

Review

# Effectiveness of Advanced Oxidation Processes in Wastewater Treatment: State of the Art

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**Abstract:** In recent years, many scientific studies have focused their efforts on quantifying the different types of pollutants that are not removed in wastewater treatment plants. Compounds of emerging concern (CECs) have been detected in different natural environments. The presence of these compounds in wastewater is not new, but they may have consequences in the future. These compounds reach the natural environment through various routes, such as wastewater. This review focuses on the study of tertiary treatment with advanced oxidation processes (AOPs) for the degradation of CECs. The main objective of the different existing AOPs applied to the treatment of wastewater is the degradation of pollutants that are not eliminated by means of traditional wastewater treatment.

**Keywords:** advanced oxidation processes; compounds of emerging concern; wastewater treatment plants; tertiary treatment



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## 1. Introduction

Today, there is strong environmental concern and a focus on minimising the impact of human activities on the environment. For years, the overexploitation to which the planet has been subjected has been unsustainable, highlighting the pressure exerted on the world's water reserves. The high demand of population centres, massive industrial production, and agricultural activities have caused an unsustainable situation for the available water resources [1]. Due to this, wastewater treatment becomes absolutely essential for the subsequent return to the natural environment in the most efficient way possible. However, current technologies used in wastewater treatment are not efficient against certain types of pollutants that are able to remain in the treated wastewater, which is returned to the natural environment, thus reaching the water reserves [2,3]. Once in the environment, they are characterized by environmental persistence and threats to human health [4,5]. Due to the low concentrations of contaminants and diversity in nature, the removal of these contaminants poses numerous challenges [6].

Due to this, the application of tertiary treatments that are effective and economically viable in wastewater treatment plants has been investigated in recent years.

These pollutants are a global problem and are not limited to just one region; they have been detected in waters around the world. In América, the Biobío River (Chile) has population settlements that, due to their economic activities, such as agriculture or forestry, incorporate compounds of emerging concern, such as pharmaceuticals, personal care products, and pesticides, into the aquatic environment [7]. The presence of 28 antibiotics was detected in six rivers and a drinking water storage catchment in watersheds of South-East Queensland, Australia [8]. In the Somes River (Transylvania, Romania), compounds including musk fragrances, pharmaceuticals, metabolites and intermediates were detected [9]. An analysis of the Ebro River (Spain) revealed the presence of 31 pharmaceuticals; these

compounds were detected in wastewater treatment plant (WWTP) effluents, with the highest concentrations found in effluents of the Zaragoza WWTP [10]. It was detected the occurrence of 20 illicit and therapeutic pharmaceuticals and metabolites in surface waters influenced by WWTP discharge and in wastewater effluents in Nebraska [11]. In the Pearl River (China), eight types of antibiotics were detected in the water [12]. Laboratory analysis revealed that antibiotics were widely distributed in Baiyangdian Lake, China [13]. In rivers and lakes in the agricultural zone of Northeast Denmark, 17 emerging contaminants (diclofenac, MCPA, caffeine and TCEPT were the most abundant) were identified and quantified in surface waters (including pesticides, personal care products [PCPs], pharmaceuticals, plasticisers, and fire retardants) [14]. In the affluents of the Delaware River (Pennsylvania, EE.UU), Triclosan (PCP), which is widely used as an antiseptic, was found in high concentrations, which proved to be a high-risk compound for aquatic life. In this river, Diphenhydramine (antibiotic) was also found whose effect is similar to Triclosan [15].

Pollution is not just limited to water; it is also 'absorbed' by sediments and living organisms that are found where waters contaminated by CECs are found. In Baiyangdian Lake (China), quinolones were detected in sediments and aquatic plants. Quinolones and macrolides are often found in aquatic animals and birds [13].

The present study focuses on the different types of advanced oxidations and their efficiency against the different polluting CECs. These pollutants are a global problem and are not limited to just one region but have been detected in waters around the world. This paper tries to give a global view of the problem by compiling the most relevant studies carried out during the last decade and centralizes other studies that review the problem.

## 2. Advanced Oxidation Processes for Wastewater Treatment

Advanced oxidation processes (AOPs) have been used in urban and industrial wastewater treatment as an effective option for the treatment of non-biodegradable compounds [16].

The complete mineralisation to water, inorganic compounds and CO<sub>2</sub>, water of the contaminants in the wastewater, or at least their transformation into more innocuous compounds, can be achieved by applying a chemical treatment using AOPs [17]. There is a wide range of advanced oxidation treatments where different reagents are used with the aim of producing OH• radicals, which are very powerful oxidising agents. AOPs are classified as either homogeneous or heterogeneous. Homogeneous processes include processes that use energy and those that do not. This classification is shown in Figure 1.

Homogeneous processes that use energy and ultraviolet radiation use reagent systems that include O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and photo-Fenton reactions. They all produce OH• radicals. For the degradation of compounds whose UV absorption range is within the corresponding range of the spectrum, these AOPs are generally used [17,18]. Homogeneous processes that use ultrasound energy form hydroxyl radicals because of the extreme conditions generated by ultrasound, which are capable of cracking water molecules. They can be combined with other AOPs. Finally, homogeneous processes that use energy have anodic oxidation, electrochemical oxidation, and electro-Fenton processes. This type of process breaks down compounds and molecules for degradation using electrical energy. The electron transfer occurs by the intervention of hydroxyl radicals [17].

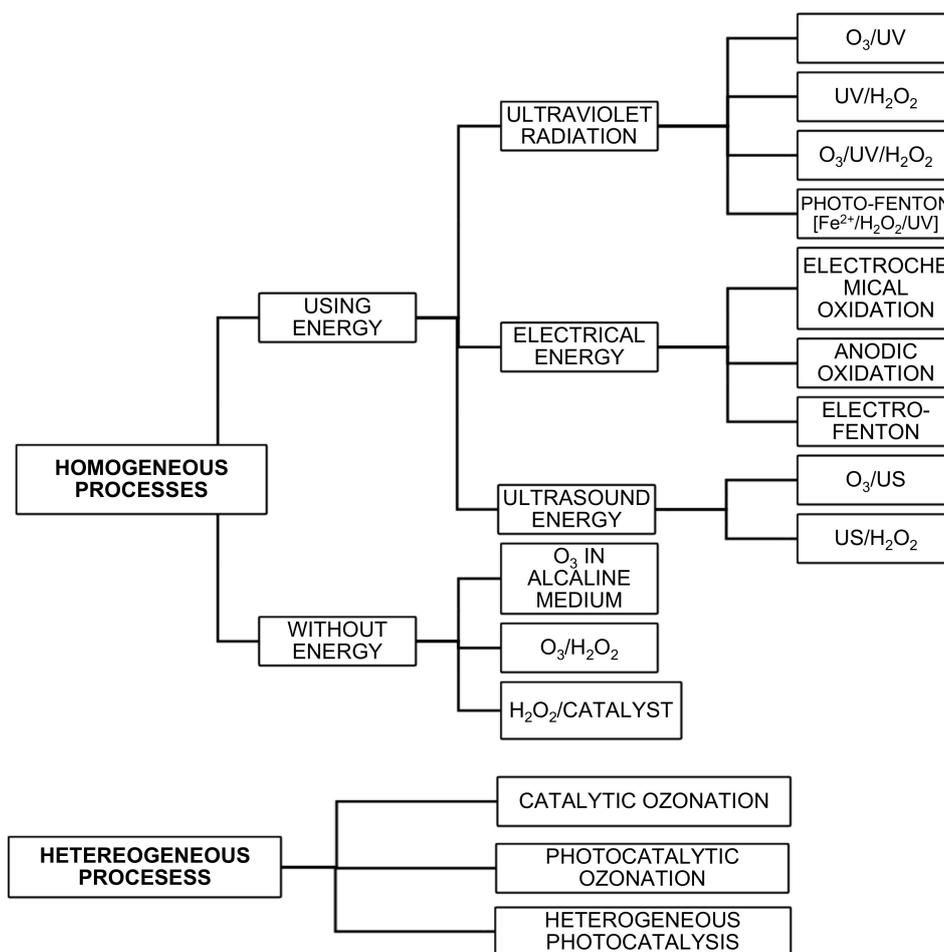
Homogeneous processes that do not use energy are hydrogen peroxide and catalyst processes, ozonation with hydrogen peroxide, and ozonation in an alkaline medium. The difference between the hydrogen peroxide process and catalysation with H<sub>2</sub>O<sub>2</sub>/UV is found in the area of radical formation of OH•, which is less in the process that does not use energy [17].

In heterogeneous AOPs, catalysts are often used to produce the degradation of the contaminant compounds. Compared to homogeneous processes, the catalysts used in heterogeneous processes have the advantage of being able to separate the product more easily [17].

The reactions produced in the different types of AOPs are exposed in Table 1.

Table 1. Reactions of the different types of advanced oxidation processes.

Advanced Oxidation Processes	Reactions	Description	Examples of Pollutants That Can Be Removed
O <sub>3</sub> /UV	$H_2O + O_3 \xrightarrow{h\nu} 2OH^\bullet + O_2$ $2OH^\bullet \rightarrow H_2O_2$	The photolysis of the ozone produces the formation of hydroxyl radicals [17].	Imidacloprid [19]
H <sub>2</sub> O <sub>2</sub> /UV	$2OH^\bullet \xrightarrow{h\nu} H_2O_2$	The formation of hydroxyl radicals is generated by photolysis of H <sub>2</sub> O <sub>2</sub> [17].	Bacterias ( <i>E. Coli</i> , <i>S. Enteritidis</i> and <i>E. Faecalis</i> ) [20] Inactivation of a multidrug resistant <i>E. Coli</i> [21]
O <sub>3</sub> /H <sub>2</sub> O <sub>2</sub> /UV	$2O_3 + H_2O_2 \xrightarrow{h\nu} 2OH^\bullet + 3O_2$	Combination of systems O <sub>3</sub> /UV and H <sub>2</sub> O <sub>2</sub> /UV. The use of H <sub>2</sub> O <sub>2</sub> it accelerates the decomposition of ozone and increases the generation of OH• [17].	Tamoxifen [22]
Fe <sup>2+</sup> /H <sub>2</sub> O <sub>2</sub> /UV	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet$	The Fenton reaction is the process most often applied when it is necessary to remove recalcitrant compounds [17].	<i>E. Faecalis</i> [23] Inactivation of a multidrug resistant <i>E. Coli</i> [21]
O <sub>3</sub> /US	$H_2O \xrightarrow{US} H^\bullet + OH^\bullet$ $O_3 \xrightarrow{US} O_2(g) + O(^3P)$ $O(^3P)(g) + H_2O \rightarrow 2OH^\bullet$ $O_3 + OH^\bullet \rightarrow O_2 + HO_2^\bullet$ $O_2 + H^\bullet \rightarrow HO_2^\bullet$ $O_3 + HO_2^\bullet \rightarrow 2O_2 + OH^\bullet$ $OH^\bullet + OH^\bullet \rightarrow H_2O$ $HO_2^\bullet + OH^\bullet \rightarrow H_2O + O_2$	Ultrasounds are represented as ‘((( [24].	7α -estradiol, 17β-estradiol, estrone, 17α-dihydroequilin, 17α-ethinyl estradiol, estriol and equilin [25]
H <sub>2</sub> O <sub>2</sub> /US	$H_2O_2 \xrightarrow{US} OH^\bullet + OH^\bullet$ $H_2O_2 + O_2 \xrightarrow{US} HO_2^\bullet + HO_2^\bullet$ $H_2O_2 + OH^\bullet \rightarrow HO_2^\bullet + H_2O$	The combination of ultrasound and H <sub>2</sub> O <sub>2</sub> achieves the formation of hydroxyl radicals [26].	7α -estradiol, 17β-estradiol, estrone, 17α-dihydroequilin, 17α-ethinyl estradiol, estriol and equilin [25]
Electrochemical oxidation	[Anode] $H_2O \rightarrow H^+ + (OH^\bullet)_{ads} + e^-$ $(OH^\bullet)_{ads} \rightarrow (O)_{ads} \text{ or } O_2 + H^+ + e^-$ $(O)_{ads} + O_2 \rightarrow O_3$ [Cathode] $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	In this type of oxidation, the compound to be degraded reacts to the oxidants, which have been electrochemically generated in situ [27].	Reactive Orange 16, Reactive Violet 4, Reactive Red 228, and Reactive Black 5 [28]
Anodic oxidation	$Anode + H_2O \rightarrow H^+ + Anode(OH^\bullet) + e^-$	In this process, organic compounds directly react with heterogeneous hydroxyl radicals (OH•), formed by oxidation of water at the surface of anode with high oxygen overpotential [29].	Acid Red 1 azo dye [30]
Electro-Fenton	$O_{2(g)} + 2H^+ + 2e^- \rightarrow H_2O_2$	Hydrogen peroxide is produced electrochemically through the cathodic reduction of dissolved oxygen on a carbon electrode [31].	Non-polar organochlorine pesticides [32] Direct yellow 9 azo dye [33]
Ozonation in an alkaline medium	$O_3 + OH^- \rightarrow O_3^{\bullet -} + OH^\bullet$ $O_3^{\bullet -} \rightarrow O_2 + O^{\bullet -}$ $O^{\bullet -} + H^+ \rightarrow OH^\bullet$	The degradation of the compound occurs through the action of the ozone itself as well as through the radicals generated in the alkaline medium [34].	Bisphenol A, paraxantina [35]
Ozonation with hydrogen peroxide	$H_2O_2 + 2O_3 \rightarrow 2OH^\bullet + 3O_2$ $HO_2^- + O_3 \rightarrow HO_2^\bullet + O_3^\bullet$	Hydrogen peroxide in an aqueous solution is partially dissociated to hydroperoxide anion which reacts with ozone [36].	Fluoroquinolone antibiotics and Clarithromycin [37]
Hydrogen peroxide and catalyst	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet$	This type of reaction is very similar to photo-Fenton processes but the formation rate of OH• radicals is lower [17].	Doxycycline (catalyst CoFe <sub>2</sub> O <sub>4</sub> ) [38]
Catalytic ozonation	$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2$ $FeO^{2+} + H_2O \rightarrow Fe^{3+} + OH^\bullet + OH^-$	In catalytic ozonation the most widely used catalyst is Fe <sup>2+</sup> [36].	Naphthalene [39]
Photocatalytic ozonation: O <sub>3</sub> /UV/TiO <sub>2</sub>	$TiO_2 \xrightarrow{h\nu} h^+ + e^-$ $e^- + O_3 \rightarrow O_3^{\bullet -}$ $O_3^{\bullet -} \rightarrow O_2 + O^{\bullet -}$ $O^{\bullet -} + H_2O \rightarrow OH^- + OH^\bullet$ $h^+ + OH^- \rightarrow OH^\bullet$	Titanium dioxide (TiO <sub>2</sub> ) is the most effective catalyst of those used in AOPs. The basic mechanism is described by [40].	Diclofenac [41]
Heterogeneous photocatalysis: UV/TiO <sub>2</sub> /H <sub>2</sub> O <sub>2</sub>	$TiO_2 \xrightarrow{h\nu} TiO_2(e^- + h^+)$ $TiO_2 h^+ + OH_{ad}^- \rightarrow TiO_2 + OH^\bullet$ $H_2O_2 + e^- \rightarrow OH^\bullet + OH^-$	In these processes, titanium dioxide is combined with hydrogen peroxide and UV radiation [42].	Inactivation of A multidrug resistant <i>E. Coli</i> [21]



**Figure 1.** Classification of advanced oxidation processes. Abbreviations used: O<sub>3</sub>, ozonation; H<sub>2</sub>O<sub>2</sub>, hydrogen peroxide; UV, ultraviolet radiation; US, ultrasound energy; Fe<sup>2+</sup>, ferrous ion, modified of [17].

### 3. Methodology

The search for relevant literature was carried out by searching the Scopus database using the following keywords: “advanced oxidation processes”, “concern emerging contaminants” and “wastewater treatment”. The first search resulted in 51 articles, and a review article for 2010 (67 additional references) was used to provide an overview since 2000. The less relevant articles were discarded following the criterion of looking for articles of removal of the same pollutants with more easily reproducible operating conditions. Once the search list was generated, it was manually checked to exclude studies that were not relevant and to give preference to articles that eliminated several contaminants. In addition, relevant studies found in the bibliography of the selected studies were included in the literature identification list. Articles were selected from the years 2000 to 2021 to check the progress of the technology studied and only articles written in English were selected. This extended range of years was selected because it was considered important to give an overview of the evolution of advanced oxidation processes.

### 4. Compounds of Emerging Concern (CECs)

Water is the essential resource for life; everybody depends on it, and because of this it is one of the most threatened resources on the planet. Aquifers and water reserves are constantly affected by overexploitation and pollution associated with human activities. For this reason, the European Union (EU), as well as most governments around the world, is focusing efforts on achieving good quality of their resources. The EU created an observation list of emerging pollutants. These substances do not currently follow an elimination legisla-

tion, but it has been studied and shown that they are present in rivers, lakes, aquifers, and natural environments; therefore, they can pose a somewhat long-term risk and the study of their elimination is essential to prevent their entry into ecosystems. These substances can be divided into four main groups: pharmaceuticals (PHs) (e.g., antibiotics and analgesics), PCPs (e.g., fragrances and antiseptics), pesticides (e.g., atrazine and dimethoate) and illicit drugs (e.g., opioids and amphetamines).

The introduction of this type of compound into the environment has its origin in human activity. Transformation products and metabolites may enter the aquatic environment and eventually reach drinking water if the CECs are not eliminated during wastewater treatment [43].

The EU, through Directive 2008/105/EC, establishes an observation list of substances for monitoring purposes at the European level. This list is updated every 24 months by the Water Framework Directive of the European Union. These modifications are made taking into account several criteria, among which are the research programmes in force and the characterisation and results obtained by the member states of the EU of their river basin districts. Each member state selects a representative monitoring station, and the monitoring frequency shall not be less than once a year. The last update of this list was made in December 2018, and a final programme of measures is foreseen for December 2021 to be fully operational by December 2024 (<https://www.boe.es/buscar/doc.php?id=DOUE-L-2013-81677> accessed on 7 April 2020). In addition, in 2005, the European Commission funded the NORMAN project. (<https://www.norman-network.net> accessed on 7 April 2020). The NORMAN network enhances the exchange of information on emerging environmental substances and encourages the validation and harmonisation of common measurement methods and monitoring tools so that the requirements of risk assessors and risk managers can be better met. It specifically seeks both to promote and to benefit from the synergies between research teams from different countries in the field of emerging substances. This network includes the competent authorities/reference laboratories, research centres and academia, industry stakeholders, government institutions and standardisation bodies. The mission of the NORMAN network is to enhance the exchange of information and collection data environmental substances, encourage the validation and harmonisation of common measurement methods and monitoring tools so that the demands of risk assessors can be better met and ensure that knowledge of emerging pollutants is maintained and developed by stimulating coordinated, interdisciplinary projects on problem-oriented research and knowledge transfer to address identified needs.

In the case of the US, the Environmental Protection Agency (EPA; <https://www.epa.gov/ccl> accessed on 28 May 2020) publishes a Contaminant Candidate List (CCL) every five years, with the last being published in 2016. The EPA has a candidate list of 97 chemical contaminants/groups of contaminants and 12 microbial contaminants (including PHs and PCPs). Within this area, each member state, as with Europe, adapts this policy to its territory. In California, the State Water Resources Control Board has a Recycled Water Policy where scientific advisors provide guidance on how to monitor CECs for prioritisation in legislation [44].

In the case of Japan and its Ministry of Health, they focus their efforts on evaluating the environmental risk posed by pharmaceutical products, and with it their marketing is approved or denied. The same occurs in the case of Canada and Australia, which are based on standard physicochemical tests to determine the biodegradability of the compounds, without following a specific list that is monitored or regulated (World Health Organization, 2012).

In China, the Ministry of Environmental Protection establishes a plan for the control and prevention of environmental risks of chemical substances, including pharmaceuticals. This was launched in 2013 [45].

In general, the release of antibiotics into the environment is believed to be a major concern as it can increase the appearance of resistant bacteria in the environment. However,

treatments done by man, as well as natural filtration, can be penetrated by emerging compounds and cause them to pose a potential risk to the supply of drinking water [46].

#### 4.1. Pharmaceuticals Compounds (PH)

The appearance of different types of pharmaceuticals in waters has been extensively studied in recent years. A large number of compounds associated with the removal of urban and industrial wastewater have been detected in groundwater and surface. The current wastewater treatment technology is insufficient for these pollutants, and they are not retained in the treatment plants, which is why many of these pharmaceutical residues reach the ecosystem, thus joining the water cycle. In primary treatments, while some pharmaceuticals remain in the water, others can be removed by adsorption, e.g., naproxen, ibuprofen, iopromide, and sulfamethoxazole [47,48]. Antibiotics and anti-inflammatories are eliminated in subsequent biological treatments by 30–75%.

The concern about pharmaceuticals is their chronic toxicity and not their acute toxic effects. In general, pharmaceuticals are biologically active compounds that are not easily biodegradable. They may cause side effects in non-target organisms or cause a similar function as they do in their intended users [49]. The evolution and spread of antimicrobial resistance are recognised as one of the major global health challenges of the 21st century by major regulatory, economic, and political bodies, including the European Commission (EC), the United Nations (UN), and the World Health Organisation (WHO), and the surveillance of critical hotspots through intensive monitoring is recommended, including urban wastewater treatment plants, aimed at reducing its propagation [50].

The uncontrolled consumption of pharmaceuticals by the population, where many of them are consumed without medical control, such as ibuprofen or diclofenac, has led to their detection in water intended for human consumption [8]. Thus, hospital wastewaters, landfill leachates, and municipal wastewaters are always considered 'hot spots' for environmental water contamination by pharmaceuticals [51].

During therapeutic periods, humans excrete pharmaceuticals and their metabolites. In the case of pharmaceuticals used for veterinary medicine, when animal wastes are sprayed on agricultural fields to fertilise them, these substances are released into the environment [52].

The different physico-chemical properties of these compounds, as well as their metabolites or degradation by-products thereof, can affect the waters they arrive at and/or be retained in the soil into which the treated waters are discharged, which causes a negative effect on the ecosystem. The annual usage of antibiotics has been estimated to be between 100,000 and 200,000 tons globally, with more than 25,000 tons used each year in China [12,53].

The pharmaceuticals are divided into several types, analgesics and antibiotics are the most widely used of them.

**Antibiotics:** These are pharmaceuticals that are used to fight bacterial infections in organisms. Their use is not limited to humans, but they are also used in animals and in the food industry to preserve food. Therefore, they are widely produced and consumed, causing large amounts of them to be present in wastewater.

**Analgesics and anti-inflammatories:** These are the pharmaceuticals with the highest global consumption and those most used by the population as self-medication [54]. Compounds such as ibuprofen and diclofenac belong to this group.

**Antidepressants and anticonvulsants:** These medications help improve the way the brain uses certain natural chemicals and can help combat depression and epileptic attacks.

**Lipid regulators:** These are regulators of compounds present in blood, such as enzymes.

**$\beta$ -blockers:** These compounds work primarily in the heart and blood vessels.

Many PHs are also thought to mimic natural hormones in the body, hence their classification as endocrine-disrupting chemicals (EDCs) [52]. These compounds are defined as natural and/or synthetic substances that can include naturally generated estrogenic

hormones, e.g., estrone (E1) and 17 $\beta$ -oestradiol (E2), and, therefore, are ubiquitous in aquatic environments receiving wastewater effluents [49]. Oestrogens and xenoestrogens are excreted into wastewater and reach wastewater treatment plants as organic contaminants, where they are only partially eliminated [55]. Some of the most studied PHs and their classifications are listed in Table 2.

**Table 2.** Classification and functions of pharmaceutical compounds.

Pharmaceutical Compounds	Use	Examples [52]
<b>Antibiotics</b>	Antibacterial activity. Human and veterinary use	Amoxicillin, ampicillin, cefaclor, cefalexin, ciprofloxacin, chlortetracycline, clarithromycin, difloxacin, doxycycline, enoxacin, erythromycin, lincomycin, levofloxacin, metromidazole, mecillinam, ofloxacin, oxytetracycline, penicillin, sulfamethoxazole, sulfadiazine, sulfamethizole, sulfathiazole, sulphapyridine, tetracyclines, trimethoprim, tylosin . . .
<b>Analgesics and anti-Inflammatory Pharmaceuticals</b>	Pain relief and the reduction of inflammation	Ibuprofen, diclofenac, paracetamol, acetaminophen, acetylsalicylic acid, fenoprofen, indomethacin, naproxen, nimesulide, mefenamic acid, fluoxetine, ketoprofen, phenazone . . .
<b>Antidepressants and Anticonvulsants</b>	Relief from mental symptoms and the treatment of epileptic seizures	Diazepam, carbamazepine, doxepin, imipramine, amitriptyline, primidone, salbutamol, meprobamate, fluoxetine, oxazepam, gabapentin, phenobarbital, thioridazine, dilantin . . .
<b>Lipid Regulators</b>	Regulation of cholesterol and blood triglycerides	Clofibric acid, clofibrate, benzafibrate, fenofibric acid, etofibrate, gemfibrozil, simvastatin, furosemide, Bendroflumethiazide . . .
<b><math>\beta</math>-blockers</b>	Reduction of blood pressure	Atenolol, metoprolol, propranolol, sotalol, timolol . . .
<b>X-ray contrasts</b>	Diagnostic contrast (organ visibility)	Iopromide, iopamidol, diatrizoate . . .
<b>Eestrogens, Progestogens, Androgens, Glucocorticoids, Phytoestrogens &amp; Hormones</b>	Regulation of female/male sexual development, maintenance of pregnancy, growth promotion in meat-producing animals, control of immune function, treatment of breast cancer, lymphomas and leukaemias	17 $\beta$ -Oestradiol (E2), estrone (E1), estriol, diethylstilbestrol (DES), 17- $\alpha$ ethynylestradiol, mestranol, zerranol, trenbolone acetate, melengestrol acetate, tamoxifen, testosterone, phytoosterols, sesquiterpenes, androstenedione, beclomethasone, progesterone, norethindrone . . .

The application of AOPs based on studies of the removal of pharmaceutical products present in wastewater that are not eliminated by other technologies will be analysed. During the oxidation of urban wastewater, transformation products (TPs) of the antibiotics present can be formed, which may be more biologically potent, less biodegradable, or more toxic compared to the parent compounds [56].

One of the most studied types of AOPs for the treatment of wastewater by the authors is the UV/H<sub>2</sub>O<sub>2</sub> process. Photolysis of hydrogen peroxide is produced under ultraviolet radiation and it does not depend on pH. A H<sub>2</sub>O<sub>2</sub>/UV system can totally mineralise any organic compound, reducing it to CO<sub>2</sub> and water [17]. In addition, in this method, you can use sunlight instead of UV lamps. This is very interesting as in places where there are many hours with sunlight, this would be a low-cost application. In the case of antibiotics, this process can degrade compounds such as ciprofloxacin, which is a compound that is observed in wastewater. Ciprofloxacin is a compound included in the observation List of substances for the EU. Michael et al. [50] studied ciprofloxacin removal using H<sub>2</sub>O<sub>2</sub>/UV and H<sub>2</sub>O<sub>2</sub>/sunlight processes by comparing them to each other. H<sub>2</sub>O<sub>2</sub>/UV treatment was able to remove ciprofloxacin (90 min, 0.9 kJ L<sup>-1</sup>), while the H<sub>2</sub>O<sub>2</sub>/sunlight process was able to remove ciprofloxacin in 60 min (8 kJ L<sup>-1</sup>). Monteoliva-García et al. [57] reported the elimination of ciprofloxacin (concentrations from 22.30 to 98.53  $\mu$ g L<sup>-1</sup>) by applying

H<sub>2</sub>O<sub>2</sub>/UV treatment ([H<sub>2</sub>O<sub>2</sub>] = 25, 50, and 100 mg L<sup>-1</sup>), with total elimination after 20 min of treatment. Yuan et al. [58] completely eliminated ciprofloxacin by applying H<sub>2</sub>O<sub>2</sub>/UV from an initial CIP concentration of 5 µM and using an LP-Hg lamp. Rosal et al. [59] studied ciprofloxacin removal using O<sub>3</sub> and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>-based AOPs under similar conditions. While removal rates were very good at 98% and more than 93%, respectively, TOC removal was much more efficient in the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process, obtaining more than 90% removal compared to 15% in the other process. De Witte et al. [60] obtained a very similar result of eliminating the TOC of 95% by applying O<sub>3</sub>-based AOPs. Most of the treatments range between pH 7.5 and 8, this is very interesting and useful as this is within the pH range detected in urban wastewater. Therefore, for ciprofloxacin, it can be accepted that it can be almost completely removed from wastewater by AOPs, with the most favourable carbon treatment being O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> treatment.

Another commonly used antibiotic is sulfamethoxazole. Michael et al. [50] studied its elimination by means of H<sub>2</sub>O<sub>2</sub>/UV and H<sub>2</sub>O<sub>2</sub>/sunlight treatment to determine which was more efficient. The H<sub>2</sub>O<sub>2</sub>/UV treatment was able to eliminate sulfamethoxazole after 90 min (0.9 kJ L<sup>-1</sup>), while the process with H<sub>2</sub>O<sub>2</sub>/UV only eliminated 46% after 300 min and 42 kJ L<sup>-1</sup>. Lekkerkerker-Teunissen et al. [61] also studied the elimination of sulfamethoxazole by applying UV/H<sub>2</sub>O<sub>2</sub> treatment, which was able to eliminate it by more than 90% (UV doses ranged from 300–700 mJ cm<sup>-2</sup>). Yang et al. [62] applied the UV/H<sub>2</sub>O<sub>2</sub> treatment and succeeded in removing sulfamethoxazole (SMX) after 60 min. Other authors applied O<sub>3</sub>-based AOPs for SMX elimination, obtaining excellent elimination results (99.9%) from a high concentration of SMX (30 mg L<sup>-1</sup>, 22 °C) [63]. The pH range of the various treatments is very wide, ranging from 2–10. This is really useful; although, the water can be treated effectively at a natural pH but would achieve satisfactory eliminations in the event of temporary fluctuations in the plant.

For the treatment of amoxicillin, an antibiotic widely used because of its great efficacy, its elimination has been studied using various POP processes. By applying UV/H<sub>2</sub>O<sub>2</sub> treatment, it was possible to irradiate the compound with a low-pressure lamp at an incident light intensity of  $8 \times 10^{-7}$  Einstein L<sup>-1</sup> s<sup>-1</sup> and one at an H<sub>2</sub>O<sub>2</sub> concentration of 0.4–10 mM at 99% in only 20 min [64]. However, in the study by Elmolla et al. [65], which carried out UV/TiO<sub>2</sub> treatment, only 20% elimination (UV 365 nm) and a high pH dependency were reported, achieving the highest degradation at pH 11. The authors also studied the addition of H<sub>2</sub>O<sub>2</sub> at pH 5 (ambient) with a TiO<sub>2</sub> concentration of 1 g/L, achieving complete degradation of amoxicillin in only 30 min of heterogeneous photocatalysis treatment (UV/H<sub>2</sub>O<sub>2</sub>/TiO<sub>2</sub>). The amoxicillin treatment with O<sub>3</sub>-based AOPs also provided very good results. At an initial amoxicillin concentration of  $5.0 \times 10^{-4}$  M, with pH 5.5 (buffer) and a flow of O<sub>3</sub>  $1.6 \times 10^{-4}$  M, 90% was eliminated [66]. Therefore, amoxicillin is a compound that reacts very well to advanced oxidation treatments, achieving very good removal performance. In conclusion, the highest degradation for this pharmaceutical compound occurs at pH 11, which can be problematic; although, high clearance is also achieved at pH 5, where mineralisation of the pharmaceutical (phenolic ring hydroxylation) occurs.

Another important antibiotic is metronidazole, which is used for bacterial infections affecting various parts of the body (vaginal infection primarily and others, such as the stomach, liver, skin, and brain). Several authors have studied their removal by applying different types of AOPs and comparing them with each other. Shemmet et al. [67] applied the UV/H<sub>2</sub>O<sub>2</sub> method under four operating conditions, obtaining elimination rates of between 58% and 67% (6.0 µM metronidazole; 1.5 mW cm<sup>-2</sup>; 50 mg L<sup>-1</sup> H<sub>2</sub>O<sub>2</sub>). Furthermore, ref. [67] applied the UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> method and obtained 94% elimination as the best result, also starting from a 6.0 µM Metronidazole concentration, and they compared it with the H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> process under the same reaction conditions, where the maximum elimination result was 76%. These results show significant differences in behaviour under equal conditions, making the advanced photo-Fenton oxidation process the most effective against this compound. Rosal et al. [59] studied metronidazole elimination using ozone

technology, comparing O<sub>3</sub>-based AOPs and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> under the same conditions, where they obtained elimination percentages of 91% (15% TOC) and 92% (above 90% TOC), respectively, highlighting the role H<sub>2</sub>O<sub>2</sub> key to eliminating toxicity, the same as other antibiotics such as ciprofloxacin. The pH ranges studied are very broad, but the data seem to indicate that better removal rates are achieved at increasingly acidic pH values in UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup> processes, with this AOP showing a removal rate of over 90%. In the case of lincomycin, Andreozzi et al. [68] applying different types of AOPs (UV/H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>-based AOPs). O<sub>3</sub>-based AOPs shown a total elimination in 2 min of treatment and no toxicity in one hour of treatment. UV/H<sub>2</sub>O<sub>2</sub> obtained the elimination percentages of 80% in 3 min of treatment and no toxic product generation. De Witte et al. [60] applying O<sub>3</sub>-based AOPs in the elimination of levofloxacin and obtained a removal of 99.9 %.

The antiepileptic pharmaceutical carbamazepine, which is present in wastewater, has been studied for its removal by the advanced UV/H<sub>2</sub>O<sub>2</sub> removal process. At low H<sub>2</sub>O<sub>2</sub> concentration, carbamazepine removal is not appropriate despite UV treatment with medium- and low-pressure lamps [61]. However, at H<sub>2</sub>O<sub>2</sub> concentrations of 5 mg/L and above, up to 99.7% removal is achieved [69]. Monteoliva-García et al. [57] achieved at laboratory scale eliminations of more than 80% until complete elimination under real plant conditions (pH natural and real wastewater). The results of the different authors seem to indicate that working with natural pH is sufficient, but nevertheless the initial H<sub>2</sub>O<sub>2</sub> concentration in the treatment is very important, since at low concentrations the UV flux applied, even if it is high, is not sufficient to achieve optimum removal yields.

Their elimination has been extensively studied lipid-lowering pharmaceuticals (lipid regulators). An example of this compound is bezafibrate, treating the waters with O<sub>3</sub>-based AOPs, eliminations of the compound have been reported ranging from 80% [70], 94% (15% TOC) [59] until reaching above 95% [71]. Another compound of the same nature, gemfibrozil also obtained elimination percentages close to 100%, but with better TOC elimination performance (>90%) when the ozone process is combined with H<sub>2</sub>O<sub>2</sub>, being the case similar to that of antibiotics [59].

Another type of pharmaceutical widely used is those known as anti-inflammatories. One example is diclofenac, a widely used anti-inflammatory that has been found in many wastewater treatment plant effluents. The advanced oxidation process H<sub>2</sub>O<sub>2</sub>/UV is able after 90 min of treatment to degrade this compound with a mineralisation of 39% [72]. Lekkerkerker-Teunissen et al. [61] reported its elimination in more than 80% by applying different intensities with low and medium pressure UV lamps two ranged from 300–700 mJ cm<sup>-2</sup> and variable concentrations of H<sub>2</sub>O<sub>2</sub> (0–10 mg L<sup>-1</sup>). Andreozzi et al. [73] obtained a 100% elimination in 2 min starting from an initial diclofenac concentration of 2.8 mg L<sup>-1</sup> and applying a UV intensity (LP-Hg lamp) of 2.51 × 10<sup>-6</sup> E s<sup>-1</sup> and variable concentrations of H<sub>2</sub>O<sub>2</sub>. It is treatment by means of an AOP based on O<sub>3</sub> also eliminates it completely [74]. At a concentration of O<sub>3</sub> of 5 mg L<sup>-1</sup> and H<sub>2</sub>O<sub>2</sub> of 1.8 mg L<sup>-1</sup>, it showed high efficacy in the elimination of ibuprofen and diclofenac, obtaining 98% mineralisation [75]. The Photo-Fenton system completely oxidised diclofenac after 60 min [76].

Another anti-inflammatory widely used by the population and detectable in practically all studies of wastewater effluents is ibuprofen. Several authors have applied O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> treatment and O<sub>3</sub>-based AOPs obtaining very good results, with eliminations reaching up to 99.4% starting from an initial ibuprofen concentration of 2 µg L<sup>-1</sup> and an ozone flow 1–5 mg L<sup>-1</sup> with a molar ratio O<sub>3</sub>:H<sub>2</sub>O<sub>2</sub> (2:1) [75]. Huber et al. [71] reported an elimination of between 40–70% treating the effluent with O<sub>3</sub> (0.1–2 mg L<sup>-1</sup>) starting from an ibuprofen concentration of 0.5 µM. Eliminations greater than 62% were also achieved for water with an initial concentration of 0.13 µg L<sup>-1</sup> and an O<sub>3</sub> (5–15 mg L<sup>-1</sup>) [77]. Monteoliva-García et al. [57] reported an ibuprofen elimination (concentrations from 54.6 to 275.0 µg L<sup>-1</sup>) applying the H<sub>2</sub>O<sub>2</sub>/UV treatment ([H<sub>2</sub>O<sub>2</sub>] = 25, 50, and 100 mg L<sup>-1</sup>) from 89.8 to 100%. This seems to indicate that despite the high elimination obtained with both treatments, the most efficient is O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, practically eliminating it completely.

In the case of naproxen, a very common anti-inflammatory, it seems to indicate that its behaviour is similar to that of ibuprofen. Rosal et al. [59] compared two AOPs to each other, obtaining with O<sub>3</sub>-based AOPs an elimination percentage of 93% and approximately 15% TOC, but nevertheless applying O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> the removal was very similar obtaining 94% and more than 90% TOC. This same author also carried out the study of another anti-inflammatory, ketoprofen, and the behaviour was the same as in the case of ibuprofen and naproxen. By means of O<sub>3</sub>-based AOPs, it was able to degrade ketoprofen by 69% and eliminate approximately 15% TOC, applying O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> the elimination performance was 70%, very similar but with a toxicity elimination of 90% TOC [59]. Although the removal result is effective, the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> treatment manages to remove a much higher percentage of the total organic carbon, making it a much more efficient treatment.

The degradation of metoprolol (MTP), a  $\beta$ -blocker commonly used for cardiovascular diseases, by UV/H<sub>2</sub>O<sub>2</sub> (LP lamp, 254 nm) process was comparatively evaluated. The results indicate that MTP can rapidly degrade and was marginally affected by changing pH, with a removal rate of 56.7% within 15 min. The MTP degradation treatment satisfied pseudo-first-order kinetic [51]. The treatment of clofibrilic acid, a lipid regulator metabolite, was completely degraded with no toxic product generation in 2 min by applying two different AOPs (UV/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>-based AOPs) [73].

Table S1 in Supplementary Materials summarises the results of different authors in the elimination of pharmaceutical compounds by applying AOPs [78–82].

#### 4.2. Personal Care Products (PCPs)

Personal care products are designated for use on the human body. They comprise a high range of products, such as moisturisers, gels, fragrances, sun creams, and mosquito repellents. Hygienic products alone include at least 8000 preparations available within the European market, with some 140.000 tonnes of shampoo used annually in Germany [83]. Most PCPs are discharged into wastewater and make their way to wastewater treatment plants in their biologically altered or original form [49]. Personal care products may be completely degraded during the wastewater treatment process, or they may remain unchanged or partially converted to metabolites in some cases [84,85]. Therefore, to ensure that TPs are nontoxic and safe, detoxifying the parent compounds becomes a vital and meaningful research focus for promoting the large-scale application of AOPs [86]. Some of the most studied PCPs and their classifications are listed in Table 3.

**Table 3.** Classification and functions of personal care products.

Personal Care Products	Use	Examples [52]
Fragrances	Pleasant odours	Polycyclic and macrocyclic musks (musk xylol and musk ketone), phthalates, tonalide, celestolide, galaxolide . . . .
Sun–screen agents	Skin protection from solar ultraviolet radiation	Benzophenone, 4-methylbenzylidene camphor, homosalate, octocrylene, oxybenzone, octylmethoxycinnamate, octyldimethyl-PABA . . .
Insect repellents	Repellent	<i>N,N</i> -diethyltoluamide, . . .
Antiseptics	Disinfectants	Clorophene, triclosan, bromoprene, 2-phenylphenol, 4-chlorocresol, 4-chloroxylenol . . .
Preservatives	Prevention of undesirable chemical changes or microbial decomposition	Methylparaben, 2-phenoxyethanol, ethyl 4-hydroxybenzoate, butyl 4-hydroxybenzoate . . .

Most of the studies show that treatment by O<sub>3</sub>-based AOP is highly efficient in the elimination of PCPs, reaching, in some cases, up to 100%; however, this method has the

drawback that it uses a large amount of energy for some minimal  $O_3$  productions. Another one of the most used AOPs is UV/ $H_2O_2$ , achieving excellent removal results [52].

UV/ $H_2O_2$  treatment was applied in the study of the elimination of triclosan, an antimicrobial agent widely used in many household and personal care products. The result was an elimination of greater than 80%, associated with this elimination at pH 8.5 the most favourable [87]. Triclosan also has a good response against the treatment of  $O_3$ -based AOPs, being almost completely eliminated (94–99.9% removal, Tric 10 mg  $L^{-1}$ , pH 7, 25 °C), but identifying several toxic by-products that are detrimental to the resulting water quality [82].

The degradation of methylparaben, ethylparaben, propylparaben, and butylparaben, was carried out by applying an  $O_3$ -based AOP. An ozone dose of 0.67 g/h resulted in the removal of 99% of parabens in 12 min, as well as the removal of 32% TOC and 61% of chemical oxygen demand [COD] in 3 h of ozonation time for a 500  $\mu M$  of solution of parabens [88]. Another paraben studied their elimination by UV/ $H_2O_2$ , butylparaben, was able to eliminate more than 95% of its presence after 20 min of treatment (29.6 W/ $cm^2$ , 0.01 M  $H_2O_2$ , pH 7.0, 22 °C) [89].

#### 4.3. Illicit Drugs

There are studies that analyse the presence of this type of compound. Zuccato et al. [90] tested the presence of drugs of abuse (opioids, amphetamines, cocaine, and cannabis derivatives), some related opioid pharmaceuticals (methadone and codeine), and/or their metabolites in Italian and British surface waters. In 2005, it was reported that kilograms of cocaine residues travel daily down the Po River (Italy). Opioids and non-opioids have for a long-time been used for pain medication because pain is a global health priority and the detection of such contaminants in wastewater serves to estimate the treatment burden of a population using wastewater-based epidemiology (WBE) [91]. In the past decade, wastewater-based epidemiology has been applied in many countries such as China [92] (where influent and effluent wastewater samples were collected from 49 wastewater treatment plants (WWTPs) in 24 major cities that cover all the geographic regions of the country), EE.UU [93], but mainly in Europe [94–97].

In the case of cocaine, it is largely excreted in the urine as metabolites (its main metabolite is benzoylecgonine) and in a small percentage without changes. If it is consumed with ethanol, the metabolite cocaethylene is also excreted. The group of opioids comprising morphine (metabolic residue like heroin), codeine, and morphine itself is also excreted, but are easily hydrolysed; they are also present in wastewater. Amphetamines, another group of illicit drugs, are excreted as is, not as metabolites. Cannabis is mainly excreted in the urine. Finally, opioid pharmaceuticals are also detected since some drugs of abuse may also have some medical applications, such as codeine for the treatment of heroin addiction, morphine as a strong pain reliever, and dronabinol THC for use in chemotherapy or AIDS patients, and all are present in the wastewater. All these compounds were detected in rivers in Italy by Zuccato et al. [90], demonstrating that they are common contaminants of the aquatic environment in populated areas.

In South Wales in the United Kingdom, a study was conducted for the detection of illicit drugs, including amphetamine, cocaine, and its main metabolite, benzoylecgonine. The illicit drugs studied were found in rivers at low levels of  $ng L^{-1}$ . The average daily load of amphetamine was 8 g  $day^{-1}$ . For cocaine, it was 1.2 g  $day^{-1}$ , and for its main metabolite, benzoylecgonine, it was 39 g  $day^{-1}$ . This frequent presence is associated with their high illegal usage and is strongly associated with the discharge of insufficiently treated wastewater effluent [98]. Methamphetamine (0.8 ng/L) and MDMA (0.5 ng/L) were detected in effluent samples from three WWTPs in the USA. The USA estimated an annual release of 0.02 kg of ecstasy in the receiving waters of one of these WWTPs [99]. A study in Northeast Spain in which influent and effluent waters from wastewater treatment plants were monitored, amphetamine was detected (maximum concentration of 210 ng/L), MDA was detected in 10 plants (maximum concentration of 200 ng/L), and methamphetamine was detected in 12 plants (3–90 ng/L). MDEA was also found in 18 effluents, and MDEA

was detected in 1 plant (12 ng/L). The main metabolite of cocaine (benzoylecgonine [BE]) was detected in 40 of 42 plants monitored at maximum concentrations of 4.7–7.5 µg/L [100].

The few studies on the application of AOP technology in the elimination of illicit drugs have mainly focused on the elimination of cocaine and its metabolite, BE, as it is one of the most consumed. Spasiano et al. [101] applied the UV/H<sub>2</sub>O<sub>2</sub> process (LP lamp mercury) for different water matrices as a reliable method. This AOP process is effective against this contaminant. BE removal was insensitive in a pH range of 4–8. Russo et al. [102] carried out a study comparing the efficacy of direct photolysis against UV/H<sub>2</sub>O<sub>2</sub> (in a microcapillary film photoreactor) for the degradation of BE. The authors did not obtain differences in BE removal for pH values of 4–8, coinciding with the results of [101]. Indirect photolysis UV<sub>254</sub> at different residence times up to 140 s obtained BE removal between 50–70% for different water matrices (pH 6–7.8), while for UV/H<sub>2</sub>O<sub>2</sub> removal rates of up to 95% were achieved for residence times of 2 s, observing various transformation products resulting from the applied treatments, with the potential toxicity of these compounds being unknown.

#### 4.4. Pesticides

These compounds are chemical substances widely used in agriculture to protect crops against insects, fungi, plants considered weeds, and other pests. They have been highly studied products due to their extensive use, and, therefore, their presence and destination in groundwater are well known. Studies have described the transport of pesticides from the soil to depths within different groundwater systems, as well as the occurrence of their metabolites [103–106].

The spatial occurrence of pesticides in an aquifer is closely related to present or historical land use. A major pathway for contaminant transport to groundwater is the leaching from soils following pesticide application. Fractures, drains, soak ways, and sumps can provide rapid transport routes to groundwater, which bypass some of the natural attenuation potential provided by shallow unsaturated zones and the soil [107]. Pesticides and insecticides have become pervasive environmental problems due to their widespread use [29].

Examples of pesticides are isoproturon, MCPP, atrazine, imazapyr, 2,4-D, glyphosate, simazine, diuron, and picloram. The presence of these compounds in the natural environment is not usual; there are data for at least three decades in which they have been found in the natural environment. Organic pesticides have been used since the discovery of their qualities as insecticides by the Swiss chemist Paul H. Muller in 1939. Due to their great utility, their world consumption has been increasing. Large amounts of pesticides applied in uncontrolled agriculture have caused environmental problems worldwide [51]. Studies have shown that the detection of herbicides is often seasonal. Detectable amounts of some s-triazine herbicides were found in 18 Swiss lakes that were analysed. Atrazine was the major herbicide present, accompanied by smaller amounts of simazine and terbuthylazine, and occasionally (methyl-thio)-s-triazines. Seasonal trends were also observed [108]. Atrazine, simazine, and lindane were found in the Guadiana River from March to November in 1993, observing a seasonal variation [4].

The new vacuum ultraviolet/ultraviolet/chlorine (VUV/UV/chlorine) vacuum process is considered a new AOP, but little is yet known about its kinetics for the degradation of contaminants in water treatment. Using this method, six typical pesticides (dimethoate [DMT], atrazine [ATZ], prometon [PMT], propoxur [PPX], bromacil [BRM], and propachlor [PPC]) were removed with 95% efficiency after 60 s [51]. This seems to indicate that this new VUV/UV/Chlorine process is a very promising AOP. This type of pollutant remains in the soil where it is directly applied. There are AOPs used in situ (ISCO) that are used for soil shadowing. An example of this is the activated persulfate process (SR-AOP), which is a promising technology [109].

Table 4 shows a representative list of PCPs, illicit drugs, and pesticides that can be removed by advanced oxidation processes.

**Table 4.** Examples of representative PCPs, illicit drugs, and pesticides that can be removed by AOPs.

Advanced Oxidation Processes	Examples of Representative PCPs, Illicit Drugs and Pesticides That Can Be Removed
O <sub>3</sub> -based AOPs	PCPs: Triclosan [84]; Ethylparaben, propylparaben, and butylparaben [90]
O <sub>3</sub> /UV	PCPs: Triclosan [88]; Butylparaben [91]; Illicit drugs: Cocaine and its metabolite [103,104,110]
VUV/UV/chlorine	Pesticides: Dimethoate [DMT], atrazine [ATZ], prometon [PMT], propoxur [PPX], bromacil [BRM], and propachlor [PPC] [109]

## 5. Discussion

In this paper, the different types of existing AOPs and their effectiveness in the removal of CECs from wastewater have been discussed. Despite being an efficient technology, they have their own limitations in terms of practical application. Two factors that limit its wide application are hard reaction conditions and high treatment costs [111]. In addition, degradation of organic pollutants leads to formation of by-products, which may be more toxic than the original contaminants. The most studied AOPs are those based on photocatalytic processes, where complete mineralization of the pollutants has generally not been possible [112–114]. Therefore, the toxicity of wastewater treated by photocatalysis is a topical issue, it is of high importance to evaluate the toxicity of treated wastewater effluent [115]. It is essential to study their toxicity conventional methods are limited to detecting reaction by-products.

Another aspect to be considered in the application of this advanced technology is its economic cost, which is very high. The trend is to combine biological and physicochemical processes to optimise the overall process cost and for each process to be pollutant selective. To make these processes more energetically more efficient and promote their application, hybrid techniques of AOP and biological treatment processes have been developed [116]. AOPs combined with biological Fenton [Fenton/biological processes] in wastewater treatment improved biodegradability with a TOC reduction of approximately 35% [117]. It was also reported to be used in synthetic wastewater where it reduced the operating costs required for the complete mineralisation of pharmaceuticals [furosemide and ranitidine] over extended periods of time [118]. The electro-Fenton/biological treatment process applied to synthetic water improved its biodegradability for a short treatment of 3 h [119]. For the removal of the pharmaceutical sulfamethoxazole and erythromycin in synthetic water, the combined membrane bioreactor/solar Fenton technology achieved complete removal [120]. The MBR/ozonation process applied to synthetic water achieved complete removal of the pharmaceutical sulfadiazine [121]. The combined MBR and H<sub>2</sub>O<sub>2</sub>/UV process applied to urban wastewater allowed high removal efficiencies of over 95% for carbamazepine and up to 98% for ibuprofen, resulting in complete removal for ciprofloxacin [1]. Studies seem to determine that in terms of contaminants degradation, the efficiency of combined processes of AOPs and biological treatments is higher than that of single AOPs [111].

Therefore, there are several limitations to the application of advanced oxidation processes such as the economic cost of their implementation, the intermediate compounds are in some cases more toxic than the starting compounds, as well as the lack of complete mineralisation in some cases. This remains a challenge to be considered for future research.

## 6. Conclusions

This paper provides a summary of the studies that have been carried out by different authors for the treatment of emerging contamination compounds that have been detected in natural environments by means of AOPs. Although these products were present in the aquatic environment for decades, due to their levels or detection in recent studies are now

recognised as potentially dangerous for natural water reserves. These contaminants are not completely removed in conventional treatment systems.

The combination of AOPs as tertiary treatment in wastewater treatment plants can provide biodegradation mechanisms for contaminating compounds that are not eliminated in previous purification processes, thus avoiding their integration into the environment.

Advanced oxidation processes are very promising alternatives for the removal of emerging contamination compounds. With them, very high removal percentages can be achieved. In the case of compounds such as amoxicillin and sulfamethoxazole, their removal percentage is around 90%. In the case of compounds such as diclofenac, ibuprofen, and ciprofloxacin, even their complete elimination from water can be achieved. In the case of the contaminant sulfamethoxazole, removal by AOPs produces removals of more than 90%, reaching complete removal for the UV/H<sub>2</sub>O<sub>2</sub> process. Other pharmaceuticals that are removed with very high or complete removal rates are oxytetracycline and doxycycline. Very promising removal rates of 69% were achieved for ketoprofen, as well as removal rates of 53–94% for metronidazole. In the case of lipid regulators bezafibrate and clofibrate, clearance rates of 50–90% were achieved.

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/article/10.3390/w13152094/s1>, Table S1: Removal percentage of pharmaceutical compounds using AOPs.

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## Abbreviations

AOPs, advanced oxidation processes; BE, benzoylecgonine; BOD5, biochemical oxygen demand; CAS, activated sludge system; CECs, compounds of emerging concern; CIP, ciprofloxacin; COD, chemical oxygen demand; DOC, dissolved organic carbon; Fe<sup>2+</sup>, ferrous ion; GAC, granular activated carbon; Hv, photolysis; HP, high pressure; HPLC-MS, high pressure liquid chromatography; H<sub>2</sub>O<sub>2</sub>, hydrogen peroxide; ISCO, in situ chemical oxidation; LP, low pressure; MCPP, mecoprop (methylchlorophenoxypropionic acid); MDA, tenamfetamine; MDEA, methylenedioxyethylamphetamine; MDMA, 3,4-metilendioxi-methamphetamine; MTP, metoprolol; O<sub>3</sub>, ozonation; PCP, personal care product; PH, pharmaceutical; SMX, sulfamethoxazole; SR-AOP, activated persulfate oxidation processes; TiO<sub>2</sub>, titanium dioxide; TOC, total organic carbon; Tric, triclosan; t-BuOH, tert-butyl alcohol, also called tert-butanol; US, ultrasound energy; UV, ultraviolet radiation; VUV, vacuum ultraviolet; WWTP, wastewater treatment plant; 2,4-D, 2,4-dichlorophenoxyacetic acid.

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