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Review

Solar Photocatalysis for Emerging Micro-Pollutants Abatement and Water Disinfection: A Mini-Review

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Abstract: This mini-review article discusses the critical factors that are likely to affect the performance of solar photocatalysis for environmental applications and, in particular, for the simultaneous degradation of emerging micro-pollutants and the inactivation of microbial pathogens in aqueous matrices. Special emphasis is placed on the control of specific operating factors like the type and the form of catalysts used throughout those processes, the intriguing role of the water matrix, and the composition of the microbial load of the sample in each case. The interplay among the visible responsive catalyst, the target pollutants/pathogens, including various types of microorganisms and the non-target water matrix species, dictates performance in an unpredictable and case-specific way. Case studies referring to lab and pilot-scale applications are presented to highlight such peculiarities. Moreover, current trends regarding the elimination of antibiotic-resistant bacteria and resistance genes by means of solar photocatalysis are discussed. The antibiotic resistance dispersion into the aquatic environment and how advanced photocatalytic processes can eliminate antibiotic resistance genes in microbial populations are documented, with a view to investigate the prospect of using those purification methods for the control-resistant microbial populations found in the environment. Understanding the interactions of the various water components (both inherent and target species) is key to the successful operation of a treatment process and its scaling up.

Keywords: microorganisms; inactivation; water matrix; catalysts; antibiotic-resistant bacteria; resistance genes

1. Introduction

The current trends in water and wastewater treatment are focused in the development and exploration of environmentally friendly and low-cost technologies. The occurrence of emerging micro-pollutants in the aquatic environment, as well as the presence of various pathogenic microorganisms, impose the application of effective purification methods in order to maintain high hygiene standards and to act toward public health protection.

In this context, advanced oxidation processes (AOPs) have been well studied during the last decades and have proven to be quite promising for the chemical treatment and disinfection of aqueous samples [1–3]. The beneficial action of AOPs is attributed firstly to the in situ generation of highly reactive oxygen species (ROS) like hydroxyl radicals ($HO^{\bullet}$, E^0 = 1.8–2.7 V), which have the potential to mineralize various organic contaminants contained in waters, classified as bio-recalcitrant [4]. Also, they are capable of causing oxidative stress to "target" microorganisms,

exhibiting remarkable biocidal action, as they can lead them to irreversible inactivation [3,5,6]. Encountering the challenge to propose a sustainable technology for the effective treatment of water/wastewater, recent studies have highlighted the application of solar photocatalysis and its variations, which are often used in environmental control processes [7–11]. The prospect of using the solar spectral range and the application at ambient temperature and pressure makes this method even more attractive [12]. Up until now, solar photocatalysis has shown high potential for the degradation of hazardous compounds and the inactivation of multiple microbes present in water and wastewater [1]. Solar and visible light is used for the activation of a substrate, such as a semiconductor photocatalyst, which remains unconsumed after the photoreaction. This activation initiates a chain reaction, through which ROS are produced as pivotal in the degradation of organic compounds and in the inactivation of water pathogens [3,13].

However, the overall performance of the process is highly dependent on various parameters and variables that interfere with the effectiveness, in terms of the satisfactory treatment of water and wastewater. This review paper presents and discusses all possible aspects of solar photocatalysis, according to recent research studies conducted in the field, which deal with this AOP and its lab- or pilot-scale application.

The most important variables that are implicated in the course of the treatment (Figure 1) are (a) the kind of the photocatalytic technique with all recorded operating parameters, (b) the type of microorganism or emerging contaminant, (c) the water matrix, and (d) the special category of antibiotic-resistant bacteria (ARB) or antibiotic resistance genes (ARGs), which have nowadays flooded the interest of the researchers, given their uncontrolled dispersion into the aquatic environment [14,15]. What is commonly accepted is the fact that there is always considerable difficulty in relation to the standardization of the operating parameters, which are applied in each case during such treatments. Apart from the extensive variety of photocatalytic approaches and catalysts that may be used, the main driving forces, which define the final outcome of the treatment, are the wide diversity of organic contaminants and the varied behavior of microbial populations after exposure to the intense conditions of photocatalysis. The latter is more pronounced when ARB and ARGs are included in the frame, considering that both of them may not be fully eliminated post disinfection [16]. In this perspective, the following sections present some of the major issues that are implicated during solar photocatalytic treatment of water and wastewater.

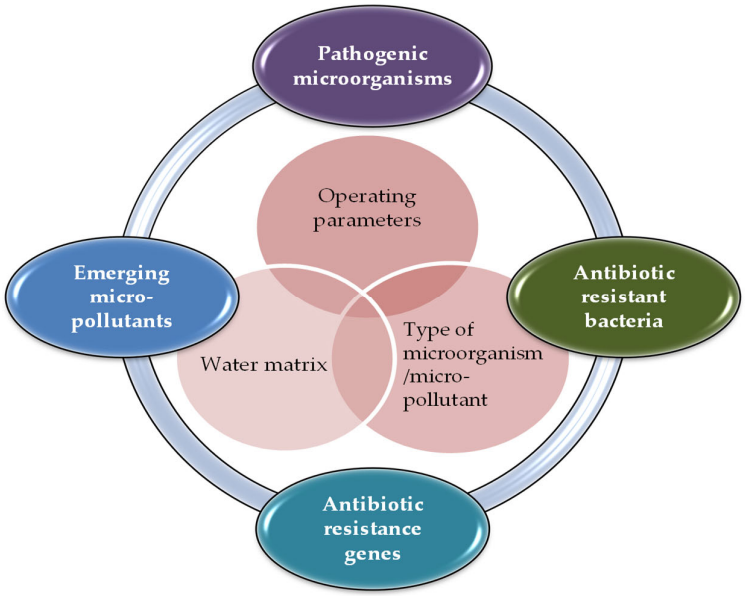

Figure 1. Basic aspects of solar photocatalysis as a treatment method for the degradation of emerging micro-pollutants and the inactivation of waterborne pathogens.

2. Solar Photocatalytic Approaches for Water and Wastewater Treatment

2.1. TiO_2 Photocatalysis

Emerging micro-contaminants such as pharmaceuticals and endocrine disruptors are treated ineffectively in conventional wastewater treatment plants (WWTPs), where they are only partially removed through sorption onto the activated sludge, hydrolysis, and biodegradation; because of the low concentration of these micro-contaminants at the ng/L to μg/L levels, though, WWTP operators have not paid particular attention in removing such compounds. Regarding drinking water supplying companies, the use of granular activated carbon alone or combined with ozone, a traditional technique for removing pesticides from waters, can also be effective for other micro-contaminants [17].

The vast majority of solar photocatalytic processes highlight the use of titanium dioxide as an effective catalyst in terms of the degradation and destruction of a wide range of emerging micro-pollutants and microorganisms, respectively [18]. The advantages of heterogeneous semiconductor photocatalysis using TiO_2 include its operation at ambient conditions, while among the assets of the catalyst are its low cost, photochemical stability, structural properties, and the fact that it is non-toxic [4]. However, the excitation of this semiconductor requires exposure under irradiation with energy greater than its high band-gap energy (~3.2 eV). This feature makes titania active mainly under the UV spectral range, which is a small fraction of the solar light [19]. Nevertheless, and despite this limitation, there are numerous studies that have investigated the efficiency of pure titania regarding the oxidation of chemical compounds and the inactivation of pathogens under solar light (Tables 1 and 2) [3,20].

Fanourgiakis et al. (2014) studied the simultaneous elimination of synthetic estrogen 17α-ethynylestradiol (EE2) and inactivation of *Escherichia coli* in wastewater, applying simulated solar light and TiO_2. According to their findings, the removal rates of EE2 and the bacterium were quite satisfactory, underlining the possible use of pure titania for wastewater purification under solar irradiation [21]. Other attempts that have taken place at the degradation of emerging micro-pollutants have been referred to in investigations that deal with antibiotics. Carbajo et al. (2016), who studied the degradation of multiple antibiotics in water, recorded firstly, the effectiveness of TiO_2 upon exposure under solar light, and secondly, the dependence of the catalyst's activity on the concentration of organic pollutants. The total removal of various pharmaceutical compounds occurred in very short periods of time (t_{30w} < 35 min), revealing the beneficial use of titania under specific operational conditions [13]. Similarly, Méndez-Arriaga et al. (2009) used TiO_2 for the removal of ibuprofen from water, but they noted an overall enhancement of the process adding H_2O_2. Nevertheless, the degradation of ibuprofen was significant with TiO_2 alone, independently on the solar device employed [22].

Table 1. Selected applications of solar photocatalysis for the elimination of emerging micro-pollutants from aqueous samples.

Emerging Micro-Pollutant		Lab-Scale Photocatalytic Process	Catalyst Concentration/Light Intensity	Aqueous Matrix	Degradation Level	Reference
Endocrine disrupting compounds (EDCs)	Bisphenol-A (BPA) and 17α-ethynylestradiol (EE2)	Various TiO_2 photocatalysts (doping with N, P, Ca, Ag, Na, K, Pt)	125–1000 mg/L/17.4 × 10^{-8} – 5.8 × 10^{-8} einstein/(L s)	Wastewater	Up to 90% in 60 min	[2]
	17α-ethynylestradiol (EE2)	TiO_2	500–1000 mg/L/5.8 × 10^{-7} einstein/(L s)	Wastewater	Up to 89.9% in 90 min	[21]
Pharmaceutical micro-contaminants	Clofibric acid	Silver loaded activated carbon (Ag–AC) nanocomposites	10 mg/L/natural sunlight *	Water	97% after 80 min	[23]
	Diclofenac and memantine	Solar-assisted photocatalysis using hydrothermal TiO_2–SnS_2	5, 27.5 and 50% wt. SnS_2/450 W xenon arc lamp *	Water	59.8% for diclofenac and <5.3% for memantine after 60 min	[24]
	Acetaminophen, ibuprofen and antipyrine	TiO_2-activated carbon heterostructures	250 mg/L/600 W/m² (107.14 klx)	Water	Complete conversion within 3–6 h	[25]
	Diclofenac	Immobilized TiO_2-based zeolite composite photocatalyst (TiO_2–FeZ)	Thin films with immobilized composite with TiO_2: FeZ wt% = 74.6: 25.4/124.78 ± 0.11 mW/cm²	Water	99.7% after 180 min	[26]
	Acetaminophen	TiO_2/activated carbon heterostructures	250 mg/L/600 W/m² (107.14 klx)	Water	Complete conversion after 6 h	[27]
	Ibuprofen, acetaminophen and antipyrine	ZnO/sepiolite heterostructured materials	250 mg/L/intensity at 450 W/m²	Wastewater	70–100% in 10 h	[28]
Emerging Micro-Pollutant		**Pilot-Scale Photocatalytic Process (CPC)**	**Catalyst Concentration/Light Intensity**	**Aqueous Matrix**	**Degradation Level**	**Reference**
Endocrine disrupting compounds (EDCs)	Endocrine disruptors	Solar photo-Fenton process assisted with ferrioxalate	Molar ratio Fe/oxalic acid = 3/mean solar intensity = 30 W/m²	Wastewater	Up to 79% of TOC (total organic carbon) removal in 2 h	[29,30]
Pharmaceutical micro-contaminants	Nalidixic acid	Solar photo-Fenton and biological treatment (immobilized biomass reactor)	20 mg/L of Fe^{2+} and 300 mg/L of H_2O_2/natural sunlight *	Pharmaceutical wastewater	Complete removal after 190 min	[31]
	Atenolol, hydrochlorothiazide, ofloxacin and trimethoprim	Ozone and solar TiO_2-photocatalytic oxidation	Ozone dosage = 18–25 mg/L; TiO_2 P25 = 200 mg L/Q_{UV} up to 40 kJ/L	Water and wastewater	Complete removal of pharmaceuticals and about 70% TOC removal	[32]
	Acetaminophen, antipyrine, caffeine, ketorolac, metoprolol,	Solar heterogeneous photocatalysis with TiO_2, solar photo-Fenton	Ozone concentration in the gas phase = 13 mg/L; TiO_2 = 250 mg/L; Fe(III) = 2.8 mg/L or Fe_3O_4	Wastewater	80–100% after 180 min	[33]

	sulfamethoxazole, carbamazepine, hydrochlorothiazide and diclofenac		= 150 mg/L/Q_{UV} = 30–38 kJ/L			
	Phenol, dichloroacetic acid and pyrimethanil	Two titania (the commercial P25 and a homemade catalyst, TiEt-450)	P25 = 200 mg/L and TiEt-450 = 500 mg/L/mean solar intensity = 30 W/m^2	Deionized water (DW) and natural ground water (NW)	Up to complete removal in t_{30w} = 50–100 min	[13]
	Ofloxacin, sulfamethoxazole, carbamazepine, flumequine and ibuprofen	Two titania (the commercial P25 and a homemade catalyst, TiEt-450)	P25 = 200 mg/L and TiEt-450 = 500 mg/L/mean solar intensity = 30 W/m^2	Deionized water (DW) and natural ground water (NW)	Up to complete removal in t_{30w} = 30 min	[13]
	Ibuprofen	TiO_2	0.1–1 g/L/Q_{UV} up to 60 kJ/L	Water	Total elimination when approximately 80% of TOC still remain in solution (Q_{UV} = 60 kJ/L)	[22]
	Acetaminophen, antipyrine, atrazine, caffeine, carbamazepine, diclofenac, flumequine, hydroxybiphenyl, ibuprofen, isoproturon, ketorolac, ofloxacin, progesterone, sulfamethoxazole and triclosan	Solar photo-Fenton	Fe = 5 mg/L/mean solar intensity = 30 W/m^2	Wastewater	Complete elimination in t_{30w} = 60–300 min	[34]
	Various contaminants including antibiotics	Conventional photo-Fenton at pH$_3$ and modified photo-Fenton at neutral pH	Fe = 5 mg/L; H_2O_2 = 50 mg/L/mean solar intensity = 30 W/m^2	Wastewater	Removal of over 95% in t_{30w} up to 150 min	[35]
	Propranolol	TiO_2	0.1–0.4 g/L/Q_{UV} up to 1.5 kJ/L	Water	81% in 240 min	[36]
Pesticides	Imazalil, acetamiprid and thiabendazole	TiO_2 supported on glass beads	Q_{UV} = 20–40 kJ/L	Wastewater	90–100%	[37]
Emerging Micro-Pollutant		**Pilot-Scale (Solar Raceway Pond Reactors)**	**Catalyst Concentration/Light Intensity**	**Aqueous Matrix**		**Reference**
Pharmaceutical micro-contaminants	Contaminants of emerging concern (CECs)—Various antibiotics	Photo-Fenton at neutral pH	Fe^{3+} = 5.6 mg/L and H_2O_2 = 30 mg/L/mean solar intensity = 30 W/m^2	Wastewater	Over 80% degradation after 15 min	[38]

* Light intensity is not provided.

Table 2. Selected applications of solar photocatalysis for the inactivation of various pathogenic microorganisms in aqueous samples.

Microorganism		Lab-Scale Photocatalytic Process	Catalyst Concentration/Light Intensity	Aqueous Matrix	Inactivation Level	Reference
Bacteria	*Escherichia coli*, *Pseudomonas aeruginosa*, *Bacillus subtilis* and *Staphylococcus aureus*	Silver-loaded activated carbon (Ag–AC) nanocomposites	10 mg/L/natural sunlight *	Water	Satisfactory antimicrobial activity (agar diffusion method)	[23]
	Escherichia coli, *Salmonella* sp., *Shigella* sp. and *Vibrio cholerae*	Bare and metal-ion (silver, copper and iron)-doped TiO_2 photocatalysts	0.1–1.0 g/L/average intensity of radiation = 37.6 mW/cm^2	Wastewater	86.8–100% in 180 min	[39]
	Escherichia coli, total coliforms, *Enterococci*, *Vibrio owensii*, *Vibrio alfacsensis* and *Vibrio harveyi*	Ink-jet printed composite TiO_2/SiO_2 thin film	UV dose up to 44.91 Wh/m^2	Water/marine water	Up to 99% in 100 min	[40]
	Escherichia coli, *Pseudomonas aeruginosa* and *Bacillus cereus*	N-doped TiO_2 photocatalysts	25–100 mg/L/irradiance = 1.31 × 10^{-2} W/m^2	Water	4–6 Logs in 15–60 min (depending on the bacterium and catalyst concentration)	[9]
	Escherichia coli and *Klebsiella pneumoniae*	Mn-, Co- and Mn/Co-doped TiO_2 catalysts	25–250 mg/L/irradiance = 1.31 × 10^{-2} W/m^2	Water	5–6 Logs in 15–30 min (depending on the bacterium and catalyst concentration)	[19]
	Staphylococcus aureus	Fe-, Al- and Cr-doped TiO_2 catalysts	5–50 mg/L/irradiance = 1.31 × 10^{-2} W/m^2	Water	5 Logs in 6–30 min	[41]
	Vibrio cholerae	Ag@ZnO core–shell-structured nanocomposites	0.5 mg/L/ *	Water	Almost 98% in at 40–60 min	[5]
	Escherichia coli	Ag core–TiO_2 shell-structured (Ag@TiO_2) nanoparticles	0.4 g/L/average light intensity = 970 × 10^2 lux	Water	8 Logs in 15 min	[42]
	Escherichia coli	TiO_2 P-25, PC500, Ruana and Bi_2WO_6	0.05–1 g/L/solar UV irradiance up to 40 W/m^2	Water	6 Logs in 15–120 min	[6]
	Heterotrophic bacteria	TiO_2	0.5 g/L/solar UV irradiance = 14–27 W/m^2	Dairy wastewater	41–97% in 30 min	[43]
	Escherichia coli	Neutral solar heterogeneous photo-Fenton (HPF) over hybrid iron/montmorillonite/alginate beads	0–20 beads with 10 ppm of H_2O_2/irradiation intensity = 1200 W m^{-2}	Water	7 Logs in 1 h	[44]
Fungi	*Fusarium* sp.	TiO_2	35 mg/L/average solar UV-A irradiance = 25.78 W/m^2	Water	3 Logs in 1-6 h	[45]
Viruses	Phages MS2, UX174 and PR772	TiO_2	50 mg/L/average solar UV-A irradiance = 19–33 W/m^2	Water	3 Logs in 1 h	[46]
	Phage MS2	Mn-, Co- and Mn/Co-doped TiO_2 catalysts	100 mg/L/average solar UV-A irradiance = 12.7–13.4 W/m^2	Wastewater	Up to 4 Logs in 60 min	[47]
	Phage MS2	Iron (hydr)oxide-mediated Fenton-like processes	200 mg/L of iron oxides and 50 μM of H_2O_2/irradiance = 320 W/m^2	Water	5 Logs in 240 min	[48]

Parasites	*Cryptosporidium parvum* oocysts	TiO_2	100–200 mg/L/irradiance = 500 W/m²	Water and simulated WWTP effluent	99 up to 50% in 5 h, in water and wastewater, respectively	[10]
Microorganism		**Pilot-Scale Photocatalytic Process (CPC)**	**Catalyst Concentration/Light Intensity**	**Aqueous Matrix**	**Inactivation Level**	**Reference**
Bacteria	*Escherichia coli*, *Enterococcus faecalis*	Synthetized Ag modified $BiVO_4$ composite	0.2–1 g/L/average solar UVA irradiance = 27 ± 2 W/m²	Water and secondary effluents	6 Logs in 60 min	[12]
	Enterococcus faecium and *Klebsiella pneumoniae*	Immobilized TiO_2 reduced graphene oxide	loading ofTiO_2-rGO = 0.89 mg/cm²/average solar UVA irradiance up to 40 W/m²	Rainwater	8–9 Logs in 240 min	[49]
	Escherichia coli K12	Industrial TiO_2-coated paper matrix fixed on a tubular support in the focus of the CPC	Coated at a dose of 20 g TiO_2/m²/average solar UVA irradiance = 22 W/m²	Water	6 Logs in 90 min	[50]
	Escherichia coli	TiO_2 (Degussa P25) in suspension or TiO_2 supported on Ahlstrom paper (NW10) fixed	50 mg/L (suspension) and dose = 11.8 g/m² (fixed)/average solar UVA irradiance up to 40 W/m²	Water	Up to 6 Logs in 50 min	[51]
	Escherichia coli	Suspended TiO_2	100 mg/L *	Urban and simulated urban effluents	Up to 5.5 Logs when Quv = 12 kJ/L	[52]
	Aeromonas hydrophila	Thin film fixed-bed reactor (TFFBR) coated with P25 DEGUSSA TiO_2	Density of TiO_2 = 20.50 g/m²/solar irradiance = 980–1100 W/m²	Water	Up to 5 Logs in 30 min, depending on operating conditions	[20]
Fungi	*Fusarium solani*	Synthetized Ag modified $BiVO_4$ composite	0.2–1 g/L/average solar UVA irradiance = 27 ± 2 W/m²	Water and secondary effluents	Almost 3 Logs in 240 min	[12]
	Fusarium solani	Suspended TiO_2	100 mg/L *	Urban and simulated urban effluents	Up to 2.5 Logs when Quv = 5 kJ/L	[52]
Microorganism		**Pilot-Scale (Solar Raceway Pond Reactors)**	**Catalyst Concentration/Light Intensity**	**Aqueous Matrix**	**Inactivation Level**	**Reference**
Bacteria	Total Coliforms, *Escherichia coli* and *Enterococcus* sp.	Solar photo-Fenton	Fe^{2+} = 2.5–20 mg/L and H_2O_2 = 30 or 50 mg/L/average solar UVA = 13–34 W/m²	Secondary wastewater effluents	4–5 Logs in 11–15 h	[53]

* Light intensity is not provided.

The biocidal effect of UVA irradiation has been long documented and is attributed to its absorption by cellular components called chromophores, causing further damage and oxidative stress to the microorganisms [4,54]. During photocatalysis the progressive generation of ROS results in detrimental effects on microbial components and on the cellular layers, beginning from the cell wall and the outer membrane. Afterwards, the lesions expand toward the inner proteins (enzymes) and the nucleic acids (genetic material) [43,55]. The primary species responsible for microbial destruction is hydroxyl radical ($HO^{\bullet}$) followed by superoxide radical anion ($O_2^{\bullet-}$), hydro-peroxyl radical ($HO_2^{\bullet}$), and hydrogen peroxide (H_2O_2) [56]. Selected applications of TiO_2 for solar disinfection purposes may be seen in Table 2. The bactericidal action of titania proved to be significant when *E. coli* was the target organism, either in water or in wastewater [6,52]. Catalyst concentrations up to 0.5 g/L seem to be sufficient for the complete removal of the bacterium with an initial concentration of 10^6 CFU/mL. Parallel performance has been observed regarding other microorganisms as well, like fungi (*Fusarium* species) [45,52] and heterotrophic bacteria in dairy wastewater [43].

During recent years, though, the trend in the broad solar photocatalytic area has been to develop and explore newly synthesized materials that potentially could serve as efficient catalysts for the process. The general concept is to improve the activity of titania and to expand its absorption spectrum toward the visible light region. Screening the current literature, various materials have arisen that show promising performance in terms of the elimination of emerging micro-pollutants and waterborne pathogens (Tables 1 and 2). Many different strategies have been adopted for either morphological or chemical modifications of the catalyst [57,58]. Those include modifications of TiO_2 surface with noble metals or other semiconductors or incorporation of additional components in the catalyst structure, like non-metal or/and noble and transition metal deposition [57]. The performance of modified titania is highly improved under simulated and natural solar light, and better removal rates are achieved with various contaminants/pathogens.

In this perspective several attempts have been made using doped-titania materials, in terms of the degradation of hazardous and emerging micro-contaminants in water and wastewater. For example Dimitroula et al. (2012) proceeded with the removal of bisphenol-A (BPA) and 17α-ethynylestradiol (EE2) from wastewater, using various TiO_2 photocatalysts doped with N, P, Ca, Ag, Na, K, and Pt. The overall photoactivity of modified titania under visible light was enhanced, but the treatment performance was not improved substantially [2]. This outcome verified the fact that modified titania do not always work well under the operating conditions in each case. Besides, there have been reports of many possible limitations to metal-doped titania materials, like photo-induced corrosion and promoted charge recombination at some metal sites [57,59]. On the other hand, more applications have been overviewed in recent studies, regarding the use of doped-titania and disinfection processes. For instance, various metal-doped TiO_2, such as Fe–, Mn–, Co– or Al–TiO_2 catalysts, have been used successfully for the inactivation of bacteria (*E. coli*, *Klebsiella pneumoniae*, *Staphylococcus aureus*) and viruses (bacteriophage MS2) in water and wastewater [19,41,47]. In all those cases microbial inactivation was 2–3 times faster, compared with the respective occurring with the pristine P25 TiO_2. The improved activity of metal-doped titania was credited to the optical absorption shifts toward the visible region and to the recombination delay of the electron–hole pair. Also, Sreeja et al. (2017) investigated the performance of Ag core–TiO_2 shell-structured (Ag@TiO_2) nanoparticles and found that those catalysts were quite efficient for the inactivation of *E. coli* in water under solar light irradiation [42]. Complete disinfection (8 Log reduction of the bacterial population) was achieved within 15 min of treatment applying 0.4 g/L Ag@TiO_2 catalyst loading. Interestingly, similar promising results were obtained testing other species such as *Bacillus cereus* with N-doped TiO_2 photocatalysts using various nitrogen precursors (urea, triethylamine-TEA, and NH_3) [9]. Although *B. cereus* exhibited high resistance, N-doped TiO_2 catalysts were more active than pure titania in water samples and under simulated solar irradiation. Generally, the use of modified titania, at least in the case of water/wastewater disinfection under solar irradiation, seems to be faster than other treatment techniques, highlighting the competitive nature of the proposed process against more conventional disinfection systems.

2.2. Slurry or Immobilized Catalysts?

One of the major concerns or debates refers to the choice of the catalyst form to be used for environmental applications. Catalysts in slurry phase are well-known for their effective performance and rather popular; however, such processes require further treatment steps so as to remove the catalyst from the treated sample (water or effluent). On the other hand, another option is to immobilize the catalyst onto appropriate surfaces, surpassing the need for post-treatment handling [37]. Nevertheless, even then, other issues are implicated in the oxidation process, like the decrease of the surface area of the catalysts that is available for the photocatalytic reactions [60]. This feature results in lower degradation rates of chemical compounds and slower inactivation of microbial pathogens in aqueous matrices when immobilized catalysts are employed, compared with the suspended systems [61]. The choice of the catalyst form should be weighed carefully, based on the treatment that is to be applied and on the special requirements in each case (type of pollutant/microorganism, initial concentration water matrix, etc.).

Salaeh et al. (2016) investigated the possibility of removing diclofenac from water using immobilized TiO_2-based zeolite composite photocatalyst (TiO_2–FeZ) and simulated solar light. Diclofenac was removed by 80.1% after 15 min of exposure, with the adsorption of the pharmaceutical playing the most significant role in the overall treatment efficiency [26]. Also, in another study TiO_2 supported on glass beads was tested for tertiary treatment of residual pesticides, achieving rates over 90%, but only with the additional contribution of hydrogen peroxide as an electron acceptor [37]. Respective attempts have been made in the field of disinfection. Khan et al. (2012) worked with a thin-film fixed-bed reactor (TFFBR) for the inactivation of aquaculture pathogen *Aeromonas hydrophila*, demonstrating that high sunlight intensities (>600 W/m^2) and low flow rates (4.8 L/h) play key role in the inactivation of this fish pathogen [20]. Sichel et al. (2007) achieved a 6 Log reduction of *E. coli* within 90 min, using TiO_2 immobilized on Ahlstrom paper in a compound parabolic collector (CPC reactor), highlighting that low flow rates contribute to a more efficient photocatalytic disinfection [50].

In an attempt to improve the photocatalytic activity when TiO_2 films are used and to counterbalance any loss that may occur, many researchers propose the application of an external electric bias. Dunlop et al. (2008), who worked with spores of *Clostridium perfringens* and TiO_2/Ti films (working electrode), proved that applying an external bias of 1 V led to 60–70% higher inactivation rates, while when no bias was applied the disinfection efficiency was inadequate [62]. Based on their research, the potential gradient forces the electrons toward the cathode, thus minimizing the rate of electron–hole recombination.

2.3. Photocatalysts Other than TiO_2

Titania nanoparticles and its composites show remarkable results during solar photocatalysis of water and wastewater. Especially the metal and non-metal-doped nanoparticles have been extensively used for multiple applications, demonstrating promising prospects of a "clean and green" aquatic environment. Nevertheless, we should not overlook some other semiconductors that have emerged as alternative approaches in this field of treatment and disinfection.

Zinc oxide nanoparticles with a wide band-gap of 3.37 eV appear to be a nice option, considering some recorded assets, such as good optoelectronic, piezoelectric, and catalytic properties [28]. However, photo-corrosion may worsen the performance of ZnO, causing limited stability. Therefore, some researchers have tested the use of supplementary materials as support to ZnO nanoparticles. For example, ZnO-supported clays have been prepared for photocatalytic applications, like ZnO/sepiolite heterostructured materials. Akkari et al. (2018) used those composited for solar photocatalytic degradation of pharmaceuticals in wastewater. According to their findings, ibuprofen, acetaminophen, and antipyrine were readily degraded in wastewater, indicating the superiority of those materials compared to other catalysts used for solar photocatalysis [28]. ZnO nanocomposites have also been used successfully for disinfection purposes of various bacterial species like *E. coli*, *Vibrio cholerae*, and multi-drug-resistant *Bacillus* sp. [5,63,64]. Given that the solar photocatalytic activity of the metal oxide nanostructures is increased by

formation of metal/metal oxide hybrid structures, Das et al. (2015) synthesized Ag@ZnO core–shell structure nanocomposites and tested their potential to inactivate *V. cholerae* in water. The results showed that this highly pathogenic bacterium may decrease up to 98% after 40–60 min of sunlight exposure with a catalyst loading of 0.5 mg/L [5]. The same group worked with Ag@SnO_2@ZnO core–shell nanocomposites and Fe-doped ZnO nanoparticles, as well, studying their biocidal properties against *Bacillus* sp. and *E. coli*, respectively. In both cases the synthesized materials exhibited satisfactory performance in terms of the inactivation of pathogens in water (Tables 2 and 3) [63,64]. In all those cases catalysts had a stable structure and no silver leaching was observed.

Further attempts have been made to explore more catalysts with acceptable solar performance. In this sense, cadmium sulfide (CdS) seems to be quite effective regarding the disinfection of aqueous matrices with high concentrations of *E. coli* and *S. aureus* under visible light [65]. Silver orthophosphate (Ag_3PO_4) is a low band-gap photocatalyst with enormous potential in harvesting solar energy. What is important regarding this catalyst is that it is characterized by a low electron–hole recombination rate, but with low long-term stability, as it is decomposed in the absence of sacrificial agent [66]. In this case, leaching of silver in the liquid phase may contribute to disinfection through homogeneous reactions. This drawback may be surpassed by synthesizing various Ag_3PO_4-based composites. Ag_3PO_4 and Ag_3PO_4/TiO_2 materials have the potential to achieve good inactivation rates of *E. coli* under solar irradiation, while other studies present the disinfection efficiency of several Ag_3PO_4/TiO_2 composites against multiple pathogens [67–69].

Among the numerous visible light active photocatalysts bismuth vanadate ($BiVO_4$) has received attention despite the fact that very few water disinfection studies have been reported. Its activity alone is not that significant, as the recombination rate of photo-induced electron–hole pair is really fast and high. Metal deposition on the surface of the catalyst seems to work toward overcoming this drawback, leading to enhanced activity under solar light. In this perspective, the silver deposition on the surface of $BiVO_4$ made this catalyst capable of inactivating three waterborne pathogens, namely, *E. coli* (Gram-negative bacteria), *Enterococcus faecalis* (Gram-positive bacteria) and spores of *Fusarium solani* (phytopathogen) under natural sunlight [12]. Finally, one more catalyst reported in current literature is Bi_2WO_6, which has the advantage of absorbing more solar photons. This catalyst has the potential to accelerate the bactericidal action of solar irradiation, given that a concentration of 0.5 g/L is sufficient for a 6 Log reduction of *E. coli* in water within 105 min [6].

2.4. Heterogeneous Photo-Fenton Systems

Among the AOPs applied for water and wastewater treatment, the photo-Fenton process has become very popular as an eco-friendly choice for organics mineralization and microbial inactivation. This process takes place in the presence of ferrous or ferric salts and hydrogen peroxide in acidic media, and hydroxyl radicals are generated through the Fe^{2+}/Fe^{3+} redox cycle. The production of hydroxyl radicals is greatly enhanced under UV–vis irradiation, as transformation of Fe^{3+} to Fe^{2+} is promoted. The main challenge when applying this method is to operate at neutral or near-neutral conditions and not in the range of 2.5–3.5, which is optimum for this AOP [70]. This pH range is prohibited for environmental applications, and further actions should be taken post treatment and prior to the disposal of treated streams into the aquatic bodies (e.g., neutralization).

In this view, current research studies have proposed heterogeneous Fenton-like systems, which operate well and efficiently at neutral or near-neutral conditions (Table 2). New organic or inorganic supports have been tested for the catalysts used in photo-Fenton processes, especially biopolymers like sodium alginate, which is biocompatible, inexpensive, and can be easily assembled into spherules or beads. Barreca et al. (2015) synthesized iron-enriched montmorillonite alginate beads for the inactivation of *E. coli* and recorded a 7 Log reduction at pH 7 after 60 min under solar irradiation with 10 mg/L H_2O_2 [44]. Also, other materials served as efficient catalysts for the removal of MS2 coliphage from water at neutral conditions [48]. This phage was inactivated successfully in water in the presence of hematite (α-Fe_2O_3), goethite (α-FeOOH), and magnetite (Fe_3O_4) and under solar light, and all materials exhibited stability with negligible iron leaching. Also, promising results have been derived regarding the wastewater treatment by means of the photo-Fenton process. De la

Obra Jiménez et al. (2019), who worked with raceway pond reactors, observed total inactivation of total coliforms *E. coli* and *Enterococcus* sp. in wastewater secondary effluents in continuous flow and neutral pH within 60 min in the presence of 50 mg/L H_2O_2 [53].

Similar studies may be overviewed regarding the degradation of emerging micro-pollutants (Table 1). Solar photo-Fenton reactions are capable of removing endocrine disruptors (EDCs) and various antibiotics from water and wastewater, either alone or combined with other processes [29,31,33,38]. For instance, Sirtori et al. (2009) investigated the degradation rate of nalidixic acid, which belongs to the quinolone group of antibiotics, by means of photo-Fenton and biological treatment. Photo-Fenton was found to be a successful enhancer of the biodegradability of wastewater, acting as a supplementary technique to an immobilized biomass reactor in order to achieve mineralization and detoxification of industrial wastewater [31]. Moreover, Soriano-Molinao et al. (2019) accomplished the removal of 80% of the concentration of chemicals of emerging concern from wastewater after 15 min of photo-Fenton at circumneutral pH in solar raceway pond reactors [38]. Based on all those results, heterogeneous photo-Fenton systems at neutral pH seem to be a feasible solution for water/wastewater treatment with acceptable results, without causing any disturbance or toxicity to the surrounding environment.

2.5 Transformation By-Products

Solar photocatalysis of contaminants may result in the formation of transformation by-products (TBPs) that are less biodegradable and/or more toxic than the original compound. This is more likely to happen if the experiments have been performed in environmental matrices rather than pure water (as this is mainly the case for the studies shown in Table 1), since less biogenic TBPs may also be generated from photocatalytic transformations involving the non-target species inherently present in the matrix (i.e., the effluent organic matter typically found in treated wastewaters and the natural organic matter found in groundwaters) [31]. The level of toxicity induced by the generation of by-products is often unpredictable and sometimes related to the duration of the process. The toxicity in short treatments usually decreases gradually in the course of the photodegradation [4].

The effect of photocatalysis on the properties of the effluent is usually assessed by means of biodegradability and/or toxicity tests. The standard BOD (biochemical oxygen demand) test is commonly employed as a measure of aerobic biodegradability, which is also assessed by means of shake flask tests, respirometry, and the Zahn–Wellens test [24]. Anaerobic biodegradability tests are less popular and usually measure the rate of biogas production. Acute toxicity is usually assessed against freshwater and marine microorganisms and the results are usually quoted in the form of EC50 values [26]. It should be pointed out that identification of TBPs, although conceptually advantageous, may not be feasible even when sophisticated analytical tools are available. This is due to the fact that the concentration of micro-contaminants may be 2–3 orders of magnitude lower than the organic and inorganic, non-target matrix components and, therefore, interferences mask the presence of TBPs in the matrix [31].

3. The Intriguing Role of the Water Matrix

The water matrix that is mainly used in research studies dealing with AOPs and water/wastewater treatment is ultrapure water. This choice is based primarily on the need to gain fundamental understanding of processes such as degradation kinetics, mechanisms, and pathways without taking into account the impact and the interference of the water matrix effect. Notwithstanding, the latter may be extremely influential to the overall performance of each technique and has the potential to lead to an unreliable outcome.

It is well established that a high level of the water matrix complexity causes deterioration of AOPs' efficacy. This occurs because the pollutants/microorganisms and the ingredients of the matrix (e.g., dissolved organic matter, inorganic constituents, etc.) develop a competitive action toward the generated ROS or the active sites of the catalysts/activators when heterogeneous processes are applied [71]. In this sense, for example, in a case of sulfamethoxazole degradation using solar photocatalysis over WO_3/TiO_2 suspensions, the pseudo-first order kinetic constant decreases as the

matrix shifts from ultrapure water to drinking water (DW: containing bicarbonates and other ions) and finally to secondary treated wastewater (WW: containing residual organics and various ions) [72]. On the other hand, the exact reverse behavior may take place under different operating conditions and when other contaminants are to be degraded, like bisphenol-A (BPA); the highest rates of BPA degradation are recorded when the sample is wastewater, compared with other matrices, like ultrapure water [73].

Apparently, the target micro-pollutants/microorganisms that are to be degraded/inactivated, the constituents of the matrix, the ROS, and the catalysts/activators, if they are present, develop tricky and challenging interactions among them with unpredictable results. Eventually, the nature of those interactions will define any reaction kinetics and mechanisms through a synergy or an antagonism, which may be generated. Moreover, the relative contribution of each individual effect may depend on the specific treatment system in question and, for a certain system, on the specific operating conditions.

Nevertheless, some cases underline the fact that the effect of water matrix on photocatalytic disinfection/degradation is case specific. The mechanisms and kinetics of photocatalytic disinfection are highly affected by the presence of inorganic ions (e.g., bicarbonates, chlorides etc.), organics (e.g., natural organic matter (NOM)) and suspended solids. Those components aid in the resistance of microorganisms, considering that they act as physical shields that interfere in the whole process [74]. That is why wastewater has always been dealt with as an aqueous matrix of special attention with special complexity and intrinsic features. Zuo et al. (2015) presented the deterioration of photocatalytic disinfection of *E. coli* due to the presence of ammonia and nitrites in the matrix. The overall effect was attributed to the partial consumption of hydroxyl radicals during the conversion of inorganic nitrogen to nitrates [75]. Similar observations were made by Marugán et al. (2010), who recorded the unfavorable effect of carbonates, phosphates, and humic acid on the inactivation of *E. coli* [76]. However, they highlighted the positive effect of chlorides on disinfection, which may further contribute to the production of toxic organochlorinated by-products. The latter may counterbalance the loss of hydroxyl radicals, leading to an improvement of disinfection efficiency. What was even more surprising was that the same components seemed to slow down the photocatalytic degradation of dyes, making the whole issue of "the water matrix effect" rather a "brain teaser" with an unpredicted outcome. The main suggestion in the literature is the careful standardization of operating conditions in each case, based on the special features of the chemical pollutants and microbial pathogens contained in the sample.

4. Type of Waterborne Pathogens Tested in Solar Photocatalysis

Water and wastewater contain a remarkably extensive variety of microorganisms, belonging to different groups with diverse structures and features. The latter affect inevitably the microbial response and their overall behavior during a disinfection process, as well as the specific mode of their inactivation. According to the recent literature many studies have been conducted so as to provide insight about the principles and mechanisms of microbial inactivation. However, there is still a lot to be revealed and clarified. Screening indicative published data, it is quite obvious that most of the disinfection studies related to solar photocatalysis are focused on the investigation of bacterial species and spores (Table 2), leaving out other virulent pathogens, which are important to public health. What is more is that although multiple bacterial species are contained in water and wastewater, the one that is always mentioned in disinfection applications is the well-known *E. coli* [6,42,44,51]. Nevertheless, focusing on just one bacterial indicator poses the risk of extracting biased conclusions in terms of the effectiveness of solar photocatalytic applications.

The extent up to which cell (or other) damages occur varies greatly, depending on the type of microorganism tested each time. Therefore, in the case of bacteria the level of damages and cell permeability caused by ROS are defined, among other parameters, by the thickness of the cell wall. The main differences are identified between Gram-positive and Gram-negative species, as the first ones possess a thick cell wall that contains many layers of peptidoglycan and teichoic acids. Those components provide the potential of preserving their viability during photocatalytic treatment, as

the penetration of free radicals is rather obstructed [40]. However, the higher resistance of Gram-positive bacteria is not always confirmed, as the operational conditions and the bacterial indicators employed in each case may reverse this precedence order [9]. In this sense, there are cases where high catalyst concentrations may be required up to 300 mg/L for the complete inactivation of Gram-negative bacteria [77]. The role of cell wall structure and complexity in the overall behavior of bacteria during photocatalysis is still under investigation and many parameters are yet to be explored. It is commonly accepted though, that the disinfection efficiency of a process should be assessed using representative indicators of both groups of bacteria, in order to obtain reliable and accurate results and an objective overview of the process' limits.

Another issue under consideration is the cellular form of the target microorganism. For instance, some pathogenic bacteria are found in the aquatic environment in the form of endospores, which are considered really resistant under the stressed conditions of disinfection. Endospores contain a thick coating made by proteins, which usually require prolonged treatment and exposure under solar irradiation. García-Fernández et al. (2015) studied the effect on the microorganism type of the solar photocatalytic treatment and found that vegetative cells are much more sensitive than spores. In that specific case *Fusarium* spores (fungus) were tested, which showed remarkable resistance to TiO_2 photocatalysis due to rigid structures composed of polymeric sugars, proteins, and glycoproteins. Also, their wall contains an outer xylan layer that confers significant resistance to oxidative stress [52]. In another case, *Clostridium perfringens* spores with a dipicolinic acid–calcium–peptidoglycan complex could be harmed only by hydrogen peroxide, which can be further activated by ferrous ion that is incorporated into the spore coating. This process is called in vivo Fenton reaction [62].

The waterborne protozoa constitute another group of pathogenic microorganisms that are found in the aquatic bodies in the resistant form of cysts/oocysts. *Cryptosporidium parvum* and *Giardia lamblia* are considered very virulent with extremely low infectious dose and yet they have not been mentioned frequently in the literature in relation to disinfection techniques. Generally, both protozoan species show significant tolerance during conventional methods, like chlorination, but also during many AOPs [74]. Oocysts of *C. parvum* require up to 5 h for a substantial decay and removal from distilled water during TiO_2 solar photocatalysis [10]. Moreover, the authors stated that because of the robustness of the oocysts, *C. parvum*'s inactivation would probably ensure the elimination of other less resistant pathogens. Even if oocysts remain as residual microorganisms after treatment, they are not considered infective as excystation occurs with the subsequent generation of sporozoites. The combination of solar light with a catalyst causes destruction of the oocyst cell walls, and the final picture is empty cells characterized as "ghosts," which remain after the process [70].

Much less research has been conducted on the photocatalytic inactivation of viruses, whose significant presence in the aquatic environment verifies their resistant nature and tolerance during conventional disinfection methods. Up until now, studies demonstrated the existence of such viruses in treated effluents, highlighting the inadequacy of conventional purification methods [78]. Viruses are traditionally known to maintain their structural properties and infectivity when hostile conditions are induced in the surrounding area [79]. Upon application of a photocatalytic process, viral inactivation may occur only when substantial oxidizing power is provided, which is necessary for the deformation of their protein capsid and the development of lesions in their nucleic acid. The absence of any enzymes or other typical cellular structure leaves capsid and genetic material as the only targets of the ROS generated during AOPs techniques [47]. Viral adsorption and general adherence onto the catalysts' nanoparticles is the first step of their inactivation in photocatalytic processes, followed by the attack on the protein capsid and other binding sites of the viruses [80]. On the other hand, certain studies proposed a different mode of action and mechanism of photocatalysis against viruses. What mostly occurs is the interaction between free hydroxyl radicals in the bulk phase and the viruses, as electrostatic repulsion does not allow the interaction and close contact between the catalyst and the virus [46]. The application of a positive potential to an immobilized TiO_2 electrode may induce an electrostatic attraction between the catalyst and the viral capsid, which

is mostly negatively charged. Also, Fenton's reagent and metal-doped titania seem to eliminate successfully MS2 coliphages, as reduction up to 5 Logs may occur within 60 min of treatment [47].

The final target of ROS in the course of photocatalysis is the genetic material of microorganisms and viruses (DNA or RNA). Nucleic acids are rather susceptible to the produced oxidative power through attacks either at the sugar or at the base [81]. All damages and lesions in the microbial genetic material are subject to restoration in the case of some bacterial species, according to their properties. This feature, the so-called "photoreactivation," is the main disadvantage of photocatalytic treatment and generally of the processes that utilize UV irradiation. Some bacteria have the potential to repair any destruction sites or "mistakes" on their genetic material through special enzymatic activity. Such enzymes mainly act under light (300–500 nm) and split the dimmers formed as a consequence of irradiation [82]. Although restoration activity takes place usually after exposure to UV-C irradiation, it has also been reported when UV-A is employed, involving not only bacteria but other microbes like protozoan cysts [83]. Therefore, having in mind that solar photocatalytic processes have no residual action, it is crucial to design properly such applications in order to ensure the durability of the disinfection and the inability of waterborne pathogens to proliferate post treatment. Catalyst loading, light energy, time of irradiation are some of the parameters that must be defined and standardized properly to cause irreversible damages in microbial components and structures. The possibility of microbial reactivation always remains, but it should be minimized, though, for public health protection and if solar photocatalysis is to be applied for water disinfection purposes.

5. Antibiotic-Resistant Bacteria (ARB) and Antibiotic Resistance Genes (ARGs)

A special group of microorganisms contained in water and wastewater is referred to the antibiotic-resistant bacteria (ARB), which have already attracted much scientific attention nowadays. The effective application of a disinfection process should always include this specific target microbial group, as it raises many concerns about human health. The uncontrolled use of antibiotics in medical, veterinary, or even agricultural practices and their incomplete removal in WWTPs has led to their uncontrolled excretion in the environment, resulting in an excessive rise of antibiotic resistance in various bacteria by the dissemination of antibiotic resistance genes (ARGs) [84]. ARB and ARGs seem to prevail in the aquatic environment, inducing further resistance within microbial communities, while they have also been documented as emerging contaminants. Many different kinds of ARGs have already been detected in aquatic systems, including WWTPs, and their effluents verify their persistence during treatment (Table 3). Water bodies and particularly WWTPs are extraordinary settlements for the proliferation of ARB and the dissemination of ARGs through horizontal transference of genetic elements, conferring resistance to multiple antibiotic compounds [16]. The main concern and question is whether current treatment processes and disinfection approaches are capable of removing all ARB and ARGs present in water/wastewater, prohibiting their revival in effluents. According to the current literature this is quite common and many multi-drug-resistant bacteria, as well as ARGs, have been detected in the end-streams of WWTPs [85,86]. Moreover, in some cases ARGs are increased in the course of treatment, resulting in extremely high concentrations in the effluents [87].

Therefore, what is mostly needed is the establishment and application of effective technologies toward the control of ARB and the elimination of ARGs from water/wastewater. Failure to limit their dispersion into the aquatic environment threatens public health and contributes to a further increase of resistant populations. The extent to which treatment and disinfection processes inactivate ARB and eliminate the genes relevant to resistance is still under discussion [88]. The question that arises is how far and under which operational conditions does disinfection eliminate ARB and ARGs.

While the risk still exists, solar photocatalysis seems to work well in this direction, providing promising results regarding the inactivation of ARB (Table 3). As already mentioned, this method overcomes many disadvantages of conventional purification processes like the toxic by-products of chlorination or certain action limitations of UV irradiation, which have the potential to remove ARB

from water and wastewater [89,90]. Doped-titania materials have the potential to inactivate sufficiently antibiotic-resistant *E. coli* or *K. pneumoniae* [15,91]. Metal and non-metal-doped TiO_2 under solar irradiation led to up to 6 Log bacterial reductions within 60 min of treatment of urban wastewater. Also, Venieri et al. (2016) studied the possible changes in the antibiotic resistance profile of *K. pneumoniae* post treatment and found out that in some cases residual cells after disinfection were more susceptible in specific antibiotic compounds [15]. The same authors documented the simultaneous loss of *K. pneumoniae*'s ARGs in the course of photocatalysis. Fe-doped ZnO nanoparticles and Ag@SnO_2@ZnO core–shell nanocomposites exhibited similar performance, adequately inactivating *E. coli* and *Bacillus* sp. in water, respectively [63,64]. Neither bacteria regrew after treatment and *Bacillus* sp. lost substantial resistance. Also, comparing the effectiveness of Ag@SnO_2@ZnO core–shell nanocomposites with traditional chemical disinfectants and UV-250 nm, it was found that they had lesser impact on the resistance profile of the bacteria.

The elimination of ARGs during solar photocatalysis has been underreported in recent studies. Although there are data regarding their prevalence in water and wastewater (Table 3), more information is needed about their response in the presence of a semiconductor and solar light. Furthermore, given that ARGs are mostly carried in bacterial plasmids, special attention should be paid to the persistence of plasmids and their integrity level during treatment. According to Mao et al. (2015), the optimum removal of ARGs from wastewater requires high irradiation intensities or the combination of UV with a photocatalytic treatment [87]. Up until now, the point of agreement is that wastewater is an important repository of ARGs that needs more effective treatment than conventional applications.

Table 3. Elimination of antibiotic-resistant bacteria (ARB) and antibiotic resistance genes (ARGs) present in the aquatic environment by means of solar photocatalysis and other disinfection methods (indicative recent literature).

Antibiotic Resistant Bacteria (ARB)	Aqueous Matrix	Treatment	Removal Level	Reference
Escherichia coli	Wastewater	Solar TiO_2 photocatalysis	93.17% removal after 10 min	[11]
Escherichia coli	Water	Solar photocatalysis using Fe-doped ZnO nanoparticles	More than 99.9% removal after 90 min	[63]
Escherichia coli	Wastewater	Solar photocatalysis using N-doped TiO_2 nanoparticles	More than 5 Log bacterial reduction after 10 min of irradiation	[91]
Klebsiella pneumoniae	Wastewater	Solar photocatalysis using Mn-, Co- and binary Mn/Co-TiO_2 nanoparticles	Bacterial decrease from 4 to 6 Logs upon 90 min of exposure to simulated solar irradiation	[15]
Bacillus sp.	Water	Solar photocatalysis using Ag@SnO_2@ZnO core–shell nanocomposites	7 Log bacterial reduction within 210 min with a catalyst concentration of 500 mg/L	[64]
Escherichia coli	Wastewater	UV irradiation	Total inactivation after 60 min	[90]
Escherichia coli	Wastewater	Chlorination	Total inactivation after 120 min	[90]
Heterotrophic bacteria resistant to various antibiotics	Wastewater	Chlorination	Total inactivation	[89]
Antibiotic Resistance Genes (ARGs)	**Aqueous Matrix**	**Treatment**	**Removal Level**	**Reference**
blaTEM, ermB, qnrS, sulI and tetW	Wastewater	Wastewater treatment plant (WWTP)	Incomplete removal	[85]
tetA, tetB, tetE, tetG, tetH, tetS, tetT, tetX, sul1, sul2, qnrB and ermC	Wastewater	WWTP	Proliferation of ARGs through biological WWTP* processes	[87]
sul1, tetX, tetG and intI1	Municipal wastewater	Chlorination	Reduction of ARGs in the range 1.20–1.49 Logs	[92]

sul1, tetX, tetG and intI1	effluent Municipal wastewater effluent	UV/chlorination	Reduction of ARGs up to 2 Logs	[92]
mecA, ermB, sul1, tetA, tetW and tetX	Wastewater	WWTP	Incomplete removal	[93]
tetA, tetB, tetE, tetM, tetZ, tetW, sul1, sul2, sul3, gryA, qnrC, qnrD and parC	Wastewater	WWTP	Concentrations of the selected ARGs were kept relatively constant during treatment procedures	[14]
tetO, tetQ, tetW, tetH and tetZ	Wastewater	WWTP	Detectable ARGs in the effluents and possible proliferation	[86]
ereA, ereB, ermA, ermB, tetA, tetB, tetM and tetO	Wastewater	Chlorination	Limited removal levels (0.1–0.4 Logs)	[89]

6. Pilot-Scale Application

Although solar photocatalytic treatment of water and wastewater has successfully been tested in the laboratory, information regarding pilot- or large-scale applications is scarce (Tables 1 and 2). The pilot-scale applications that have been mainly tested are compound parabolic collectors (CPCs) and raceway ponds. Generally, both systems prove to be effective for the removal of persistent micro-contaminants of emerging concern and the elimination of waterborne pathogens.

Special key aspects for successful water treatment applications are the design and configuration of the photo-reactor. CPC solar reactors are one of the best approaches in order to enhance the efficacy of solar photocatalytic purification and disinfection of water [12]. These reactors are easy to use, cost-effective, and appropriate for point-of-use applications, since they can be constructed in various sizes. Raceway pond reactors were originally developed for micro-algal mass culture and are applied for the degradation of emerging micro-contaminants like pharmaceuticals and disinfection via solar photo-Fenton process [38,53]. Although they have less efficient optics than CPCs, they have a low construction cost and a large volume/surface ratio, which make them a quite competitive option for the treatment of secondary effluents [53]. Recent studies highlighted the prospect of scaling-up solar photocatalytic applications for water and wastewater treatment, considering those pilot-scale reactors as a post-secondary treatment step in WWTPs. This trend was followed by Barwal and Chaudhari, who designed and tested a hybrid bio-solar system with a moving bed biofilm reactor and a CPC for the purification and disinfection of municipal wastewaters [94].

Based on the above, large-scale applications of solar photocatalysis can serve as advanced tertiary treatment of wastewater and as an effective disinfection step in the water industry, especially in cases where other techniques are not suitable or feasible.

7. Future Perspectives

Although several AOPs have demonstrated supreme performance on water/wastewater treatment and disinfection over the last decades, solar photocatalysis is a relatively new area and there is lot yet to be explore and developed. The challenges are still numerous and many problems have to be overcome; however, the prospect of using solar light and energy combined with newly developed materials stands out as one sustainable alternative for environmental applications. Environmental protection and the economic cost are among the most important driving forces for the development of new methods that will be preserved and feasible in the course of time. In this respect, solar processes have all the characteristics and potential to be applied on a routine basis as efficient disinfection/decontamination treatment technologies. Also, they offer an ideal set-up for the synthesis of new, environmentally friendly materials that will serve as photocatalysts. Finally, the process scale-up, which has already begun, is a challenging task that will add to the overall science of water/wastewater treatment in an era where public health and environmental protection are the

ultimate values for human beings. In a nutshell, water and wastewater purification and disinfection are listed among the topics that are balanced in the interface of science and engineering, and different disciplines must cooperate to deal with them successfully and constructively.

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