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Review

Application of O_3/PMS Advanced Oxidation Technology in the Treatment of Organic Pollutants in Highly Concentrated Organic Wastewater: A Review

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Abstract: The ozone/peroxymonosulfate (O_3/PMS) system has attracted widespread attention from researchers owing to its ability to produce hydroxyl radicals (•OH) and sulfate radicals ($SO_4^{\bullet-}$) simultaneously. The existing research has shown that the O_3/PMS system significantly degrades refinery trace organic compounds (TrOCs) in highly concentrated organic wastewater. However, there is still a lack of systematic understanding of the O_3/PMS system, which has created a significant loophole in its application in the treatment of highly concentrated organic wastewater. Hence, this paper reviewed the specific degradation effect, toxicity change, reaction mechanism, various influencing factors and the cause of oxidation byproducts (OBPs) of various TrOCs when the O_3/PMS system is applied to the degradation of highly concentrated organic wastewater. In addition, the effects of different reaction conditions on the O_3/PMS system were comprehensively evaluated. Furthermore, given the limited understanding of the O_3/PMS system in the degradation of TrOCs and the formation of OBPs, an outlook on potential future research was presented. Finally, this paper comprehensively evaluated the degradation of TrOCs in highly concentrated organic wastewater by the O_3/PMS system, filling the gaps in scale research, operation cost, sustainability and overall feasibility.

Keywords: ozone/peroxymonosulfate; advanced oxidation process; highly concentrated organic wastewater; hydroxyl radicals; sulfate radicals; organic pollutants

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1. Introduction

With the industrial activities that humans operate, all kinds of organic wastewater are inevitably produced. Among them, the highest concentration of organic wastewater is produced in animal husbandry and medical industries. Studies have shown that such highly concentrated organic wastewater still shows high TrOC concentration and toxicity after being treated by a conventional wastewater treatment plant (WWTP) [1–4]. Discharging TrOCs into the natural water body leads to the eutrophication of the water body and a decrease in the oxygen content in the water, which in turn result in the formation of a black and odorous water body [5–7]. Therefore, treating highly concentrated organic wastewater is a significant challenge for traditional WWTP treatment [8,9]. Some researchers have solved this problem using a chemically enhanced primary treatment, reducing chlorination byproducts, and applying a machine learning model to pH and chemical dose control [10–12]. However, subsequent observation of the receiving waters revealed that the microbial community in the river was significantly affected [13]. This showed that compared with the activated sludge and chemical precipitation methods in the traditional WWTP, this new enhanced primary and secondary treatment scheme had improved effects; however, there are still limitations in treating TrOCs [14,15].

Several scholars are focusing on advanced oxidation processes (AOPs) due to the water quality problem in WWTPs. Traditional AOPs mainly degrade various TrOCs by producing •OH, and the treatment effect is not ideal. However, the O_3/PMS system can simultaneously produce •OH and $SO_4^{\bullet-}$, which eliminates the limitation of traditional AOPs in terms of degradation effect [16–24]. Relevant experiments showed that [25], in the O_3/PMS system, the more types and contents of TrOCs present in wastewater, the higher the proportion of •OH is in the oxidation contribution. The experiment of tert-Butyl alcohol quenching •OH showed that [26] the O_3/PMS process demonstrated a higher removal efficiency than most AOPs dominated by •OH, especially at a higher pH. At that time, $SO_4^{\bullet-}$ played a significant role in the degradation of TrOCs, which is the advantage of the process that produced two kinds of active free radicals compared with the process that only produced a single free radical. However, at that time, the degradation efficiency of chemical oxygen demand (COD) and biochemical oxygen demand (BOD) in the system decreased, mainly because the selectivity of $SO_4^{\bullet-}$ to TrOCs was higher than that of •OH [20,27]. In addition, when PMS was used alone for degradation, the toxicity of the treated water was often much higher than that of the O_3/PMS process. Therefore, it was likely that O_3 and hydroxyl inhibited the generation of disinfection byproducts (DBPs) [28].

Given the advantages of the O_3/PMS process—environmental sustainability, high efficiency and strong anti-interference ability—the development of the O_3/PMS process has been paid more and more attention by scholars. However, there are still some gaps when the O_3/PMS system is applied to the degradation of highly concentrated organic wastewater, such as the specific degradation effect of various TrOCs, the toxicity changes in the degradation process, the reaction mechanism, various influencing factors and OBPs generated by them. Therefore, in this paper, the reaction mechanism of O_3/PMS was summarised, and various influencing factors of the system and a series of chemical changes in the treatment of highly concentrated organic wastewater were described in detail. Furthermore, it introduces the latest research progress on the O_3/PMS process in highly concentrated wastewater treatment, which provides a valuable reference for future studies to carry out in-depth research on the O_3/PMS process. In addition, future research directions were proposed, given the limited understanding of the O_3/PMS system in the degradation of TrOCs and the formation of OBPs.

2. Mechanism and Influence Factors of O_3/PMS Process

2.1. Reaction Mechanism

As shown in Figure 1, from a microscopic perspective, the structural formula of PMS (H_2SO_5) is such that a hydrogen atom in H_2O_2 is replaced by a sulfo group (–SO_3H) and HOO– is combined with –SO_3H. Therefore, some characteristics of PMS are similar to those of H_2O_2, but the difference is that the free radicals ($SO_4^{\bullet-}$ and •OH) produced by breaking the O-O bonds are different. There are many effective oxidants in the O_3/PMS system. As a strong oxidant, O_3 can effectively degrade many organic substances that are difficult to deal with in the traditional oxidation process [29,30]. Generally, O_3 attacks only the double bonds, activated aromatic groups and nonprotonated amines of TrOCs [31,32], but it has strong selectivity. PMS slowly hydrolyses sulfuric acid and H_2O_2 in water and reacts slowly with TrOCs, mainly acting as the primary source of $SO_4^{\bullet-}$ in the system. •OH is a strong nonselective oxidant, which can diffuse rapidly in the system and react with various TrOCs, with a reaction rate range of 1×10^9–3×10^{10} $M^{-1} \cdot s^{-1}$ [33].

In general, the degradation of micropollutants by O_3 is achieved through the joint activities of molecular O_3 and OH [34]. The degradation selectivity of $SO_4^{\bullet-}$ is higher than that of •OH, but its higher redox potential (E0 = 2.5~3.1 V) indicates that $SO_4^{\bullet-}$ has a more efficient degradation rate in the system. Further, the reaction between $SO_4^{\bullet-}$ and TrOCs has less alkali resistance and is less interfered with by natural organic matter (NOM) and inorganic nonmetallic ions [35–37]. Therefore, $SO_4^{\bullet-}$ produced by PMS activation can exist in the system for a long time and effectively and continuously oxidise TrOCs. In each reaction process in Figure 1, the direct oxidation and indirect oxidation of •OH in reaction processes 1, 2 and 3 are dominant. However, for some TrOCs, the indirect oxidation of $SO_4^{\bullet-}$ produced in process 4 plays an important role. On the other hand, the selectivity of •OH and $SO_4^{\bullet-}$ produced in the O_3/PMS system is lower than that of O_3, especially •OH. This means that the process has a broader application range [38–41].

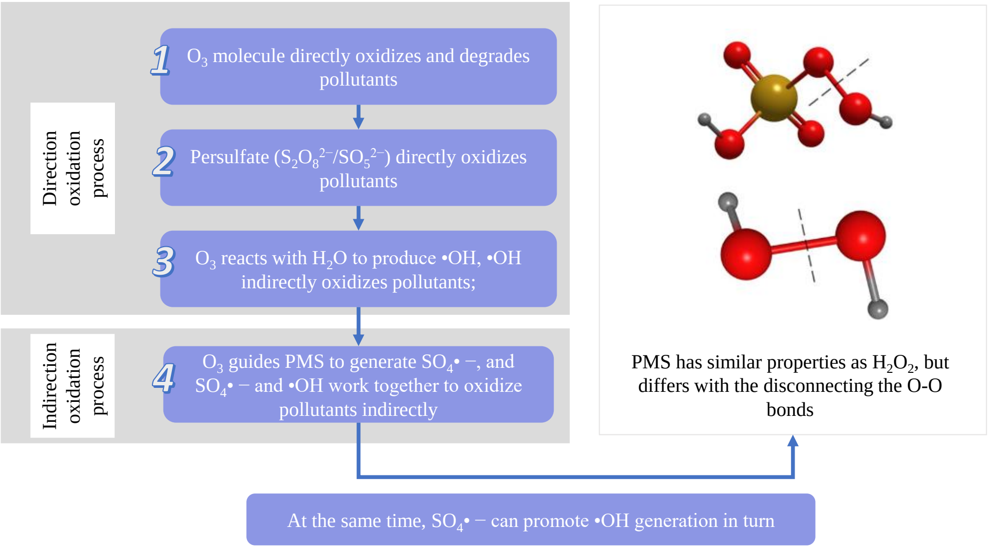

Figure 1. Free radical generation process in O_3/PMS process and bond breaking of PMS and H_2O_2.

As shown in Table 1, deprotonated PMS first reacts with O_3 to generate SO_8^{2-} (Reaction 1). Then, this substance decays in the form of biomolecules for decomposition (Reactions 2 and 3). $O_3^{\bullet-}$ (superoxide radical) is converted into •OH (Reactions 4 and 5) in water. The $SO_5^{\bullet-}$ produced by Reaction 2 can not only react with ozone again to generate $SO_4^{\bullet-}$ (Reaction 6) but also self-decompose to generate a sulfate radical (Reaction 7) or decay to $S_2O_8^{2-}$ (Reaction 8). At the same time, excessive $SO_4^{\bullet-}$ in the system further oxidises H_2O or OH^- to form •OH (Reaction 9, 10) [17,35,42,43].

Table 1. The reaction equations for the formation of •OH and $SO_4^{\bullet-}$ and the corresponding reaction rate constants.

No.	Reaction	Reaction Rate Constant	References
1	$SO_5^{2-}+O_3 \rightarrow SO_8^{2-}$	2.12×10^4	[17]
2	$SO_8^{2-} \rightarrow SO_5^{\bullet-}+O_3^{\bullet}$	none	[17]
3	$SO_8^{2-} \rightarrow SO_4^{2-}+2O_2$	none	[17]
4	$O_3^{\bullet-} \rightleftharpoons O_2+O^{\bullet-}$	none	[43]
5	$O^{\bullet-}+H_2O \rightleftharpoons \bullet OH + OH^-$	none	[43]
6	$SO_5^{\bullet-}+O_3 \rightarrow SO_4^{\bullet-}+2O_2$	$1.6 \times 10^5\ M^{-1}{\cdot}s^{-1}$	[43,44]
7	$2SO_5^{\bullet-} \rightarrow 2SO_4^{\bullet-}+O_2$	$2.1 \times 10^8\ M^{-1}{\cdot}s^{-1}$	[43,44]
8	$2SO_5^{\bullet-} \rightarrow S_2O_8^{2-}+O_2$	$2.2 \times 10^8\ M^{-1}{\cdot}s^{-1}$	[43,44]
9	$SO_4^{\bullet-}+H_2O \rightarrow H^+ + SO_4^{2-}+\bullet OH$	$<3 \times 10^3\ M^{-1}{\cdot}s^{-1}$	[36,43]
10	$SO_4^{\bullet-}+OH^- \rightarrow SO_4^{2-}+\bullet OH$	$7.3 \times 10^7\ M^{-1}{\cdot}s^{-1}$	[36,43]

In addition, When PMS in the system is excessive, under an alkaline environment, it hydrolyses to produce H_2O_2 (Reaction 11 and 12) [17,44], and then the H_2O_2 reacts with O_3 to produce •OH (Reaction 13) [45]. Excess $SO_4^{\bullet-}$ in the system hydrolyses to produce •OH or forms new •OH with OH^- (Reaction 14 and 15) [44,46]. Table 2 shows the reaction formulas and corresponding reaction rate constants of PMS and $SO_4^{\bullet-}$ promoting •OH formation [17,44–46].

Table 2. Reaction equations and corresponding reaction rate constants for PMS- and $SO_4^{\bullet-}$-promoted •OH formation.

No.	Reaction	Reaction Rate Constant	References
11	$HSO_5^- + H_2O \rightarrow HSO_4^- + H_2O_2$	none	[17]
12	$SO_5^{2-} + H_2O \rightarrow SO_4^{2-} + H_2O_2$	none	[44]
13	$H_2O_2 + 2O_3 \rightarrow 3O_2 + 2\bullet OH$	none	[45]
14	$SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + \bullet OH$	$(6.5 \pm 1.0) \times 10^7\ M^{-1}\cdot s^{-1}$	[46]
15	$SO_4^{\bullet-} + H_2O \rightarrow H^+ + SO_4^{2-} + \bullet OH$	$<3 \times 10^3\ M^{-1}\cdot s^{-1}$	[44]

2.2. Influence Factors

2.2.1. pH Value

pH value significantly influences the degradation efficiency of the O_3/PMS process. When the pH value rises from 6 to 7, the contribution rate of •OH to the degradation in the system is the highest, but it shows a trend of gradual decline. When the pH value rises from 7 to 9, the degradation rate in the system gradually increases. This may be attributed to two phenomena: (1) the increase in hydroxyl concentration further enhances the decomposition rate of O_3 to •OH. (2) The essence of PMS catalysing O_3 is the reaction with deprotonated PMS (SO_5^{2-}), and their reaction rate constant is $2.12 \times 10^4\ M^{-1}\cdot s^{-1}$ (Reaction 1). The secondary dissociation constant of PMS dissociation to SO_5^{2-} is 9.4. Therefore, within the studied pH range, the closer it is to 9.4, the higher the concentration of deprotonated PMS, and the faster the catalytic decomposition of $O_{3.}$ When the pH increased to more than 9.4, the degradation rate decreased slightly or remained unchanged, and then the decline increased. The main reason is that PMS decomposes in a nonfree radical way, the production rate of $SO_4^{\bullet-}$ decreases, and a too-high pH concentration makes the free radicals in the system lose their reactivity [17,47–51].

2.2.2. O_3 Dosage

The concentration of O_3 is critical to the yield of two free radicals in the system, and a higher O_3 concentration can significantly increase the rate of free radicals, especially ·OH. However, when excessive O_3 is introduced, excessive molecular O_3 in the system can quench the free radicals, resulting in a decrease in the reaction rate [17,52–54].

2.2.3. PMS Dosage

The effect of the concentration of PMS is similar to that of O_3, which shows that a slight increase can improve the free radical generation rate. The only difference is that when PMS is slightly excessive, the growth rate of $SO_4^{\bullet-}$ generation rate is greater than that of •OH. Excessive PMS reduces the pH value of the solution, and undissolved PMS produces the phenomenon of quenching free radicals [42,55,56].

2.2.4. Ratio of O_3 to PMS

The system's molar mass ratio of O_3 to PMS is also critical to the degradation process. Research has shown that [23,24] the ratio of O_3 to PMS of 1:1 is the optimal ratio, at which point the degradation rate in the system is the fastest, indicating that sufficient O_3 is the key to producing free radicals efficiently. However, when further analysing the influence of the concentration of O_3 and PMS on the degradation rate, it was found that when the degradation rate reached it is maximum, further increasing the concentration of O_3 and PMS reduced the removal efficiency. This may be due to the quenching effect of excessive O_3 and PMS on the two free radicals [57–59].

2.2.5. Temperature

A significant number of studies have confirmed that, in the range of 5–40 °C, with the increase in temperature, the degradation rate increases in the experiment. This may be that the O-O bond in PMS breaks at high temperatures, which increases the conversion of $SO_4{}^{\bullet-}$ [60,61]. However, when the temperature is higher than 40 °C, increasing the temperature causes the reaction rate of the system to decrease. This is probably because the temperature is too high at this time, so O_3 escapes from the solution into the air before it decomposes.

2.2.6. Inorganic Anions

The influence of inorganic ions on the O_3/PMS system is summarised in Table 3, which is described as follows.

Common inorganic ions in solution, such as chloride ions, can react with •OH and $SO_4{}^{\bullet-}$ to generate chlorine-containing free radicals ($Cl^{\bullet}$, $Cl_2{}^{\bullet-}$, etc.) with strong selectivity. It can be seen from Reactions 16 and 17 that chloride ions and •OH can easily generate $ClOH^{\bullet-}$ and Cl^- under acidic conditions. When the concentration of H^+ is higher (i.e., the pH value is lower), $ClOH^{\bullet-}$ then reacts with H^+ to generate $Cl^{\bullet}$ (Reaction 22). However, when in a neutral or alkaline environment, the hydrogen ion concentration is low, so the capture effect of chloride ions on •OH is weak, and the degradation reaction dominated by •OH is less affected. The reaction of chloride ions with $SO_4{}^{\bullet-}$ (Reaction 18) is independent of pH, so it has a noticeable capture effect on $SO_4{}^{\bullet-}$ under experimental conditions and generates $Cl^{\bullet}$ and $Cl_2{}^{\bullet-}$ through Reactions 18–21 [62,63].

Carbonate is also the capture agent of •OH and $SO_4{}^{\bullet-}$, and its reaction formula for capturing free radicals is shown in Reactions 24–27. Carbonate reduces the decomposition rate of ozone and captures •OH and $SO_4{}^{\bullet-}$ to generate a carbonate radical ($CO_3{}^{\bullet-}$), a more selective free radical. This enhances the selectivity of the reaction in the system and reduces the applicability of the O_3/PMS process [62,64,65].

Nitrite and phosphate ions can also capture free radicals; see Reactions 26–35. However, the generated nitrate radical ($NO_2{}^{\bullet}$) and the phosphate radical ($HPO_4{}^{\bullet-}$) have higher reaction selectivities and lower oxidation capacities, negatively affecting the system. Therefore, when a phosphate buffer solution is used in the O_3/PMS system, the concentration of phosphate ions should be controlled [62,66,67].

Table 3. The reaction formula of each inorganic ion in the O_3/PMS system.

Inorganic Anions	No.	Reaction	Reaction Rate Constant ($L{\cdot}M^{-1}{\cdot}s^{-1}$)	References
Cl^-	16	$\bullet OH + Cl^- \rightarrow ClOH^{\bullet-}$	4.3×10^9	[68]
	17	$ClOH^{\bullet-} \rightarrow \bullet OH + Cl^-$	6.1×10^9	[68]
	18	$SO_4{}^{\bullet-} + Cl^- \rightarrow SO_4{}^{2-} + Cl^{\bullet}$	3.0×10^8	[69]
	19	$SO_4{}^{2-} + Cl^{\bullet} \rightarrow SO_4{}^{\bullet-} + Cl^-$	2.5×10^8	[69]
	20	$Cl^- + Cl^{\bullet} \rightarrow Cl_2^{\bullet-}$	8.5×10^9	[70]
	21	$Cl_2^{\bullet-} \rightarrow Cl^- + Cl^{\bullet}$	6.0×10^4	[71]
	22	$ClOH^{\bullet-} + H^+ \rightarrow Cl^{\bullet} + H_2O$	2.1×10^{10}	[68]
	23	$Cl_2^{\bullet-} + \bullet OH \rightarrow HOCl + Cl^-$	1.0×10^9	[72]
$HCO_3{}^-$	24	$HCO_3^- + \bullet OH \rightarrow CO_3^{\bullet-} + H_2O$	8.6×10^6	[33]
	25	$HCO_3^- + SO_4{}^{\bullet-} \rightarrow CO_3^{\bullet-} + SO_4{}^{2-} + H^+$	3.9×10^8	[73]
$CO_3{}^{2-}$	26	$CO_3^{2-} + \bullet OH \rightarrow CO_3^{\bullet-}$	2.8×10^6	[33]
	27	$CO_3^{2-} + SO_4{}^{\bullet-} \rightarrow CO_3^{\bullet-} + SO_4{}^{2-}$	6.1×10^6	[74]
$NO_2{}^-$	28	$NO_2^- + \bullet OH \rightarrow NO_2^{\bullet} + OH^-$	None	[75]
	29	$NO_2^- + SO_4{}^{\bullet-} \rightarrow NO_2^{\bullet} + SO_4{}^{2-}$	None	[75]
	30	$NO_2^- + HSO_5^- \rightarrow NO_3^- + HSO_4^-$	None	[76]
	31	$NO_2^- + O_3 \rightarrow NO_3^- + O_2$	None	[76]
$HPO_4{}^{2-}$	32	$\bullet OH + HPO_4^{2-} \rightarrow HPO_4^{\bullet-} + OH^-$	1.5×10^5	[35]
	33	$\bullet OH + H_2PO_4^{2-} \rightarrow HPO_4^{\bullet-} + H_2O$	2.0×10^4	[35]
	34	$SO_4{}^{\bullet-} + HPO_4^{2-} \rightarrow HPO_4^{\bullet-} + SO_4{}^{2-}$	1.2×10^6	[77]
	35	$SO_4{}^{\bullet-} + H_2PO_4^{2-} \rightarrow HPO_4^{\bullet-} + HSO_4{}^{2-}$	5.0×10^4	[77]

2.2.7. NOM

NOM widely exists in actual water bodies, and some functional groups (such as phenols and amines) can react with ozone to form •OH; further, their reaction with •OH can also promote the reaction process, thus promoting the decomposition of O_3 and the generation of free radicals [78–80]. At the same time, NOM competes with the target for oxidants such as O_3, •OH and $SO_4^{\bullet-}$, thus reducing the removal rate of the target. Therefore, a low concentration of NOM promotes ozone decomposition to produce •OH, but when the concentration of NOM is too high, it competes with TrOCs in the system for two free radicals, inhibiting the degradation efficiency. NOM accelerates the formation of •OH from O_3, resulting in the concentration of •OH being greater than that of $SO_4^{\bullet-}$ [69,81–84].

To sum up, the main influencing factors in the O_3/PMS system are presented in Table 4.

Table 4. The main influencing factors in the O_3/PMS system.

Influence Factors	Performance			References
	pH = 6→7	pH = 7→9.4	pH > 9.4	
pH	1. The contribution rate of •OH is greater than that of $SO_4^{\bullet-}$, but it first increases and then decreases with the increase in pH value.	1. The decomposition rate of O_3 and PMS is improved. 2. The contribution rate of $SO_4^{\bullet-}$ degradation gradually increases. 3. $SO_4^{\bullet-}$ increases the generation rate of •OH.	1. The degradation rate decreases gradually. 2. PMS decomposes with nonfree radicals, and $SO_4^{\bullet-}$ generation rate decreases gradually.	[17,47–51]
O_3 dosage	1. Higher O_3 concentration can improve the yield of free radicals and degradation efficiency. 2. Excessive O_3 concentration quenches free radicals.			[17,52–54]
PMS dosage	1. Higher PMS concentration increases the decomposition rate of O_3. 2. Excessive PMS causes the pH value of the solution to drop, and the undecomposed PMS quenches free radicals.			[42,55,56]
O_3: PMS	1. When the ratio of O_3 to PMS is 1:1, the decomposition rate of O_3 is the highest. 2. When the ratio of O_3 to PMS is 1:2 or 2:1, the reaction rate has no significant change.			[57–59]
Temperature	1. The decomposition of O_3 is accelerated with the increase in temperature. 2. Higher temperature promotes the formation of free radicals and improves degradation efficiency. 3. There is no obvious thermodynamic control effect within 5–40 °C. 4. When the temperature is higher than 40 °C, the formation rate of free radicals decreases.			[60,61]
Inorganic anions	1. Chloride ions: when the concentration is low, the degradation of TrOCs is promoted, the degradation effect gradually decreases as the concentration increases until the effect is the same as that of no addition, and then if the chloride ions are further increased, the degradation is inhibited. 2. Bicarbonate ions and carbonate ions: reduce the decomposition rate of ozone, reduce the reaction rate and improve the selectivity of the reaction, reducing the applicability of the O_3/PMS process. 3. Nitrite ions and phosphate ions: have a strong inhibitory effect.			[62–67]
NOM	1. Low concentration of NOM promotes ozone decomposition to generate •OH, but when the concentration of NOM is too high, it competes with TrOCs in the system for two free radicals and inhibits the degradation efficiency. 2. NOM accelerates O_3 to generate •OH, resulting in •OH concentration being greater than that of $SO_4^{\bullet-}$.			[69,79–84]

3. Research Status of the O_3/PMS Process on Highly Concentrated Wastewater

The essence of the advanced oxidation process is to produce enough free radicals to oxidise and degrade organics in water [85]. The advanced oxidation system is dominated by •OH. It has a broader scope of application as it does not produce secondary pollution and the cost of equipment and consumables is low, but it still faces problems such as insufficient mineralisation capacity. While the advanced oxidation system based on $SO_4^{\bullet-}$ shows the advantages of a fast reaction and short cycle, compared with the system based on •OH, $SO_4^{\bullet-}$ has a more substantial selectivity for the reaction environment and smaller scope of application [86,87]. As described below, extensive research has been carried out on the O_3/PMS process in treating highly concentrated organic wastewater.

TrOCs in high-concentration organic wastewater are challenging to degrade efficiently in sewage treatment plants, resulting in pollution of receiving water bodies [17,88,89]. This usually requires pretreatment or advanced treatment of this organic wastewater [90]. When the O_3/PMS process is used for pretreatment, O_3 can decompose macromolecular organic pollutants into small molecular organic pollutants with low toxicity and easy biochemical degradation, and then $SO_4^{\bullet-}$ and •OH degrade a part of TrOCs to improve the biochemical index of the wastewater. On the other hand, when the O_3/PMS process is used for advanced treatment, TrOCs are directly oxidised by O_3 or •OH or co-oxidised by $SO_4^{\bullet-}$ and •OH radicals and are eventually mineralised directly into CO_2 and H_2O, which significantly reduces the COD and BOD in the water [91–94].

In terms of pretreatment, Ghanbari F. et al. [95] added ultraviolet (UV) to treat polluted water with landfill leachate (PWLL) based on the O_3/PMS system. In the O_3/PMS/UV process under the optimum conditions of pH 7, PMS = 5.7 g/L and O_3 = 1.7 $mg \cdot min^{-1}$, after 75 min of reaction, the total organic carbon (TOC) in the system and chromaticity, ammonia nitrogen, COD and BOD removal rates reached 74%, 98%, 93%, 81% and 69%, respectively. The results showed that the generation rates of $SO_4^{\bullet-}$ and •OH active radicals were increased under the action of UV, and the removal ability of TOC in PWLL was significantly improved. At the same time, adding ferrous ions could further increase the TOC removal rate to 77%. The removal of TOC by O_3/PMS/UV conformed to the quasi-first-order kinetic model, and the pseudo-first-order rate constants (K_{obs}) were 0.0203 min^{-1}. Compared with H_2O_2/UV, O_3/PMS/UV had higher removal rates of TOC, COD, chromaticity and ammonia nitrogen. Wang H.W. et al. [96] added polymerised ferric sulfate (PFS) and nanoscale zero-valent iron (NZVI) to the O_3/PMS system to form a NZVI/PMS/O_3 process to treat the reverse osmosis concentrated leachate (ROCL). Under the optimum conditions of PFS concentration of 8 $g \cdot L^{-1}$, O_3 dosage of 100 $mg \cdot min^{-1}$, PMS dosage of 1.71 g/L and NZVI dosage of 5.58 g/L, the maximum removal rates of COD and TOC were 89.1% and 83.2%, respectively, and the biochemical index (BOD_5/COD) was increased from 0.02 to 0.32. The analysis of excitation–emission matrix (EEM) fluorescence spectroscopy showed that humus-like and fulvic-acid-like substances in ROCL were effectively removed, indicating that most of the macromolecular organics in the system can be transformed into small molecule organics, and the biodegradability was significantly improved after treatment. Jaafarzadeh N. et al. [75] used the magnetic copper ferrite nanoparticle (MCFN) $CuFe_2O_4$ as a catalyst to treat 2,4-dichlorophenoxyacetic acid (2,4-D) based on the O_3/PMS system to reduce the toxicity of highly concentrated organic wastewater. After treatment with the O_3/PMS/MCFNs system, its biochemical index increased from 8.3% to 58.9%, toxicity decreased from 76.5% to 3.8%, TOC removal rate was 67.3% and 2,4-D removal rate was 42.7%. Based on the breath measurement test, the O_3/MCFNs/PMS process significantly degraded the 2,4-D solution and improved the biodegradability of wastewater. Tan C.Q. et al. [97] studied the degradation of aspirin (ASA) and phenacetin (PNT) by the O_3/PMS system. After O_3 preoxidation, the toxicity of DBPs in the system decreased significantly. It was found that the increase in pH value significantly promoted the degradation effect of the above two TrOCs, and the K_{obs} values of ASA and PNT increased by 3.3×10^{-2} min^{-1} and 8.3×10^{-2} min^{-1}, respectively. The degradation rates of $SO_4^{\bullet-}$, •OH and O_3 for ASA were 44.5%, 32.9% and 22.6%, respectively, which were relatively balanced, while •OH had the best degradation effect for PNT, which was 71.4%, followed by $SO_4^{\bullet-}$ and O_3 with 16.7% and 11.9%, respectively.

In terms of advanced treatment, Zheng Z.W. et al. [98] studied the synergistic effect of the O_3/PMS process on the degradation of isothiazolinone fungicide. It was found that at pH 7, the degradation efficiency of methylisothia-zolinone (MIT) and chloro-methyl-isothiazolinone (CMIT) increased to 91.0% and 81.8%, respectively, within 90 s. The total radical formation value (R_{ct}, •R) of the O_3/PMS process was 24.6 times that of the O_3 process. Because O_3/PMS has a low selectivity for macromolecular organic pollutants in the system and a good activation effect for some inorganic anions (such as HCO_3^-) precipitated by PMS, O_3/PMS shows better adaptability to actual wastewater. Therefore, the O_3/PMS process has a good application prospect for the degradation of TrOCs in highly concentrated organic wastewater. Tang G.M. et al. [99] combined the O_3/PMS system with upflow biological aerated filter (UBAF) for the biological treatment of biotreated Chinese patent medicine wastewater (BCPMW). Under the conditions of an initial pH of 7.4–8.9, O_3 concentration of 20 $mg{\cdot}L^{-1}$, potassium bisulfate dosage of 50 $mg{\cdot}L^{-1}$, UBAF gas–liquid ratio of 4:1, UBAF hydraulic retention time of 4 h, UBAF backwash time of 7 d and temperature of 16–28 °C, the O_3/PMS/UBAF combined process could effectively degrade organic pollutants in the waste liquid. The removal rates of dissolved organic carbon (DOC), COD and chromaticity were 77.60%, 85.68% and 81.79%, respectively. After O_3/PMS/UBAF treatment, the COD load was less than 48 $mg{\cdot}L^{-1}$, and the BCPMW chromaticity grade was less than 25, meeting the requirements of the emission standard (GB21906-2008). In addition, O_3/PMS oxidation improved the overall removal rate and biodegradation rate of dissolved organic matter (DOM) in BCPMW. Ghanbari F. et al. [48] investigated the effects of different operating parameters on the degradation of benzotriazole (BTA) by ultrasonic (US) combined with the O_3/PMS process. The results showed that the O_3/PMS/US process was the best under the conditions of pH 7, O_3 = 6.8 $mg{\cdot}L^{-1}$, PMS = 1.71 g/L and US power = 200 W. After 60 min of reaction, BTA with a concentration of 40 $mg{\cdot}L^{-1}$ was completely degraded, with a COD removal rate of about 85%, a TOC removal rate of 75% and a total organic nitrogen (TON) removal rate of 73.3%. The removal test of BTA found that •OH was the main oxidant for the oxidation of BTA in the O_3/PMS/US collaborative process. The inhibition of anions on BTA removal was $NO_2^- > HCO_3^- > Cl^- > NO_3^- > SO_4^{2-}$. The degradation intermediates of BTA were identified, and the oxidation pathway of BTA was proposed, as shown in Figure 2.

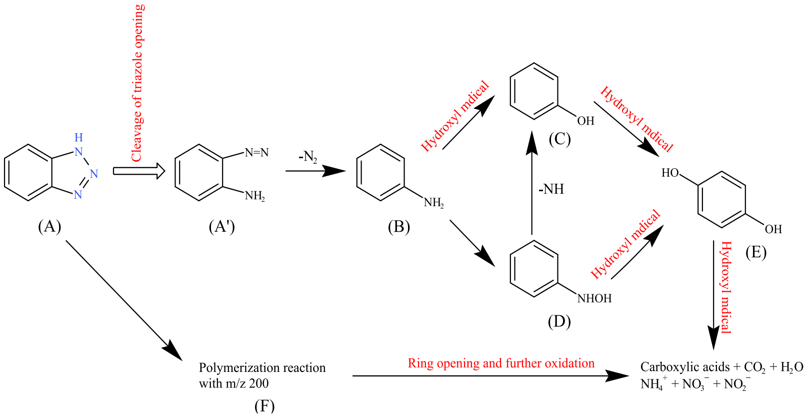

Figure 2. Degradation mechanism of BTA (O_3 = 6.8 $mg{\cdot}L^{-1}$, pH = 7.0, PMS = 1.71 g/L, US power = 200 W and 60 min).

The above studies showed that the O_3/PMS process, as a sustainable and efficient AOP, is feasible in treating highly concentrated organic wastewater, but there are still some challenges. Firstly, the optimal reaction conditions of the O_3/PMS process are neutral and weakly alkaline. However, it is often difficult to control the pH value of the reaction due to the complexity of various organic substances in the actual wastewater owing to complex organic substances in real wastewater. Secondly, for most TrOCs, it is often •OH that plays the main role in oxidation. Nevertheless, for the degradation of some TrOCs, O_3 and $SO_4^{\bullet-}$ both play a role that cannot be ignored. Therefore, in practical application, it is necessary to summarise and form a systematic quantitative dosing standard to realise the optimisation of the effectiveness and economy of the O_3/PMS process. The applications of the O_3/PMS method in highly concentrated organic wastewater treatment are summarised briefly in Table 5.

Table 5. O_3/PMS method applications in organic degradation in highly concentrated organic wastewater.

Application Scenario	Process Category	Research Findings	Ref.
High-concentration organic wastewater	O_3/PMS	At pH = 7.0, the degradation efficiency of MIT and CMIT increased to 91.0% and 81.8%, respectively, within 90 s. R_{ct}, •R of the O_3/PMS process was 24.6 times that of ozonation alone.	[63]
		After O_3 preoxidation, the toxicity of DBPs in the system reduced from 6.63×10^{-2} min^{-1} to 5.27×10^{-2} min^{-1}. However, the increase in pH value could significantly promote the degradation of the two TrOCs, and the k_{obs} values of ASA and PNT increased by 3.3×10^{-2} min^{-1} and 8.3×10^{-2} min^{-1}, respectively.	[62]
	PMS/O_3/UV	Under the optimal conditions of pH = 7, PMS = 5.7 g/L and O_3 = 1.7 mg/min, the removal rates of TOC, chromaticity, ammonia, COD and BOD by PMS/O_3/UV at 75 min were 74%, 98%, 93% and 69%, respectively.	[59]
	NZVI/PMS/O_3	Under the optimal conditions of 8 g/L FPS, 100 mg/min O_3, 1.71 mg/L PMS and 5.58 g/L NZVI, the maximum removal rates of COD and TOC were 89.1% and 83.2%, respectively, and the biodegradability index (BOD_5/COD) was increased from 0.02 to 0.32.	[60]
	PMS/MCFNs/O_3	The biodegradability of activated sludge containing 2,4-D increased from 8.3% to 58.9%, the toxicity decreased from 76.5% to 3.8%, the removal rate of TOC was 67.3% and the removal rate of 2,4-D was 42.7%.	[61]
	O_3/PMS-UBAF	After O_3/PMS/UBAF treatment, the COD load was less than 48 $mg \cdot L^{-1}$, and the BCPMW chromaticity grade was lower than 25. In addition, the overall removal rate and biodegradation rate of DOM in BCPMW were improved by O_3/PMS oxidation.	[64]
	O_3/PMS/US	Hydroxyl radical was the main oxidant of BTA oxidation by the O_3/PMS/US combined process. The inhibition of anions on BTA removal was $NO_2^- > HCO_3^- > Cl^- > NO_3^- > SO_4^{2-}$.	[36]

4. Evaluation of O_3/PMS Process Operation Characteristics

Currently, the O_3/PMS process research is still in the laboratory stage, and the relevant economic evaluation is still relatively lacking. Therefore, researchers should optimise the treatment parameters in their different environments to achieve maximum effectiveness and economic benefits.

In the previous combined process based on O_3, the reaction between O_3 and OH^- was often mistaken as the main source of •OH. As a result, the rate constant of this reaction was very low, and a considerable reaction rate could be achieved only at a very high pH, while other competitive reactions are usually much faster, such as the ozone reaction with DOM [100,101]. However, in this process, some O_3 enters the system and reacts with TrOCs and inorganic ions in the system too early, leading to the premature consumption of O_3 and the generation of various OBPs [59,102]. Researchers have gradually solved this defect; that is, by adding other catalysts and optimising the reaction device, O_3 is preferentially consumed to produce two free radicals [103,104]. Subsequently, H_2O_2 generated by PMS hydrolysis is also converted into •OH. At the same time, excess $SO_4^{\bullet-}$ in the system also reacts with H_2O or hydroxide ions to form •OH, reaching dynamic equilibrium [34,35]. During the degradation process, the concentration of O_3, the concentration of PMS and the molar mass ratio of O_3 to PMS are the keys to an efficient reaction. Sufficient O_3 and PMS can keep the reaction at a high level. See Figure 3 for details.

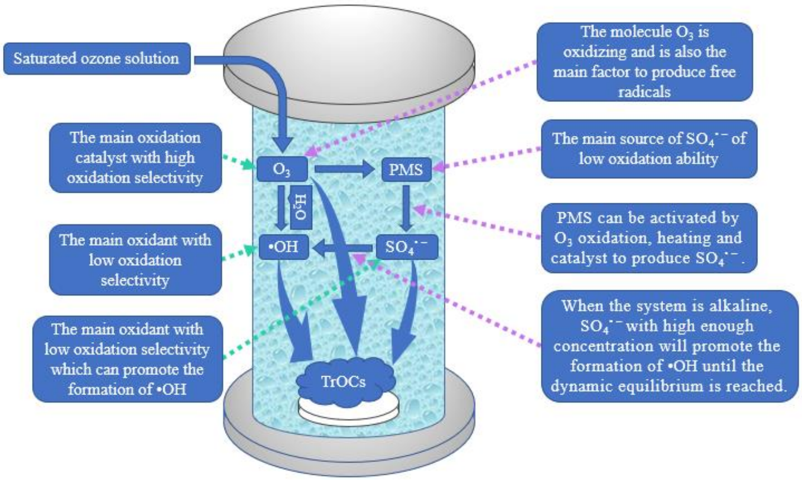

Figure 3. Main oxidants and catalytic processes in O_3/PMS system.

Therefore, to ensure the production rate of •OH in a neutral environment, it usually needs to be achieved by adding a catalyst or by electrolysis [105]. In addition, the decomposition of O_3 is very slow when •OH is used as the main active oxidation free radical under acidic conditions in an OH^--deficient system. This can affect the formation of •OH and $SO_4^{\bullet-}$ active free radicals [106]. At this time, TrOCs were directly oxidised in the form of O_3 molecules in the system. Neutral and alkaline environments can often improve the degradation efficiency of TrOCs. However, in a system where $SO_4^{\bullet-}$ is the main active oxidation radical or •OH does not occupy the main degradation position, the increase in pH has a minor impact on the degradation efficiency of TrOCs. The main reason is that increasing pH can increase the O_3 consumption rate constant, OH^- triggers the decomposition of ozone to generate •OH, and •OH can accelerate the decomposition of PMS [107]. O_3/PMS usually shows the strongest oxidation performance when the pH is about 9. More free radicals are produced in the system with increasing pH, and these free radicals may quench each other, resulting in a decline in the degradation effect, which may be the reason for the decline in the oxidation effect of the O_3/PMS process in a high-pH environment.

Generally, •OH and $SO_4^{\bullet-}$ are the main reactive oxygen species (ROS) in O_3/PMS. Researchers deduced the degradation path of TrOCs in the system by considering the preferential attack sites of these two free radicals. On the one hand, $SO_4^{\bullet-}$ was electrophilic and was easy to react with electron donor groups such as hydroxyl (•OH), alkoxy ($^{\bullet}$RO) and amino ($^{\bullet}NH_2$) but not easy to react with nitro ($^{\bullet}NO_2$), carbonyl (C=O), or other electron-withdrawing groups [23,108]. On the other hand, •OH had a low selectivity for most TrOCs in the system. Therefore, the two active radicals had good synergy under general conditions. For example, prometon (PMT)'s aromatic ring or side chain (isopropylamino and alkoxy) may be attacked by •OH and $SO_4^{\bullet-}$, mainly through addition to unsaturated carbon, H-abstraction and electron abstraction [109–111]. $SO_4^{\bullet-}$ mainly degrades organics through electron transfer, while •OH degrades TrOCs through its addition. This also reflects how selective $SO_4^{\bullet-}$ is in the degradation of organic matter.

Generally speaking, the greater the amount of O_3 added, the higher the degradation rate of TrOCs. In this process, O_3 can directly oxidise TrOCs or react with H_2O to generate •OH to further improve the oxidation capacity of the system. The higher the concentration of O_3, the faster the rate of •OH formation. However, there is an optimal value for the additional amount of PMS. If the addition exceeds this optimal value, the reaction rate remains unchanged, and the degradation rate does not increase significantly. This phenomenon may be because excessive HSO_5^- can react with •OH and $SO_4^{\bullet-}$, so only a few oxide species can be generated. Another reason may be that excessive PMS quenches free radicals. It can be seen that excessive PMS can promote not only the degradation of pollutants but also increase the operation cost [47,112].

Additionally, the impact of other reaction parameters (such as reactant concentration), reaction conditions (such as pH and temperature), water quality (such as the concentration of inorganic substances (Cl^-, Br^- and I^{3-}) and organic compounds) on the reaction system is also one of the urgent key points in the O_3/PMS process to explore. The $SO_4^{\bullet-}$-based traditional advanced oxidation technology can be used for degrading organic pollutants in the O_3/PMS system to realise technical iteration in the future.

5. Outlook

The above analysis concludes that the following improvements can be made in the future use of the O_3/PMS process to obtain a broader application scenario. See Table 6 for details.

Table 6. Recommendations for improvement of the O_3/PMS process.

Scheme	Advantages	Disadvantages
Enhancing reactor [113]	It can enable a rapid consumption of O_3 to produce free radicals. On the one hand, it can reduce the production of OBPs in the system and the toxicity of secondary effluent. On the other hand, it can reduce the consumption of O_3, thereby reducing energy consumption and cost.	It increases equipment costs.
Adding catalyst [114]	The addition of a catalyst can increase the formation rate of two free radicals by adding metal ions such as Fe^{2+}, M^{2+} or other catalysts.	The catalyst can react with other inorganic ions or NOM in the system to form DBPs.
Integrating with other processes [115]	Integration with UV, US and other processes can increase the generation rate of the two free radicals.	Currently, this scheme does not qualitatively improve the degradation efficiency of the O_3/PMS process but increases the cost.
Preremoval of inorganic ions and NOM [116]	Inorganic ions with adverse effects in the system can be removed in advance, or the concentration of NOM can be controlled by biosorption or sludge method.	The cost increases, and the degradation process becomes complex and lengthy.

At present, there is still a lack of a comprehensive understanding of the O_3/PMS system, including specific degradation effects and mechanisms of various TrOCs in high-concentration organic wastewater, OBPs generated in the degradation process, toxicity changes in the degradation process, residual toxicity of the secondary effluent and reliable economic research of this process. Therefore, the above problems limit the application of this process to specific water treatment schemes.

6. Conclusions

The O_3/PMS process has the characteristics of high efficiency. When used in the pretreatment of highly concentrated organic wastewater, O_3/PMS can decompose macromolecular organic pollutants into small molecular organic pollutants with low toxicity and easy biochemical degradation to improve the efficiency of subsequent biochemical degradation. When used as an advanced treatment, TrOCs are directly oxidised by O_3 or •OH or co-oxidised by $SO_4^{\bullet-}$ and •OH. In the future, the traditional advanced oxidation technology based on $SO_4^{\bullet-}$ can be used for degrading organic pollutants in the O_3/PMS system. The O_3/PMS process has high degradation efficiency for TrOCs, but there are differences in the treatment effects of different organics under different pH environments, so the optimal reaction conditions still need to be further studied.

Finally, it is proposed that further research should explore the relevant reaction mechanism further; that is, the concentration of a single oxidant is relatively accurately detected in the oxidation system containing many oxidising substances, and the system displays relatively accurate identification of reactive oxygen species. When used for pretreatment, it is essential to distinguish the individual effects of each reactive oxygen species relatively and accurately on subsequent biological treatment. When used for advanced treatment, identifying the type or structure of organic matter in nonbiodegradable or biodegradable parts is crucial. In addition, at present, the economy of the O_3/PMS process is relatively poor. Therefore, researchers should also focus on sustainable economic development and develop more cost-effective advanced oxidation water treatment schemes.

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Abbreviations

AOPs	advanced oxidation processes
ASA	aspirin
BCPMW	biotreated Chinese patent medicine wastewater
BOD	biochemical oxygen demand
BTA	benzotriazole
COD	chemical oxygen demand
CMIT	chloro-methyl-isothiazolinone

DBPs	disinfection byproducts
DOC	dissolved organic carbon
DOM	dissolved organic matter
EEM	excitation-emission matrix
MCFNs	magnetic copper ferrite nanoparticles
MIT	methyl-isothiazolinone
NZVI	nanoscale zerovalent iron
NOM	natural organic matter
OBPs	oxidation byproducts
O_3	ozone
PMS	peroxymonosulfate
PMT	prometon
PNT	phenacetin
PFS	polymerised ferric sulfate
PWLL	polluted water with landfill leachate
R_{ct}, •R	total radical formation value
ROCL	reverse osmosis concentrated leachate
ROS	reactive oxygen species
TOC	total organic carbon
TON	total organic nitrogen
TrOCs	refractory trace organic compounds
UBAF	upflow biological aerated filter
US	ultrasound
UV	ultraviolet
WWTP	wastewater treatment plant
2,4-D	2,4-dichlorophenoxyacetic

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