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Review

Recent Advances in Advanced Oxidation Processes for Degrading Pharmaceuticals in Wastewater—A Review

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Abstract: A large variety of pharmaceutical compounds have recently been detected in wastewater and natural water systems. This review highlighted the significance of removing pharmaceutical compounds, which are considered indispensable emerging contaminants, from wastewater and natural water systems. Various advanced oxidation processes (AOPs), including UV-H_2O_2, Fenton and photo-Fenton, ozone-based processes, photocatalysis, and physical processes, such as sonolysis, microwave, and electron beam irradiation, which are regarded as the most viable methods to eliminate different categories of pharmaceutical compounds, are discussed. All these AOPs exhibit great promising techniques, and the catalytic degradation process of the emerging contaminants, advantages, and disadvantages of each technique were deliberated. Heterogeneous photocatalysis employing metal oxides, particularly anatase TiO_2 nanoparticles as catalysts activated by UV light irradiation, was reviewed in terms of the electron–hole separation, migration of the charge carriers to the catalyst surfaces, and redox potential of the charge carriers. This brief overview also emphasized that anatase TiO_2 nanoparticles and TiO_2-based nanomaterials are promising photocatalysts, and a combination of photocatalysis and other AOPs enhanced photocatalytic degradation efficiency. Finally, the challenges of applying anatase TiO_2-based photocatalysis in environmental remediation and wastewater treatments to degrade pharmaceutical compounds, including mass spectroscopic analysis and a biological activity test of by-products of the emerging contaminants resulting from photocatalysis, are summarized.

Keywords: advanced oxidation process; emergence contaminant; Fenton; pharmaceutical waste; photocatalysis; catalytic process; wastewater treatment

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1. Introduction

In recent years, the consumption of pharmaceuticals used in medical treatments, public healthcare, and upholding a high standard of living, increased inevitably along with the global population at an annual rate of 5.8% [1]. This prompts the occurrence of pharmaceuticals in the environment, particularly in wastewater and sewage systems of hospitals, clinics, pharmaceutical industries, and residential areas, due to their uncontrolled discharge, non-metabolized in humans and animals, or expiry date [2–4]. Pharmaceuticals that are mostly organic compounds with complex aromatic structures and persistent in

aquatic systems have specific biological activities, so their existence in the environment is considered indispensable emerging contaminants [5–7]. The majority of pharmaceuticals found in wastewater are antibiotics, analgesics, painkillers, β-blockers, blood–lipid regulators, cytostatic drugs, steroidal hormones, anti-inflammatory drugs, antidepressants, stimulants, and other medications used for the treatment of various diseases [3–5]. As these pharmaceuticals are resistant to light, physical, and chemical treatments, they are not effectively degraded using the existing conventional methods in wastewater treatments and could reach and pollute surface water, groundwater, and water systems [8,9].

The accumulation of active pharmaceutical compounds in water systems results in the emergence of antimicrobial resistance genes and antibiotic resistance genes, causing serious threats to aquatic organisms, the environment, and eventually human health through trophic transfer [10,11]. Moreover, the presence of multiple pharmaceuticals in water systems could induce synergistic effects, enhancing their ecotoxicity and other considerable impacts [12]. Ecotoxicological risks of the active pharmaceutical compounds have been linked to various cancers in humans, as well as physiological perturbation and reproduction dysfunction of fishes and microorganisms. Therefore, the increasing emerging contaminants in the environment have become a serious global concern. With this in mind, in addition to regulations for the proper handling and disposal of unused pharmaceuticals, cost-effective and highly efficient methods are being developed and implemented in wastewater treatments as part of the global efforts to remove pharmaceuticals from water systems [13].

In general, there are various methods of removing pharmaceuticals from water systems, and most of them are based on biological, chemical, and physical approaches. Among the promising methods, adsorption [14–16], nanofiltration and nanoadsorption [17,18], membrane bioreactors [19,20], biological degradation [21,22], and advanced oxidation processes (AOPs) [23,24] have been explored and demonstrated to be successful in the removal of pharmaceuticals from aqueous solutions. Considering the respective advantages and disadvantages of each method, adsorption, biological degradation, and AOPs have attracted great attention [25].

Using the adsorption method, for instance, a large variety of adsorbents with their functional groups being protonated or deprotonated, pharmaceutical compounds are easily immobilized through hydrogen-bonding or electrostatic interactions. Given these advantages, the adsorptive removal of pharmaceuticals has been intensively explored on different adsorbents, such as sludge-derived biochar [26], biochar [27], activated carbon [28], clay [29], alkali-activated clay [16], and polymeric materials [15]. This method has been demonstrated to be successful in removing and decreasing the bioavailability of a large number of pharmaceuticals from aquatic media. These extensive research studies also revealed that the adsorption behavior of pharmaceuticals depends strongly on their functional groups, molecular conformation, ionic nature, and solubility in water, while the functional groups and net surface charge on the adsorbent surfaces play an important role in adsorbent–pharmaceutical interactions. It is worth noting that several key issues related to the post-adsorption steps to treat pharmaceuticals remain crucial challenges [30]. Similar problems are also accounted for in other techniques, such as flocculation, coagulation, and membrane filtration. From this point of view, these techniques are less practical in comparison with AOPs, which could degrade the organic pollutants and pharmaceuticals instantaneously into smaller chemical compounds that could possibly be less toxic.

In order to eliminate the pharmaceuticals in water systems, a biological degradation method, employing aerobic or anaerobic biological reactors using microorganisms, such as bacteria, fungi, algae, yeast, nematodes, and protozoa, has also been developed [31,32]. This method relies on breaking down organic polymers using normal cellular processes of those microorganisms. Although this method is the most cost-effective and ecological, its application is limited to biodegradable pharmaceuticals. Furthermore, the biological process in employed microorganisms can be altered in the presence of pharmaceuticals [33]. In addition, this method requires excessive energy consumption and intensive labor to

grow the employed microbes, and it has been pointed out that this method has low efficacy, rapid saturation, and unpleasant smell [34].

An interesting breakthrough in eliminating pharmaceuticals in aqueous solutions is the use of AOPs that can generate reactive oxygen species (ROS) in aqueous solutions or on the catalyst surfaces, which are capable of oxidizing and degrading pharmaceuticals into small compounds. AOPs have been proven to be a good alternative for the rapid degradation and elimination of refractory and non-biodegradable pharmaceutical compounds, such as antibiotics [35,36]. Therefore, AOPs are considered to be highly effective in the remediation of pharmaceuticals and other emerging pollutants. Although the detailed fragmentation pathways of pharmaceuticals upon oxidation still remain a research challenge, the by-products have been reported to be biologically inactive, suggesting that ROS eventually oxidizes the emerging contaminants into smaller sizes that are biodegradable and environmentally benign oxidation end products [37]. There are various established AOPs, which are dominantly classified into UV–hydrogen peroxide (UV/H_2O_2), Fenton and photo-Fenton, ozone-based processes, photocatalysis, and physical processes (including sonolysis, microwave, and electron beam irradiation) [24]. Among these AOPs, photocatalysis is the simplest method, and photocatalysts can be reused multiple times in wastewater treatment [38]. A large number of research efforts employing metal oxides, such as TiO_2, ZnO, WO_3, and $ZnWO_3$ nanoparticles as photocatalysts activated by UV light irradiation, have been devoted to the removal of pharmaceutical compounds from aqueous solutions [39].

Considering that all AOPs are flexible and are based on the same principle, where they generate ROS with high oxidation capacities to initiate the oxidization of organic pollutants, they can be combined to improve the removal efficiency of pharmaceutical compounds [40]. The combination of AOPs could also enhance cost-effectivity in terms of speed, the use of chemicals, and energy consumption. Therefore, it is crucial to outline the knowledge of photocatalytic degradation of pharmaceutical compounds by AOPs, including UV/H_2O_2, Fenton and photo-Fenton, ozone-based processes, photocatalysis, and sonolysis. Several articles reviewing this topic have been devoted by different research groups [24,41,42]. Thus, this review article focuses on pharmaceuticals in wastewater and provides an overview of the recent research and its efforts on photocatalytic degradation, highlighting the AOPs and degradation process of pharmaceuticals and other organic pollutants in aqueous solutions. The degradation mechanism of pharmaceutical compounds and the advantages and disadvantages of each AOP are discussed. In particular, this review also summarizes the important role of the photocatalytic activity of different catalysts in the heterogeneous photocatalytic degradation of pharmaceutical compounds in aqueous solutions, highlighting that photocatalysis on anatase-TiO_2 nanoparticles activated by UV light irradiation is the most promising method. This review article is divided into several sections, providing detailed pharmaceuticals found in wastewater and their degradation by various AOPs, delving into the mechanisms and recent studies on the degradation of the pharmaceutical compounds by various AOPs. Finally, future perspectives on the prospects and potential practical applications of anatase TiO_2-based nanoparticles and nanocomposites in removing pharmaceuticals in wastewater treatment are highlighted.

2. Pharmaceuticals in the Environment

Global consumption and demand for pharmaceuticals have significantly increased along with population growth, economic development, and standard of living improvement. Increasing the awareness of chronic diseases and the establishment of healthcare practices also have elevated the market of pharmaceuticals [43]. For instance, it is reported that over thirty million tons of pharmaceuticals have been consumed worldwide in 2023 [44]. As some portions (10−90%) of pharmaceuticals consumed by patients who receive medical treatments are not metabolized, the pharmaceutical compounds and their derivatives are excreted into the sewage system. The presence of pharmaceuticals in the environment, particularly in urban wastewater, should be proportional to their consump-

tion, and the pharmaceuticals in wastewater finally enter wastewater treatment plants and water systems [45].

Based on their therapeutic applications, the pharmaceuticals found in wastewater mainly include antibiotics, analgesics, antidepressants, antihistamines, anti-inflammatory drugs, painkillers, cardiovascular drugs, antidyskinetic medicines, diuretic drugs, statins, anti-epileptic drugs, and antihypertensive agents [46,47]. These pharmaceuticals are commonly used to treat fever, reduce inflammation and allergic diseases, and alleviate symptoms, such as pain, headaches, cold, flu, arthritis, musculoskeletal injuries, dyskinesia and Parkinson's disease, high blood pressure, and high cholesterol, as summarized in Table 1. As mentioned above, these pharmaceutical compounds are not effectively degraded by conventional methods in water treatment plants, and these emerging contaminants could eventually enter the water systems. In this sense, the presence of these pharmaceutical compounds in the aquatic environment, such as water systems, freshwater ecosystems, marine environments, and groundwater [20], was detected in the order between ng/L and µg/L [48,49]. Although, with this concentration, the therapeutic effects of these pharmaceutical compounds are negligible, and bioaccumulation, chronic toxicity, and mutagenicity of their pharmacologically active components in water systems pose potential hazards to aquatic life, the environment, and human health. In fact, long-term exposure to low-concentrated antibiotics, nonsteroid anti-inflammatory drugs (NSAIDs), antihypertensive drugs, and antidepressants has been demonstrated to affect the cardiovascular and cardiac irregularities in zebrafish [50,51] and water fleas (*Daphnia magna*) [52], as well as hypoglycemia, growth inhibition, and sexual development alteration in aquatic organisms [2,53].

Table 1. Pharmaceutical compounds commonly found in wastewater, their chemical formula, pKa, and therapeutic applications.

Pharmaceutical	Chemical Formula	pKa	Therapeutic Applications
Acetaminophen (Paracetamol)	$C_8H_9NO_2$	9.4	Analgesic and antipyretic pharmaceuticals widely used to treat pain and fever.
Aspirin (Acetylsalicylic acid)	$C_9H_8O_4$	3.5	An NSAID to reduce pain, fever, and/or inflammation.
Amantadine	$C_{10}H_{17}N$	10.5	An antidyskinetic medicine to treat dyskinesia and Parkinson's disease.
Ampicillin	$C_{16}H_{19}N_3O_4S$	2.5	An antibiotic to treat acute otitis media caused by susceptible organisms.
Amoxicillin	$C_{16}H_{19}N_3O_5S$	3.2, 11.7	An antibiotic widely used to treat bacterial infections, including chest infections, such as pneumonia and odontogenic abscesses
Azithromycin	$C_{38}H_{72}N_2O_{12}$	8.7	An antibiotic prescribed to children for the treatment of acute otitis media caused by Haemophilus influenzae, Moraxella catarrhalis, or Streptococcus pneumoniae.
Bupropion	$C_{13}H_{18}ClNO$	8.2	An antidepressant medication used for treating conditions like depression and mental disorders and aiding in smoking cessation.
Carbamazepine	$C_{15}H_{12}N_2O$	13.9	An anticonvulsant or anti-epileptic drug for the treatment of nerve pain and seizures.
Cefotaxime	$C_{16}H_{17}N_5O_7S_2$	3.75	A β-lactam antibiotic used to treat gram-positive, gram-negative, and anaerobic bacteria.
Cephalexin	$C_{16}H_{17}N_3O_4S$	4.5	A β-lactam antibiotic used to treat bacterial infections caused by bacteria such as pneumonia.

Table 1. *Cont.*

Pharmaceutical	Chemical Formula	pKa	Therapeutic Applications
Chloramphenicol	$C_{11}H_{12}Cl_2N$	1.14	An antibiotic useful for the treatment of severe bacterial infections.
Ceftriaxone	$C_{18}H_{18}N_8O_7S_3$	3.0	A cephalosporin antibiotic used to treat various bacterial infections.
Cetirizine	$C_{21}H_{27}Cl_3N_2O_3$	3.6, 7.6	A non-drowsy antihistamine used to relieve allergy symptoms.
Ciprofloxacin	$C_{17}H_{18}FN_3O_3$	6.1, 8.7	A fluoroquinolone antibiotic used to treat various bacterial infections.
Clarithromycine	$C_{38}H_{69}NO_{13}$	8.5	An antibiotic used to treat skin problems and chest infections.
Cloxacillin	$C_{19}H_{18}ClN_3O_5S$	2.8	A penicillin-type antibiotic to treat a wide range of bacterial infections.
Diclofenac	$C_{14}H_{11}Cl_2NO_2$	4.15	An NSAID used to treat pain and inflammation, such as gout and arthritis.
Erythromycin	$C_{37}H_{67}NO_{13}$	8.88	An antibiotic used to treat a variety of bacterial infections, such as skin infections and respiratory tract infections.
Fenofibrate	$C_{20}H_{21}ClO_4$	4.0	A fibrate class of medication used to treat abnormal blood lipid levels.
Hydrochlorothiazide	$C_7H_8ClN_3O_4S_2$	7.9, 9.2	A diuretic drug used to treat high blood pressure, edema, and swelling due to fluid build-up.
Ibuprofen	$C_{13}H_{18}O_2$	4.85	An NSAID used to relieve fever, pain, and inflammation.
Isoniazid	$C_6H_7N_3O$	1.82	An antibiotic used in the treatment of latent mycobacterium tuberculosis infection.
Ketoprofen	$C_{16}H_{14}O_3$	3.88	An NSAID used to treat inflammation, pain, swelling, stiffness, rheumatoid arthritis, and osteoarthritis.
Levofloxacin	$C_{18}H_{20}FN_3O_4$	5.7, 7.9	A fluoroquinolone antibiotic used to treat accute sinusitis and pneumonia bacterial infections.
Memantine	$C_{12}H_{21}N$	10.7	An antiparkinson agent used to suppress memory loss, dementia, and Alzheimer's disease.
Metoprolol	$C_{12}H_{21}N$	13.9	A β-blocker and antihypertensive medication used to treat high blood pressure, fast heart rate, and chest pain.
Metamizole	$C_{13}H_{17}N_3O_4S$	1.4	An antipyretic, analgesic, painkiller drug used to relieve severe and persistent fever and pain.
Metronidazole	$C_6H_9N_3O_3$	2.38	An antibiotic and antiprotozoal medication used to treat bacterial infections and inflammatory diseases.
Nabumetone	$C_{15}H_{16}O_2$	4.8	An NSAID used to treat mild to moderate pain and help to relieve symptoms of arthritis and reduce pain.
Naproxen	$C_{14}H_{14}O_3$	4.15	An NSAID used to treat pain, fever, rheumatoid arthritis, and inflammatory diseases.
Norfloxacin	$C_{16}H_{18}FN_3O_3$	6.34, 8.75	A fluoroquinolone antibiotic used in the treatment of a variety of bacterial infections.
Oflaxacin	$C_{18}H_{20}FN_3O_4$	5.45	A quinolone antibiotic used for the treatment of various bacterial infections.
Oxytetracycline	$C_{22}H_{24}N_2O_9$	3.22, 7.46, 8.94	A tetracycline class of antibiotic used to treat various infectious diseases.

Table 1. *Cont.*

Pharmaceutical	Chemical Formula	pKa	Therapeutic Applications
Promethazine	$C_{17}H_{20}N_2S$	9.05	Antihistamine used to relieve allergy symptoms.
Ranitidine	$C_{13}H_{22}N_4O_3S$	8.4	Antihistamine used to decrease acid produced in the stomach.
Ribavirin	$C_8H_{12}N_4O_5$	12.25	An antiviral drug for the treatment of hepatitis C and respiratory viral infections.
Rifampicin	$C_{43}H_{58}N_4O_{12}$	1.7, 7.9	An antibiotic used to treat a variety of mycobacterial and gram-positive bacterial infections.
Rimantadine	$C_{12}H_{21}N$	10.4	An antiviral drug used to prevent and treat respiratory tract infections caused by influenza A virus.
Simvastatin	$C_{25}H_{38}O_5$	4.7	Hydroxymethylglutaryl-CoA reductase inhibitors used to treat high cholesterol and reduce the risk of heart disease.
Streptomycin	$C_{21}H_{39}N_7O_{12}$	7.4, 13.5	An antibiotic isolated from Streptomyces griseus used to inhibit gram-positive and gram-negative bacteria and that is useful to treat cavitary lung disease.
Sulfamethoxazole	$C_{10}H_{11}N_3O_3S$	3.9	An antibiotic used to treat bacterial infections and is useful against gram-positive and gram-negative bacteria.
Tetracycline	$C_{22}H_{24}N_2O_8$	3.3, 7.8, 9.6	An antibiotic used to treat a variety of infections, acne, brucellosis, cholera, malaria, and plague.
Tramadol	$C_{16}H_{25}NO_2$	9.2	An opioid painkiller to treat moderately severe pain.
Trimethoprim	$C_{14}H_{18}N_4O_3$	7.6, 8.3	An antibiotic used to treat and prevent different types of infections.
Valsartan	$C_{24}H_{29}N_5O_3$	3.9, 4.7	An angiotensin receptor blocker used to treat high blood pressure, heart failure, and diabetic kidney disease.

In addition, Rodríguez et al. evaluated the toxicity and risk of pharmaceuticals present in wastewater and reported highly hazardous pharmaceuticals detected in the hospital wastewater samples, such as azithromycin, clarithromycin, doxycycline, cephalexin, ciprofloxacin, and ofloxacin [54]. Other antibiotics, such as sulfamethoxazole, could cause mutations in genes and chronic health effects [55]. In general, the presence of antibiotics in the environment can lead to the enhancement of antibiotic-resistant genes and multi-drug-resistant microbes that have been part of the global public health crisis [56,57]. Therefore, the removal of these emerging contaminants from wastewater is indispensable.

As displayed in Figure 1, pharmaceutical compounds generally have homocyclic and/or heterocyclic aromatic rings attached to primary and secondary amine ($-NH_2$ and $-NH$), carbonyl ($-CO$), ether ($-O-$), hydroxyl ($-OH$), methoxyl ($-OCH_3$), or sulfoxide ($-SO$) functional groups. These functional groups could be protonated or deprotonated, depending on the acidity of the aqueous medium, as represented by their respective pKa values. With the pKa value in either an acidic or basic condition, as listed in Table 1, most pharmaceutical compounds are in their protonated, deprotonated, or zwitterionic forms at ambient pH. From the chemistry viewpoint, pharmaceutical compounds easily make intermolecular interactions through hydrogen-bonding and/or ionic interactions with any biological and non-biological substances [58]. Therefore, they can diffuse and immobilize efficiently on the surfaces of solid substances. By optimizing these facts, adsorption and AOPs have been demonstrated to degrade pharmaceutical compounds efficiently [59,60].

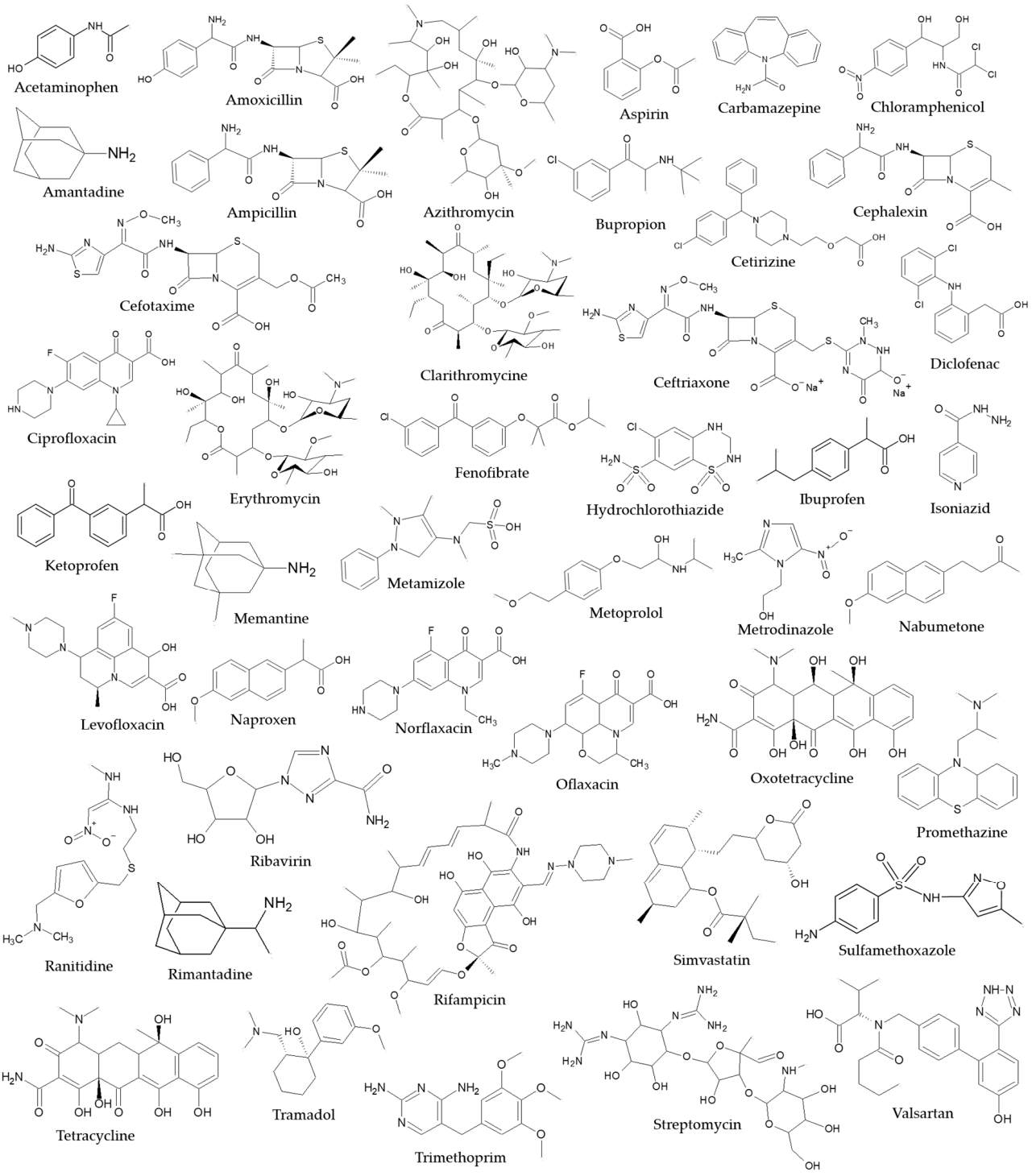

Figure 1. Chemical structures of pharmaceuticals commonly found in wastewater.

3. Degradation of Pharmaceuticals by Advanced Oxidation Processes in Aqueous Solution

As mentioned above, pharmaceuticals are highly resistant organic compounds that are toxic and difficult to eliminate using conventional methods in wastewater treatment plants, while AOPs have attracted great attention due to their notable performance in degrading pharmaceuticals in aqueous solutions. The COVID-19 virus outbreak globally has prompted more studies on AOPs to decontaminate and disinfect hospital wastewater. AOPs are believed to be ecofriendly and innovative methods that could be involved in wastewater treatments to enhance the existing anti-pollutant technology procedures. AOPs

are also considered as clean methods, generating free radicals that have at least a single unpaired electron, such as superoxide anion radicals ($O_2 + e^- \rightarrow {}^{\bullet}O_2^-$; E = +0.33 V), hydroxyl radicals ($H_2O \rightarrow {}^{\bullet}OH + H^+ + e^-$; E = +2.8 V), hydroperoxyl radicals ($O_2 + H^+ + e^- \rightarrow {}^{\bullet}HO_2$; E = +1.7 V), singlet oxygen ($^1O_2 + e^- \rightarrow {}^{\bullet}O_2^-$; E = +1.48 V), ozone ($O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$; E = +2.07 V), hydroperoxide anions ($HO_2^- + 2e^- + H_2O \rightarrow 3OH^-$; E = −0.88 V), sulfate anion radicals ($SO_4^{2-} \rightarrow {}^{\bullet}SO_4^- + e^-$; E = +2.6 V), and carbonate anion radicals ($CO_3^{2-} \rightarrow {}^{\bullet}CO_3^- + e^-$; E = +1.81 V). These free radicals are the most common ROS that are responsible for oxidizing pharmaceuticals in aqueous solutions or on catalyst surfaces [61,62]. Among the AOPs, UV-H_2O_2, Fenton and photo-Fenton, ozone-based processes, sonolysis, and photocatalysis, as individuals or a combination of them, have been demonstrated to be feasible to degrade pharmaceutical compounds in aqueous solutions [24]. These methods will be discussed in detail in the subsequent sections, taking into account the specific characteristics and capabilities of each AOP as well as the oxidation process related to the chemical structure of pharmaceutical compounds.

3.1. UV–Hydrogen Peroxide

In the UV-H_2O_2 process, UV light irradiation accelerates the photolysis of H_2O_2, generating active ${}^{\bullet}OH$ radicals in aqueous solutions due to the O-O bond cleavage of H_2O_2 [24,63], according to the following general reaction:

$$H_2O_2 + hv \rightarrow 2{}^{\bullet}OH \quad (1)$$

The Gibbs free energy and enthalpy of this light-induced dissociation reaction of H_2O_2 are $\Delta G = -237$ kJ mol^{-1} and $\Delta H = -190$ kJ mol^{-1} [64], suggesting that the reaction is spontaneous and thermodynamically feasible. The rate of photolysis is enhanced either with the pH of the medium or with the concentration of H_2O_2, suggesting that the light-induced dissociation of H_2O_2 is favorable in solutions with less acidic conditions and follows the first-order reaction kinetics. The ${}^{\bullet}OH$ radical is a strong oxidant with a standard reduction potential of +2.80 V, which is higher compared with that of most oxidizing agents, so this radical is able to oxidize a wide variety of organic compounds, including pharmaceuticals [65,66]. It is important to note that the oxidation reaction by the radical is ultrafast with a rate constant typically in the range of $10^8 - 10^{11}$ ms^{-1}, and the ${}^{\bullet}OH$ radical has a short lifetime within a few tens of ns [67,68]. These suggest that the reaction is actually controlled by the diffusion of both the radical and organic compounds and, hence, the degradation rate of the organic compounds is extremely low. In this sense, the degradation rate can be enhanced by increasing the concentration of H_2O_2 in the contaminated water solution. Moreover, in solutions with high H_2O_2 concentrations, the ${}^{\bullet}OH$ radicals could react with H_2O_2 to form a hydroperoxyl (${}^{\bullet}HO_2$) radical, which is also capable of oxidizing organic compounds [68]. Although the UV-H_2O_2 method is considered to consume a relatively cheap chemical agent, the use of high concentrations of H_2O_2 makes this method non-cost-effective [68].

3.2. Fenton, Photo-Fenton, and Electro-Fenton

In principle, Fenton utilizes homogenous catalytic ferric (Fe^{2+}) ions in the photolysis of H_2O_2 in aqueous solutions under acidic conditions [69]. The spontaneous dissociation of H_2O_2 to the formation of ${}^{\bullet}OH$ radicals is catalyzed by dissolved Fe^{2+} ions, according to the Haber–Weiss mechanism [70] as follows:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (2)$$

In the Fenton reaction, the Fe^{2+} ion is the most frequently employed due to its abundance, low toxicity, and simplicity in the removal of pollutants from water. The additional UV radiation in the photo-Fenton method accelerates the dissociation of H_2O_2 and degrades organic compounds more efficiently compared to the Fenton method. Both Fenton and photo-Fenton are preferable due to their less technological complexity and less specialized

equipment, and they could be environmentally beneficial upon the cyclic reaction to from Fe^{2+} ions as follows:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + {}^{\bullet}O_2H \quad (3)$$

Reactions (2)–(3) have to occur efficiently to realize the entire Fenton process. Therefore, the drawback of the Fenton and photo-Fenton methods is that they are non-regenerated catalysts. When the latter reaction is inefficient, the former reaction leads to the formation of Fe-containing sludge, and the buildup of Fe^{3+} ions inhibits the whole process and produces secondary iron pollution [68]. Another downside of the Fenton and photo-Fenton processes is the excessive usage of acid to maintain acidic conditions at pH 3 [24].

Electro-Fenton has also been demonstrated to be a promising water treatment technology to remove a variety of organic pollutants from water [71]. This method also utilizes Fe^{2+} ions to accelerate the dissociation of H_2O_2 to form $^{\bullet}OH$ radical as an effective oxidation agent for the decomposition of stubborn pollutants [71]. In an electro-Fenton cell, the $^{\bullet}OH$ radical is produced in situ in the acidic aqueous solution and is positively related to the applied electric field. In this method, there are few possibilities to generate $^{\bullet}OH$, including (i) the use of a sacrificial Fe anode as a source of Fe^{2+} ions and the direct addition of H_2O_2, (ii) the generation of H_2O_2 by an oxygen-sparging cathode and the addition of Fe^{2+} ions into the solution, (iii) the use of a sacrificial Fe anode and the generation of H_2O_2 by an oxygen-sparging cathode, and (iv) the generation of an $^{\bullet}OH$ radical and Fe^{2+} through the dissociation of H_2O_2 in the solution and the reduction in Fe^{3+} ions on the cathode. The disadvantages of this method are a decrease in the catalytic activity associated with the scavenging of the $^{\bullet}OH$ radical by Fe^{2+} ion, the precipitation of $Fe(OH)_3$ at high pHs, and the poisoning effect due to the formation of a polymer layer on the anode surface.

3.3. Ozone-Based Processes

The application of ozone has been successfully demonstrated to degrade pharmaceuticals, such as antibiotic, anticancer, antipsychotic, and painkiller drugs contained in artificial wastewater [72] and other organic pollutants, industrial effluents, and pesticides [24]. Ozone is a strong oxidant with a reduction potential of 2.07 V and can oxidize organic compounds in two ways: (i) a direct electrophilic attack by ozone molecules and (ii) an indirect attack through the generation of an H_2O_2 and $^{\bullet}OH$ radical when ozone breaks down in water, as given by

$$2O_3 + 2H_2O \rightarrow H_2O_2 + 2O_2 + 2\,{}^{\bullet}OH \quad (4)$$

Ozone-based processes employ either ozonation or the formation of ozone microbubbles to produce ROS by dissolving ozone in an aqueous medium. The degradation efficiency of pharmaceuticals or organic pollutants in water by ozone-based processes can be increased by additional H_2O_2 or UV light irradiation in order to enhance the production of the $^{\bullet}OH$ radical [73].

The drawbacks of ozone-based processes include low solubility of ozone in water, high energy consumption to generate ozone that leads to high costs, and the formation of by-products with genotoxic aldehydes, like formaldehyde [74]. Another disadvantage is the low efficiency against compounds with amide linkages due to their ozone-resistant properties [75]. Therefore, ozonation could be used as a pre-treatment process rather than in the purification of water [24]. However, adding a catalyst can alleviate the formation of toxic by-products with the same principle. This method is commonly employed and known as catalytic ozonation. Exploiting several metals, metal oxides, minerals, and carbon materials as a catalyst promotes the complete degradation of organic compounds and reduces partial oxidation in forming harmful intermediates [76]. In this sense, activated carbon is widely utilized in achieving the complete mineralization of antibiotics due to their inertness, stability, large specific surface area, and porosity [77,78]. Their high adsorptive properties enhance an excellent mass transfer in developing an efficient catalytic ozonation process. These properties and ozone decomposition determine catalytic activity and can

influence the complete removal of pollutants. Incorporating catalysts into ozone-based processes favors indirect oxidation compared to direct electrophilic ozone reactions with organic compounds. In other words, ozone saturation adsorbing onto the catalyst surface reduces the ozone availability for direct electrophilic attack.

A study of the removal of cephalexin via catalytic ozonation catalyzed using Mn-anchored zeolite reported excellent catalytic performance with a removal efficiency of 97% within only 2 min of retention time [78]. A comparison between non-catalytic ozonation was also conducted, and the difference between the two approaches showed that the degradation of cephalexin was 79.2-fold higher with the addition of the Mn@zeolite catalyst [78].

3.4. Ultrasonic Irradiation

Ultrasonic irradiation or sonolysis is an innovative and sustainable method for the removal of pharmaceutical waste from an aqueous medium. This technique employs ultrasound to alter and modify the target compounds, without any addition of chemicals, through water fragmentation upon collapsing the generated sonic microcavities. In principle, high-frequency sound waves are passed through a specific area within a liquid medium to generate sonic cavitation, which results in the formation of microcavities that rapidly expand and then violently collapse, producing shock waves within a short period of time [79–81]. The extremely high local temperature and pressure induce a pyrolysis process inside the cavity, where the dissociation of water generates an $^{\bullet}OH$ radical, which oxidizes organic pollutants if the radicals efficiently diffuse into the solution. As a result, volatile and non-volatile molecules within and in close proximity to the microcavities are oxidized and degraded [82]. Diffusion of the generated $^{\bullet}OH$ radical in the solution is governed by several parameters, including reactor geometry and frequency of the ultrasound wave. The application of sonolysis has been recently demonstrated in the degradation of azo dyes, but the sonolysis of pharmaceuticals is very new and is rarely investigated [83]. The drawback of sonolysis is mainly related to its high energy consumption and low electrical efficiency.

An interesting finding has been reported by Alishiri et al. on the ultrasonic removal of 15 mg/L ciprofloxacin and cephalexin using Fe_3O_4/GO nanocomposites, where the sonolysis of ciprofloxacin and cephalexin resulted in 96.39% and 97.69% removal efficiency, respectively [84]. In another study, the removal of 20 mg/L sulfamethoxazole, sulfadimethoxine, and sulfamerazine antibiotics using a magnetic Fe_3O_4–bentonite nanocomposite (Fe_3O_4-Bt) with a 17 min ultrasonication time showed the removal of 98.06%, 95.49%, and 96.52% [85].

3.5. Photocatalysis

Photocatalysis utilizes the transformation of the photonic energy into chemical energy, employing the intrinsic photoactivity of metal oxide, perovskite-type metal oxide, or metal sulfide nanoparticles activated by light irradiation [86,87]. Compared with homogeneous photocatalysis, which utilizes all the reactants and reagents in the same physical states, heterogeneous photocatalysis is preferable to degrade organic pollutants due to the easy separation of the catalysts after the photocatalytic process [88]. Moreover, heterogeneous photocatalysis has been demonstrated as a promising approach for destroying organic pollutants in wastewater due to its high efficiency, non-selectivity, and robustness with respect to the regeneration of photocatalysts. Photocatalytic degradation of organic pollutants is initiated by light irradiation, causing the excitation of electrons and creating holes in the lattice of the photocatalysts. When electrons and holes escape from recombination and migrate to the catalyst surfaces, depending on their reduction potential, the charge carriers could generate $^{\bullet}O_2^-$ and $^{\bullet}OH$ radicals, which initiate oxidation reactions to degrade organic pollutants [89].

Intensive studies have been devoted to finding photocatalysts with good photoactivity, biological and chemical inertness, relatively low bandgap, strong catalytic activity, non-toxicity, long charge carrier diffusion length, high charge mobility, abundant quantity, and inexpensive [90]. These criteria could be fulfilled by several metal oxides and

perovskite-type metal oxides, including TiO_2, ZnO, CeO_2, Mn_3O_4, $SrTiO_3$, $BiVO_4$, and Bi_2WO_6 nanoparticles. Supplementing to this, metal oxides, such as TiO_2 and ZnO nanoparticles, not only show good photoactivity in the removal of pharmaceuticals, pesticides, and organic dyes, but they can also exhibit antibacterial, antioxidant, and self-cleaning properties due to their morphology, structure, capacity to scavenge free radicals, inhibition of toxic by-products, and hydrophilicity [91,92]. These multifunctional properties give this photocatalytic material potential for the future of nanotechnology, biomedical applications, coatings, and window glass applications. Hence, these photoactive metal oxides can be synthesized with a variety of morphologies and nanostructures, such as nanospheres, nanofibers, nanowires, and nanorods [93]. With the bandgap energy being in the range of 3.0−3.5 eV, the photocatalytic activity of these catalysts depends on light irradiation in the UV region below 420 nm [94–96].

Incorporation of a small number of metallic dopants into the crystal lattice of the photocatalysts could reduce their bandgap energy to allow them to be activated by visible light irradiation. However, visible light also excites some organic pollutants, particularly dyes, leading to their spontaneous photolysis, so that the photocatalytic degradation of the dyes on such visible-light-responsive catalysts competes with their spontaneous photolysis [97,98]. In many studies, it has been pointed out that the incorporation of dopants creates trapping states, accelerating electron–hole recombination and decreasing the photocatalytic activity of the metal oxides and perovskite-type metal oxides [99,100].

In efforts to increase active sites, narrow the band gap for wider light absorption, and improve charge migration dynamics, current research highlighted the employment of structural modification, surface sensitization, and the formation of heterojunction [101]. The specific engineering schemes have been designed toward per surface and interfacial engineering, defects engineering, metals as cocatalysts and plasmonic materials, and heterostructured materials [101]. For instance, Zhou et al. have developed novel 0D/2D $Bi_4V_2O_{11}$/g-C_3N_4 S-scheme heterojunctions to absorb light within the visible spectrum with a wavelength of up to 450 nm [102]. This study revealed high photocatalytic degradation efficiency of oxytetracycline and reactive red 2 to be 74.1% and 84.2%, respectively. The combination of two n-type photocatalysts utilizes a more positive valance band and a more negative conduction band, which facilitates high redox capacity and delays charge recombination. Nevertheless, although sunlight can be considered as an alternative cost-effective light source for practical purposes, photocatalyst activated by UV light irradiation has a higher photoactivity, resulting in higher degradation efficiency of organic contaminants and better reproducibility [103]. Another study on the development of a photocatalyst highlighted the fabrication of a Fenton-like catalyst using FeOCl/MoS_2 [104]. The catalytic performance has shown 97.3% degradation of methylene blue (dye) and over 89% degradation of tetracycline (antibiotic), atrazine (pesticides), Bisphenol A (endocrine disruptor), carbamazepine (pharmaceutical), and rhodamine B (dye). This high catalytic performance was achieved due to the increased $^{\bullet}OH$ radicals from the reduction in Fe^{3+} to Fenton-active Fe^{2+} via the oxidation of Mo^{4+} to Mo^{6+} [104].

It is worth noting that the photocatalytic activity of metal oxides and perovskite-type metal oxides depends on the suppression of the electron–hole recombination and the efficient migration of the charge carriers to the catalyst surfaces, as well as the redox potential of the charge carriers, which is associated with the reduction potential of conduction and a valence band [105]. The lower reduction potential of the conduction band with respect to that of $O_2/^{\bullet}O_2^-$ (E = +0.33 V) facilitates the reduction in solvated oxygen to form an $^{\bullet}O_2^-$ radical, whereas a higher reduction potential of the valence band with respect to that of $OH^-/^{\bullet}OH$ (E = +2.8 V) is required to oxidize the water molecules on the catalyst surfaces to generate the $^{\bullet}OH$ radical [106]. Based on the reduction potentials of the conduction band and valence band, TiO_2 and $SrTiO_3$ nanoparticles are the most promising photocatalysts, as the excited electrons and holes could generate $^{\bullet}O_2^-$ and $^{\bullet}OH$ radicals, respectively. Other metal oxides, such as ZnO and WO_3 nanoparticles, could only generate either an $^{\bullet}O_2^-$ or $^{\bullet}OH$ radical. This fact emphasizes the high photocatalytic activity of TiO_2 and $SrTiO_3$

nanoparticles compared with ZnO and WO_3 nanoparticles. Supporting this notion, the degradation rate constant of amoxicillin, ampicillin, and cloxacillin on TiO_2 nanoparticles is higher than those on ZnO nanoparticles [107,108]. Figure 2 illustrates the band edge positions of the most commonly used photocatalysts [109]. Metal oxides, such as TiO_2, ZnO, WO_3, MnO, and CuO nanoparticles, are suitable for pollution degradation due to their strong oxidation properties.

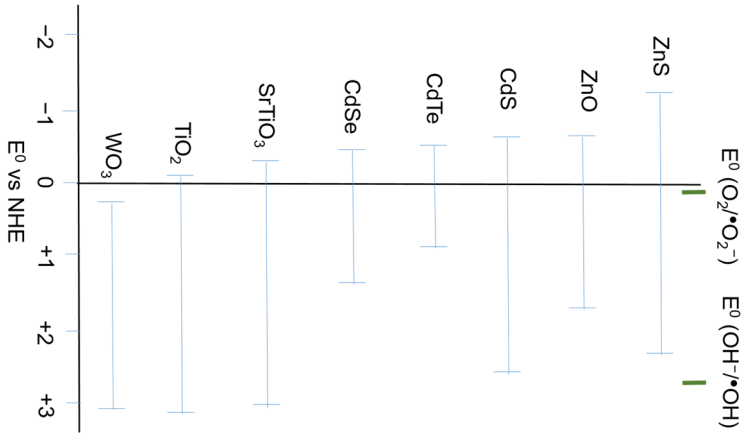

Figure 2. The reduction potential and band edge position of some common semiconductors.

It should be noted that $^{\bullet}O_2^-$ and $^{\bullet}OH$ radicals, which are generated on the catalyst surfaces, have short lifetimes within ns to µs, and photocatalysis is an ultrafast process [67,68]. Therefore, the photocatalytic degradation rate of organic pollutants depends strongly on the diffusion and immobilization of the target organic pollutants onto the catalyst surfaces, where the organic pollutants are readily oxidized by the radicals [87]. Using several established diffusion models, highly effective photocatalytic degradation of the organic contaminants has been revealed to take place in early irradiation times due to their rapid external film diffusion to the catalyst surfaces. It was then followed by a slower photocatalytic degradation before saturation at longer irradiation times. It is conceivable that the organic pollutants should be in contact with the radicals on the catalyst surface. With this in mind, one could consider that, if the external mass transfer and intraparticle diffusion of the organic pollutants onto the catalyst surfaces is much slower than the radical formation, the generated active radicals are dissolved in the solution and quickly decay into non-reactive species, so that no photocatalytic processes are observed.

4. Parameters Governing Advanced Oxidation Processes in the Degradation of Pharmaceuticals

The photocatalytic degradation of most organic pollutants triggered by reactive radicals has been attributed to the breaking down of their conjugated system. The oxidation reaction follows several fragmentation pathways and reductive hydrolysis, producing small organic molecules, carbon dioxide, and ammonium hydroxide as final products [110,111]. The photocatalytic degradation of organic compounds should be an ultrafast reaction [112]. The degradation kinetics should be governed by several conventional non-fundamental parameters, including light irradiation power, irradiation time, catalyst dosage, initial concentration, and temperature. The degradation kinetics of the heterogeneous photocatalysis has been well described by the Langmuir–Hinshelwood (L–H) model [113,114], emphasizing that the oxidation reaction of organic pollutants is the pseudo-first-order. The L–H model provides the average photocatalytic degradation process observable in the steady state measurement, although the photocatalytic degradation of organic pollutants should involve rapid multistep or complex reactions. In this sense, photocatalytic degradation should involve many reaction pathways and intermediates, and in most cases, the existence

of backward reactions would result in an equilibrium at prolonged irradiation times, so that a complete photocatalytic degradation cannot be reached.

Nevertheless, based on the generalized Smoluchowski equation, the observed rate constant obtained from the L–H model could be positively related to the diffusion constant of organic pollutants in the solution, highlighting an important role of molecular size, molecular conformation, functional groups, and classes of the organic pollutants. Supporting this notion, Suhaimi et al. demonstrated that the photocatalytic degradation of the planar conformation and relatively smaller size of methylene blue on TiO_2 nanoparticles surpasses rhodamine B in their binary solution [96]. A similar finding has also been reported by Wang et al. in the photocatalytic degradation of the ternary solution of methylene blue, rhodamine B, and methyl orange on $BaTiO_3/Bi_2WO_6$ heterojunction photocatalysts [115]. Furthermore, the energetic diffusion and oxidation reaction between organic contaminants and reactive oxygen species can be enhanced by increasing the temperature of the photocatalytic degradation.

Taking into account that the photocatalytic degradation of pharmaceutical compounds depends on the generated $^{\bullet}O_2^-$ and $^{\bullet}OH$ radicals, adding a small amount of H_2O_2, which efficiently produces $^{\bullet}OH$ radicals on the catalyst surfaces, should enhance the degradation rate of organic pollutants. Although dissociation of H_2O_2 is also accelerated under UV light irradiation, leading to the formation of $OH^{\bullet}$ radicals in the solution [116], as given by reaction (1) in Section 3.1, the direct oxidation reaction of organic pollutants by the formation of $OH^{\bullet}$ radicals in the solution is relatively slow and inefficient and undergoes through different mechanisms from that of the photocatalytic process on the catalyst surfaces. Moreover, the excessive addition of H_2O_2 would negatively affect degradation efficiency due to the increased scavenging effect of $^{\bullet}OH$ radicals. Based on similar phenomena, one could anticipate that a similar effect of additional H_2O_2 would be observed in the photocatalytic degradation of pharmaceutical compounds.

It is worth noting that the stability and reusability of photocatalysts have also been of interest [117]. Several metal oxides, such as TiO_2 and ZnO nanoparticles, are amphoteric and have poor chemical stability at a high pH in the medium [118]. $BiVO_4$ and Fe_2O_3 nanoparticles have poor charge carrier mobility in the crystal lattice and slow oxygen kinetics on the particle surface, whereas WO_3 nanoparticles undergo peroxidation and photocorrosion during the photocatalytic process [119]. However, as the crystal structure and the surface of TiO_2, ZnO, SiO_2, and Fe_3O_4 nanoparticles remain unchanged after photoexcitation, these photoactive catalysts can be regenerated and reused [120].

The effect of the pH of a medium, the pKa value of the organic contaminants, and the pH_{pzc} (point of zero charge) of the photocatalyst play important roles in the degradation of pharmaceuticals. By taking into account the pH_{pzc} value of the catalyst, one could predict the changeability of ionic charges of the catalyst surface. The effect of pH involves the protonation and deprotonation of functional groups for electrostatic and ionic interactions between organic compounds and catalyst surfaces. Hence, a variation of the results was reported by several studies on the effect of pH on pharmaceutical degradation. The investigation of photocatalytic degradation of 60.76 µmol/L rifampicin with the addition of 10 mg TiO_2 NPs under UV light irradiation shows an increase in the efficiency values from pH 3 to pH 5.63. This indicates favorable degradation of rifampicin antibiotic in an acidic medium, which can be rationalized by the conservation of the rifampicin zwitterion structure between pH 3 and pH 7.9. A decreasing degradation efficiency was reported with increasing basicity of the medium from pH 6 to pH 10 due to the deprotonation of piperazine nitrogen of rifampicin above its pK_b value of 7.9, which induces electrostatic repulsion among negative surface charges of TiO_2 NPs [121]. In another finding by Yousefi et al., the photocatalytic degradation efficiency of rifampicin by BiOCl/BiOI nanocomposites was optimal in an acidic environment (pH 3 and pH 5) due to the attraction of rifampicin-free electron pairs to the positive surface of the catalyst [122]. The pH_{pzc} of BiOCl/BiOI was 7.5, leading to an unsatisfactory rifampicin removal at pH 8 to pH 10. In addition to this discussion, the pH of the reaction medium also affects the degradation

efficiency of pharmaceutical compounds using different AOP techniques, particularly homogenous Fenton and photo-Fenton. Several studies reveal that the optimal degradation efficiency by these techniques could only be achieved at pH 3 [123]. Above this pH, the formation of hydroxyl radicals is insufficient, as the concentration of H^+ ions decreases. On the other hand, below pH 3, the degradation of organic compounds is inefficient due to slow H_2O_2 dissociation in the formation of $^{\bullet}HO_2$ radicals.

5. A Combination of Advanced Oxidation Processes

Although individual AOPs can be used to degrade pharmaceutical compounds and other organic pollutants in wastewater, a combination of AOPs has been employed in many studies and reached satisfactory results [24]. In particular, a combination of sonolysis with ozonation has been demonstrated to efficiently degrade various pharmaceuticals, such as diclofenac, sulfamethoxazole, and carbamazepine in an aqueous solution [124]. A coupled Fenton reaction with high-frequency sonolysis (862 kHz) has been demonstrated to degrade ibuprofen from both distilled water and wastewater [125]. Another important combination is photocatalysis and sonication [126,127], where applying ultrasonic waves (20–1000 kHz) in photocatalysis could induce cavitation bubbles, enhancing the generation of $^{\bullet}OH$ radicals and the degradation of organic pollutants. It is worth noting that, in these combinations of AOPs, the mechanisms of respective sonolysis, ozonation, and photocatalytic degradation of the organic pollutants are unchanged. Applying additional sonication provides more kinetic energy and enhances the diffusion and immobilization of the organic pollutants on the microbubble or catalyst surfaces, resulting in higher degradation efficiency.

6. Reported Studies of the Advanced Oxidation Processes of Pharmaceuticals

Various AOPs, such as UV-H_2O_2, Fenton-based, ozone-based, and semiconductor-based photocatalytic processes, have been employed for the degradation of organic pollutants, including pharmaceutical compounds [128–132]. Among these AOPs, a heterogeneous photocatalytic process employing metal oxides, metal sulfides, and perovskite-type materials as photocatalysts is more widely used for the removal of persistent pollutants, creating safe end products [133]. More specifically, photocatalysis using anatase TiO_2 nanoparticles is the most promising method due to their high photocatalytic activity, cost-effectivity, environmental friendliness, and chemical and physical inertness [134–137]. Therefore, several research groups have published numerous papers on the usage of AOPs using TiO_2-based nanoparticles as catalysts in the photocatalytic degradation of pharmaceuticals in water [138–140].

Light-driven AOPs have been applied to degrade carbamazepine, ciprofloxacin, ibuprofen, and a mixture of these pharmaceutical compounds on TiO_2 nanoparticles as catalysts. It was found that ciprofloxacin showed the highest degradation rate, followed by ibuprofen and carbamazepine [141]. The removal of levofloxacin upon photocatalysis using TiO_2 nanoparticles as catalysts has also been investigated. The degradation of levofloxacin was confirmed by decreasing the antibacterial activity of its by-products against *Escherichia coli* (E. coli), where the antibacterial activity of the treated levofloxacin solution decreases gradually with the irradiation time [142].

Effective photocatalytic degradation of three antiviral pharmaceuticals, namely 1-amantadine, 2-amantadine, and rimantadine, under UV irradiation in the presence of TiO_2 nanoparticles has been established [143]. The removal of cefotaxime upon photocatalysis under UV light radiation of two types of nanocatalysts, i.e., TiO_2 and TiO_2/kaolin, has been investigated and compared with the degradation of this β-lactam antibiotic under UV-H_2O_2 treatment. It was reported that the UV-H_2O_2 treatment is more effective and promising in removing cefotaxime from an aqueous solution [144].

The photocatalytic degradation of ibuprofen from synthetic wastewater has been reported under UV-LED irradiation in the presence of TiO_2, ZnO, H_2O_2, potassium peroxomonosulfate (KSO_5), and potassium peroxodisulfate ($K_2S_2O_8$). Compared to other systems investigated, ibuprofen was found to degrade most efficiently on TiO_2 nanoparti-

cles [145]. On the other hand, the photodegradation of sulfamethoxazole, metronidazole, and ciprofloxacin on TiO_2 nanoparticles under UV light irradiation has also been investigated [146]. The effective degradation of metoprolol, a medication to treat blood pressure and heart rate, through photocatalytic activity under the visible light of a Xenon lamp in the presence of B-doped TiO_2 nanoparticles has been performed. The photocatalytic degradation of this antibiotic was enhanced by a B dopant in the lattice structure of TiO_2 nanoparticles [147]. The photocatalytic degradation of isoniazid and rifampicin using TiO_2 and ZnO catalysts has been investigated and compared with the degradation of these antibiotics upon the UV-A photo-Fenton process [148]. A radical scavenging assay was also conducted to determine the effects of free radicals, electron vacancy, and singlet oxygen, and it was revealed that isoniazid was degraded by various ROS, while rifampicin was degraded by electron vacancy.

The degradation of norfloxacin has been investigated using different AOPs, including UV/H_2O_2, Fenton, photo-Fenton process, and UV/TiO_2 [149], highlighting that this antibiotic is efficiently degraded by the photo-Fenton process. The degradation of ribavirin using the $UV/TiO_2/H_2O_2$ system has also been reported. The results revealed that ribavirin was degraded, and the formation of its transformation products was found to contribute to ecotoxicity. Although the method was effective in degrading ribavirin, it also led to the formation of toxic transformation products, which require further processes to degrade [150]. Similarly, upon the photocatalytic degradation of memantine using UV-C/H_2O_2 and UV-A/TiO_2, it has been reported that the presence of ROS, especially $^{\bullet}OH$ radicals, is more prominent than $^{\bullet}O_2^-$ radicals, while intermediate species in the degradation process of memantine are non-biodegradable and are considered relatively toxic [151].

It is interesting to note that the photocatalytic degradation of anti-epileptic carbamazepine in the presence of the BiOCl/AgCl composite catalyst activated by simulated sunlight irradiation is more efficient than that in the presence of BiOCl [152]. The high photocatalytic activity of the BiOCl/AgCl composite is attributed to efficient electron–hole separation and the migration of the charge carriers to the catalyst surfaces. The degradation pathways of carbamazepine involve oxidation by photo-induced radicals, aromatic ring rearrangement, and hydroxylation [152]. In contrast, the photodegradation of carbamazepine in estuarine water is enhanced by the presence of chloride ions [153], which form reactive chlorine species (RCS). This highlights that the UV/H_2O_2, Fenton, photo-Fenton processes, and UV/TiO_2 in the presence of chlorine, have multiple reactive species (ROS and RCS) to oxidize the emerging contaminants [154].

A study of the degradation of metronidazole treated using various methods, including ultrasonic irradiation, UV light irradiation, H_2O_2, ozonation, and peroxonium, has been recently reported [155]. In addition, the degradation of this antibiotic was also investigated via UV and $UV/H_2O_2/O_3$ associated with heterogeneous catalysis of TiO_2 nanoparticles ($UV/H_2O_2/O_3/TiO_2$@PU) that have been functionalized in polyurethane macroporous structures. It was found that both ultrasonic and UV light irradiation had less efficacy in degrading metronidazole, but this antibiotic was efficiently degraded in the $UV/H_2O_2/O_3/TiO_2$@PU system [155].

Metal-doped TiO_2 nanoparticles have been intensively utilized as photocatalysts in the degradation of a variety of pharmaceuticals in water under solar light. For instance, Ni-doped TiO_2 nanoparticles have been utilized and found to be an excellent photocatalyst to degrade ofloxacin [156], cephalexin, and tetracycline in water and wastewater with high photocatalytic degradation efficiency [157]. On the other hand, Ag-doped TiO_2 nanoparticles under UV light irradiation also could efficiently degrade chloramphenicol [158]. Fe-doped TiO_2 nanoparticles under UV light have successfully mediated the photocatalytic degradation of metronidazole from aqueous solutions and other pharmaceutical compounds from industrial pharmaceutical wastewater [159]. Carbon-doped TiO_2 nanoparticles activated by visible UV light were successfully utilized to degrade carbamazepine and diclofenac, where complete depletion was achieved at a concentration of the catalyst of 244 mg/L [160].

The effect of supporting materials in the photodegradation of pharmaceuticals is demonstrated in the degradation of carbamazepine on mesoporous dendritic silica-supported TiO_2 nanoparticles (TiO_2/MDS) in the presence of persulfate [161]. The high photocatalytic activity of the TiO_2/MDS/persulfate system is further revealed in the photocatalytic degradation of amoxicillin, sulfamethoxazole, bisphenol A, and naproxen [161]. It was speculated that the high photocatalytic activity of TiO_2/MDS is due to the suppression of electron–hole recombination. The degradation of ceftriaxone through photocatalytic degradation using light irradiation in the presence of heterogeneous activated carbon-supported TiO_2 nanoparticles has also been investigated [162]. The findings suggest that the photocatalyst made of activated carbon–TiO_2 composites can be utilized in the removal of pharmaceutical wastes by the photocatalytic process in an environmentally friendly, reliably efficient, effective, reusable, and sustainable manner [162]. Another important TiO_2-based composite to degrade pharmaceutical wastes from aqueous solutions is multi-walled carbon nanotube–TiO_2-SiO_2 nanocomposites. It has been demonstrated that the introduction of MWCNT reduces the bang gap, allowing visible light excitation, enhancing the surface area, and improving the photocatalytic degradation efficiency of acetaminophen in an aqueous solution [163].

Ali et al. investigated the photocatalytic degradation of the endocrine-disrupting drug (estrone hormone (E1)) using silica-supported g-C_3N_4/WO_3 under UV and visible light irradiation [164]. The result shows excellent estrone hormone removal of 100% and 96.2% using UV light and visible light irradiation, respectively, under the set parameters of 3000 µg of photocatalyst dosage, pH 7, and 300 µg/L hormone concentration.

Finally, a combination of nanofiltration with AOPs, including UV, UV/TiO_2, and UV/H_2O_2, has been employed to degrade commonly consumed anticancer drugs, such as etoposide, paclitaxel, cyclophosphamide, and ifosfamide. The results revealed that direct photolysis was able to effectively degrade etoposide and paclitaxel, whereas the degradation of cyclophosphamide and ifosfamide was found to be ineffective [165]. It is also notable that a combination of ozonation and the photocatalytic degradation of metronidazole and cephalexin using the Urea/TiO_2/$ZnFe_2O_4$/Clinoptilolite catalyst under visible-light irradiation and ozone injection showed higher potential for the degradation of these pharmaceuticals due to a large number of generated ROS [166].

7. Pilot Test of Advanced Oxidation Processes on Industrial Wastewater

Intending to promote the various AOPs on an industrial scale, some studies conducted pilot tests using advanced technological prototypes on the practical applications of AOPs on wastewater remediation. Actual wastewater samples were collected from the influent drains of industries, hospitals, and urban wastewater plants and experimented for their removal efficiencies and toxicities. The pre- and post-assessments for water quality in the potentiality of AOPs in eliminating toxicity were analyzed based on several parameters and types of contaminants. The physical assessment may include parameters such as temperature, pH, electrical conductivity, chemical oxygen demand (COD), total organic carbon (TOC), dissolved organic carbon (DOC), particulate matter (turbidity), hardness, color, and salinity. Supplemental chemical analysis may require the identification of organic substances, heavy metals, nitrogen, nitrates, nitrites, ammonia, chlorine, phosphates, and phosphorus found in water. In addition to this, the presence of *E. coli,* coliform bacteria pathogenic microorganisms, *Klepsiella pneumonia* (K. pneumonia), *Staphylococcus aureus* (S. aureus), abiotic particles, and viruses in water content are often investigated. Hence, most methods of identification use inductively coupled plasma for detecting heavy metals; a UV-Vis spectrophotometer for analyzing color, COD, DOC, TOC, organic substances, and turbidity; ion chromatography for measuring significant anions and cations in water content; and a real-time bacteria sensor, polymerase chain reaction, surface-enhanced Raman scattering, and laser-induced fluorescence spectroscopy for detecting *E.coli*, *K. pneumonia*, *S. aureus,* bacteria, and viruses [167].

Most of the reported pilot tests, as tabulated in Table 2, show successful pharmaceutical waste removal that follow a realistic wastewater treatment approach. Research focusing on developing small-scale AOP models still requires some improvements, with economic and operational costs being the main limitations. The cost can be reduced by improving the light absorptivity of a photocatalyst toward a wider solar spectrum. Solar irradiation can lower the expenses for electrical consumption and UV light generation. Hence, several strategies were implemented to optimize the photocatalytic activity to overcome its limitations and the occurrence of charge recombination, as mentioned in Section 3.5.

Table 2. Reported studies using AOPs and combination methods for real wastewater treatment and evidence of their effectiveness.

AOP Method	Wastewater	Light Source	Catalyst	Results	Ref.
UV-H_2O_2	Northeast of Spain: two from urban wastewater plants. One from graywater, a psychiatric hospital, and the pharmaceutical industry. The wastewater was composed of 30 pharmaceuticals and 13 transformation products.	UV-C lamp (30 min)	None	The pharmaceuticals were approximately 6–86% removed from urban wastewater plants, and 59% from graywater, with electrical energy per order (E_{EO}) values of 0.9–1.5 kWh/(m^3·order). The removals were lower for hospitals and industries (36% and 17%), with electrical energy per order (E_{EO}) values of 7.3–9.1 kWh/(m^3·order).	[168]
Photo-Fenton	Porto Alegre City, local hospital: paracetamol (297 µg/L) and dipyrone (55 µg/L).	Solar irradiation (30 min)	Fe^{3+}-EDDS (1:2 ratio)	77% pharmaceutical removal. Most of the transformation products show low toxicity, mutagenicity, and bioaccumulation.	[169]
Catalytic ozonation	Zhejiang Province, China, industrial treatment plant: 8% pharmaceutical waste.	None	Mn-Fe/Al_2O_3	99% removal of DOC and 14.5 mg/L average removal of COD. The effluent has a low total transcriptional effect level index value of ≤1.50.	[170]
Biological-photocatalysis	Kharagpur Subdivisional Hospital, India: containing carbamazepine.	UV-A irradiation	Al–ZnO/Fe	85% carbamazepine removal from aerated horizontal flow-constructed wetland. The biological method removed 30% carbamazepine.	[171]

Wastewater contains several impurities and contaminants; for example, soluble ions, such as nitrate ions, chloride ions, and carbonate ions, could act as free radical scavengers and inhibit the efficient degradation of organic compounds and pharmaceuticals. The laboratory-scale removal efficiency of antibiotics in ultra-pure water has resulted in a high degradation rate. However, evidence of intermediate by-products and possible toxicity caused by secondary products is insufficient and requires additional examination [172].

8. Conclusions and Future Perspectives

In this review, the presence of pharmaceuticals in water systems that pose potential hazards to aquatic life, the environment, and humans due to their bioaccumulation, chronic toxicity, and mutagenicity was comprehensively summarized. Advanced oxidation processes (AOPs), including UV-H_2O_2, Fenton and photo-Fenton, ozone-based processes, photocatalysis, and physical processes, are the most viable and fascinating methods to eliminate pharmaceuticals and other organic pollutants in wastewater and water systems. AOPs are radical-based processes where the generated radicals act as reactive oxygen species (ROS) and are apparently considered the most feasible radicals to degrade the emerging

contaminants. Among these AOPs, photocatalysis is initiated by light radiation in the presence of metal oxide or perovskite-type metal oxide nanoparticles as photocatalysts to degrade pharmaceuticals in water systems due to their simplicity and eco-friendliness. The photoactivity of the photocatalysts is determined by the electron–hole separation and migration of the charge carriers to the catalyst surfaces and the redox potential of the charge carriers. With these criteria, TiO_2 and $SrTiO_3$ nanoparticles were found to be the most promising photocatalysts, as their excited electrons and holes could generate $^{\bullet}O_2^-$ and $^{\bullet}OH$ radicals, respectively, which are responsible for initiating the degradation of pharmaceutical compounds. Until now, anatase TiO_2 nanoparticles have been revealed to have the best photocatalytic activity and have been intensively explored in the degradation of various pharmaceuticals and other organic pollutants in aqueous solutions. For that reason, anatase TiO_2-based nanomaterials activated by UV light irradiation have also been successfully applied in the photocatalysis of pharmaceutical compounds. In this brief overview, anatase TiO_2 nanoparticles and their nanocomposites have been emphasized to be the most promising photocatalysts. A combination of photocatalysis and other AOPs has been highlighted to be a promising efficient method for enhancing the photocatalytic degradation of pharmaceutical compounds. Finally, the effects of diffusion, polarizability, steric hindrance, molecular structure, and the optical properties of pharmaceutical compounds on their degradation by AOPs are conceivable factors to be evaluated in future studies to provide a better understanding of the photocatalytic degradation of these indispensable emerging contaminants. This should include mass spectroscopic analysis and biological activity tests of by-products of pharmaceutical compounds resulting from photocatalysis, as well as the development of new metal oxide, perovskite-type metal oxide, or metal sulfide and their nanocomposite photocatalysts for environmental remediation and wastewater treatment.

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