

Review



Degradation of Micropollutants and Formation of Oxidation By-Products during the Ozone/Peroxymonosulfate System: A Critical Review

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Abstract: The O_3 /PMS system has appeared as an effective wastewater treatment method because of the simultaneous generation of hydroxyl radicals ($^{\circ}OH$) and sulfate radicals ($SO_4^{\circ-}$). Many research achievements have been made on the degradation of micropollutants and the reaction mechanism of the O_3 /PMS system. However, an integral understanding of the O_3 /PMS system is lacking, which limits the development of safe and effective AOP-based water treatment schemes. Therefore, in this review, the degradation effects, toxicity changes, and reaction mechanisms of various micropollutants in the O_3 /PMS system are reviewed. The formation of oxidation by-products (OBPs) is an important issue that affects the practical application of O_3 /PMS systems. The formation mechanism and control methods of OBPs in the O_3 /PMS system are overviewed. In addition, the influence of different reaction conditions on the O_3 /PMS system are comprehensively evaluated. Finally, future research needs are proposed based on the limited understanding of O_3 /PMS systems in the degradation of micropollutants and formation of OBPs. Specifically, the formation rules of several kinds of OBPs during the O₃/PMS system are not completely clear yet. Furthermore, pilot-scale research, the operational costs, sustainability, and general feasibility of the O_3/PMS system also need to be studied. This review can offer a comprehensive assessment on the O3/PMS system to fill the knowledge gap and provide guidance for the future research and engineering applications of the O₃/PMS system. Through this effort, the O₃/PMS system can be better developed and turned towards practical applications.

Keywords: ozone; peroxymonosulfate; micropollutants; oxidation by-products

1. Introduction

At present, the emergence of some pollutants (such as drugs, personal care products, endocrine disruptors, and other refractory organics) pose a threat to water quality and safety, which has aroused widespread concern [1–3]. Sulfate radicals ($SO_4^{\bullet-}$)-based advanced oxidation processes (AOPs) have received widespread attention owing to their strong oxidation ability, fast reaction rate, and wide applicability to contaminants in wastewater [4–6]. $SO_4^{\bullet-}$ can be obtained by activation of PMS through various methods, which include ultraviolet light (UV) irradiation, heating, or addition of transition metals, carbon materials and ozone (O_3) [4,7–9]. As a strong oxidant, O_3 can activate PMS to produce $SO_4^{\bullet-}$, while at the same time it will decompose to produce a large amount of hydroxyl radicals ($^{\bullet}OH$) [10–12]. In addition, singlet oxygen ($^{1}O_2$) and superoxide radicals ($O_2^{\bullet-}$) also can be generated in the process of O_3 activating PMS [13,14]. Under the combined action of these reactive oxygen species (ROS), different types of micropollutants can be



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). efficiently degraded. Specifically, the results of studies showed that O_3/PMS achieved 81% removal of ATZ in 10 min [10], and PMT was eliminated by 99.27% approximately in O_3/PMS system within 10 min [15], while *p*CBA was fully degraded by O_3/PMS in less than 5 min [16]. Furthermore, Gholikandi et al. reported that in terms of sludge stabilization and dewatering, O_3/PMS was a better choice than other processes (i.e., O_3 , O_3/H_2O_2 , O_3/PS) [17]. The study of Andrés et al. indicated that the O_3/PMS combination produced a synergistic effect in the inactivation of microorganisms [18]. All these studies have shown that the O_3/PMS system has a very great application potential in water treatment.

However, ROS will unavoidably react with co-existing substances in aqueous solution, leading to the generation of large amounts of oxidation by-products (OBPs). The formation and control of OBPs is an important issue that has been relatively neglected in the study of AOPs. The common OBPs in AOPs-treated water include: (1) low-molecular-weight carbonyls (LMWCs) (e.g., carboxylic acids, benzoic compounds, aldehydes, ketones, ketoacids), (2) organic halogenated OBPs (X-OBPs) (e.g., trihalomethane (THM), haloacetic acids (HAA), chloral hydrate (CH)), and (3) inorganic OBPs (e.g., nitrite (NO_2^{-}) , chlorite (CIO_2^{-}) , chlorate (ClO_3^{-}) , and bromate (BrO_3^{-}) [19–22]. Many of these low-molecular-weight carbonyls constitute assimilable organic carbon (AOC) easily, which can be rapidly utilized by microorganisms, leading to an increase in biomass [23,24]. In the United States, it is stipulated that chloroform (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform (TBM) should be controlled below 80 μ g·L⁻¹, and chloroacetic acid (CAA), bromoacetic acid (BAA), dichloroacetic acid (DCAA), dibromoacetic acid (DBAA), and trichloroacetic acid (TCAA)) should be controlled below 60 μ g·L⁻¹ [25]. Both the World Health Organization (WHO) and China have issued individual guidelines for ClO_2^- and ClO_3^- , each of which should be below 700 µg L^{-1} in drinking water [26,27]. BrO₃⁻ is a class 2B carcinogen stipulated by the WHO and the U.S. Environmental Protection Agency (USEPA), and 10 μ g/L is set to be the maximum contaminant level of BrO₃⁻ in drinking water [27]. It should be noted that the difference between OBPs and disinfection by-products (DBPs) is only that the former is a kind of by-product of AOPs, and the latter is a kind of product of conventional disinfection (i.e., adding chlorine (Cl₂), monochloramine (NH_2Cl) , chlorine dioxide (ClO_2) [28,29]. As an AOP, the O₃/PMS system will produce many kinds of OBPs during the process of treating micropollutants, which greatly limits the application of an O_3 /PMS system in the actual water treatment.

In addition, the influence of different reaction parameters (e.g., concentration of reactive substances), reaction conditions (e.g., pH, temperature), and water quality (e.g., concentration of inorganic and organic substances) on the reaction system is also one of the key points that needs to be studied urgently in AOPs. The results of several studies have shown that the concentration of O_3 and PMS have an appropriate range. Excessive dosage of O_3 and PMS would have a negative impact on the degradation of micropollutants in the O_3 /PMS system [30–32]. Temperature affects the decomposition of O_3 and the activation of PMS [33–35]. In addition, pH also shows influence on the conversion of free radicals [30,31,36]. Inorganic ions (e.g., Cl⁻, NO₂⁻, CO₃²⁻, HCO₃⁻, phosphate) usually inhibit the degradation of micropollutants in the O_3 /PMS system by scavenging free radicals [37–40]. Natural organic matter (NOM) in water acts as a promoter or inhibitor for the generation of free radicals [41–43]. Therefore, the influence of these external conditions on the O_3 /PMS system needs to be comprehensively considered in both the analysis of the degradation effect of O_3 /PMS system on micropollutants and the study of the generation and control of OBPs in O_3 /PMS system.

To the best of our knowledge, the current research on the O_3 /PMS system mainly focuses on the theoretical exploration of a single direction. There has been no specific review on the O_3 /PMS system so far, which stimulated us to write this review article on this fast-growing research area with emphasis on the introduction, influence factors, degradation of micropollutants and formation and control of OBPs of O_3 /PMS system. The aim of this work is to develop an integrated understanding of the O_3 /PMS system through a critical evaluation of the relevant publications. As a result, the knowledge gaps in related research and future research directions are explored, so that the O_3/PMS system can be better developed and used for practical applications.

2. Background of the O₃/PMS System

2.1. Proposal of the O₃/PMS System

As a strong oxidant, O_3 can effectively degrade many organic substances which are refractory to traditional oxidation processes [44,45]. However, O_3 has strong selectivity and tends to attack the double bonds, activated aromatic groups and non-protonated amines of organic substances [21,41]. On the other hand, •OH produced in the process of O_3 decomposition is a non-selective strong oxidant (Equations (1) and (2)), which can rapidly react with various micropollutants at nearly diffusion-controlled rates, and the diffusion-controlled rate of •OH is ~10⁸–10¹⁰ M⁻¹s⁻¹ [46,47]. Typically, the degradation of micropollutants by O_3 is achieved by the combined activities of molecular O_3 and •OH. However, the oxidation efficiency of O_3 alone is very low for the refractory micropollutants in water due to the smaller amount of •OH produced by O_3 decomposition and the selectivity of molecular O_3 .

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \ 70 \ M^{-1} s^{-1}$$
 (1)

$$O_3 + HO_2^- \rightarrow^{\bullet}OH + O_2^{\bullet-} + O_2 2.8 \times 10^6 M^{-1} s^{-1}$$
 (2)

The •OH-based AOPs have attracted widespread attention. The reaction between O₃ and hydrogen peroxide (H₂O₂) is one of the most common AOPs to produce •OH for contaminant degradation [48]. The O₃/H₂O₂ system was firstly proposed in a study by Staehelin and Hoigne [49]. Subsequently, the underlying mechanism of the O₃/H₂O₂ system through quantum–chemical and thermokinetic analysis was revised [46,50]. O₃ and H₂O₂ firstly react to form the adduct HO₅⁻ (Equation (3)), which subsequently decomposes in two ways (Equations (4) and (5)). Eventually, •OH is generated through Equations (6)–(8).

$$\mathrm{HO}_2^- + \mathrm{O}_3 \rightarrow \mathrm{HO}_5^- \tag{3}$$

$$\mathrm{HO}_{5}^{-} \rightarrow \mathrm{O}_{3}^{\bullet -} + \mathrm{HO}_{2}^{\bullet} \tag{4}$$

$$HO_5^- \rightarrow 2O_2 + OH^- \tag{5}$$

$$O_3^{\bullet-} \rightleftharpoons O^{\bullet} + O_2 \tag{6}$$

$$O^{\bullet-} + H_2 O \rightleftharpoons^{\bullet} OH + OH^{-}$$
(7)

$$HO_2^{\bullet} \rightleftharpoons O_2^{\bullet-} + H^+ \tag{8}$$

$$O_2^{\bullet-} + O_3 \rightarrow O_3^{\bullet-} + O_2 \tag{9}$$

 $SO_4^{\bullet-}$, as a strong oxidant, has a higher selectivity and higher redox potential $(E_0 = 2.5-3.1 \text{ V})$ than •OH, and can react with many micropollutants at nearly diffusioncontrolled rates [51]. Additionally, compared with \bullet OH, the reactions between SO₄ \bullet^- and micropollutants are less affected by alkalinity and NOM [51–53]. In many studies, the formation of $SO_4^{\bullet-}$ was achieved through activating persulfate (i.e., peroxodisulfate (PDS) and peroxymonosulfate (PMS)). The activation strategies include ultraviolet light (UV) irradiation, heating, or addition of transition metals and carbon materials [54–57]. The structure of PDS and PMS are shown in Figure 1. PMS has an asymmetric structure and a parallel peroxy bond (O–O) with H_2O_2 , indicating that it is likely to substitute H_2O_2 by PMS in the O_3/H_2O_2 system to achieve a synergistic effect [58]. Wen et al. reported that O_3 -activated PMS enhanced the degradation of pCBA, proving that PMS had a similar effect as H_2O_2 in promoting the generation of free radicals during ozonation [16]. Furthermore, the study of Li et al. theoretically demonstrated that high chemical reactivity and low kinetic stability of PMS prompted its reaction with O_3 [13]. However, according to Figure 1, PDS exists in the form of symmetric structure, where the peroxy group of it is stable and can hardly react with O_3 [46]. The research by Yuan et al. also indicated that no radical

signal was detected in the O₃/PDS system [36]. Wen et al. reported that O₃ decomposition was only slightly enhanced in the presence of PDS [16]. Therefore, extensive research has used O₃ to activate PMS to generate •OH and SO₄•- simultaneously, which could quickly and effectively degrade a variety of micropollutants.



Figure 1. The structure of PDS and PMS. Yellow color is the sulfur atom and the red color is the oxygen atom. Dashed line represents the fission position of O–O bond for the formation of sulfate radicals.

2.2. Mechanism and Influencing Factors

2.2.1. Mechanism

Yang et al. reported the mechanism of the simultaneous production of ${}^{\bullet}OH$ and $SO_4{}^{\bullet-}$ in the O_3/PMS system [10]. The TBA assay and competition kinetics were used to determine the yields of ${}^{\bullet}OH$ and $SO_4{}^{\bullet-}$, respectively. As shown in Figure 2, O_3 firstly reacted with $SO_5{}^{2-}$ (PMS) to produce ${}^{-}O_3SO_5{}^{-}$ (Equation (10)), which is decomposed in two ways (Equations (11) and (12)). Next, $SO_5{}^{\bullet-}$ would further transform into $SO_4{}^{\bullet-}$ by reacting with O_3 or decaying bimolecularly (Equations (13) and (14)), and $O_3{}^{\bullet-}$ would convert into ${}^{\bullet}OH$ (Equations (16) and (17)). Equations (12) and (15) are termination reactions with formation of $SO_4{}^{2-}$ and $S_2O_8{}^{2-}$.

$$^{-}O_{3}SOO^{-} + O_{3} \rightarrow ^{-}O_{3}SO_{5}^{-} 2.12 \times 10^{4} \text{ M}^{-1} \text{s}^{-1}$$
(10)

$$^{-}O_{3}SO_{5}^{-} \rightarrow SO_{5}^{\bullet-} + O_{3}^{\bullet-}$$

$$\tag{11}$$

$$^{-}O_{3}SO_{5}^{-} \rightarrow SO_{4}^{2-} + 2O_{2}$$
 (12)

$$SO_5^{\bullet-} + O_3 \rightarrow SO_4^{\bullet-} + 2O_2 \ 1.6 \times 10^5 \ M^{-1} s^{-1}$$
 (13)

$$2SO_{\text{E}}^{\bullet-} \rightarrow 2SO_{\text{A}}^{\bullet-} + O_{2} 21 \times 10^{8} \text{ M}^{-1} \text{s}^{-1}$$
 (14)

$$2SO_5^{\bullet -} \rightarrow S_2O_8^{2-} + O_2 \ 2.2 \times 10^8 \ \mathrm{M}^{-1} \mathrm{s}^{-1}$$
(15)

$$O_3^{\bullet-} \rightleftharpoons O^{\bullet-} + O_2 2.1 \times 10^3 \,\mathrm{M}^{-1} \mathrm{s}^{-1}$$
 (16)

$$O^{\bullet-} + H_2 O \rightarrow^{\bullet} O H + O H^{-} 10^8 s^{-1}$$
 (17)

In addition, some studies reported that both HSO_5^- and SO_5^{2-} could also react with H_2O to produce H_2O_2 , thus enhancing •OH generation during the O_3/PMS system (Equations (18)–(20)). Moreover, $SO_4^{\bullet-}$ could react with H_2O or OH^- to produce •OH according to Equations (21) and (22) [13,15,59]. On the other hand, 1O_2 and $O_2^{\bullet-}$ would be produced in ozonation system. The self-decomposition of PMS would also produce 1O_2 according to Equation (23) [14].

$$HSO_5^- + H_2O \rightarrow H_2O_2 + HSO_4^-$$
(18)

$$SO_5^{2-} + H_2O \rightarrow H_2O_2 + SO_4^{2-}$$
 (19)

$$2O_3 + H_2O_2 \rightarrow 2^{\bullet}OH + 3O_2 \tag{20}$$

$$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + {}^{\bullet}OH \quad (6.5 \pm 1.0) \times 10^7 \,\mathrm{M}^{-1} \mathrm{s}^{-1}$$
 (21)

$$SO_4^{\bullet-} + H_2O \rightarrow H^+ + SO_4^- + {}^{\bullet}OH \qquad <3 \times 10^3 \, \mathrm{s}^{-1}$$
 (22)

$$SO_5^{2-} + HSO_5^{-} \rightarrow HSO_4^{-} + SO_4^{2-} + {}^1O_2$$
 (23)



Figure 2. The mechanism of the simultaneous production of ${}^{\bullet}OH$ and $SO_4 {}^{\bullet-}$ in the O_3/PMS system.

2.2.2. Influencing Factors

The influence of reaction conditions on the O_3/PMS system is shown in Table 1. Related research mainly focuses on the influence of pH, concentration and molar ratio of O_3 and PMS, temperature, inorganic ions, and NOM on the O_3/PMS system. These studies have explored the internal mechanism by analyzing the impact of the changes in external conditions on the O_3/PMS system. These factors mainly influence the O_3/PMS system by affecting the decomposition of O_3 , the activation of PMS, and the generation and conversion of free radicals.

Table 1. The influence of reaction conditions on the O_3/PMS system.

Influence Factor	Performance	Refs.
рН	 The amount of SO₄^{•-} and •OH generation increased with the increase of pH. The consumption of O₃ increased with the increase of pH. PMS would decomposed in non-radical pathway at alkaline conditions due to the pK_{a2} of PMS being 9.4. As the pH increased, the presence of OH⁻ led to the transformation of SO₄^{•-} to •OH. 	[10,30,59–62]
O3 dosage	 The promoting effects on the generation of radicals was stronger under higher O₃ dosage. Excessive O₃ dosage could influence the amount of effective free radicals and acted as scavenger. 	[15,36,63]
PMS dosage	 Increased PMS dosage accelerated the O₃ decomposition. Excessive PMS scavenged the free radicals (*OH and SO4*-) via unreacted PMS and reducing pH. 	[13–15,36,59,64,65]

Influence Factor	Performance	Refs.
O3:PMS	 No significant difference between the removal efficiency was obtained when the ratio of O₃:PMS was 1:1 or 1:2. The O₃ decomposition rate was the maximum when the molar ratio of PMS:O₃ was 1:1. 	[16,60]
Temperature	 O₃ decomposition rate increased with the increase of temperature. The O-O bond in PMS was easily broken at high temperature. The high reaction temperature could facilitate the formation of •OH and SO₄•⁻. O₃/PMS system was not thermodynamically controlled in the 5-40 °C temperature range. 	[14,15,32,34]
Ionic strength	• Various ionic strength by different buffer concentrations had no effect on the O ₃ /PMS system.	[10]
Inorganic ions	 HCO₃⁻ and CO₃²⁻ could react with •OH and SO₄•⁻ to produce the carbonate radical. The reaction between Cl⁻ and SO₄•⁻ could cause the formation of •OH and Cl-containing radicals. Cl⁻ had no significant effect on •OH-based AOPs at neutral pH. NO₂⁻ and phosphate ions signified a strong inhibition effect. 	[10,14,15,32,47,64,66–69]
NOM	 NOM acted as a promoter and inhibitor for the generation of •OH. NOM was a stronger scavenger for •OH and SO₄ •- than HCO₃ 	[10,14,15,32,70]

Table 1. Cont.

pH is an important factor in the O₃/PMS system because of its remarkable effect on the decomposition of O₃, the speciation of PMS, and the conversation of free radicals. In acidic conditions, the presence of excessive proton (H⁺) could scavenge •OH and SO₄•⁻ based on Equations (24) and (25) [31]. As the pH increases up to alkaline, the decomposition of O₃ accelerates, resulting in the formation of more •OH [71]. In addition, since pK_{a2} of PMS is 9.4, the dominant species of PMS would change from HSO₅⁻ to SO₅²⁻ under alkaline conditions, which could induce more SO₄•⁻ generation [36,72]. Besides, according to Equations (1), (2), (26), and (27), O₃ and PMS could react with OH⁻ to produce HO₂⁻, which then reacts with O₃ and PMS to generate •OH and SO₄•⁻ to •OH based on Equation (21) [13,15,30].

$$^{\bullet}OH + H^{+} + e^{-} \rightarrow H_2O \tag{24}$$

$$SO_4^{\bullet-} + H^+ + e^- \rightarrow HSO_4^-$$
(25)

$$HSO_5^- + OH^- \rightarrow HO_2^- + SO_4^{2-} + H^+$$
 (26)

$$HSO_5^{-} + HO_2^{-} \rightarrow SO_4^{\bullet -} + O_2^{\bullet -} + H_2O \quad (6.5 \pm 1.0) \times 10^7 \text{ M}^{-1}\text{s}^{-1}$$
(27)

The dosage and the molar ratio of O_3 and PMS are also very important influencing factors in the O_3 /PMS system. The increase of O_3 and PMS dosage leads to the generation of more free radicals in a proper range [10,36], while self-consumption between free radicals also occurs when there are too many •OH and $SO_4^{\bullet-}$ in the solution, according to Equations (28)–(30) [13,15,47,51,74]. On the other hand, excessive O_3 and PMS would exhibit an inhibitory effect on the reaction. Specifically, excessive O_3 could influence the amount of free radicals and act as scavenger based on Equations (31) and (32) [32,63,75]. Excessive PMS could act as a scavenger of •OH and $SO_4^{\bullet-}$ and facilitate the transformation of abundant $SO_4^{\bullet-}$ into SO_4^{2-} , as described in Equations (33) and (34) [10,13–15,36,72].

In addition, the high concentration of PMS would reduce the pH value and excessive H⁺ could scavenge free radicals [31,32]. When the molar ratio of PMS: O_3 was 1:1, the amount of PMS that could be activated by O_3 tended to stabilize [60]. By contrast, $H_2O_2:O_3 = 0.5$ was the optimal molar ratio for the O_3/H_2O_2 system [76,77].

$$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \quad 7.0 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$$
 (28)

$$\bullet OH + \bullet OH \rightarrow H_2O_2 \tag{29}$$

$$SO_4^{\bullet-} + {}^{\bullet}OH \rightarrow HSO_5^{-}$$
 (30)

$$O_3 + {}^{\bullet}OH \rightarrow HO_2 {}^{\bullet} + O_2 \quad 1.0 \times 10^8 M^{-1} s^{-1}$$
 (31)

$$O_3 + SO_4^{\bullet-} \rightarrow SO_5^{\bullet-} + O_2 \tag{32}$$

$$HSO_5^{-} + {}^{\bullet}OH \rightarrow SO_5^{\bullet-} + H_2O = 5.0 \times 10^6 M^{-1} s^{-1}$$
(33)

$$HSO_5^{-} + SO_4^{\bullet -} \rightarrow SO_5^{\bullet -} + HSO_4^{-} \quad 1.0 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$$
(34)

Temperature is a very important influencing factor in all reaction systems. Although the study by Shao et al. indicated that the O_3 /PMS system was not controlled by thermodynamics in the temperature range of 5–40 °C [32], other studies have shown that the amount of free radicals in the O_3 /PMS system increased with the increase of temperature [33,78,79]. Specifically, the O–O bond of PMS was easily broken at a higher temperature while PMS activation was reduced at a lower temperature, leading to the reduction of SO₄•⁻. Furthermore, the solubility and availability of O_3 to produce free radicals in aqueous solution were reduced at a higher temperature [80–82].

The presence of some kinds of inorganic ions has a significant impact on the O₃/PMS system [14], while the impact of different ionic strengths on the O₃/PMS system is very limited. According to Equations (35)–(37), Cl⁻ had limited effect on •OH because the reaction between Cl⁻ and •OH was reversible and the generation of Cl[•] occurred only at low pH conditions [21]. On the other hand, Cl⁻ could scavenge SO₄^{•-} to produce less reactive Cl[•] (Equations (38) and (39)) [32,37,38]. The reaction between Cl⁻ and SO₄^{•-} could lead to the generation of •OH [40,83]. Br⁻ affected the O₃/PMS system through rapid and irreversible reacting with •OH and SO₄^{•-} (Equations (40) and (41)) [84,85]. Equations (42)–(45) describe the reaction of free radicals with CO₃²⁻ and HCO₃⁻ [32]. CO₃²⁻ and HCO₃⁻ could quench the free radicals effectively to generate CO₃^{•-}, with lower redox potential ($E_0 = 1.78$ V) than •OH and SO₄^{•-} [14]. NO₂⁻ influenced oxidants and free radicals due to its reducibility (Equations (46) and (47)) [14,86]. Phosphate ions showed a strong inhibitory effect on O₃ decomposition [87]. Therefore, the use of phosphate buffer solution in the O₃/PMS system should control the concentration of phosphate ions.

•OH + Cl⁻
$$\rightarrow$$
ClOH•- 4.3 × 10⁹ M⁻¹s⁻¹ (35)

$$ClOH^{\bullet-} \to OH + Cl^{-} \qquad 6.1 \times 10^9 \,M^{-1} s^{-1}$$
 (36)

$$ClOH^{\bullet-} + H^+ \rightarrow H_2O + Cl^{\bullet} = 2.1 \times 10^{10} M^{-1} s^{-1}$$
 (37)

$$SO_4^{\bullet-} + Cl^- \rightarrow SO_4^{2-} + Cl^{\bullet} \qquad 3.0 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$$
 (38)

$$SO_4^{2-} + Cl^{\bullet} \rightarrow SO_4^{\bullet-} + Cl^{-} \qquad 2.5 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$$
 (39)

$$^{\bullet}OH + Br^{-} \rightarrow BrOH^{\bullet -} \qquad 1.1 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$$
(40)

$$SO_4^{\bullet-} + Br^- \rightarrow SO_4^{2-} + Br^{\bullet} \qquad 3.5 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$$
 (41)

$$^{\bullet}OH + CO_3{}^{2-} \rightarrow CO_3{}^{\bullet-} + OH^- \qquad 3.9 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$$
(42)

$${}^{\bullet}\text{OH} + \text{HCO}_{3}^{-} \rightarrow \text{CO}_{3}^{\bullet-} + \text{H}_{2}\text{O} \qquad 8.6 \times 10^{6} \,\text{M}^{-1}\text{s}^{-1} \tag{43}$$

$$SO_4^{\bullet-} + CO_3^{2-} \rightarrow CO_3^{\bullet-} + SO_4^{2-} \qquad 6.1 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$$
(44)

$$SO_4^{\bullet-} + HCO_3^{-} \rightarrow CO_3^{\bullet-} + HSO_4^{-} = 2.8 \times 10^6 \text{ M}^{-1} \text{s}^{-1}$$
 (45)

$$NO_2^- + {}^{\bullet}OH \text{ or } SO_4^{\bullet-} \rightarrow NO_2^{\bullet} + HO^- \text{ or } SO_4^{2-}$$
(46)

$$NO_2^- + HSO_5^- \text{ or } O_3 \rightarrow NO_3^- + HSO_4^- \text{ or } O_2$$
 (47)

NOM plays a dual role in the O_3/PMS system [41,42]. The low concentration of NOM enhanced the decomposition of O_3 to produce °OH [43]. However, NOM acted as a scavenger for °OH and $SO_4^{\bullet-}$ at relatively high concentrations [70]. HA, as an important component of NOM, also played an obvious dual role in the O_3/PMS system [15].

3. Degradation of Micropollutants Using the O₃/PMS System

3.1. Degradation Effect and Energy Efficiency

The O₃/PMS system can quickly and effectively generate •OH and SO₄•⁻, so it is widely used in the research of micropollutant degradation. As shown in Table 2, the O₃/PMS system exhibits a good degradation effect when treating sewage-containing general chemicals, agricultural chemicals, and medical chemicals. The SO₄•⁻ formed by PMS activation exists in the system for a long time, so it can oxidize micropollutants more effectively. Specifically, the O₃/PMS system has high efficiency in degrading typical micropollutants in agricultural and medical industries, so it can be used for soil remediation and medical wastewater treatment. There are many factors that affect the degradation effect of O₃/PMS on micropollutants, such as the type and concentration of micropollutants, the concentration and molar ratio of O₃ and PMS, pH, and temperature. Tang et al. studied the effect of the O₃/PMS system on the degradation of micropollutants with different molecular weights (MW). The MW distributions were divided into five fractions: F1 (<3 kDa), F2 (3–10 kDa), F3 (10–100 kDa), F4 (100 kDa–0.45 µm), and F5 (>0.45 µm) (low: F1; lower: F2; higher: F3, F4; high: F5). The results indicated that O₃/PMS oxidation degraded higher MW fractions more efficiently than low MW fractions in DOM [88].

The reaction rate constants between different micropollutants with O₃ and free radicals are shown in Table 3. The reaction rate constants determine which ROS plays a key role in the degradation of target micropollutants in the O_3 /PMS system. For example, when the solution pH shifted from neutral to alkaline, the proportion of O_3 that directly reacted with ACE decreased, resulting in an enhanced formation of SO₄^{•-} and suppressed formation of \bullet OH. Considering that SO₄ \bullet^- degraded ACE more slowly than \bullet OH did, the oxidation capacity of the system was weakened due to the decrease of •OH formation [32]. On the other hand, the synergy between the various ROS (i.e., O_3 , ${}^{\bullet}OH$, $SO_4 {}^{\bullet-}$, $O_2 {}^{\bullet-}$, ${}^{1}O_2$) produced by the O_3 /PMS system results in the degradation efficiency of micropollutants faster than other O₃-based oxidation processes (i.e., O₃, O₃/H₂O₂, O₃/PDS). Wen et al. reported that the degradation efficiency of pCBA by O_3 alone and O_3/H_2O_2 was only 48.9% and 54.7% after 5 min, respectively. On the contrary, pCBA was fully degraded by O₃/PMS in less than 5 min [16]. In the study by Yang et al., it was found that the removal rate of ATZ by O_3 /PMS reached 81% in 10 min, while the removal rate of O_3 alone in 20 min was only 27% [10]. Besides, the removal rate of PMT within 10 min in the O_3 /PMS system was about 99.27%, while the removal rate of PMT by O_3 alone and O_3 /PDS was 46.16% and 53.45%, respectively [15].

Yu et al. studied the electrical energy per order (EE/O) of ATL in several AOPs. Specifically, the EE/O of UV/O₃/PMS, UV/O₃, O₃/PMS, UV/PMS and O₃ was 4.48×10^{-4} , 2.37×10^{-4} , 5.37×10^{-4} , 4.40×10^{-4} , and 2.80×10^{-4} kW·h/L, respectively, which followed the order: O₃/PMS > UV/O₃/PMS \approx UV/PMS > O₃ > UV/O₃. The results indicated that the O₃/PMS system was the most energy-intensive process for ATL degradation [89]. Besides, Miklos et al. also reported the higher energy efficiency for the SO₄^{•-}-based AOPs [90]. This is mainly due to the selectivity of SO₄^{•-}, which will consume more energy when degrading the target micropollutants at a low reaction rate with SO₄^{•-}.

Туре	Object	Reaction Conditions	Performance	Oxidizing Agent	Ref.
General chemicals	рСВА	 <i>p</i>CBA = 5 μM, O₃ = 5 mg/L, PMS:O₃ (molar ratio) = 1:1, pH = 7.5 	• >90% removed in 1 min	O ₃ , ●OH, SO ₄ ●−	[60]
		 <i>p</i>CBA = 9 μM, O₃ = 0.103 mM, PMS:O₃ (molar ratio) = 1:1, pH = 6.0, T = 20 °C 	• 100% removed in 5 min	•OH, SO4●−	[16]
	4-nitrophenol	 4-nitrophenol = 50 mg/L, O₃ = 30 mg/L, PMS = 100 mg/L, T = 25 °C, catalyst loading (MnO₂/rGO) = 0.1 g/L 	• 100% removed in 45 min	•OH, SO4●−	[91]
	CN	• CN = 50 mg/L, O ₃ = 0.4 g/h, PMS = 100 mg/L, pH = 10.0, T = 25 °C	• 100% removed in 10 min	•OH, SO ₄ •−	[34]
	OA	 OA = 15 μM, O₃ = 1.135 mg/min, PMS = 100 μM, pH = 7.0, T = 20 ± 2 °C, (GO = 10 mg/L) 	 67% removed in 25 min; (74% removed in 25 min) 		[92]
	BTA	• BTA = 40 mg/L, O ₃ = 6.8 mg/L, PMS = 1.5 mM, US power = 200 W, pH = 7.0	• 100% re- moved in 60 min	•ОН	[30]
Agricultural chemicals	ACE	• ACE = 8.0 mg/L, O ₃ = 60 ± 5 μg/min, PMS = 0.4 μM, pH = 7.4, T = 15 ± 1 °C	 >90% removed in 15 min 	O ₃ , ●OH, SO ₄ ●−	[32]
	ATZ	• ATZ = 5 μM, O ₃ = 5 mg/L, PMS:O ₃ (molar ratio) = 1:1, pH = 7.5	 >90% removed in 1 min 	O ₃ , ●OH, SO ₄ ●−	[60]
		• ATZ = 1 μ M, O ₃ = 1 mg/L, PMS = 10 μ M, pH = 8, T = 15 \pm 1 °C	• 81% removad in 10 min	•OH, SO ₄ •−	[10]
	PMT	• PMT = 2 mg/L, O ₃ = 7.5 mg/min, PMS = 100 mg/L, pH = 6.5, T = 20 °C	 >99.27% removed in 10 min 	•OH, SO4●-	[15]
	2,4-D	 2,4-D = 200 mg/L, O₃ = 16 mg/L, PMS = 2.0 mM, pH = 6.0, catalyst dosage (MCFNs) = 0.2 g/L 	• 100% re- moved in 40 min	•OH, $SO_4^{\bullet-}, O_2^{\bullet-}, O_1^{\bullet-}, O_2^{\bullet-}$	[14]
Medical chemicals	KET	 KET = 5 μM, O₃ = 5 mg/L, PMS:O₃ (molar ratio) = 1:1, pH = 7.5 	 >90% removed in 1 min 	O ₃ , ●OH, SO ₄ ●−	[60]
	METR	• METR = 5 μM, O ₃ = 5 mg/L, PMS:O ₃ (molar ratio) = 1:1, pH = 7.5	• >90% removed in 1 min	O ₃ , SO ₄ •-	[60]

Table 2. Degradation effect of O_3/PMS process on micropollutants.

Туре	Object	Reaction Conditions	Performance	Oxidizing Agent	Ref.
	SMT	• SMT = 10 mg/L, O ₃ = 100 mg/h, PMS = 0.4 g/L, T = 25 °C, catalyst dosage (Co-Ce/MCM-48) = 0.2 g/L	• 67.2% mineralized at 90 min	•OH, SO ₄ •-, O ₂ •-, ¹ O ₂	[13]
	IPM	• IPM = 1 μ M, O ₃ = 41.7 μ M, PMS = 10 μ M, pH = 7.0, T = 25 \pm 1 °C	• 100% removed in 4 min	•OH, SO4 •−	[59]
	IBP	 IBP = 5 μM, O₃ = 31.3 μM, PMS = 6.5 μM, Intial pH = 7.0, T = 20 °C 	• 72% removed in 20 min	•OH, SO ₄ •−	[36]
	RBV	• RBV = 10 μ M, O ₃ = 0.025 μ M, PMS = 0.025 μ M, pH = 7.0	• 50% removed in 5 min	O ₃ , ●OH, SO ₄ ●−	[65]
	ATL	• ATL = 10 mg/L, O ₃ = 2.6 mg/min, PMS = 66.4 mg/L, UV (unknown), pH = 6.0	• 97.36% removed in 7 min	•OH, SO4 •−	[89]
	ASA	• ASA = 55 μM, O ₃ = 1 mg/L, PMS = 1.0 mM, pH = 7.0	• The pseudo- first-order rate constants was $6.01 \times 10^{-2} \text{ min}^{-1}$	O ₃ , ●OH, SO ₄ ●−	[93]
	PNT	• PNT = 55 μM, O ₃ = 1 mg/L, PMS = 1.0 mM, pH = 7.0	• The pseudo- first-order rate constants was $1.77 \times 10^{-1} \text{ min}^{-1}$	O ₃ , ●OH, SO ₄ ●−	[93]
	CAP	• $CAP = 5 \ \mu M, O_3 = 2.4 \ mg/L,$ $PMS = 50 \ \mu M, pH = 7.0$	• 60% removed in 30 min	•OH, SO ₄ •−	[70]
	SMX	• SMX = 0.04 mM, O ₃ = 20 mg/L, PMS = 1.2 mM, Intial pH = 3.4 (SNRP-O ₃)	• 76.4% removed in 30 min	O ₃	[94]
	BCPMW	 COD = 320.0 mg/L, TOC = 125 mg/L, DOC = 88.0 mg/L, color = 118 times, O₃ = 50 mg/L, PMS = 22.5 mg/L, Intial pH = 7.4–8.9, T = 16–28 °C 	• 60.28% COD, 44.06% TOC, 52.49% DOC, 75.26% color removed		[88]

Table 2. Cont.

Object	$k_{ m O3}$ (M $^{-1}{ m s}^{-1}$)	$k_{ m OH}$ (M $^{-1}{ m s}^{-1}$)	$k_{{ m SO4}-}$ (M $^{-1}{ m s}^{-1}$)	Refs.
рСВА	0.15	$5.0 imes 10^9$	$3.6 imes10^8$	[16,95]
KET	0.40	$8.4 imes10^9$	n.d.	[96]
ATZ	6.3–16	$(2.5-3.0) \times 10^9$	$(2.4-2.6) \times 10^9$	[10,93,97]
METR	253	$3.54 imes10^9$	$2.74 imes10^9$	[98,99]
METO	$2 imes 10^3$	$6.8 imes10^9$	$5.11 imes 10^9$	[99–101]
VEN	$8.5 imes10^3$	$8.15 imes10^9$	$3.53 imes10^9$	[99,102,103]
CBZ	$3 imes 10^5$	$8.8 imes10^9$	$1.92 imes 10^9$	[103-105]
NB	0.09	$(3.9-5.9) \times 10^9$	<10 ⁶	[10,65,106]
PMT	0.76	$1.9 imes10^9$	$1.7 imes10^9$	[15]
MeOH	n.d.	$9.7 imes10^8$	$2.5 imes10^7$	[47,51]
EtOH	n.d.	$(1.2-2.8) \times 10^8$	$(1.6-7.7) \times 10^7$	[51,54]
AcOH	$3 imes 10^{-5}$	$1.0 imes 10^8$	$5.0 imes10^6$	[93]
TBA	0.01	$(3.8-7.6) \times 10^8$	$(4.0-9.1) imes 10^5$	[54]
BA	n.d.	$4.2 imes10^9$	$1.2 imes 10^9$	[107,108]
IPM	18	n.d.	$1.6 imes 10^9$	[59,105]
ACE	n.d.	$3.8 imes10^9$	$<2.0 imes 10^7$	[109]
IBP	n.d.	$5.23 imes 10^9$	$1.08 imes10^9$	[36,110]
DEP	n.d.	n.d.	<10 ⁶	[111,112]
RBV	9.8	$1.9 imes10^9$	$7.9 imes10^7$	[65]
BTA	17–23	n.d.	n.d.	[92]
ASA	7.32	$4.18 imes10^9$	$3.46 imes 10^8$	[93]
PNT	37.3	$4.99 imes 10^9$	$5.64 imes10^8$	[93]
CAP	0.291	$2.27 imes10^9$	$1.02 imes 10^8$	[70]
NOM	n.d.	$3.0 imes10^8$	$2.35 imes10^7$	[69,113]
CO_{3}^{2-}	n.d.	$3.9 imes10^8$	$6.1 imes10^6$	[89]
HCO_3^-	n.d.	$8.5 imes10^6$	$1.6 imes10^6$	[47,114]
NO_2^-	n.d.	$1.0 imes10^{10}$	$8.8 imes10^8$	[47,51]

Table 3. The reaction rate constant between the substance and O_3 , ${}^{\bullet}OH$ and $SO_4{}^{\bullet-}$.

n.d.: no data available.

3.2. Toxicity Changes and Degradation Pathway

The O₃/PMS system can significantly reduce the toxicity of micropollutants. Specifically, the biodegradability of activated sludge containing 2,4-D was increased from 8.3% to 58.9%, and the toxicity was reduced from 76.5% to 3.8% after treatment by the PMS/MCFNs/O₃ system [14]. With the oxidation of O₃/PMS, the toxic equivalent (TE) and the relative inhibition light ratio (RILR) of BCPMW were significantly lowered from 0.08 mg/L to 0.02 mg/L and 36% to 9%, respectively [88]. Tan et al. studied the degradation effect of O₃/PMS system on micropollutants containing a variety of anti-inflammatory drugs. Toxicity was calculated based on the toxicity parameter 50% lethal concentration (LC50) of each DBP. The results indicated that the toxicity of the system was decreased after O₃/PMS pre-oxidation. Specifically, the toxicity of disinfection by-products (DBPs) reduced from $6.63 \times 10^{-2} \text{ min}^{-1}$ to $5.27 \times 10^{-2} \text{ min}^{-1}$ under neutral conditions [93].

Among the ROS generated in the O₃/PMS system, •OH and SO₄•⁻ have the strongest oxidizing ability. Therefore, the priority attack sites of these two free radicals should be firstly considered when analyzing the degradation path of micropollutants. SO₄•⁻ has electrophilicity and tends to react with electron-donating groups such as hydroxyl (–OH), alkoxy (–RO) and amino (–NH₂) groups, but does not easily react with the nitro (–NO₂), carbonyl (C=O), or other electron-withdrawing groups [115,116]. On the other hand, •OH is nonselective toward organic pollutants in the oxidation reaction. For some examples, the aromatic ring or the side chains (isopropylamino and alkoxy) of PMT are likely to be attacked by •OH and SO₄•⁻ mainly through addition to unsaturated carbon, H-abstraction, and electron abstraction [15,117–119]. In addition, •OH and SO₄•⁻ participated in the degradation of ACE and the attack sites were C=C, C–O, and C–N bonds [32].

4. Formation and Control of OBPs during the O₃/PMS System

4.1. Formation Pathway and Influencing Factors

The OBPs formed in the O₃-based oxidation process are mainly low-molecular-weight carbonyls, organic halogenated OBPs, and inorganic OBPs. Among them, the inorganic OBPs generally includes chlorinated OBPs, brominated OBPs, and iodinated OBPs. Compared to brominated OBPs, the production of chlorinated and iodinated OBPs during the O_3 /PMS system is negligible [65]. On the other hand, Frederik et al. reported the formation rule of AOC in O_3 alone, but there is no relevant research on the O_3 /PMS system [120,121]. As typical brominated OBPs, the formation mechanism of bromate (BrO_3^{-}) in the treatment of bromide-containing water by O_3 /PMS has been reported in detail by Wen et al., as shown in Figure 3 [64]. The interaction between bromide (Br^-) and molecular O₃, ${}^{\bullet}OH$, and $SO_4^{\bullet-}$ in the O_3/PMS system leads to the formation of BrO_3^- [64,122,123]. The $Br^$ would be oxidized into Br^{\bullet} by ${}^{\bullet}OH$ and $SO_4{}^{\bullet-}$, then Br^{\bullet} would transform into BrO^{\bullet} by reacting with O₃ and finally convert into BrO₃⁻. Furthermore, Br⁻ would react with O₃ to produce hypobromous acid (HOBr/OBr⁻), which would also convert into BrO[•] by reacting with $^{\circ}OH$ and $SO_4^{\circ-}$ [64]. Compared with the BrO_3^{-} generation path of the traditional ozone oxidation process, the $SO_4^{\bullet-}$ path is added in the O_3/PMS system. Therefore, the O_3 /PMS system will generate more BrO_3^- than O_3 alone. In addition, the research by Liu et al. indicated that some brominated OBPs including dibromoacetaldehyde and tribromoacetaldehyde may possess much higher cytotoxicity than BrO_3^{-} [65]. Thus, more attention should be paid to the formation and control of organic halogenated OBPs during O₃-based processes [124].



Figure 3. The mechanism of bromate formation (red: ozonation; blue: O_3 /PMS). Reprinted with permission of refs. [64,124].

The influence of reaction conditions on the OBP formation is shown in Table 4. The amount of BrO_3^- produced increases with the increase of Br^- concentration within a certain range. However, too much Br^- exhibits an inhibition effect [64]. The pH value of the solution comprehensively affects the formation of OBPs in the O₃/PMS system by affecting O₃ decomposition, $R_{ct,oOH}$ and $R_{ct,SO4\bullet}^-$, and PMS speciation [64,125]. According to the research results, BrO_3^- formation would increase as O₃ and PMS dosage increases [64,125,126]. However, according to the reaction mechanism of the O₃/PMS system, this promotion effect may be reduced with the addition of excessive O₃ and PMS. The HCO₃⁻ in the inorganic ions inhibits the formation of BrO_3^- by scavenging free radicals. On the other hand, NH_4^+ prevented the conversion of Br^- into BrO_3^- by masking important intermediate products (HOBr/OBr⁻) [64]. HA, as an important constituent of NOM, could scavenge ROS and thus reduce the formation of BrO_3^- [78,127]. In addition, HA could readily capture the intermediates, providing an additional inhibitory effect [122].

Influence Factor	Performance	Refs.
The concentration of $Cl^-/Br^-/I^-$	 Excessive Br⁻ would compete for reactive substances, lowering the yield of BrO₃⁻. The formation of iodinated OBPs increased with the increase of I⁻ concentration. 	[64,65]
рН	 The formation of BrO₃⁻ was significantly promoted with pH increasing from 4.0 to 10.0. More available Br• would be formed for further oxidation to BrO• at lower pH. The change of pH values would affect HOBr/OBr⁻ balance (pKa = 8.8–9.0). 	[64,92,125]
O ₃	• BrO_3^- formation was enhanced with the increase in O_3 dosage.	[125]
PMS	• BrO ₃ ⁻ formation was enhanced with the increase in PMS dosage.	[64]
Inorganic ions	 The presence of HCO₃⁻ significantly reduced the formation of BrO₃⁻. NH₄⁺ could mask HOBr/OBr⁻ into NH₂Br, thus inhibited the formation of BrO₃⁻. 	[64]
NOM	 HA could scavenge °OH, SO₄ • -, and molecular O₃ to reduce the formation of BrO₃ HA could capture the intermediates (i.e., Br • and HOBr/OBr -), thus inhibiting the formation of BrO₃ 	[64]

Table 4. The influence of reaction conditions on OBP formation.

4.2. Control Strategy

The current research on the control methods of OBP formation in the O₃/PMS system focuses on inhibiting the formation of BrO₃⁻. Several methods were used to control the formation of BrO₃⁻ in O₃ alone: reducing pH [125], adding carbon materials [128,129], H₂O₂ [130], and ammonia (NH₃) and chlorine (Cl₂) [123,131]. pH depression shifts the equilibrium of HOBr/OBr⁻ into HOBr (pKa = 8.8), thus slowing down the reaction between HOBr/OBr⁻ and O₃ ($k_{(O3,HOBr)} = 0.01 \text{ M}^{-1}\text{s}^{-1}$, $k_{(O3,OBr}^{-}) = 100 \text{ M}^{-1}\text{s}^{-1}$), and finally reducing BrO₃⁻ formation. Besides, pH depression can lower the •OH exposure, and thus inhibits the BrO₃⁻ formation from the oxidation pathways by •OH [125]. Carbon materials suppress the BrO₃⁻ formation by reducing HOBr/OBr⁻, which is crucial to the formation of BrO₃⁻. [132]. H₂O₂ can inhibit BrO₃⁻ formation during ozonation because H₂O₂ can also reduce HOBr/OBr⁻ into Br⁻ (k = 7.6 × 10⁸ M⁻¹s⁻¹) [21,130]. Therefore, BrO₃⁻ formation is negligible in O₃/H₂O₂ system with excess H₂O₂ [90]. In the pretreatment strategies of NH₃-Cl₂ and Cl₂-NH₃, Br⁻ is mainly masked as bromine-containing haloamines (i.e., NH₂Br, NHBr₂ and NHBrCl) to inhibit the formation of BrO₃⁻ [123,131].

At present, only Wen et al. have reported the control of BrO_3^- formation in the O_3/PMS system [92]. The research results indicated that the addition of carbon materials significantly inhibited the BrO_3^- formation, and the order of the inhibition efficiency was as follows: graphene (GO) > carbon nano tube (CNT) > powdered activated carbon (PAC). According to the study, the carbon materials could block the BrO_3^- formation by reducing HOBr/OBr⁻ in the reaction system [92]. Besides, Wen et al. synthesized a catalyst (CuCo₂O₄-GO), which could simultaneously inhibit the formation of BrO_3^- and enhance the degradation of micropollutants in the O_3/PMS system. Specifically, when 100 mg/L CuCo₂O₄-GO was added, the BrO_3^- inhibition efficiency reached 96.17% and the degradation efficiency of SMX increased from 0.163 min⁻¹ to 0.422 min⁻¹ [133]. The pretreatment strategy (i.e., NH₃, Cl₂-NH₃ and NH₃-Cl₂) was also used to inhibit BrO_3^- generated in the O_3/PMS system. All the pretreatment strategies reduced 90% or more of the overall BrO_3^- formation, while the NH₃-Cl₂ pretreatment strategy was prior to that of

the NH₃ and Cl₂-NH₃ [134]. The inhibitory effects of the common BrO_3^- control strategies, lowering pH and adding H₂O₂, in the O₃/PMS system have not been studied yet. Many studies have reported that lowering pH could effectively inhibit the formation of BrO_3^- in an O₃-only system. This is because the intermediate substance HOBr/OBr⁻ (pKa = 8.8–9.0) exists in the form of OBr⁻ under alkaline conditions, which is more likely to react with O₃ to form BrO_3^- [125,135,136]. On the other hand, adding excess H₂O₂ could suppress the formation of BrO_3^- in O₃ alone system by reducing HOBr/OBr⁻ to Br⁻ [137–140]. These two kinds of BrO_3^- inhibition strategies may be able to inhibit the formation of BrO_3^- in the O₃/PMS system through similar mechanisms. In general, as shown in Figure 4, the control strategies are used to inhibit the formation of BrO_3^- by affecting the initial Br⁻ or HOBr/OBr⁻.



Figure 4. The mechanism of the inhibition of bromate formation (gray: bromate formation; orange: carbon materials; red: NH_3 ; blue: Cl_2 - NH_3 ; green: NH_3 - Cl_2 ; violet: The bromate control strategies that have not been verified in the O_3/PMS system). Reprinted with permission [64,92,133,134].

5. Recommendations and Future Prospects

In terms of micropollutant degradation, the research on the O_3 /PMS system is still at the laboratory level. The investigation using real water should be strengthened to reflect the feasibility of O_3 /PMS system in practical applications, because many substances contained in actual water will affect the O_3 /PMS system. Besides, the degradation efficiency under different actual water conditions (i.e., surface water and groundwater) should be studied and comparable to explore the water quality condition which is suitable for the application of the O_3 /PMS system. At the same time, more pilot-scale research is needed to promote the conversion of O_3 /PMS system to practical applications.

Due to the generation of $SO_4^{\bullet-}$, the O_3/PMS system has higher selectivity than the O_3/H_2O_2 system. Therefore, the degradation rules of different types of micropollutants in the O_3/PMS system should be extensively researched. The toxicity changes of the treated micropollutants also need to be studied, which are important indicators for evaluating the practical application potential of the O_3/PMS system. In order to evaluate the advantages and disadvantages of the O_3/PMS system and the suitable application conditions, the O_3/PMS system should be compared with the O_3 -alone and O_3/H_2O_2 systems when conducting the above research.

The formation rules of several kinds of OBPs under different conditions during the O_3 /PMS system are not completely clear yet. Notable are the structure change of NOM and the formation rule of small molecular organic matter after treatment by O_3 /PMS system. At the same time, the effectiveness of various OBP control methods in the O_3 /PMS system has not been widely studied. Since the O_3 /PMS system can generate several kinds of ROS, the formation and control of the OBPs need to be compared with the O_3 alone and O_3 /H₂O₂ systems to explore the mechanism. In addition, micropollutants are not fully mineralized by the O_3 /PMS system but degraded into transformation products (TPs), which arouse a growing concern because of the unknown structures and potential biological effects. Therefore, more research needs to pay attention to the TPs formed during the degradation of micropollutants in the O_3 /PMS system.

The operational costs (e.g., energy consumption, chemical input), sustainability (e.g., resource use, carbon footprint), and general feasibility (e.g., physical footprint and oxidation by-product formation) of the O_3 /PMS system need to be studied to enable to compare their efficiency with other AOPs and alternative treatment processes (i.e., O_3/H_2O_2 , O_3/UV). In addition, the combination of O_3 and biological activated carbon (BAC) is a very common water treatment process in practical applications, which can enhance the degradation efficiency of organic matter while reducing OBPs in the effluent. Therefore, the combined effect of O_3 /PMS and BAC is also worth studying.

6. Conclusions

As a new advanced oxidation process, O3/PMS degrades many refractory micropollutants rapidly and effectively by generating many strong oxidizing ROS simultaneously. Compared with the widely used O_3 and O_3/H_2O_2 systems, the O_3/PMS system produces more types of free radicals and has higher selectivity. Based on the current research, the O₃/PMS system has a good degradation efficiency on general chemicals, agrochemicals and medical chemicals, and the degradation effect is affected by a variety of influencing factors (e.g., pH, the concentration of O_3 and PMS, temperature, and inorganic ions). These factors mainly influence the O_3 /PMS system by affecting the decomposition of O_3 , the activation of PMS, and the generation and conversion of free radicals. The generation and control of OBPs during the degradation of micropollutants in the O_3/PMS system is another current research focus. According to the research results, the BrO_3^- produced in the O_3 /PMS system is mainly due to the interaction between Br⁻ and molecular O_3 , $^{\bullet}OH$ and $SO_4^{\bullet-}$, and the BrO_3^{-} formation can be effectively inhibited by addition of carbon materials, or NH₃ and Cl₂ combined pretreatment strategy. However, it is not practical enough to apply the O_3 /PMS system to actual water treatment processes, and there are still many key problems that need to be addressed. Specifically, the degradation rule and toxicity change of different types of micropollutants in the O_3 /PMS system should be extensively studied. The formation rules of several kinds of OBPs during the O_3 /PMS system are not completely clear yet. Furthermore, pilot-scale research, the operational costs, sustainability, and general feasibility of the O_3 /PMS system also need to be studied. Currently, there is no integrated understanding of the O_3 /PMS system. It is expected that the findings of this review may advance future research and application of O_3/PMS system. Specifically, the continuous exploration in the research directions proposed by this article will not only make the O_3 /PMS system perform better in the degradation of micropollutants, but also enhance the potential of applications of the O_3 /PMS process in other areas such as sludge stabilization, dewatering, and inactivation of microorganisms.

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Nomenclatures

Abbreviation	Full Name
рCBA	4-chlorobenzoic acid
KET	Ketoprofen
ATZ	Atrazine
METR	Metronidazole
HA	Humic acid
PMT	Prometon
2,4-D	2,4-dichlorophenoxyacetic acid
MCFNs	CuFe ₂ O ₄ magnetic nanoparticles
SMT	sulfamethazine
BCPMW	Biotreated Chinese patent medicine wastewater (e.g., cellulose, lignin, etc.)
ACE	Acesulfame
DEP	Diethyl phthalate
CN	Cyanide
BTA	Benzotriazole
ASA	Aspirin
CAP	Chloramphenicol
METO	Metoprolol
VEN	Venlafaxine
CBZ	Carbamazepine
MOX	Moxifloxacin
NB	Nitrobenzene
MeOH	Methanol
TBA	Tert-Butanol
BA	Benzoic acid
IPM	Iopamidol
MCFN	Magnetic copper ferrite nano-particle (CuFe ₂ O ₄)
IBP	Ibuprofen
RBV	Ribavirin
OA	Oxalic acid
ATL	Atenolol
PNT	Phenacetin
SMX	Sulfamethoxazole

References

- 1. Bilal, M.; Adeel, M.; Rasheed, T.; Zhao, Y.; Iqbal, H.M. Emerging contaminants of high concern and their enzyme-assisted biodegradation—A review. *Environ. Int.* **2019**, *124*, 336–353. [CrossRef] [PubMed]
- Feng, G.; Huang, H.; Chen, Y. Effects of emerging pollutants on the occurrence and transfer of antibiotic resistance genes: A review. J. Hazard. Mater. 2021, 420, 126602. [CrossRef]
- 3. Patel, N.; Khan, Z.A.; Shahane, S.; Rai, D.; Chauhan, D.; Kant, C.; Chaudhary, V.K. Emerging Pollutants in Aquatic Environment: Source, Effect, and Challenges in Biomonitoring and Bioremediation—A Review. *Pollution* **2020**, *6*, 99–113.
- 4. Matzek, L.W.; Carter, K.E. Activated persulfate for organic chemical degradation: A review. *Chemosphere* **2016**, *151*, 178–188. [CrossRef]
- 5. Wacławek, S.; Lutze, H.V.; Grübel, K.; Padil, V.V.T.; Černík, M.; Dionysiou, D.D. Chemistry of persulfates in water and wastewater treatment: A review. *Chem. Eng. J.* **2017**, *330*, 44–62. [CrossRef]
- 6. Ushani, U.; Lu, X.; Wang, J.; Zhang, Z.; Dai, J.; Tan, Y. Sulfate radicals-based advanced oxidation technology in various en-vironmental remediation: A state-of-the-art review. *Chem. Eng. J.* **2020**, 402, 126232. [CrossRef]

- Xia, Y.C.; Wan, Q.Q.; Xu, X.Q.; Cao, R.H.; Li, Y.F.; Wang, J.Y.; Xu, H.N.; Huang, T.L.; Wen, G. Solar disinfection of fungal spores in water: Kinetics, influencing factors, mechanisms and regrowth. *Chem. Eng. J.* 2022, 428, 132065. [CrossRef]
- 8. Hou, J.; He, X.; Zhang, S.; Yu, J.; Feng, M.; Li, X. Recent advances in cobalt-activated sulfate radical-based advanced oxidation processes for water remediation: A review. *Sci. Total Environ.* **2021**, 770, 145311. [CrossRef]
- 9. Addison, F.; Offiong, N.-A.; Han, Q.; Wang, R.; Liu, N. Nitrogen-doped mesoporous carbon material (NCMK-3) as a catalyst for the removal of 4-chlorophenol during persulfate oxidation and its efficiency after reuse. *Environ. Technol.* 2020, 1–7. [CrossRef]
- 10. Yang, Y.; Jiang, J.; Lu, X.; Ma, J.; Liu, Y. Production of Sulfate Radical and Hydroxyl Radical by Reaction of Ozone with Per-oxymonosulfate: A Novel Advanced Oxidation Process. Environ. *Sci. Technol.* **2015**, *49*, 7330–7339. [CrossRef] [PubMed]
- Deniere, E.; Alagappan, R.P.; Van Langenhove, H.; Van Hulle, S.; Demeestere, K. The ozone-activated peroxymonosulfate process (O₃/PMS) for removal of trace organic contaminants in natural and wastewater: Effect of the (in)organic matrix composition. *Chem. Eng. J.* 2021, 133000. [CrossRef]
- Huang, Y.; He, Z.; Liao, X.; Cheng, Y.; Qi, H. NDMA reduction mechanism of UDMH by O₃/PMS technology. *Sci. Total Environ.* 2022, 805, 150418. [CrossRef]
- 13. Li, S.; Huang, J.; Li, X.; Li, L. The relation of interface electron transfer and PMS activation by the H-bonding interaction between composite metal and MCM-48 during sulfamethazine ozonation. *Chem. Eng. J.* **2020**, *398*, 125529. [CrossRef]
- Jaafarzadeh, N.; Ghanbari, F.; Ahmadi, M. Efficient degradation of 2,4-dichlorophenoxyacetic acid by peroxymonosulfate/magnetic copper ferrite nanoparticles/ozone: A novel combination of advanced oxidation processes. *Chem. Eng. J.* 2017, 320, 436–447. [CrossRef]
- 15. Wu, G.; Qin, W.; Sun, L.; Yuan, X.; Xia, D. Role of peroxymonosulfate on enhancing ozonation for micropollutant degradation: Performance evaluation, mechanism insight and kinetics study. *Chem. Eng. J.* **2019**, *360*, 115–123. [CrossRef]
- Cong, J.; Wen, G.; Huang, T.; Deng, L.; Ma, J. Study on enhanced ozonation degradation of para-chlorobenzoic acid by peroxymonosulfate in aqueous solution. *Chem. Eng. J.* 2015, 264, 399–403. [CrossRef]
- Gholikandi, G.B.; Zakizadeh, N.; Masihi, H. Application of peroxymonosulfate-ozone advanced oxidation process for simultaneous waste-activated sludge stabilization and dewatering purposes: A comparative study. *J. Environ. Manag.* 2018, 206, 523–531. [CrossRef] [PubMed]
- Moreno-Andres, J.; Morillo-Ponce, J.; Ibáñez-López, M.E.; Acevedo-Merino, A.; García-Morales, J.L. Disinfection enhance-ment of single ozonation by combination with peroxymonosulfate salt. J. Environ. Chem. Eng. 2020, 8, 104335. [CrossRef]
- 19. Ike, I.A.; Karanfil, T.; Cho, J.; Hur, J. Oxidation byproducts from the degradation of dissolved organic matter by advanced oxidation processes—A critical review. *Water Res.* **2019**, *164*, 114929. [CrossRef]
- 20. Wu, Q.-Y.; Zhou, Y.-T.; Li, W.; Zhang, X.; Du, Y.; Hu, H.-Y. Underestimated risk from ozonation of wastewater containing bromide: Both organic byproducts and bromate contributed to the toxicity increase. *Water Res.* **2019**, *162*, 43–52. [CrossRef] [PubMed]
- von Gunten, U. Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine. *Water Res.* 2003, 37, 1469–1487. [CrossRef]
- Ji, Y.; Ferronato, C.; Salvador, A.; Yang, X.; Chovelon, J.M. Degradation of ciprofloxacin and sulfamethoxazole by ferrous-activated persulfate: Implications for remediation of groundwater contaminated by antibiotics. *Sci. Total Environ.* 2014, 472, 800–808. [CrossRef] [PubMed]
- 23. van der Kooij, D. Assimilable organic carbon as an indicator of bacterial regrowth. *J. Am. Water Works Assoc.* **1992**, *84*, 57–65. [CrossRef]
- 24. Escobar, I.C.; Randall, A.A.; Taylor, J.S. Bacterial Growth in Distribution Systems: Effect of Assimilable Organic Carbon and Biodegradable Dissolved Organic Carbon. *Environ. Sci. Technol.* **2001**, *35*, 3442–3447. [CrossRef]
- 25. U.S. Environmental Protection Agency. National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfection Byproducts Rule: Final Rule. *Fed. Regist.* **2006**, *71*, 388–493.
- 26. Jin, Y.; Chen, E.; Chen, C.; Zhang, X.; Chen, L. *Standards for Drinking Water Quality (GB-5749-2006)*; Beijing Ministry of Health of the People's Republic of China: Bejing, China, 2006.
- 27. Edition, F. Guidelines for drinking-water quality. WHO Chrzonicle 2011, 38, 104–108.
- 28. Mazhar, M.A.; Khan, N.A.; Ahmed, S.; Khan, A.H.; Hussain, A.; Changani, F. Chlorination disinfection by-products in Mu-nicipal drinking water–A review. J. Clean. Prod. 2020, 273, 123159. [CrossRef]
- 29. Liu, X.; Chen, L.; Yang, M.; Tan, C.; Chu, W. The occurrence, characteristics, transformation and control of aromatic disinfection by-products: A review. *Water Res.* 2020, 184, 116076. [CrossRef] [PubMed]
- Ghanbari, F.; Khatebasreh, M.; Mahdavianpour, M.; Lin, K.-Y.A. Oxidative removal of benzotriazole using peroxymonosulfate/ozone/ultrasound: Synergy, optimization, degradation intermediates and utilizing for real wastewater. *Chemosphere* 2020, 244, 125326. [CrossRef] [PubMed]
- Ghanbari, F.; Moradi, M. Application of peroxymonosulfate and its activation methods for degradation of environmental organic pollutants: Review. Chem. Eng. J. 2017, 310, 41–62. [CrossRef]
- Shao, Y.; Pang, Z.; Wang, L.; Liu, X. Efficient Degradation of Acesulfame by Ozone/Peroxymonosulfate Advanced Oxidation Process. *Molecules* 2019, 24, 2874. [CrossRef] [PubMed]
- Li, Y.; Yuan, X.; Wang, D.; Wang, H.; Wu, Z.; Jiang, L.; Mo, D.; Yang, G.; Guan, R.; Zeng, G. Recyclable zero-valent iron acti-vating peroxymonosulfate synchronously combined with thermal treatment enhances sludge dewaterability by altering physicochemical and biological properties. *Bioresour. Technol.* 2018, 262, 294–301. [CrossRef] [PubMed]

- 34. Chegini, Z.G.; Hassani, H.; Torabian, A.; Borghei, S.M. Enhancement of PMS activation in an UV/ozone process for cyanide degradation: A comprehensive study. *Pigment Resin Technol.* **2020**, *49*, 409–414. [CrossRef]
- Jung, Y.; Hong, E.; Kwon, M.; Kang, J.-W. A kinetic study of ozone decay and bromine formation in saltwater ozonation: Effect of O₃ dose, salinity, pH, and temperature. *Chem. Eng. J.* 2017, 312, 30–38. [CrossRef]
- 36. Yuan, Z.; Sui, M.; Yuan, B.; Li, P.; Wang, J.; Qin, J.; Xu, G. Degradation of ibuprofen using ozone combined with peroxymonosulfate. Environ. *Sci. Water Res.* 2017, *3*, 960–969.
- 37. Wang, Y.; Chu, W. Degradation of a xanthene dye by Fe(II)-mediated activation of Oxone process. *J. Hazard. Mater.* **2011**, *186*, 1455–1461. [CrossRef]
- 38. Sharma, J.; Mishra, I.; Dionysiou, D.; Kumar, V. Oxidative removal of Bisphenol A by UV-C/peroxymonosulfate (PMS): Kinetics, influence of co-existing chemicals and degradation pathway. *Chem. Eng. J.* **2015**, *276*, 193–204. [CrossRef]
- 39. Muthukumar, M.; Selvakumar, N. Studies on the effect of inorganic salts on decolouration of acid dye effluents by ozonation. *Dye. Pigment.* **2004**, *62*, 221–228. [CrossRef]
- 40. Lutze, H.V.; Kerlin, N.; Schmidt, T.C. Sulfate radical-based water treatment in presence of chloride: Formation of chlorate, inter-conversion of sulfate radicals into hydroxyl radicals and influence of bicarbonate. *Water Res.* 2015, 72, 349–360. [CrossRef]
- Von Gunten, U. Ozonation of drinking water: Part I. Oxidation kinetics and product formation. Water Res. 2003, 37, 1443–1467.
 [CrossRef]
- Okawa, K.; Nakano, Y.; Nishijima, W.; Okada, M. Effects of humic substances on the decomposition of 2,4-dichlorophenol by ozone after extraction from water into acetic acid through activated carbon. *Chemosphere* 2004, 57, 1231–1235. [CrossRef] [PubMed]
- 43. Buffle, M.O.; von Gunten, U. Phenols and amine induced HO[•] generation during the initial phase of natural water ozonation. *Environ. Sci. Technol.* **2006**, *40*, 3057–3063. [CrossRef] [PubMed]
- 44. Chen, H.; Wang, J. Degradation and mineralization of ofloxacin by ozonation and peroxone (O₃/H₂O₂) process. *Chemosphere* **2021**, *269*, 128775. [CrossRef] [PubMed]
- Guo, Y.; Zhao, E.; Wang, J.; Zhang, X.; Huang, H.; Yu, G.; Wang, Y. Comparison of emerging contaminant abatement by conventional ozonation, catalytic ozonation, O₃/H₂O₂ and electro-peroxone processes. *J. Hazard. Mater.* 2020, 389, 121829. [CrossRef] [PubMed]
- 46. Von Sonntag, C.; Von Gunten, U. Chemistry of Ozone in Water and Wastewater Treatment: From Basic Principles to Applications; IWA Publishing: London, UK, 2012. [CrossRef]
- 47. Buxton, G.V.; Greenstock, C.L.; Helman, W.P.; Ross, A.B. Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (·OH/·O—In Aqueous Solution. *J. Phys. Chem. Ref. Data* **1988**, 17, 513–886. [CrossRef]
- Piras, F.; Santoro, O.; Pastore, T.; Pio, I.; De Dominicis, E.; Gritti, E.; Caricato, R.; Lionetto, M.; Mele, G. Controlling micropollutants in tertiary municipal wastewater by O₃/H₂O₂, granular biofiltration and UV254/H₂O₂ for potable reuse applications. *Chemosphere* 2020, 239, 124635. [CrossRef]
- 49. Staehelin, J.; Hoigne, J. Decomposition of ozone in water: Rate of initiation by hydroxide ions and hydrogen peroxide. *Environ. Sci. Technol.* **1982**, *16*, 676–681. [CrossRef]
- Merényi, G.; Lind, J.; Naumov, S.; von Sonntag, C. Reaction of Ozone with Hydrogen Peroxide (Peroxone Process): A Revision of Current Mechanistic Concepts Based on Thermokinetic and Quantum-Chemical Considerations. *Environ. Sci. Technol.* 2010, 44, 3505–3507. [CrossRef]
- 51. Neta, P.; Huie, R.E.; Ross, A.B. Rate Constants for Reactions of Inorganic Radicals in Aqueous Solution. *J. Phys. Chem. Ref. Data* **1988**, 17, 1027–1284. [CrossRef]
- 52. Lutze, H.V.; Bircher, S.; Rapp, I.; Kerlin, N.; Bakkour, R.; Geisler, M.; von Sonntag, C.; Schmidt, T.C. Degradation of chlo-rotriazine pesticides by sulfate radicals and the influence of organic matter. *Environ. Sci. Technol.* **2015**, *49*, 1673–1680. [CrossRef]
- 53. Gara, P.M.D.; Bosio, G.N.; Gonzalez, M.; Martire, D. Kinetics of the sulfate radical-mediated photo-oxidation of humic substances. *Int. J. Chem. Kinet.* 2007, 40, 19–24. [CrossRef]
- 54. Anipsitakis, G.P.; Dionysiou, D.D. Radical Generation by the Interaction of Transition Metals with Common Oxidants. *Environ. Sci. Technol.* **2004**, *38*, 3705–3712. [CrossRef]
- 55. Guan, Y.-H.; Ma, J.; Li, X.-C.; Fang, J.-Y.; Chen, L.-W. Influence of pH on the Formation of Sulfate and Hydroxyl Radicals in the UV/Peroxymonosulfate System. *Environ. Sci. Technol.* **2011**, *45*, 9308–9314. [CrossRef] [PubMed]
- Zhang, T.; Zhu, H.; Croué, J.-P. Production of Sulfate Radical from Peroxymonosulfate Induced by a Magnetically Separable CuFe₂O₄ Spinel in Water: Efficiency, Stability, and Mechanism. *Environ. Sci. Technol.* 2013, 47, 2784–2791. [CrossRef] [PubMed]
- 57. He, X.; de la Cruz, A.A.; Dionysiou, D.D. Destruction of cyanobacterial toxin cylindrospermopsin by hydroxyl radicals and sulfate radicals using UV-254nm activation of hydrogen peroxide, persulfate and peroxymonosulfate. *J. Photochem. Photobiol. A Chem.* **2013**, 251, 160–166. [CrossRef]
- Wang, J.; Wang, S. Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants. *Chem. Eng. J.* 2018, 334, 1502–1517. [CrossRef]
- Mao, Y.; Dong, H.; Liu, S.; Zhang, L.; Qiang, Z. Accelerated oxidation of iopamidol by ozone/peroxymonosulfate (O₃/PMS) process: Kinetics, mechanism, and simultaneous reduction of iodinated disinfection by-product formation potential. *Water Res.* 2020, 173, 115615. [CrossRef]

- 60. Deniere, E.; Van Hulle, S.; Van Langenhove, H.; Demeestere, K. Advanced oxidation of pharmaceuticals by the ozone-activated peroxymonosulfate process: The role of different oxidative species. *J. Hazard. Mater.* **2018**, *360*, 204–213. [CrossRef]
- Yang, N.; Cui, J.; Zhang, L.; Xiao, W.; Alshawabkeh, A.N.; Mao, X. Iron electrolysis-assisted peroxymonosulfate chemical oxidation for the remediation of chlorophenol-contaminated groundwater. J. Chem. Technol. Biotechnol. 2016, 91, 938–947. [CrossRef]
- Chen, Q.; Ji, F.; Liu, T.; Yan, P.; Guan, W.; Xu, X. Synergistic effect of bifunctional Co-TiO₂ catalyst on degradation of Rho-damine B: Fenton-photo hybrid process. *Chem. Eng. J.* 2013, 229, 57–65. [CrossRef]
- 63. Akbari, S.; Ghanbari, F.; Moradi, M. Bisphenol A degradation in aqueous solutions by electrogenerated ferrous ion activated ozone, hydrogen peroxide and persulfate: Applying low current density for oxidation mechanism. *Chem. Eng. J.* **2016**, *294*, 298–307. [CrossRef]
- 64. Wen, G.; Qiang, C.; Feng, Y.; Huang, T.; Ma, J. Bromate formation during the oxidation of bromide-containing water by ozone/peroxymonosulfate process: Influencing factors and mechanisms. *Chem. Eng. J.* **2018**, 352, 316–324. [CrossRef]
- 65. Liu, X.; Hong, Y.; Ding, S.; Jin, W.; Dong, S.; Xiao, R.; Chu, W. Transformation of antiviral ribavirin during ozone/PMS in-tensified disinfection amid COVID-19 pandemic. *Sci. Total Environ.* **2021**, *790*, 148030. [CrossRef]
- Das, T.N. Reactivity and Role of SO₅^{•-} Radical in Aqueous Medium Chain Oxidation of Sulfite to Sulfate and Atmospheric Sulfuric Acid Generation. *J. Phys. Chem. A* 2001, 105, 9142–9155. [CrossRef]
- 67. Matthew, B.M.; Anastasio, C. A chemical probe technique for the determination of reactive halogen species in aqueous solution: Part 1—Bromide solutions. *Atmos. Chem. Phys. Discuss.* **2006**, *6*, 2423–2437. [CrossRef]
- 68. Grebel, J.E.; Pignatello, J.J.; Mitch, W.A. Effect of Halide Ions and Carbonates on Organic Contaminant Degradation by Hydroxyl Radical-Based Advanced Oxidation Processes in Saline Waters. *Environ. Sci. Technol.* **2010**, *44*, 6822–6828. [CrossRef]
- Hoigné, J. Chemistry of Aqueous Ozone and Transformation of Pollutants by Ozonation and Advanced Oxidation Processes. In *Quality and Treatment of Drinking Water II. The Handbook of Environmental Chemistry (Part C: Water Pollution)*; Hrubec, J., Ed.; Springer: Berlin/Heidelberg, Germany, 1998; Volume 5, pp. 83–141.
- Cao, Y.; Qiu, W.; Zhao, Y.; Li, J.; Jiang, J.; Yang, Y.; Pang, S.-Y.; Liu, G. The degradation of chloramphenicol by O₃/PMS and the impact of O₃-based AOPs pre-oxidation on dichloroacetamide generation in post-chlorination. *Chem. Eng. J.* 2020, 401, 126146. [CrossRef]
- 71. Sehested, K.; Holcman, J.; Bjergbakke, E.; Hart, E.J. Formation of ozone in the reaction of hydroxyl with O₃⁻ and the decay of the ozonide ion radical at pH 10–13. *J. Phys. Chem.* **1984**, *88*, 269–273. [CrossRef]
- 72. Maruthamuthu, P.; Neta, P. Radiolytic chain decomposition of peroxomonophosphoric and peroxomonosulfuric acids. *J. Phys. Chem.* **1977**, *81*, 937–940. [CrossRef]
- 73. Furman, O.S.; Teel, A.L.; Watts, R.J. Mechanism of Base Activation of Persulfate. *Environ. Sci. Technol.* 2010, 44, 6423–6428. [CrossRef] [PubMed]
- 74. Klaning, U.K.; Sehested, K.; Appelman, E.H. Laser flash photolysis and pulse radiolysis of aqueous solutions of the fluoroxysulfate ion, SO4F-. *Inorg. Chem.* **1991**, *30*, 3582–3584. [CrossRef]
- 75. Guo, L.; Zhong, Q.; Ding, J.; Lv, Z.; Zhao, W.; Deng, Z. Low-temperature NOx (x = 1, 2) removal with •OH radicals from catalytic ozonation over a RGO-CeO₂ nanocomposite: The highly promotional effect of oxygen vacancies. *RSC Adv.* 2016, *6*, 87869–87877. [CrossRef]
- Katsoyiannis, I.A.; Canonica, S.; von Gunten, U. Efficiency and energy requirements for the transformation of organic micropollutants by ozone, O₃/H₂O₂ and UV/H₂O₂. *Water Res.* 2011, 45, 3811–3822. [CrossRef] [PubMed]
- 77. Pisarenko, A.N.; Stanford, B.D.; Yan, D.; Gerrity, D.; Snyder, S.A. Effects of ozone and ozone/peroxide on trace organic contaminants and NDMA in drinking water and water reuse applications. *Water Res.* **2012**, *46*, 316–326. [CrossRef] [PubMed]
- Elovitz, M.S.; Von Gunten, U.; Kaiser, H.-P. Hydroxyl Radical/Ozone Ratios during Ozonation Processes. II. The Effect of Temperature, pH, Alkalinity, and DOM Properties. *Ozone Sci. Eng.* 2000, 22, 123–150. [CrossRef]
- 79. Ikehata, K.; El-Din, M.G. Aqueous Pesticide Degradation by Ozonation and Ozone-Based Advanced Oxidation Processes: A Review (Part I). *Ozone Sci. Eng.* 2005, 27, 83–114. [CrossRef]
- 80. Yao, Y.; Xu, C.; Qin, J.; Wei, F.; Rao, M.; Wang, S. Synthesis of Magnetic Cobalt Nanoparticles Anchored on Graphene Nanosheets and Catalytic Decomposition of Orange II. *Ind. Eng. Chem. Res.* **2013**, *52*, 17341–17350. [CrossRef]
- 81. Shi, P.; Su, R.; Zhu, S.; Zhu, M.; Li, D.; Xu, S. Supported cobalt oxide on graphene oxide: Highly efficient catalysts for the removal of Orange II from water. *J. Hazard. Mater.* **2012**, 229–230, 331–339. [CrossRef]
- 82. Beltrán, F.J.; Rivas, J.; Montero-De-Espinosa, R. Catalytic ozonation of oxalic acid in an aqueous TiO2 slurry reactor. *Appl. Catal. B Environ.* **2002**, *39*, 221–231. [CrossRef]
- 83. McElroy, W.J. A laser photolysis study of the reaction of sulfate(1-) with chloride and the subsequent decay of chlorine(1-) in aqueous solution. *J. Phys. Chem.* **1990**, *94*, 2435–2441. [CrossRef]
- Wang, Z.; An, N.; Shao, Y.; Gao, N.; Du, E.; 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]
- Yang, Y.; Pignatello, J.J.; Ma, J.; Mitch, W. Comparison of Halide Impacts on the Efficiency of Contaminant Degradation by Sulfate and Hydroxyl Radical-Based Advanced Oxidation Processes (AOPs). *Environ. Sci. Technol.* 2014, 48, 2344–2351. [CrossRef] [PubMed]

- 86. Naumov, S.; Mark, G.; Jarocki, A.; von Sonntag, C. The reactions of nitrite ion with ozone in aqueous solution–new exper-imental data and quantum-chemical considerations. *Ozone Sci. Eng.* **2010**, *32*, 430–434. [CrossRef]
- 87. Morozov, P.A.; Ershov, B.G. The influence of phosphates on the decomposition of ozone in water: Chain process inhibition. *Russ. J. Phys. Chem. A* 2010, *84*, 1136–1140. [CrossRef]
- Tang, G.; Zhang, Y.; Wei, Y.; Wang, S.; Liu, P.; Jia, Z.; Yu, X.; Ma, F. Advanced treatment of bio-treated Chinese patent medicine wastewater using ozone/peroxymonosulfate-upflow biological aerated filter. *Chem. Eng. J.* 2020, 390, 124527. [CrossRef]
- 89. Yu, X.; Qin, W.; Yuan, X.; Sun, L.; Pan, F.; Xia, D. Synergistic mechanism and degradation kinetics for atenolol elimination via integrated UV/ozone/peroxymonosulfate process. *J. Hazard. Mater.* **2021**, 407, 124393. [CrossRef] [PubMed]
- 90. Miklos, D.B.; Remy, C.; Jekel, M.; Linden, K.G.; Drewes, J.E.; Hübner, U. Evaluation of advanced oxidation processes for water and wastewater treatment—A critical review. *Water Res.* **2018**, *139*, 118–131. [CrossRef] [PubMed]
- Wang, Y.; Xie, Y.; Sun, H.; Xiao, J.; Cao, H.; Wang, S. 2D/2D nano-hybrids of γ-MnO2 on reduced graphene oxide for catalytic ozonation and coupling peroxymonosulfate activation. *J. Hazard. Mater.* 2016, 301, 56–64. [CrossRef] [PubMed]
- 92. Wen, G.; Wang, S.; Wang, T.; Feng, Y.; Chen, Z.; Lin, W.; Huang, T.; Ma, J. Inhibition of bromate formation in the O₃/PMS process by adding low dosage of carbon materials: Efficiency and mechanism. *Chem. Eng. J.* **2020**, 402, 126207. [CrossRef]
- Tan, C.; Cui, X.; Sun, K.; Xiang, H.; Du, E.; Deng, L.; Gao, H. Kinetic mechanism of ozone activated peroxymonosulfate system for enhanced removal of anti-inflammatory drugs. *Sci. Total Environ.* 2020, 733, 139250. [CrossRef]
- 94. Wang, S.; Wang, J. Successive non-radical and radical process of peroxymonosulfate-based oxidation using various activation methods for enhancing mineralization of sulfamethoxazole. *Chemosphere* **2021**, *263*, 127964. [CrossRef]
- 95. Jung, H.; Choi, H. Catalytic decomposition of ozone and para-Chlorobenzoic acid (pCBA) in the presence of nanosized ZnO. *Appl. Catal. B Environ.* **2006**, *66*, 288–294. [CrossRef]
- 96. Real, F.J.; Benitez, F.J.; Acero, J.L.; Sagasti, J.J.P.; Casas, F. Kinetics of the Chemical Oxidation of the Pharmaceuticals Primidone, Ketoprofen, and Diatrizoate in Ultrapure and Natural Waters. *Ind. Eng. Chem. Res.* **2009**, *48*, 3380–3388. [CrossRef]
- 97. Acero, J.L.; Stemmler, K.; von Gunten, U. Degradation Kinetics of Atrazine and Its Degradation Products with Ozone and OH Radicals: A Predictive Tool for Drinking Water Treatment. *Environ. Sci. Technol.* **2000**, *34*, 591–597. [CrossRef]
- Sanchez-Polo, M.; Rivera-Utrilla, J.; Prados-Joya, G.; García, M.; Ángeles, F.; Bautista-Toledo, I. Removal of pharmaceutical compounds, nitroimidazoles, from waters by using the ozone/carbon system. *Water Res.* 2008, 42, 4163–4171. [CrossRef] [PubMed]
- Lian, L.; Yao, B.; Hou, S.; Fang, J.; Yan, S.; Song, W. Kinetic Study of Hydroxyl and Sulfate Radical-Mediated Oxidation of Pharmaceuticals in Wastewater Effluents. *Environ. Sci. Technol.* 2017, *51*, 2954–2962. [CrossRef] [PubMed]
- Benner, J.; Ternes, T.A. Ozonation of Metoprolol: Elucidation of Oxidation Pathways and Major Oxidation Products. *Environ. Sci. Technol.* 2009, 43, 5472–5480. [CrossRef] [PubMed]
- Benitez, F.J.; Acero, J.L.; Real, F.J.; Roldán, G. Ozonation of pharmaceutical compounds: Rate constants and elimination in various water matrices. *Chemosphere* 2009, 77, 53–59. [CrossRef] [PubMed]
- Santoke, H.; Song, W.; Cooper, W.J.; Peake, B.M. Advanced oxidation treatment and photochemical fate of selected anti-depressant pharmaceuticals in solutions of Suwannee River humic acid. J. Hazard. Mater. 2012, 217, 382–390. [CrossRef] [PubMed]
- Lee, Y.; Kovalova, L.; McArdell, C.S.; von Gunten, U. Prediction of micropollutant elimination during ozonation of a hospital wastewater effluent. *Water Res.* 2014, 64, 134–148. [CrossRef] [PubMed]
- 104. McDowell, D.C.; Huber, M.M.; Wagner, M.; von Gunten, U.; Ternes, T.A. Ozonation of Carbamazepine in Drinking Water: Identification and Kinetic Study of Major Oxidation Products. *Environ. Sci. Technol.* **2005**, *39*, 8014–8022. [CrossRef] [PubMed]
- 105. Matta, R.; Tlili, S.; Chiron, S.; Barbati, S. Removal of carbamazepine from urban wastewater by sulfate radical oxidation. *Environ. Chem. Lett.* **2010**, *9*, 347–353. [CrossRef]
- 106. Hoigné, J.; Bader, H. Rate constants of reactions of ozone with organic and inorganic compounds in water—II: Dissociating organic compounds. *Water Res.* **1983**, *17*, 185–194. [CrossRef]
- 107. Oh, W.-D.; Dong, Z.; Lim, T.-T. Generation of sulfate radical through heterogeneous catalysis for organic contaminants removal: Current development, challenges and prospects. *Appl. Catal. B Environ.* **2016**, *194*, 169–201. [CrossRef]
- Liang, C.; Su, H.-W. Identification of Sulfate and Hydroxyl Radicals in Thermally Activated Persulfate. Ind. Eng. Chem. Res. 2009, 48, 5558–5562. [CrossRef]
- Toth, J.E.; Rickman, K.A.; Venter, A.R.; Kiddle, J.J.; Mezyk, S.P. Reaction Kinetics and Efficiencies for the Hydroxyl and Sulfate Radical Based Oxidation of Artificial Sweeteners in Water. J. Phys. Chem. A 2012, 116, 9819–9824. [CrossRef]
- 110. Shu, Z.; Bolton, J.R.; Belosevic, M.; El Din, M.G. Photodegradation of emerging micropollutants using the medium-pressure UV/H2O2 Advanced Oxidation Process. *Water Res.* 2013, 47, 2881–2889. [CrossRef]
- Ma, J.; Graham, N.J. Degradation of atrazine by manganese-catalysed ozonation: Influence of humic substances. *Water Res.* 1999, 33, 785–793. [CrossRef]
- 112. Lau, T.K.; Chu, W.; Graham, N.J.D. The Aqueous Degradation of Butylated Hydroxyanisole by UV/S₂O₈²⁻: Study of Reaction Mechanisms via Dimerization and Mineralization. *Environ. Sci. Technol.* **2007**, *41*, 613–619. [CrossRef]
- 113. Xie, P.; Ma, J.; Liu, W.; Zou, J.; Yue, S.; Li, X.; Wiesner, M.R.; Fang, J. Removal of 2-MIB and geosmin using UV/persulfate: Contributions of hydroxyl and sulfate radicals. *Water Res.* **2015**, *69*, 223–233. [CrossRef]
- 114. Zuo, Z.; Cai, Z.; Katsumura, Y.; Chitose, N.; Muroya, Y. Reinvestigation of the acid–base equilibrium of the (bi)carbonate radical and pH dependence of its reactivity with inorganic reactants. *Radiat. Phys. Chem.* **1999**, *55*, 15–23. [CrossRef]

- Yang, S.; Yang, X.; Shao, X.; Niu, R.; Wang, L. Activated carbon catalyzed persulfate oxidation of Azo dye acid orange 7 at ambient temperature. J. Hazard. Mater. 2011, 186, 659–666. [CrossRef]
- 116. Wen, G.; Wang, S.-J.; Ma, J.; Huang, T.-L.; Liu, Z.-Q.; Zhao, L.; Su, J.-F. Enhanced ozonation degradation of di-n-butyl phthalate by zero-valent zinc in aqueous solution: Performance and mechanism. *J. Hazard. Mater.* **2014**, *265*, 69–78. [CrossRef] [PubMed]
- 117. Antoniou, M.G.; de la Cruz, A.A.; Dionysiou, D.D. Intermediates and reaction pathways from the degradation of micro-cystin-LR with sulfate radicals. *Environ. Sci. Technol.* **2010**, *44*, 7238–7244. [CrossRef] [PubMed]
- 118. Méndez-Díaz, J.; Sánchez-Polo, M.; Rivera-Utrilla, J.; Canonica, S.; von Gunten, U. Advanced oxidation of the surfactant SDBS by means of hydroxyl and sulphate radicals. *Chem. Eng. J.* 2010, *163*, 300–306. [CrossRef]
- 119. Song, W.; Yan, S.; Cooper, W.J.; Dionysiou, D.D.; O'Shea, K.E. Hydroxyl radical oxidation of cylindrospermopsin (cyano-bacterial toxin) and its role in the photochemical transformation. *Environ. Sci. Technol.* **2012**, *46*, 12608–12615. [CrossRef] [PubMed]
- Hammes, F.; Salhi, E.; Köster, O.; Kaiser, H.P.; Egli, T.; Von Gunten, U. Mechanistic and kinetic evaluation of organic disin-fection by-product and assimilable organic carbon (AOC) formation during the ozonation of drinking water. *Water Res.* 2006, 40, 2275–2286. [CrossRef]
- 121. Hammes, F.; Meylan, S.; Salhi, E.; Köster, O.; Egli, T.; Von Gunten, U. Formation of assimilable organic carbon (AOC) and specific natural organic matter (NOM) fractions during ozonation of phytoplankton. *Water Res.* **2007**, *41*, 1447–1454. [CrossRef]
- 122. Fang, J.-Y.; Shang, C. Bromate Formation from Bromide Oxidation by the UV/Persulfate Process. *Environ. Sci. Technol.* **2012**, *46*, 8976–8983. [CrossRef] [PubMed]
- 123. Von Gunten, U.; Hoigne, J. Bromate Formation during Ozonization of Bromide-Containing Waters: Interaction of Ozone and Hydroxyl Radical Reactions. *Environ. Sci. Technol.* **1994**, *28*, 1234–1242. [CrossRef]
- 124. Fischbacher, A.; Löppenberg, K.; von Sonntag, C.; Schmidt, T.C. A New Reaction Pathway for Bromite to Bromate in the Ozonation of Bromide. *Environ. Sci. Technol.* 2015, 49, 11714–11720. [CrossRef]
- 125. Yang, J.; Li, J.; Dong, W.; Ma, J.; Yang, Y.; Li, J.; Yang, Z.; Zhang, X.; Gu, J.; Xie, W.; et al. Enhancement of bromate formation by pH depression during ozonation of bromide-containing water in the presence of hydroxylamine. *Water Res.* **2017**, *109*, 135–143. [CrossRef]
- 126. Legube, B.; Parinet, B.; Gelinet, K.; Berne, F.; Croue, J.-P. Modeling of bromate formation by ozonation of surface waters in drinking water treatment. *Water Res.* **2004**, *38*, 2185–2195. [CrossRef] [PubMed]
- 127. Naumov, S.; von Sonntag, C. Standard Gibbs free energies of reactions of ozone with free radicals in aqueous solution: Quantumchemical calculations. *Environ. Sci. Technol.* 2011, 45, 9195–9204. [CrossRef] [PubMed]
- 128. Bao, M.L.; Griffini, O.; Santianni, D.; Barbieri, K.; Burrini, D.; Pantani, F. Removal of bromate ion from water using granular activated carbon. *Water Res.* **1999**, *33*, 2959–2970. [CrossRef]
- 129. Huang, W.-J.; Cheng, Y.-L. Effect of characteristics of activated carbon on removal of bromate. *Sep. Purif. Technol.* 2008, *59*, 101–107. [CrossRef]
- 130. Yang, J.; Dong, Z.; Jiang, C.; Wang, C.; Liu, H. An overview of bromate formation in chemical oxidation processes: Occurrence, mechanism, influencing factors, risk assessment, and control strategies. *Chemosphere* **2019**, 237, 124521. [CrossRef]
- 131. Ling, L.; Deng, Z.; Fang, J.; Shang, C. Bromate control during ozonation by ammonia-chlorine and chlorine-ammonia pretreatment: Roles of bromine-containing haloamines. *Chem. Eng. J.* **2020**, *389*, 123447. [CrossRef]
- Huang, X.; Zhou, X.; Zhou, J.; Huang, Z.; Liu, S.; Qian, G.; Gao, N. Bromate inhibition by reduced graphene oxide in ther-mal/PMS process. *Water Res.* 2017, 122, 701–707. [CrossRef] [PubMed]
- 133. Liu, Z.; Wang, S.; Ma, W.; Wang, J.; Xu, H.; Li, K.; Huang, T.; Ma, J.; Wen, G. Adding CuCo₂O₄-GO to inhibit bromate formation and enhance sulfamethoxazole degradation during the ozone/peroxymonosulfate process: Efficiency and mechanism. *Chemosphere* 2022, 286, 131829. [CrossRef] [PubMed]
- Liu, Z.; Wen, G.; Ni, Y.; Wang, S.; Yuang, S.; Yu, Y.; Huang, T.; Ma, J. Inhibition of bromate formation in the ozone/peroxymonosulfate process by ammonia, ammonia-chlorine and chlorine-ammonia pretreatment: Comparisons with ozone alone. *Sep. Purif. Technol.* 2022, 278, 119600. [CrossRef]
- 135. Zehavi, D.; Rabani, J. Oxidation of aqueous bromide ions by hydroxyl radicals. Pulse radiolytic investigation. *J. Phys. Chem.* **1972**, 76, 312–319. [CrossRef]
- 136. Zuo, J.; Xu, X.; Wan, Q.; Cao, R.; Liang, Z.; Xu, H.; Li, K.; Huang, T.; Wen, G.; Ma, J. Inactivation of fungal spores in water with peracetic acid: Efficiency and mechanism. *Chem. Eng. J.* **2022**, *427*, 131753. [CrossRef]
- 137. Hoigné, J.; Bader, H. The role of hydroxyl radical reactions in ozonation processes in aqueous solutions. *Water Res.* **1976**, *10*, 377–386. [CrossRef]
- 138. Von Gunten, U.; Bruchet, A.; Costentin, E. Bromate formation in advanced oxidation processes. *J. Am. Water Work. Assoc.* **1996**, *88*, 53–65. [CrossRef]
- 139. Wang, L.; Jing, K.; Hu, B.; Lu, J. Hydrogen peroxide suppresses the formation of brominated oxidation by-products in heatactivated peroxydisulfate oxidation process. *Chem. Eng. J.* 2021, 417, 129138. [CrossRef]
- Wan, Q.Q.; Cao, R.H.; Wen, G.; Xu, X.Q.; Xia, Y.C.; Wu, G.H.; Li, Y.F.; Wang, J.Y.; Lin, Y.Z.; Huang, T.L. Sequential use of UV-LEDs irradiation and chlorine to disinfect waterborne fungal spores: Efficiency, mechanism and photoreactivation. *J. Hazard. Mater.* 2022, 423, 127102. [CrossRef]