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Treatment of Antibiotics in Wastewater Using Advanced Oxidation Processes (AOPs)

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Abstract

Antibiotics are nonbiodegradable, can survive at aquatic environments for long periods and they have a big potential bio-accumulation in the environment. They are extensively metabolized by humans, animals and plants. After metabolization, antibiotics or their metabolites are excreted into the aquatic environment. Removal of these compounds from the aquatic environment is feasible by different processes. But antibiotics are not treated in conventional wastewater treatment plants efficiently. During the last years studies with advanced oxidation processes (AOPs) for removal of these pharmaceuticals from waters has shown that they can be useful for removing them fully. Advanced oxidation processes (AOPs) can work as alternatives or complementary method in traditional wastewater treatment, and highly reactive free radicals, especially hydroxyl radicals (OH) generated via chemical (O_3/H_2O_2 , O_3/OH^-), photochemical (UV/ O_3 , O_3/H_2O_2) reactions, serve as the main oxidant. This study presents an overview of the literature on antibiotics and their removal from water by advanced oxidation processes. It includes almost all types of antibiotics which are consumed by human and veterinary processes. It was found that most of the investigated advanced oxidation treatment processes for the oxidation of antibiotics in water are direct and indirect photolysis with the combinations of H_2O_2 , TiO_2 , ozone and Fenton's reagent.

Keywords: wastewater, antibiotics, endocrine disrupter, advanced oxidation

1. Introduction

The “antibiotic” term qua generic is used to specify any class of organic molecule that blocks or ravage microbes by specific interactions with bacterial marks, without considering any compound or class [1]. Antibiotics are designed to act very effectively even at low doses and, in case of intracorporal administration, to be completely excreted from the body after a short time of residence [2]. They are nonbiodegradable and can survive in aquatic environments for long periods [3]. The entrance of these compounds into the environment owing to anthropogenic sources can result in a potential risk for organisms. Although antibiotics exist at residual levels, they can cause resistance in bacterial populations, making them inactive in the treatment of several diseases in the near future [4, 5]. And they cause endocrine-disrupting effects when they are consumed by living organisms. They interfere with the synthesis, secretion, transport, binding, action, and elimination of hormones in the human body [6].

The annual usages of antibiotics are determined between 100,000 and 200,000 t globally [7]. Traditionally, these compounds were not accepted as environmental contaminants, but their existence in the aquatic ecosystems has become an apprehension as biological impacts and potential threat to the environment [8–10]. Furthermore, it has been shown up that residual antibiotics are able to support the election of genetic variants of microorganisms concluding in the existence of antibiotic-resistant pathogens [11, 12].

Removal of these compounds from the aquatic environment is feasible by different processes. This can be carried out using biotic (biodegradation) or nonbiotic (chemical oxidation and advanced oxidation) ways. But antibiotics are not treated in conventional wastewater treatment plants efficiently. During the last years, studies with advanced oxidation processes (AOPs) for removal of these pharmaceuticals from waters have shown that they can be useful for removing them completely. In this chapter, we aim to introduce a review of literature on antibiotics and their removal from water by advanced oxidation processes. An effort to include as many studies as possible was made in order to highlight important findings and present the knowledge currently available on the removal efficiency of antibiotics from wastewater.

2. General description of antibiotics

Antibiotic as a word is reproduced from the Greek anti (=against) and biotikos (=living).

Most of the living organisms are able to compose matters that can influence other organisms' capacity for growth, endurance, and reproduction. Microorganisms have a versatile ability to inhibit the growth and purpose of other microorganisms and produce and release biologically effective substances at the appropriate moment. We denominate substances of this kind as *antibiotics* [13].

In addition, organisms' ability to compose antibiotics has been of great importance for the development of different life forms and their capability to accommodate to new circumambient. Nowadays, antibiotics are important components for the functions of various biological systems.

With the development of synthetic antibiotics, a large number of substances with specific areas of application have been given to access. Today, the level of usage of synthetic antibiotics and their effects to the environment are at a critical rate. Since antibiotics are bioavailable, they can show long-term biological effects in the environment.

Antibiotics can be grouped according to their chemical structure or mechanism of action. There are various groups of chemicals that can be arranged to different subgroups, such as β -lactams, quinolones, tetracyclines, macrolides, sulphonamides, and others. They are complicated molecules, which may have different functionalities within the same molecule. Consequently, they act as neutral, cationic, anionic, or zwitterionic under different pH conditions. Owing to different functionalities in a single molecule, their physico-chemical and biological properties (like octanol-water partition coefficients ($\log P_{ow}$), sorption behavior, photoreactivity and antibiotic activity, and toxicity) may change with pH [14].

b-Lactam antibiotics contain cefradine, amoxicillin, ceftriaxone, sulfamycin, and penicillins G and VK. Actually, these antibiotics have been insulated from molds and have been adapted to obtain different physicochemical and pharmacological properties [15]. They suppress bacterial cell wall synthesis.

Sulfonamides are synthetic antibiotics, and they inhibit generation of bacteria by behaving as competitive inhibitors of *p*-aminobenzoic acid in the folic acid metabolism cycle [15]. A diversity of sulfonamides have been developed, consumed, and finally detected in the environment, and some of them have been studied for their degradation by ozonation and AOPs. These compounds include sulfadiazine, sulfadimethoxine, sulfachlopyridazine, sulfamethazine, sulfamethizole, sulfamethoxazole, sulfisoxazole, sulfapyridine, sulfathiazole, sulfamoxole, and sulfamerazine.

Most common quinolone antibiotics are enrofloxacin and ofloxacin. They have been examined in terms of their degradation by ozonation and AOPs. More particularly, both are fluoroquinolones. While enrofloxacin is utilized as a veterinary antibiotic, despite that ofloxacin is designed for human uptake. These compounds have a benefit to suppress the activity of bacterial DNA gyrase. It is known that the quinolones are metabolized in the liver and eliminated in the urine [15, 16].

When we examine other antibiotics, clarithromycin, azithromycin, erythromycin, and roxithromycin are macrolide antibiotics, and lincomycin is a lincosamide antibiotic. These antibiotics are described by a property to inhibit bacterial protein synthesis. These antibiotics are mostly eliminated in the bile [15, 16].

Antibiotic is a chemotherapeutic agent that inhibits the growth of microorganisms (bacteria, fungi, protozoa, or viruses) even at very low concentrations. They are nonbiodegradable and can survive in aquatic environments for long periods. So they can bio-accumulate in the environment [3]. Also antibiotics in the environment may contribute to the emergence of antibiotic-resistant bacteria [17]. And they cause endocrine-disrupting effects when they are consumed by living organisms. They interfere with the synthesis, secretion, transport, binding, action, and elimination of hormones in the human body [6].

Releasing of antibiotics into the aquatic environment by human beings and animals depends mainly on the consumption rates of antibiotics [14, 18]. According to the investigations, some

antibiotics have toxic effects on humans, animals, and also microorganisms even at low concentrations. At the same time, they are nonbiodegradable and can survive in the environment even in the conventional wastewater treatments. So they cause bio-accumulation [3]. Therefore, the presence of antibiotics in the environment can cause the occurrence of antibiotic-resistant bacteria [17]. They are not treated in the conventional wastewater treatment plants completely. According to the recent studies, advanced oxidation processes (AOPs) are useful to remove these toxic compounds completely from waters.

2.1. Sources of antibiotics in the environment

In these last years, the use of antibiotics in veterinary and human medicine has been widespread, and consequently, the possibility of water contamination with such compounds has been increased [19]. These pollutants are continually discharged into the natural environment as parent compounds, metabolites/degradation products, or both forms by a diversity of input sources as shown in **Figure 1** [5].

Fertilizers present in the fields can contaminate soil and consequently surface and groundwater through runoff or filtration [20]. Likewise, human antibiotics which are present into the environment through discharge, entering in the sewage and reaching the Waste-water treatment plants (WWTP). Despite most of WWTPs are not projected to remove highly polar micropollutants [19], they can be transferred to surface waters and reach groundwater after leaching.

The sludge produced in WWTPs is utilized as soil manure and can cause problems when used as a fertilizer. Some other significant pollution source is the direct delivery of veterinary antibiotics through the implementation in aquaculture. Inappropriate elimination of unused/expired

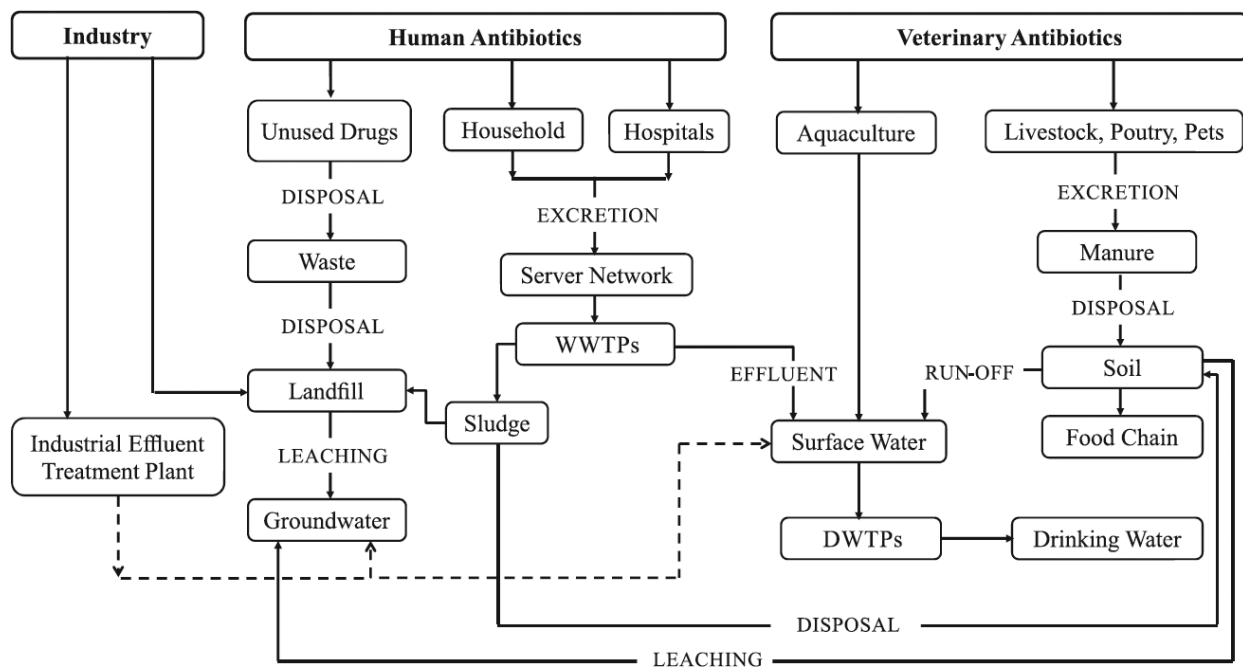


Figure 1. Pathways of antibiotics in the environment [5, 16].

drugs can also be considered as significant points of contamination. These are derived directly from sewage discharge or landfills deposition, waste effluents from manufacture, or accidental spills during manufacturing or distribution [5].

2.2. Occurrence

Research has quite extensively studied the presence of antibiotics in the environment (for a short overview, see **Table 1**). With respect to other pharmaceuticals, the concentrations of antibiotics measured in different countries were found in the same range of concentrations in the different compartments [14, 21–23]. The antibiotic groups that have been analyzed up to now include a number of different important classes of antibiotics. They include primarily macrolides, aminoglycosides, tetracyclines, sulfonamides, sulfanilamides, and quinolones to name just a few [14, 23–29].

Antibiotic	Sewage treatment plant effluent (ng L ⁻¹)	Surface water (ng L ⁻¹)	Ground water*/bank filtrate (ng L ⁻¹)	References
<i>Penicillins</i>				
Penicillin	up to 200	up to 3		[32]
Flucloxacillin		7		[33]
Piperacillin		48		[33]
<i>Macrolides</i>				
Macrolide	up to 700	up to 20	up to 2*	[32]
Azithromycin		up to 3		[33]
Erythromycin-H ₂ O	up to 287		up to 49	[34, 35] [36]
	up to 6000	up to 1700		[8]
		up to 190		[33]
		up to 15.9		[37]
		up to 220		[38]
	up to 400			[30]
Clarithromycin	up to 328	up to 65		[34, 35]
	up to 240	up to 260		[8]
		up to 37		[33]
		up to 20.3		[37]
		up to 20.3		[39]
	up to 38			[30]
Roxithromycin	up to 68			[30]
	up to 72			[34, 35]
			up to 26	[36]

Antibiotic	Sewage treatment plant effluent (ng L ⁻¹)	Surface water (ng L ⁻¹)	Ground water*/bank filtrate (ng L ⁻¹)	References
	up to 1000	up to 560		[8]
		up to 14		[33]
		up to 180		[38]
		up to 350		[31]
<i>Chinolones</i>				
Fluorchinolone	up to 100	up to 5		[32]
Fluorchinolone	up to 106	up to 19		[34, 35]
Ciprofloxacin		9		[33]
		up to 30		[38]
		up to 26.2		[37]
		up to 1300		[31]
		up to 26		[39]
Norfloxacin		up to 120		[38]
Ofloxacin	up to 82			[30]
		20		[33]
<i>Sulfonamides</i>				
Sulfamethoxazole	up to 370			[30]
	up to 2000	up to 480	up to 470	[8]
		up to 52		[33]
		up to 1900		[38]
		up to 2000		[31]
Sulfamethazin			up to 160	[8]
		up to 220		[38]
Sulfamethizole		up to 130		[38]
Sulfadiazine			up to 17	[36]
Sulfadimidine			up to 23	[36]
		up to 7		[33]
<i>Tetracyclines</i>				
Tetracycline (no more specified)	up to 20	up to 1		[32]
Tetracycline		up to 110		[38]
Chlortetracycline		up to 690		[38]
		up to 600		[31]
		up to 100		[38]
Oxytetracycline		up to 340		[38]
		up to 19.2		[37]

Antibiotic	Sewage treatment plant effluent (ng L ⁻¹)	Surface water (ng L ⁻¹)	Ground water*/bank filtrate (ng L ⁻¹)	References
<i>Others</i>				
Trimethoprim	up to 38			[30]
		up to 24		[36]
	up to 660	up to 200		[8]
		up to 12		[33]
		up to 710		[38]
Ronidazol			up to 10	[36]
Chloramphenicol	up to 68			[30]
	up to 560	up to 60		[8]
Clindamycin	up to 110			[30]
		up to 24		[33]
Lincomycin		up to 730		[38]
		up to 248.9		[39]
Spiramycin		up to 74.2		[37]
Oleandomycin		up to 2.8		[37]
Tylosin		up to 280		[38]
		up to 2.8		[37]

*Directly impacted by surface water.

Table 1. Examples of measured concentrations of antibiotics in the aquatic environment [14, 18, 30, 31].

3. Advanced oxidation processes (AOPs)

During the oxidation of organic contaminants, the ultimate goal is to produce simple, relatively harmless inorganic molecules [40]. Advanced oxidation processes are characterized by their production of the hydroxyl radical ($\cdot\text{OH}$), a very strong oxidant, in sufficiently high concentrations to affect water quality. The symbol “ \cdot ” represents the radical center, a single unpaired electron [41].

At optimum operation conditions, for instance sufficient contact time, it is possible to mineralize the target contaminant to CO_2 and H_2O , the most stable end products of chemical oxidation. For this reason, the extraordinary definition of AOPs on chemical processes is that they are completely described as “environmentally friendly” [42].

The basic treatment of AOPs can be explained in two steps: one is the generation of hydroxyl radicals and the other is the oxidative reaction of these radicals with molecules [43]. The dissolved organic pollutants can be converted into CO_2 and H_2O by AOPs. The generation of hydroxyl radical might be by the use of UV, UV/ H_2O_2 , UV/ O_3 , $\text{TiO}_2/\text{H}_2\text{O}_2$, $\text{Fe}^{+2}/\text{H}_2\text{O}_2$ and one or two processes [44].

AOPs can be classified in two groups: (1) nonphotochemical AOPs and (2) photochemical AOPs. Nonphotochemical AOPs include cavitation, ozonation, Fenton and Fenton-like processes, wet air oxidation, ozone/hydrogen peroxide, etc. Photochemical oxidation processes include homogeneous and heterogeneous processes [45].

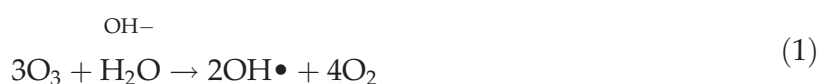
3.1. Nonphotochemical oxidation processes

Nonphotochemical oxidation processes can be classified as follows: ozonation, peroxide, Fenton process, ozone/hydrogen, supercritical water oxidation, electrochemical oxidation, cavitation, gamma-ray, X-ray, electrical discharge-based nonthermal plasma, and electron beam.

3.1.1. Ozonation

Ozone is a powerful oxidizer and has been increasingly used for the treatment of wastewater [46]. High pH values (>11.0) causes high efficiency and ozone behaves randomly with all organic and inorganic compositions present in the reacting medium [45]. Ozone reacts with substances in two different ways: indirect and direct. These two reaction pathways are managed by different type of kinetics and lead to different oxidation products [47].

Simplified reaction mechanism of ozone at high pH is given in below:



3.1.2. Ozone/hydrogen peroxide (peroxone) process ($\text{O}_3/\text{H}_2\text{O}_2$)

The principle of peroxonation is based on the coupling between ozone (O_3) and H_2O_2 , resulting in the generation of oxidizing radicals. As pointed out by Zaviska et al. [47], the peroxonation mechanism could be more productive than ozonation alone, and H_2O_2 impacts on increasing the decomposition percentage of O_3 in water, which generates a larger number of very reactive $\cdot\text{OH}$ radicals [49]. Because of the high cost of ozone generation, this combination makes the process economically feasible [50]. Several factors limit the usefulness of the peroxonation process such as important energetic consumption, low water solubility of ozone, and its sensitivity to several factors [51]. A general mechanism of peroxon process is given below:



Solution pH is critical as well for the process output like other AOPs. Higher production rates of hydroxyl radicals will be obtained by the addition of hydrogen peroxide to the aqueous O_3 solution at high pH conditions. Independence of peroxone process from any light source or UV delivers a certain benefits to this operation [44].

3.1.3. Fenton process

Fenton's reaction is known as the dark reaction of ferrous iron (Fe(II)) with H_2O_2 (Eq.(15)) [6]. $\cdot\text{OH}$ radical is generated through the agency of reaction between H_2O_2 and Fe^{+2} salts as described below.



Thus, composed hydroxyl radical can react with Fe(II) to develop ferric ion (Fe(III)) (Eq. (16))



As an alternative, hydroxyl radicals are able to react with organic pollutants and start oxidation in a waste stream,



Reactions can result into the degradation of Fe^{+3} to Fe^{+2} at a value of pH between 2.7 and 2.8.



In these circumstances, iron can be considered as a true catalyst [156].

Process efficiency is closely related to the solution pH whose optimal values are between 2 and 4 as well as the COD:H₂O₂:catalyst ratio in the feed [52].

Basically, the Fenton process possesses several important advantages for water/wastewater treatment [48, 53]:

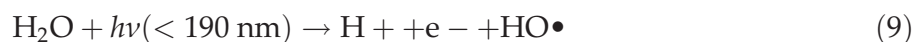
- A plain and adaptable operation permitting easy execution in existing plants
- Easy-to-use and relatively cheap chemicals
- No need of energy input

3.2. Photochemical oxidation processes

3.2.1. Homogeneous photochemical oxidation processes

3.2.1.1. Vacuum UV (VUV) photolysis

The vacuum ultraviolet (UV) is absorbed by all the materials from water to air, therefore can only be transferred in a vacuum. The absorption of a VUV photon causes breaking of one or more bond. As an example, water is decomposed by



VUV photolysis has a high feasibility for the oxidative degradation of organic pollutants in water. In spectral domain (approx. 140–200 nm), it produces hydrogen atoms and hydroxyl radicals. Due to the high absorption cross-section of water and quantum yields of water homolysis of 0.45–0.3 at stimulation wavelengths (between 140 and 185 nm) provide productive local concentrations of hydroxyl and hydrogen radicals. VUV photolysis is a new technique for water

treatment and suggests the benefit to generate unusually high local concentrations of oxidative reactive intermediates without the addition of supplementary oxidant [44, 54].

3.2.1.2. Hydrogen peroxide/UV (H_2O_2/UV) process

Hydrogen peroxide can be photolyzed by UV radiations by producing the homolytic scission of the O–O bond of the H_2O_2 and resulting the formation of $\bullet OH$ radicals which can also be supplied to the decomposition of H_2O_2 by secondary reactions [48]. The main reaction is given below:



UV/ H_2O_2 process is effective in mineralizing organic pollutants. As an disadvantage the process cannot use solar light as the source of UV light owing to the fact that the required UV energy is not available in the solar spectrum [55]. Over and above, H_2O_2 has poor UV absorption characteristics. At last, special reactors designed for UV illumination are required [56].

The major factors influencing the process are the amount of H_2O_2 used, presence of bicarbonate, wastewater pH, the initial concentration of the object compound, and reaction time [57].

3.2.1.3. Ozone/UV (O_3/UV) process

The advanced oxidation process with ozone and UV radiation is initiated by the photolysis of ozone. Hydroxyl radicals can be composed by those in hydrogen peroxide under UV and/or ozone. The equations are given below:



All kinds of UV light origins can be utilized for this process, especially low-pressure mercury vapor lamps. The O_3/UV process does not have the same limitations as that of H_2O_2/UV process. Many variables (temperature, pH, UV intensity, turbidity, lamp spectral characteristics, and pollutant type, etc.) affect the performance of the system [42, 44].

3.2.1.4. Ozone/hydrogen peroxide/UV ($O_3/H_2O_2/UV$) process

This method is considered to be the most effective and powerful method, which provides a fast and complete mineralization of pollutants [42, 50]. The addition of H_2O_2 to the O_3/UV process accelerates the decomposition of ozone, which results in an increased rate of $\cdot OH$ generation.

The main short mechanism of the $O_3/H_2O_2/UV$ process is given below:



The capital and operating costs for the system vary widely depending on the wastewater flow rate, types, and concentrations of contaminants present and the degree of removal required [58].

3.2.1.5. Photo-Fenton process

The Photo-Fenton process occurs by the combination of H₂O₂ and UV radiation with Fe(II) or Fe(III). The main factor of the mechanism is that iron salts act as photocatalysts and H₂O₂ as an oxidizing agent. It offers a productive and cheap method for wastewater treatment and produces hydroxyl radicals to a greater extent [59].

The reaction is given below:



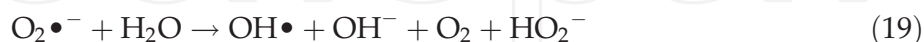
A highly low reaction time is required for the photo-Fenton process, and depending on the operating pH value, the concentrations of H₂O₂ and iron are added.

3.2.2. Heterogeneous photochemical oxidation processes

Widely investigated and applied heterogeneous photochemical oxidation processes are semiconductor-sensitized photochemical oxidation processes.

A semiconductor consists of two energy bands: one is high energy conduction and the other is low energy valence band. This kind of photolytic chemical oxidation is used for the generation of OH radical in heterogeneous processes. Zinc oxide, strontium titanium trioxide, and TiO₂ have been used for commercial implementation. Valance and conduction bands of a semiconductor material are distinguished by energy gap/band gap [60].

Moreover, the photocatalyst TiO₂ is a wide band gap semiconductor (3.2 eV) and is successfully used as a photocatalyst for the treatment of organic pollutants [61, 62]. To summarize, in the TiO₂ process, the photon energy given to achieve the band gap energy and to induce an electron into the transmission band from the valence band can be fed with a wavelength shorter than 387.5 nm. Clarified reaction mechanisms of TiO₂/UV process are given below [Eq. (16)–(19)].



The basic reason of this reversal is the production of photons. The reversal mechanism importantly decreases the photocatalytic efficiency of a semiconductor. Main benefit of TiO₂/UV process is low energy consumption thus sunlight can be utilized as a light source [44].

AOPs have been examined in terms of limitations and summarized below.

As an example, UV oxidation process with H₂O₂ is just effective at low wavelengths (especially under 200 nm). The treated aqueous flux must supply good transmission of UV light. Scavengers and high doses of chemical subscriptions may limit the process. Insoluble oil and grease,

heavy metal ions, insoluble oil and grease, carbonates, and high alkalinity may cause clogging of the UV quartz handle. Air emission problems with O₃ may arise. The cost of the AOPs is expensive when compared to rival technologies [42].

3.3. Assessment of AOPs performance for antibiotic removal

Ozonation and AOPs are required for efficient degradation of antibiotics in water and wastewater. These treatment processes have an advantage of elimination of such pollutants through mineralization or conversion to the products that are less harmful to human health and the aquatic environment.

Various studies have published the effective AOPs treatment for the removal of antibiotics from wastewater [63–67]. High-quality and effective publications relevant with the AOP studies on the mechanisms and applications of water and wastewater treatments have been pronounced for last two decades. From the theoretical, environmental, and economical point of view, they demonstrate a great and increasing interest. As shown in **Table 2**, several studies have been conducted on the applicability of AOPs on different antibiotic classes.

Ozone is a potent oxidant and has been progressively applied for the treatment of wastewater. Ozone and/or hydroxyl radicals passivate bactericidal characteristics of antibiotics by disrupting or modulating their pharmaceutically active functional groups, such as N-etheroxime and dimethylamino groups of macrolides [68, 69], aniline moieties of sulfonamides [70], thioether groups of penicillins, unsaturated bonds of cephalosporin, and the phenol ring of trimethoprim [69]. High removal rates (>90%) were achieved by ozonation of the compounds with electron-rich aromatic systems, such as hydroxyl, amino (e.g., sulfamethoxazole), acylamino, alkoxy, and alkyl aromatic compounds, as well as those compounds with deprotonated amine (e.g., erythromycin, ofloxacin, and trimethoprim) and nonaromatic alkene groups, since these structural moieties are highly amendable to oxidative attack [1]. Ozonation process was found to be effective for the removal of b-lactams, macrolides, sulfonamides, trimethoprim, quinolones, tetracyclines, and lincosamides [5].

The performance of ozone treatment can be improved providing ozone is combined with UV irradiation, hydrogen peroxide, or catalysts such as iron or copper complexes [52]. Regardless, optimum process and operational circumstances have still been determined for the different water and wastewater types together with various types of antibiotics [152].

In general, Fenton process has been widely used successfully for the oxidation of many groups of antibiotics, including b-lactams, quinolones, trimethoprim, and tetracyclines. Fenton's oxidation is a homogeneous oxidation process and considered to be a metal-catalyzed oxidation reaction, in which iron acts as a catalyst [65, 153]. The main handicap of the process is the low pH value. It is required to avoid iron precipitation that takes place at high pH [154, 155].

Heterogeneous photocatalysis with TiO₂ semiconductor is generally accomplished by the illumination of a suspension of TiO₂ in aqueous solution with light energy which is greater than its bandgap energy. This causes the generation of high energy electron-hole pairs (e⁻/h⁺), which may migrate to the surface of the catalyst and may either reunite producing thermal

Compound name	AOP	Concentration	Reaction conditions	References
Amoxicillin, sulfamethoxazole, and ciprofloxacin	Direct photolysis with UV	1 mgL ⁻¹	250 W lamp (254 nm), UV doses: 0–2.5 × 10 ⁴ μW s cm ⁻² , urban wastewater	[71]
β-Lactam antibiotics (amoxicillin and ampicillin)	Ferrate (VI)	0.1 mM	Fe(VI): 0.1–10 mM, pH 7.0, synthetic wastewater	[72]
Amoxicillin and cloxacillin	Photo-Fenton	150 mgL ⁻¹	Solar intensity 0.85 kWm ⁻² , pH 3, synthetic wastewater	[73]
Enrofloxacin	Wet air oxidation and ozonation	0.2 mM	<i>Wet air oxidation</i> : 50 mL Teflon-lined stainless steel autoclave, 0.5 MPa, 150°C stirring speed: 300 rps <i>Ozonation</i> : Pyrex glass tubular photoreactor, flow rate: 7.3 L h ⁻¹ , OGV-500 catalyst, synthetic wastewater	[74]
Amoxicillin, ampicillin, and cloxacillin	Fenton	AMX, AMP, CLX: 104, 105, 103 mgL ⁻¹	pH 3, COD: 520 mgL ⁻¹ , synthetic wastewater	[75]
Amoxicillin, ampicillin, and cloxacillin	Photo-Fenton	AMX, AMP, CLX: 104, 105, 103 mgL ⁻¹	UV lamp, 230 V, 0.17 A, 6 W, 365 nm, synthetic wastewater	[76]
Amoxicillin, ampicillin and cloxacillin	UV/TiO ₂ and UV/H ₂ O ₂ /TiO ₂	AMX, AMP, CLX: 104, 105, 103 mgL ⁻¹	pH ~ 5, COD: 520 mgL ⁻¹ , BOD ₅ /COD ~0 and DOC 145 mgL ⁻¹ , synthetic wastewater	[77]
Amoxicillin and cloxacillin	UV/TiO ₂ /H ₂ O ₂	AMX: 138 mgL ⁻¹ CLX: 84 mgL ⁻¹	6-W lamp, wavelength ≈ 365 nm, pharmaceutical industry wastewater	[67]
Amoxicillin	UV-A/TiO ₂	2.5–30 mgL ⁻¹	Degussa P25 TiO ₂ , TiO ₂ : 100–750 mgL ⁻¹ , pH 5 or 7.5, photon flux of 8 × 10 ⁻⁴ E/(L min), 9 W lamp, 350–400 nm, 25°C, synthetic wastewater	[78]
Amoxicillin, ampicillin, and cloxacillin	Fenton, photo-Fenton, TiO ₂ photocatalytic and UV/ZnO	AMX, AMP, CLX: 104, 105, 103 mgL ⁻¹	UV lamp, 230 V, 0.17 A, 6 W, 365 nm, synthetic wastewater	[77]
Amoxicillin	O ₃ /OH ⁻ , H ₂ O ₂ /UV, Fe ²⁺ /H ₂ O ₂ , Fe ³⁺ /H ₂ O ₂ , Fe ²⁺ /H ₂ O ₂ /UV and Fe ³⁺ /H ₂ O ₂ /UV	AMX: 400 mgL ⁻¹	O ₃ generated from O ₂ , 21W Hg lamp (253.7 nm), flow rate: 1.3 L/min, light intensity: 3.65 WL ⁻¹ (1.73 × 10 ⁻⁴ EinsteinL ⁻¹ s ⁻¹), effective pathlength: 1.72 cm, pharmaceutical wastewater	[3]
Amoxicillin and cloxacillin	Fenton	AMX and CLX: 150 mgL ⁻¹	pH 3.0, H ₂ O ₂ /COD: 1.0–3.0, H ₂ O ₂ /Fe ²⁺ : 2–150 and reaction time: 60–120 min, synthetic wastewater	[79]
Amoxicillin, oxacillin, and ampicillin	Nonthermal plasma	OX, AMX, AMP: 100 mgL ⁻¹	Discharge was generated at the gas-liquid interface at room temperature and atmospheric pressure, in	[80]

Compound name	AOP	Concentration	Reaction conditions	References
Amoxicillin	UV, O ₃ , Fenton, Fenton-like, photo-Fenton, UV/O ₃ /H ₂ O ₂ , TiO ₂ , Fe(II), and Fe(III)	1 μM	oxygen flow rate: 600 sccm, power: 2 W, pH 8, synthetic wastewater Temperature: 20°C, 15 W Hg lamp (254 nm), light intensity: 1.81 micro Einstein s ⁻¹ , optical path: 5.09 cm, O ₃ was generated from O ₂ . flow rate of O ₃ : 16 mg h ⁻¹ photo-Fenton and photo-Fenton: pH 3 and other experiments were carried out at natural pH for Fenton and photo-Fenton Fe(II) and H ₂ O ₂ concentration: 10 μM, ultra-pure water, reservoir water, groundwater, secondary effluents from municipal WWTP	[81]
Amoxicillin	Photo-Fenton	0.1 mM	15-W black-light fluorescent lamp (365 nm), pharmaceutical solution flow rate: 80 mL min ⁻¹ , pH 2.5, ferric nitrate or FeOx conc.: 0.2 mmol L ⁻¹ , H ₂ O ₂ conc.: 1.0–10.0 mmol L ⁻¹ , sewage treatment plant effluent	[82]
Amoxicillin	Microwave assisted Fenton	450 μg L ⁻¹	H ₂ O ₂ conc.: 2 g L ⁻¹ , FeSO ₄ .7H ₂ O conc.: 0.2 g L ⁻¹ , pH 3.5, microwave-assisted oxidation reactions were performed with a modified version of the domestic electric oven: power of 1200 W, of 2450 MHz, synthetic wastewater	[83]
Amoxicillin	Ozonation	5.0 × 10 ⁻⁴ M	Ozonation were performed in a semicontinuous stirred gas–liquid reactor. 25°C, flow rate: 361 h ⁻¹ , synthetic wastewater	[84]
Amoxicillin	Photo-Fenton	50 mg L ⁻¹	Solar simulator: 1100-W xenon arc lamp (290 nm), minimum intensity (250 W m ⁻²) pH 6.2, TOC: 26.3 mg C L ⁻¹ , FeSO ₄ .7H ₂ O or FeOx conc.: 0.05 mM, H ₂ O ₂ concentration used was 120 mg L ⁻¹ , pH 2.5–2.8, synthetic wastewater	[85]
Amoxicillin	Sulfate radicals under ultrasound irradiation	0.095 mmol L ⁻¹	Ultrasonic generator: 20 kHz, Ti probe, synthetic wastewater	[86]
Amoxicillin	UV and UV/H ₂ O ₂	00 μM	Low-pressure Hg arc-UV (254 nm) Photon fluence rate: 8 × 10 ⁻⁷ Einstein L ⁻¹ s ⁻¹ , effective light path: 5.5 cm, T: 20 ± 2°C pH 7	[87]

Compound name	AOP	Concentration	Reaction conditions	References
Trimethoprim, sulfamethoxazole, clarithromycin, erythromycin, and roxithromycin	Ozonation and UV	TMP:0.34 $\mu\text{g L}^{-1}$ SMX: 0.62 $\mu\text{g L}^{-1}$ CMI: 0.21 $\mu\text{g L}^{-1}$ EMC: 0.62 $\mu\text{g L}^{-1}$ RXM:0.54 $\mu\text{g L}^{-1}$	H ₂ O ₂ : 0.4, 2, 3, 4, 5, and 10 mM, synthetic wastewater pH: 7.2, DOC: 23.0 mg L^{-1} , COD: 30.0 mg L^{-1} AOX: 100 mg L^{-1} , BOD ₅ : 2.8 mg L^{-1} , low-pressure UV unit (254 + 185 nm, 110 W power rating, 400 J m ⁻² by a flowrate: 2 m ³ h ⁻¹), municipal wastewater	[88]
Beta lactam antibiotics	Sulfate radical oxidation	-	Linear accelerator (LINAC) electron pulse radiolysis system was used, T: 20–22°C, 4–6 ns pulses of 8.0 MeV electrons generating sulfate Radical concentrations of 5–10 μM per pulse were used, synthetic wastewater	[89]
Flumequine, ofloxacin, and sulfamethoxazole	Photo-Fenton	100 $\mu\text{g L}^{-1}$	pH 5, Fe ²⁺ conc.: 5 mg L^{-1} , natural water	[90]
Cefalexin	Electro Fenton	50, 100, 200, and 300 mg L^{-1}	Cathode: activated carbon fiber (ACF), resistivity: 18.2 M Ω cm, T: 25°C, FeSO ₄ ·7H ₂ O conc.: 0.5–1 mM, pH 2–5, wastewater	[91]
Cefazolin	TiO ₂ /UV and sunlight	1.0 $\times 10^{-2}$ mol L ⁻¹	TiO ₂ Degussa P25 and the N-doped TiO ₂ were used; 5 \times 8 W blacklight Fluorescent lamps (max. 365 nm), photonic fluence: 3.1 $\times 10^{-7}$ Einstein s ⁻¹ , T: 23 \pm 2°C, pH 6.4 \pm 0.1, synthetic wastewater	[92]
Ceftriaxone, cephalosporine, penicillin VK, penicillin group, enrofloxacin, and quinolone	O ₃ and O ₃ /H ₂ O ₂	COD: 450 mg L^{-1}	Ozone generated from O ₂ , pH 3, 7, and 10.6, oxygen flow rate: 100 Lh ⁻¹ , T: 20°C \pm 2, synthetic wastewater	[93]
Chloramphenicol	Photo-Fenton	200 mg L^{-1} ,	400 W high-pressure Hg vapor lamp (295–390 and 295–710 nm), photonic flux: 6.0 $\times 10^{-7}$ and 3.3 $\times 10^{-6}$ Einstein s ⁻¹ , T: 25–30°C, synthetic wastewater	[94]
Chloramphenicol	Solar photoelectro-Fenton	245 mg L^{-1}	pH 3.0, T:35°C, synthetic wastewater	[95]
Chloramphenicol	UV/H ₂ O ₂	100 mg L^{-1}	T: 20°C \pm 2, 6-W low-pressure Hg lamp (254 nm), pH 5.5 \pm 0.1, synthetic wastewater	[96]
Chloramphenicol	Direct photolysis (UVC), hydrogen peroxide/UVC and solar radiation	20 mg L^{-1}	30W three UVC lamps, illuminance: 2500 lux, 53 $\mu\text{W cm}^{-2}$ (290 and 390 nm) and 18.6 $\mu\text{W cm}^{-2}$ (254 nm), synthetic wastewater	[97]

Compound name	AOP	Concentration	Reaction conditions	References
Chlortetracycline, doxycycline, oxytetracycline	Ozone	5×10^{-6} M	Flow rate: 80 cm ³ /min, T: 20–21°C, synthetic wastewater	[98]
Chlortetracycline, sulfamethoxazole	UV, electron beam, ozone	30 mgL ⁻¹	pH 4.63 and 4.33, atmospheric pressure T: 22 ± 2°C, 6-W single UV-C lamp (254 nm), ozone was produced from O ₂ , electron accelerator (1 MeV and 40 kW), synthetic wastewater	[99]
Chlortetracycline	Photocatalytic ozonation	0.15 mM	Ozone generated from O ₂ (air pressure: 5 bar, air flow rate: 1200 L h ⁻¹), ozone input: 20 g m ⁻³ and flow rate of the ozone/air: 20 L h ⁻¹ , T: 25°C, 15-W UV low-pressure lamp (254 nm), synthetic wastewater	[100]
Chlortetracycline	Photocatalytic ozonation	0.5 mM	Ozone generated from pure oxygen. flow rate: 20 mg min ⁻¹ , T: 20 ± 2°C, 125-W high-pressure UV lamp (260, 275, 290, 302, 307, 315, 336, 366, 406, and 434 nm), TiO ₂ : Degussa P25 and 0.1 g L ⁻¹ , synthetic wastewater	[101]
Ciprofloxacin and sulfamethoxazole	persulfate	0.15 mM	Initial pH 6 and decreased to 3–4. K ₂ S ₂ O ₈ and Fe (II)/Fe(II)-chelate: 4.8 and 4.8 mM, river water	[102]
Ciprofloxacin, moxifloxacin	UV and TiO ₂ /UV	CIP:45.3 μM and MOX: 37.4 μM	Photocatalyst: TiO ₂ -P25, TiO ₂ : 0.5 g L ⁻¹ , T: 298 ± 1°K, synthetic wastewater	[103]
Ciprofloxacin	Electron ionization	100 mg L ⁻¹	10 MeV, 10-kW electron ionizing energy unit, synthetic wastewater	[104]
Ciprofloxacin	O ₃ /H ₂ O ₂	45.27 μM	A bubble reactor was used for ozonation. Ozone generated from O ₂ . T: 6.0–62°C, ozone conc.: 2500 ppm, gas flow rate: 120 mL min ⁻¹ , T: 27.5°C, H ₂ O ₂ : 2–990 μmol L ⁻¹ , synthetic wastewater	[105]
Ciprofloxacin	UV, TiO ₂ /UV, O ₃ and H ₂ O ₂	200 μg L ⁻¹	Photocatalyst: TiO ₂ -P25, 125W medium-pressure Hg lamp, pH 3 (UV and TiO ₂ /UV), TiO ₂ conc.: 571 ppm, ozone generated from O ₂ , flowrate: 8 L min ⁻¹ , pH 9 (O ₃ and H ₂ O ₂), H ₂ O ₂ conc.: 500 and 1000 mg L ⁻¹ , hospital wastewater	[106]
Ciprofloxacin	Photo-Fenton	0.15 mM	T: 298 K, 125-W high-pressure lamp, photonic flux (9×10^4 μEs m ⁻² s ⁻¹), synthetic wastewater	[100]

Compound name	AOP	Concentration	Reaction conditions	References
Ciprofloxacin	Pulsed radiolysis, UV	100 mM	Electron pulse radiolysis 8-MeV TBS-8/16-1S linear accelerator, pulse lengths: 2.5–10 ns, $\lambda = 472$ nm, $((Ge) = 5.2 \times 10^{-4} \text{ m}^2 \text{ J}^{-1}, 3-5 \text{ Gy per 2-3 ns pulse, 8-12 replicate pulses, } T: 25 \pm 1^\circ\text{C, 125-W high-pressure Hg lamp } (E_{\text{max}} = 365 \text{ nm})$ Light intensity: 0.38 mWcm^{-2} , TiO_2 : 1.5 gL^{-1} (Degussa P25), synthetic wastewater	[107]
Amoxicillin and cloxacillin	Photo-Fenton	AMX: $138 \pm 5 \text{ mgL}^{-1}$ CLX: $84 \pm 4 \text{ mgL}^{-1}$	230 V, 0.17 A, 6-W UV lamp (365 nm), antibiotic wastewater	[67]
Dicloxacillin and ceftazidime	Ozonation	1.5 mg L^{-1}	Ozone gas-phase concentration (mg L^{-1}): $5 \pm 0.5-30 \pm 0.5$, volumetric ozone-gas flow rate (mL min^{-1}): 40 ± 0.5 , ozone inlet pressure (bar): 2.5 ± 0.1 , transmembrane pressure (TMP) (bar): 2.1 ± 0.1 , volumetric cross-flow rate (Lmin^{-1}): 0.55 ± 0.05 , temp. ($^\circ\text{C}$): 24 ± 1 , surface water	[108]
Doxycycline and norfloxacin	UV C, ozonation	$5 \times 10^{-5} \text{ M}$	Ozone was produced from pure oxygen, gas flow rate: 30 L h^{-1} , 15-W low-pressure Hg vapor lamp (254 nm), commercial activated carbon Hydraffin P-110 was used in granular form. Titanium dioxide Degussa P-25 was also used. Synthetic wastewater.	[109]
Enrofloxacin	Anodic oxidation, electro-Fenton (EF), photoelectro-Fenton (PEF) and solar photo electro-Fenton	158 mgL^{-1}	Fluorescent lamp (360 nm, 1.4 Wm^{-2}), pH 3.0, T: 35°C , synthetic wastewater	[110]
Enrofloxacin, ciprofloxacin	UV/H ₂ O ₂ , UV/H ₂ O ₂ /Fe(II), O ₃ , O ₃ /UV, O ₃ /UV/H ₂ O ₂ and O ₃ /UV/H ₂ O ₂	0.15 mM	Ozone, generated from pure oxygen air Pressure: 5 bar, air flow rate 1200 L h^{-1} Flow rate of the ozone/air mixture: 20 L h^{-1} , T: 25°C , 15W UV low-pressure lamp (254 nm), synthetic wastewater	[100]
Ciprofloxacin, erythromycin, ofloxacin, sulfamethoxazole, trimethoprim	Ozonation	ERYC: 346 ngL^{-1} CIP: 5524 ngL^{-1} OFX: 2275 ngL^{-1} SMX: 279 ngL^{-1} TMP: 104 ngL^{-1}	pH 7.54, COD (mgL^{-1}) 269, BOD ₅ (mgL^{-1}) 42, T: 25°C , ozone was produced by a corona discharge ozonator (Ozomatic, 119 SWO100) fed by an AirSep AS-12 PSA oxygen generation unit. gas flow rate: $0.36 \text{ Nm}^{-3}\text{h}^{-1}$, pH value of 8.5 ± 0.1 urban	[111]

Compound name	AOP	Concentration	Reaction conditions	References
Flumequine, ofloxacin, sulfamethoxazole	Modified photo-Fenton	100 $\mu\text{g L}^{-1}$	wastewaters were taken from Alcalá de Henares (Madrid) 5 mg L^{-1} Fe, 35 mg L^{-1} , 50 mg L^{-1} H_2O_2 , oxalic acid, initial pH \approx 7, $\lambda < 400$ nm Solar UV power: 30 W m^{-2} , municipal wastewater treatment plant effluent was taken downstream of the MWTP secondary biological treatment in El Ejido (province of Almería, Spain). pilot compound parabolic collector (CPC) was used for photo-Fenton experiment	[112]
Flumequine	Fenton and photo-Fenton	500 $\mu\text{g L}^{-1}$	Low-pressure mercury lamp, 15 W, $\lambda_{\text{max}} = 254$ nm, irradiance: 8.3 mW cm^{-2} , H_2O_2 : 0.5–10.0 mmol L^{-1} , Fe(II): 0.25–1.0 mmol L^{-1} . $\text{NaHSO}_4/\text{H}_2\text{O}_2$: 1	[97]
Levofloxacin	Ozonation and TiO_2/UV	20 mg L^{-1}	Ozone flow rate: 3.3 gh^{-1} , oxygen was used as a feed gas, commercial TiO_2 Degussa P25 was used as catalyst, T: 17°C, pH 6.5, synthetic wastewater	[113]
Metronidazole	Electro-Fenton	80 mg L^{-1}	T: 20°C, synthetic wastewater	[114]
Moxifloxacin	TiO_2/UV	37.4 and 124.6 μM	T: 25°C, pH: 3.0, 7.0 and 10.0, stirring speed: 13.2 rps, reactor volume: 200 mL, catalyst loading: 1.0 g L^{-1} , air flow: 60 mL min^{-1} , phosphate buffer conc.: 10 mM, light intensity UV-A 104 mW , synthetic wastewater	[115]
Moxifloxacin	TiO_2/UV	12.5, 24.9, 37.4, 49.9, 62.3 and 124.6 μM	T: 5, 15, 25, 35, 45, and 65°C, pH 7, stirring speed 2.3, 7.9 and 13.2 rps, reactor volume 200 mL, catalyst loading 0.25, 0.5, 1, 3, 5, and 8 g L^{-1} , oxygen, air, nitrogen flow: 60 mL min^{-1} , buffer concentration 10 mM, light intensity UV-A at 3 cm, 485 W cm^{-2} , ISO concentration $\mu\text{mol L}^{-1}$ 37.4, 374, 3740, 37.4×10^3 , 74.8×10^3 , and 18.7×10^4 , KI concentration 3.74, 37.4, 374, 3740, and 7480 mol L^{-1} , synthetic wastewater	[116]
Ofloxacin and trimethoprim	Solar photo-Fenton process	100 $\mu\text{g L}^{-1}$	T: 25°C, UV power: 30 W m^{-2} , secondary treated domestic effluents	[117]

Compound name	AOP	Concentration	Reaction conditions	References
Oxfloxacin	Solar Fenton	10 mg L ⁻¹	T: 20°C, H ₂ O ₂ conc.: 2.5 mg L ⁻¹ and Fe ²⁺ conc.: 2 mg L ⁻¹ , demineralized water, simulated natural freshwater, simulated effluent from municipal wastewater treatment plant and pre-treated real effluent from municipal wastewater treatment plant	[1]
Oxolinic acid	TiO ₂ /UV	20 mg L ⁻¹	Titanium dioxide Degussa P-25 with a surface area of 50 m ² g ⁻¹ (size ~20–30 nm) was used as provided. 14 Wm ⁻² , emission maximum at 365 nm, synthetic wastewater	[118]
Oxytetracycline	Photo-Fenton	20 mg L ⁻¹	T: 25°C, I = 500 Wm ⁻² , wastewater	[119]
Oxytetracycline	TiO ₂ /UV	20 mg L ⁻¹	T: 25°C, photocatalyst: Titanium dioxide Degussa P-25, 1000-W Xe-OP lamp, radiant power: 3.55 J s ⁻¹ , synthetic wastewater	[120]
Roxithromycin, sulfamethoxazole, and trimethoprim	H ₂ O ₂ /UV, Fenton, photo-Fenton, UV, ozon	50–100 µg L ⁻¹	Membrane bioreactor Hollow-fiber ultrafiltration (UF) membranes, nominal pore size: 0.04 µm, pH: 7.2 municipal wastewater UV radiation, O ₃ and AOP T: 20°C, pH: 3.0, synthetic wastewater and MBR permeate	[121]
Sulfachlorpyridazine, sulfapyridine, and sulfisoxazole	TiO ₂ /UV	50–200 µM	Xe arc lamp, 172 nm, power: 125 W, T: 20°C, photocatalyst: degussa P25, synthetic wastewater	[122]
Sulfamethazine	Electrochemical incineration	193 mg dm ⁻³	Synthetic wastewater	[123]
Sulfamethazine	Gamma irradiation/H ₂ O ₂	20 mg L ⁻¹	Dose rate: 339 Gymin ⁻¹ , pH: 6.0–7.5, H ₂ O ₂ concentration: 0, 10, and 30 mg L ⁻¹ , synthetic wastewater	[124]
Sulfamethoxazole and acetaminophen	Ozone, Fenton-like	30 mg L ⁻¹	Ozone was produced from pure oxygen, gas flow rate: 20 Lh ⁻¹ , 15-W black light lamps, 365-nm radiation, synthetic wastewater	[125]
Sulfamethoxazole, ciprofloxacin, clarithromycin, erythromycin, sulfamethoxazole	UV	763.31 and 2.32 µg L ⁻¹	Two different UV lamps: medium pressure (MP) lamp with power of 2–10 kW and low-pressure (LP) UV lamp with power of 0.25 kW LP lamp wavelengths: 254 nm and 185 nm. MP	[126]

Compound name	AOP	Concentration	Reaction conditions	References
Sulfamethoxazole, roxithromycin, erythromycin, ciprofloxacin and sulfathiazole	UV	1 $\mu\text{g mL}^{-1}$	lamp has polychromatic emission, hospital wastewater Mercury vapor lamp (UV 254 nm) or black light phosphor bulb (UV 350 nm), xenon lamp (750 W cm^{-2} , 250 W cm^{-2} , pH: 5.5–8.1, T : 20°C, synthetic wastewater	[127]
Sulfamethoxazole, sulfamethazine, sulfadiazine, trimethoprim	UV and UV/H ₂ O ₂	4 μM	Low-pressure UV lamps, fluence = 540 mJ cm^{-2} , H ₂ O ₂ dose = 6 mg L^{-1} , synthetic wastewater, surface water, wastewater treatment plant effluent	[128]
Sulfamethoxazole	Anodic oxidation and electro-Fenton	1.3 mM	Catalyst: 0.2 mM Fe ²⁺ and/or 0.2 mM Cu ²⁺ , pH 3.0 and T : 23 ± 2°C, current: 30–450 mA, synthetic wastewater	[129]
Sulfamethoxazole	Photoelectro-Fenton	200–300 mg L^{-1}	T : 20°C, anode: RuO ₂ /Ti, cathode: RuO ₂ /Ti, UV Lamp SLUV-8, 254/365 nm, energy input: 1407 W cm^{-2} , current: 0.36 A, synthetic wastewater	[130]
Sulfamethoxazole	Ozone	0.150 mM	Ozone generated from pure oxygen, pH: 2 and 8, H ₂ O ₂ : 0.013 M, flow: 3.0 ml min^{-1} , T : 25°C, gas flow: 8.5 g Nm^{-3} , synthetic wastewater	[131]
Sulfamethoxazole	Ozone	200 $\mu\text{g L}^{-1}$	Ozone generated from pure oxygen, 15-W black light lamps (365 nm), flux of radiation: 7.05 ± 0.05 × 10 ⁻⁵ Einstein min^{-1} , primary wastewater effluent	[132]
Sulfamethoxazole	Photo-Fenton	200 mg L^{-1}	Black-light blue lamps with power of 8W (350 and 400 nm), photon flow: 6.85–5.67 Einstein s^{-1} . T : 25 ± 0.8°C; TOC = 94.5 mg L^{-1} and COD = 290 $\text{mg O}_2 \text{L}^{-1}$, synthetic wastewater	[133]
Sulfamethoxazole	Solar photo-Fenton	10 mg L^{-1}	1100-W xenon arc lamp (below 290 nm), intensity: 250 W m^2 , T : 25°C, synthetic wastewater, seawater	[134]
Sulfamethoxazole	TiO ₂ /UV	100 mg L^{-1}	Catalyst: TiO ₂ Degussa P25, T : 25°C, xenon lamp (1000 W), wavelength: below 290 nm, synthetic wastewater	[135]
Sulfamethoxazole	TiO ₂ /UV	2.5–30 mg L^{-1}	9W lamp (350–400 nm), photon flux: 2.81 × 10 ⁻⁴ Einstein min^{-1} , T : 25°C, synthetic wastewater	[136]

Compound name	AOP	Concentration	Reaction conditions	References
Sulfasalazine	Fenton-like	100 mgL ⁻¹	Initial pH:3.0, industrial wastewater	[137]
Sulfadiazine	Gamma irradiation	10–30 mgL ⁻¹	The dose rate of gamma-ray: 103 Gymin ⁻¹ , pH: 5.5–6.5, wastewater	[138]
Sulfamethoxazole	Catalytic ozonation	50 ppm	Catalysts: commercial activated carbon and commercial multi-walled carbon nanotubes, pH: 4.8, flow rate: 150 cm ³ min ⁻¹ , ozone concentration: 50 g m ⁻³ , T: 20°C, synthetic wastewater	[139]
Sulfamethoxazole	UV/H ₂ O ₂	1 mg L ⁻¹	0.45-kW polychromatic (200–300 nm) medium-pressure (MP) Hg vapor lamp, H ₂ O ₂ concentrations: 0–4.41 mM, synthetic wastewater	[140]
Sulfamethoxazole	UV, O ₃ , O ₃ /TiO ₂ , O ₃ /UVA, O ₂ /TiO ₂ /UVA, O ₃ /TiO ₂ /UVA	30–80 mg L ⁻¹	Ozone was generated from pure oxygen. catalyst: TiO ₂ Degussa P25, high-pressure mercury lamp (700 W, 238–579 nm) Radiation intensity: 0.111 Einstein h ⁻¹ , synthetic wastewater	[141]
Sulfamethazine	Gamma irradiation	20 mgL ⁻¹	Dose rate: 320 Gymin ⁻¹ , G (Fe ³⁺): 15.6 (per 100eV), Fe ²⁺ concentrations: 0, 0.1, 0.2, 0.4, and 0.6 mM, pH: 6.0–7.5, irradiation: 200, 400, 600, 800, and 1000 Gy, synthetic wastewater	[142]
Sulfamethazine	Sonophotolytic goethite/oxalate Fenton-like	25 mg L ⁻¹	T: 20°C, 9-W UVA lamp (λ_{\max} = 365 nm), light intensity: 7.7 mW cm ⁻² , ultrasonic shockwave Frequency: 20 kHz, purified air flow:1.0 L min ⁻¹ , synthetic wastewater	[143]
Sulfanilamide	Electro-Fenton and UVA photoelectro-Fenton	239–2511 mg L ⁻¹	6-W fluorescent black light blue tube (320–400 nm), photoionization energy: 5 Wm ⁻² , synthetic wastewater	[123]
Tetracycline, chlortetracycline, oxytetracycline, doxycycline	Electron pulse radiolysis, gamma radiolysis	0.5 mM	Pulse radiolysis $k = 472$ nm, dose of radiolysis:3–5 Gy per 2–3 ns pulse, pH 7, T: 22°C, Xe arc lamp (172 nm), synthetic wastewater γ -radiolysis pH 7, T: 22°C, synthetic wastewater	[12]

Compound name	AOP	Concentration	Reaction conditions	References
Tetracycline	Electrochemical oxidation	TC = 200 mg L ⁻¹	The process was performed using a DSA (mixed metal oxide, Ti/RuO ₂ -IrO ₂) anode carbon-felt from cathode. synthetic wastewater	[144]
Tetracycline	Electrochemical oxidation, electro-Fenton	100 mg L ⁻¹	Three electrodes as anode: commercial pure Pt, boron-doped diamond (BDD, thin-film deposited on a niobium substrate), and commercial DSA (mixed metal oxide Ti/RuO ₂ -IrO ₂), and a tridimensional, carbon-felt electrodes as cathode were used. <i>T</i> : 23°C, synthetic wastewater	[145]
Tetracycline	Ozonation	20–100 mgL ⁻¹	O ₃ was generated from oxygen. <i>T</i> : 25°C, synthetic wastewater	[146]
Tetracycline	Photo-Fenton	TOC: 13 mg L ⁻¹	15-W black-light lamp (365 nm), irradiance: 19 Wm ⁻² , flow rate: 80 mL min ⁻¹ , synthetic wastewater, surface water and a sewage treatment plant effluent	[147]
Tetracycline	Photocatalysis	67 mgL ⁻¹	Medium mercury lamp, synthetic wastewater	[148]
Tinidazole	Ozone	30 mgL ⁻¹	<i>T</i> : 25°C, synthetic wastewater, surface water and a sewage treatment plant effluent	[149]
Tinidazole	Sonolysis	45, 80, and 100 ppm	pH: 3, 5, 7, 9; H ₂ O ₂ conc.: 83, 167, 250, 333, and 417 mM L ⁻¹ , frequency: 40, 80, 120, and 160 kHz, input power: 750 W, pharmaceutical wastewater (Tehran, Iran), synthetic wastewater	[150]
Trimethoprim	Anodic oxidation, electro-Fenton, photoelectro-Fenton, solar photoelectro-Fenton	20.0 mg L ⁻¹	6-W fluorescent blacklight blue lamp (350–410 nm), synthetic wastewater, wastewater	[151]
Trimethoprim	BDD, electrochemical oxidation	1.72 × 10 ⁻⁴ mol L ⁻¹	<i>T</i> : 25°C, synthetic wastewater	[120]

Table 2. Summary of reaction conditions for antibiotic removal from water by AOP.

energy or participate in redox reactions with the compounds that are adsorbed on the catalyst's surface [1].

Due to some disadvantages of the heterogeneous photocatalysis (e.g., rather small quantum efficiency of the process; comparatively narrow light-response reach of TiO_2 ; the requirement of postseparation and recovery of the catalyst particles from the reaction mixture in aqueous slurry systems), TiO_2 appear to have some interesting properties, such as high chemical stability in a wide pH range, strong resistance to chemical breakdown and photocorrosion, and high efficiency. The catalyst is also inexpensive and can be reprocessed [134, 156]. The characteristics of antibiotics to be treated like pKa and molecular structure will identify not only the performance of their photocatalytic breakdown but also the mechanisms of the oxidation products formation.

Ultraviolet (UV) disinfection is progressively discovering practices in UWTPs. Photolytic breakdown can be either direct or indirect. In direct photolysis, the target pollutant assimilates a solar photon, which causes to a breakup of the molecule. In an indirect photolysis mechanism, as a matter of course occurring molecules in the system such as dissolved organic matter (DOM) behave as sensitizing species, which creates strong reactive agents such as hydroxyl radicals, singlet oxygen, and hydrate electrons under solar radiation [1, 117].

Ultraviolet irradiation has been greatly used for the treatment of waters and wastewaters worldwide. Different studies have stated the effective treatment of UV irradiation for the removal of antibiotics in wastewater effluents [63]. It has been lately stated that at high UV doses of almost 11,000–30,000 mJ cm^2 , a nearly complete removal of tetracyclines and ciprofloxacin was obtained. Kim et al. [99] noticed that sulfonamides and quinolones demonstrate high removal efficiency in the reach of 86–100% throughout the UV process [1].

Many of the antibiotics have aromatic rings, structural moieties (such as phenol and nitro groups) heteroatoms, and other functional chromophore groups that can either absorb solar radiation or react with photogenerated transient species in natural. The organic material, UV dosage, contact time, and the chemical construction of the compound are significant agents ruling the removal performance of antibiotics throughout direct photolysis. This technique is only practicable to wastewater-containing photosensitive compounds and waters with low COD concentrations [5].

Most traditional operation performed in WWTPs and DWTPs (such as coagulation, flocculation, sedimentation, and filtration) were ineffective in the removal of these compounds [63], taking the improvement of new effective methodologies. Owing to the recalcitrant nature of the effluents including antibiotics residues, the implementation of the AOPs arises as an alternate. In fact, ozonation and Fenton's oxidation are the most tried methodologies. Although ozonation has the benefit of being used to fluctuate flow rates and compositions, the high cost of material and the energy required to provide the process constitute a primary disadvantage. Oxyhydroxides produce precipitate (if the pH range is not controlled well) when a homogeneous process is used and the necessity of recovering dissolved catalyst is a disadvantage. This is another process that is applied often to the group of beta-lactam antibiotics, combined with UV irradiation (photo-Fenton).

4. Conclusions

The consumption of antibiotics worldwide by human and veterinary uses has been increasing significantly. This is an important public concern because they have endocrine-disrupting properties even in trace concentrations and can cause microorganism resistance in aquatic environments. According to the researches made in recent years, advanced oxidation processes are promising treatment methods for the removal of the antibiotic compounds from water.

In the event of the photochemical technologies, we can determine that the photochemical AOPs are usually easy, clean, comparatively inexpensive, and productive against the classical, chemical AOPs. Four basic types of photochemical AOPs ($\text{H}_2\text{O}_2/\text{UV}$, O_3/UV , $\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$, and TiO_2/UV) have been enforced to reduce and/or mineralize organic pollutants. We have defined that, within these photochemical processes, the photocatalytic ones had mainly a better performance.

Furthermore, it is significant to point that heterogeneous photocatalysis has been the aim of an enormous improvement in the last decade. In fact, TiO_2 is a semiconductor approach that exists, for example, as a chemically very stable, biologically inefficient, very easy to manufacture, cheaper than the photocatalytic viewpoint, active and several important photocatalysts with an energy vacancy comparable to solar photons.

The economic robust of AOPs for full-scale wastewater treatment needs to be extensively investigated. These technologies should be modified to achieve both technical efficiency and cost effectiveness so that water industries could afford the adaptation of such technologies.

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