Journal of Environmental Chemical Engineering 10 (2022) 107859

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

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

A critical view of the contributions of photoelectrochemical technology to pharmaceutical degradation

Roberta Yonara Nascimento Reis [a], Lorena Athie Goulart [a], Lucia Helena Mascaro [a], Suellen Aparecida Alves [b,1,*]

[a] Chemistry Department, Federal University of São Carlos, São Paulo, Brazil
[b] Chemistry Department, State University of Ponta Grossa, Paraná, Brazil

ARTICLE INFO

Editor: Despo Kassinos

Keywords:
Photoelectrocatalysis
Pharmaceutical degradation
Photocatalytic fuel cells

ABSTRACT

The deterioration of water quality and its reuse has generated the necessity to develop water treatment processes with different qualities for industry, agriculture, and human consumption. The types of water contaminants have grown and diversified with different types of processes and activities such as urbanization, industrialization, agriculture, and livestock. In this sense, recalcitrant contaminants stand out, which are not easily removed by conventional water treatment methods. These recalcitrant compounds include pharmaceuticals, whose use has increased significantly, causing long-term danger to humans, animals, and the environment through cumulative exposure. Considering this aspect, it is not surprising that photoelectrochemical processes have become more popular in recent years due to the capacity to generate alternatively oxidizing species which lead to mineralization of organic compounds, improving the quality of water for reusing, even if such species are present in minimal concentrations. In this review, we highlight the main semiconductor materials used in photoelectrocatalysis for the degradation of pharmaceutical compounds, as well as their efficiency in degrading some drugs including antibiotics, analgesics, anti-inflammatories, antivirals, and antidepressants. The main semiconductors used are TiO_2, WO_3, ZnO, CuO, Cu_2O, and $BiVO_4$ photoelectrocatalysts pure or doped and in the presence of cocatalysts or heterostructures. Photocatalytic fuel cells (PFCs) were also investigated in relation to degradation and electricity generation. The system provides a double benefit to the environment: waste materials can be consumed, and solar radiation can be converted into useful energy sources, such as electricity, hydrogen, or fuel. Therefore, photoelectrochemical approaches are currently being considered as a viable method of degrading drugs in water.

1. Introduction

Pharmaceutical compounds have an important role in the development of human life, presenting themselves as essential agents in the treatment of diseases. A recent public health crisis, the COVID-19 Pandemic, and the process of reusing drugs to determine promising treatments for this disease has highlighted the importance of pharmaceutical compounds even further [1]. These therapeutic compounds can be classified according to their structure, origin, mechanism of action and response to the disease, thus ensuring the well-being of living beings by preventing pain and treating diseases.

The various mechanisms by which these compounds work include the suppression of replication of bacteria and viruses with the interruption of protein synthesis and the inhibition of enzymes [2,3]. Some of the classes of drugs applied in the treatment of diseases are antibiotics, analgesics, anti-inflammatory drugs, antivirals, antidepressants, among others [4]. As a result of a large number of diseases and people who are affected by them, the production of medicines and their consumption has increased dramatically in recent years.

Due to the high consumption of drugs, these compounds have become an environmental threat, being identified in water resources, causing the compromise of the aquatic ecosystem, the development of microorganisms (bacteria, parasites, and viruses) resistant to antimicrobials and thus generating risks to humans [5,6]. In this context, photoelectrochemical technology has played an important and promising role with high efficiency in the treatment of complex effluents such

* Corresponding author.
E-mail address: saalves@uepg.br (S.A. Alves).
[1] ORCID 0000-0002-9332-4252

https://doi.org/10.1016/j.jece.2022.107859
Received 27 December 2021; Received in revised form 20 April 2022; Accepted 3 May 2022
Available online 6 May 2022

as pharmaceutical compounds. Photoelectrocatalysis (PEC) is an electrochemically based Advanced Oxidative Process (AOPs) that combines the properties of photocatalysis with electrolytic reactions applied in the mineralization of various contaminants [7,8].

In PEC, the applied photocatalyst is immobilized on a support with a conductive interface, thus being called a photoelectrode. When irradiated with a light source (visible or UV) with a range equal to or greater than the bandgap of the semiconductor material used. Generally, the mechanism in PEC relates the electrons in the valence band (VB) being promoted to the conduction band (CB) of the semiconductor, generating electron/ holes (e^-/h^+) and, from the application of a positive external bias, the photoexcited electrons being transferred to the cathode and the holes becoming available on the photoelectrode surface (Eq. 1) [9]. The processes that occur in the PEC are illustrated in Fig. 1.

Thus, this process results in delayed recombination of the photogenerated charge carriers and leaves them for a more available time for the generation of high oxidative power radials such as •OH and/or directly participating in the degradation of organic compounds (Eqs. (2–4)). In addition to the reactions that occur at the photoelectrode, at the cathode, there is the formation of oxidants such as $O_2^{\bullet-}$, which also

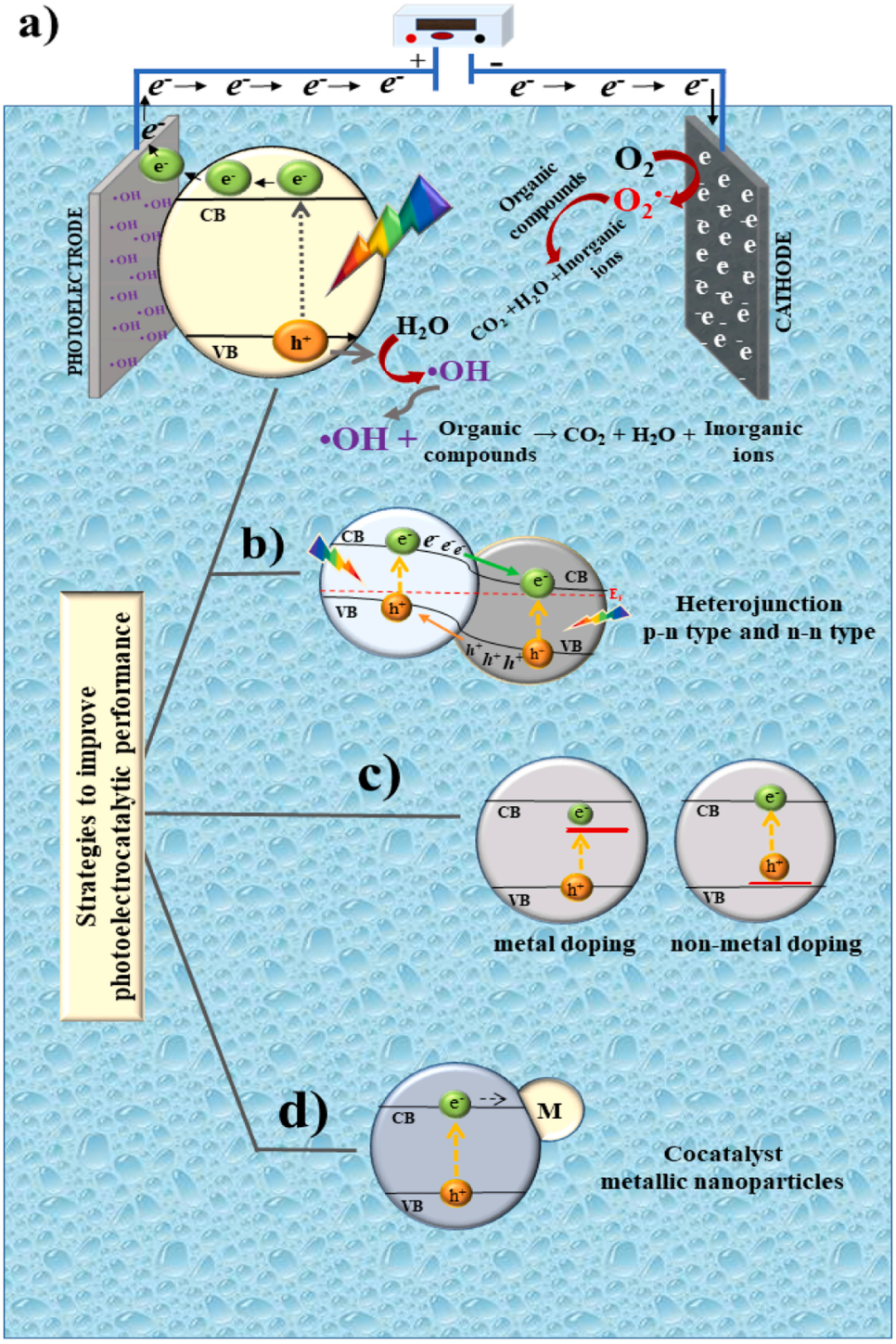

Fig. 1. Schematic representation of the PEC process and the different forms applied to a photocatalyst to improve the photoelectrocatalytic response: a) PEC mechanism in degradation of pharmaceutical compounds, b) heterojunction, c) doping with metals and non-metals, and d) cocatalyst.

directly participate in the degradation of recalcitrant compounds (Eqs. (5–10)). Therefore, in PEC, oxidizing species are formed from photogenerated charges on the catalyst capable of degrading organic compounds (Eqs. (11–14)) [9,10].

The photogenerated radicals and charge carriers in the PEC can mineralize the contaminants present in the reaction medium. The formed intermediates should be less or non-toxic than the recalcitrant organic compounds of origin [11]. The steps described above for the PEC process are summarized by Eq. 1 to 14.

$$Semiconductor + h\nu \rightarrow Semiconductor\ (e^-_{BC}) + (h^+_{BV}) \quad (1)$$

$$\text{Semiconductor } (h^+_{BV}) + H_2O \rightarrow \text{Semiconductor} + H^+ + {}^\bullet OH \quad (2)$$

$$\text{Semiconductor}(h^+_{BV}) + OH^- \rightarrow \text{Semiconductor} + {}^\bullet OH \quad (3)$$

$$\text{Semiconductor} + (e^-_{BC}) + O_2 \rightarrow \text{Semiconductor} + O_2^{\bullet -} \quad (4)$$

$$\text{Semiconductor} + \text{bias potential} \rightarrow \text{external circuit} \quad (5)$$

$$O_2^{\bullet -} + H^+ \rightarrow HO_2^\bullet \quad (6)$$

$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2 \quad (7)$$

$$\text{Semiconductor } (e^-_{BC}) + H_2O_2 \rightarrow {}^\bullet OH + OH^- \quad (8)$$

$$H_2O_2 + O_2^{\bullet -} \rightarrow {}^\bullet OH + OH^- + O_2 \quad (9)$$

$$H_2O_2 + h\nu \rightarrow 2\,{}^\bullet OH \quad (10)$$

$$\text{Organic pollutants} + {}^\bullet OH \rightarrow Intermediates \quad (11)$$

$$Intermediates \rightarrow CO_2 + H_2O \quad (12)$$

Cathode reactions:

$$e^- + O_2 \rightarrow O_2^{\bullet -} \quad (13)$$

$$O_2^{\bullet -} + \text{Organic Pollutants} \rightarrow \text{degradation products} \quad (14)$$

In comparison to other conventional methods for removing pharmaceutical compounds, such as physically, chemically, and biologically, the synergistic effect of combining the processes that occur in the PEC offers significant advantages. Since some pharmaceutical compounds generate metabolites that are not fully metabolized by the body, removing them by conventional wastewater treatment networks is often inefficient and ineffective due to their complex and recalcitrant nature [7]. Nevertheless, the PEC method of action can be considered more effective than other AOPs such as Photocatalysis, which has been widely applied in recent years in studies of degradation and mineralization processes of pharmaceutical compounds. However, this large usage, conventional Photocatalysis has some limitations, such as difficulties in separating the reaction medium, loss of catalyst, and high recombination of photogenerated charge carriers, which compromises its performance efficiency and percentage of degradation [12].

The limitations of photocatalysis can be addressed by PEC, which suppresses recombination processes and simplifies separation of the photocatalyst, minimizing losses and enhancing reproducibility. However, the quantity of studies and publications in the field of Photoelectrocatalysis, for the pharmaceutical compound's degradation and especially in specific conditions such as the use of visible irradiation, is limited by a much smaller number in the last ten years when compared to photocatalysis, as evidenced from data collected in Web of Science searches as shown in Fig. 2.

We aimed here to present an overview of the differences between photocatalysis and photoelectrocatalysis in terms of degradation of this class of pollutants, showing that PEC, despite demonstrating high rates of degradation for recalcitrant organic compounds [13–15], still has drawbacks [13–15].

In the last ten years, there has not been any work that investigates the use of ultraviolet and visible radiation, in PEC, to degrade

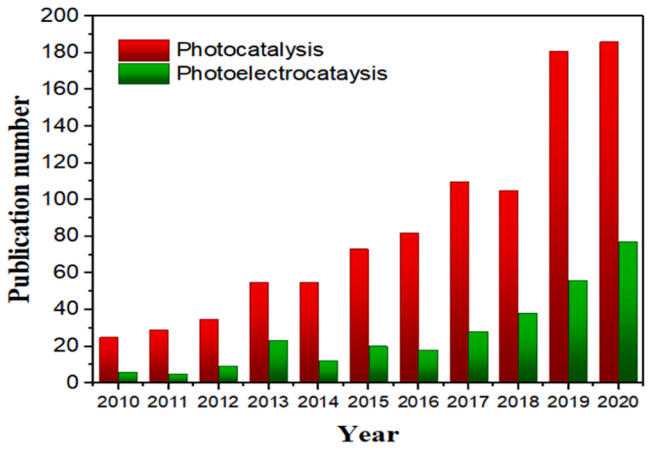

Fig. 2. Comparison between publication number in photocatalysis and photoelectrocatalysis in degradation of pharmaceutical compounds (Web of Science data, keywords: photocatalysis* and degradation and pharmaceutical* and photoelectrochemical degradation* and drugs*).

pharmaceutical compounds in real matrices such as river water, domestic waste, or hospital effluents, with most research concentrating on smaller-scale applications. The development of studies that expand the application of PEC to real matrices or that simulate this type of matrix is extremely important given the growing increase and detection of pharmaceutical effluents and water contaminated with drugs residues such as antibiotics in the aquatic environment [16,17].

The development of PEC technology is directly related to the study and development of materials with excellent photoactivity to be used as photoanodes. Semiconductor materials, such as TiO_2, WO_3, ZnO, CuO, Cu_2O, and $BiVO_4$, have been widely investigated to be applied as electrodes in the photoelectrocatalysis of organic compounds in water treatment [18]. Although some semiconductors have high photosensitivity and photocatalytic activity, some of these materials suffer photocorrosion and are unstable during photoelectrocatalytic processes, making their use unfeasible for long periods during PEC. Another disadvantage is related to the high recombination of photogenerated charges and the absorption of light in a small range of the light radiation spectrum, as is the case of TiO_2 and ZnO, which only absorb in the UV light region. Thus, different strategies have been investigated to improve the photocatalytic properties of candidate materials for photoanodes [19–21].

The formation of heterojunction between semiconductors, doping, and addition of cocatalysts decreases the recombination of the photogenerated charges and improves the formation of oxidizing species during PEC, thus being efficient strategies for the photoelectrocatalytic properties of these materials (Fig. 1b-d) [22,23]. In the formation of a heterojunction, semiconductors with a different bandgap energy (E_{BG}) are combined in such a way the photoexcited electrons, at different CB energy levels of these semiconductors, can be quickly transferred from one semiconductor to another, thus increasing the separation of photogenerated charges [24].

Doping, in turn, allows an atom with different characteristics to be added to the semiconductor network, replacing its atoms or generating oxygen vacancies that contributed to improving the charge transfer of the material and its spectral response [25]. Also, the addition of a cocatalyst on the surface of a semiconductor slows down recombination, increasing the time of photogenerated charge carriers and greater oxidation of the species in the reaction medium [26].

Accordingly, this review aims to critically assess the studies performed recently for the application of PEC technology for the degradation of pharmaceutical compounds by application of radiation in the ultraviolet and visible region, concentrating its description on the drug classes such as antibiotics, anti-inflammatories, analgesics, hormones,

and other classes reported to be among the main emerging contaminants in water resources. The review focused on TiO_2, WO_3, ZnO, CuO, Cu_2O, and $BiVO_4$ photoelectrocatalysts in their pure form and their most usual forms with the generation of heterostructures, using cocatalysts and dopants.

Searches in the Web of Science, Science Direct, Scopus, and Google Scholar databases were conducted to produce this study, focusing on the keywords:

- photoelectrocatalysis,
- photoelectrocatalysis*pharmaceutical,
- photoelectrocatalysis*drugs*visible light,
- photoelectrocatalysis*drugs.

Additionally, we searched the database to locate the covered photoelectrocatalysts.

This critical review provides a discussion of photoelectrocatalytic technology, its development, and advantages over the degradation process applied to the most prominent classes of pharmaceutical compounds in recent studies using ultraviolet and visible radiation, as well as the limitations addressed by this technology.

2. Main therapeutic classes with photoelectrochemical degradation results

According to Statista, in 2020, the following therapeutic classes represented the largest market share for pharmaceutical products: oncology, antidiabetic, respiratory, autoimmune diseases, antibiotics and vaccines, pain, mental health, immunology, and hypertension generate over $500 billion in revenue [27].

While these statistics are noteworthy for the world economic context, they raise concerns about both the health status of the world population and the discharge into the environment of the chemicals and their metabolites that can be harmful to human health. According to Peña et al., the types of pharmaceuticals studied (such as pharmaceutical detection in water and effluents, disposal, destination, environmental impacts and concerns, and environmental treatment) do not reflect the types of pharmaceuticals most commonly produced and consumed today [28]. From this perspective, we identified the main classes of therapeutics with studies on degradation via photoelectrocatalysis, which are presented on the following topics.

2.1. Antibiotics

The increase in health problems influenced by population growth, industrial development, social and economic factors (such as food and basic survival conditions), lead to greater use of pharmaceutical products, such as antibiotics. These pharmaceutical products have both human and veterinary use, and their use has intensified in recent decades and are drugs capable of eliminating or preventing the multiplication of bacteria. However, its wide use results in two main problems: *i)* presence in aquatic systems since they are considered persistence and *ii)* enhancement bacterial resistance.

Public health faces a lot of problems due to the widespread use of this drug by society without a prescription. Furthermore, an additional concern is given to expired medicines that are not disposed of correctly and end up reaching water resources. According to data from the World Health Organization (WHO), published in 2018 for the years 2016–2018, Brazil is one of the countries that consumes the most antibiotics in the world and is the largest consumer in America [29]. Also, according to reported data, the main antibiotic sub-groups in Brazil are:

- Beta-lactam antibacterials, penicillins;
- Macrolides, lincosamides, and Streptogramins;
- Quinolone antibacterials;
- Other beta-lactam antibacterials;
- Sulfonamides and trimethoprim;
- Tetracyclines.

A recent WHO report has also raised concerns about the intensity of antibiotic use during the new Coronavirus pandemic (COVID-19). In this regard, a guide was released in May 2020 expressly recommending not using antibiotics in the treatment of the new disease in suspected or mild cases, except in cases of bacterial infection. The reason is related to its use without scientific proof of early therapeutic efficacy can increase bacterial resistance rates, which can impact society today and in the near future [29].

Böger et al. recently investigated the occurrence of antibiotics and antibiotic-resistant bacteria in Brazilian rivers. The authors report that the concentrations of antibiotic drugs in water were higher than those reported in the literature for the same rivers (Belém and Barigui, Curitiba-PR) and suggest that this increase is due to the greater amount of domestic effluent. Furthermore, in all samples analyzed, bacteria resistant to antibiotics were detected [30].

Regarding the legislation that regulates the detection or maximum concentration of these substances in drinking water or effluents (domestic or hospital), there is still a great lack considering world terms. Khan et al. recently published an investigation into guidelines and legislation scenarios around the world. For the authors, hospital effluents are considered hazardous with a high concentration of chemical substances and drugs excreted in patients' urine and these are not removed by conventional water and/or effluent treatment systems [31].

In this sense, our approach sought to relate the main scientific investigations of recent years into the photoelectrochemical degradation of different types of antibiotics, which were divided into the following subgroups:

2.1.1. β-lactams antibiotics

Initially, we will approach studies related to antibiotics of the most consumed class in Brazil, the β-lactams, which are of natural origin and semi-synthetic derivatives and present a mechanism of action related to the irreversible inhibition of the enzyme transpeptidase, which catalyzes the reaction of transpeptidation between bacterial cell wall peptidoglycan chains [32].

Penicillins are β-lactam antibiotics that can be of natural origin (penicillins) or semi-synthetic (amoxicillin, for example). In this sense, CuS/TiO_2 nanotube arrays photoelectrode was successfully prepared by an anodization process, with galvanostatic electrodeposition strategy and applied photoelectrodes in the degradation of penicillin G. The results indicated that CuS nanoparticles have significantly enhanced the photoelectrocatalytic activity by red shifting the light absorption to the visible region and increasing the photoinduced charge separation efficiency. The CuS/TiO_2 nanotube photoelectrodes arrays showed a photoelectrocatalytic performance for the elimination of penicillin G (99.1%) and mineralization to H_2O, CO_2, NH_4, and NO_3 within 150 min under visible light illumination. The authors concluded that CuS/TiO_2 NTAs photoelectrode showed potential in applications of environmental remediation [33].

Zheng et al. synthesized the ZnO / ZnSe / CdSe / MoS_2 materials with excellent photoelectrocatalytic activity under UV–visible light that was applied in the degradation of the antibiotic amoxicillin. This photoanode promoted the complete degradation of amoxicillin in just 30 min, despite the complexity of the target molecule. The high photoactivity of this material was attributed to increased absorption of light and active sites of the different deposited layers, which promoted the separation of photogenerated charges. In addition, there was a reduction in CdSe photocorrosion by protecting MoS_2 on the surface [34].

Concerning semi-synthetic β-lactam drugs, the subclass of cephalosporins stands out, which are semi-synthetic and can be divided into generations (1st to 5th generation). In recent years, studies have been carried out for the degradation of 2nd and 3rd generation cephalosporins via photoelectrocatalysis [35].

The Cefotaxime (CFX) photoelectrocatalytic degradation was studied using a TiO_2 electrode in an aqueous solution varying the pH under UV illumination. Nanostructured TiO_2 thin films were fabricated via a facile, economical, and energy-efficient microwave-assisted dip-coating (MWDC) technique. The TiO_2 photoelectrode showed no change in the PEC activity in recycling tests after 1 month and repeated up to 5 months, indicating that TiO_2 films display long-term stability and do not suffer from photocorrosion [36]. This result is interesting from the perspective of electrode useful life since few studies are successful without modifications via doping, heterojunction, or the use of cocatalysts.

Therefore, the degradation of the CFX antibiotic was carried out with $MoSe_2$-modified TiO_2 electrodes. The photoelectrodes were prepared by anodization followed by cyclic voltammetry method using titanium foil as substrate and $MoSe_2$ nanoparticles were deposited on TiO_2 nanotubes, and the electrodes were denoted as $MoSe_2$/ TiO_2 NTs. The modification of TiO_2 NTs with $MoSe_2$ improved the photoelectric properties, including more abundant surface oxygen vacancies and enhanced visible-light absorption. Based on the synergistic effect of surface oxygen vacancies and direct Z-scheme heterojunction a mechanism of photo-induced charge carriers on the $MoSe_2/TiO_2$ NTs photoanode was proposed. The CFX photoelectrode achieved 95% in 3 h showing this as a highly efficient photoelectrode system for removal of this antibiotic in wastewater [37].

Sheydaei et al. showed that the g-C_3N_4/Ce-ZnO/Ti material was an effective photocatalyst for the PEC process under visible light in the degradation of the cefixime antibiotic. This molecule shows side-chain variation in the chemical structure of CFX. After the PEC process, 80% of cefixime was degraded in 180 min and 96% TOC (total organic carbon) removal in 330 min of treatment. Comparing the PEC degradation results with the sorption, electrosorption, and PEC processes it was verified a synergistic effect of photocatalysis and electrosorption on the antibiotic degradation [38].

To determine whether the photoelectrocatalytic process is efficient it is also necessary to analyze TOC data when it comes to mineralization, that is, how the organic component converts into CO_2.

2.1.2. *Quinolones antibiotics*

Quinolones are bactericidal drugs widely used in the treatment of urinary tract infections and the treatment of infections caused by microorganisms resistant to the most common antibacterial agents. Therefore, it is a substance that should not be administered in the first line of treatment. This antibiotic subclass is derived from nalidixic acid, which was first synthesized in 1962 [39]. Nowadays, nearly all quinolone antibiotics in use contain a fluorine atom in their chemical structure and they are called fluoroquinolones. Photoelectrochemical degradation has been verified for this class in recent years, highlighting the following drugs: norfloxacin (NOR), ciprofloxacin (CIP), ofloxacin (OFL), and levofloxacin (LFX).

These antibiotics are classified into four generations/classes based on their antibacterial spectra. They show activity against gram-negative and gram-positive microorganisms and are usually administered orally, after which they are well absorbed reaching therapeutic concentrations in most body fluids, and are partially metabolized in the liver. The kidneys are the main route of elimination, with approximately 30–60% of an oral dose excreted unchanged in the urine [39].

Many newer fluoroquinolones have been removed from the US market due to toxicity; among them trovafloxacin (severe liver toxicity), gatifloxacin (hypoglycemia and hyperglycemia), grepafloxacin (cardiac toxicity), temafloxacin (acute renal failure, hepatotoxicity, hemolytic anemia, coagulopathy, and hypoglycemia) and lomefloxacin, sparfloxacin and enoxacin [39].

In this sense, we initiate the approach with degradation studies for 2nd generation drugs: NOR, CIP, and OFL with different semiconductors and architectures. The degradation of the NOR antibiotic was also performed using different heterojunctions. For example, [115] reported the development of a $BiVO_4/WO_3$ film with 67% photoelectrochemical degradation of an aqueous solution of 50 mL of NOR, with a concentration of 10 mg L^{-1} applying a potential of 1.0 V vs. SCE under irradiation from a 300 W Xe lamp with a cut filter ($\lambda > 420$ nm), being higher to the photocatalysis process of heterogeneous and electrocatalysis with 19% and 22%, respectively.

The authors identified that the main ROS produced during the degradation process was the h^+, $\bullet O_2^-$ and •OH radicals, being the main active species in the environment, and with the measurements of HPLC and LC-MS, it was determined that the main route of degradation NOR's PEC was by piperazine ring cleavage. The morphological modifications together with increased visible light absorption and a redshift resulted in bandgap energy of 2.21 eV and a photocurrent density of ca. 38 times larger than pure WO_3 film. Therefore, the modifications presented by the formed heterojunction, together with the application of the photoelectrocatalysis method were responsible for the suppression of recombination of the e^-/h^+ pair and high performance in the degradation of the NOR [40].

For the PEC degradation of NOR antibiotic, heterojunction also using WO_3 but with Bi_2O_3 was evaluated. The synthetic process to obtain the heterojunction was carried out via a hydrothermal route with FTO substrate and the heterojunction presented a flower-like morphological structure. The efficiency of degradation of the antibiotic NOR, with a concentration of 10 mg L^{-1} and cell volume of 50 mL, was 88.4% after 6 h of the experiment using radiation in the visible region.

Comparing the efficiency of the photoelectrochemical activity of the separated source materials, that is, Bi_2O_3 and only WO_3 films, it became clear that heterojunction promotes an increase in this activity and the results were evaluated from the ease of electronic transfer as well as the separation more efficient charge carriers, preventing recombination. Furthermore, the authors made an important consideration about the degradation intermediates formed by this process. This is indeed essential from an environmental and toxicity point of view and a possible degradation route was described from LC-MS results [41].

$BiVO_4$ electrodes are photoanodes that have shown high performance in PEC applications, such as water separation and organic pollutant oxidation. For example, Di Cao and collaborators produced an $Ag_3PO_4/BiVO_4$ electrode of the $Ag_3PO_4/BiVO_4$ on FTO substrate. Initially synthesized with the electrodeposition of $BiVO_4$, followed by a heat treatment at 450ºC for 2 h with the subsequent addition of 5 mM Ag_3PO_4 nanoparticles in situ under the formed $BiVO_4$ film.

The heterojunction completely degraded a solution of 5 mg L^{-1} of NOR after 90 min under visible irradiation ($\lambda > 420$ nm) by a photoelectrocatalytic system with the application of 0.5 V vs. SCE, having a removal efficiency evaluated by TOC of 27%. The investigation of degradation products by the HPLC-MS method showed that the main route of degradation of NOR involved the cleavage of the piperazine ring caused by the attack of $\bullet OH/h^+$, the main radicals acting in the environment of reaction. The PEC activity of the $Ag_3PO_4/BiVO_4$ on FTO was also tested against sulfamethoxazole and oxytetracycline antibiotics, obtaining total degradation after a time of 3 h. The application of PEC provided a greater separation of charge carriers and the heterojunction system increased the lifetime of the materials used, delaying the photocorrosion process (Fig. 3)[42].

The degradation of CIP, also a 2nd generation drug of quinolones, was performed with different semiconductors and systems. Ni-doped ZnO was used under UVA light irradiation and sunlight for CIP degradation. Doping with Ni in the ZnO network increased the performance of PEC in the visible region, since the antibiotic degradation rate improved after doping. About 100% degradation of ciprofloxacin under different sources of irradiation was achieved after treatment with PEC and 83.7% removal of TOC and the formation of non-toxic products was observed during the degradation of ciprofloxacin [43].

Considering the heterojunction, TiO_2 and g-C_3N_4 electrodes were used to photodegradation assays of CIP. The g-C_3N_4/TiO_2/HNTs heterostructure was prepared via sol-gel and calcination methods. The

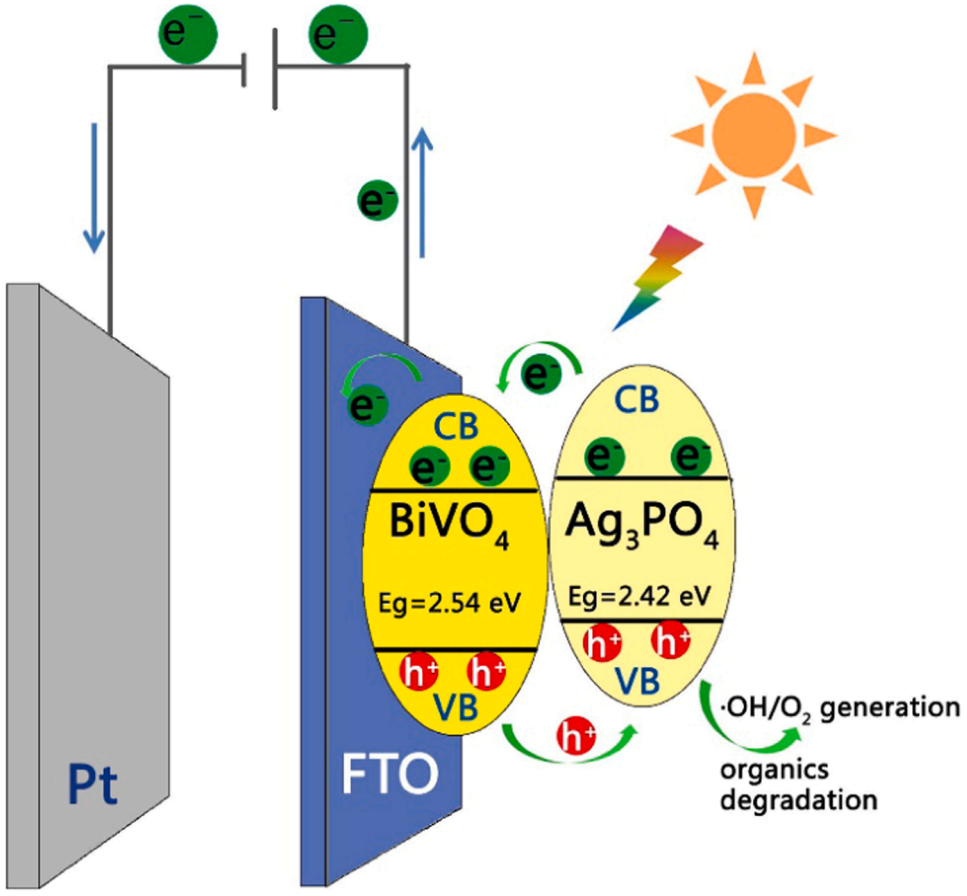

Fig. 3. Schematic illustration of norfloxacin degradation in the PEC process with composite Ag3PO4/BiVO4 electrode.
Reprinted with permission from [42] Copyright © 2020 Elsevier Ltd.

introduction of HNTs and the g-C_3N_4/TiO_2 heterojunction effectively enhanced the charge transfer and separation efficiency of photogenerated electron-hole pairs, providing the system with good stability and photoelectrochemical performance.

Compared to pure TiO_2, the heterojunction composite exhibited higher visible light photocatalytic activity towards degradation of ciprofloxacin and 87% of CIP was degraded by g-C_3N_4-TiO_2/HNTs heterojunction composites [44]. Heterojunction of TiO_2 nanotubes (NTAs) with a p-type semiconductor, such as copper oxide I (Cu_2O) was used. The union of these semiconductors in a heterojunction combines the high electronic mobility properties of TiO_2 NTA with adjustment of the energy absorption region provided by the bandgap narrow of Cu_2O.

Therefore, a heterostructured electrode of TiO_2 NTA/Cu_2O produced by anodization followed by calcination at 500 °C and electrodeposition, was applied in a photoelectrocatalytic system for degradation of 50 mL of a solution of CIP in Na_2SO_4 (0.1 mol L^{-1}) with concentration initial 10 mg L^{-1}. This test was performed with a polarization potential of 1.5 V and a percentage of degradation of ca. 73% was achieved after 4 h of irradiation with a solar simulator with UV cut ($\lambda > 400$ nm). The scavenger studies revealed that photogenerated holes were the main oxidative species in the photoelectrocatalytic process. The factors as the reduction of the bandgap energy of the TiO_2 NTA/Cu_2O film to 2.38 eV, as well as the investigation of the applied potential and the established time in PEC were decisive for the obtained result [45].

Another study applied heterostructured Cu_2O with $BiVO_4$ in film form for the PEC degradation of CIP. In this study, Li and coauthors reported, for the first time, the functionalization of the Cu_2O/$BiVO_4$ film with the cobalt phosphate (Co-Pi) cocatalyst as a strategy for the suppression of the photocorrosion of Cu_2O, the outer layer of the heterojunction, originated of the self-oxidation of this material from excess h^+ photogenerated and accumulated in the valence band of copper oxide I.

For this purpose, the authors performed the photodeposition of a thin layer of Co-Pi on the Cu_2O/$BiVO_4$ film with a charge of deposition 0.05 C.cm^{-2}. The $BiVO_4$/Cu_2O/Co-Pi photoanode obtained showed high stability and photocurrent density ca. 1.8 times greater than the initial heterojunction. Therefore, from this modification with Co-Pi, it was possible to reach a degradation efficiency of 96.17% using the PEC system for 50 mL of a solution with 30 mg L^{-1} of CIP prepared in electrolyte mixed with KPI (0. 1 mol L^{-1}) as an auxiliary electrolyte. For this process, the amperometric mode was used with polarization potential fixed at 0.6 V vs. Ag/AgCl under irradiation of sunlight simulated AM 1.5 G (100 mW cm^{-2}) for a time of 2.5 h. The reduction of recombination of photogenerated pairs and the increase in the lifetime of these carriers provided by PEC combined with the holes-receiving trap generated by the Co-Pi cocatalyst were responsible for this high efficiency of CIP degradation [46].

The study of Orimolade et al. described the solar photoelectrocatalytic degradation of CIP by applying an FTO/$BiVO_4$/MnO_2 anode as an n-n heterojunction. The incorporation of MnO_2 in the $BiVO_4$ film was a usual strategy to overcome the limitation of this material in charge transfer and recombination, the addition of MnO_2 was carried out by electrodeposition with a total number of 50 cycles. Among the methods investigated for the application of FTO/$BiVO_4$/MnO_2 film for CIP degradation, photoelectrocatalysis showed superior results with a removal efficiency of 73% after a total time of 2 h under a solar simulator with a 100 W xenon lamp.

This result was obtained from the optimization of the parameters applied in the photoelectrochemical tests, in which a solution with 10 mg L^{-1} of CIP prepared in Na_2SO_4 (0.1 mol L^{-1}) had pH adjusted to 7 and the application of a potential 1.5 V vs. Ag/AgCl. The percentage of

mineralization determined was 71% according to TOC analysis and the main route of degradation of CIP established by the authors was via oxidation of the piperazine ring from hydroxyl radicals and photogenerated holes [47].

Hosseini et al. degraded the OFL with a larger scale reactor (800 mL) with NaCl solution, using as photocatalyst Ni-doped ZnO. In this study, operational variables such as initial pH, applied current, OFL concentration, and reaction time during PEC under UV-A irradiation were evaluated. In the best condition, about 100% of the antibiotic was degraded. It was found that photocatalytic processes have a much lower efficiency for OFL removal compared to PEC. Furthermore, there was a decrease in the toxicity of the solution at different reaction times and eight possible degradation intermediates were identified [48].

The degradation of the OFL antibiotic was also studied by [49] using Co-Doped ZnO as a photocatalyst in 50 mL of Na_2SO_4 solution. After a 6-hour treatment PEC, under xenon lamp irradiation ($\lambda > 420$ nm), 86.7% of ofloxacin was removed from the solution. The visible light photoelectrochemical activity of ZnO film electrodes was improved by Co doping. The PEC of antibiotics with ZnO-based materials used as photoanode is still very scarce in usual electrolyte solutions (Na_2SO_4 and NaCl) and especially in real samples, such as wastewater and natural water under visible light irradiation [49].

Despite having a similar chemical structure to OFL, LFX was inserted in the 3rd generation since it has activity against *Streptococcus*. In this sense, Cristino et al. synthesized films with the n-n heterojunction formed by $WO_3/BiVO_4$. The semiconductor was deposited on WO_3 mesoporous film via electrochemical deposition using a modified potentiostatic method and after that, the films were calcined at 500 °C for 2 h. For the 10 mg L^{-1} degradation experiments of LFX, the authors used a volume of 10 mL solution, a system containing 2 electrodes, and under potentiostatic conditions (0.4 and 1.5 V) with a total of 5 h of photoelectrolysis (simulated lighting system 1.5 G with appropriate cut off). Longer experiments were carried out to identify the process intermediates via LC-MS. It was observed that more than 80% degradation was found after 5 h under visible (>400 nm) illumination and 1.5 V vs. Pt electrode. Moreover, the degradation intermediates were progressively consumed by further oxidation at the $WO_3/BiVO_4$ interface [50].

Cristino et al. also carried out the degradation of ketoprofen and the antibiotic LFX but using WO_3 and zeolite. An interesting approach of this study is the incorporation of a non-conductive material, synthetic zeolite with a ratio of 25 between SiO_2/Al_2O_3 and being called β25. This combination of photocatalyst material and adsorbent material allows to collect and trap contaminants near the surface, where % •OH photogeneration occurs, allowing to increase the chance of bimolecular encounter between the target and this highly reactive oxidant.

The results showed high efficiency of photoelectrochemical degradation of the combination between WO_3 and β25 zeolite, reaching up to 90% efficiency after 5 h of testing under radiation incidence (AM 1.5 G with the appropriate cut-offs) with 10 mL of cell volume, the antibiotic concentration of 10 mg L^{-1} and total electrode area of the 1 cm^2. The tests were carried out under potentiostatic conditions (0.4 V) for 5 h. A 20 h trial was performed to identify intermediates by LC-MS. In total, 6 degradation intermediates were identified and they disappeared after 20 h of testing [51].

In this way, drugs of the Quinolone class were successfully degraded via a photoelectrochemical process. Different strategies were carried out about the semiconductor material such as pure, heterojunction, doping, among others. It is still interesting that, despite the complexity of the molecules, the studies showed a high rate of efficiencies but still in systems that do not use real samples or large-scale flow reactors. For the successful application of photoelectrochemical processes aimed at mineralization or the formation of less toxic compounds, the importance of degradation intermediates should not be underestimated.

2.1.3. Sulfonamides antibiotics

Sulfonamides, such as sulfadiazine (SD) and sulfamethazine (SMZ), are some of the most frequently used antibiotics worldwide in veterinary medicine. However, few studies have been carried out in recent years addressing the degradation of this class of antibiotics via the photoelectrochemical process. Data were summarized in Table 1.

Teng et al. investigated the decomposition of SD by $Ag_3PO_4/MoS_2/TiO_2$ nanotube array electrode, under visible light excitation. Nearly 70% of SD was degraded in 240 min. A higher degradation value was only reached in the presence of Ag_3PO_4 and MoS_2, compared to electrodes of the type of MoS_2/TiO_2 and Ag_3PO_4/TiO_2 NTAs. This behavior was explained considering that Ag_3PO_4 nanoparticles enhanced the visible light absorption and the MoS_2 nanosheet promoted the separation of photogenerated charges. The authors explain by the proposed mechanism that superoxide and hydroxyl radicals could be generated by $Ag_3PO_4/MoS_2/TiO_2$ NTAs under visible light e then react with organic compounds, or the holes could directly oxidize the organic compounds into CO_2, H_2O, and other intermediates [52].

Considering the SMZ degradation, different approaches were used with the semiconductors TiO_2, Cu_2O, and Ag_3PO_4. The use of the hybrid photoelectrode of semiconductor-metal organic frameworks (MOFs) was successfully addressed. ZIF-8 (Zeolitic imidazolate framework) nanoparticles were deposited on the hollow TiO_2 nanotubes and N and F were added as co-doping and the electrode as nominated ZIF-8/NF-TiO_2. The percentage of SMZ degradation was 81% and TOC of 40% after 180 min, implying that SMZ could be partially mineralized by ZIF-8/NF-TiO_2 under visible light irradiation. The authors compared the degradation rate of the prepared electrode with unmodified anatase TiO_2, and the rate increased by 21.7 times. This behavior was attributed to the porous structure of ZIF-8, and the intrinsic band difference between anatase and rutile TiO_2 which greatly improved light utilization and promoted electron-hole separation. Fig. 4 shows the proposed mechanism for this system [53].

Peleyeju et al. reported the photoelectrocatalytic SMX at a TiO_2–exfoliated graphite (TiO_2–EG) anode. After optimizing the experimental conditions, was applied a current density of 10 mA cm^{-2} in 0.1 M Na_2SO_4 solution, pH 6.3, and simulated sunlight with a 100 W xenon lamp to photodegradation of SMX. It is observed that SMX was almost completely degraded and 90% of the COD of the solution was removed after 6 h [54].

A heterojunction of Cu_2O with Ag_3PO_4 was used as an adequate strategy for the photoelectrochemical degradation of SMZ by Koiki et al. The authors reported for the first time the application of a Cu_2O/Ag_3PO_4 heterojunction photoanode illuminated by sunlight in the photoelectrochemical degradation of emerging pharmaceutical pollutants, with SMZ as the target contaminant. This study reports the obtainment of a Cu_2O/Ag_3PO_4 film deposited in FTO by drop–coating, which was applied in a quartz reactor of 50 mL to degrade a SMX solution with an initial concentration of 10 mg L^{-1}. The PEC had its performance conditions optimized with the polarization of + 1.5 V vs. Ag/AgCl and the pH of the electrolyte solution adjusted to 6.2. From this, a removal percentage of 67% was achieved after 2 h of irradiation under simulated sunlight (100 W xenon lamp and 1.5 G AM filter). This result was 1.2 and 3.2 times higher than the PEC values of the separate Cu_2O and Ag_3PO_4 films, respectively [55].

From Table 1, it is possible to state that the degradation of sulfonamides is still not widely applied despite being one of the most consumed classes in the world, according to the WHO. The chemical structures are not as complex as those of other antibiotics already mentioned in this article, but a possibility of few studies may be due to the difference in solubility as a function of pH and at certain values, they may behave like zwitterions. In addition, they are usually sold in combination, as is the case with trimethoprim/sulfamethoxazole.

2.1.4. Tetracyclines

Tetracyclines (TC) are broad-spectrum bacteriostatic polyketide antibiotics that are very effective against several Gram-positive and Gram-negative aerobic and anaerobic bacteria. Also, this subclass can be

Table 1
Experimental conditions and removal rates during PEC with Sulfonamides antibiotics.

Material	Synthesis method	Experimental conditions	Removal efficiency (%)	Reference
Sulfadiazine (SD)				
$Ag_3PO_4/MoS_2/TiO_2$	electrodeposition and chemical immersion method	C = 10 mg L^{-1} Irradiation source: Visible light excitation V = 100 mL E = + 0.2 V vs. SCE	70% in 4 h ph= 8.0	[52]
Sulfamethazine (SMZ)				
ZIF-8/NF-TiO_2	electro-anodization and in-situ growth	C = 10 mg L^{-1} Matrix: 0.5 mol L^{-1} Na_2SO_4 Irradiation source: Visible light excitation E = + 2 V vs. Ag/AgCl	81.3% in 3 h pH= 3.5	[53]
Sulfamethoxazole (SMX)				
TiO_2–EG	Sol-gel and microwave techniques	C = 25 mg L^{-1} Matrix: 0.1 mol L^{-1} Na_2SO_4 Irradiation source: simulated sunlight with a 100 W xenon lamp V= 75 mL j = 10 mA cm^{-2}	90% of the COD pH 6.3	[54]
Cu_2O/Ag_3PO_4	deposited in FTO by drop–coating	C = 10 mg L^{-1} Matrix: 0.1 mol L^{-1} Na_2SO_4 Irradiation source: Oriel LCA-100 Solar Simulator (USA) equipped with 100 W xenon lamp and AM 1.5 G V= 50 mL E = + 1.5 V vs. ag/AgCl	67% in 2 h pH= 6.2 TOC= 38%	[55]

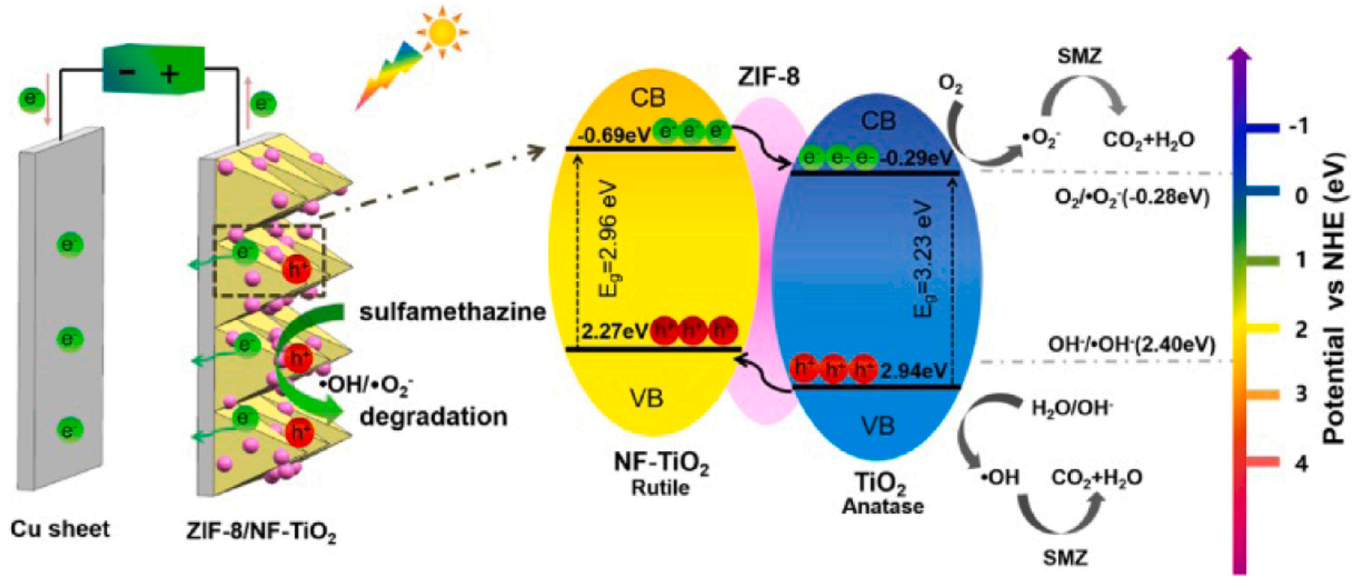

Fig. 4. Proposed mechanisms in ZIF-8/NF-TiO_2.
Reprinted with permission from [53] Copyright © 2020 Elsevier Ltd.

natural or semi-synthetic and they have intense worldwide consumption. Tetracyclines have several favorable properties, such as a broad spectrum of action, low toxicity, and low cost. In addition to the pharmacological importance of tetracyclines, these drugs have a very interesting chemical structure, being able to form chelates in various positions of the molecule due to the presence of several donor groups (N, O) [56].

Several studies were carried out using different semiconductors for the degradation of tetracycline. The chemical structures of tetracyclines, as the name already says, have four rings, which may at first be a difficulty for the efficient degradation process. Zhang et al. developed films on FTO substrate with the structure of WO_3 nanoplates using the hydrothermal method. To assess this effect, the authors performed photoelectrochemical assays for the degradation of the TC antibiotic which has therapeutic indications from acne and rosacea to respiratory and systemic infections.

The degradation efficiency of this antibiotic, which has a complex chemical structure, was at a maximum of 72% after 80 min of the experiment. The authors also report that the success of the photoelectrochemical results is due to the film thickness and the increase in the oxygen deficiency content of the WO_3 nanoplate films, which further promoted the high light absorption and low recombination rate of electron-hole pairs in the interface [57]. This study deserves to be highlighted for its high efficiency using only the semiconductor, in the WO_3 case, without another strategy such as doping or heterojunction formation. It becomes clear that the morphology of the material influences the efficiency since the authors reported nanoplate-like structures that help both transport loads and reduce defects.

The TiO_2 semiconductor was used with different architectures for TC degradation. Tang et al. presented a system composed of g-C_3N_4 nanosheets/TiO_2 nanotube mesh arrays where TC was removed almost completely (TOC 93%) from the solution in 2 h, using simulated solar

irradiation with electrode polarized at 1 V vs. Ag/AgCl. In this study theoretical calculations were also performed in search of to predict the reactive sites for the formation of radical species. Thus, in the proposed mechanism the species $\bullet O_2^-$, $\bullet OH$, and h^+ jointly participated in the degradation of TC.

The system was tested using a water matrix sampled from Taozi Lake, Changsha, China, and it is observed that TOC reached the value of about 80% in 5 h and remained stable for up to 20 h, showing the good performance of the material. This study deserves attention for the use of a real matrix and for using two types of system: static and in flux. Few studies in the area of photoelectrochemistry have reported degradation results in flow systems, although this is still far from a system with a pilot-scale application since the treated volume is only 50 mL and the active area is only 4 cm^2. The determination of intermediates was performed via LC-MS and ecotoxicity studies with *E. coli*. Also, despite the sample being real, the study was carried out with fortification with 10 mg L^{-1} of the drug. Fig. 5 shows the mechanism proposed by the authors [58].

Also using carbon nitrides, Rabé et al. proposed an electrode g-C_3N_4/Fe^0 (1%)/TiO_2 as photoanode and WO_3 as photocathode to degradation of TC. The electrodes were irradiated by a halogen lamp of 50 W employing 0.05 M Na_2SO_4 at different pH and external resistance of 10 ohms and 97.3% was removed at 90 min at pH 5 [59].

TiO_2 catalysts co-doped with I and P (ITP) were prepared via a hydrolysis method at the decomposition of TC. The photoanodes were prepared with different P dopants amounts and the synergistic effect of I and P co-doping was observed, such as improving the charge separation rate and enhancing the light absorption capacity of TiO_2. The better result to TC degradation was achieved when the doping content of P was at 4% (ITP-4 photoelectrode) at pH 11.02 under visible light where the velocity constant was 4.20×10^{-2} min^{-1} and the TC degradation reached almost 100% in 3 h [60].

Li et al. studied the degradation of the TC with a photoanode composed of three semiconductor oxides of ZnO, Cu_2O and TiO_2 immobilized in FTO, forming the n-ZnO/p-Cu_2O/n-TiO_2 electrode, under a visible irradiation source and a solar simulator. The results of this work showed high removal of tetracycline both in visible light (85% in 3 h) and in sunlight (90% in 3 h), indicating an excellent photoelectrocatalytic activity of the n-ZnO/p-Cu_2O/n-TNA material [24]. Therefore, the results indicate that the simulated light presented a result compared to sunlight but the latter still with superior performance and still shows the feasibility of using sunlight as a source of energy and sustainability of the photoelectrochemical process.

Two combinations of bismuth vanadate oxides $BiVO_4$ and ZnO were also applied in the removal of TC in sulfate electrolyte medium. Feng et al. studied the deposition of ZnO under $BiVO_4$ forming the $BiVO_4$/ZnO electrode and evaluated the efficiency of this catalyst under the PEC of tetracycline under irradiation of sunlight with a xenon lamp. The results of the study indicated that the introduction of $BiVO_4$ into the ZnO extended the film absorption to the visible region and improved the visible light PEC activity of the ZnO film. Under optimized conditions, the $BiVO_4$/ZnO film was successfully applied to PEC degradation of tetracycline under visible light illumination, with a degradation percentage of 66.1% [61].

Li et al. studied the degradation of the TC antibiotic and which oxidizing species, formed during the photocatalytic process of ZnO/$BiVO_4$, is responsible for the degradation of the compound. From this study, it was found that the ZnO/$BiVO_4$ is capable of producing active species $\bullet O_2^-$ and $\bullet OH$ under visible light and that this material degraded about 84.5% of the antibiotic after 60 min of PEC (Fig. 6) [18].

Eswar et al. report the use of CuO nanoparticles obtained by combustion in solution with ascorbic acid as fuel (described as NPs CuO-CSA) in the degradation of photoelectrocatalytic TC and *E. coli* bacteria (wild-type K12 strain). In this study, the authors compared the properties of CuO-CSA NPs with continuous arrangement morphology of high porosity Cuo NPs with CuO nanorods in three degradation configurations, PC, CE, and PEC.

In summary, an optimized amount of 0.5 g L^{-1} of CuO-CSA NPs was deposited in FTO for the formation of a film applied in the PEC degradation of a 25 mg L^{-1} TC solution applying a potential of 3 V vs. calomel, and the complete degradation of tetracycline was achieved in 1 h under irradiation of a metal halides lamp 400 W with a cut filter of UV solution ($K_2Cr_2O_7$) and λ_{max} of lamp approximately 510 nm. With the application of PEC, this degradation result was superior and much faster when compared to the other applied configurations. The CuO-CSA NPs film was still active after 10 cycles, evidencing the high level of reuse of this material [62].

In addition to the PEC evaluation of TC with the CuO-CSA NPs film, a pioneering study was carried out evaluating the application of this same degradation method in a system with the simultaneous presence of the antibiotic tetracycline and the bacteria *E. Coli*, which the centrifuged bacterial cell mass was suspended in 25 mg L^{-1} tetracycline solution. In this procedure, PEC degradation had high performance, inactivating both analytes in less than 30 min. Therefore, PEC degradation was identified as a method applied to prevent the increase in antibiotic resistance among microorganisms exposed to them [62].

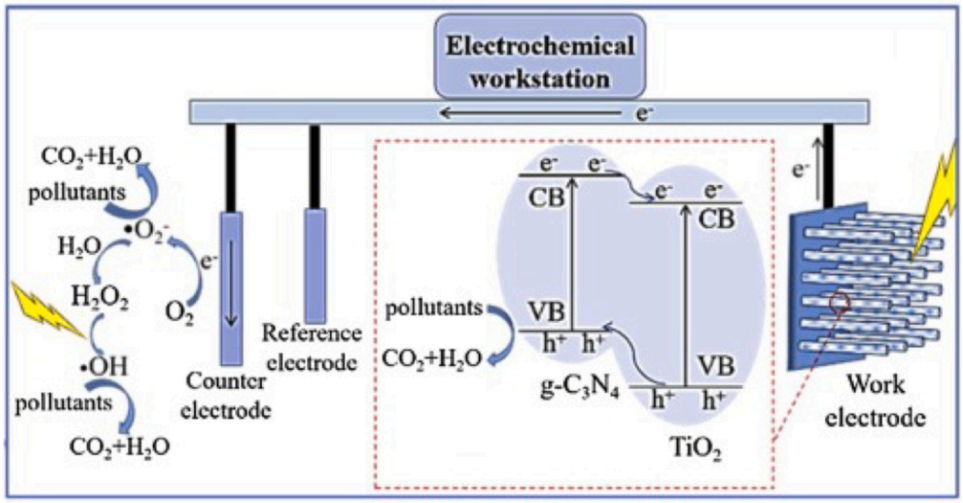

Fig. 5. Schematic of PEC degradation of TC over TCN-2.
Reprinted with permission from [58]. Copyright © 2020 Elsevier Ltd.

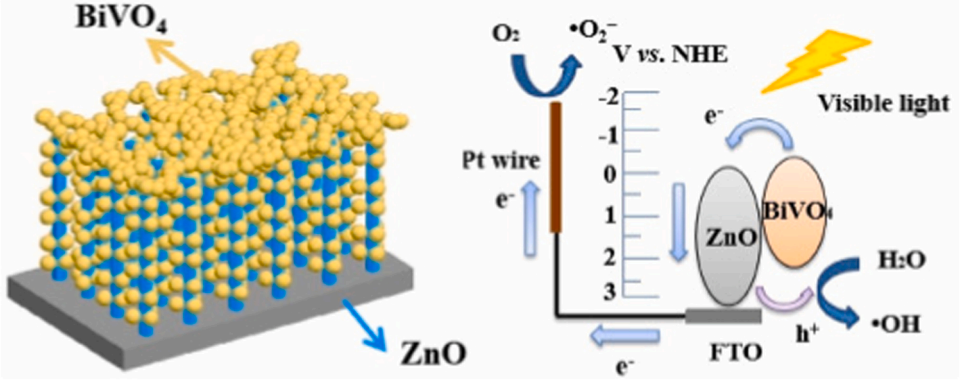

Fig. 6. Schematic diagram of the ZnO/$BiVO_4$ nanocomposite V vs NHE.
Reprinted with permission from [18] Copyright © 2020 Elsevier Ltd.

Among the studies presented for photoelectrochemical degradation of the tetracycline class by Cu_2O, Cheng et al. studied the application of a p-n heterojunction film of Cu_2O/α-Fe_2O_3 deposited in FTO and the photoelectrocatalytic performance of this for oxytetracycline (OTC) degradation, one of the derivations of the tetracycline antibiotic. In this study, the synthesized heterojunction was able to remove 73.3% of OTC in 1 h with the application of + 0.5 V vs. Ag/AgCl by photoelectrocatalysis showing a removal rate of 5.4 times higher than the photocatalytic process applied in the same study.

The results obtained in the application efficiency of PEC are linked to factors such as a lower recombination rate, a greater separation of the photogenerated charge carriers and the electron interfacial transfer obtained when combined α-Fe_2O_3 of n-type and Cu_2O of type- p in the form of heterojunction, having inferior results for both separately. The Cu_2O electrodeposition time (1–5 min) on the α-Fe_2O_3 surface is pointed out as an important factor in the improved response of the obtained heterojunction, in which 5 min Cu_2O deposition proved to be ideal for the results obtained and its viability in visible light [63].

Changanaqui et al. studied the degradation of the antibiotic oxytetracycline in Na_2SO_4 and urban wastewater with the tertiary film ZnO/TiO_2/Ag_2Se deposited under FTO by chronoamperometry and dip coating. This work is the only one to date that addresses the degradation of antibiotics with ZnO under visible light using the PEC process in a real sample, which was observed that the ZnO/TiO_2/Ag_2Se photoanode mainly promoted the formation of •OH radicals, the species responsible for the degradation of the antibiotic. Furthermore, the presence of NOM (fulvic and humic acids) and active chlorine in urban wastewater led to partial destruction of radicals formed during PEC, which promoted a decrease in the removal rate of oxytetracycline in this reaction medium, compared to the solution of Na_2SO_4 [64].

Nanostructured nitrogen-doped TiO_2 photoanode was used for chlortetracycline (CTC) photoelectrocatalytic oxidation under visible light by Daghrir et al. The electrode consists of nanostructured anatase N-doped TiO_2 prepared with different nitrogen contents. The authors observed that nitrogen doping produced the redshift of the absorption onset of the TiO_2 coatings (from $\lambda = 380$ nm to $\lambda = 550$ nm). With the optimal N content of 3.4%, the current intensity of 0.6 A, and 180 min of treatment CTC, the processes of oxidation and mineralization reached the value of 99.6% and 92.5%, respectively [65].

The antibiotic tetracycline hydrochloride was degraded by Wang et al. using a WO_3 electrode decorated with FeOOH and Au nanoparticles. For the photoelectrochemical degradation tests, a three-electrode system was used with a 20 mg L^{-1} solution of the drug molecule and a volume of 80 mL under potentiostatic conditions. (0.9 V

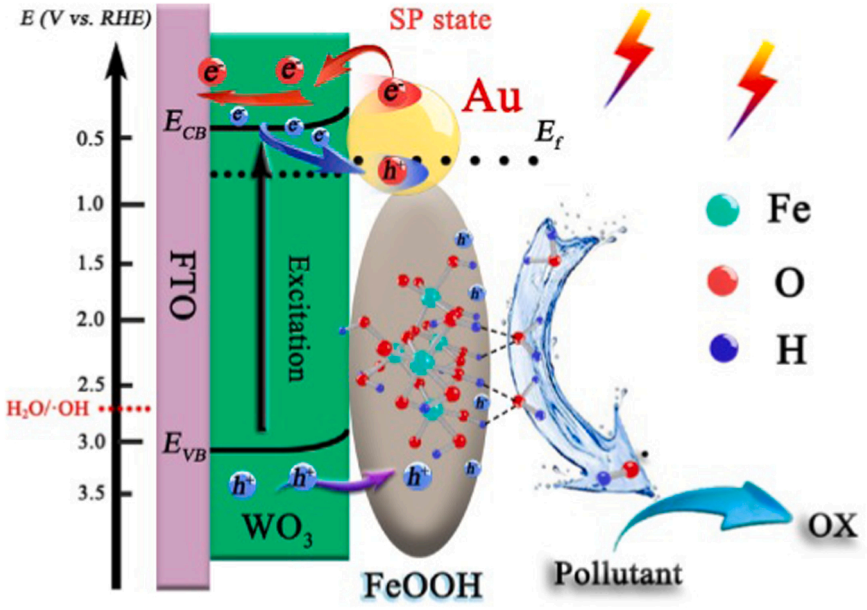

Fig. 7. Proposed mechanism of WO_3/Au/FeOOH composite photoanode for PEC degradation towards TC-HCl pollutant.
Reprinted with permission from [66]. Copyright © 2021 Elsevier Ltd.

vs. RHE) e illumination provided by a solar simulator (AM 1.5 G). The process efficiency was interesting with 99% removal after 50 min and the proposed mechanism for photoelectrochemical degradation is shown in Fig. 7 [66].

Table 2 presents the main experimental conditions and results of the degradation efficiency of the tetracycline class antibiotics.

In all studies presented, degradations were successfully performed with high tetracycline degradation rates. However, these studies were not conducted using real matrices and the solution volumes were still relatively small (up to 800 mL), not representative of real applications. Furthermore, the authors used lamps to simulate radiation rather than sunlight to simulate light.

2.1.5. Amphenicol antibiotics

The amphenicol subclass comprises drugs produced by *Streptomyces venezuelae*, which was introduced into clinical practice in 1948. Chloramphenicol (CAP) is the best-known drug of this subclass, and some studies have been conducted on its photoelectrochemical degradation.

Cheng et al. used WO_3 electrodes with CdS quantum dots as photoanode to CAP degradation. Coupled photoelectrocatalysis (PEC) and electroenzymatic (EEC) processes were carried out to the degradation experiments, using a quartz photoreactor containing 60 mL aqueous solution of CAP with 0.1 M Na_2SO_4 with a Xenon lamp with an optical filter ($\lambda > 420$ nm) was used as the irradiation source. Also, during the degradation experiments, the air was continuously purged into the solution to supply oxygen for the generation of H_2O_2 via oxygen reduction on the cathode. The preparation of graphene-hemin hybrid materials and immobilization of graphene-hemin on graphite electrode (cathode) was carried out using chitosan as a binder. Thus, the PEC-EEC system reached a CAP degradation of 98.7 ± 0.4% after 10-h treatment [67].

Gupta et al. studied the ZnO/CuI electrode, p–n junction-based obtained by hydrothermally grown. In this study, the electrode promoted simultaneous inactivation of antibiotic-resistant bacteria (ARB) and CAP antibiotic degradation, due to its excellent photoactivity. Therefore, holes and superoxide radicals were identified as the responsible species for the inactivation of bacterial cells, confirmed by scavenger studies [68].

He and coauthors presented a PEC system constructed using TiO_2 nanotube arrays (TNTs) decorated with Ag/SnO_2-Sb nanoparticles (TNTs-Ag/SnO_2-Sb) as the anode and Ti-Pd/SnO_2-Sb as the cathode and in the removal of antibiotic-resistant bacteria (ARB) and antibiotic resistance genes (ARGs). The good performance of this system was observed, and the results showed a removal and inactivation of 99.9% of ARB and ARGs, at 20 min and 30 min, respectively. At the same time, the degradation of CAP solution occurred at the cathode chamber within 1 h. In this paper, the authors demonstrated that the PEC system presented an excellent ability to remove contaminants and sterilize bacteria and it also could remove antibiotics, ARB and ARGs in the anode or reduce in the cathode contaminants that have great oxidation resistance [69].

Chatzitakis et al. compared the performance of particulate TiO_2 (SGT) layers grown on Ti substrates and TiO_2 nanotubes (TNTs) in the photoelectrolysis of CAP. The authors observed that TNTs showed a 4-fold enhancement in the CAP photoelectrodegradation rate under + 0.5 V reverse bias compared to the SGT and conclude TNTs electrodes present the best accomplishment due to their higher surface area [70].

Bai et al. studied the formation of a uniform heterojunction electrode p-Cu_2O/n-TiO_2 prepared by electrochemical anodization followed by pulse electrodeposition having as application the photoelectrocatalysis of the target CAP under simulated sunlight irradiation (300 W xenon lamp and100 mW cm^{-2}). The authors reported a reduction in the resistance of transports of e^- and an increase in the absorption of the visible region, and the results were confirmed by the photoluminescence and electrochemical impedance spectra.

The photoelectrochemical degradation of CAP was evaluated using 50 mL of an aqueous solution with 10 mg L^{-1} of CAP with an application of a constant potential of 0.5 V vs. Ag/AgCl, the pH of the CAP solution was 5.3. The p-Cu_2O/n-TiO_2 electrode had a degradation efficiency of CAP by the PEC process of 66.8% in 4 h, being superior to the photolysis, electrocatalysis, and photocatalysis systems. The polarization potential applied in the PEC process was responsible for increasing the separation of the photogenerated e^-/h^+ pairs, prolonging the life of the charge carriers, and inducing the transfer of photogenerated electrons from the anode to the cathode. The PEC degradation of CAP was mainly attributed to •OH radicals and was facilitated by the synergistic effect of active species in the •OH, $•O_2^-$ and h^+ medium [71].

2.1.6. Combined processes: degradation of antibiotic and generation of hydrogen or energy

Wastewater contaminated with pharmaceutical agents such as tetracycline hydrochloride and other compounds noted in this study is a recurring environmental problem. Nevertheless, wastewater contaminated with refractory organics can be a potentially renewable resource, since the organics they contain are rich in chemical energy, making it possible to produce electricity and hydrogen from their degradation [72]. In this particular case, we point out the aspects of this approach from a technological point of view concerning the studies published on the degradation of antibiotics.

Dai et al. proposed a bio-photoelectrochemical system (BPES) composed of a reduced graphene oxide/ TiO_2/Ag (RGO/TiO_2/Ag) photocathode with a bioanode. The interesting thing about this work was to propose a system in which TC degradation and electricity generation occur simultaneously. The BPES showed a TC removal rate of 95.21% within 8 h under illumination with a xenon lamp (300 W, 100 mW cm^2). In addition, the TOC removal rate of the system with the RGO/TiO_2/Ag photocathode was about 3.4, 2.5, and 2.2 times higher than the system with the TiO_2, RGO/ TiO_2, and TiO_2/Ag photocathode, respectively. The performance of the system is greater in light than in dark and it is assumed that TC removal under illumination is due to the synergistic effect of the photocathode and biological anode, with the $•O_2$ species being dominant in the mechanism of the BPES reaction followed by the species •OH [73].

In another study, conducted by Rabé et al., the coupling of the waste photodegradation process and energy generation in a Photocatalytic Fuel Cell (PFC) was carried out with a visible light Z-scheme g-C_3N_4/Fe^0/TiO_2 anodic catalyst, tested with cathodic WO_3. In this case, the organic molecule to be degraded in the photoanode was the berberine chloride (BC) antibiotic and simultaneously generate electricity in the photocathode. The phytotherapeutic berberine is a quaternary ammonium salt of the protoberberine group of benzylisoquinoline alkaloids used in various treatments and more recently, as an antibiotic. The highest removal of BC, cell voltage, and power density were 91%, 0.8 V, and 16.4 W m^{-2} at a current density of 2.02 mA cm^{-2}, respectively after 90 min irradiation in 0.05 M Na_2SO_4 electrolyte, with 10 Ω external resistance [74]. The Photocatalytic fuel cell (PFC) was also evaluated, by Deng et al., for degradation of 4-chlorophenol (4-CP), phenol, and tetracycline (TC), and power generation in a dual-chamber. The degradation efficiency of 4-CP, phenol, and TC reached 32.6%, 37.9%, and 96.4% in 6 h [75].

Zeng et al. reported for the first time a new self-sustaining monolithic photoelectrocatalytic/photovoltaic (SMPP) system for efficient organic degradation and simultaneous production of electricity and hydrogen using sunlight with the photoanode WO_3/$BiVO_4$, the rear Si photovoltaic cell (PVC), and a counter Pt-black/Pt cathode. The developed SMPP system follows the following mechanism: when illuminating sunlight from the photoanode side, the WO_3/$BiVO_4$ film absorbs light of relatively short wavelength for photoelectrochemical degradation of the contaminant, and the Si PVC absorbs the transmitted light, from a relatively long wavelength, to generate polarization potential and facilitate the transfer of photogenerated electrons in the WO_3/$BiVO_4$ photoanode to the black Pt/Pt cathode to generate hydrogen.

For the PEC of tetracycline hydrochloride, a 100 mL solution with

Table 2
Experimental conditions and removal rates during PEC with TC antibiotics.

Material	Synthesis method	Experimental conditions	Removal efficiency (%)	Ref
Tetracycline				
WO_3 Nanoplates	Hydrothermal method	C = 5 mg L^{-1} Matrix: 0.5 M Na_2SO_4 Irradiation source: 300 W xenon lamp source E = 1.20 V_{RHE}	72% after 80 min of the experiment	[57]
g-C_3N_4 nanosheets/ TiO_2 nanotube	Thermal condensation	C = 10 mg L^{-1} Matrix: 0.1 M Na_2SO_4 Irradiation source: 300 W Xe lamp V = 50 mL E = 1 V vs. Ag/AgCl Reactor: quartz beaker	TOC 93% after 2 h (water sample) TOC reached the value of about 80% in 5 h (river sample)	[58]
g-C_3N_4/ Fe^0(1%)/TiO_2	Chemical reduction for Fe^0 /TiO_2 and g-C_3N_4 from melamine	C = 10 − 60 mg L^{-1} Matrix: 0.05 M Na_2SO_4 Irradiation source: halogen lamp of 50 W V = 500 mL R = 10 Ω of an external resistor Reactor: single reactor	97.3% and the power density is 24 W m^{-2} when the original pH is 5	[59]
TiO_2 catalysts co-doped with I and P	Hydrolysis method	C = 10 mg L^{-1} Matrix: 0.1 M Na_2SO_4 Irradiation source: metal halogen lamp 400 W V = 100 mL E = 1.4 V bias T: 25 °C Reactor: photochemical reactor	Almost 100% in 3 h	[60]
n-ZnO/p-Cu_2O/n-TiO_2	Anodization, sonoelectrochemical deposition (SED) and hydrothermal method	C = 20 mg L^{-1} Matrix: 0.2 M Na_2SO_4. Irradiation source: Xenon lamp (100 mW cm^{-2}) and visible light with filter of 380 and 800 nm. V = 20 mL pH = 5.5 E = + 0.5 V T: 25 °C Reactor: a rectangular shaped quartz reactor (20 mm × 30 mm × 50 mm.	85% of removal of tetracycline after 3 h degradation under visible light. 90% of tetracycline was degraded after 3 h under solar light.	[24]
$BiVO_4$/ZnO	The composite film was prepared by liquid phase deposition (LPD) and SILAR process followed by calcination at 500° and 450 °C.	C = 20 mg L^{-1} Matrix: 0.1 M Na_2SO_4. Irradiation source: PLS-SXE300 xenon lamp (($\lambda > 420$ nm) V = 80 mL E = + 0.8 V T: 25 °C. Reactor: round-bottom quartz beaker	26.1% and 35.9% of tetracycline were degraded by ZnO and BiVO4, respectively. 66.1% of tetracycline was degraded by $BiVO_4$/ZnO.	[61]
ZnO/$BiVO_4$	electrodeposition and chemical water bath deposition on FTO substrate.	C = 20 mg L^{-1} Matrix: 0.1 M Na_2SO_4. Irradiation source: Xenon lamp (300 W) with a filter of $\lambda \geqq 420$ nm – visible light) V = 50 mL E = + 1.2 V T: 25 °C Reactor: quartz reactor	Under visible light illumination and 1.2 V, about 84.5% of tetracycline was degraded in 60 min with ZnO/$BiVO_4$ during PEC	[18]
Chlortetracycline (CTC)				
N-doped TiO_2	N-doped TiO_2 coatings onto Ti by radiofrequency magnetron sputtering (MS) process	C = 100 μg L^{-1} Matrix: 0.07 M Na_2SO_4 Irradiation source: 150 W xenon lamp V = 0.6 L i_{app} = 0.6 A Reactor: batch recirculation mode	Oxidation and mineralization reached the value of 99.6% and 92.5%, respectively	[65]
Oxytetracycline				
ZnO/TiO_2/Ag_2Se	Hydrothermal treatment	C = 5 mg L^{-1} Matrix: 0.05 M Na_2SO_4 Irradiation source: Higrow 36-W blue LED lamp V = 0.1 L E = + 1.0 V vs Ag=AgCl T: 25 °C Reactor: jacketed, an undivided three-electrode glass cell	96.5% of the antibiotic was removed after 360 min of electrolysis	[64]
Tetracycline hydrochloride				
WO_3/Au NP/FeOOH	Chemical bath deposition method	C = 20 mg L^{-1} Matrix: 0.1 M Na_2SO_4	99% removal after 50 min	[66]

(*continued on next page*)

Table 2 (*continued*)

Material	Synthesis method	Experimental conditions	Removal efficiency (%)	Ref
		Irradiation source: 300 W Xe with optical filter, Solarlight V = 80 mL E = 0.9 V vs. RHE Reactor: Simple reactor		

10 mg L^{-1} of tetracycline hydrochloride was prepared in Na_2SO_4 (0.1 mol L^{-1}) and irradiated with a solar simulator (300 W Xe lamp with an AM filter 1.5) having the $WO_3/BiVO_4$ film as the working electrode. The potential used in the PEC process was + 1.35 V vs. SCE. The SMPP system, applied with a tri-cell array, showed a removal rate of 90.6% after 3 h of operation, which is about 220% improvement compared to the PEC system without PVC of Si. The electricity production of the SMPP system was almost 14 times higher when compared to the traditionally applied PFC, having a maximum power output density (Pmax) of 1112 μW cm^{-2}. Therefore, the SMPP system using the $WO_3/BiVO_4$ photoanode showed to be a new efficient way to purify wastewater and produce clean energy under sunlight, simultaneously [76].

Another structure prepared from $BiVO_4$ was developed and applied in the photoelectrodegradation of tetracycline hydrochloride. An electrode of the F-$BiVO_4$ @NiFe-LDH developed from the surface/interface engineering of core-shell composition was prepared from the doping of $BiVO_4$ with F by electrodeposition in FTO followed by a surface attack with HF (2 min) and a process of chemical-thermal. Soon after, the surface of the F-$BiVO_4$ nanoparticles film was modified with double hydroxide coated with NiFe (F-$BiVO_4$ @ NiFe-LDH), which has a cocatalyst action contributing to the oxidation reactions' acceleration speed of organic compounds and water splitting.

The F-$BiVO_4$ @NiFe-LDH electrode was efficient in the photoelectrocatalytic degradation of a TC solution with 20 mg L^{-1} prepared in 0.1 mol L^{-1} PBS with pH 7 and application of + 0.5 V vs. Ag/AgCl under irradiation of sunlight simulated of 100 mW cm^{-2} achieving a degradation percentage of 86% in 2 h. This PEC result was 2.9 times and 6.5 times higher than the photocatalysis (29.3%) and electrocatalysis (13.3%) systems, respectively. A PEC test was also performed for a higher concentration of antibiotics with C_0 = 100 mg L^{-1} having a degradation efficiency of 50.5% after 2 h. The developed F-$BiVO_4$ @NiFe-LDH electrode showed good stability even after four cycles of reuse, thus being appointed as a promising strategy for advanced performance in the areas of solar energy conversion and wastewater treatment [77].

2.2. Anti-inflammatory or analgesic

Several over-the-counter (OTC) analgesics are available over-the-counter and are commonly used by the public, such as paracetamol, weak opioids, and anti-inflammatory drugs such as aspirin and ibuprofen, which are non-steroidal [78].

Medications such as antibiotics and anti-inflammatories/analgesics are the most widely consumed compounds for therapeutic use. These pharmaceutical products have been considered potential contaminants in aquatic environments, mainly due to their excessive use over the years, especially painkillers [79]. However, the impact of chronic drug exposure in the aquatic environment is still unknown, and therefore, no legislation limits the presence of these pharmaceutical compounds in wastewater [80]. The treatment of wastewater contaminated by painkillers is also being studied by advanced oxidative processes. Nevertheless, there are still few works in the literature that report the removal of these compounds by PEC under visible light irradiation.

2.2.1. Salicylic acid

Salicylic acid (SA) is known for its anti-inflammatory, antipyretic, antithrombotic, and analgesic effects. Various symptoms associated with viral infections can be alleviated by this drug, and it is currently being tested in the treatment of patients with COVID-19 [81]. However, large amounts of this medication can cause vomiting, acidosis, abdominal pain, and other symptoms. Therefore, SA in the aquatic environment constitutes a potential hazard to human health. However, the biological effects of SA in aquatic environments are hardly reported, and to date, the degradation of SA by PEC has largely not been documented [82].

Suryavanshi et al. combined the photoactive oxides of iron and zinc synthesized by the spray pyrolysis method under FTO, for the formation of the Fe_2O_3/ZnO electrode applied as a photoanode in the process of PEC of SA and the dye methyl orange (MO). In this work, PEC was carried out under sunlight, which is a highlight in the degradation of organic compounds with ZnO-based materials. The Fe_2O_3/ZnO photo electrocatalyst exhibited good absorption in the visible light region (the gap between 2.69 and 2.73 eV) and the PEC degradation results of SA and MO show the removal of almost 100% of organic compounds under sunlight up to 320 min. The results show COD values as a function of time, decreasing from 59 to 8.5 mg L^{-1} for SA and from 56 to 6.7 mg L^{-1} for MO, showing the good removal of pollutants after PEC [83].

2.2.2. Paracetamol

Paracetamol is a medicine used as an antipyretic, for mild pain, and has no anti-inflammatory action. Non-steroidal anti-inflammatory drugs produce analgesic effects, can reduce inflammation, and are antipyrexial. Opioids, on the other hand, are drugs that produce effects similar to those of morphine, reducing moderate or severe pain [78]. Due to its widespread use and incomplete degradation, high amounts of paracetamol have been found in rivers, groundwater, and wastewater [84]. Furthermore, ecotoxicological studies using algae, Daphnia, fish embryos, and bacteria have shown that this drug is classified as harmful to aquatic organisms [85]. Therefore, the regulation and degradation of this compound and its metabolites in water are extremely important.

ZnO doped with different metals and in the form of heterostructures with other oxides presents good results as a photocatalyst material in the removal of organic compounds by PEC. Alternatively, the incorporation of semiconductor oxide nanoparticles in carbon-based materials has also shown potential as catalysts in water treatment. The interest in carbonaceous materials is related to their high dimensional stability and surface area, in addition to good conductivity. Thus, Nada et al. studied the photo-electroactivity of an electrode of carbon nanofibers (CNFs) modified with ZnO and palladium (CZnO–Pd) in the degradation of the antipyretic paracetamol. The complete drug removal was achieved after about 3 h of PEC with 71.20% removal of TOC after 4 h. The reaction mechanism proposed in this study shows that photogenerated holes and hydroxyl radicals are the main responsible for the drug degradation when CZnO–Pd was used under visible light irradiation (420–600 nm), Fig. 8 [86].

The photoelectrocatalytic oxidation of paracetamol was also carried out by a p-n heterojunction of $BiVO_4$ with bismuth oxyiodide (BiOI), which was first described by Orimolade et al. [87]. This electrode was synthesized by two-step electrodeposition in FTO, which was confirmed by the graphics of Mott Schottky with an improved charge separation mechanism. The photoelectrochemical degradation experiments were carried out with 50 mL of a 10 mg L^{-1} solution of the drugs prepared in Na_2SO_4 at 0.1 mol L^{-1} under radiation from a solar simulator equipped with a 100 W xenon lamp and the application of potential 1.5 V vs. Ag/AgCl.

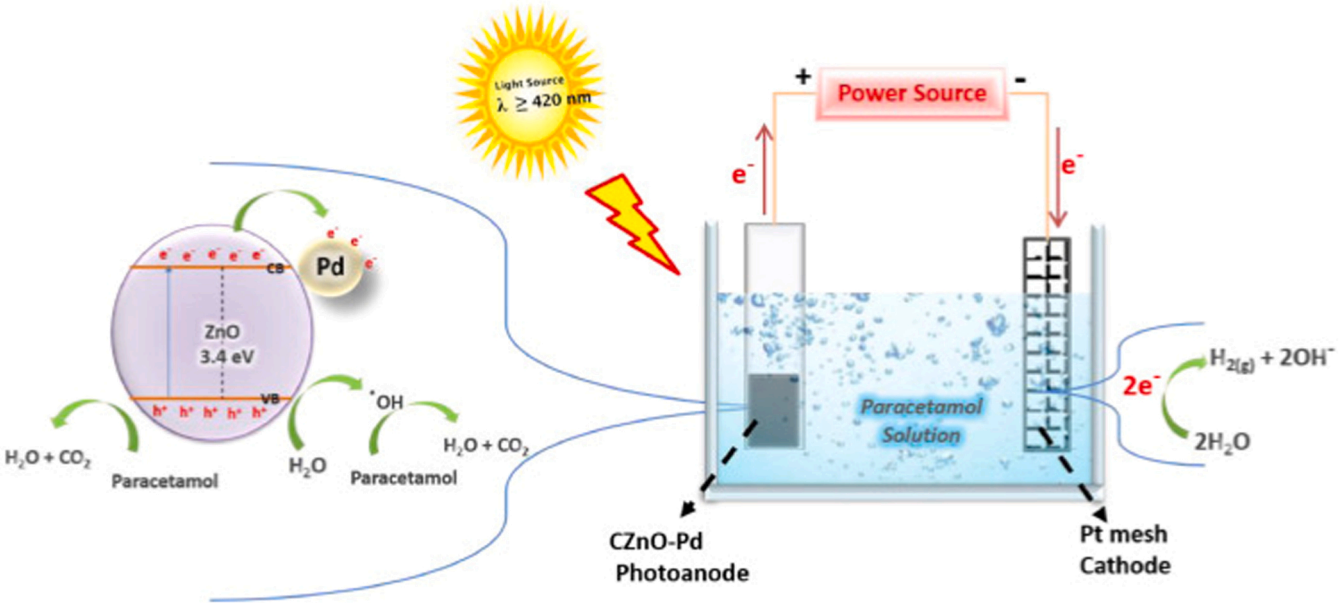

Fig. 8. Mechanism PEC degradation process using CZnO-Pd100 photoanode (2 h, 0.1 mM paracetamol; 10 mA cm^{-2}; CZnO-Pd100). Reprinted with permission from [86]. Copyright © 2021 Elsevier Ltd.

The degradation efficiencies obtained for the $BiVO_4$/BiOI film were 68% and 62% for paracetamol and ciprofloxacin, respectively. The maximum percentages of TOC removal were also determined in this study and resulted in 59% for paracetamol and 48% for ciprofloxacin. In addition to the reported degradation tests, the authors performed a simultaneous PEC test of acetaminophen and ciprofloxacin obtaining a degradation of ca. 60% for both drugs. The efficiency in removing an analyte by the degradation is described by the direct influence of the applied polarization potential, as the potential can promote the separation of the photogenerated charge carriers [87].

Multilayer-type TiO_2/Au/TiO_2 nanocomposites films were prepared by pulsed laser deposition (PLD) and employed as photoanode in electro-oxidation (EO) and photoelectrooxidation (PEO) of paracetamol in sulfate medium. The PEO treatment was 2 times faster than EO, with 95% degradation of paracetamol in the first and only 47% in the second in 3 h. The rate of paracetamol degradation in a hybrid process involving PEO + photoelectron-Fenton (PEF) was also evaluated and the PEC + PEF process exhibited an excellent synergy, achieving the complete disappearance of paracetamol in only 5 min [88].

2.2.3. *Ibuprofen*

Non-steroidal anti-inflammatory drugs (NSAIDs) are among the most widely determined drugs in environmental samples as well as the most widespread drugs in the world. Ibuprofen belongs to this family of drugs, and its concentration in the environment is reported to be between 10 and 160 ng L^{-1} [89]. Ibuprofen is one of the most widely used anti-inflammatories and has been found in surface water, wastewater, and drinking water due to its stability to biodegradation and photolysis. Also, Ibuprofen may have an endocrine-disrupting effect, and exposure to this drug may induce various ecotoxicological risks to aquatic wildlife [90]. Thus, its removal from the environment has been studied.

A p-n junction based on doping of nanotube matrices of TiO_2 with Cu_2O (Cu_2O/TNAs) synthesized by chemical bath deposition method was applied as an anode for the photoelectrodegradation of ibuprofen (IBP), an anti-inflammatory with high stability and difficult biodegradation, persistent in bodies of water. In this study, Sun and colleagues performed the photoelectrocatalytic tests of the IBP in an H-type reactor separating the anode from the cathode to improve the degradation of this persistent contaminant [91].

The degradation experiments were conducted at various pH (pH 3–6) in the anode chamber, while the pH was 5.5 for the NaCl solution in the cathode chamber. The Cu_2O/TNAs electrode with an active area of 2 cm^2 totally degraded a solution of 10 mg L^{-1} of IBP with application of 1.0 V vs. Ag/AgCl under irradiation a 100 W Hg lamp in 120 min, the pH 3 in the anode chamber was ideal for obtaining this result, showing that the degradation of IBP is favored under acidic conditions. The modifications presented by the addition of Cu_2O in the structure of the nanotubes contribute to greater use in the visible region (EBG = 2.07 eV), and this combined with the photoelectrocatalysis method, provided a significant increase in electron mobility and reduction in the recombination of electron-hole pairs, increasing the life of the electrons [91].

Gomes et al. prepared Ti/Zn-TiO_2 electrodes by the co-deposition method and applied them to photoelectrochemical degradation of Ibuprofen (Ibu). The results showed that Ibuprofen was efficiently degraded after a 3 h period in an apparent first-order rate constant with a value of 5.07×10^{-5} s^{-1}. The COD and TOC removals were 34% and 23% after 3 h, respectively. The authors concluded that the results reveal that this nanocomposite material has a huge potential to be applied as a photoelectrocatalyst [92].

2.3. *Other pharmaceutical products in wastewater*

Although antibiotics and anti-inflammatories are the most commonly used drugs and, therefore, the most studied products on PEC, other pharmaceutical products are also noteworthy due to the potential problems they can cause to water resources. The following drug classes will be discussed in this review: β-blockers, antidepressants, anti-anxiolytics, diuretics, hormones, and endocrine disruptors (EDCs). Yet again, the idea is to report the articles according to each drug studied using different semiconductor oxides used in PECs aiming at photodegradation. These semiconductors, as in the previous cases, can be pure, heterostructured, heterojunctions, and cocatalysts.

In the case of atenolol, the novel four-electrode combined cells containing Pt or boron-doped diamond with the coupled in parallel anode a carbon-felt an air-diffusion cathode for H_2O_2 electron generation, have been used to degradation. A carbon-felt cathode strongly enhances the mineralization rate in the photoelectron-Fenton process due to the rapid photolysis of Fe(III) and/or Fe(II) complexes under UVA irradiation which favors the •OH production. The efficient regeneration

of Fe^{2+} with larger •OH production in the combined cells causes a quicker atenolol decay, which always follows a pseudo-first-order reaction, with a TOC removal of 97% in 360 min at a constant rate of 2.03×10^{-3} s^{-1} [93].

In another work of the same group the degradation, beta-blockers were made using electro-Fenton (EF) and solar photoelectron-Fenton (SPEF) with an electrode similar to the previous work, BDD/ADEePt/CF with 95% removal of TOC in 360 min at a constant rate of 2.14×10^{-3} s^{-1}. The advantage was the use of a solar collector, which reduced energy consumption by up to 4 times, showing that SPEF can be a viable method for the remediation of wastewaters with beta-blocker [93].

In the case of a system using only PEC for atenolol degradation, only one study was found, in which Longobucco et al. used WO_3 electrode and near UV–Vis illumination (360 nm). The electrodes were illuminated in the area of the 1 cm^2 and they were placed in a quartz photoelectrochemical cell with aqueous solutions of ATN or CBZ and an initial concentration of the 10 mg L^{-1}. The experiment times were 1;3 and 5 h and the solutions were analyzed by HPLC DAD [94].

The authors also evaluate the photoelectrocatalytic processes in natural waters or domestic wastewaters which should be more representative of naturally occurring wastewaters. Compared to previous systems, the reaction rate constant was much lower ($k = 0.65$ h^{-1} @ pH $= 3$ and $k = 0.41$ h^{-1} @ pH $= 6$) and the degradation reached only 90% of ATN after 5 h of irradiation. This shows that the system is much less efficient which leads to higher energy consumption, so the association of the photo-Fenton process to degrade atenolol can be advantageous.

To CBZ degradation in PEC devices, pure or modified WO_3 and TiO_2 electrodes have been used. In one of the studies, the visible-light-driven Z-scheme TiO_2-carbon dots-polyaniline (PANI) was used. The presence of carbon dots and PANI improved the light adsorption and decrease the bandgap, increasing the photocurrent density by 18.8 times under visible light and leading to good simultaneous carbamazepine degradation (44.67%) then Cr(VI) reduction (11.94%) performance [95].

The highest CBZ degradation efficiency (73.08% ± 1.67%) after a 4 h reaction was obtained using TiO_2 thin film as photoanode and Ag plate as cathode, as proposed by Wang et al. [94]. This system also allowed the reduction of CO_2 and production of H_2 simultaneously with the degradation of CBZ. There was a production of CO and HCOOH of 108.23 ± 8.96 and 10.77 ± 0.75 μmol, respectively, and also H_2 production (152.6 ± 4.34 μmol). The good performance of this electrode was attributed to the surface control of oxygen vacancies and defects of the photoanodes, which was important for the photogeneration of electron-hole pairs and charge transfer.

The same electrode of WO_3 was applied by Longobucco et al. for CBZ degradation. After 5 h irradiation, the thin films achieve degradation of about 40–60% of CBZ. The advantage of this material was that in the WO_3 driven photo-electrocatalytic process, no intermediate having $m/z = 180$ was observed, therefore the process significantly reduces the possibility of formation of toxic products of CBZ, in particular, acridine. Also, the process was evaluated under more real conditions using two different concentrations of sodium sulfate and in the presence of perchlorate in natural waters or domestic wastewaters and a good response was obtained [93].

The application of thermally prepared Sb-doped Sn80%-W20%-oxide thin film electrodes for the CBZ photoelectrocatalytic and photocatalytic degradation was evaluated in the study of Ghasemian et al. [96]. In this work, the lower overall toxicity of the final solution treated by the photoelectrocatalytic method was also observed. This electrode showed a low energy consumption, a decrease in the initial concentration of CBZ by 80% using a current of 10 mA cm^{-2}, and a decrease in the concentration of toxic intermediates at about 60 min indicating excellent performance.

Other possibilities of application of electrodes of TiO_2 and TiO_2/WO_3, when it comes to photoelectrodegradation of drugs, its related to hormones. To remediate 17-alpha-ethinylestradiol (EE2), which is the active component of most oral contraceptives, an electrode of TiO_2/WO_3 electrode was used and resulted in 45% degradation of EE2 after 4 h compared with the result of 35% when using TiO_2 electrode. Higher performance was achieved under solar irradiation when an electrochemically heterogeneous photocatalysis (EHP) system was employed and the photoelectrodes were biased at + 0.7 V. Thus, the EE2 removal corresponded to 48% and 54% for the TiO_2 and TiO_2/WO_3, respectively [97].

Costa et al. developed WO_3 electrodes functionalized with Ag and Pt nanoparticles to evaluate the performance in photoelectrochemical degradation of this hormone. The WO_3 films surface was modified with a silver (Ag^0) or platinum (Pt^0) and applied and the degradation of progesterone by photo (HP) and photoelectrocatalysis (EHP) with an initial concentration of 0.35 mg L^{-1} in a 0.1 mol L^{-1} Na_2SO_4 electrolyte. For photoelectrochemical assays, the photoelectrodes were polarized in + 0.7 V vs Ag/AgCl. In HP configuration pure and Ag or Pt-modified WO_3 electrodes exhibited an increase in degradation efficiency of 6.4%, 6.8%, and 7.0%, respectively. However, for the EHP configuration, the WO_3, Ag/WO_3, and Pt/WO_3 photocatalysts degradation occurred more efficiently with results of 21.6%, 22.6%, and 26.7%, respectively, indicating that the nanoparticles improved progesterone degradation, even though, the authors report the stability of the electrodes, which five times were used with low photocurrent loss.

For this study, the authors report that the functionalization with metallic NPs accelerates the electron transport and increases the separation of the electrons and photogenerated holes, thus, reducing the recombination time of the e^- /h^+ pair. Also, the highest photocatalytic activity was obtained for the WO_3 electrode functionalized with Pt NPs. Another interesting point of this article is related to the stability of the electrodes. With NPs electrodes, they could be used five times with less photocurrent loss and greater hormone photooxidation [98]. Nevertheless, the intermediates formed were not assessed, so it is not possible to say whether progesterone degradation involved the mineralization of part of the hormone or not.

Another important class identified within the environmental issue as emerging contaminants is the endocrine disruptors (EDCs). These compounds can mimic hormones and so disrupt the regulation of human endocrine functions. Bisphenol A (BPA) is an endocrine disruptor widely used in industry and has been identified as a recurrent contaminant in effluents and bodies of water. Studies indicate that BPA disturbs the hormonal system, causes reproductive abnormalities, birth defects, infertility, and breast cancer [99]. Therefore, photoelectrocatalysis, as previously mentioned as an important technique for the degradation of these contaminants, has been applied in the degradation of BPA with high removal values. Importantly, most articles refer to the use of $BiVO_4$ for use in the photoelectrodegradation of BPA.

In this context, Goulart and coauthors describe the fabrication of a WO_3 electrode doped with Cu, deposited in FTO by drop-casting from a suspension of $[(NH_4)_{10}H_2(W_2O_7)_6]$ and $CuSO_4{\cdot}5\ H_2O$, and prepared by a modified sol-gel method applied to degradation photoelectrocatalytic of BPA under visible light radiation and the aid of H_2O_2 as an oxidizing agent. The PEC test with the Cu-WO_3 electrode was performed under optimized conditions in which a solution of 200 mL of BPA with 60 ppm in 0.5 mol L^{-1} Na_2SO_4 pH 8 and 10 mmol L^{-1} H_2O_2 had an 80% degradation efficiency in 8 h with a current density of 10 mA cm^{-2} under irradiation with a Metal Vapor lamp (HQI-TS Osram, 150 C).

The monitoring of the BPA oxidation was carried out by an electrochemical method (cyclic voltammetry), demonstrated to be efficient in the determination of the oxidation potential and the identification of the reaction intermediates from a glassy carbon electrode, modified with nickel oxide nanoparticles and nickel nanotubes carbon (NiO/MWCNT/GCE). For this experiment was a 75% BPA mineralization after the degradation test by TOC, confirming the good performance of the Cu-WO_3 electrode and the applied degradation method [100].

There have been other studies published on the degradation of BPA by PEC using BiVO4 electrodes. A $BiVO_4$ photoanode was applied in a

photoelectrocatalytic system with the introduction of peroxymonosulfate (PMS) to enhance the oxidation of BPA. The PMS solution helps to a better separation of charges in the medium from the presence of $SO_4^{\bullet-}$ radicals, which together with •OH radicals promote higher oxidation of organic compounds in the medium [101].

The PEC study was carried out in a plate and frame electrolytic cell reactor, divided into two chambers by a proton exchange membrane with 100 mL of BPA ($C_0 = 10$ mg L^{-1}) in sodium perchlorate as a supporting electrolyte. BPA degradation occurred with the application of + 0.25 V vs. SCE under irradiation from a 300 W Xe lamp with a 420 nm cut-off filter. The addition of 5 mM PMS to anode chamber with $BiVO_4$ film resulted in 100% BPA degradation in 2 h with ca. 65.8% TOC removal. Sulfate radicals generated from PMS were identified as a dominant active species in the control of the BPA oxidation reaction, making the degradation process even more efficient [101].

Another report has been described in the literature applying $BiVO_4$ films using PMS to improve the BPA oxidation reaction. Bacha et al. describe a Co-$BiVO_4$ electrode with an active area of 3 cm^2 applied for efficient activation of peroxymonosulfate (PMS) and used later for degradation of BPA. In this study, the photoelectrocatalytic degradation conditions were optimized to 50 mL of a 20 ppm BPA solution with pH 7, the addition of PMS the 2 mM, and application of a 1.2 V polarization potential under simulated visible irradiation with a 300 W Xe lamp with a light intensity of 100 mW cm^{-2}. In this process, Co-$BiVO_4$ film and a Pt-wire in a Teflon socket (length = 70 mm with platinum purity 99.99%) were used as a working electrode and counter electrode, respectively. The PEC process together with the synthesis conditions applied in the study promoted the total degradation of BPA in 1 h, having achieved the removal of TOC from ca. 59% [102].

A nanoporous MoS_2 @$BiVO_4$ photoanode was applied by Zheng et al. for enhanced degradation of bisphenol-A by photoelectrocatalysis. MoS_2 cocatalyst was added to the $BiVO_4$ film surface by the chemical bath to achieve recombination suppression and increase charge transfer capability. The authors reported that the synthesized MoS_2 @$BiVO_4$ composite was capable of fully degrading by photoelectrocatalysis a 250 mL solution of 10 ppm BPA in 100 mM NaCl (support electrolyte) with the application of + 1.5 V vs. Ag/AgCl in 75 min under irradiation. The degradation rate constants of BPA in the photoelectrocatalytic system increased to 0.0512 min^{-1}, which was 10.2 times of photocatalytic treatment and 6.2 times of electrocatalytic treatment, respectively. The superior photoelectrocatalytic activity of MoS_2 @$BiVO_4$ photoanodes was mainly attributed to the reduced recombination of photogenerated charge carriers [103].

Cong and coauthors have also developed an electrode based on MoS_2 and $BiVO_4$, synthesizing a new electrochemically modified thin-film electrode $BiVO_4$-MoS_2-Co_3O_4 obtained by hydrothermal methods, electrodeposition, and calcination. PEC degradation of 50 mL of a 10 mg L^{-1} BPA solution in 0.2 mol L^{-1} Na_2SO_4 and pH of 6.3 was performed on a two-electrode system. $BiVO_4$-MoS_2-Co_3O_4 film prepared with an active area of 4 cm^2 was used as the anode and a titanium plate was used as the cathode, at an applied potential of 3.5 V under visible irradiation with a xenon lamp.

The authors reported that the degradation efficiency of $BiVO_4$-MoS_2-Co_3O_4 for the BPA pollutant was 81.56% by photoelectrochemical process and the TOC removal rate achieved was 61.5% under the conditions applied for BPA removal, which indicates the high BPA mineralization. The $BiVO_4$-MoS_2-Co_3O_4 film exhibited good stability and improved performance in PEC degradation due to the synergistic effects of reduced interfacial charge transfer resistance, the formation of oxygen vacancies, and greater separation efficiency of e^-/h^+ pairs photogenerated [104].

Zheng et al. produced a nanoporous MoS_2 @$BiVO_4$ for photoelectrocatalytic degradation of BPA under visible light illumination and 14 intermediates were detected and identified during photoelectrocatalytic degradation. The authors observed that that applying 1.5 V vs. Ag/AgCl in 75 min BPA can be completely removed in the presence of 0.1 mM of NaCl and 10 ppm of that BPA. The film exhibited high stability and reusability at 5 consecutives tests [103].

Like BPA, tetrabromobisphenol A (TBBPA) can be considered a widely-concerned emerging pollutant with industrial application, such as the manufacturing of thermoplastics, insulated wires, textiles. The tip-decorated ZnO/Bi_2S_3 thin films were used successfully at photoelectrochemical TBBPA degradation under full light spectrum irradiation. During degradation 11 intermediates were identified by UPLC–MS analysis and 71.9% of the TBBPA (10 mg L^{-1}) can be degraded in 30 min. The authors concluded that well-aligned band-structures and the strong interaction in the intimate interface between ZnO and Bi_2S_3 accelerate charge separation, which results in excellent photocatalytic activity [105].

3. Pharmaceutical products in the environment: actions and challenges

Chemicals considered emerging have not been elucidated as to the effects on the ecosystem, and are without established monitoring programs in water systems, whether for drinking water or effluents (industrial, domestic, or hospital). Therefore, our contribution in this review paper is meant to increase public discussion and emphasize the need for public agencies to monitor and encourage the development of technologies for the degradation of emerging contaminants, in particular, pharmaceutical products.

In this context, it is inevitable to ask what the perspectives and contributions of the area of photoelectrocatalysis for the degradation of pharmaceutical products are. This brief analysis reveals that the field of photoelectrocatalysis still presents challenges that must be addressed not only to increase the number of scientific publications but also to reach a broad audience of civil society to minimize the potential harm that these compounds can cause.

Furthermore, it's crucial to emphasize that the release of these products into the environment, especially in the case of pharmaceuticals, from incorrect disposal of expired, unused drugs and human excreta in domestic and hospital sewage, can increase the problems associated with environmental toxicity. Fig. 9 shows our critical analysis of the actions needed to improve this area and provide adequate drinking water conditions for society.

Before evaluating the challenges of applying photoelectrochemical technology in the degradation of drugs, we must mention that adequate public and private policies are necessary to reduce or eliminate the risks that today's society lives due to invisible chemical substances that are present in water resources. Such policies arise from the collaborative efforts of government power, public and private organizations (such as hospitals and pharmaceutical manufacturing industries), and science. In the context of drug degradation, we can cite the importance of the following areas of study:

- *Studies on ecotoxicity, bioaccumulation, and biomagnification:* assessment of the effects of chemical substances on human health and communities of organisms are extremely relevant and important. Also, the potential for bioaccumulation and biomagnification as well as the transport and destination of different species in different ecosystems, and degradation processes related to environmental matrices, natural, and biological systems. In addition to substances already on the market, new pharmaceutical products are released every year that may harm the environment, including not only the final products but also their metabolites and raw materials used in the manufacturing process.
- *Monitoring in drinking water and domestic, industrial, and hospital effluents:* the development of analytical methods for analysis and sample preparation are necessary to assess the presence and quantity of drugs and their metabolites in the environment. In this case, the detection of lower concentration and the analysis of complex matrices, are the two big challenges. However, several studies in the

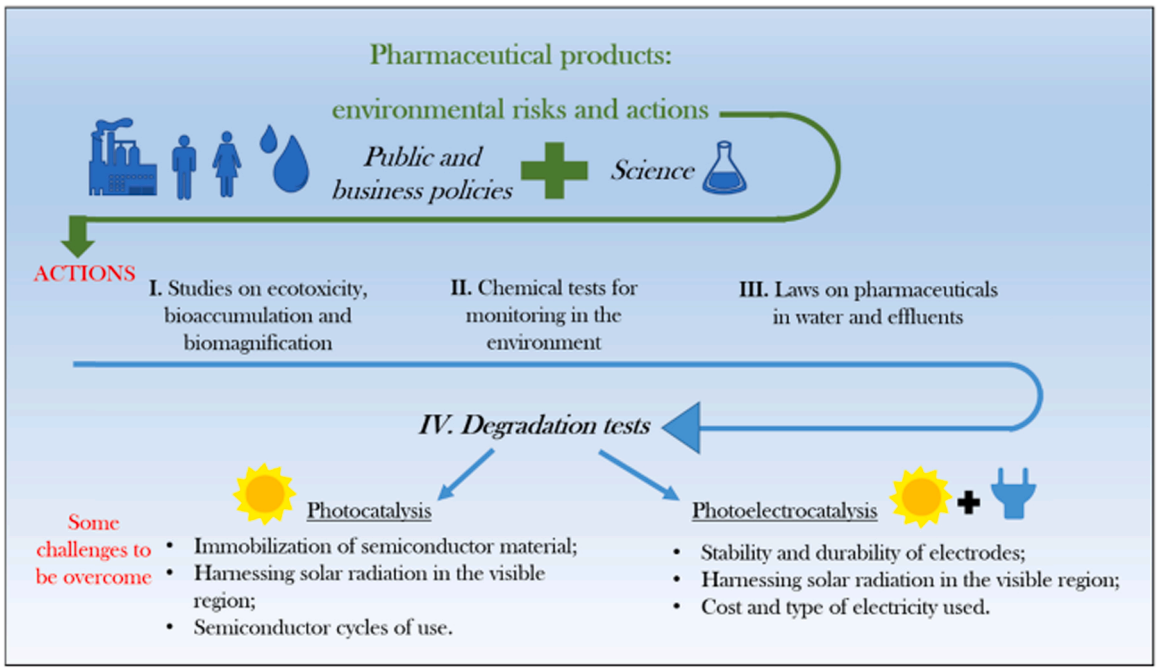

Fig. 9. Schematic representation of actions and challenges on pharmaceutical products in the environment.

world literature point out advances in this case (some data from WoS), especially for drug detection in rivers and waters before and after treatment.

With this information and the government's involvement, it is possible to have improvements to legislation and inspections to identify persistent pharmaceutical compounds. A quick review of Brazilian legislation and UN and EPA-US recommendations are shown in Table 3.

As expressed in this Table, Brazilian legislation recommends parameters, skills, and responsibilities regarding the treatment of water and effluents. However, maximum concentrations of pharmaceutical products in both water and effluents (industrial or domestic), are not directly established. UNESCO International Initiative on Water Quality already refers to the so-called emerging contaminants (pharmaceuticals are included) as well as the need to monitor them to guarantee drinking water for society. In the case of the EPA-US Guide for effluents, we see a global and important reference for evaluating new chemical substances introduced every year and their potential to cause risks to the environment and public health.

4. Challenges and trends of photoelectrochemical degradation

In recent years, numerous studies using photoelectrocatalytic (PEC) technology for addressing environmental remediation and energy crisis

Table 3
Brief assessment of legislation or recommendations for water and effluent treatments by different agencies at national and international levels.

Country/ Regulatory Authority	Type	General description	Any specific mention of pharmaceutical products?	Ref.
Brazil/ Ministério do Meio Ambiente Conselho Nacional do MeioAmbiente (CONAMA). Resoluç ão No.430/2011	Effluent	- Provides for the conditions and standards for the release of effluents (industrial and domestic); - Effluents from any polluting source can only be discharged directly into the receiving body as long as they comply with the conditions and standards provided; - - Those responsible for polluting sources of water resources must carry out self-monitoring to control and periodically monitor the effluents released into the receiving bodies, based on a representative sampling thereof.	No	[106]
Brazil/ Portaria GM/MS n. 888; 2021	Drinking Water	- Provides for the quality control and surveillance procedures of the water for human consumption and its drinking standard; - Nominate the skills and responsibilities to promote clean water for society; - Establishes the physical-chemical parameters of drinking water; - - Sets maximum limits for metal ions, pesticides, cyanobacteria, and other organic chemicals that pose a health risk.	No	[107]
Global/ International Initiative on Water Quality- UNESCO	Water and wastewater	- Describes the global challenge regarding the right to safe drinking water and adequate wastewater treatment; - The initiative raises awareness of emerging pollutants, such as pesticides, pharmaceuticals, personal care products, industrial waste, among others that are not normally monitored and that can affect the ecosystem.	Yes	[108]
US/ EPA, Preliminary Effluent Guidelines Program Plan 15–2021	Effluent	- Preliminary plans describe the EPA's annual review of effluent guidelines and pretreatment standards. - - Preliminary plans identify new or existing industrial categories selected for effluent guidelines or pretreatment standards rulemakings and provide a schedule for such rulemakings.	Yes	[109]

have been reported, such as water splitting [110], fuel production [111], and organic molecules degradation [112]. A great advantage of using PEC on the organic pollutant's degradation, in wastewaters, is the fact that different semiconductor materials, electrolytes, pH's, and cell configurations can be used.

Furthermore, the oxidant species, which are formed directly in the photoanodes and indirectly by the electrochemical process combined with light irradiation, lead to efficient degradation of organic compounds, resulting in their complete mineralization. Another advantage of PEC devices is that they are clean, low-cost, and environment-friendly, as well as being versatile, durable, reliable, and robust. They also operate under mild conditions and ambient temperature/pressure, as well as using less land space because of compact reactors.

Recently the coupling of pollutants degradation and power generation by photocatalytic fuel cells (PFC) has been discussed with promising results [113,114]. In PFC two processes occur simultaneously, that is the reduction of water or CO_2 in photocathode and photocatalytic oxidation of organic wastes in photoanode. This system presents double environmental benefits: waste material can be consumed, and solar radiation can be converted into useful forms of energy, such as electricity, hydrogen, or fuels.

Despite all the advantages, there are some challenges and key factors for advancing the practical large-scale implementation of PEC devices for drug degradation. Special attention must be given to the different kinds of photocatalysts employed and preparation methods of materials. It is necessary to choose the appropriate material so that the holes generated in the valence band are present an adequate potential so that they can oxidize the molecule of interest or generate oxidizing species. In addition, it is recommended that the material absorbs into the visible spectrum so that it can better utilize solar energy, be durable, not suffer from photocorrosion, be abundant, non-toxic, and inexpensive. Table 4 shows a summary of the main challenges and trends in the photoelectrochemical degradation process of pharmaceuticals.

In this context, the short-term durability of a PEC device depends fundamentally on the semiconductor material and its interface with the electrolyte, so the architecture and operating conditions of devices are also important factors. The degradation process can be impacted by irradiation intensity, electrolyte, analyte concentration, and current density. Also, the understanding of the reaction mechanisms about their photoactivities is of fundamental importance for rational design of high-performing photoactive materials. Thus, all these parameters and experimental conditions may serve as a general guideline for the fabrication of good photoelectrocatalyst toward drug degradation and sustainable solar fuel generation.

Lastly, in order for PEC approaches and devices to be considered a viable alternative for the removal of contaminants, they must satisfy four requirements: they must be (*i*) effective, (*ii*) affordable, (*iii*) consistent and (*iv*) durable. In order to implement PEC in a real scenario, many more research efforts are required and proper selections of pH, nature of the electrolyte, photo-anode, cathode, and reactor design are crucial.

Table 4
Summary of necessary advances in photoelectrochemical degradation of pharmaceuticals products.

Challenges	Trends
Reuse of electrodes for multiple cycles	*Combined systems involving energy*
Use of sunlight	*Application of nanotechnology for materials development*
Affordable cost (materials and systems)	*Sustainability concept applied in the development of materials*
Ecotoxicity tests	
Identification of degradation intermediates and by-products	
Use of flow reactors	
Pilot-scale application	
Degradation of concentrations of compounds close to those detected in rivers	

5. Conclusion

The development of efficient and low-cost technologies for the degradation of organic pollutants, especially pharmaceutical products, is extremely relevant and urgent. Pharmaceutical compounds can be found in water resources as well as their metabolites and, due to their chemical complexity, they are not easily degraded by conventional water or sewage treatments. In addition, the concern of the scientific society is related to the toxic effects that these can offer to living beings, as well as the increase in bacterial resistance.

In this sense, several studies point to the development of semiconductor materials and photoelectrochemical degradation systems for pharmaceutical products, in particular antibiotics, anti-inflammatory drugs and analgesics. These studies are still significantly reduced in number when compared to articles published in recent years in the field of photocatalysis for degradation of the same compounds. The evolution in the field of materials sciences is quite clear since the increase in the degradation efficiency and durability of the electrode material are among the main objectives of the studies.

Semiconductors in their pure form have several limitations, in particular, the recombination of electron-hole pairs and the photocorrosion process. However, interesting strategies have been employed, such as: formation of heterojunctions, use of metallic nanoparticles and QDs, cocatalysts, and association of carbonaceous materials. Another interesting point is that the technologies are far from applications in real systems or on a pilot scale. Because the matrix used for testing is still only electrolyte, or, in rare cases, a fortified matrix. Furthermore, the experiments are carried out with small volumes of solution ($\leq$ 100 mL) in simple reactors that do not present studies as a function of the temperature of the system. As a light source, lamps are used to mimic sunlight, and electrode durability is often not reported.

Our view is therefore that this area is extremely relevant in the current context where the provision of clean drinking water and sanitation for the entire population is essential. For photoelectrocatalysis to become a reality, it still requires investment, particularly in consideration of recalcitrant molecules and the development of reactor architectures that enable efficient degradation, with high electrode durability and especially low cost, so that it is accessible to all, in particular to those communities who are socioeconomically vulnerable. Furthermore, systems that can generate hydrogen at the same time must be considered as a new possibility in the field of clean energy.

Among the different systems reported, there are large differences in the percentage of mineralization (when informed by the authors), in the intermediates detected, and the time needed to achieve significant degradation. The comparison between these systems is not simple considering the experimental conditions used in each case vary a lot, such as cell configuration, electrode type and morphology, lighting system, application of fixed potential or current, etc. However, comparing HP and EHP systems, it can be concluded that the latter system has better degradation time and a lower formation of intermediate products.

Although these studies are certainly already a good indication of the possibility of using these systems in the degradation of these recalcitrant compounds, it is difficult to assess whether the PEC process will prove equally efficient for more complex matrices based on the literature discussed has shown very little analysis on matrices in real conditions.

CRediT authorship contribution statement

Roberta Yonara Nascimento Reis: Conceptualization, Investigation, Validation, Visualization, Writing – original draft, Writing – review & editing. **Lorena Athie Goulart:** Conceptualization, Investigation, Validation, Visualization, Writing – original draft, Writing – review & editing. **Lucia Helena:** Conceptualization, Investigation, Validation,

Visualization, Writing – original draft, Writing – review & editing. **Suellen Aparecida Alves:** Conceptualization, Investigation, Validation, Visualization, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

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

Acknowledgements

Financial support by Brazilian research funding agencies is gratefully acknowledged: São Paulo Research Foundation (FAPESP, grant #2018/16401-8, #2013/07296-2 and FAPESP/SHELL #2017/11986-15). Shell and the strategic importance of the support given by ANP (Brazil's National Oil, Natural Gas and Biofuels Agency) through the R&D levy regulation.Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brazil (CAPES) - Finance Code 001 and Conselho Nacional de Pesquisa e Desenvolvimento (CNPq).

References

[1] A. Das, R. Ahmed, S. Akhtar, K. Begum, S. Banu, An overview of basic molecular biology of SARS-CoV-2 and current COVID-19 prevention strategies, Gene Rep. 23 (2021), 101122, https://doi.org/10.1016/j.genrep.2021.101122.
[2] N. Upmanyu, V.N. Malviya, Antibiotics: mechanisms of action and modern challenges, INC (2020), https://doi.org/10.1016/b978-0-12-819001-2.00018-8.
[3] H.J. Hijma, G.J. Groeneveld, Analgesic drug development: proof-of-mechanism and proof-of-concept in early phase clinical studies, Med. Drug Discov. 10 (2021), 100083, https://doi.org/10.1016/j.medidd.2021.100083.
[4] M.A. Sousa, C. Gonçalves, E. Cunha, J. Hajšlová, M.F. Alpendurada, Cleanup strategies and advantages in the determination of several therapeutic classes of pharmaceuticals in wastewater samples by SPE-LC-MS/MS, Anal. Bioanal. Chem. 399 (2011) 807–822, https://doi.org/10.1007/s00216-010-4297-0.
[5] S. Gaw, K.V. Thomas, T.H. Hutchinson, Sources, impacts and trends of pharmaceuticals in the marine and coastal environment, Philos. Trans. R. Soc. B Biol. Sci. 369 (2014), https://doi.org/10.1098/rstb.2013.0572.
[6] T.M. Uddin, A.J. Chakraborty, A. Khusro, B.R.M. Zidan, S. Mitra, T. Bin Emran, K. Dhama, M.K.H. Ripon, M. Gajdács, M.U.K. Sahibzada, M.J. Hossain, N. Koirala, Antibiotic resistance in microbes: history, mechanisms, therapeutic strategies and future prospects, J. Infect. Public Health 14 (2021) 1750–1766, https://doi.org/10.1016/j.jiph.2021.10.020.
[7] M. de Oliveira Klein, S.V. Serrano, Á. Santos-Neto, C. da Cruz, I.A. Brunetti, D. Lebre, M.P. Gimenez, R.M. Reis, H.C.S. Silveira, Detection of anti-cancer drugs and metabolites in the effluents from a large Brazilian cancer hospital and an evaluation of ecotoxicology, Environ. Pollut. 268 (2021), https://doi.org/10.1016/j.envpol.2020.115857.
[8] G. Divyapriya, S. Singh, C.A. Martínez-Huitle, J. Scaria, A.V. Karim, P. V. Nidheesh, Treatment of real wastewater by photoelectrochemical methods: an overview, Chemosphere 276 (2021), 130188, https://doi.org/10.1016/j.chemosphere.2021.130188.
[9] D. Mijin, M. Savić, P. Snežana, A. Smiljanić, O. Glavaški, M. Jovanović, S. Petrović, A study of the photocatalytic degradation of metamitron in ZnO water suspensions, Desalination 249 (2009) 286–292, https://doi.org/10.1016/j.desal.2008.10.030.
[10] C.B. Ong, L.Y. Ng, A.W. Mohammad, A review of ZnO nanoparticles as solar photocatalysts: synthesis, mechanisms and applications, Renew. Sustain. Energy Rev. 81 (2018) 536–551, https://doi.org/10.1016/j.rser.2017.08.020.
[11] R.N. Padovan, L.S. de Carvalho, P.L. de Souza Bergo, C. Xavier, A. Leitão, Á.J. dos Santos Neto, F.M. Lanças, E.B. Azevedo, Degradation of hormones in tap water by heterogeneous solar TiO2-photocatalysis: optimization, degradation products identification, and estrogenic activity removal, J. Environ. Chem. Eng. 9 (2021), https://doi.org/10.1016/j.jece.2021.106442.
[12] P. Alulema-Pullupaxi, P.J. Espinoza-Montero, C. Sigcha-Pallo, R. Vargas, L. Fernández, J.M. Peralta-Hernández, J.L. Paz, Fundamentals and applications of photoelectrocatalysis as an efficient process to remove pollutants from water: a review, Chemosphere 281 (2021), https://doi.org/10.1016/j.chemosphere.2021.130821.
[13] N. Philippidis, S. Sotiropoulos, A. Efstathiou, I. Poulios, Photoelectrocatalytic degradation of the insecticide imidacloprid using TiO2/Ti electrodes, J. Photochem. Photobiol. A Chem. 204 (2009) 129–136, https://doi.org/10.1016/j.jphotochem.2009.03.007.
[14] D.M. De Araújo, S. Cotillas, C. Sáez, P. Cañizares, C.A. Martínez-Huitle, M. A. Rodrigo, Activation by light irradiation of oxidants electrochemically generated during Rhodamine B elimination, J. Electroanal. Chem. 757 (2015) 144–149, https://doi.org/10.1016/j.jelechem.2015.09.025.
[15] H. Rubí-Juárez, S. Cotillas, C. Sáez, P. Cañizares, C. Barrera-Díaz, M.A. Rodrigo, Use of conductive diamond photo-electrochemical oxidation for the removal of pesticide glyphosate, Sep. Purif. Technol. 167 (2016) 127–135, https://doi.org/10.1016/j.seppur.2016.04.048.
[16] N.A. Khan, S. Ahmed, I.H. Farooqi, I. Ali, V. Vambol, F. Changani, M. Yousefi, S. Vambol, S.U. Khan, A.H. Khan, Occurrence, sources and conventional treatment techniques for various antibiotics present in hospital wastewaters: a critical review, TrAC - Trends Anal. Chem. 129 (2020), https://doi.org/10.1016/j.trac.2020.115921.
[17] L.R.D. Brito, S.O. Ganiyu, E.V. dos Santos, M.A. Oturan, C.A. Martínez-Huitle, Removal of antibiotic rifampicin from aqueous media by advanced electrochemical oxidation: role of electrode materials, electrolytes and real water matrices, Electrochim. Acta 396 (2021), 139254, https://doi.org/10.1016/j.electacta.2021.139254.
[18] Y. Li, X. Sun, Y. Tang, Y.H. Ng, L. Li, F. Jiang, J. Wang, W. Chen, L. Li, Understanding photoelectrocatalytic degradation of tetracycline over three-dimensional coral-like ZnO/BiVO4 nanocomposite, Mater. Chem. Phys. 271 (2021), 124871, https://doi.org/10.1016/j.matchemphys.2021.124871.
[19] X. Zhang, G. Wang, W. Zhang, Y. Wei, B. Fang, Fixure-reduce method for the synthesis of Cu2O/MWCNTs nanocomposites and its application as enzyme-free glucose sensor, Biosens. Bioelectron. 24 (2009) 3395–3398, https://doi.org/10.1016/j.bios.2009.04.031.
[20] B. Subash, B. Krishnakumar, M. Swaminathan, M. Shanthi, Highly Effic., Sol. Act. reusable Photocatal., Zr loaded Ag. -ZnO React. Red. 120 Dye Degrad. Synerg. Eff. Dye sensitized Mech. Highly Effic., Sol. Act. reusable Photocatal., Zr loaded Ag. -ZnO React. (2012), https://doi.org/10.1021/la303842c.
[21] M.G. Peleyeju, O.A. Arotiba, Recent trend in visible-light photoelectrocatalytic systems for degradation of organic contaminants in water/wastewater, Environ. Sci. Water Res. Technol. (2018) 1–45, https://doi.org/10.1039/C8EW00276B.
[22] Y. Liu, Y. Ao, C. Wang, P. Wang, Enhanced photoelectrocatalytic performance of TiO2 nanorod array under visible light irradiation: Synergistic effect of doping, heterojunction construction and cocatalyst deposition, Inorg. Chem. Commun. 108 (2019), 107521, https://doi.org/10.1016/j.inoche.2019.107521.
[23] J. Xue, S. Li, D. Lei, Q. Bi, C. Tang, N. Xu, Multi-component Zn2SnO4/MoS2/Ag/AgCl for enhancing solar-driven photoelectrocatalytic activity, Appl. Surf. Sci. 544 (2021), 148922, https://doi.org/10.1016/j.apsusc.2020.148922.
[24] J. Li, S. Lv, Y. Liu, J. Bai, B. Zhou, X. Hu, Photoeletrocatalytic activity of an n-ZnO/p-Cu2O/n-TNA ternary heterojunction electrode for tetracycline degradation, J. Hazard. Mater. 262 (2013) 482–488, https://doi.org/10.1016/j.jhazmat.2013.09.002.
[25] K. Huang, C. Li, X. Zhang, X. Meng, L. Wang, W. Wang, Z. Li, TiO2 nanorod arrays decorated by nitrogen-doped carbon and g-C3N4 with enhanced photoelectrocatalytic activity, Appl. Surf. Sci. 518 (2020), 146219, https://doi.org/10.1016/j.apsusc.2020.146219.
[26] M. Zhang, J. Wang, Y. Wang, J. Zhang, X. Han, Y. Chen, Y. Wang, Z. Karim, W. Hu, Y. Deng, Promoting the charge separation and photoelectrocatalytic water reduction kinetics of Cu2O nanowires via decorating dual-cocatalysts, J. Mater. Sci. Technol. 62 (2021) 119–127, https://doi.org/10.1016/j.jmst.2020.05.068.
[27] M. Mikulic, Mikulic, M. Statistics & Facts, Global Pharmaceutical, Industry; Statista: Hamburg, Germany, 2020, 2020. ⟨https://www.statista.com/topics/1764/global-pharmaceutical-industry/#editorialPicks⟩.
[28] O.I. González Peña, M.Á. López Zavala, H. Cabral Ruelas, Pharmaceuticals market, consumption trends and disease incidence are not driving the pharmaceutical research on water and wastewater, Int. J. Environ. Res. Public Health 18 (2021) 1–37, https://doi.org/10.3390/ijerph18052532.
[29] E. implementation WHO report on Surveillance of Antibiotic Consumption, WHO Report on Surveillance of Antibiotic Consumption, 2018. ⟨http://apps.who.int/iris%0Ahttps://apps.who.int/iris/bitstream/handle/10665/277359/9789241514880-eng.pdf⟩.
[30] B. Böger, M. Surek, R. de, O. Vilhena, M.M. Fachi, A.M. Junkert, J.M. Santos, E. L. Domingos, A. de, F. Cobre, D.R. Momade, R. Pontarolo, Occurrence of antibiotics and antibiotic resistant bacteria in subtropical urban rivers in Brazil, J. Hazard. Mater. 402 (2021), 123448, https://doi.org/10.1016/j.jhazmat.2020.123448.
[31] N.A. Khan, V. Vambol, S. Vambol, B. Bolibrukh, M. Sillanpaa, F. Changani, A. Esrafili, M. Yousefi, Hospital effluent guidelines and legislation scenario around the globe: a critical review, J. Environ. Chem. Eng. 9 (2021), 105874, https://doi.org/10.1016/j.jece.2021.105874.
[32] K. Bush, P.A. Bradford, b -Lactams and b -Lactamase Inhibitors: An Overview, 2016).
[33] Q. Ma, H. Zhang, R. Guo, B. Li, X. Zhang, X. Cheng, M. Xie, Q. Cheng, Construction of CuS/TiO2 nano-tube arrays photoelectrode and its enhanced visible light photoelectrocatalytic decomposition and mechanism of penicillin G, Electrochim. Acta 283 (2018) 1154–1162, https://doi.org/10.1016/j.electacta.2018.07.026.
[34] Z. Zheng, X. Li, L. Li, Y. Tang, Photoelectrocatalytic degradation of amoxicillin over quaternary ZnO/ZnSe/CdSe/MoS2 hierarchical nanorods, Int. J. Hydrog. Energy 44 (2019) 20826–20838, https://doi.org/10.1016/j.ijhydene.2018.06.150.
[35] A.P. Nath, A. Balasubramanian, K. Ramalingam, Cephalosporins: an imperative antibiotic over the generations, Int. J. Res. Pharm. Sci. 11 (2020) 623–629, https://doi.org/10.26452/ijrps.v11i1.1866.
[36] V.V. Kondalkar, R.M. Mane, P.B. Dandge, S. Choudhury, C.K. Hong, P.S. Patil, S. R. Patil, J.H. Kim, P.N. Bhosale, Photo Cefotaxime Using Nanostruct. TiO 2 Photo: Identi fi cation Degrad. Prod. Determ. Toxic. Lev. (2014).
[37] T. Li, P. Zhang, H. He, Z. Wang, X. Tu, D.D. Dionysiou, Highly efficient photoelectrocatalytic degradation of cefotaxime sodium on the MoSe2/TiO2

nanotubes photoanode with abundant oxygen vacancies, J. Solid State Chem. 303 (2021), https://doi.org/10.1016/j.jssc.2021.122455.
[38] M. Sheydaei, B. Ayoubi-Feiz, G. Abbaszade-Fakhri, A visible-light active g-C3N4/Ce–ZnO/Ti nanocomposite for efficient photoelectrocatalytic pharmaceutical degradation: modelling with artificial neural network, Process Saf. Environ. Prot. 149 (2021) 776–785, https://doi.org/10.1016/j.psep.2021.03.037.
[39] L. Mandell, G. Tillotson, Safety of fluoroquinolones, update 13 (2002).
[40] H. Du, W. Pu, Y. Wang, K. Yan, J. Feng, J. Zhang, C. Yang, J. Gong, Synthesis of BiVO4/WO3 composite film for highly efficient visible light induced photoelectrocatalytic oxidation of norfloxacin, J. Alloy. Compd. 787 (2019) 284–294, https://doi.org/10.1016/j.jallcom.2019.01.390.
[41] T. Jiang, L. Cheng, Y. Han, J. Feng, J. Zhang, One-pot hydrothermal synthesis of Bi2O3-WO3 p-n heterojunction film for photoelectrocatalytic degradation of norfloxacin, Sep. Purif. Technol. 238 (2020), 116428, https://doi.org/10.1016/j.seppur.2019.116428.
[42] D. Cao, Y. Wang, M. Qiao, X. Zhao, Enhanced photoelectrocatalytic degradation of norfloxacin by an Ag3PO4/BiVO4 electrode with low bias, J. Catal. 360 (2018) 240–249, https://doi.org/10.1016/j.jcat.2018.01.017.
[43] M. Hosseini, A. Esrafili, M. Farzadkia, M. Kermani, M. Gholami, Degradation of ciprofloxacin antibiotic using photo-electrocatalyst process of Ni-doped ZnO deposited by RF sputtering on FTO as an anode electrode from aquatic environments: Synthesis, kinetics, and ecotoxicity study, Microchem. J. 154 (2020), 104663, https://doi.org/10.1016/j.microc.2020.104663.
[44] D. Wu, J. Li, J. Guan, C. Liu, X. Zhao, Z. Zhu, C. Ma, P. Huo, C. Li, Y. Yan, Improved photoelectric performance via fabricated heterojunction g-C3N4/TiO2/HNTs loaded photocatalysts for photodegradation of ciprofloxacin, J. Ind. Eng. Chem. 64 (2018) 206–218, https://doi.org/10.1016/j.jiec.2018.03.017.
[45] B.A. Koiki, B.O. Orimolade, B.N. Zwane, D. Nkosi, N. Mabuba, O.A. Arotiba, Cu2O on anodised TiO2 nanotube arrays: a heterojunction photoanode for visible light assisted electrochemical degradation of pharmaceuticals in water, Electrochim. Acta 340 (2020), 135944, https://doi.org/10.1016/j.electacta.2020.135944.
[46] X. Li, J. Wan, Y. Ma, Y. Wang, X. Li, Study on cobalt-phosphate (Co-Pi) modified BiVO4/Cu2O photoanode to significantly inhibit photochemical corrosion and improve the photoelectrochemical performance, Chem. Eng. J. 404 (2021), 127054, https://doi.org/10.1016/j.cej.2020.127054.
[47] B.O. Orimolade, B.N. Zwane, B.A. Koiki, L. Tshwenya, G.M. Peleyeju, N. Mabuba, M. Zhou, O.A. Arotiba, Solar photoelectrocatalytic degradation of ciprofloxacin at a FTO/BiVO4/MnO2 anode: kinetics, intermediate products and degradation pathway studies, J. Environ. Chem. Eng. 8 (2020), https://doi.org/10.1016/j.jece.2019.103607.
[48] M. Hosseini, A. Esrafili, M. Farzadkia, M. Kermani, M. Gholami, Application of Ni-doped ZnO deposited by RF magnetron sputtering technique on FTO as a photoanod in Photo-Electrocatalysis process of Ofloxacin degradation: synthesis, kinetics, and ecotoxicity study, Int. J. Environ. Anal. Chem. 0 (2020) 1–17, https://doi.org/10.1080/03067319.2020.1737038.
[49] Y. Tian, L. Cheng, J. Zhang, Fabrication of Co-doped ZnO photoanode by liquid phase deposition for photoelectrocatalytic degradation of ofloxacin under visible light, J. Electrochem. Soc. 165 (2018) H284–H290, https://doi.org/10.1149/2.1321805jes.
[50] V. Cristino, L. Pasti, N. Marchetti, S. Berardi, C.A. Bignozzi, A. Molinari, F. Passabi, S. Caramori, L. Amidani, M. Orlandi, N. Bazzanella, A. Piccioni, J. Kopula Kesavan, F. Boscherini, L. Pasquini, Photoelectrocatalytic degradation of emerging contaminants at WO3/BiVO4 photoanodes in aqueous solution, Photochem. Photobiol. Sci. 18 (2019) 2150–2163, https://doi.org/10.1039/c9pp00043g.
[51] V. Cristino, G. Longobucco, N. Marchetti, S. Caramori, C.A. Bignozzi, A. Martucci, A. Molinari, R. Boaretto, C. Stevanin, R. Argazzi, M. Dal Colle, R. Bertoncello, L. Pasti, Photoelectrochemical degradation of pharmaceuticals at β25 modified WO3 interfaces, Catal. Today 340 (2020) 302–310, https://doi.org/10.1016/j.cattod.2018.09.020.
[52] W. Teng, J. Xu, Y. Cui, J. Yu, Photoelectrocatalytic degradation of sulfadiazine by Ag3PO4/MoS2/TiO2 nanotube array electrode under visible light irradiation, J. Electroanal. Chem. 868 (2020), 114178, https://doi.org/10.1016/j.jelechem.2020.114178.
[53] M. Jia, Z. Yang, H. Xu, P. Song, W. Xiong, J. Cao, Y. Zhang, Y. Xiang, J. Hu, C. Zhou, Y. Yang, W. Wang, Integrating N and F co-doped TiO2 nanotubes with ZIF-8 as photoelectrode for enhanced photo-electrocatalytic degradation of sulfamethazine, Chem. Eng. J. 388 (2020), 124388, https://doi.org/10.1016/j.cej.2020.124388.
[54] M.G. Peleyeju, E.H. Umukoro, L. Tshwenya, R. Moutloali, J.O. Babalola, O. A. Arotiba, Photoelectrocatalytic water treatment systems: Degradation, kinetics and intermediate products studies of sulfamethoxazole on a TiO2-exfoliated graphite electrode, RSC Adv. 7 (2017) 40571–40580, https://doi.org/10.1039/c7ra07399b.
[55] B.A. Koiki, B.O. Orimolade, B.N. Zwane, O.V. Nkwachukwu, C. Muzenda, D. Nkosi, O.A. Arotiba, The application of FTO-Cu2O/Ag3PO4 heterojunction in the photoelectrochemical degradation of emerging pharmaceutical pollutant under visible light irradiation, Chemosphere 266 (2021), 129231, https://doi.org/10.1016/j.chemosphere.2020.129231.
[56] E.C. Pereira-Maia, P.P. Silva, W.B. de Almeida, H.F. dos Santos, B.L. Marcial, R. Ruggiero, W. Guerra, Tetraciclinas e glicilciclinas: uma visão geral, Quim. Nova. 33 (2010) 700–706, https://doi.org/10.1590/s0100-40422010000300038.
[57] W. Zhang, H. Chen, Q. Peng, X. Liu, L. Dian, W. Ye, Y. Chang, X. Ma, H. Wang, Controlled fabrication of WO3 nanoplate films and its photoelectrochemical properties, Mater. Res. Express 6 (2019), https://doi.org/10.1088/2053-1591/ab2cc3.
[58] H. Tang, Q. Shang, Y. Tang, X. Yi, Y. Wei, K. Yin, M. Liu, C. Liu, Static and continuous flow photoelectrocatalytic treatment of antibiotic wastewater over mesh of TiO2 nanotubes implanted with g-C3N4 nanosheets, J. Hazard. Mater. 384 (2020), 121248, https://doi.org/10.1016/j.jhazmat.2019.121248.
[59] K. Rabé, L. Liu, N.A. Nahyoon, Electricity generation in fuel cell with light and without light and decomposition of tetracycline hydrochloride using g-C3N4/Fe0 (1%)/TiO2 anode and WO3 cathode, Chemosphere 243 (2020), https://doi.org/10.1016/j.chemosphere.2019.125425.
[60] D. Liu, H. Li, R. Gao, Q. Zhao, Z. Yang, X. Gao, Z. Wang, F. Zhang, W. Wu, Enhanced visible light photoelectrocatalytic degradation of tetracycline hydrochloride by I and P co-doped TiO2 photoelectrode, J. Hazard. Mater. 406 (2021), 124309, https://doi.org/10.1016/j.jhazmat.2020.124309.
[61] J. Feng, L. Cheng, J. Zhang, O.K. Okoth, F. Chen, Preparation of BiVO4/ZnO composite film with enhanced visible-light photoelectrocatalytic activity, Ceram. Int. 44 (2018) 3672–3677, https://doi.org/10.1016/j.ceramint.2017.11.124.
[62] N.K.R. Eswar, S.A. Singh, G. Madras, Photoconductive network structured copper oxide for simultaneous photoelectrocatalytic degradation of antibiotic (tetracycline) and bacteria (E. coli), Chem. Eng. J. 332 (2018) 757–774, https://doi.org/10.1016/j.cej.2017.09.117.
[63] L. Cheng, Y. Tian, J. Zhang, Construction of p-n heterojunction film of Cu2O/α-Fe2O3 for efficiently photoelectrocatalytic degradation of oxytetracycline, J. Colloid Interface Sci. 526 (2018) 470–479, https://doi.org/10.1016/j.jcis.2018.04.106.
[64] K. Changanaqui, E. Brillas, H. Alarcón, I. Sirés, ZnO/TiO2/Ag2Se nanostructures as photoelectrocatalysts for the degradation of oxytetracycline in water, Electrochim. Acta 331 (2020), https://doi.org/10.1016/j.electacta.2019.135194.
[65] R. Daghrir, P. Drogui, N. Delegan, M.A.El Khakani, Electrochemical degradation of chlortetracycline using N-doped Ti/TiO2 photoanode under sunlight irradiations, Water Res. 47 (2013) 6801–6810, https://doi.org/10.1016/j.watres.2013.09.011.
[66] J. Wang, L. Jiang, F. Liu, M. Jia, M. Liu, J. Li, Y. Lai, Enhanced photoelectrochemical degradation of tetracycline hydrochloride with FeOOH and Au nanoparticles decorated WO3, Chem. Eng. J. 407 (2021), 127195, https://doi.org/10.1016/j.cej.2020.127195.
[67] L. Cheng, L. Liu, K. Yan, J. Zhang, Visible light-driven photoelectrocatalysis coupling with electroenzymatic process for degradation of chloramphenicol, Chem. Eng. J. 330 (2017) 1380–1389, https://doi.org/10.1016/j.cej.2017.07.170.
[68] R. Gupta, J.M. Modak, G. Madras, Behavioral analysis of simultaneous photo-electro-catalytic degradation of antibiotic resistant: E. coli and antibiotic via ZnO/CuI: A kinetic and mechanistic study, Nanoscale Adv. 1 (2019) 3992–4008, https://doi.org/10.1039/c9na00483a.
[69] H. He, T. Zhao, Q. Ma, X. Yang, Q. Yue, B. Huang, X. Pan, Photoelectrocatalytic coupling system synergistically removal of antibiotics and antibiotic resistant bacteria from aquatic environment, J. Hazard. Mater. 424 (2022), 127553, https://doi.org/10.1016/j.jhazmat.2021.127553.
[70] A. Chatzitakis, N.Karanasios Papaderakis, J. Georgieva, E. Pavlidou, G. Litsardakis, I. Poulios, S. Sotiropoulos, Comparison of the photoelectrochemical performance of particulate and nanotube TiO2 photoanodes, Catal. Today 280 (2017) 14–20, https://doi.org/10.1016/j.cattod.2016.07.017.
[71] X. Bai, L. Ma, Z. Dai, H. Shi, Electrochemical synthesis of p-Cu2O/n-TiO2 heterojunction electrode with enhanced photoelectrocatalytic activity, Mater. Sci. Semicond. Process. 74 (2018) 319–328, https://doi.org/10.1016/j.mssp.2017.10.049.
[72] Q. Chen, J. Bai, J. Li, K. Huang, X. Li, B. Zhou, W. Cai, Aerated visible-light responsive photocatalytic fuel cell for wastewater treatment with producing sustainable electricity in neutral solution, Chem. Eng. J. 252 (2014) 89–94, https://doi.org/10.1016/j.cej.2014.04.046.
[73] Y. Dai, S. Li, Y. Guo, J. Ren, L. Zhang, X. Wang, P. Zhang, X. Liu, Enhanced tetracycline degradation and power generation in a solar-illuminated bio-photoelectrochemical system, J. Power Sources 497 (2021), 229876, https://doi.org/10.1016/j.jpowsour.2021.229876.
[74] K. Rabé, L. Liu, N.A. Nahyoon, Y. Zhang, A.M. Idris, Visible-light photocatalytic fuel cell with Z-scheme g-C3N4/Fe0/TiO2 anode and WO3 cathode efficiently degrades berberine chloride and stably generates electricity, Sep. Purif. Technol. 212 (2019) 774–782, https://doi.org/10.1016/j.seppur.2018.11.089.
[75] B. Deng, S. Fu, Y. Zhang, Y. Wang, D. Ma, S. Dong, Simultaneous pollutant degradation and power generation in visible-light responsive photocatalytic fuel cell with an Ag-TiO2 loaded photoanode, Nano-Struct. Nano-Objects 15 (2018) 167–172, https://doi.org/10.1016/j.nanoso.2017.09.011.
[76] Q. Zeng, L. Lyu, Y. Gao, S. Chang, C. Hu, A self-sustaining monolithic photoelectrocatalytic/photovoltaic system based on a WO3/BiVO4 photoanode and Si PVC for efficiently producing clean energy from refractory organics degradation, Appl. Catal. B Environ. 238 (2018) 309–317, https://doi.org/10.1016/j.apcatb.2018.07.005.
[77] J. Liu, J. Li, Y. Li, J. Guo, S.M. Xu, R. Zhang, M. Shao, Photoelectrochemical water splitting coupled with degradation of organic pollutants enhanced by surface and interface engineering of BiVO4 photoanode, Appl. Catal. B Environ. 278 (2020), 119268, https://doi.org/10.1016/j.apcatb.2020.119268.
[78] K.G. Sandeep, Use and understanding of analgesics (painkillers) by Aston university students, Biosci. Horiz. 4 (2011) 72–78.

[79] A. Kaur, A. Umar, S.K. Kansal, Heterogeneous photocatalytic studies of analgesic and non-steroidal anti-inflammatory drugs, Appl. Catal. A Gen. 510 (2016) 134–155, https://doi.org/10.1016/j.apcata.2015.11.008.
[80] J. Rivera-Utrilla, M. Sánchez-Polo, M.Á. Ferro-García, G. Prados-Joya, R. Ocampo-Pérez, Pharmaceuticals as emerging contaminants and their removal from water. A review, Chemosphere 93 (2013) 1268–1287, https://doi.org/10.1016/j.chemosphere.2013.07.059.
[81] M. Daescu, M. Iota, C. Serbschi, A.C. Ion, M. Baibarac, The influence of uv light on photodegradation of acetylsalicylic acid, Int. J. Mol. Sci. 22 (2021), https://doi.org/10.3390/ijms22084046.
[82] G.Liu Gangwang, H. Liu, N. Zhang, Y. Wang, Photodegradation of salicylic acid in aquatic environment: effect of different forms of nitrogen, Sci. Total Environ. 435– 436 (2012) 573–577, https://doi.org/10.1016/j.scitotenv.2012.05.068.
[83] R.D. Suryavanshi, S.V. Mohite, A.A. Bagade, K.Y. Rajpure, Photoelectrocatalytic activity of spray deposited Fe2O3/ZnO photoelectrode for degradation of salicylic acid and methyl orange dye under solar radiation, Mater. Sci. Eng. B Solid-State Mater. Adv. Technol. 248 (2019), 114386, https://doi.org/10.1016/j.mseb.2019.114386.
[84] C. Calas-Blanchard, G. Istamboulié, M. Bontoux, G. Plantard, V. Goetz, T. Noguer, Biosensor-based real-time monitoring of paracetamol photocatalytic degradation, Chemosphere 131 (2015) 124–129, https://doi.org/10.1016/j.chemosphere.2015.03.019.
[85] C. Huber, B. Bartha, R. Harpaintner, P. Schröder, Metabolism of acetaminophen (paracetamol) in plants-two independent pathways result in the formation of a glutathione and a glucose conjugate, Environ. Sci. Pollut. Res. 16 (2009) 206–213, https://doi.org/10.1007/s11356-008-0095-z.
[86] A.A. Nada, B.O. Orimolade, H.H. El-Maghrabi, B.A. Koiki, M. Rivallin, M. F. Bekheet, R. Viter, D. Damberga, G. Lesage, I. Iatsunskyi, E. Coy, M. Cretin, O. A. Arotiba, M. Bechelany, Photoelectrocatalysis of paracetamol on Pd–ZnO/ N-doped carbon nanofibers electrode, Appl. Mater. Today 24 (2021), 101129, https://doi.org/10.1016/j.apmt.2021.101129.
[87] B.O. Orimolade, B.A. Koiki, G.M. Peleyeju, O.A. Arotiba, Visible light driven photoelectrocatalysis on a FTO/BiVO 4 /BiOI anode for water treatment involving emerging pharmaceutical pollutants, Electrochim. Acta 307 (2019) 285–292, https://doi.org/10.1016/j.electacta.2019.03.217.
[88] I. Olvera-Rodríguez, R. Hernández, A. Medel, C. Guzmán, L. Escobar-Alarcón, E. Brillas, I. Sirés, K. Esquivel, TiO2/Au/TiO2 multilayer thin-film photoanodes synthesized by pulsed laser deposition for photoelectrochemical degradation of organic pollutants, Sep. Purif. Technol. 224 (2019) 189–198, https://doi.org/10.1016/j.seppur.2019.05.020.
[89] P. Iovino, S. Chianese, S. Canzano, M. Prisciandaro, D. Musmarra, Ibuprofen photodegradation in aqueous solutions, Environ. Sci. Pollut. Res. 23 (2016) 22993–23004, https://doi.org/10.1007/s11356-016-7339-0.
[90] K. Patterson, K. Howlett, K. Patterson, B. Wang, L. Jiang, Photodegradation of ibuprofen and four other pharmaceutical pollutants on natural pigments sensitized TiO2 nanoparticles, Water Environ. Res. 92 (2020) 1152–1161, https://doi.org/10.1002/wer.1310.
[91] Q. Sun, Y.P. Peng, H. Chen, K.L. Chang, Y.N. Qiu, S.W. Lai, Photoelectrochemical oxidation of ibuprofen via Cu2O-doped TiO2 nanotube arrays, J. Hazard. Mater. 319 (2016) 121–129, https://doi.org/10.1016/j.jhazmat.2016.02.078.
[92] A. Gomes, T. Frade, K. Lobato, M.E.M. Jorge, M.I. Da Silva Pereira, L. Ciriaco, A. Lopes, Annealed Ti/Zn-TiO 2 nanocomposites tested as photoanodes for the degradation of Ibuprofen, J. Solid State Electrochem 16 (2012) 2061–2069, https://doi.org/10.1007/s10008-011-1608-0.
[93] E. Isarain-Chávez, C. Arias, P.L. Cabot, F. Centellas, R.M. Rodríguez, J.A. Garrido, E. Brillas, Mineralization of the drug β-blocker atenolol by electro-Fenton and photoelectro-Fenton using an air-diffusion cathode for H2O2 electrogeneration combined with a carbon-felt cathode for Fe2+ regeneration, Appl. Catal. B Environ. 96 (2010) 361–369, https://doi.org/10.1016/j.apcatb.2010.02.033.
[94] G. Longobucco, L. Pasti, A. Molinari, N. Marchetti, S. Caramori, V. Cristino, R. Boaretto, C.A. Bignozzi, Photoelectrochemical mineralization of emerging contaminants at porous WO3 interfaces, Appl. Catal. B Environ. 204 (2017) 273–282, https://doi.org/10.1016/j.apcatb.2016.11.007.
[95] J. Cui, Y. Pei, J. Hou, Y. Zheng, Y. Zhang, K. Wei, X. He, B. Xi, Construction of a carbon dots-based Z-scheme photocatalytic electrode with enhanced visible-light-driven activity for Cr(VI) reduction and carbamazepine degradation in different reaction systems, Chem. Eng. J. 420 (2021), 127571, https://doi.org/10.1016/j.cej.2020.127571.
[96] S. Ghasemian, D. Nasuhoglu, S. Omanovic, V. Yargeau, Photoelectrocatalytic degradation of pharmaceutical carbamazepine using Sb-doped Sn80%-W20%-oxide electrodes, Sep. Purif. Technol. 188 (2017) 52–59, https://doi.org/10.1016/j.seppur.2017.07.007.
[97] H.G. Oliveira, L.H. Ferreira, R. Bertazzoli, C. Longo, Remediation of 17-α-ethinylestradiol aqueous solution by photocatalysis and electrochemically-assisted photocatalysis using TiO2 and TiO2/WO3 electrodes irradiated by a solar simulator, Water Res. 72 (2015) 305–314, https://doi.org/10.1016/j.watres.2014.08.042.
[98] M. Joseita dos Santos Costa, G. dos Santos Costa, A. Estefany Brandão Lima, G. Eduardo da Luz Júnior, E. Longo, L. Santos Cavalcante, R. da Silva Santos, Photocurrent response and progesterone degradation by employing WO3 films modified with platinum and silver nanoparticles, Chempluschem 83 (2018) 1153–1161, https://doi.org/10.1002/cplu.201800534.
[99] T.T. Schug, A.F. Johnson, L.S. Birnbaum, T. Colborn, L.J. Guillette, D.P. Crews, T. Collins, A.M. Soto, F.S. Vom Saal, J.A. McLachlan, C. Sonnenschein, J. J. Heindel, Minireview: Endocrine disruptors: Past lessons and future directions, Mol. Endocrinol. 30 (2016) 833–847, https://doi.org/10.1210/me.2016-1096.
[100] L.A. Goulart, S.A. Alves, L.H. Mascaro, Photoelectrochemical degradation of bisphenol A using Cu doped WO 3 electrodes, J. Electroanal. Chem. 839 (2019) 123–133, https://doi.org/10.1016/j.jelechem.2019.03.027.
[101] H. Shao, Y. Wang, H. Zeng, J. Zhang, Y. Wang, M. Sillanpää, X. Zhao, Enhanced photoelectrocatalytic degradation of bisphenol a by BiVO4 photoanode coupling with peroxymonosulfate, J. Hazard. Mater. 394 (2020), 121105, https://doi.org/10.1016/j.jhazmat.2019.121105.
[102] A.U.R. Bacha, I. Nabi, H. Cheng, K. Li, S. Ajmal, T. Wang, L. Zhang, Photoelectrocatalytic degradation of endocrine-disruptor bisphenol – A with significantly activated peroxymonosulfate by Co-BiVO4 photoanode, Chem. Eng. J. 389 (2020), 124482, https://doi.org/10.1016/j.cej.2020.124482.
[103] Z. Zheng, Y.H. Ng, Y. Tang, Y. Li, W. Chen, J. Wang, X. Li, L. Li, Visible-light-driven photoelectrocatalytic activation of chloride by nanoporous MoS2@BiVO4 photoanode for enhanced degradation of bisphenol A, Chemosphere 263 (2021), 128279, https://doi.org/10.1016/j.chemosphere.2020.128279.
[104] Y. Cong, W. Zhang, W. Ding, T. Zhang, Y. Zhang, N. Chi, Q. Wang, Fabrication of electrochemically-modified BiVO4-MoS2-Co3O4composite film for bisphenol A degradation, J. Environ. Sci. 102 (2021) 341–351, https://doi.org/10.1016/j.jes.2020.09.027.
[105] X. Sun, H. Wu, Y. Tang, Z. Zheng, Y. Li, L. Li, Q. Zhang, Enhanced photoelectrocatalytic degradation of tetrabromobisphenol a from tip-decorated ZnO nanorod electrode with Bi2S3 nanoparticles, Mater. Sci. Semicond. Process. 128 (2021), 105724, https://doi.org/10.1016/j.mssp.2021.105724.
[106] CONAMA, Efluentes, Diário Of. União. , 2011 8.
[107] D.E. Mar, Diário oficial da união, Diário Of. Da União. (2021) 2020–2021.
[108] N. United, Int. Initiat. Water Qual. (2015) 1–4.
[109] United States Environment Protection Agency (US EPA), Preliminary Effluent Guidelines Program Plan, Effl. Guidel. (2021). ⟨https://www.epa.gov/eg/preliminary-effluent-guidelines-program-plan⟩.
[110] T. Yao, X. An, H. Han, J.Q. Chen, C. Li, Photoelectrocatalytic materials for solar water splitting, Adv. Energy Mater. 8 (2018) 1–36, https://doi.org/10.1002/aenm.201800210.
[111] R. Sun, Z. Zhang, Z. Li, L. Jing, Review on photogenerated hole modulation strategies in photoelectrocatalysis for solar fuel production, ChemCatChem 11 (2019) 5875–5884, https://doi.org/10.1002/cctc.201901581.
[112] S. Garcia-Segura, E. Brillas, Applied photoelectrocatalysis on the degradation of organic pollutants in wastewaters, J. Photochem. Photobiol. C. Photochem. Rev. 31 (2017) 1–35, https://doi.org/10.1016/j.jphotochemrev.2017.01.005.
[113] P. Lianos, Production of electricity and hydrogen by photocatalytic degradation of organic wastes in a photoelectrochemical cell, Concept Photo. A Rev. A re-Emerg. Res. Field J. Hazard. Mater. 185 (2011) 575–590, https://doi.org/10.1016/j.jhazmat.2010.10.083.
[114] Y. Vasseghian, A. Khataee, E.N. Dragoi, M. Moradi, S. Nabavifard, G. Oliveri Conti, A. Mousavi Khaneghah, Pollutants degradation and power generation by photocatalytic fuel cells: a comprehensive review, Arab. J. Chem. 13 (2020) 8458–8480, https://doi.org/10.1016/j.arabjc.2020.07.016.
[115] H. Du, W. Pu, Y. Wang, K. Yan, J. Zhang, C. Yang, J. Guong, Synthesis of BiVO4/WO3 composite film for highly efficient visible light induced photoelectrocatalytic oxidation of norfloxacin, J. Alloys Compd. 787 (2019) 284–294, https://doi.org/10.1016/j.jallcom.2019.01.390.