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

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Additional information is available at the end of the chapter

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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

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## 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  $\beta$ -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, sultamicillin, 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

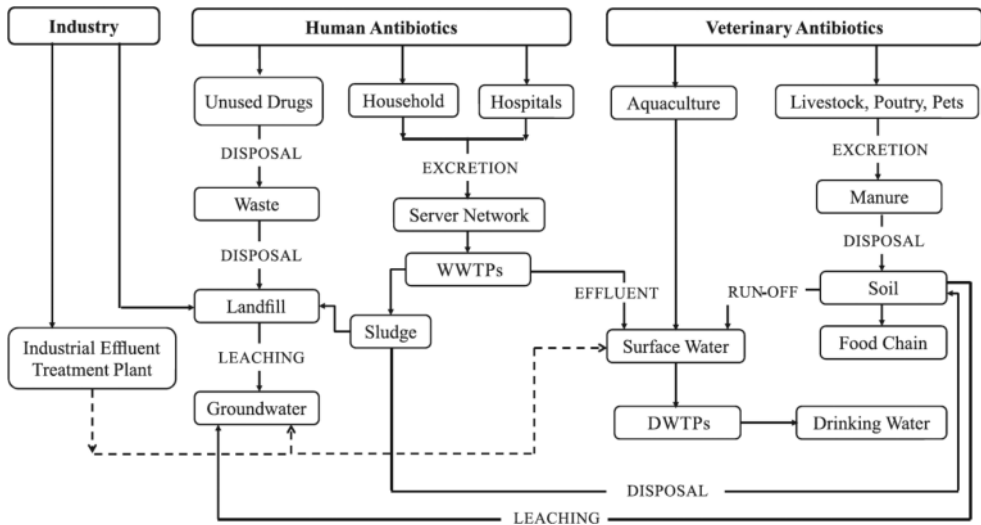
antibiotics have toxic effects on humans, animals, and also microorganisms even at low concentrations. At the same time, they are nonbiodegradable and can survive in the environment even in the conventional wastewater treatments. So they cause bio-accumulation [3]. Therefore, the presence of antibiotics 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 <sup>-1</sup> )	Surface water (ng L <sup>-1</sup> )	Ground water*/bank filtrate (ng L <sup>-1</sup> )	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 <sub>2</sub> 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 <sup>-1</sup> )	Surface water (ng L <sup>-1</sup> )	Ground water*/bank filtrate (ng L <sup>-1</sup> )	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 <sup>-1</sup> )	Surface water (ng L <sup>-1</sup> )	Ground water*/bank filtrate (ng L <sup>-1</sup> )	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  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , 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  $\text{CO}_2$  and  $\text{H}_2\text{O}$  by AOPs. The generation of hydroxyl radical might be by the use of UV, UV/ $\text{H}_2\text{O}_2$ , UV/ $\text{O}_3$ ,  $\text{TiO}_2/\text{H}_2\text{O}_2$ ,  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$  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 ( $\text{O}_3$ ) and  $\text{H}_2\text{O}_2$ , 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  $\text{H}_2\text{O}_2$  impacts on increasing the decomposition percentage of  $\text{O}_3$  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  $\text{O}_3$  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 ( $\text{Fe(II)}$ ) with  $\text{H}_2\text{O}_2$  (Eq.(15)) [6].  $\cdot\text{OH}$  radical is generated through the agency of reaction between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{+2}$  salts as described below.





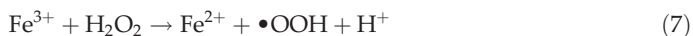
Thus, composed hydroxyl radical can react with Fe(II) to develop ferric ion (Fe(III)) (Eq. (16))



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  $\text{Fe}^{+3}$  to  $\text{Fe}^{+2}$  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:H<sub>2</sub>O<sub>2</sub>:catalyst ratio in the feed [52].

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

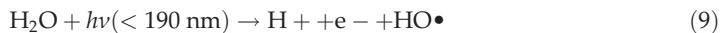
- A plain and adaptable operation permitting easy execution in existing plants
- Easy-to-use and relatively cheap chemicals
- No need of energy input

### 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  $\bullet OH$  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 H<sub>2</sub>O<sub>2</sub> and UV radiation with Fe(II) or Fe(III). The main factor of the mechanism is that iron salts act as photocatalysts and H<sub>2</sub>O<sub>2</sub> 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:



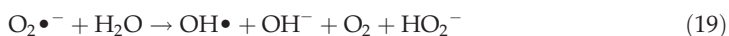
A highly low reaction time is required for the photo-Fenton process, and depending on the operating pH value, the concentrations of H<sub>2</sub>O<sub>2</sub> and iron are added.

### 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 TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub> 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 TiO<sub>2</sub>/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 TiO<sub>2</sub>/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 H<sub>2</sub>O<sub>2</sub> 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 O<sub>3</sub> 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  $\beta$ -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  $\beta$ -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 TiO<sub>2</sub> semiconductor is generally accomplished by the illumination of a suspension of TiO<sub>2</sub> in aqueous solution with light energy which is greater than its bandgap energy. This causes the generation of high energy electron-hole pairs (e<sup>-</sup>/h<sup>+</sup>), 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 <sup>-1</sup>	250 W lamp (254 nm), UV doses: 0–2.5 × 10 <sup>4</sup> μW s cm <sup>-2</sup> , 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 <sup>-1</sup>	Solar intensity 0.85 kWm <sup>-2</sup> , 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 rpm <i>Ozonation</i> : Pyrex glass tubular photoreactor, flow rate: 7.3 L h <sup>-1</sup> , OGV-500 catalyst, synthetic wastewater	[74]
Amoxicillin, ampicillin, and cloxacillin	Fenton	AMX, AMP, CLX: 104, 105, 103 mgL <sup>-1</sup>	pH 3, COD: 520 mgL <sup>-1</sup> , synthetic wastewater	[75]
Amoxicillin, ampicillin, and cloxacillin	Photo-Fenton	AMX, AMP, CLX: 104, 105, 103 mgL <sup>-1</sup>	UV lamp, 230 V, 0.17 A, 6 W, 365 nm, synthetic wastewater	[76]
Amoxicillin, ampicillin and cloxacillin	UV/TiO <sub>2</sub> and UV/H <sub>2</sub> O <sub>2</sub> /TiO <sub>2</sub>	AMX, AMP, CLX: 104, 105, 103 mgL <sup>-1</sup>	pH ~ 5, COD: 520 mgL <sup>-1</sup> , BOD <sub>5</sub> /COD ~0 and DOC 145 mgL <sup>-1</sup> , synthetic wastewater	[77]
Amoxicillin and cloxacillin	UV/TiO <sub>2</sub> /H <sub>2</sub> O <sub>2</sub>	AMX: 138 mgL <sup>-1</sup> CLX: 84 mgL <sup>-1</sup>	6-W lamp, wavelength ≈ 365 nm, pharmaceutical industry wastewater	[67]
Amoxicillin	UV-A/TiO <sub>2</sub>	2.5–30 mgL <sup>-1</sup>	Degussa P25 TiO <sub>2</sub> , TiO <sub>2</sub> : 100–750 mgL <sup>-1</sup> , pH 5 or 7.5, photon flux of 8 × 10 <sup>-4</sup> E/(L min), 9 W lamp, 350–400 nm, 25°C, synthetic wastewater	[78]
Amoxicillin, ampicillin, and cloxacillin	Fenton, photo-Fenton, TiO <sub>2</sub> photocatalytic and UV/ZnO	AMX, AMP, CLX: 104, 105, 103 mgL <sup>-1</sup>	UV lamp, 230 V, 0.17 A, 6 W, 365 nm, synthetic wastewater	[77]
Amoxicillin	O <sub>3</sub> /OH <sup>-</sup> , H <sub>2</sub> O <sub>2</sub> /UV, Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub> , Fe <sup>3+</sup> /H <sub>2</sub> O <sub>2</sub> , Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub> /UV and Fe <sup>3+</sup> /H <sub>2</sub> O <sub>2</sub> /UV	AMX: 400 mgL <sup>-1</sup>	O <sub>3</sub> generated from O <sub>2</sub> , 21W Hg lamp (253.7 nm), flow rate: 1.3 L/min, light intensity: 3.65 WL <sup>-1</sup> (1.73 × 10 <sup>-4</sup> EinsteinL <sup>-1</sup> s <sup>-1</sup> ), effective pathlength: 1.72 cm, pharmaceutical wastewater	[3]
Amoxicillin and cloxacillin	Fenton	AMX and CLX: 150 mgL <sup>-1</sup>	pH 3.0, H <sub>2</sub> O <sub>2</sub> /COD: 1.0–3.0, H <sub>2</sub> O <sub>2</sub> /Fe <sup>2+</sup> : 2–150 and reaction time: 60–120 min, synthetic wastewater	[79]
Amoxicillin, oxacillin, and ampicillin	Nonthermal plasma	OX, AMX, AMP: 100 mgL <sup>-1</sup>	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 <sub>3</sub> , Fenton, Fenton-like, photo-Fenton, UV/O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> , TiO <sub>2</sub> , 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 <sup>-1</sup> , optical path: 5.09 cm, O <sub>3</sub> was generated from O <sub>2</sub> flow rate of O <sub>3</sub> : 16 mg h <sup>-1</sup> 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 <sub>2</sub> O <sub>2</sub> 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 <sup>-1</sup> , pH 2.5, ferric nitrate or FeOx conc.: 0.2 mmol L <sup>-1</sup> , H <sub>2</sub> O <sub>2</sub> conc.: 1.0–10.0 mmol L <sup>-1</sup> , sewage treatment plant effluent	[82]
Amoxicillin	Microwave assisted Fenton	450 μg L <sup>-1</sup>	H <sub>2</sub> O <sub>2</sub> conc.: 2 g L <sup>-1</sup> , FeSO <sub>4</sub> ·7H <sub>2</sub> O conc.: 0.2 g L <sup>-1</sup> , 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 <sup>-4</sup> M	Ozonation were performed in a semicontinuous stirred gas-liquid reactor: 25°C, flow rate: 361 h <sup>-1</sup> , synthetic wastewater	[84]
Amoxicillin	Photo-Fenton	50 mg L <sup>-1</sup>	Solar simulator: 1100-W xenon arc lamp (290 nm), minimum intensity (250 W m <sup>-2</sup> ) pH 6.2, TOC: 26.3 mg C L <sup>-1</sup> , FeSO <sub>4</sub> ·7H <sub>2</sub> O or FeOx conc.: 0.05 mM, H <sub>2</sub> O <sub>2</sub> concentration used was 120 mg L <sup>-1</sup> , pH 2.5–2.8, synthetic wastewater	[85]
Amoxicillin	Sulfate radicals under ultrasound irradiation	0.095 mmolL <sup>-1</sup>	Ultrasonic generator: 20 kHz, Ti probe, synthetic wastewater	[86]
Amoxicillin	UV and UV/H <sub>2</sub> O <sub>2</sub>	00 μM	Low-pressure Hg arc-UV (254 nm) Photon fluence rate: 8 × 10 <sup>-7</sup> Einstein L <sup>-1</sup> s <sup>-1</sup> , 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 $\mu\text{g L}^{-1}$ L-CMI: 0.21 $\mu\text{g L}^{-1}$ L-EMC: 0.62 $\mu\text{g L}^{-1}$ RXM:0.54 $\mu\text{g L}^{-1}$	$\text{H}_2\text{O}_2$ : 0.4, 2, 3, 4, 5, and 10 mM, synthetic wastewater pH: 7.2, DOC: 23.0 $\text{mg L}^{-1}$ , COD: 30.0 $\text{mg L}^{-1}$ AOX: 100 $\text{mg L}^{-1}$ , BOD <sub>5</sub> : 2.8 $\text{mg L}^{-1}$ , low-pressure UV unit (254 + 185 nm, 110 W power rating, 400 J $\text{m}^{-2}$ by a flowrate: 2 $\text{m}^3 \text{h}^{-1}$ ), 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 $\mu\text{M}$ per pulse were used, synthetic wastewater	[89]
Flumequine, ofloxacin, and sulfamethoxazole	Photo-Fenton	100 $\mu\text{g L}^{-1}$	pH 5, $\text{Fe}^{2+}$ conc.: 5 $\text{mg L}^{-1}$ , natural water	[90]
Cefalexin	Electro Fenton	50, 100, 200, and 300 $\text{mg L}^{-1}$	Cathode: activated carbon fiber (ACF), resistivity: 18.2 $\text{M}\Omega \text{cm}$ , T: 25°C, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ conc.: 0.5–1 mM, pH 2–5, wastewater	[91]
Cefazolin	$\text{TiO}_2$ /UV and sunlight	$1.0 \times 10^{-2} \text{ mol L}^{-1}$	$\text{TiO}_2$ Degussa P25 and the N-doped $\text{TiO}_2$ were used; 5 × 8 W blacklight Fluorescent lamps (max. 365 nm), photonic fluence: $3.1 \times 10^{-7} \text{ Einstein s}^{-1}$ , T: 23 ± 2°C, pH 6.4 ± 0.1, synthetic wastewater	[92]
Ceftriaxone, cephalosporine, penicillin VK, penicillin group, enrofloxacin, and quinolone	$\text{O}_3$ and $\text{O}_3/\text{H}_2\text{O}_2$	COD: 450 $\text{mg L}^{-1}$	Ozone generated from $\text{O}_2$ , pH 3, 7, and 10.6, oxygen flow rate: 100 $\text{L h}^{-1}$ , T: 20°C ± 2, synthetic wastewater	[93]
Chloramphenicol	Photo-Fenton	200 $\text{mg L}^{-1}$ ,	400 W high-pressure Hg vapor lamp (295–390 and 295–710 nm), photonic flux: $6.0 \times 10^{-7}$ and $3.3 \times 10^{-6} \text{ Einstein s}^{-1}$ , T: 25–30°C, synthetic wastewater	[94]
Chloramphenicol	Solar photoelectro-Fenton	245 $\text{mg L}^{-1}$	pH 3.0, T:35°C, synthetic wastewater	[95]
Chloramphenicol	UV/ $\text{H}_2\text{O}_2$	100 $\text{mg L}^{-1}$	T: 20°C ± 2, 6-W low-pressure Hg lamp (254 nm), pH 5.5 ± 0.1, synthetic wastewater	[96]
Chloramphenicol	Direct photolysis (UVC), hydrogen peroxide/UVC and solar radiation	20 $\text{mg L}^{-1}$	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	$5 \times 10^{-6}$ M	Flow rate: $80 \text{ cm}^3/\text{min}$ , $T: 20\text{--}21^\circ\text{C}$ , synthetic wastewater	[98]
Chlortetracycline, sulfamethoxazole	UV, electron beam, ozone	$30 \text{ mgL}^{-1}$	pH 4.63 and 4.33, atmospheric pressure $T: 22 \pm 2^\circ\text{C}$ , 6-W single UV-C lamp (254 nm), ozone was produced from $\text{O}_2$ , electron accelerator (1 MeV and 40 kW), synthetic wastewater	[99]
Chlortetracycline	Photocatalytic ozonation	0.15 mM	Ozone generated from $\text{O}_2$ (air pressure: 5 bar, air flow rate: $1200 \text{ L h}^{-1}$ ), ozone input: $20 \text{ g m}^{-3}$ and flow rate of the ozone/air: $20 \text{ L h}^{-1}$ , $T: 25^\circ\text{C}$ , 15-W UV low-pressure lamp (254 nm), synthetic wastewater	[100]
Chlortetracycline	Photocatalytic ozonation	0.5 mM	Ozone generated from pure oxygen. flow rate: $20 \text{ mg min}^{-1}$ , $T: 20 \pm 2^\circ\text{C}$ , 125-W high-pressure UV lamp (260, 275, 290, 302, 307, 315, 336, 366, 406, and 434 nm), $\text{TiO}_2$ : Degussa P25 and $0.1 \text{ g L}^{-1}$ , synthetic wastewater	[101]
Ciprofloxacin and sulfamethoxazole	persulfate	0.15 mM	Initial pH 6 and decreased to 3–4, $\text{K}_2\text{S}_2\text{O}_8$ and Fe (II)/Fe(II)-chelate: 4.8 and 4.8 mM, river water	[102]
Ciprofloxacin, moxifloxacin	UV and $\text{TiO}_2/\text{UV}$	CIP: $45.3 \text{ }\mu\text{M}$ and MOX: $37.4 \text{ }\mu\text{M}$	Photocatalyst: $\text{TiO}_2\text{-P25}$ , $\text{TiO}_2$ : $0.5 \text{ g L}^{-1}$ , $T: 298 \pm 1^\circ\text{K}$ , synthetic wastewater	[103]
Ciprofloxacin	Electron ionization	$100 \text{ mg L}^{-1}$	10 MeV, 10-kW electron ionizing energy unit, synthetic wastewater	[104]
Ciprofloxacin	$\text{O}_3/\text{H}_2\text{O}_2$	$45.27 \text{ }\mu\text{M}$	A bubble reactor was used for ozonation. Ozone generated from $\text{O}_2$ . $T: 60\text{--}62^\circ\text{C}$ , ozone conc.: 2500 ppm, gas flow rate: $120 \text{ mL min}^{-1}$ , $T: 27.5^\circ\text{C}$ , $\text{H}_2\text{O}_2$ : 2–990 $\mu\text{mol L}^{-1}$ , synthetic wastewater	[105]
Ciprofloxacin	UV, $\text{TiO}_2/\text{UV}$ , $\text{O}_3$ and $\text{H}_2\text{O}_2$	$200 \text{ }\mu\text{g L}^{-1}$	Photocatalyst: $\text{TiO}_2\text{-P25}$ , 125W medium-pressure Hg lamp, pH 3 (UV and $\text{TiO}_2/\text{UV}$ ), $\text{TiO}_2$ conc.: 571 ppm, ozone generated from $\text{O}_2$ , flowrate: $8 \text{ L min}^{-1}$ , pH 9 ( $\text{O}_3$ and $\text{H}_2\text{O}_2$ ), $\text{H}_2\text{O}_2$ conc.: 500 and 1000 $\text{mg L}^{-1}$ , hospital wastewater	[106]
Ciprofloxacin	Photo-Fenton	0.15 mM	$T: 298 \text{ K}$ , 125-W high-pressure lamp, photonic flux ( $9 \times 10^4 \text{ }\mu\text{Es m}^{-2} \text{ s}^{-1}$ ), 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, $((Ge) = 5.2 \times 10^{-4} \text{ m}^2 \text{ l}^{-1}, 3\text{--}5 \text{ Gy per } 2\text{--}3 \text{ ns pulse, } 8\text{--}12 \text{ replicate pulses, } T: 25 \pm 1^\circ \text{C, } 12.5\text{--}W \text{ high-pressure Hg lamp } (E_{\text{max}} = 365 \text{ nm}))$ Light intensity: $0.38 \text{ mW cm}^{-2}$ , $\text{TiO}_2$ : $1.5 \text{ g L}^{-1}$ (Degussa P25), synthetic wastewater	[107]
Amoxicillin and cloxacillin	Photo-Fenton	AMX: $138 \pm 5 \text{ mg L}^{-1}$ CLX: $84 \pm 4 \text{ mg L}^{-1}$	$230 \text{ V, } 0.17 \text{ A, } 6\text{--}W \text{ UV lamp (365 nm), antibiotic wastewater}$	[67]
Dicloxacillin and ceftazidime	Ozonation	$1.5 \text{ mg L}^{-1}$	Ozone gas-phase concentration ( $\text{mg L}^{-1}$ ): $5 \pm 0.5\text{--}30 \pm 0.5$ , volumetric ozone-gas flow rate ( $\text{mL min}^{-1}$ ): $40 \pm 0.5$ , ozone inlet pressure (bar): $2.5 \pm 0.1$ , transmembrane pressure (TMP) (bar): $2.1 \pm 0.1$ , volumetric cross-flow rate ( $\text{L min}^{-1}$ ): $0.55 \pm 0.05$ , temp. ( $^\circ\text{C}$ ): $24 \pm 1$ , surface water	[108]
Doxycycline and norfloxacin	UV C, ozonation	$5 \times 10^{-5} \text{ M}$	Ozone was produced from pure oxygen, gas flow rate: $30 \text{ L h}^{-1}$ , 15-W low-pressure Hg vapor lamp (254 nm), commercial activated carbon Hydrafilm 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	$158 \text{ mg L}^{-1}$	Fluorescent lamp (360 nm, $1.4 \text{ W m}^{-2}$ ), pH 3.0, T: $35^\circ \text{C}$ , synthetic wastewater	[110]
Enrofloxacin, ciprofloxacin	UV/H <sub>2</sub> O <sub>2</sub> , UV/H <sub>2</sub> O <sub>2</sub> /Fe(II), O <sub>3</sub> , O <sub>3</sub> /UV, O <sub>3</sub> /UV/H <sub>2</sub> O <sub>2</sub> and O <sub>3</sub> /UV/H <sub>2</sub> O <sub>2</sub>	0.15 mM	Ozone, generated from pure oxygen air Pressure: 5 bar, air flow rate $1200 \text{ L h}^{-1}$ Flow rate of the ozone/air mixture: $20 \text{ L h}^{-1}$ , T: $25^\circ \text{C}$ , 15W UV low-pressure lamp (254 nm), synthetic wastewater	[100]
Ciprofloxacin, erythromycin, ofloxacin, sulfamethoxazole, trimethoprim	Ozonation	ERYC: $346 \text{ ng L}^{-1}$ CIP: $5524 \text{ ng L}^{-1}$ OFX: $2275 \text{ ng L}^{-1}$ SMX: $279 \text{ ng L}^{-1}$ TMP: $104 \text{ ng L}^{-1}$	pH 7.54, COD ( $\text{mg L}^{-1}$ ) 269, BOD <sub>5</sub> ( $\text{mg L}^{-1}$ ) 42, T: $25^\circ \text{C}$ , 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 $8.5 \pm 0.1$ 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 $\text{mg L}^{-1}$ Fe, 35 $\text{mg L}^{-1}$ $\text{H}_2\text{O}_2$ , oxalic acid, initial $\text{pH} \approx 7$ , $\lambda < 400$ nm Solar UV power: 30 $\text{W m}^{-2}$ , 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 $\text{mW cm}^{-2}$ , $\text{H}_2\text{O}_2$ : 0.5–10.0 $\text{mmol L}^{-1}$ , Fe(II): 0.25–1.0 $\text{mmol L}^{-1}$ , $\text{NaHSO}_4/\text{H}_2\text{O}_2$ : 1	[97]
Levofloxacin	Ozonation and $\text{TiO}_2/\text{UV}$	20 $\text{mg L}^{-1}$	Ozone flow rate: 3.3 $\text{g h}^{-1}$ , oxygen was used as a feed gas, commercial $\text{TiO}_2$ Degussa P25 was used as catalyst, T: 17°C, pH 6.5, synthetic wastewater	[113]
Metronidazole	Electro-Fenton	80 $\text{mg L}^{-1}$	T: 20°C, synthetic wastewater	[114]
Moxifloxacin	$\text{TiO}_2/\text{UV}$	37.4 and 124.6 $\mu\text{M}$	T: 25°C, pH: 3.0, 7.0 and 10.0, stirring speed: 13.2 rps, reactor volume: 200 mL, catalyst loading: 1.0 $\text{g L}^{-1}$ , air flow: 60 $\text{mL min}^{-1}$ , phosphate buffer conc.: 10 mM, light intensity UV-A 104 mW, synthetic wastewater	[115]
Moxifloxacin	$\text{TiO}_2/\text{UV}$	12.5, 24.9, 37.4, 49.9, 62.3 and 124.6 $\mu\text{M}$	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 $\text{g L}^{-1}$ , oxygen, air, nitrogen flow: 60 $\text{mL min}^{-1}$ , buffer concentration 10 mM, light intensity UV-A at 3 cm, 485 $\text{W cm}^{-2}$ , ISO concentration $\mu\text{mol L}^{-1}$ 37.4, 374, 3740, $37.4 \times 10^3$ , $74.8 \times 10^3$ , and $18.7 \times 10^4$ , KI concentration 3.74, 37.4, 374, 3740, and 7480 $\text{mol L}^{-1}$ , synthetic wastewater	[116]
Ofloxacin and trimethoprim	Solar photo-Fenton process	100 $\mu\text{g L}^{-1}$	T: 25°C, UV power: 30 $\text{W m}^{-2}$ , secondary treated domestic effluents	[117]

Compound name	AOP	Concentration	Reaction conditions	References
Ofloxacin	Solar Fenton	10 mg L <sup>-1</sup>	T: 20°C, H <sub>2</sub> O <sub>2</sub> conc.: 2.5 mg L <sup>-1</sup> and Fe <sup>2+</sup> conc.: 2 mg L <sup>-1</sup> , 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 <sub>2</sub> /UV	20 mg L <sup>-1</sup>	Titanium dioxide Degussa P-25 with a surface area of 50 m <sup>2</sup> g <sup>-1</sup> (size ~20–30 nm) was used as provided. 14 W m <sup>-2</sup> , emission maximum at 365 nm, synthetic wastewater	[118]
Oxytetracycline	Photo-Fenton	20 mg L <sup>-1</sup>	T: 25°C, I = 500 W m <sup>-2</sup> , wastewater	[119]
Oxytetracycline	TiO <sub>2</sub> /UV	20 mg L <sup>-1</sup>	T: 25°C, photocatalyst: Titanium dioxide Degussa P-25, 1000-W Xe-OP lamp, radiant power: 3.55 J s <sup>-1</sup> , synthetic wastewater	[120]
Roxithromycin, sulfamethoxazole, and trimethoprim	H <sub>2</sub> O <sub>2</sub> /UV, Fenton, photo-Fenton, UV, ozon	50–100 µg L <sup>-1</sup>	Membrane bioreactor Hollow-fiber ultrafiltration (UF) membranes, nominal pore size: 0.04 µm, pH: 7.2 municipal wastewater UV radiation, O <sub>3</sub> and AOP T: 20°C, pH: 3.0, synthetic wastewater and MBR permeate	[121]
Sulfachlorpyridazine, sulfapyridine, and sulfisoxazole	TiO <sub>2</sub> /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 <sup>-3</sup>	Synthetic wastewater	[123]
Sulfamethazine	Gamma irradiation/H <sub>2</sub> O <sub>2</sub>	20 mg L <sup>-1</sup>	Dose rate: 339 Gy min <sup>-1</sup> , pH: 6.0–7.5, H <sub>2</sub> O <sub>2</sub> concentration: 0, 10, and 30 mg L <sup>-1</sup> , synthetic wastewater	[124]
Sulfamethoxazole and acetaminophen	Ozone, Fenton-like	30 mg L <sup>-1</sup>	Ozone was produced from pure oxygen, gas flow rate: 20 L h <sup>-1</sup> , 15-W black light lamps, 365-nm radiation, synthetic wastewater	[125]
Sulfamethoxazole, ciprofloxacin, clarithromycin, erythromycin, sulfamethoxazole	UV	763.31 and 2.32 µg L <sup>-1</sup>	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 $\text{W cm}^{-2}$ , 250 $\text{W cm}^{-2}$ , pH: 5.5–8.1, T: 20°C, synthetic wastewater	[127]
Sulfamethoxazole, sulfamethazine, sulfadiazine, trimethoprim	UV and UV/ $\text{H}_2\text{O}_2$	4 $\mu\text{M}$	Low-pressure UV lamps, fluence = 540 $\text{mJ cm}^{-2}$ , $\text{H}_2\text{O}_2$ dose = 6 $\text{mg L}^{-1}$ , synthetic wastewater, surface water, wastewater treatment plant effluent	[128]
Sulfamethoxazole	Anodic oxidation and electro-Fenton	1.3 mM	Catalyst: 0.2 mM $\text{Fe}^{2+}$ and/or 0.2 mM $\text{Cu}^{2+}$ , pH 3.0 and T: $23 \pm 2^\circ\text{C}$ , current: 30–450 mA, synthetic wastewater	[129]
Sulfamethoxazole	Photoelectro-Fenton	200–300 $\text{mg L}^{-1}$	T: 20°C, anode: RuO <sub>2</sub> /Ti, cathode: RuO <sub>2</sub> /Ti, UV Lamp SLUV-8, 254/365 nm, energy input: 1407 $\text{W cm}^{-2}$ , current: 0.36 A, synthetic wastewater	[130]
Sulfamethoxazole	Ozone	0.150 mM	Ozone generated from pure oxygen, pH: 2 and 8, $\text{H}_2\text{O}_2$ : 0.013 M, flow: 3.0 $\text{ml min}^{-1}$ , T: 25°C, gas flow: 8.5 $\text{gNm}^{-3}$ , 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: $7.05 \pm 0.05 \times 10^{-5}$ Einstein $\text{min}^{-1}$ , primary wastewater effluent	[132]
Sulfamethoxazole	Photo-Fenton	200 $\text{mg L}^{-1}$	Black-light blue lamps with power of 8W (350 and 400 nm), photon flow: 6.85–5.67 Einstein $\text{s}^{-1}$ , T: 25 $\pm 0.8^\circ\text{C}$ , TOC = 94.5 $\text{mg L}^{-1}$ and COD = 290 $\text{mgO}_2 \text{L}^{-1}$ , synthetic wastewater	[133]
Sulfamethoxazole	Solar photo-Fenton	10 $\text{mg L}^{-1}$	1100-W xenon arc lamp (below 290 nm), intensity: 250 $\text{W m}^{-2}$ , T: 25°C, synthetic wastewater, seawater	[134]
Sulfamethoxazole	TiO <sub>2</sub> /UV	100 $\text{mg L}^{-1}$	Catalyst: TiO <sub>2</sub> Degussa P25, T: 25°C, xenon lamp (1000 W), wavelength: below 290 nm, synthetic wastewater	[135]
Sulfamethoxazole	TiO <sub>2</sub> /UV	2.5–30 $\text{mg L}^{-1}$	9W lamp (350–400 nm), photon flux: $2.81 \times 10^{-4}$ Einstein $\text{min}^{-1}$ , T: 25°C, synthetic wastewater	[136]

Compound name	AOP	Concentration	Reaction conditions	References
Sulfasalazine	Fenton-like	100 mgL <sup>-1</sup>	Initial pH:3.0, industrial wastewater	[137]
Sulfadiazine	Gamma irradiation	10–30 mgL <sup>-1</sup>	The dose rate of gamma-ray: 103 Gymin <sup>-1</sup> , pH: 5.5–6.5, wastewater	[138]
Sulfamethoxazole	Catalytic ozonation	50 ppm	Catalysis: commercial activated carbon and commercial multi-walled carbon nanotubes, pH: 4.8, flow rate: 150 cm <sup>3</sup> min <sup>-1</sup> , ozone concentration: 50 g m <sup>-3</sup> , T: 20°C, synthetic wastewater	[139]
Sulfamethoxazole	UV/H <sub>2</sub> O <sub>2</sub>	1 mg L <sup>-1</sup>	0.45-kW polychromatic (200–300 nm) medium-pressure (MP) Hg vapor lamp, H <sub>2</sub> O <sub>2</sub> concentrations: 0–4.41 mM, synthetic wastewater	[140]
Sulfamethoxazole	UV, O <sub>3</sub> /TiO <sub>2</sub> , O <sub>3</sub> /UVA, O <sub>2</sub> /TiO <sub>2</sub> /UVA, O <sub>3</sub> /TiO <sub>2</sub> /UVA	30–80 mg L <sup>-1</sup>	Ozone was generated from pure oxygen. catalyst: TiO <sub>2</sub> Degussa P25, high-pressure mercury lamp (700 W, 238–579 nm) Radiation intensity: 0.111 Einstein h <sup>-1</sup> , synthetic wastewater	[141]
Sulfamethazine	Gamma irradiation	20 mgL <sup>-1</sup>	Dose rate: 320 Gymin <sup>-1</sup> , G (Fe <sup>3+</sup> ), 15.6 (per 100eV), Fe <sup>2+</sup> 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 <sup>-1</sup>	T: 20°C, 9-W UVA lamp ( $\lambda_{max}$ = 365 nm), light intensity: 7.7 mW cm <sup>-2</sup> , ultrasonic shockwave Frequency: 20 kHz, purified air flow:1.0 L min <sup>-1</sup> , synthetic wastewater	[143]
Sulfanilamide	Electro-Fenton and UVA photoelectro-Fenton	239–2511 mg L <sup>-1</sup>	6-W fluorescent black light blue tube (320–400 nm), photoionization energy: 5 Wm <sup>-2</sup> , 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 <sup>-1</sup>	The process was performed using a DSA (mixed metal oxide, Ti/RuO <sub>2</sub> -IrO <sub>2</sub> ) anode carbon-felt from cathode, synthetic wastewater	[144]
Tetracycline	Electrochemical oxidation, electro Fenton	100 mg L <sup>-1</sup>	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 <sub>2</sub> -IrO <sub>2</sub> ), and a tridimensional, carbon-felt electrodes as cathode were used. T: 23°C, synthetic wastewater	[145]
Tetracycline	Ozonation	20–100 mgL <sup>-1</sup>	O <sub>3</sub> was generated from oxygen. T: 25°C, synthetic wastewater	[146]
Tetracycline	Photo-Fenton	TOC: 13 mg L <sup>-1</sup>	15-W black-light lamp (365 nm), irradiance: 19 Wm <sup>-2</sup> , flow rate: 80 mL min <sup>-1</sup> , synthetic wastewater, surface water and a sewage treatment plant effluent	[147]
Tetracycline	Photocatalysis	67 mgL <sup>-1</sup>	Medium mercury lamp, synthetic wastewater	[148]
Timidazole	Ozone	30 mgL <sup>-1</sup>	T: 25°C, synthetic wastewater, surface water and a sewage treatment plant effluent	[149]
Timidazole	Sonolysis	45, 80, and 100 ppm	pH: 3, 5, 7, 9; H <sub>2</sub> O <sub>2</sub> conc.: 83, 167, 250, 333, and 417 mM L <sup>-1</sup> , 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 <sup>-1</sup>	6-W fluorescent blacklight blue lamp (350–410 nm), synthetic wastewater, wastewater	[151]
Trimethoprim	BDD, electrochemical oxidation	1.72 × 10 <sup>-4</sup> mol L <sup>-1</sup>	T: 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  $\text{TiO}_2$ ; the requirement of postseparation and recovery of the catalyst particles from the reaction mixture in aqueous slurry systems),  $\text{TiO}_2$  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  $\text{mJ cm}^2$ , 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 ( $\text{H}_2\text{O}_2/\text{UV}$ ,  $\text{O}_3/\text{UV}$ ,  $\text{H}_2\text{O}_2/\text{Fe}^{2+}/\text{UV}$ , and  $\text{TiO}_2/\text{UV}$ ) 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,  $\text{TiO}_2$  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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## References

- [1] Michael I, Rizzo L, McArdeell CS, Manaia CM, Merlin C, Schwartz T, Dagot C, Fatta-Kassinos D. Urban wastewater treatment plants as hotspots for the release of antibiotics in the environment: A review. *Water Res.* 2013;**47**:957–995. DOI:10.1016/j.watres.2012.11.027
- [2] Thiele-Brühn S. Pharmaceutical antibiotic compounds in soils: A review. *J. Plant Nutr. Soil Sci.* 2003;**166**:145–167. DOI: 10.1002/jpln.200390023



- [3] Alaton I, Dogruel S. Pre-treatment of penicillin formulation effluent by advanced oxidation processes. *J. Hazard. Mater.* 2004;**B112**:105–113. DOI:10.1016/j.jhazmat.2004.04.009
- [4] Schwartz T, Volkmann H, Kirchen S, Kohnen W, Schon-Holz K, Jansen B, Obst U. Real-time PCR detection of *Pseudomonas aeruginosa* in clinical and municipal wastewater and genotyping of the ciprofloxacin-resistant isolates. *FEMS Microbiol. Ecol.* 2006;**57**:158–167. DOI: 10.1111/j.1574-6941.2006.00100.x 1
- [5] Homem V, Santos L. Degradation and removal methods of antibiotics from aqueous matrices: A review. *J. Environ. Manage.* 2011;**92**:2304–2347. DOI:10.1016/j.jenvman.2011.05.023
- [6] EPA. Handbook on Advanced Non-Photochemical Oxidation Process, US. EPA, Washington, DC; 2001.
- [7] Kümmerer K. Significance of antibiotics in the environment. *J. Antimicrob. Chemother.* 2003;**52**:5–7. DOI: 10.1093/jac/dkg293
- [8] Hirsch R, Ternes T, Haberer K, Kratz KL. Occurrence of antibiotics in the aquatic environment. *Sci. Total Environ.* 1999;**225**:109–118. DOI:10.1016/S0048-9697(98)00337-4
- [9] Boxall ABA, Kolpin DW, Halling-Sorensen B, Tolls J. Peer reviewed: Are veterinary medicines causing environmental risks? *Environ. Sci. Technol.* 2003;**37**(15):286A–294A. DOI: 10.1021/es032519b
- [10] Banik KK, Hossain S. Pharmaceuticals in drinking water: A future water quality threat. *Indian J. Environ. Prot.* 2006;**26**:926–932.
- [11] Chee-Sanford JC, Aminov RI, Krapac IJ, Garrigues-Jeanjean N, Mackie RI. Occurrence and diversity of tetracycline resistance genes in lagoons and groundwater underlying two swine production facilities. *Appl. Environ. Microbiol.* 2001;**67**:1494–1502. DOI: 10.1128/AEM.67.4.1494-1502.2001
- [12] Jeong J, Song W, Cooper WJ, Jung J, Greaves J. Degradation of tetracycline antibiotics: Mechanisms and kinetic studies for advanced oxidation/reduction processes. *Chemosphere.* 2010;**78**:533–540. DOI:10.1016/j.chemosphere.2009.11.024
- [13] Johansson N. Antibiotics in the environment. Environment and pharmaceuticals. Swedish Environmental Protection Agency, and Roland Möllby, Karolinska Institute; 2006.
- [14] Kümmerer K. Antibiotics in the aquatic environment-a review-Part I. *Chemosphere.* 2009;**75**:417–434. DOI:10.1016/j.chemosphere.2008.11.086
- [15] Merck and Co. The Merck Manual of Diagnosis and Therapy. 17<sup>th</sup> edition. John Wiley & Sons, Indianapolis, IN; 1999.
- [16] Ikehata K, Naghashkar NJ, El-Din MG. Degradation of aqueous pharmaceuticals by ozonation and advanced oxidation processes: A review. *Ozone Sci. Eng.* 2006;**28**:353–414.
- [17] Rozas O, Contreras D, Mondaca MA, Pérez-Moya M, Mansilla HD. Experimental design of Fenton and photo-Fenton reactions for the treatment of ampicillin solutions. *J. Hazard. Mater.* 2010;**177**:1025–1030. DOI:10.1016/j.jhazmat.2010.01.023

- [18] Alexy R, Kümpe l T, Kümmerer K. Assessment of degradation of 18 antibiotics in the closed bottle test. *Chemosphere*. 2004;**57**:505–512. DOI:10.1016/j.chemosphere.2004.06.024
- [19] Xu WH, Zhang G, Zou SC, Li XD, Liu YC. Determination of selected antibiotics in the Victoria Harbour and the Pearl River, South China using high performance liquid chromatography electrospray ionization tandem mass spectrometry. *Environ. Pollut.* 2007;**145**:672–679. DOI:10.1016/j.envpol.2006.05.038
- [20] Kemper N. Veterinary antibiotics in the aquatic and terrestrial environment. *Ecol. Indic.* 2008;**8**:1–13. DOI:10.1016/j.ecolind.2007.06.002
- [21] Botitsi E, Frosyni C, Tsi pi D. Determination of pharmaceuticals from different therapeutic classes in wastewaters by liquid chromatography electrospray ionization-tandem mass spectrometry. *Anal. Bioanal. Chem.* 2007;**387**:1317–1327. DOI: 10.1007/s00216-006-0804-8
- [22] Chang H, Hu J, Asami M, Kunikane S. Simultaneous analysis of 16 sulfonamide and trimethoprim antibiotics in environmental waters by liquid chromatography-electrospray tandem mass spectrometry. *J. Chromatogr. A.* 2008;**1190**:390–393. DOI:10.1016/j.chroma.2008.03.057
- [23] Duong HA, Pham NH, Nguyen HT, Hoang TT, Pham HV, Pham VC, Berg M, Giger W, Alder AC. Occurrence, fate and antibiotic resistance of fluoroquinolone antibacterials in hospital wastewaters in Hanoi, Vietnam. *Chemosphere*. 2008;**72**:968–973. DOI:10.1016/j.chemosphere.2008.03.009
- [24] Hartmann A, Alder AC, Koller T, Widmer RM. Identification of fluoroquinolone antibiotics as the main source of umuC genotoxicity in native hospital wastewater. *Environ. Toxicol. Chem.* 1998;**17**:377–382. DOI: 10.1002/etc.5620170305
- [25] Lindberg R, Jarnheimer PA, Olsen B, Johansson M, Tysklind M. Determination of antibiotic substances in hospital sewage water using solid phase extraction and liquid chromatography/mass spectrometry and group analogue internal standards. *Chemosphere*. 2004;**57**:1479–1488. DOI:10.1016/j.chemosphere.2004.09.015
- [26] Turiel E, Bordin G, Rodríguez AR. Study of the evolution and degradation products of ciprofloxacin and oxolinic acid in river water samples by HPLC–UV/MS/MS–MS. *J. Environ. Monitor.* 2005;**7**:189–195. DOI: 10.1039/B413506G
- [27] Brown KD, Kulis J, Thomson B, Chapman TH, Mawhinney DB. Occurrence of 24 antibiotics in hospital, residential, and dairy effluent, municipal wastewater, and the Rio Grande in New Mexico. *Sci. Total Environ.* 2006;**366**:772–783. DOI:10.1016/j.scitotenv.2005.10.007
- [28] Thomas KV, Dye C, Schlabach M, Langford KH. Treatment works. *J. Environ. Monitor.* 2007;**9**:1410–1418. DOI: 10.1039/B709745J
- [29] Martins AF, Vasconcelos TG, Henriques DM, Frank CD, König A, Kümmerer K. Concentration of ciprofloxacin in Brazilian hospital effluent and preliminary risk assessment: A case study. *Clean.* 2008;**36**:264–269. DOI: 10.1002/clen.200700171

- [30] Alexy R, Sommer A, Lange FT, Kümmerer K. Local use of antibiotics and their input and fate in a small sewage treatment plant—Significance of balancing and analysis on a local scale vs. nationwide scale. *Acta Hydroch. Hydrob.* 2006;**34**:587–592. DOI: 10.1002/aheh.200400657
- [31] Watkinson AJ, Murby EJ, Kolpin DW, Constanzo SD. The occurrence of antibiotics in an urban watershed: From wastewater to drinking water. *Sci. Total Environ.* 2009;**407**:2711–2723. DOI: 10.1016/j.scitotenv.2008.11.059
- [32] Färber H. Antibiotika im Krankenhausabwasser (Antibiotics in the hospital sewage). *Hyg. Med.* 2002;**27**:35.
- [33] Christian T, Schneider RJ, Färber HA, Skutlarek D, Meyer MT, Goldbach HE. Determination of antibiotic residues in manure, soil, and surface waters. *Acta Hydroch. Hydrob.* 2003;**31**:36–44. DOI: 10.1002/aheh.200390014
- [34] Giger W, Alder AC, Golet EM, Kohler HPE, McArdell CS, Molnar E, Siegrist H, Suter MJF. Occurrence and fate of antibiotics as trace contaminants in wastewaters, sewage sludges, and surface waters. *Chimia.* 2003a;**57**:485–491. DOI:10.2533/000942903777679064
- [35] Giger W, Alder AC, Golet EM, Kohler HPE, McArdell CS, Molnar E, Pham Thi NA, Siegrist H. Antibiotikaspuren auf dem Weg von Spital- und Gemeindeabwasser in die Fließgewässer: Umweltanalytische Untersuchungen über Einträge und Verhalten (Traces of antibiotics on the way from hospital and local sewage treatment plant in flowing bodies of water: Environmental analytical investigations on their entry and behavior). In: Track, T., Kreysa, G. (Eds.), *Spurenstoffe in Gewässern. Pharmazeutische Reststoffe und endokrinwirksame Substanzen (Trace materials in bodies of water. Pharmaceutical trace materials and endocrine active substances)*. Wiley-VCH GmbH & Co, New Jersey, USA. 2003b p. 21–33.
- [36] Sacher F, Gabriel S, Metzinger M, Stretz A, Wenz M, Lange FT, Brauch HJ, Blankenhorn I. Arzneimittelwirkstoffe im Grundwasser – Ergebnisse eines Monitoring-Programms in Baden-Württemberg (Active pharmaceutical ingredients in ground water – the results of a monitoring program in Baden-Württemberg (Germany)). *Vom Wasser.* 2002;**99**:183–196. ISSN 0083-6915
- [37] Calamari D, Zuccato E, Castiglioni S, Bagnati R, Fanelli R. Strategic of therapeutic drugs in the rivers Po and Lambro in Northern Italy. *Environ. Sci. Technol.* 2003;**37**:1241–1248. DOI: 10.1021/es020158e
- [38] Kolpin DW, Furlong ET, Meyer MT, Thurman EM, Zaugg SD, Barber LB, Buxton HT. Pharmaceuticals, hormones, and others organic wastewater contaminants in US streams, 1999–2000: A national reconnaissance. *Environ. Sci. Technol.* 2002;**36**:1202–1211. DOI: 10.1021/es011055j
- [39] Zuccato E, Chiabrando C, Castiglioni S, Calamari D, Bagnati R, Schiarea S, Fanelli R. Cocaine in surface waters: A new evidence-based tool to monitor community drug abuse. *Environ. Health.* 2005;**5**:4–14. DOI: 10.1186/1476-069X-4-14

- [40] Parsons SA, Williams M. Introduction. In: Parsons, S. (Ed.). *Advanced Oxidation Processes for Water and Wastewater Treatment*. IWA Publishing, London, UK. 2004, p. 1–6.
- [41] Ince NH, Apikyan IG. Combination of activated carbon adsorption with light enhanced chemical oxidation via hydrogen peroxide. *Water Res.* 2000;**34**:4169–4176. DOI:10.1016/S0043-1354(00)00194-9
- [42] Azbar N, Kestioglu K, Yonar T. Application of Advanced Oxidation Processes (AOPs) to Wastewater Treatment. Case Studies: Decolourization of Textile Effluents, Detoxification of Olive Mill Effluent, Treatment of Domestic Wastewater, Ed. A.R. BURK. *Water Pollution: New Research*, Nova Science Publishers, New York, 2005 p. 99–118. ISBN-1-59454-393-3
- [43] Mandal A, Ojha K, De AK, Bhattacharjee S. Removal of catechol from aqueous solution by advanced photo-oxidation process. *Chem. Eng. J.* 2004;**102**:203–208. DOI:10.1016/j.cej.2004.05.007
- [44] Yonar T. Decolorisation of Textile Dyeing Effluents Using Advanced Oxidation Processes. Eds. Hauser PJ. In: *Advances in Treating Textile Effluent*. Intech Publisher, Rijeka, Croatia, 2011.
- [45] Litter MI. Introduction to photochemical advanced oxidation processes for water treatment. *Environ. Photochem. Part II.* 2005;**2**:325–326. DOI:10.1007/b138188
- [46] Gottschalk C, Libra JA, Saupe A. *Ozonation of Water and Wastewater*. Wiley-Vch, Weinheim, Deutschland, 2009 ISBN:978-3-527-31962-6.
- [47] Zaviska F, Drogui P, Mercier G, Blais JF. Procédés d'oxydation avancée dans le traitement des eaux et des effluents industriels: Application à la dégradation des polluants réfractaires. *Rev. Sci. Eau.* 2009;**22**(4):535–564. DOI: 10.7202/038330ar
- [48] Oturan MA, Aaron JJ. Advanced oxidation Processes in water/wastewater treatment: Principles and Applications: A review. *Crit. Rev. Environ. Sci. Technol.* 2014;**44**:2577–2641. DOI:10.1080/10643389.2013.829765
- [49] Buxton GU, Greenstock CL, Helman WC, Ross AB. Critical review of rate constant for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (HO/O<sup>-</sup>) in aqueous solution. *J. Phys. Chem. Ref. Data.* 1988;**17**(2):513–886. DOI: 10.1063/1.555805
- [50] Mokrini M, Oussi D, Esplugas S. Oxidation of aromatic compounds with UV radiation/ozone/hydrogen peroxide. *Water Sci. Technol.* 1997;**35**:95–102
- [51] Hernandez R, Zappi M, Colluci J, Jones R. Comparing the performance of various advanced oxidation process for treatment of acetone contaminated water. *J. Hazard. Mater.* 2002;**92**(1): 33–50. DOI:10.1016/S0304-3894(01)00371-5
- [52] Klavarioti M, Mantzavinos D, Kassinos D. Removal of residual pharmaceuticals from aqueous systems by advanced oxidation process. *Environ. Int.* 2009;**35**:402–417. DOI:10.1016/j.envint.2008.07.009
- [53] Bautista P, Mohedano AF, Casas JA, Zazo JA, Rodriguez JJ. An overview of the application of Fenton oxidation to industrial wastewaters treatment. *J. Chem. Technol. Biotechnol.* 2008;**83**(10):1323–1338. DOI: 10.1002/jctb.1988

- [54] Gonzalez MG, Oliveros E, Worner M, Braun AM. Vacuum-ultraviolet photolysis of aqueous reaction systems. *J. Photochem. Photobiol. C Photochem. Rev.* 2004;**5**:225–246. DOI: 10.1016/j.jphotochemrev.2004.10.002
- [55] Niaounakis M, Halvadakis CP. Olive processing waste management—Literature review and patent survey, 2nd ed., Elsevier, Amsterdam, The Netherlands, 2006. ISSN:1478-7482
- [56] Crittenden JC, Trussell RR, Hand DW, Howe KJ, Tchobanoglous G. *Water treatment: Principles and Design*, 2nd ed., Wiley, Oxford, UK, Estonian Academy Publishers, Tallinn, Estonia, 2005.
- [57] Stasinakis AT. Use of selected advanced oxidation processes (AOPs) for wastewater treatment—A mini review. *Global Nest J.* 2008;**10**(3):376–385.
- [58] Munter R. Advanced oxidation processes-currents status and prospects. Proceedings of the Estonian Academy of Sciences. Aben, H., editor; 2001 ISSN: 1406-0124.
- [59] Ghaly MY, Härtel G, Mayer R, Haseneder R. Photochemical oxidation of *p*-chlorophenol by UV/H<sub>2</sub>O<sub>2</sub> and photo-Fenton process. A comparative study. *Waste Manage.* 2001;**21**:41–47. DOI: 10.1016/S0956-053X(00)00070-2
- [60] Gosavi VD, Sharma S. A general review on various treatment methods for textile wastewater. *JECET.* 2014;**3**(1):29–39. E-ISSN: 2278–179X
- [61] Kormann C, Bahnemann DF, Hoffmann MR. Photolysis of chloroform and other organic molecules in aqueous TiO<sub>2</sub> suspensions. *Environ. Sci. Technol.* 1991;**25**:494–500. DOI: 10.1021/es00015a018
- [62] Zahraa O, Chen HY, Bouchy M. Adsorption and photocatalytic degradation of 1,2-dichloroethane on suspended TiO<sub>2</sub>. *J. Adv. Oxid. Technol.* 1999;**4**:167–173.
- [63] Adams C, Asce M, Wang Y, Loftin K, Meyer M. Removal of antibiotics from surface and distilled water in conventional water treatment processes. *J. Environ. Eng.* 2002;**128**:253–260. DOI: 10.1061/(ASCE)0733-9372
- [64] Arslan Alaton I, Dogruel S, Baykal E, Gerone G. Combined chemical and biological oxidation of penicillin formulation effluent. *J. Environ. Manag.* 2004;**73**:155–163. DOI: 10.1016/j.jenvman.2004.06.007
- [65] Saritha P, Aparna C, Himabindu V, Anjaneyulu Y. Comparison of various advanced oxidation processes for the degradation of 4-chloro-2nitrophenol. *J. Hazard. Mater.* 2007;**149**:609–614. DOI:10.1016/j.jhazmat.2007.06.111
- [66] Naddeo V, Meric S, Kassinos D, Belgiorno V, Guida M. Fate of pharmaceuticals in contaminated urban wastewater effluent under ultrasonic irradiation. *Water Res.* 2009;**43**:4019–4027. DOI:10.1016/j.watres.2009.05.027
- [67] Elmolla ES, Chaudhuri M. The feasibility of using combined TiO<sub>2</sub> photocatalysis-SBR process for antibiotic wastewater treatment. *Desalination.* 2011;**272**:218–224. DOI: 10.1016/j.desal.2011.01.020

- [68] Lange F, Cornelissen S, Kubac D, Sein MM, Von Sonntag J, Hannich CB, Golloch A, Heipieper HJ, Moder M, Von Sonntag C. Degradation of macrolide antibiotics by ozone: A mechanistic case study with clarithromycin. *Chemosphere*. 2006;**65**(1):17–23. DOI: 10.1016/j.chemosphere.2006.03.014
- [69] Dodd MC. Potential impacts of disinfection processes on elimination and deactivation of antibiotic resistance genes during water and wastewater treatment. *J. Environ. Monit.* 2012;**14**:1754–1771. DOI: 10.1039/C2EM00006G
- [70] Huber MM, Göbel A, Joss A, Hermann N, Löffler D, McArdell CS, Ried A, Siegrist H, Ternes TA, Von Gunten U. Oxidation of pharmaceuticals during ozonation of municipal wastewater effluents: A pilot study. *Environ. Sci. Technol.* 2005;**39**:4290–4299. DOI: 10.1021/es048396s
- [71] Rizzo L, Fiorentino A, Anselmo A. Advanced treatment of urban wastewater by UV radiation: Effect on antibiotics and antibiotic-resistant *E. coli* strains. *Chemosphere*. 2013;**92**:171–176. DOI: 10.1016/j.chemosphere.2013.03.021
- [72] Sharma VK, Liu F, Tolan S, Sohn M, Kim H, Oturan MA. Oxidation of b-lactam antibiotics by ferrate(VI). *Chem. Eng. J.* 2013;**221**:446–451. DOI: 10.1016/j.cej.2013.02.024
- [73] Chaudhuri M, Wahap M, Affam AC. Treatment of aqueous solution of antibiotics amoxicillin and cloxacillin by modified photo Fenton process. *Desalination and Water Treatment*. 2013;**51**:7255–7268. DOI:10.1080/19443994.2013.773565
- [74] Li Y, Zhang F, Liang X, Yediler A. Chemical and toxicological evaluation of an emerging pollutant (enrofloxacin) by catalytic wet air oxidation and ozonation in aqueous solution. *Chemosphere*. 2013;**90**:284–291. DOI:10.1016/j.chemosphere.2012.06.068
- [75] Elmolla ES, Chaudhuri M. Photocatalytic degradation of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution using UV/TiO<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub>/TiO<sub>2</sub> photocatalysis. *Desalination*. 2010a;**252**:46–52. DOI:10.1016/j.desal.2009.11.003
- [76] Elmolla ES, Chaudhuri M. Degradation of the antibiotics amoxicillin, ampicillin and cloxacillin in aqueous solution by the photo-Fenton process. *J. Hazard. Mater.* 2009;**172**:1476–1481. DOI: 10.1016/j.jhazmat.2009.08.015
- [77] Elmolla ES, Chaudhuri M. Comparison of different advanced oxidation processes for treatment of antibiotic aqueous solution. *Desalination*. 2010b;**256**:43–47. DOI: 10.1016/j.desal.2010.02.019
- [78] Dimitrakopoulou D, Rethemiotaki I, Frontistis Z, Xekoukoulotakis N, Venieri D, Mantzavino, D. Degradation, mineralization and antibiotic inactivation of amoxicillin by UV-A/TiO<sub>2</sub> photocatalysis. *J. Environ. Manag.* 2012;**98**:168–174. DOI: 10.1016/j.jenvman.2012.01.010
- [79] Affamand AC, Chaudhuri M. Optimization of Fenton treatment of amoxicillin and cloxacillin antibiotic aqueous solution. *Desalination Water Treatment*. 2013;**52**:1878–1884. DOI: 10.1080/19443994.2013.794015

- [80] Magureanu M, Piroi D, Mandache NB, David V, Medvedovici A, Bradu C, Parvulescu VI. Degradation of antibiotics in water by non-thermal plasma treatment. *Water Res.* 2011;**45**:3407–3416. DOI: 10.1016/j.watres.2011.03.057
- [81] Benitez FJ, Acero JL, Real FJ, Roldan G, Casas F. Comparison of different chemical oxidation treatments for the removal of selected pharmaceuticals in water matrices. *Chem. Eng. J.* 2011;**168**:1149–1156. DOI: 10.1016/j.cej.2011.02.001
- [82] Trovo AG, Melo SAS, Nogueira RFP. Photodegradation of the pharmaceuticals amoxicillin, bezafibrate and paracetamol by the photo-Fenton process-Application to sewage treatment plant effluent. *J. Photochem. Photobiol. A Chem.* 2008;**198**:215–220. DOI: 10.1016/j.jphotochem.2008.03.011
- [83] Homem V, Alves A, Santos L. Microwave-assisted Fenton's oxidation of amoxicillin. *Chem. Eng. J.* 2013;**220**:35–44. DOI: 10.1016/j.cej.2013.01.047
- [84] Andreozzi R, Canterino M, Marotta R, Paxeus N. Antibiotic removal from wastewaters: The ozonation of amoxicillin. *J. Hazard. Mater.* 2005;**122**:243–250. DOI:10.1016/j.jhazmat.2005.03.004
- [85] Trovo AG, Nogueira RFP, Aguera A, Fernandez-Alba AR, Malato S. Degradation of the antibiotic amoxicillin by photo-Fenton process, chemical and toxicological assessment water research. 2011;**45**:1394–1402. doi:10.1016/j.watres.2010.10.029
- [86] Su S, Guo W, Yi C, Leng Y, Ma Z. Degradation of amoxicillin in aqueous solution using sulphate radicals under ultrasound irradiation. *Ultrasonics Sonochem.* 2012;**19**:469–474. DOI: 10.1016/j.ultsonch.2011.10.005
- [87] Jung YJ, Kim WG, Yoon Y, Kang JW, Hong YM, Kim HW. Removal of amoxicillin by UV and UV/H<sub>2</sub>O<sub>2</sub> processes. *Sci. Total Environ.* 2012;**420**:160–167. DOI: 10.1016/j.scitotenv.2011.12.011
- [88] Ternes TA, Stuber J, Herrmanna N, McDowella D, Ried A, Kampmann M, Teiser B. Ozonation: A tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater? *Water Res.* 2003;**37**:1976–1982. DOI:10.1016/S0043-1354(02)00570-5
- [89] Biń AK, Madej SS. Comparison of the Advanced Oxidation Processes (UV, UV/H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>) for the Removal of Antibiotic Substances during Wastewater Treatment. *Ozone Sci. Eng.* 2012;**34**:136–139. DOI: 10.1080/01919512.2012.650130
- [90] Cuevas SM, Arqués A, Maldonado MI, Pérez JAS, Rodríguez SM. Combined nanofiltration and photo-Fenton treatment of water containing micropollutants. *Chem. Eng. J.* 2013;**224**:89–95. DOI: 10.1016/j.cej.2012.09.068
- [91] Estrada AL, Li YY, Wang A. Biodegradability enhancement of wastewater containing cefalexin by means of the electro-fenton oxidation process. *J. Hazard. Mater.* 2012;**227–228**:41–48. DOI: 10.1016/j.jhazmat.2012.04.079

- [92] Gurkan YY, Turkten N, Hatipoglu A, Cinar Z. Photocatalytic degradation of cefazolin over N-doped TiO<sub>2</sub> under UV and sunlight irradiation: Prediction of the reaction paths via conceptual DFT. *Chem. Eng. J.* 2012;**184**:113–124. DOI: 10.1016/j.cej.2012.01.011
- [93] Balçioğlu IA, Ötoker M. Treatment of pharmaceutical wastewater containing antibiotics by O<sub>3</sub> and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> processes. *Chemosphere.* 2003;**50**:85–95. DOI:10.1016/S0045-6535(02)00534-9
- [94] Trovo AG, Paiva VAB, Machado AEH, Oliveira CA, Santos RO. Degradation of the antibiotic chloramphenicol by photo-fenton process at lab-scale and solar pilot plant: Kinetic, toxicity and inactivation assessment. *Solar Energy.* 2013;**97**:596–604. DOI: 10.1016/j.solener.2013.09.017
- [95] Segura SG, Cavalcanti EB, Brillasa E. Mineralization of the antibiotic chloramphenicol by solar photoelectro-Fenton. From stirred tank reactor to solar pre-pilot plant. *Appl. Catal. B Environ.* 2014;**144**:588–598. DOI:10.1016/j.apcatb.2013.07.071
- [96] Zuorro A, Fidaleo M, Fidaleo M, Lavecchia R. Degradation and antibiotic activity reduction of chloramphenicol in aqueous solution by UV/H<sub>2</sub>O<sub>2</sub> process. *J. Environ. Manag.* 2014;**133**:302–308. DOI: 10.1016/j.jenvman.2013.12.012
- [97] Rocha ORS, Pinheiro RB, Duarte MMB, Dantas RF, Ferreira AP, Benachour M, Silva VL. Degradation of the antibiotic chloramphenicol using photolysis and advanced oxidation process with UV C and solar radiation, *Desalination Water Treatment.* 2013;**51**:7269–7275. DOI: 10.1080/19443994.2013.792148
- [98] Hopkins ZR, Blaney L. A novel approach to modeling the reaction kinetics of tetracycline antibiotics with aqueous ozone. *Sci. Total Environ.* 2014;**468–469**:337–344. DOI: 10.1016/j.scitotenv.2013.08.032
- [99] Kim TH, Kim SD, Kim HY, Lim SJ, Lee M, Yu S. Degradation and toxicity assessment of sulfamethoxazole and chlortetracycline using electron beam, ozone and UV. *J. Hazard. Mater.* 2012;**227–228**:237–242. DOI: 10.1016/j.jhazmat.2012.05.038
- [100] Bobu M, Yediler A, Siminiceanu I, Zhang F, Hostede S. Comparison of different advanced oxidation processes for the degradation of two fluoroquinolone antibiotics in aqueous solutions. *J. Environ. Sci. Health, Part A.* 2013;**48**:251–262. DOI: 10.1080/10934529.2013.726805
- [101] Khanet MH, Jung HS, Lee W, Jung JY. Chlortetracycline degradation by photocatalytic ozonation in the aqueous phase: Mineralization and the effects on biodegradability. *Environ. Technol.* 2013;**34**:495–502. DOI:10.1080/09593330.2012.701332
- [102] Jiet Y, Ferronato C, Salvador A, Yanga X, Chovelon J. Degradation of ciprofloxacin and sulfamethoxazole by ferrous-activated persulfate: Implications for remediation of groundwater contaminated by antibiotics. *Sci. Total Environ.* 2014;**472**:800–808. DOI: 10.1016/j.scitotenv.2013.11.008



- [103] Doorslaer XV, Demeestere K, Heynderickx PM, Langenhove HV, Dewulf J. UV-A and UV-C induced photolytic and photocatalytic degradation of aqueous ciprofloxacin and moxifloxacin: Reaction kinetics and role of adsorption. *Appl. Catal. B Environ.* 2011;**101**:540–547. DOI: 10.1016/j.apcatb.2010.10.027
- [104] Cho JY, Chung BY, Lee K, Geon-Hwi Lee Hwang SA. Decomposition reaction of the veterinary antibiotic ciprofloxacin using electron ionizing energy. *Chemosphere.* 2014;**117**:158–163. DOI: 10.1016/j.chemosphere.2014.06.039
- [105] Witte BD, Dewulf J, Demeestere K, Langenhove HV. Ozonation and advanced oxidation by the peroxone process of ciprofloxacin in water. *J. Hazard. Mater.* 2009;**161**:701–708. DOI: 10.1016/j.jhazmat.2008.04.021
- [106] Vasconcelos TG, Kümmerer K, Henriques DM, Martins AF. Ciprofloxacin in hospital effluent: Degradation by ozone and photoprocesses. *J. Hazard. Mater.* 2009;**169**:1154–1158. DOI: 10.1016/j.jhazmat.2009.03.143
- [107] An T, Yang H, Li G, Song W, Cooper WJ, Nie X. Kinetics and mechanism of advanced oxidation processes (AOPs) in degradation of ciprofloxacin in water. *Appl. Catal. B Environ.* 2010;**94**:288–294. DOI: 10.1016/j.apcatb.2009.12.002
- [108] Alpatova AL, Davies SH, Masten SJ. Hybrid ozonation-ceramic membrane filtration of surface waters: The effect of water characteristics on permeate flux and the removal of DBP precursors, dicloxacillin and ceftazidime. *Sep. Purif. Technol.* 2013;**107**:179–186. DOI: 10.1016/j.seppur.2013.01.013
- [109] Rivas J, Encinas Á, Beltrán F, Graham N. Application of advanced oxidation processes to doxycycline and norfloxacin removal from water. *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.* 2011;**46**:9:944–951. DOI: 10.1080/10934529.2011.586249
- [110] Guinea E, Garrido JA, Rodríguez RM, Cabot P, Arias C, Centellas F, Brillas E. Degradation of the fluoroquinolone enrofloxacin by electrochemical advanced oxidation processes based on hydrogen peroxide electrogeneration. *Electrochim. Acta.* 2010;**55**:2101–2115. DOI: 10.1016/j.electacta.2009.11.040
- [111] Rosal R, Rodriguez A, Perdigon-Melon JA, Petre A, Calvo EG, Gomez MJ, Agüera A, Fernandez-Alba AR. Occurrence of emerging pollutants in urban wastewater and their removal through biological treatment followed by ozonation. *Water Res.* 2010;**44**:578–588. DOI:10.1016/j.watres.2009.07.004
- [112] Klammerth N, Malato S, Maldonado MI, Agüera A, Fernández-Alba A. Modified photo-Fenton for degradation of emerging contaminants in municipal wastewater effluents. *Catal. Today.* 2011;**161**:241–246. DOI:10.1016/j.cattod.2010.10.074
- [113] Nasuhoglu D, Rodayan A, Berk D, Yargeau V. Removal of the antibiotic levofloxacin (LEVO) in water by ozonation and TiO<sub>2</sub> photocatalysis. *Chem. Eng. J.* 2012;**189–190**:41–48. DOI: 10.1016/j.cej.2012.02.016

- [114] Cheng W, Yang M, Xie Y, Liang B, Fang Z, Tsang EP. Enhancement of mineralization of metronidazole by the electro-Fenton process with a Ce/SnO<sub>2</sub>-Sb coated titanium anode. *Chem. Eng. J.* 2013;**220**:214–220. DOI: 10.1016/j.cej.2013.01.055
- [115] Doorslaer XV, Demeestere K, Heynderickx PM, Caussyn M, Langenhove HV, Devlieghere F, Vermeulen A, Dewulf J. Heterogeneous photocatalysis of moxifloxacin: Identification of degradation products and determination of residual antibacterial activity. *Appl. Catal. B Environ.* 2013;**138–139**:333–341. DOI: 10.1016/j.apcatb.2013.03.011
- [116] Doorslaer XV, Heynderickx PM, Demeestere K, Debevere K, Langenhove HV, Dewulf J. TiO<sub>2</sub>, mediated heterogeneous photocatalytic degradation of moxifloxacin: Operational variables and scavenger study. *Appl. Catal. B Environ.* 2012;**111–112**:150–156. DOI:10.1016/j.apcatb.2011.09.029
- [117] Michael I, Hapeshi E, Michael C, Varela AR, Kyriakou S, Manaia CM, Fatta-Kassinos D. Solar photo-Fenton process on the abatement of antibiotics at a pilot scale: Degradation kinetics, ecotoxicity and phytotoxicity assessment and removal of antibiotic resistant enterococci. *Water Res.* 2012;**46**:5621–5634. DOI: 10.1016/j.watres.2012.07.049
- [118] Giraldo A, Penuela G, Torres-Palma R, Pino N, Palominos R, Mansilla H. Degradation of the antibiotic oxolinic acid by photocatalysis with TiO<sub>2</sub> in suspension. *Water Res.* 2010;**44**:5158–5167. DOI: 10.1016/j.watres.2010.05.011
- [119] Pereira J, Queirós D, Reis A, Nunes O, Borges M, Boaventura R, Vilar V. Process enhancement at near neutral pH of a homogeneous photo-Fenton reaction using ferric-carboxylate complexes: Application to oxytetracycline degradation. *Chem. Eng. J.* 2014;**253**:217–228. DOI: 10.1016/j.cej.2014.05.037
- [120] Pereira J, Vilar V, Borges M, Gonzalez O, Esplugas S, Boaventura R. Photocatalytic degradation of oxytetracycline using TiO<sub>2</sub> under natural and simulated solar radiation. *Solar Energy.* 2011;**85**:2732–2740. DOI: 10.1016/j.solener.2011.08.012
- [121] Tambosi JL, de Sena RF, Gebhardt WRFPM, Moreira, José HJ, Schröder HF. Physico-chemical and advanced oxidation processes—A comparison of elimination results of antibiotic compounds following an MBR treatment. *Ozone Sci. Eng. J. Int. Ozone Assoc.* 2009;**31**:428–435. DOI: 10.1080/01919510903324420
- [122] Yang H, Li G, An T, Gao Y, Fu J. Photocatalytic degradation kinetics and mechanism of environmental pharmaceuticals in aqueous suspension of TiO<sub>2</sub>: A case of sulfa drugs. *Catal. Today.* 2010;**153**:200–207. DOI: 10.1016/j.jhazmat.2010.03.079
- [123] El-Ghenymy A, Oturan N, Oturan MA, Garrido JA, Cabot PL, Centellas F, Rodríguez RM, Brillas E. Comparative electro-Fenton and UVA photoelectro-Fenton degradation of the antibiotic sulfanilamide using a stirred BDD/air-diffusion tank reactor. *Chem. Eng. J.* 2013;**234**:115–123.
- [124] Liu Y, Wang J. Degradation of sulfamethazine by gamma irradiation in the presence of hydrogen peroxide. *J. Hazard. Mater.* 2013;**250–251**:99–105. DOI: 10.1016/j.jhazmat.2013.01.050

- [125] Aguinaco A, Beltrán FJ, Sagasti JJP, Gimeno O. In situ generation of hydrogen peroxide from pharmaceuticals single ozonation: A comparative study of its application on Fenton like systems. *Chem. Eng. J.* 2014;**235**:46–51. DOI: 10.1016/j.cej.2013.09.015
- [126] Köhler C, Venditti S, Igos E, Klepiszewski K, Benetto E, Cornelissen A. Elimination of pharmaceutical residues in biologically pre-treated hospital wastewater using advanced UV irradiation technology: A comparative assessment. *J. Hazard. Mater.* 2012;**239–240**:70–77. DOI:10.1016/j.jhazmat.2012.06.006
- [127] Batchu SR, Panditi VR, O’Shea KE, Gardinali PR. Photodegradation of antibiotics under simulated solar radiation: Implications for their environmental fate. *Sci. Total Environ.* 2014;**470–471**:299–310. DOI: 10.1016/j.scitotenv.2013.09.057
- [128] Baeza C, Knappe DRU. Transformation kinetics of biochemically active compounds in low-pressure UV Photolysis and UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation processes. *Water Res.* 2011;**45**:4531–4543. DOI: 10.1016/j.watres.2011.05.039
- [129] Dirany A, Sirés I, Oturan N, Oturan MA. Electrochemical abatement of the antibiotic sulfamethoxazole from water. *Chemosphere.* 2010;**81**:594–602. DOI: 10.1016/j.chemosphere.2010.08.032
- [130] Wang A, Li Y, Estrada AL. Mineralization of antibiotic sulfamethoxazole by photoelectro-Fenton treatment using activated carbon fiber cathode and under UVA irradiation. *Applied Catal. B Environ.* 2011;**102**:378–386. DOI:10.1016/j.apcatb.2010.12.007
- [131] Ramos MMG, Mezcuca M, Agüera A, Alba ARF, Gonzalo S, Rodríguez A, Rosal R. Chemical and toxicological evolution of the antibiotic sulfamethoxazole under ozone treatment in water solution. *J. Hazard. Mater.* 2011;**192**:18–25. DOI: 10.1016/j.jhazmat.2011.04.072
- [132] Espejo A, Aguinaco A, Amat AM, Beltrán FJ. Some ozone advanced oxidation processes to improve the biological removal of selected pharmaceutical contaminants from urban wastewater. *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.* 2014;**49**:410–421. DOI: 10.1080/10934529.2014.854652
- [133] Gonzalez O, Sans C, Esplugas S. Sulfamethoxazole abatement by photo-Fenton toxicity, inhibition and biodegradability assessment of intermediates. *J. Hazard. Mater.* 2007;**146**:459–464. DOI: 10.1016/j.jhazmat.2007.04.055
- [134] Trovo AG, Nogueira RFP, Agüera A, Alba ARF, Sirtori C, Malato S. Degradation of sulfamethoxazole in water by solar photo-Fenton: Chemical and toxicological evaluation. *Water Res.* 2009;**43**:3922 – 3931. DOI: 10.1016/j.watres.2009.04.006
- [135] Abellan MN, Bayarri B, Gimenez J, Costa J. Photocatalytic degradation of sulfamethoxazole in aqueous suspension of TiO<sub>2</sub>. *Appl. Catal. B Environ.* 2007;**74**:233–241. DOI: 10.1016/j.apcatb.2007.02.017
- [136] Xekoukoulotakis NP, Drosou C, Brebou C, Chatzisyneon E, Hapeshi E, Kassinos DF, Mantzavinos D. Kinetics of UV-A/TiO<sub>2</sub> photocatalytic degradation and mineralization

- of the antibiotic sulfamethoxazole in aqueous matrices. *Catal. Today*. 2011;**161**:163–168. DOI: 10.1016/j.cattod.2010.09.027
- [137] Fan X, Hao H, Shen X, Chen F, Zhang J. Removal and degradation pathway study of sulfasalazine with Fenton-like reaction. *J. Hazard. Mater.* 2011;**190**:493–500. DOI: 10.1016/j.jhazmat.2011.03.069
- [138] Liu Y, Hu J, Wang J. Radiation-induced removal of sulphadiazine antibiotics from wastewater. *Environ. Technol.* 2014a;**35**(16):2028–2034. DOI: 10.1080/09593330.2014.889761
- [139] Goncalves AG, Órfão JJM, Pereira MFR. Catalytic ozonation of sulphamethoxazole in the presence of carbon materials: Catalytic performance and reaction pathways. *J. Hazard. Mater.* 2012;**239–240**:167–174. DOI: 10.1016/j.jhazmat.2012.08.057
- [140] Lester Y, Avisar D, Mamane H. Photodegradation of the antibiotic sulphamethoxazole in water with UV/H<sub>2</sub>O<sub>2</sub> advanced oxidation process. *Environ. Technol.* 2010;**31**(2):175–183. DOI: 10.1080/09593330903414238
- [141] Beltran FJ, Aguinaco A, Araya JFG, Oropesa A. Ozone and photocatalytic processes to remove the antibiotic sulfamethoxazole from water. *Water Res.* 2008;**42**:3799–3808. DOI: 10.1016/j.watres.2008.07.019
- [142] Liu Y, Hu J, Wang J. Fe<sup>2+</sup> enhancing sulfamethazine degradation in aqueous solution by gamma irradiation. *Radiation Phys. Chem.* 2014b;**96**:81–87. DOI: 10.1016/j.radphyschem.2013.08.018
- [143] Zhou T, Wu X, Zhang Y, Li J, Lim T. Synergistic catalytic degradation of antibiotic sulfamethazine in a heterogeneous sonophotolytic goethite/oxalate Fenton-like system. *Appl. Catal. B Environ.* 2013;**136–137**:294–301. DOI: 10.1016/j.apcatb.2013.02.004
- [144] Wu J, Zhang H, Oturan N, Wang Y, Chen L, Oturan MA. Application of response surface methodology to the removal of the antibiotic tetracycline by electrochemical process using carbon-felt cathode and DSA(Ti/RuO<sub>2</sub>-IrO<sub>2</sub>) anode. *Chemosphere.* 2012;**87**:614–620. DOI: 10.1016/j.chemosphere.2012.01.036
- [145] Oturan N, Wu J, Zhang H, Sharma VK, Oturan MA. Electrocatalytic destruction of the antibiotic tetracycline in aqueous medium by electrochemical advanced oxidation processes: Effect of electrode materials. *Appl. Catal. B: Environ.* 2013;**140–141**:92–97. DOI: 10.1016/j.apcatb.2013.03.035
- [146] Pacheco CV, Polo MSJ, Utrilla R, Penalver JL. Tetracycline removal from waters by integrated technologies based on ozonation and biodegradation. *Chem. Eng. J.* 2011;**178**:115–121. DOI: 10.1016/j.cej.2011.10.023
- [147] Bautitz IR, Nogueira RFP. Degradation of tetracycline by photo-fenton process-solar irradiation and matrix effects. *J. Photochem. Photobiol. A Chem.* 2007;**187**:33–39. DOI: 10.1016/j.jphotochem.2006.09.009

- [148] Mboula VM, Héquet V, Gru Y, Colin R, Andrès Y. Assessment of the efficiency of photocatalysis on tetracycline biodegradation. *J. Hazard. Mater.* 2012;**209–210**:355–364. DOI: 10.1016/j.jhazmat.2012.01.032
- [149] Utrilla JR, Polo MS, Joya GP, García MAF, Toledo IB. Removal of tinidazole from waters by using ozone and activated carbon in dynamic regime. *J. Hazard. Mater.* 2010;**174**:880–886. DOI: 10.1016/j.jhazmat.2009.09.059
- [150] Rahmani H, Gholami M, Mahvi AH, Alimohammadi M, Azarian G, Esrafil A, Rahmani K, Farzadkia M. Tinidazole removal from aqueous solution by sonolysis in the presence of hydrogen peroxide. *Bull. Environ. Contam. Toxicol.* 2014;**92**:341–346. DOI: 10.1007/s00128-013-1193-2
- [151] Moreira FC, Segura S, Boaventura RAR, Brillas E, Vilar VJP. Degradation of the antibiotic trimethoprim by electrochemical advanced oxidation processes using a carbon-PTFE air-diffusion cathode and a boron-doped diamond or platinum anode. *Appl. Catal. B Environ.* 2014;**160–161**:492–505. DOI:10.1016/j.apcatb.2014.05.052
- [152] Yargeau V, Leclair C. Impact of operating conditions on decomposition of antibiotics during ozonation: A review. *Ozone Sci. Eng.* 2008;**30**:175–188. DOI: 10.1080/01919510701878387
- [153] Tekin H, Bilkay O, Ataberk SS, Balta TH, Ceribasi IH, Sanin FD. Use of Fenton oxidation to improve the biodegradability of a pharmaceutical wastewater. *J. Hazard. Mater.* 2006;**136**:258–265. DOI: 10.1016/j.jhazmat.2005.12.012
- [154] Melero JA, Calleja G, Martinez F, Molina R, Pariente MI. Nanocomposite Fe<sub>2</sub>O<sub>3</sub>/SBA-15: An efficient and stable catalyst for the catalytic wet peroxidation of phenolic aqueous solutions. *Chem. Eng. J.* 2007;**131**:245–256. DOI: 10.1016/j.cej.2006.12.007
- [155] Santos A, Yustos P, Rodriguez S, Simon E, Garcia-Ochoa F. Abatement of phenolic mixtures by catalytic wet oxidation enhanced by Fenton's pretreatment: Effect of H<sub>2</sub>O<sub>2</sub> dosage and temperature. *J. Hazard. Mater.* 2007;**146**:595–601. DOI: 10.1016/j.jhazmat.2007.04.061
- [156] Andreozzi R, Insola A, Caprio V, Amore MGD. Ozonation of pyridine aqueous solution: Mechanistic and kinetic aspects. *Water Res.* 1991;**25**:655–659. DOI: 10.1016/0043-1354(91)90040-W

