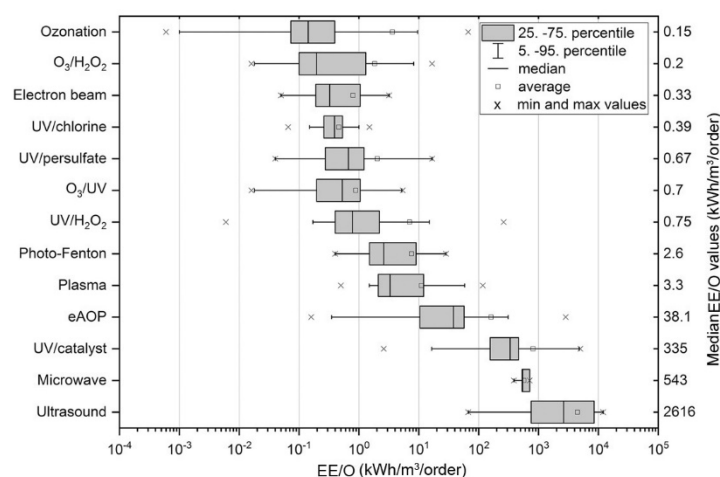


Figure 6. EE/O values of different AOPs, adapted from Reference (Miklos et al., 2018) with permission from Elsevier.

4. PWT patents

PWT has attracted considerable commercial interest over the past two decades. According to The Orbit Platform from Questel, 4301 inventions relevant to photocatalytic water/wastewater treatment have been patented from 1999 to 2020 (searching strategies are shown in SI). However, only approximately 10% (446) of the patents are relevant to photocatalytic reactors, while most disclosures relate to photocatalysts synthesis, including their use in wastewater treatment. Thus, disclosures and publication of scientific papers have followed the same path. However, over the past few years, 812 patents (accounting for ~18.9% of the total patents) have ceased, somehow indicating that many of the photocatalysts developed in the laboratories were not suitable for commercial exploitation. Among the 446 patents on photocatalytic reactors for wastewater treatment, China has the largest share of patent families among all the other countries: 235 for China, 42 for the United States, 31 for South Korea, 18 for France (Figure 7). It is interesting to note that the numbers of patents have been stable until 2016, beyond which the number of patents significantly increased from 13 in 2015 to 67 in 2016 with Chinese inventions taking the largest

share. This fact mirrors the ambitious plan for clean water released by the Chinese government in 2015, reported as a 10-point Water Pollution Prevention and Control Action Plan. On the other hand, as the two biggest economies, both China and the U.S., have the largest patent numbers, implying PWT as a novel water treatment process still attracts interest in the water treatment within academia and industries.

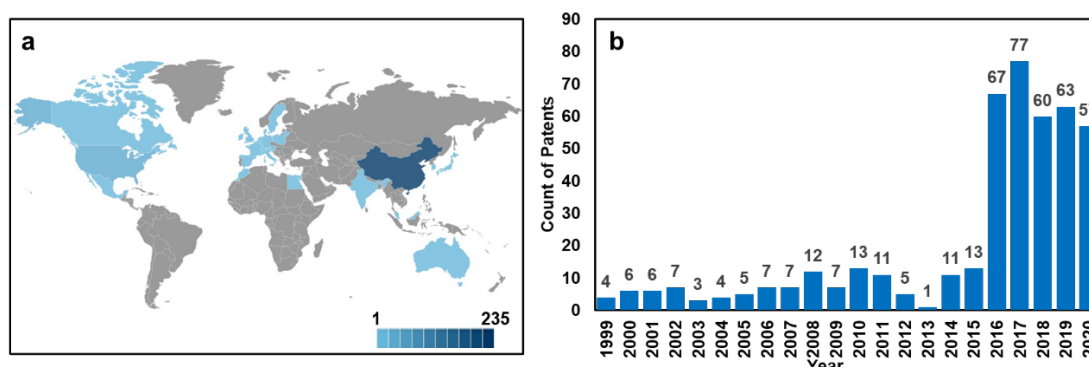


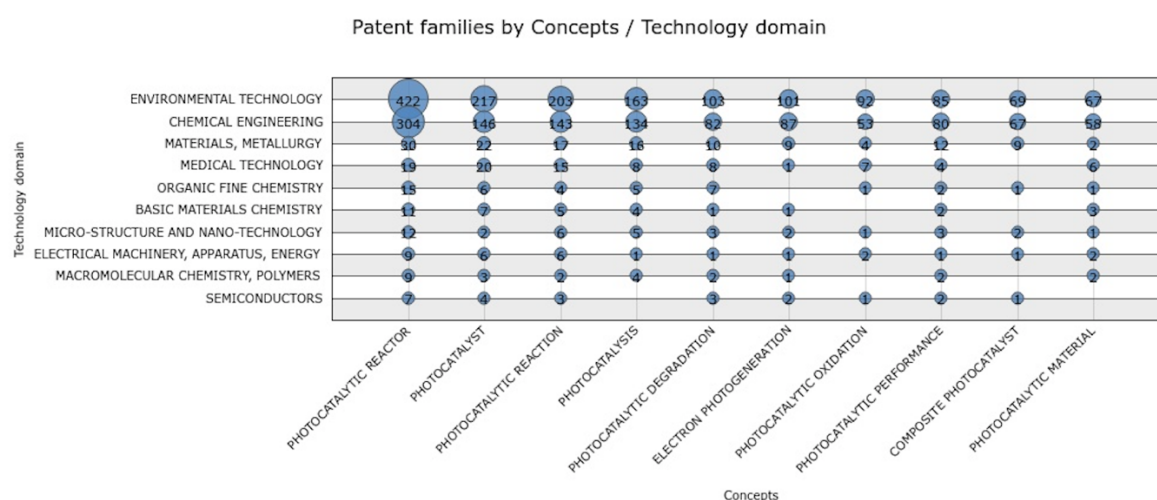
Figure 7. Patents on photocatalytic reactors for wastewater treatment (a) map and (b) trend over the last 20 years.

Espacenet database yielded similar results as the Orbit Platform. Further patent search using Espacenet shows that the most relevant domains for the current paper are found within the Cooperative Patent Classification (CPC) codes C02F-2201/00 and C02F-2305/10, which are related to apparatus for water treatment and the use of photocatalysts in water treatment, respectively as follows: C02F Treatment of water, waste water, sewage, or sludge; C02F-2201/00 Apparatus for treatment of water, waste water or sewage; C02F-2305 Use of specific compounds during water treatment; C02F-2305/10 Photocatalysts.

A summary of the patent search with the main claims and figures of selected patent highlights are shown in Table S1 (see Supporting Information). The fundamental configurations of the reactors are similar with that reported in Figure 4. For example, one of the oldest patents for solar PWT reactors is patent EP0738686

(A1) demonstrated the serpentine-like geometry of photocatalytic reactor, as shown in Figure 4i (Benz et al., 1996). A concentrating solar photoreactor (Patent 6 in Table S1) has similar geometry as in Figure 4a. Some other key points were observed among the documents: (1) Most patents focus on engineering aspects, such as how to install light source (Patents 2, 4, 6, 11, and 25 in Table S1) and improve mass transfer rate (Patents 12, 14, 25, and 33). Some on-line monitoring systems are also demonstrated (Patent 24 and 32); (2) Coupling with other treatment processes, such as membranes, microwave, and ozone, are widely demonstrated (Patents 3 and 9); (3) Prototypes of reactors with unconventional light source, such as VUV and UV LED, show that PWT reactors can be compact and operated under continuous flow mode (Patents 13, 22, 23, and 31); (4) Some patents demonstrated the system for treatment of wastewater with large volumes (e.g., Patent 18). It was noted that some of the ideas demonstrated in the patents are not feasible even though some portions of the ideas can be innovative and patentable. For example, even though many patents mentioned the use of immobilized catalysts, information on the long-term stability of the PWT treatment process is usually omitted (Patents 4, 7, 10, 11, 15, 16, 17, 19, 26, 28, 29, and 35). Moreover, the production of immobilized catalyst over large supporting areas in large-scale reactors could be challenging and expensive. More importantly, some of the reactors in the patents seem inefficient as the slurry film is very thick, while thin slurry film has been proven to be the most efficient, by both simulation and experimental works. Because of above facts, few of the patents have progressed to industrial applications. It was also noted that most of these patents were pursued by universities (~ 85%), where the patent costs and benefits are less carefully considered than in profit-based companies.

The photoreactors devices reported in patents (Figure 8) are related with environmental technology, chemical engineering and materials, and the fundamental concepts mainly focus on light distribution, the type of light, the type and use of the catalyst, and the fluid distribution in the reactor. The technical information found in the patents mirrors closely the main characteristics of photoreactors designs described in literature.



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Figure 8. Relationship between technology domains and main concepts related to photoreactors.

5. Outlook

Photocatalysts. While manufacturing cost, durability, and ease of separation/recovery are all the key factors for the development of novel catalytic materials, continuous advances in photocatalytic material gives PWT potential advantages over other conventional AOPs. Semiconductor materials with appropriate band-gaps and efficient charge separation can perform the degradation of recalcitrant contaminants, such as PPCPs and PFAS, which are difficult to be removed by conventional AOPs. For example, bismuth phosphate and boron nitrate have been

demonstrated to be highly efficient in the degradation of perfluorooctanoic acid (PFOA) via a hole-initiated pathway, while TiO_2 photocatalysis and H_2O_2 based AOP were ineffective (Duan et al., 2020; Sahu et al., 2018b). However, effective photocatalytic materials presenting finely tuned bandgaps, high photon absorption efficiency, and quantum yield should also be produced at a reasonable cost, they should not use exotic materials, they should be robust and durable, and should be easily recovered and reused.

Photocatalytic Reactors. Reuse of catalyst, transmittance coefficients of photoreactors building materials, pumping, and arrays of multi-reactors systems can be modified to decrease the footprints of solar PWT or energy consumption of UV PWT. Scaling up of the photocatalytic reactors is another critical issue for PWT. Coupling PWT with other AOPs, including ozonation, electrochemical systems, and heterogeneous photo-Fenton (i.e., goethite), have been proven to be efficient to remove emerging contaminants, while few efforts have been devoted to the design of modular reactors integrating different PWT with AOPs. In terms of configuration, photocatalytic reactors should be designed based on their purpose and should always be operated under optimum optical thicknesses. Thus, highly efficient thin-film slurry PWT should be used for higher organic loads, while reactors with wider body shapes should be used for removal of microcontaminants. Reactors using immobilized catalysts provide a simpler solution to slurry reactors, however, these should overcome mass-transfer and radiation transfer limitations and potential catalyst losses and inactivation.

Modeling. Mathematical modeling and simulation of PWT reactors should focus on scaling-up the process from laboratory to pilot-scale to industrial-scale solving real applied engineering problems. Future modeling studies can explore new construction

materials, include the fouling coefficients of the surface of reactors (such as glass wall and pipelines), light diffraction by the transparent walls, the dynamic change of the catalyst optical properties and catalyst deactivation, recovery and reuse of the catalyst, the impact of weather conditions and atmospheric emission radiation models and the application of SFM-HG to a wider range of photocatalytic materials other than TiO_2 . Simplified radiation models that retain the essential features of complex model, such as the SFM-HG, should be integrated into commercial and open-source CFD codes to allow the modeling of a wide range of reactor geometries, the full impact of the water matrix species on the radiation field and the hydrodynamics inside the reactor. This requires the development of full mechanistic kinetics models incorporating the impact of all reacting species. It is also noted fewer studies have been directed to the modeling of reactors with immobilized photocatalysts and greater efforts should focus on processes that can achieve simultaneous water treatment and catalyst separation/retention.

Integration with renewable energy technologies. The exciting achievement on renewables and photovoltaics also provides opportunities for their integration with PWT, as already shown in electrochemical processes for water treatment (Cid et al., 2018). Integration of PWT with renewables should enable solar light-based PWT to operate also when the solar flux is absent, weak or unstable. Moreover, artificial light-based PWT could become more energy efficient by integration with photovoltaics and LEDs, increasing the sustainability of PWT. A patent following this approach has been reported (Patent 20, Table S3). Moreover, environmental remediation coupled with energy generation enabled by photocatalysis has also the potential to reduce the overall energy consumption of PWT (Wang et al., 2017; Wang et al., 2015a), even though a range of engineering challenges need to be addressed.

Conceptual design of photocatalytic plants. Different aspects of process engineering must be considered to achieve a satisfactory operation arrangement in a photocatalytic water treatment unit (Figure 9). The source of UV photons and how the catalyst is used determines the reactor geometry, and these factors impact the reactor design. The semi-batch operational regime seems to be the most versatile in terms of selection of UV photons source, catalyst, reactor geometry, and fluid residence time, as it can own a long fluid residence time with a relatively small footprint area.

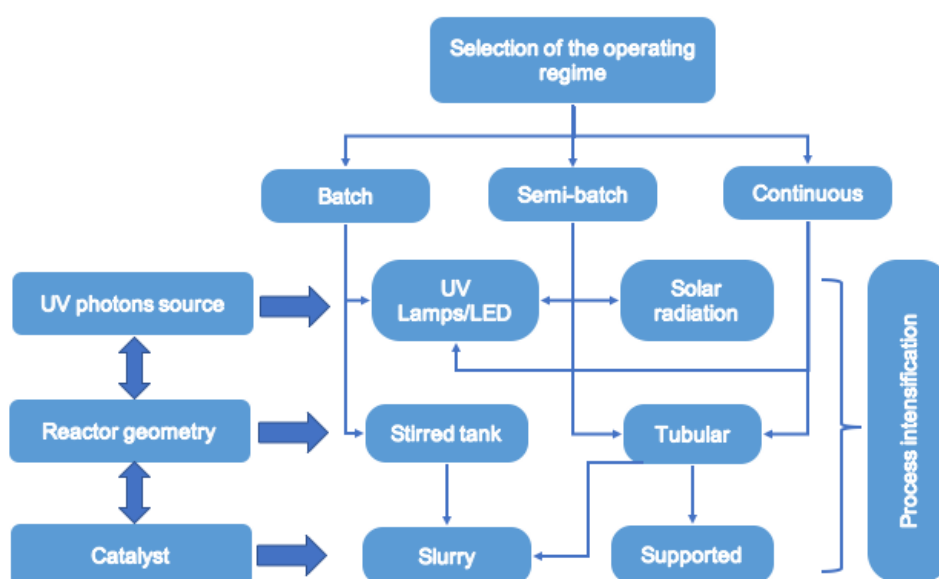


Figure 9. General scheme for conceptual design of photocatalytic plants.

The use of process intensification principles and the need of a continuous operational regime for pilot and full scale PWT plants are potential ways to make PWT feasible as a commercial alternative for wastewater treatment. According to the current modeling theory and experimental data for slurry system, a “thin film”, which usually corresponded to small volume, is still most favorable for efficient treatment. As a result, a long or a series of tall photocatalytic reactors are usually required to treat large volumes. However, advances on the production of efficient light sources (e.g., LEDs) may provide opportunities to design more compact photocatalytic reactors (Casado et al., 2017b) for domestic water treatment at the point of use, where the volume

requirements are much smaller. To make PWT more cost effective, solar light PWT designs should be directed towards small footprint designs, which can also provide water disinfection in rural areas, whereas developing more efficient photocatalysts is likely the most feasible approach to improve the energy efficiency of UV light designs. Regarding immobilized photocatalyst systems, future studies should be directed to demonstrate their water treatment capacities at pilot- or greater scale. The evaluation of the energy efficiency of such systems over a long-term continuous operation (days to months) is essential to appraise the stability of the catalysts, which is often a disadvantage.

5. Conclusions

The bridge between novel photocatalysts and widespread application of PWT for water treatment is always reactor design and its relevant engineering considerations, which have been widely neglected. This perspective has discussed the key photocatalytic reactor design principles, which can lead to efficient PWT. Compared to the efforts presented in scientific papers, patents have focused more on the practical challenges of PWT systems. However, the technology transfer from a patent to an industrial application requires a careful assessment, which should consider both long term performance and cost viability. Although several industrial applications of PWT have been demonstrated, more efforts are needed to bring it to a competitive level. As research continue to advance in the development of visible-light and plasmonic photocatalysts, the use of highly efficient and inexpensive visible LEDs powered with renewables and matching the resonance wavelength of plasmonic photocatalysts may provide the awaited breakthrough in PWT overall efficiency.

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