

Review

Recent Trends in Pharmaceuticals Removal from Water Using Electrochemical Oxidation Processes

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Abstract: Nowadays, the research on the environmental applications of electrochemistry to remove recalcitrant and priority pollutants and, in particular, drugs from the aqueous phase has increased dramatically. This literature review summarizes the applications of electrochemical oxidation in recent years to decompose pharmaceuticals that are often detected in environmental samples such as carbamazepine, sulfamethoxazole, tetracycline, diclofenac, ibuprofen, ceftazidime, ciprofloxacin, etc. Similar to most physicochemical processes, efficiency depends on many operating parameters, while the combination with either biological or other physicochemical methods seems particularly attractive. In addition, various strategies such as using three-dimensional electrodes or the electro-synthesis of hydrogen peroxide have been proposed to overcome the disadvantages of electrochemical oxidation. Finally, some guidelines are proposed for future research into the applications of environmental electrochemistry for the degradation of xenobiotic compounds and micropollutants from environmental matrices. The main goal of the present review paper is to facilitate future researchers to design their experiments concerning the electrochemical oxidation processes for the degradation of micropollutants/emerging contaminants, especially, some specific drugs considering, also, the existing limitations of each process.

Keywords: pharmaceuticals; advanced oxidation processes; boron doped diamond; operating parameters; water matrix; degradation; micropollutants



Citation: Bamos, G.; Petala, A.; Frontistis, Z. Recent Trends in Pharmaceuticals Removal from Water Using Electrochemical Oxidation Processes. *Environments* **2021**, *8*, 85. <https://doi.org/10.3390/environments8080085>

Academic Editor: Alfredo Cassano

Received: 30 July 2021

Accepted: 20 August 2021

Published: 22 August 2021

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1. Introduction

In recent decades, the intense environmental contamination was mostly attributed to the rapid industrialization of the modern societies dictated by the increased human needs, raising serious concerns in the international scientific community [1,2]. Among the various wastes present in water bodies, pharmaceuticals (PhCs) hold a special place since their presence even at low concentrations can cause irreversible damage to the ecosystem and human health [3]. PhCs can be divided into various categories concerning their characteristics such as anti-inflammatory (e.g., diclofenac), antiepileptic (e.g., carbamazepine), stimulant (e.g., caffeine), β -blockers (e.g., propranolol), antibiotics (sulfamethoxazole), psychiatric (e.g., venlafaxine), antimicrobials (e.g., triclosan), etc. [1].

Since pharmaceutical wastewater includes compounds of high complexity, the processes related to their degradation are quite demanding [2]. Various methods were applied to remove PhCs from water and wastewater, such as coagulation or biological treatment [4–7]. However, the complete removal and mineralization of PhCs cannot be achieved with these conventional methods [8], and the demand for more advanced methods for wastewater treatment resulted in the development of advanced oxidation processes (AOPs) during the 1980s [2]. Based on the in situ generation of oxygen species of high reactivity (ROS), such as hydroxyl (\bullet OH) or superoxide radicals ($O_2^{\bullet-}$), the most significant advantage

of AOPs is that they can completely mineralize even non-biodegradable pharmaceutical wastewater employing specific conditions under an environmentally friendly manner [9]. Various AOPs are applied to degrade organic compounds divided into different categories concerning the employed methodology for the generation of reactive oxygen species (photochemical or non-photochemical) or the use or not of catalytic materials during the process (homogeneous or heterogeneous). Some of the most common AOPs are ozonation, UV/hydrogen peroxide, and photocatalysis [10].

Among the applied AOPs, the electrochemical oxidation processes (EOPs) are highly efficient technologies with a facile operation. They are easily combined with other AOPs and biological treatment [8]. The electrochemical oxidation of PhCs can be performed on the surface of the anodic electrode of the electrochemical cell (direct) or via the ROS produced from the water oxidation performed on the anode surface (indirect) [8,11,12], as depicted in Figure 1. In addition, some ROS produced during electrolysis can diffuse to the bulk solution, thus enhancing the efficiency and partially bypassing mass transfer limitations. Moreover, the coupling of the EOPs with other physicochemical technologies is considered a highly efficient combination, with a typical example of this technology being the reactive electrochemical membrane [13].

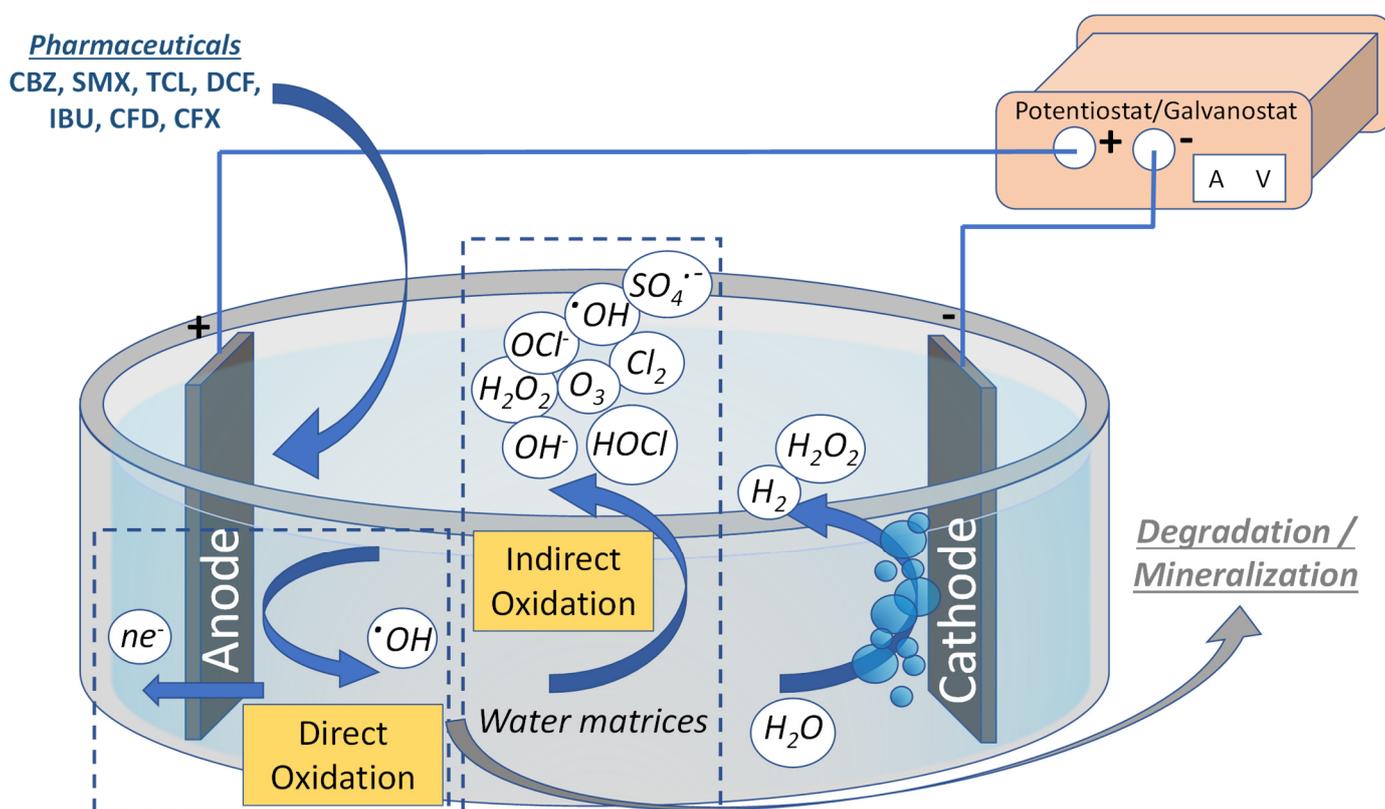


Figure 1. Direct and indirect electrochemical oxidation process for the mineralization of PhCs.

Recently, Dao et al. [12] and Zhang et al. [8] published two exceptional works relevant to the recent progress concerning the electrochemical oxidation processes for PhCs degradation. Dao et al. [12] studied the recent advances in removing various PhCs from aqueous solutions applying EOPs. They focused their research efforts on the various parameters affecting the efficient PhCs degradation using EOPs such as the reactor design, the electrode materials (BDD, lead, etc.) or the operational parameters (current density, pH, etc.). Zhang et al. [8] studied the recent advances in electrochemical anodic oxidation processes focusing mainly on the parameters affecting the efficiency of the process. Most of the examined parameters that the aforementioned research groups have found to affect the EOPs for PhCs removal are practically the same such as the design of the electrochemical

reactor, the electrode material, the applied current density, the electrolyte concentration, the initial PhCs concentration or the pH of the solution.

However, the large number of PhCs as well as the various parameters affecting their treatment and the different water matrices result in a multiparametric system, which must be examined for an effective experimental design. Although there are a large number of studies, one major drawback is that the available information is fragmented. It would be of interest to study the progress concerning the employed electrochemical oxidation technologies for the degradation of each drug separately. The latter would further facilitate the literature study for the researchers who want to be informed as it concerns the recent progress in the EOPs for the degradation of some PhCs of particular interest.

Towards this direction, the present review article examines the EOPs applied for PhCs wastewater degradation concerning specific PhCs that were examined in a larger extent. Specifically, carbamazepine (CBZ), sulfamethoxazole (SMX), tetracycline (TCL), diclofenac (DCF), ibuprofen (IBU), ceftazidime (CFD), and ciprofloxacin (CFX) were examined in separate sections, whereas various other PhCs were examined together in Section 3.8, since the number of recent publications concerning their degradation applying EOPs was significantly smaller than that of those PhCs, such that their study was presented in separate sections. The aim of the present review paper is to ease the experimental design of various EOPs which would be applied by future researchers for the elimination of recalcitrant micropollutants, especially, some specific PhCs considering, however, the existing limitations of each process.

2. Contamination of Aquatic Environment by PhCs

The contamination of the water bodies by the PhCs is attributed to hospital or pharmaceutical industry waste, personal hygiene products or therapeutic drugs [14]. The most frequently detected PhCs in water bodies are antibiotics, antiepileptics, antidepressants, anti-inflammatories, antihistamines, and β -blockers [15]. The unknown negative long-term effect that PhCs may have on human health through drinking water as well as the problems that the presence of these organic compounds may cause to the ecosystem, resulted in the development of a research field relevant to this issue. The special features of the structure of most PhCs distinguish them from other industrial wastes and make their degradation quite demanding. Typically, large polar molecules of high complexity with various structures and weights are combined to form PhCs. The composition of these molecules is characterized by the presence of various ionizable compounds, whereas their ionization degree strongly depends on the pH of the solution. Common PhCs such as SMX may remain in the environment for ca. a year or even more, as in the case of clofibrac acid [16]. The persistency of these PhCs may result in their accumulation, which is possible to increase their biological activity [14].

The consumption of PhCs may follow two possible pathways, either being excreted without being chemically converted or undergoing biochemical reactions during the metabolism process. These biochemical reactions include the redox reactions, hydrolysis and alkylation reactions, and the formation and subsequent extraction of glucuronide and sulfates as metabolites [17,18]. PhCs are introduced into the environment either by their disposal in rubbish that could be prevented or via biological wastewater produced by humans or animals, which is difficult to prevent [14].

3. Recent Developments of EOPs for Specific PhCs

As mentioned in the introduction, some of the PhCs were investigated to a larger extent concerning their removal from the aquatic environment employing EOPs or applying a combination of an EOP with another AOP (e.g., ozonation), biological treatment methods or physical processes such as membrane technology. To the best of our knowledge, the number of works published in the last decade concerning the applied electrochemical removal technology for the degradation of these seven PhCs is depicted below (Figure 2).

The most studied PhCs towards their applied EOP technology are the CBZ (11), SMX (10), TCL (8), and DCF (7).

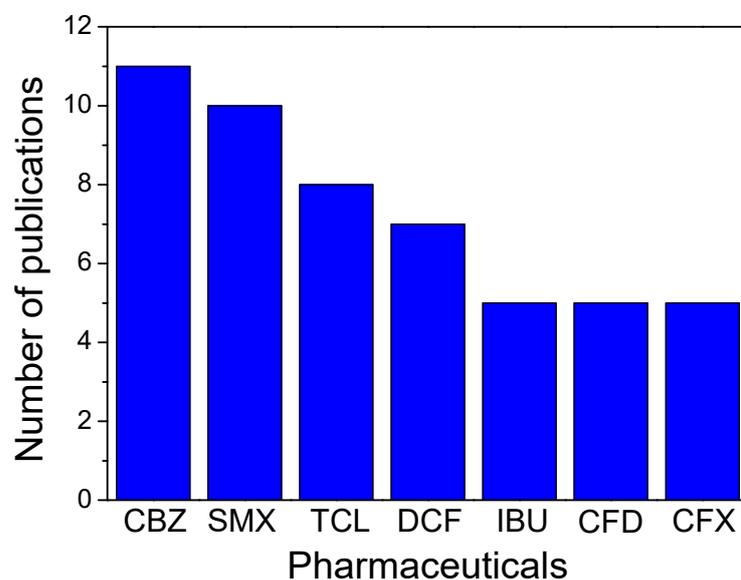


Figure 2. Number of publications of the most studied PhCs as it concerns their removal using EOPs during the last decade.

Details concerning the used anode electrode material, the applied electrolyte solution, and the obtained removal efficiency of each of the aforementioned PhCs are listed in Table 1.

Table 1. Recent publications on electrochemical oxidation processes for the selected PhCs (CBZ, SMX, TCL, DCF, IBU, CFD, CFX).

PhCs	Anode Electrode Material	Electrolyte	Removal Efficiency	Reference
Carbamazepine (CBZ)	Activated carbon powder (PAC) 3-D electrode	NaCl	89.8% (10 min)	[19]
	BDD	Na ₂ SO ₄	100% (0.98 min)	[20]
	Nb/BDD	Na ₂ SO ₄	82% (90 min)	[21]
	Nb/BDD	NaCl	88.7% (12.45 min)	[22]
	Ti/PbO ₂	NaSO ₄	88% (101 min)	[23]
	Ti/PbO ₂ (EOP coupled with eMBR)	NaSO ₄	99.99% (101 min)	[24]
	TiO ₂ meshes	KCl	100% (45 min)	[25]
	BDD	NaSO ₄	50% (1 min) k _{app} = 0.73 min ⁻¹	[26]
	Nb/BDD (EOP coupled with eMBR)	(NH ₄) ₂ SO ₄ , KH ₂ PO ₄	97% (40 min)	[27]
Aluminium	NH ₄ -N, NO ₃ -N, PO ₄ -P	50% (19 h)	[28]	

Table 1. Cont.

PhCs	Anode Electrode Material	Electrolyte	Removal Efficiency	Reference
Sulfamethoxazole (SMX)	Nb/BDD	Na ₂ SO ₄	86% (90 min)	[21]
	Ti/Ru _{0.3} Ti _{0.7} O ₂	NaCl	98% (30 min)	[29]
	BDD	K ₂ SO ₄	75% (60 min)	[30]
	Ti/SnO ₂ -Sb/Ce-PbO ₂	NaOH, Na ₂ SO ₄ , NaNO ₃ , NaNO ₂ , NaClO ₄ , NH ₄ Cl, H ₃ PO ₄ , HClO ₄	95% (60 min)	[31]
	Graphite	NaCl	99.6% (30 min) k _{app} = 0.170 min ⁻¹	[32]
	BDD	-	72.9% (180 min)	[33]
	BDD	NaOH	100% (50 min)	[34]
	Pt	Na ₂ SO ₄	98% (90 min)	[35]
	Ti/SnO ₂ -Sb/Er-PbO ₂	Na ₂ SO ₄	k _{app} = 0.299 min ⁻¹ (9.2 min)	[36]
	Tetracycline (TCL)	Graphite felt	Na ₂ SO ₄	99%
BDD		Na ₂ SO ₄	99% (120 min)	[38]
Magnéli phase Ti ₄ O ₇		H ₂ SO ₄	98.4% (56.4 min)	[39]
Ti/Ti ₄ O ₇		Na ₂ SO ₄	97.2% (11.2 min)	[40]
DSA (mixed metal oxide, Ti/RuO ₂ -IrO ₂)		Na ₂ SO ₄	100% (20 min)	[41]
Pb/PbO ₂		H ₂ SO ₄	86.7% (DOC) (60 min)	[42]
Ti ₄ O ₇		Na ₂ SO ₄	97.2% (120 min)	[43]
Diclofenac (DCF)	BDD	Na ₂ SO ₄	100% (200 min)	[44]
	Aluminium	NH ₄ -N, NO ₃ -N, PO ₄ -P	47% (6 h)	[28]
	Graphite	NaCl	99.2% (60 min)	[32]
	BDD	-	73.7% (180 min)	[33]
	BDD	methanol/phosphate buffer	79.4% (175 min)	[45]
	Pt	Na ₂ SO ₄	98% (90 min)	[35]
Ibuprofen (IBU)	BDD	NaCl	96% (TOC) (8 h)	[46]
	BDD	Na ₂ SO ₄	95% (COD) 92% (TOC) (6 h)	[47]
	TiO ₂ nanoflower-modified porous titanium gas diffuser (TiO ₂ -NF @PTGD)	Na ₂ SO ₄	k _{app} = 0.0195 min ⁻¹ (30 min)	[48]
	Nb/BDD (EOP coupled with eMBR)	(NH ₄) ₂ SO ₄ , KH ₂ PO ₄	93% (120 min)	[27]
	Ti/SnO ₂ -Sb/Ce-PbO ₂	Na ₂ SO ₄	93.2% (60 min) k _{app} = 0.094 min ⁻¹	[49]
Ceftazidime (CFD)	Ti/SnO ₂ -Cu	Na ₂ SO ₄	90% (60 min)	[50]
	CeO ₂ -ZrO ₂ /TiO ₂ /CNT	Na ₂ SO ₄	83.47% (60 min)	[51]
	La ₂ O ₃ -CuO ₂ /CNTs	Na ₂ SO ₄	90% (30 min)	[52]
	CeO ₂ /MWCNTs	Na ₂ SO ₄	100% (60 min)	[53]
	Ti/TiO ₂ /SnO ₂ -Sb-Cu	Na ₂ SO ₄	97.65% (20 h)	[54]
Ciprofloxacin (CFX)	BDD	K ₂ SO ₄	100% (250 min)	[30]
	BDD	K ₂ SO ₄	100% (180 min)	[55]
	Sb-doped SnO ₂	Na ₂ SO ₄	100% (60 min)	[56]
	Ti-Pt/β-PbO ₂	Na ₂ SO ₄	100% (120 min)	[57]
	SnO ₂ -Sb/Ti	Na ₂ SO ₄	99.5% (120 min)	[58]

3.1. Carbamazepine (CBZ)

CBZ belongs to the antiepileptic drugs treating various psychiatric diseases, epilepsy or trigeminal neuralgia [59]. Regarding the fact that the reported consumption per year of CBZ is quite large as mentioned by Zhang et al. [60] as well as the fact that CBZ is not easily

degradable under biological treatment or hydrolysis [61], the presence of CBZ in water bodies varies from 0.08 to 3.1 $\mu\text{g/L}$ posing a significant threat for the ecosystem affecting in turn human health [62]. The elimination of CBZ from wastewaters was examined applying various AOPs such as ozonation [63] or photocatalysis [64].

Recently, various research groups studied EOPs for CBZ degradation with quite interesting results [19–28,65]. Alighardashi et al. [19] compared the efficiency of a three-dimensional electrochemical process (3-EC) with that obtained by a two-dimensional electrochemical process (2-EC) applying activated carbon as a particle electrode concerning the CBZ degradation. Various factors affecting the electrochemical oxidation process were examined, such as initial CBZ loading, current density, activated carbon concentration, reaction time, and other operating parameters. The optimum values achieving the highest CBZ removal efficiency (89.8%) were 9 mA/cm^2 applied current density, initial activated carbon concentration equal to 0.5 g/L , and 10 min operational time concerning the three-dimensional electrochemical system. In this particular work, the role of activated carbon as a particle electrode material was underlined as crucial, especially for the production of superoxides employed for the degradation of CBZ.

Domínguez et al. [20] studied the electrochemical oxidation of CBZ applying boron-doped diamond (BDD) anodes under galvanostatic mode, whereas the process was optimized concerning four parameters, namely applied current density, pH, electrolyte concentration, and flow rate. The most significant parameter was current density and the process achieved complete CBZ elimination. Nb/BDD and Ti/IrO₂ were examined as anodic electrodes for electrochemical oxidation of CBZ applying NaCl as a supporting electrolyte providing additional active chlorine species by García-Espinoza et al. [22]. The most critical parameters affecting the effectiveness of the electrochemical oxidation of CBZ were the current density and the treatment time. Nb/BDD was the most effective anode electrode, whereas the 88.7% CBZ degradation efficiency was achieved applying specific operational conditions (1 A applied current, 12.45 min operational time, and 14 mM NaCl). According to the researchers, the Nb/BDD was more effective than the Ti/IrO₂ anode electrode due to the increased production of $\cdot\text{OH}$ radicals and HClO as well as Cl^\cdot and ClO^- species. However, the anodic electrode material does not affect the overall process drastically as the other examined parameters and especially the current density.

García-Gómez et al. published two interesting works [23,24] related to the experimental design methodology of the electrochemical oxidation of CBZ employing Ti/SnO₂, Ti/PbO₂, and Ti/BDD anodic electrodes [23], as well as a proposed technology combining a membrane bioreactor (MBR) with an anodic oxidation process employing Ti/PbO₂ as an anodic material for CBZ removal [24]. As in the previous studies, the effect on the CBZ electrochemical degradation of the applied current, time, anodic electrode material, and the flow rate was tested. A CBZ removal efficiency of 88% was obtained for the Ti/PbO₂ anode material, for an applied current value equal to 1.37 A and an electrolysis time equal to 101 min. The flow rate was 232 mL/min [23]. The proposed combination of the MBR with the electrochemical oxidation process was introduced as a promising combination since the coupling of these two technologies resulted in complete removal of the CBZ (99.9%) [24]. The MBR exhibited high capacity in the COD removal. In contrast, the CBZ degradation was relatively low (20%) after 120 d implying that the CBZ was not poisonous for the MBR microorganisms. At the same time, the electrochemical oxidation resulted in the complete removal of the CBZ.

Moreover, a very interesting work examining the electrochemical degradation of CBZ in various water matrices namely ultrapure water, surface lake water, and urban wastewater treatment plant effluent using Si/BDD as the anode material and stainless steel as the cathode material was demonstrated by Palo et al. [26], punctuating one more time the significance of the current density, as well as the CBZ initial concentration in the electrochemical system removal efficiency.

Finally, the works of Ouarda et al. [27], García-Espinoza et al. [21], Borea et al. [65], and Ensano et al. [28] were related to EOPs or combinations of EOPs with other AOPs for

the degradation of CBZ alone or as a mixture with other PhCs. The coupling of the MBR technology with the electrooxidation (EO) process was investigated by Ouarda et al. [27] for the degradation of three different PhCs, namely CBZ, ibuprofen (IBU), estradiol (E2), as well as venlafaxine (VEN). The results concerning the IBU will be discussed later in the corresponding section. The EO process was applied either before or after the MBR treatment and the differences in the removal efficiency of the various examined PhCs were discussed. The most effective combination concerning the degradation of CBZ was the application of EO after the MBR as a post treatment/polishing step, achieving high removal efficiency (>97%) corroborating in that way the results of Palo et al. [26] presented earlier.

The effect of current density, pH values, operational time, and oxygen injection on the efficiency of the oxygenated electrochemical destruction of CBZ, SMX, and propranolol (PRO) was examined applying the Nb/BDD anode material and Na₂SO₄ as a supporting electrolyte by García-Espinoza et al. [21]. The accumulation on the electrode surface of the injected oxygen increased the number of ROS present in the electrolyte solution, which, combined with the increase of the mass transfer, resulted in an enhanced CBZ degradation efficiency equal to 82%. Moreover, the electrolyte composition was found to play a crucial role in the effect of injected oxygen in the EOP. An electro membrane bioreactor (eMBR) was used for the degradation of amoxicillin (AMX), diclofenac (DCF), and CBZ by Borea et al. [65]. Higher degradation of both conventional and emerging pollutants and effective control on membrane fouling was obtained when the current density increased from 0.3 to 1.15 mA/cm². Authors underline the significance of the current density on the synergistic effects of electrochemical and microbial processes stating that the proposed eMBR technology is a novel step towards an effective chemical free wastewater treatment. The electrocoagulation treatment of the same PhCs as in the previous case were examined from Ensano et al. [28]. The hydrophobicity of CBZ resulted in an enhanced tendency to be adsorbed by the coagulants.

3.2. Sulfamethoxazole (SMX)

SMX belongs to the functional group of sulfonamides and is a common bacteriostatic antibiotic applied to inhibit the folic acid precursor (dihydropteroate synthase), which may be responsible for bacterial growth [66]. SMX, as well as its metabolites, are often detected in water bodies. It has the ability to travel long distances with the water flow due to the co-presence of its acetyl metabolites, which enables SMX to increase by transforming itself into a parent compound [66]. The durability of SMX against microbes results in its persistence in the ecosystem threatening human life and environmental balance. Various techniques were used during the years for SMX removal such as adsorption applying carbonaceous materials as adsorbent-like activated carbon [67], biochar [68], carbon nanotubes (CNTs) [69] or graphene materials [70]. Fenton process [71], photocatalysis [72], cavitation [73] or radiation assisted catalysis [74] were also used for SMX degradation.

EOPs have recently attracted significant interest for the elimination of SMX from water matrices. Hussain et al. [29] investigated the electrochemical oxidation process using a commercial Ti/Ru_{0.3}Ti_{0.7}O₂ electrode material as the anode. The researchers achieved almost 98% SMX degradation after 30 min in 0.1 M NaCl for a pH value equal to 3 applying current density ca. 20 mA/cm². The rapid SMX destruction was attributed to the increase in the charge transfer and the enhancement of the formation of the oxidizing species due to the increased applied current density and the concentration of supporting electrolyte (NaCl). Lin et al. [31] investigated the Ti/SnO₂-Sb/Ce-PdO₂ electrocatalytic material as a possible anode in the electrocatalytic oxidation of SMX in aqueous solution. The researchers examined a series of parameters affecting the SMX mineralization such as the distance between the electrodes, the applied current density, the initial concentration of SMX, and the initial pH value. The significance of these factors in the SMX removal varied, with the current density being one more time a quite important parameter for the enhanced rate constant (k).

In contrast, the initial SMX concentration did not significantly affect the k values. A similar anode material (Ti/SnO₂-Sb/Er-PbO₂) was tested by Wang et al. [36] towards the electrochemical removal of SMX as well as acetyl-SMX (Ac-SMX), which is an SMX metabolite. The rate constant value was equal to 0.268 and 0.072 min⁻¹ under the optimum applied current density value (10 and 14 mA/cm², for SMX and Ac-SMX, respectively). The authors also studied the degradation pathways and punctuated the importance of the simultaneous investigation of the SMX metabolites along with the SMX removal, since some of them, such as Ac-SMX, are characterized by toxicity and more refractory than SMX.

Two works published by Lan et al. [30,55] examined the electrochemical degradation of SMX and other PhCs studying various parameters affecting the efficiency of the process. In the manuscript published in 2017 [30], the effect of salts on the electrochemical degradation of SMX, ciprofloxacin (CFX), and salbutamol (SBT) in wastewaters was studied using a BDD anode electrode. The elimination of SMX was enhanced by the presence of sulfates, while no effect was found in the case of SBT. In contrast, the current density and treatment time played a significant role in reducing the formation of toxic species such as ClO⁴⁻ and halogenated organic compounds. The electrochemical degradation of the same PhCs were further investigated by the same research group [55] in the presence of other organics and a model was proposed to predict the experimental results. The model's input parameters were the electronic activity of the applied BDD anode, the number of electrons participated in the direct oxidation and the obtained reaction rate as estimated after the formation of the oxidant species derived from the salts.

The direct and indirect electrochemical oxidation of SMX, DCF, and acetaminophen (ACT) were studied by Liu et al. [32] applying graphite electrodes and Na₂SO₄ or NaCl as supporting electrolytes. Additionally, 81.6% SMX removal efficiency was achieved under 0.5 A applied current value, after 60 min with an apparent rate constant equal to 0.027 min⁻¹ in the case of the direct electrooxidation system. For the indirect electrochemical oxidation, the SMX degradation efficiency was 99.6% applying the aforementioned current density after 30 min of treatment with a significantly higher rate constant equal to 0.17 min⁻¹.

Various operational parameters such as applied current density, initial PhCs concentration, and wastewater matrix (simulated vs. real effluent of hospital wastewater) were examined by Loos et al. [33] for the removal of SMX, DCF, iopromide (IOP), and 17- α -ethinyloestradiol (EE2) using BDD as the anode. The effects of supporting electrolyte (Na₂SO₄ or potassium phosphate) as well as the material (carbon or Pt) of the anodic electrode were investigated for the electrochemical removal of SMX and DCF by Sifuna et al. [35]. The superior performance of Pt as an anodic electrode using Na₂SO₄ as the electrolyte was confirmed. Moreover, the SMX removal rate was found to follow second-order kinetics. Finally, a very interesting work published by Rodríguez-Nava et al. [34] studying the coupling of electrochemical oxidation with a biological treatment for the simultaneous degradation of bexafibrate, gemfibrozil, indomethacin, and SMX (BIGS) from wastewater demonstrated interesting results, since this was the first time that the simultaneous removal of various PhCs was investigated applying a combination of degradation technologies.

3.3. Tetracycline (TCL)

TCL antibiotics have a remarkable antibiotic activity against various infections such as chlamydia or mycoplasma and have been successfully used for veterinary purposes [75]. Their presence in the aquatic system after being biologically excreted by humans or animals may cause problems to human health by the possible presence in drinking water and fruits and vegetables, since they enhance the development of antibiotic resistance microorganisms disturbing the intestine microflora leading to infections [76]. Membrane technology [77], adsorption [78], photodegradation [79], photocatalysis [80], and various other processes are applied for the degradation of TCL.

Electrochemical processes used for the TCL antibiotics elimination gained significant interest recently due to their flexibility and their effectiveness towards the PhCs removal [81]. Remarkable are the works of Brinzila et al. [38,82], studying the electrochemi-

cal degradation of TCL using BDD as the anode material. The effect of the pH value, the applied current, and the supporting electrolyte on the TCL removal were examined. The highest COD removal was obtained for pH equal to 2. At the same time, the use of Na_2SO_4 as a supporting electrolyte was accompanied by a complete TCL degradation after 2 h of treatment. The presence of chloride ions was found to accelerate the TCL removal, but obstructed the TCL mineralization. It is quite interesting that increasing the applied current results in a decrease in organic matter degradation.

Frontistis et al. [83] used the BDD for the electrochemical oxidation of tetracycline. BDD showed higher activity from platinum and stainless steel. Scavengers such as bicarbonates (200 mg/L) decreased the observed kinetic constant from 0.328 to 0.212 min^{-1} , while the addition of 200 mg/l chlorides enhanced almost four times the apparent kinetic constant. Using BDD as both anode and cathode material increased the process efficiency by about 20%, while UVA or simulated solar radiation enhanced performance by 14%. Interestingly, the removal of tetracycline was favored in environmental matrices such as bottled water and secondary effluent.

Liang et al. [39] studied the electrooxidation of TCL over Magnéli phase titanium oxide (Ti_4O_7) as the anodic material, considering possible reaction mechanisms, kinetics, and toxicity altering experimental parameters such as current density and TCL initial concentration. Furthermore, salicylic acid (SA) was added as a well-known hydroxyl radical scavenger to investigate the oxidation reaction mechanism. TCL oxidation facilitated by $\bullet\text{OH}$ was responsible for 40% of the total TCL degradation. These radicals were yielded on Ti_4O_7 under a flow rate equal to $2 \times 10^{-9} \text{ mol cm}^{-2} \text{ min}^{-1}$ applying 0.5 mA/cm^2 current density. The $\text{Ti/Ti}_4\text{O}_7$ anode material was used for the electrochemical oxidation of TCL, achieving 95.8% removal efficiency after 40 min of treatment. This efficiency was invariable after five experimental cycles, as demonstrated by Wang et al. [40]. The effect of current density, the distance between the electrodes, and the initial TCL concentration were examined and a relatively comprehensive effort towards the elucidation of the oxidation mechanism was presented.

Wu et al. [41] studied the EOP of TCL employing carbon felt and DSA ($\text{Ti/RuO}_2\text{-IrO}_2$) as cathode and anode material, respectively, of the electrochemical cell scrutinizing the effect of operational parameters such as initial TCL concentration, pH value, and the applied current density. The latter was found to enhance the TCL removal, whereas the former two parameters negatively affected the electrooxidation process. TCL hydrochloride degradation was investigated using a Pb/PbO_2 anodic material combined with the conventional activated sludge process, as shown by Yahiaoui et al. [42]. Once again, the applied current was a significant factor concerning the effective TCL removal. In addition, the increase of the initial TCL concentration acted negatively towards its removal. The optimal operating conditions derived by the central composite design (CCD) were a temperature value of 26 °C, applied current density equal to 25 mA/cm^2 , 100 mg/L initial TCL concentration, and 720 rpm agitation rate. Applying the optimal values resulted in 86.7% removal of the dissolved organic carbon (DOC). Coupling the electrooxidation process as pretreatment with the activated sludge resulted in the total removal of TCL.

Zhi et al. [43] studied the combination of ozonation with a reactive electrochemical membrane technology to degrade TCL. The TCL degradation was performed by ozonation over the Ti_4O_7 reactive electrochemical membrane reactor (REM). Almost total removal of TCL was achieved and 9.1% TOC removal efficiency was recorded. After the ozonation, 33 intermediates (nitrogen species, etc.) were detected, whereas their number was decreased to 18 after the EOP process. Finally, Belkheiri et al. [37] investigated the electrochemical oxidation as a pretreatment followed by a biological process for TCL degradation.

3.4. Diclofenac (DCF)

DCF is one of the most widely used non-steroidal anti-inflammatory PhCs, typically used to control renal colic [44]. It is a persistent PhC that is often detected in water bodies

in concentrations up to 4.4 $\mu\text{g/L}$ [84]. Sonolysis [85], ozonation [86], as well as solar photo-Fenton [87] are among the various AOPs applied for DCF degradation.

Brillas et al. [44] studied the anodic oxidation of DCF employing Pt or BDD as anode material. Complete elimination of DCF was achieved with a pH value equal to 6.5 and using BDD as the anode. The superior performance of BDD compared to Pt was attributed to the smaller number of generated reactive $\text{Pt}(\cdot\text{OH})$ species compared to $\text{BDD}(\cdot\text{OH})$. Sifuna et al. [35] investigated the electrooxidation of SMX and DCF over Pt and graphite carbon as an anodic electrode. The observed kinetic constant of DCF decomposition was equal to $0.006 \text{ mol}^2 \text{ L}^{-2} \text{ min}^{-1}$ using Na_2SO_4 as a supporting electrolyte. Electrochemical oxidation for the degradation of DCF and paracetamol was used over BDD anode material and stainless steel cathode by García-Montoya et al. [45]. The mineralization of DCF was accompanied by the evolution of NH_4^+ and NO_3^- species, whereas the efficiency concerning the degradation of DCF increased with increasing the DCF concentration.

As shown earlier, among various PhCs Loos et al. [33] investigated also the degradation of DCF using BDD anode. The flow rate affected the removal of DCF. As demonstrated in a previous section, the direct and indirect oxidation process using graphite electrodes was investigated by Liu et al. [32] concerning the degradation of aminophen, SMX, and DCF. Applying the optimum current value (0.5 A) and employing the direct oxidation process, the removal efficiency of DCF was equal to 90%, whereas the rate constant was 0.037 min^{-1} , and the TOC removal was 85.9% after 60 min of electrooxidation. Complete DCF removal was achieved after 30 min operational time using the same optimum current value considering the indirect oxidation process, whereas the TOC removal and the rate constant were 92.6% and 0.307 min^{-1} , respectively, implying the superior performance of the indirect process compared to that of the direct electrooxidation, as in the case of SMX.

The electrocoagulation process was applied to remove CBZ, DCF, and AMX from municipal wastewater, as presented earlier by Ensano et al. [28]. The electro-flotation and the charge neutralization are believed to aid the DCF degradation in contrast with the process occurring in the case of SMX where its hydrophobic characteristics seem to facilitate its adsorption on the coagulants. Moreover, as presented by Borea et al. [65], the removal of DCF, CBZ, and AMX and the membrane fouling in an eMBR were also studied concerning the effect of the applied current density. Degradation efficiency did not differ significantly among the three examined PhCs, whereas the effect of the applied current in the entire process was crucial.

3.5. Ibuprofen (IBU)

Another common non-steroidal anti-inflammatory PhC is IBU, which is acidic and typically prescribed to relieve pain or treat rheumatoid arthritis and osteoarthritis [88]. Except AOPs, various methods such as adsorption, biological treatment or filtration were employed for the IBU removal [88]. During the last decade, some interesting works were published concerning EOPs for the IBU removal from the aquatic environment [27,46–49].

The electrochemical removal of IBU was investigated by Ambuludi et al. [46] using an electrolytic cell equipped with Pt or BDD as anode electrode material, and carbon felt as the cathode. According to the researchers, the larger $\cdot\text{OH}$ amounts were responsible for the enhanced performance of the BDD compared to Pt. Moreover, the rate constant increased with increasing the applied current density value and adding NaCl rather than Na_2SO_4 as the supporting electrolyte. However, the initial IBU concentration did not seem to affect the removal efficiency.

Ciríaco et al. [47] investigated the electrochemical oxidation of IBU applying Ti/Pt/PbO₂ and BDD as anode electrode materials. Experiments were conducted varying the initial IBU concentration from 0.22 to 1.75 mM in the case of Ti/Pt/PbO₂ electrode and the current density value from 10 to 30 mA/cm², while the supporting electrolyte (Na_2SO_4) concentration was 0.035 M. The performance of the BDD concerning the IBU removal was higher than that obtained for the Ti/Pt/PbO₂ electrode.

An interesting work was demonstrated by Li et al. [48] who studied the coupling of ozonation with the electrocatalytic oxidation (E-catazone process) over a novel TiO₂ nanoflower (TiO_{2-NF}) anode material towards IBU degradation. The combined process (E-catazone) resulted in a significantly larger production of hydroxyl radicals than those produced by each process (ozonation and electrochemical oxidation) separately, enhancing the IBU removal since these radicals were the most significant ROS for IBU degradation. TiO_{2-NF} was also found to facilitate the adsorption and subsequent transformation of O₃ to ·OH and ease the generation of H₂O₂ in the cell's cathode by reducing its overpotential value, enhancing further the ·OH production.

Various Ti-based electrodes were investigated towards their electrocatalytic activity concerning the IBU removal by Wang et al. [49]. The electrochemical oxidation of IBU was found to follow pseudo-first-order kinetics, whereas the rate constant values were equal to 9.4×10^{-2} , 4.7×10^{-2} , and $5.6 \times 10^{-2} \text{ min}^{-1}$ for the Ti/SnO₂-Sb/Ce-PbO₂, Ti/Ce-PbO₂, and Ti/SnO₂-Sb electrode materials, respectively. As it is obvious, the Ti/SnO₂-Sb/Ce-PbO₂ exhibited the highest IBU removal efficiency. The latter was also reflected in the high TOC removal (93.2%). Hydroxylation, decarboxylation, and loss of isopropanol and isopropyl may occur to achieve complete mineralization. Finally, the coupling of a membrane bioreactor technology with an electrochemical oxidation process for removing CBZ, IBU, estradiol, and VEN from synthetic hospital wastewater was mentioned earlier by Ouarda et al. [27].

3.6. Cefotaxime (CFD)

CFD belongs to the cephalosporin family (third generation) and is commonly applied against headaches and infections of the respiratory and urinary systems. CFD has been detected in environmental matrices in concentrations ranging from 200 to 10 mg/L [89]. Among the various treatment methods employed for the CFD elimination, such as physical processes (e.g., membrane separation) [90], biodegradation [91], and chemical oxidation processes such as Fenton and UV radiation [92], EOPs arose as a quite effective alternative [93].

Quite remarkable are the works demonstrated by Duan et al. [50–52]. The optimum applied current value was estimated at 20 mA, the optimum distance between the electrodes was 1 cm with an agitation rate equal to 150 rad/min and 1 g/L of Na₂SO₄ as the electrolyte was used to achieve 97.5% CFD degradation efficiency after 60 min of treatment, as shown by Duan et al. [50] in their work published in 2018 investigating the performance of Ti/SnO₂-Cu as an anodic electrode material. The researchers proposed a CFD removal mechanism resulting in the complete mineralization of CFD after the formation of various intermediates. Moreover, Duan et al. investigated the CFD degradation applying oxidation over an innovative CeO₂-ZrO₂/TiO₂/CNT anodic electrocatalytic material [51]. The achieved degradation efficiency was 83.47%, while the initial CFD concentration was 1 mg/L and the applied current density was 3 mA/cm². Increasing the applied current density up to 4 mA/cm² resulted in complete CFD removal. The optimum stirring rate (400 rad/min) and the optimum electrode distance (2 cm) were also obtained in this study and correlated with the degradation efficiency and energy consumption. Furthermore, the unique structural characteristics of carbon nanotubes (CNTs) were studied in an innovative La₂O₃-CuO₂/CNTs anode material towards the CFD electrooxidation [52]. Using an initial CFD concentration of 1 mg/L and an electrolysis time equal to 30 min the optimum conditions applied in order to achieve a 90% CFD removal were 0.8 mA/cm² current density, 1 g/L supporting electrolyte (Na₂SO₄), and 2 cm distance between the anodic and cathodic electrode in an operating volume of 100 mL.

The doping with Ce in multiwalled CNTs (MWCNTs) was studied as a possible anode electrode for the electrooxidation of CFD by Hu et al. [53]. Complete degradation of CFD was obtained applying mA/cm² current density, 1 cm distance between the electrodes, 1 g/L Na₂SO₄ for 60 min, while the initial CFD concentration was 1 mg/L. Finally, the electrochemical oxidation of CFD was examined over a synthesized Ti/TiO₂/SnO₂-Sb-Cu

anode electrode by Li et al. [54]. The different electrode's removal efficiency was 97.65% and 81.87% after 20 cycles of continuous usage. The optimum current density, pH value, electrode distance, and supporting electrolyte concentration were equal to 1.25 mA/cm², 6, 6.4 cm, and 1 g/L, respectively, for the decomposition of 5 mg/L CFD.

3.7. Ciprofloxacin (CFX)

CFX is a third-generation fluoroquinolone (antibiotic) with an enhanced antibacterial activity and relatively stable in the environment [56]. The latter makes its degradation a process of high emergency. Researchers investigated various treatment methods to eliminate CFX from water bodies such as the Fenton reaction [94] or photodegradation applying UV or xenon lamps [95]. As in the previous cases concerning removing various PhCs using EOPs, the high cost of BDD electrodes limits the use of electrooxidation processes. However, some interesting works concerning the CFX degradation via EOPs were already published.

Mu et al. [56] studied the electrochemical oxidation of CFX employing a Sb-doped SnO₂ anodic electrode. The optimal experimental conditions for the complete removal of 30 mg/L CFX after 60 min were experimentally determined (current density: 20 mA/cm², supporting electrolyte (Na₂SO₄) concentration: 25 g/L, pH value: 3). The synthesized electrode, which was subjected 16 times in a coating operation, exhibited the highest performance towards CFX oxidation.

A flow reactor equipped with a Ti-Pt/ β -PbO₂ anode electrode was studied towards the electrochemical removal of 50 mg/L CFX using 0.1 M Na₂SO₄ as the supporting electrolyte by Wachter et al. [57]. Complete CFX removal was achieved after 2 h of treatment, where after 5 h, the TOC removal was equal to 75%. The latter efficiencies were obtained using an applied current density of 30 mA/cm², a pH value of 10, a flow rate adjusted at 6.5 L/min, while the operational temperature was equal to 25 °C.

Nevertheless, the CFX, COD, and TOC removal efficiencies were equal to 99.5%, 86%, and 70%, respectively, and were obtained for the treatment of 50 mg/L CFX applying a current density of 30 mA/cm² and 120 min electrolysis time as demonstrated by Wang et al. [58] in their work, where they studied the SnO₂-Sb/Ti as a potential anodic material. Finally, the presence of sulfates facilitated the electrochemical removal of CFX, as noted in the case of SMX earlier in a study presented by Lan et al. [30]. Moreover, Lan et al. in another study, found that the presence of SMX and CFX did not affect the latter's degradation [55].

3.8. Other PhCs

Except for the above seven PhCs, numerous other drugs are studied as it concerns their degradation by EOPs. Some recent scientific works focusing on EOPs for the removal of other PhCs are presented below.

Al-Qaim et al. [96] investigated the electrochemical degradation of caffeine employing a graphite-PVC anode electrode material. It was found that the co-presence of H₂O₂ with NaCl has a negative impact on the oxidation rate. Brocenschi et al. [97] studied the electrochemical degradation of estrone using a BDD anode electrode. The highest removal efficiency for 500 µg/L estrone was achieved using 0.1 M Na₂SO₄ as the supporting electrolyte, and using 10 mA/cm² of applied current density. Moreover, optimum results were obtained for a pH value equal to 7 and 2 L/min flow rate. The electrochemical removal of omeprazole was investigated by Cavalcanti et al. [98] in an electrochemical cell equipped with Pt or BDD as the anode electrode. The superior performance towards the electrooxidation of omeprazole was confirmed in the case of the latter.

The BDD anode electrode material was also studied concerning the electrochemical degradation of norfloxacin [99] and cephalexin [100] by Coledam et al. The complete removal of norfloxacin was obtained by applying 10 mA/cm² at 40 °C, whereas the initial norfloxacin concentration was 100 mg/L and the supporting electrolyte (Na₂SO₄) concentration was equal to 0.1 M [99]. The electrochemical degradation of cephalexin was

studied, varying the applied current density and pH values [100]. It was found that the cephalixin removal efficiency depended on both the parameters mentioned above since they affect ROS production.

Da Silva et al. [101] studied the electrochemical oxidation process towards the atenolol removal from aqueous solutions. They found that in the conditions studied, the atenolol electrochemical oxidation happens independently by the applied current density value or the pH value. However, the atenolol oxidation pathway was affected by the above-mentioned parameters. Electrochemical oxidation of naproxen was investigated by Díaz et al. [102] and González et al. [103]. Modified MWCNTs were applied as anode electrode material achieving a removal efficiency of 82.5%, whereas the complete naproxen mineralization was ca. 70% after 20 h of operational time [102]. The BDD anode material was also used for the naproxen electrochemical oxidation [103]. Applying a current density equal to 194 mA/cm², a pH value 10.7, a flow rate equal to 4.1 cm³/min, and a supporting electrolyte (Na₂SO₄) concentration equal to 0.392 M resulted in complete naproxen removal in only 0.305 min.

A graphite electrode was used as anode material for the electrooxidation of 20 mg/L paracetamol by Periyasamy et al. [104]. The researchers observed 90%, 82%, and 65% paracetamol, COD, and TOC removal, respectively after 240 min of reaction with 5.1 mA/cm² applied current density, a pH value equal to 4, and 0.1 M Na₂SO₄. A modified carbon paste electrode was used as anode material employed for the electrochemical oxidation of ranitidine as demonstrated by Pinar et al. [105].

A three-dimensional carbon felt/ β -PbO₂, as well as planar graphite sheet/ β -PbO₂, were used as anode electrode materials for the electrocatalytic removal of the herbicide diuron by Rahmani et al. [106]. Applying the optimized experimental conditions (pH 5.42, applied current density 14.2 mA/cm², and 0.043 M Na₂SO₄) as derived by the RCCD method the superior performance was exhibited by the carbon felt containing material reaching a 98.8% degradation efficiency compared to 74.2% in the case of the graphite sheet containing material after 50 min electrolysis time. The superior performance of the former was also reflected in the obtained energy consumption values, which were equal to 2077 and 3195 kWh/kg_{TOC} for the carbon felt and the graphite sheet, respectively. In addition, the lifetime of the latter was smaller (91 h) than that obtained for the former (115 h). The superior performance of a three-dimensional electrochemical oxidation system using activated carbon as 3D electrode material over a conventional two-dimensional system towards the electrochemical oxidation of amoxicillin was highlighted by Shi et al. [107].

Frontistis et al. [108] examined the electrooxidation of commercial amoxicillin over a BDD anode with particular emphasis on the electrolyte effect. According to the researchers, the presence of NaCl significantly enhanced the removal rate and altered the decomposition mechanism and the identified by-products. Interestingly, *K. pneumoniae* and *E. faecalis* were inactivated by almost 25% in the presence of electrooxidised samples even when the AMX was removed.

The electrochemical oxidation of methyl paraben, chloramphenicol, and iohexol was investigated by Steter et al. [109], Sun et al. [110], and Turkay et al. [111], respectively. The complete mineralization of 100 mg/methyl paraben was obtained after 300 min, under 10.8 mA/cm², and 0.05 M K₂SO₄ applying BDD as the anode electrode material [109].

Frontistis et al. [112] demonstrated the simultaneous use of low-frequency ultrasound and electrochemistry could enhance the degradation of the micropollutant propyl paraben. However, the synergistic ratio *S* was decreased in real matrices as the indirect oxidation that occurred mainly by active chlorine species became the dominant mechanism in environmental matrices.

A 70% removal efficiency of 100 mg/L chloramphenicol was achieved applying 0.1 A current, a pH value equal to 6 using a Ti-Sn/ γ -Al₂O₃ as 3D electrode particles [110]. Various Ti-based anode materials and a Pt/SnO₂ anode material were applied towards the electrooxidation of iohexol, among the examined electrocatalytic systems, Ti/RuO₂ exhibited the highest performance [111]. The investigation of the electronic structure and

the electron density distribution in iohexol revealed the significance of these parameters on the iohexol degradation into fragments.

Frontistis et al. [113] examined the persulfate assisted electrochemical oxidation of ampicillin using BDD. They found that the electro activation of persulfate can significantly increase the ampicillin removal, while the complex nature of real effluents increased the process efficiency due to alteration of the mechanism and the contribution of indirect oxidation inside the bulk solution.

A Ti/SnO₂-Sb/La-PbO₂ material was applied as anode material for the electrocatalytic removal of enrofloxacin by Wang et al. [114]. It was found that by applying 8 mA/cm² current density the TOC degradation rate was equal to 95.1%. The energy cost estimated for the proposed process was equal to 2.1 Wh/L. The electrooxidation of lamivudine was investigated by Wang et al. [115] using a Ti/SnO₂-Sb/Ce-PbO₂ as anode material. The lamivudine removal ranged from 91.4% to 96% during five consecutive experiments implying that the employed electrode was quite stable. This performance was reflected in the obtained rate constants.

Grey cast iron material was used as anodic electrode towards the electrochemical degradation of ethanethiol in alkaline medium (using NaOH) by Wang et al. [116]. Once again, the significance of the applied current density in the electrooxidation (direct and indirect) process was underlined. Indium doped PbO₂ was used as anode electrode towards the electrocatalytic degradation of aspirin from water bodies by Xia et al. [117]. The insertion of indium into the electrocatalytic structure acted beneficially towards the aspirin removal, since the obtained catalytic structure was characterized by a more efficient orientation of the formatted crystallites and smaller size resulting in higher production of ROS and higher oxygen evolution overpotential. In addition, the charge transfer resistance value was reduced, increasing the electrode stability.

4. Conclusions and Future Perspectives

In recent years, the scientific community has shown particular interest in investigating the electrochemical decomposition of pharmaceutical compounds. Many innovative or non-innovative materials have been tested in various operating parameters to eliminate different pharmaceutical compounds. The efficiency of the process is not a one-size-fits-all function. It depends on the nature of the electrode materials and pollutants in question, operating parameters with the role of the applied current standing out, and the significant effect of the aqueous matrix. The latter can change the extent of the destruction and affect the removal mechanism and consequently the observed toxicity. Moreover, major drawbacks of applied EOPs such as: Expensive catalytic materials, low mass transfer rate, low current efficiency, and high energy consumption or formation of intermediates with high toxicity should be considered before an effective treatment. The separate study of several experimental parameters along with the various disadvantages of each process are essential in order to perform an integrated research effort.

In the coming years, searching for new materials with excellent properties such as BDD will continue, leading to a significant increase in efficiency and bringing us one step closer to industrial application. On the other hand, the continuation of the research towards the combination of processes is considered imperative. This combination may either involve biological processes where possible or focus on physicochemical processes. Some directions where the research could be directed in the coming years are:

- The study of three-dimensional electrodes seems to be an exciting strategy to address the limitations of the active surface of the electrodes.
- The further study of the (photo) electrochemical generation of hydrogen peroxide at the cathode, in combination with other processes, such as (Photo) Fenton reaction and UV/H₂O₂, will allow additional reaction mechanisms in the main volume (bulk) of the solution.
- The gradual shift of investigations in the case of mixtures of drugs where the observed results mainly concern toxicity have not been studied in full detail.

- The simultaneous study of the process for the removal of micro-pollutants, pathogens, and organic material in conditions that resemble the tertiary treatment of domestic wastewater or in real effluent.
- Coupling with renewable energy sources and the study of integrated systems on a pilot scale under realistic conditions.

Funding: This research is co-financed by Greece and the European Union (European Social Fund—ESF) through the Operational Programme ‘Human Resources Development, Education and Lifelong Learning 2014–2020’ in the context of the project ‘Development of an innovative biomass-based hybrid electrochemical process for the removal of endocrine disruptors’ (MIS 5050535).

Conflicts of Interest: The authors declare no conflict of interest.

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