Photocatalytic, electrocatalytic and photoelectrocatalytic degradation of pharmaceuticals in aqueous media: Analytical methods, mechanisms, simulations, catalysts and reactors

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ABSTRACT

Pharmaceuticals are used every day in most parts of the world and great proportions of these substances are excreted unaltered or as active sub-products, posing a threat of pollution. To protect the aquatic ecosystems, innovative solutions such as photocatalysis, electrocatalysis and photoelectrocatalysis are required. In this article we provide a comprehensive review of photo- and electrocatalytic techniques for the removal of pharmaceuticals from water and wastewaters. The analytical and toxicity methods commonly used to study the degradation of pharmaceuticals are presented, and it is pointed high performance liquid chromatography analysis as the most common analytical method to evaluate the efficiency in the pharmaceutical's degradation. However, it is also highlighted that the evaluation of the toxicity is fundamental to ensure adequate treatment. The determination of the reactive species and the mechanistic evaluation of pharmaceuticals degradation are essential to understanding and enhancing the degradation process. A deep discussion of photocatalysis, electrocatalysis and photoelectrocatalysis principles and practical examples of their application in pharmaceuticals treatment is presented. The catalytic materials and the reactors used in these processes for the removal of pollutants are reviewed focusing on some representative examples. The reusability of catalysts is still restricted to a few reuse cycles. It was observed very limited results in the treatment of larger amounts of effluent and a lack of information about process costs, which were correlated to the difficulty of application of these techniques on real scale. Finally, the main advantages of photocatalysis, electrocatalysis and photoelectrocatalysis as high efficiency on pharmaceuticals degradation, and the main drawbacks, as the low quantum efficiency and/or high energetic consume are pointed out along with alternatives to overcome these limitations.

1. Introduction

Pharmaceuticals are an important class of substances used for healing and preventing diseases as well as improving the quality of life. Nevertheless, they are also emerging as environmental pollutants that can adversely affect the aquatic environment and so have long-term consequences for human health (Zhou et al., 2020). They reach the natural environment in its development stage as raw materials, during the production, transportation and storage, as well as through domestic sewage, hospitals and industrial wastewater, livestock farming, and solid-waste leachate, among other daily human activities (Rodriguez-Mozaz et al., 2020). The situation is worsened by their indiscriminate use (without medical planning) coupled with improper disposal (de Oliveira et al., 2020). Several classes of pharmaceuticals used in human medicine are only partially metabolized by the organism, and are excreted unaltered or in active forms. For example, more than 75% of the antibiotics from the tetracyclines family are excreted as active metabolites (Xu et al., 2021).

Numerous pharmaceuticals were already found in surface, ground and drinking water in concentrations from parts-per-trillion (ng/L) to

parts-per-billion (μg/L) (Yang et al., 2017). In Europe, the most frequently detected and quantified pharmaceuticals in environmental samples include three antibiotics (sulfamethoxazole, trimethoprim and clarithromycin), four analgesic anti-inflammatory drugs (diclofenac, ibuprofen, naproxen, paracetamol (acetaminophen) and ketoprofen) and two psychotropic drugs (carbamazepine and venlafaxine) (Fekadu et al., 2019).

Once pharmaceuticals or their by-products reach the environment, they can cause multiple adverse effects, such as aquatic toxicity, the growth of resistant and multi-resistance pathogenic bacteria, the transference of an antibiotic-resistant gene to a new generation of microorganisms (making them more resistant than before), genotoxicity, endocrine disorders and other harmful ecotoxicological effects (Jose et al., 2020).

There are still no specific laws or discharge limits for effluents containing pharmaceuticals. However, the Decision (EU) 2018/840 introduces a watch list of substances for EU-wide monitoring, which includes four pharmaceutical compounds/classes (17-alpha-ethinylestradiol, macrolide antibiotics, amoxicillin, ciprofloxacin) (European Commission, 2018). The Swiss Water Protection Act proposes evaluating the effectiveness of wastewater treatment in plants that have implemented advanced treatments with either ozone or activated carbon. This act lists 12 indicator substances that must be abated, on average, by 80% over the whole treatment plant. Among the 12 indicator substances, 10 of them are pharmaceuticals (amisulpride, carbamazepine, citalopram, clarithromycin, diclofenac, hydrochlorothiazide, metoprolol, venlafaxine, candesartan, irbesartan) (Joint Norman Water Europe Position Paper, 2019). Despite not specifying the monitoring of pharmaceuticals, the US Unregulated Contaminant Monitoring Rule (UCMR) and the Australian Drinking Water Guidelines (ADWG) list 30 chemical contaminants to be monitored and strategies for managing drinking-water systems, respectively (NHMRC, 2018; U.S.EPA, 2016).

Conventional water- and wastewater-treatment plants (WWTPs) were originally designed for the removal of suspended solids and biodegradable organic matter; as such they exhibit variable removal efficiencies (from 0 to 100%) for pharmaceuticals (Desbiolles et al., 2018). For antibiotics, values of 4% for ofloxacin and 74% for amoxicillin removal were already reported (Yang et al., 2017). It is clear that conventional wastewater treatments fall short of the required efficiency. Several alternative technologies have been studied and applied to reduce the potential risk of pharmaceuticals to the environment and human health, including membrane filtration (Bhattacharya et al., 2020; Heo et al., 2019; Reddy et al., 2017), adsorption (Escudero-Curiel et al., 2021; Jaria et al., 2021; Jia et al., 2021; Liu et al., 2021), Fenton processes (Hong et al., 2020; Mitsika et al., 2021; Scaria et al., 2021; Talwar et al., 2021), ozonation (Kharel et al., 2020; Kim et al., 2020; Mathon et al., 2021; C. Wang et al., 2020), sulfate radical-based oxidation (Smaali et al., 2021; Telegang Chekem et al., 2020; Wang et al., 2020 ; Zhang et al., 2021), and ionizing radiation (Reinholds et al., 2017; Sági et al., 2018; Shen et al., 2019a, 2019b). However, an effective, safe, low-cost, high-technology-readiness-level (TRL) alternative, which could be a concrete option to be used together with a conventional treatment, still needs to be developed. The combination of an appropriated catalyst with an optimized reactor design allows the effective use of the catalyst active sites and should enhance the system efficiency along with economic advantages (Darvishi et al., 2016).

In this context, photocatalysis, electrocatalysis and photoelectrocatalysis with immobilized catalysts are promising technologies because of their environmental friendliness, easy operation, lack of sludge generation, high removal rate of emerging pollutants (>80%), effectiveness in disinfection and the possibility of solar-energy utilization (Espíndola and Vilar, 2020). In fact, concerning the research on pharmaceuticals' degradation, these three technologies combined exhibit exponential growth and correspond to almost 20% of the published studies in the past 20 years (between 2000 and 2020), as shown in Fig. 1.
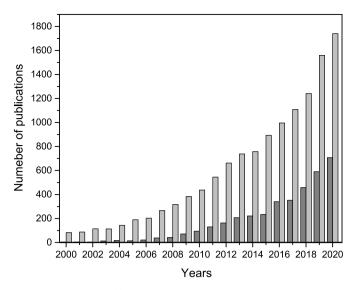

Fig. 1. Number of publications per year (2000–2020). Search terms: ■ "pharmaceutica* and (photocataly* or electrocataly* or photoelectrocataly*)". Results: total of 3724 documents; ■ "pharmaceutica* and degradation". Results: total of 12,572 documents. Source: Web of Science on August 2021.

Review articles focused on the treatment of water and wastewater contaminated with pharmaceuticals are generally: i) very specific, limited to a single treatment technique or contaminant (Abdurahman and Abdullah, 2020; Awofiranye et al., 2020; Mohapatra et al., 2014b; Prasannamedha and Kumar, 2020; Sodhi et al., 2021), or ii) very embracing, exploring several classes of treatment or compounds (Alharbi and Price, 2017; Bourgin et al., 2018; de Oliveira et al., 2020; Dhangar and Kumar, 2020; Espíndola and Vilar, 2020; Kanakaraju et al., 2018). There is a lack of reviews that cover pharmaceuticals' degradation by photocatalytic, electrocatalytic, and photoelectrocatalytic processes. This review will critically review and compare the fundamentals, efficiencies and applicability potential of photocatalysis (PC), electrocatalysis (EC) and photoelectrocatalysis (PEC) in terms of the degradation of the pharmaceutical. Since Fenton and other Iron-based processes are already very well discussed and reviewed in other works (Brillas, 2020; Ismail et al., 2021; Moreira et al., 2017), in this review we will focus on the use of other catalysts, including TiO_2, BDD and heterostructured materials. We present an overview of the analytical techniques necessary to follow the concentration of pharmaceuticals and by-products formed, along with the toxicity tests more appropriate to evaluate the final quality of the treated water. The catalysts commonly used and their characteristics, as well as the design of the reactors combined with different sources of radiation for batch and continuous treatment, are also discussed. The high efficiency on pharmaceuticals degradation is one of the main advantages of PC, EC and PEC processes. However, some drawbacks, including the low quantum efficiency of commercial catalysts and/or high energetic consumption, still difficult the application of these processes on larger scale. Some challenges and alternatives to overcome these limitations are emphasized in the prospects section.

2. Detection, quantification and toxicity evaluation of pharmaceuticals

During the degradation of pharmaceuticals, it is essential to monitor the specific compound's decay, its mineralization, the formation of by-products, and the toxicity of the final effluent. To understand the steps involved in the degradation process, it is desirable to evaluate the oxidative ($OH^•$, $O_2^{•-}$, $HO_2^•$, $SO_5^{•-}$) and reducing (e_{aq}^-) species formed during the catalytic reaction. Only an evaluation of all these parameters provides a complete view of the degradation process. Table 1 shows the

Table 1
Techniques most used to check the viability of a particular degradation process.

PERFORMANCE	BY-PRODUCTS IDENTIFICATION	REACTIVE SPECIES IDENTIFICATION	TOXICITY
<u>MINERALIZATION</u> • TOC <u>GENERAL ANALYSIS</u> • UV-VIS • COD <u>COMPOUNDS DECAY</u> • HPLC/GC • UV-VIS • ELECTROCHEMISTRY	• HPLC • GC-MS • LC-MS • IC	• FLUORESCENCE • QUENCHING • HPLC • EPR	• *Pseudokirchneriella subcapitata* • *Vibrio fischeri* • *Daphnia magna*

techniques most used to check the viability of a particular degradation process.

The decay kinetics of the initial pollutant is usually evaluated by high-performance liquid chromatography (HPLC) or gas chromatography (GC), noting that sample preparation for HPLC is usually easier than that for GC (Feier et al., 2018). Furthermore, the low volatility and/or poor thermal stability of some pharmaceuticals can limit the applicability of GC analysis (Brillas and Sirés, 2015). In fact, as shown in Table 2, liquid chromatography with separation through a reverse-phase C18 column is the primary method used to follow the decay of pharmaceuticals. Nevertheless, for specific compounds, including ampicillin, paracetamol and ciprofloxacin, alternative, simpler methods, such as electrochemical sensors (Raymundo-Pereira et al., 2017; Yang et al., 2017), Raman (He et al., 2010) and ultraviolet–visible spectroscopies (Gupta et al., 2021), can also be used. It is important to mention that for all techniques, depending on the pharmaceutical's initial concentration and the method's sensibility, pre-concentration of the samples might be required. Solid-phase extraction (SPE), liquid-liquid extraction (LLE), liquid-liquid micro-extraction (LLME) and solid-phase microextraction (SPME) are the most common sample-preparation techniques used for pharmaceutical monitoring (Feier et al., 2018).

Evaluating the decay of the total organic carbon (TOC), chemical oxygen demand (COD) and UV–vis spectra (200–300 nm) can also provide useful information about the mineralization, organics oxidation, and aromatic or unsaturated molecules' abatement, respectively (Brillas and Sirés, 2015).

A crucial task that concerns pharmaceuticals' degradation is the elucidation of the reaction mechanism, which can be achieved through the detection of intermediates and by-products, and the detection/determination of the reactive species that are formed (Brillas and Sirés, 2015; Zhang et al., 2021).

Cyclic and aromatic intermediates and low-molecular-weight carboxylic acids are usually detected by liquid chromatography with a variety of mass-spectrometry detectors (LC-MS, LC-MS-MS, LC-QTOF-MS, LC-QTOF-MS-MS, UPLC-MS, UPLC-MS-MS, etc.). Gaseous chromatography is an alternative for detecting small molecules containing –OH groups, because they can be derivatized. In this case, both polar and non-polar columns can be used for the separation of intermediates (Brillas and Sirés, 2015). Another strategy is determining low-molecular-weight carboxylic acids, formed through the successive oxidative cleavage of aromatic products, by ion-exclusion chromatography. In this case, a regular HPLC can be equipped with an appropriated column (Bio-rad Aminex HPX 87H column 300 mm × 7.8 mm (i.d.) or Phenomenex RezexTM ROA-Organic Acid H+ (8%) 300 mm × 7.8 mm) and a simple 4 mM H_2SO_4 solution can be used as the mobile phase (Espíndola et al., 2019; Guinea et al., 2010). Finally, inorganic ions that can form (e.g., Cl^-, SO_4^{2-}, F^-, NH_4^+, NO_3^-, etc.) can be accurately quantified by ionic chromatography, using appropriate anion/cation columns and a conductivity detector (Brillas and Sirés, 2015).

Concerning the identification, quantification and determination of the reactive species' contribution during the pharmaceuticals' removal by advanced oxidation processes (AOPs), the most common methods are electron paramagnetic resonance (EPR), HPLC and quenching

experiments, respectively (M. He et al., 2021). EPR is a technique capable of identifying molecules with one or more unpaired electrons, as radicals, providing an effective way to detect the reactive species formed during the catalytic processes. However, as the reactive species are very reactive and have a short lifetime (~μs), their direct detection is difficult. Thus, the EPR spin-trap method is based on the use of trap agents to derivatize the reactive species into longer-lifetime species, allowing their identification. The commonly employed trap agents are 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) for $OH^•$, $SO_4^{•-}$ and, $O_2^{•-}$, and 2,2,6,6-Tetramethylpiperidine (TEMP) for singlet oxygen ($^1O_2$) (Wang et al., 2020). After the spin-adduct DMPO-$OH^•$ forms, the molecule's lifetime is increased to 55 min (He et al., 2021).

The principle of using HPLC to quantify the reactive species is also based on the strategy of generating stabilized intermediates through the reaction with trap agents. In this case, the preferable trap agents include benzoic acid, hydroxybenzoic acid, terephthalic acid and dimethyl sulfoxide (Wang and Wang, 2020). By correlating the concentration of the intermediates with the reactive species, it is possible to determine their concentration. Another approach to quantifying $OH^•$ radicals is to use the fluorescence-probe method, through the combination of a non-fluorescent probe with $OH^•$ radicals to form a stable adduct. Benzoic and terephthalic acids are examples of molecules that can scavenge $OH^•$ and form fluorescent compounds (Wang et al., 2020).

Quenching experiments can be used to determine the reactive species' contribution and indirectly identify the main species involved in the degradation process. It is fundamental to choose the appropriate scavenger agents to suppress the target reactions and thus allow an indirect identification of the reactive species. Furthermore, the scavenger concentration is also important and should be in large excess, with the molar ratio of the scavenger:reactive species being at least 500:1 (Wang and Wang, 2020). Some examples of reactive species and their usual scavenger agents include i) hydroxyl radicals: tertiary butanol, methanol, ethanol, n-butanol, isopropanol; ii) sulfate radicals: ethanol, methanol, 1-octanol; iii) superoxide radicals: benzoquinone, chloroform; iv) singlet oxygen: sodium azide; v) electron: potassium dichromate, silver nitrate; vi) electron-hole: EDTA, potassium iodine, ammonium oxalate (Diao et al., 2015; M. He et al., 2021; Wang and Wang, 2020; Wang et al., 2020).

Another fundamental study to evaluate the viability of a degradation process is the evolution of the solution's toxicity with time, or at least the toxicity of the final effluent (Brillas and Sirés, 2015). For this purpose, organisms from different trophic levels can be used, for instance, the crustacean *Daphnia magna,* the algae *Pseudokirchneriella subcapitata* and the bacteria *Vibrio fischeri*, which are the most used species for assessing the toxicity of pharmaceuticals (Desbiolles et al., 2018). Nonetheless, it is important to consider that different species could be more sensitive for acute or chronic exposure, according to the type of pharmaceutical. Thus, it is important to identify which organisms are the most relevant for specific pharmaceuticals. For anti-inflammatory drugs, such as ibuprofen and naproxen, crustaceans are reported to be the most sensitive organisms (Harada et al., 2008). Crustaceans are also reported to be sensitive to betablockers such as propranolol (Ferrari et al., 2004). While for antibiotics, like amoxicillin and clarithromycin,

Table 2
HPCL operating conditions for monitoring pharmaceutical compounds during degradation processes for their removal.

Therapeutic class	Compound	Initial concentration and sample preparation	Degradation process	Analytical method/ Equipment	Operating conditions	LOD and LOQ	Ref.
Antibiotics	amoxicillin	10–30 mg L^{-1}	Sonocatalysis/ electrolysis with magnesium oxide nanocatalyst	HPLC system coupled with a UV detector	Reversed-phase C18 column (250 × 4.6 mm, 5 μm); mobile phase of 40:60 methanol: phosphate buffer (pH 4.5) with flow rate of 1 mL/min; the detection wavelength was 254 nm	–	Darvishi Cheshmeh Soltani et al. (2018)
	azithromycin	20 mg L^{-1}; Centrifugation to remove the photocatalyst	Photocatalysis with ZrO$_2$/Ag@TiO$_2$ nanocomposite	HPLC system coupled with a UV detector (HPLC-UV)	Reversed-phase C18 column (150 × 4.6 mm, 5 μm); mobile phase of 0.1% of formic acid solutions in acetonitrile and water with flow rate of 0.8 mL/ min in gradient mode; the detection wavelength was 274 nm	–	Naraginti et al. (2019)
	ciprofloxacin	~35 mg L^{-1}	Fenton-like system	HPLC system coupled with a UV detector (HPLC-UV)	Reversed-phase C18 column (150 × 4.6 mm, 5 μm); mobile phase of water (containing 0.1% formic acid) and acetonitrile with flow rate of 0.5 mL/min at 30 °C; injection volume of 20 μL and detection wavelength at 278 nm	–	Diao et al. (2017)
	norfloxacin	20 mg L^{-1}	Iron based reactions	HPLC system coupled with a UV detector (HPLC-UV)	Reversed-phase C18 column (150 × 4.6 mm, 5 μm); mobile phase of water (containing 0.1% formic acid) and acetonitrile with volume ratio 73:27 and flow rate of 0.8 mL/min at 30 °C; injection volume of 20 μL and detection wavelength at 278 nm	–	(J. J. Liu et al., 2018)
	oxytetracycline	20 mg L^{-1}; Filtration with 0.45 μm nylon membrane filter	Photocatalysis with TiO$_2$	HPLC equipped with a diode array detector (HPLC-DAD)	Reversed-phase C18 column (125 × 4 mm, 5 μm); mobile phase of mixture of acetonitrile/ methanol/0.014 M oxalic acid in gradient mode; injection volume of 50 μL and flow rate of 0.8 mL/ min. Retention time of 5.8 min the DAD detector was set at 354 nm	0.3 and 1.2 mg L^{-1}, respectively	Espíndola et al. (2019)
Anti-cancer drugs	Anastrozole	50–500 mg L^{-1}; Filtration with 0.22 μm PVDF membrane filter	Photo-Fenton	LC system coupled to QTOF mass spectrometer (LC-QTOF MS)	Reversed-phase C18 column (150 × 2.1 mm, 3 μm); mobile phase of acetonitrile and ultrapure water acidified with 0.1% formic acid at a flow rate of 0.5 mL/min; gradient mode; injection volume of 10 μL and retention time of 18.5 min. Detection with QTOF MS operated in positive ionization mode, with the following conditions: capillary at 4000 V, nebulizer at 4 bar, drying gas at 8 L min^{-1}, and gas temperature at 200 °C. Broadband collision-induced dissociation acquisition of 25 and 50 eV. MS information obtained in scan mode, in the m/ z range 50–1200	–	Sanabria et al. (2021)
Psychotropic drugs	carbamazepine	Filtration with 0.45 μm membrane filter	UV/chlorine	LC coupled with triple quadrupole mass spectrometer (LC-MS-MS)	Reversed-phase C18 column (250 × 4.6 mm, 5 μm); mobile phase of aqueous and methanolic 5 mM ammonium acetate solutions at a flow rate of 0.6 mL/min; gradient mode; retention time of 18.5 min. Detection with the following settings for the ion source and mass spectrometer: curtain gas 25 psi, spraying gas 65 psi, drying gas 45 psi, temperature of 650 °C, collision gas value 7	LOQ of 10 ng L^{-1}	(Seitz et al., 2006; Sichel et al., 2011)

Table 2 (*continued*)

Therapeutic class	Compound	Initial concentration and sample preparation	Degradation process	Analytical method/ Equipment	Operating conditions	LOD and LOQ	Ref.
	diazepam	10 mg L^{-1}	Photo-Fenton	UPLC system coupled with a diode array detector (UPLC-DAD)	(range 1–12), and an ion spray voltage of 4500 V Reversed-phase C18 column (100 × 2.1 mm, 1.7 μm); mobile phase of aqueous and methanolic formic acid solutions (0.3% v/v) at a flow rate of 0.3 mL/min; gradient mode; retention time of 16.5 min. Injection volume of 20 μL and the analytical column was thermostated at 40 °C	–	Mitsika et al. (2021)
Analgesic anti-inflammatory drugs	diclofenac	5 mg L^{-1}; Filtration with 0.23 μm membrane filter	Photoelectro-catalysis with TiO$_2$ nanotube	HPLC system coupled with a UV detector (HPLC-UV)	Reversed-phase C18 column (250 × 4.6 mm, 5 μm); mobile phase of 75% of methanol and 25% of acetic acid aqueous solution (1%) at a flow rate of 1 mL/min; injection volume of 10 μL and detection at 276 nm	–	Cheng et al. (2016)
Beta-blockers	propranolol	Filtration with 0.45 μm membrane filter	Photocatalysis with TiO$_2$/ONLH	HPLC system coupled with a diode array detector (HPLC-DAD)	Reversed-phase C18 column (250 × 2.1 mm, 1.7 μm); mobile phase of 65% of water acidified phosphoric acid (pH = 3) and 35% acetonitrile at a flow rate of 1 mL/min; retention time of 16.5 min. Injection volume of 20 μL and detection at 213 nm	0.02 and 0.05 mg L^{-1}, respectively	(Q. Zhang et al., 2021)

growth inhibition on algae has shown high sensitivity (Andreozzi et al., 2004; Yamashita et al., 2006). Lastly, the determination of biological oxygen demand after a 5-day incubation (BOD5) is also useful for indicating effluent biodegradability (Brillas and Sirés, 2015).

Despite all the advances and possibilities with these analytical techniques, there is still a lack of studies that properly relate and discuss the effect of the by-products' formation with the radicals formed during the reaction and the toxicity of the final effluent. Many reported studies identify the by-products and even the radicals formed, but fail to properly evaluate the toxicity of the final effluent. The opposite is also common. Studies with a global evaluation, which take advantage of the analytical technology available, are fundamental in supporting real applications and ensuring the security of these treatment technologies.

3. Photocatalysis, electrocatalysis and photoelectrocatalysis

3.1. Photocatalysis

3.1.1. Fundamentals

Heterogeneous photocatalysis is an effective and promising technology based on the photo-activation of semiconductors (photocatalysts) such as TiO$_2$, ZnO, CeO$_2$, ZrO$_2$, WO$_3$, V$_2$O$_5$, CdS and ZnS, which act as active catalytic surfaces for the degradation and mineralization of persistent organic pollutants, including pharmaceuticals and their possible intermediate products in aqueous media (Bergamonti et al., 2019; Chaker et al., 2020). Among the cited semiconductors, TiO$_2$ is the most commonly used in photocatalysis (PC), since it has several advantages, such as chemical stability, resistance to acids and alkalis, large production, ability to use a small percentage of ultraviolet solar radiation for activation, possibility to be easily synthesized in laboratories as both colloidal dispersions and thin films deposited on inert supports (Antonopoulou et al., 2021). Recently, new metal-free photocatalysts, as the graphitic carbon nitride (g-C$_3$N$_4$), have been identified as favorable photocatalysts for environmental application on water and wastewater treatment. g-C$_3$N$_4$ presents good photochemical stability and appropriate bandgap energy (2.7 eV). However, it also presents the low-charge carrier mobility and low surface area, which limits its applications in PC (Ismael, 2020). To overcome these limitations, and improve the charge separation, the majority of the works regarding g-C$_3$N$_4$ applications on PC take use of the synthesis of heterojunction composites, by coupling g-C$_3$N$_4$ with a large bandgap semiconductor. This approach for g-C$_3$N$_4$ and other photocatalysts modification is discussed in section "*4.3. Heterostructured Materials*".

In the degradation of pharmaceuticals, photocatalytic oxidation is the primary process. It is based on the non-selective production of highly reactive species, starting with the generation of electron (e$_{cb}^-$) and hole (h$_{vb}^+$) pairs (Eq. (1)), after the semiconductor absorbs a photon with equal (or higher) energy than the band gap (Fig. 3) (Mehrabadi and Faghihian, 2018). In the sequence, successive reactions can occur with the oxidizing holes and both the organic contaminants and the water/-hydroxyl anion (Eqs. (2) and (3)), forming smaller fragments of the pollutants and the OH$^\bullet$ radical, respectively (Marinho et al., 2019). When using semiconductors with a conduction band redox potential below that of O$_2$, the dissolved oxygen can act as an electron acceptor, forming superoxide radicals (O$_2^{\bullet-}$, HO$_2^\bullet$) or other reactive species (Eqs. (4)–(8)) (Antonopoulou et al., 2021; Wang and Zhuan, 2020). The oxidation of pharmaceuticals can occur through a reaction with reactive oxygen radicals or by a direct reaction with the photohole (Eqs. (9) and (10)), eventually converting them to H$_2$O and CO$_2$ (Awfa et al., 2018; Mehrabadi and Faghihian, 2018). Fig. 2 shows a schematic representation of these reactions and the process flow diagram of PC.

$$\text{semiconductor} + hv \rightarrow e_{cb}^- + h_{vb}^+ \tag{1}$$

$$h_{vb}^+ + H_2O + O_2 \rightarrow OH^\bullet + H^+ + O_2^{\bullet-} \tag{2}$$

$$h_{vb}^+ + OH^- \rightarrow OH^\bullet \tag{3}$$

$$O_2 + e_{cb}^- \rightarrow O_2^{\bullet-} \tag{4}$$

$$O_2^{\bullet-} + H^+ \rightarrow HO_2^\bullet \tag{5}$$

$$2HO_2^\bullet \rightarrow O_2 + H_2O_2 \tag{6}$$

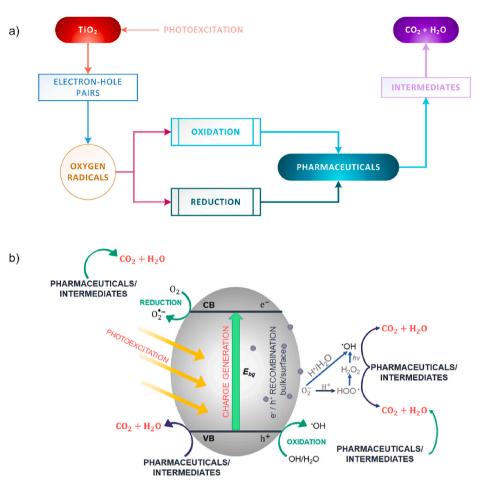$$HO_2^\bullet + e^- \rightarrow HO_2^- \tag{7}$$

Fig. 2. Schematic of the photocatalysis process: a) process flow diagram; b) schematic representation PC reactions. Adapted from (Marinho et al., 2021) and (Cheng et al., 2016).

$$H_2O_2 + O_2^{\bullet-} \rightarrow OH^{\bullet} + OH^- + O_2 \tag{8}$$

$$\text{Pharmaceutical} + OH^{\bullet} / O_2^{\bullet-}/2HO_2^{\bullet} \rightarrow \text{Degradation product} + H_2O \tag{9}$$

$$\text{Pharmaceutical} + h^+ \rightarrow \text{Degradation product} + H_2O \tag{10}$$

3.1.2. Affecting parameters

To scale up the photocatalytic process, it is important that visible light is used and absorbed by the photocatalyst. A crucial characteristic of the material is its band gap, which denotes the energy needed to promote an electron from the valence band to the conduction band. TiO_2, the most widely used photocatalyst, has a band gap corresponding to UV light (~3.2 eV) (J. Zhang et al., 2021), which represents only 5% of the incident solar (Islam et al., 2021). Several strategies, which will be discussed latter, have been proposed and tested to improve the performance of TiO_2 under visible light: doping, co-doping, the use of co-catalysts, the exploitation of defects and using different semiconductors (Z-scheme).

The process efficiency is also controlled by several parameters, including the loading, particle size and surface area of the photocatalyst, the initial concentration of the contaminant, the type and intensity of the irradiation, the presence or absence of oxygen, the pH and the temperature (Attia and Mohamed, 2019; Bergamonti et al., 2019). Regarding the process kinetics, it is agreed that both the reaction constants and orders are apparent and that the heterogeneous photocatalysis usually follows a pseudo-first-order kinetics (Marinho et al., 2019). The kinetic studies are useful to understand the reaction mechanism and to the development of the reaction network, which is the first step for simulation and design of commercial reactors. Furthermore, the reactions can be modeled using a reaction network and the kinetic parameters for each reaction can be obtained after the algorithm optimization with experimental data (Vafajoo et al., 2014).

The number of reactive sites driving the photocatalytic reactions is related to the particle size and the surface area: as the particle size is reduced and the surface area is increased, the photocatalytic efficiency is improved due to a more favorable area/size ratio, which justifies the use of nanocatalysts (Bergamonti et al., 2019). Another parameter that affects the number of reactive sites is the loading: as the concentration of the photocatalyst is increased, the reaction rate is also improved, up to a limit. For pharmaceuticals' degradation in slurry conditions, the optimum catalyst loading is usually between 250 mg L^{-1} (Achilleos et al., 2010) and 1000 mg L^{-1} (Marinho et al., 2017), depending on the reactor design and the working conditions. Higher catalyst loadings typically yield no additional efficiency gain or cause a decrease in efficiency since the excess catalyst (bulk) can block the photons from penetrating and/or cause shielding, reflection and scattering of light (Wang and Zhuan, 2020). In systems with supported photocatalysts, the increase of the loading is usually linked to the catalyst's film thickness. Thus, the enhancement of efficiency is limited to the point where the light is completely absorbed by the catalyst layer. Any further increase in the catalyst loading will not affect the process efficiency, since the diffusional length of the charge carrier to the catalyst-liquid interface remains constant (Marinho et al., 2017).

The intensity of the light and the photon flux are intimately related to the reactor geometry. For instance, with an increase in the number of photons that reaches the reactor, the photogeneration of the reactive species is usually increased. Nevertheless, after a limiting photon flux,
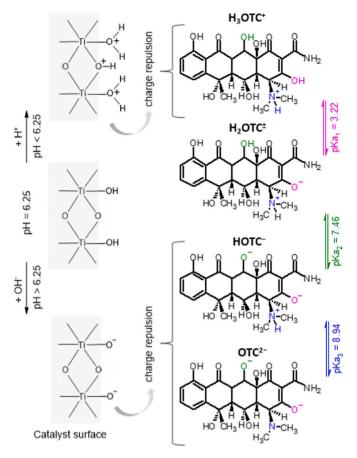
Fig. 3. Schematic of protonation/deprotonation of the TiO$_2$ surface and oxytetracycline molecule. Adapted from (Pereira et al., 2013) and (Beranek, 2011).

the photogenerated species will remain in excess and a high rate of e^-_{cb}/ h^+_{vb} pairs' recombination will be observed. As a consequence, the reaction rate becomes constant even with the increased availability of photons (Marinho et al., 2019).

The pH of the solution is a crucial property of the aqueous system in heterogeneous photocatalysis, since the pH affects the semiconductor particles' charge as well as the protonation/deprotonation of the pharmaceuticals. When the pH of the solution is lower or higher than the pH of the zero point charge (pH$_{zpc}$), i.e., the pH where the photocatalyst surface is uncharged, the catalyst is positively or negatively charged, respectively (Fig. 3) (Marinho et al., 2021). Similarly, at pH values below or above the pKa of the substrates, species with different charges are formed, which can facilitate or impede the reaction with the catalyst's surface (Wang and Zhuan, 2020). Fig. 3 highlights this behavior for oxytetracycline, which has three acidic hydrogens (pKa_1 = 3.22, pKa_2 = 7.46, pKa_3 = 8.94) and can exist in four different forms (H$_3$OTC$^+$, H$_2$OTC$^\pm$, HOTC$^-$, OTC^{2-}), depending on the pH of the solution. The H$_3$OTC$^+$ species is dominant under more acidic conditions and is electrostatically repulsed by the positively charged TiO$_2$ surface. Similarly, under basic conditions, the dominant HOTC$^-$ and OTC^{2-} species at equilibrium will be repelled from the negatively charged TiO$_2$ surface. Close to neutral pH values, the zwitterion H$_2$OTC$^\pm$ species are dominant and can interact with the positive, negative and neutral TiO$_2$ surfaces, facilitating the oxidation process (Espíndola et al., 2019).

One of the main advantages of heterogenous photocatalysis is the possibility of working at room temperature. Since the irradiation activates the photocatalyst, it is not necessary to heat the system. It has been reported that the optimum temperature range is 20–80 °C; at lower temperatures, the adsorption of reactants can block the photocatalyst

surface, while at higher temperatures, the concentration of dissolved oxygen is diminished. Temperatures near the boiling point of water are also rate-limiting due to the increase of kinetic energy in the system, which hinders the reactions on the photocatalyst surface (Malato et al., 2016).

The stability of the catalyst, which is related to its capability of being reused, is an important aspect for industrial or commercial applications. Despite the existence of commercial catalysts with excellent photocatalytic efficiency, full-scale, heterogeneous, photocatalysis systems are still rare due to the aggregation during the operation and difficult recovery and reuse after the process. This also poses an environmental problem since the quality of the treated effluent might be compromised by the catalyst release (Linley et al., 2014; Paredes et al., 2019; Valério et al., 2020). In addition, commercial photocatalysts often have other shortcomings, such as a high rate of recombing electrons and holes as well as low efficiency for removing contaminants at low concentrations (Kim and Kan, 2016). To solve these problems, various techniques have been proposed to increase the process efficiency, including immobilization on appropriate supports, which facilitate the photocatalyst's recovery and reduce the costs of treatment. In addition, it can also contribute to minimizing the e^-_{cb}/ h^+_{vb} pairs' recombination and enhance the activity of the photocatalyst in the UV–vis range (Savun-Hekimoğlu et al., 2020). Nevertheless, due to there being less active surface available, a reduction in the efficiency can occur when supported photocatalysts are used. As a result, the selection of appropriate support material is of fundamental importance for the fabrication of this type of photocatalysts (Paredes et al., 2019). The supports can be: i) a mechanically and chemically stable material, such as glass, alumina or stainless steel (Jayasree and Remya, 2020; Paredes et al., 2019); ii) an active support, such as activated carbon, biochar, zeolites, polymer beads, membranes, or magnetic nanoparticles (Behravesh et al., 2020; Bergamonti et al., 2019; Linley et al., 2014; C. M. Liu et al., 2018); or iii) floating supports, such as perlite and low-density polyethylene (Hartley et al., 2017). Various methods have been applied to immobilize the photocatalysts, including sol-gel processes, chemical vapor deposition, dip-coating, electron-beam evaporation, and sputtering (Katal et al., 2021). Consecutive cycles with immobilized catalysts are fundamental to evaluate the adhesion of the catalyst on the support and the potential reusability of the material, since the catalyst can leach from the support of can be poisoned by the sub-products generated during the reaction (Diao et al., 2020). Table 3 shows different support materials, immobilization methods and photocatalysts applied for the photocatalytic treatment of pharmaceuticals, as well as the evaluated reusability/durability.

Electrical energy is a significant fraction of the operating costs for heterogeneous photocatalysis. Its consumption is influenced by several experimental parameters, such as the type and concentration of the pollutant, the photocatalyst dosage, the reactor design, and the radiation source. For the removal of pharmaceuticals by photocatalysis, the Electrical Energy per Order (EEO) ranges from 25 to 13,000 kWh m^{-3} and indicates the amount of electrical energy (in kWh) necessary to degrade a pollutant by one order of magnitude per cubic meter of contaminated water (Durán et al., 2018). Note that the type of the irradiation source influences this value. For systems that use UVA lamps almost three times more electrical energy is required than for those that utilize UVC radiation. Nevertheless, natural solar UVA radiation can be an alternative that contributes substantially towards decreasing energy costs (Babić et al., 2015). In addition, the feasibility of the process at neutral pH is one of the major advantages of heterogeneous photocatalysis (Antonopoulou et al., 2021). After the optimization of the operating conditions, the values of the EEO can be significantly decreased (Durán et al., 2018). Nevertheless, few studies of the degradation of pharmaceuticals by photocatalysis evaluate the energetic consumption, and even fewer estimate the costs of the whole process. Since it is very difficult to compare studies with different photocatalysts,

Table 3

Supported photocatalysts for pharmaceuticals' degradation and reusability.

Pharmaceutical	Support	Photocatalyst	Immobilization method	Number of reuse cycles/hours of continuous use[a]	Removal of the starting compound	Ref.
Amoxicillin	Chitosan scaffolds	TiO_2 P25	3D printing	3 cycles	From ~90 to ~80% in 180 min, after 3 cycles	Bergamonti et al. (2019)
Ibuprofen	Raschig rings	TiO_2 anatase	Immersion in TiO_2-containing ink for 5 min and heating at 650 °C for 30 min	6 h	Unchanged 87%, after 6 h of continuous treatment	Cerrato et al. (2019)
Oxytetracycline	Kenics static mixer	Fe_2O_3	Spray coating	3 cycles	The kinetic constant remained almost unchanged (85×10^{-3} min^{-1}), after 3 cycles	Díez et al. (2018)
Tetracycline	Floating hollow acrylic spheres	TiO_2 P25	Dip coating	35 days	The kinetic constant changed from 1.88×10^{-3} to 1.82×10^{-3} min^{-1}, after 35 days of solar light exposition while floating in water	Hartley et al. (2017)
Oxytetracycline	Glass	TiO_2 P25	Spray coating	4 cycles	The kinetic constant changed from 44×10^{-3} to 39×10^{-3} min^{-1}, after 5 cycles	Espíndola et al. (2019)
Paracetamol	Aluminosilicate	TiO_2 (from titanium isopropoxide)	Sol-gel	3 cycles	From 99 to 94% in 30 min, after 3 cycles	Jayasree and Remya (2020)
Metronidazole	Chitosan (CS) and polyvinyl alcohol/chitosan blend (PVA-CS)	TiO_2 P25	Sol-gel	15 cycles	98% using CS and 100% using PVA-CS in 90 min, after 15 cycles	Neghi et al. (2019)
Chlorhexidine digluconate	Alginate	TiO_2 P25	Entrapping	5 cycles	From 99 to 85%, after 5 cycles	Sarkar et al. (2015)
Guaifenesin	Fumed silica	Catalyst residue from petrochemical plant containing Ti (2.5%)	Sol-gel	5 cycles	From 49 to 45% in 60 min, after 5 cycles	da Silva et al. (2015)
Tetracycline	Floating expanded perlite	z-scheme composite $FeMo_3O_x/g$-C_3N_4	Dip-calcination method	5 cycles	From 98 to 85%, after 5 cycles	Liu et al. (2022)
Sulfamethoxazole	Biochar	TiO_2 doped with zinc elements (Zn–TiO_2/pBC)	Sol-gel	5 cycles	From 81 to 77%, after 5 cycles	Xie et al. (2019)
Cefoperazone	Zeolite	CdS/g-C_3N_4	Co-precipitation	3 cycles	From ~95 to ~80%, after 3 cycles	AttariKhasraghi et al. (2021)

[a] Without significant efficiency lost.

reactor designs and sources of radiation, a cost analysis would be useful to enable this comparison and stimulate the implementation of this technology in real applications.

3.1.3. Degradation mechanisms - first-principles calculations

Electrons can be excited to any of the unoccupied energy states. However, in conventional photocatalysis, all the transitions from a higher to the lowest excited state are considered fast and do not contribute significantly to the reaction rate (Fig. 4). This means that the molecules will spend most of their excited lifetime in the lowest excited state. This simplifies the catalyst design and reaction modeling considerably, necessitating that only the first excited states are considered when modeling reaction mechanism and molecule properties using density functional theory (DFT). Proposed by Michael Kasha in 1950,
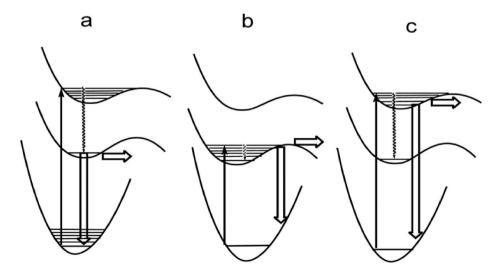

Fig. 4. Electronic states in reactions proceeding from (a) first excited state, (b) higher vibrational levels of the first excited state and (c) higher excited states. According to the Kasha rule, the contribution of (c) is negligible. Adapted from (Turro et al., 1978).

the eponymous rule, postulated with respect to emission and absorption spectra (Kasha, 1950), has only recently been circumvented, paving the way to the anti-Kasha approach (Demchenko et al., 2017; Shi et al., 2020).

While there is a vast body of research on the photo(electro)chemical degradation of pharmaceuticals, most focus either on the development of catalysts and associated techniques or on the performance. First-principles calculations, which can shed additional light on the processes by explaining the reaction steps and/or the catalyst structure, are rarely used. In degradation studies, DFT is generally employed in a supplementary fashion to calculate the band gap of the catalyst material, the Fukui function, work functions, or similar (Zhuangzhuang Wang et al., 2021). For the studies of photoactive catalytic materials, the band structure, densities of state and the electronic location function (ELF) are often calculated (Ding et al., 2019). Proper mechanistic studies are very rare. A common reaction pathway is the attack of the hydroxyl radical, which is formed upon irradiation in aqueous media. A typical reaction scheme involves decarboxylation, oxidation (dehydrogenation), C–C bond cleavage and addition to aromatic rings, as shown in Fig. 5.

The most often calculated Fukui functions are popular tools to predict the regioselectivity of the reactions with radicals (Li et al., 2021). The Fukui function ($f(r)$) is defined as a derivative of the electron density function with respect to a change in the number of electrons:

$$f(r) = \left[\frac{\partial \mu}{\partial v(\mathbf{r})}\right]_N = \left[\frac{\partial \rho(\mathbf{r})}{\partial N}\right]_v$$

where μ is the electronic chemical potential, $\rho(\mathbf{r})$ is the electron density at $\mathbf{r}$, N is the number of electrons and v is the constant external potential. The first equality gives the formal definition of the Fukui function (Fukui, 2006). As it is an exact differential, this definition lends itself to be rewritten as the second equality following the Maxwell relations between derivatives. Two finite versions, corresponding to the addition or removal of one electron, are most easily calculated and describe the susceptibility of a particular site to nucleophilic or electrophilic attack. The electronic band structure is commonly calculated as it gives the band gap value and other useful information stemming from the arrangement of the energy levels that the electrons can occupy. The band gap, being the difference between the valence and conduction bands, is intimately connected to the photo-activity of the material. Only photons with an energy greater than the band gap can be absorbed. The work function is sometimes calculated. It describes the work required to remove an electron from a solid material to a point adjacent to the surface.

Very few studies try to computationally elucidate the reaction mechanism of the photodegradation of pharmaceuticals. Even those that attempt this, often fail to include the effect of irradiation or excited sites instead of simulating the process after the OH$^\bullet$ has been formed. Wang et al. (2021b) studied the photochemical degradation of ibuprofen (IBP) with experiments and DFT. However, the authors performed conventional thermocatalytic DFT calculations at the B3LYP-D3/6-31G(d,p) level with the integral equation formalism version of the polarizable continuum model (IEFPCM) solvation and did not model the photocatalytic effects explicitly. Instead, they assumed that OH$^\bullet$ and NO$_2^\bullet$ form and then modeled their reactions with IBP. They showed that OH$^\bullet$ plays a crucial role in the process, calculating the second-order kinetic constant for IBP degradation with OH$^\bullet$ as $3.93 \times 10^6\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}$ using the transition state theory. NO$_2^\bullet$ was found to be a potent inhibiter, as its addition lowered the overall reaction rate. The second-order kinetic constant for the reaction with NO$_2^\bullet$ was found to be $5.59 \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}$. The reactivity of O$_2^{\bullet-}$ was smaller than that of OH$^\bullet$.

One of very few fully mechanistic studies was focused on the oxidation of phenazopyridine (PhP) over iron(iii) oxyhydroxide structures in a O$_3^+$PTNL/N$_2$ process. Using the M062X/6-31 + G(d) DFT approach, Pelalak et al. (2021) proposed a full reaction mechanism to support their experimental data. They calculated the Fukui functions for a radical attack on PhP and showed the most reactive site in the molecule, the intermediates and transition states for an OH$^\bullet$-mediated degradation, ultimately causing the breakup of the azo bond. The activation barrier for the initial attack is 28 kcal mol^{-1}. A frontier molecular orbital (FMO) analysis of different intermediate structures and transition states of PhP and OH$^\bullet$ confirmed that the azo nitrogen is the most susceptible to attack. Lastly, other chemical parameters of the structures were calculated: global hardness, ionization potential and electron affinity (EA), and electrophilicity index.

A complex mechanistic study of carbamazepine (CBZ) degradation using a biosource composite by El Mouchtari et al. (2021) featured DFT calculations heavily. At the B3LYP/6-31G (d,p) level with the conductor-like polarizable continuum model (CPCM), the authors calculated the structures of the CBZ and all the intermediates/products in a OH$^\bullet$-mediated degradation. The Fukui functions were also calculated. A comprehensive study of pindolol (PIN) photodegradation by Armaković et al. (2020) also relied heavily on theory. After identifying all the possible conformers of PIN at a force-field level (OPLS3e) and optimizing them at a B3LYP level, the bond-dissociation energies (BDEs) of the cleavage of single acyclic bonds and hydrogen abstraction were calculated using the LACV3P basis set. As PIN has a HOMO-LUMO gap of 5.2 eV, which is indicative of a stable molecule, the molecular electrostatic potential (MEP) and the average local ionization energy (ALIE)
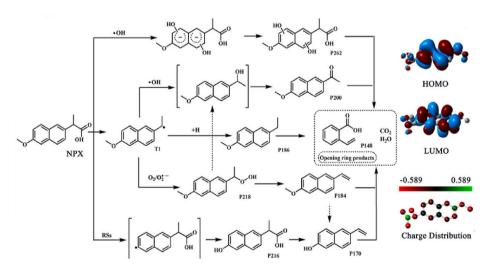

Fig. 5. A degradation pathway of naproxen (NPX) by crystalline carbon nitride (CCN) upon irradiation. Reprinted from Wang et al., 2020. Copyright© (2020), with permission from Elsevier.

were used as proxies to estimate the most susceptible part of the molecule to an attack. High values for H-BDE show that the molecule does not readily undergo auto-oxidation. Instead, cleavage of the C–O bond is the most probable site of attack. Molecular dynamic simulations showed that the molecule is stable in aqueous solutions. For an insight into the photodegradation route, the Fukui functions were calculated.

Gurkan et al. (2012) used DFT to predict the degradation pathway of cefazolin over N-doped TiO_2 under UV and visible light. Assuming that the $OH^\bullet$ is formed under the irradiation conditions, they calculated the reaction network for the interaction of cefazolin with $OH^\bullet$ at the B3LYP/6-31G* level. Additionally, reactivity parameters such as the global hardness and the Fukui function were obtained. Being a β-lactam antibiotic, cefazolin was predicted to degrade via the intramolecular β-lactam, thiadiazole, tetrazole and dihydrothiazin ring cleavages, which further on react with the $OH^\bullet$.

Wang et al. (2020e) studied the photodegradation of pharmaceuticals and personal-care products (PRCP) on bulk and crystalline carbon nitrides (BCNs and CCNs, respectively) and showed that the crystalline structure is more effective. Theoretical calculations at the PBE level were used to underpin the experiments. The authors focused on the mechanism of active-species generation, i.e., the oxygen-reduction reaction (ORR) pathway. They calculated the reaction energies on BCNs and CCNs for the adsorption of O_2 (−0.10 and −0.44 eV), the transformation to OOH (−0.31 eV and −0.73 eV) and the formation of H_2O_2 (+0.01 eV and +0.50 eV). The reaction is much more exothermic on CCNs. A projected density-of-state analysis of the adsorbed $HO_2^\bullet$ was used to show that a BCN is a poorer electron acceptor, while O_2 is crucial to the degradation process.

Tang et al. (2017) investigated the mechanism for the photocatalytic degradation of carbamazepine (CBZ) on $BiVO_4$ with graphene quantum dots. The calculations were performed at the B3LYP/6-31 + G(d,p) level with water as the solvent. The active species was modeled as $OH^\bullet$. The calculations of its reaction with CBZ showed that it preferentially attacks the heterocyclic (azepine) ring rather than the aromatic ring.

TiO_2–SnS_2 was evaluated as a photocatalyst for the degradation of a polar and non-polar pharmaceutical compound: diclofenac (DCF) and memantine (MEM) (Kovacic et al., 2020). The SnS_2 decoration on the TiO_2 lowered the band gap and improved the photo-oxidation of the DCF, while the MEM remained stable. Theoretical calculations performed on a 4×4 supercell of a SnS_2 monolayer showed that the DCF adsorbs about three times more strongly than the MEM because of the interaction of the π-electrons of the DCF's phenyl group and the negatively charged S surface atoms. The MEM binds solely through the amine group. The solvation effect was checked on a $Sn_{36}S_{72}$ finite section using a continuum water model and found to be < 1 kcal mol^{-1}.

3.1.3.1. Fukui-function calculations.
In many studies, first-principles calculations are employed solely to provide the Fukui functions or other similar descriptors, which are used to postulate a probable reaction mechanism. Huang et al. (2021) studied the photocatalytic degradation of amoxicillin (AMX) on carbon-rich g-C_3N_4. They used DFT to calculate the natural population analysis (NPA) charge distribution and the Fukui functions of AMX, which were then used to postulate the degradation pathway. The Fukui functions were calculated for the photocatalytic degradation of diclofenac (DCF) on quantum-dots-modified g-C_3N_4 (W. Liu et al., 2019), for amoxicillin and cefotaxime degradation under visible light over g-C_3N_4 (Dou et al., 2020), for carbamazepine photodegradation over g-C_3N_4 (Zhao et al., 2020) and for meropenem degradation over g-C_3N_4 nanosheets with nitrogen defects (Wang et al., 2020).

F. Liu et al. (2019) investigated the photocatalytic removal of diclofenac using a Ti-doped BiOI microsphere. They established that h^+, $O_2^{\bullet-}$ and H_2O_2 play crucial roles in the reaction. The Fukui functions were also calculated in a study of naproxen degradation over a Bi_2MoO_6/g-C_3N_4 heterojunction under visible light (Fu et al., 2021),

diclofenac degradation over activated carbon-fiber-supported titanate nanotubes (Dang et al., 2020), and for the photodegradation of ofloxacin by perovskite-type $NaNbO_3$ nanorods modified g-C_3N_4 heterojunction (D. Zhang et al., 2020). X. Liu et al. (2019) showed that graphene modifications of anatase/titanate nanosheets improve their photocatalytic activity in the photodegradation of sulfamethazine using the Fukui functions.

3.1.3.2. Other electronic properties.
When Yin et al. (2020) showed that peroxymonosulfate enhances the photocatalytic ability of Pd/g-C_3N_4 in bezafibrate degradation, the DFT calculations were used to ascribe the electron transfer to the chemical bond between the Pd and the g-C_3N_4. In the plane-wave approach, the electronic band structure, density of state, electronic location function and charge-difference function were calculated for g-C_3N_4 and Pd/g-C_3N_4.

Regmi et al. (2019a) showed that phosphate-doped $BiVO_4$ is an effective photocatalyst for degrading IBP and p-amino salicylic acid. They used DFT (in the PBE + U approach) to calculate the density of states of the catalyst, the band gap (2.11 eV vs. experimental 2.4 eV), the charge-density difference and the bond lengths. They showed that phosphate doping increases the electron density of states in the valence band, improves the carrier mobility and thus enhances the photocatalytic efficiency. They also studied the N-doped catalyst. The presence of nitrogen in the catalyst led to an increase in ibuprofen degradation from 71 (undoped catalyst) to 90% in 150 min (Regmi et al., 2019b).

Z. Yang et al. (2021) used DFT to elucidate the photocatalytic degradation pathway of tetracycline (TC) over Z-scheme Ag_3PO_4/mixed-valence MIL-88A(Fe) heterojunctions. They used the periodic approach with the Perdew–Burke-Ernzerhof (PBE) functional and Hubbard corrections (DFT + U) to calculate the catalyst's band structure and charge-density difference. For calculating the Fukui functions of TC, an atomic-orbital approach at the B3LYP/6–31(d,p) with solvation (IEFPCM) was employed. Huang et al. (2015) showed that $Bi_2O_2(OH)$ (NO_3) works as a $[Bi_2O_2]^{2+}$ layered catalyst for the photo-oxidation of phenol, bisphenol A, 2,4-dichlorophenol and tetracycline hydrochloride. They used DFT to investigate the electronic band structure and dipole moment at the local-density approximation (LDA) level of theory. In a study of ciprofloxacin photodegradation in aqueous bismuth oxybromide by photohole oxidation, Zhang et al. (2015) used theory to pinpoint the active sites with a spin-distribution analysis on the ciprofloxacin radical. Similarly, Zhang et al. (2019) calculated the highest occupied and lowest unoccupied molecular orbitals for a polymeric O and N co-linked carbon nitride framework with carbon dots, which was 11.6 times more active in the photodegradation activity of diclofenac than g-C_3N_4.

Armaković et al. (2019) studied La-doped TiO_2 as a photocatalyst for the degradation of metoprolol tartrate (MET) and propranolol hydrochloride (PRO). The authors calculated the opto-electronic properties, the e^- and h^+ reorganization energies (ERE and HRE), the hydrophobic areas, the HOMO-LUMO gap, the chemical hardness, the chemical potential and the electrophilicity index.

Xing et al. (2018) tested the photoelectrochemical properties of a bismuth oxybromide heterostructure and employed DFT as a supporting technique for determining the band gap energy, the conduction band minimum and the valence band maximum. The photodegradation of levofloxacin by Fe-doped BiOCl nanosheets was studied by Zhong et al. (2020), who used DFT to prove the shrinkage of the unit cell upon Fe substitution and to calculate the band gap structure and the density of states of the undoped and Fe-doped BiOCl.

3.2. Electrocatalysis

3.2.1. Fundamentals
Instead of light, electricity can be used to guide the desired chemical

reaction. In this context, electrochemical advanced oxidation processes (EAOPs) have emerged as a promising alternative for treating and remediating water streams. Conceptually, electrocatalysis is a way to convert electrical energy into chemical energy. In practice, the EAOPs are based on the electrochemical generation of oxidizing species, mainly the hydroxyl radical (OH$^\bullet$). Since electrical energy can be obtained from renewable sources, this technique can be considered as a green oxidation process (Suhadolnik et al., 2019a).

The EAOPs can be divided in homogeneous (electroFenton, photo-electroFenton and sonoelectrolysis) and heterogeneous processes (anodic oxidation and photoelectrocatalysis), in the function of the OH$^\bullet$ generation in the bulk solution or at the anode surface, respectively (Sirés et al., 2014).

In heterogeneous electrocatalysis, the electrode is a solid conductive material, usually a metal. This is one of the main reasons for the over-potential, which depends on the reactants and the products at the interphase, the electrolyte and the electrode material. The overpotential is the potential required in excess of the thermodynamic minimum and represents the kinetic barrier for the reaction. Thus, the aim of electrocatalysts' development is to lower the overpotential for the desired reaction.

3.2.2. Anodic oxidation

Anodic oxidation (AO) is one of the most common electrocatalytic processes among EAOPs to remove organic pollutants from water (Martínez-Huitle et al., 2015). This section will deal with the treatment of water and wastewater containing pharmaceuticals by applying AO, as well as a discussion of its fundaments and the main parameters that affect this process.

AO's advantages include high efficiency, the possibility of automation, the simple equipment required, the mild operating conditions (room temperature and pressure), and versatility, since it can be used for effluents with up to 100 g L^{-1} of COD. Nevertheless, there are still some drawbacks that limit the industrial applications, such as the high costs of electricity and some electrode materials, the mass-transfer limitations, foam formation, the temperature increase during the process, the need to add electrolytes to wastewaters with low conductance, and the deposition of organic material on the electrode's surface, so shortening its lifetime (Martínez-Huitle et al., 2015; Sirés et al., 2014).

Pharmaceuticals and organic pollutants in general can be degraded by AO using direct AO when there is a direct electron transfer to the anode, or indirect reactions with the electrogenerated species in the bulk

solution (Fig. 6). The most relevant species generated are the hydroxyl radicals and active chlorine (when the electrolyte contains chlorine) (Suhadolnik et al., 2019a). In both cases the type of electrode is of fundamental importance and directly influences the efficiency of the process. Actually, the Gibbs free energy of any reaction is also a function of the electric potential, which is non-zero at the electrodes in electrocatalysis. This means that the electrode does not act merely as an acceptor or donor of electrons, but actively modifies the reaction rates.

An ideal electrode should have a high surface area and current efficiency as well as a long lifetime and low cost. Several types of electrode materials have already been reported for the electrocatalytic degradation of pharmaceuticals, among which boron-doped diamond (BDD) (Lan et al., 2018), platinum (Guitaya et al., 2017) and metal oxides (e.g., TiO$_2$) (Arredondo Valdez et al., 2012) are the most common. However, an electrode that has all the desired characteristics remains to be found.

The formation of radical species that are able to react in the bulk solution occurs first through the direct oxidation of these species on the anode surface. It depends on the anode material and the electrolyte type. When using anode materials like BDD and PbO$_2$ coatings, the formation of radicals from anions such as sulfate, phosphate, carbonate and chloride are explained by Eqs. (11)–(14) (Sirés et al., 2014). The formation of OH$^\bullet$ occurs during the anodic oxidation of water (Eq. (15)). However, due to its high reactivity, it can rapidly react to form H$_2$O$_2$ and/or HO$_2^\bullet$ (Eqs. (16) and (17)) (Oturan et al., 2012). Since the oxidation of organic compounds to CO$_2$ is favored by the reaction with OH$^\bullet$, anodes with a high O$_2$-evolution overpotential (such as BDD) are preferable to anodes with a low O$_2$-evolution overpotential for the removal of pharmaceuticals (Martínez-Huitle et al., 2015).

$$2SO_4^{\bullet-} \rightarrow S_2O_8^- \tag{11}$$

$$2PO_4^{\bullet-} \rightarrow P_2O_8^{4-} \tag{12}$$

$$2CO_3^{\bullet-} \rightarrow C_2O_6^{2-} \tag{13}$$

$$2Cl^\bullet \rightarrow Cl_2 \tag{14}$$

$$H_2O \rightarrow OH^\bullet + H^+ + e^- \tag{15}$$

$$2OH^\bullet \rightarrow H_2O_2 \tag{16}$$

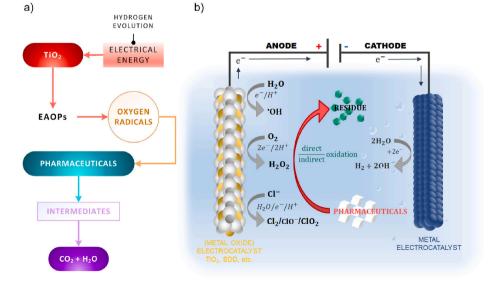$$OH^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O \tag{17}$$

Fig. 6. Schematic of the electrocatalysis process (anodic oxidation): a) process flow diagram; b) schematic representation EC reactions. Adapted from (Lan et al., 2018) and (Feier et al., 2018).

Another important reaction that should be considered is the production of H_2O_2 by reducing oxygen on the cathode surface. Thus, a strong oxidant can be produced instead of other unproductive reactions at the cathode. It can occur in most cathode materials when dissolved oxygen is available; however, it demands a large contact area, which is usually found with porous cathodes (Zhou et al., 2012).

3.2.2.1. Affecting parameters. Some figures of merit that are important to evaluate the AO performance from the electrochemical point of view, such as the current efficiency (the ratio of the charge needed to oxidize the pollutant to the total charge required in the process), the space-time yield (electrochemical oxidation capacity), the specific energy consumption (the energy used to remove a unit mass of COD) and the limiting current density (for maximum production rate), can be found in detail elsewhere (Panizza and Cerisola, 2009).

Other parameters such as the current density and the stirring rate, the effluent conductivity, the pollutant type and concentration, the pH and the temperature, can also influence the process performance and sometimes are not fully evaluated in all reports.

The operating current density is a parameter of fundamental importance in the AO process, since the distance between the electrodes is fixed and the current is continuously supplied. This is the one parameter that can be directly controlled during the process (Martí-nez-Huitle et al., 2015). Typically, when the current density is increased, the rate of pollutant removal also rises; however, it is often followed by a fall in the current efficiency. Despite the simplicity, undesirable reactions can also occur and affect the performance of the process. Sopaj et al. (2015) reported the influence of the current density for different anode materials during the EC treatment of amoxicillin. For almost all the materials tested (Pt, PbO_2, DSA, carbon-fiber and carbon-graphite) a weak influence of the current density was observed in the range 2–20 mA/cm^2. The exceptions were BDD and carbon-felt anodes, which exhibited higher efficiencies when using current densities of 20 and 15 mA/cm^2, respectively. The current density applied for the EC degradation of pharmaceuticals normally remains between 1 and 50 mA/cm^2, and the best condition depends on the materials and the reactor design. However, it is important to ensure appropriate stirring of the system, to minimize the mass-transfer limitations and to ensure homogeneous conditions (Macpherson, 2015). In an experimental set-up with a recirculation system (10 L capacity), the limited influence of the flow rate in the range 125–500 L/h was reported (Loos et al., 2018). Since the mass-transfer coefficient's enhancement affects the reaction rate to a limited extent, even for the minimum flow rate tested, the system was adequately homogenized and the reaction was not mass-transfer limited.

The electrolyte concentration determines the solution's conductivity, while its type is related to the reactive species formed, with both being very significant for the AO efficiency. Normally, NaCl or Na_2SO_4 are used as electrolytes, but ideally the wastewater itself should be the electrolyte. It is worth noting that chloride-mediated reactions are favored in the presence of NaCl, while in the presence of Na_2SO_4, persulfates can be produced (Cheng et al., 2003). Y. J. Liu et al. (2019) evaluated the influence of the electrolyte type (NaCl and Na_2SO_4) at different current intensities (0.1–0.5 A) for the EC degradation of acetaminophen, diclofenac and sulfamethoxazole. The results showed there was little influence of the current intensities when using Na_2SO_4, reaching degradations of about 80% for all the pharmaceuticals in 60 min at all the current intensities tested. On the other hand, when using NaCl the EC efficiency was greatly improved by increasing the current intensity from 0.1 to 0.5 A, increasing the pharmaceuticals' removal from 50 to 60% to more than 90% in 20 min (Y. J. Liu et al., 2019). These results indicate that for the reaction with Na_2SO_4 as the electrolyte, the oxidation mainly occurs on the anode surface, while in the system with NaCl indirect reactions also occur, promoting the synergy between the hydroxyl radicals and the active chlorine. Nevertheless, the presence of chlorine must be cautiously monitored since there is the possibility of

toxic by-products being formed (Lan et al., 2017). Longer reaction times can be an alternative to ensure the mineralization of the organic species and avoid the residual presence of organochlorine species. Furthermore, to confirm that the final effluent is not dangerous, toxicity tests and TOC analysis should be performed.

Welter et al. (2020) studied the influence of the electrolyte in the EC degradation of prednisone by comparing the efficiencies when using synthetic and real matrices. The EC was able to oxidize the prednisone in all the tested conditions. When using a synthetic solution with 1 g L^{-1} of Na_2SO_4 as the electrolyte, it was possible to achieve a degradation of 78% and a mineralization of 42%. However, the results were improved when the process was applied to a real wastewater matrix spiked with the same amount of prednisone, which can be attributed to the different ions in the real wastewater matrix that allow the greater electro-generation of oxidizing agents. In fact, the presence of different ions seems to be more important for the EC efficiency than the single electrolyte concentration since the efficiency in the unmodified wastewater matrix (84% of prednisone removal and 63% of TOC removal) was higher than the one with the addition of 1 g L^{-1} Na_2SO_4 matrix (82% of prednisone removal and 55% of TOC removal). Furthermore, excess sulfate ions at high concentrations of Na_2SO_4 can lead to a decrease in the pharmaceuticals' removal efficiency, since the adsorption of the excess ions at the anode surface reduces the number of accessible active sites for the generation of $OH^\bullet$ (Samarghandi et al., 2021).

The effect of the pH on the AO process is related to the pollutant type, which is sometimes easily oxidized in an alkaline or acidic medium, depending on its pK_a. Furthermore, pollutants can preferentially adsorb/desorb on the surface of the electrodes at different pH values. In addition, the pH can also influence the availability of the $OH^\bullet$ and other oxidants in the bulk solution (Macpherson, 2015). Despite the inexistence of a general rule for the influence of pH, the AO process generally has an optimum pH value for its maximum efficiency, which must be experimentally determined. For the EC removal of antibiotics from the fluoroquinolone family, different studies with different electrodes have found a diversity of optimum pH values. For ciprofloxacin the best pH evaluated was 4 (C. Yang et al., 2021), while for ofloxacin (Xie et al., 2017) and levofloxacin (Meng et al., 2021), high efficiencies were found in more basic conditions, at pH values of 11 and 10, respectively.

Regarding the pollutant's initial concentration, for higher initial concentrations, greater current efficiencies are usually observed; however, longer reaction times are required. On the other hand, the temperature has a minimum influence on the AO efficiency when oxidation by $OH^\bullet$ is the primary reaction for the pollutants' removal (Martí-nez-Huitle et al., 2015).

Despite the promising results obtained in AO laboratory-scale tests and its feasibility to be utilized in small-scale decentralized treatment plants, its practical application for treating real pharmaceutical effluents is still limited. This behavior can be attributed to its high energy consumption (50–1000 kWh kg^{-1} COD) when compared to the aerobic biological treatment (3 kWh kg^{-1} COD) (Yang and Hoffmann, 2016), as well as to the need for more information about the by-products formed during the process and the theoretical description of the systems.

3.2.2.2. Degradation mechanisms. While the theoretical description of thermocatalytic reactions at solid-vacuum or solid-gas interfaces has traditionally shown good agreement with experiments, electrocatalytic-reaction modeling suffers from three drawbacks: (i) the processes are influenced by the electrode potential, (ii) the description of liquid electrolytes is computationally expensive and imprecise, and (iii) the density functional theory's description of the transition states involved falls short of the elusive chemical accuracy (<1 kcal mol^{-1}). These shortcomings have prevented researchers from developing a universal or generally accepted approach to modeling electrocatalysis.

While thorough theoretical studies of electrochemical reaction mechanisms exist, they are limited to smaller molecules or industrially

relevant processes. For the degradation of pharmaceuticals, theoretical calculations are used as a supporting technique with limited predictive power. Some authors used DFT to calculate adsorption energies and use them to infer the reaction mechanism. Zichen Wang et al. (2021) used waste 1D-FeOOH as an electrocatalyst for peroxymonosulfate (PMS) activation and metronidazole degradation. First-principle calculations were used to calculate the adsorption energy of PMS on 1D-FeOOH and 1D-FeOOH@Mo and the surface-electron density, relating the superior activity of FeOOH@Mo to its strong interaction with PMS. Meng et al. (2021) synthesized FeOOH nanoneedles with quantum carbon dots (CQDs@FeOOH) for the electrodegradation of levofloxacin and then calculated the adsorption energies of OH on (221), (111) and (110) facets. The oxygen-reduction reaction (ORR), which is instrumental in the electro-Fenton degradation of sulfonamides on N,S co-doped cathodes, was explored by calculating the adsorption energy of O_2 over graphene in pure, N-doped, S-doped and co-doped forms, finding the strongest interaction in the last of these (Zhu et al., 2021).

Even more often, the use of DFT is relegated to calculations of the principal electronic properties of the materials and substrates involved. The HOMO-LUMO gap is important for activity and was calculated for Turkay et al. (2018) in a study of its electro-oxidation over several Ti-containing electrodes and boron-doped diamond. Acetaminophen and its analogs are common substrates for testing electrocatalysts and mechanism investigations. Q. Zhang et al. (2020a) focused on sulfur-doped graphene (SGN), which has edge and thiophene structured sulfur species. The authors used DFT to help postulate a reaction mechanism by calculating the HOMO and LUMO and the electron-density difference upon Cl^- adsorption, concluding that the thiophene structure S catalyzes the reaction. When using a boron-doped graphene electrode, boron was found to slightly change the charge density, the HOMO-LUMO gap and the magnetic moment, as confirmed by DFT calculations on six different models (Q. Zhang et al., 2020b). The same properties were calculated in a study of N-(4-hydroxyphenyl) ethanamide electrodegradation on phosphorus-graphene (Yu et al., 2021), acetaminophen degradation on S-doped graphene/Pt/TiO_2.

3.3. Photoelectrocatalysis

3.3.1. Fundamentals

The combination of photocatalysis and electrochemistry emerged at the beginning of this century, leading to photoelectrocatalysis (PEC) technology, which finds extensive use in environmental applications as a promising alternative for degrading refractory organic pollutants in water and wastewater as well as water splitting (Garcia-Segura and Brillas, 2017; D. Liu et al., 2017; S. Liu et al., 2017). The electrical potential is used to make the desired reaction exothermic (a negative Gibbs free-energy change) and irradiation then increases the reaction rate further. Artificial photosynthesis (solar fuel production) is an example of a photo-electrocatalytic system. Photo-electrocatalysis has numerous advantages, such as better performance over refractory contaminants and a faster mineralization of organic pollutants, the possibility of automation, modularity and portability, as well as a small footprint (Ghasemian et al., 2017; Suhadolnik et al., 2019b). However, since PEC is a relatively new technology, most of its reported applications relate to synthetic wastewater that had the electrolytes added. Nonetheless, it is important to mention that urban and industrial wastewaters generally already contain electrolytes such as sulfate, chloride and carbonate salts, which guarantee enough conductivity to effectively perform the PEC treatment, making this technology more attractive for the treatment of real wastewater.

This technique is based on the use of a semiconductor photo-anode, which is composed of a semiconductor photocatalyst (commonly TiO_2 or ZnO) supported on a conductive substrate, and a cathode with an active metal surface that allows the desired reactions (Fig. 6) (Jaramillo-Gutiérrez et al., 2016). When the anode is irradiated by light with an energy equal to or higher than the semiconductor's band gap,

electrons and holes are photogenerated. This system is simultaneously biased by a gradient of potential, which drives the electrons from the anode to the cathode, preventing electron-hole recombination, while additional reactions on the cathode can help the oxidation of the pollutants and enhance the photocatalytic efficiency (Liu et al., 2017; Suhadolnik et al., 2019b). In fact, although the reduction of water to produce H_2 is the conventional reaction on the cathode (Fig. 7), the use of carbonaceous cathodes can lead to the formation of H_2O_2 by reducing the O_2 in accordance with Eq. (18) (Brillas and Martínez-Huitle, 2015). The formed H_2O_2 is able to react with e_{cb}^- and contributes to the formation of additional $OH^\bullet$ radicals (Eq. (19)) (Garcia-Segura and Brillas, 2017). Furthermore, when an anodic potential (E_{anod}) is applied over the semiconductor, anodic oxidation (AO) is also feasible since the water can be oxidized with the subsequent formation of a hydroxyl radical ($OH^\bullet$), as exemplified in Eq. (20) (Cavalcanti et al., 2013).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{18}$$

$$e_{cb}^- + H_2O_2 \rightarrow OH^\bullet + OH^- \tag{19}$$

$$\text{Semiconductor} + H_2O \overset{E_{anod}}{\rightarrow} OH^\bullet + H^+ + e^- \tag{20}$$

Since the recombination of the electron/hole is suppressed in PEC, the hole's lifetime is increased, readily oxidizing the pharmaceutical compounds directly (Eq. (10)), as well as reacting with water, producing a hydroxyl radical by conventional PC (Eq. (2)) (Garcia-Segura and Brillas, 2017). With all possible reactions that can occur in the PEC process, it is challenging to determine the contribution of every individual process. Nevertheless, the greater efficiency of PEC over conventional EC can be explained by the photocatalytic reactions that take place only in PEC systems (Garcia-Segura et al., 2013). The choice of appropriate anode materials is a fundamental step that strongly influences the process efficiency, cost and selectivity (Ghasemian et al., 2017). The most suitable electrode should exhibit a high catalytic activity and stability, facilitating its recovery and recycling along successive treatments, without losing its efficiency (Garcia-Segura and Brillas, 2017). Consequentially, a key aspect of a successful PEC system is a strong adhesion of the photocatalyst to the conductive support (anode) (Suhadolnik et al., 2019b). Several immobilization techniques can be used to prepare anodes, such as sol-gel, thermal, chemical vapor deposition, electrodeposition and anodization methods (Garcia-Segura et al., 2013). Each method leads to different characteristics of the anodes, such as a high catalytic activity or strong adherence.

3.3.2. Affecting parameters

The use of PEC systems for the treatment of pharmaceuticals and organic pollutants at low concentrations usually follows pseudo-first-order kinetics and the global efficiency is influenced by other operational variables, such as current voltage and intensity, catalyst layer thickness, electrolyte types and concentration, effluent/solution pH, light intensity and pollutant concentration (Zanoni et al., 2003).

The efficiency of the PEC process is enhanced by an anodic potential increase, since it slows down the electron-hole recombination and allows for the formation of additional reactive species on the cathode. Nevertheless, this enhancement is observed only until a certain anodic potential value, at which the maximum amounts of photoexcited electrons are driven to the cathode and the reaction becomes dependent only on the photon flux. With a further increase in the anodic potential, the space-charge layer can exceed the thickness of the photocatalyst, leading to a redistribution of the charges, reducing the PEC efficiency and increasing the energy consumption (Yang et al., 2016). This behaviour was observed by Wang et al. (2021) during the photo-electrocatalytic degradation of carbamazepine. With an increase of the bias voltage from 0.5 to 1.5 V, the carbamazepine degradation rate increased from 47 to 73%. Nevertheless, with a further increase up to 2.0 V, only 63% of the initial carbamazepine concentration was degraded. The authors
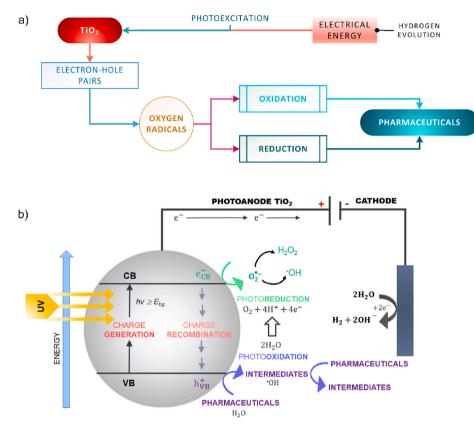
Fig. 7. Schematic of the photo-electrocatalysis process: a) process flow diagram; b) schematic representation PEC reactions. Adapted from (Jeon et al., 2018) and (Divyapriya et al., 2021).

attributed this reduced efficiency at a bias voltage of 2.0 V to the oxygen-evolution reaction at an elevated overpotential. On the other hand, if the catalyst layer thickness is too large, the material resistivity will rise, making the charge carriers moving to the catalyst surface more difficult and facilitating the charge recombination (Chaplin, 2014).

In addition to influencing the material conductivity, the catalyst thickness is also related to the light penetration into the film. Therefore, the catalyst thickness increases will enhance the process efficiency up to a limit, and a further increase will diminish the PEC performance (Garcia-Segura and Brillas, 2017). It is worth to mention that the incident radiation with a certain wavelength presents a maximum penetration depth into TiO$_2$ film according to the relation $1/\alpha$, where α is the TiO$_2$ absorption coefficient at the light wavelength (Hitchman and Tian, 2002). Furthermore, the surface area also plays an important role in PEC efficiency. While the reduction in the grain size increase of the active surface area, it also increases the grain boundaries and the defects associated with small grains. These boundaries and defects can act as trapping sites for electrons and holes, which slow down the charge carriers transport to the film active surface, and consequentially decrease the photocatalytic activity (Jelovica Badovinac et al., 2020).

The mass transfer between the catalyst surface and the bulk solution is directly related to the reactor geometry and flow profiles. It is expected that the system design is projected to minimize the resistance in the mass transfer. However, even in small scale reactors, deviations from the ideal mix configuration may happen. Computational fluid dynamics (CFD) is a tool that can consider these deviations in the models and provides information that helps to understand these complexities (Ješić et al., 2021).

The electrolyte type and concentration can strongly influence the PEC efficiency as they affect the solution's conductivity and can contribute to the formation of strong oxidant species (such as active chlorine species), the scavenging of OH$^\bullet$ (by inorganic anions, Eqs. (21)–(24)), and lead to the production of recalcitrant and toxic by-products

(chlorine derivatives) (Moreira et al., 2017). The common electrolytes applied in PEC systems include sodium and potassium salts like Na$_2$SO$_4$, NaCl, KCl, NaClO$_4$, NaNO$_3$, and Na$_2$CO$_3$. Of these, sodium sulfate (Na$_2$SO$_4$) is the most commonly used.

$$SO_4^{2-} + OH^\bullet \rightarrow SO_4^{\bullet 2-} + OH^- \tag{21}$$

$$Cl^- + OH^\bullet \rightarrow [ClOH]^{\bullet -} \tag{22}$$

$$PO_4^{3-} + OH^\bullet \rightarrow PO_4^{\bullet 3-} + OH^- \tag{23}$$

$$CO_3^{2-} + OH^\bullet \rightarrow CO_3^{\bullet 2-} + OH^- \tag{24}$$

Jia et al. (2020) evaluated the effect of Na$_2$SO$_4$ concentration in a PEC system on the degradation of sulfamethazine. An increase in the pharmaceutical degradation rate from 60 to 82% in 180 min was observed when the electrolyte concentration increased from 0.1 to 0.5 mol/L. With a further increase of the electrolyte concentration to 1 mol/L, no significant improvement in the degradation rate was observed. The authors also evaluated the effect of the presence of inorganic anions (Cl$^-$, CO$_3^{2-}$, PO$_4^{3-}$) and humic acid (HA) in the same PEC system. The sulfamethazine degradation rate was decreased with the ionic strength increase in all cases, with the lowest efficiency being observed in the system with HA. The interference in the sulfamethazine degradation was HA > PO$_4^{3-}$ > CO$_3^{2-}$ > Cl$^-$. The authors attributed the adverse impact of the inorganic anions and HA on the sulfamethazine degradation to the scavenging of active oxidants (h$_{vb}^+$ and OH$^\bullet$).

The light intensity (a photon flux with sufficient energy to promote the band gap) and the stirring rate influence the amount of photogenerated electrons and the mass transfer, respectively, in a PEC system. However, both parameters are not usually evaluated in most studies. Researchers normally use irradiation sources of high intensity and high stirring rates to ensure the maximum efficiency. The same behavior is observed for the influence of temperature, which is typically kept at

20–25 °C (Garcia-Segura and Brillas, 2017; Moreira et al., 2017). Nonetheless, it is important to mention that by optimizing the light intensity and the stirring rate, it is possible to achieve higher PEC efficiencies and reduce the operational costs.

The pH value influences the PEC efficiency. However, the best condition has to be determined experimentally, since this influence cannot be explained by PZC (as in photocatalysis) and depends on the interactions of the pollutant molecule and the photocatalyst surface, which will be positively charged at the anodic potential (Garcia-Segura and Brillas, 2017). Different optimum pH values were reported for different PEC systems during the degradation of target pharmaceuticals, such as pH 2.7 for sulfamethoxazole (TiO$_2$/Ti photoanode) (Su et al., 2016), pH 3.5 for sulfamethazine (zeolitic imidazolate frameworks with N and F co-doped TiO$_2$ nanotubes photoanode) (Jia et al., 2020), pH 5.4 for ciprofloxacin (expanded graphite supported p-n MoS$_2$–SnO$_2$ photoanode) (Umukoro et al., 2018), pH 5.6 for diclofenac (γ-Bi$_2$MoO$_6$ photoanode) (S. Liu et al., 2017) and pH 9.0 for tetracycline (K$_2$Ti$_6$O$_{13}$ nanobelt/TiO$_2$ microflower - ITO photoanode) (Wang et al., 2019). In PEC system where the anodic and cathodic reactions take place in separated tanks, the pH in the anode tank may decrease during the reaction. To solve this problem, the conventional salt bridge can be replaced by a cation exchange membrane, which allows the transport of H$^+$ generated in the anode tank to the cathode tank (Diao et al., 2013).

Regarding the initial pollutant concentration, the usual observation is that for high initial concentrations longer treatment times are required. This is the case for sulfamethoxazole photoelectrocatalytic degradation, reported by Su et al. (2016), where it was necessary to increase the reaction time from 50 to 250 min for the complete degradation when the initial concentration was increased from 0.7 to 13 mg L^{-1}. However, R. Daghrir et al. (2013) reported similar degradation rates (97–92%) for the degradation of chlortetracycline with initial concentrations ranging from 32 to 230 μg/L, indicating that for low pharmaceutical concentrations, the PEC efficiency can be maintained.

Since the degradation kinetics typically follows pseudo first order, the initial concentration should not influence the kinetic constant values. Nevertheless, lower pseudo-first-order kinetic constants for higher pollutant concentrations are often observed. This behavior can be attributed to a possible shift from the pseudo-first-order kinetic to the zero-order kinetic or limitations of this kinetic model to precisely describe the decay, since it simplifies the many reactions that occur simultaneously in a PEC system (Moreira et al., 2017).

3.3.3. Degradation mechanisms

First-principle theoretical methods already struggle to describe photo-induced processes and electrochemical reactions, which is in no small part due to the enormous computational cost. Since a theoretical description of photoelectrocatalysis compounds presents difficulties, few papers on this topic employ any first-principle calculations.

When DFT is employed, it does not account for the photo-activation and the electric field. When investigating water splitting and the photoelectrochemical degradation of tetracycline over a F–BiVO4@NiFe-LDH photoanode, Liu et al. (2020) used DFT to study the structure-property relations. They focused on calculating the binding energies between F$^-$ doped and undoped BiVO$_4$, and NiFe-LDH, showing that F$^-$ increases the interaction. The band structure calculations, band gap, density of states and work function confirmed that F$^-$ increases the range of the light absorption and improves the function of the catalyst. Similarly, Ma et al. (2021) calculated the band structure, density of state and work function for p-chloronitrobenzene photodegradation by BiO-Br/TiO$_2$ nanotube arrays. Sometimes, DFT is used to calculate the charge distribution and bond orders, such as in a study of sulfamethoxazole degradation in plasma (Zheng et al., 2019).

3.3.3.1. Chemical micro-kinetics or Monte Carlo at mesoscale. Understanding the mechanisms on the mesoscale is vital to link the atomic-

scale, first-principles catalysis to continuum-based reactor unit operation design or optimization. The mesoscale thus calls for the integration of adsorption, desorption, kinetics, diffusion and/or convection, or at least a comparison of these in terms of the assessment of process-rate-determining steps, simplifying it enough for control later. Indeed, looking at the literature, little has been completed in this specific direction, highlighting the opportunity and necessity to develop an integrated understanding of both (photo)(electro)catalytic degradation mechanisms and reactor unit design.

Manassero et al. (2015) were the first to apply a Monte Carlo methodology to the photocatalytic degradation reactions of a drug, focusing on the modeling of radiation itself. Pharmaceutical clofibric acid was subjected to detailed kinetic modeling in a reactor. Manassero et al. (2017) later advanced this by implementing the Monte Carlo simulations to optimize the conditions under photocatalytic degradation reactions, immobilizing TiO$_2$ on packing to provide a continuous process operation. Jalali and Dezhampanah (2021) applied a genuine kinetic Monte Carlo model simulation so as to describe the catalytic surface photodegradation of amoxicillin, ampicillin and cloxacillin, tackling the complexity of the intermediates as well.

As photo-, electro- and photo-electro-catalysis bring about an increase in complexity, the latter is an emerging research field, while in thermo-catalysis such a methodology is much more common to date. However, model integration is still performed intuitively.

In our recent work (Suhadolnik et al., 2019a) we demonstrated how micro-kinetics could be usefully put to work to understand, predict, and optimize reactions as complex as the electro-catalytic phenol degradation, which proceeds through various intermediate/product steps. The concentrations of all bulk/surface intermediates or products can thus be simulated for multiple process times, reactor positions, as well as operating process conditions (Fig. 8).

4. Catalytic materials

The development of new materials for applications in water and wastewater treatment is growing fast in recent years. The need for efficient and at the same time low-cost materials is an issue for the removal of different water contaminants, including pharmaceuticals as well as heavy metals (Khandaker et al., 2021), endocrine disruptors (Diao et al., 2018), rare earths (Kubra et al., 2021), nitrate reduction (Diao et al., 2019b), dyes (Katheresan et al., 2018), algae inactivation (Diao et al., 2019a), among others. Furthermore, many reviews on catalytic materials were published (Atkinson et al., 2019; Gadipelly et al., 2014; Khetan and Collins, 2007; Kitanosono et al., 2018; Patel et al., 2019; Singh et al., 2018). They focus on synthesis methods and characterization of various groups of materials that can be used for the degradation of pharmaceuticals. They include non-metal materials, metals on in/organic supports, metal-organic frameworks, bulk metals, metal hydro/oxides, metal nanoparticles and surfactant-based catalysts. This section of the review will focus on titanium dioxide (TiO$_2$) as a catalytic material for photocatalysis, electrocatalysis and photo-electrocatalysis, as well as on boron-doped diamond (BDD) and heterostructured materials. They are among the most promising materials for the photo-electro-catalytic oxidation of pharmaceuticals or their conversion into biocompatible compounds.

It is important to mention that many catalyst properties can influence photo(electro)catalytic performance, such as size, specific surface area, pore volume, pore structure, crystalline phase, and exposed surface facets. Thus, a precise characterization of the catalyst materials is crucial for comprehending the photocatalytic mechanism and enabling the synthesis of enhanced photo(electro)catalysts (Luo et al., 2017; Nakata and Fujishima, 2012). Fig. 9 summarizes the techniques most utilized for the characterization of photo(electro)catalysts.
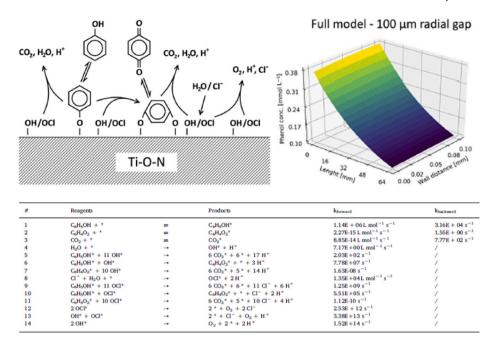
#	Reagents		Products	$k_{forward}$	$k_{backward}$
1	$C_6H_5OH + *$	$\rightleftharpoons$	C_6H_5OH*	$1.14E+06 \, L\,mol^{-1}\,s^{-1}$	$3.16E+04 \, s^{-1}$
2	$C_6H_4O_2 + *$	$\rightleftharpoons$	$C_6H_4O_2*$	$2.27E-15 \, L\,mol^{-1}\,s^{-1}$	$1.55E+00 \, s^{-1}$
3	$CO_2 + *$	$\rightleftharpoons$	CO_2*	$8.85E-14 \, L\,mol^{-1}\,s^{-1}$	$7.77E+02 \, s^{-1}$
4	$H_2O + *$	$\rightarrow$	$OH* + H^+$	$7.17E+00 \, L\,mol^{-1}\,s^{-1}$	/
5	$C_6H_5OH* + 11\,OH*$	$\rightarrow$	$6\,CO_2* + 6\,* + 17\,H^+$	$2.03E+02 \, s^{-1}$	/
6	$C_6H_5OH* + OH*$	$\rightarrow$	$C_6H_4O_2* + * + 3\,H^+$	$7.78E+07 \, s^{-1}$	/
7	$C_6H_4O_2* + 10\,OH*$	$\rightarrow$	$6\,CO_2* + 5\,* + 14\,H^+$	$1.63E-08 \, s^{-1}$	/
8	$Cl^- + H_2O + *$	$\rightarrow$	$OCl* + 2\,H^+$	$1.35E+04 \, L\,mol^{-1}\,s^{-1}$	/
9	$C_6H_5OH* + 11\,OCl*$	$\rightarrow$	$6\,CO_2* + 6\,* + 11\,Cl^- + 6\,H^+$	$1.25E+09 \, s^{-1}$	/
10	$C_6H_5OH* + OCl*$	$\rightarrow$	$C_6H_4O_2* + * + Cl^- + 2\,H^+$	$5.51E+05 \, s^{-1}$	/
11	$C_6H_4O_2* + 10\,OCl*$	$\rightarrow$	$6\,CO_2* + 5\,* + 10\,Cl^- + 4\,H^+$	$1.12E-10 \, s^{-1}$	/
12	$2\,OCl*$	$\rightarrow$	$2\,* + O_2 + 2\,Cl^-$	$2.53E+12 \, s^{-1}$	/
13	$OH* + OCl*$	$\rightarrow$	$2\,* + Cl^- + O_2 + H^+$	$3.38E+13 \, s^{-1}$	/
14	$2\,OH*$	$\rightarrow$	$O_2 + 2\,* + 2\,H^+$	$1.52E+14 \, s^{-1}$	/

Fig. 8. Example of mechanism (top left), the reactions with constants (below) and the predictions of the process of degradation (top right), applying chemical micro-kinetics; results are reproduced from our previous work (Suhadolnik et al., 2019a), taking phenol as a model compound. Copyright© (2019), with permission from Elsevier.

Fig. 9. Characterization techniques used for photo(electro)catalysts.

4.1. Titanium dioxide (TiO_2)

TiO_2 is the most widely studied photocatalyst, since it combines important physical-chemical properties such as chemical stability, long durability, and transparency to visible light, with the advantage of low cost and high photocatalytic activity (Luo et al., 2017; Nakata and Fujishima, 2012). Crystalline TiO_2 can exist in three different phases: anatase, rutile, and brookite. The first two can be easily synthesized in the laboratory and are widely used in photocatalytic studies. Rutile is the most stable form, while anatase exhibits better photocatalytic activity (Pelaez et al., 2012). Meanwhile, there is a lack of studies using

brookite for the degradation of pharmaceuticals. Table 4 shows some physical and structural properties of the anatase and rutile phases.

The high photocatalytic activity of anatase, when compared to rutile, is related to characteristics that include: i) lower packing density (~3.8 g/cm³) (Liu et al., 2010); ii) presence of [0 0 1] facets with remarkable photocatalytic activity due to the abundance of under-bonded Ti atoms as well as large Ti–O–Ti bond angles (Gong and Selloni, 2005); iii) longer recombination lifetimes and, iv) photocarriers with faster migrations to the catalyst surface (Zhang et al., 2014). The combination of two different phases produces a synergetic effect in photocatalysis, as is the case for the most common TiO_2 commercial powder, P25 (80% anatase,

Table 4
Physical and structural properties of TiO$_2$ (anatase and rutile) (Burnside et al., 1999; Luo et al., 2017; Pelaez et al., 2012).

Property	Crystalline phases	
	Anatase	Rutile
Band gap (eV)	3.2	3.0
Valence band (eV)	−2.8	−2.4
Conduction band (eV)	0.4	0.6
pH$_{ZPC}$	6.4	5.8
Density (g/cm^3)	3.79	4.13
Light absorption (nm)	<390	<415
Dielectric constant	31	114
Refractive index	2.55	2.75
Crystal structure	Tetragonal	Tetragonal
Mohr's Hardness	5.5	6.5–7.0
Melting point	1825	1825
Boiling point	2500–3000	2500–3000
Lattice constants (Å)	$a = 3.78$	$a = 4.59$
	$c = 9.52$	$c = 2.96$
Ti–O bond length (Å)	1.94 (4)	1.95 (4)
	1.97 (2)	1.98 (2)
Electron mobility (cm^2/V s)	10	1

20% rutile). It was also found that the optimum mixture rate is up to 60% anatase and 40% rutile, and that this approach can also be applied to the anatase and brookite mixtures (Luo et al., 2017).

TiO$_2$ nanoparticles can be produced by different synthesis techniques, including sol-gel (Dolatabadi et al., 2021), hydrothermal (Li et al., 2020), solvothermal (Das et al., 2008), anodic oxidation (Marinko et al., 2021), chemical vapor deposition (Khanna et al., 2020), electrospinning (Marinho et al., 2021), etc. Depending on the methodology utilized for TiO$_2$ production, the nanoparticles can present different structural dimensionalities, such as powders and 1 to 3D, which imparts different properties to the produced material (Fig. 10). Furthermore, a significant enhancement of the photocatalytic performance of TiO$_2$ can be achieved with strategies like surface modification and doping (Luo et al., 2017).

The nanostructured TiO$_2$ powders are the most widely studied and used in TiO$_2$-related materials. Commercial TiO$_2$ powders include P25,

which is composed of a mixture of anatase and rutile phases, and PC105, PC500, which are pure anatase (Marinho et al., 2018). The main advantage of this type of structure is a larger specific surface area and the high pore volume and size, which facilitates the rate of mass transfer and the pollutants' adsorption (Nakata and Fujishima, 2012). Using these materials in slurry systems brings about the need for a post-step (such as filtration) to remove the photocatalysts or a previous immobilization of the nanoparticles in inert supports. The same behavior occurs with 2D nanosheets and 3D nanostructured TiO$_2$ materials.

This could be avoided with the use of TiO$_2$ 1D structures, such as fibers and tubes, which can be synthetized with electrospinning and anodization methods, respectively. Electrospinning is a simple and effective method of producing nanofibers through a high-voltage electric field, in which the TiO$_2$ can be electrospun with a polymer solution (Marinho et al., 2021). Anodization is a useful tool for producing nanotubes in which TiO$_2$ structures are grown directly in an electrode foil/mesh (Nakata et al., 2011). In both cases the TiO$_2$ is already strongly attached to the produced material, eliminating the need for nanoparticle immobilization or a post-step to remove the nanoparticles from the solution/effluent.

The structural characteristics of these 1D materials result in superior photocatalytic activity since they enable a facile diffusion of organic pollutants over the TiO$_2$ nanofibers/nanotubes. Furthermore, for TiO$_2$ nanotubes, a reduction in the electron/hole recombination is also observed since the thickness of the nanotube walls is smaller than the TiO$_2$ carriers' diffusion length (Almquist and Biswas, 2002).

Doping is an attractive strategy to overcome the limitations of TiO$_2$ related to the need for irradiation with wavelengths below 385 nm to promote its activation. Doping or co-doping TiO$_2$ with non-metals (N, F, C, S, B) (Dozzi and Selli, 2013; Li et al., 2005; H. Yu et al., 2021), transition metals (Cu, Ni, Cr, Fe) (A. S. Chen et al., 2021; Ferreira et al., 2021; Lee et al., 2021; Mancuso et al., 2021), noble metals (Pt, Ag, Au) (J. He et al., 2021; Komaraiah et al., 2020; Mohammed, 2020) and rare earths (La, Ce, Eu) (Chaker et al., 2020; Prakash et al., 2021), are approaches that change the crystalline structure and significantly improve the TiO$_2$'s photocatalytic activity by shorting the band gap and expanding the absorption wavelength to visible light. The synthesis of

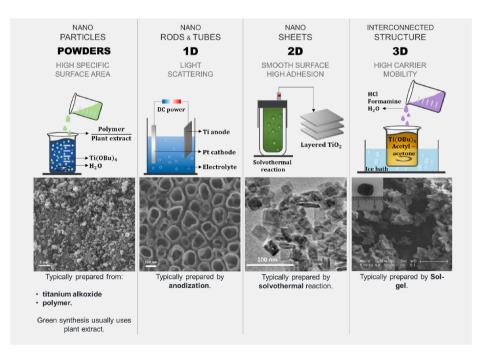**Fig. 10.** Schematic of the structural dimensionality of materials with the expected properties. SEM/TEM images reprinted from: powders – Nabi et al., 2021, Copyright© (2021), with permission from Elsevier; 1D – Koiki et al., 2020, Copyright© (2020), with permission from Elsevier; 2D – Qu et al., 2021, Copyright© (2021), with permission from Elsevier; Chen et al., 2010, Copyright© (2010), with permission from Elsevier.

TiO₂ composites can also contribute to the enhancement of the photo (electro)catalytic efficiency. As an example, the GO/TiO₂ composite is generally more efficient than pure TiO₂, since the GO sheets can accept and transport the photo-generated electrons, reducing the electron/hole recombination (Garmroudi et al., 2020). Xie et al. (2019) evaluated the efficiency of titanium dioxide doped with zinc, fixed on reed straw biochar (Zn–TiO₂/pBC), for the degradation of sulfamethoxazole (SMX). The material showed visible light response due to the presence of zinc, which also hindered the combination of photogenerated electrons and holes. The biochar proved to be a suitable support, facilitating the adsorption of the SMX and its by-products. Fig. 11 shows a schematic diagram of the mechanism of Zn–TiO₂/pBC photocatalytic activity and SMX degradation. The removal rate of SMX was increased from 50%, when using only TiO₂, to 81%, when using Zn–TiO2/pBC (Xie et al., 2019). It is clear that these improvements provide beneficial effects for the photodegradation of pharmaceuticals; however, it is necessary to evaluate whether the oxidative strength of photogenerated holes is lower than in undoped TiO₂ or if the use of expensive or potentially toxic materials could hamper the use of these new materials.

4.2. Boron-doped diamond (BDD)

BDD is a material that combines diamond-like properties like chemical inertness, extreme hardness, thermal conductivity, low friction, high charge-carrier mobilities and versatility with boron's electrical conductivity due to its incorporation into the diamond lattice (Guillery, 1993). Other electrochemical characteristics that increase the material's popularity are a wide solvent window, low capacitance, reduced resistance to fouling and mechanical robustness (Cobb et al., 2018). When synthesizing a diamond electrode, four different thin-diamond-electrode outcomes can be fabricated. They are presented in Fig. 12 (Luong et al., 2009).

There are many diamond thin-film syntheses procedures and post modifications, such as etching/shaping (Yang et al., 2005), high-pressure, high-temperature (Ekimov and Kondrin, 2020), vacuum annealing (Watanabe et al., 2002), surface transfer doping (Strobel et al., 2004) and chemical vapor deposition (CVD). Of these, CVD is the most favored and widely used due to the possibility of the film growing on any substrate geometry (May, 2000). However, the harsh conditions limit the substrates that can be used for diamond-film synthesis. The most suitable are niobium (Jum'h et al., 2017), tungsten (Vokhmyanin and Oglezneva, 2019), silicon (May, 2000) and titanium (Askari, 2012). Interestingly, more flexible substrates, such as polymers (Parylene-C
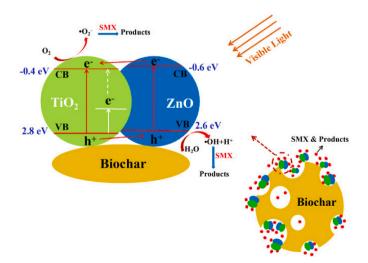

Fig. 11. Mechanism of photocatalytic activity of Zn–TiO2/pBC under visible light irradiation. Reprinted from (Xie et al., 2019). Copyright© (2019), with permission from Elsevier.
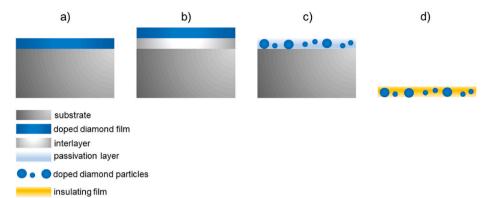
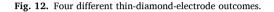(Fan et al., 2017)), can be used if the film is transferred to the substrate.

The CVD synthesis of a thin diamond film is schematically presented in Fig. 13 and can be described as a four-step sequence. First, a mixture of hydrogen/hydrocarbon gas (usually methane and hydrogen (Butler et al., 2009)) is activated via hot-filament CVD (HF-CVD) or a microwave plasma CVD (MW-CVD). Second, hydrogen atoms react with the hydrocarbon and create a mixture of hydrocarbon species. The hydrogen atoms also create radical surface sites for the adsorption of carbon species and the recombination of hydrogen atoms. In the last step, the hydrogen atoms and other gaseous species react with sp/sp² carbon sites and convert them into sp³ carbon. The hydrogen-terminated surface drives the carbon to incorporate into the diamond lattice (Butler et al., 2009; Srikanth et al., 2012). Competition between the surface-activation reaction and hydrogen-atom recombination with the radical surface site is linked to the number of nucleation sites. The growth continues as the carbon diffuses over the surface until the diamond seeds eventually merge and form a highly controlled thin film.

Regardless of the crystallinity, a diamond has a wide band gap of 5.47 eV. As diamond is inherently an insulator, the conductivity is achieved with doping. One possible route is the so-called surface-transfer doping. In this case, dopant atoms are not incorporated into the diamond lattice. Instead, they are evaporated and adsorbed onto the hydrogen-terminated surface (Strobel et al., 2004). Another possibility is annealing in different atmospheres (Seshan et al., 2013), high-temperature diffusion (Seo et al., 2014), and ion implantation with heteroatoms (Prawer and Kalish, 1995). Depending on the dopant, new energy levels are formed, forming a *n-* or *p-*type semiconductor. However, the method is invasive and demands harsh conditions, often leading to a resistive material (Goss et al., 2008). The possibility of damaging the substrate is high, but if the ion implantation is controlled, the controlled growth of a doped diamond film is possible (Achard and Tallaire, 2018).

By far the most popular method is doping with gas during the CVD synthesis of the diamond thin film. Besides the typical CVD setting for a diamond-film synthesis, the addition of boron in gaseous form is needed (Macpherson, 2015). The substitution of the sp³ hybridized carbon atoms in a tetrahedral diamond lattice with boron atoms occurs during the process, which results in the formation of a BDD film (Luong et al., 2009). The boron atom is the most favorable for diamond doping since i) it can easily incorporate into the packed lattice due to its small size, ii) it acts as an electron acceptor, iii) it modifies the material electrical properties (Yang et al., 2005), and iv) it has a small activation energy (0.37 eV) (Macpherson, 2015). Doping diamonds with boron introduces holes into the lattice and makes the diamond film a *p-*type semiconductor. Time, pressure, gas ratio, the addition of other gases and other parameters influence the grain size of BDD films. An important characteristic is that the crystalline facets will increase with the growth period or the film thickness.

According to Macpherson (2015), the following issues must be considered when working with BDD: i) surface morphology, ii) amount of boron that contributes to the conductivity, and iii) surface termination. Because the surface morphology has a considerable impact on the electrochemical behavior, a complete surface characterization must be performed before analyzing results, emphasizing the crystallinity, the surface roughness and the grain size (Šelešovská et al., 2016; Zhao et al., 2010). Understanding the material properties and electrode characteristics is vital for achieving the maximum growth of the material. The boron concentration can be determined with the methods mentioned in Table 5; its values are usually expressed in *ppm, %* or *the number of atoms* per *cm³*. Approximately one boron atom per 1000 carbon atoms must be placed to ensure optimal semiconductor properties (Macpherson, 2015). Lastly, the BDD surface can be oxygen-terminated (*hydrophilic, positive electron affinity*) or hydrogen-terminated (*hydrophobicity, negative electron affinity*). Surface termination has a considerable impact on the electron transfer, wettability and electrostatic interactions (Bhardwaj et al., 2020; Hoffmann et al., 2010). Immediately after the synthesis, the
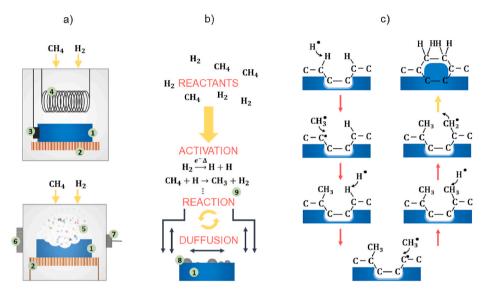
Fig. 12. Four different thin-diamond-electrode outcomes.

Fig. 13. Schematic of processes occurring during diamond CVD. a) overview of the process. 1-Substrate, 2-substrate heater, 3-thermocouple, 4-filament, 5-plasma, 6-microwave generator, 7-tuner. b) details of the process. 1-substrate, 8-diffusion layer, 9-generation of free radicals.

BDD electrode is hydrogen terminated. However, the oxygen-terminated surface possesses better electrochemical characteristics (Hutton et al., 2013). Therefore, the surface termination needs to be checked periodically and acted upon if a change is needed.

BDD's popularity for wastewater treatment is attributed to the absence of hydrogen and oxygen evolution reactions that could interfere with the degradation and analysis. This is a consequence of the very low capacitance, the absence of surface oxide, the high overpotential and the reduced reactions between oxygen and hydrogen evolution (Santana et al., 2005). Moreover, its use allows the rapid production of hydroxyl radicals with a high standard reduction potential (E^o OH$^\bullet$/H$_2$O, 2.8 V), contributing to a significant unselective reactivity with organic contaminants. However, if the electrochemical conditions during degradation are severe, delamination of diamond film from the BDD electrode can occur (Chaplin et al., 2011, 2013). This can result in lower efficiency and, possibly, electrode failure. Delamination results from etching the sp^2 carbon that acts as a deactivation site for the OH$^\bullet$ radicals (Wang et al., 2014). If the phenomenon is detected in time, it can be slowed by changing the electrochemical conditions.

Li et al. (2019) investigated the degradation of 300 mL of an aqueous solution of ciprofloxacin in a differential column batch reactor where the BDD anode was 15 mm from the titanium foil cathode. Different concentrations (1, 5, 10, 20 mg L^{-1}), process times (5, 25, 30, 50 min), current densities (5, 10, 20, 30, 40 mA cm^{-2}), supporting electrolyte concentrations (5, 50, 100, 500 mmol L^{-1}), pHs (3, 4.5, 7, 9) and

voltages (between 3.5 and 8.6 V) were monitored, and the best degradation conditions determined.

4.3. Heterostructured materials

The construction of heterojunctions based on coupling two different semiconductors is an efficient strategy to reduce the recombination of electron-hole pairs and to overcome one of the main drawbacks in photocatalytic applications. When semiconductors have different Fermi energy levels (E_F), the electrons of the semiconductor with higher E_Fs are spontaneously diffused to the one with the lower E_F, forming an electric field at the heterojunction interface, which inhibits the recombination of the carriers (Yang, 2021). It is important to mention that this electric field depends on many factors, such as the semiconductivity (*p-type* or *n-type*), the Fermi level, and the conduction and valence band potentials of the semiconductors. Heterojunction photocatalysts can be divided into four types: i) semiconductor-semiconductor (S–S); ii) semiconductor-metal (S-M); iii) semiconductor-carbon (S–C); and iv) tandem heterojunctions (Xue and Bao, 2021). Low et al. (2017) presented a detailed review of the basic principles of various heterojunction photocatalysts.

An important example of a heterostructured material for photo-electrocatalytic processes is the combination of the *p-type* BDD with the *n-type* TiO$_2$. This makes it possible to enhance the material's quantum yield by reducing the recombination of electron-holes (photogenerated

Table 5

Experimental parameters of BDD film synthesis.

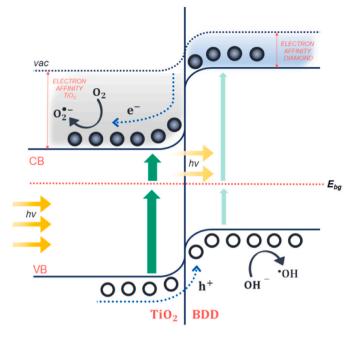|	SUBSTRATE	SYNTHESIS CONDITIONS	ANALYSIS	REF.
HF-CVD	Silicon wafers (100), niobium-coated under diamond seeds.	**Filaments:** 16 kW, 12 pcs of 32 cm long tantalum filament **Time:** 12 and 60 h **Temperature:** 0 °C **Pressure:** 4000 Pa **Gas flux:** $(CH_3)_2CO$ 90 sccm, $B(OCH_3)_3$ 6 sccm (7902 ppm of B) and H 400 sccm	FE-SEM RAMAN XRD CV	(Song et al., 2020)
	• After 12 h the film resulted in 1.22 μm thickness and 5.91 μm after 60 h of the • The electrochemical performance was influenced by the intrinsic properties of the particles exposed and not by the density and thickness of the BDD film. deposition.			
	Silicon wafers (single-crystal), polished with 1 μm diamond paste	**Filaments:** Helical-shaped filaments, 0.127 mm diameter tungsten wire, operated at 1800 °C **Time:** 20–90 h **Temperature:** 750–800 °C **Pressure:** 5300 Pa **Gas flux:** H 100 sccm, Ar 2–10 sccm and B 200–6300 ppm. Feed gas was a mixture of argon, bubbled through a solution of B_2O_3 in C_2H_6O, and H. The B_2O_3/C_2H_6O ratios ranged from 10 g L^{-1} for the lowest doping level to 50 g L^{-1} for the highest doping level.	SEM RAMAN XRD TGA SIMS AES	Farabaugh et al. (1995)
	• The following parameters had the most significant influence on the growth rate: argon flow rate between 8 and 10 sccm, a substrate temperature of 800 °C, increased amount of carbon and hydrogen flow rate of 100 sccm.			
MW-CVD	Silicon wafers (*p-type* <111> oriented single-crystalline), polished with 0.25 μm diamond paste for 1 h	**Time:** 7 h **Temperature:** 800 °C **Pressure:** 35 Torr **Gas flux:** B_2H_6 0, 0.005, 0.01, 0.1, 0.5, 1 ppm, CH_4 and H, B/C ratios were 0, 2, 4, 40, 200, 400 ppm, CH_4 to H volumetric ratio 0.5%, gas flow rate 100 cm^3 min^{-1}	SIMS SEM STM TEM EELS RAMAN	Wang et al. (1992)
	• With a growth rate of 0.15 μm h^{-1}, the film resulted in 1.1 μm thickness. • Boron increased structural perfection but reduced diamond grain size.			
	Oriented diamond films (001), etched *in situ* in hydrogen microwave plasma for 20 min to remove the surface contamination	**Time:** 4–6 h **Temperature:** 770 °C **Pressure:** 1.3–5 bar **Ga flux:** CH_4 0.5% (2 sccm), H 99.5% (498 sccm), trimethylborate (TMB)/ triethylborate (TEB)/tripropylborate (TPB) 93 ppm (up to 550 ppm), B/H ratios were 1–10 sccm	SEM AFM RAMAN SIMS EPMA ERD	Jiang et al. (1999)
	• *In situ* doping.			
	Silicon wafers (100) coated with silicon dioxide grown via a thermal growth process. Surfaces were seeded with nanocrystalline diamond particles via immersion in an ultrasonic system and grown in plasma	**Thermal diffusion:** Diffusion was carried on 3 samples of ultra-nanocrystalline diamond films grown on a silicon substrate. Annealing at low oxygen atmosphere at 800, 900, 1000 °C for 180 s for inducing the process of boron diffusion inside the diamond film	RAMAN XRD SEM SIMS XPS UPS	Tirado et al. (2018)
	• An approximately 200 nm thick boron coating was deposited on the surface of ultra-nanocrystalline diamond films using the spin-on-dopant solution.			
	Nanodiamond with a diameter of 4.7 nm and specific surface area of 270 m^2 g^{-1}	**Post - heat treatment:** air at 425 °C for 8 h to minimize the amount of sp^2 carbon impurities **Time:** 8 h **Temperature:** 800 °C **Gas flux:** 70% $B(OCH_3)_3/CH_4$ and acetone (the B/C atomic concentration ratio was 20,000 ppm)	RAMAN TEM BET CV	Miyashita et al. (2019)
	• Post - heat treatment was necessary to minimize the amount of sp^2 carbon impurities.			
	Polypyrrole films (*coral-like polypyrrole*), coated with a dense layer of diamond nanoparticles using an electrostatic grafting process	**Time:** Until a continuous boron doped nanocrystalline diamond layer was obtained (6 and 12 h) **Temperature:** seeds grown at a temperature below 450 °C **Pressure:** 20 Torr **Gas:** CH_4 1%, $B(OCH_3)_3$ 2.4%	SEM RAMAN EIS CV	Hébert et al. (2015)
	• The thickness of a diamond layer is 90 and 170 nm. • Incredible electrochemical performances, porous diamond material and no limitation for the process to reach larger surface areas.			
	Silicon pillar array 10 μm diameter and 50 μm height, silicon wafer as a blank	**Special:** Photolitography **Gas:** $B(OCH_3)_3$, CH_4 and $(CH_3)_2CO$ 70%. B/C atomic concentration ratio of 20,000 ppm	SEM RAMAN CV EIS	Kondo et al. (2017)
	• CV measurements indicated successful enhancement of the double-layer current up to 2800 μF cm^{-2}, maintaining a wide potential window and short time constant (18 ms). • The use of photolithography increased the specific surface area of BDD (use of silicon pillar array).			

Fig. 14. Schematic band diagram of the *n-type* TiO$_2$ nanotubes and *p-type* BDD heterojunction.

charge carriers), making it more efficient for the degradation process. BDD can be used directly or as a substrate for other materials. By immobilizing the TiO$_2$ on a conductive material, it is possible to suppress the electron-hole recombination and, consequently, improve the photocatalytic efficiency by forming a heterojunction. This type of structure acts as an internal electrostatic potential in the space-charge region, allowing for an efficient separation of the photo-induced charge carriers (Fig. 14).

There are three possibilities for electrodes: i) separate TiO$_2$ and BDD electrode; ii) TiO$_2$ films on the BDD electrode where the morphology of the deposition of TiO$_2$ films can vary (nanocrystals, nanosheets, nanorods, etc.), and iii) BDD on the TiO$_2$ electrode. Han et al. (2011) reported that the p-n junction elevates the photoelectrocatalytic activity over the oxidation of organic compounds in wastewaters. Additionally, the heterostructure electrode has an excellent resistance to acids (due to the BDD). Yuan et al. (2010) also reported that the heterojunction shows no loss of activity in the recycling experiments. Han et al. (2013) also reported on a very high chemical stability.

The evidence of the heterojunction formation can be observed by TEM and HRTEM micrographs. As an example, in Fig. 15 it is possible to observe the heterojunction between the rGO, g-C$_3$N$_4$ and CoFe$_2$O$_4$

nanoparticles (rGO/g-CN/CFO). In Fig. 15a it is highlighted the g-CN/CFO composite is well attached on rGO nanosheet, which is fundamental to the heterojunction formation. In Fig. 15b it can be noted d-spacing of CFO nanoparticle (0.239 nm, (311) plane), which makes the interface formation with g-CN and rGO nanosheets (Palanivel et al., 2021).

Graphitic carbon nitride (g-C$_3$N$_4$) has low-charge carrier mobility and low surface area, which limits its application in photocatalysis. However, it has a unique band structure, capable of coupling it with a large bandgap semiconductor to produce Z-scheme heterojunction composites (Ismael, 2020). Wu et al. (2022) have evaluated the tetracycline degradation using a floral and lamellar interlaced double Z-scheme ternary heterojunction Bi$_2$O$_2$CO$_3$/g-C$_3$N$_4$/Bi$_2$O$_3$ (CNBB-5). The synthesized heterostructured material showed enhanced photocatalytic than the single catalysts, under simulated solar irradiation. All individual catalysts presented less than 50% of TC degradation, while the ternary heterojunction material was capable to degrade up to 100% of TC in the same reaction time. In this dual Z-scheme structure (Fig. 16), the photogenerated (e$_{cb}^-$) of Bi$_2$O$_2$CO$_3$ and Bi$_2$O$_3$ can be transmitted to the VB of g-C$_3$N$_4$ so that photogenerated electrons can reduce O$_2$ to produce O$_2^{\bullet-}$ in the CB of g-C$_3$N$_4$. At the same time, the (h$_{vb}^+$) of Bi$_2$O$_2$CO$_3$ and Bi$_2$O$_3$, are able to oxidize TC to small molecules, while (h$_{vb}^+$) of Bi$_2$O$_2$CO$_3$ can also react with water to produce OH$^\bullet$ (Wu et al., 2022).
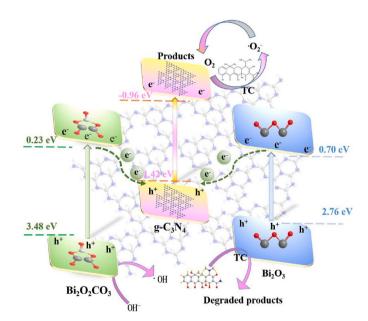

Fig. 16. Schematic heterojunction mechanism of CNBB-5. Reprinted from (Wu et al., 2022). Copyright© (2022), with permission from Elsevier.
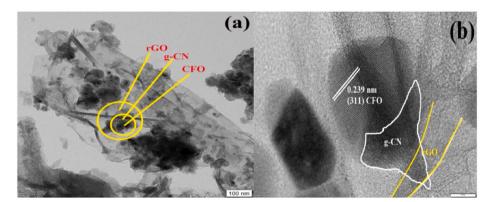

Fig. 15. Evidence of heterojunction formation on rGO/g-C$_3$N$_4$/CoFe$_2$O$_4$ (rGO/g-CN/CFO) photocatalyst confirmed by a) TEM and b) HRTEM images. Reprinted from (Palanivel et al., 2021). Copyright© (2021), with permission from Elsevier.
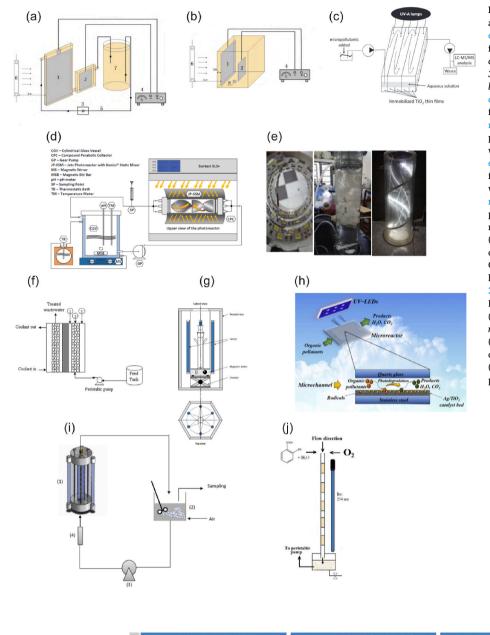
Fig. 17. The most common types of catalytic reactors. a) TNAs based thin-layer PEC reactor (Bai et al., 2010), Copyright© (2010), with permission from Elsevier; b) conventional PEC reactor *(for both a and b: 1-double-faced TNAs electrode, 2-Pt electrode, 3-peristaltic pump, 4-DC power supply, 5-hose, 6-UV lamp, 7-solution container, 8-magnetic stirrer)* (Bai et al., 2010), Copyright© (2010), with permission from Elsevier; c) continuous-flow reactor (Carbonaro et al., 2013), Copyright© (2013), with permission from Elsevier; d) low system equipped with two Kenics® static mixing elements (Díez et al., 2018), Copyright© (2018), with permission from Elsevier; e) fluidized bed type LED reactor with immobilized catalyst on MBBR media (Surenjan et al., 2019), Copyright© (2019), with permission from Elsevier; f) packed bed photoreactor (PBPR) (Sarkar et al., 2015), Copyright© (2015), with permission from Elsevier; g) cylindrical batch photoreactor (Palmisano et al., 2015), Copyright© (2015), with permission from Elsevier; h) microchannels microreactor (Eskandarloo et al., 2015), Copyright© (2015), with permission from Elsevier; i) fluidized bed photocatalytic reactor (FBPR) *(1-FBPR, 2-storage tank, 3-pump, 4-flow-meter)* (Rezaei and Mohseni, 2017), Copyright© (2017), with permission from Elsevier; j) quartz capillaries as multiphase photocatalytic reactors (Hurtado et al., 2016), Copyright© (2016), with permission from Elsevier.

Fig. 18. Parameters of photocatalytic, electrocatalytic and photoelectrocatalytic degradation. 1-flow rate, 2-light source, 3-light intensity, 4-surface-to-volume ratio, 5-mixing, 6-applied potential, 7-distance between electrodes, 8-solution conductivity.

5. Design of laboratory reactors

Photocatalytic, electrocatalytic or photoelectrocatalytic reactor is a device where the conversion of pharmaceuticals occurs. Depending on the process being used to degrade organic contaminants, there are several different reactor types. While a photoelectrocatalytic reactor can also be used for a photocatalytic or electrocatalytic process, this is not the case with the other two reactor types, which significantly differ in terms of device design and operation. Electrocatalytic reactors require electrically conductive electrodes positioned parallel to one another

Table 6
Results of the degradation of pharmaceuticals published in the literature.

Degradation process and catalyst	Pharmaceutical compound(s)	Initial concentration	Reactor type	Experimental conditions	Removal of the starting compound [%]	Ref.
Photocatalysis Three forms of TiO_2	Ibuprofen	10 mg L^{-1}	Batch photoreactor	10 mg of photocatalyst 250 mL aqueous suspension UV light source (60 W, 370–400 nm) Reaction time: 5 h	97	Tran et al. (2017)
Photocatalysis TiO_2/Fe_2O_3 core-shell nanostructures	Paracetamol	50 mg L^{-1}	Batch photoreactor	2.5 mg of photocatalyst 50 mL aqueous suspension 450W medium-pressure mercury vapor lamp Reaction time: 90 min	100	Abdel-Wahab et al. (2017)
Photocatalysis TiO_2	Ibuprofen	6 mg L^{-1}, 60 mg L^{-1} or 213 mg L^{-1}	Batch photoreactor	0.5, 1.0 or 1.5 g L^{-1} photocatalyst 250 mL of aqueous suspension 40 W UV LEDs with peak intensity at 382 nm Reaction time: 90 min	70% dissolved organic carbon	Jallouli et al. (2018)
Photocatalysis C-doped TiO_2	Tetracycline hydrochloride	5 mg L^{-1}	Batch photoreactor	300 mg L^{-1} photocatalyst 200 mL aqueous suspension 25 W visible-light LED strip with peak intensity at 450 nm Reaction time: 2 h	83% after 4 cycles	Oseghe and Ofomaja (2018)
Photocatalysis TiO_2	Sulfamethoxazole	1 mg L^{-1}	Recirculating photoreactor	100 mg of photocatalyst 1 L of solution with simulated seawater or deionized water Illuminated volume: 77 mL 1500 W Xenon lamp with solar spectrum Reaction time: 6 h	100% in deionized water and 91% for seawater	Porcar-Santos et al. (2020)
Photocatalysis TiO_2 and oxidized multi-walled carbon nanotube/anatase	Diclofenac	8 mg L^{-1}	Batch photoreactor under O_2/Ar atmosphere	50 mg–1000 mg of photocatalyst 500 mL aqueous suspension UV light with intensity of 8.33×10^{-6} E s^{-1} at peak wavelength of 254 nm or NUV-vis with photon flux at 366 nm of 2.38×10^{-6} E s^{-1} 200 mL/min O_2/Ar (50% vol. of oxygen) stream was continuously supplied to the reactor Reaction time: 1 h	100%	Martínez et al. (2011)
Photocatalysis Whey stabilized TiO_2 and ZnO	Carbamazepine	295 ng L^{-1}	Batch photoreactor with immobilized film	Photocatalytic geometric surface: 1 cm^2 UV light with intensity of 6.9 mW cm^{-2} at peak wavelength of 254 nm Reaction time: 2 h	100% for TiO_2 and 92% for ZnO after 55 min	Mohapatra et al. (2014a)
Photocatalysis TiO_2	Sulfamethoxazole	10–50 mg L^{-1}	Fixed-bed recirculating photoreactor	Photocatalytic geometric surface: 190 cm^2 250 mL aqueous solution Flow rate: 0.11–0.48 L min^{-1} 18 W UV lamp (peak intensity at 365 nm) or 18 W white lamp (400–600 nm and insignificant amount of 365 nm) Reaction time: 7.5 h	100% for 10 ppm of SFX	Ahmed et al. (2014)
Photocatalysis TiO_2 and Fe_2O_3	Oxytetracycline	20 mg L^{-1}	Fixed-bed recirculating photoreactor	Photocatalytic geometric surface: 190 cm^2 1.8 L aqueous solution Flow rate: 0.42–1.67 L min^{-1} 1700 W Xenon lamp with solar spectrum (radiation intensity at the	100% for TiO_2 and >90% for Fe_2O_3	Díez et al. (2018)

Table 6 (*continued*)

Degradation process and catalyst	Pharmaceutical compound(s)	Initial concentration	Reactor type	Experimental conditions	Removal of the starting compound [%]	Ref.
				photoreactor surface of 44 W m^{-2}) 77 mg L^{-1} H$_2$O$_2$ for TiO$_2$ and 154 mg L^{-1} H$_2$O$_2$ for Fe$_2$O$_3$ Reaction time: 180 min for TiO$_2$ and 40 min for Fe$_2$O$_3$		
Photocatalysis TiO$_2$	Iopromide acetaminophen sulfamethoxazole carbamazepine	50 µg L^{-1} each	Fixed-bed continuous-flow photoreactor	Photocatalytic geometric surface: 469 cm^2 325 mL reactor volume Flow rate: 2.7 mL/min 5–15 W UV-A lamps with spectrum centered at ~365 nm pH 8.2 Reaction time: 7 days	In the continuous-flow mode only the overall reactor and photocatalyst stability was evaluated. App. 60–90% of pharmaceuticals were degraded	Carbonaro et al. (2013)
Photocatalysis TiO$_2$@nZVI/persulfate	Amoxicillin	20 mg L^{-1}	Batch photoreactor	1000 mg L^{-1} of photocatalyst 50 mL aqueous solution containing 0.5 mM of persulfate 10 W UV lamp (peak intensity at 254 nm) pH 5.0 Reaction time: 1 h	99%	Diao et al. (2021)
Photocatalysis TiO$_2$	Diclofenac	2.37 mg L^{-1}	Batch photoreactor	105 mg of photocatalyst 80 mL aqueous suspension UV light with intensity of 3.04×10^{-7} E s^{-1} at peak wavelength of 365 nm pH 6.0 Reaction time: 3 h	100% in 156 min	Perisic et al. (2016)
Photocatalysis TiO$_2$	Diclofenac	5–20 mg L^{-1}	Batch photoreactor	17.5 mg of photocatalyst 350 mL aqueous suspension 9 W UVA (350–400 nm) light with intensity of 3.37×10^{-6} E s^{-1} pH 6.0 Reaction time: 4 h	85%	Achilleos et al. (2010)
Photocatalysis TiO$_2$	Sulfamethoxazole	10 mg L^{-1}	Batch photoreactor	500 mg of biochar supported TiO$_2$ 100 mL aqueous suspension 15 W UV lamp (peak intensity at 254 nm) pH 4 Reaction time: 6 h	91%	Kim and Kan (2016)
Photocatalysis TiO$_2$	Sulfamethoxazole trimethoprim	0.4 mg L^{-1} of each	Continuous photoreactor with air purging	0.05 mg L^{-1} of photocatalyst 500 mL reactor volume Flow rate: 8 mL/min 32 W UV light with intensity of 4.32×10^3 mW cm^{-2} at peak wavelength of 365 nm Reaction time: 5 h	90% in 20 min	Cai and Hu (2017)
Photocatalysis TiO$_2$/Fe^0	Ciprofloxacin (simultaneously with Cr(VI) reduction)	30 mg L^{-1} of ciprofloxacin and 20 mg L^{-1} of Cr(VI)	Batch photoreactor	1000 mg L^{-1} of photocatalyst 10 W UV lamp (peak intensity at 254 nm) pH 3.0 Reaction time: 1 h	95% of ciprofloxacin and 98% of Cr(VI)	Diao et al. (2017)
Electrocatalysis BDD anode Zr cathode	Ciprofloxacin sulfamethoxazole salbutamol	69 µmol L^{-1}	Recirculating electrocatalytic reactor	BDD anode geometric surface: 69 cm^2 Distance between the electrodes: 10 mm 1 L aqueous solution 0.1 M (pH 4, adjusted with H$_2$SO$_4$) or 0.02 M K$_2$SO$_4$ Applied current density: 0.72–7.24 mA/cm^2 Flow rate: 6 L min^{-1} Reaction time: 5 h	100%	Lan et al. (2018)
Electrocatalysis Ti/Pt or Ti/PbO$_2$ anodes and carbon felt	Carbamazepine	4.5 µg L^{-1}	Recirculating electrocatalytic reactor	Anode geometric surface area: 130 cm^2 Distance between the electrodes: 10 mm	75% for Ti/PbO$_2$ anodes	Guitaya et al. (2017)

Table 6 (*continued*)

Degradation process and catalyst	Pharmaceutical compound(s)	Initial concentration	Reactor type	Experimental conditions	Removal of the starting compound [%]	Ref.
covered with titanium cathode				Anode surface area to reactor volume: 1.9 m²/m³ 500 mg L^{-1} Na$_2$SO$_4$ Flow rate: 1–6 L min^{-1} Applied current: 1–3 A Reaction time: 100 min		
Electrocatalysis BDD anode and stainless-steel cathode	Amoxicillin	1000 or 2000 mg L^{-1}	Batch electrocatalytic reactor	BDD anode geometric surface: 10 cm² Distance between the electrodes: 15 mm 0.2 L aqueous solution with 2–4 g L^{-1} NaCl Applied current density: 30–50 mA/cm² Reaction time: 1.5 h	84.1%	Frontistis et al. (2017)
Electrocatalysis Nb/BDD or Ti/IrO$_2$ anode and Ti mesh cathode	Carbamazepine	10 mg L^{-1}	Recirculating electrocatalytic reactor	Anode geometric surface area: 62 cm² Distance between the electrodes: 5 mm 2 L aqueous solution with 7 or 14 mM NaCl Flow rate: 0.8 L min^{-1} Applied current: 0.5–1.5 A Reaction time: 30 min	88.7%	García-Espinoza et al. (2018)
Electrocatalysis BDD anode and cathode	Iopromide, sulfamethoxazo-le, 17-alpha-ethinylestradiol, diclofenac	0.5 or 10 mg L^{-1} of each component	Recirculating electrocatalytic reactor	Electrodes geometric surface: 189 cm² 10 L of simulated or real waste water Flow rate: 250 L min^{-1} Applied current: 0.9 A Reaction time: 180 min	32.3%–73.7%	Loos et al. (2018)
Electrocatalysis BDD anode and stainless-steel cathode	Losartan	377 mol/L	Batch electrocatalytic reactor	Anode geometric surface area: 5 cm² Distance between the electrodes: 10 mm 100 mL aqueous solution with 0.05 M Na$_2$SO$_4$ Applied current density: 10 mA cm^{-2} pH 7 Reaction time: 360 min	100%	Salazar et al. (2016)
Electrocatalysis CuO/TiO$_2$/Al$_2$O$_3$/RVC anode and RVC cathode	Paracetamol	96 mg L^{-1}	Batch electrocatalytic reactor	Anode geometric surface area: 3 cm² Ag/AgCl reference electrode 150 mL aqueous solution with 10 mM H$_2$O$_2$ and 0.5 M Na$_2$SO$_4$ Electrode potential of 1.3 V vs. SCE pH 5 Reaction time: 1 h	98%	Arredondo Valdez et al. (2012)
Electrocatalysis Boron doped graphene anode and Cu cathode	Acetaminophen	10 mg L^{-1}	Batch electrocatalytic reactor	Anode geometric surface area: 2.5 cm² Distance between the electrodes: 15 mm 200 mL aqueous solution with 17 mM NaCl Applied current: 20 mA Reaction time: 90 min	100%	(Q. Zhang et al., 2020b)
Electrocatalysis g-C$_3$N$_4$/Ti/PbO$_2$ anode and Ti cathode	Acetaminophen	100 mg L^{-1}	Batch electrocatalytic reactor	Anode geometric surface area: 15 cm² Distance between the electrodes: 20 mm 1 L aqueous solution with 6 g L^{-1} Na$_2$SO$_4$ Current density: 15 mA cm^{-2} pH 7 Reaction time: 3 h	83%	(S. Chen et al., 2021)
Photoelectrocatalysis TiO$_2$ anode, Pt cathode	Tetracycline	10 mg L^{-1}	Batch photoelectrocatalytic reactor	Catalyst (anode) geometric surface area: less than 10 cm² Ag/AgCl reference electrode 20 mL aqueous solution with 20 mM Na$_2$SO$_4$	80%	Liu et al. (2009)

Table 6 (*continued*)

Degradation process and catalyst	Pharmaceutical compound(s)	Initial concentration	Reactor type	Experimental conditions	Removal of the starting compound [%]	Ref.
Photoelectrocatalysis Reduced TiO_2 anode, Pt cathode	Diclofenac	5 mg L^{-1}	Batch photoelectrocatalytic reactor with air purging	Electric bias: 0.5 V 4 W UV light with intensity of 2.5 mW cm^{-2} and peak wavelength of 254 nm pH 5.5 Reaction time: 3 h Catalyst (anode) geometric surface area: 4 cm^2 SCE reference electrode 80 mL aqueous solution with 0.1 M Na_2SO_4	100% in 8 h	Cheng et al. (2016)
Photoelectrocatalysis TiO_2 anode, Pt cathode	Tetracycline	20–120 mg L^{-1}	Fixed-bed recirculating photoelectrocatalytic reactor	Electric bias: 0.4 V 35 W Xenon lamp Reaction time: 12 h Catalyst (anode) geometric surface area: less than 20 cm^2 Ag/AgCl reference electrode 50 mL aqueous solution with 0.1 M Na_2SO_4 Flow rate: 10 mL/min	96.4% for 20 mg L^{-1} and 54.8% for 120 mg L^{-1}	Bai et al. (2010)
Photoelectrocatalysis N-doped TiO_2 anode, 2 vitreous carbon plates cathodes	Chlortetracycline	100 µg L^{-1}	Fixed-bed recirculating photoelectrocatalytic reactor	Electric bias: 2 V 4 W UV light with intensity of 5 mW cm^{-2} and peak wavelength of 254 nm pH 8 Reaction time: 1 h Catalyst (anode) geometric surface area: 24 cm^2 1 L aqueous solution with 0.07 M Na_2SO_4 Flow rate: 250 mL/min Applied electric current: 0.1–0.8 A AM 1.5 solar illumination conditions (150 W xenon lamp) Reaction time: 20–240 min	99.6% in 180 min	(Rimeh Daghrir et al., 2013)
Photoelectrocatalysis TiO_2 anode, Pt cathode	Acyclovir	20 mg L^{-1}	Continuous-flow photoelectrocatalytic reactor	Catalyst (anode) geometric surface area: less than 0.785 cm^2 Ag/AgCl reference electrode 100 µL aqueous solution with 0.2 M $NaNO_3$ Electric bias: 1 V UV light with intensity of 10 mW cm^{-2} and peak wavelength of 365 nm Reaction time: 0–370 s	97.1% at 370 s residence time	Nie et al. (2013)
Photoelectrocatalysis TiO_2 anode, Pt cathode	Tetracycline	120 mg L^{-1}	Fixed-bed recirculating photoelectrocatalytic reactor	Catalyst (anode) geometric surface area: 40 cm^2 50 mL aqueous solution with 0.1 M Na_2SO_4 Electric bias: 2 V UV light with intensity of 5 mW cm^{-2} and peak wavelength of 355 nm Reaction time: 2 h	54.8% in 1 h	Bai et al. (2010)
Photoelectrocatalysis Sb-doped Sn80%-W20%-oxide anode, Stainless-steel cathode	Carbamazepine	0.2 mg L^{-1}	Batch photoelectrocatalytic reactor	Catalyst (anode) geometric surface area: less than 50 cm^2 550 mL aqueous solution with 0.1 M KH_2PO_4 Current densities of 1, 2, 4, 6 and 10 mA/cm^2 10 W UV lamp with peak wavelength of 254 nm pH 7 Reaction time: 1 h	100%	Ghasemian et al. (2017)

Table 6 (*continued*)

Degradation process and catalyst	Pharmaceutical compound(s)	Initial concentration	Reactor type	Experimental conditions	Removal of the starting compound [%]	Ref.
Photoelectrocatalysis $BiVO_4/Ag_2S$ anode, Pt cathode	Ciprofloxacin sulfamethoxazole	10 mg L^{-1}	Batch photoelectrocatalytic reactor	Catalyst (anode) geometric surface area: less than 6.5 cm^2 Ag/AgCl reference electrode 70 mL aqueous solution with 0.1 M Na_2SO_4 Electric bias: 0.2–1.5 V Solar illumination conditions (100 W xenon lamp) pH 7 Reaction time: 2 h	80% for ciprofloxacin and 86% for sulfamethoxazole at 1.2 V	Orimolade and Arotiba (2020)
Photoelectrocatalysis Cu_2O/TiO_2 anode, Pt cathode	Ibuprofen	10 mg L^{-1}	Batch photoelectrocatalytic reactor	Catalyst (anode) geometric surface area: 2 cm^2 Ag/AgCl reference electrode Electric bias: 0.5 V 100 W Hg lamp Reaction time: 4 h	100% of ibuprofen removal after 1.5 h and ~50 of mineralization (TOC decay) after 4 h	Chang et al. (2016)
Photoelectrocatalysis I and P co-doped TiO_2 anode and stainless steel cathode	Tetracycline	10 mg L^{-1}	Batch photoelectrocatalytic reactor	Catalyst (anode) geometric surface area: 30 cm^2 100 mL aqueous solution with 0.1 M Na_2SO_4 Electric bias: 1.4 V Metal halide lamp with 420 nm cut-off filter (average light intensity: 30 mW cm^{-2}) pH 7 Reaction time: 3 h	100%	(Liu et al., 2021)
Photoelectrocatalysis Cu/TiO_2 anode, Pt cathode	Diclofenac	5 mg L^{-1}	Batch photoelectrocatalytic reactor	Catalyst (anode) geometric surface area: 1 cm^2 Ag/AgCl reference electrode 50 mL aqueous solution with 0.1 M Na_2SO_4 Electric bias: 0.5 V 300 W xenon arc lamp with intensity on the photoanode surface of 100 mW cm^{-2} pH 6.2 Reaction time: 6 h	71%	Hua et al. (2016)
Photoelectrocatalysis TiO_2/Ti anode and Pt cathode	Sulfamethoxazole	2 mg L^{-1}	Batch photoelectrocatalytic reactor	Catalyst (anode) geometric surface area: 4 cm^2 Ag/AgCl reference electrode 50 mL aqueous solution with 0.01 M NaCl 4 W UVA lamp pH 5.4 Reaction time: 70 min	100%	(Su et al., 2016)
Photoelectrocatalysis g-C_3N_4/TiO_2 anode and Pt cathode	Tetracycline	10 mg L^{-1}	Batch photoelectrocatalytic reactor	Catalyst (anode) geometric surface area: 4 cm^2 Ag/AgCl reference electrode 50 mL aqueous solution with 0.5 M Na_2SO_4 Electric bias: 1 V 300 W Xe lamp (200–800 nm) Reaction time: 2 h	100%	Tang et al. (2020)
Photoelectrocatalysis Cu_2O/TiO_2 anode, Pt cathode	Ciprofloxacin	10 mg L^{-1}	Batch photoelectrocatalytic reactor	Catalyst (anode) geometric surface area: 15 cm^2 Ag/AgCl reference electrode 50 mL aqueous solution with 0.1 M Na_2SO_4 Electric bias: 1.5 V Solar simulator with a 400 nm cut-off filter pH 6 Reaction time: 4 h	73%	Koiki et al. (2020)

Table 6 (*continued*)

Degradation process and catalyst	Pharmaceutical compound(s)	Initial concentration	Reactor type	Experimental conditions	Removal of the starting compound [%]	Ref.
Photoelectrocatalysis TiO$_2$/Ti anode stainless steel cathode	5-fluorouracil	~5 mg L^{-1}	Batch photoelectrocatalytic reactor	Catalyst (anode) geometric surface area: 4 cm^2 Ag/AgCl reference electrode 80 mL aqueous solution with 42 mM Na$_2$SO$_4$ Electric bias: 1 V Solar simulator equipped with a xenon lamp with irradiation intensity 4.5 mW cm^{-2} pH 6.4 Reaction time: 3 h	100%	Mazierski et al. (2019)
Photoelectrocatalysis CuS/TiO$_2$ anode and Pt cathode	Penicillin G	5 mg L^{-1}	Batch photoelectrocatalytic reactor	Catalyst (anode) geometric surface area: 4 cm^2 SCE reference electrode 80 mL aqueous solution with 0.1 M Na$_2$SO$_4$ Electric bias: 0.4 V Xenon lamp (35 W) with a 420 nm cut-off filter Reaction time: 2.5 h	99%	Ma et al. (2018)

with a small gap in between where the generated reactive oxygen species degrade the pollutants when a potential bias is applied. On the other hand, photocatalytic reactors require a light source that has to illuminate the largest possible area of a photocatalyst with light of sufficient energy to excite the electrons in the photocatalyst in use. Due to the light illumination requirement, photocatalytic reactors have to be at least in part made of a transparent material. In general, photocatalytic reactors can be classified based on the photocatalyst form. Slurry reactors have suspended photocatalytic nanoparticles, whereas photocatalytic reactors with immobilized photocatalysts have the catalyst attached to the support via physical surface forces or chemical bonds. Immobilized photocatalytic reactors can be further divided into different types of fixed-bed reactors like monolith reactors, thin-film reactors and packed-bed reactors. Both main photocatalytic reactor types possess certain advantages and/or disadvantages. Slurry reactors provide a high surface area of photocatalyst per unit volume and therefore exhibit a larger photocatalytic activity than the immobilized photocatalyst reactors. However, the most important advantage of the latter reactor types is that they do not require catalyst recovery and permit the continuous use of the photocatalyst. Furthermore, immobilized photocatalysts can also be used for photoelectrocatalytic degradation if they are incorporated into a photoelectrocatalytic reactor. This reactor type is the most difficult to design since an effective photoelectrocatalytic reactor has to ensure an efficient exposure of the photocatalyst to irradiation, good contact between the illuminated catalyst and water, the optimal position and relative surface area of anode(s) and cathode(s) as well as optimal photocatalytic surface-to-volume ratio. In the case of a large-scale reactor, mixing and mass-transfer limitations also need to be considered.

Regardless of the degradation process and the catalyst form, various catalytic reactors can be operated in a continuous-flow or batch mode. The most common types of catalytic reactors used for the degradation of pharmaceuticals are shown in Fig. 17.

Regardless of the degradation process, catalytic reactors can be operated in a continuous-flow or batch mode. A degradation reaction inside a continuous-flow reactor can be efficiently controlled by the flow rate of the treated fluid, whereas in batch mode the reaction time is the parameter mostly used to control the degradation process. In Fig. 18, all the most important parameters for the photocatalytic, electrocatalytic and photoelectrocatalytic degradation of pharmaceuticals are shown together with the most frequently used values. As is clear from Fig. 18, the photoelectrocatalytic process is the most complicated one, which is why there are the fewest reactor-design variations developed for this type of process.

Finally, Table 6 shows the results of the degradation of pharmaceuticals by photocatalysis, electrocatalysis and photoelectrocatalysis published in the literature. The degradation of pharmaceutical compounds with different initial concentrations was performed in many reactor types with one of the three degradation processes covered in this review paper. The operating conditions influencing the degradation process are also listed. Based on the published literature, it can be concluded that all the photocatalytic experiments were carried out at 20–25 °C and mixing in the reactor is usually achieved with a Teflon-covered stirring bar when needed. In the case of the flow reactors, the mixing is achieved with the flow of the treated water. If recirculating conditions are used, the flow rate does not influence the degradation rate (Ahmed et al., 2014). On the other hand, the degradation rate strongly depends on the flow rate in the case of a continuous-flow reactor. However, when studying the degradation process, the residence time is commonly selected so that 50–90% degradation of the target micropollutants is achieved, since this range of micropollutant degradation permits better quantification of the matrix effects than if the design was based on a higher level of treatment where changes in catalyst activity would be more difficult to quantify (Carbonaro et al., 2013). The use of UVC light significantly increases the degradation rate, when compared to the degradation rate when UVA or solar light is used. Furthermore, the degradation under UV irradiation is more effective than under near-UV–Vis (Martínez et al., 2011). The reason for the better results achieved using UVC irradiation is the high degradation rate achieved with direct photolysis alone (Kim and Kan, 2016). In any case, it can be seen in Table 4 that although a 100% degradation of the starting pharmaceutical compounds can be achieved, this does not indicate the overall quality of the degradation process. More attention should be paid to the formation of intermediate products, which can be even more harmful and resistant to different subsequent water treatments. A study by Porcar-Santos et al. (2020) shows that reactive halogen species can form from chlorine and bromine radicals when using TiO$_2$ to treat pharmaceuticals in seawater. The generation of reactive halogen species resulted in the formation and accumulation of harmful halogenated organic byproducts. For identification purposes, the photocatalytic decomposition of pharmaceuticals is usually conducted in batch mode with optimal catalyst loading and sufficient reaction time to ensure the amount of intermediates generated is above the LC–MS–MS and GC–MS detection limit (Cai and Hu, 2017). The working conditions where enough intermediate products are formed depend on

the photoreactor's geometry and the amount of catalyst. However, the degradation rate is generally found to increase with the photocatalyst concentration towards a limiting value at relatively high concentrations.

Electrocatalytic degradation studies mainly use the BDD electrodes as anodes and titanium or stainless steel as cathodes for the degradation of pharmaceuticals. When simulated or real wastewater is not used as the matrix solution, NaCl or Na_2SO_4 are used as supporting electrolytes. NaCl increases the degradation rate through the indirect oxidation by electro-generated active chlorine, which is accelerated in acidic media in comparison to alkaline media (Brillas and Sirés, 2015). Guitaya et al. (2017) determined that the anode type is the most important parameter affecting the pharmaceutical degradation rate followed by the treatment time, the applied current, and then the recirculation flow rate.

Few papers have reported the treatment of pharmaceuticals solutions by photoelectrocatalysis. All of them report on the better performance of photoelectrocatalytic process when compared to photocatalytic and electrocatalytic processes. A significant synergetic effect usually results in at least a five-times higher degradation-rate constant than the one of the photocatalytic process using the same catalytic material. Studies also show that the photoelectrocatalytic method results in lower levels of intermediate transformation products than the photolytic and photocatalytic methods. This suggests a potentially lower overall toxicity of the final solution when treated by the photoelectrocatalytic method. Furthermore, the photoelectrocatalytic process was determined to be the most energy efficient (Ghasemian et al., 2017). However, similar to the results of the photocatalytic degradation, continuous-flow reactors are very rarely used for the photoelectrocatalytic degradation of pharmaceuticals since one pass of the treated pharmaceutical solution through the reactor is not enough to degrade a relatively high concentration of pharmaceuticals at low retention times/high flow rates with the catalysts and reactor designs developed so far. Therefore, continuous-flow reactors (also listed in Table 6) have a very small volume of less than 1 mL to intensify the degradation reaction of the pharmaceuticals (Nie et al., 2013). It can be concluded that the currently developed catalysts and reactors are not applicable yet for the treatment of large wastewater volumes existing in sewage treatment plants.

6. Prospects

In this review major aspects involving the degradation of pharmaceuticals by photocatalysis, electrocatalysis and photoelectrocatalysis are discussed and the main challenges were indicated. Based on the information reported, the following can be prospect:

- Since the analytical methods to determine pharmaceuticals concentration in aquatic media are already well established, regulation limits should be addressed by environmental agencies to regulate the discharge of these compounds in the aquatic environment. However, the lack of techniques capable of efficiently treating these compounds in large scale still limits this regulation. For now, the analytical techniques are utilized for scientists to monitor the presence of pharmaceuticals in the environment. They are also a powerful instrument to evaluate the efficiency of new treatment techniques.
- Theoretical modeling of PC, EC and PEC from first principles remains limited to small molecules; instead, the theory is used solely to provide partial insights into the catalyst or substrate structure (such as HOMO/LUMO) but not their interplay. The studies regarding theoretical calculations and modeling methods should attract much more attention. These tools are useful for a deeper understanding of the mechanism and charge-migration kinetics in the catalysts. Further advances in theoretical calculations are highly desirable to understand more complex systems, such as water and wastewater contaminated with pharmaceuticals.
- The existing photocatalytic materials feature various drawbacks such as high cost, large bandgaps, low active surface area, limited

reusability, etc. Significant challenges still remain in the development of new, efficient and low cost catalysts, capable to be applied and produced on large scale for practical applications, is one of the key research goals.
- Future research directions in this field should be focused on cost-effective systems for treating large amounts of effluents in studies using more complex matrices (and not pure aqueous solutions), to enable scaling-up of this technology.

7. Conclusions

Based on the information reported in this review, it can be concluded that water and wastewater containing pharmaceuticals can be effectively treated by photocatalysis, electrocatalysis and photoelectrocatalysis. These processes have been extensively studied by several researcher groups and evaluated for the treatment of a wide range of pharmaceuticals compounds. The analytical tools necessary for the evaluation of the processes are well developed and the HPLC analysis is the most common one to determine pharmaceuticals concentration decay during the treatment. The toxicity tests are also well established; however, they are not present in great part of the revised works. The evaluation of oxidative and reductive species formed during the catalytic reaction and theoretical modeling, help to provide a full view of the degradation process and become more popular in recent years. There is a wide variety of catalyst materials already synthesized and well characterized, but only a few are available on commercial scale. Among them TiO_2 and BDD are the most utilized catalysts for photocatalysis and electrocatalysis, respectively. Furthermore, the development of strongly attached photocatalysts, such as TiO_2 nanotubes, on conductive materials, as BDD, forming heterostructured materials, seems to be a good way to overcome some limitations of these treatment technologies. Different reactor designs can be chosen for applications in PC, EC and PEC, however, the great majority of the studied reactors are capable to treat only a few milliliters of simulated effluent (or pure aqueous solutions), poising a major challenge for applications in larger and real scale. In conclusion, we have summarized recent work related to PC, EC and PEC and their application of pharmaceuticals in aqueous media. The studies in this field provide a meritorious platform for accelerating the practical applications of these techniques. We hope that this review can stimulate further exploration of these techniques to fulfill the present challenges.

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.

Nomenclature

1D	One-dimensional shape
2D	Two-dimensional shape
3D	Three-dimensional shape
ADWG	Australian drinking water guidelines
AES	Auger electron spectroscopy
AFM	Atomic force microscopy
ALIE	Average local ionization energy
AMX	Amoxicillin
AO	Anodic oxidation

AOPs	Advanced oxidation processes
B3LYP	Becke, 3-parameter, Lee–Yang–Parr
BC	Biochar
BCN	Bulk carbon nitride
BDD	Boron-doped diamond
BDEs	Bond-dissociation energies
BET	Brunauer-Emmett-Teller surface area analysis
CBZ	Carbamazepine
CCN	Crystalline carbon nitride
CFO	$CoFe_2O_4$
CN	$g-C_3N_4$
CNBB-5	$Bi_2O_2CO_3/g-C_3N_4/Bi_2O_3$
COD	Chemical oxygen demand (mg L-1)
CPCM	Conductor-like polarizable continuum model
CV	Capacitance–voltage profiling
CVD	Chemical vapor deposition
DCF	Diclofenac
DFT	Density functional theory
DMPO	5,5-Dimethyl-1-pyrroline N-oxide
DRS	Diffuse reflectance spectroscopy
E_{anod}	Anodic potential
EAOPs	Electrochemical advanced oxidation processes
EC	Electrocatalysis
EC	European commission
EDTA	Ethylenediamine tetraacetic acid
EELS	Electron energy loss spectroscopy
EEO	Electrical Energy per Order
E_F	Fermi energy levels
EIS	Electrochemical impedance spectroscopy
ELF	Electronic location function
E^o	Standard reduction potential
EPMA	Electron probe microanalysis
EPR	Electron paramagnetic resonance
ERD	Elastic recoil detection
ERE	Electron reorganization energy
EU	European union
$f(r)$	Fukui function
FMO	Frontier molecular orbital
FTIR	Fourier-transform infrared spectroscopy
GC	Gas chromatography
GO	Graphene oxide
HA	Humic acid
HF-CVD	Hot-filament chemical vapor deposition
HOMO	Highest occupied molecular orbital
HPLC	High performance liquid chromatography
HPLC-DAD	High performance liquid chromatography with diode-array detection
HPLC-UV	High performance liquid chromatography with UV detector
HRE	Hole reorganization energy
HRTEM	High resolution transmission electron microscopy
IBP	Ibuprofen
IEFPCM	Integral equation formalism version of the polarizable continuum model
LC/MS/MS	Liquid chromatography tandem mass spectrometry
LC-MS	Liquid chromatography mass spectrometry
LC-QTOF MS	Liquid chromatography quadrupole time-of-flight mass spectrometry
LC-QTOF-MS-MS	Liquid chromatography tandem quadrupole time-of-flight mass spectrometry
LDA	Local-density approximations
LDH	Layered double hydroxide
LED	Light-emitting diode
LLE	Liquid-liquid extraction
LLME	Liquid-liquid micro-extraction
LUMO	Lowest unoccupied molecular orbital
MEM	Memantine

MEP	Molecular electrostatic potential
MET	Metoprolol tartrate
MW-CVD	Microwave plasma chemical vapor deposition
N	Number of electrons
NPA	Natural population analysis
NPX	Naproxen
nZVI	Nano zerovalent iron
ORR	Oxygen-reduction reaction
OTC	Oxytetracycline
PBE	Perdew–Burke-Ernzerhof functional
PC	Photocatalysis
PEC	Photoelectrocatalysis
PhP	Phenazopyridine
pH_{pzc}	Ph of the zero point charge
PIN	Pindolol
pKa	Negative log base ten of the acid dissociation constant value
PMS	Peroxymonosulfate
ppb	Parts per billion
ppm	Parts per million
PRCP	Pharmaceuticals and personal-care products
PRO	Propranolol hydrochloride
PZC	Point of zero charge
rGO	Reduced graphene oxide
RVC	Reticulated vitreous carbon
SCE	Saturated calomel electrode
SEM	Scanning electron microscope
SGN	Sulfur-doped graphene
SIMS	Secondary ion mass spectrometry
SPE	Solid-phase extraction
SPME	Solid-phase microextraction
STM	Scanning tunneling microscopy
TC	Tetracycline
TEB	Triethylborate
TEM	Transmission electron microscopy
TEMP	2,2,6,6-tetramethylpiperidine
TGA	Thermogravimetric analysis
TMB	Trimethylborate
TOC	Total organic carbon (mg L^{-1})
TPB	Tripropylborate
TRL	Technology readiness level
UCMR	Unregulated contaminant monitoring rule (usa)
UPLC	Ultra performance liquid chromatography
UPS	Ultraviolet photoelectron spectroscopy
UV	Ultraviolet
UVA	Ultraviolet A
UVC	Ultraviolet C
Vis	Visible
WWTPs	Water- and wastewater-treatment plants
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction analysis
μ	Electronic chemical potential
ν	Constant external potential
$\rho(r)$	Electron density

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