



Advanced Oxidation Processes for the Removal of Antibiotics from Water. An Overview

Eduardo Manuel Cuerda-Correa *, María F. Alexandre-Franco and Carmen Fernández-González

Department of Organic & Inorganic Chemistry, University of Extremadura, Avda de Elvas s/n, ES-06006 Badajoz, Spain; malexandre@unex.es (M.F.A.-F.); mcfernan@unex.es (C.F.-G.)

* Correspondence: emcc@unex.es; Tel.: +34-924-489-121

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Abstract: In this work, the application of advanced oxidation processes (AOPs) for the removal of antibiotics from water has been reviewed. The present concern about water has been exposed, and the main problems derived from the presence of emerging pollutants have been analyzed. Photolysis processes, ozone-based AOPs including ozonation, O₃/UV, O₃/H₂O₂, and O₃/H₂O₂/UV, hydrogen peroxide-based methods (i.e., H₂O₂/UV, Fenton, Fenton-like, hetero-Fenton, and photo-Fenton), heterogeneous photocatalysis (TiO₂/UV and TiO₂/H₂O₂/UV systems), and sonochemical and electrooxidative AOPs have been reviewed. The main challenges and prospects of AOPs, as well as some recommendations for the improvement of AOPs aimed at the removal of antibiotics from wastewaters, are pointed out.

Keywords: advanced oxidation processes; antibiotics; photolysis; ozone; hydrogen peroxide; Fenton; heterogeneous photocatalysis; sonochemical oxidation; electrooxidation

1. Introduction.

Water is a natural resource, scarce, and indispensable for human life that also allows the sustainability of the environment. It is an essential part of any ecosystem, both qualitatively and quantitatively. However, water is unevenly distributed in different regions of the world, and its quality is not the same in all of them. For example, more than one-half of the world's major rivers are severely depleted or polluted, so they degrade contaminating ecosystems and threaten the health of living beings. According to WHO and UNICEF data, 780 million people do not have access to drinking water, of which 185 million use surface water to meet their daily needs [1,2].

As noted in the second United Nations report on the development of water resources in the world [3], poor water quality slows down economic growth and can have adverse effects on health and livelihoods. Chemical contamination of surface waters, mainly due to industrial and agricultural discharges, is also a significant health risk in some developing countries. Pollution and industrial waste are endangering water resources, damaging and destroying the ecosystems of the entire world.

In recent decades, one of the biggest concerns in the environmental field is the risk associated with the pollution derived from persistent organic compounds (POPs). POPs are a group of chemical compounds that resist to a different extent the photochemical, chemical, and biochemical degradation, which causes their average life to be high in the environment. As a consequence, many POPs have been detected in low quantities (mg·L⁻¹) in rivers, lakes, and oceans around the world, and even in drinking water [4]. Although the carcinogenic, mutagenic, and bactericidal properties of most POPs remain unknown, there is a great interest in their elimination from the waters to avoid their potential toxic consequences and the possible dangerous effects on the health of living organisms, including humans. Organic pollutants, not just POPs, are responsible for severe damages when they are accumulated in the environment [5].

For a long time, the scientific community has focused its efforts on the study of chemical pollutants that are regulated in different legislations. These include mostly apolar, toxic, persistent, and bioaccumulative pollutants, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), or dioxins. However, in recent years, the development of new and more sensitive methods of analysis has made it possible to detect the presence of other potentially dangerous contaminants, globally referred to as "emerging pollutants". These are defined as previously unknown or unrecognized pollutants, not regulated by legislation, and whose effects on health and environment are not sufficiently known yet. They can be included in various sub-groups: Steroids and hormones, pharmaceutical and personal care products, antiseptics, surfactants, disinfection products, dyes, preservatives, etc. Their presence in the environment is not necessarily new, but concern about its possible consequences is arising since its impact on the different environments is unknown. However, due to their high production, consumption, and continuous introduction into the environment, they do not need to be persistent to cause adverse effects [6].

In the last few decades, advances in analytical methods have allowed the detection of very low concentrations (of the order of ng/L) of various compounds in waters that were not analyzed until now [7]. Even though these so-called emerging compounds are not always subjected to the existing regulations on water quality, their effects on human health and the environment make their elimination convenient [8]. The risk associated with the presence of these pollutants in the environment is not only due to their acute toxicity, but also to their genotoxicity, their capacity to develop resistance in pathogens, and the risk of endocrine alterations due to the continued exposure of aquatic organisms to these contaminants [9]. On the other hand, these products designed to be biologically active can significantly affect fishes and aquatic plants, even at very low concentrations [10]. The synergistic effect of some products on other pollutants is also known.

The degradation of the aquatic environment caused by these pollutants must be prevented [11], and control is particularly challenging due to the wide dispersion of their emission sources ranging from domestic or industrial waste to landfills. Very frequently, due to the demands of their design, they are relatively non-biodegradable compounds. For this reason, the conventional treatment of active sludge, widely used in urban wastewater treatment plants, is insufficient for the elimination of these compounds [12,13].

Therefore, it is necessary to use other technologies for the elimination of these compounds. Within these technologies, advanced oxidation processes (AOPs) have a high application potential, mainly derived from the high reactivity and low selectivity of the hydroxyl radicals. However, the presence of natural organic matter and low concentration of these micropollutants are factors to consider when applying these treatments since •OH radicals oxidize both substrates. Furthermore, the high reaction rate of these radicals with the micropollutants does not necessarily imply greater process efficiency [14].

Among all types of pollutants, a group of recalcitrant compounds is formed by antibiotics (ABs), which are discharged into the aquatic environment in large quantities from industrial activities or excreted by humans or animals. The accumulation of ABs in the environment constitutes a risk for the aquatic flora and fauna and may cause resistance in some bacterial strains. These compounds are tough to degrade, mainly because they tend to have a very complex structure that makes them quite stable and, consequently, poorly biodegradable [15,16]. Hence, the removal of antibiotics from aqueous medium constitutes one of the most significant challenges in the field of water treatment. A wide variety of conventional treatments have been developed to remove pollutants from waters.

These conventional treatments can be classified into three broad groups, namely physical, chemical, and biological treatments. Table 1 summarizes the advantages and disadvantages of these traditional treatments.

	Physical or Physicochemical Treatment	Biological Treatment	Chemical Treatment
Kind of pollutant	Industrial (organic, inorganic, metals)	Industrial and domestic (low concentrations of organic and some inorganic)	Industrial (organic, inorganic, metals)
Methods	Filtration Adsorption Air flotation Extraction Flocculation Sedimentation	Anaerobic Aerobic Activated muds	Thermal oxidation (combustion) Chemical oxidation Ion exchange Chemical precipitation
Advantages	Low cost of capital Relatively safe Easy to operate	Easy maintenance Relatively safe elimination of the dissolved contaminants Easy to operate	High degree of treatment Elimination of the dissolved contaminants
Disadvantages	Volatile emissions High energetic cost Complex maintenance	Volatile emissions Require elimination of residual muds Susceptible to toxins or antibiotics	High costs of capital and operation. Difficult operation

Table 1. Advantages and disadvantages of the different kinds of water treatments.

This conventional approach, hence, makes combined use of physical, chemical, and biological treatments, with the main goal of removing sediments and organic matter that could promote both, the growth of microorganisms, and the eutrophication of water bodies. Moreover, the use of conventional methods is not wholly accepted nowadays because of the high costs and operational problems [17,18]. Also, they are not very efficient for the treatment of persistent or emerging pollutants in water, such as antibiotics, since many of these compounds have complex structures and, therefore, exhibit high chemical stability that hinders their complete degradation. The generation of harmful wastes in these processes is also a significant disadvantage. Consequently, it is necessary to adopt more modern systems such as advanced oxidation processes (AOPs).

The implementation of cleaner production programs framed in the reduction of discharges and polluting effluents, and especially the application of environmentally sustainable technologies in industrial processes, is of the utmost importance nowadays. That is why the use of AOPs technologies is currently under development. AOPs were defined by Glaze et al. [19] as water treatment processes performed at pressure and temperature close to environmental conditions, which involve the generation of hydroxyl radicals in sufficient quantity to interact with the organic compounds of the medium. Wastewater treatment plants (WWTPs) generally do not reach the complete elimination of many contaminants. Therefore, they behave as an important source of release of some polluting products into the environment. The implementation of sustainable technologies is imposed as a possible solution for the recovery of high-quality treated effluent. AOPs are new water purification technologies that have been widely used in the last years due to their versatility and a broad spectrum of applicability [20] and constitute a group of very efficient methods for water and wastewater treatment [21–23].

AOPs include all the catalytic and non-catalytic processes that take advantage of the high oxidizing capacity of the hydroxyl radical (OH), and they differ from each other in the way in which this radical is generated. These processes are mainly based on the "in situ" generation of the hydroxyl radical that reacts rapidly with most organic compounds, except chlorinated alkanes [24]. Thus, such radical is generated in sufficient quantity to interact with organic compounds [4,25]. AOPs can be classified into two broad groups: Homogeneous processes and heterogeneous processes, distinguishing between those that operate with an external input of energy (radiant energy, ultrasonic energy, electrical energy) and those that do not.

Hydroxyl radicals are optimal within the group of powerful oxidants because they meet a series of requirements:

- They do not generate additional waste.
- They are not toxic and have a very short lifetime
- They are not corrosive to pieces of equipment.
- They are usually produced by assemblies that are simple to manipulate.

According to these considerations, AOPs are technologies compatible with the environment and based on them, competitive processes from an economic point of view are being developed. The viability of the AOPs depends on the efficacy of the OH radical, which is the second known species with higher oxidant power after fluorine [4,26] (Table 2).

The OH radical acts in a non-selective manner on organic and organometallic contaminants in the aqueous medium, ideally leading to their complete mineralization to CO₂, water, and inorganic ions [27–31].

Oxidizer	Reduction Reaction	E°/V
Fluorine	$\begin{array}{c} F_2(g) + 2H^+ + 2e^- \rightarrow 2HF \\ F_2(g) + 2e^- \rightarrow 2F^- \end{array}$	3.05
Hydroxyl radical	$OH + H^+ + e^- \rightarrow H_2O$	2.80
Sulfate radical anion	SO_4^- + $e^- \rightarrow SO_4^{2-}$	2.60
Ferrate	$FeO_{4^{2-}} + 8H^+ + 3e^- \rightarrow Fe^{3+} + 4H_2O$	2.20
Ozone	$O_3(g)$ + 2H ⁺ + 2e ⁻ \rightarrow $O_2(g)$ + H ₂ O	2.08
Peroxodisulfate	$S_2O_{8^{2-}}+2e^-\rightarrow 2SO_{4^{2-}}$	2.01
Hydrogen peroxide	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.76
Permanganate (a)	$MnO_{4^-} + 4H^+ + 3e^- \rightarrow MnO_2(s) + 2H_2O$	1.67
Hydroperoxyl radical ^(a)	$HO_2 + 3H^+ + 3e^- \rightarrow 2H_2O$	1.65
Permanganate ^(b)	$MnO_{4^-} + 8H^{\scriptscriptstyle +} + 5e^{\scriptscriptstyle -} \rightarrow Mn^{2\scriptscriptstyle +} + 4H_2O$	1.51
Hydroperoxiyl radical ^(b)	$HO_2 + H^+ + e^- \rightarrow H_2O_2$	1.44
Dichromate	$Cr_2O7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.36
Chlorine	$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	1.36
Manganese dioxide	$MnO_2 + 4H^{\scriptscriptstyle +} + 2e^{\scriptscriptstyle -} \rightarrow Mn^{2 \scriptscriptstyle +} + 2H_2O$	1.23
Oxygen	$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23
Bromine	$Br_2(l) + 2e^- \rightarrow 2Br^-$	1.07

Table 2. Standard reduction potentials in aqueous medium of the most commonly used oxidizing agents.

^(a) Circumneutral or weakly acidic medium; ^(b) Strongly acidic medium.

The OH radical is a highly reactive species, and therefore does not accumulate in the medium but can react efficiently with organic pollutants that are refractory to the action of other oxidants, giving rise to rate constants in the order of 10⁶–10¹⁰ M⁻¹ s⁻¹ [32,33]. The most important advantage of the advanced oxidation processes is that they are respectful of the environment [34].

Hydroxyl radicals can degrade organic or organometallic compounds by three degradation mechanisms, depending on the nature of the compound:

1. Dehydrogenation or abstraction of a hydrogen atom to form water (if the substrate has C-H bonds, e.g., alkanes) and radical R that in the presence of molecular oxygen can generate the peroxyl radical ROO and thus initiate an oxidative sequence that can lead to mineralization, Reactions (1) and (2).

$RH + OH \rightarrow H_2O + R$	Reaction (1)

2. Hydroxylation of the organic compound by the attack of OH in the high electron density sites, adding to the unsaturated bonds of aromatic or aliphatic compounds and initiating a chain of oxidation reactions, Reactions (3)–(6).

$ROO + n(OH/O_2) \rightarrow xCO_2 + yH_2O$	Reaction (3)
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$$ArH + OH \rightarrow ArH(OH)$$
 Reaction (4)

$$ArH(OH) + O_2 \rightarrow [ArH(OH)OO]$$
 Reaction (5)

$$[ArH(OH)OO] \rightarrow ArH(OH) + HO_2$$
 Reaction (6)

3. Charge transfer by oxidation-reduction, causing the ionization of the molecule, Reaction (7).

$$OH + RX \rightarrow RX + OH^{-}$$
 Reaction (7)

The radical mechanisms are complicated so that the oxidation of organic matter by OH radicals involves several types of species and reactions:

1. Initiation reactions during which radical species R are formed, Reaction (1).

$$RH + OH \rightarrow H_2O + R$$
 Reaction (1)

2. Propagation reactions involving radical species R that react with other neutral organic molecules, Reaction (8), or with dissolved oxygen in the solution, Reaction (2).

$$R + R'H \rightarrow RH + R'$$
 Reaction (8)

$$R + O_2 \rightarrow ROO$$
 Reaction (2)

3. Termination reactions where the radicals combine, Reactions (9)–(11).

$$R \rightarrow R - R$$
 Reaction (9)

$$R \rightarrow R - OH$$
 Reaction (10)

$$OH + OH \rightarrow H_2O_2$$
 Reaction (11)

Many AOPs are based on the combination of a strong oxidizing agent (e.g., ozone or hydrogen peroxide) with a catalyst (e.g., transition metal ions or photocatalysts) and/or radiation (e.g., UV or ultrasound).

One of the possible classifications of the AOPs is based on the source of generation of the oxidizing species; that is, the method to generate the hydroxyl radicals. This classification is shown in Table 3, which lists the main types of AOPs: photolytic, based on the use of ozone, based on the use of hydrogen peroxide, photocatalytic, electrochemical, or by ultrasound. The wide variety of available techniques evidences the versatility of AOPs.

In short, the most positive characteristics of the AOPs can be summarized as follows:

- Potential capacity to carry out mineralization of organic pollutants to carbon dioxide and water, and oxidation of inorganic compounds and ions such as chlorides, nitrates, etc.
- Non-selective reactivity with the vast majority of organic compounds, especially attractive to
 avoid the presence of potentially toxic byproducts from the primary pollutants that can be
 originated by other methods that do not achieve complete oxidation.

The main disadvantage of AOPs lies in their high cost due to the use of expensive reagents (for example, H₂O₂) and energy consumption (generation of O₃ or UV radiation). Therefore, the future prospects of these processes include a renewed technology combined with adequate use of kinetic-chemical models.

	Generic Name	Source of OH Radicals	
	Photolysis	UV radiation	
Processes		O3	
	O have d processo	O ₃ /UV	
	O3-based processes	O3/H2O2	
Pro		$O_3/H_2O_2/UV$	
н <u>–</u>		H ₂ O ₂ /UV	
tio 's)	H2O2-based processes	H ₂ O ₂ /Fe ²⁺ (Fenton)	
dаt ОР		H2O2/Fe ³⁺ (Fenton-like)	
xi (A		H2O2/Fe2+/UV (Photo-Fenton)	
0	Heterogeneous	TiO ₂ /UV	
ed	photocatalysis	TiO ₂ /UV/H ₂ O ₂	
nc	Conschemical ovidation	Ultrasounds 20kHz–2MHz (water	
var		sonolysis)	
Аd	Electrochemical	Electricity, 2-20A	

Table 3. A classification of advanced oxidation processes (AOPs) according to the source of •OH radicals.

In the following sections, a bibliographic review dealing with the most important contributions to each of the AOPs summarized in Table 3 is presented. Most of the works referred to have been published in the last decade, although references to papers published in the first decade of the 21st Century have been included, too. On the contrary, references to works published in the 1970s, 1980s, and 1990s have been reduced to a minimum. This paper follows the path of some previously published reviews dealing with the removal of antibiotics in water by AOPs [35–47].

oxidation

In this review, after some preliminary considerations concerning the scarcity and necessity of water worldwide, the concerns on water pollution by persistent pollutants, and the main drawbacks of the use of conventional methods to remove them, an update is presented on the novel approaches for wastewater remediation based on advanced oxidation processes. The main challenges and future prospects of AOPs, as well as some recommendations for the improvement of AOPs aimed at the removal of antibiotics from wastewaters, have been dealt with in the final sections of this work.

2. Photolysis

Photolytic methods for the degradation of pollutants dissolved in water are based on providing energy to chemical compounds in the form of radiation, which is absorbed by different molecules to reach excited states for the time necessary to undergo different chemical reactions. Molecules absorb radiant energy in the form of quantized units called photons, which provides the energy required to excite specific electrons and form free radicals that undergo a series of chain reactions to give the reaction products. These free radicals can be generated by homolysis of weak bonds, or by electronic transfer from the excited state of the organic molecule to molecular oxygen, resulting in the superoxide radical (O_2^{-}), or other chemical reagents such as ozone or hydrogen peroxide (reactions that will be discussed later) so that hydroxyl radicals are produced. These photolytic methods use UV radiation due to the higher energy of their photons as indicated by the Planck's equation:

$$E_{\lambda} = hc/\lambda$$
 ec. (1)

(water electrolysis)

where E_{λ} is the energy of a photon associated with the wavelength (λ) of the radiation; h is the Planck's constant; and c is the speed of light.

Thus, direct photolysis involves the interaction of light with molecules to cause their dissociation into simpler fragments. For this reason, in any process in which UV radiation is used, photolysis could take place. The intensity and wavelength of the radiation or the quantum yield of the compound to be eliminated are factors that influence the performance of the process. As a source of UV radiation, mercury vapor lamps are usually used [48].

Indirect photodegradation is due to oxidation mediated by radicals that are generated when light excites some molecules, commonly known as *photosensitizers*. Dissolved organic matter—particularly humic and fulvic acids—and nitrate ions are two examples of photosensitizers usually found in aquatic environments. It is worth noting that the generation of radicals by sensitizers is a UV light-mediated process and, hence, indirect photodegradation takes place to the detriment of direct photolysis.

The data summarized in Table 4 illustrate the mechanisms and removal efficiencies of the different photolytic processes aimed at abating a wide variety of antibiotics in aqueous solution.

Antibiotic	Mechanism	Maximum Removal Efficiency	Remarks	Reference
Amoxicillin (AMX) Ampicillin (AMP) Piperacillin (PPR) Penicillin V (PNV)	Mainly indirect photolysis	~100% AMX & AMP ~95% PNV ~90% PPR	Photodegradation by sunlight may play a role in the degradation of these antibiotics together with hydrolysis and microbial degradation	[49]
Cefalexin (CFL) Cefradine (CFR) Cefapirin (CFP) Cefazolin (CFZ) Cefotaxime (CFT)	Direct photolysis (CFP, CFZ) Indirect photolysis (CFL, CFR) Direct and indirect photolysis equally (CFT)	86%–89% in all cases	Photo byproducts were found to be less photolabile and more toxic than precursors	[50]
Cefradine (CFR) Cefuroxime (CFX) Ceftriaxone (CFN) Cefepime (CFM)	Direct photolysis (CFN); Indirect Photolysis (CFR, CFX, CFM)	~90% CFM ~80% CFX ~70% CFN ~60% CFR	Abiotic hydrolysis was responsible for the elimination of the cephalosporins. Direct photolysis significantly stimulated the abiotic degradation	[51]
Ceftiofur (CFF) Cefapirin (CFP)	Direct photolysis with some pH-dependent hydrolysis	~96% CFP ~92% CFF	Both compounds are relatively stable under neutral and acid environment, whereas base-catalyzed reactions (pH > 9) led to fast degradation	[52]
Ciprofloxacin (CPR)	Direct photolysis (Photooxidation, defluorination, and cleavage of the piperazine ring)	n.a.	Fast process, particularly at slightly basic pH	[53]
Difloxacin (DFL) Sarafloxacin (SRF)	Direct photolysis	>99% in both cases	SRF is the primary photoproduct of DFL and shows relatively higher persistence	[54]
Enofloxacine (ENF)	Direct and (some) indirect photolysis	Very close to 100%	Self-sensitized fluoroquinolone photooxidation via •OH radicals and singlet oxygen also plausible	[55]

Table 4. Removal efficiency of antibiotics in waters by photodegradation.

Norfloxacin (NRF) Ofloxacin (OFX) Ciprofloxacin (CPR) Enrofloxacin (ENR) Sparfloxacin (SPR) Danofloxacin (DNF) Sulfanilamide (SND) Sulfaguanidine (SGD) Sulfadiazine (SDZ) Sulfamethoxazole (SLF) Sulfathiazole (STZ) Sulfamethizole (STX) Sulfamethizole (SMT) Sulfamethazine (SMZ)	Direct photolysis and collateral processes (e.g., hydrolysis)	>98.5% in all cases	Photo byproducts derived from desulfonation and/or denitrification, as well as hydroxylation of photo- oxidized heterocyclic rings were identified	[56]
Sulfamethoxazole (SLF)	Direct photolysis, hydroxylation, cleavage of the sulfonamide bond and fragmentation of the isoxazole ring	Very close to 100%	Fast process, particularly under acidic pH. Indirect photolysis results in a decrease in degradation rate	[57]
Tetracycline (TTR) Oxytetracycline (OXY) Chlortetracycline(CHL)	Mainly indirect photolysis	89.59% TTR 100% OXY 100% CHL	Effectiveness of the process is lower at higher initial concentrations for all three tetracyclines. Low concentrations of dissolved organic matter in these waters act as a photosensitizer. Higher toxicity of byproducts	[58]
Trimethoprim (TRM) Sulfamethoxazole (SLF)	Direct photolysis (48% for SLF, 18% for TRM) Indirect photolysis (52% for SLF, 82% for TRM)	~90% in both cases	Indirect photolysis is attributable to the production of •OH radicals and triplet excited state organic matter	[59]

It is widely accepted that direct photolysis is a fast process. However, pollutants are removed by direct photolysis to a limited extent. Photosensitizers-mediated processes contribute to improving removal efficiencies.

Among the main advantages of this group of AOPs, it is worth noting that photolysis is a chemical-free treatment that requires relatively low maintenance and operational costs. Moreover, UV has proven its versatility and capacity to promote the cleavage of the chemical bonding of a wide variety of refractory compounds. Hence, the use of UV irradiation in AOPs aimed at the treatment of wastewater is rising in the last years.

However, the use of UV-alone treatments has some crucial limitations. For instance, the occurrence of organic molecules suitable to behave as photosensitizers may also cause an increase in the turbidity of the aqueous media, thus hindering the penetration of UV radiation in the polluted medium. This latter hinders the contribution of indirect photolysis so that the process becomes less efficient.

It should be noted, however, that ultraviolet radiation alone is not usually applied as an advanced oxidation process (AOP). The use of UV irradiation, together with other oxidants, may contribute to the degradation of the parental pollutants as well as that of potentially harmful byproducts [60,61]. Furthermore, most of the low-pressure UV lamps that are commercially available emit approximately 5% of the radiation of a wavelength close to 185 nm, which produces ozone in the reactor. Hence, UV has been widely used combined with oxidizing agents such as ozone or hydrogen peroxide to enhance the generation of hydroxyl radicals, as will be exposed in the next sections of this work.

In general, direct photolysis is less effective in the degradation of pharmaceuticals present in wastewaters and also requires more energy than, for example, ozonation [62]. Hence, in the next section, advanced oxidation processes based on the use of ozone are presented.

3. Ozone-Based AOPs

Ozone is a powerful oxidizing agent capable of reacting with a large number of organic and inorganic compounds. Its high oxidation potential ($E^\circ = 2.08$ V, see Table 2) and the absence of the formation of dangerous byproducts during the process have increased the importance of this technique in water treatment during the past decades. The main drawback is the need to generate ozone from oxygen, for which an electric discharge over a stream of air or pure oxygen is used. This step consumes large amounts of energy, thus handicapping the scaling of the process.

3.1. Ozonation

The mechanism of oxidation by ozone is a complex process that takes place in two ways: Direct reaction with dissolved ozone (O₃) or indirect oxidation through the formation of radicals (·OH). The extension of both mechanisms throughout the degradation of a compound depends on factors such as the nature of the contaminant, the dose of ozone, or the pH of the medium. Normally, under acidic conditions (pH < 4) direct ozonation prevails, Reaction (12):

$$3O_3 + OH^- + H^+ \rightarrow 2 OH + 4O_2$$
 Reaction (12)

On the contrary, at pH > 9, the indirect route is the most important one. As a rule, degradation rates in ozonation processes increases as pH does, since high pH favors ozone decomposition into free radicals as shown in Reaction (13). Other chemical reactions involved in the indirect oxidation with ozone are as follows:

$O_3 + OH^- \rightarrow O_2 + HO_2^-$	Reaction (13)
$O_3 + HO_2^- \rightarrow HO_2 + O_3^-$	Reaction (14)
$HO_2 \rightarrow H^+ + O_2^-$	Reaction (15)

$O_2^- + O_3 \rightarrow O_2 + O_3^-$	Reaction (16)
$O_3^- + H^+ \rightarrow HO_3$	Reaction (17)
$HO_3 \rightarrow HO + O_2$	Reaction (18)

Under alkaline conditions, however, a fast side-reaction must be taken into account:

$$HO + O_3 \rightarrow HO_2 + O_2$$
 Reaction (19)

This latter reaction results in a rapid generation of hydroperoxyl radicals ($E^{\circ} = 1.65V$) to the detriment of the \cdot OH radicals ($E^{\circ} = 2.80$ V) and leads to a decrease in the oxidation ability.

Table 5 lists some selected papers dealing with conventional ozonation treatments of a wide variety of antibiotics, indicating the aqueous matrix and the main experimental conditions.

Antibiotic	Matrix	Operation Conditions	Maximum Removal Efficiency	Remarks	Reference
Amoxicilin (AMX)	Deionised water	0.16 mM O ₃ 2.5 < pH < 7.2	~90%	Fast process, low mineralization degree	[63]
Amoxicilin (AMX)	Formulation washwater	57.5 mM O₃ 3 < pH < 11.5	100%	Complete removal after 40 min treatment at pH = 11.5	[64]
Amoxicillin (AMX) Doxycycline (DXY) Ciprofloxacin (CPR) Sulphadiazine (SDZ)	Deionized water	0.003–1.5 mM O ₃ pH = 6.8	70% AMX 92%–98% for DXY, CPR, and SDZ	Maximum removal achieved for 1.5 mM O3	[65]
Azithromycin (AZT) Clarithromycin (CLR) Roxithromycin (RXT)	Spiked WWTP effluent	0.01–0.1 mM O ₃ pH = 7	~99%	Excellent removal efficiencies above 0.042 mM O ₃	[10]
Ciprofloxacin (CPR)	Deionized water	52 mM O₃ 3 < pH < 10	95%	O ₃ supply rather than reaction kinetics is rate limiting. Desethylene-CPR was identified as the major CPR degradation product	[66]
Ciprofloxacin (CPR) Erythromycin (ERY) Metronidazole (MTR) Trimethoprim (TRM)	Spiked STP effluent	0.145 mM O ₃ pH = 7	100% CPR 94% ERY 100% MTR 94% TRM	Ozonation treatment was successfully used to improve conventional STP treatments	[67]
Clarithromycin (CLR) Erythromycin (ERY) Roxithromycin (RXT)	Spiked STP effluent	0.1-0.3 mM O_3 pH = 7.2	76% (CLR) 92% (ERY) 91% (RXT) Below limit of quantification in all cases	Hydroxylated antibiotics should not further promote the formation of antibiotic-resistant strains	[68]

Table 5. Removal efficiency of antibiotics in waters by ozonation.

Clarithromycin (CLR)	Distilled water	0.05 mM O ₃ 3.2 < pH < 4.4	100%	High rate of reaction. Antibiotics fully eliminated even at a low ozone dose	[69]
Flumequine (FLM)	Ultrapure water	140.6 mg O3 L ⁻¹ (in gas phase) 3 < pH < 11	~100%	Hydroxylation, decarboxylation and defluorination were mainly involved in the FLM ozonation. Removal efficiency increases with increasing pH	[70]
Lincomycin (LNC)	Distilled water	0.06-0.10 mM O3 2 < pH <9	~100%	Fast process, particularly at neutral pH	[71]
Lincomycin (LNC)	Distilled water	0.4 mM O ₃ 5.5 < pH < 7.5	~100%	Total removal achieved in 2 min	[72]
Ofloxacin (OFX) Trimethoprim (TRM) Norfloxacin (NRF) Ciprofloxacin (CPR)	Ultrapure water	0.09 mM O ₃ pH = 7	~100%	All drugs completely removed within 10 s	[73]
Oxytetracycline (OXY)	Ultrapure water	0.23 mM O₃ 3 < pH < 7	100%	Removal efficiency increases with increasing pH. Complete removal in 20 min	[74]
Roxithromycin (RXT)	Spiked lake, river and well water	0.002–0.042 mM O ₃ pH = 8	>90%	Remarkable influence of water matrix on ozone stability, formation of radicals and scavenging	[75]
Spectinomycin (SPC)	Distilled water	0.06-0.10 mM O3 2 < pH <9	~100%	Fast process, particularly at neutral pH	[71]
Sulfadiazine (SDZ) Sulfamethozaxole (SLF) Sulfapyridine (SLP) Sulfathiazole (STZ)	Spiked WWTP effluent	0.01–0.1 mM O ₃ pH = 7	99%	Excellent removal efficiencies above 0.042 mM O ₃	[10]
Sulfadiazine (SDZ) Sulfamethoxazole (SLF) Sulfathiazole (STZ) Sulfamethizole (SMT)	Deionized water	0.02–0.067 mM O ₃ 2 < pH < 10	~100%	Complete removal from contaminated water. Increasing the pH from 2.0 to 10.0 resulted in enhanced removal of the sulfonamides	[76]
Sulfamethoxazole (SLF)	Spiked lake, river and well water	0.002-0.042 mM O ₃ pH = 8	>90%	Remarkable influence of water matrix on ozone stability and formation of radicals.	[75]

Trimethoprim

(TRM)

Sulfamethoxazole (SLF)	Spiked STP effluent	0.1–0.3 mM O ₃ pH = 7.2	92% Below limit of quantification	Hydroxylated antibiotics should not further promote the formation of antibiotic-resistant strains	[68]
Sulfamethoxazole (SLF)	Distilled water	3.125–31.25 mM O ₃ 3 < pH < 11	100%	Removal efficiency increases with increasing pH. Complete removal in 60 min, 31.25 mM O ₃	[77]
Sulfamethoxazole (SLF) Chlortetracycline (CHL)	Distilled water	O ₃ concentration not provided pH = 4.63 (SLF) or 4.33 (CHL)	~100%	Total degradation achieved after 90 min. CHL was more quickly oxidized than SLF	[78]
Triclosan (TRC)	Ultrapure water	0.04 mM O ₃ pH = 7	~100%	2,4-dichlorophenol, chlorocatechol, mono- hydroxy-TRC, and dihydroxy-TRC were the main byproducts. Increasing O ₃ concentrations leads to decreased concentration of TRC and byproducts	[79]
		0.1–0.3 mM		Hydroxylated antibiotics should not	

If O_3 mediated oxidation is performed under acidic or near-neutral pH, the degradation of the pollutants mainly takes place through direct reactions between O_3 and the organic molecules. The main targets of ozone attack are -C = C- or -N = N- double bonds.

85%

further promote the

formation of

antibiotic resistant strains [68]

Several operational parameters strongly influence the formation of O_3 and its subsequent transformation into $\cdot OH$ radicals. Among these parameters, the chemical structure and concentration of the pollutant, the quality of the effluent, pH (as indicated above), and temperature must be taken into consideration. The main advantages of ozonation are:

(i) The volume of effluent remains constant along the process and sludge is not formed,

O3

pH = 7.2

(ii) Installations are relatively simple and require only a little space,

Spiked STP

effluent

- (iii) O₃ is generated in situ, so that no stock solutions of H₂O₂, iron salts, or other chemicals are needed on-site,
- (iv) It can be applied even if the effluent fluctuates both in terms of flow rate and/or composition and
- (v) O₃ remnants can be eliminated as ozone tends to decompose into oxygen.

As indicated above, the main inconvenience is the relatively high cost of equipment and maintenance, together with the high requirements of energy that must be supplied to carry on the process.

Another key point to be taken into consideration is the necessity to ensure an adequate mass transfer. It must be born in one's mind that O₃ molecules must be transferred from the gas phase to the liquid phase so that the attack on the chemical bonds of the organic molecules may occur. Very frequently, the mass transfer may be regarded as the limiting step of the process. An inadequate mass

transfer can negatively affect the removal efficiency of the process and, hence, result in increasing the operating costs. An adequate reactor design helps to avoid this critical drawback of ozonation, as will be discussed later.

Furthermore, if high levels of bromide ions are present in the effluent, ozonation can lead to the generation of bromate, which has been proved to act as a carcinogen [80].

The ozonation treatment can be improved by coupling with hydrogen peroxide and/or UV (O₃/UV, O₃/H₂O₂, or O₃/H₂O₂/UV processes). The next sections are devoted to these binary or ternary systems.

3.2. The O₃/UV System

Ozonation alone poses several advantages over conventional chemical oxidants such as chlorine or chlorine dioxide; however, it does not generate enough concentration of hydroxyl radicals to degrade organic compounds until total mineralization. This latter is due to the low value of the kinetic constant of the direct ozone-pollutant reaction. Hence, the concentration of hydroxyl radicals generated by decomposition of the ozone is insufficient, unless the pH of the medium rises, which would imply the use of external chemical agents. In short, higher concentrations of these radicals are required for the reduction of the pollutants.

The O₃/UV combination generates large concentrations of hydroxyl radicals in a fast manner so that this technique is adequate for this type of mineralization processes. Therefore, ozonation in the presence of UV irradiation has become one of the most used AOPs for the degradation of organic compounds in general as acids, alcohols, and organochlorines of low molecular weight (dihalomethanes, trihalomethanes, etc.). Another essential advantage of the combined use of UV and O₃ is the fact that the generation of bromate is inhibited.

The molar extinction coefficient of O_3 is 3300 M⁻¹·cm⁻¹. Ozone strongly absorbs UV light of wavelength λ = 254 nm. To explain the generation of hydroxyl radicals from O_3 , a two-stage process has been proposed. In the first stage, the photoinduced homolysis of the ozone molecule takes place, Reaction (20), and in the second stage, the production of hydroxyl radicals as a consequence of the reaction of atomic oxygen O (¹D) with water, Reaction (21), takes place [81]:

$$O_3 + h \rightarrow O_2 + O(^1D)$$
 Reaction (20)

$$O(^{1}D) + H_{2}O \rightarrow 2HO$$
 Reaction (21)

However, the hydroxyl radicals recombine generating hydrogen peroxide; therefore, the photolysis of ozone in solution can be represented by Reaction (22).

Hν

$$O_3 + H_2O \rightarrow [2 OH] + O_2 \rightarrow H_2O_2 + O_2$$
 Reaction (22)

The H₂O₂ molecules generated in this latter reaction may undergo different chemical reactions in the presence of ozone as follows [82]:

 $O_2 \rightarrow O_3 \rightarrow O_2 + O_3$

$H_2O_2 \rightarrow HO_2^- + H^+$	Reaction (23)
$HO_2^- + O_3 \rightarrow HO_2 + O_3^-$	Reaction (24)

$$HO_2 \rightarrow O_2 \rightarrow H^+$$
 Reaction (25)

Reaction (26)

- $O_3 \rightarrow H^+ \rightarrow HO_3$ Reaction (27)

$$HO_3 \rightarrow HO \rightarrow O_2$$
 Reaction (28)

Next,

$$R \rightarrow ROO$$
 Reaction (2)

Peyton and Glaze [81] suggest that initiation may occur either by the reaction of ozone with the HO^{-} or HOO^{-} species or by the photolysis of hydrogen peroxide. The reaction with water of the radical anion ozonate, O_{3}^{-} is rapid, Reaction (29). The spontaneous decomposition of the ozonate has also been proposed [83], Reaction (30).

$$O^- + H_2O \rightarrow OH + HO^-$$
 Reaction (29)

$$O_3 \rightarrow O_2 + O^-$$
 Reaction (30)

Hence, as described in Reaction (1), the hydroxyl radicals react with the organic substances, and the kinetics of the process is speeded up by the presence of UV radiation. Of course, as indicated in the previous section, UV light itself can degrade some compounds by direct photolysis. Moreover, UV radiation can excite the organic molecules of the pollutant, increasing their susceptibility towards an attack by the hydroxyl radicals.

Nevertheless, since both UV and ozone are quite expensive to generate and need the consumption of large amounts of electric energy, there are relatively few works in the literature devoted to the study of the removal of pollutants by O₃/UV processes in comparison with other UV-or ozone-based systems. Table 6 summarizes some research works dealing with the removal of several antibiotics by the O₃/UV process.

Antibiotic	Matrix	Operation Conditions	Maximum Removal Efficiency	Remarks	Reference
Amoxicillin (AMX)	Ultrapure water	O ₃ flow:16 mg·h ⁻¹ T = 20 °C Low-pressure mercury vapor lamp (λ = 254 nm)	~100%	Synergistic effect of direct ozonation, direct photolysis, and hydroxyl radical oxidation. ·OH radicals generated in the photolysis of O ₃	[84]
Azithromycin (AZT) Norfloxacin (NRF) Ofloxacin (OFX) Roxithromycin (RXT)	Ultrapure water WWTP effluent	0.08 mM O ₃ T = 20 °C Low-pressure mercury vapor lamp (λ = 254 nm)	≥98% (water) >87% (effluent)	Synergetic effect between O3 and UV irradiation	[85]

Table 6. Removal efficiency	of antibiotics in wate	ers by the O ₃ /UV process
-----------------------------	------------------------	---------------------------------------

Azithnomia						
$(\Delta 7T)$						
Ciprofloyacin						
(CPR)						
Clarithromycin			CPR SI M			
(CLR)			LNC NLD			
Frythromycin		Pilot-scale	SLE IVE			
(FRV)		nlant	FRV and	31 out of 38		
Levofloxacin		0.02-0.12 mM	TRM below	PPCPs		
(I VF)		O_2	detection	detected in the		
Lincomycin	ММТР	Room	limit (LOD)	secondary		
(INC)	offluont	temperature	$CIR \ A7T$	offluent were	[86]	
Nalidivic acid	ennuent	I ow-pressure	and RXT	degraded to or		
(NILD)		mercury yapor	inconsitivo	below their		
Rovithromycin		lamp ($\lambda = 254$	or very			
(RXT)		nm)	stable in the	LOD		
Sulfadimethoxine		iiii)	$\Omega_2/I IV$			
(SI M)			process			
Sulfamethoxazole			process			
(SLF)						
Trimethoprim						
(TRM)						
()		2–20 mM O ₃				
		Medium-		O3-based		
Ciprofloxacin		pressure (MP)		processes more		
(CPR)	Ultrapure	polychromatic	~100%	efficient than	[87]	
Trimethoprim	water	UV lamp		UV-based		
(TRM),		$(\lambda = 200 - 300)$		processes		
		nm)		1		
		,		Abatement		
	anoun deseter	I our process		efficiencies		
	groundwater	Low-pressure		only		
Chloramphenicol	surface	mercury vapor	> 000/	moderately	1001	
(CHL)	water	$lamp (\Lambda = 254)$	>90%	increased	[88]	
	WWIP	nm)		compared to		
	effluent	pH = 8.0–8.2		conventional		
				ozonation		
		0.03 mM O ₃				
		High-pressure		Complete		
Sulfamethoxazole	Ultrapure	mercury lamp	~100%	removal	[80]	
(SLF)	water	$(\lambda = 313 \text{ nm})$	100 /0	achieved in 10	[۲۵]	
		Room		min		
		temperature				

The literature review suggests that the use of UV light combined with O3 increases the removal efficiency of refractory pollutants. This fact is attributable to the photolysis-mediated generation of larger amounts of ·OH radicals. However, the economic viability of this method is limited because of the remarkable energy requirement for the production of O3 and UV light.

3.3. The O_3/H_2O_2 System

The direct action of ozone on certain typical water pollutants is advantageous, as discussed above, due to its ability to degrade high molecular weight electron-rich organic compounds. However, the decomposition of these large molecules usually gives rise to the generation of low molecular weight byproducts that may be refractory or recalcitrant towards both further ozone oxidation or degradation through ·OH radical-mediated pathways. Hence, it is possible that though the primary pollutants are entirely degraded by single ozonation, the degree of mineralization can be deficient [77]. This is, perhaps, the most critical disadvantage of the use of single ozonation as an AOP, since these low molecular weight byproducts may exhibit more acute toxicity than the primary pollutants. The concomitant use of hydrogen peroxide in ozonation may help to improve the process efficiency, since the reaction of O_3 with H_2O_2 results in the generation of OH radicals. The O_3/H_2O_2 combined oxidation system (commonly known as "peroxone") produces higher conversion yields than ozonation in those cases in which the direct ozone-pollutant reaction follows a slow kinetic regime due to gas-liquid matter transfer problems. Under these circumstances, an advanced oxidation process such as the one that can be achieved by adding a small amount of hydrogen peroxide to the aqueous solution through which ozone is being bubbled is convenient [90].

Hydrogen peroxide in aqueous solution is partially dissociated into its conjugate base, the hydroperoxide ion (HO₂⁻), according to Reaction (23). Hydroperoxide ions react with ozone causing its decomposition, Reaction (24), and giving rise to a series of chain reactions in which the hydroxyl radical is involved [32]. Such reactions are much the same as indicated above as Reactions (25)–(28). Furthermore, ozone can react with hydroxyl radicals, Reaction (31), giving rise to more hydroperoxide ions that can further react with ozone, thus making the process continue. This way, the pollutant dissolved in water is susceptible to undergo oxidation through two simultaneous routes: The direct route (molecular reaction with ozone) or the indirect radical pathway (reaction with the hydroxyl radical).

$\mathrm{H_2O_2} \rightarrow \mathrm{HO_2^-} + \mathrm{H^+}$	Reaction (23)
$\mathrm{HO}_{2^{-}} + \mathrm{O}_{3} \rightarrow \mathrm{HO}_{2^{-}} + \mathrm{O}_{3^{-}}$	Reaction (24)
$HO_2 \rightarrow H^+ + O_2^-$	Reaction (25)
$O_2^{-} \cdot + O_3 \rightarrow O_2 + O_3^{-}$	Reaction (26)
$O_3 - H \to HO_3$	Reaction (27)
$\mathrm{HO}_3 \longrightarrow \mathrm{HO} + \mathrm{O}_2$	Reaction (28)
$\mathrm{HO} \cdot + \mathrm{O}_3 \rightarrow \mathrm{HO}_2 \cdot + \mathrm{O}_2$	Reaction (31)

Additionally, ozone may also react directly with hydrogen peroxide and more hydroxyl and ozonate radicals are generated:

$$2 \text{ H}_2\text{O}_2 + \text{O}_3 \rightarrow 2 \text{ HO} + \text{O}_3^{-}$$
 Reaction (32)

Some selected results obtained in the O₃/H₂O₂ process are listed in Table 7.

Table 7. Removal efficiency of antibiotics in waters by the O₃/H₂O₂ process.

Antibiotic	Matrix	Operation Conditions	Maximum Removal Efficiency	Remarks	Reference
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Amoxicillin (AMX)	Ultrapure water Reservoir water Groundwater, Two secondary WWTP effluents	O ₃ flow: 16 mg·h ⁻¹ H ₂ O ₂ = 10 μM T = 20 °C	~100% in all cases	O ₃ /H ₂ O ₂ process leads to the highest rate constants. Degradation rate higher in the UP. Dissolved organic matter results in slower degradation process	[84]
Ciprofloxacin (CPR)	Ultrapure water	O3 = 0.1 mM H2O2 = 2– 990 μM	95% degradation reached after 60–75 min	No effect of temperature (6.0–62.0 °C). Low [H2O2] (2– 50 μM) increased CPR degradation Large concentrations (990 μM) decreased degradation rates at pH 7	[91]
Ciprofloxacin (CPR)	WWTP effluent	$O_3 = 0.23$ mM $H_2O_2 = 20$ mM 0.15 mL H_2O_2 (30% w/v) injected every 5 min	>99% after 5 min >99.5% after 10 min	High degree of mineralization (>90%)	[92]
Levofloxacin (LVF)	Ultrapure water	$O_3 = 0.1 \text{ mM}$ $H_2O_2 = 2-$ $100 \ \mu\text{M}$ pH = 3-10	95% (40 min) 99% (50 min)	Strong influence of pH on levofloxacin degradation rate and reaction pathways H2O2 addition had only a limited effect	[66]
Metronidazole (MTR)	WWTP effluent	$ \begin{array}{r} O_3 = 0.23 \\ mM \\ H_2O_2 = 20 \\ mM \\ 0.15 mL \\ H_2O_2 (30\% \\ w/v) \\ injected \\ every 5 min \end{array} $	>92% after 5 min	Low molecular weight carboxylates (mostly oxalates) as the final product	[92]

Sulfamethoxazole (SLF)	Ultrapure water Spiked WWTP effluent	$O_3 = 0.42$ mM $H_2O_2 = 5$ mM	~100%	Water matrix has no significant impact on SLF removal. Total	[93]
			~100%	removal. Total degradation achieved in 45 min	[93]

Researchers agree that the O_3/H_2O_2 system is highly effective in achieving fast and complete mineralization of recalcitrant organic pollutants that can be found in wastewaters. The addition of H_2O_2 accelerates O_3 decomposition and the subsequent formation of $\cdot OH$ radicals. This, in turn, makes the overall process faster since the reaction rate constant of the hydroxyl radical (i.e., 10^6-10^9 M⁻¹ s⁻¹) is several orders of magnitude higher than that of O_3 .

3.4. The O₃/H₂O₂/UV System

In the $H_2O_2/O_3/UV$ system, there is a wide variety of individual processes that can give rise to the generation of $\cdot OH$ radicals. Hence, this ternary system can be considered as the result of the integration of different unitary or binary systems, namely:

- (a) Direct photolysis.
- (b) Ozonation alone.
- (c) UV photolysis of O₃.
- (d) The combined effect of O_3 and H_2O_2 .
- (e) UV photolysis of H₂O₂.

The methods (a) to (d) have been considered in previous sections of this work, whereas the UV photolysis of hydrogen peroxide will be dealt with in depth in Section 4.1.

All these processes result in the formation of \cdot OH radicals through a sequence of reactions that directly or indirectly are related to the formation of (and/or the reaction with) H₂O₂ as suggested by reactions

Hν

$$O_3 + H_2O \rightarrow [2 \text{ OH}] + O_2 \rightarrow H_2O_2 + O_2$$
 Reaction (22)
2 $H_2O_2 + O \rightarrow 2 \text{ HO} + O_3^-$ Reaction (32)

among others.

The main advantage of the ternary $O_3/H_2O_2/UV$ system lies in the fact that the decomposition of ozone is speeded up by the simultaneous presence of hydrogen peroxide and UV irradiation, thus yielding an increased rate of generation of \cdot OH radicals. Furthermore, it can also be applied under mild conditions (namely, atmospheric pressure and room temperature). However, the high costs of the three elements that constitute the system (i.e., ozone, hydrogen peroxide, and UV light) pose a remarkable disadvantage that limits a broader use of this process. Consequently, the use of this ternary system is usually restricted to the treatment of highly polluted effluents to achieve adequate degradation and mineralization of recalcitrant pollutants.

Some examples of the use of the $O_3/H_2O_2/UV$ system in the removal of antibiotics are summarized in Table 8.

Table 8. Removal efficiency of antibiotics in waters by the O₃/H₂O₂/UV process.

Antibiotic	Matrix	Operation Conditions	Maximum Removal Efficiency	Remarks	Reference
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Berberine (BRB)	Synthetic & real wastewater spiked with 1500 mg/L of BRB	$H_2O_2 = 0.5-4.0$ mM Low-pressure mercury vapor lamp ($\lambda = 254$ nm) pH = 5-11	94.1%	Performance of the process mainly relied on the H2O2 and O3 dosages, water alkalinity, and contact time	[94]
Chlortetracycline (CHL)	Livestock wastewater	$O_3 = 0.012 \text{ mM}$ $H_2O_2 = 0-5.9 \text{ mM}$ Low-pressure mercury vapor lamp ($\lambda = 254$ nm) pH = 8.5	100% in less than 15 min	Complete mineralization not achieved	[95]
Ciprofloxacin (CPR) Trimethoprim (TRM)	2.5 mM phosphate buffer saline (PBS) at pH 7	$O_3 = 0.1 \text{ mM}$ $H_2O_2 = 0.05-0.1 \text{ mM}$ Medium- pressure (MP) polychromatic UV lamp (λ =200-300 nm)	>90%	Larger contribution of O3-mediated degradation pathways (O3 for TRM and O3/H2O2 for CPR). UV contributes to a lesser extent	[87]
Penicillin G (PNG)	Ultrapure water	$O_3 = 0.03 \text{ mM}$ $H_2O_2 = 3 \text{ mM}$ Low-pressure mercury vapor lamp ($\lambda = 254$ nm)	~80% in 30 min	O3 alone was very effective A complete degradation or mineralization was not achieved	[96]
Sulfamethoxazole (SLF)	Spiked ultrapure and tap water	$O_3 = 0.04 \text{ mM}$ $H_2O_2 = 1 \text{ mM}$ Low-pressure mercury vapor lamp ($\lambda = 254$ nm) pH = 3-10	100%	100% removal obtained in O3/UV system	[97]

4. Hydrogen Peroxide-Based AOPs

Hydrogen peroxide is a safe, abundant, and easy to use chemical reagent, widely used for the prevention of contamination. However, H₂O₂ itself does not exhibit good oxidizing properties and must be combined with other substances or catalysts to become more effective. The combined use of H₂O₂ with ozone has been described under Section 3.2. Hydrogen peroxide can be used in combination with the UV radiation but has also been widely applied together with Fe²⁺ and/or Fe³⁺ ions giving rise to the well-known Fenton and Fenton-like processes. Finally, a ternary combination of UV irradiation, H₂O₂, and Fe²⁺/Fe³⁺ ions, commonly known as the "Photo-Fenton process," has been broadly reported in the literature. In the next sections, these processes will be described in some detail.

Ultraviolet radiation has been widely used for the treatment of water and wastewater around the world and has more and more applications in this field. Numerous studies show that this treatment is useful for the elimination of pharmaceuticals found in different types of surface water [59,98,99]. However, this technology is only applicable to waters containing photosensitive compounds and with low levels of COD (for example, river and drinking water) [41]. On the other hand, effluents from sewage treatment plants may contain high concentrations of organic compounds that can inhibit the process [100]. In these cases, UV/H₂O₂ is a particularly attractive alternative for the removal of organic molecules that exhibit low reactivity towards ozone and hydroxyl radicals, but that are markedly photoactive.

The UV/H2O2 system takes advantage of the joint action of two chemical processes, namely

- (a) The UV photolytic ability (regardless it is direct or indirect),
- (b) The reaction of the dissolved pollutants with the ·OH radicals generated in the homolytic cleavage of the O-O bond in H₂O₂.

It can be stated that the photolysis of an organic compound in aqueous solution catalyzed by the presence of hydrogen peroxide is a very complex process. The success of the H₂O₂/UV system lies in the stoichiometric formation of hydroxyl radicals (·OH) from the photocatalytic decomposition of H₂O₂ in the first stage of the photolytic degradation [101]:

Hν

$$H_2O_2 \rightarrow 2 \text{ OH}$$
 Reaction (33)

The quantum yield of this process is very high, forming a maximum of two hydroxyl radicals as absorbed, and invariable with the applied wavelength [102].

Next, a series of radical reactions takes place:

$$H_2O_2 + OH \rightarrow HO_2 + H_2O$$
 Reaction (34)

$$H_2O_2 + HO_2 \rightarrow OH + O_2 + H_2O \qquad \text{Reaction (35)}$$

$$2 \text{ HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$$
 Reaction (36)

$$OH + HO_2 \rightarrow H_2O_2 + O_2$$
 Reaction (37).

From Reactions (34)–(37) it becomes evident that although the photolytic cleavage of hydrogen peroxide gives rise to the formation of \cdot OH radicals (Reaction (33)), the occurrence of high concentrations of H₂O₂ may have a scavenging effect on the hydroxyl radicals and, hence, may hinder the effectiveness of the oxidation process. Consequently, the H₂O₂ initial concentration must be carefully adjusted to maximize the efficiency of the removal process. Moreover, H₂O₂ is an expensive reagent that increases the total operating costs of the process [103].

Once the highly reactive \cdot OH radicals are formed, they react with the organic compound by different mechanisms: Abstraction of a hydrogen atom, addition to C=C double bonds, or electron transfer, depending on the nature and functional groups of the molecule. The most general reaction route is the abstraction of a hydrogen atom and the generation of the resulting organic radical R \cdot , which in turn reacts rapidly with dissolved O₂ to form the peroxide organic radical RO₂·[21]. These organic radicals decompose by bimolecular reactions giving rise to the different degradation products of the starting compound together with other byproducts such as hydrogen peroxide, hydroperoxide radicals, formaldehyde, etc.

Finally, the dimerization reactions of the hydroxyl radicals themselves, i.e., the reverse process of Reaction (33) [104] and the hydroperoxide radicals, Reaction (36) [105], lead to the regeneration of hydrogen peroxide, which in turn can sequester hydroxyl radicals and re-form hydroperoxide radicals, Reaction (34) [106].

At the same time, one must consider the dissociation equilibria of the organic compound itself and of the different intermediates formed, such as hydrogen peroxide, hydroperoxide radicals, etc., which are shown below:

$$RH \leftrightarrow R^{-} + H^{+} \qquad \text{Reaction (38)}$$

$$H_2O_2 \rightarrow HO_2^{-} + H^{+} \qquad \text{Reaction (23)}$$

$$HO_2 \rightarrow H^+ + O_2^-$$
 Reaction (25)

In summary, a cycle of decomposition and simultaneous formation of hydrogen peroxide can be established. The overall result of such a cycle will depend on several variables as, for instance, the intensity of the ultraviolet radiation, temperature, pH, and the nature of the organic compounds.

It must be noted, however, that the H₂O₂/UV system is considered one of the most viable advanced oxidation processes. For instance, on many occasions, it is preferable to ozonation because it is less sensitive to the nature and concentration of the polluting species.

Table 9 summarizes some examples of removal processes of antibiotics by the H₂O₂/UV process. From the literature review, it may be concluded that the UV/H₂O₂ is a fast and efficient technology for the removal of antibiotics from aqueous matrices, due to a fast generation of OH radicals in solution. However, the overall performance of the process is remarkably dependent on different operational parameters such as the UV wavelength and intensity (i.e., the UV light source) and the inherent properties of the wastewater (i.e., pH, initial concentration of pollutants, etc.).

			Maximum		
Antibiotic	Matrix	Operation Conditions	Removal	Remarks	Reference
			Efficiency		
Amoxicillin (AMX)	Ultrapure water	$H_2O_2 = 0.4-10 \text{ mM}$ Low-pressure mercury lamp $(\lambda = 254 \text{ nm})$ pH = 2-10	99% in 20 min	Low mineralization Antibacterial activity effectively eliminated	[107].
Cefalexin (CFL) Norfloxacin (NRF) Ofloxacin (OFX)	Ultrapure water and tap water	$H_2O_2 = 0.25-5.0 \text{ mM}$ Low-pressure mercury vapor lamp ($\lambda = 254 \text{ nm}$)	~100% within 3–5 min	Scavenging effect if large concentrations of H ₂ O ₂ are used Presence of halides in tap water accelerates the degradation rate	[108]
Ceftriaxone (CFN)	Ultrapure water and tap water	H_2O_2 = 0.15–2.9 mM Low-pressure mercury vapor lamp (λ = 254 nm) pH = 5–9	~100%	Optimum removal efficiency reached for [H2O2] = 0.3 mM Up to 35% synergistic effect achieved with respect to the photolysis process 58.1% mineralization reached	[109]
Ciprofloxacin (CPR) Doxycycline (DXY) Oxytetracycline (OXY)	Ultrapure water Surface water Wastewater	$H_2O_2 = 0.7-4.2 \text{ mM}$ Low-pressure mercury lamp $(\lambda = 254 \text{ nm})$ pH = 2-10	100%	Toxicity firstly increases, then decreases 10% mineralization, total mineralization needed much more energy	[99]
Norfloxacin (NRF)		$H_2O_2 = 0.7-4.2 \text{ mM}$ Low-pressure mercury lamp $(\lambda = 254 \text{ nm})$ pH = 2-10	100% in 100 min	Direct photolysis infeasible (high reaction time and low mineralization)	[110]
Ofloxacin (OFX) Sulfaquinoxaline(SLQ)	Ultrapure water	$H_2O_2 = 0.8-9.0 \text{ mM}$ Low-pressure mercury lamp ($\lambda = 254 \text{ nm}$)	>99% in 11 min	OFX is degraded faster than SLQ Degradation products of OFX and SLQ are harmful to microorganisms	[111]

Table 9. Removal efficiency of antibiotics in waters by the H₂O₂/UV process.

Roxithromycin (RXT)	Ultrapure water Secondary wastewater effluent	$H_2O_2 = 2-20 \text{ mM}$ High-pressure mercury lamp ($\lambda = 365$ nm) pH = 4-9	~100% in appr 45 min	Slightly alkaline favorable for the RXT degradation Degradation products more toxic than the parent compound	[112]
Sulfadiazine (SDZ) Sulfathiazole (STZ) Sulfamerazine (SMR) Sulfisoxazole (SSX) Sulfamethazine (SMZ) Sulfamethoxypyridazine (SMP) Sulfamonomethoxine (SMM) Sulfadimethoxypyrimidine (SDM)	Synthetic wastewater Hydrolyzed urine 5 mM phosphate buffer (pH = 7)	$H_2O_2 = 0.9 \text{ mM}$ Low-pressure mercury lamp ($\lambda = 254 \text{ nm}$)	>99%	Sulfonamides with five-membered heterocyclic group undergo rapid direct photolysis.	[113]
Sulfamethazine (SMZ)	Ultrapure water	$H_2O_2 = 1-10 \text{ mM}$ Low-pressure mercury lamp ($\lambda = 254 \text{ nm}$)	100% in 10 min	57% mineralization in 120 min	[114]
Sulfamethoxazole (SLF)	Ultrapure water	$H_2O_2 = 0, 0.15, and 0.30$ mM Low-pressure and medium-pressure mercury lamps ($\lambda = 254$ and 365 nm)	~100%	Removal largely attributed to direct photodegradation Lower UV or H2O2 doses yielded different relative abundances of certain transformation products as compared to higher doses	[115]

4.2. The Fe²⁺/H₂O₂ System. Fenton Reagent

The Fenton process is a viable alternative for the removal of organic pollutants from wastewater and has been applied in many industrial sectors. However, it has some disadvantages derived from the use of iron salts as a catalyst for the decomposition of hydrogen peroxide to hydroxyl radicals.

On the one hand, large amounts of these dissolved iron salts are necessary, which makes the process more expensive. On the other hand, the directives of the European Union on water quality allow a very low concentration of iron dissolved in the effluents, which forces to introduce some treatment aimed at eliminating iron salts from the effluents of the Fenton process. These complementary processes, typically physical–chemical coagulation–flocculation processes, produce large quantities of metal sludge as a waste, which must be managed appropriately too. These drawbacks of the conventional Fenton process have promoted the development of new systems, which allow minimizing the presence of iron species dissolved in the environment, without critically affecting the efficiency of the process.

Different alternatives can be distinguished to achieve this objective [116]. Firstly, technological options have been proposed to accelerate the regeneration of Fe(II) species, which is mainly responsible for the decomposition of hydrogen peroxide and the generation of hydroxyl radicals. This would reduce the amount of iron (II) needed in the reaction medium. One of these alternatives is the combined use of the Fenton process together with near-visible ultraviolet radiation, which constitutes the so-called "photo-Fenton process." This process will be dealt with in detail in Section 4.4. Secondly, the development of solid catalysts for Fenton processes has attracted the attention of the scientific community in recent years. The use of highly active and stable solid catalysts would help to minimize the presence of iron (II) salts dissolved in the medium, besides facilitating the recovery and reuse of the catalyst. This latter alternative gives rise to a broad group of process commonly known as "heterogeneous Fenton processes." Finally, the combined use of Fenton's reagent and electric current receives the generic denomination of "electro-Fenton techniques" [117].

The addition of iron salts as a catalyst in the presence of hydrogen peroxide is one of the classical methods of producing hydroxyl radicals, being one of the most powerful oxidizing agents at acidic pH (namely, pH = 3–5). The Fenton reagent has a great oxidizing capacity towards a wide range of organic substances, both aromatic (phenols, polyphenols, etc.) and aliphatic compounds (alcohols, aldehydes, etc.). The main oxidizing species is again the hydroxyl radical, which is generated in the initial reaction between hydrogen peroxide and Fe^{2+} salts [118]. While the exact mechanism of the oxidation of an organic compound by the reagent mentioned above is complex and not completely known, several authors agree on its main stages. Thus, it can be assumed that the overall process takes place through the following individual stages:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-$$
 Reaction (39)

 $R + H_2O_2 \rightarrow P1$ Reaction (40)

$$R + OH \rightarrow P2$$
 Reaction (41)

where R represents the organic compound, and P1 and P2 are the formed intermediates and final products of the oxidation. The first reaction of the mechanism is responsible for the formation of hydroxyl radicals [118] that will later attack organic compound R in Reaction (41), the main degradation pathway in the Fenton reaction.

On the other hand, Reactions (34) and (42) represent the sequestering effect of such radicals exerted by Fe^{2+} itself or H_2O_2 [119]:

$H_2O_2 + OH \rightarrow HO_2 + H_2O$	Reaction (34	ł)
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$$Fe^{2+} + OH \rightarrow Fe^{3+} + OH^{-}$$
 Reaction (42)

Finally, reactions (43), (44), and (45) indicate the possible reaction pathways of the Fe(III) generated in reaction (42) with H₂O₂ and with the hydroperoxide (HO₂·) or superoxide (O₂-·) radicals.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2 \qquad \text{Reaction (43)}$$

$$Fe^{3+} + HO_2 \rightarrow Fe^{2+} + H^+ + O_2$$
 Reaction (44)

$$Fe^{3+} + O_2 \rightarrow Fe^{2+} + O_2$$
 Reaction (45)

It is worth noting that in Reactions (43)–(45), Fe^{2+} is regenerated, so that the Fenton process can be regarded as catalytic with respect to iron. Therefore, the reaction of formation of OH radicals can continue to take place as long as there is hydrogen peroxide in the medium.

For the procedure to be effective, the following requirements are necessary:

- (a) The pH of the water to be treated must be in the range 3–5 since at higher pH values, iron precipitates as Fe(OH)₃, thus inactivating the system. Furthermore, if the pH is high, the decomposition of hydrogen peroxide into oxygen and water is favored.
- (b) The addition of the Fe²⁺ salt is necessary, generally as FeSO₄, even though other sources of Fe²⁺ or Fe³⁺ can be added. In the case of Fe³⁺, which is also useful, a small initial delay of the reaction is observed.
- (c) The addition of H₂O₂ must be very slow to avoid decomposition phenomena.

The rate of \cdot OH radical generation, which in turn depends on the concentration of ferrous catalyst, generally limits the reaction rate of this system. The typical Fe²⁺: H₂O₂ molar ratio is 1: 5–10, although Fe²⁺ levels below 25–50 mg·L⁻¹ may require a considerable reaction time (10–48 h).

The main advantages of this oxidation process are:

- (a) Fe^{2+} is abundant and non-toxic.
- (b) Hydrogen peroxide is easy to handle and environmentally benign.
- (c) No chlorinated compounds are formed as in other techniques.
- (d) There are no limitations of matter transfer since the system is homogeneous. Hence, the design of reactors for this technology is quite simple.
- (e) An additional advantage of the Fenton process is the formation of complexes that promote the coagulation of suspended solids after oxidation reactions [120].

However, the Fenton process has some shortcomings, including:

- (a) The regeneration rate of Fe²⁺ from Fe³⁺ according to Reactions (43)–(45) is very low if compared with the depletion rate of Fe²⁺ (Reaction (42))
- (b) If pH increases above 3 or 3.5, large amounts of sludge are produced due to iron hydroxide precipitation, and additional treatment is necessary.
- (c) Fe²⁺ or Fe³⁺ ions may undergo complexation reactions with organic or inorganic ligands that may be present in solution.
- (d) Scavenging reactions may take place, for instance, Reaction (42).

In the absence of ferrous or ferric salt, there is no evidence of hydroxyl radical formation. As the iron concentration increases, the oxidation rate of organic compounds increases to a point at which an additional increase in iron concentration is ineffective. For most applications, it does not matter if Fe²⁺ or Fe³⁺ is used; the catalyst cycle starts quickly if hydrogen peroxide and organic material are in sufficient concentration.

When the H₂O₂ dose is increased, a noticeable reduction in organic matter is obtained, whereas a small or negligible change in toxicity may occur. Once a minimum threshold has been reached, small increases in the H₂O₂ dose result in evident decreases in the toxicity of the effluent. However, it must be kept in one's mind that high concentrations of hydrogen peroxide lead to the scavenging of \cdot OH radicals (see Reactions (34)–(37)).

The reaction rate in the Fenton process increases with temperature, the effect being more pronounced at temperatures below 20 °C. However, when the temperature rises to 40–50 °C, the

effectiveness of the reagent decreases. This is due to the accelerated decomposition of H_2O_2 into oxygen and water. From a practical standpoint, most of the commercial applications of this reagent occur at a temperature between 20–40 °C.

As indicated above, the optimum operational pH is between 3 and 3.5. The inefficiency of a basic pH is attributed to the transformation of the hydrated iron species to colloidal ferric species. In this last form, iron catalytically decomposes hydrogen peroxide into oxygen and water, without forming hydroxyl radicals.

This process can be applied to wastewater, sludge, or contaminated soils producing the oxidation of organic pollutants, reduction of toxicity, reduction of COD, reduction of BOD₅, and elimination of odor and color. Some examples of the use of the Fenton process are summarized in Table 10.

Antibiotic	Matrix	Operation Conditions	Maximum Removal Efficiency	Remarks	Reference
Amoxicillin (AMX)	Spiked wastewater	$H_2O_2 = 0.3-15 \text{ mM Fe}^{2+} = 0-0.9 \text{ mM}$	100% in 2.5 min	Box-Behnken-statistical design 37% mineralization in 15 min	[121]
Amoxicillin (AMX)	Ultrapure water	$H_2O_2 = 0.1-0.125 \text{ mM}$ $Fe^{2+} = 0.004-0.006 \text{ mM}$ $pH = 3.5 \text{ T} = 20-30 ^{\circ}\text{C}$	100% in 30 min	Central composite factorial design Only T and [Fe ²⁺] affect statistically the removal efficiency	[122]
Amoxicillin (AMX)	Synthetic wastewater	$H_2O_2 = 5-50 \text{ mM}$ $Fe^{2+} = 0.5-5 \text{ mM}$ pH = 2-7	83%	Optimum Fe ²⁺ /H2O2 molar ratio = 1/15 66% mineralization	[123]
Ampicillin (AMP)	Ultrapure water	$H_2O_2 = 0.373 \text{ mM}$ $Fe^{2+} = 0.087 \text{ mM}$ pH = 3.5	100% in 10 min	Central composite factorial experimental design Degradation products without antibacterial activity	[124]
Chlortetracycline (CHL)	Wastewater	$H_2O_2 = 0.3 \text{ mM}$ Fe ²⁺ = 0.003–0.3 mM pH = 7	76%	Complete mineralization not achieved	[125]
Ciprofloxacin (CPR)	Ultrapure water	H2O2 = 20–84 mM Fe ²⁺ = 5–21 mM pH = 5	74% in 25 min	Optimal conditions: $H_2O_2 = 74.5 \text{ mM}$ $Fe^{2+} = 17.46 \text{ mM}$ pH = 4.6 Hydroxylation of both piperazine and quinolone rings; oxidation and cleavage of the piperazine ring, and defluorination (OH/F substitution) are the main degradation mechanisms	[126]
Ciprofloxacin (CPR)	Ultrapure water	$H_2O_2 = 26-51 \text{ mM}$ $Fe^{2+} = 5-10 \text{ mM}$ pH = 3	76% in 45 min	Optimal conditions: $H_2O_2 = 26 \text{ mM}$ $Fe^{2+} = 5 \text{ mM}$ pH = 3 Complete mineralization could not be achieved	[127]

Table 10. Removal efficiency of antibiotics in waters by the Fenton process.

Ciprofloxacin (CPR)	Spiked wastewater	$H_2O_2 = 14.2 \text{ mM}$ $Fe^{2+} = 0.284-2.84 \text{ mM}$ pH = 3	70% in 15 min	55% mineralization achieved Considerable reduction in toxicity of the treated wastewater	[128]
Doxycycline (DXY)	Ultrapure water	$H_2O_2 = 2.9-26.5 \text{ mM}$ $Fe^{2+} = 0.09-2.1 \text{ mM}$ T = 0-40 °C pH = 5	100% in 10 min	Optimal conditions: $H_2O_2 = 18 \text{ mM}$ $Fe^{2+} = 0.44 \text{ mM}$ T = 35 °C	[129]
Flumequine (FLM)	Ultrapure water	$H_2O_2 = 0.5-10 \text{ mM}$ $Fe^{2+} = 0.25-1 \text{ mM}$ pH = 2.8	40% in 15 min	Low mineralization degree Deactivation of antimicrobial activity	[130]
Levofloxacine (LVF)	Ultrapure water	$H_2O_2 = 0.375-1.5 \text{ mM}$ $Fe^{2+} = 0.0375-0.15 \text{ mM}$ pH = 3	100%	Total removal achieved within 5–90 min according to experimental conditions Defluorination, piperazinyl substituent transformation, and quinolone moiety modifications are the main degradation pathways	[131]
Sulfamethoxazole (SLF)	Ultrapure water Synthetic wastewater	$H_2O_2 = 0.5-4 \text{ mM}$ $Fe^{2+} = 0.025-0.2 \text{ mM}$ pH = 3	100% in 10 min (ultrapure water) 53% in 30 min (synthetic wastewater)	Wastewater components had a negative effect on sulfamethoxazole degradation Degradation pathways: (a) Oxidation of –NH2 in benzene ring by ·OH radicals followed by hydroxylation (b) -SH-Ph bond cleavage	[132]
Trimethoprim (TRM)	Ultrapure water Synthetic wastewater	$H_2O_2 = 0.5-4 \text{ mM}$ $Fe^{2+} = 0.025-0.2 \text{ mM}$ pH = 3	100% in ultrapure water 36% in synthetic wastewater	Hydroxylation is the first degradation step, followed by the cleavage of the C-C bond between the pyrimidine and the benzene rings	[133]

4.3. The Fe³⁺/H₂O₂ System. Fenton-Like Reagent

The main drawback of using the Fenton system described above is the cost of the reagents, namely H_2O_2 and Fe^{2+} . For this reason, several methods have been developed to substitute Fe^{2+} with Fe^{3+} salts, whose price is lower than that of the Fe^{2+} salts.

Originally, the "Fenton-like" term was used in reference to a similar process to that described in the previous section, with the only difference that the reagent used is a mixture of Fe³⁺ and H₂O₂ where the hydrogen peroxide decomposes into hydroxyl radicals, and the Fe(III) is reduced to Fe(II) following the reaction:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OH^- + OH$$
 Reaction (46)

Several studies have shown that the decomposition rate of H_2O_2 and the oxidation rate of organic solutes are markedly slower using Fe^{3+}/H_2O_2 than Fe^{2+}/H_2O_2 , with an optimal being achieved at pH = 3 [134,135].

Additionally, the Fenton-like process produces peroxyl radicals (HO2·):

$$Fe^{3+} + H_2O_2 \rightarrow H^+ + FeOOH^{2+}$$
 Reaction (47)

$$FeOOH^{2+} \rightarrow HO_{2^{+}} + Fe^{2+}$$
 Reaction (48)

Despite the fact that the homogeneous Fenton or Fenton-like processes have been largely used due to their effectiveness in terms of pollutant removal as well as to their ease of operation, both of them exhibit important disadvantages such as excessive sludge production and limited range of operational pH (usually below 3). Heterogeneous Fenton oxidation was developed to overcome these problems. In heterogeneous Fenton oxidation, a reaction takes place between hydrogen peroxide and Fe(III) in different forms, e.g., Fe₂O₃ or α -FeOOH, among others. If solid catalysts are used, in addition to the chemical reactions described above, physical adsorption occurs at the surface of the solid catalyst, which reduces sludge generation.

For all the exposure, the Fenton-like system is becoming progressively less used in recent years, and the number of manuscripts published is decreasing. On the contrary, heterogeneous Fenton-like processes, as well as those using different precursors to generate Fe(II) or Fe(III) ions in solution, are gaining importance. Hence, in this section, results corresponding not only to the Fenton-like process in its traditional sense, but also to some new alternatives will be presented.

Fe(II) used in the traditional Fenton process can be efficiently substituted by nanoscale zerovalent iron (nZVI) that is commonly synthesized by the reaction of Fe(II) with sodium borohydride:

$$Fe(H_2O)_{6^{2+}} + 2 BH_4 \rightarrow Fe^0 \downarrow + 2 B(OH)_3 + 7 H_2 \uparrow \qquad \text{Reaction (49)}$$

Once synthesized and/or isolated, Fe⁰ reacts with hydrogen peroxide or dissolved oxygen in the acidic medium required for the Fenton process (pH ~ 2.5–3.5) yielding Fe²⁺ as follows:

$$Fe^{0} + H_{2}O_{2} + 2 H^{+} \rightarrow Fe^{2+} + 2H_{2}O$$
 Reaction (50)

$$Fe^0 + O_2 + 2 H^+ \rightarrow Fe^{2+} + H_2O_2$$
 Reaction (51)

Fe(II) undergoes the series of reactions described in the previous section. It is worth noting that Reaction (50) involves the degradation of hydrogen peroxide, whereas in Reaction (51), H_2O_2 is generated. Hence, the global reaction is:

$$2 \text{ Fe}^{0} + \text{O}_{2} + 4 \text{ H}^{+} \rightarrow 2 \text{ Fe}^{2+} + 2 \text{ H}_{2}\text{O}$$
 Reaction (52)

However, the heterogeneous process appears to be less effective than a homogeneous Fenton process due to mass-transfer limitation. To solve this problem, different metal oxides, MO_x (e.g., ceria [136], Fe₃O₄ [137], Mn₃O₄ [138], WMoO [139], FeCuO₂, NiCuO₂ [140], etc.) have been recently tested

as catalysts or as a support of Fe⁰ in a series of alternative Fenton-like processes. The use of these oxides involves either a faster kinetic removal or the broadening of the operational pH range, that may reach up to 10 in some of these processes, which is not suitable for conventional Fenton or Fenton-like processes due to Fe(II) and/or Fe(III) precipitation in the form of hydroxides or oxyhydroxides.

The improvement in the performance of the MO_x/ Fe⁰-catalyzed systems is attributable to different factors, mainly:

- (a) MO_x usually exhibit larger specific surface areas than iron-based materials, thus favoring the adsorption of pollutants in the active sites of the solid's surface.
- (b) MO_x may act as catalysts for the homolytic break of H_2O_2 into two $\cdot OH$ radicals.
- (c) MO_x used to have a relatively large number of oxygen vacancies that are suitable for pollutants to react rapidly with the reactive oxygen species (ROS) generated on the material's surface.

Biochar has also been used as catalyst support in Fenton-like processes [141]. It is well-known that the surface of biochars possesses a vast number and variety of redox-active sites (e.g., quinone, hydroquinone, conjugated π -electron systems, aromatic rings, etc.). These active sites are suitable to act as electron donors or acceptors in many redox processes such as Fenton-like, among others. Further details can be found in the excellent review recently published by Wang et al. (see reference [141] and citations therein).

Finally, the outstanding properties of graphene and graphene oxide have also been applied to the heterocatalytic Fenton-like process [142].

Table 11 summarizes some recent contributions regarding the removal of antibiotics through heterogeneous Fenton-like process

Antibiotic	Matrix	Operation Conditions	Maximum Removal Efficiency	Remarks	Reference
Amoxicilin (AMX)	Ultrapure water	H ₂ O ₂ = 3.3–12.2 mM nZVI = 0.5–2.0 g/L pH = 2.0–5.0 T = 15–45 °C	~90% in 20 min	^(a) Optimal conditions: H ₂ O ₂ = 6.6 mM, nZVI = 0.5 g/L pH = 3.0 T = 30 °C Adsorption of AMX onto nZVI or its (hydr)oxide surface plays an important role	[143]
Ciprofloxacin (CPR)	Ultrapure water	H2O2 = 100 mM nZVI = 0.056– 0.28 g/L pH = 7 Room temperature	100% in 30 min	^(a) Reaction at the piperazinyl ring and defluorination followed by hydroxyl substitution appear to be the main degradation pathways	[144]
Ciprofloxacin (CPR)	Ultrapure water	H2O2 = 10 mM Catalysts (0.5 g/L): MnCuO2 FeCuO2 CoCuO2 NiCuO2 pH = 6	~90%	^(b) CPR degradation mainly occurs in solution. Scarce contribution of adsorption Degradation of CPR should be due to the cleavage of piperazine ring, followed by loss of formaldehyde, replacement of F with OH and/or loss of ethylamine	[140]

	Table 11.	Removal	efficiency o	of antibiotics	in waters	through	heterogen	eous Fenton-li	ke process
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Ciprofloxacin (CPR)	Ultrapure water	H2O2 = 10–100 mM Sludge Biochar Catalyst (SBC) = 0.2 g/L pH = 2–12	90% in 4 h	(c)Fe ²⁺ and Fe ³⁺ were released in the SBC/H2O2 system Piperazine ring cleavage, pyridine cleavage, hydroxylation, F/OH substitution, and defluorination were the dominant degradation pathways	[145]
Metronidazol (MTR)	Ultrapure water	nZVI = 0.03-0.13 g L ⁻¹ pH = 3.03-9.04	96.4% in 5 min	^(a) H2O2 generated according to Reaction (51)	[146]
Metronidazole (MTR)	Ultrapure water	Absence of Fe and H2O2 Addition of 2 mM H2O2 in one experiment	92%	 ^(d)Three-dimensional macroporous graphene- wrapped zero-valent copper nanoparticles (3D- GN@Cu⁰) used as the catalyst H₂O₂ generated in situ by reduction of O₂ on the surface of 3D-GN@Cu⁰ Addition of 2 mM H₂O₂ had little effect on the degradation of MTR 	[142]
Tetracycline (TTR)	Ultrapure water	$H_2O_2 = 100 \text{ mM}$ Fe ⁰ @CeO ₂ catalyst = 0.1 g/L pH = 5.8 T = 26 °C	94%	(b)A combined adsorption/reduction mechanism enhances removal efficiency	[136]
Tetracycline (TTR)	Ultrapure water	$H_2O_2 = 3-20 \text{ mM}$ Fe(III) concentration not specified WMoO _x catalyst = 0.2-1.6 g/L pH = 3-8 T = 25 °C	86%	^(b) The system avoids solution chroma and sludge formation caused by the dissolved ferric species	[139]
Tetracycline (TTR)	Ultrapure water Spiked wastewater	H ₂ O ₂ = 5 mM pH = 7.4 T = 25 °C Fe substituted by a mixture of three biochars from corn stalks, bamboo, and pig manure	100%	^(c) Pig manure showed the best performance in TTR removal	[147]

				^(d) α-FeOOH/RGO hydrogels	
				could generate reactive	
				oxygen species (ROS)	
		$H_2O_2 = 1.1 - 3.3$		without the addition of	
		mM		H2O2	
Tetracycline	Ultrapure		100% in	TTR acts as an electron	[1.40]
(TTR)	water	α-FeOOH/RGO	120 min	donor.	[148]
		hydrogels used		e^{-} are transferred through	
		as catalysts		$\pi - \pi$ interactions (TTR -	
				graphene) and π –Fe	
				interactions	
				(graphene- FeOOH)	

KEY: Catalysts used: ^(a)nZVI; ^(b)MO_x; ^(c)Biochars; ^(d)Graphene/graphene oxide.

4.4. The Fe²⁺/H₂O₂/UV System (Photo- Fenton).

It is commonly accepted that UV radiation accelerates Fenton reactions, thus favoring the degree of degradation of organic pollutants, including aromatic and aliphatic compounds, and presenting greater effectiveness at acidic pH. The photo-Fenton system, therefore, includes ultraviolet radiation, hydrogen peroxide, and iron salts. This system has been considered one of the most promising ways of purifying highly contaminated wastewater [149,150].

The main advantages of the photo-Fenton process over the Fenton or Fenton-like reagents discussed in the previous section are the following:

(a) The photolysis of hydrogen peroxide, produced according to Reaction (33), provides a supplementary source of OH radicals [101].

Hν

$$H_2O_2 \rightarrow 2 \text{ OH}$$
 Reaction (33)

(b) The reduction of Fe³⁺ to Fe²⁺ by ultraviolet radiation, shown in Reaction (53), also contributes to the generation of hydroxyl radicals. Furthermore, this reaction facilitates the formation of Fe(II), which reacts rapidly with hydrogen peroxide to yield more ·OH radicals by the conventional Fenton reaction (39). Hence, it can be stated that UV radiation accelerates the Fe(III)–Fe(II) cycle, thus facilitating the production of hydroxyl radicals in both reactions (53) and (39)

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH \qquad \text{Reaction (53)}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-$$
Reaction (39)

In addition to these important advantages, Bossman et al. [151] proposed that Fe(III) in the presence of ultraviolet radiation is promoted into an excited state of Fe(III) that reacts faster with hydrogen peroxide to form Fe(II) and OH radicals, Reaction (46), or even with organic compounds.

$$Fe^{3+} + H_2O_2 \rightarrow 2 Fe^{2+} + OH^- + OH$$
 Reaction (46)

All these advantages make the photo-Fenton system a promising procedure in the treatment of water purification, since hydroxyl radicals are generated and secondary chlorinated oxidation products are not produced, as in the case of oxidation by chlorine or chlorine dioxide.

Table 12 summarizes some recent papers reporting the use of the photo-Fenton process for the removal of pharmaceuticals from water.

Table 12. Removal efficiency of antibiotics in waters by photo-Fenton	processes
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Amoxicillin (AMX)	Spiked synthetic wastewater Spiked real wastewater	$H_2O_2 = 0.08$ mM Fe ³⁺ = 0.05 mM Natural solar radiation (pilot-plant scale CPC photoreactor) pH = 7–8	90% in 9 min	No mineralization of the drug. Hydroxylation of the aromatic ring, opening of the β - lactam ring, and subsequent formation of amoxilloic and amoxicilloic acids are the main transformation pathways.	[152]
Ampicillin (AMP)	Spiked WWTP effluent	Solar photo- Fenton $H_2O_2 = 0.74-$ 2.94 mM $Fe^{2+} = 0.09$ mM pH = 3	100% in 20 min	Optimal conditions: $H_2O_2 = 2.2 \text{ mM}$ $Fe^{2+} = 0.09 \text{ mM}$ Beyond the optimal H_2O_2 concentration, scavenging effects might occur	[153]
Chloramphenicol (CHL)	Spiked WWTP effluent	$H_2O_2 = 0.044-$ 0.088 mM $Fe^{2+} = 0.016-$ 0.064 mM Black light lamps (λ = 350-400 nm) or solar irradiation pH = 5.8-7.7	79% in 20 min	Optimal conditions: $H_2O_2 = 0.088 \text{ mM}$ $Fe^{2+} = 0.048 \text{ mM}$ pH = 5.8 Acidification and neutralization before the discharge are avoided	[154]
Ciprofloxacin (CPR)	Ultrapure water	H ₂ O ₂ = 5–25 mM High-pressure mercury lamp $(\lambda = 362 \text{ nm})$ T = 25 °C Fe ²⁺ = 0.25–2 mM pH = 2–9	93% in 45 min	Optimal conditions: $H_2O_2 = 10 \text{ mM}$ $Fe^{2+} = 1.25 \text{ mM}$ pH = 3.5 70% mineralization reached Piperazine ring degradation is the main degradation pathway	[155]

Oxacillin (OXC)	Ultrapure water	$H_2O_2 = 0.09-10$ mM $Fe^{2+} = 0.0036-$ 0.09 mM High-pressure mercury lamp ($\lambda = 365$ nm) pH = 6 T = 25 °C	100% in 20 min	Optimal conditions $H_2O_2 = 10 \text{ mM}$ $Fe^{2+} = 0.09 \text{ mM}$ Light intensity = 30 W Effluent has no antimicrobial activity Near-neutral conditions are used	[156]
Trimethoprim (TRM)	Ultrapure water	$H_2O_2 = 0.03-5$ mM High-pressure mercury lamp ($\lambda = 360$ nm) T = 25 °C Fe ²⁺ = 0.03-2 mM pH = 2.5-4.5	99.5% in 6 min	Optimal conditions: $H_2O_2 = 0.09 \text{ mM}$ $Fe^{2+} = 0.09 \text{ mM}$ pH = 4.56	[157]

According to the literature, the photo-Fenton process is economical, technically simple, and highly efficient for the removal of pollutants in general and antibiotics in particular from wastewaters. Fe(II) salts, the H_2SO_4 required for acidic pH, and hydrogen peroxide are readily available chemicals. Furthermore, the use of UV radiation speeds up the generation of $\cdot OH$ radicals, thus reducing the H_2O_2 consumption in comparison with the traditional Fenton process.

5. Heterogeneous Photocatalysis with TiO₂

Photocatalysis is defined as the acceleration of a photochemical reaction by the presence of a semiconductor that is activated by the absorption of radiation with energy above its bandgap. The term *heterogeneous* refers to the fact that the contaminants are present in a fluid phase while the catalyst is in the solid phase. The most commonly used catalyst is titanium dioxide (TiO₂) due to its high chemical stability, low cost, and excellent results it has proven to provide [158,159].

The first reaction of the photocatalysis process is the absorption of UV radiation by the catalyst, with the formation of hollow-electron (h⁺/e⁻) pairs according to Reaction (54). In environmental applications, the photocatalytic processes are carried out under aerobic conditions, and oxygen can be adsorbed onto the catalyst's surface. Hence, the aforementioned electrons, due to their high reducing power, reduce the oxygen adsorbed on the TiO₂ surface, thus giving rise to the generation of superoxide radical ion (O₂⁻)·as indicated in Reaction (55); conversely, the holes are capable of causing the oxidation of water and/or HO⁻ adsorbed species into OH radicals according to Reactions (56) and (57), which will subsequently oxidize the organic compounds. When organic matter is also adsorbed on the surface of the catalyst, it can be directly oxidized by the transfer of an electron from the catalyst [160]. Certainly, in the presence of redox species adsorbed on the semiconductor particle and under irradiation, oxidation and reduction reactions co-occur on the catalyst's surface. The photogenerated holes give rise to photooxidation reactions, while the electrons in the conduction band give rise to photoreduction reactions:

$11O_2 + hv \rightarrow 11O_2 (e^-) + 11O_2(h^+)$ Reaction (54)	→ TiO_2 (e ⁻) + TiO_2 (h ⁺) Reaction (54)
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 $TiO_2(e^-) + O_2 \rightarrow TiO_2 + O_2^-$. Reaction (55)

$$TiO_2(h^+) + H_2O \rightarrow TiO_2 + OH + H^+$$
 Reaction (56)

Reaction (57)

 $TiO_2(h^+) + HO^- \rightarrow TiO_2 + OH$

The main advantages of this AOP are that it can be operated under pressure and at room temperature, the possibility of using sunlight for the irradiation of the catalyst, and the low cost and reusability of the catalyst. Also, this system is capable of achieving the complete mineralization of many compounds. However, it has significant disadvantages, such as the difficulties of attaining uniform radiation over the entire surface of the catalyst on a larger scale or the need for a subsequent separation treatment to recover the catalyst in suspension, which makes the process more expensive.

5.1. The TiO₂/UV System

The process of photocatalytic oxidation, that is, the simultaneous application of air or oxygen, UV radiation, and a semiconductor (mainly TiO₂), is a widely known process that is applied in the removal of numerous compounds but that is not fully developed on a large scale, mostly by the need to separate the photocatalyst, as indicated above. If used in powder (particle size in the range of tens of nm), TiO₂ exhibits high effectiveness. It is also required that the incident radiation on the surface of the photocatalyst has a minimum of energy so that the electrons of the valence band of the semiconductor can be promoted to the conduction band and the generation of hole–electron pairs may take place. In the particular case of titanium dioxide, radiation in the near-ultraviolet is required. This is so because, unfortunately, TiO₂ can absorb no more than 5% of the solar spectrum (i.e., the near UV light with $\lambda < 380$ nm) due to its relatively large bandgap (3.2 eV) [161]. As a consequence, the enhancement of the catalytic activity of TiO₂ within the visible zone of the solar spectrum has received a great deal of attention by the scientific community in recent years. Different strategies have been followed to improve the photocatalytic properties of TiO₂ under visible irradiation, such as surface modification with organic molecules [162] or nanoparticles [163,164] or doping with metal [163,165–167] and non-metal [165,168,169] ions, among others.

From the results summarized in Table 13, it may be concluded that the UV-TiO₂ system is quite useful for the removal of antibiotics from water. However, authors agree that it is not the choice method to be applied for effluents showing high concentrations of pollutants. Furthermore, when large catalyst doses are used, the efficiency of the process decreases. Nevertheless, perhaps the main inconvenience that hinders the applicability of this method is the difficulty of separating and recycling an expensive photocatalyst as TiO₂.

Antibiotic	Matrix	Operation Conditions	Maximum Removal Efficiency	Remarks	Reference
Ciprofloxacin (CPR)	Ultrapure water	Graphitized mesoporous carbon (GMC)- TiO ₂ nanocomposite used as a catalyst (0.35 g/L) Low-pressure UV lamp (λ = 254 nm)	100% in 45 min	Total mineralization achieved in 90 min Hydroxylation, cleavage of piperazine ring and decarboxylation are the main degradation pathways	[170]

Table 13. Removal efficiency of antibiotics in waters by TiO2/UV advanced oxidation processes.

Cloxacillin (CLX)	Ultrapure water; Synthetic pharmaceutical wastewater	TiO ₂ = 2.0 g/L; UV light = 150 W	~100%	TiO ₂ photocatalysis exhibits larger degradation and mineralization efficiencies than other systems also tested	[171]
Metronidazole (MTR)	Complex aqueous matrix (contains anions, cations, humic acid, and glucose)	TiO ₂ = 1.5 g/L UV light intensity = 6.5 mW cm ⁻²	~88% in max 30 min	The presence of common water matrix components hinders drug degradation (except glucose)	[172]
Norfloxacin (NRF)	Ultrapure water	TiO ₂ = 0.3 g/L Low-pressure UV lamp (λ = 254 nm)	~90%	TiO2 photocatalysis is the second most effective method for the removal of NRF, after photo-Fenton (96%)	[173]
Oxacillin (OXC)	Ultrapure water	$TiO_2 = 0.5 g/L$ High-pressure mercury lamp ($\lambda = 365 nm$) UV = 150 W	100% in 45 min	~90% mineralization achieved in 135 min	[156]
Oxacillin (OXC)	Synthetic pharmaceutical effluent	TiO ₂ = 0.5 g/L High-pressure mercury lamp $(\lambda = 365 \text{ nm})$ UV = 150 W	100% in 45 min (without additives) 100% in 60 min (with additives)	TiO2 photocatalytic treatment was the least inhibited by additives	[174]

5.2. The TiO₂/H₂O₂/UV System

It has already been stated that the simultaneous presence of H_2O_2 and UV radiation results in the homolytic photodissociation of the hydrogen peroxide molecule, thus giving rise to two hydroxyl radicals according to Reaction (33), see Section 5.1. Furthermore, the addition of hydrogen peroxide to the TiO₂/UV system produces a considerable increase in the photodegradation rate. This effect may be due to the generation of more hydroxyl radicals by the reaction of H_2O_2 with the TiO₂(e⁻) generated when titanium dioxide is excited by radiation of the adequate wavelength (not necessarily UV light, as indicated under the previous section).

The reaction between $TiO_2(e^-)$ and H_2O_2 generates additional $\cdot OH$ radicals easily available to contribute to oxidation processes:

$$TiO_2(e^-) + H_2O_2 \rightarrow TiO_2 + OH^- + OH$$
 Reaction (58)

As it is the case for the TiO₂/UV system, the introduction of doping elements or surface modifications results in a better performance of the TiO₂/H₂O₂/UV system both in terms of removal and mineralization efficiencies. For instance, Jiang et al. [175] have recently reported on the important role played by ferrihydrite (Fh) in the transference of the photo-generated electrons from TiO₂ to

H₂O₂. According to these authors, Fh deposited on the surface of the catalyst enables an improved separation of electron–hole pairs. These electrons are more available to be transferred to H₂O₂, thus enhancing its decomposition, Reaction (58), which results in more efficient degradation of the target antibiotic, cefotaxime. The Fh-TiO₂ catalyst is highly active from the catalytic standpoint, is easy to prepare at relatively low cost, and exhibits good stability. Furthermore, according to the experimental data, catalytic activity continues even after the complete decomposition of H₂O₂ has taken place. Of course, the photo-generated electrons can also be directly transferred to dissolved O₂, water, or H₂O₂ so that more hydroxyl and superoxide radicals are generated according to Reactions (55), (56), and (58), respectively.

Similarly, García-Muñoz et al. [176] have recently prepared a mesoporous Fe₂O₃-TiO₂ catalyst that exhibited norfloxacin (NRF) degradation rates more than 60% greater than non-doped mesoporous titania. The maximum enhancement of the degradation rate occurs for 3 wt% Fe₂O₃-TiO₂ catalyst, yielding 100% degradation and 90% mineralization within 120 min of reaction. According to the authors, in the hybrid photocatalyst iron oxidation-reduction reactions take place in the presence of H₂O₂, thus generating HO_x· radical species that also contribute to the removal of NRF:

$$Fe(II)-TiO_2 + H_2O_2 \rightarrow Fe(III)-TiO_2 + HO + OH^-$$
Reaction (59)

$$Fe(II)-TiO_2 + H_2O_2 \rightarrow Fe(III)-TiO_2 + HOO + H^+ \qquad \text{Reaction (60)}$$

Furthermore, oxidation of NRF in aqueous solutions occurs under mild reaction conditions, namely 25 °C and pH 7.

6. Sonochemical Advanced Oxidation Processes

Ultrasounds (US) are sound waves that have frequencies higher than those that can be perceived by the human ear (16 kHz) and lower than 1 GHz. US can be classified into different categories according to their frequency and intensity.

US of very high frequency and low intensity does not generate physicochemical modifications to the medium in which it is applied. US is used, for example, in medicine for diagnosis. High-intensity US, meanwhile, may interact with the medium. The interactions can be physical so that US is used to ease emulsification, cleaning up, and degassing. If the interactions are chemical, US can find applications in the synthesis of organic compounds and the degradation of pollutants in the environment, among others. This latter field of use of ultrasound is called sonochemistry.

In environmental applications, sonochemistry involves the application of US fields to an effluent, with a frequency between 20 kHz and 2 MHz. Among the various phenomena that appear in the water when an ultrasonic field propagates, ultrasonic cavitation stands out. Cavitation is defined as the phenomenon of formation, growth, and implosion of microbubbles or cavities within the liquid that takes place in a brief time interval (milliseconds) and releases a large amount of energy [158,159].

The generation of the phenomenon of cavitation depends mainly on the frequency and power of the US field. During this process, temperatures close to 5000 °C inside the bubbles and extremely high pressures (100 MPa) are generated locally and in a very short time, conditions that allow complicated chemical reactions to be carried out [177].

An aqueous solution in which cavitation takes place can be assimilated to an environment full of chemical microreactors (the cavitating bubbles) where at least the sonolysis of water takes place; that is, the homolytic breakdown of the molecule into highly reactive ·OH and H· radicals. The subsequent participation of these radicals, especially the OH radicals, in the oxidation of toxic and dangerous molecules that could be found in solution, makes it possible to suggest, at least theoretically, the feasibility of eliminating this type of pollutants without the need to use additional reagents—that can be dangerous—and under mild conditions of temperature or pressure [178]. Thus, the degradation of organic compounds can take place through the action of hydroxyl radicals (an oxidative mechanism) or due to high temperatures (a pyrolytic mechanism) [179].

When US is applied to an aqueous solution of a pollutant, the sonolysis of water may take place [180]:

$$2 \text{ H}_2\text{O} +))) \longrightarrow \text{H}_2 + \text{H}_2\text{O}_2 \qquad \qquad \text{Reaction (61)}$$

and the generated H2O2 may also undergo sonolysis:

$$H_2O_2 +))) \rightarrow 2 \cdot OH$$
 Reaction (62)

Recently, Serna et al. [181] have reported the removal of up to 17 pharmaceuticals (nine of them antibiotics) by sonochemical oxidation. The authors propose a double mechanism for the degradation of the pollutants, namely pyrolysis, and interaction between pollutants and hydroxyl radicals. The former mechanism is responsible for the removal of hydrophobic and volatile species that undergo thermal degradation in the liquid–bubble interface. On the contrary, hydrophilic and nonvolatile compounds (including antibiotics) are oxidized by the •OH radicals in the bulk solution.

However, the degradation efficiency and rate for most of the pollutants are far from being entirely satisfactory. The total mineralization of contaminants by the application of US alone is extremely difficult to achieve, particularly for refractory pollutants. Furthermore, the use of US in AOPs is inefficient from the energy consumption standpoint.

Nevertheless, sonication has successfully been applied as an auxiliary treatment in conjunction with other widely used AOPs and, particularly, with the Fenton reagent and some other derived from it.

For instance, in the so-called sono-Fenton process ($Fe^{2+}/H_2O_2/US$), the following reactions are proposed [182]. The process initiates with two reactions that are coincident with the first stages of the Fenton process:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-$$
 Reaction (39)

$$H_2O_2 + Fe^{3+} \rightarrow Fe(OOH)^{2+} + H^+ \qquad \text{Reaction (47)}$$

Next, the Fe(OOH)²⁺ decomposes sonochemically giving rise to hydroperoxyl radicals:

$$Fe(OOH)^{2+} +))) \rightarrow Fe^{2+} + HOO$$
 Reaction (63)

Finally, additional sonochemically generated hydroxyl radicals become available for acting as oxidizing agents:

$$Fe^{2+} + HOO \rightarrow Fe^{2+} + H^+ + O_2$$
 Reaction (64)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO$$
 Reaction (39)

According to Serna et al. [181] the removal of the pollutants in the effluent is more effective in the sono-Fenton process when compared with sonochemical oxidation alone, due to the generation of extra ·OH through reactions between Fe(II) and the sonogenerated hydrogen peroxide.

A similar situation has been described for the nZVI-based hetero-Fenton process, where nanoscaled Fe⁰ particles substitute Fe(II) in the initial stages of the process [182] as well as in the sono-Fenton-like process, where Fe(III) salts are used instead of Fe(II) [183]. This suggests that the use of a catalyst may improve energy consumption due to the occurrence of synergistic effects.

Zhou et al. [184] reported on the use of a goethite catalyst in the heterogeneous sonophotolytic Fenton-like (SP-FL) treatment of antibiotic sulfamethazine. The authors integrated the in situ H₂O₂ generation under UV illumination with a heterogeneous Fenton-like process and suggested that the synergistic role of US in the SP-FL system could be most ascribed to its promotional effect in Fenton-like reaction. Efficient Fe(II) species regeneration, improved mineralization degree, and successful wastewater detoxification were achieved.

Synergy appears to be more remarkable as the particle size of the catalyst decreases. Hence, the use of nanostructured catalysts is receiving a great deal of attention from the scientific community at present. Ghoreishian et al. [185] recently used flowerlike rGO/CdWO₄ solar-light-responsive photocatalysts for the US-assisted heterogeneous degradation of tetracycline. Excellent

photoelectrochemical behavior, superior sonophotocatalytic activity, and good mineralization efficiency were achieved under optimal conditions. Tetracycline was removed entirely at a pH of 5.7, an initial antibiotic concentration of 13.54 mg L⁻¹, a treatment time of 60 min, and a catalyst dosage of 0.216 g L⁻¹. Furthermore, rGO/CdWO4 exhibited a sonophotocatalytic efficiency that was 1.5 and 3 times higher than commercial nano-ZnO and nano-TiO2, respectively. Tetracycline was also chosen as the target pollutant by Vinesh et al. [186], which used a reduced graphene oxide (rGO)-supported electron-deficient B-doped TiO₂ (Au/B-TiO₂/rGO) nanocomposite. A considerable synergistic effect of ~1.3 was observed when the reaction was performed in the presence of US and photocatalysis. The total degradation of the antibiotic was also confirmed by TOC analysis. The enhanced sonophotocatalytic activity was mainly attributed to the generation of more reactive species by the combination of US and photocatalysis. Also, Abazari et al. [187] applied Ni-Ti layered double hydroxide@graphitic carbon nitride nanosheet for photocatalytic and sonophotocatalytic removal of amoxicillin from aqueous solution. The authors related the enhancement in the sonophotocatalytic activity of the nanocomposites to their higher specific surface areas, the intimacy of the contact interfaces of their components, the synergistic effect between these components, and the restriction of electron-hole recombination. The optimum sonophotocatalysis conditions were 500 W light intensity, 9 s on/1 s off US pulse mode, and 1.25 g/L of g-C₃N₄@Ni-Ti LDH catalyst. Under these conditions, 99.5% removal within 75 min was attained.

7. Electro-Oxidative Advanced Oxidation Processes.

The application of electric current (from 2 to 20 A) between two electrodes in water produces the generation of hydroxyl ·OH radicals coupled with the production of hydrogen peroxide in the reaction medium.

$$H_2O \rightarrow OH + H^+ + e^-$$
 Reaction (65)

$$O_2 + 2 H^+ + 2 e^- \rightarrow H_2O_2$$
 Reaction (66)

The global reaction is:

$$2 \text{ H}_2\text{O} + \text{O}_2 \rightarrow \text{H}_2\text{O}_2 + 2 \text{ OH}$$
 Reaction (67)

Hence, the OH radicals can be regarded as the product of the anodic oxidation of water and are readily available to oxidize the organic matter in aqueous solution. At the same time, hydrogen peroxide is generated by cathodic reduction of oxygen [188].

Electro-oxidation, also called anodic oxidation or electrochemical incineration, is one of the most popular electrochemical advanced oxidation processes for the elimination of organic contaminants contained in wastewater [28,189].

This procedure involves the oxidation of the contaminants in an electrolytic cell through the following routes:

- (a) Direct electron transfer to the anode.
- (b) Indirect or mediated oxidation with oxidizing species formed from the electrolysis of water at the anode, by physisorbed OH radicals or by the chemisorbed "active oxygen."

The existence of these species allows two different approaches to be proposed [190]:

- (1) Electrochemical conversion, where the refractory organic compounds are selectively transformed into biodegradable compounds, such as carboxylic acids, by the chemisorbed "active oxygen."
- (2) Electrochemical combustion, where the physisorbed OH radicals mineralize the organic compounds.

Anodic oxidation can achieve the oxidation of water pollutants, either by direct contact or by oxidative processes that take place on the anodic surface of the electrochemical cell. Hence, the oxidation process does not necessarily have to occur in the anode, but it is initiated on its surface. As a consequence, this treatment combines two main types of processes [191]:

- a. Heterogeneous oxidation of contaminants on the surface of the anode. This is a complex process that consists of a series of simple steps: The transport of pollutants to the surface of the electrode, the adsorption of the contaminant on the electrode's surface, the direct electrochemical reaction by electron transfer, the desorption of products, and the transport of such products to the dissolution.
- b. Homogeneous oxidation of contaminants by oxidants produced on the surface of the anode. These oxidizing species can be produced by the heterogeneous anodic oxidation of the water or from ions contained in the water acting in the dissolution of the electrolytic cell. The most important oxidant is the hydroxyl radical, which can be generated by the oxidation of water, Reaction (65), or by oxidation of the hydroxyl ion, Reaction (68):

$$H_2O \rightarrow OH_{ads} + H^+ + e^- \qquad \text{Reaction (65)}$$

$$OH^- \rightarrow OH_{ads} + e^-$$
 Reaction (68)

The generation of this OH radical is the main argument for considering anodic oxidation as an AOP. Due to the high oxidation capacity of hydroxyl radicals, these promote the formation of many other oxidizing species (persulfates, peroxophosphates, ferrates, etc.) from different species contained in real water matrices [192]. It has been shown that the presence of these species has a significant effect on the increase in degradation efficiency [193]. The synergistic effects of all these mechanisms can explain the high efficiencies obtained in the elimination of pollutants and the high mineralization achieved with this technology in comparison with other AOPs [194].

Some materials lead to powerful oxidation of the pollutant, yielding CO₂ and H₂O as the major final products and a small number of intermediates, while other materials produce less oxidation and generate a large number of oxidation byproducts. Comminellis [195] proposed an integral model for the destruction of organic compounds in an acidic medium that assumes the existence of "non-active" and "active" anodes. According to this model, "active" anodes, which promote the electrochemical reaction of oxygen evolution, favor the electrochemical conversion of organic matter, while the "non-active", which are less electrocatalytic for the evolution of oxygen, requiring higher anodic overpotentials, favor the electrochemical combustion of organic matter. In both types of anodes, denoted as M, the water oxidizes giving rise to the formation of physisorbed hydroxyl radicals (M (OH)):

$$M + H_2O \rightarrow M(\cdot OH)_{\text{physisorbed}} + H^+ + e^-$$
 Reaction (69)

In the case of "active" anodes, this radical interacts strongly with the surface, transforming into chemisorbed "active oxygen" or superoxide MO:

$$M(OH)_{physisorbed} \rightarrow MO_{chemisorbed} + H^+ + e^-$$
 Reaction (70)

The MO/M pair is a mediator in the electrochemical conversion of organic compounds (R):

$$MO + R \rightarrow M + RO$$
 Reaction (71)

On the contrary, the surface of the "non-active" anodes interacts weakly with the OH species, so that these radicals react directly with the organic products until total mineralization is at least ideally achieved. These radicals are physisorbed on electroactive electrode sites and do not undergo modification during the electron transfer reaction.

Graphite electrodes, with sp² carbon, metal (Pt, Ti/Pt), metal oxide (IrO₂, RuO₂), and mixed metal oxides electrodes, are considered as "active" anodes and behave as low-efficiency electrodes for the oxidation of organic compounds, generating a large number of intermediate byproducts. Most aromatic compounds treated with these anodes degrade slowly due to the generation of carboxylic acids that are difficult to oxidize [196]. Small mineralization efficiencies are obtained, and in some cases, polymeric species are generated, thus hindering the perspectives of application of these materials as anodes for electrooxidation processes.

Some metallic oxides and mixed metal oxides (those containing PbO₂ and/or SnO₂) and conductive diamond electrodes, in particular, the boron-doped diamond (BDD) electrodes are considered "non-active" anodes and behave as highly efficient electrodes for the oxidation of organic compounds. These anodes promote the mineralization of pollutants, whose extent is limited only by the mass transfer, and in general, virtually total mineralization of the contaminant is achieved. The surface material of BDD electrodes represents a promising technology for the electroanalysis of different biologically relevant active compounds [197–201].

In practice, all anodes exhibit a mixed behavior, since both mechanisms take place simultaneously. The "non-active" anodes may have defects in their surface or partially oxidized sites, while in the case of the "active" electrodes, the formation of physisorbed radicals at very positive potentials cannot be excluded, even if the surface is highly reactive. It should be mentioned that, as a general rule, the less positive the potential at which the evolution of oxygen occurs, the higher the participation of the anode surface in the reaction.

The generalized reaction pathway for the oxidation of an organic compound, R, and the simultaneous electrochemical formation of oxygen (over an anode, M), for the two types of anodes proposed, includes the following stages [202]:

- (1) Generation and adsorption of the OH radical.
- (2) Oxygen production by electrochemical oxidation of adsorbed OH radicals.
- (3) Formation of a site with a higher oxidation state by electrochemical oxidation of the radical OH.
- (4) Production of oxygen by chemical decomposition of the site with a higher oxidation state.
- (5) Combustion of the organic compound, R, by physisorbed OH radicals.
- (6) Chemical oxidation of the organic compound at a site with a higher oxidation state.

The BDD anode is the most potent known "non-active" electrode [191]. It is considered as the most suitable anode for the treatment of organic compounds by anodic oxidation. Furthermore, the BDD electrodes have high anodic stability and a broad working potential range [203,204]. The use of BDD has considerably increased the interest in the application of this method in the treatment of waters since excellent mineralization efficiencies are obtained.

It should be noted that this anode exhibits excellent chemical and electrochemical stability, an inert surface with low adsorption properties, long life, and a wide range of potential for water discharge [205,206], and therefore, it turns out to be a promising electrode for the decontamination treatment.

The main limitation of technology based on BDD electrodes is its high price, which hinders its use at the industrial scale. It has been shown that many biorecalcitant compounds including phenols, chlorophenols, nitrophenols, pesticides, synthetic dyes, pharmaceuticals, and industrial leachates can be completely mineralized with high current efficiency, even close to 100%, using a BDD anode [207–213].

The composition of the supporting electrolyte or the different ions present in real industrial effluents can vary the effectiveness of the electrooxidation process. During the electrolysis with BDD anodes, simultaneously with the generation of active oxygen species that give rise to the generation of •OH radicals, numerous reactions take place that can also lead to other oxidants depending on the ions present in the treated volume. In sulfate medium, oxidation of sulfate ions to peroxodisulfate can occur [209,214]:

$$2 \text{ SO}_{4^2} \longrightarrow \text{S}_2 \text{O}_{8^2} + 2 \text{ e}^- \qquad \text{Reaction (72)}$$

A very particular behavior is found when the solution contains chloride ions since the electrogeneration of active chlorine in the form of chlorine gas, hypochlorous acid, or hypochlorite ion occurs through Reactions (73)–(75). Under these conditions, organic matter can be competitively attacked by the ·OH radicals produced on the surface of the anode and the active chlorine produced and diffused into the solution. As a counterpoint, the formation of organochlorine intermediates can occur, which can be even more stubborn and more toxic than the primary pollutants.

$$Cl_{2(aq)} + H_2O \leftrightarrow HClO + Cl^- + H^+$$
 Reaction (74)

$$HClO \leftrightarrow ClO^- + H^+$$
 Reaction (75)

When a "non-active" anode such as BDD is used, hypochlorite ions are also generated from the oxidation of chloride ions by the ·OH radicals adsorbed on the BDD anode according to Reaction (76). The resulting ion can be oxidized consecutively to chlorite, chlorate, and perchlorate according to Reactions (76)–(79) [215,216]:

$Cl^- + OH \rightarrow ClO^- + H^+ + e^-$	Reaction (76)
$ClO^- + OH \rightarrow ClO_2^- + H^+ + e^-$	Reaction (77)
$ClO_{2^-} + OH \rightarrow ClO_{3^-} + H^+ + e^-$	Reaction (78)
$ClO_{3^-} + OH \rightarrow ClO_{4^-} + H^{+} + e^-$	Reaction (79)

It is worth mentioning that one of the most advanced large-scale applications in the field of electrochemical AOPs is the electrochemical disinfection of pool and spa water using automated equipment with BDD anodes. In this field, specialized products such as OxineoTM and SysneoTM have been developed for private and public facilities. Compared to other methods of disinfection, these systems have several advantages, since the chlorine smell typical of saline chlorination disappears, there is no accumulation of chemicals in the pool water—with the consequent reduction of allergic reactions—and there is no need to use anti-algae chemicals.

8. Prospects and Challenges of AOPs

From all the exposed in this review, AOPs arise as beneficial technologies for the removal of pollutants in general and antibiotics, in particular, that may be found in wastewaters. However, the applicability of these processes at the industrial scale is relatively limited at present.

Very recently, Rodríguez-Chueca et al. [217] have reported that AOPs, in general, improved the efficiency of UV-C on the removal of antibiotics. When applying the harshest operating conditions (0.5 mM dosage of oxidants and 7s of UV-C contact time), three antibiotics (ciprofloxacin, metronidazole, and sulfamethoxazole) were similarly removed using peroxymonosulfate and H₂O₂ as oxidants, four antibiotics (azithromycin, clindamycin, ofloxacin, and trimethoprim) were removed more efficiently using peroxymonosulfate, and three (clarithromycin, sulfadiazine, and sulfapyridine) using H₂O₂. The addition of Fe(II) only improved the degradation of four antibiotics (sulfamethoxazole, sulfadiazine, sulfapyridine, and metronidazole) compared to the photolytic process.

Chowdhury et al. [218] have studied the direct UV photolysis of different pharmaceutical compounds, including tetracycline antibiotics (chlortetracycline), sulfa drugs (sulfamethoxazole, sulfathiazole, and sulfisoxazole), and fluoroquinolones (ciprofloxacin) at full-scale. Except for ciprofloxacin, the remaining drugs showed considerable pH-dependent photolysis in the pH range under study (namely, 5–8). High removal by UV photolysis was attained, although a much higher UV fluence than that used for water disinfection was required. This latter finding suggests that additional treatments are necessary for water recycling.

Östman et al. [67] analyzed the effect of full-scale ozonation on the removal of up to eight antibiotics (namely, ciprofloxacin, norfloxacin, ofloxacin, pentamidine, clarithromycin, erythromycin, metronidazole, and trimethoprim) in Sweden's first sewage treatment plant with full-scale ozonation. Ozonation proved to be effective in most cases. Total (100%) removal of ciprofloxacin and metronidazole was reported, whereas 94% was achieved for erythromycin (versus 79% in the conventional treatment). Trimethoprim was poorly removed (41%) in the traditional treatment process, but 94% removal efficiency was reached by ozonation.

Rame et al. [219] also indicate that FLASH technology that uses physical and biological pretreatment, followed by an advanced oxidation process based on catalytic ozonation and followed by GAC and PAC filtration, has demonstrated good removal efficiency of macro-pollutants present in hospital wastewaters, including antibiotics.

Some years before, Sui et al. [220] reported that the sequential UV and ozonation process in a full-scale WWTP in Beijing was able to remove up to 13 pharmaceuticals and personal care products (PPCPs) including chloramphenicol. According to these authors, notwithstanding the fact that the UV exhibited a limited removal ability for most of the PPCPs under study, the sequential use of UV and ozone made it possible to minimize PPCPs in the final effluent of WWTPs.

To increase the feasibility of AOPs to be used at large scale, several aspects should be improved. With such an aim, further research work should be—and is currently being—performed on different topics such as, for instance, costs of the process, toxicity of effluents and byproducts, (photo)catalysts technology, and reactors design.

Many papers dealing with operational costs of AOPs at bench scale are available. However, articles focusing on operational expenses of full-scale advanced oxidation processes are scarce, and attention has been paid to this issue only in the last few years [46,221–227]. From the literature review, it may be concluded that treatment costs tend to decrease as the pollutant's concentration in water increases. Moreover, the ozonation and Fenton processes appear to be more economically viable and, as a consequence, have been more frequently implemented at the industrial scale. However, authors do not agree on which of these treatments is the most cost-effective one. When integrating UV radiation to other AOPs, it can be stated that removal efficiencies increase, but operational costs are higher, too. Also, it is commonly accepted that photocatalysis (mainly using TiO₂) is a relatively expensive AOP but also quite useful for the removal of pollutants.

In many cases, AOPs can be successfully applied for the removal of pollutants present in wastewaters and chemically degrade the parent compounds leading to their complete mineralization, thus generating CO₂ and water as the leading products and without generation of any toxicity. However, it is not infrequent that the oxidation leads to different byproducts that may have similar—or even higher—toxicity than the original pollutants themselves. Changes in the molecular structure of the pollutant may give rise to an entirely new kind of chemical toxicity or even to mutagenic [228] or estrogenic activity [229]. For instance, during ozonation, the bromide naturally occurring in wastewater can be oxidized to bromate [230], with increasing yields as ozone dose rises [231]. Bromate is included in the EPA's and EU's lists of potential carcinogens. However, the addition of H₂O₂ largely mitigates the formation of bromate [232]. Similarly, if wastewaters contain large amounts of nitrate, the treatment by UV/H₂O₂ AOP may result in increased mutagenicity of the treated effluent [233]. According to the literature, the incorporation of the nitrate-nitrogen into the organic matrix and the subsequent formation on nitrated/nitrosated compounds could be the reason that mutagenicity levels increase in treated waters. Other authors have reported similar results in terms of increased toxicity after the treatment of wastewaters containing antibiotics [77,234–238].

Among the different alternatives to generate •OH radicals in AOPs, heterogeneous photocatalysis appears as an up-and-coming solution in wastewater treatment. Photocatalysis is a nonselective process that can degrade a wide variety of pollutants. A photocatalyst (i.e., a semiconductor material) and light are the only requirements of this process. However, to the date, most of the results published in the literature focus on the use of UV irradiation, with wavelengths ranging from 320 to 400 nm, mainly because the bandgap of the semiconductor must be high enough to avoid fast recombination of the electron/hole pairs generated when the photoexcitation of the catalyst takes place. Different metal oxide semiconductors have been tested and used as potential photocatalysts for wastewater treatment. According to the literature [239], TiO₂ and ZnO are the most widely used metal oxides in AOPs, even though other metal oxides (such as V₂O₅, WO₃, MoO₃, or some of their derivatives) or even sulfides (CdS, ZnS) could also be used. However, their performance is below that of TiO₂. Furthermore, TiO₂ exhibits essential advantages: It can be used under ambient conditions, is relatively inexpensive, commercially available, non-toxic, and photochemically stable.

An adequate modification of the chemical composition of the catalyst may result in enhanced efficiency and reusability. For instance, noble metals (Au, Pt, Ag, and Pd), transition metals (Cr, Mn, Fe, Co, Ni, Cu, and Zn) or lanthanides (La, Nd, Sm, Eu, Gd, Yb, or Pr) have been used as dopants in

order to improve the photocatalytic activity of TiO₂. The main goals of the chemical modification of TiO₂ by using these dopants are: (i) To reduce the bandgap of the photocatalyst so that it is compatible with solar light (and not only with UV) to a solar light-compatible level; (ii) to maximize electronhole generation; and (iii) to increase the adsorption ability of TiO₂ towards organic pollutants by increasing its specific surface area [240–242].

Recently, a new group of materials, commonly known as two-dimensional (2D) nanomaterials, has shown promising properties to be used as novel photocatalysts and are receiving increasing attention from the scientific community [243]. These nanomaterials exhibit unique optical, electronic, and physicochemical properties, but their eventual applicability may be limited due to high production costs. 2D nanomaterials include graphene, graphitic carbon nitride (g-C₃N₄), 2D metal oxides and metallates, metal oxyhalides, and transition metal dichalcogenides. These materials can be applied alone as highly efficient photocatalysts. However, some of them exhibit better performance if they are combined with other "traditional" photocatalysts (e.g., TiO₂), which, in turn, make them more affordable. For instance, it has been demonstrated that the use of graphene and TiO₂ in the form of a heterojunction provides much higher photocatalytic efficiency than pure TiO₂ [244].

Finally, another critical aspect to be taken into consideration is the proper design of the reactor. Fluidized bed reactor (FBR) has been successfully used in the full-scale application of AOPs in treatment plants [245] and is perhaps the most versatile option for this kind of processes. FBR has proven to be more effective in wastewater treatment compared to other conventional reactors such as, for instance, fixed-bed column and activated sludge. If FBR technology is combined with AOPs sludge production—one of the main disadvantages of the Fenton process—can be minimized [246], the reusability of the catalyst is increased [245], and the overall performance of the process is improved. FBRs exhibit remarkable advantages such as low operating cost, high resistance, uniformity of mixing, and high mass transfer rates. This latter is particularly important in the implementation of full-scale O3-based AOPS since one of the most significant drawbacks of ozone technologies is the difficulty of achieving an adequate mass transfer of gaseous ozone into the bulk solution. The most commonly investigated FBR-integrated AOPs are fluidized bed Fenton and fluidized bed photocatalysis. In the case of FBR heterogeneous Fenton process, high degradation efficiency has been achieved and the sludge generation has been reduced simultaneously [247]. On the other hand, in addition to its excellent mixing and mass transfer ability, in photocatalytic processes, the use of FBR can also enhance light penetration and exposure of the interior of the reaction matrix, thus improving the overall yield of the process in terms of pollutant(s) degradation.

9. Conclusions and Final Recommendations

Antibiotics are almost ubiquitous pollutants that have been found in different kinds of surface waters, wastewaters, and WWTP and hospital effluents. Furthermore, the presence of antibiotics in water may cause harmful effects to human beings as well as promote the spread of resistant bacterial strains. After several decades of research on AOPs, these technologies have proven their efficiency for the removal of a wide variety of pollutants in general and antibiotics in particular. However, most of the literature published to the date is devoted to bench- or pilot-scale studies. The implementation of AOPs at the full-scale is still quite limited. Probably, the main difficulty for the development of these processes at an industrially operative scale is the high operational cost of AOPs, especially if compared with the conventional methods that are commonly applied nowadays. Thus, if the overall cost per unit mass of pollutant that is removed from water or unit volume of water, wastewater, or effluent that is lowered, the industrial implementation of these technologies will become much more attractive for companies and/or public administrations. Some suggestions on the way to achieve this goal are as follows:

(i) To avoid unnecessary expenses in terms of time, facilities, and reagents, AOPs should be integrated with other treatments and only with specific and clearly defined goals (i.e., the removal of recalcitrant (micro)pollutants, the polishing of previously treated effluents, etc.). Furthermore, synergistic effects between processes should be studied at least at the pilot-scale.

- (ii) Energy costs must also be reduced. In this connection, the search for novel, affordable photocatalysts that may use a broader part of the light spectrum instead of only UV is a priority. Furthermore, the application of renewable energy sources in the treatment plants should also be investigated.
- (iii) The generation of wastes (e.g., sludge in the Fenton process and/or exhausted or poisoned catalysts in photocatalyzed AOPs), should be minimized and possible alternatives for the valorization of such wastes should be explored.

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