

Article

Zero-Valent Manganese Promoted $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ Oxidation for Acid Orange 7 Degradation: Performance, Mechanism and Water Matrix Effects

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Abstract

Fenton oxidation is effective for degrading refractory organic contaminants, but slow Fe^{3+} -to- Fe^{2+} regeneration under acidic conditions limits continuous H_2O_2 activation. Here, Acid Orange 7 (AO7) was used as a model pollutant to evaluate a coupled $\text{Mn}^0/\text{Fe}/\text{H}_2\text{O}_2$ system designed to promote iron redox cycling and enhance H_2O_2 activation. AO7 degradation was examined under different operating conditions, and reactive species and mechanisms were identified using electron spin resonance spectroscopy, chemical probes, and quenching experiments. Under optimized conditions (pH 3.0, 10 μM AO7, 2 mM H_2O_2 , 9 μM Fe^{2+} , and 0.05 g/L Mn^0), 88% of AO7 was degraded within 30 min. Hydroxyl radicals ($\bullet\text{OH}$) and FeO^{2+} were identified as the main reactive species, accounting for 88.6% and 11.4% of AO7 degradation, respectively. Mn^0 promoted AO7 degradation by directly activating H_2O_2 to form $\bullet\text{OH}$ and by reducing Fe^{3+} to Fe^{2+} , thereby sustaining $\text{Fe}^{2+}/\text{Fe}^{3+}$ cycling and facilitating $\bullet\text{OH}$ and FeO^{2+} generation. Sulfate and carbonate had negligible effects, whereas fulvic acid, nitrate, and chloride inhibited degradation. AO7 degradation decreased to 40% in lake water and 60% in river water. These results demonstrate that Mn^0 addition can enhance Fenton-like oxidation by accelerating iron redox cycling, suggesting its potential in treating dye-contaminated wastewater under controlled operational conditions.

Keywords: zero-valent manganese; hydrogen peroxide activation; $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycling; Acid Orange 7

1. Introduction

Dyes are extensively used in a wide range of industrial sectors, including textile, leather, paper, printing, and food processing industries. Due to incomplete fixation during manufacturing and application processes, substantial amounts of dyes are discharged into industrial effluents, resulting in wastewater with high organic load, intense color, complex composition, and elevated suspended solids [1]. In addition to causing serious aesthetic deterioration of water bodies, many dyes and their degradation intermediates exhibit persistence, toxicity, and potential ecological risks [2]. Therefore, the efficient treatment of dye-containing wastewater has become an important issue in water pollution control.

Hydrogen peroxide (H_2O_2)-based advanced oxidation processes (AOPs) have attracted extensive attention because of their simplicity, strong oxidation capacity, and effectiveness in degrading refractory organic pollutants [3–5]. Among them, the Fenton process is one of the most widely studied systems, in which Fe^{2+} activates H_2O_2 to generate hydroxyl radicals



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(•OH) for rapid oxidation of organic compounds (Equation (1)) [6]. However, the practical efficiency of the Fenton process is often limited by the slow regeneration of Fe^{2+} from Fe^{3+} , which suppresses the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox cycle and lowers H_2O_2 utilization efficiency. Therefore, accelerating Fe^{2+} regeneration is crucial for improving the performance of Fenton oxidation systems.



Various approaches have been developed to enhance the $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycle in the Fenton process. For example, several reducing agents, such as thiosulfate [7], gallic acid [8], hydroxylamine [9] and ascorbic acid [10], have been introduced to promote the reduction of Fe^{3+} to Fe^{2+} , and their effectiveness in enhancing contaminant degradation has been demonstrated. However, the addition of soluble organic or inorganic reductants may introduce secondary contaminants, consume reactive oxygen species, or compete with target pollutants for •OH, thereby lowering the overall oxidation efficiency [11]. Zero-valent iron (Fe^0) has also been employed to strengthen Fenton systems because it can continuously provide Fe^{2+} through corrosion under acidic conditions [12]. Nevertheless, the corrosion and electron-transfer processes of Fe^0 are strongly affected by the formation and thickening of surface oxide layers, which increase electron-transfer resistance and hinder the reduction of Fe^{3+} by Fe^0 . In addition, external energy-assisted methods, such as ultraviolet irradiation [13] and electric assistance [14], have been reported to effectively promote Fe^{3+} reduction and enhance H_2O_2 activation. However, these methods generally require additional energy input and may show limited resistance to water matrix interference, which constrains their practical application in complex wastewater treatment. Accordingly, it is highly necessary to explore novel, feasible modification strategies to optimize and upgrade traditional Fenton technology.

Compared with the direct addition of soluble reductants, zero-valent metals are attractive because they can continuously donate electrons and facilitate Fe^{3+} reduction without introducing large amounts of dissolved organic additives. Among them, zero-valent copper (Cu^0) has been reported to effectively accelerate the $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycle, thereby improving H_2O_2 activation and pollutant degradation efficiency [15]. However, Cu^+ generated during the corrosion of Cu^0 can be readily oxidized by dissolved oxygen to Cu^{2+} , leading to inefficient electron utilization and potentially limiting the long-term performance of the system [16]. In this context, zero-valent manganese (Mn^0) may represent a promising alternative. Owing to the lower redox potential of the $\text{Mn}^{2+}/\text{Mn}^0$ couple relative to that of $\text{Cu}^{2+}/\text{Cu}^0$, Mn^0 is expected to exhibit a stronger reducing ability and thus greater potential to promote Fe^{3+} reduction in Fenton systems [17]. Moreover, manganese species are generally considered less toxic than copper species, which may make Mn^0 more favorable for practical water treatment applications [18]. Although Mn-based materials have been investigated in some oxidation systems, the performance and mechanism of the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ process for pollutant degradation have not yet been systematically clarified. In particular, the role of Mn^0 in promoting H_2O_2 activation, the dominant reactive oxygen species involved, and the applicability of this process in complex water matrices remain insufficiently understood.

In this study, dye degradation by the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system was systematically investigated. Among dyes, Acid Orange 7 (AO7), a typical azo dye with high chromaticity and recalcitrance, was chosen as a target pollutant. The objectives of this work were: (i) to evaluate the enhancement effect of Mn^0 on AO7 degradation in the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system; (ii) to elucidate the dominant reactive oxygen species and the associated H_2O_2 activation mechanism; and (iii) to assess the applicability of the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system in real water matrices and its resistance to interference from common coexisting substances. This work is expected to provide mechanistic insight into Mn^0 -assisted Fenton oxidation and

to support the development of efficient and practical advanced oxidation technologies for dye-containing wastewater treatment.

2. Results and Discussion

2.1. AO7 Degradation in Different Reaction Systems

Figure 1a shows the AO7 degradation performance of five reaction systems, including H_2O_2 , Mn^0 , $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, $\text{Mn}^0/\text{H}_2\text{O}_2$, and $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ systems. Negligible AO7 degradation was observed in the H_2O_2 system and Mn^0 systems within 30 min, indicating that neither H_2O_2 nor Mn^0 alone was effective for AO7 degradation under the tested conditions. In the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system, approximately 25% of AO7 was rapidly degraded in the initial 1 min, after which the pollutant concentration remained nearly unchanged. This trend is consistent with previous studies, in which Fe^{2+} rapidly activated H_2O_2 at the initial stage, whereas the slow reduction of Fe^{3+} to Fe^{2+} limited the sustained generation of reactive oxidizing species [9]. By contrast, the $\text{Mn}^0/\text{H}_2\text{O}_2$ system achieved about 30% AO7 degradation within 30 min, suggesting that Mn^0 was able to activate H_2O_2 to some extent. More importantly, the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system exhibited the best performance, achieving 88% AO7 degradation within 30 min. This efficiency was substantially higher than those of the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and $\text{Mn}^0/\text{H}_2\text{O}_2$ systems, suggesting a synergistic effect between Mn^0 and Fe^{2+} in promoting H_2O_2 activation. Furthermore, a systematic comparison of AO7 degradation performance among various Fenton-like processes is summarized in Table S1. Compared to mineral-catalyzed or energy-assisted Fenton processes, the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system exhibits highly competitive degradation efficiency rapidly (within 30 min) at remarkably lower chemical dosages and without external energy input. Its primary advantage lies in the rapid and sustained regeneration of Fe^{2+} driven by Mn^0 .

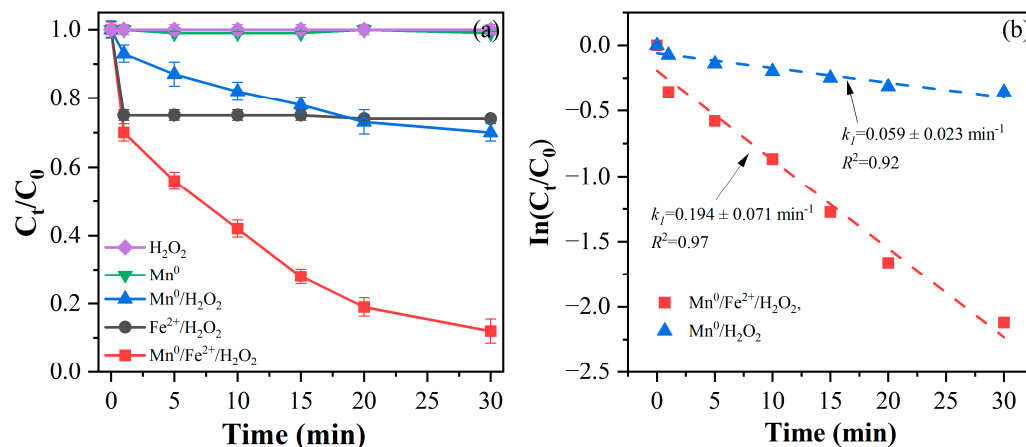


Figure 1. (a) AO7 degradation and (b) pseudo-first-order fitting kinetic curve in different reaction systems. Conditions: $[\text{AO7}]_0 = 10 \text{ }\mu\text{M}$, $[\text{Fe}^{2+}]_0 = 9 \text{ }\mu\text{M}$, $[\text{Mn}^0]_0 = 0.05 \text{ g/L}$, $[\text{H}_2\text{O}_2]_0 = 2.0 \text{ mM}$, $\text{pH}_0 = 3.0 \pm 0.1$ and $25 \pm 2 \text{ }^\circ\text{C}$.

To quantitatively compare the reaction kinetics, a pseudo-first-order kinetic model was applied (Figure 1b). However, this model was not suitable for the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system. In that system, the reaction exhibited a rapid initial burst but virtually stalled within the first minute due to the swift depletion of Fe^{2+} and the slow regeneration from Fe^{3+} , leading to a premature plateau. Consequently, kinetic fitting for the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system was omitted to avoid statistically invalid comparisons. For the applicable systems, the rate constants (k_1) were calculated over the 30 min fitting range. The $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system exhibited a k_1 of $0.194 \pm 0.071 \text{ min}^{-1}$ ($R^2 = 0.97$), which was notably higher than that of the $\text{Mn}^0/\text{H}_2\text{O}_2$ system ($k_1 = 0.059 \pm 0.023 \text{ min}^{-1}$, $R^2 = 0.92$). These kinetic results quantitatively support

that the introduction of Mn^0 helps sustain the catalytic oxidation and mitigates the rapid stagnation typically observed in the Fenton process.

2.2. Identification of Reactive Oxygen Species in the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ System

The identification of reactive oxygen species (ROS) is critical for elucidating the oxidation mechanism of advanced oxidation processes. In Fe^{2+} -activated H_2O_2 systems, $\bullet\text{OH}$ has traditionally been considered the predominant oxidizing species [14,15]. However, increasing evidence suggests that ferryl $\text{Fe}(\text{IV})$, such as FeO^{2+} , may also be formed during Fenton-like reactions and contribute to pollutant oxidation [19,20]. Accordingly, both $\bullet\text{OH}$ and FeO^{2+} were considered potential reactive species for the degradation of target pollutants in the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system.

To clarify the ROS involved in AO7 degradation, ESR analysis and scavenging experiments were performed. As shown in Figure 2a, a characteristic four-line ESR signal with an intensity ratio of 1:2:2:1 was observed in the presence of DMPO, which is attributable to the $\text{DMPO}\cdot\bullet\text{OH}$ adduct. This result confirms the generation of $\bullet\text{OH}$ in the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system.

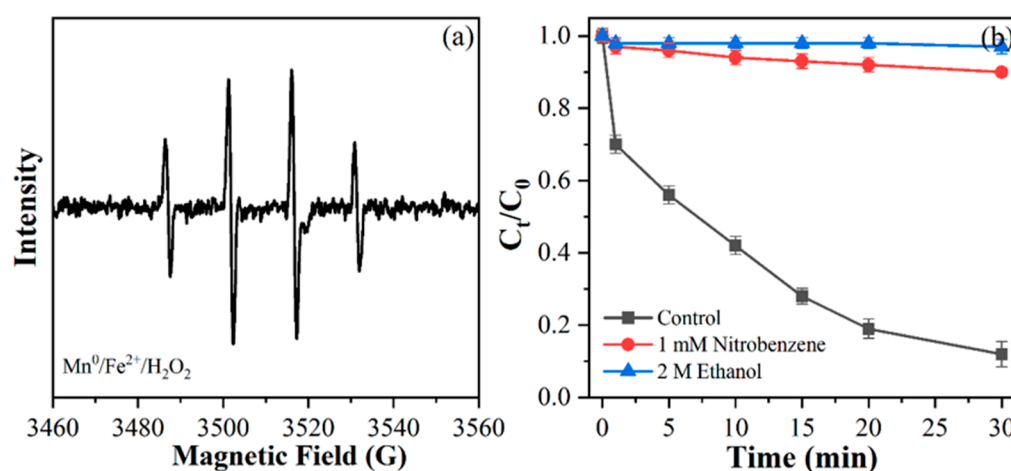


Figure 2. (a) ESR spectra obtained in the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system; (b) effect of nitrobenzene and ethanol on AO7 degradation in the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system. Conditions: (a) $[\text{DMPO}]_0 = 2 \text{ mM}$, $[\text{Fe}^{2+}]_0 = 9 \text{ }\mu\text{M}$, $[\text{Mn}^0]_0 = 0.05 \text{ g/L}$, $[\text{H}_2\text{O}_2]_0 = 2.0 \text{ mM}$, $\text{pH}_0 = 3.0 \pm 0.1$ and $25 \pm 2 \text{ }^\circ\text{C}$; (b) $[\text{AO7}]_0 = 10 \text{ }\mu\text{M}$, $[\text{Fe}^{2+}]_0 = 9 \text{ }\mu\text{M}$, $[\text{Mn}^0]_0 = 0.05 \text{ g/L}$, $[\text{H}_2\text{O}_2]_0 = 2.0 \text{ mM}$, $\text{pH}_0 = 3.0 \pm 0.1$ and $25 \pm 2 \text{ }^\circ\text{C}$.

To further evaluate the contributions of different oxidizing species, nitrobenzene and ethanol were employed as chemical scavengers. Nitrobenzene is known to react rapidly with $\bullet\text{OH}$ but negligibly with FeO^{2+} [21]. As shown in Figure 2b, the addition of 1 mM nitrobenzene markedly suppressed AO7 degradation, and the degradation efficiency decreased to approximately 10%, indicating that $\bullet\text{OH}$ was the dominant oxidizing species in the system. In contrast, ethanol was capable of simultaneously scavenging both $\bullet\text{OH}$ and FeO^{2+} [22]. When 2 M ethanol was introduced, AO7 degradation was almost completely inhibited (Figure 2b). The stronger inhibition observed with ethanol than with nitrobenzene suggests that FeO^{2+} also participated in AO7 oxidation, although its contribution was secondary to that of $\bullet\text{OH}$.

In addition, PMSO was adopted as a specific probe for FeO^{2+} . It has been documented that FeO^{2+} can selectively oxidize PMSO to produce PMSO_2 , whereas $\bullet\text{OH}$ tends to yield other byproducts such as hydroxylated derivatives and biphenyl substances [23]. As shown in Figure S1, nearly $5 \text{ }\mu\text{M}$ PMSO_2 was detected after 1 mM PMSO was added to the

$\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system, providing additional evidence for the formation of FeO^{2+} . The generation of FeO^{2+} may be described by Equation (2) [24]:

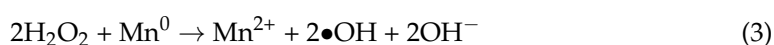


Although classical Fenton chemistry predominantly generates $\bullet\text{OH}$ at bulk $\text{pH} < 3.0$ (consistent with the 88.6% contribution of $\bullet\text{OH}$ in this study), the detection of FeO^{2+} (11.4% contribution) indicates the co-existence of the two-electron transfer pathway. This could be attributed to the corrosive consumption of protons by Mn^0 at the solid-liquid interface, which increases the pH near the Mn^0 surface, creating a microenvironment that favors the heterolytic cleavage of H_2O_2 to generate FeO^{2+} .

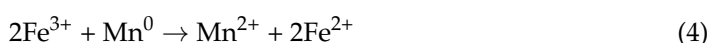
Collectively, all of the above results indicate that $\bullet\text{OH}$ and FeO^{2+} were involved in AO7 degradation in the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system, with $\bullet\text{OH}$ serving as the predominant reactive species. Based on the inhibition extents observed in the scavenging experiments, the relative contributions of $\bullet\text{OH}$ and FeO^{2+} to AO7 degradation were estimated to be 88.6% and 11.4%, respectively.

2.3. Enhancement Mechanism of $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ System

The superior AO7 degradation observed in the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system suggests a synergistic interaction between Mn^0 and Fe^{2+} during H_2O_2 activation. As shown in Figure S2, negligible AO7 degradation occurred in the H_2O_2 , Mn^0 , and $\text{Mn}^{2+}/\text{H}_2\text{O}_2$ systems, indicating that dissolved Mn^{2+} contributed little to H_2O_2 activation under the tested conditions. During the reaction, Mn^0 was gradually oxidized and released predominantly as Mn^{2+} . Therefore, the reactivity observed in the $\text{Mn}^0/\text{H}_2\text{O}_2$ system can be reasonably ascribed to direct H_2O_2 activation at the Mn^0 surface. Specifically, the solid-liquid interfacial electron transfer from Mn^0 to H_2O_2 is likely to promote the cleavage of the O-O bond, generating $\bullet\text{OH}$ as proposed in Equation (3). Previous studies have likewise shown that the coupling of Fe^{2+} and Mn^0 can enhance H_2O_2 activation [17,25], thereby greatly improving the degradation efficiency of AO7.



To further elucidate the enhancement mechanism, the variations in Fe^{2+} and Mn^0 concentrations were monitored. As shown in Figure 3, Fe^{2+} in the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system decreased from 9 μM to 0 μM , whereas 0.5–1 μM Fe^{2+} remained in the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system throughout the reaction. The persistence of Fe^{2+} suggests that Mn^0 facilitated the regeneration of Fe^{2+} from Fe^{3+} . To experimentally verify this, we monitored the generation of Fe^{2+} in a control $\text{Mn}^0/\text{Fe}^{3+}$ system ($[\text{Mn}^0]_0 = 0.05 \text{ g/L}$, $[\text{Fe}^{3+}]_0 = 10 \mu\text{M}$, $\text{pH}_0 = 3.0 \pm 0.1$ and $25 \pm 2 \text{ }^\circ\text{C}$). The results revealed that $9.50 \pm 0.21 \mu\text{M}$ of Fe^{2+} was rapidly produced within 5 min of reaction, providing direct evidence that Mn^0 efficiently reduces Fe^{3+} to maintain the iron redox cycle (as shown in Equation (4)).



In addition, Mn^{2+} release increased slightly from 246 to 259 μM after Fe^{2+} was introduced into the $\text{Mn}^0/\text{H}_2\text{O}_2$ system (Figure 3), which is consistent with Mn^0 oxidation coupled with Fe^{3+} reduction. Given the initial Mn^0 dosage of 0.05 g/L (approximately 0.91 mM), the released Mn^{2+} accounts for a sacrificial consumption of 28.5% of the initial Mn^0 , with the remaining 71.5% remaining in the solid phase. Meanwhile, the homogeneous iron species remained dissolved and 100% conserved in the liquid phase under the

acidic conditions. These results indicate that Mn^0 promoted $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox cycling in the coupled system.

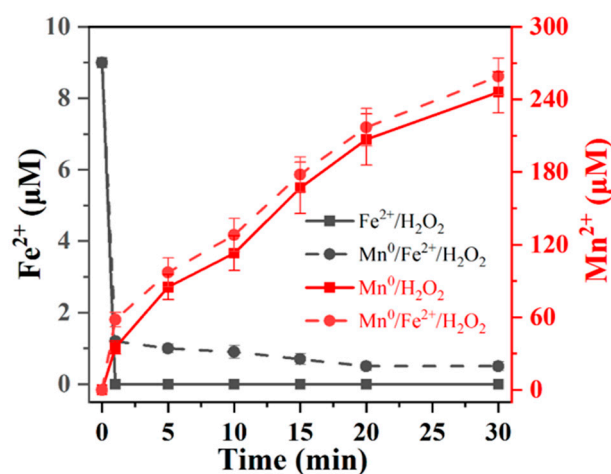


Figure 3. Change of Fe^{2+} and Mn^{2+} in the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system. Conditions: $[\text{AO7}]_0 = 10 \mu\text{M}$, $[\text{Fe}^{2+}]_0 = 9 \mu\text{M}$, $[\text{Mn}^0]_0 = 0.05 \text{ g/L}$, $[\text{H}_2\text{O}_2]_0 = 2.0 \text{ mM}$, $\text{pH}_0 = 3.0 \pm 0.1$ and $25 \pm 2 \text{ }^\circ\text{C}$.

It should be noted that while this sacrificial dissolution of Mn^0 effectively drives the iron cycle, it leads to a final Mn^{2+} accumulation of $259 \mu\text{M}$ (14.2 mg/L). This value exceeds the Mn discharge limit of 2.0 mg/L specified in the Integrated Wastewater Discharge Standard (GB 8978-1996) [26]. Therefore, to prevent secondary metal contamination in practical applications, a subsequent alkaline precipitation step (e.g., adjusting effluent pH to ≥ 9.0) is necessary as a post-treatment to efficiently recover the dissolved Mn as solid precipitates.

The accelerated iron redox cycle also enhanced H_2O_2 utilization. As shown in Figure S3, H_2O_2 decomposition in the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system was significantly higher than that in either the $\text{Mn}^0/\text{H}_2\text{O}_2$ or $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system. At the end of the reaction, the H_2O_2 consumed in the ternary system reached 0.36 mM (corresponding to an utilization efficiency of 2.4% for AO7 degradation), whereas the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system only consumed 0.03 mM (with a nominal efficiency of 8.3%). This result suggests that Mn^0 not only participated in H_2O_2 activation directly, but also sustained the availability of Fe^{2+} through Fe^{3+} reduction, thereby promoting continuous H_2O_2 decomposition and ROS generation.

Overall, the enhanced performance of the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system can be attributed to a highly efficient heterogeneous–homogeneous redox coupling mechanism involving two synergistic pathways: (i) direct activation of H_2O_2 by Mn^0 and (ii) Mn^0 -mediated regeneration of Fe^{2+} from Fe^{3+} , which accelerated the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox cycle and improved H_2O_2 activation efficiency. In this process, Fe^{2+} activated H_2O_2 to generate $\bullet\text{OH}$ and FeO^{2+} via Equations (1) and (2), while Mn^0 continuously replenished Fe^{2+} through Equation (4), thereby sustaining ROS production and enhancing AO7 degradation. A schematic illustration of the proposed mechanism is presented in Figure 4.

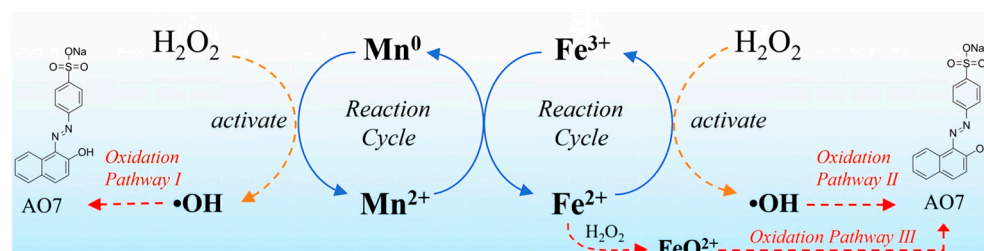


Figure 4. Possible reaction mechanism of $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system.

2.4. Effects of Reaction Factors on AO7 Degradation in the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ System

Based on the results discussed above, Fe^{2+} played an important role in enhancing AO7 degradation capacity in the $\text{Mn}^0/\text{H}_2\text{O}_2$ system. Thus, investigating the impact of Fe^{2+} concentration on AO7 degradation in the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system was of great significance. As shown in Figure 5a, AO7 degradation increased continuously as the Fe^{2+} concentration increased from 0 to 15 μM . Specifically, the degradation efficiency after 30 min increased from 30% to 96%. This enhancement can be attributed to the greater availability of Fe^{2+} for H_2O_2 activation, which facilitated $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox cycling and promoted the formation of $\bullet\text{OH}$ and FeO^{2+} for AO7 degradation.

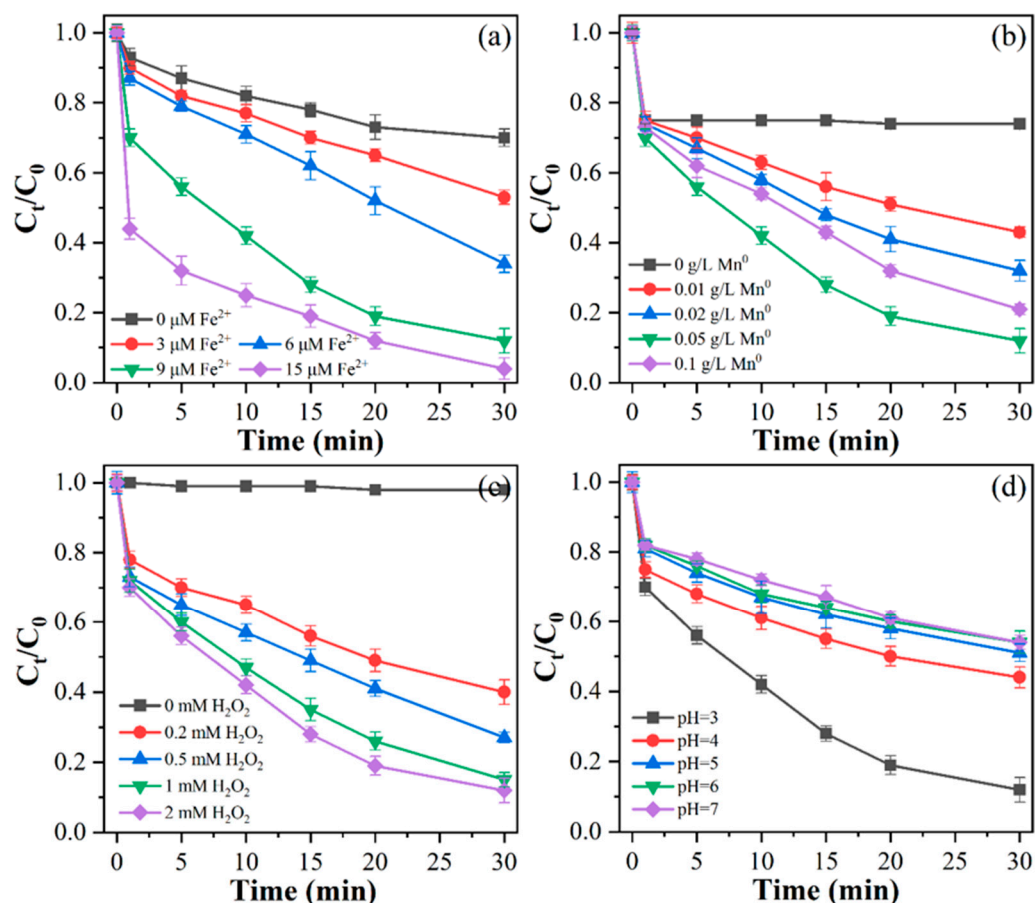


Figure 5. Effect of (a) initial Fe^{2+} concentration, (b) Mn^0 dosage, (c) H_2O_2 concentration and (d) initial pH on AO7 degradation in the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system. Conditions unless otherwise specified: $[\text{AO7}]_0 = 10 \mu\text{M}$, $[\text{Fe}^{2+}]_0 = 9 \mu\text{M}$, $[\text{Mn}^0]_0 = 0.05 \text{ g/L}$, $[\text{H}_2\text{O}_2]_0 = 2.0 \text{ mM}$, $\text{pH}_0 = 3.0 \pm 0.1$ and $25 \pm 2 \text{ }^\circ\text{C}$.

The dosage of Mn^0 directly dictates the availability of reactive sites for H_2O_2 activation. As shown in Figure 5b, increasing the Mn^0 dosage from 0 to 0.05 g/L significantly enhanced AO7 degradation from 26% to 88% within 30 min. This profound improvement indicates that an adequate Mn^0 supply provides sufficient reactive sites to trigger H_2O_2 decomposition, ensuring continuous $\bullet\text{OH}$ production and rapid $\text{Fe}^{3+}/\text{Fe}^{2+}$ interconversion. However, a further increase in Mn^0 dosage to 0.1 g/L resulted in a slight decline in degradation efficiency to 79%. This inhibitory effect is likely due to the parasitic scavenging of $\bullet\text{OH}$ and FeO^{2+} by excess Mn^0 particles.

The oxidant dosage is another critical parameter governing reactive species yield. The effect of H_2O_2 dosage is shown in Figure 5c. Within the investigated range of 0–2.0 mM, AO7 degradation increased with increasing H_2O_2 concentration. After 30 min, the degradation efficiency increased from 2% to 88%. The improved performance can be ascribed

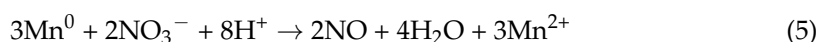
to the increased availability of H_2O_2 for activation by Fe^{2+} and Mn^0 , which enhanced the production of $\bullet\text{OH}$ and FeO^{2+} responsible for AO7 degradation.

pH fundamentally governs iron speciation and redox potential, heavily influencing the performance of advanced oxidation processes [27]. As illustrated in Figure 5d, the AO7 degradation efficiency exhibited a strong pH dependence, declining steadily from 88% to 46% as the initial pH increased from 3.0 to 7.0 in the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system. As discussed in Section 2.3, efficient $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox cycling is essential for sustained H_2O_2 activation in this system. Ferric speciation is strongly pH-dependent, and the dominant Fe^{3+} species shift from soluble Fe^{3+} and FeOH^{2+} to $\text{Fe}(\text{OH})_2^+$ and insoluble $\text{Fe}(\text{OH})_3$ as pH increases from 3 to 7 (Figure S4). Compared with soluble ferric species under acidic conditions, these hydrolyzed forms are less reactive and more prone to precipitation as iron hydroxides. Consequently, the regeneration of Fe^{2+} from Fe^{3+} becomes less efficient at higher pH due to the surface passivation by precipitates and the decreased redox potential of iron couples [28,29], leading to suppressed H_2O_2 activation and lower AO7 degradation.

Overall, these results demonstrate that AO7 degradation in the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system was strongly dependent on Fe^{2+} concentration, Mn^0 dosage, H_2O_2 dosage, and initial pH. Efficient degradation was achieved at higher Fe^{2+} and H_2O_2 concentrations, an appropriate Mn^0 dosage, and acidic conditions.

2.5. Effects of Water Matrix Constituents and Performance in Real Water Samples

Coexisting inorganic anions and natural organic matter are ubiquitous in natural waters and may affect contaminant degradation during advanced oxidation processes [30]. A unified concentration of 1 mM for inorganic anions (and 1 mg/L for HA) was selected. This value was adopted as a standardized condition, commonly utilized in fundamental AOP studies, to clearly observe and compare the distinct inhibitory impacts and fundamental radical-scavenging mechanisms of different water matrix constituents on AO7 degradation. As shown in Figure 6a, the addition of 1 mM carbonate species or SO_4^{2-} caused little change in AO7 degradation in the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system under the tested conditions. In contrast, the presence of Cl^- slightly decreased the AO7 degradation efficiency from 88% to 83%. This inhibition was mainly attributed to the reaction of Cl^- with $\bullet\text{OH}$, which can convert $\bullet\text{OH}$ into less reactive chlorine-based radicals/species and thereby reduce the overall oxidation efficiency [31,32]. Among the tested anions, NO_3^- exhibited a more pronounced inhibitory effect, decreasing the AO7 degradation efficiency from 88% to 73%. This result may be related to the direct reaction between NO_3^- and Mn^0 (Equation (5)), which consumes Mn^0 and reduces its availability for H_2O_2 activation and Fe^{3+} reduction [33]. Humic acid showed the strongest suppression effect, and AO7 degradation decreased sharply to 35%. This substantial inhibition can be ascribed to the competitive scavenging of reactive oxidizing species, including $\bullet\text{OH}$ and FeO^{2+} , by humic substances [34].



To further evaluate the practical applicability of the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ process, AO7 degradation was examined in authentic water samples, including lake water and river water. As shown in Figure 6b, both real water matrices substantially suppressed AO7 degradation, with final degradation efficiencies of 40% in lake water and 60% in river water, respectively. The stronger inhibition in lake water is likely due to its typically higher accumulation of natural organic matter and salinity compared to flowing river water. Moreover, the background impurities in natural water, particularly natural organic matter (NOM) and inorganic ions (e.g., Cl^- and NO_3^-), competed with AO7 for reactive oxygen species such as $\bullet\text{OH}$ and FeO^{2+} . This competitive effect was the key reason for the weakened pollutant degradation capacity in real water environments. Consequently,

overcoming this scavenging effect in complex matrices would inevitably increase chemical demands, such as higher H_2O_2 consumption.

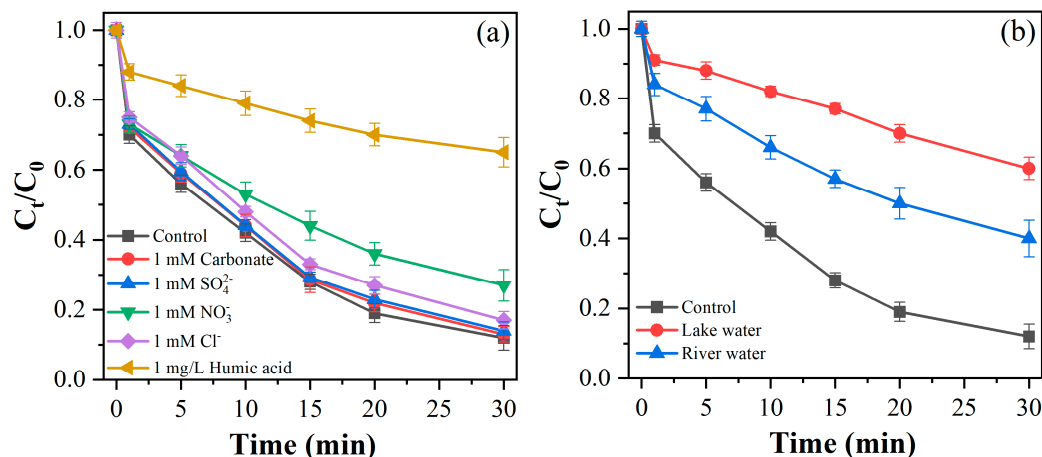


Figure 6. (a) Effect of water matrix on degrading AO7 in the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system and (b) AO7 degradation in authentic water samples with the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system. Conditions: $[\text{AO7}]_0 = 10 \mu\text{M}$, $[\text{Fe}^{2+}]_0 = 9 \mu\text{M}$, $[\text{Mn}^0]_0 = 0.05 \text{ g/L}$, $[\text{H}_2\text{O}_2]_0 = 2.0 \text{ mM}$, $\text{pH}_0 = 3.0 \pm 0.1$ and $25 \pm 2 \text{ }^\circ\text{C}$.

Furthermore, scaling up this system for real wastewater treatment presents several operational limitations. The optimal performance strictly depends on an acidic environment ($\text{pH } 3.0$), which necessitates costly acidification prior to treatment and subsequent neutralization. Additionally, the sacrificial dissolution of Mn^0 introduces metal ions into the effluent, requiring post-treatment alkaline precipitation to meet discharge standards, which inevitably generates metal hydroxide sludge. These results and operational constraints indicate that although the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system exhibits high degradation efficiency in model solutions, its practical application potential requires further evaluation.

3. Materials and Methods

3.1. Chemicals

Acid Orange 7 (AO7, $\text{C}_{16}\text{H}_{11}\text{N}_2\text{NaO}_4\text{S}$, >85%), zero-valent manganese (Mn^0 , >99.9%), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, >99%), hydrogen peroxide (H_2O_2 , 30 wt%), sodium hydroxide (NaOH , >96%), sulfuric acid (H_2SO_4 , 95–98%), and 1,10-phenanthroline monohydrate ($\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$, >98%), sodium carbonate (Na_2CO_3 , >99%), sodium chloride (NaCl , >99.8%), sodium sulfate (Na_2SO_4 , >99%), sodium nitrate (NaNO_3 , >99%), humic acid ($\geq 90\%$), nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$, >99.5%), 5,5-dimethyl-1-pyrroline N-oxide ($\text{C}_6\text{H}_{11}\text{NO}$, DMPO, >97%), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$, >99%), methyl phenyl sulfoxide (PMSO, >95%), methyl phenyl sulfone (PMSO₂, >97%) and tert-butyl alcohol ($\text{C}_4\text{H}_{10}\text{O}$, >98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Deionized water was used to prepare all solutions. In addition, lake water from Taiping Lake and river water from the Xin'an River were used as water matrices for AO7 solution preparation.

3.2. Experimental Procedures

Batch degradation experiments were carried out in 250 mL conical flasks with continuous magnetic stirring (500 rpm) at room temperature ($25 \pm 2 \text{ }^\circ\text{C}$). Before each experiment, the initial pH of the AO7 solution was adjusted to the desired value using 0.01 M NaOH solutions and 0.01 M H_2SO_4 . In a typical experiment with the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system, 100 mL of AO7 solution (initial concentration of $10 \mu\text{M}$) was transferred into the flask, followed by the addition of a predetermined volume of H_2O_2 and FeSO_4 solution. Mn^0 was then added within a few seconds to initiate the reaction. At predetermined time inter-

vals, 1 mL samples were collected and immediately quenched with 1 mL of 0.5 M sodium thiosulfate solution, followed by filtration through a 0.45 µm membrane before analyzing. For comparison, control experiments using $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, $\text{Mn}^0/\text{H}_2\text{O}_2$, Fe^{2+} alone, and Mn^0 alone were also conducted. For the active species quenching experiments, the quencher at a specified concentration was mixed with the AO7 solution prior to the addition of other substances. The relative contributions of $\bullet\text{OH}$ and FeO^{2+} were estimated from the differences in AO7 degradation efficiencies in the presence of selective scavengers. Each experiment was performed in triplicate, and the results are reported as mean values with standard deviations.

3.3. Analytical Methods

The residual AO7 concentration was determined from its absorbance at 484 nm using a UV–visible spectrophotometer (U-3900, Hitachi Limited, Tokyo, Japan) based on a standard calibration curve. The degradation efficiency of AO7 was calculated using the following Equation (6), and the degradation kinetics were fitted to the pseudo-first-order model described by Equation (7):

$$\text{Degradation Efficiency (\%)} = (C_0 - C_t)/C_0 \times 100\% \quad (6)$$

$$\ln(C_t/C_0) = -k_1 t \quad (7)$$

where C_0 and C_t are the initial concentration and the concentration of AO7 at reaction time t (µM), respectively; k_1 represents the pseudo-first-order rate constant (min^{-1}), and t is the reaction time (min).

Solution pH was monitored with a PH2-25 pH meter (Shanghai INESA Scientific Instrument Co., Ltd., Shanghai, China). The content of Fe^{2+} was quantified at 510 nm using the 1,10-phenanthroline monohydrate colorimetric method [35], while H_2O_2 concentration was determined by the ABTS method at 415 nm [36]. The concentration of M^{2+} was determined using a Flame Atomic Absorption Spectrophotometer (FAAS, TAS-990, Beijing Purkinje General Instrument Co., Ltd., Beijing, China). The analysis was conducted using an air-acetylene flame. The analytical wavelength for Mn was set at 279.5 nm with a slit width of 0.3 nm. Standard calibration curves were established prior to the measurements, exhibiting excellent linearity ($R^2 > 0.999$). To ensure the reliability of the results, all samples were filtered through a 0.22 µm membrane and appropriately diluted before measurement, and the analyses were performed in triplicate. An electron spin resonance (ESR) spectrometer (Bruker EMXplus, Bruker Corporation, Karlsruhe, Germany) was employed to detect reactive oxygen species using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the spin-trapping agent.

4. Conclusions

In this study, we developed an efficient $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system for rapid AO7 degradation, achieving 88% removal within 30 min under optimized conditions. It was demonstrated that the synergistic coupling of zero-valent manganese (Mn^0) and Fe^{2+} significantly enhances H_2O_2 activation. Specifically, Mn^0 plays a crucial dual role: it facilitates direct H_2O_2 cleavage and continuously regenerates Fe^{2+} from Fe^{3+} , thereby sustaining the iron redox cycle. Both hydroxyl radicals ($\bullet\text{OH}$) and high-valent iron species (FeO^{2+}) cooperatively drive the oxidation process. While the system exhibits exceptional reactivity in model solutions, its efficiency is attenuated in authentic water matrices due to competitive scavenging by natural constituents.

Overall, this work deepens the understanding of reactive species generation and iron cycling in Mn^0 -assisted systems, providing a feasible strategy for strengthening Fenton-like

oxidation via metal-mediated redox coupling. Nevertheless, for future applications in complex wastewater treatment, operational limitations, including the need for pH adjustment, H_2O_2 consumption, and the management of metal-hydroxide sludge, must be carefully addressed. Additionally, comprehensive evaluations of mineralization efficiency (e.g., TOC/COD removal), transformation by-products, and effluent toxicity will be imperative to ensure the environmental safety of the treated water. Addressing these engineering and environmental aspects will ultimately improve the overall techno-economic viability of this advanced oxidation technology.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/catal16070608/s1>. Figure S1: Changes of PMSO and PMSO₂ in the $\text{Mn}^0/\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system. Conditions: $[\text{PMSO}]_0 = 1 \text{ mM}$, $[\text{Fe}^{2+}]_0 = 9 \text{ }\mu\text{M}$, $[\text{Mn}^0]_0 = 0.05 \text{ g/L}$, $[\text{H}_2\text{O}_2]_0 = 2.0 \text{ mM}$, $\text{pH}_0 = 3.0 \pm 0.1$ and room temperature; Figure S2: Degradation of AO7 in different systems. Conditions: $[\text{AO7}]_0 = 10 \text{ }\mu\text{M}$, $[\text{Mn}^{2+}]_0 = 0.05 \text{ mM}$, $[\text{Mn}^0]_0 = 0.05 \text{ g/L}$, $[\text{H}_2\text{O}_2]_0 = 2.0 \text{ mM}$, $\text{pH}_0 = 3.0 \pm 0.1$ and room temperature; Figure S3: Consumed H_2O_2 in the various systems. Conditions: $[\text{AO7}]_0 = 10 \text{ }\mu\text{M}$, $[\text{Fe}^{2+}]_0 = 9 \text{ }\mu\text{M}$, $[\text{Mn}^0]_0 = 0.05 \text{ g/L}$, $[\text{H}_2\text{O}_2]_0 = 2.0 \text{ mM}$, $\text{pH}_0 = 3.0 \pm 0.1$ and room temperature. (* and ** indicate statistical significance at $p < 0.05$ and $p < 0.01$, respectively); Figure S4: Form distribution of Fe^{3+} in different pH. Conditions: $[\text{Fe}^{3+}] = 10 \text{ }\mu\text{M}$. Table S1: Comparison of AO7 degradation efficiency by various Fenton-like processes. References [37–40] are cited in the Supplementary Materials.

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Conflicts of Interest: There are no conflicts to declare.

Abbreviations

The following abbreviations are used in this manuscript:

AOPs	Advanced oxidation processes
AO7	Acid Orange 7
ESR	Electron spin resonance
DMPO	5,5-dimethyl-1-pyrroline N-oxide
ROS	Reactive oxygen species

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