

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur



Removal of paracetamol (acetaminophen) by photocatalysis and photoelectrocatalysis. A critical review

Enric Brillas^{a,*}, Juan Manuel Peralta-Hernández^{b,**}

^a Laboratori d'Electroquímica dels Materials i del Medi Ambient, Secció de Química Física, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain

^b Departamento de Química, DCNE, Universidad de Guanajuato, Cerro de la Venada s/n, Pueblito de Rocha, Guanajuato C.P. 36040, Mexico

ARTICLE INFO

Keywords: Hybrid photocatalysis and photoelectrocatalysis Pure TiO₂ and TiO₂-based photocatalysts Pure ZnO and ZnO-based photocatalysts Real wastewater treatment Sunlight UV light

ABSTRACT

Paracetamol (PCT) is widely used as an antipyretic and analgesic drug by animals and humans, and it is detected in most natural waters and wastewaters because it is not completely removed by conventional methods in wastewater treatment plants. Since it is toxic to living beings such as microorganisms, algae, and fishes, powerful methods for its removal from the aquatic environment need to be developed. Over the last years, many research works have shown the effectiveness of photocatalysis (PC) and photoelectrocatalysis (PEC) to remediate waters contaminated with PCT. This article presents a critical and comprehensive review of such studies up to June 2022. Once the fundamentals of both techniques have been described, the review summarizes the fast removal and low mineralization of PCT by PC with pure TiO2 under UV light to further remark the better performance achieved with UV than visible light using TiO₂-based nanocomposites. The treatments with other photocatalysts like pure ZnO, ZnO-based nanocomposites, WO₃-based, bismuth-based, and g-C₃N₄-based with UV or visible light are summarized as well. Commercial and synthesized materials used for each class of these photocatalysts are described, considering their nature, composition, and band gap potential. The effect of pH and/or components of the aqueous matrix are examined, showing a lower degradation in natural waters and real wastewaters than in pure water, The different photocatalytic mechanisms proposed to originate reactive oxygen species from the photogenerated electron/hole pairs in the semiconductors are explained, along with the oxidation products detected. The PEC treatments are analyzed from the nature and composition of the photoanode, light irradiated, and electrical properties of the photoelectrochemical cells to produce the reactive oxygen species for PCT destruction. The larger drug decay with hybrid PEC + PEF treatments under sunlight is finally remarked.

1. Introduction

Over the last decades, increasing quantities of many drugs have been consumed by animals and humans worldwide to heal from their illnesses. Because of their widespread use and abuse, mixtures of drugs are usually detected in natural waters and wastewaters as concerning emerging pollutants, which are hazardous by their possible toxic effects on living beings and the environment [1].

Acetaminophen or paracetamol (PCT) is a well-known antipyretic and analgesic drug commonly prescribed to treat fever and mild to moderate pain. This compound of CAS number 130–90-2 has a chemical formula of C₈H₉NO₂ with M = 151.165 g mol⁻¹, solubility in water of 14 g/L at 20 °C, and pK_a = 9.53. It is partially metabolized after uptake by animals and humans and excreted through the urine to contaminate aquatic/natural environments, including wastewater treatment plants (WWTPs) [2]. Other important contributions to the release of PCT to the environment are the waste of overdue or unused drugs and its industrial manufacturing process [3]. This drug has been detected up to concentrations as high as 0.1–300 mg/L in effluents of many European, Asian, and American countries. Unfortunately, in developing countries, PCT prevails in surface water because wastewaters are often not collected and treated properly. Up to 33 ng/L of this drug has been found in Asian rivers, whereas contents from 0.4 to 71 ng/L have been reported in rivers of Spain and France [4].

Conventional methods used in WWTPs like filtration with membranes, sedimentation, activated sludge with adsorption,

* Corresponding author.

** Corresponding author.

https://doi.org/10.1016/j.seppur.2022.122982

Received 3 November 2022; Received in revised form 19 December 2022; Accepted 19 December 2022 Available online 23 December 2022

1383-5866/© 2023 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

E-mail addresses: brillas@ub.edu (E. Brillas), juan.peralta@ugto.mx (J. Manuel Peralta-Hernández).

biodegradation, and solar photolysis are usually inefficient for the total abatement of drugs. The analysis of WWTP effluents in many European countries has shown a PCT reduction from 65 to $< 10 \mu g/L$ [3]. Long-term exposure to trace amounts of this drug over bacteria, plants, animals, and humans can potentially produce endocrine disruption and chronic disease since it can oxidize the lipids in cells and denature the proteins with damage to their genetic code [4]. So, PCT toxicity has been well-proven in some protozoan, macrophytes, algae, bacteria, and fishes. As an example, it has been documented the existence of toxicological liver affectations in Zebrafish as well as morphological alterations in Zebrafish embryos and Zebrafish larvae upon exposition to this drug in waters [5].

To avoid the harmful health effects of PCT on living beings, many research efforts at laboratory and pilot scales have been made to destroy this pollutant and its degradation/metabolites products from wastewaters before their discharge to the environment. The most potent technologies developed are the so-called advanced oxidation processes (AOPs), which are environment-friendly methods based on the oxidation of organics by generated reactive oxygen species (ROS). Single and combined processes based on sonolysis [6]. Fenton, photo-Fenton, and derived treatments [5], UV/H₂O₂ [7,8] and catalyzed ozonation [9] have been widely studied. Over the last decade, increasing attention has been paid to the destruction of PCT in waters and wastewaters by photocatalysis (PC) using many kinds of semiconductors as photocatalysts and with a large variety of different incident lights [10-13]. Table 1 collects the main reactions involved in PC to generate ROS like superoxide radical anion ($O_2^{\bullet-}$), hydroperoxyl radical (HO_2^{\bullet} , E° = 1.51 V vs SHE), H_2O_2 ($E^\circ = 1.78$ V vs SHE), and hydroxyl radical (•OH, $E^{\circ} = 2.8 \text{ V vs SHE}$ [14–16]. An electrochemical variety of PC is photoelectrocatalysis (PEC), which has been less explored. This method possesses higher oxidation power because more quantity of ROS is generated, including 'OH formed at the anode surface from water oxidation [17]. The latter ROS is the strongest oxidant in the PC and PEC systems. To date, any review considering the destruction of PCT in waters and waters by such processes considering the semiconductors tested as photocatalysts and photoanodes as well as the kind of light irradiation to them has been published. The analysis of the properties and behavior of new materials to enhance the PCT removal efficiency, as model molecule, is needed to know their potential use in future applications of PC and PEC.

This paper presents a critical and comprehensive review over the application of PC and PEC to PCT removal in waters and wastewater. The fundamentals of these techniques, the characteristics of commercial and synthesized semiconductors, pure or as composites, used, the light irradiated for their photoexcitation, and the effect of the pH and components of the aqueous matrix, are widely.

detailed and discussed. The photocatalytic mechanisms to generate ROS are explained, and the reaction by-products detected from the drug

Table 1

Generation reactions of main oxidizing agents by a photocatalyst (M) activated by light irradiation to degrade organics (R) in a water matrix [14–16].

Reaction	Number
$M + h\nu (>E_g) \rightarrow h_{VB}^+ + e_{CB}^-$	(1)
$h_{VB}^+ + e_{CB}^- \rightarrow M + heat$	(2)
$h_{VB}^+ + H_2O \rightarrow {}^\bullet OH + H^+$	(3)
$h_{VB}^+ + OH^- \rightarrow {}^{\bullet}OH$	(4)
$h_{VB}^+ + R \rightarrow R^+$	(5)
$e_{CB}^- + O_2 \rightarrow O_2^{\bullet -}$	(6)
$O_2^{\bullet-} + H^+ \rightarrow HO_2^{\bullet-}$	(7)
$2HO_2^{\bullet} (or \ 2O_2^{\bullet^-} + 2H^+) \rightarrow H_2O_2 + O_2$	(8)
$HO_2^{\bullet} + H^+ \rightarrow H_2O_2$	(9)
$H_2O_2 + h\nu (UVC) \rightarrow 2^{\bullet}OH$	(10)
$H_2O_2 + e_{CB}^- \rightarrow \bullet OH + OH^-$	(11)

 h_{VB}^{+} : Photogenerated hole, e_{CB}^{-} : photogenerated electron, •OH: Hydroxyl radical, $O_2^{\bullet-}$: Superoxide anion radical, $HO_2^{\bullet-}$: Hydroperoxyl radical.

oxidation are reported. First, the review separately analyzes the PCT removal from the type of photocatalysts tested in PC, considering their nature, composition, and band gap potential (E_g), mainly in a single process but also in combination with other AOPs. The degradation rate of the drug, the mineralization power of the photocatalyst, and its reproducibility in consecutive runs, are examined. A final section is devoted to the PEC treatment, considering the irradiated light and the applied current (I), bias potential to the anode (E_{an}), or cell voltage (E_{cell}) required to generate efficient amounts of ROS to rapidly destroy the drug.

2. Search strategy and bibliometric analysis

The four keywords "acetaminophen AND photocatalysis", "paracetphotocatalysis", "acetaminophen AND amol AND photoelectrocatalysis", and "paracetamol AND photoelectrocatalysis" were introduced in the Scopus database to retrieve the peer-review reviews and scientific articles related to the destruction of this drug in waters by photocatalysis and photoelectrocatalysis. The title, authors, abstract, and reference data of each paper were collected covering up to June 2022 to be further selected as appropriate publications of the matter. Reviews and scientific articles written in English were only analyzed, whereas other publications including book chapters and communications, and conferences in congresses were excluded. The publications included in the present review verified the following criteria:

- (i) The correct application of PC and PEC to PCT remediation,
- (ii) the degradation and/or mineralization of PCT alone or mixed with other organic pollutants in synthetic waters and/or real wastewaters,
- (iii) a detailed description of the experimental method and materials used, including the synthesis of new semiconductors as photocatalysts or photoanodes tested, the photoreactor or photoelectrochemical cell used, the experimental conditions applied, and the analyses made along with their equipment, and
- (iv) an acceptable discussion of the results obtained, with a good characterization of the prepared photocatalysts or photoanodes from their physicochemical, optical, and electrochemical properties, the removal of PCT concentration with reaction time and its kinetic analysis, the influence of the kind of incident irradiation applied and of the nature of the aqueous matrix on drug removal, the clarification and identification of the different oxidizing agents generated, the determination of mineralization parameters like total organic carbon (TOC) and/or chemical oxygen demand (COD) abatement as well as energetic parameters, the detection of by-products, the photoactivation mechanism of semiconductors to generate the oxidants, and the proposal of a reaction sequence for PCT removal. The present review reports 28 figures and 5 tables specially designed to remark on these results.

The above analysis allowed identifying the application of many commercial and synthesized semiconductors to the remediation of waters contaminated with PCT by PC. The photocatalysts were classified from their chemical and structural nature as (i) pure TiO₂, (ii) TiO₂-based, (iii) pure ZnO, (iv) ZnO-based, (v) WO₃-based, (vi) bismuth-based, (vii) g-C₃N₄-based, and (viii) other photocatalysts. The latter group contained many different semiconductors that can also be attractive for PC processes. The action of UVA, UVB, UVC, and visible lights, as well as solar simulation with Xe lamps and direct sunlight irradiation, as energy sources over the performance of the photocatalysts, has been considered. Most articles described the removal of PCT as a model molecule in pure water to show the effectiveness of the photocatalyst and light irradiation checked, and only a few works reported combined (hybrid) processes with other AOPs. Some articles studied the influence of the reaction medium by adding ions or organic

pollutants to the water or taking natural or WWTP effluents. In contrast, a reduced number of articles have been devoted to the PEC treatment of the drug, in which oxidation power has been jointly analyzed. The present review briefly describes the fundamentals of the PC and PEC processes for further analysis of PCT removal with the photocatalysts and photoanodes above mentioned. Special emphasis has been made on the systems used, the effect of operating parameters, the role of generated oxidants, and the mechanisms proposed for the photoactivation of semiconductors.

From the above criteria, 9 specific review articles were selected, most of them published over the last three years. A recent review of our group was devoted to PCT removal by Fenton and Fenton-based processes [5]. Two reviews considered a general application of AOPs including PC to organics destruction in which PCT was cited [6.7]. The other reviews described the destruction of pharmaceuticals including PCT and other organics by PC using TiO₂-based nanocomposites [11,13], graphenebased nanocomposites [12], g-C₃N₄-based nanocomposites [18], halloysite-based nanocomposites [10], and the structural modification of common photocatalysts [19]. However, any article related to a general review of the remediation of waters contaminated with PCT by PC and PEC, as presented in this paper, has been previously published.

The bibliometric analysis was completed by the identification of 159 scientific articles dealing with the destruction of PCT by PC and the other 9 scientific articles considering PEC. Fig. 1a highlights the annual distribution of these papers alongside the 9 review articles. These data make evidence of the great interest in the application of these technologies to PCT abatement since 2016, with a higher number of papers (51



Fig. 1. Bibliometric analysis of the literature on photocatalysis and photoelectrocatalysis. (a) Several publications by year. (b) Percentage of treatment by: (1) pure TiO₂, (2) TiO₂-based nanocomposites, (3) pure ZnO, (4) ZnO-based nanocomposites, (5) WO₃-based photocatalysts, (6) bismuth-based photocatalysts, (7) g-C₃N₄-based photocatalysts, and (8) other photocatalysts.

in total) published since 2021. Considering both PC and PEC treatments, Fig. 1b shows the preferential use of TiO₂-based nanocomposites with other materials (33.3 %) followed by pure TiO₂ (23,2%). Other photocatalysts (16.1 %), as well as ZnO-based nanocomposites (9.6 %), bismuth-based photocatalysts (6.6 %), g-C₃N₄-based photocatalysts (4.8 %), pure ZnO (3.6 %), and WO₃-based photocatalysts (3.0 %), were tested in a lesser extent. It should be mentioned that a high number of scientific articles reported the synthesis and characterization of photocatalysts and photoanodes and their efficient application to the oxidation removal of PCT in waters with different light irradiations, offering key information on the role of oxidizing agents and the photoactivation mechanism of the semiconductors checked. In some works, the study was completed by identifying the by-products of the drug formed.

3. Treatment of paracetamol wastewater by photocatalysis

This section is devoted to the description of the application of different PCT treatments to the removal of PCT from water and wastewater. The fundamentals of this technique are initially and briefly explained. Further, the separated oxidation power of photocatalysts is analyzed and discussed with the semiconductors grouped as: TiO₂ and TiO₂-based nanocomposites, ZnO and ZnO-based nanocomposites, WO₃-based photocatalysts, bismuth-based photocatalysts, g-C₃N₄-based photocatalysts, and other photocatalysts. Tables 2-5 summarize the best results reported in selected papers published for such semiconductors considering the system used and the experimental conditions applied.

3.1. Fundamentals

The initial process of PC consists of the photoexcitation of an electron of the valence band (VB) to the conduction band (CB) of a semiconductor upon light exposition. This originates an electron in the empty CB ($\bar{e_{CB}}$) and a positively charged hole in the fully VB (h_{VB}^+) via reaction (1) (see Table 1). The photogeneration of e_{CB}^-/h_{VB}^+ pairs is feasible when the energy of the photons (hv) of the incident irradiation is higher than the E_{g} -value of the semiconductor. The incident light can be provided either by artificial lamps of UVC (190-280 nm), UVB (280-315 nm), and UVA (315-400 nm), light emitting diode (LED), or by direct sunlight or mimicked with a Xe lamp, whereas visible light can be supplied by white lamps or cutting-off the λ values <400--420 nm of Xe lamps by filters. However, the lifetime of the photogenerated pairs depends on their recombination rate via reaction (2), thus limiting the ability of the separated e_{CB}^- and h_{VB}^+ charges to oxidize organics from ROS generation. Apart from these basic reactions, the light irradiation can photoexcite the O₂ dissolved in water to form the oxidant singlet oxygen (¹O₂), directly detected by electron paramagnetic resonance (EPR) with 4-amino-2,2,6,6-tetramethylpiperidine (TEMP) in PC processes [20].

Photogenerated h_{VB}^+ can produce the strong oxidant •OH from either H_2O by reaction (3) or OH⁻ by reaction (4), or directly attack the organic R by reaction (5). In contrast, the promoted e_{CB}^- is reductor of dissolved O_2 to form the strong superoxide anion radical O_2^{\bullet} ⁻ from reaction (6), which evolves to H_2O_2 and •OH via reactions (7)-(11). So, the protonation of O_2^{\bullet} ⁻ in acid medium gives the hydroperoxyl radical HO₂[•] by reaction (7), which evolves to H_2O_2 via reaction (8) or (9). Finally, H_2O_2 can originate •OH either from homolytic photolysis with incident UVC light ($\lambda < 280$ nm) by reaction (10) or direct reduction by e_{CB}^- from reaction (11). The generated •OH and $O_2^{\bullet-}$ are evidenced by their characteristic EPR spectra with 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) [20]. The generation of all these ROS and the action of h_{VB}^+ can be highlighted using scavengers.

Fig. 2 schematizes the above reactions for a single or pure photocatalyst that oxidizes PCT, remarking the photo-oxidation and photoreduction processes involved. Moreover, this figure presents the main reactions of an alternative and more complex PEC process with a photoanode in an electrolytic cell, where the above photoreactions also take place. The PEC treatments of PCT will be discussed in section 4. From

Table 2

Selected results obtained for the treatment by photocatalysis (PC) of paracetamol (PCT) in different aqueous media using pure TiO₂ photocatalysts.

TiO ₂ material	System	Experimental conditions	Best results	Ref.
TiO ₂ suspension P 25 (NPs ^a with 80 % anatase and 20 % rutile)	Like Fig. 4a under an inner 8 W UVA light or 15 W UVC lamp	150 mL of 2–10 mM drug in pure water. 0.04–7 g/L photocatalyst, pH 3.5–11.0, O_2 concentration: 1.3–36.3 mg/L, 26 °C, 330 min	No degradation with only UVA. For 4 mM drug, 0.4 g/ L P25, pH 5.5, and 36.3 mg/L O_2 , higher degradation: Ti O_2 /UVA < UVA < Ti O_2 /UVC, with total PCT removal. Degradation raised to 0.8 g/L P 25, with increasing O_2 concentration, and up to pH 9.5, but dropped with raising PCT content.	[23]
P 25	Solar pilot-plant like Fig. 4c with a 36 L CPC $^{\rm b}$ photoreactor	150 L of 10 mg/L drug in pure water or synthetic WWTP effluent, 0.2 g/L photocatalyst, natural pH, time measured as t_{30W} ^c	Total degradation at t_{30W} : 30 min (k_1 d = 0.1072 min ⁻¹) in pure water, faster than 80 min (k_1 = 0.059 min ⁻¹) in synthetic WWTP. TOC abatement: 18 % in pure water, higher than 8 % in synthetic WWTP. 6 final short-linear carboxylic acids detected by HPLC. NH \dot{a} and NO $_3$ quantified	[30]
P 25	Solar pilot-plant like Fig. 4c with a 24 L CPC photoreactor	50 L of a secondary WWTP effluent with 9 drugs (1.57 ng/L PCT), 0.2 g/L photocatalyst, 180 min	>98 % degradation of PCT and the other 8 drugs from the secondary WWTP. After addition of 5 mg/L of each drug, 27 % PCT removal at $t_{30W} = 55$ min. At that time, all fecal contamination removed	[31]
P 25	Stirred crystallizer under external 10 mW UVA, UVB, or UVC light, or 3000 mW UVA (UVAH) light	140 mL of 20 mg/L drug in pure water, 0.5 g/L photocatalyst, natural pH, 25 °C, 180 min	Degradation: 17 % (UVB) < 23 % (UVC) < 30 % (TiO ₂ / UVA) < 34 % (TiO ₂ /UVAH) < 37 % (TiO ₂ / UVB) < 47 % (TiO ₂ /UVC)	[32]
Anatase NPs	Fig. 4b under a low-pressure Hg vapor lamp with a photon flow of 13 $\mu Es~L^{-1}~s^{-1}$ (200–700 nm)	500 mL of 20 mg/L drug in pure water, 0.5 g/L photocatalyst, 0.5 g/L H ₂ O ₂ , pH 7.2, 20 °C, LFR e = 2.5 L min ⁻¹ , 60 min	Degradation: 13 % ($k_1 = 0.0031 \text{ min}^{-1}$) by direct photolysis < 51 % ($k_1 = 0.0135 \text{ min}^{-1}$) by PC < 60 % by PC + H ₂ O ₂ addition ($k_1 = 0.0178 \text{ min}^{-1}$). For PC, 46 % COD and 30 % TOC reductions	[27]
Hollow mesoporous anatase microspheres P. 25	Stirred beaker externally irradiated with a 500 W Hg lamp	50 mg/L drug in pure water, 0.1 g/L of each photocatalyst, natural pH, 60 min	Degradation: 85 % for TiO ₂ P 25 $<$ 93 % for hollow anatase with 8 % water. Loss of \approx 30 % performance after 10 consecutive cycles with the above hollow anatase	[39]
Anatase NPs Rutile NPs P 25	Stirred beaker externally irradiated with UVA or UVC light.	200 mL of 1 mM drug in pure water, 1 g/L of each photocatalyst, natural pH, O_2 concentration: 7.1 mg/L, up to 2880 min	Degradation for TiO ₂ /UVA: Rutile $(k_1 = 0.021 h^{-1}) < P 25 (k_1 = 0.073 h^{-1}) < Anatase$ $(k_1 = 0.110 h^{-1})$. For TiO ₂ /UVC: Rutile $(k_1 = 0.018 h^{-1}) < Anatase (k_1 = 0.080 h^{-1}) < P 25$ $(k_1 = 0.100 h^{-1})$. For 20 µM drug, faster degradation using TiO ₂ /UVC for all photocatalysts and with increasing photon flux. 6 primary by-products detected by HPLC	[40}
TiO ₂ NTs ^f prepared from P 25	Stirred cylindrical photoreactor with an inner UVC lamp providing 25 W $\rm cm^{-2}$	250 mL of 20 mg/L drug in pure water, 0.4 g/L TiO ₂ NTs, pH 2.5–10.5, 25 °C, 180 min	99 % degradation with $k_1 = 0.039 \text{ min}^{-1}$ at pH 6.5. Lower degradation and $k_1 \text{ (min}^{-1)}$ for the other pH: 46 % and 0.016 at pH 2.5, 83 % and 0.029 at pH 4.5, 71 % and 0.027 at pH 7.5, 68 % and 0.024 at pH 8.5, and 32 % and 0.008 at pH 10.5	[41]
P 25 onto a ceramic γ-Al ₂ O ₃ tubular ultrafiltration membrane	Continuous tube-in-tube photoreactor with P 25 ceramic and radial H_2O_2 addition upon four external 6 W UVA or UVC lights	1 L of a mixture of 4 drugs, including PCT, at 0,2 mg $L^{\rm 1}$ each in simulated WWTP and secondary WWTP effluent, pH 5.0–6.0, 25 °C, LFR: 40 L h^{-1}	Degradation in simulated WWTP: 1 % for UVA < 10 % for UVC by PC, and 13 % for UVA < 27 % for UVC by PC with 20 mg/L H ₂ O ₂ . Degradation in secondary WWTP effluent: 9 % for UVC by PC with 20 mg/L H ₂ O ₂	[16]
Suspended P 25 P 25 onto glass spheres	Like Fig. 4a with an inner 150 W UV light for suspended P 25. Like Fig. 4b with a packed bed of P 25/glass spheres illuminated with a 400 W solar sodium vapor lamp	Suspended P 25: 800 mL of 50 mg/L drug in pure water, 0.05–1.0 g/L photocatalyst, pH 3.2–10.1, 20 °C, 120 min. Packed bed of P 25/glass spheres: 250 mL of the same solution, pH 8.0, 20 °C, 23 h	For suspended P 25, faster total degradation at pH 8.0, practically independent of photocatalyst content. k_1 varied between 0.36 and 0.45 min ⁻¹ for 0.05 and 0.5 g/L of photocatalyst, respectively For a packed bed of P 25/glass spheres, 42 % and 45 % degradation at 8 and 23 h, respectively, and LER = 0.8 mL s ⁻¹	[44]
Suspended P 25 P 25 onto a cellulosic fiber	Like Fig. 4b with an inner 11 W UVC for suspended P25. Like Fig. 4b but with a solar tubular photoreactor for P 25/cellulosic fiber	For UVC, 1.5 L of 0.0264 mM drug in pure water, 0.4 g/L photocatalyst, pH 2.5–11.0, 150 min. For sunlight, 6.7 L of the same solution, pH 9.0, 150 min	For UVC, faster degradation at pH 9.0 up to 91 % with $k_{1:} = 0.0180 \text{ min}^{-1}$ Under sunlight, 79 % degradation with $k_{1:} = 0.0102 \text{ min}^{-1}$. Low reusability of the P 25/cellulosic fiber after 5 consecutive tests. Detection of 4 primary aromatics by HPLC	[46]
P 25 onto stainless steel (SS) mesh	Quartz photoreactor externally irradiated with six 4 W UVA lights	50 mL of 10 μ M drug in distilled water (DW) and secondary WWTP effluent, TiO ₂ /SS-90 photocatalyst (2.120 mg of TiO ₂ per 2.5–5.0 cm ² SS), pH not controlled, 80 min of irradiation	No drug adsorption over the photocatalyst and scarce drug decay by direct UVA photolysis. Degradation: 66 % for the secondary WWTP effluent < 100 % for DW (k_1 : 0.089 min ⁻¹) High drug content reduction up to 40 % in DW in 10 mM <i>t</i> -butanol as °OH scavenger, but no change in 10 mM <i>c</i> -butanol as "OH scavenger.	[47]
Suspended anatase NPs Anatase in a fixed bed	Solar pilot-plant of Fig. 4c with a 1.11 L CPC at LFR = 26 mL s ⁻¹ and Fig. 4d with 3 fixed beds of 40 cm \times 20 cm \times 1 cm at LFR = 39.3 mL s ⁻¹	2.5–20 mg/L drug in pure water, 0.4 g/L anatase NPs for CPC, 1.1 mg anatase per m^2 for fixed bed, pH 3.0–11.0, 360 min	Degradation for 10 mg/L drug in CPC, k_1 (10 ⁻³ min ⁻¹): 3.4 at pH 3.0 < 8.6 at pH free < 11.3 at pH 9.5. In fixed bed, k_1 (10 ⁻³ min ⁻¹): 21.0 at pH 3.0, 12.0 at pH free, 27.0 at pH 9.5, and 13.0 at pH 11.0. Gradual k_1 decay with raising drug content. TOC removal: 100 % for fixed bed > 77 % for CPC.	[28]

(continued on next page)

Table 2 (continued)

TiO ₂ material	System	Experimental conditions	Best results	Ref.
Hybrid processes				
P 25 and US ⁸	Stirred sono- reactor with a US of 317 kHz frequency and 13.8 W power upon an external 450 W Xe	250 mL of 0.09 mM drug in pure water, 1 g/L photocatalyst, 0.05 mM Fe ³⁺ , pH 2.7, 25 °C, 180 min	$k_1 (\min^{-1}): 0.007 \text{ for P } 25/US < 0.009 \text{ for US } < 0.021 \text{ for Xe/Fe}^{3+} < 0.033 \text{ for Xe/P } 25 < 0.044 \text{ for Xe/P } 25/US < 0.052 \text{ for Xe/US/ Fe}^{3+}. \text{ For the two latter processes, about 90 \% TOC reduction}$	[53]
P 25 and PMS ^h	Stirred beaker photoreactor with air conditioned under an external 300 W Xe lamp	50 mL of 0.1 mM drug in pure water, 0.5 g/L photocatalyst, 0.5 mM PMS, pH 5.0, 240 min	81 % degradation with $k_1 = 0.20$ h ⁻¹ . Excellent reusability of the photocatalyst after 4 consecutive steps, much better than using analogous Co ₃ O ₄ /PMS process	[54]
Anatase NPs and Cr (VI)	Stirred double-wall beaker photoreactor with an external Xe lamp of 2000 W m^{-2} providing visible light with a cut-off at 420 nm	100 mL of 50 mg/L drug in pure water, 0.5 g/L of photocatalyst, 10 mg/L Cr(VI), pH 5.36, 25 °C, 60 min	67 % degradation with 60 % conversion of Cr(VI) into Cr(III). Dramatic loss of efficiency in the second consecutive cycle	[57]

^a NPs: Nanoparticles. ^b CPC: Compound parabolic collector. ^c t_{30W} : time referred to a solar UV power of 30 W m⁻². ^d k_1 : Pseudo-first-order rate constant for PCT decay. ^e LFR: Liquid flow rate. ^f NTs: Nanotubes. ^g US: Ultrasound. ^h PMS: Peroxymonosulfate (HSO₅).

Fig. 2, one can infer the following features: (i) the application of a constant bias potential to the anode (E_{an}), a constant E_{cell} , or a constant I promotes the extraction of photogenerated e_{CB}^- by the external electrical circuit, giving rise to efficient separation of the e_{CB}^-/h_{VB}^+ pairs, and (ii) O_2 and H_2 are evolved at the photoanode (M) and cathode from H_2O oxidation and reduction, respectively, with the peculiarity, that the former reaction originates extra adsorbed hydroxyl radical M([•]OH) as follows [17]:

 $M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^-$ (12).

Several strategies have been proposed to enhance the efficiency of the adsorbed photons for the abatement of organic pollutants in PC aiming to decelerate the recombination of e_{CB}^-/h_{VB}^+ pairs from reaction (2). Nanoparticulated semiconductors with a high specific area in suspension in the effluent, which are difficult to recover after treatment, or immobilized onto substrates, with loss of active specific area and drop of pollutant removal, are frequently tested. Other research efforts have been published dealing with the synthesis of more cost-effective semiconductors, pure or as composites, able to be photoexcited with visible irradiation from natural sunlight and with less E_{g} -value than the most common TiO₂ photocatalyst requiring artificial UVA light. Composites of two semiconductors or a semiconductor with a metal or like-metal in contact form heterojunctions in which the photogenerated electrons and/or holes can circulate between them causing a drop in the E_{g} -value of the individual components [21,22]. This is feasible following different mechanisms like Type II, Schottky, Z-scheme, and p-n, which will be exemplified in the next subsections.

Most scientific papers reported the physicochemical, optical, and electrochemical properties of pristine or synthesized semiconductors. Scanning electron microscopy (SEM) along with energy dispersive X-ray spectroscopy (EDS) are typically used to analyze the surface and qualitatively composition of materials. Their crystallinity and structure are elucidated by X-ray diffraction (XRD) spectroscopy, which is sometimes corroborated with Raman spectroscopy. Fourier-transform infrared (FT-IR) spectra and X-ray photoelectron spectroscopy (XPS) allow the identification of the chemical bonds and the elements of their surface, respectively. UV-vis diffuse-reflectance spectroscopy is measured to construct the Kubelka-Munk function curve and so, determine the E_{g} value of the semiconductors from the corresponding Tauc plot. The electrochemical characteristics are assessed from the photocurrent generated and faradaic impedance. Other parameters such as porosity, active surface area, and the pH of zero-point charge (pHzpc) are determined to understand the adsorption of PCT onto the photocatalyst, which is needed for their reaction with photogenerated oxidants. As a first approach, the adsorption of PCT obeys a Langmuir-Hinshelwood model [23,24] and the rate (r) of the drug decay (mM min⁻¹) can be expressed as a pseudo-first-order reaction kinetics by Eq. (13):

 $r = - = -k_1$ [PCT] (13).

where k_1 is the pseudo-first-order rate constant for PCT decay (min⁻¹), k_{int} is the intrinsic rate constant (mM min⁻¹), and K is the

adsorption constant of PCT onto the photocatalyst (mM⁻¹). Integration of Eq. (13) gives Eq. (14) whose slope corresponds to the k_1 -value of the reaction:

$$\ln ([PCT]_0/[PCT]) = k_1 t (14).$$

3.2. TiO₂ and TiO₂-based photocatalysts

 TiO_2 is the more extensively used semiconductor for the PCT treatments by PC (see Fig. 1b). This subsection describes the oxidation power of these processes. The PC with pure TiO_2 nanoparticles is first detailed considering this material in suspension or immobilized onto substrates, as well as its combination in hybrid processes. Subsequently, TiO_2 -based nanocomposites are separately analyzed with carbon materials, metals, organics, oxides, and other materials.

3.2.1. Pure TiO₂

 TiO_2 is an inert, cheap, non-toxic, and *n*-type metal oxide semiconductor with three crystalline phases called rutile, brookite, and anatase. Fig. 3 shows the structure of these phases, where rutile is.

the most stable one [25]. The metastable anatase and brookite phases can be converted into the rutile one by annealing between 600 and 800 °C [17]. The $E_{\rm g}$ -value of these phases is 3.02 eV for rutile < 3.14 eV for brookite < 3.23 eV for anatase. They are photoexcited with UV light and anatase with the higher $E_{\rm g}$ value is the most active phase. This is ascribed to the more prolonged lifetime of the photogenerated $e_{\rm CB}$ and $h_{\rm VB}^+$ charges due to their larger spatial separation in the crystalline structure of anatase [17]. The PCT destruction from these materials is described below and Table 2 lists the selected results reported.

3.2.1.1. TiO_2 suspension. The most ubiquitous commercial TiO_2 photocatalyst is the so-called P25 from Degussa. It is composed of 80 % of anatase and 20 % of rutile nanoparticles (NPs), with an $E_g = 3.20$ eV, and it acts.

suspended in solution upon strong stirring and exposed to UV light. Fig. 4 depicts the schemes of representative photoreactors tested for these trials. Fig. 4a shows a typical stirred tank reactor equipped with an inner UV lamp and air/O₂ injection [26], whereas a flow photoreactor with an inner UV lamp is schematized in Fig. 4b [27]. Fig. 4c and d present two solar pilot-plant photoreactors, the first one with a compound parabolic collector (CPC) and the second one with a fixed bed TiO₂ under recirculation of the wastewater [28].

Several authors have reported the PCT removal from waters using suspended $TiO_2 P 25 [14.23,29-35]$, black TiO_2 prepared from P 25 [36], and unspecified $TiO_2 NPs [15.37.38]$. Fig. 5 shows the pioneering study made by Yang et al. [23] with 150 mL of 2–10 mM drug and. 0.04–7 g/LP 25 in pure water at pH 3.5–11.0 and 26 °C. The solution was treated in a photoreactor like Fig. 4a equipped with an inner 8 W UVA light or 15 W UVC lamp and flowing with an O₂ concentration of

Table 3

Selected results determined for the destruction of PCT in different aqueous media using PC with TiO₂-based photocatalysts.

Photocatalyst	System	Experimental conditions	Best results	Ref.
Carbon materials				
P 25/activated carbon (AC)	Like Fig. 4a with an inner 125 W medium pressure Hg lamp (cut-off for $\lambda \leq$ 285 nm).	1 L of a suspension in pure water with 25 mg/L drug and 0.75–25 mg/L photocatalyst, pH 3.0–11.0, 240 min	Degradation: 4 % by direct photolysis and 9 % by adsorption for 1.5 mg/L of 10 % P 25/activated carbon at pH 9.0. Under these optimum conditions in PC: 75 % degradation > 50 % found for P 25 alone. Good reproducibility after 4 consecutive cycles	[24]
TiO ₂ NTs/graphene	Stirred beaker externally illuminated with a 14 W UVA light	500 mL of suspensions in pure water with 5 mg/L drug, 0.1 g/L of photocatalyst, pH 3.0–11.0, 180 min	E_{g}^{-3} -values: 3.18 eV for TiO ₂ NTs > 2.98 eV for TiO ₂ NTs/5% graphene. For the latter composite at pH 9.0: 96 % degradation and $k_1 = 0.0248 \text{ min}^{-1}$. Good reproducibility after 5 successive cycles, Detection of 3 aromatic by-products by GC–MS.	[60]
Anatase/carbon	Stirred beaker externally illuminated with five 1 W LED ($\lambda = 400-490 \text{ nm}$)	500 mL of suspensions in pure water with 0.1 mM ¹ drug, 1.0 g/L photocatalyst, pH 6.9, 540 min	Degradation: 54 % for P25 < 94 % for the composite calcined at 300 °C ($k_1 = 0.005 \text{ min}^{-1}$)	[61]
Anatase/graphite	Stirred beaker illuminated with two inner 8 W UVA lights	50 mL of a suspension in pure water with 25 mg/L drug, 0.19–6 g/L anatase, and/or 5–50 % graphite, 180 min	Similar E_{g} -value for anatase and composite. Larger performance for 3 g/L of anatase/10 % graphite: 100 % drug abatement at 120 min and 86 % TOC removal at 180 min. Excellent reproducibility after 4 consecutive cycles	[66]
Anatase/rGO ^b	Stirred beaker with external illumination with eighteen 3 W UVA-LED lights	25 mL of suspension in pure water with 50 mg/L drug, 0.4–4.0 g/L of photocatalyst, pH 4.0–9.0, 50 min	$E_{\rm g}$ -values: 3.23 eV for anatase $>$ 3.11 eV for anatase/1% rGO $>$ 3.05 eV for anatase/3% rGO $>$ 2.78 eV for anatase/10 % rGO. Degradation with 2.0 g/L of the above photocatalysts at pH 5.4: 56 % $<$ 85 % $<$ 100 % $>$ 69 %. Faster degradation at pH 9.0. Oxidants detected with scavengers. Loss of 10 % of reproducibility after 5 successive steps	[68]
Anatase/SiO ₂ / MWCNTs ^c	Like Fig. 4a with an inner high- pressure Hg lamp with emission at $500-550$ nm, intensity 7.31–7.53 mW cm ⁻²	700 mL of suspension in pure water with 10 mg/L drug, anatase/ SiO ₂ /1.0–9.0 %wt MWCNTs, nearly neutral pH, 60 min	$E_{\rm g}$ -value for anatase/SiO ₂ /1.72 %wt MWCNTs: 2.94 eV. 81 % degradation ($k_1 = 0.013 \text{ min}^{-1}$) and 61 % mineralization. Detection of oxidants with scavengers.	[69]
O,P-anatase/CNTs	Stirred beaker with external illumination with a 300 W Xe lamp (cutoff filter at $\lambda <$ 400 nm)	50 mL of suspensions in pure water with 5 mg/L drug, 0.5 g/L photocatalyst, 120 min	$E_{\rm g}$ -value: 2.98 eV. Degradation; 7 % for pure anatase < 95 % for the composite (k_1 : 0.025 min ⁻¹). In the latter case, 58 % mineralization. Effect of scavengers to elucidate the oxidants. Loss of 8 % of reproducibility after 4 consecutive cycles. Identification of 3 aromatic derivatives and 2 final carboxylic acids by LC/MS	[71]
Anatase/Fe, P, Zn, or K- AC	Stirred beaker externally illuminated with a 600 W m 2 Xe lamp (cutoff filters for $\lambda \leq$ 290 nm)	150 mL of a suspension in pure water with 5 mg/L drug, 250 mg/L of anatase in each photocatalyst, 25 °C, 360 min	$E_{\rm g}\text{-values:}$ 3.28 eV for anatase/Fe-AC $<$ 3.33 for anatase $<$ 3.42 eV for anatase/Zn-AC $<$ 3.45 eV for anatase/K-AC $<$ 3.50 eV for anatase/P-AC. Degradation and TOC removal: 100 % at 120 min and 59 % for anatase $>$ 100 % and 43 % for anatase/Fe-AC $>$ 90 % and 35 % for anatase/P-AC $>$ 90 % and 30 % for anatase/K-AC $>$ 75 % and 24 % for anatase/Zn-AC. Loss of 10 % performance after 4 cycles with anatase/Fe-AC	[72]
Metals P 25/Ag	Stirred beaker illuminated with external UVA or visible light	250 mL of suspensions in the pure water of 20–100 µg/L drug, 1 g/L P 25/5% Ag photocatalyst, O_2 flow rate: 100 mL min ⁻¹ , 300 min	$E_{\rm g}$ -value: 2.9 eV. Degradation under UVA light > under visible light. In the former case, 92 %-98 % drug decay was achieved for all concentrations. k_1 dropped from 0.035 min ⁻¹ for 20 ug/l, to 0.016 min ⁻¹ for 100 ug/l.	[76]
TiO ₂ /Sb	Glass vial submitted to 7 mW $\rm cm^{-2}$ UVA-LED light	7.0 mL of a suspension in the pure water of 4.6 mg/L drug, 5 mg of photocatalyst, 120 min	Degradation: 50 % for TiO ₂ , 71 % for TiO ₂ /0.05 % Sb, 72 % for TiO ₂ /0.1 % Sb, 60 % for TiO ₂ /0.2 % Sb, and 32 % for TiO ₂ /2.0 % Sb	[81]
Anatase + brookite/Ta Anatase/Ta	Stirred beaker illuminated with a 30 $\rm mW~cm^{-2}$ UVA light	600 mL of a suspension in the pure water of 35 mg/L drug, 0.5 g/L of photocatalyst, O_2 flow rate: 9 L h^{-1} , 120 min	Degradation, \bar{k}_1 (min ⁻¹), and mineralization: 83 %, 0.0124, and 59 % for anatase + brookite, 70 %, 0.0094, and 44 % for anatase + brookite/Ta, 70 %, 0.0104, and 50 % for anatase/Ta. Identification of 1 aromatic by-product, acetamide, and 1 carboxylic acid by GC-MS	[83]
TiO ₂ NFs ^d /BN ^e /Pd	Stirred beaker illuminated with external 400 W UVA or visible light	250 mL of suspensions in the pure water of 1 mg/L drug, 0.5 g/L of photocatalysts, 240 min	$E_{\rm g}$ -values: 3.2 eV for TiO ₂ NFs $>$ 3.17 eV for TiO ₂ NFs/Pd $>$ 3.11 eV for TiO ₂ NFs/BN $>$ 3.09 eV for TiO ₂ NFs/BN/Pd. Degradation in the same order under UV light at 15 min: 89 %, 100 %, 24 %, and 100 %. Under visible light at 240 min: 40 %, 60 %, 12 %, and 100 %. For the latter composite, good reproducibility after 5 successive runs	[84]
P 25/Pt for hybrid process with US	Stirred sono-reactor with a US of 572 kHz frequency and 120 W power upon 107.4 W cm $^{-2}$ UVC low-pressure Hg vapor lamp	250 mL of a suspension in the pure water of 40 μM drug, 5 mg/L of photocatalyst, natural pH of 6.5, 60 min	Total degradation using P 25 and P 25/1 mM Pt, P 25/ 2 mM Pt, and P 25/4 mM Pt, but with: $k_1 = 0.074 \text{ min}^{-1}$ for the second and third, and $k_1 = 0.108 \text{ min}^{-1}$ for the latter. The corresponding mineralization was: 32 %, 40 %, 42 %, and 48 %. Study of the oxidizing species with scavengers for P 25/4 mM Pt	[79]
Organics				

(continued on next page)

Table 3 (continued)

Photocatalyst	System	Experimental conditions	Best results	Ref.
P 25/Zn(II) phthalocyanine	Stirred annular reservoir with an inner 400 W UV/Visible light (295–710 nm)	850 mL of suspensions in the pure water of 10 mg/L drug, 100 mg/L of photocatalyst, 16–332 mg L H_2O_2 , pH 3.0–10.0, 25 °C, 120 min	Mineralization at pH 3.0 and 10.0: 33 % and 76 % without H_2O_2 and 69 % and 67 % with 33 mg/L H_2O_2 for P 25. In the case of P 25/2.5 % Zn(II) phthalocyanine, 67 % and 72 % without H_2O_2 and 79 % and 69 % with 33 mg/L H_2O_2	
TiO ₂ NTs/ carboxymethyl- β-cyclodextrine	Stirred beaker with an external 10 W UV lamp	Suspensions in the pure water of 20 mg/L drug, 1 g/L of photocatalyst, pH 4.0, 20 °C, 150 min	Degradation: 43 % for TiO ₂ NTs and 97 % ($k_1 = 0.0234$ min ⁻¹) for TiO ₂ NTs/carboxymethyl- β -cyclodextrine. Oxidants detected with scavengers for the nanocomposite	[88]
Oxides P 25/Fe ₃ O ₄ P 25/SiO ₂ /Fe ₃ O ₄	Like of Fig. 4a with an inner UVC light providing 3.8 \times 10 6 Es L^{1} s^{-1}	400 mL of phosphate-buffered suspensions of 30 mg/L drug, 1.16 g/L for P $25/Fe_3O_4$ and 1.34 g/L for P $25/SiO_2/Fe_3O_4$, pH 7.0, air flow rate: 50 L h ⁻¹ , 25 °C, 300 min	Characterization of the magnetic properties of photocatalysts. Degradation: 90 % for P 25/ Fe ₃ O ₄ < 97 % for P 25 and P 25/SiO ₂ /Fe ₃ O ₄ . $k_1 = 0.0071, 0.0098, and 0.0102 min-1, respectively. Good reusability after 4 cycles only for P 25/SiO2/Fe3O4$	[90]
P 25/Fe ₂ O ₃	Stirred beaker illuminated with external 450 W medium-pressure Hg vapor lamp (297–578 nm)	50 mL of suspensions in the pure water of 50 mg/L drug, 0.1 g/L of magnetic photocatalysts, without and with an O_2 flow rate of 100 mL min ⁻¹ , 60 or 90 min	Degradation at 90 min and k_1 (min ⁻¹) without O_2 : 52 % and 0.008 for Fe ₂ O ₃ < 64 % and 0.011 for 15 % P 25/ Fe ₂ O ₃ < 75 % and 0.015 for 33 % P 25/Fe ₂ O ₃ < 88 % and 0.022 for 50 % P 25/Fe ₂ O ₃ < 99 % and 0.060 for P 25. Large enhancement with O ₂ : 98 % degradation and 66 % mineralization in 60 min for 50 % P 25 Fe ₂ O ₃ . Detection of 3 aromatics, acetamide, and 7 carboxylic acids by GC–MS	[91]
Anatase/Nb ₂ O ₅	Stirred cuboid photoreactor under an external 40 W LED white lamp	50 mL of suspensions in the pure water of 10 mg/L drug, 30 mg of photocatalyst, 120 min	$E_{\rm g}$ values: 2.43 eV for Nb ₂ O ₅ > 2.05 eV for 4 anatase/ Nb ₂ O ₅ > 1.79 eV for 2 anatase/Nb ₂ O ₅ . Degradation: 36 % < 80 % < 91 %, also linked to the greater adsorption of the drue onto the photocatalyst	[94]
TiO ₂ /MnO _x for hybrid US process	Jacketed glass reactor upon 20 W US and an external 160 W UVA light	150 mL of suspensions in cooking water of 25 mg/L drug, 0.1 g/L of photocatalyst, 180 min	As-synthesized TiO ₂ with anatase, rutile, and brookite. E_g values varied between 1.60 and 1.91 eV. Degradation: 12 % with only US < 26 % for the hybrid process	[95]
Other materials Anatase/K ₃ [Fe(CN) ₆]	Stirred beaker with five external blue 1 W LED lights (440–490 nm)	2 L of suspensions in the pure water of 0.1–0.2 mM drug, 0.5–1.0 g/L of	Optimization by response surface methodology: 91 % degradation for 0.1 mM drug, 1 g/L photocatalyst, and	[97]
Anatase/K ₂ S ₂ O ₈	Stirred beaker with five external LED lights (up to 450 nm)	photocatalyst, pH 6.9–8.2, 30 °C, 540 min 500 mL of suspensions in the pure water of 0.1 mM drug, 1 g/L of anatase/ 0.50-1.25 %wt K ₂ S ₂ O ₈ , calcination temp. and time: 200–500 °C, and 120–300 min, pH 9.0 510 min	pH 6.9. Faster total degradation was attained with anatase/ 0.50 %wt K ₂ S ₂ O ₈ prepared with a calcination temp. of 300 °C for 180 min. $E_{\rm g}$ -value: 1.94 eV. $k_1 = 0.0084 {\rm min}^{-1}$	[101]
Anatase/halloysite and/ or sepiolite	Stirred annular photoreactor with an inner 400 W UVA lamp	200 mL of suspensions in the pure water of 30 mg/L drug, 0.85 g/L of photocatalyst, 120 min	$E_{\rm g}$ -values: 3.20 eV for anatase and \approx 3.0 eV for the other nanocomposites, Degradation: 83 % for anatase/ halloysite < 88 % for anatase/ halloysite + sepiolite < 93 % for anatase/ sepiolite < 97 % for anatase. 40 % TOC removal for anatase/sepiolite	[103]
Anatase/ aluminosilicate	Two stirred vessels with an external 125 W UV lamp (280–365 nm)	100 mL of suspensions in the pure water of 1–10 mg/L drug, 0.5–4.0 g/L of photocatalyst, pH 4.0–10.0, air sparging, 30 min	Optimization by response surface methodology: 99 % degradation and 83 % TOC reduction for 2.74 mg/L drug, 2.71 g/L photocatalyst, and pH 9.5. Energy consumption per unit PCT mass: 0.224 kWh g ⁻¹ . Loss of 4.6 % degradation after 3 successive cycles	[104]
TiO ₂ NRs ^f /MoS ₂	Stirred beaker under direct sunlight	Suspensions in the pure water of 2 mM drug, 25 mg/L of the nanocomposite, 25 min	Degradation: 5 % for $TiO_2 NRs < 39$ % for $TiO_2 NRs/MoS_2$ (k ₁ : 0.021 min ⁻¹). Excellent reusability after 3 consecutive runs	[106]
TiO ₂ (anatase + rutile)/ B or N	Like Fig. 4a with an inner 125 W UVA light	150 mL of suspensions in the pure water of 10–100 mg/L drug, 0.05–2.5 g/L of $TiO_2/$ 4.64 %wt B or $TiO_2/0.50$ %wt N as a photocatalyst, 180 min	$E_{\rm g}$ -values. 2.98 eV for TiO ₂ > 2.96 eV for TiO ₂ /4.64 %wt B > 2.51 eV for TiO ₂ /0.50 %wt N. Faster degradation for 10 mg/L drug and 1 g/L photocatalyst dose: 95 % for TiO ₂ /4.64 %wt B > 75 % for TiO ₂ /0.50 %wt N. Lower degradation with raising drug concentration	[108]

^a E_o: band gap potential. ^b rGO: Reduced graphene oxide. ^c MWCNTs: Multi-walled carbon nanotubes. ^d NFs: Nanofibers, ^e BN: Boron nitride. ^f NRs: Nanorod.

1.3–36.3 mg/L. For 4 mM drug and 0.4 g/Lphotocatalyst at pH 5.5 and 36.3 mg/L O₂, Fig. 5a highlights a very small removal for TiO₂ alone or under UVA light in 330 min, meaning the existence of low adsorption of the drug onto the photocatalyst and a large photostability under this irradiation. In contrast, the UVC irradiation caused a higher 52 % of drug decay due to its slow photolysis because it absorbed this light with $\lambda^{max} = 243$ nm. Less potent was the PC process with UVA yielding a 46 % reduction, whereas the alternative use of UVC led to 98 % of almost total PCT removal. The UVA photons with higher energy than the E_g -value of P 25 (3.20 eV) then photogenerated e_{CB}^-/h_{VB}^+ pairs from reaction (1) to produce oxidants as •OH and O₂•⁻ to destroy the drug. The greater oxidation with UVC can be ascribed to its additional photolysis that

largely enhances its destruction. The by-products thus generated can be much more easily mineralized, as deduced from Fig. 5b showing the TOC decay, since only the PC with UVC yielded up to a 60 % mineralization in 330 min. The change of k_1 for PCT decay with key experimental operating variables of the latter process is shown in Fig. 5c-f. As can be seen in Fig. 5c, an increase in the P 25 loading caused the rise of k_1 up to an optimum.

content of 0.8 g/L, whereupon it reached a plateau because higher photocatalyst loadings decreased the light penetration and enhanced the collision between the nanoparticles, thus activating less P 25 in the suspension. Fig. 5d highlights the gradual drop of k_1 at higher initial drug content as a result of the slower attack of the same amount of

Table 4

Selected results for PCT removal from different aqueous media by PC with photocatalysts containing ZnO, WO₃, Bi, or g-C₃N₄.

Photocatalyst	System	Experimental conditions	Best results	Ref.
Pure ZnO				
Thermally or mechanically activated ZnO	Stirred beaker with an external UVA light (315–400 nm)	250 mL of suspensions in the pure water of 50 mg/L drug, 1 g/L of photocatalyst, 23 $^\circ\text{C},$ 240 min	Degradation and $k_1 (min^{-1})$: 96 % and 0.0136 (annealed at 100 °C) > 95 % and 0.0124 (annealed at 200 °C) > 92 % and 0.0104 (unannealed) > 76 % and 0.0057 (annealed at 500 °C). In the case of mechanical activation with ethanol, air, and methanol, $k_1 = 0.0085$. 0.0062. and 0.0049 min ⁻¹	[111]
Molecularly imprinted ZnO nanonuts	Quartz cuvette under an external 4 mW cm^{-2} UVA lamp ($\lambda=368$ nm)	2.0 mL of suspensions in the pure water of 0.05 mM drug, 0.5 g of photocatalyst, 180 min	Degradation and k_1 (min ⁻¹): 19 % and 0.00112 for ZnO < 92 % and 0.0132 for molecularly imprinted ZnO nanonuts	[113]
Packed bed ZnO	A vial coated with a ZnO thin film irradiated with a UVA-LED light	5 mL of 400 μM drug in pure water with a phosphate buffer of pH 11.5, 0–1.8 % (v/v) of $\rm H_2O_2,$ 68 min	E_g value: 2.9 eV. Rapid decay of drug concentration with raising $\rm H_2O_2$ content to 0.35 % (v/v). Under these conditions, 69 % of drug removal	[110]
ZnO-based nanocomposites ZnO/La	Stirred beaker upon three external compact 20 W fluorescent lamps	100 mL of suspensions in the pure water of 100 mg/L drug, 1 g/L of photocatalyst, 25 $^\circ$ C, 180 min	$E_{\rm g}\text{-values: }3.15$ eV for ZnO >3.09 eV for ZnO/1.5 % wt La >3.02 eV for ZnO/0.5 %wt La >2.97 eV for ZnO/1.0 %wt La. Degradation and TOC removal for photocatalysts: 5 % and 2 % $<$ 81 % and 63 % $<$ 80 % and 69 % $<$ 93 % and 80 %. Identification of 3 aromatic derivatives and 3 carboxylic acids by GC–MS	[116]
ZnO/Nd,V	Stirred beaker externally illuminated with a 500 W halogen lamp	180 mL of suspensions in the pure water of 10 mg/L drug, 1 g/L of photocatalyst, 25 $^\circ \rm C,$ 150 min	E_{g} -values: 3.25 eV for ZnO > 2,97 eV for ZnO/2% Nd 1 % V > 2.92 eV for ZnO/4% Nd 1 % V > 2.82 eV for ZnO/6% Nd 1 % V, Degradation for these photocatalysts: 5 %, 49 %, 70 % (39 % TOC removal), and 59 %. Oxidants detected with scavengers	[118]
ZnO/Ag	Like of Fig. 4a with an inner 300 W halogen lamp providing visible light	A suspension in a WWTP effluent of 5 mg/L drug, 1 g/L of pure ZnO or ZnO/Ag, pH 8.5, 120 min	$E_{\rm g}\text{-values: 3.31 eV}$ for pure ZnO and 3.02 eV for ZnO/ Ag. Degradation: 42 % for pure ZnO < 91 % for ZnO/ Ag (k_1 : 0.020 min ⁻¹). After 5 consecutive cycles, loss of performance of up to 75 % degradation	[122]
ZnO/sepiolite ZnO/SiO ₂ /sepiolite ZnO//Fe ₃ O ₄ /sepiolite	Stirred beaker with an external 450 W m ⁻² Xe light (cutoff filter for $\lambda < 320$ nm) Stirred beaker externally irradiated	250 mL of suspensions in the pure water of 10 mg/L drug, 1 g L ⁻¹ of photocatalyst, air flow rate: 50 mL min ⁻¹ , 38 °C, 600 min 50 mL of a suspension in the pure water of	Degradation and k_1 (10 ⁻³ min ⁻¹): 31 % and 0.66 for ZnO/SiO ₂ /sepiolite < 58 % and 1.32 for ZnO// Fe ₃ O ₄ /sepiolite < 85 % and 3.12 for ZnO/Sepiolite	[124]
A <u>8</u> 29-210/100	with a 350 W Xe light	20 mg/L drug, 2 g/L of TiO ₂ P 25, ZnO/rGO, or Ag ₂ S-ZnO/rGO, pH 5.4, 60 min	Degradation: 34.96 for P 25 < 47 % for ZnO/ rGO < 100 % for Ag ₂ S-ZnO/rGO. In the latter case, 68 % mineralization. Detection of oxidizing agents with different scavengers. Scarce reusability after 5 successive steps	[12/]
ZnO/Fe ₃ O ₄ -GO/ZIF-8 ^a	Stirred beaker upon external irradiation with a 50 W Xe light	Suspension in the pure water of 10 mg/L drug, 0.5 g/L of photocatalyst, 45 min	99 % degradation and 99 % TOC abatement. Detection of oxidizing agents with scavengers. Excellent reproducibility after 10 consecutive cycles	[128]
WO ₃ -based photocatalysts Pure WO ₃ in the presence of Fe(III) and/or H ₂ O ₂	Stirred beaker under an external 4 W fluorescent light (350–650 nm)	Suspensions in the pure water of 0.10 mM drug, 0.5 g/L of photocatalyst, 0.25 mM Fe (III), 5 mM H_2O_2 , pH 7.0, equilibrated air, 22 °C	$k_1 = 0.026 \text{ min}^{-1}$ for WO ₃ /H ₂ O ₂ $< 0.030 \text{ min}^{-1}$ for WO ₃ /Fe(III)/H ₂ O ₂	[132]
WO3 nanoplates/AC	Stirred beaker with an external 400 W metal halide lamp	100 mL of suspensions in the pure water of 1 mg/L drug, 1 g/L of photocatalyst, 180 min	$E_{\rm g}\text{-values:}$ 2.78 eV for WO ₃ nanoplates $>$ 2.42 eV for WO ₃ nanoplates/1% AC $>$ 2,26 eV for WO ₃ nanoplates/2% AC. Degradation: 45 % $<$ 56 % $<$ 97 %	[133]
WO ₃ /g-C ₃ N ₄	Stirred beaker externally irradiated with a 300 W Xe lamp (visible light with IR and 400 nm cut filters)	50 mL of suspensions in the pure water of 10 mg/L drug, 50 mg of g -C ₃ N ₄ or WO ₃ /g-C ₃ N ₄ , 1 mM of scavengers, 60 min	$E_{\rm g}$ -values: 2.78 eV for g-C ₃ N ₄ and 2.70 eV for WO ₃ . Drug removal: 97 % at 60 min for g-C ₃ N ₄ < 98 % at 30 min for WO ₃ /g-C ₃ N ₄ . Study of oxidants formed in each photocatalyst with different scavengers. Identification by EPR with DMPO. Loss of 15 % of drug degradation after 5 consecutive cycles	[135]
Bismuth-based photocatalysts Four morphological forms of BiVO ₄	Stirred tubes upon external 300 W Xe lamp as visible light source $(\lambda > 420 \text{ nm})$	50 mL suspensions in the pure water of 5–25 mg/L drug, 20–120 mg/L of each photocatalyst, pH 2.0–11.0, 300 min	$E_{\rm g}$ -values: 2.37, 2.36, 2.39, and 2.39 eV for cube, granular, plate, and spindle forms. Degradation and $k_1 (\min^{-1})$ for 10 mg/L drug, 80 mg/L of each photocatalyst at pH 6.0 in the above order: 95 % and 0.0135 > 90 % and 0.074 > 76 % and 0.0046 > 55 % and 0.0024. For the cube form, near 73–76 % TOC removal was maintained during 5 consecutive cycles	[137]
BiVO ₄ /Pd	Stirred beaker externally illuminated with visible light at $\lambda > 420 \text{ nm}$ from a 300 W Xe lamp	40 mL of suspensions in the pure water of 10 mg/L drug, 1 g/L of photocatalyst, 15 $^\circ C$, 60 min	$E_{\rm g}$ -values: 2.38 eV for BiVO ₄ and 2.29 eV for BiVO ₄ /Pd. Degradation and $k_1 ({\rm min}^{-1})$ for these photocatalysts: 30 % and 0.0101 < 100 % and 0.0308. 40 % TOC removal for BiVO ₄ /Pd. Oxidants detected using scavengers and FPR with DMPO	[140]
Bi ₃ O ₄ Br hierarchical hollow spheres with (0,0,1)-facets nanosheets	Stirred beaker externally illuminated with visible light at $\lambda > 420 \text{ nm}$ from a 1000 W Xe lamp	50 mL of suspensions in the pure water of 10 mg/L drug, 1 g/L of photocatalyst, 100 min	$E_{\rm g}$ -values: 2.34 eV for hollow spheres, very close to 2.39 eV for Bi ₃ O ₄ Br nanoplates. 96 % degradation and $k_1 = 0.342$ min ⁻¹ for hollow spheres but only 64 % degradation with $k_1 = 0.098$ min ⁻¹ for nanoplates.	[143]
			(continued on ne	л page)

Table 4 (continued)

Photocatalyst	System	Experimental conditions	Best results	Ref.
BiOCl	Stirred beaker with external illumination with four 15 W fluorescent lamps (300–500 nm)	100 mL of suspensions in the pure water of 0.05 mM drug, 0.3 g/L of photocatalyst, 1 mM of H_2O_2 and $S_2O_8^{2-}$, pH 3.0–10.0, 20 °C, 180 min	Detection of oxidizing agents with scavengers and EPR with DMPO. Loss of 10 % performance after 5 successive runs Degradation with BiOCI: 98 % at pH 3.0 and about 65 % for pH 5.8–10.0. TOC removal at pH 5.8: 10 % for H ₂ O ₂ < 14 % for S ₂ O ₈ ²⁻ < 60 % for BiOCI/ H ₂ O ₂ < 66 % for BiOCI < 85 % for BiOCI/H ₂ O ₂ / S ₂ O ₈ ²⁻ . Detection of oxidants with scavengers and EPR with DMPO	[145]
BiOCl/BiPO ₄	Stirred beaker externally illuminated with UV light provided by a 300 W Xe lamp ($\lambda < 400$ nm)	50 mL of suspensions in the pure water of 30 mg/L drug, 25 mg of HBIP (BiPO ₄ uncalcined), <i>n</i> -type twinned BiPO ₄ (calcined at 500 °C), <i>p</i> -type BiClO, and BiClO/BiPO ₄ , 18 min	Er with Diro's 1.8 and 4.2 eV for the two forms of the twinned BiPO ₄ > 3.34 eV for BiClO. Degradation and k_1 (min ⁻¹) at 15 min: 4 % and 0.0017 for HBIP < 6 % and 0.0042 for twinned BiPO ₄ < 69 % and 0.074 for BiClO < 100 % and 0.25 for BiClO/BiPO ₄ . For the latter photocatalyst, oxidants detected with scavengers	[146]
g-C ₃ N ₄ -based photocatalysts g-C ₃ N ₄ /Au P 25/Au	Stirred beaker externally illuminated with a 15 W UVA lamp. For visible light, a photoreactor like Fig, 4a with four inner 10 W white LED lamps	70 mL of suspensions in the pure water of 0.3 mg/L drug, 40.5 mg of photocatalyst, pH 2.9–11.0, 25 $^\circ \rm C$	<i>E</i> _g -values: 3.23 eV for P 25 > 3.10 eV for P 25 ₂ / Au > 2.75 eV for g-C ₃ N ₄ > 2.67 eV for g-C ₃ N ₄ /Au. Overall degradation of these photocatalysts at natural pH 5.9: 40, 31, 48, and 24 min with UV light. Using g-C ₃ N ₄ under visible light, total degradation: 15 min at pH 2.9 < 30 min at pH 9.5 (p <i>K</i> _a) < 47 min at natural pH 5.9 < 60 min at pH 11.0. Excellent reproducibility after 8 cycles at pH 5.9 for 50 min	[147]
g-C ₃ N ₄ /Ni-ZnS	Stirred beaker externally illuminated with visible light from a 500 W tungsten halogen lamp $(\lambda > 400 \text{ nm})$	220 mL of a suspension in the pure water of 30 mg/L drug, 0.22 g of g-C ₃ N ₄ /10 % mol Ni-ZnS, O ₂ flow rate: 1 L min ⁻¹ , 25 °C, 100 min	E_{g} -values: 3.40 eV (ZnS) > 2.70 eV (g- C ₃ N ₄) > 2.61 eV (g-C ₃ N ₄ /10 % mol Ni-ZnS. For the latter photocatalyst, 86 % degradation in 100 min	[148]
g-C ₃ N ₄ /K and N defects	Stirred beaker with an external 300 W Xe lamp (visible light with IR and 400 nm cutoff filters)	50 mL of suspensions in the pure water of 10 mg/L drug, 1 g/L of photocatalyst, 120 min	$E_{\rm g}$ -values: 2.72 eV for g-C ₃ N ₄ > 2.65–2.66 eV for g-C ₃ N ₄ with 1.0 % K, 2,4% K, 5.9 % K, and 7.9 % K. Degradation and $k_1 ({\rm min}^{-1})$ for these photocatalysts: 50 % and 0.0109 < 61 % and 0.0147 < 74 % and 0.0199 < 80 % and 0.0285 < 100 % and 0.0651. Detection of oxidants with scavengers and EPR with DMPO and TEMP. Low reproducibility after 7 consecutive cycles	[20]
g-C ₃ N ₄ -K,I/CeO ₂	Hollow cylindrical photoreactor with external eight 8 W visible light lamps ($\lambda = 465 \pm 40$ nm)	20 mL of suspensions in pure water of 10 mg/ L dtug, 0.5–2.0 g/L of g-C ₃ N ₄ -K,I/15 % CeO ₂ , pH 3.0–11.0, 25 °C, 90 min	$E_{\rm g}$ -values: 2.98 eV (15 % CeO ₂) > 2.77 eV (g-C ₃ N ₄ -K, I) > 2.36 eV (g-C ₃ N ₄ -K,I/15 % CeO ₂). For 2.0 g/L of the latter photocatalyst at pH 9.0, 98 % degradation and $k_1 = 0.039~{\rm min}^{-1}$. Good reproducibility after 3 consecutive cycles. Detection of oxidants with scavengers.	[150]

^a ZIF-8: Zeolitic imidazolate framework-8.

photogenerated oxidants over more organic matter, whereas Fig. 5e reveals a continuous rise of k_1 with increasing O_2 concentration due to the production of more oxidant $O_2^{\bullet-}$ from reaction (6). Another interesting result is depicted in Fig. 5f where a maximum k_1 -value was attained at pH = 9.5, related to the p K_a (=9.53) of the drug and the pH_{2pc} (=6.2) of the photocatalyst. At pH < 6.2 the nanoparticle surface was positively charged, whereas at pH > 6.2 it was negatively charged, and then, the neutral form of the drug can be more adsorbed and more rapidly removed at pH 9.5, being its negative form less adsorbed and more slowly destroyed at pH > 9.5. All these optimum conditions are given in Table 2. Additionally, these authors identified 10 by-products of HPLC and GC–MS. Other works have confirmed this degradation behavior, but with a lack of techno-economic studies to benchmark its possible industrial application with that of other AOPs.

Aiming to demonstrate the effectiveness of PC for WWTP remediation, Radjenovic et al. [30] and Bernabeu et al. [31] applied solar pilotplants like Fig. 4c with CPC photoreactors to treat large volumes (150 and 50 L) of synthetic and real WWTPs with PCT and other organic contaminants. The runs were performed with a small amount of 0.2 g/L of P 25 at natural pH and the time was measured whit respect to a solar UV power ($\lambda > 300$ nm) of 30 W m⁻² (t_{30W}). The former authors treated suspensions of 10 mg/L drug and at $t_{30W} = 30$ min, they found a faster total degradation with $k_1 = 0.1072$ min⁻¹ and 18 % TOC removal in pure water than $k_1 = 0.059$ min⁻¹ and 8 % TOC abatement for a synthetic WWTP due to the competitive oxidation of its components (see Table 2). They also detected 6 final short-linear carboxylic acids by HPLC and quantified the released NH_4^+ and NO_3^- ions. In contrast, the latter authors considered a real WWTP containing 9 drugs including 1.57 ng/L of PCT, and obtained a 98 % of degradation of all pollutants after 180 min of reaction. Upon the addition of 5 mg/L PCT, the degradation process was slower and only 27 % of the drug was removed at $t_{30W} = 55$ min as a positive result, fecal contamination was completely abated (see Table 2). Although these findings evidence that solar PC with TiO₂ P5 can be useful for PCT destruction, more active photocatalysts have been synthesized and applied, as discussed below.

More information about the influence of the light irradiation has been reported by Eskandarian et al. [32] by using a 10 mW UVA, UVB, or UVC light, or a more potent 3000 mW UVA (UVAH) light to illuminate a crystallizer with 140 mL of a suspension of 20 mg/L drug and 0.5 g/LP 25 at natural pH and 25 °C. Fig. 6 depicts the variation of the normalized drug concentration with time showing that at 180 min, the most efficient process was PC with UVC, followed by PC with UVB, PC with UVA, UVC, and UVB (see Table1). It can be inferred again that the quicker drug photolysis by UVC enhanced the PC process due to the larger photolysis of the drug. Moreover, the more potent UVAH (3000 mW) than UVA (only 10 mW) did not practically improve the degradation process in PC, suggesting that the little influence of the higher light power over the PC process is due to the saturation of active sites for photoexcitation already under the application of the less potent 10 mW UVA light.

Several works on PC with TiO2 have detected and identified the main

Table 5

Selected results obtained for the destruction of PCT from different aqueous media by PC with other photocatalysts.

Photocatalyst	System	Experimental conditions	Best results	Ref.
Ag/AgBr NPs	Stirred beaker with an external 300 W Xe light (cutoff filters for IR and $\lambda <$ 420 nm)	100 mL of suspensions in pure water with 5 mg/L drug, 30 mg of photocatalyst, 50 min	$E_{\rm g}$ -values: 2.56 eV for AgBr > 2.42 eV for Ag/AgBr. Degradation for these photocatalysts: 90 % < 99 %. Using TiO ₂ and TiO ₂ /N, 6 % and 76 % degradation, respectively. Detection of oxidants with scavengers	[154]
Ag/AgCl/ZIF-8	Stirred beaker externally illuminated with a 500 W metal halogen lamp (cutoff filters for IR and $\lambda < 400$ nm)	100 mL of suspensions in pure water with 0.5–2 mg/L drug, 0.1–0.8 g/L of photocatalyst, pH 3.0–11.0, room temperature, 60 min	<i>E</i> _g -value for ZIF-8: 5.06 eV. Degradation for 1 mg/L drug and 0.5 g/L of photocatalyst at pH 7.0: 4 % without catalyst < 19 % for ZIF-8 < 79 % for Ag/AgCl < 100 % for Ag/AgCl/ZIF-8 ($k_1 = 0.058 \text{ min}^{-1}$). Faster and total degradation with $k_1 = 0.142 \text{ min}^{-1}$ at pH 5.0. Low reusability after 3 consecutive cycles. Detection of oxidants with scavengers. Identification of 2 aromatic by-products and 4 final carboxylic acids by HPLC	[155]
Zn-Al/Ce MMO ^a	Stirred beaker upon an external visible light at $\lambda > 420 \text{ nm}$ using a 300 W Xe lamp	50 mL of suspensions in the pure water of 10 mg/L drug, 0.5 g/L of photocatalyst. 240 min	Degradation: 11 % by photolysis < 99 % by PC using Zn-Al/ 5% Ce calcined at 750 °C. Detection of oxidizing agents by EPR with DMPO	[156]
ZnFe- CLDH ^b /rGO	Like Fig. 4a with an inner 500 W Xe lamp	50 mL of suspensions in the pure water of 5 mg/L drug, 25 mg of photocatalyst, neutral pH, room temperature, 420 min	k_1 (10 ⁻³ min ⁻¹): 0.15 for direct photolysis < 1.4 for LDH < 2.1 for CLDH < 7.4 for ZnFe-CLDH. For the latter process, 96 % degradation and 50 % mineralization. Detection of oxidants by scavengers and EPR with DMPO. Excellent reproducibility after 5 successive trials	[158]
In ₂ S ₃ /Zn ₂ GeO ₄	Stirred customized photoreactor with an external 300 W Xe light (cutoff filters providing $\lambda > 420$ nm).	100 mL of suspensions in pure water with air equilibrated of 5–25 mg/L drug, 0.5–2.5 g/L of photocatalyst, pH 3.0–7.0, 25 °C, 360 min	E_{g} -value: 2.2 eV for $\ln_2 S_3$ and 4.67 eV for $2n_2 GeO_4$. Faster degradation up to 95 % with $k_1 = 0.0087 \text{ min}^{-1}$ for 5 mg/L drug and 1.0 g/L photocatalyst at pH 9.0. TOC only dropped 53 % at pH 7.0. Good reusability after 5 consecutive cycles. Detection of oxidizing agents using different scavengers. Study of the influence of HCO ₃ ⁻ and humic acid	[160]
SnO ₂ /ZnS	Heraeus photoreactor upon a 7.53 mW cm $^{-2}$ high-pressure Hg lamp (550 nm)	750 mL of suspensions in pure water with 10 mg/L drug, 1 g/L of photocatalyst, pH 6.5, 120 min	Degradation and $k_1 \text{ (min}^{-1}$): 41 % and 0.0443 for pure ZnS < 65 % and 0.00786 for pure SnO ₂ < 70 % and 0.01067 for 1:2 ZnS/SnO ₂ . In the latter case, 38 % of TOC removal. Detection of oxidants with scavengers	[161]
Fe ₃ O ₄ /Fe ₂ O ₃ NPs	Ace glass photoreactor externally illuminated with 450 W medium-pressure Hg lamp	150 mL of suspensions in pure water of 5–30 mg/L drug, 0.13 g/L of photocatalyst, N_2 or air bubbling, 120 min	Total degradation with air: 20 min for 5 and 10 mg/L drug < 30 min for 20 mg/L drug < 60 min for 30 mg/L drug. By bubbling N ₂ , 45 min for 10 mg/L drug. Evaluation of photogenerated *OH with 2-hydroxyterephthalic acid. Detection of 3 aromatic derivatives and 1 carboxylic acid by LC/MS	[164]
Nb ₂ O ₅	Stirred beaker under an external 125 W UVA light	250 mL of suspensions in pure water of 10 mg/L drug, 0.5–1.5 g/L of photocatalyst, pH 4.0–10.0, 25 °C, O ₂ flow rate: 5 mL min ⁻¹ , 120 min	$E_{\rm g}$ values: 3.09 to 3.34 eV depending on it is uncalcined or calcined between 100 and 600 °C. Faster degradation of 47 % with uncalcined photocatalyst at pH 4.0 with $k_1 = 0.01201 \text{ min}^{-1}$	[166]
Poly(3,4- ethylenedioxythiophene) or PEDOT	Stirred beaker under eight external 15 W UV/visible lights	Suspensions in pure water and secondary WWTP effluent with 1 mg/ L drug, 0.5 g/L of photocatalyst, pH 5.6. 60 min	Degradation: 100 % in pure water > 44 % in secondary WWTP effluent. Oxidants detected with scavengers	[168]
Ti-Zr/MOF ^c (NH ₂ -MIL-125)	Stirred beaker externally illuminated with a 600 W m ⁻² Xe lamp (cutoff filters for $\lambda \leq$ 290 nm)	150 mL of suspensions in pure water with 5 mg/L drug, 0.125–1.0 g/L of photocatalyst, pH 3.0–11.0, 20 °C, 180 min	<i>E</i> _g -values: 2.74 eV for Ti/MOF > 2.70 eV for Ti-15 % molar Zr/MOF. Overall degradation for 0.250 mg/L of these photocatalysts at pH 6.9: 180 min $(k_1 = 0.0073 \text{ min}^{-1}) > 120 \text{ min} (k_1 = 0.0121 \text{ min}^{-1})$. Detection of oxidizing agents with scavengers. Decay of 13 % performance after 3 consecutive steps	[173]
NH ₂ -MIL-125 (Ti)/Pd, Pt, or Ag	Stirred beaker under external irradiation of a 600 W m ⁻² Xe lamp (cutoff filter for $\lambda < 290$ nm)	150 mL of suspensions in the pure water of 5 mg/L drug, 0.25 g/L of each photocatalyst, 180 min	E_{g} -values: 2.48 eV for Pt/NH ₂ -MIL-125 < 2.50 eV for Pd/ NH ₂ -MIL-125 < 2.56 eV for NH ₂ -MIL-125 < 2.70 eV for Ag/ NH ₂ -MIL-125. Decreasing degradation rate for metal-coated photocatalysts in the same order, although attaining > 97 % removal. Oxidants detected with scavengers for Pt/NH ₂ -MIL- 125. Identification of 3 dimers, 1 aminoaliphatic derivative, and 4 final carboxylic acids by LC/ESI-MS and IC	[174]
Ce-Fe/MOF (with 2-amino- terephthalic acid)	Stirred Erlenmeyer flask exposed to direct sunlight	100 mL of suspensions in the pure water of 10 mg/L drug, 0.1 g/L of photocatalyst, pH 3.0–10.0, 270 min	$E_{\rm g}$ -values: 2.54 eV for Ce/MOF $>$ 1.45 eV for Fe/MOF $>$ 1.18 eV for Ce-Fe/MOF. Degradation and $k_1~({\rm min}^{-1})$ for these photocatalysts at pH 5.6: 60 % and 0.0038 $<$ 71 % and 0.0057 $<$ 96 % and 0.0138. Using TiO ₂ : 35 % and 0.0018	[176]
Chitosan/COF ^d thin film	Stirred beaker with an external 300 W Xe light (cutoff filter for $\lambda \leq$ 420 nm)	60 mL of pure water with 3 mg/L drug, 5–20 mg of films, pH 5.0–11.0, 25 $^\circ\text{C},$ 180 min	100 % degradation with $k_1 = 0.029 \text{ min}^{-1}$ for 20 mg of photocatalyst (pH 7.0). Little effect of common anions except CO_3^{2-} and using 3 natural waters. Detection of oxidants by EPR with DMPO. Excellent reusability after 5 successive cycles	[179]

^a MMO: Metal mixed oxides. ^b CLDH: Calcined layered double hydroxides. ^c MOF: Metal-organic framework. ^d COF: Covalent organic framework.



Fig. 2. Mechanism for the photocatalysis (PC)/photoelectrocatalysis (PEC) treatment of paracetamol (PCT) under UV light. Adapted from [17]



Fig. 3. Crystalline phases of TiO₂. Adapted from [25]

by-products formed from PCT oxidation [14,15,30,37]. Based on these compounds, Fig. 7 proposes a reaction sequence for its mineralization with •OH as the pre-eminent oxidizing agent. The initial hydroxylation of paracetamol can take place either on the C(2) or C(3) of the benzenic ring to yield: (i) the corresponding dihydroxylated derivatives, (ii) cause the loss of acetamide to form hydroquinone, or (iii) release the aceto group to give 4-aminophenol. Further hydroxylation/oxidation of these 4 primary by-products led to the generation of trihydroxybenzene, pbenzoquinone, and p-nitro-phenol. The cleavage of the benzene moiety of all these derivatives originates from a mixture of short-linear aliphatic carboxylic acids like succinic, maleic, malonic, hydroxyacetic, oxalic, and formic. The two latter acids are ultimate compounds directly transformed into CO_2 [1]. In parallel, acetamide is oxidized to oxamic acid that is mineralized to CO_2 , NH⁺₄, and NO⁻₃.

Commercial anatase NPs [26,27] and hollow core–shell mesoporous anatase microspheres prepared from TiOSO₄ [39] have also been applied to PCT abatement. Trousil et al. [27] studied the behavior of a suspension of 20 mg/L drug in pure water with 0.5 g/L anatase at pH 7.2 and 20 °C under recirculation in a system like Fig. 4b with a lowpressure Hg vapor lamp emitting from 200 to 700 nm at a liquid flow rate (LFR) of 2.5 L min⁻¹. While a 13 % degradation in 60 min with $k_1 = 0.0031 \text{ min}^{-1}$ was found by direct photolysis due to the photodecomposition with the UVC region adsorbed, the PC process gave 51 % drug decay with $k_1 = 0.0135 \text{ min}^{-1}$, along with 46 % COD and 30 % TOC abatements. It is interesting to remark the PC assays made by adding 0.5 g/L H_2O_2 that yielded a larger degradation of 60 % with $k_1 = 0.0178 \text{ min}^{-1}$ (see Table 2). This enhancement can be related to the formation of more •OH from the homolytic photolysis of H₂O₂ by reaction (10) or its reduction by reaction (11). Lin et al. [39] prepared hollow mesoporous anatase microsphere materials, as confirmed by SEM and XRD, with large porosity that presented higher photoactivity than P 25. This was checked by degrading suspensions with 50 mg/L of PCT and 0.1 g/L of each photocatalyst in pure water at natural pH for 60 min using a stirred beaker exposed to a 500 W Hg lamp. Table 2 shows that up to 93 % drug removal was obtained with hollow anatase containing 8 % water, a value higher than 85 % determined for P 25. However, the hollow anatase lost about 30 % of photocatalytic performance in 10 successive runs, demonstrating that is not useful in practice because larger reusability is needed to ensure large-duration experiments.

An interesting work by Chen et al. [40] compared the photocatalytic behavior of commercial anatase, rutile, and P 25 (80 % anatase + 20 % rutile). Fig. 8a-c depicts the comparative abatement of the normalized PCT concentration with time for 200 mL of 1 mM PCT and 1 g/L of the above photocatalysts in pure water at natural pH with a stirred beaker under UVA or UVC irradiation and keeping the O₂ concentration of 7.1 mg/L. As expected, a slightly higher degradation can be observed for all photocatalysts by irradiating with UVC as compared with UVA due to the additional drug photodecomposition. Moreover, the degradation increased in the order: rutile < P 25 < anatase.

(see Table 2). The superiority of anatase can also be easily deduced from the corresponding k_1 -values collected in Fig. 8d, which were low because of the small photon flow provided by the lamp tested without reaching the saturation of the photocatalytic active sites and requiring long reaction times. This can be confirmed for anatase from Fig. 8e, where the rise of the photon flux from 0.2 to 3.3 Es m⁻² s⁻¹ increased near 3.5-fold the k_1 -value for each light. These findings indicate that the photon flux of the irradiating lamps should be optimized to just saturate the photocatalytic active sites and so, obtain the best degradation rate of PCT. Finally, up to 6 primary by-products were detected by HPLC.

Lozano-Morales et al. [41] synthesized TiO₂ nanotubes (NTs) from a



Fig. 4. Schemes of photoreactors used for PCT removal by PC. (a) Stirred tank reactor with inner UV lamp and air/O_2 injection (adapted from [26]). (b) Flow photoreactor with inner UV lamp (adapted from [27]). Solar pilot-plant photoreactor with (c) a compound parabolic collector (CPC) or (d) a fixed bed TiO₂ under recirculation of the wastewater (adapted from [28]).

hydrothermal method with P 25 as a precursor to treating 250 mL of 20 mg/L PCT with 0.4 g/L of such photocatalyst in pure water at 25 °C using a stirred cylindrical photoreactor with an inner 25 W cm⁻² UVC lamp. The assays were made in the pH range 2.5–10.5 and the faster drug removal was achieved at pH 6.5 with 99 % degradation in 180 min and $k_1 = 0.039 \text{ min}^{-1}$ (see Table 2), i.e., at the pH_{zpc} of the photocatalyst was achieved. No study about the reusability of the TiO₂ NTs was made.

3.2.1.2. Immobilized TiO2. The PCT removal from waters has been investigated with several immobilized P 25 [16,42-49] and anatase [25,28,50-52] nanomaterials. Nevertheless, the photocatalytic power reported for these materials is usually low. Cuervo-Lumbaque et al. [16] deposited P 25 onto a ceramic γ -Al₂O₃ tubular ultrafiltration membrane to treat 1 L of simulated or secondary WWTP in a continuous tube-intube photoreactor illuminated with four external 6 W UVA or UVC lights. Each wastewater at pH 5.0-6.0 contained PCT mixed with the other 3 drugs at 0.2 mg/L each and recirculated at an LFR = 40 L h⁻¹. Very low PCT degradations of 10 % and 13 % were obtained in the simulated wastewater (without organic pollutants) for UVA and UVC lights, respectively (see Table 2). To improve the UVC process, 20 mg/L of H₂O₂ was added to the simulated WWTP to profit its photodecomposition into the strong oxidant •OH from reaction (10), but the drug removal only grew up to 27 %. When the run was performed with the secondary WWTP, a lower PCT degradation of 9 % was found due to the loss of oxidants by their attack on its organic components. These treatments are not useful in practice.

Suspended and immobilized P 25 treatments have been reported in several papers demonstrating the superiority of the former procedure under UV light as compared to the latter one with sunlight. The study of Borges et al. [44] over the degradation of 800 mL of suspensions of 50 mg/LPCT with 0.05–1.0 g/LP 25 in pure water at pH 3.2–10.1 by PC using a system like Fig. 4a with a 150 W UV light revealed that the bestoperating conditions were found at pH 8.0 with total degradation in 120 min (see Table 2). The same solution at pH 8.0 but with a smaller volume of 250 mL was further treated with a packed bed of P 25 onto glass spheres in a system like Fig. 4b illuminated with a 400 W solar sodium vapor lamp at LFR = 0.8 mL s^{-1} . Due to the much lower intensity of this lamp in the UV region in front of the 150 W UVA light above applied, the duration of the degradation was enlarged to 23 h and only reached 45 %. Jallouli et al. [46] using recirculation systems like Fig. 4b with 11 W UVC light for suspended P 25 or with a solar tubular photoreactor for P 25 immobilized onto cellulosic fiber found that 0.0264 mM of PCT were degraded more rapidly in the former case (91 % vs 79 %) at pH 9.0 (see Table 2). However, these results were not completely comparable since different solution volumes (1.5 vs 6.7 L) were treated. Four by-products were detected by HPLC.

An interesting work by Ramasundaram et al. [47] considered the deposition of P 25 onto stainless steel (SS) mesh prepared by electrospraying with several volumes of P 25 dispersion (x = 30, 60, and 90 mL), followed by heating to favor its adhesion. The as-materials thus obtained were so-called P 25/SS-x. Fig. 9a presents the XRD spectra for the pristine-SS, control, P 25/SS-30, P 25/SS-60, P 25/SS-90, and TiO₂ P 25. The spectra related to the P 25/SS-x materials showed the



Fig. 5. (a) PCT concentration and (b) normalized TOC content vs reaction time for the treatment of a 150 mL suspension of 4 mM drug and 0.4 g/L TiO₂ P 25 at pH 5.5, O₂ concentration of 36.3 mg/L, and 26 °C by PC using a photoreactor like of Fig. 4a under an inner 8 W UVA light or 15 W UVC lamp. Change of the pseudo-first-order rate constant (k_1) for PCT decay with (c) TiO₂ P 25 content for 4 mM PCT, pH 5.5, and O₂ concentration of 36.3 mg/L, (d) PCT concentration for 0.4 g/L TiO₂ P 25 pH 5.5, and O₂ concentration of 36.3 mg/L, (e) O₂ concentration for 4 mM drug, 0.4 g/L TiO₂ P 25, and pH 5.5, and (f) pH for 4 mM drug, 0.4 g/L TiO₂ P 25, and O₂ concentration of 36.3 mg/L. Adapted from [23]

characteristic crystal planes of γ -Fe of SS as stronger peaks, although those associated with P 25 (anatase (A) and rutile (R)) were more visible at higher volumes of PA dispersion, meaning its greater adsorption onto the substrate. The best P 25/SS-90 material was selected as a photocatalyst. These assays were carried out with a quartz photoreactor exposed to six 4 W UVA lights that contained.

50 mL of 10 μ M PCT in distilled water (DW) or secondary WWTP effluent at uncontrolled pH. The solutions were kept for 30 min under the dark to ensure that the drug was not adsorbed onto the photocatalyst surface during the next 80 min of irradiation. Fig. 9b highlights the scarce drug removal found when only UVA was irradiated according to its photostability in the light region. In contrast, the PC process led to 100 % degradation with $k_1 = 0.089 \text{ min}^{-1}$ in DW, which was reduced to 66 % in the secondary WWTP due to the oxidation of other organic contaminants (see Table 2). It is noteworthy the high deceleration of drug removal in DW up to 40 % by adding *t*-butanol as •OH scavenger, indicating that this radical was the main oxidant of the PC process.

Moreover, h_{VB}^{+} was disregarded as oxidizing species because no change in drug decay was observed in the presence of 10 mM oxalate as a scavenger.

Chekir et al. [28] reported better PCT destruction with a solar pilotplant containing fixed anatase beds than suspended anatase NPs with a CPC photoreactor. In both cases, the photocatalyst was commercial anatase of $320 \text{ m}^2 \text{ g}^{-1}$ of surface area and 6.04 nm of average size, which XRD spectrum with its characteristic peaks is shown in Fig. 10a. The systems schematized in Fig. 4c and d were used for the CPC and fixed bed assays to treat 1.1 L of 2.5–20 mg/L PCT in pure water at pH 3.0–11.0 respectively. For 10 mg/L drug, Fig. 10b and c disclose a quicker degradation always at pH 9.5, as also reported in [23] for P 25. However, quicker total drug removal was attained for the fixed bed (90 min) than with the CPC (300 min) because much more photocatalyst was used in the former case (8.8 vs 0.44 mg). Fig. 10d shows the k_1 values obtained for these runs with a maximal of 0.027 min⁻¹ for a fixed bed, whereas Fig. 10e highlights the progressive decay of k_1 when the



Fig. 6. Variation of normalized drug concentration with reaction time for the photocatalytic degradation of a 140 mL suspension of 20 mg/L PCT and 0.5 g/L TiO₂ P 25 at natural pH and 25 °C with a crystallizer photoreactor under external 10 mW UVA, UVB, or UVC light, or 3000 mW UVA (so-called UVAH) light.

Adapted from [32]

drug content was risen, as expected from the greater quantity of organic matter destroyed (see also Table 2). The treatment for 10 mg/L drug with the fixed bed was so effective that yielded 100 % mineralization at 360 min, whereas the CPC system only achieved a 77 % TOC reduction (see Fig. 10f). These excellent results allow inferring the need of optimizing the amount of immobilized photocatalyst in a system to lead to a very effective PCT removal from waters.

3.2.1.3. Hybrid processes. To enhance the oxidation power of PC with

TiO₂, several hybrid processes have been proposed under simulated sunlight by combining this procedure with P 25 and ultrasounds (US) [53], peroxymonosulfate (PMS) [54], peroxysulfate (PS) [55], and biodegradation with a membrane bioreactor [56], or with anatase in the presence of Cr(VI) [57]. Preliminary results were only given for such processes that need deeper research to be considered attractive potential methods in practice. US is well-known to produce the cavitation phenomenon with bubbles formation in which 'OH is produced from the water molecules entrapped inside them. Jagannathan et al. [53] studied the coupling of PC with P 25 and US for the treatment of 250 mL of 0.09 mM PCT with 1 g/L photocatalyst in pure water at pH 2.7 and 25 $^\circ\text{C}$ using a sono-reactor illuminated with an external 450 W Xe light. Results of Table 2 show a very poor degradation with the US alone or the US with suspended P 25, which rose for the classical Xe/P 25 $(k_1 = 0.033 \text{ min}^{-1})$ process and even more strongly for the hybrid Xe/P 25/US ($k_1 = 0.044 \text{ min}^{-1}$) one. Aiming to accelerate the process, 0.05 mM Fe^{3+} was added to the solution to obtain more oxidant •OH from the photo-Fenton reaction (15) [17]:

 $Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + \bullet OH + H^+$ (15).

This reaction favored the PCT degradation using Xe/Fe³⁺ ($k_1 = 0.021 \text{ min}^{-1}$) and Xe/US/Fe³⁺ ($k_1 = 0.052 \text{ min}^{-1}$). Note that TOC was reduced by 90 % after 180 min of Xe/P 25/US and Xe/US/Fe³⁺.

PMS and PS produce the strong oxidant sulfate radical anion (SO₄•⁻) upon light activation. Jo et al. [54] confirmed the improvement of the degradation of 0.1 mM PCT in pure water with the system Xe/P 25/PMS using 0.5 g/L photocatalyst and 0.5 mM PMS at pH 5.0 in a stirred beaker photoreactor with air-conditioned and upon a 300 W Xe lamp. An 81 % of degradation at 240 min with $k_1 = 0.20$ h⁻¹ was found, along with excellent reproducibility after 4 cycles due to the inert surface of P 25 (see Table 2). They remarked on the latter positive issue as compared to another photocatalyst like Co₃O₄ that was oxidized by PMS. On the other hand, Sun et al. [57] proposed the simultaneous reduction of Cr



Fig. 7. Reaction sequence proposed for PCT mineralization by PC. Adapted from [14,15,30,37]



Fig. 8. Change of normalized PCT concentration with reaction time for the photocatalytic treatment of 200 mL suspensions of 1 mM drug and 1 g/L of (a) anatase, (b) rutile, or (c) TiO₂ P 25 photocatalyst at natural pH and O₂ concentration of 7.1 mg/L with a quartz beaker as photoreactor externally irradiated with UVA or UVC light. (d) Pseudo-first-order rate constants for PCT decay determined for the above trials. (e) Variation of the pseudo-first-order rate constants for PCT decay with incident photon flux for a 20 μ m drug suspension with 1 g/L anatase. Adapted from [40]

(VI) to Cr(III) and PCT oxidation using a Xe (visible)/anatase process. In this hybrid process, Cr(VI) was reduced by the photogenerated e_{CB}^- in the photocatalyst, thus decelerating the recombination of the $e_{CB}h_{YB}^+$ pair and favoring the drug oxidation with •OH formed from reaction (3) or (4). They described a 67 % PCT degradation with 60 % conversion of Cr (VI) into Cr(III) after 60 min of treatment of 100 mL of 50 mg/L drug, 0.5 g/L of anatase, and 10 mg/L Cr(VI) at pH 5.36 using a stirred beaker illuminated with a 2000 W m⁻²Xe lamp providing visible light with a cutoff at 420 nm (see Table 2). Unfortunately, the efficiency of the process dramatically decayed in consecutive cycles discarding its practical application.

3.2.2. TiO₂-based nanocomposites

A high number of researchers have investigated the role of many TiO_2 -based nanocomposites on the photocatalytic behavior of PCT

remediation. The articles searched to enhance the adsorption of the drug onto the photocatalyst and/or to diminish its E_g -value for better efficiency of the process and for using free and renewable sunlight as an energy source for more cost-effective treatment. Carbon materials, metals, organics, oxides, and other materials have been used to prepare such composites, as detailed in this subsection. Table 3 summarizes the relevant results reported in these works.

3.2.2.1. Carbon materials. Nanocomposites of P 25 NPs with activated carbon (AC) prepared by an impregnation method upon ultrasonication of both pristine components have been checked by Basha et al. [24]. Fig. 11a depicts the change of the FT-IR spectrum of a 10 % P25/AC nanocomposite when it adsorbed PCT and then when the drug was strongly removed after the PC process. The assay was carried out with 1 L of a suspended solution of 25 mg/L drug and 1.5 mg/L photocatalyst in



Fig. 9. (a) XRD patterns for pristine stainless steel (SS) support, control support before P 25 electrospraying and heating, synthesized TiO₂/SS-x materials at several electrospraying TiO₂ dispersion volumes (x = 30, 60, and 90 mL), and pristine TiO₂ P 25. Main crystal planes are given in each diffractogram. (b) Evolution of normalized PCT content for the degradation of 50 mL of 10 μ M drug and TiO₂/SS-90 photocatalyst (2.120 mg of TiO₂ per 2.5–5.0 cm² SS) in distilled water (DW), DW in the presence of 10 mM *t*-butanol (t.BuOH) as •OH scavenger, and secondary WWTP effluent. A quartz photoreactor externally irradiated with six 4 W UVA lights was used, and pH was not controlled. The trials of drug adsorption with the immobilized photocatalyst and only UVA irradiation (without the photocatalyst) are also reported. Adapted from [47]

pure water at pH 9.0 with a photoreactor like Fig. 4a with an inner 125 W medium pressure Hg lamp providing $\lambda > 285$ nm and lasting 240 min. Although it was confirmed that the drug adsorption onto the photocatalyst followed a Langmuir-Hinshelwood isotherm, Fig. 11b highlights that it only caused a small reduction of a 9 %.

of its content in solution. Despite this apparent low adsorption, Fig. 11b makes evidence that the PCT concentration was reduced by

50 % and more rapidly by 75 % upon PC with P 25 and with 10 % P25/ AC, respectively (see Table 3). This enhancement in oxidation power for the nanocomposite was ascribed to its greater drug adsorption promoted by the AC component that favors the attack of photogenerated oxidants on the P 25 surface. Fig. 11c-e makes evidence that the above solution (25 mg/L PCT, 10 % P 25/AC, and pH 9.0) gave the best performance, confirming the oxidation by P 25 near the pK_a of the drug. The composite presented excellent reproducibility after 4 successive runs and hence, could be useful in practice.

Other works have considered nanocomposites like TiO₂/AC [58] and Ni/P 25-W/graphene [59] with mixtures of anatase and rutile. Tao et al. [60] synthesized TiO₂ nanotubes (NTs) from a hydrothermal method with commercial titania to prepare composites with various percentages of graphene. They determined from UV–vis diffuse reflectance spectroscopy a decrease of E_g from 3.18 eV for TiO₂ NTs to 2.98 eV for TiO₂ NTs/graphene, increasing its photocatalytic efficiency under UVA light along with greater drug adsorption. Suspensions in the pure water of 500 mL of 5 mg/L PCT and 0.1 g/L of the nanocomposite in a stirred beaker illuminated with 14 W UVA light were more rapidly degraded at pH 9.0, giving rise to 96 % drug removal in 180 min with $k_1 = 0.0248 \text{ min}^{-1}$ (see Table 3). The nanocomposite was stable and yielded good reproducibility after 5 consecutive steps. GC–MS analysis of treated suspensions allowed identifying 3 aromatic derivatives.

Most of the nanocomposites with carbon materials were prepared by hydrothermal or sol–gel methods with a titanium precursor to obtaining pure anatase phases. Articles reporting the synthesis and use of anatase combined with carbon [61,62], carbon microspheres [63], AC [64,65], carbon xerogel [66], graphite [67], reduced graphene oxide (rGO) [68], SiO₂ and multi-walled carbon nanotubes (MWCNTs) [69,70], doping with oxygen vacancies and P and CNTs [71], and doping with Fe, P, Zn or K and AC [72,73] have been published. The hybrid application of nanocomposites with graphene and PS has been described by Yang et al. [74].

De Luna et al. [61] prepared anatase/carbon nanocomposites by a sol-gel method with titanium tetrabutoxide and ethanol followed by optimized calcination at 300 °C. The tests were made in a stirred beaker exposed to visible light upon five 1 W LED lamps for 540 min containing 500 mL of suspensions of 0.1 mM of PCT and 1.0 g/L of nanocomposite at pH 6.9. While only 54 % of degradation was achieved using P 25 as a photocatalyst, the nanocomposite was much more efficient and led to 94 % drug abatement but with a small $k_1 = 0.005 \text{ min}^{-1}$. Better performance has been described by Vaiano et al. [67] with nanocomposites obtained by mixing anatase formed from titanium tetraisopropoxide and 5-50 % of graphite. Fig. 12a shows that all anatase/x% graphite nanocomposites upgraded the PCT degradation with anatase that reached 97 % after 180 min of PC of 50 mL suspensions with 25 mg/L drug and 3 g/L of photocatalyst in pure water filling a stirred beaker illuminated with two inner 8 W UVA lights. Optimum conditions were found for anatase/10 % graphite where overall drug decay took place at 120 min and TOC was reduced by 86 % at 180 min (see Fig. 12b and Table 3). Fig. 12c and d confirm that 3 g/L of anatase/10 % graphite led to the best degradation and TOC removal as compared to other nanocomposite loads. The similar E_{g} -value found for this nanocomposite and pure anatase suggests again the important role of drug adsorption in the former case to enhance its destruction under the PC process. Moreover, the photocatalyst showed good stability yielding excellent reproducibility after 4 consecutive cycles. In contrast, a loss of 10 % of reproducibility from 100 % degradation was found after 5 consecutive cycles under the optimum conditions of 2.0 g/L of anatase/3% rGO suspended in 25 mL of 50 mg/L drug in pure water at pH 9.0 in a stirred beaker with eighteen 3 W UVA-LED lights [68]. The continuous decrease of E_g from 3.23 eV for anatase with raising the percent of rGO is given in Table 3 and the photogeneration of •OH as the main oxidant was confirmed with scavengers. The authors proposed that rGO acted as an electron-sink so that the photogenerated e_{CB}^- in anatase was transferred to the rGO to produce •OH, whereas the drug adsorption was considered negligible.



Fig. 10. (a) XRD pattern of pristine anatase NPs (surface area: $320 \text{ m}^2 \text{ g}^{-1}$, average size: 6.04 nm) showing main peaks (crystal planes) at 25° (101), 37° (112), 47° (200), 55° (211) and 63° (204). (b) Normalized PCT concentration vs reaction time for the solar photocatalytic process of 10 mg/L drug in pure water at pH 9.5 and 20–30 °C using (b) the CPC photoreactor of Fig. 4c with 0.4 g/L anatase TiO₂ at a liquid flow rate (LFR) = 26 mL s^{-1} and (c) the fixed bed photoreactor of Fig. 4d with 1.1 mg of anatase TiO₂ per m² at LFR = 39.3 mL s^{-1} . (d) Pseudo-first-order rate constant for PCT decay determined for the above experiments. (e) Pseudo-first-order rate constant for PCT decay obtained for 2.5–20 mg/L drug at pH free or 9.5 for the CPC or fixed bed photoreactor, respectively. (f) Evolution of the percent of TOC removal for 10 mg/L drug (6.5 mg/L initial TOC) at pH 9.5 in both systems. Adapted from [28]

Stable nanocomposites with three components, namely anatase, SiO₂, and pristine MWCNTs, were synthesized by Czech and Tyszczuk-Rotko [69]. SiO₂ was deposited as an intermediate layer to ensure strong adhesion of the carbon material. The best material was obtained for anatase/SiO₂/1.72 %wt MWCNTs with $E_g = 2.94$ eV, being able to operate with visible light in a photoreactor like Fig. 4a with a high-pressure Hg lamp emitting at 500–550 nm. PC was applied to 700 mL of suspensions in pure water with 10 mg/L drug at nearly neutral pH attaining 81 % degradation in 60 min with $k_1 = 0.013 \text{ min}^{-1}$ (see Table 3), The use of scavengers revealed that the main oxidant was h_{VB}^+ , with less relevant action of •OH and O₂•⁻. It was proposed that the visible light was absorbed by the electrons of the VB of MWCNTs promoting the formation of e_{CB}/h_{VB}^+ pairs that were further separately transferred to the CB and VB of anatase where the photogenerated

oxidants acted over PCT. A nanocomposite with oxygen vacancies and P co-doped anatase-coated CNTs with $E_g = 2.98$ eV was prepared by Feng et al. [71] for the PC process of suspensions of 50 mL of 5 mg/L drug and 0.5 g/L in a stirred beaker with a 300 W Xe lamp with a cutoff filter to provide visible light at $\lambda > 400$ nm. While only 7 % of degradation was found for pure anatase, the nanocomposite gave 95 % drug removal with $k_1 = 0.025 \text{ min}^{-1}$ and 58 % mineralization in 120 min, although the reproducibility decayed an 8 % after 4 consecutive cycles (see Table 3). Three aromatic by-products and two final carboxylic acids were identified by LC/MS. •OH was detected as the main oxidizing species with scavengers. The proposed photocatalytic mechanism involved the combination of drug adsorption with the generation of donor states from the oxygen vacancies and P below the CB of anatase to such donor states,



Fig. 11. (a) Fourier-transform infrared (FT-IR) spectra obtained for as-synthesized 10 % P 25/activated carbon (AC) photocatalyst and after adsorption and PC of PCT in 1 L of a suspended solution in pure water with 25 mg/L drug and 1.5 mg/L photocatalyst at pH 9.0 using a photoreactor like of Fig. 4a equipped with an inner 125 W medium pressure Hg lamp (cut-off of 285 nm). (b) Normalized PCT concentration vs reaction time for different processes of the above suspension. Effect of: (c) the percent of P 25 in 0.15 mg/L photocatalyst at pH 9.0, (d) pH with 0.15 mg/L of 10 % P 25/AC, and (e) the 10 % P 25/AC content in the suspension at pH 9.0. Adapted from [24]

which were subsequently transferred to the CB of anatase to originate the ROS. Other interesting work dealing with anatase/Fe-AC, anatase/ Zn-AC, anatase/K-AC, and anatase/P-AC nanocomposites has been published by Peñas-Garzón et al. [72]. The E_g -value of these materials varied between 3.28 and 3.50 eV (see Table 3) and their photocatalytic behavior was checked with a stirred beaker upon simulated sunlight mimicked by a Xe lamp containing 150 mL of 5 mg/L PCT in suspensions with 250 mg/L of anatase in each material. The best results were found for anatase/Fe-AC leading to total degradation in 120 min with 58 % TOC reduction in 360 min, with a loss of 10 % of reproducibility after 4 successive cycles. The PC process was related to the combination of adsorption and oxidation by photogenerated ROS. 3.2.2.2. *Metals.* Several metals like Bi [75], Ag [76–78], Au [77], Pt [77,79], Fe [80], Sb [81], Sn [82], Ta [83], and Pd [84] have been used to improve the performance of TiO₂ in PC by decelerating the recombination of the photogenerated charges with generation of more oxidizing agents. Photocatalytic characteristics of TiO₂|Pd nanocomposites are also reported in [85]. Aguilar et al. [76] photodeposited given amounts of Ag from an Ag⁺ solution onto P 25 with further calcination at 500 °C to form a TiO₂/Ag nanocomposite. The SEM micrograph of Fig. 13a shows a homogeneous size of Ag nanoparticles over the P 25. Fig. 13b presents the UV–vis diffuse reflectance spectrogram of several TiO₂/Ag nanocomposite compared to that of P 25. For all these materials, an $E_g = 2.9$ eV was then obtained from the



Fig. 12. (a) Variation of normalized PCT concentration with time and (b) percentage of TOC removal at 180 min for the treatment of 50 mL of a suspension in pure water with 25 mg/L drug and 3 g/L of different photocatalysts containing anatase and/or various graphite contents by PC using a stirred beaker as photoreactor illuminated with two inner 8 W UVA lights.(c) Evolution of normalized drug content and (d) percent of TOC removal at 180 min for the above suspension with different anatase/10 % graphite concentrations. Adapted from [67]

corresponding Tauc plots, a value lower than 3.20 eV found for P 25. This decay of E_{σ} in the composite was explained by the formation of a Schottky heterojunction in which the photoexcited e_{CB}^- originated in P 25 upon irradiation was moved to the Ag NPs surface where they react with O2 to form ROS. This heterojunction aligned the Fermi levels of both materials, minimize the recombination of charges formed due to the surface plasmonic resonance effect and increased the photocatalytic activity. This was tested by suspending 1 g L⁻¹ of a P 25/5% Ag nanocomposite in 250 mL of pure water with 20-100 µg/L drug upon bubbling an O₂ flow rate of 100 mL min⁻¹ using a stirred beaker illuminated with UVA and visible light. Fig. 13c confirms the superiority of UVA in front of visible light, and in the former case, with a drug decay between 92 % and 98 % in 300 min within the concentration range (see also Table 3). Nevertheless, Fig. 13d shows a gradual decrease of k_1 from 0.035 to 0.016 \min^{-1} with increasing the drug content from 20 to 100 µg/L, as expected from the gradual attack on the more organic matter of a similar quantity of photogenerated oxidants.

Gandelman et al. [81] synthesized a TiO₂ (with anatase + rutile)/Sb nanocomposite by mixing titanium tetraisopropoxide as a precursor and calculated amounts of an acid antimony solution followed by calcination at 350 °C. The PC process was studied with glass vials exposed to UVA light-.

filled with 7.0 mL of suspensions of 4.6 mg/L PCT and 5 mg/L of P 25 and P 25 with 0.05–2.0 % Sb lasting 120 min. Table 3 shows that up to 0.2 % of Sb doping upgraded the photoactivity of undoped TiO₂, with maximum degradation of 71–72 % for 0.05–0.1 % Sb. The loss of photocatalytic activity for the higher Sb doping of 2 % was ascribed to the increase of the specific surface area with the adsorption of more PCT that inhibits part of the active sites of Sb. Rimoldi et al. [83] synthesized pure

anatase + brookite, along with doped anatase + brookite/Ta and anatase nanocomposites, by several sol-gel methods with titanium tetraisopropoxide followed by impregnation with TaCl₅ and calcination at 400 °C. The treatment of a suspension of 35 mg/L PCT and 0.5 g/L of each photocatalyst with an O_2 flow rate of 9 L h^{-1} for 120 min in a stirred beaker with a UVA light showed a worse performance for the Tadoped TiO_2 nanocomposite than the pure anatase + brookite (see Table 3). These negative results were associated with the higher number of surface acid sites of the nanocomposites yielding lesser adsorption of organics to be oxidized. This means that Ta is inappropriate as a metal doping agent. The authors identified 1 aromatic derivative, acetamide, and 1 carboxylic acid by GC-MS. Recently, Sayegh et al. [84] described the efficient PC process of PCT with a TiO₂ nanoflowers (NFs)/boron nitride (BN)/Pd nanocomposites in a stirred beaker under a 400 W UVA or visible light. This nanocomposite was prepared by electrospinning of a titanium tetraisopropoxide solution and calcination at 400 °C, followed by atomic layer deposition of boron hydride and Pd. Its E_g -value of 3.09 eV was smaller than that of 3.2 eV for TiO₂ NFs (see Table 3). A 100 % vs 89 % degradation after 15 min of UVA irradiation of 250 mL of suspensions in the pure water of 1 mg/L drug and 0.5 g/L of such photocatalysts was found. It is also remarkable that the drug was completely abated using the TiO₂ NFs/BN/Pd nanocomposite under visible light, although this required a longer time of 240 min, with excellent reproducibility after 5 consecutive cycles.

A hybrid treatment with P 25/Pt nanocomposites and US has been tested by Ziylan-Yavaş and Ince [79] using a stirred sono-reactor under a UVC light. Nanocomposites were sonolytically synthesized with solutions of P 25 and 3 H₂PtCl₂ concentrations (1, 2, and 4 mM), and the PC treatments were carried out with 250 mL of suspensions of 40 μ M drug



Fig. 13. (a) Scanning electron microscopy (SEM) images of the surface of as-synthesized P 25/5% Ag photocatalysts from Ag electrodeposition. (b) UV–vis diffusereflectance spectrogram of different as-synthesized photocatalysts and P 25 used for the determination of the E_g -value of the Schottky heterojunction. (c) Percent of PCT degradation after 300 min of treatment of 250 mL of suspensions of different drug concentrations in pure water with 1 g/L P 25/5% Ag photocatalyst upon an O₂ flow rate of 100 mL min⁻¹ using a stirred beaker illuminated with external UVA or visible light. (d) Pseudo-first-order rate constant determined for the assays of UVA light.

Adapted from [76]

and 5 mg/L of each photocatalyst at pH 6.5 during 60 min. The best performance was obtained for P 25/4 mM Pt yielding overall degradation with $k_1 = 0.108 \text{ min}^{-1}$ and 48 % mineralization (see Table 3). The study with different scavengers revealed the main oxidative action of photogenerated •OH.

3.2.2.3. Organics. A reduced number of papers have reported the rise of PCT destruction by PC with some specific organic materials like Zn(II)phthalocyanine [86], β -cyclodextrine [87,88], and dissolved organic matter [89 coated onto TiO₂. This behavior has been explained by the light-harvesting of such organics upon UV/Vis irradiation that decelerates the recombination of the photogenerated e_{CB}^{-}/h_{VB}^{+} pairs in the TiO₂ NPs to upgrade the formation of oxidants. França et al. [86] treated suspensions of 850 mL with 10 mg/L of the drug and 100 mg/L of P 25/ Zn(II) phthalocyanine in pure water at pH 3.0–10.0 and 25 °C with a stirred annular reservoir upon an inner 400 W UV/Vis light ($\lambda = 295-710$ nm). After 120 min of reaction, the mineralization increased from 33 % with P 25 to 67 % with P 25/Zn(II) phthalocyanine at pH 3.0, but after the addition of 33 mg/L H₂O₂, it grew from 69 % to 79 % due to the formation of more •OH from the reduction of this species by reaction (11). In contrast, similar TOC removal between 67 % and 76 % were obtained in all the above conditions operating at pH 10.0 (see Table 3). For a TiO₂ NTs/ carboxymethyl-β-cyclodextrine nano-composite, a 97 % degradation with $k_1 = 0.0234$ min⁻¹ in front of 43 % with TiO₂ NTs was obtained after 150 min of treating suspensions of 20 mg/L of PCT and 1 g/L of each photocatalyst at pH 4.0 and 20 °C using a stirred beaker upon a 10 W UV light [88] (see Table 3). •OH and $O_2^{\bullet^-}$ were detected as main oxidants with scavengers.

3.2.2.4. Oxides. Nanocomposites of P25 with magnetite (Fe₃O₄) [90] and P 25 or TiO₂ with hematite (Fe₂O₃) [91–93] were prepared by simple Fe₃O₄ or Fe₂O₃ coating and a sol–gel method with titanium tetraisopropoxide and Fe₂O₃, respectively. An advantage of these magnetic materials is that they are easily separable by a magnetic field from treated solutions. Álvarez et al. [90] treated 400 mL of phosphate-buffered suspensions with 30 mg/L of PCT and 1.16 g/L of P 25/Fe₃O₄ or 1.34 g/L of P 25/SiO₂/Fe₃O₄ at pH 7.0 with an airflow rate = 50 L h⁻¹ at 25 °C using a photoreactor like of Fig. 4a with a UVC

light. A greater degradation of 97 % in 300 min with $k_1 = 0.0102 \text{ min}^{-1}$ was found for P 25/SiO₂/Fe₃O₄, like that P 25 alone with $k_1 = 0.0098 \text{ min}^{-1}$ and superior to the 90 % drug decay with $k_1 = 0.0071 \text{ min}^{-1}$ determined by P 25/Fe₃O₄ (see Table 3). These authors do not justify the photocatalytic mechanism of the nanomaterials and considered that the intermediate layer of the insulating SiO₂ gave stability and larger photoactivity since good reproducibility was obtained after 4 consecutive steps for P 25/SiO₂/Fe₃O₄. More recently, Abdel-Wahab et al. [91] studied the PC process of suspensions of 50 mL of 50 mg/L PCT and 0.1 g/L of x(15–50 %)% P 25/Fe₂O₃ with a stirred beaker illuminated with a 450 W medium-pressure Hg vapor lamp ($\lambda = 297-578$ nm). Fig. 14a depicts the magnetization curves for Fe₂O₃ and the prepared nanocomposites, showing the expected decrease in the magnetization saturation with increasing the percentage of P 25 due to



Fig. 14. (a) Magnetization curves of pure Fe_2O_3 and several P $25/Fe_2O_3$ core-shells. (b) Schematic representation of the Type-II heterojunction in the core-shell structure formed between TiO₂ and Fe₂O₃. (c) Percentage of drug removal after 90 min of PC and the corresponding pseudo-first-order rate constant for 50 mL of suspensions in the pure water of 50 mg/L PCT and 0.1 g/L of various photocatalysts in a stirred beaker illuminated with an external 450 W medium-pressure Hg vapor lamp (297–578 nm). (d) Percent of drug and mineralization at 60 min of the above assays under an O₂ flow rate of 100 mL min⁻¹. Adapted from [91]

the presence of less magnetic Fe₂O₃. Fig. 14b schematizes the Type-II heterojunction proposed for the core–shell structure formed between TiO₂ and Fe₂O₃. In this photocatalytic mechanism, both materials are photoexcited, and then, the photogenerated e_{CB}^- in Fe₂O₃ is transferred to the lower energetic CB of P 25 where the photo-reduction of O₂ takes place, while the h_{VB}^+ of P 25 is moved to the higher energetic VB of Fe₂O₃ where H₂O is photo-oxidized. The action of this mechanism can be observed in Fig. 14c for the percent of degradation and k_1 -values obtained for the different photocatalysts, which progressively increased with increasing the P 25 percentage in the nanocomposite up to P 25 alone (see Table 3). The same behavior was found when 100 mL min⁻¹ of O₂ were bubbled through the suspensions, giving rise to higher degradation and mineralization due to the acceleration of the photoreduction of this dissolved gas from reaction (6) in the CB of P 25 (see Fig. 14d). In this case,

98 % degradation and 66 % mineralization in 60 min for 50 % P 25 Fe_2O_3 were determined. Three aromatic derivatives, acetamide, and seven carboxylic acids were detected by GC–MS.

Mixtures of 4:1 and 2:1 M ratio of peroxotitanium:peroxoniobium hydrosols as precursors were prepared by Bi et al. [94] to form 4 anatase/Nb₂O₅ and 2 anatase/Nb₂O₅ nanocomposites. The E_{q} -value of these photocatalysts (2.05 and 1.79 eV) was lower than that of Nb₂O₅ (2.43 eV) and anatase with Ti³⁺ impurities (2.16 eV), all being photoexcited by visible light. The proposed photocatalytic mechanism of nanocomposites involved the pass of e_{CB}^- from the CB of Nb₂O₅ to the less energetic CB level of Ti³⁺ impurities to photoreduce O₂. The trials performed with 50 mL of suspensions in the pure water of 10 mg/L PCT and 30 mg of each photocatalyst with a stirred cuboid photoreactor upon a 40 W LED white (visible) lamp demonstrated that the higher degradation of 91 % was achieved after 120 min using the 2 anatase/Nb₂O₅ nanocomposite, with the participation of drug adsorption. In contrast, Khani et al. [95] described a small PCT degradation of 26 % in front of 12 % with the only US when a hybrid process combining this method and PC with TiO₂/MnO_x was applied for 180 min to 150 mL of suspensions of 25 mg/L of the drug and 0.1 g/L of photocatalyst in cooking water using a glass reactor equipped with a 20 W US and a 160 W UVA light (see Table 3). The TiO₂/MnO_x nanomaterials were synthesized by a sol-gel method assisted by US with calculated solutions of Mn(NO₃)₂ and titanium tetrabutoxide, and final calcination at 450 °C. Different proportions of both components presented low $E_{\rm g}$ values between 1.60 and 1.91 eV due to the rise of light absorption in the visible region between 390 nm and 730 nm of the MnO_v species. The low drug removal achieved by the hybrid process can then be related to the parallel oxidation of the organic pollutants of the cooking water used as the reaction medium.

3.2.2.5. Other materials. Nanocomposites with different TiO₂ phases and other inorganic or organic materials have been synthesized and checked for PCT destruction from waters. These materials include K₃[Fe $(CN)_6$ [96–99], KAl $(SO_4)_2$) or NaAl $((SO_4)_2)$ [100], K₂S₂O₈ [101], 13 X molecular sieves [102], halloysite and/or sepiolite [103], aluminosilicate [104], Bi₄O₅I₂ [105], MoS₂ [106], g-C₃N₄ [107], and doping with B or N [108]. Lin et al. [97] prepared anatase/K₃[Fe(CN)₆ nanocomposites by a sol-gel method with titanium tetrabutoxide as a precursor and K₃[Fe(CN)₆ as a dopant. No explanation of the visible photocatalytic mechanism of this material was made and its oxidation power over PCT was studied by response surface methodology using a stirred beaker with five external blue 1 W LED lights ($\lambda = 440-490$ nm) filled with 2 L of suspensions of 0.1-0.2 mM drug and 0.5-1.0 g/L of photocatalyst in pure water at pH 6.9-8.2 and 30 °C lasting 540 min. Optimized conditions were found for 0.1 mM drug, 1 g/L photocatalyst, and pH 6.9, yielding 91 % degradation (see Table 3). Similar behavior has been described by de Luna et al. [101] with an anatase/K₂S₂O₈ nanocomposite. They prepared different photocatalysts using titanium tetrabutoxide as the precursor of the anatase phase, followed by doping

with $K_2S_2O_8$ and calcination at 200–500 °C for 120–300 min. All these materials were photoexcited with visible light by treating 500 mL of suspensions of 0.1 mM drug and 1 g/L of anatase/0.50–1.25 %wt $K_2S_2O_8$ in pure water at pH 9.0 during 510 min with a stirred beaker with five external LED lights (up to $\lambda = 450$ nm). The best degradation was attained with anatase/0.50 %wt $K_2S_2O_8$ (see Fig. 15a) synthesized at 300 °C (see Fig. 15b) for 180 min (see Fig. 15c), with overall PCT abatement with $k_1 = 0.0084 \text{ min}^{-1}$. The photoactivity of this nanomaterial was ascribed to its low E_g -value of 1.94 eV due to the presence of the $K_2S_2O_8$ dopant. However, the well-known generation of the oxidant SO_4 ·⁻ from the photoactivation of this compound was not investigated, which could contribute to destroying PCT in conjunction with the photogenerated ROS.

Halloysite and sepiolite are two clay minerals that were selected by Papoulis et al. [103] to support anatase synthesized from a hydrothermal method with titanium tetraisopropoxide as a precursor. The nanocomposites thus prepared had an $E_{\rm g} \approx 3.0$ eV, slightly lower than that of anatase (3.20 eV), then being operative with UVA light. This was tested for 200 mL of suspensions of 30 mg/L PCT and 0.85 g/L of each photocatalyst in pure water for 120 min with a stirred annular photoreactor with an inner 400 W UVA light. The best photocatalyst was anatase/ sepiolite leading to.

93 % mineralization and 40 % mineralization, although it possessed less oxidation power than pure anatase due to its lower concentration in the aqueous matrix (see Table 3). Jayasree and Remya [104] prepared a nanocomposite of anatase supported onto aluminosilicate and studied the treatment of 100 mL of suspensions of PCT by response surface methodology using two stirred vessels with an external 125 W UV lamp ($\lambda = 280-365$ nm). Optimum conditions of 99 % degradation and 83 % TOC reduction were obtained for 2.74 mg/L drug, 2.71 g/L photocatalyst, and pH 9.5 (see Table 3). These authors also calculated that the energy consumption per unit PCT mass of the process was 0.224 kWh g⁻¹. However, the anatase/aluminosilicate photocatalyst did not yield good reproducibility losing 4.6 % degradation after 3 successive steps.

Kumar et al. [106] detailed the treatment of PCT with a TiO₂ nanorod (NRs)/MoS₂ nanocomposite. This photocatalyst was obtained by mixing solutions of MoS₂ (another *n*-type semiconductor) and TiO₂ NRs previously synthesized by a hydrothermal process with a commercial TiO₂ as the precursor. Stirred beakers with suspensions of 2 mM drug and 25 mg/L photocatalyst were tested in direct sunlight. The treatment was well-efficient and gave 39 % degradation in 25 min with $k_1 = 0.021 \text{ min}^{-1}$, much greater than the 5 % determined for pure TiO₂ NRs (see Table 3). The nanocomposite showed excellent reproducibility after 3 consecutive steps. A Type II charge transfer mechanism like Fig. 14b was proposed to explain the solar photoactivity of the heterojunction formed between these two materials, with the pass of the e_{CB} from MoS₂ to TiO₂ NRs and the inverse movement of the h_{VB} that diminished the E_{g} -value of the nanocomposite with respect its individual components, making it operative under sunlight irradiation.

A recent work by Yadav et al. [108] reported the synthesis of nanocomposites of TiO_2 doped with inorganic elements like B or N. The TiO_2 material was synthesized following a sol–gel route with titanium tetraisopropoxide and the precursors of the B or N dopant were boric acid and urea, respectively. The resulting nanocomposites were analyzed by FT-IR and Fig. 16a presents the recorded spectra for TiO_2 , TiO_2 /B, and TiO_2 /N showing characteristics surface bands of the dopants.

From UV–vis diffuse reflectance spectroscopy, $E_{\rm g}$ values of 2.96 and 2.51 eV were determined for TiO₂/4.64 %wt B and TiO₂/0.50 %wt N, respectively. Despite this, faster PCT degradation was obtained with the former catalyst, which was explained by a larger stabilization of Ti³⁺ impurities on the TiO₂ surface from B that enlarged the lifetime of the photogenerated $e_{\rm CB}^-/h_{\rm VB}^+$ pairs giving greater production of oxidants. This was determined when treating 150 mL of suspensions of 10–100 mg/L drug and 0.05–2.5 g L of each nanomaterial in pure water lasting 180 min with a photoreactor like Fig. 4a illuminated with a



Fig. 15. (a) Effect of the percentage in weight of $K_2S_2O_8$ in the composite over the variation of normalized PCT concentration with reaction time for the degradation of 500 mL of suspensions in the pure water of 0.1 mM drug and 1 g/L of anatase/K₂S₂O₈ photocatalysts obtained with a calcination temperature of 300 °C lasting 180 min by PC at pH 9.0 using a stirred beaker with five external LED lights (450 nm as maximal). (b) Influence of the calcination temperature for the assays with 1 g/L of anatase/0.50 %wt K₂S₂O₈ and calcination time of 180 min. (c) Effect of the calcination time for the trials with 1 g/L of anatase/0.50 %wt K₂S₂O₈ and calcination temperature of 300 °C. Adapted from [101]

125 W UVA light. Fig. 16b makes evidence that the best degradations were obtained for photocatalyst concentrations > 0.5 g/L, always higher for TiO₂/4.64 %wt B, whereas Fig. 16c discloses the slower degradation achieved at higher drug content with 1 g/L of this nanocomposite. It yielded a faster degradation of 95 % for the smaller drug content of 10 mg/L, a value much higher than 75 % found for TiO₂/0.50 %wt N



Fig. 16. (a) FT-IR spectra recorded for the as-synthesized TiO₂ (with anatase and rutile phases), TiO₂/4.64 %wt B, and TiO₂/0.50 %wt N. (b) Effect of the photocatalyst dose over the normalized PCT concentration decay determined after 180 min of treatment of 150 mL of suspensions in the pure water of 50 mg/L drug and different contents of TiO₂/4.64 %wt B or TiO₂/0.50 %wt N photocatalyst using a photoreactor like of Fig. 4a with an inner 125 W UVA light, (c) Effect of the drug content over its normalized decay after 180 min of irradiation with 1 g/L of each catalyst. Adapted from [108]

(see Table 3).

3.3. ZnO and ZnO-based photocatalysts

ZnO is another widely used nanomaterial as photocatalyst because it is a cheap material extensively found in nature and is innocuous over the health of animals and humans [17]. This subsection deals with the application of pure ZnO and ZnO-based nanocomposites to the treatment of PCT from water and wastewater, with the most relevant results listed in Table 4.

3.3.1. Pure ZnO

- Hexagonal wurtzite is the most thermodynamically stable structure of synthesized ZnO NPs at ambient conditions with an $E_{\rm g}$ = 3.3 eV [109]. A peculiarity of synthesized ZnO thin films is its transparency that upgrades the light penetration into and decreases the $E_{\rm g}$ -value enhancing the photogeneration of $e_{\rm CB}^-/h_{\rm VB}$ + pairs from reaction (1), even under sunlight irradiation [110]. Works related to PCT remediation by PC were carried out with ZnO NPs [109], thermally or mechanically activated

ZnO [111], immobilization of ZnO onto glass spheres [112], molecularly imprinted ZnO nanonuts [113], ZnO thin films [110], and packed bed of ZnO [114].

Kaneva et al. [111] activated commercial ZnO NPs in two ways: (i) thermally annealing between 100 and 500 °C and (ii) mechanically milling with balls at 200 rpm in ethanol, air, and methanol. Hexagonal wurtzite was always obtained, with nanoparticles between 20 and 40 nm in the former case and undefined aggregates in the second one. Their photocatalytic behavior was studied with 250 mL of suspensions of 50 mg/L PCT and 1 g L⁻¹ of each photocatalyst in pure water at 23 °C with a stirred beaker exposed to UVA light. The best degradation of 96 % in 240 min with $k_1 = 0.0136 \text{ min}^{-1}$ was determined for the thermally annealed nanomaterial at 100 °C (see Table 4). Lower k_1 -values were



Fig. 17. (a) SEM image, (b) XRD pattern, and (c) Tauc plot for the determination of E_g for pure ZnO deposited as thin films on glass (α is the absorption coefficient of the light). (d) Normalized PCT concentration vs the percentage of H₂O₂ (30 %) added to 5 mL of 400 μ M drug in pure water with a phosphate buffer of pH 11.5 using a vial coated with a ZnO thin film irradiated during 34 min with a UVA-LED light. (d) Time course of the normalized drug concentration for the assays with 0.35 % (v/v) H₂O₂ under the above conditions. Adapted from [110]

found for the aggregated materials due to their higher $E_{\rm g}$ -values. Molecularly imprinted ZnO nanonuts composed of wurtzite were prepared by Cantarella et al. [113] through a coprecipitation method involving Zn(II) acetate and PCT, with further removal of PCT by washing with water. The imprinted area of the synthesized nanonuts selectively interacted with dissolved PCT and ZnO surface with large effectiveness of its removing process. This was confirmed from the PC process of 2.0 mL of suspensions of 0.05 mM drug and 0.5 g of photocatalyst in pure water-filling quartz cuvettes upon.

A 4 mW UVA light. After 180 min of irradiation, 92 % degradation with $k_1 = 0.0132 \text{ min}^{-1}$ was determined for molecularly imprinted ZnO nanonuts much higher than only 19 % drug abatement with $k_1 = 0.00112 \text{ min}^{-1}$ found for ZnO NPs (see Table 4).

ZnO thin film coating vials were prepared by Hernández-Carabalí et al. [110] by ultrasonic spray pyrolysis of Zn(II) acetate. Fig. 17a depicts the compact and granular surface with particles close to 1 µm in diameter obtained in these films, whereas Fig. 17b presents their XRD pattern with the characteristic peaks of the crystal planes of wurtzite. Its E_{g} -value was 2.9 eV as determined from the corresponding Tauc plot shown in Fig. 17c. The vials were filled with 5 mL of 400 µM PCT in a phosphate buffer of pH 11.5 with the addition of 0-1.8 % (v/v) of H₂O₂ and irradiated with a UVA-LED light. Fig. 17d reveals the rapid decay of drug concentration with raising H₂O₂ content to 0.35 % (v/v) after 34 min of PC, whereupon it was unaffected by this compound indicating the saturation of the active sites of the ZnO surface for its decomposition to •OH via reaction (11). The exponential concentration decay for the assay with 0.35 % (v/v) H₂O₂ up to 69 % degradation in 68 min is presented in Fig. 17e, meaning that it followed a pseudo-first-order reaction mainly with •OH.

3.3.2. ZnO-based nanocomposites

Nanocomposites of ZnO with La [115.116], Fe and Cu [117], Nd and V [118], Ce [119], Ag [120–122], Ph-g-C₃N₄ [123], sepiolite [124.125], and polystyrene pellets [126] have been synthesized and checked for PCT destruction. Other studies have considered Ag₂S-ZnO/rGO [127], ZnO/Fe₃O₄-GO/zeolitic imidazolate framework (ZIF)-8 [128], and the hybrid process with Ag/ZnO/NiFe₂O₄ NRs and PMS [129]. Interesting photocatalytic characteristics of ZnO nanocomposites with MgO [130] and TiO₂ and CuO [131] have beed described.].

ZnO/La nanomaterials photoactive with visible light were prepared by Thi and Lee [116] by coprecipitation of Zn(NO₃)₂ and La(NO₃)₃ with final calcination at 400 °C. The $E_{\rm g}=3.15$ eV of ZnO decreased up to 3.02 eV with 0.5 % La and 2.97 eV with 1.0 % La, but increased up to 3.09 eV with 1.5 % La. The decay of E_g up to 1.0 % La was ascribed to the formation of a lower energetic CB level with respect to that of ZnO due to the La impurities where O_2 was reduced by the promoted e_{CB}^- from the VB of ZnO. In contrast, the presence of higher impurities with 1.5 % La overlapped their energetic CB levels with those of ZnO, thus increasing the E_{g} -value. The faster degradation of 93 % and TOC reduction of 80 % was obtained after 180 min of PC of 100 mL of suspensions in the pure water of 100 mg/L of PCT and 1 g/L of ZnO/1.0 %wt La (with the lowest E_{g}) with a stirred beaker upon compact 20 W fluorescent lamps (see Table 4). GC-MS analysis of treated solutions allowed the detection of 3 aromatic derivatives and 3 carboxylic acids. Alam et al. [118] synthesized ZnO co-doped with different mol percent of Nd and V from a sol--gel method with Zn(NO₃)₂, Nd(NO₃)₃, and NH₄VO₃ and final calcination at 500 °C. The best nanocomposite for visible light application was ZnO/4% Nd 1 % V with an $E_g = 2.92$ eV. This lower E_g -value as compared to that of ZnO (3.25 eV) was ascribed to the formation of two energetic levels between the CB and VB of ZnO by Nd (near the VB) and V (near the CB) impurities introduced in it. The photogenerated h_{VB}^+ from the VB of ZnO passed to the slightly higher energetic level of Nd to photo-oxidize the organics, while the e_{CB} accumulated in the slightly lower energetic level of V to photoreduce O₂. For 1 g/L of this co-doped photocatalyst, 70 % of PCT and 39 % of TOC removals were found after 150 min of treating 180 mL of a suspension of 10 mg/L drug at 25 °C

using a stirred beaker upon a 500 W halogen lamp (see Table 4). Treatments with scavengers demonstrate the main oxidation with photogenerated *OH.

The work of Ramasamy et al. [122] presented good degradation results for PCT with a ZnO/Ag photocatalyst synthesized by coprecipitation of Ag NPs from AgNO₃ and ZnO NPs previously obtained from ZnSO₄, with final calcination at 300 °C. Fig. 18a presents the SEMEDX spectrum of the as-synthesized ZnO/Ag nanomaterial, along with the atomic percent of each element. The Schottky heterojunction mechanism proposed for this nanomaterial to explain its lower $E_g = 3.02$ eV concerning 3.31 eV for ZnO is schematized in Fig. 18b. It is like the TiO₂/Ag photocatalyst explained by Aguilar et al. [74] in subsection 3.2.2.2. In the case of ZnO/Ag, the e_{CB} passed from the CB of ZnO to the lower energetic level of the Ag NPs surface where O₂ was photoreduced. Fig. 18c shows a much faster PCT removal during the application of 1 g/L of ZnO/Ag vs ZnO to suspensions of.

5 mg/L drug in a WWTP effluent at pH 8.5 by PC with a photoreactor like Fig. 4a under a 300 W halogen lamp. Fig. 18d makes evidence that such concentration decays obeyed pseudo-first-order kinetics. For ZnO/Ag, 91 % drug decay in 120 min with $k_1 = 0.020 \text{ min}^{-1}$ was found. However, the nanomaterial was not useful to be reusable in practice because the degradation process was largely reduced from 91 % to 75 % after 5 consecutive cycles of 120 min.

The preparation of several nanocomposites of ZnO deposited onto the clay mineral sepiolite, including insulating SiO₂ or magnetic Fe₃O₄ as intermediate layers, for sunlight irradiation has been described by Akkari et al. [124]. The tests were carried out with 250 mL of suspensions of 10 mg/L of the drug and 1 g L⁻¹ of each photocatalyst in pure water at 38 °C upon an airflow rate of 50 mL min⁻¹ during a long time of 600 min using a stirred beaker with simulated sunlight irradiation ($\lambda > 320$ nm) provided by a Xe lamp. The higher degradation of 85 % with a small $k_1 = 0.00312 \text{ min}^{-1}$ was determined for the ZnO/sepiolite nanomaterial (see Table 4). The lower photoactivity with ZnO/SiO₂/ sepiolite and ZnO/Fe₃O₄/sepiolite was explained by the partial blocking of the active sites of ZnO by the intermediate materials.

Khavar et al. [127] synthesized Ag₂S-ZnO/rGO nanomaterials sensible to visible light by combining Zn(II) acetate, 10 % mol of AgNO₃, and a solution with 0.2 g/L GO. The E_g -value of 1.0 eV for Ag₂S was much smaller than 3.25 eV for ZnO. Fig. 19a depicts that the visible light photoexcites the Ag₂S nanomaterial involving the photo-oxidation of PCT and the photoreduction of O₂ in its VB and CB levels, respectively. The photogenerated e_{CB}^- in the Ag₂S then passed to the CB of ZnO and subsequently to the rGO structure, promoting the O₂ photoreduction in both cases. The effectiveness of this photocatalyst can be easily deduced from Fig. 19b by the overall degradation and 68 % mineralization reached with 2 g/L of it after 60 min of the PC process of 50 mL of a suspension of 20 mg/L drug in pure water at pH 5.4 using a stirred beaker with a 350 W Xe light. In contrast, much smaller PCT removals of 34 % and 47 % were obtained for TiO₂ P 25 and ZnO/rGO, respectively (see also Table 4). Fig. 19c shows the effect of several scavengers on the performance.

of PCT decay under the above conditions upon the addition of 200 mg/L of *tert*-butanol (*t*-BuOH) (scavenger of •OH), persulfate (scavenger of $O_2^{\bullet-}$), p-benzoquinone (p-Bq) (scavenger of e_{CB}^{-}), and EDTA-2Na (scavenger of h_{VB}^+). The two latter photogenerated charges contributed more largely to the PCT removal. The main drawback of the photocatalyst was its scarce reusability, as found after 5 consecutive steps. In contrast, the addition of a metal–organic framework (MOF) like ZIF-8 to a nanocomposite of ZnO/Fe₃O₄-GO conferred great stability after 10 successive steps of 45 min, along with an excellent 99 % degradation and 99 % TOC removal of a suspension with 10 mg/L PCT after this time under simulated sunlight [128] (see Table 4).

3.4. WO₃-based photocatalysts

 WO_3 is another *n*-type semiconductor metal oxide as TiO_2 , with a



Fig. 18. (a) SEM-Energy dispersive X-ray (EDX) spectrum of the as-synthesized ZnO/Ag. (b) Schematic diagram of the photocatalytic destruction of PCT in the Schottky heterojunction formed by the composite between ZnO and Ag. (c) Evolution of the normalized PCT concentration and (d) its pseudo-first-order kinetic analysis for the treatment of a suspension in a WWTP effluent of 5 mg/L drug and 1 g/L of pure ZnO or ZnO/Ag as photocatalyst at pH 8.5 by PC with a photoreactor like of Fig. 4a with an inner 300 W halogen lamp providing visible light. Adapted from [122]

monoclinic crystalline structure between 17 and 330 °C, and an E_g near 2.7 eV. This E_g -value is much lower than that of TiO₂ and hence, it presents a better performance under visible light irradiation [17]. However, it is a hazardous, toxic, and irritant metal oxide that represents a clear disadvantage for practical application. Only a reduced number of papers have reported the use of this nanomaterial for PCT remediation, including pure WO₃ in the presence of Fe(III) and/or H₂O₂ [132], WO₃ nanoplates/AC [133], WO₃/Ag/AgCl [134], and WO₃/gC₃N₄ [135]. The photocatalytic behavior of coal fly ash decorated with WO₃/GO [136] has been described as well.

Lee et al. [132] studied the PC process of suspensions of 0.10 mM PCT with 0.5 g/L of pristine WO₃ and 5 mM of H₂O₂ in pure water at pH 7.0 with equilibrated air at 22 °C using a stirred beaker exposed to a 4 W fluorescent light ($\lambda = 350-650$ nm) and found a rapid degradation with

 $k_1 = 0.026 \text{ min}^{-1}$ (see Table 4). When they tested the addition of 0.25 mM Fe(III) to enhance the •OH production from the photo-Fenton reaction (15), the degradation rate only increased slightly and a $k_1 = 0.030 \text{ min}^{-1}$ was determined. This scarce enhancement is not surprising because the experimental conditions tested were not appropriate for the photo-Fenton reaction (15) since it is very efficient at pH 3.0, but its rate at pH 7.0 becomes practically insignificant [1]. Shahzad et al. [133] synthesized WO₃.

Nanoplates from a tungstate salt, which were subsequently doped with 1 % and 2 % of AC nanoparticles by a hydrothermal method. The lower $E_g = 2.26$ eV was found for the nanocomposite with 2 % AC (see Table 4) that yielded 97 % of PCT removal for 100 mL of suspensions in pure water of 1 mg/L of the drug and 1 g/L of photocatalyst during180 min with a stirred beaker under a 400 W metal halide lamp. A more



Fig. 19. (a) Scheme of the separation and transfer of the photogenerated charges to remove PCT by PC of the as-synthesized Ag₂S-ZnO/rGO composite. (b) Percent of degradation and mineralization determined after 60 min of the PC process of 50 mL of a suspension in the pure water of 20 mg/L drug with 2 g/L TiO₂ P 25, ZnO/rGO, or Ag₂S-ZnO/rGO as photocatalyst at pH 5.4 for 60 min using a stirred beaker externally irradiated with a 350 W Xe light. (d) Effect of different scavengers at 200 mg/L over the percent of the degradation achieved for the above suspension with Ag₂S-ZnO/rGO. Scavenger: *tert*-butanol (*t*-BuOH), persulfate, p-benzoquinone (p-Bq), and EDTA-2Na. Adapted from [127]

recent work by Meng et al. [135] considered a WO₃/g-C₃N₄ nanocomposite prepared from a hydrothermal procedure involving a tungstate salt and acetic acid. The $E_g = 2.78$ eV for g-C₃N₄ was quite like 2.70 eV for WO₃, but the WO₃/g-C₃N₄ nanomaterial was much more photoactive under visible light. Fig. 20a schematizes the Z-scheme heterojunction mechanism proposed for such nanomaterial, where the visible light photoexcites both, WO3 and g-C3N4, with the movement of the e_{CB}^- from the CB of the former to the VB of the latter. It is then expected that PCT is oxidized by photoreduced O₂^{•-} from O₂ at the CB of g- C_3N_4 and by photo-oxidized •OH from H_2O/OH^- at the VB of WO₃. The generation of these radicals was confirmed by EPR with DMPO. The PCT degradation was assessed for 50 mL of suspensions of 10 mg/L drug and 50 mg of each photocatalyst in pure water using a stirred beaker irradiated with a 300 W Xe lamp providing $\lambda >$ 400 nm. While 97 % degradation in 60 min was attained for g-C₃N₄, the WO₃/g-C₃N₄ yielded 98 % drug decay in only 30 min (see Table 4). Further study was focused on the detection of the oxidizing agents by using 1 mM of scavengers such as p-Bq, t-BuOH, and EDTA-Na. Fig. 20b reveals that O2. scavenged by p-Bq was the main oxidant for g-C₃N₄, whereas Fig. 20c depicts that •OH scavenged by t-BuOH prevailed for WO₃/g-C₃N₄. Note the

surprising enhancement of drug removal using EDTA-2Na in Fig. 20b, which was related to the rise of $O_2{}^{\bullet-}$ photogeneration when the scavenger blocked the h_{VB}^{+} . Unfortunately, the WO_3/g-C_3N_4 was rather unstable losing 15 % of drug removal after 5 consecutive cycles.

3.5. Bismuth-based photocatalysts

Several bismuth-based nanomaterials have been used as photocatalysts to treat PCT from water under UV or visible light. They include BiVO₄ [137], BiVO₄ NTs/RGO [138], BiVO₄/Gd³⁺ [139], BiVO₄/Pd [140], β -Bi₂O₃ [141], Bi₂O₃/rGO/Mo_nO_{3n-1} [142], Bi₃O₄Br [143], Bi₃O₄Br/AgI [144], BiOCl [145], and BiOCl/BiPO₄ [146].

Hu et al. [137] synthesized four morphological forms of BiVO₄, socalled cube, granular, plate, and spindle, from a hydrothermal procedure with stoichiometric amounts of a mixture of Bi(NO₃)₃ and NH₄VO₃ at different conditions of pH between 2.0 and 5.0, temperature between 180 and 200 °C, and reaction time between 2 and 48 h. Fig. 21a depicts the SEM image of such forms showing their different morphologies, Fig. 21b presents their UV–vis diffuse reflectance spectra, and Fig. 21c the corresponding Tauc plots from which similar E_g -values near 2.39 eV



Fig. 20. (a) Scheme of the band structure alignment and Z-scheme of the charge carrier transfer mechanism of a $WO_3/g-C_3N_4$ heterojunction. Change of normalized drug concentration with reaction time for the degradation of 50 mL of suspended solutions in pure water of 10 mg/L PCT and 50 mg of (b) g-C₃N₄ or (c) $WO_3/g-C_3N_4$ as photocatalysts by PC using a stirred beaker externally irradiated with a 300 W Xe lamp providing visible light with IR and 400 nm cut filters. In these assays, the effect of 1 mM scavengers like p-benzoquinone, *tert*-butanol, and EDTA-2Na was studied. Adapted from [135]

were determined for all the forms (see Table 4). Nevertheless, the four morphological forms showed very different photoactivity under visible light. This was revealed from the treatment of 50 mL suspensions of 5-25 mg/L of PCT and 20-120 mg/L of each photocatalyst in pure water at pH 2.0–11.0 using stirred tubes under a 300 W Xe lamp at $\lambda > 420$ nm. Fig. 21d shows that the profiles of normalized drug content vs time decreased in order. cube > granular > plate > spindle forms for 10 mg/L drug and 80 mg/L of each photocatalyst at pH 6.0. The cube form with a smaller nanoparticle size and larger surface area (see Fig. 21a) led to the maximum 95 % degradation and about 73-76 % TOC decay in 300 min with the higher $k_1 = 0.0135 \text{ min}^{-1}$ (see Table 4). Fig. 21e and f make evidence that the best degradation was achieved for 80 mg/L of the cube form and pH 6.0. Under these conditions, the photocatalyst was very stable and maintained the TOC removal during 5 consecutive cycles. BiVO₄ plates coated with Pd by impregnation with PdCl₂ were prepared by Wang and Bian [140]. The $E_g = 2.38$ eV for BiVO₄ decreased up to 2.29 eV for BiVO₄/Pd due to the Schottky heterojunction formed. The BiVO₄/Pd nanocomposite was then more photoactive giving overall PCT decay and 40 % TOC abatement in 60 min with $k_1 = 0.0308 \text{ min}^{-1}$ for 40 mL of suspensions in the pure water of 10 mg/L of drug and 1 g/L of photocatalyst at 15 °C filling a stirred beaker upon a 300 W Xe lamp at $\lambda > 420$ nm (see Table 4). The photogeneration of •OH and O₂•⁻ was confirmed with scavengers and EPR with DMPO.

Mao et al. [143] synthesized Bi₃O₄Br hierarchical hollow spheres

with (0,0,1)-facets nanosheets with $E_{\rm g} = 2.34$ eV, slightly lower than 2.39 eV for Bi₃O₄Br nanoplates. The enlarged surface area of the hollow spheres enhanced the photoactivity of this nanomaterial under visible light. When 50 mL of suspensions in pure water with 10 mg/L of PCT and 1 g/L of each photocatalyst were treated for 100 min in a stirred beaker exposed to a 1000 W Xe lamp at $\lambda > 420$ nm, 96 % drug decay with $k_1 = 0.342$ min⁻¹ was determined for the hollow spheres, whereas only a 64 % degradation with $k_1 = 0.098$ min⁻¹ was found for nanoplates (see Table 4). The oxidative action of O₂·-, HO₂·, and h⁺_{VB} was confirmed by means of scavengers and EPR with DMPO. However, the nanomaterial of hollow spheres was unstable losing 10 % of performance after 5 consecutive runs.

BiOCl nanomaterial synthesized by mixing Bi(NO₃)₃ and KCl is a *p*-type semiconductor with photoactivity in the UVA region due to its high $E_g = 3.34 \text{ eV}$ [145,146]. Wang et al. [145] degraded 100 mL of suspensions in the pure water of 0.05 mM PCT and 0.3 g/L BiOCl at pH 3.0–10.0 and 20 °C during 180 min using a stirred beaker with four 15 W fluorescent lamps ($\lambda = 300-500$ nm). The quicker almost overall degradation of 98 % was reached at pH 3.0, with 65 % drug abatement in the interval 5.8–10.0. Aiming to enhance its photocatalytic power, assays by adding 1 mM of H₂O₂ and/or S₂O₈²⁻ as oxidants at pH 5.8 were assessed. Table 4 indicates that only the BiOCl/H₂O₂/S₂O₈²⁻ system improved the degradation up to 85 %, a value higher than 66 % found for BiOCl alone. The addition of scavengers and EPR spectra with DMPO



Fig. 21. (a) SEM images of the four morphological as-synthesized BiVO₄ photocatalysts by a hydrothermal method at different pH, temperature, and reaction times. (b) UV–vis diffuse reflectance spectra of the four photocatalysts and (c) the corresponding Tauc plots to determine the corresponding E_g values. (d) Percent of PCT degradation with reaction time for the PC process of 50 mL of suspensions in the pure water of 10 mg/L drug and 80 mg/L of each photocatalyst at pH 6.0 using stirred tubes upon an external 300 W Xe lamp as a visible light source ($\lambda > 420$ nm). Influence of: (e) the cube photocatalyst dose at pH 6.0 and (b) the pH for 80 mg/L of cube photocatalyst over the percent of drug degradation of suspensions with 10 mg/L drug. Adapted from [137].

demonstrates the production of oxidants •OH, $O_2 \bullet^-$, and $SO_4 \bullet^-$. An interesting work of Guo et al. [146] synthesized a twinned BiPO₄ photocatalyst with two homojunctions, so-called nBIP with $E_g = 3.8$ eV and mBIP with $E_g = 4.2$ eV (see Fig. 22a), by a hydrothermal method with Bi (NO₃)₃ and NaH₂PO₄. The twinned BiPO₄ was then mixed with BiOCl using a solvothermal procedure to form a BiOCl/BiPO₄ photocatalyst. Fig. 22a highlights that after contact of both nanomaterials, the UV light promoted a Type-II mechanism in which the e_{CB}^- of the CB of BiOCl dropped in cascade to the CB levels of the twinned BiPO₄ to be accumulated in that of mBIP level and the inverse movement of h_{VB}^+ led to its accumulation in the VB of BiOCl. O₂ photoreduction and H₂O/OH⁻ photo-oxidation took place on such accumulation levels, respectively. This mechanism allowed a larger photoactivity of the BiOCl/BiPO₄

nanocomposite with respect to its separated components, as can be in Fig. 22b. Total degradation in only 15 min with a high $k_1 = 0.25 \text{ min}^{-1}$ was found for 50 mL of suspensions of 30 mg/L PCT and 25 mg photocatalyst in a stirred beaker with a UV light provided by a 300 W Xe lamp at $\lambda < 400 \text{ nm}$. O₂*⁻ was detected as the main oxidant from the addition of scavengers.

3.6. $g-C_3N_4$ -based photocatalysts

 $g\text{-}C_3N_4$ with $E_g=2.78$ eV is a versatile nanomaterial with excellent photocatalytic power under visible light. It has been checked for PCT treatments with TiO_2/g-C_3N_4 [107] and WO_3/g-C_3N_4 [135] nanocomposites involving Z-scheme heterojunction mechanisms, as stated



Fig. 22. (a) Sketch of the charge separations of p-type BiClO and n-type twinned BiPO4 semiconductors under UV light irradiation before contact and the p-n heterojunction photocatalytic mechanism of the BiClO/ BiPO₄ composite after contact. The n-type twinned BiPO₄ contained two crystalline phases, so-called nBIP and mBPI in homojunction. PCT is oxidized by the holes photogenerated in the VB of BiClO and by •OH formed from O2 reduction with the photogenerated electrons in the CB of mBIP. (b) Change of normalized PCT concentration with electrolysis time for 50 mL of suspensions in the pure water of 30 mg/L drug with 25 mg of as-synthesized HBIP (BiPO₄ uncalcined), n-type twinned BiPO4 (calcinated at 500 °C), p-type BiClO, and BiClO/BiPO4 (1:2 M ratio) photocatalysts using a stirred beaker externally illuminated with UV light provided by a 300 W Xe lamp (the cutoff for $\lambda > 400$ nm).

Adapted from [146]

above, and has also been recently used as photocatalyst with nanocomposites of g-C₃N₄/Au [147], g-C₃N₄/Ni-ZnS [148], g-C₃N₄/K and N defects [20], g-C₃N₄/K,Li [149], g-C₃N₄-K,I/CeO₂ [150], and g-C₃N₄/ CuSm_{0.06}Fe_{1.94}O₄ [151]. Hybrid processes with g-C₃N₄/Ag and ozonation [152] and with g-C₃N₄ and PS [153] have been described as well.

Jiménez-Salcedo et al. [147] synthesized g-C₃N₄ by direct heating of melamine at 520 °C, which was mixed with Au(C_6F_5) to obtain a g- $C_3N_4/$ Au nanocomposite. With the same Au precursor, another P 25/Au nanocomposite was prepared. Decreasing E_{g} -values were determined in the order: 3.23 eV for P 25 > 3.10 eV for P 25/Au > 2.75 eV for g- $C_3N_4 > 2.67$ eV for g-C₃N₄/Au. The drop of E_g in the nanocomposites with respect to pure nanomaterials was explained by the formation of Schottky heterojunctions with the transference of the corresponding photoexcited e_{CB} to the Au surface to form ROS from O₂ photoreduction via reaction (6). The first series of trials were made with a stirred beaker illuminated with a 15 W UVA lamp containing 70 mL of suspensions of 0.3 mg/L of PCT and 40.5 mg of each photocatalyst at natural pH 5.9 and 25 °C. Shorter times for overall degradation were found with decreasing the E_g -value, with a smaller time of 24 min for g-C₃N₄/Au (see Table 4). This nanomaterial was then more photoactive than P 25/Au under UVA light. Further assays were focused on the treatment of the same solution with g-C₃N₄/Au at pH 2.9–11.0 using a photoreactor like Fig. 4a upon four 10 W white LED lamps. Slower PCT degradation was determined under such visible light, requiring 47 min for its total disappearance at natural pH 5.9. A shorter time of 15 min was found at pH 2.9 that was prolonged up to 60 min at pH 11.0 (see Table 4). Good reproducibility of the degradation with g-C₃N₄/Au at pH 5.9 lasting 50 min under visible light was obtained after 8 consecutive cycles.

Danish and Muneer [148] mixed g-C₃N₄ with Ni-ZnS, with final calcination at 400 °C, to prepare a g-C₃N₄/10 % mol Ni-ZnS nanocomposite with $E_g = 2.61$ eV, lower than 2.70 eV of the undoped g-C₃N₄. The proposed Schottky heterojunction mechanism under visible light for this photocatalyst is schematized in Fig. 23a. The visible light only photogenerated e_{CB}^-/h_{VB}^+ pairs in the g-C₃N₄ and then, the e_{CB}^- moved first to the CB of ZnS and further, to the Ni surface. O₂ was photoreduced on the latter surface while PCT was photo-oxidized at the VB of g-C₃N₄. An 86 % PCT removal was determined after 100 min of PC of 220 mL of a suspension with 30 mg/L of drug and 0.22 g of g-C₃N₄/10 % mol Ni-ZnS in pure water under an O₂ flow rate of 1 L min⁻¹ at 25 °C filling a stirred beaker exposed to a 500 W tungsten halogen lamp with $\lambda > 400$ nm (see Table 4).

Nanocomposites of g-C₃N₄ doped with 1.0–7.9 % K containing N defects were synthesized by mixing melamine and KOH solutions followed by calcination at 500 °C [20]. The $E_{\rm g}$ -value of all the nanomaterials was of 2.65–2.66 eV, regardless of the percent of K dopant, but the g-C₃N₄/7.9 % K remarkably boosted the generation-transferseparation-transportation process of photogenerated charges under visible light yielding the faster photocatalytic PCT removal. So, total abatement with $k_1 = 0.0651 \text{ min}^{-1}$ was found for 50 mL of suspensions of 10 mg/L of drug and 1 g/L of such photocatalyst in pure water after 120 min of PC in a stirred beaker under a 300 W Xe lamp providing $\lambda > 400 \text{ nm}$ (see Table 4). Unfortunately, a low reproducibility was



Fig. 23. (a) Graphic for the photocatalytic destruction of PCT by the Schottky heterojunction of a $g-C_3N_4/Ni-ZnS$ composite (adapted from [143]). (b) Schematic illustration of the Type-II heterojunction mechanism for PCT removal over $g-C_3N_4$ -K,I/CeO₂ under visible light (adapted from [150]).

obtained after 7 successive steps. The EPR spectra with DMPO revealed the generation of oxidants ${}^{\circ}OH$, $O_{2}{}^{\bullet-}$, and ${}^{1}O_{2}$.

Paragas et al. [150] prepared a g-C₃N₄ co-doped with K and I nanomaterial with further deposition of 15 % CeO₂ by mixing., which had an $E_g = 2.36$ eV lower than 2.77 eV for g-C₃N₄-K,I and 2.98 eV for CeO₂. The proposed Type-II heterojunction mechanism for the g-C₃N₄-K, I/15 % CeO₂ photocatalyst is shown in Fig. 23b. Its photoactivity was assessed for 20 mL of suspensions in pure water with 10 mg/L of PCT and 0.5–2.0 g/L of g-C₃N₄-K,I/15 % CeO₂ at pH 3.0–11.0 and 25 °C during 90 min using a hollow cylindrical photoreactor with eight 8 W visible lamps of $\lambda = 465 \pm 40$ nm. The greater degradation of 98 % with $k_1 = 0.039 \text{ min}^{-1}$ was obtained for 2.0 g/L of the photocatalyst at pH 9.0. Good reproducibility was found after 3 successive runs. •OH and O₂•-

3.7. Other photocatalysts

Other kinds of photocatalysts have been tested for PCT remediation from waters under UV, visible, or sunlight irradiation. Some papers considered nanomaterials with Ag [154,155], Zn [156–163], Fe [164,165], and Nb [166]. Other works focus the behavior of photocatalysts with organic compounds like tris(4,7-diphenyl-1,10phenanthroline)Ru(II) [167], PEDOT or poly(3,4ethylenedioxythiophene) [168], and 10-phenylphenothiazine [169]. C60 aminofullerene [170], MOF [171–176], and covalent organic framework (COF) [177–179] materials were checked as well. Table 5 summarizes the best findings obtained for selected scientific papers.

Ma et al. [154] prepared Ag/AgBr NPs by US-precipitation of KBr and AgNO₃ solutions, followed by immersion in a hydrazine hydrate solution at 105 °C. Ag presented a surface plasmonic resonance by accepting photogenerated e_{CB}^- of AgBr under visible light in the Schottky heterojunction and the E_g -value of Ag/AgBr was 2.42 eV, a value lower than 2.56 eV for AgBr. This explained the 99 % and 90 % PCT removals obtained for 30 mg/L of such photocatalysts in 100 mL of suspensions in pure water with 5 mg/L drug in a stirred beaker after 50 min of visible light irradiation supplied by a 300 W Xe lamp. The superior photoactivity of Ag/AgBr NPs with respect to TiO₂ was confirmed by determining lower degradations of 6 % and 76 % with classical TiO₂ NPs and TiO₂/N NPs (see Table 5). The use of scavengers allowed the detection of the formation of •OH and photogenerated h_{VB}^+ . Fan et al. [155] described the behavior of similar Ag/AgCl NPs deposited onto particles of a MOF such as ZIF-8, which is unable to be photoexcited due to its high $E_{\rm g} = 5.06$ eV. Fig. 24a schematizes the photocatalytic mechanism proposed for Ag/AgCl/ZIF-8 under visible light. The irradiation originated $e_{\rm CB}^-/h_{\rm VB}^+$ pairs in the AgCl, and then, the $e_{\rm CB}^-$ passed to the Ag surface and further, to the ZIF-8 surface where O_2^{\bullet} was produced to oxidize the PCT adsorbed onto it. Its good photoactivity can be deduced from the decay of the normalized PCT concentration vs time plots in the order ZIF-8 < Ag/AgCl < Ag/AgCl/ZIF-8 shown in Fig. 24b for the PC of 100 mL of suspensions of 1 mg/L of drug and 0.5 g/L of each photocatalyst in pure water at pH 7.0 and room temperature using a stirred beaker exposed to visible light supplied by a 500 W metal halogen lamp. Overall degradation with $k_1 = 0.058$ min⁻¹ was more quickly reached after 60 min of

irradiation with Ag/AgCl/ZIF-8 (see also Table 5). Fig. 24c highlights that pH 5.0 yielded the faster drug abatement with total disappearance in only 20 min and $k_1 = 0.142 \text{ min}^{-1}$. However, this material presented low reusability after 3 consecutive cycles. The photogenerated oxidants were elucidated at pH 7.0 by adding 1 mM of oxalate (scavenger of h_{VB}^{+}), isopropanol (IPA) (scavenger of •OH), and p-Bq (scavenger of $O_2^{\bullet-}$). Fig. 24d reveals the stronger oxidation action of $O_2^{\bullet-}$ in the PC process according to the proposed mechanism of Fig. 24a. Additionally, 2 aromatic by-products and 4 final carboxylic acids were identified by HPLC.

Several Zn-based nanomaterials have also shown good effectiveness to destroy PCT. Zhu et al. [156] obtained Zn-Al/x% Ce MMO by co-



Fig. 24. (a) Sketch of the photocatalytic destruction of PCT over an Ag/AgCl/ZIF-8 composite under visible light. (b) Time course of the normalized PCT degradation for the treatment of 100 mL of suspensions in pure water with 1 mg/L drug and 0.5 g/L of different photocatalysts at pH 7.0 and room temperature by PC using a stirred beaker externally illuminated with a 500 W metal halogen lamp (cutoff filters for IR and $\lambda < 400$ nm). (c) Effect of pH on the normalized drug degradation for PC assays with 1 mg/L drug and 0.5 g/L Ag/AgCl/ZIF-8. (d) Influence of 1 mM of different scavengers over the percent of drug decay after 60 min of degradation of suspensions with 1 mg/L drug and 0.5 g/L Ag/AgCl/ZIF-8 at pH 7.0. Adapted from [155]

precipitation of a mixture of Zn(NO₃)₂, Al(NO₃)₃, and Ce(NO₃)₃ solutions with final calcination at 750 °C. The nanocomposite contained ZnO NPs and ZnAl₂O₄ NPs as photocatalysts, alongside Ce doping as reductor of the recombination of their photogenerated e_{CB}^-/h_{VB}^+ pairs. Suspensions in the pure water of 50 mL of 10 mg/L of PCT and 0.5 g/L of Zn-Al/5% Ce in a stirred beaker yielded 99 % degradation with $k_1 = 0.014 \text{ min}^{-1}$ after 240 min under a visible light using a 300 W Xe lamp (see Table 5). Oxidants •OH and O₂•⁻ were identified by EPR with DMPO. The

behavior of another material composed of ZnFe-CLDH (at 450 °C)/rGO was studied by Zhu et al. [158]. Fig. 25a highlights that it was formed of a mixture of ZnO NPs ($E_g = 3.2 \text{ eV}$) and ZnFe₂O₄ NPs ($E_g = 1.92 \text{ eV}$) with a Z-scheme heterojunction that was photoactive upon simulated sunlight. The photoexcited e_{CB} in the CB of ZnO was then transferred to the VB of ZnFe₂O₄ decreasing the recombination of the photogenerated charges and enhancing the oxidation of the pollutants studied (As(III) and PCT) in the VB of the former nanomaterial and the photoreduction



Fig. 25. (a) Sketch of the proposed Z-scheme heterojunction mechanism for the photocatalytic degradation of PCT or oxidation of As(III) to As(V) over ZnFe-calcined layered double hydroxides (CLDH)/rGO upon simulated sunlight. (b) Pseudo-first-order rate constants determined for the direct photolysis, and PC with LDH, CLDH, and ZnFe-CLDH of 50 mL of suspensions in the pure water of 5 mg/L PCT and 25 mg of each catalyst at neutral pH and room temperature using a photoreactor like of Fig. 4a with an inner 500 W Xe light. (c) Percentage of drug degradation after 420 min of the assays with ZnFe-CLDH in the absence and presence of 0.5 mM of scavengers like isopropyl alcohol (IPA), p-benzoquinone, and EDTA-2Na. EPR spectra of: (d) DMPO-OH (in water) and (e) DMPO-O₂·⁻ adducts (in methanol) detected in ZnFe-CLDH dispersions in the dark or after 10 min upon simulated sunlight. Adapted from [158]

of O_2 to $O_2^{\bullet-}$ in the CB of the latter one to destroy such pollutants. Fig. 25b shows that 25 mg of this.

photocatalyst led to a low $k_1 = 0.0074 \text{ min}^{-1}$ for the degradation of 50 mL of suspensions of 5 mg/L PCT in pure water at neutral pH and room temperature using a photoreactor like Fig. 4a with a 500 W Xe lamp, much higher than individual treatments. Under these conditions, 96 % drug abatement and 50 % mineralization in 420 min were found (see Table 5). Fig. 25c-e makes evidence that •OH and O₂•⁻ are formed in the PC process, although Fig. 25c reveals that h_{VB}^+ scavenged by EDTA-

2Na was the main oxidizing species. The presence of rGO stabilized the photocatalyst and allowed excellent reproducibility after 5 consecutive trials.

Other metal-based photocatalysts were also useful for PCT destruction, as shown in Table 5. Yan et al. [160] studied an In_2S_3/Zn_2GeO_4 nanocomposite prepared by a hydrothermal co-precipitation method of both materials. Zn_2GeO_4 NRs were previously synthesized via a hydrothermal reaction of GeO₂ and Zn(II) acetate. The E_g -value for In_2S_3 was 2.2 eV and for Zn_2GeO_4 , 4.67 eV, meaning that the latter one was not



Fig. 26. (a) Scheme of the photocatalytic removal of PCT in the Schottky heterojunction of an In_2S_3/Zn_2GeO_4 composite. (b) Effect on the percentage of PCT degradation of (b) the dosage of the above photocatalyst with 5 mg/L drug at pH 7.0, (c) the initial drug concentration with 1.0 g/L photocatalyst at pH 7.0, and (d) the initial pH with 5 mg/L drug and 1.0 g/L photocatalyst. The trials were carried out for 360 min with 100 mL of suspensions in pure water with air equilibrated at 25 °C using a stirred customized photoreactor upon an external 300 W Xe light (cutoff filters providing $\lambda > 420$ nm). (e) Effect of 2 mM scavengers on the percent of PCT degradation for 5 mg/L drug and 1.0 g/L photocatalyst at pH 7.0. Adapted from [160]

photoactive. Upon visible irradiation, Fig. 26a shows the Schottky heterojunction formed where the promoted e_{CB}^- in the CB of In₂S₃ passed to the CB of Zn₂GeO₄ to produce the oxidant O₂., while the photooxidation took place in the VB of In₂S₃, thus facilitating PCT removal. The trials were made with 100 mL of suspensions in pure water with air equilibrated of 5-25 mg/L of drug and 0.5-2.5 g/L of photocatalyst at pH 3.0-7.0 and 25 °C lasting 360 min using a stirred customized photo reactor upon a 300 W Xe light at $\lambda > 420$ nm. From the data of Fig. 26b-d, one can infer that the maximum degradation of 95 % with $k_1 = 0.0087 \text{ min}^{-1}$ was obtained for 5 mg/L PCT and 1.0 g/L In₂S₃/ Zn₂GeO₄ at pH 9.0. Excellent reusability of the photocatalyst was obtained after 5 successive steps. It also found a small TOC reduction of 53 % at pH 7.0 (see Table 5). It was confirmed that the presence of $HCO_3^$ and humic acid, typical pollutants of wastewaters, caused a drastic abatement of PCT decay due to the parallel consumption of oxidizing agents. Fig. 26e depicts the inhibition of drug removal after the addition of 2 mM of different scavengers under optimum conditions. As can be seen, h⁺_{VB} and O₂•⁻ scavenged by EDTA and p-Bq, respectively, were the main oxidants photogenerated.

Nanocomposites with different SnO2 and ZnS ratios were hydrothermally synthesized by Hojamberdiev et al. [163] by mixing SnCl₄ and ZnS solutions at 180 °C. These x:v SnO₂/ZnS nanocomposites presented a Type-II heterojunction with the migration of the e_{CB}^- of ZnS to the CB of SnO_2 and the h_{VB}^+ of SnO_2 to the VB of ZnS, promoting an efficient separation of the photogenerated charges. It was found that the adsorption of PCT in the order: 1:2 SnO₂/ZnS > SnO₂ > ZnS also played a key role in the degradation of 750 mL of suspensions in pure water with 10 mg/L drug and 1 g/L of each photocatalyst at pH 6.5 using a Heraeus photoreactor with visible light at $\lambda = 550$ nm. After 120 min, drug decays of 70 %, 65 %, and 41 %, respectively, were determined (see Table 5). A 38 % TOC removal was obtained for 1:2 SnO₂/Zn. The main oxidizing agent was •OH, as detected by scavengers. Fernandes et al. [164] synthesized magnetic nanoparticles of magnetite covered with hematite, easily separable from treated solutions with a magnetic field. The photoactivity of 0.13 g/L of the Fe₃O₄/Fe₂O₃ nanocomposite was examined for the degradation of 150 mL of suspensions of 5-30 mg/L PCT in pure water with air or N₂ bubbling in an Ace glass photoreactor upon a 450 W medium-pressure Hg lamp. Results of Table 5 highlight that faster overall removal in 20 min was achieved for the lower drug contents of 5 and 10 mg/L upon air bubbling, as expected from the slower destruction of higher drug amounts by similar quantities of photogenerated oxidants. The degradation was inhibited under N₂ by the loss of •OH formed from O₂ photoreduction at the CB of a photocatalyst. The evolution of •OH under air was followed with 2-hydroxyterephthalic acid. Moreover, 3 aromatic derivatives and 1 carboxylic acid were identified by LC/MS of treated solutions. Abreu et al. [166] reported the PCT degradation by PC with uncalcined and calcined (between 100 and 600 °C) commercial Nb₂O_{5.} These photocatalysts were checked under UVA light because their E_{g} -values varied between 3.09 for uncalcined and 3.34 eV for calcined nanomaterials. Introducing 0.5 g/L of the uncalcined nanomaterial in 250 mL of a suspension in pure water at pH 4.0 and 25 $^{\circ}$ C with an O₂ flow rate of 5 mL min⁻¹ in a stirred beaker with a 125 W UVA light, a low degradation of 47 % with $k_1 = 0.01201 \text{ min}^{-1}$ was obtained as the best result for 10 mg/L PCT, suggesting that it is not a useful alternative to TiO₂ nanomaterials.

PEDOT can be easily synthesized by chemical polymerization of 3,4ethylenedioxythiophene (EDOT) and FeCl₃ [168]. It is a curious conducting polymer that can be photoexcited with UV/visible light originating separated charges that produce •OH and O_2 •⁻ oxidants, as confirmed by scavengers. Tests performed with suspensions of 1 mg/L PCT and 0.5 g/L PEDOT at pH 5.6 with a stirred beaker under eight 15 W UV/visible lights revealed excellent photoactivity, attaining 100 % and 44 % degradations in pure water and secondary WWTP effluent, respectively, after 60 min of irradiation (see Table 5).

MOF nanomaterials with NH₂-MIL-125 (Ti) have received increasing attention in nanocomposites for PC under solar irradiation. Gómez-

Avilés et al. [173] synthesized Ti-x% molar Zr/MOF with NH₂-MIL-125 nanocomposites by a solvothermal procedure by mixing solutions of 2aminobenzene dicarboxylic acid, titanium tetraisopropoxide, and Zr (IV) butoxide. The $E_g = 2.70$ eV for the best Ti-15 % molar Zr/MOF was only slightly lower than 2.74 eV for Ti%/MOF. However, the former nanocomposite gave a faster total PCT degradation (120 min with $k_1 = 0.0121 \text{ min}^{-1}$ vs 180 min with $k_1 = 0.0073 \text{ min}^{-1}$) when suspensions of 150 mL with 5 mg/L of drug and 0.125-1.0 g/L of each photocatalyst at optimum pH 6.9 and 20 °C were treated in a stirred beaker with a Xe lamp irradiating at $\lambda > 290$ nm (mimicking solar irradiation). It was confirmed through scavengers that •OH and O2•- were the predominant oxidizing species. Unfortunately, the nanocomposite presented low reusability because of the loss of 13 % performance after 3 consecutive cycles. Better results have been reported by the same group for NH₂-MIL-125 (Ti) decorated with Pd, Pt, or Ag [174]. Fig. 27a depicts the UV-vis diffuse reflectance spectra recorded for such photocatalysts and Fig. 27b the corresponding Tauc plots, allowing determining E_{g} -values of 2.48 eV for Pt/NH₂-MIL-125 < 2.50 eV for Pd/ NH₂-MIL-125 < 256 eV for NH₂-MIL-125 < 2.70 eV for Ag/NH₂-MIL-125. For 150 mL of suspensions in the pure water of 5 mg/L PCT and 0.25 g/L of each photocatalyst filling a stirred.

beaker with a Xe lamp irradiating at $\lambda > 290$ nm. Fig. 27c shows a decreasing degradation rate in the same order as the decreasing Egvalues stated above, always reaching > 97 % removal in 180 min. The k_1 -value for the best Pt/NH₂-MIL-125 was 0.017 min⁻¹, higher than 0.0121 min⁻¹ obtained for the above Ti-15 % molar Zr/MOF. The preeminent oxidant formed under these conditions was O2*, according to the higher k_1 decay depicted in Fig. 27d for 1 mM p-Bq. It is noticeable the acceleration of the PC process by adding 1 mM AgNO₃, which can be ascribed to the adsorption of visible light by Ag⁺ that photogenerated separated e_{CB}^- and h_{VB}^+ with the subsequent transference of e_{CB}^- to the CB of NH2-MIL-125 (Ti). LC/ESI-MS and IC analysis of irradiated solutions identified 3 dimers, 1 aminoaliphatic derivative, and 4 final carboxylic acids. Kuila and Saravanan [176] prepared Ce/MOF, Fe/MOF, and Ce-Fe/MOF nanomaterials by mixing Ce(NO₃)₃ and/or Fe(NO₃)₃ with 2aminoterephthalic acid and heating at 180 °C. Their Eg-values determined by UV-vis reflectance spectroscopy decreased in the sequence: 2.54 eV for Ce/MOF > 1.45 eV for Fe/MOF > 1.18 eV for Ce-Fe/MOF, then being photoactive in the visible light region. They explained that light irradiation promoted the separation of electron-holes between the LUMO of MOF and the HOMO of metals, where ROS were formed. The tests performed in a stirred Erlenmeyer flask upon direct sunlight with 100 mL of suspensions in the pure water of 10 mg/L of PCT and '0.1 g/L of each photocatalyst at optimum pH 5.6 lasting 270 min revealed growing 60 %, 71 %, and 96 % of drug decay with raising the E_{g} -value. The corresponding k_1 -values raised from 0.0038 to 0.0138 min⁻¹ (see Table 5). It is noticeable that all these photocatalysts upgraded the oxidation power of TiO₂, which only yielded a $k_1 = 0.0018 \text{ min}^{-1}$ under the same conditions. However, their reusability was not studied.

Recently, thin films of chitosan-coated with a COF composed of a mixture of 1,3,5-triformylphloroglucinol, 3,6-diaminepyridazine, and Teflon, were prepared by Zhang et al. [179]. The film presented a good ability for visible light absorption with the production of e_{CB}^- and h_{VB}^+ separated charges. Several assays were carried out by treating 60 mL of pure water with 3 mg/L of PCT and 5–20 mg of films at pH 0.0–11.0, 25 °C for 180 min using a stirred beaker exposed to visible light at $\lambda > 420$ nm provided by a 300 W Xe light. Overall degradation with $k_1 = 0.029 \text{ min}^{-1}$ was found for the optimum conditions of 20 mg of photocatalyst at pH 7.0. Drug removal was decelerated in 3 natural waters due to the competence of their organic components and in the presence of CO_3^{2-} , whereas it was practically unaffected with other common anions. O_2^{*-} and e^- was detected as the pre-eminent oxidant by EPR with DMPO. As an interesting result, large stability with excellent reusability after 5 consecutive cycles was described.

It is difficult to compare the data of the PC processes collected in Tables 2-5 due to the large variety of cells, photocatalysts, and



Fig. 27. (a) UV–vis diffuse reflectance spectra and (b) Tauc plots obtained for the as-prepared NH₂-MIL-125, Ag/NH₂-MIL-125, Pd/NH₂-MIL-125, and Pt/NH₂-MIL-125 photocatalysts. (b) Change of the normalized PCT concentration with the reaction for the degradation of 150 mL of suspensions in the pure water of 5 mg/L drug and 0.25 g/L of each of the above photocatalysts by PC with a stirred beaker under external irradiation of a 600 W m⁻² Xe lamp (cutoff filter for λ < 290 nm). (c) Pseudo-first-rate constants determined for the trials with the Pt/NH₂-MIL-125 photocatalyst with 1 mM of different scavengers. Adapted from [174]

experimental conditions used including the power and kind of irradiated light. As a first approach, the determined k_1 -value for PCT degradation can be taken as comparative term between different works. This parameter is usually lower than 0.01 min⁻¹, as expected for a rather slow drug removal. The highest $k_1 = 0.45$ min⁻¹ has been reported using TiO₂ P 25 under simulated sunlight [44], reinforcing the priority use of this nanomaterial as photocatalyst. No better degradation has been described with TiO₂-based nanomaterials, with a maximum k_1 -value of 0.108 min⁻¹ for a hybrid process of TiO₂/Pt with US upon UVC light [79]. Worse results have been found for thermally activated ZnO under UVA light with $k_1 = 0.0136$ min⁻¹ [111] and ZnO/Ag under visible light with $k_1 = 0.020$ min⁻¹ [122], For the other photocatalysts tested, it is only remarkable the higher k_1 -value of 0.342 min⁻¹ obtained with Bi₃O₄Br hollow spheres under visible light [143].

4. Treatment of paracetamol wastewater by photoelectrocatalysis

As stated in section 2, the PEC process is an electrochemical variety of PC in which the photocatalyst acts as a photoanode submitted to light irradiation in an electrolytic cell like the two-electrode undivided one schematized in Fig. 2. In this system, a constant bias E_{cell} or *I* is applied to extract the photogenerated e_{CB}^- from the photoanode by the external electrical circuit yielding a larger separation with lower recombination of the photogenerated e_{CB}^-/h_{VB}^+ pairs as compared to PC. This originates much higher quantities of h_{VB}^+ in the photoanode that produce more •OH from reaction (3) or (4) or directly oxidize the organics via reaction (5). When a three-electrolytic cell is used, the e_{CB}^- extraction is regulated by the bias E_{an} applied to the photoanode vs a third reference electrode. In all the electrolytic cells, the radical oxidant M(•OH) additionally originated from water oxidation at the photoanode M by reaction (12). M (•OH) causes the electrochemical oxidation (EO) of organics that competes with their PEC destruction. Although the contribution of EO to the overall process is difficult to know, it is usually assumed the predominance of PEC because low E_{cell} , I, or E_{an} values are applied producing small amounts of M(•OH) with very low ability to mineralize the pollutants [17]. A drastic loss of the photocatalyst properties occurs if high E_{cell} , I, or E_{an} values are applied.

The PEC process for PCT destruction has been examined with TiO_2 and TiO_2 -based photoanodes composed of faceted TiO_2 NPs [180], TiO_2 NTs-coated discs [181], TiO_2 coated membranes [182], $CuO/TiO_2/Al_2O_3/reticulated$ vitreous carbon [183], Pr-polyethylene glycol-PbO₂/ $Ti//TiO_2$ NTs [184], TiO_2/Au [185], and $TiO_2/Au/TiO_2$ multilayer [186]. Other photoanodes of ZnO-Pd/*N*-carbon nanofibers [187] and FTO/BiVO₄/BiOI [188] have also been considered.

It is remarkable the work of Montenegro-Ayo et al. [181] using a flow tubular reactor with TiO_2 NTs-coated discs upon UVC irradiation. TiO_2 NTs with anatase structure were anodically deposited at 40 V for

120 min in a solution of ethylene glycol with NH₄F, being further annealed at 450 °C. The runs with 1 L of 10 mg/L PCT in 0.02 M Na₂SO₄ as supporting electrolyte recirculating at 180 mL min⁻¹ showed that PEC with an internal 14 W UVC light and $E_{cell} = 8$ V was the more efficient process. Fig. 28a depicts that after 310 min of irradiation, the drug content was reduced by 93 % by PEC, much higher than 63 % by PC, whereas it remained practically invariant under direct photolysis and EO (without irradiation). Fig. 28b shows the expected increase of PCT removal with increasing E_{cell} from 0 to 62 V in PEC as a result of the generation of more oxidants. The kinetics always followed a pseudo-first order reaction with maximum oxidation power for $E_{cell} = 8$ V with $k_1 = 0.0085$ min⁻¹ and a minimum electrical energy per order (E_{EO}) of 67 kWh m⁻³ order⁻¹. At higher E_{cell} , the PEC became less inefficient due to the enhancement of parasitic reactions of oxidants and the $\mathrm{E}_{\mathrm{EO}}\text{-value}.$

grew enormously up to 330 kWh m⁻³ order⁻¹ at 62 V. The calculation of E_{EO} is then a good option to optimize the process with the minimum energetic requirements. PCT dropped more slowly with raising its initial concentration, as can be seen in Fig. 28c for 5–50 mg/L drug at $E_{cell} = 8$ V with the corresponding pseudo-first-order kinetic analysis, as expected from the slower attack of oxidants over higher organic amounts. The faster PEC process occurred for the lower 5 mg/L drug with $k_1 = 0.0123$ min⁻¹. For 10 mg/L drug under these conditions, TOC was reduced by 59 % (see Fig. 28d). Ion-exclusion HPLC analysis of this solution allowed the detection of the generation of formic and oxalic acids as final carboxylic acids. Fig. 28e highlights the difficulty of destroying these acids, remaining at contents of 33 and < 2 mg/L in the



Fig. 28. (a) PCT concentration abatement with time during the treatment of 1 L of 10 mg/L drug in 0.02 M Na₂SO₄ using a flow tubular reactor with TiO₂ NTs-coated discs as anode/photocatalyst/photoanode at liquid flow rate of 180 mL min⁻¹ by (\bullet) direct photolysis, (\blacksquare) electrochemical oxidation (EO), (\bullet) PC, and (\bullet) PEC. Photo-assisted methods used an internal 14 W UVC light and electrolytic processes were made at cell voltage (E_{cell}) of 8.0 V. (b) Effect of E_{cell} over drug decay for the above solution under PEC and the corresponding pseudo-first-order kinetic analysis (inset). $E_{cell} = (\bullet) 0$ (PC), (\blacksquare) 4.0, (\bullet) 8.0, (\bullet) 16.0, (\checkmark) 32.0, and (\circ) 62.0 V. (c) Effect of PCT content on drug removal by PEC at $E_{cell} = 8.0$ V and the corresponding pseudo-first-order kinetic analysis (inset). Concentration: (\bullet) 5, (\blacksquare) 10, (\bullet) 20, (\bullet) 35, and (\checkmark) 50 mg/L. Time-course of (d) TOC, (e) the concentration of detected (\blacksquare) formic and (\bullet) oxalic acids, and (f) the concentration of released (\checkmark) NH₄⁺ and (\bullet) NO₃⁻ ions during the PEC treatment of 10 mg/L PCT at $E_{cell} = 8.0$ V. Adapted from [181]

final solution, respectively. Fig. 28f depicts a quicker release of the N of PCT in the form of NH_4^+ than NO_3^- . Hybrid processes of PEC with photoelectro-Fenton (PEF) have shown a greater oxidation power using TiO₂/Au [185] and TiO₂/Au/TiO₂ multilayer [186] photoanodes. The PEF process consists of the generation of H₂O₂from the two-electron O₂ reduction at an air-diffusion cathode from reaction (16) and the addition of Fe²⁺ generates homogeneous •OH in the bulk solution from the well-known Fenton reaction (17) [1]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{16}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^-$$
 (17)

In the hybrid PEC + PEF process, the irradiation photogenerated e_{CB}^-/h_{VB}^+ pairs in TiO₂ from reaction (1) and the e_{CB}^- passed to the Au surface by a Schottky heterojunction mechanism to be extracted through the external electric circuit to the cathode. Heterogenous •OH was formed in PEC from the oxidation of H₂O and OH⁻ by h_{VB}^+ via reactions (3) and (4), respectively. The combined PEF process originated homogeneously •OH from reactions (16) and (17), and additionally from the photo-Fenton reaction (15) because Fe³⁺ was generated by reaction (17).

Hernández et al. [185] prepared a TiO₂/Au photoanode by mixing titanium tetraisopropoxide and $AuCl_3$ solutions, followed by electrophoretic deposition on carbon cloth. It was placed in a three-electrode undivided electrolytic cell with a SS cathode for EO or an air-diffusion cathode for PEF, along with an Ag|AgCl reference electrode, upon nine 2 W UVA-LED lamps or direct sunlight. In the latter case, solar PEC (SPEC) and solar PEF (SPEF) were applied. Solutions of 100 mL of 78.5 mg/L PCT in pure water with 0.050 M Na₂SO₄ at pH 3.0 (optimal for PEF) and 25 °C were treated for 180 min. Low degradations of 3 %, 57 %, 62 %, and 66 % were obtained for PC, EO, PEC, and SPEC, respectively, at $E_{an} = +0.82$ V vs Ag|AgCl in the electrolytic tests. In contrast, total drug abatement in 45 min for PEC + PEF and in 25 min for SPEC + SPEF was found after adding 0.50 mM FeSO₄ to the solution. From these promising results and trying to improve the application of the two latter hybrid processes, the same group extended the study to a TiO₂/Au/TiO₂ multilayer thin film photoanode synthesized by pulsed laser deposition [186]. The photoanode composed of six TiO₂ and five Au alternate layers was deposited on a conductive substrate and was designed to optimize the absorption of photons and minimize the recombination of the separated photogenerated charges. The processes were performed with the same electrochemical system stated above upon a 36 W UVA-LED light containing 100 mL of 39-157 mg/L PCT in $0.050~M~\text{Na}_2\text{SO}_4$ or $0.035~M~\text{Na}_2\text{SO}_4 + 0.015~M$ NaCl (mimicking urban wastewater) at pH 3.0. Degradations lower than 50 % were obtained for EO after 150 min of applying a small I = 0.50 mA due to the low generation of M(•OH) from reaction (12). In contrast, 95 % degradation was found in 150 min for 39 mg/L drug by PEC with 0.050 M Na₂SO₄ and total degradation in 120 min with 0.035 M Na₂SO₄ + 0.015 M NaCl because of the additional attack of active chlorine formed from Cloxidation at the anode. Much faster drug decay was determined by means of PEC + PEF in 0.035 M Na₂SO₄ + 0.015 M NaCl, with total disappearance in 4–5 min, by adding 0.50 mM Fe²⁺ and applying an E_{an} = +4.0 V vs Ag|AgCl, due to the extra oxidative action of homogeneous •OH produced by reactions (15) and (17). GC-MS analysis of treated solutions by EO and PEC identified hydroquinone, p-benzoquinone, and hydroxylated products as drug derivatives, whereas the chlorine derivative N-(4-chloro-2-hydroxyphenyl)acetamide formed by active chlorine was detected in PEC + PEF. These results encourage the development of new PEC + PEF processes, or better the more costeffective SPEC + SPEF ones, for the destruction of PCT in real waters for feasible industrial application.

5. Conclusions and prospects

 TiO_2 is the preferred nanomaterial used for PCT removal from water and wastewater. The drug was more rapidly degraded in suspensions in

pure water with rutile < P 25 < anatase and using UVC as compared to UVB, UVA, or visible light due to its photolysis. Photon flux of the irradiating lamps, PCT content, and pH are main factors affecting the process efficiency that need to be well characterized to optimize the treatment. The former parameter should saturate the photocatalytic active sites to achieve the best degradation rate. The drug decay raised to an optimum photocatalyst content where the active sites were saturated, and its percentage of degradation decreased at higher initial drug content because of the slower oxidation of more organic matter with similar amounts of generated oxidizing agents. Usually, the optimum pH was 9.5, near the pK_a -value of PCT, where it was adsorbed to a larger extent by the photocatalyst. The treatments with solar pilot plants with CPC photoreactors confirmed that the drug was more slowly removed from WWTP effluents than in pure water due to the competitive oxidation of its components. More powerful photocatalysts are required to improve the degradation rate in WWTP effluents. Hollow mesoporous anatase microsphere materials showed good drug decay but with very low reusability in the consecutive cycle, making it not useful in practice. This results from the low mineralization of the by-products that remained adsorbed on the photocatalyst surface blocking its active sites. A reaction sequence for PCT mineralization involving the initial generation of aromatic derivatives followed by their cleavage to final carboxylic acids is proposed based on the by-products identified in the literature. Immobilized P 25 onto a ceramic y-Al₂O₃ tubular ultrafiltration membrane, glass spheres, and SS gave smaller drug removal than suspended P 25. In contrast, 100 % mineralization was reported using a solar pilot plant with fixed anatase beds, much greater than with suspended anatase NPs, suggesting that the amount of immobilized photocatalyst should be optimized for PCT removal. Hybrid processes of PC with P 25 and US or PMS had superior performance to degrade the drug with respect to single PC and with good reusability of the photocatalyst. Further research should consider techno-economic studies to benchmark the PC with pure TiO2 technology with other AOPs to clarify its potential interest in treating natural waters and WWTPs at the industrial level. The development of hybrid processes by adding powerful oxidants seems a good way to attain better efficiencies in future research.

TiO₂-based nanocomposites have been synthesized to enhance the adsorption of the drug onto the photocatalyst and/or to diminish its E_{g} value for a better process efficency and for using renewable sunlight as an energy source aiming to more cost-effective treatment. Stable photocatalysts with carbon materials increased the PCT removal by its adsorption on them and with good reproducibility to be useful in practice, as reported for P 25/AC under simulated sunlight, TiO₂ NTs/graphene and anatase/graphite upon UVA light, and anatase/SiO2/ MWCNTs under visible light. The photocatalytic performance was notably enhanced when TiO2 NPs and TiO2 NFs were coated with metals like Ag, Fe, Pd, and Pt upon UV light by the decrease of their E_{g} -values, but with smaller relevance under visible light. The Schottky heterojunction formed between semiconductor/metal largely enhances the separation of the photogenerated e_{CB}/h_{VB} species. However, Ta was found an inappropriate metal for such nanocomposites. Magnetic P 25 with Fe_3O_4 or Fe_2O_3 allowed quicker drug destruction with UV/Vis light thanks to the reduction of their E_{g} -value by a Type II heterojunction mechanism, showing the advantage of a rapid extraction from the medium by a magnetic field. Positive photocatalysts have also been described for anatase coated with K₃[Fe(CN)₆ and K₂S₂O₈ under visible light, and anatase/sepiolite, TiO2 NRs/MoS2, and TiO2/B upon UVA light. However, their reusability was not checked, which is a key parameter to knowing their practical applicability. Most papers related to TiO₂-based nanocomposites used pure water as a reaction medium, then further research should consider the treatments of natural waters and WWTPs effluents to clarify their oxidation power for possible application. Techno-economic studies should be reported and more attention should be made to achieving large COD and/or TOC abatements that are necessary to remove toxic and undesired by-products in the final solutions. Simple and cost-effective nanocomposites should be

E. Brillas and J. Manuel Peralta-Hernández

next developed to be useful in practice.

Pure ZnO presented a similar photoactivity to remove PCT than pure TiO_2 because of their analogous E_g -values. The treatment with ZnO NPs was improved with molecularly imprinted ZnO nanonuts and ZnO films by adding small contents of H₂O₂, always using UVA light. The drug degradation was strongly enhanced with ZnO/La and ZnO/Nd,V nanocomposites because the added metals originated intermediate energetic levels absorbing visible light. Similar behavior was found for ZnO/Ag nanocomposites with a Schottky heterojunction photoactive upon UV/ Vis light. An Ag₂S-ZnO/rGO photocatalyst also operative under visible light presented scarce reproducibility in successive runs. In contrast, a MOF nanomaterial of ZnO/Fe₃O₄-GO/ZIF-8 showed great stability and excellent results with 99 % PCT degradation and 99 % TOC reduction with simulated sunlight. MOF derivatives are a good option to obtain more efficient ZnO-based nanocomposites for PCT removal and need to be more extensively developed in next future to operate with free and renewable sunlight.

WO₃ is another nanomaterial that efficiently removed PCT from waters under visible light due to its low E_g -value, although it is not recommendable for its toxicity. Some nanocomposites such as WO₃ nanoplates/AC and WO₃/g-C₃N₄ also showed excellent photoactivity, but the latter with a Z-scheme heterojunction rapidly lost reproducibility. Several bismuth-based nanomaterials have been used as photocatalysts to treat PCT from water under UV or visible light. Good results have been reported for the cube form of BiVO₄, BiVO₄ nanoplates/Pd, and BiOCl/H₂O₂/S₂O₈²⁻, where generated oxidants •OH, O₂•⁻, and SO₄•⁻ were detected with scavengers and EPR with DMPO. Other interesting works have described the fast drug destruction with BiClO/twinned BiPO₄, and g-C₃N₄ doped with Au and Ni-ZnS and co-doped with K and I that presented high photoactivity under visible light. The toxicity of the PCT treatment with these nanomaterials should be reported to clarify their feasible applicability at industrial level.

Other photocatalysts have been tested for PCT remediation from waters under UV, visible, or sunlight irradiation. Good photoactivity has been described for nanocomposites of Ag/Br, ZnFe- CLDH/rGO, $In_2S_3/$ Zn_2GeO₄, Fe₃O₄/Fe₂O₃, PEDOT, Pt/NH₂-MIL-125 (Ti), and Ce-Fe/MOF, as well as chitosan/COF thin films. However, most studies were made in pure water, disregarding the loss of drug removal in the presence of typical pollutants of natural waters and wastewater. Future work should clarify the photocatalytic behavior of the above materials on real waters by means of pilot recirculation plants preferentially under solar irradiation to propose their application to remediate natural waters and WWTP effluents with PCT pollutants at an industrial scale. Techno-economic studies should also be made to corroborate their possible use.

A reduced number of articles have been published dealing with the PCT abatement by the PEC process. Some works have reported the superiority of PEC over PC and EO for TiO₂, TiO₂-based, ZnO-based, and bismuth-based photoanodes. Hybrid processes of PEC + PEF, and more powerful SPEC + SPEF, using TiO₂/Au and Au/TiO₂/Au multilayer thin film photoanodes largely outperformed the PEC process. These results should encourage next research developing new PEC + PEF processes, or better the more cost-effective SPEC + SPEF ones, to destroy PCT in real waters as a first step to assess their industrial application.

CRediT authorship contribution statement

Enric Brillas: Conceptualization, Investigation, Methodology, Formal analysis, Supervision, Writing – original draft, Writing – review & editing. **Juan Manuel Peralta-Hernández:** Conceptualization, Investigation, Methodology, Formal analysis, Funding acquisition, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

Acknowledgments

The authors are grateful for the economic support from the Universidad de Guanajuato under grant 013/2022 and Laboratorio Nacional UG- UAA-CONACyT.

References

- E. Brillas, Fenton, photo-Fenton, electro-Fenton, and their combined treatments for the removal of insecticides from waters and soils. A review, Sep. Purif. Technol. 284 (2022) 120290. https://doi.org/10.1016/j.seppur.2021.120290.
- [2] A.J. dos Santos, M.S. Kronka, G.V. Fortunato, M.R.V. Lanza, Recent advances in electrochemical water technologies for the treatment of antibiotics: a short review, Curr. Opin. Electrochem. 26 (2021), 100674, https://doi.org/10.1016/j. coelec.2020.100674.
- [3] W.J. Lee, P.S. Goh, W.J. Lau, A.F. Ismail, Removal of pharmaceutical contaminants from aqueous medium: a state-of-the-art review based on paracetamol, Arab. J. Sci. Eng. 45 (2020) 7109–7135, https://doi.org/10.1007/ s13369-020-04446-1.
- [4] H.N. Phong Vo, G.K., Le, T.M. Hong Nguyen, X.-T. Bui, K.H. Nguyen, E.R. Rene, T. D.H. Vo, N.-D. Thanh Cao, R. Mohan, Acetaminophen micropollutant: historical and current occurrences, toxicity, removal strategies and transformation pathways in different environaments, Chemosphere 236 (2019) 124391. https://doi.org/10.1016/j.chemosphere.2019.124391.
- [5] M. Pacheco-Álvarez, R. Picos Benítez, O.M. Rodríguez-Narváez, E. Brillas, J. M. Peralta-Hernández, A critical review on paracetamol removal from different aqueous matrices by Fenton and Fenton-based processes, and their combined methods, Chemosphere 303 (2022), 134883, https://doi.org/10.1016/j. chemosphere.2022.134883.
- [6] M. Salimi, A. Esrafili, M. Gholami, A. Jonidi Jafari, R. Rezaei Kalantary, M. Farzadkia, M. Kermani, H.R. Sobhi, Contaminants of emerging concern: a review of new approach in AOP technologies, Environ. Monit. Assess. 189 (2017), https://doi.org/10.1007/s10661-017-6097-x.
- [7] A. Ziylan, N.H. Ince, The occurrence and fate of anti-inflammatory and analgesic pharmaceuticals in sewage and fresh water: treatability by conventional and nonconventional processes, J. Hazard. Mater. 187 (2011) 24–36, https://doi.org/ 10.1016/j.jhazmat.2011.01.057.
- [8] W. Yang, H. Zhou, N. Cicek, Treatment of organic micropollutants in water and wastewater by UV-based processes: a literature review, Crit. Rev. Environ. Sci. Technol. 44 (2014) 1433–1476, https://doi.org/10.1080/ 10643389 2013 790745
- [9] M.A. Prada-Vásquez, S.E. Estrada-Flórez, E.A. Serna-Galvis, R.A. Torres-Palma, Developments in the intensification of photo-Fenton and ozonation-based processes for the removal of contaminants of emerging concern in Ibero-American countries, Sci. Total Environ. 765 (2021), 142699, https://doi.org/ 10.1016/j.scitotenv.2020.142699.
- [10] D. Papoulis, Halloysite based nanocomposites and photocatalysis: a review, Appl. Clay Sci. 168 (2019) 164–174, https://doi.org/10.1016/j.clay.2018.11.009.
- [11] O.S. Awofiranye, S.J. Modise, E.B. Naidoo, Overview of polymer-TiO₂ catalyst for aqueous degradation of pharmaceuticals in heterogeneous photocatalytic process, J. Nanopart. Res. 22 (2020), https://doi.org/10.1007/s11051-020-04877-9.
- [12] O.C. Olatunde, D.C. Onwudiwe, Graphene-based nanocomposites as catalysts for the degradation of pharmaceuticals, Int. J. Env. Res. Public Health 18 (2021) 1–36, https://doi.org/10.3390/ijerph18041529.
- [13] R.M.S. Sendão, J.C.G. Esteves da Silva, L. Pinto da Silva, Photocatalytic removal of pharmaceutical water pollutants by TiO₂-carbon dots nanocomposites: a review, Chemosphere 301 (2022), 134731, https://doi.org/10.1016/j. chemosphere.2022.134731.
- [14] L. Yang, L.E. Yu, M.B. Ray, Photocatalytic oxidation of paracetamol: dominant reactants, intermediates, and reaction mechanisms, Environ. Sci. Technol 43 (2009) 460–465, https://doi.org/10.1021/es8020099.
- [15] E. Moctezuma, E. Leyva, C.A. Aguilar, R.A. Luna, C. Montalvo, Photocatalytic degradation of paracetamol: intermediates and total reaction mechanism, J. Hazard. Mater. 243 (2012) 130–138, https://doi.org/10.1016/j. ihazmat.2012.10.010.
- [16] E. Cuervo-Lumbaque, C. Sirtori, V.J.P. Vilar, Heterogeneous photocatalytic degradation of pharmaceuticals in synthetic and real matrices using a tube-intube membrane reactor with radial addition of H₂O₂, Sci. Total Environ. 743 (2020), 140629, https://doi.org/10.1016/j.scitotenv.2020.140629.
- [17] S. Garcia-Segura, E. Brillas, Applied photoelectrocatalysis on the degradation of organic pollutants in wastewaters, J. Photochem. Photobiol. C: Photochem. Rev. 31 (2017) 1–35, https://doi.org/10.1016/j.jphotochemrev.2017.01.005.
- [18] S. Vinoth, K.S. Shalini Devi, A. Pandikumar, A comprehensive review on graphitic carbon nitride based electrochemical and biosensors for environmental and healthcare applications. TrAC -, Trends Anal. Chem. 140 (2021), 116274, https:// doi.org/10.1016/j.trac.2021.116274.

- [19] K. Bisaria, S. Sinha, R. Singh, H.M.N. Iqbal, Recent advances in structural modifications of photo-catalysts for organic pollutants degradation-A comprehensive review, Chemosphere 284 (2021), 131263, https://doi.org/ 10.1016/j.chemosphere.2021.131263.
- [20] J. Meng, X. Zhang, Y. Liu, M. Ren, Y. Guo, X. Yang, Y. Yang, Engineering of graphitic carbon nitride with simultaneous potassium doping sites and nitrogen defects for notably enhanced photocatalytic oxidation performance, Sci. Total Environ. 796 (2021), 148946, https://doi.org/10.1016/j.scitotenv.2021.148946.
- [21] C. Yu, X. Chen, N. Li, Y. Zhang, S. Li, J. Chen, L. Yao, K. Lin, Y. Lai, X. Deng, Ag₃PO₄-based photocatalysts and their application in organic-polluted wastewater treatment, Environ. Sci. Pollut. Res. 29 (2022) 18423–18439, https:// doi.org/10.1007/s11356-022-18591-7.
- [22] Y. Wang, X. Wu, J. Liu, Z. Zhai, Z. Yang, J. Xia, S. Deng, X. Qu, H. Zhang, D. Wu, J. Wang, C. Fu, Q. Zhang, Mo-modified band structure and enhanced photocatalytic properties of tin oxide quantum dots for visible-light driven degradation of antibiotic contaminants, J. Environ Chem. Eng. 10 (2022), 107091, https://doi.org/10.1016/j.jecc.2021.107091.
- [23] L. Yang, L.E. Yu, M.B. Ray, Degradation of paracetamol in aqueous solutions by TiO₂ photocatalysis, Water Res. 42 (2008) 3480–3488, https://doi.org/10.1016/ j.watres.2008.04.023.
- [24] S. Basha, D. Keane, K. Nolan, M. Oelgemüller, J. Lawler, J.M. Tobin, A. Morrissey, UV-induced photocatalytic degradation of aqueous acetaminophen: the role of adsorption and reaction kinetics, Environ. Sci. Pollut. Res. 22 (2015) 2219–2230, https://doi.org/10.1007/s11356-014-3411-9.
- [25] S. Rawal, S.H. Buer, W. Hawkins, J.R. Sanders, P.E. Arce, Photocatalytic degradation of acetaminophen from water solutions via thin films part I: preparation, characterization, and analysis of titanium dioxide thin films, Int. J. Chem. React. Eng. 20 (2022) 97–112, https://doi.org/10.1515/ijcre-2021-0039.
- [26] K. González-Labrada, I. Quesada-Peñate, F. Velichkova, C. Julcour-Lebigue, C. Andriantsiferana, M.-H. Manero, C. Albasi, U.J. Jáuregui-Haza, Degradation of paracetamol in aqueous solution: comparison of different UV induced advanced oxidation processes, Latin Am. Appl. Res. 46 (2016) 115–120.
- [27] V. Trousil, J. Palarcik, Z. Blazkova, J. Korlnkova, O. Machalicky, J. Cakl, Paracetamol and ibuprofen removal from aqueous solutions by ozonation and photochemical processes, Environ. Prot. Eng. 44 (2018) 159–175, https://doi. org/10.5277/epe180411.
- [28] N. Chekir, D. Tassalit, O. Benhabiles, N. Sahraoui, M. Mellal, Effective removal of paracetamol in compound parabolic collectors and fixed bed reactors under natural sunlight, Water Sci. Technol. 82 (2020) 2460–2471, https://doi.org/ 10.2166/wst.2020.511.
- [30] J. Radjenovic, C. Sirtori, M. Petrovic, D. Barceló, S. Malato, Solar photocatalytic degradation of persistent pharmaceuticals at pilot-scale: kinetics and characterization of major intermediate products, Appl. Catal. B: Environ. 89 (2009) 255–264, https://doi.org/10.1016/j.apcatb.2009.02.013.
- [31] A. Bernabeu, R.F. Vercher, L. Santos-Juanes, P.J. Simón, C. Lardín, M. A. Martínez, J.A. Vicente, R. González, C. Llosa, A. Arques, A.M. Amat, Solar photocatalysis as a tertiary treatment to remove emerging pollutants from wastewater treatment plant efluents, Catal. Today 161 (2011) 235–240, https:// doi.org/10.1016/j.cattod.2010.09.025.
- [32] M.R. Eskandarian, H. Choi, M. Fazli, M.H. Rasoulifard, Effect of UV-LED wavelengths on direct photolytic and TiO₂ photocatalytic degradation of emerging contaminants in water, Chem. Eng. J. 300 (2016) 414–422, https://doi. org/10.1016/j.cej.2016.05.049.
- [36] R. Katal, M. Salehi, M.H. Davood Abadi Farahani, S. Masudy-Panah, S.I. Ong, J. Hu, Preparation of a new type of black TiO₂ under a vacuum atmosphere for sunlight photocatalysis, ACS Appl. Mater. Interfaces 10 (2018) 35316-35326. https://doi.org/10.1021/acsami.8b14680.
- [37] X. Zhang, F. Wu, X. Wu, P. Chen, N. Deng, Photodegradation of acetaminophen in TiO₂ suspended solution, J. Hazard. Mater. 157 (2008) 300–307, https://doi.org/ 10.1016/j.jhazmat.2007.12.098.
- [39] C.J. Lin, W.-T. Yang, C.-Y. Chou, S.Y.H. Liou, Hollow mesoporous TiO₂ microspheres for enhanced photocatalytic degradation of acetaminophen in water, Chemosphere 152 (2016) 490–495, https://doi.org/10.1016/j. chemosphere.2016.03.017.
- [40] Y. Chen, X. Zhang, L. Mao, Z. Yang, Dependence of kinetics and pathway of acetaminophen photocatalytic degradation on irradiation photon energy and TiO₂ crystalline, Chem. Eng. J. 330 (2017) 1091–1099, https://doi.org/10.1016/ j.cej.2017.07.148.
- [41] S.A. Lozano-Morales, G. Morales, M.A. López Zavala, A. Arce-Sarria, F. Machuca-Martínez, Photocatalytic treatment of paracetamol using TiO₂ nanotubes: effect of pH, Processes 7 (2019), https://doi.org/10.3390/pr7060319.
- [42] N. Miranda-García, S. Suárez, B. Sánchez, J.M. Coronado, S. Malato, M. I. Maldonado, Photocatalytic degradation of emerging contaminants in municipal wastewater treatment plant effluents using immobilized TiO₂ in a solar pilot plant, Appl. Catal. B: Environ. 103 (2011) 294–301, https://doi.org/10.1016/j. apcatb.2011.01.030.
- [43] N. Miranda-García, S. Suárez, M.I. Maldonado, S. Malato, B. Sánchez, Regeneration approaches for TiO₂ immobilized photocatalyst used in the elimination of emerging contaminants in water, Catal. Today 230 (2014) 27–34, https://doi.org/10.1016/j.cattod.2013.12.048.
- [44] M.E. Borges, D.M. García, T. Hernández, J.C. Ruiz-Morales, P. Esparza, Supported photocatalyst for removal of emerging contaminants from wastewater in a continuous packed-bed photoreactor configuration, Catalysts 5 (2015) 77–87, https://doi.org/10.3390/catal5010077.
- [45] C. Calas-Blanchard, G. Istamboulié, M. Bontoux, G. Plantard, V. Goetz, T. Noguer, Biosensor-based real-time monitoring of paracetamol photocatalytic degradation,

Chemosphere 131 (2015) 124–129, https://doi.org/10.1016/j. chemosphere.2015.03.019.

- [46] N. Jallouli, K. Elghniji, H. Trabelsi, M. Ksibi, Photocatalytic degradation of paracetamol on TiO₂ nanoparticles and TiO₂/cellulosic fiber under UV and sunlight irradiation, Arab. J. Chem. 10 (2017) S3640-S3645. https://doi.org/ 10.1016/j.arabjc.2014.03.014.
- [47] S. Ramasundaram, M.G. Seid, H.-E. Kim, A. Son, C. Lee, E.-J. Kim, S.W. Hong, Binder-free immobilization of TiO₂ photocatalyst on steel mesh via electrospraying and hot-pressing and its application for organic micropollutant removal and disinfection, J. Hazard. Mater. 350 (2018) 62–70, https://doi.org/ 10.1016/j.jhazmat.2018.07.100.
- [48] I. Rouibah, W. Hassen, O.F. Sallem, N. Khellaf, A. Hassen, H.B. Mansour, Photocatalytic and biodegradation treatments of paracetamol: investigation of the in vivo toxicity, Environ. Sci. Pollut. Res. 28 (2021) 14530–14545, https:// doi.org/10.1007/s11356-020-11615-0.
- [49] M.O. Chijioke-Okere, Z. Adlan Mohd Hir, C.E. Ogukwe, P.C. Njoku, A.H. Abdullah, E.E. Oguzie, TiO₂/Polyethersulphone films for photocatalytic degradation of acetaminophen in aqueous solution, J. Mol. Liq. 338 (2021) 116692. https://doi.org/10.1016/j.molliq.2021.116692.
- [50] V.G. Bessergenev, M.C. Mateus, I.M. Morgado, M. Hantusch, E. Burkel, Photocatalytic reactor, CVD technology of its preparation and water purification from pharmaceutical drugs and agricultural pesticides, Chem. Eng. J. 312 (2017) 306–316, https://doi.org/10.1016/j.cej.2016.11.148.
- [51] L. Rimoldi, D. Meroni, E. Falletta, V. Pifferi, L. Falciola, G. Cappelletti, S. Ardizzone, Emerging pollutant mixture mineralization by TiO₂ photocatalysts. The role of the water mèdium, Photochem. Photobiol. Sci. 16 (2017) 60-66. https://doi.org/10.1039/c6pp00214e.
- [52] S. Rawal, S.H. Buer, J.R. Sanders, P.E. Arce, Photocatalytic degradation of acetaminophen in water via ultraviolet light and titanium dioxide thin films part II: chemical and kinetic aspects, Int. J. Chem. React. Eng. 20 (2022) 113–127, https://doi.org/10.1515/ijcre-2021-0040.
- [53] M. Jagannathan, F. Grieser, M. Ashokkumar, Sonophotocatalytic degradation of paracetamol using TiO₂ and Fe³⁺, Sep. Purif. Technol. 103 (2013) 114–118, https://doi.org/10.1016/j.seppur.2012.10.003.
- [54] Y. Jo, C. Kim, G.-H. Moon, J. Lee, T. An, W. Choi, Activation of peroxymonosulfate on visible light irradiated TiO₂ via a charge transfer complex path, Chem. Eng, J 346 (2018) 249–257, https://doi.org/10.1016/j. cei.2018.03.150.
- [55] E.C. Lumbaque, D.C. Lüdtke, D.D. Dionysiou, V.J.P. Vilar, C. Sirtori, Tube-in-tube membrane photoreactor as a new technology to boost sulfate radical advanced oxidation processes, Water Res. 191 (2021), 116815, https://doi.org/10.1016/j. watres.2021.116815.
- [56] C. Joannis-Cassan, A.S. Rodriguez Castillo, C. Dezani, C. Gómez-Canela, B. Reoyo-Prats, C. Calas-Blanchard, C. Barata, S. Lacorte, G. Plantard, Towards an innovative combined process coupling biodegradation and photo-oxidation for the removal of pharmaceutical residues, J. Chem. Technol. Biotechnol. 96 (2021) 755–763, https://doi.org/10.1002/jctb.6589.
- [57] Y. Sun, L. Xu, P. Jin, X. Bai, X. Jin, Simultaneous removal of colorless micropollutants and hexavalent chromium by pristine TiO₂ under visible light: an electron transfer mechanism, Chem. Eng. J. 405 (2021), 126968, https://doi.org/ 10.1016/j.cej.2020.126968.
- [58] M. Gar Alalm, A. Tawfik, S. Ookawara, Enhancement of photocatalytic activity of TiO₂ by immobilization on activated carbon for degradation of pharmaceuticals, J. Environ Chem. Eng. 4 (2016) 1929–1937, https://doi.org/10.1016/j. jecc.2016.03.023.
- [59] C. Gomez-Solis, R. Mendoza, J.F. Rios-Orihuela, G. Robledo-Trujillo, L.A. Diaz-Torres, J. Oliva, V. Rodriguez-Gonzalez, Efficient solar removal of acetaminophen contaminant from water using flexible graphene composites functionalized with Ni@TiO₂: W nanoparticles, J. Environ. Manage. 290 (2021), 112665, https://doi. org/10.1016/j.jenvman.2021.112665.
- [60] H. Tao, X. Liang, Q. Zhang, C.-T. Chang, Enhanced photoactivity of graphene/ titanium dioxide nanotubes for removal of acetaminophen, Appl. Surf. Sci. 324 (2015) 258–264, https://doi.org/10.1016/j.apsusc.2014.10.129.
- [61] M.D.G. de Luna, J.-C.-T. Lin, M.J.N. Gotostos, M.-C. Lu, Photocatalytic oxidation of acetaminophen using carbon self-doped titanium dioxide, Sust. Environ. Res. 26 (2016) 161–167, https://doi.org/10.1016/j.serj.2016.02.001.
- [62] A. Gómez-Avilés, M. Peñas-Garzón, J. Bedia, J.J. Rodriguez, C. Belver, C-modified TiO₂ using lignin as carbon precursor for the solar photocatalytic degradation of acetaminophen, Chem. Eng. J. 358 (2019) 1574–1582, https://doi.org/10.1016/ j.cej.2018.10.154.
- [63] M. Peñas-Garzón, W.H.M. Abdelraheem, C. Belver, J.J. Rodriguez, J. Bedia, D. D. Dionysiou, TiO₂-carbon microspheres as photocatalysts for effective remediation of pharmaceuticals under simulated solar light, Sep. Purif. Technol. 275 (2021), 119169, https://doi.org/10.1016/j.seppur.2021.119169.
- [64] S. Benjedim, J. Castelo-Quibén, E. Bailón-García, E.M. Lotfi, A.F. Pérez-Cadenas, V. Slovák, J. Kalina, F. Carrasco-Marín, Activated carbon-based coloured titania nanoparticles with high visible radiation absorption and excellent photoactivity in the degradation of emerging drugs of wastewater, Carbon 178 (2021) 753–766, https://doi.org/10.1016/j.carbon.2021.03.044.
- [65] S. Üstün Odabaşi, I. Boudraà, R. Aydin, H. Büyükgüngor, Photocatalytic removal of pharmaceuticals by immobilization of TiO₂ on activated carbon by LC-MS/MS monitoring, Water Air Soil Pollut. 233 (2022), https://doi.org/10.1007/s11270-022-05579-9.
- [66] R. da Cunha, W.V.F. do Carmo Batista, H.L. de Oliveira, A.C. dos Santos, P.M. dos Reis, K.B. Borges, P.B. Martelli, C.A. Furtado, H. de Fátima Gorgulho, Carbon Xerogel/TiO₂ composites as photocatalysts for acetaminophen degradation, J.

Photochem. Photobiol. A: Chem. 412 (2021) 113248. https://doi.org/10.1016/j. jphotochem.2021.113248.

- [67] V. Vaiano, O. Sacco, M. Matarangolo, Photocatalytic degradation of paracetamol under UV irradiation using TiO₂-graphite composites, Catal. Today 315 (2018) 230–236, https://doi.org/10.1016/j.cattod.2018.02.002.
- [68] A.H.C. Khavar, G. Moussavi, A.R. Mahjoub, The preparation of TiO₂@rGO nanocomposite efficiently activated with UVA/LED and H₂O₂ for high rate oxidation of acetaminophen: catalyst characterization and acetaminophen degradation and mineralization, Appl. Surf. Sci. 440 (2018) 963–973, https://doi.org/10.1016/j.apsusc.2018.01.238.
- [69] B. Czech, K. Tyszczuk-Rotko, Visible-light-driven photocatalytic removal of acetaminophen from water using a novel MWCNT-TiO₂-SiO₂ photocatalysts, Sep. Purif. Technol. 206 (2018) 343–355, https://doi.org/10.1016/j. seppur.2018.06.025.
- [70] B. Czech, K. Tyszczuk-Rotko, Caffeine hinders the decomposition of acetaminophen over TiO₂-SiO₂ nanocomposites containing carbon nanotubes irradiated by visible light, J. Photochem. Photobiol. A: Chem. 376 (2019) 166–174, https://doi.org/10.1016/j.jphotochem.2019.03.017.
- [71] X. Feng, P. Wang, J. Hou, J. Qian, C. Wang, Y. Ao, Oxygen vacancies and phosphorus codoped black titania coated carbon nanotube composite photocatalyst with efficient photocatalytic performance for the degradation of acetaminophen under visible light irradiation, Chem. Eng. J. 352 (2018) 947–956, https://doi.org/10.1016/j.cej.2018.06.037.
- [72] M. Peñas-Garzón, A. Gómez-Avilés, J. Bedia, J.J. Rodriguez, C. Belver, Effect of activating agent on the properties of TiO₂/activated carbon heterostructures for solar photocatalytic degradation of acetaminophen, Materials 12 (2019), https:// doi.org/10.3390/ma12030378.
- [73] M. Peñas-Garzón, A. Gómez-Avilés, C. Belver, J.J. Rodriguez, J. Bedia, Degradation pathways of emerging contaminants using TiO₂-activated carbon heterostructures in aqueous solution under simulated solar light, Chem. Eng. J. 392 (2020), 124867, https://doi.org/10.1016/j.cej.2020.124867.
- [74] L. Yang, L. Xu, X. Bai, P. Jin, Enhanced visible-light activation of persulfate by Ti³ ⁺ self-doped TiO₂/graphene nanocomposite for the rapid and efficient degradation of micropollutants in water, J. Hazard. Mater. 365 (2019) 107–117, https://doi.org/10.1016/j.jhazmat.2018.10.090.
- [75] G. Fan, H. Peng, J. Zhang, X. Zheng, G. Zhu, S. Wang, L. Hong, Degradation of acetaminophen in aqueous solution under visible light irradiation by Bi-modified titanate nanomaterials: morphology effect, kinetics and mechanism, Catal, Sci. Technol. 8 (2018) 5906–5919, https://doi.org/10.1039/c8cy01614c.
- [76] C.A. Aguilar, C. Montalvo, B.B. Zermeño, R.M. Cerón, J.G. Cerón, F. Anguebes, M. A. Ramírez, Photocatalytic degradation of acetaminophen, tergitol and nonylphenol with catalysts TiO₂/Ag under UV and Vis light, Int. J. Environ. Sci. Technol. 16 (2019) 843–852, https://doi.org/10.1007/s13762-018-1707-x.
- [77] O. Nasr, O. Mohamed, A.-S. Al-Shirbini, A.-M. Abdel-Wahab, Photocatalytic degradation of acetaminophen over Ag, Au and Pt loaded TiO₂ using solar light, J. Photochem. Photobiol. A: Chem. 374 (2019) 185–193, https://doi.org/ 10.1016/j.jphotochem.2019.01.032.
- [78] I. Bergamonti, C. Graiff, C. Bergonzi, M. Potenza, C. Reverberi, M.C. Ossiprandi, P.P. Lottici, R. Bettini, L. Elviri, Photodegradation of pharmaceutical pollutants: new photocatalytic systems based on 3d printed scaffold-supported Ag/TiO₂ nanocomposite, Catalysts 12 (2022), https://doi.org/10.3390/catal12060580.
- [79] A. Ziylan, N.H. Ince, Enhanced photo-degradation of paracetamol on n-platinumloaded TiO2: the effect of ultrasound and OH/hole scavengers, Chemosphere 162 (2016) 324–332, https://doi.org/10.1016/j.chemosphere.2016.07.090.
- [80] S. Puri, I. Thakur, A. Verma, S. Barman, Degradation of pharmaceutical drug paracetamol via UV irradiation using Fe-TiO₂ composite photocatalyst: statistical analysis and parametric optimization, Environ. Sci. Pollut. Res. 28 (2021) 47327-47341. https://doi.org/10.1007/s11356-021-13895-6.
- [81] H. Gandelman, A.L. da Silva, B. Ramos, D. Gouvêa, Interface excess on Sb-doped TiO₂ photocatalysts and its influence on photocatalytic activity, Ceram. Int. 47 (2021) 619–625, https://doi.org/10.1016/j.ceramint.2020.08.169.
- (2021) 619–625, https://doi.org/10.1016/j.ceramint.2020.08.169.
 [82] D.A. Solís-Casados, L. Escobar-Alarcón, L.M. Gómez-Oliván, E. Haro-Poniatowski, T. Klimova, Photodegradation of pharmaceutical drugs using Sn-modified TiO₂ powders under visible light irradiation, Fuel 198 (2017) 3–10, https://doi.org/ 10.1016/j.fuel.2017.01.059.
- [83] L. Rimoldi, D. Meroni, E. Falletta, A.M. Ferretti, A. Gervasini, G. Cappelletti, S. Ardizzone, The role played by different TiO₂ features on the photocatalytic degradation of paracetamol, Appl. Surf. Sci. 424 (2017) 198–205, https://doi. org/10.1016/j.apsusc.2017.03.033.
- [84] S. Sayegh, F. Tanos, A. Nada, G. Lesage, F. Zaviska, E. Petit, V. Rouessac, I. Iatsunskyi, E. Coy, R, Viter, D, Damberga, M. Weber, A. Razzouk, J. Stephan, M. Bechelany, Tunable TiO₂-BN-Pd nanofibers by combining electrospinning and atomic layer deposition to enhance photodegradation of acetaminophen, Dalton Trans. 51 (2022) 2674-2695. https://doi.org/10.1039/d1dt03715c.
- [85] D. Ashkezari, H. Sid kalal, H. Hoveidi, M.R. Almasian, M. Ashoor, Fabrication of UV/TiO₂ nanotubes/Pd system by electrochemical anodization for furfural photocatalytic degradation, Caspian J. Environ. Sci. 15 (2017) 1-11. https://doi. org/10.22124/cjes.2017.2213.
- [86] M.D. França, L.M. Santos, T.A, Silva, K.A., Borges, V.M. Silva, A.O.T. Patrocinio, A.G. Trovó, A.E.H. Machado, Efficient mineralization of paracetamol using the nanocomposite TiO₂/Zn(II) phthalocyanine as photocatalyst, J. Braz. Chem. Soc. 27 (2016) 1094-1102. https://doi.org/10.5935/0103-5053.20160007.
- [87] X. Zhang, F. Wu, N. Deng, Degradation of paracetamol in self assembly β-cyclodextrin/TiO₂ suspension under visible irradiation, Catal. Commun. 11 (2010) 422–425, https://doi.org/10.1016/j.catcom.2009.11.013.

- [88] Y. Zhou, Q. Liu, X. Li, L. Ling, Y. Zhou, Efficient oxidation of paracetamol triggered by molecular-oxygen activation at β-cyclodextrin-modified titanate nanotubes, Chem. Asian J. 17 (2022), https://doi.org/10.1002/asia.202200352.
- [90] P.M. Álvarez, J. Jaramillo, F. López-Piñero, P.K. Plucinski, Preparation and characterization of magnetic TiO₂ nanoparticles and their utilization for the degradation of emerging pollutants in water, Appl. Catal. B: Environ. 100 (2010) 338–345, https://doi.org/10.1016/j.apcatb.2010.08.010.
- [91] A.-M. Abdel-Wahab, A.-S. Al-Shirbini, O. Mohamed, O. Nasr, Photocatalytic degradation of paracetamol over magnetic flower-like TiO₂/Fe₂O₃ core-shell nanostructures, J. Photochem. Photobiol. A: Chem. 347 (2017) 186–198, https:// doi.org/10.1016/j.jphotochem.2017.07.030.
- [92] O.F.S. Khasawneh, P. Palaniandy, L.P. Teng, Large-scale study for the photocatalytic degradation of paracetamol using Fe₂O₃/TiO₂ nanocomposite catalyst and CPC reactor under natural sunlight radiations, MethodsX 6 (2019) 2735–2743, https://doi.org/10.1016/j.mex.2019.11.016.
- [93] O.F.S. Khasawneh, P. Palaniandy, P. Palaniandy, M. Ahmadipour, H. Mohammadi, M.R. Bin Hamdan, Removal of acetaminophen using Fe₂O₃-TiO₂ nanocomposites by photocatalysis under simulated solar irradiation: optimization study, J. Environ Chem. Eng. 9 (2021), 104921, https://doi.org/10.1016/j. jecc.2020.104921.
- [94] X. Bi, G. Du, A. Kalam, D. Sun, W. Zhao, Y. Yu, Q. Su, B. Xu, A.G. Al-Sehemi, Constructing anatase TiO₂/Amorphous Nb₂O₅ heterostructures to enhance photocatalytic degradation of acetaminophen and nitrogen oxide, J. Colloid Interface Sci. 601 (2021) 346–354, https://doi.org/10.1016/j.jcjs.2021.05.120.
- [95] Z. Khani, D. Schieppati, C.L. Bianchi, D.C. Boffito, The sonophotocatalytic degradation of pharmaceuticals in water by MnO_x-TiO₂ systems with tuned bandgaps, Catalysts 9 (2019), https://doi.org/10.3390/catal9110949.
- [96] M.J.N. Gotostos, C.-C. Su, M.D.G. de Luna, M.-C. Lu, Kinetic study of acetaminophen degradation by visible light photocatalysis, J. Environ, Sci. Health A 49 (2014) 892–899, https://doi.org/10.1080/10934529.2014.894310.
- [97] J.C.T. Lin, M.D.G. de Luna, M.J.N. Gotostos, M.-C. Lu, Optimization of visiblelight photocatalytic degradation of acetaminophen by K₃[Fe(CN)₆]-modified TiO₂, J. Taiwan Inst. Chem. Eng. 49 (2015) 129–135, https://doi.org/10.1016/j. jtice.2014.11.030.
- [98] J.C.T. Lin, M.D.G. de Luna, G.I. Aranzamendez, M.-C. Lu, Degradations of acetaminophen via a K₂S₂O₈-doped TiO₂ photocatalyst under visible light irradiation, Chemosphere 155 (2016) 388–394, https://doi.org/10.1016/j. chemosphere.2016.04.059.
- [99] J.-C.-T. Lin, M.D.G. de Luna, M.J.N. Gotostos, M.-C. Lu, Effects of doping amounts of potassium ferricyanide with titanium dioxide and calcination durations on visible-light degradation of pharmaceuticals, Environ. Sci. Pollut. Res. 23 (2016) 22721–22733, https://doi.org/10.1007/s11356-016-7470-y.
- [100] M.L.P. Dalida, K.M.S. Amer, C.-C. Su, M.-C. Lu, Photocatalytic degradation of acetaminophen in modified TiO₂ under visible irradiation, Environ. Sci. Pollut. Res. 21 (2014) 1208–1216, https://doi.org/10.1007/s11356-013-2003-4.
- [101] M.D.G. de Luna, G.L. Aranzamendez, N.C. Tolosa, M.-C. Lu, Synthesis of novel potassium peroxodisulfate-modified titanium dioxide for photocatalytic oxidation of acetaminophen under visible light irradiation, Int. J. Environ. Sci. Technol. 14 (2017) 973–982, https://doi.org/10.1007/s13762-016-1193-y.
- [102] M. Malakootian, M. Pourshaban-Mazandarani, H. Hossaini, M.H. Ehrampoush, Preparation and characterization of TiO₂ incorporated 13X molecular sieves for photocatalytic removal of acetaminophen from aqueous solutions, Process Saf. Environ. Prot. 104 (2016) 334–345, https://doi.org/10.1016/j. psep.2016.09.018.
- [103] D. Papoulis, D. Panagiotaras, P. Tsigrou, K.C. Christoforidis, C. Petit, A. Apostolopoulou, E. Stathatos, S. Komarneni, I. Koukouvelas, Halloysite and sepiolite-TiO₂ nanocomposites: synthesis characterization and photocatalytic activity in three aquatic wastes, Mater. Sci. Semicond. Process. 85 (2018) 1–8, https://doi.org/10.1016/j.mssp.2018.05.025.
- [104] P. Jayasree, N. Remya, Photocatalytic degradation of paracetamol using aluminosilicate supported TiO₂, Water Sci. Technol. 82 (2020) 2114–2124, https://doi.org/10.2166/wst.2020.484.
- [105] R. Mu, Y. Ao, T. Wu, C. Wang, P. Wang, Synthesis of novel ternary heterogeneous anatase-TiO₂(B) biphase nanowires/Bi₄O₅I₂ composite photocatalysts for the highly efficient degradation of acetaminophen under visible light irradiation, J. Hazard. Mater. 382 (2020), 121083, https://doi.org/ 10.1016/j.jhazmat.2019.121083.
- [106] N. Kumar, A.S. Bhadwal, B. Mizaikoff, S. Singh, C. Kranz, Electrochemical detection and photocatalytic performance of MoS₂/TlO₂ nanocomposite against pharmaceutical contaminant: paracetamol, Sens. Bio-Sens. Res. 24 (2019), 100288, https://doi.org/10.1016/j.sbsr.2019.100288.
- [107] Y. Liu, M. Ren, X. Zhang, G. Yang, L. Qin, J. Meng, Y. Guo, Supramolecule selfassembly approach to direct Z-scheme TiO₂/g-C₃N₄ heterojunctions for efficient photocatalytic degradation of emerging phenolic pollutants, Appl. Surf. Sci. 593 (2022), 153401, https://doi.org/10.1016/j.apsusc.2022.153401.
- [108] V. Yadav, H. Sharma, A. Rana, V.K. Saini, Facile synthesis of boron and nitrogen doped TiO₂ as effective catalysts for photocatalytic degradation of emerging micro-pollutants, J. Ind. Eng. Chem. 107 (2022) 126–136, https://doi.org/ 10.1016/j.jiec.2021.11.035.
- [109] E.D.M. Isa, K. Shameli, H.J. Ch'ng, N.W. Che Jusoh, R. Hazan, Photocatalytic degradation of selected pharmaceuticals using green fabricated zinc oxide nanoparticles, Adv. Powder Technol. 32 (2021) 2398–2409, https://doi.org/ 10.1016/j.apt.2021.05.021.
- [110] L.A. Hernández-Carabalí, R. Sachdeva, J.B. Rojas-Trigos, E. Marín, C.D. Garcia, Monitoring the advanced oxidation of paracetamol using ZnO films via capillary

electrophoresis, J. Water Process Eng. 41 (2021), 102051, https://doi.org/10.1016/j.jwpe.2021.102051.

- [111] N. Kaneva, A. Bojinova, K. Papazova, D. Dimitrov, K. Zaharieva, Z. Cherkezova-Zheleva, A. Eliyas, Effect of thermal and mechano-chemical activation on the photocatalytic efficiency of ZnO for drugs degradation, Arch. Pharm. Res. 39 (2016) 1418–1425, https://doi.org/10.1007/s12272-016-0789-6.
- [112] B. Ramos, A.O.G. Silva, A.C.S.C. Teixeira, Immobilization of ZnO nanoparticles onto glass spheres: effects of annealing temperature, zinc oxide concentration, and number of coating rounds on the photocatalytic activity under visible light, Braz. J. Chem. Eng. 39 (2022) 403–414, https://doi.org/10.1007/s43153-021-00160-z.
- [113] M. Cantarella, A. di Mauro, A. Gulino, L. Spitaleri, G. Nicotra, V. Privitera, G. Impellizzeri, Selective photodegradation of paracetamol by molecularly imprinted ZnO nanonuts, Appl. Catal. B: Environ. 238 (2018) 509–517, https:// doi.org/10.1016/j.apcatb.2018.07.055.
- [114] B. Ramos, J.G.M. Carneiro, L.I. Nagamati, A.C.S.C. Teixeira, Development of intensified flat-plate packed-bed solar reactors for heterogeneous photocatalysis, Environ. Sci. Pollut. Res. 28 (2021) 24023–24033, https://doi.org/10.1007/ s11356-020-11806-9.
- [116] V.H.-T Thi., B.-K. Lee, Effective photocatalytic degradation of paracetamol using La-doped ZnO photocatalyst under visible light irradiation, Mater. Res. Bull. 96 (2017) 171-182. https://doi.org/10.1016/j.materresbull.2017.04.028.
- [117] U. Alam, A. Khan, D. Bahnemann, M. Muneer, Synthesis of iron and copper cluster-grafted zinc oxide nanorod with enhanced visible-light-induced photocatalytic activity, J. Colloid Interface Sci. 509 (2018) 68–72, https://doi. org/10.1016/j.jcjs.2017.08.093.
- [118] U. Alam, T.A, Shah, A. Khan, M. Muneer, One-pot ultrasonic assisted sol-gel synthesis of spindle-like Nd and V codoped ZnO for efficient photocatalytic degradation of organic pollutants, Sep. Purif. Technol. 212 (2019) 427-437. https://doi.org/10.1016/j.seppur.2018.11.048.
- [119] R. Al Abri, F. Al Marzouqi, A.T. Kuvarega, M.A. Meetani, S.M.Z. Al Kindy, S. Karthikeyan, Y. Kim, R. Selvaraj, Nanostructured cerium-doped ZnO for photocatalytic degradation of pharmaceuticals in aqueous solution, J. Photochem. Photobiol. A: Chem. 384 (2019), 112065, https://doi.org/ 10.1016/j.jphotochem.2019.112065.
- [120] A. di Mauro, C. Farrugia, S. Abela, P. Ref Alo, M. Grech, L. Falqui, G. Nicotra, G. Sfuncia, A. Mio, M.A. Buccheri, G. Rappazzo, M.V. Brundo, E.M. Scalisi, R. Pecoraro, C. Iaria, V. Privitera, G. Impellizzeri, Ag/ZnO/PMMA nanocomposites for efficient water reuse, ACS Appl, Bio Mater. 3 (2020) 4417–4426, https://doi.org/10.1021/acsabm.0c00409.
- [121] M.A. Al-Gharibi, H.H. Kyaw, J.N. Al-Sabahi, M.T. Zar Myint, Z.A. Al-Sharji, M. Z. Al-Abri, Silver nanoparticles decorated zinc oxide nanorods supported catalyst for photocatalytic degradation of paracetamol, Mater. Sci. Semicond. Process. 134 (2021), 105994, https://doi.org/10.1016/j.mssp.2021.105994.
- [122] B. Ramasamy, J. Jeyadharmarajan, P. Chinnaiyan, Novel organic assisted Ag-ZnO photocatalyst for atenolol and acetaminophen photocatalytic degradation under visible radiation: performance and reaction mechanism, Environ. Sci. Pollut. Res. 28 (2021) 39637–39647, https://doi.org/10.1007/s11356-021-13532-2.
- [123] M.Z.A. Warshagha, M. Muneer, Synthesis of ZnO Co-doped Ph-g-C₃N₄ for enhanced photocatalytic organic pollutants removal under visible light, Int. J. Environ. Anal. Chem. (2020), https://doi.org/10.1080/ 03067319.2020.1808631.
- [124] M. Akkari, P. Aranda, C. Belver, J. Bedia, A. Ben Haj Amara, E. Ruiz-Hitzky, Reprint of ZnO/sepiolite heterostructured materials for solar photocatalytic degradation of pharmaceuticals in wastewater, Appl. Clay Sci. 160 (2018) 3–8, https://doi.org/10.1016/j.clay.2018.02.027.
- [126] V. Vaiano, M. Matarangolo, O. Sacco, UV-LEDs floating-bed photoreactor for the removal of caffeine and paracetamol using ZnO supported on polystyrene pellets, Chem. Eng. J. 350 (2018) 703–713, https://doi.org/10.1016/j.cej.2018.06.011.
- [127] A.H.C. Khavar, G. Moussavi, A.R. Mahjoub, R. Luque, D. Rodríguez-Padrón, M. Sattari, Enhanced visible light photocatalytic degradation of acetaminophen with Ag₂₅S-ZnO@rGO core-shell microsphere as a novel catalyst: catalyst preparation and characterization and mechanistic catalytic experiments, Sep. Purif. Technol. 229 (2019), 115803, https://doi.org/10.1016/j. seppur.2019.115803.
- [128] L. Chen, J. Peng, F. Wang, D. Liu, W. Ma, J. Zhang, W. Hu, N. Li, P. Dramou, H. He, ZnO nanorods/Fe₃O₄-graphene oxide/metal-organic framework nanocomposite: recyclable and robust photocatalyst for degradation of pharmaceutical pollutants, Environ. Sci. Pollut. Res. 28 (2021) 21799–21811, https://doi.org/10.1007/s11356-020-12253-2.
- [129] M. Kohantorabi, G. Moussavi, S. Mohammadi, P. Oulego, S. Giannakis, Photocatalytic activation of peroxymonosulfate (PMS) by novel mesoporous Ag/ ZnO@NiFe₂O₄ nanorods, inducing radical-mediated acetaminophen degradation under UVA irradiation, Chemosphere 277 (2021), 130271, https://doi.org/ 10.1016/j.chemosphere.2021.130271.
- [130] M. Mohammadnia, E. Derakhshani, A. Naghizadeh, Photochemical degradation of an environmental pollutant by pure ZnO and MgO doped ZnO nanocatalysts, Iranian J. Chem. Chem. Eng. (IJCCE) 40 (2020) 83–91, https://doi.org/ 10.30492/ijcce.2019.36825.
- [131] M. Mansouri, M. Nademi, M.E. Olva, H. Lotfi, Study of methyl tert-butyl ether (MTBE) photocatalytic degradation with UV/TiO₂-ZnO-CuO nanoparticles, J. Chem. Health Risks 7 (2017) 19–32, https://doi.org/10.22034/ jchr.2017.544161.
- [132] H. Lee, J. Choi, S. Lee, S.-T. Yun, C. Lee, J. Lee, Kinetic enhancement in photocatalytic oxidation of organic compounds by WO₃ in the presence of Fenton-

like reagent, Appl. Catal. B: Environ. 138–139 (2013) 311–317, https://doi.org/ 10.1016/j.apcatb.2013.03.006.

- [133] K. Shahzad, M.B. Tahir, M. Ashraf, T. Nawaz, N.R. Khalid, M.R. Kabli, Interfacial growth of activated carbon on WO₃ nanoplates for enhanced photocatalytic activity by surface plasmon resonance, Plasmonics 15 (2020) 1205–1212, https:// doi.org/10.1007/s11468-020-01135-5.
- [134] P. Hasse Palharim, B. Lara Diego dos Reis Fusari, B. Ramos, L. Otubo, A.C. Silva Costa Teixeira, Effect of HCl and HNO₃ on the synthesis of pure and silver-based WO₃ for improved photocatalytic activity under sunlight, J. Photochem. Photobiol. A: Chem. 422 (2022) 113550. https://doi.org/10.1016/j. jphotochem.2021.113550.
- [135] J. Meng, X. Wang, Y. Liu, M. Ren, X. Zhang, X. Ding, Y. Guo, Y. Yang, Acidinduced molecule self-assembly synthesis of Z-scheme WO₃/g-C₃N₄ heterojunctions for robust photocatalysis against phenolic pollutants, Chem. Eng. J. 403 (2021), 126354, https://doi.org/10.1016/j.cej.2020.126354.
- [136] E.C. Umejuru, E. Prabakaran, K. Pillay, Coal fly ash decorated with graphene oxide-tungsten oxide nanocomposite for rapid removal of Pb²⁺ ions and reuse of spent adsorbent for photocatalytic degradation of acetaminophen, ACS Omega 6 (2021) 11155–11172, https://doi.org/10.1021/acsomega.0c04194.
- [137] C. Hu, J. Xu, Y. Zhu, A. Chen, Z. Bian, H. Wang, Morphological effect of BiVO₄ catalysts on degradation of aqueous paracetamol under visible light irradiation, Environ. Sci. Pollut. Res. 23 (2016) 18421–18428, https://doi.org/10.1007/ s11356-016-6975-8.
- [138] J. Sun, C. Wang, T. Shen, H. Song, D. Li, R. Zhao, X. Wang, Engineering the dimensional interface of BiVO₄-2D reduced graphene oxide (RGO) nanocomposite for enhanced visible light photocatalytic performance, Nanomaterials 9 (2019), https://doi.org/10.3390/nano9060907.
- [139] C. Orona-Návar, I. Levchuk, J. Moreno-Andrés, Y. Park, A. Mikola, J. Mahlknecht, M. Sillanpää, N. Ornelas-Soto, Removal of pharmaceutically active compounds (PhACs) and bacteria inactivation from urban wastewater effluents by UVA-LED photocatalysis with Gd³⁺ doped BiVO₄, J. Environ. Chem. Eng. 8 (2020), 104540, https://doi.org/10.1016/j.jece.2020.104540.
- [140] L. Wang, Z. Bian, Photocatalytic degradation of paracetamol on Pd-BiVO4 under visible light irradiation, Chemosphere 239 (2020), 124815, https://doi.org/ 10.1016/j.chemosphere.2019.124815.
- [141] X. Xiao, R. Hu, C. Liu, C. Xing, C. Qian, X. Zuo, J. Nan, L. Wang, Facile large-scale synthesis of β-Bi₂O₃ nanospheres as a highly efficient photocatalyst for the degradation of acetaminophen under visible light irradiation, Appl. Catal. B; Environ. 140–141 (2013) 433–443, https://doi.org/10.1016/j. apcatb.2013.04.037.
- [142] R. Rubio-Govea, C. Orona-Návar, S.F. Lugo-Bueno, N. Hernández, J. Mahlknecht, A. Garcia-Garcia, N. Ornelas-Soto, Bi₂O₃/rGO/Mo_nO_{3n-1} all-solid-state ternary Zscheme for visible-light driven photocatalytic degradation of bisphenol A and acetaminophen in groundwater, J. Environ. Chem. Eng. 8 (2020), 104170, https://doi.org/10.1016/j.jece.2020.104170.
- [143] D. Mao, J. Yuan, X. Qu, C. Sun, S. Yang, H. He, Size tunable Bi₃O₄Br hierarchical hollow spheres assembled with {0 0 1}-facets exposed nanosheets for robust photocatalysis against phenolic pollutants, J. Catal. 369 (2019) 209–221, https:// doi.org/10.1016/j.jcat.2018.11.016.
- [144] R. Zhou, D. Zhang, P. Wang, Y. Huang, Regulation of excitons dissociation in AgI/ Bi₃O₄Br for advanced reactive oxygen species generation towards photodegradation, Appl. Catal. B: Environ. 285 (2021), 119820, https://doi.org/ 10.1016/j.apcatb.2020.119820.
- [145] X. Wang, M. Brigante, W. Dong, Z. Wu, G. Mailhot, Degradation of acetaminophen via UVA-induced advanced oxidation processes (AOPs). Involvement of different radical species: HO, SO₄ and HO₂/O₂, Chemosphere 258 (2020), 127268 https://doi.org/10.1016/j.chemosphere.2020.127268.
 [146] Y. Guo, P. Wang, J. Qian, J. Hou, Y. Ao, C. c, Construction of a composite
- [146] Y. Guo, P. Wang, J. Qian, J. Hou, Y. Ao, C. c, Construction of a composite photocatalyst with significantly enhanced photocatalytic performance through combination of homo-junction with hetero-junction, Catal. Sci. Technol. 8 486–498. doi: 10.1039/c7cy02027a.
- [148] M. Danish, M. Muneer, Excellent visible-light-driven Ni-ZnS/g-C₃N₄ photocatalyst for enhanced pollutants degradation performance: insight into the photocatalytic mechanism and adsorption isotherm, Appl Surf. Sci. 563 (2021), 150262, https:// doi.org/10.1016/j.apsusc.2021.150262.
- [149] X. Liu, M. Cui, K. Cui, Y. Ding, X. Chen, C. Chen, X. Nie, Construction of Li/K dopants and cyano defects in graphitic carbon nitride for highly efficient peroxymonosulfate activation towards organic contaminants degradation, Chemosphere 294 (2022), 133700, https://doi.org/10.1016/j. chemosphere.2022.133700.
- [150] L.K.B. Paragas, V. Dien Dang, R.S. Sahu, S. Garcia-Segura, M.D.G. de Luna, J.A. I. Pimentel, R.-A. Doong, Enhanced visible-light-driven photocatalytic degradation of acetaminophen over CeO₂,/K-codoped C₃N₄ heterojunction with tunable properties in simulated water matrix, Sep. Purif. Technol. 272 (2021), 117567, https://doi.org/10.1016/j.seppur.2020.117567.
- [151] N. Masunga, B.B. Mamba, K.K. Kefeni, Magnetically separable samarium doped copper ferrite-graphitic carbon nitride nanocomposite for photodegradation of dyes and pharmaceuticals under visible light irradiation, J. Water Process Eng. 48 (2022), 102898, https://doi.org/10.1016/j.jwpe.2022.102898.
- [152] Y. Ling, G. Liao, P. Xu, L. Li, Fast mineralization of acetaminophen by highly dispersed Ag-g-C₃N₄ hybrid assisted photocatalytic ozonation, Sep. Purif. Technol. 216 (2019) 1–8, https://doi.org/10.1016/j.seppur.2019.01.057.

- [153] M. Shen, X. Zhang, S. Zhao, S. Wang, gCN-P: a coupled g-C₃N₄/persulfate system for photocatalytic degradation of organic pollutants under simulated sunlight, Environ. Sci. Pollut. Res. 29 (2022) 23280–23291, https://doi.org/10.1007/ s11356-021-17540-0.
- [154] Q. Ma, H. Zhang, R. Guo, Y. Cui, X. Deng, X. Cheng, M. Xie, Q. Cheng, B. Li, A novel strategy to fabricate plasmonic Ag/AgBr nano-particle and its enhanced visible photocatalytic performance and mechanism for degradation of acetaminophen, J. Taiwan Inst. Chem. Eng. 80 (2017) 176–183, https://doi.org/ 10.1016/j.jtice.2017.06.033.
- [155] G. Fan, X. Zheng, J. Luo, H. Peng, H. Lin, M. Bao, L. Hong, J. Zhou, Rapid synthesis of Ag/AgCl@ZIF-8 as a highly efficient photocatalyst for degradation of acetaminophen under visible light, Chem. Eng. J. 351 (2018) 782–790, https:// doi.org/10.1016/j.cej.2018.06.119.
- [156] J. Zhu, Z. Zhu, H. Zhang, H. Lu, Y. Qiu, L. Zhu, S. Küppers, Enhanced photocatalytic activity of Ce-doped Zn-Al multi-metal oxide composites derived from layered double hydroxide precursors, J. Colloid. Interface Sci. 481 (2016) 144–157, https://doi.org/10.1016/j.jcis.2016.07.051.
- [157] G. Di, Z. Zhu, H. Zhang, J. Zhu, H. Lu, W. Zhang, Y. Qiu, L. Zhu, S. Küppers, Simultaneous removal of several pharmaceuticals and arsenic on Zn-Fe mixed metal oxides: Combination of photocatalysis and adsorption, Chem. Eng. J. 328 (2017) 141–151, https://doi.org/10.1016/j.cej.2017.06.112.
- [158] J. Zhu, Z. Zhu, H. Zhang, H. Lu, W. Zhang, Y. Qiu, L. Zhu, S. Küppers, Calcined layered double hydroxides/reduced graphene oxide composites with improved photocatalytic degradation of paracetamol and efficient oxidation-adsorption of As(III), Appl. Catal. B: Environ. 225 (2018) 550–562, https://doi.org/10.1016/j. apcatb.2017.12.003.
- [159] K.M. Girish, S.C. Prashantha, H. Nagabhushana, C.R. Ravikumar, H. P. Nagaswarupa, R. Naik, H.B. Premakumar, B. Umesh, Multi-functional Zn₂TiO₄: Sm³⁺ nanopowders: excellent performance as an electrochemical sensor and an UV photocatalyst, J. Sci. Adv. Mater. Dev. 3 (2018) 151–160, https://doi.org/ 10.1016/j.jsand.2018.02.001.
- [160] T. Yan, T. Wu, Y. Zhang, M. Sun, X. Wang, Q. Wei, B. Du, Fabrication of In₂S₃/ Zn₂GeO₄ composite photocatalyst for degradation of acetaminophen under visible light, J. Colloid Interface Sci. 506 (2017) 197–206, https://doi.org/10.1016/j. jcis.2017.06.079.
- [161] P. Uddandarao, T.A. Hingnekar, R.M. Balakrishnan, E.R. Rene, Solar assisted photocatalytic degradation of organic pollutants in the presence of biogenic fluorescent ZnS nanocolloids, Chemosphere 234 (2019) 287–296, https://doi. org/10.1016/j.chemosphere.2019.05.265.
- [162] A. Khan, M. Danish, U. Alam, S. Zafar, M. Muneer, Facile synthesis of a Z-scheme ZnIn₂S₄/MoO₃ heterojunction with enhanced photocatalytic activity under visible light irradiation, ACS Omega 5 (2020) 8188–8199, https://doi.org/10.1021/ acsomega.0c00446.
- [163] M. Hojamberdiev, B. Czech, A.C. Göktaş, K. Yubuta, Z.C. Kadirova, SnO₂@ZnS photocatalyst with enhanced photocatalytic activity for the degradation of selected pharmaceuticals and personal care products in model wastewater, J. Alloys Compd. 827 (2020), 154339, https://doi.org/10.1016/j. iallcom.2020.154339.
- [164] T.A. Fernandes, S.G. Mendo, L.P. Ferreira, N.R. Neng, M.C. Oliveira, A. Gil, M. D. Carvalho, O.C. Monteiro, J.M.F. Nogueira, M.J. Calhorda, Photocatalytic degradation of acetaminophen and caffeine using magnetite-hematite combined nanoparticles: kinetics and mechanisms, Environ. Sci. Pollut. Res. 28 (2021) 17228–17243, https://doi.org/10.1007/s11356-020-12016-z.
- [165] Ö. Tuna, E.B. Simsek, Anchoring LaFeO₃ perovskites on the polyester filters for flowthrough photocatalytic degradation of organic pollutants, J. Photochem. Photobiol. A: Chem. 418 (2021), 113405, https://doi.org/10.1016/j. jphotochem.2021.113405.
- [166] E. Abreu, M.Z. Fidelis, M.E. Fuziki, R.M. Malikoski, M.C. Mastsubara, R.E. Imada, J.L. Diaz de Tuesta, H.T. Gomes, M.D. Anziliero, B. Baldykowski, D.T. Dias, G. G. Lenzi, Degradation of emerging contaminants: effect of thermal treatment on Nb₂O₅ as photocatalyst, J. Photochem. Photobiol. A: Chem. 419 (2021), 113484, https://doi.org/10.1016/j.jphotochem.2021.113484.
- [167] E. Díez-Mato, F.C. Cortezón-Tamarit, S. Bogialli, D. García-Fresnadillo, M. D. Marazuela, Phototransformation of model micropollutants in water samples by photocatalytic singlet oxygen production in heterogeneous mèdium, Appl. Catal. B: Environ. 160–161 (2014) 445–455, https://doi.org/10.1016/j. apcatb.2014.05.050.
- [168] R. Kumar, A. Akbarinejad, T. Jasemizad, R. Fucina, J. Travas-Sejdic, L.P. Padhye, The removal of metformin and other selected PPCPs from water by poly(3,4ethylenedioxythiophene) photocatalyst, Sci. Total. Environ. 751 (2021), 142302, https://doi.org/10.1016/j.scitotenv.2020.142302.
- [169] D. González-Muñoz, A. Gómez-Avilés, C.B. Molina, J. Bedia, C. Belver, J. Alemán, S. Cabrera, Anchoring of 10-phenylphenothiazine to mesoporous silica materials: a water compatible organic photocatalyst for the degradation of pollutants, J. Mater. Sci. Technol. 103 (2022) 134–143, https://doi.org/10.1016/j. jmst.2021.07.004.
- [170] J. Lee, S. Hong, Y. MacKeyev, C. Lee, E. Chung, I.J. Wilson, J.-H. Kim, P.J. J. Alvarez, Photosensitized oxidation of emerging organic pollutants by tetrakis C 60 aminofullerene-derivatized silica under visible light irradiation, Environ. Sci. Technol. 45 (2011) 10598–10604, https://doi.org/10.1021/es2029944.
- [171] R.R. Solís, A. Gómez-Avilés, C. Belver, J.J. Rodriguez, J. Bedia, Microwaveassisted synthesis of NH₂-MIL-125(Ti) for the solar photocatalytic degradation of aqueous emerging pollutants in batch and continuous tests, J. Environ. Chem. Eng. 9 (2021), 106230, https://doi.org/10.1016/j.jece.2021.106230.
- [172] V. Muelas-Ramos, M. Peas-Garzón, J.J. Rodriguez, J. Bedia, C. Belver, Solar photocatalytic degradation of emerging contaminants using NH₂-MIL-125 grafted

by heterocicles, Sep. Purif. Technol. 297 (2022), 121442, https://doi.org/10.1016/j.seppur.2022.121442.

- [173] A. Gómez-Avilés, M. Peñas-Garzón, J. Bedia, D.D. Dionysiou, J.J. Rodríguez, C. Belver, Mixed Ti-Zr metal-organic-frameworks for the photodegradation of acetaminophen under solar irradiation, Appl. Catal. B: Environ. 253 (2019) 253–262, https://doi.org/10.1016/j.apcatb.2019.04.040.
- [174] V. Muelas-Ramos, C. Belver, J.J. Rodriguez, J. Bedia, Synthesis of noble metaldecorated NH₂-MIL-125 titanium MOF for the photocatalytic degradation of acetaminophen under solar irradiation, Sep. Purif. Technol. 272 (2021), 118896, https://doi.org/10.1016/j.seppur.2021.118896.
- [175] H.E. Emam, M. El-Shahat, R.M. Abdelhameed, Observable removal of pharmaceutical residues by highly porous photoactive cellulose acetate@MIL-MOF film, J. Hazard. Mater. 414 (2021), 125509, https://doi.org/10.1016/j. jhazmat.2021.125509.
- [176] A. Kuila, P. Saravanan, Intramolecular orbital engineered hetero bimetallic Ce-Fe MOF with reduced transition energy and enhanced visible light property, Appl. Organomet. Chem. 34 (2020), https://doi.org/10.1002/aoc.5728.
- [177] F. Liu, C. Nie, Q. Dong, Z. Ma, W. Liu, M. Tong, AgI modified covalent organic frameworks for effective bacterial disinfection and organic pollutant degradation under visible light irradiation, J. Hazard. Mater. 398 (2020), 122865, https://doi. org/10.1016/j.jhazmat.2020.122865.
- [178] F. Liu, Z. Ma, Y. Deng, M. Wang, P. Zhou, W. Liu, S. Guo, M. Tong, D. Ma, Tunable covalent organic frameworks with different heterocyclic nitrogen locations for efficient Cr(VI) reduction, Escherichia coli disinfection, and paracetamol degradation under visible-light irradiation, Environ. Sci. Technol. 55 (2021) 5371–5381, https://doi.org/10.1021/acs.est.0c07857.
- [179] B. Zhang, F. Liu, C. Nie, Y. Hou, M. Tong, Photocatalytic degradation of paracetamol and bisphenol A by chitosan supported covalent organic framework thin film with visible light irradiation, J. Hazard. Mater. 435 (2022), 128966, https://doi.org/10.1016/j.jhazmat.2022.128966.
- [180] R. Katal, M.H. Davood Abadi Farahani, H. Jiangyong, Degradation of acetaminophen in a photocatalytic (batch and continuous system) and photoelectrocatalytic process by application of faceted-TiO₂, Sep. Purif. Technol. 230 (2020) 115859. https://doi.org/10.1016/j.seppur.2019.115859.
- [181] R. Montenegro-Ayo, J.C. Morales-Gomero, H. Alarcon, S. Cotillas, P. Westerhoff, S. Garcia-Segura, Scaling up photoelectrocatalytic reactors: a TiO₂ nanotubecoated disc compound reactor effectively degrades acetaminophen, Water (Switzerland) 11 (2019), https://doi.org/10.3390/w11122522.
- [182] P. Kumari, N. Bahadur, X.A. Conlan, M. Laleh, L. Kong, L.A. O'Dell, L.F. Dumée, A. Merenda, Atomically-thin Schottky-like photo-electrocatalytic cross-flow membrane reactors for ultrafast remediation of persistent organic pollutants, Water Res. 218 (2022), 118519, https://doi.org/10.1016/j.watres.2022.118519.
- [183] H.C. Arredondo Valdez, G. García Jiménez, S. Gutiérrez Granados, C. Ponce de León, Degradation of paracetamol by advance oxidation processes using modified reticulated vitreous carbon electrodes with TiO₂ and CuO/TiO₂/Al₂O₃, Chemosphere 89 (2012) 1195–1201, https://doi.org/10.1016/j. chemosphere.2012.07.020.
- [184] B. Zhao, H. Yu, Y. Liu, Y. Lu, W. Fan, W. Qin, M. Huo, Enhanced photoelectrocatalytic degradation of acetaminophen using a bifacial electrode of praseodymium-polyethylene glycol-PbO₂//Ti//TiO₂-nanotubes, Chem. Eng. J. 410 (2021), 128337, https://doi.org/10.1016/j.cej.2020.128337.
- [185] R. Hernández, I. Olvera-Rodríguez, C. Guzmán, A. Medel, L. Escobar-Alarcón, E. Brillas, I. Sirés, K. Esquivel, Microwave-assisted sol-gel synthesis of an Au-TiO₂ photoanode for the advanced oxidation of paracetamol as model pharmaceutical pollutant, Electrochem. Commun. 96 (2018) 42–46, https://doi.org/10.1016/j. elecom.2018.09.009.
- [186] I. Olvera-Rodríguez, R. Hernández, A. Medel, C. Guzmán, L. Escobar-Alarcón, E. Brillas, I. Sirés, K. Esquivel, TiO₂/Au/TiO₂ multilayer thin-film photoanodes synthesized by pulsed laser deposition for photoelectrochemical degradation of organic pollutants, Sep. Purif. Technol. 224 (2019) 189–198, https://doi.org/ 10.1016/j.seppur.2019.05.020.
- [187] A.A. Nada, B.O. Orimolade, H.H. El-Maghrabi, B.A. Koiki, M. Rivallin, M. F. Bekheet, R. Viter, D. Damberga, G. Lesage, I. Iatsunskyi, E. Coy, M. Cretin, O. A. Arotiba, M. Bechelany, Photoelectrocatalysis of paracetamol on Pd-ZnO/Ndoped carbon nanofibers electrode, Appl. Mater. Today 24 (2021), 101129, https://doi.org/10.1016/j.apmt.2021.101129.
- [188] B.O. Orimolade, B.A. Koiki, G.M. Peleyeju, O.A. Arotiba, Visible light driven photoelectrocatalysis on a FTO/BiVO₄/BiOI anode for water treatment involving emerging pharmaceutical pollutants, Electrochim. Acta 307 (2019) 285–292, https://doi.org/10.1016/j.electacta.2019.03.217.

Further reading

- [29] N. Klamerth, N. Miranda, S. Malato, A. Agüera, A.R. Fernández-Alba, M. I. Maldonado, J.M. Coronado, Degradation of emerging contaminants at low concentrations in MWTPs effluents with mild solar photo-Fenton and TiO₂, Catal. Today 144 (2009) 124–130, https://doi.org/10.1016/j.cattod.2009.01.024.
- [33] C.M. Lee, N.A.B.A. Aziz, P. Palaniandy, S.S. Abu Amr, Performance of natural sunlight on paracetamol removal from synthetic pharmaceutical wastewater using heterogeneous TiO₂ photocatalyst, Desal, Water Treat. 78 (2017) 341–349, https://doi.org/10.5004/dwt.2017.20879.
- [34] O. Alvarado-Rolon, R. Natividad, J. Ramírez-García, J. Orozco-Velazco, J.
 A. Hernandez-Servin, A. Ramírez-Serrano, Kinetic modelling of paracetamol degradation by photocatalysis: Incorporating the competition for photons by the

E. Brillas and J. Manuel Peralta-Hernández

organic molecule and the photocatalyst, J. Photochem. Photobiol. A: Chem. 412 (2021), 113252, https://doi.org/10.1016/j.jphotochem.2021.113252.

- [35] D.A. Pino-Sandoval, L. Hinojosa-Reyes, J.L. Guzmán-Mar, J.C. Murillo-Sierra, A. Hernández-Ramírez, Solar photocatalysis for degradation of pharmaceuticals in hospital wastewater: influence of the type of catalyst, aqueous matrix, and toxicity evaluation, Water Air Soil Pollut. 233 (2022), https://doi.org/10.1007/s11270-021-05484-7.
- [38] B. Boutra, A. Sebti, M. Trari, Response surface methodology and artificial neural network for optimization and modeling the photodegradation of organic pollutants in water, Int. J. Environ. Sci. Technol. (2022), https://doi.org/10.1007/s13762-021-03875-1.

- Separation and Purification Technology 309 (2023) 122982
- [89] H. Peng, Y. Chen, L. Mao, X. Zhang, Significant changes in the photo-reactivity of TiO₂ in the presence of a capped natural dissolved organic matter layer, Water Res. 110 (2017) 233–240. https://doi.org/10.1016/j.watres.2016.12.025.
- 110 (2017) 233–240, https://doi.org/10.1016/j.watres.2016.12.025.
 [115] M. Shakir, M. Faraz, M.A. Sherwani, S.I. Al-Resayes, Photocatalytic degradation of the paracetamol drug using lanthanum doped ZnO nanoparticles and their invitro cytotoxicity assay, J. Lumin. 176 (2016) 159–167, https://doi.org/10.1016/j.jlumin.2016.03.027.
- [125] M. Akkari, P. Aranda, C. Belver, J. Bedia, A. Ben Haj Amara, E. Ruiz-Hitzky, ZnO/ sepiolite heterostructured materials for solar photocatalytic degradation of pharmaceuticals in wastewater, Appl. Clay Sci. 156 (2018) 104–109, https://doi. org/10.1016/j.clay.2018.01.021.