Review

Removal of Pharmaceuticals and Personal Care Products (PPCPs) by Free Radicals in Advanced Oxidation Processes

Jiao Jiao 1, Yihua Li 1,∗, Qi Song 1, Liu Jin Wang 2, Tianlie Luo 2, Changfei Gao 3, Lifen Liu 4 and Shengtao Yang 1,∗

1 Key Laboratory of Pollution Control Chemistry and Environmental Functional Materials for Qinghai-Tibet Plateau of the National Ethnic Affairs Commission, School of Chemistry and Environment, Southwest Minzu University, Chengdu 610041, China
2 State of Environmental Protection Key Laboratory of Synergetic Control and Joint Remediation for Soil & Water Pollution, College of Ecology and Environment, Chengdu University of Technology, Chengdu 610059, China
3 School of Environmental and Material Engineering, Yantai University, Yantai 264005, China
4 Key Laboratory of Industrial Ecology and Environmental Engineering, Ministry of Education, School of Ocean Science and Technology, Dalian University of Technology, Panjin 124221, China
∗ Correspondence: yihuali@swun.edu.cn (Y.L.); yangst@pku.edu.cn (S.Y.)

Abstract: As emerging pollutants, pharmaceutical and personal care products (PPCPs) have received extensive attention due to their high detection frequency (with concentrations ranging from ng/L to µg/L) and potential risk to aqueous environments and human health. Advanced oxidation processes (AOPs) are effective techniques for the removal of PPCPs from water environments. In AOPs, different types of free radicals (HO·, SO4·−, O2·−, etc.) are generated to decompose PPCPs into non-toxic and small-molecule compounds, finally leading to the decomposition of PPCPs. This review systematically summarizes the features of various AOPs and the removal of PPCPs by different free radicals. The operation conditions and comprehensive performance of different types of free radicals are summarized, and the reaction mechanisms are further revealed. This review will provide a quick understanding of AOPs for later researchers.

Keywords: pharmaceuticals and personal care products; advanced oxidation processes; free radicals; water treatment

1. Introduction

Pharmaceutical and personal care products (PPCPs) are attracting increasing concern [1–3] due to the fact that they have been extensively detected in aqueous environments, solids and sediments [4–10]. PPCPs are defined as widespread chemicals including pharmaceuticals (such as hormones, antibiotics, antidepressants, non-steroidal anti-inflammatory drugs, and lipid regulators) and personal care products (such as preservatives, disinfectants, fragrances, and sunscreens) [2,11]. PPCPs are widely used in high quantities throughout the world, and are known to be released into aquatic environments from multiple discharges, including domestic wastewater, pharmaceutical wastewater [11], daily washing, swimming, excreting after human ingestion [12], livestock, aquaculture and households (excretion and littering) [13]. Meanwhile, in terms of household medicine, the inappropriate disposal of pharmaceutical products could adversely infect the environment and increase the risk of accidental poisoning [14]. It was revealed that domestic sewage was the primary source of PPCP emissions in the surface water of China [15,16]. These pollutants, along with their transformed intermediate products, have been prevalent in most environmental matrices [17].

To evaluate the per-capita emission rates of some PPCPs, in Korea, Subedi et al. [18] found that the per-capita emission rates of triclocarban and acetaminophen (ACE) were 158 and 59 µg/capita/day, respectively. In the long run, trace concentrations of 1 ng/L–100 µg/L of PPCPs in aqueous environments pose potential risks to animals and human health [19].
The detection results of partial PPCPs in various aquatic environments from different countries were summarized in Table 1. PPCPs have been widely detected in surface water, groundwater, and even drinking water, with concentrations ranging from ng/L to mg/L. Additionally, the concentrations of PPCPs in sediment and soil are at the level of mg/kg [19–22]. Recently, Chaves et al. [23] revealed the frequencies of detection of PPCPs in surface water with 104 articles (Figure 1a). Among them, carbamazepine (CBZ), diclofenac (DCF), sulfamethoxazole (SMX), caffeine (CAF), ACE and ibuprofen (IBP) have the highest detection frequency. The maximum concentrations (ng/L) of the most frequent PPCPs in each analyzed continent are shown in Figure 1b. Although the concentrations of PPCPs are not enough to cause acute toxicity to humans or animals, most of the PPCPs will gradually accumulate in the aqueous organisms for their refractory properties, causing potential threats to human health [24–26]. Meanwhile, the ubiquitous presence of PPCPs would cause trepidation in maintaining the homeostasis of the ecological environment [27]. Thus, it is of great importance to remove PPCPs from the environment. In recent decades, the number of publications on PPCPs had been increased annually (Figure 2).

Table 1. The detection of partial PPCPs in various aquatic environments from different countries.

| Location | Aquatic Environment | Chemical | Category | Concentration | Ref. |
|----------|---------------------|----------|----------|---------------|------|
| Poland   | Groundwater         | N,N-diethyl-meta-toluamide (DEET) | Mosquito and insect repellants | 17.28 µg/L | [28] |
|          |                     | 17β-oestradiol | Hormones | 48 ng/L |      |
|          | Surface water       | CAF      | Stimulants | 29.9955 µg/L |      |
|          | Drinking water      | Bisphenol A (BPA) | Hormones | 3.113 µg/L | [28] |
|          | Drinking water      | Azithromycin (AZM) | Antibiotics | 193 ng/L |      |
|          | Drinking water      | Paracetamol | Non-steroidal anti-inflammatory drugs | 173 ng/L |      |
|          | Drinking water      | IBP      | Non-steroidal anti-inflammatory drugs | 224 ng/L |      |
|          | CAF                 | Stimulants | 159 ng/L |      |
| Brazil   | Surface water       | Avobenzone (ABZ) | Sunscreen agents | 340 ng/L |      |
|          | Glibenclamide (GBC) | Hypoglycemic drugs | 50–120 ng/L |      |
|          | Drinking water      | Nimesulide (NI) | Non-steroidal anti-inflammatory drugs | 181 ng/L | [29] |
|          | Methylparaben       | Preservatives | 234 ng/L |      |
|          | ABZ                 | Sunscreen agents | 290 ng/L |      |
| China    | Surface water       | SMX      | Antibiotics | <LOQ–2.92 ng/L | [30] |
|          | 4-n-nonylphenol     | Hormones | 9.90–457.40 ng/L |      |
|          | Salicylic acid (SA) | Analgesics | 2.92–34.12 ng/L |      |
|          | Drinking water      | Sulfamethoxypyridazine | Antibacterial | 107.14 ng/L | [31] |
|          | Lincomycin          | Antibiotics | 1.00–29.32 ng/L |      |
|          | SMX                 | Antibiotics | <LOQ–2.18 ng/L |      |
|          | Drinking water      | CBZ      | Antiepileptics | <LOQ–57.4 ng/L | [32] |
|          | LCM                 | Antibiotics | <LOQ–378 ng/L |      |
| Vietnam  | Surface water       | SMZ      | Antibiotics | 3.65–2778 ng/L |      |
### Table 1. Cont.

| Location   | Aquatic Environment | Chemical              | Category                        | Concentration       | Ref. |
|------------|---------------------|-----------------------|---------------------------------|---------------------|------|
| India      | Groundwater         | Ketoprofen (KPF)      | Non-steroidal anti-inflammatory drugs | <LOQ–23.4 ng/L     | [33] |
|            |                     | IBP                   | Non-steroidal anti-inflammatory drugs | <LOQ–49.4 ng/L     |      |
| Pakistan   | Groundwater         | Tigecycline           | Antibiotics                     | 21.3 ng/L           | [34] |
| Pakistan   | Groundwater         | Ciprofloxacin (CIP)   | Antibiotics                     | 15.2–262 ng/L       |      |
| United States | Drinking water     | CBZ                   | Antiepileptic                   | 51 ng/L             |      |
| United States | Drinking water     | DCF                   | Non-steroidal anti-inflammatory drugs | 1.2 ng/L           | [35] |
| United States | Drinking water     | SMX                   | Antibiotics                     | 110 ng/L            |      |
|            |                     | Naproxen              | Non-steroidal anti-inflammatory drugs | 32 ng/L            |      |

**Figure 1.** Detection results of PPCPs in surface water. (a) Detection frequencies of 104 articles; (b) the maximum concentrations (ng/L) of the most detected PPCPs in each analyzed continent. Reproduced with permission from [23].
Herein, the removal performance of PPCPs of different free radicals generated in various AOPs were analyzed and summarized systematically by in-depth analysis of the reaction mechanisms. Current status, future directions, perspectives and challenges of AOPs were further discussed.
Herein, the removal performance of PPCPs of different free radicals generated in various AOPs were analyzed and summarized systematically by in-depth analysis of the reaction mechanisms. Current status, future directions, perspectives and challenges of AOPs were further discussed.

2. Various AOPs

AOPs is the general term for the photochemical oxidation process, the electrochemical oxidation process, the wet air oxidation process, the ultrasonic oxidation process, the gamma ray/electron beam radiation process, the Fenton oxidation process, the ozone oxidation process, the persulfate-based oxidation process, etc. AOPs are employed either independently or in combination with other chemical processes for the removal of PPCPs. Prior to revealing the degradation mechanism of PPCPs, it is needed to analyze and summarize the generation of possible free radicals in different AOPs. Figure 4 summarized the possible free radicals generated in different AOPs.

2.1. Photochemical Oxidation

Photochemical oxidation processes can be achieved by two approaches—the photocatalytic oxidation method and the photo-excited oxidation method. The former uses a semiconductor (such as TiO$_2$ [67,68] and WO$_3$ [69,70]) as a photocatalyst. When the semiconductor makes contact with water, strongly oxidizing free radicals (i.e., HO·) are generated on its surface (as shown in Equations (1) and (2) [71,72]), which react with PPCPs and degrade them in water. As among the most promising photocatalyst materials, nano-TiO$_2$ is highly utilized to remove PPCPs from water, and nano-TiO$_2$ has been studied by numerous studies [73–75].

\[
\text{TiO}_2 + h\nu \rightarrow e_{\text{CB}}^- + h_{\text{VB}}^+ \quad (1)
\]

\[
h_{\text{VB}}^+ + \text{OH}^- \rightarrow \text{HO}· \quad (2)
\]
The latter method aims at enhancing the oxidation potential of oxidants under ultraviolet (UV) irradiation. In the process, free radicals with strong oxidizing properties such as \( \text{O}_2 \cdot^- \) and \( \text{HO}^- \) are generated by different oxidants [76]—during which, when \( \text{H}_2\text{O}_2 \) and peroxysulfate are employed as oxidants separately, \( \text{HO}^- \) and \( \text{SO}_4^{2-} \) are the main free radicals, respectively (Equations (3) and (4)) [77,78]. Otherwise, when peroxymonosulfate (PMS) is employed as an oxidant (Equation (4)), both \( \text{HO}^- \) and \( \text{SO}_4^{2-} \) are the main free radicals (Equation (5)) [78].

\[
\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \text{HO}^- \quad (3)
\]
\[
\text{S}_2\text{O}_8^{2-} + \text{hv} \rightarrow 2 \text{SO}_4^{2-} \quad (4)
\]
\[
\text{HSO}_5^- + \text{hv} \rightarrow \text{HO}^- + \text{SO}_4^{2-} \quad (5)
\]

New insights were provided by these innovative methods for the potential application of photochemical oxidation in water pollution remediation. For instance, improving the structure and properties of catalysts would have an impact on the generation of free radicals, and further on the removal of PPCPs. Fu et al. [79] investigated a three-dimensional core-shell composite material for PPCPs degradation, which exhibited a >90% removal efficiency of CBZ. Wang et al. [80] synthesized \( \text{Sr}@@\text{TiO}_2/\text{Uio-66-NH}_2 \) heterostructures as a photocatalyst for the degradation of ACE. In the report, strontium titanate was used as a precursor to obtain the heterostructures, resulting in the anchoring and dispersing of \( \text{Sr}@@\text{TiO}_2 \) on the surface of \( \text{Uio-66-NH}_2 \). The process exhibited an excellent removal rate towards ACE (over 90%). This method provides a new platform for the application of MOF materials in photocatalytic oxidation processes.

With mild reaction conditions and high oxidation capacity, the photochemical oxidation process is acknowledged as an eco-friendly method. Nevertheless, it has several limitations: (1) most of the catalysts used in photochemical oxidation are nanoparticles that are difficult to recover; (2) the electron–hole pairs generated by light are easily recombined and inactivated; (3) the UV radiation has a narrow absorption range and a low utilization rate of light energy. These limitations are urgently to be improved in later research.

### 2.2. Electrochemical Oxidation

The electrochemical oxidation method is among the most acclaimed methods to remove PPCPs from aqueous environments. In the process, free radicals (i.e., \( \text{HO}^- \)) are generated by the decomposition of \( \text{H}_2\text{O} \) and simultaneously the oxidation of hydroxyl ions via direct or indirect electrochemical oxidation. The reactions were expressed in Equations (6) and (7) [78,81].

\[
\text{H}_2\text{O} \rightarrow \text{HO}^- + \text{H}^+ + e^- \quad (6)
\]
\[
\text{OH}^- \rightarrow \text{HO}^- + e^- \quad (7)
\]

Recently, Guo et al. [82] fabricated single-atom copper (Cu) and nitrogen (N) atom-codoped graphene (Cu@NG) and used it as electrocatalytic anode. The efficient degradation of ACE was achieved with a current of 15 mA within 90 min. Although this method was beneficial to improve the electrocatalytic performance (100% degradation efficiency), there was a lack of toxicity analysis of intermediate products. Xia et al. [83] prepared a self-made \( \text{Ti/SnO}_2\text{Sb}_2\text{O}_3/\alpha,\beta-\text{Co-PbO}_2 \) electrode to degrade norfloxacin (NOR). After electrolysis for 60 min, the removal efficiency of NOR, chemical oxygen demand (COD) and total organic carbon (TOC) were 85.29%, 43.65% and 41.89%, respectively. However, as the results revealed, in the processes of decomposing PPCPs, the toxic intermediates which perhaps harm the environment might be produced because of the low TOC removal efficiency. Therefore, later studies are expected to investigate how to achieve high efficiency of TOC.

Due to the simple assembly, easy operation and convenient control, the electrochemical oxidation device provides a facile approach to large-scale application. Nonetheless, satisfactory decomposition of PPCPs may need high energy consumption and high equipment cost, and there is a shortage of electrochemical oxidation that needs to be further solved.
Furthermore, the preparation of inexpensive and efficient electrode materials for practical engineering applications is also needed.

2.3. Wet Air Oxidation

Wet air oxidation (WAO) uses O\(_2\) as an oxidant at high temperature (473–593 K) and high pressure (20–200 bar) to generate free radicals (i.e., HO·) [84]. A radical chain reaction is involved in the process of WAO [85]. In general, alkyl radical (R·) and hydroperoxide radicals (HO\(_2\)·) are generated by the reaction of PPCPs and O\(_2\), which is known as a chain induced reaction. The reaction was expressed in Equation (8) [78]. HO\(_2\)· can be converted to HO· via the chain transfer reaction, as shown in Equations (9) and (10).

\[
\begin{align*}
RH + O_2 &\rightarrow R\cdot + HO_2\cdot \\
2 HO_2\cdot &\rightarrow H_2O_2 + O_2 \\
HO_2\cdot + H_2O_2 &\rightarrow HO\cdot + H_2O + O_2
\end{align*}
\]

Zhu et al. [86] employed the WAO method to treat antibiotic wastewater, with the optimum TOC removal reached being 87.3%. Likewise, Boucher et al. [87] used the WAO method as a pretreatment technology in the removal of pharmaceuticals from hospital effluents. Significant removal rates (>90%) were achieved for all pharmaceuticals under 300 °C within 60 min. This experiment indicated the potential application of WAO to remove pharmaceuticals from hospital wastewater, which could effectively prevent the release of pharmaceuticals into surface water.

The WAO method has the advantages of eco-friendliness and splendid degradation performance; however, the operation conditions are harsh, which leads to high cost in the practical application. Thus, in further studies, inexpensive WAO technologies should be explored to realize the large-scale application for the removal of PPCPs in sewage treatment plants.

2.4. Ultrasonic Oxidation

The ultrasonic oxidation method is a process that applies acoustic waves with frequencies ranging from 15 kHz to 1 MHz at high temperature and high pressure to remove refractory PPCPs by oxidants (i.e., HO·) [52]. During the ultrasonic oxidation of pure water, the reaction chains progressed, as expressed in Equations (11)–(14) [88].

\[
\begin{align*}
H_2O + \text{\textsuperscript{\large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Large\Large\Large\\\Larger
Perea et al. [91] utilized ultrasonic oxidation to degrade seven types of pharmaceuticals with different chemical structures in distilled water environments. The highest removal of DCF was obtained at 24.4 W (a complete degradation efficiency was achieved within 30 min). To extend practical applications, experiments on various aqueous mixtures need to be explored.

The ultrasonic oxidation method has typical advantages such as no addition of chemicals and selective degradation depending on the nature of various PPCPs. Meanwhile, the ultrasonic oxidation method is simple to operate and convenient to use, and can degrade toxic PPCPs into small molecules with less toxicity or no toxicity. In addition, the ultrasonic oxidation method could be utilized as an assistive technology in combination with other AOPs to remove PPCPs from water.

However, ultrasonic degradation of wastewater is still at the laboratory stage—the degradation mechanism, reaction kinetics, reactor design and amplification of the ultrasonic degradation process have not been sufficiently studied. Moreover, it takes a lot of energy to produce ultrasonic waves. The above shortages make ultrasonic degradation difficult to realize practically in environmental remediation.

2.5. Gamma Ray/Electron Beam Radiation

Gamma ray/electron beam radiation can activate H$_2$O molecules, and cause the ionization of plenty of H$_2$O molecules simultaneously in a few seconds to generate free radicals (HO·, H·) [92,93]. The reactions were expressed in Equation (19).

$$8 \text{H}_2\text{O} \rightarrow 4 \text{HO}^- + 2 \text{e}_{\text{aq}}^- + 2 \text{H}^- + \text{H}_2 + \text{H}_2\text{O}_2 + 2 \text{H}_3\text{O}^+ \quad (19)$$

Chen et al. [92] used the electron beam method for the degradation of benzothiazole (BTH) in aqueous solution. Experiments showed that the method had an effective removal rate (up to 90%) towards BTH when the electron beam reaches 5 kGy. Toxicity calculations exhibited that the toxicity of most of the intermediates had been significantly reduced after radiation. As shown in Figure 5, most of the produced intermediates were non-toxic during the degradation of BTH, although there are still a few intermediates with higher toxicity than BTH. Trojanowicz et al. [93] utilized gamma ray radiation for the removal of endocrine disruptor BPA from wastewater. The degradation rate of BPA reached more than 90% in 5.5 min. These novel approaches provide new platforms for the removal of PPCPs from water.

![Figure 5. The results of the toxicity calculation of BTH and degradation intermediates in the electron beam irradiation system: (a) oral rat LD$_{50}$; (b) developmental toxicity; (c) bioaccumulation factor; and (d) mutagenicity. Reproduced with permission from [92].](image-url)
Compared with other AOPs, the advantage of radiation processes is that it can simultaneously generate $\text{HO}^\cdot$, $\text{e}_{\text{aq}}^-$, and $\text{H}^-$ with high efficiency, which will help to achieve high degradation rates towards target contaminants. However, the defects of gamma ray radiation are also obvious, such as the requirement of a long exposure time, the regular replacement of radionuclides, and the persistent potential risk of radiation contamination.

2.6. Fenton Oxidation

The mixture of $\text{Fe}^{2+}$ and $\text{H}_2\text{O}_2$ is defined as Fenton’s reagent [94]. The core process of Fenton oxidation is the reaction of $\text{Fe}^{2+}$ and $\text{H}_2\text{O}_2$—during which, $\text{H}_2\text{O}_2$ is activated by $\text{Fe}^{2+}$ to generate free radical $\text{HO}^\cdot$ and $\text{HO}_2^\cdot$, which are performed as the primary product and the secondary product, respectively (Equations (20)–(22)) [78,94].

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^\cdot + \text{HO}^- \tag{20}
\]

\[
\text{H}_2\text{O}_2 + \text{HO}^- \rightarrow \text{H}_2\text{O} + \text{HO}_2^- \tag{21}
\]

\[
2 \text{HO}^- \rightarrow \text{H}_2\text{O}_2 \tag{22}
\]

In recent research, the removal of CBZ and CAF from tap water by the Fenton oxidation process was studied by Sönmez et al. [95]. The results showed that the removal efficiencies of CBZ and CAF were calculated as 99.77% and 99.66%, respectively. The optimum performance was exhibited when the concentrations of $\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}$ were either 0.6 mg $\text{H}_2\text{O}_2$/L corresponding to 8 mg $\text{Fe}^{2+}$/L or 7.5 mg $\text{H}_2\text{O}_2$/L corresponding to 6 mg $\text{Fe}^{2+}$/L. The reaction conditions of Fenton oxidation are mild without high temperature or high pressure, and the device is also easy to operate independently or combined with other treatment technologies. However, there are several disadvantages of Fenton oxidation, such as the limit of the acidic condition and the production of a large amount of iron-containing sludge which is difficult to remove [96]. To overcome these disadvantages, Fe-based porous catalysts are used to replace the role of the dissolved ion $\text{Fe}^{2+}$, to get access to recycle, based on which the process are called as Fenton-like oxidation process, including photo-Fenton oxidation and electro-Fenton oxidation [97]. In the above Fenton-like oxidation processes, the removal of PPCPs in aqueous solution can be achieved within an expanded applicable pH range, and the degradation performance is also superior to that of the classical Fenton oxidation process.

2.7. The Ozone Oxidation Process

The ozone oxidation process is a widely used AOP in the removal of PPCPs. Ozone has high oxidizing ability with a redox potential of 2.07 eV [98]. In the process of ozone oxidation, $\text{HO}^\cdot$, $\text{O}_2^\cdot$, $\text{O}_3^\cdot$, and $\text{HO}_2^\cdot$ are generated by chain reactions, as shown in Equations (23)–(27) [99], which can decompose recalcitrant PPCPs efficiently.

\[
\text{O}_3 + \text{OH}^- \rightarrow \text{HO}_2^- + \text{O}_2 \tag{23}
\]

\[
3 \text{HO}_2^- + 2 \text{O}_3 \rightarrow 3 \text{O}_2^- + 3 \text{HO}_2^\cdot \tag{24}
\]

\[
\text{HO}_2^\cdot \rightarrow \text{O}_2^- + \text{H}^+ \tag{25}
\]

\[
\text{O}_2^- + \text{O}_3 \rightarrow \text{O}_3^- + \text{O}_2 \tag{26}
\]

\[
\text{O}_3^- + \text{H}_2\text{O} \rightarrow \text{HO}^- + \text{O}_2 + \text{OH}^- \tag{27}
\]

Yang et al. [100] employed a catalytic ozone oxidation/membrane filtration process to degrade SMX in aqueous environments. The catalyst was prepared by the method of impregnation combined with in situ precipitation. The degradation efficiency was up to 81.3% after the treatment of the oxidation–filtration combined process, which provides new ideas for the combination of AOPs and other technologies. Paucar et al. [101] investigated the degradation performance of the ozone oxidation process towards PPCPs in the secondary effluent of a sewage treatment plant. The results exhibited that the ozone oxidation process
is absolutely capable of decomposing a wide range of PPCPs in 10–15 min. These attempts provide novel methods for future studies [102–104].

The ozone oxidation process is a promising technology to decompose PPCPs from water environments, which has no secondary pollution. However, to date, there is no consensus on the mechanisms of the ozone oxidation process, and this needs further investigation. Meanwhile, the low utilization efficiency of ozone is also a significant issue for further water treatment applications.

2.8. Persulfate-Based Oxidation

Persulfate, including PDS (peroxodisulfate, $S_2O_8^{2-}$) and PMS ($HSO_5^-$), can be activated to produce free radical $SO_4^{2-}$, which has the characteristic of strong oxidation. Commonly, the persulfate can be activated by methods including thermal activation [105,106], mechanochemical activation [107,108], carbonaceous materials activation [109,110], alkali activation [111,112], electrochemical activation [113,114], UV activation [115,116], and transition metal activation [117,118]. The possible activation mechanisms were shown in Figure 6. Generally, in addition to $SO_4^{2-}$, free radicals including $SO_5^-$ and $HO_2^-$ can also be generated during various processes of persulfate activation [119,120].

![Possible activation mechanisms of persulfate](image_url)

**Figure 6.** Possible activation mechanisms of persulfate. Reproduced with permission from [78].

In a recent study [121], the heat-activated PMS process was introduced to remove ACE from water environments, during which sodium tetraborate was used as a catalyst. The results indicated that the degradation efficiencies of ACE were significantly high (nearly 100%) in multiple mediums including ultrapure water, lake water and groundwater within 15 minutes of reaction time. Weng et al. [122] utilized Fe$^0$ to activate the persulfate oxidation system via hydrodynamic cavitation. The removal rate of tetracycline (TC) was up to 97.80%. These studies have shed light on the potential implementation of the persulfate oxidation process on the removal of PPCPs.

Despite the fact that the persulfate-based oxidation process has been widely reported, it is still at the experimental stage. The industrial application needs to be studied thoroughly. Furthermore, later studies on persulfate-based oxidation processes should focus on evaluating their comprehensive performance, i.e., activation rates of persulfate, energy cost, toxicity and yield of by-products.

To evaluate the electrical energy per order ($E_{EO}$) values of various AOPs, significant differences among AOP efficiency were observed by Miklos et al. [123]. As shown in Figure 7, based on reported $E_{EO}$ values, AOPs were classified into (1) AOPs with median $E_{EO}$ values of <1 kWh/m$^3$, (2) processes with median $E_{EO}$ values in the range of 1–100 kWh/m$^3$ and (3) median $E_{EO}$ values of >100 kWh/m$^3$ (i.e., UV-based photocatalysis, ultrasound, and microwave-based AOPs), which are considered as not (yet) energy efficient AOPs. The
research provides an excellent figure of merit to directly compare and evaluate AOPs based on energy efficiency.

Figure 7. Overview of published EEO values of different AOPs sorted according to median values. For O₃- and UV-based AOP data, only substances resistant to direct ozonation/photolysis are shown. Median values and number of data points are reported on the second and third y-axis, respectively. Reproduced with permission from [123].

Overall, to efficiently remove PPCPs from aqueous environments, there has been a lot of effort to develop different types of AOPs or their combined technologies. Table 2 summarized the dominant free radicals, experimental conditions, and removal efficiencies of different processes on the removal of several PPCPs with the highest detection frequencies. However, among all the developed AOPs, there is still no process which can simultaneously achieve the goals of high efficiency, low cost and simple operation on the removal of PPCPs. Thus, further studies should focus on combining different types of free radicals and explore more advanced processes to make AOPs more considerable for industrial application.

Table 2. Degradation compilation of frequently detected PPCPs via various AOPs.

| PPCP | AOPs                                      | Dominant Radicals | Concentration of PPCPs | Reaction Time (min) | pH | Removal Rate (%) | Ref. |
|------|-------------------------------------------|-------------------|------------------------|---------------------|----|------------------|------|
|      | Photochemical oxidation                    | HO·, O₂⁻          | 8.75 mg/L              | 45                  | 6  | 99.77            | [124]|
| CBZ  | Persulfate-based + photochemical oxidation | SO₄²⁻, HO·, O₂⁻   | 5 ppm                  | 30                  | 7  | 97.1             | [125]|
|      | UV/chlorine oxidation                      | HO·, Cl⁻          | 40 µM                  | 60                  | 7  | 83.9             | [126]|
|      | Electrochemical oxidation                  | HO·, SO₄²⁻        | 1 µM                   | 5                   | 2  | 100              | [127]|
|      | Photo Fenton oxidation                     | HO·               | 285 ng/L               | 30                  | 6–7| 94               | [128]|
|      | Photo-assisted ozone oxidation             | HO·               | 5 mg/L                 | 2                   | 7 ± 0.2| >99.99| [44] |
|      | Sono-photocatalytic oxidation              | O₂⁻              | 10 ppm                 | 240                 | 7  | 93.37            | [129]|
|      | Electron beam radiation                    | HO·, H·           | 75 mg/L                | /                   | 6.3| 99.9             | [130]|
| DCF  | Photochemical oxidation                    | HO·               | 20 mg/L                | 270                 | 5  | 76               | [131]|
|      | Persulfate-based oxidation                 | HO·               | 50 µg/L                | 5                   | 4  | 96.8             | [132]|
|      | Fenton-like oxidation                      | HO·               | 20 mg/L                | 60                  | 5  | 86.62            | [133]|
|      | Ozone oxidation                           | HO·               | 29.6 mg/L              | 60                  | 7  | 73.3             | [134]|
|      | Persulfate-based oxidation                 | SO₄²⁻             | 20 mg/L                | 15                  | 5  | 90               | [135]|
Table 2. Cont.

| PPCP        | AOPs                         | Dominant Radicals | Concentration of PPCPs | Reaction Time (min) | pH   | Removal Rate (%) | Ref. |
|-------------|------------------------------|-------------------|------------------------|---------------------|------|------------------|------|
| SMX         | Photochemical oxidation      | HO·, O₂⁻          | 10 mg/L                | 60                  | 7.5  | 84               | [136]|
|             | Electrochemical oxidation    | HO·               | 74.45 mg/L             | 51.49               | 4.78 | 100              | [137]|
|             | Ultrasonic oxidation         | HO·               | 10 µM                  | 60                  | 7    | 97               | [138]|
|             | Photo-Fenton oxidation       | HO·               | 25 mg/L                | 15                  | 3    | 98.06            | [139]|
|             | Persulfate-based oxidation   | SO₄²⁻             | 0.04 mM                | 120                 | 3.4  | 100              | [140]|
|             | Gamma ray radiation          | HO·               | 39.48 µM               | /                   | 6.7  | 88.6             | [141]|

3. Different Free Radicals in the Removal of PPCPs

3.1. Hydroxyl Radical (HO·)

Free radical HO· has a redox potential of 2.80 V and extremely strong oxidizing potential [142]. In AOPs, the HO· is mainly generated via hydrogen abstraction and hydroxylation [143]. The HO· is a strong oxidant which can react with the unsaturated carbon-carbon bond, the carbon-nitrogen bond, the carbon-sulfur bond and other chemical bonds to decompose PPCPs, with non-selective chemical oxidation [144]. The Fenton oxidation process is a typical AOP, which generates HO· by chain reactions between H₂O₂ and Fe²⁺ under acidic conditions. Nevertheless, the Fenton oxidation process has the disadvantages of using excessive amounts of Fe²⁺ and H₂O₂, which resulted in low utilization of H₂O₂. Compared to the conventional Fenton oxidation process, the required H₂O₂ could be in situ generated by the electro-Fenton process, which saves cost and improves decomposition efficiency. Currently, Cui et al. [145] designed an electro-Fenton (EF) oxidation device to degrade carbamazepine (CBZ) in water. In the report, FeS₂/carbon felt was used as the cathode and Ti/IrO₂-RuO₂ was used as the anode of the EF device. The reaction between H₂O₂ and Fe²⁺ was accelerated by the cathode, which helped to produce more HO· to remove CBZ. The possible degradation pathways of CBZ were shown in Figure 8. Under the attack of HO·, CBZ molecules were finally mineralized and decomposed into harmless and small molecules with a degradation rate of 99.99%.

Du et al. [146] investigated Fe/Fe₃C@PC hybrid materials with core-shell structures as catalysts for the degradation of sulfadimethoxine (SMT) in the non-homogeneous Fenton process. The MIL-101(Fe) precursor was prepared by the solvothermal method. Then, the activated precursor was put in a tube furnace under a flowing argon atmosphere and heated to 800 °C for 6 h at a heating rate of 5 °C min⁻¹ to produce Fe/Fe₃C@PC. The removal of SMT was up to 96% at pH = 4 with a microcurrent of 25 mA. Furthermore, the degradation rate decreased with the increase in pH, due to decomposition into H₂O and O₂ when pH ≥ 4.5, which hindered the generation of HO· [147]. The oxidation potential of HO· decreased with the increase in pH (E⁰ = +2.8 V at pH = 0 and E⁰ = +1.98 V at pH = 14) [148]. As shown in Figure 9a, the dominant free radical was HO·. Density functional theory (DFT) calculations indicated the presence of internal microelectrolysis (IME) in Fe/Fe₃C@PC hybrid materials has greatly promoted the activation of H₂O₂ to generate HO·. During the electrolysis process, SMT molecules were attacked by HO· and ultimately decomposed into innocuous CO₂ and H₂O.
Figure 8. Degradation pathway of CBZ in the EF process with FeS₂/CF as a cathode. Reproduced with permission from [145].

Figure 9. Illustrations of mechanisms of different AOPs. (a) Proposed scheme of the mechanism of the hetero-EF process catalyzed by Fe/Fe₃C@PC. Reproduced with permission from [146]. (b) Activation of PDS and PMS through a electron transfer and b energy transfer reactions. Reproduced with permission from [149]. (c) Schematic illustration of the photocatalytic mechanism using carbon quantum dots modified tubular graphitic carbon nitride as material. Reproduced with permission from [150]. (d) Possible mechanisms of the visible light-driven MoS₂/PMS system. Reproduced with permission from [151].
In summary, HO·-based AOPs can effectively remove PPCPs from water environments. Nevertheless, there are still some difficulties in HO·-radicals-based AOPs. On the one hand, HO·-based AOPs have several limitations. For instance, to the best of our knowledge, HO·-based AOPs have the disadvantages of a large amount of reagents, no selectivity towards target substances, and narrow pH conditions (pH 3~4). Therefore, further optimization and exploration of degradation conditions are expected. On the other hand, the identification of HO· is significantly imprecise. Recently, Chen et al. [152] found that in the UV-based AOPs, the widely used scavenger alcohol will accidentally generate H2O2 in the process of eliminating HO·. These generated H2O2 will be photodissociated into HO·, thus affecting the accuracy of HO· quantification. Therefore, researchers should select suitable scavenger to eliminate HO· like N-butyl alcohol, and more accurate identification technologies should be proposed and promoted. Lastly, the HO·-based AOPs are still at the experimental research stage, when it comes to industrial application, existing problems such as high operation cost need to be solved. In the later research, how to realize practical application and improve the selectivity oxidation of target PPCPs are the current challenges of Fenton-like technologies. Meanwhile, efficient and stable catalysts should be developed to increase utilization efficiency and reduce energy cost.

3.2. Sulfate Radical (SO4−·)

Studies on sulfate radical (SO4−·) for pollutants removal began in 1996 [153]. Compared to HO·, SO4−· has a higher average redox potential (E0 = 2.5–3.1 V), a wider pH range (2–10) and a longer half-life (30–40 µs) [154]. The decomposition of SO4−· towards PPCPs was mainly achieved via electron transfer [155,156]. By activation through electron transfer, PDS or PMS molecules are converted to SO4−· [149,157]. Generally, persulfates are the main precursors of SO4−· (Figure 9b) [47,149]. Compared with the process without PDS, the decomposition efficiency of organic pollutants in the process with PDS was greatly accelerated [47,158]. In this system, the procedure of persulfate activization was a crucial process in AOPs. Theoretically, most of the organic matters in water environments could be removed by the oxidation of SO4−· [159]. Zhang et al. [160] used carbon nanofiber-loaded Co/Ag bimetallic nanoparticles (Co@CNFS-Ag) as catalysts for the heterogeneous activation of PMS and the efficient oxidation of amoxicillin (AMX). The excellent removal performance of AMX was realized by adjusting the dosage of catalyst, the reaction temperature and the pH condition. The results indicated that the optimal pH of this system was 7, which was environmentally friendly.

Affected by impurities and other interference, the degradation of some PPCPs in the actual water environments by SO4−· may produce intermediates, byproducts and residues that are even more toxic and difficult to degrade. Thus, the utilization of SO4−·-based AOPs needs to be further improved to eliminate their negative impacts. In addition, in the quenching identification process of SO4−·, the high concentration of added scavengers would cause numerous confounding effects on the persulfate-based process, thus affecting the generation of SO4−·. Therefore, adding scavengers may seriously mislead the interpretation of the mechanism of SO4−·-based AOPs [161]. Thus, the mechanism of adding scavengers to explain SO4−·-based AOPs should be cautious, and some controversial conclusions obtained by adding scavengers may need to be re-examined.

3.3. Superoxide Radical (O2−·)

Recently, superoxide radical (O2−·) has attracted increasing concern in environmental remediation because of its potential to destroy highly toxic organic chemicals which are carcinogenic in most cases [162]. The redox potential of O2−· is 2.4 V. O2−· can induce the degradation of PPCPs through an initial hydrogen abstraction step, which results in the formation of carbon-based radicals [163,164]. Then, carbon-based radicals combine with O2 to form peroxide intermediates. Afterwards, the formation of degradation products was realized [165]. O2−· is an important species involved in natural aquatic systems exposed to sunlight [166].
Photocatalysis, an AOP, has been shown to be an effective method for the generation of \( \text{O}_2^2^- \). Zhao et al. [150] prepared novel carbon quantum dots (CQDs)-modified tubular graphitic carbon nitride (g-C3N4) by an adsorption–polymerization method, which showed up to a 100% removal rate towards CBZ under visible light irradiation. It was further confirmed by electron spin resonance (ESR) analysis that the main active species for CBZ degradation were \( \text{O}_2^2^- \) and photogenerated holes (h\(^+\)). The detailed mechanism was shown in Figure 9c. Under the attack of \( \text{O}_2^2^- \) and h\(^+\), CBZ molecules were mineralized to harmless CO\(_2\) and H\(_2\)O. Dong et al. [151] established a visible light-driven PMS activation process dominated by \( \text{O}_2^2^- \). In the study, the generation of radicals was confirmed via combination with the scavenger test and electron paramagnetic resonance (EPR) detection. During the scavenger test, HO\(^-\) and SO\(_4^2^-\) were captured by methanol, HO\(^-\) was captured by isopropanol, \( \text{O}_2^2^- \) was captured by p-BQ, and the results indicated that HO\(^-\), SO\(_4^2^-\) and \( \text{O}_2^2^- \) were all generated in this system, among which \( \text{O}_2^2^- \) played a dominant role (Figure 10a). To further verify the generation of free radicals, EPR was employed to detect these free radicals, coupled with 5,5-dimethyl-1-pyrroline (DMPO) as a spin-trapping reagent to capture both SO\(_4^2^-\) and HO\(^-\). The intensity of characteristic peaks for DMPO-SO\(_4^2^-\) and DMPO-HO\(^-\) was observed (Figure 10b), verifying the existence of SO\(_4^2^-\) and HO\(^-\). As shown in Figure 10c, after the addition of methanol and DMPO, the characteristic peaks of DMPO-O\(_2^2^-\) were observed, confirming the generation of \( \text{O}_2^2^- \). The possible mechanism was exhibited in Figure 9d. Once irradiated with visible light, the charge carriers (i.e., electrons and holes) were generated on the surface of MoSe\(_2\) (Equation (28)). Additionally, photo-generated electrons react with O\(_2\) to produce O\(_2^2^-\) (Equation (29)). Due to the generation of photoelectrons, IBP, benzophenone-3 (BZP) and CBZ were decomposed in aqueous environments (Equation (30)). These studies on the generation and identification of \( \text{O}_2^2^- \) could provide mechanisms and theoretical bases for understanding the comprehensive processes of photocatalysis.

\[
\text{MoSe}_2 + \text{hv} \rightarrow e^- + h^+ \tag{28}
\]

\[
\text{O}_2 + e^- \rightarrow \text{O}_2^- \tag{29}
\]

\[
\text{O}_2^- + \text{target PPCP} \rightarrow \text{intermediates} + \text{CO}_2 + \text{H}_2\text{O} \tag{30}
\]

![Figure 10. (a) Scavenger test for the degradation of CBZ; (b) EPR spectra for the detection of HO\(^-\) and SO\(_4^2^-\) in the presence of 5,5-dimethyl-1-pyrrolineN-oxide (DMPO) at room temperature; (c) EPR spectra for the detection of O\(_2^2^-\) in the presence of DMPO and methanol, (CH\(_3\)OH) at room temperature. Reproduced with permission from [151]].

In photocatalysis reactions, \( \text{O}_2^- \) is an important reactive oxygen species. The study of the generation and presence of \( \text{O}_2^- \) could help to promote the understanding of the photocatalysis mechanism. Moreover, it could provide a guideline and theoretical basis for improving photocatalysis efficiency.
3.4. Reactive Chlorine Species (RCS)

The reactive chlorine species (RCS) of the UV/chlorine process is an emerging AOP used for the removal of PPCPs [167]. RCS (including Cl·, Cl2− and ClO−) were found to exhibit excellent removal rates towards many types of PPCPs including chlorine-resistant and UV-resistant PPCPs, i.e., CBZ and CAF [168]. Compared with HO·, Cl· has a high redox potential (2.5 V) as well as high selectivity [169]. Cl· can degrade PPCPs by the reactions of hydrogen abstraction, one-electron oxidation and chlorine addition [170].

As known, the UV/chlorine process is a more effective technology to remove PPCPs (i.e., CBZ, sulfamethoxazole and IBP) than the UV/H2O2 process for the reason that more effective free radicals are generated in the former process. In addition, the residual chlorine could be used for water disinfection in the former process. Thus, the UV/chlorine process could be considered as a possible alternative to the UV/H2O2 process for water treatment plants. Xiang et al. [171] investigated the degradation kinetics and pathways of IBP in the UV/chlorine process. In the same reaction condition, the primary rate constant of in UV/chlorine process was 3.3-fold higher than that of the UV/H2O2 process. Guo et al. [172] used a UV/chlorine process to treat various types of different PPCPs. Experimental results showed that HO·, Cl·, Cl2− and ClO− were generated in the process. The concentration of HO· decreased significantly with the increase in pH, while the concentration of ClO− decreased gradually, and the concentration of ClO− remained essentially constant. The concentration of ClO− was 3–4-fold higher than that of HO·, Cl· or Cl2−, so ClO− played a key role in the effective removal of PPCPs. In summary, the UV/chlorine process provides a new idea for the removal of PPCPs from waters.

It is worth noting that although the UV/chlorine process is more effective than the UV/H2O2 process, the toxicity of chlorinated products needs to be further evaluated. Meanwhile, when it comes to practical application, the high requirement of equipment and relatively high cost are also crucial issues which need to be further evaluated.

In addition to the above-mentioned free radicals, secondary radicals such as Br·, Br2−, ClBr−, and CO3− generated during the UV/chlorine process also contribute to promote the removal rates of PPCPs in waste water [173–178].

In future studies, the AOPs with different types of free radicals could be combined to achieve efficient removal towards PPCPs under facilitated and environmentally friendly conditions, to make it acceptable for large-scale industrial applications finally. Recently, Wang et al. [179] established a novel AOP of bisulfite (BS)/chlorine dioxide (ClO2) concomitant system, and the removal efficiency of atrazine (ATZ) in water was more than 85% within 3 min. In the above process, the BS was activated by ClO2. The scavenger experiments and ESR detection results indicated that the dominant radicals were ClO− and SO4−. Cheng et al. [180] used a combination process of solar irradiation and free available chlorine (FAC) to remove PPCPs from drinking water. It was found that that the in situ generation of HO·, RCS and ozone by FAC under solar irradiation contributed greatly to the degradation of PPCPs. PPCPs containing electron-donating groups were degraded more rapidly and preferentially by RCS and/or HO·. Paracetamol, IBP and ATZ that contain electron-withdrawing groups were degraded mainly by HO·. The combination of solar irradiation and FAC was well-established and inexpensive, which provided a novel idea for the combination of AOPs. In the removal of PPCPs, based on the structure and physicochemical properties of the target PPCPs, studies are expected to develop the combined activation technologies to achieve selective degradation or mineralization of PPCPs.

4. Perspective

This review briefly summarized multiple free radicals generated by AOPs for the removal of PPCPs and look towards the recent progress of various AOPs. In the process of contaminants remediation, AOPs have the advantages of strong oxidation potential, a rapid reaction rate and complete degradation compared to conventional oxidation processes, especially for low-concentration and recalcitrant pollutants. Thus, AOPs are acknowledged as ideal and prospecting technologies in the removal of PPCPs from practical water en-
environments. However, AOPs have disadvantages such as high operation cost and harsh experimental conditions, which make it difficult to apply AOPs at a large scale for industrial application. To achieve efficient degradation of PPCPs, the following suggestions were made for further studies.

1. To precisely identify the concentration of free radicals, more accurate approaches should be employed. The conventional radical identification methods are challenged because adding scavengers would cause negative effects on AOPs and influence the generation of free radicals. Other methods such as probe-based kinetic models, EPR and laser flash photolysis should be developed and employed to assist in identification of the free radicals in AOPs.

2. To achieve the practical application of AOPs, convenient and inexpensive approaches should be studied. At present, there are still some issues with AOPs, which need to be further studied. For example, the experimental operations are still complicated and have a high cost. Thus, while researchers focus on the efficiency of water treatment, convenient and inexpensive approaches should be studied to realize large-scale application.

3. To further study the reaction process and reveal the impacts of AOPs, the mechanism of AOPs in multiple mixture systems should be investigated in depth and the interference of impurity ions on the degradation reaction should be minimized.

4. To remove PPCPs from complex aqueous mixtures, a pilot-scale plant on the treatment of practical wastewater should be implemented instead of a laboratory scale experiment. Currently, most studies on the removal of PPCPs are focused on water environments containing limited given substances, which is unrealistic. Thus, practical wastewater (i.e., pharmaceutical discharges) should be used in later studies.

5. To selectively remove PPCPs from aqueous environments, AOPs should be further developed to adjust them to multiple water environments. In the later studies, the removal of PPCPs is expected to be achieved without affecting the existence of trace nutritious natural organic matters (NOMs) in water environments [181].

In addition, eco-friendly AOPs should be studied by adjusting experimental conditions, such as ultrasonic power, radiation dose, current density, temperature, pH, reaction time and chemical dosage. Future studies are advised to focus on the combination of AOPs and other available technologies to selectively and efficiently remove PPCPs from water environments in a green and environmental way.

Author Contributions: Conceptualization, Y.L. and S.Y.; methodology, L.L.; software, J.J.; validation, C.G., Y.L. and T.L.; formal analysis, Q.S.; investigation, L.W.; data curation, J.J.; writing—original draft preparation, J.J.; writing—review and editing, Y.L.; visualization, S.Y.; supervision, Y.L.; project administration, J.J. All authors have read and agreed to the published version of the manuscript.

Funding: This review was funded by the National Natural Science Foundation of China (NO. 42107090), the National Natural Science Foundation of Sichuan Province (2022NSFSC1076), and the Innovative Research Project for Graduate Students of Southwest Minzu University (NO. YB2022193).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare that the work is original research that has not been published previously, and is not under consideration for publication elsewhere. No conflict of interest exist in the submission of this review, and the review is approved by all authors for publication.

References
1. Noguera-Oviedo, K.; Aga, D.S. Lessons learned from more than two decades of research on emerging contaminants in the environment. J. Hazard. Mater. 2016, 316, 242–251. [CrossRef]
2. Wang, J.; Wang, S. Removal of pharmaceuticals and personal care products (PPCPs) from wastewater: A review. J. Environ. Manag. 2016, 182, 620–640. [CrossRef]
3. Arpin-Pont, L.; Bueno, M.J.M.; Gomez, E.; Fenet, H. Occurrence of PPCPs in the marine environment: A review. Environ. Sci. Pollut. Res. 2016, 23, 4978–4991. [CrossRef]

4. Caliman, F.A.; Gavriluce, M. Pharmaceuticals, Personal Care Products and Endocrine Disrupting Agents in the Environment—A Review. Clean-Soil Air Water 2009, 37, 277–303.

5. Ngo, T.H.; Van, D.A.; Tran, H.L.; Nakada, N.; Tanaka, H.; Huynh, T.H. Occurrence of pharmaceutical and personal care products in Cau River, Vietnam. Environ. Sci. Pollut. Res. 2021, 28, 12086–12091. [CrossRef]

6. Spurgeon, D.; Wilkinson, H.; Civil, W.; Hutt, L.; Armenise, E.; Kieboom, N.; Sims, K.; Besien, T. Worst-case ranking of organic chemicals detected in groundwater as surface waters in England. Sci. Total Environ. 2022, 835, 155101. [CrossRef]

7. Wang, Y.Q.; Lei, Y.; Liu, X.; Song, L.Y.; Hamid, N.; Zhang, R. Sulfonamide and tetracycline in landfill leachates from seven municipal solid waste (MSW) landfills: Seasonal variation and risk assessment. Sci. Total Environ. 2022, 825, 153956. [CrossRef]

8. Pisetta, A.M.; Roveri, V.; Guimaraes, L.L.; de Oliveira, T.M.N.; Correia, A.T. First report on the occurrence of pharmaceuticals and cocaine in the coastal waters of Santa Catarina, Brazil, and its related ecological risk assessment. Environ. Sci. Pollut. Res. 2022, 29, 63099–63111. [CrossRef]

9. Korkmaz, N.E.; Suvan-Hekimoglu, B.; Aksu, A.; Burak, S.; Caglar, N.B. Occurrence, sources and environmental risk assessment of pharmaceuticals in the Sea of Marmara, Turkey. Sci. Total Environ. 2022, 819, 152996. [CrossRef]

10. Anand, U.; Adelodun, B.; Cabreros, C.; Kumar, P.; Suresh, S.; Dey, A.; Ballesteros, F.; Bontempi, E. Occurrence, transformation, bioaccumulation, risk and analysis of pharmaceutical and personal care products from wastewater: A review. Environ. Chem. Lett. 2022. [CrossRef]

11. Liu, J.L.; Wong, M.H. Pharmaceuticals and personal care products (PPCPs): A review on environmental contamination in China. Environ. Int. 2013, 59, 208–224. [CrossRef]

12. Rahman, M.F.; Yanful, E.K.; Jasim, S.Y. Endocrine disrupting compounds (EDCs) and pharmaceuticals and personal care products (PPCPs) in the aquatic environment: Implications for the drinking water industry and global environmental health. J. Water Health 2009, 7, 224–243. [CrossRef]

13. Pereira, A.L.; Barros, R.T.D.; Pereira, S.R. Pharmacopollution and Household Waste Medicine (HWM): How reverse logistics is environmentally important to Brazil. Environ. Sci. Pollut. Res. 2017, 24, 24061–24075. [CrossRef]

14. Insani, W.N.; Qonita, N.A.; Jannah, S.S.; Nuraliyah, N.M.; Supadmi, W.; Gatera, V.A.; Alfian, S.D.; Abdulah, R. Improper disposal practice of unused and expired pharmaceutical products in Indonesian households. Heliyon 2020, 6, e04551. [CrossRef]

15. Yang, L.; Wang, T.Y.; Zhou, Y.Q.; Shi, B.; Bi, R.; Meng, J. Contamination, source and potential risks of pharmaceuticals and personal care products in wastewater treatment plant in Jordan. Environ. Sci. Process Impacts 2022, 28, 22716–22728. [CrossRef]

16. Chen, H.Z.; Chen, W.F.; Guo, H.G.; Lin, H.; Zhang, Y.B. Pharmaceuticals and personal care products in the seawater around a typical subtropical tourist city of China and associated ecological risk. Environ. Sci. Pollut. Res. 2021, 28, 22716–22728. [CrossRef]

17. Khan, S.A.; Hussain, D.; Abbasi, N.; Khan, T.A. Deciphering the adsorption potential of a functionalized green hydrogel nanocomposite for aspartame from aqueous phase. Chemosphere 2022, 289, 133232. [CrossRef]

18. Subedi, B.; Lee, S.; Moon, H.B.; Kannan, K. Emission of artificial sweeteners, select pharmaceuticals, and personal care products through sewage sludge from wastewater treatment plants in Korea. Environ. Int. 2014, 68, 33–40. [CrossRef]

19. Wang, Y.J.; Yin, T.R.; Kelly, B.C.; Gin, K.Y.H. Bioaccumulation behaviour of pharmaceuticals and personal care products in a constructed wetland. Chemosphere 2019, 222, 275–285. [CrossRef]

20. Sugihara, K. Effect of Environmental Factors on the Ecotoxicity of Pharmaceuticals and Personal Care Products. Yakugaku Zasshi J. Pharm. Soc. Jpn. 2018, 138, 277–280. [CrossRef]

21. Al-Mashaqbeh, O.; Alsafadi, D.; Dalahmeh, S.; Bartelt-Hunt, S.; Snow, D. Removal of Selected Pharmaceuticals and Personal Care Products in Wastewater Treatment Plant in Jordan. Water 2019, 11, 204. [CrossRef]

22. Ismanto, A.; Habibah, T.; Kristanti, R.A.; Maslukah, L.; Safinatah, N.; Sathishkumar, P. The abundance of endocrine-disrupting chemicals (EDCs) in downstream of the Bengawan Solo and Brantas rivers located in Indonesia. Chemosphere 2022, 297, 134151. [CrossRef]

23. Chaves, M.D.S.; Kulzer, J.; de Lima, P.D.P.; Barbosa, S.C.; Primel, E.G. Updated knowledge, partitioning and ecological risk of pharmaceuticals and personal care products in global aquatic environments. Environ. Sci. Process Impacts 2022. [CrossRef]

24. Xie, J.Y.; Liu, Y.F.; Wu, Y.F.; Li, L.R.; Fang, J.; Lu, X.Q. Occurrence, distribution and risk of pharmaceutical and personal care products in the Haihe River sediments, China. Environ. Sci. Pollut. Res. 2022, 30, 134874. [CrossRef]

25. Priya, A.K.; Gnanasekaran, L.; Rajendran, S.; Qin, J.Q.; Vasseghian, Y. Occurrences and removal of pharmaceutical and personal care products from aquatic systems using advanced treatment—A review. Environ. Res. 2022, 204, 112986. [CrossRef]

26. Mendoza, A.; Acena, J.; Perez, S.; de Alda, M.L.; Barcelo, D.; Gil, A.; Valcarcel, Y. Pharmaceuticals and iodinated contrast media in a hospital wastewater: A case study to analyse their presence and characterise their environmental risk and hazard. Environ. Res. 2015, 140, 225–241. [CrossRef]

27. Khan, S.A.; Hussain, D.; Khan, T.A. Mechanistic evaluation of metformin drug confiscation from liquid phase on itaconic acid/kaolin hydrogel nanocomposite. Environ. Sci. Pollut. Res. 2021, 28, 53298–53313. [CrossRef]

28. Slosarczyk, K.; Jakobczyk-Karpierz, S.; Rozkowski, J.; Witkowski, A.J. Occurrence of Pharmaceuticals and Personal Care Products in the Water Environment of Poland: A Review. Water 2021, 13, 2283. [CrossRef]
55. Chavez, A.M.; Gimeno, O.; Rey, A.; Plegio, G.; Oropesa, A.L.; Alvarez, P.M.; Beltran, F.J. Treatment of highly polluted industrial wastewater by means of sequential aerobic biological oxidation-ozone based AOPs. *Chem. Eng. J.* 2019, 361, 89–98. [CrossRef]

56. Gholami, M.; Souraki, B.A.; Pendashteh, A. Electro-activated persulfate oxidation (EC/PS) for the treatment of real oilfield produced water: Optimization, developed numerical kinetic model, and comparison with thermal/EC/PS and EC systems. *Process Saf. Environ. Protect.* 2021, 153, 384–402. [CrossRef]

57. Nashat, M.; Mossad, M.; El-Etribly, H.K.; Alalm, M.G. Optimization of electrochemical activation of persulfate by BDD electrodes for rapid removal of sulfamethazine. *Chemosphere* 2022, 286, 131579. [CrossRef]

58. Khodadadi, T.; Solgi, E.; Mortazavi, S.; Nourmoradi, H. Comparison of advanced oxidation methods of Fenton, UV/Fenton, and O-3/Fenton in treatment of municipal wastewater. *Desalin. Water Treat.* 2020, 206, 108–115. [CrossRef]

59. Rueda-Marquez, J.J.; Levchuk, I.; Manzano, M.; Sillanpaa, M. Toxicity Reduction of Industrial and Municipal Wastewater by Advanced Oxidation Processes (Photo-Fenton, UVC/H₂O₂, Electro-Fenton and Galvanic Fenton): A Review. *Catalysts* 2020, 10, 612. [CrossRef]

60. Zhu, H.; Ning, S.Y.; Li, Z.Z.Q.; Wang, X.P.; Fujita, T.; Wei, Y.Z.; Yin, X.B. Synthesis of bimetallic NbCo-piperazine catalyst and study on its advanced redox treatment of pharmaceuticals and personal care products by activation of permonosulfate. *Sep. Purif. Technol.* 2022, 285, 120345. [CrossRef]

61. Wang, J.L.; Wang, S.Z. Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants. *Chem. Eng. J.* 2018, 334, 1502–1517. [CrossRef]

62. Bojanowska-Czajka, A. Application of Radiation Technology in Removing Endocrine Micropollutants from Waters and Wastewaters—A Review. *Appl. Sci.* 2021, 11, 12032. [CrossRef]

63. Penalver, J.J.L.; Pacheco, C.V.G.; Polo, M.S.; Utrilla, J.R. Degradation of tetracyclines in different water matrices by advanced oxidation/reduction processes based on gamma radiation. *J. Chem. Technol. Biotechnol.* 2013, 88, 1096–1108. [CrossRef]

64. Ghasemian, S.; Nasuhoglu, D.; Omanovic, S.; Yargeau, V. Photoelectrocatalytic degradation of pharmaceutical carbamazepine using Sn-doped Sn-80%-W-20%-oxide electrodes. *Sep. Purif. Technol.* 2017, 188, 52–59. [CrossRef]

65. Prado, T.M.; Silva, F.L.; Carrico, A.; Lanza, M.R.D.; Fatibello, O.; Moraes, F.C. Photoelectrocatalytic degradation of caffeine using bismuth vanadate modified with reduced graphene oxide. *Mater. Res. Bull.* 2022, 145, 111539. [CrossRef]

66. Lee, J.; von Gunten, U.; Kim, J.H. Persulfate-Based Advanced Oxidation: Critical Assessment of Opportunities and Roadblocks. *Environ. Sci. Technol.* 2020, 54, 3064–3081. [CrossRef]

67. Lang, X.J.; Ma, W.H.; Chen, C.C.; Ji, H.W.; Zhao, J.C. Selective Aerobic Oxidation Mediated by TiO₂ Photocatalysis. *Accounts Chem. Res.* 2014, 47, 355–363. [CrossRef]

68. Augugliaro, V.; Bellardita, M.; Loddo, V.; Palmissano, G.; Palmissano, L.; Yurdakal, S. Overview on oxidation mechanisms of organic compounds by TiO₂ in heterogeneous photocatalysis. *J. Photochem. Photobiol. C Photochem. Rev.* 2012, 13, 224–245. [CrossRef]

69. Zhang, J.; Nosaka, Y. Generation of OH radicals and oxidation mechanism in photocatalysis of WO₃ and BiVO₄ powders. *J. Photochem. Photobiol. A Chem.* 2015, 303, 53–58. [CrossRef]

70. Yang, J.; Xiao, J.D.; Cao, H.B.; Guo, Z.; Rabeah, J.; Bruckner, A.; Xie, Y.B. The role of ozone and influence of band structure in WO3 photocatalysis and ozone integrated process for pharmaceutical wastewater treatment. *J. Hazard. Mater.* 2018, 360, 481–489. [CrossRef]

71. Savun-Hekimoglu, B.; Eren, Z.; Ince, N.H. Photocatalytic Destruction of Caffeine on Sepiolite-Supported TiO₂ Nanocomposite. *Sustainability* 2020, 12, 10314. [CrossRef]

72. Lan, Y.C.; Lu, Y.L.; Ren, Z.F. Mini review on photocatalysis of titanium dioxide nanoparticles and their solar applications. *Nano Energy* 2013, 2, 1031–1045. [CrossRef]

73. Ran, Z.L.; Fang, Y.H.; Sun, J.; Ma, C.; Li, S.F. Photocatalytic Oxidative Degradation of Carbamazepine by TiO₂ Irradiated by UV Light Emitting Diode. *Catalysts* 2020, 10, 540. [CrossRef]

74. Khraisheh, M.; Kim, J.; Campos, L.; Al-Muhtaseb, A.H.; Al-Hwari, A.; Al Ghouti, M.; Walker, G.M. Removal of pharmaceutical and personal care products (PPCPs) pollutants from water by novel TiO₂–Coconut Shell Powder (TCNSP) composite. *J. Ind. Eng. Chem.* 2014, 20, 979–987. [CrossRef]

75. Kumar, A.; Khan, M.; Fang, L.P.; Lo, J.M.C. Visible-light-driven N-TiO₂@SiO₂@Fe₃O₄ magnetic nanophotocatalysts: Synthesis, characterization, and photocatalytic degradation of PPCPs. *J. Hazard. Mater.* 2019, 370, 108–116. [CrossRef]

76. Cao, T.T.; Cui, H.; Zhou, D.D.; Ren, X.; Cui, C.W. Degradation mechanism of BPA under UUV irradiation: Efficiency contribution and DFT calculations. *Environ. Sci. Pollut. Res.* 2022. [CrossRef]

77. Chuang, Y.H.; Chen, S.; Chinn, C.J.; Mitch, W.A. Comparing the UV/Monochloramine and UV/Free Chlorine Advanced Oxidation Processes (AOPs) to the UV/Hydrogen Peroxide AOP under Scenarios Relevant to Potable Reuse. *Environ. Sci. Technol.* 2017, 51, 13859–13868. [CrossRef]

78. Wang, J.L.; Wang, S.Z. Reactive species in advanced oxidation processes: Formation, identification and reaction mechanism. *Chem. Eng. J.* 2020, 401, 126158. [CrossRef]

79. Fu, H.; Gray, K.A. TiO₂ (Core)/Crumpled Graphene Oxide (Shell) Nanocomposites Show Enhanced Photodegradation of Carbamazepine. *Nanomaterials* 2021, 11, 2087. [CrossRef]

80. Wang, Y.; Penas-Garzon, M.; Rodriguez, J.J.; Bedia, J.; Belver, C. Enhanced photodegradation of acetaminophen over Sr@TiO₂/UiO-66-NH₂ heterostructures under solar light irradiation. *Chem. Eng. J.* 2022, 446, 137229. [CrossRef]
81. Lozano, I.; Perez-Guzman, C.J.; Mora, A.; Mahlknecht, J.; Aguilar, C.L.; Cervantes-Aviles, P. Pharmaceuticals and personal care products in water streams: Occurrence, detection, and removal by electrochemical advanced oxidation processes. *Sci. Total Environ.* 2022, 797, 154348. [CrossRef]

82. Guo, D.; Huang, Z.; Liu, Y.Y.; Zhang, Q.; Yang, Y.L.; Hong, J.M. Incorporation of single-atom copper into nitrogen-doped graphene for acetaminophen electrocatalytic deactivation. *Appl. Surf. Sci.* 2022, 604, 154561. [CrossRef]

83. Xia, Y.J.; Yan, Y.; Hu, L.B.; Dai, Q.Z.; Ma, X.J.; Lou, J.Q.; Xia, Y. Enhanced Mechanism of Electrochemical Oxidation of Antibiotic Norfloxacin using a Ti/SnO2-Sb2O3/alpha, beta-Co-PbO2 Electrode. *J. Electrochem. Soc.* 2021, 168, 106510. [CrossRef]

84. Mishra, VS.; Mahajani, V.V.; Joshi, J.B. Wet air oxidation. *Ind. Eng. Chem. Res.* 1995, 34, 2–48. [CrossRef]

85. Luck, F. Wet air oxidation: Past, present and future. *Catal. Today* 1999, 53, 81–91. [CrossRef]

86. Zhu, L.B.; Sheng, D. Study on wet oxidation of antibiotic wastewater. *Oxid. Commun.* 2016, 39, 1640–1645.

87. Boucher, V.; Beaudon, M.; Ramirez, P.; Lemoine, P.; Volk, K.; Vargue, V.; Segura, P.A. Comprehensive evaluation of non-catalytic wet air oxidation as a pretreatment to remove pharmaceuticals from hospital effluents. *Environ. Sci. Wat. Res. Technol.* 2021, 7, 1301–1314. [CrossRef]

88. Boffito, D.C.; Crocella, V.; Pirola, C.; Neppolian, B.; Cerrato, G.; Ashokkumar, M.; Bianchi, C.L. Ultrasonic enhancement of the acidity, surface area and free fatty acids esterification catalytic activity of sulphated ZrO2-TiO2 systems. *J. Catal.* 2013, 297, 17–26. [CrossRef]

89. Joseph, J.M.; Destaillats, H.; Hung, H.M.; Hofmann, M.R. The sonochemical degradation of azobenzene and related azo dyes: Rate enhancements via Fenton’s reactions. *J. Phys. Chem. A* 2000, 104, 301–307. [CrossRef]

90. Sierra, R.S.C.; Zuniga-Benitez, H.; Penuela, G.A. Elimination of cephalixin and doxycycline under low frequency ultrasound. *Ultrason. Sonochem.* 2021, 79, 105777. [CrossRef]

91. Camargo-Perea, A.L.; Serna-Galvis, E.A.; Lee, J.; Torres-Palma, R.A. Understanding the effects of mineral water matrix on degradation of several pharmaceuticals by ultrasound: Influence of chemical structure and concentration of the pollutants. *Ultrason. Sonochem.* 2021, 73, 105500. [CrossRef]

92. Chen, L.; Yin, W.T.; Shao, H.Y.; Tu, M.X.; Ren, Y.F.; Mao, C.K.; Huo, Z.H.; Xu, G. The performance and pathway of benzothiazole degradation by electron beam irradiation. *Chemosphere* 2022, 303, 134964. [CrossRef]

93. Trojanowicz, M.; Bojanowska-Czajka, A.; Szreder, T.; Meczynska-Wielgosz, S.; Bobrowski, K.; Fornal, E.; Nichipor, H. Application of ionizing radiation for removal of endocrine disruptor bisphenol A from waters and wastewaters. *Chem. Eng. J.* 2021, 403, 126169. [CrossRef]

94. Wang, J.L.; Zhuan, R. Degradation of antibiotics by advanced oxidation processes: An overview. *Sci. Total Environ.* 2020, 701, 135023. [CrossRef]

95. Sonmez, G.; Bahadir, T.; Isik, M. Removal of selected pharmaceuticals from tap water by the Fenton process. *Int. J. Environ. Anal. Chem.* 2020. [CrossRef]

96. Wang, S.Z.; Wang, J.L. Triethanolammonium degradation by Fenton and Fe(II)-activated persulfate processes. *Chemosphere* 2018, 191, 97–105. [CrossRef]

97. El-Ghenemy, A.; Rodriguez, R.M.; Arias, C.; Centellas, F.; Garrido, J.A.; Cabot, P.L.; Brillas, E. Electro-Fenton and photocatalytic degradation of the antimicrobial sulfamethazine using a boron-doped diamond anode and an air-diffusion cathode. *J. Electroanal. Chem.* 2013, 701, 7–13. [CrossRef]

98. Wang, J.L.; Bai, Z.Y. Fe-based catalysts for heterogeneous catalytic ozonation of emerging contaminants in water and wastewater. *Chem. Eng. J.* 2017, 312, 79–98. [CrossRef]

99. Wang, J.L.; Chen, H. Catalytic ozonation for water and wastewater treatment: Recent advances and perspective. *Sci. Total Environ.* 2020, 704, 135249. [CrossRef]

100. Yang, Y.L.; Fu, W.Y.; Chen, X.X.; Chen, L.; Hou, C.Y.; Tang, T.H.; Zhang, X.H. Ceramic nanofiber membrane anchoring nanosized Mn2O3 catalytic ozonation of sulfamethoxazole in water. *J. Hazard. Mater.* 2022, 436, 129168. [CrossRef]

101. Paucar, N.E.; Kim, I.; Tanaka, H.; Sato, C. Ozone treatment process for the removal of pharmaceuticals and personal care products in wastewater. *Ozone Sci. Eng.* 2019, 41, 3–16. [CrossRef]

102. Verinda, S.B.; Muniroh, M.; Yulianto, E.; Maharani, N.; Gunawan, G.; Amalia, N.F.; Hobley, J.; Usman, A.; Nur, M. Degradation of ciprofloxacin in aqueous solution using ozone microbubbles: Spectroscopic, kinetics, and antibacterial analysis. *Helionyx* 2022, 8, e10137. [CrossRef]

103. Esquerrro, A.A.; Gadea, I.S.; Galvan, P.J.V.; Rico, D.P. Efficacy of atrazine pesticide reduction in aqueous solution using activated carbon, ozone and a combination of both. *Sci. Total Environ.* 2021, 764, 144301. [CrossRef]

104. Azuma, T.; Usui, M.; Hayashi, T. Inactivation of Antibiotic-Resistant Bacteria in Wastewater by Ozone-Based Advanced Water Treatment Processes. *Antibiotics* 2022, 11, 210. [CrossRef]

105. Johnson, R.L.; Tratnyek, P.G.; Johnson, R.O. Persulfate Persistence under Thermal Activation Conditions. *Environ. Sci. Technol.* 2008, 42, 9350–9356. [CrossRef]

106. Li, N.; Wu, S.; Dai, H.X.; Cheng, Z.J.; Peng, W.C.; Yan, B.B.; Chen, G.Y.; Wang, S.B.; Duan, X.G. Thermal activation of persulfates for organic wastewater purification: mechanism and influencing factors. *Chem. Eng. J.* 2022, 450, 137976. [CrossRef]

107. Liang, Z.L.; Peng, G.W.; Hu, J.P.; Hou, H.J.; Cai, C.; Yang, X.R.; Chen, S.J.; Liu, L.; Liang, S.; Xiao, K.K.; et al. Mechanochemically assisted persulfate activation for the facile recovery of metals from spent lithium ion batteries. *Waste Manag.* 2022, 150, 290–300. [CrossRef]

108. Liu, X.T.; Zhang, X.H.; Shao, K.; Lin, C.Y.; Li, C.B.; Ge, F.Z.; Dong, Y.J. Fe-0 activated persulfate-assisted mechanochemical destruction of expired compound sulfamethoxazole tablets. *RSC Adv.* 2016, 6, 20938–20948. [CrossRef]
109. Huang, W.Q.; Xiao, S.; Zhong, H.; Yan, M.; Yang, X. Activation of persulfates by carbonaceous materials: A review. Chem. Eng. J. 2021, 418, 129297. [CrossRef]

110. Oyekunle, D.T.; Zhou, X.Q.; Shahzad, A.; Chen, Z.Q. Review on carbonaceous materials as persulfate activators: Structure-performance relationship, mechanism and future perspectives on water treatment. J. Mater. Chem. A 2019, 7, 8012–8050. [CrossRef]

111. Huang, M.J.; Han, Y.; Xiang, W.; Zhong, D.L.; Wang, C.; Zhou, T.; Wu, X.H.; Mao, J. In situ-formed phenoxyl radical on the CuO surface triggers efficient persulfate activation for phenol degradation. Environ. Sci. Technol. 2021, 55, 15361–15370. [CrossRef]

112. Zheng, M.; Xu, G.; Zhao, L.; Pei, J.C.; Wu, M.H. Comparison of EB-radiolysis and UV/H<sub>2</sub>O<sub>2</sub> pathways. Water Res. 2017, 113, 80–88. [CrossRef]

113. Song, H.R.; Yan, L.X.; Jiang, J.; Ma, J.; Zhang, Z.X.; Zhang, J.M.; Liu, P.X.; Yang, T. Electrochemical activation of persulfates at BDD anode: Radical or nonradical oxidation? Water Res. 2018, 128, 393–401. [CrossRef]

114. Li, J.; Liu, Y.H.; Huang, S.; Zhang, Y.; Song, Z.J.; Shi, Y.J.; Jin, M.C.; Wang, Q.; Wei, Z.S. Hydrodynamic cavitation-enhanced heterogeneous activation of persulfate for tetracycline degradation: Synergistic effects, degradation mechanism and pathways. Chem. Eng. J. 2022, 431, 134238. [CrossRef]

115. Miklos, D.B.; Remy, C.; Jekel, M.; Linden, K.G.; Drewes, J.E.; Hubner, U. Evaluation of advanced oxidation processes for water and wastewater treatment—A critical review. Water Res. 2018, 139, 118–131. [CrossRef]

116. Constantin, M.A.; Chiriac, F.L.; Gheorghe, S.; Constantin, L.A. Degradation of Carbamazepine from Aqueous Solutions via TiO<sub>2</sub>-Assisted Photo Catalyze. Toxics 2022, 10, 168. [CrossRef]

117. Yang, L.W.; Jia, Y.Y.; Peng, Y.Q.; Zhou, P.; Yu, D.A.; Zhao, C.L.; He, J.J.; Zhan, C.A.L.; Lai, B. Visible-light-induced activation of persulfate by self-assembled EHPDI/TiO<sub>2</sub> photocatalyst toward efficient degradation of carbamazepine. Sci. Total Environ. 2021, 783, 146996. [CrossRef]

118. Zheng, M.; Xu, G.; Zhao, L.; Pei, J.C.; Wu, M.H. Comparison of EB-radiolysis and UV/H<sub>2</sub>O<sub>2</sub>-degradation of CBZ in pure water and solutions. Nucl. Sci. Tech. 2015, 26, 020302. [CrossRef]

119. Feijoo, S.; Kamali, M.; Pham, Q.K.; Assoumani, A.; Lestremau, F.; Cabooter, D.; Dewil, R. Electrochemical Advanced Oxidation of Carbamazepine: Mechanism and optimal operating conditions. Chem. Eng. J. 2022, 446, 137114. [CrossRef]

120. De la Cruz, N.; Gimenez, J.; Esplugas, S.; Grandjean, D.; de Alencastro, L.F.; Pulgarin, C. Degradation of 32 emergent contaminants via visible-light for enhanced degradation of sulfonamides without catalyst. Water Res. 2022, 173, 464–474. [CrossRef]

121. Weng, M.T.; Cai, M.Q.; Xie, Z.Q.; Dong, C.Y.; Zhang, Y.; Song, Z.J.; Shi, Y.J.; Jin, M.C.; Wang, Q.; Wei, Z.S. Hydrodynamic cavitation-enhanced heterogeneous activation of persulfate for tetracycline degradation: Synergistic effects, degradation mechanism and pathways. Chem. Eng. J. 2022, 431, 134238. [CrossRef]

122. Huang, W.Q.; Xiao, S.; Zhong, H.; Yan, P.; Gao, N.Y. Degradation of carbamazepine by UV/chlorine advanced oxidation process and formation of disinfection by-products. Environ. Sci. Pollut. Res. 2016, 23, 16448–16455. [CrossRef]

123. Cheng, X.; Guo, H.G.; Zhang, Y.L.; Wu, X.; Liu, Y. Non-photochemical production of singlet oxygen via activation of persulfate by carbon nanotubes. Water Res. 2017, 113, 80–88. [CrossRef]

124. Deng, X.Y.; Zhao, Z.W.; Wang, C.; Chen, R.; Du, J.Y.; Shi, W.X.; Cui, F.Y. Insight into the nonradical mechanism of persulfate activation via visible-light for enhanced degradation of sulfonamides without catalyst. Appl. Catal. B-Environ. 2022, 316, 121653. [CrossRef]

125. Feijoo, S.; Kamali, M.; Pham, Q.K.; Assoumani, A.; Lestremau, F.; Cabooter, D.; Dewil, R. Electrochemical Advanced Oxidation of Carbamazepine: Mechanism and optimal operating conditions. Chem. Eng. J. 2022, 446, 137114. [CrossRef]

126. De la Cruz, N.; Gimenez, J.; Esplugas, S.; Grandjean, D.; de Alencastro, L.F.; Pulgarin, C. Degradation of 32 emergent contaminants by UV and neutral photo-fenton in domestic wastewater effluent previously treated by activated sludge. Water Res. 2012, 46, 1947–1957. [CrossRef]
135. Xian, G.; Zhang, G.M.; Chang, H.Z.; Zhang, Y.; Zou, Z.G.; Li, X.Y. Heterogeneous activation of persulfate by Co$_3$O$_4$-CeO$_2$ catalyst for diclofenac removal. J. Environ. Manag. 2019, 234, 265–272. [CrossRef]
136. Makropoulou, T.; Kortidis, I.; Davididou, K.; Motaung, D.E.; Chatzisyimeon, E. Photocatalytic facile ZnO nanostructures for the elimination of the antibiotic sulfamethoxazole in water. J. Water Process. Eng. 2020, 36, 101299. [CrossRef]
137. Wan, J.T.; Jin, C.J.; Liu, B.H.; She, Z.L.; Gao, M.C.; Wang, Z.Y. Electrochemical oxidation of sulfamethoxazole using Ti/SnO$_2$-Sc/Co-PbO$_2$ electrode through AN-PSO. J. Sbr. Chem. Soc. 2019, 84, 713–727. [CrossRef]
138. Al-Hamadani, Y.A.J.; Chu, K.H.; Flora, J.R.V.; Kim, D.H.; Jang, M.; Sohn, J.; Joo, W.; Yoon, Y. Sonocatalytic degradation enhancement for ibuprofen and sulfamethoxazole in the presence of glass beads and single-walled carbon nanotubes. Ultrason. Sonochem. 2016, 32, 440–448. [CrossRef]
139. Rostami, F.; Ramavandi, B.; Arefeinia, H.; Nasrzadeh, F.; Hashemi, S. Sulfamethoxazole antibiotic removal from aqueous solution and hospital wastewater using photo-Fenton process. Desalin. Water Treat. 2020, 184, 388–394. [CrossRef]
140. Wang, S.Z.; Wang, J.L. Synergistic effect of PMS activation by Fe$_{0.1}$Fe$_{0.9}$O$_4$ anchored on N, S O co-doped carbon composite for degradation of sulfamethoxazole. Chem. Eng. J. 2022, 427, 131960. [CrossRef]
141. Kim, H.Y.; Kim, T.H.; Cha, S.M.; Yu, S. Degradation of sulfamethoxazole by ionizing radiation: Identification and characterization of radiolytic products. Chem. Eng. J. 2017, 313, 556–566. [CrossRef]
142. Gligorovski, S.; Strekowski, R.; Barbati, S.; Vione, D. Environmental Implications of Hydroxyl Radicals (center dot OH). J. Environ. Manag. 2019, 247–254. [CrossRef]
143. Sirtori, C.; Aguera, A.; Carra, I.; Perez, J.A.S. Identification and monitoring of thiabendazole transformation products in water during Fenton degradation by LC-QTOF-MS. Anal. Bioanal. Chem. 2014, 406, 5323–5337. [CrossRef]
144. Babu, S.G.; Ashokkumar, M.; Neppolian, B. The Role of Ultrasound on Advanced Oxidation Processes. Top. Curr. Chem. 2016, 374, 75. [CrossRef]
145. Cui, T.Y.; Xiao, Z.H.; Wang, Z.B.; Liu, C.; Song, Z.L.; Wang, Y.P.; Zhang, Y.T.; Li, R.Y.; Xu, B.B.; Qi, F.; et al. FeS$_2$/carbon felt as an efficient electro-Fenton cathode for carbamazepine degradation and detoxification: In-depth discussion of reaction contribution and empirical kinetic model. Environ. Pollut. 2021, 282, 110723. [CrossRef]
146. Du, X.; Fu, W.; Su, P.; Cai, J.; Zhou, M. Internal-micro-electrolysis-enhanced heterogeneous electro-Fenton process catalyzed by Fe/FesCe@PC core-shell hybrid for sulfamethazine degradation. Chem.Eng.J. 2020, 398, 125681. [CrossRef]
147. Oturan, M.A.; Aaron, J.J. Advanced Oxidation Processes in Water/Wastewater Treatment: Principles and Applications. A Review. Crit. Rev. Environ. Sci. Technol. 2014, 44, 2577–2641. [CrossRef]
148. Xu, L.J.; Wang, J.L. Fenton-like degradation of 2,4-dichlorophenol using Fe$_3$O$_4$ magnetic nanoparticles. Appl. Catal. B Environ. 2012, 123, 117–126. [CrossRef]
149. He, S.; Chen, Y.; Li, X.; Zeng, L.; Zhu, M. Heterogeneous Photocatalytic Activation of Persulfate for the Removal of Organic Contaminants in Water: A Critical Review. ACS EST Engg. 2022, 2, 527–546. [CrossRef]
150. Zhao, C.; Liao, Z.; Liu, W.; Liu, F.; Ye, J.; Liang, J.; Li, Y. Carbon quantum dots modified tubular g-C$_3$N$_4$ with enhanced photocatalytic activity for carbamazepine elimination: Mechanisms, degradation pathway and DFT calculation. J. Hazard. Mater. 2020, 381, 120957. [CrossRef]
151. Dong, C.; Wang, Z.; Ye, Z.; He, J.; Zheng, Z.; Gong, X.; Zhang, J.; Lo, I.M.C. Superoxide radicals dominated visible light driven peroxymonosulfate activation using molybdenum selenide (MoSe$_2$) for boosting catalytic degradation of pharmaceuticals and personal care products. Appl. Catal. B Environ. 2021, 296, 120223. [CrossRef]
152. Wang, L.; Li, B.Q.; Dionysiou, D.D.; Chen, B.Y.; Yang, J.; Li, J. Overlooked Formation of H$_2$O$_2$ during the Hydroxyl Radical-Scavenging Process When Using Alcohols as Scavengers. Environ. Sci. Technol. 2022, 56, 3386–3396. [CrossRef]
153. Anipsitakis, G.P.; Dionysiou, D. Degradation of organic contaminants in water with sulfate radicals generated by the conjunction of peroxymonosulfate with cobalt. Environ. Sci. Technol. 2003, 37, 4790. [CrossRef]
154. Hu, P.D.; Long, M.C. Cobalt-catalyzed sulfite radical-based advanced oxidation: A review on heterogeneous catalysts and applications. Appl. Catal. B Environ. 2016, 181, 103–117. [CrossRef]
155. Ahmed, M.M.; Barbati, S.; Doumenq, P.; Chiron, S. Sulfate radical anion oxidation of diclofenac and sulfamethoxazole for water decontamination. Chem. Eng. J. 2012, 197, 440–447. [CrossRef]
156. Norman, R.O.C.; Storey, P.M.; West, P.R. Electron spin resonance studies. Part XXV. Reactions of the sulphate radical anion with organic compounds. J. Chem. Soc. B Phys. Org. 1970, 1087–1095. [CrossRef]
157. Yang, Y.; Li, X.; Zhou, C.Y.; Xiong, W.P.; Zeng, G.M.; Huang, D.L.; Zhang, C.; Wang, W.J.; Song, B.A.; Tang, X.; et al. Recent advances in application of graphitic carbon nitride-based catalysts for degrading organic contaminants in water through advanced oxidation processes beyond photocatalysis: A critical review. Water Res. 2020, 184, 116200. [CrossRef]
158. Gong, J.; Zhang, J.S.; Lin, H.J.; Yuan, J.Y. “Cooking carbon in a solid salt”: Synthesis of porous heteroatom-doped carbon foams for enhanced organic contaminant degradation under visible light. Appl. Mater. Today 2018, 12, 168–176. [CrossRef]
159. Watts, R.J.; Ahmad, M.; Hohner, A.K.; Teel, A.L. Persulfate activation by glucose for in situ chemical oxidation. Water Res. 2018, 133, 247–254. [CrossRef]
160. Zhang, Y.; Zhang, B.T.; Teng, Y.G.; Zhao, J.J.; Kuang, L.L.; Sun, X.J. Carbon nanofibers supported Co/Ag bimetallic nanoparticles for heterogeneous activation of peroxymonosulfate and efficient oxidation of amoxicillin. J. Hazard. Mater. 2020, 400, 123290. [CrossRef]
161. Gao, L.W.; Guo, Y.; Zhan, J.H.; Yu, G.; Wang, Y.J. Assessment of the validity of the quenching method for evaluating the role of reactive species in pollutant abatement during the persulfate-based process. Water Res. 2022, 221, 118730. [CrossRef]
162. Fang, G.D.; Dionysiou, D.D.; Al-Abed, S.R.; Zhou, D.M. Superoxide radical driving the activation of persulfate by magnetite nanoparticles: Implications for the degradation of PCBs. Appl. Catal. B Environ. 2013, 129, 325–332. [CrossRef]

163. Baum, R.M. Superoxide theory of oxygen-toxicity is center of heated debate. Chem. Eng. News 1984, 62, 20–26. [CrossRef]

164. Sawyer, D.T.; Valentine, J.S. How super is superoxide. Accounts Chem. Res. 1981, 14, 393–400. [CrossRef]

165. Frimer, A.A.; Farkashsolomon, T.; Aljadeff, G. Mechanism of the superoxide anion radical (·O2−) mediated oxidation of diarylmethanes. J. Org. Chem. 1986, 51, 2093–2098. [CrossRef]

166. Ma, J.; Zhou, H.; Yan, S.; Song, W. Kinetics studies and mechanistic considerations on the reactions of superoxide radical ions with dissolved organic matter. Water Res. 2018, 149, 56–64. [CrossRef]

167. Sharma, V.K.; Triantis, T.M.; Antoniou, M.G.; He, X.X.; Pelaez, M.; Han, C.S.; Song, W.H.; O’Shea, K.E.; de la Cruz, A.A.; Kaloudis, T.; et al. Destruction of microcystins by conventional and advanced oxidation processes: A review. Sep. Purif. Technol. 2012, 91, 3–17. [CrossRef]

168. Yang, X.; Sun, J.L.; Fu, W.J.; Shang, C.; Li, Y.; Chen, Y.W.; Gan, W.H.; Fang, J.Y. PPCP degradation by UV/chlorine treatment and its impact on DBP formation potential in real waters. Water Res. 2016, 98, 309–318. [CrossRef]

169. Hirakawa, T.; Nosaka, Y. Properties of O·(center dot)- and OH center dot formed in TiO2 aqueous suspensions by photocatalytic reaction and the influence of H2O2 and some ions. Langmuir 2002, 18, 3247–3254. [CrossRef]

170. Minakata, D.; Kamath, D.; Maetzold, S. Mechanistic Insight into the Reactivity of Chlorine-Derived Radicals in the Aqueous-Phase UV Chlorine Advanced Oxidation Process: Quantum Mechanical Calculations. Environ. Sci. Technol. 2017, 51, 6918–6926. [CrossRef]

171. Xiang, Y.Y.; Fang, J.Y.; Shang, C. Kinetics and pathways of ibuprofen degradation by the UV/chlorine advanced oxidation process. Water Res. 2016, 90, 301–308. [CrossRef]

172. Guo, K.H.; Wu, Z.H.; Shang, C.; Yao, B.; Hou, S.D.; Yang, X.; Song, W.H.; Fang, J.Y. Radical Chemistry and Structural Relationships of PPCP Degradation by UV/Chlorine Treatment in Simulated Drinking Water. Environ. Sci. Technol. 2017, 51, 10431–10439. [CrossRef]

173. Wang, Z.Y.; An, N.; Shao, Y.S.; Gao, N.Y.; Du, E.D.; Xu, B. Experimental and simulation investigations of UV/persulfate treatment in presence of bromide: Effects on degradation kinetics, formation of brominated disinfection byproducts and bromate. Sep. Purif. Technol. 2020, 242, 116767. [CrossRef]

174. Lei, Y.; Lei, X.; Westerhoff, P.; Tong, X.Y.; Ren, J.N.; Zhou, Y.J.; Cheng, S.S.; Ouyang, G.F.; Yang, X. Bromine Radical (Br(·center dot)) and Br-2(center dot-) Reactivity with Dissolved Organic Matter and Brominated Organic Byproduct Formation. Environ. Sci. Technol. 2022, 56, 5189–5199. [CrossRef]

175. Liu, Y.Q.; He, X.X.; Duan, X.D.; Fu, Y.S.; Fatta-Kassinos, D.; Dionysiou, D.D. Significant role of UV and carbonate radical on the degradation of oxytetracycline in UV-AOPs: Kinetics and mechanism. Water Res. 2016, 95, 195–204. [CrossRef]

176. Gao, J.; Duan, X.D.; O’Shea, K.; Dionysiou, D.D. Degradation and transformation of bisphenol A in UV/Sodium percarbonate: Dual role of carbonate radical anion. Water Res. 2020, 171, 115394. [CrossRef]

177. Zhu, S.M.; Tian, Z.C.; Wang, P.; Zhang, W.Q.; Bu, L.J.; Wu, Y.T.; Dong, B.Z.; Zhou, S.Q. The role of carbonate radicals on the kinetics, radical chemistry, and energy requirement of UV/chlorine and UV/H2O2 processes. Chemosphere 2021, 278, 130499. [CrossRef]

178. Li, Y.; Dong, H.; Xiao, J.; Li, L.; Chu, D.; Hou, X.; Xiang, S.; Dong, Q.; Zhang, H. Advanced oxidation processes for water purification using percarbonate: Insights into oxidation mechanisms, challenges, and enhancing strategies. J. Hazard. Mater. 2022, 442, 130014. [CrossRef]

179. Wang, Z.Y.; Li, J.; Song, W.; Ma, R.; Yang, J.X.; Zhang, X.L.; Huang, F.; Dong, W.Y. Rapid degradation of atrazine by a novel advanced oxidation process of bisulfite/chlorine dioxide: Efficiency, mechanism, pathway. Chem. Eng. J. 2022, 445, 136558. [CrossRef]

180. Cheng, S.S.; Zhang, X.R.; Song, W.H.; Pan, Y.H.; Lambropoulou, D.; Zhong, Y.; Du, Y.; Nie, J.X.; Yang, X. Photochemical oxidation of PPCPs using a combination of solar irradiation and free available chlorine. Sci. Total Environ. 2019, 682, 629–638. [CrossRef]

181. Yang, Z.C.; Qian, J.S.; Shan, C.; Li, H.C.; Yin, Y.Y.; Pan, B.C. Toward Selective Oxidation of Contaminants in Aqueous Systems. Environ. Sci. Technol. 2021, 55, 14494–14514. [CrossRef]