

Article

Ru-Modified α -MnO₂ as an Efficient PMS Activator for Carbamazepine Degradation: Performance and Mechanism

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Abstract

Although Ru-based catalysts have been investigated in various oxidation systems, their application in sulfate radical-based AOPs, particularly as heterogeneous activators for acidic wastewater treatment, remains limited. Herein, Ru was incorporated into α -MnO₂ via lattice doping and surface loading to construct Ru_{latt}/ α -MnO₂ and Ru_{surf}/ α -MnO₂, and their PMS activation performance toward carbamazepine (CBZ) degradation was evaluated. Ru_{latt}/ α -MnO₂ exhibited superior activity, achieving near-complete CBZ removal within minutes under acidic conditions. PMS dosage, catalyst loading, and pH affected the degradation efficiency, with acidic environments significantly enhancing PMS activation. Cl[−] slightly promoted CBZ degradation, whereas HCO₃[−] and natural organic matter inhibited it. Mechanistic analysis revealed that Ru activated PMS through a nonradical pathway, continuously generating ¹O₂ via a reversible Ru (II)/Ru (III)/Ru (IV) cycle, while the Mn (III)/Mn (IV) redox couple acted as an electron buffer to sustain Ru cycling and improve durability. The catalyst maintained high activity in complex water matrices, demonstrating strong potential for practical remediation of CBZ-contaminated acidic wastewater.

Keywords: peroxymonosulfate activation; ruthenium; α -MnO₂; heterogeneous PMS activator; electron buffer effect



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1. Introduction

With the continuous advancement of society and the increasing public awareness of human health, the production and consumption of organic pharmaceuticals have markedly expanded. Nevertheless, their extensive application, together with the insufficient removal efficiency of conventional wastewater treatment technologies, has resulted in the widespread occurrence of these pharmaceuticals in wastewater [1]. Among various organic pharmaceuticals, carbamazepine (CBZ) is recognized as a particularly recalcitrant compound due to its chemically stable molecular structure and extremely low degradation rate in natural attenuation processes such as photolysis, volatilization, and biodegradation [2].

Owing to its high consumption and persistent resistance to degradation, CBZ has been identified as a globally monitored persistent organic pollutant (POP) of great environmental concern [3]. Pharmaceutical production and some hospital/laboratory activities often generate acid-containing process waters (e.g., synthesis, solvent washes, and equipment cleaning); when not fully neutralized or when mixed with other acidic discharges, these streams can produce acidic wastewater that still contains detectable carbamazepine [4]. Furthermore, carbamazepine, excreted by humans, enters domestic and hospital wastewater; when these drug-containing streams mix with inadequately neutralized industrial acidic effluents in the sewer network, they can produce composite wastewater that is both acidic and contaminated with carbamazepine [5,6]. In addition, numerous industrial activities, including pharmaceutical manufacturing, metal processing, and chemical synthesis, often generate acidic wastewater. Conventional treatment technologies for organic contaminants generally exhibit poor efficiency under such acidic conditions. This inefficiency arises from both the suppression of degradation pathways in acidic environments and the inherent chemical stability of CBZ. Without effective treatment strategies, these wastewaters may pose long-term ecological risks, including endocrine disruption, genotoxicity, and potential threats to human health. Therefore, developing efficient and cost-effective approaches for CBZ removal under acidic conditions remains a significant challenge.

Advanced oxidation processes (AOPs) based on peroxymonosulfate (PMS) activation have emerged as one of the most attractive technologies for the removal of organic contaminants, including carbamazepine (CBZ). This is mainly because they feature a short treatment time and high degradation efficiency [7]. Compared with conventional Fenton-based processes, sulfate radical ($\text{SO}_4^{\bullet-}$) driven advanced oxidation processes (AOPs) exhibit stronger oxidative potential, a longer half-life (30–40 μs), and a broader operational pH range (2–9). Although peroxymonosulfate (PMS) itself can oxidize organic compounds with relatively low reactivity, the reactive oxygen species (ROS) generated during PMS activation—such as singlet oxygen ($^1\text{O}_2$), sulfate radicals ($\text{SO}_4^{\bullet-}$), hydroxyl radicals ($\cdot\text{OH}$), and superoxide radicals ($\text{O}_2^{\bullet-}$)—play a more decisive role in pollutant removal [8–10]. Various approaches have been developed to activate PMS, including ultraviolet irradiation [11], ultrasound [12], alkali activation [13], and catalyst activation [14–17]. Among these, activation by metal-based catalysts is particularly attractive due to its high efficiency, low energy consumption, and minimal secondary pollution, showing great potential for water treatment. Among noble metal catalysts, ruthenium (Ru)-based activators have attracted increasing attention owing to their high catalytic activity and excellent redox performance. Compared with other platinum-group metal catalysts, Ru exhibits a relatively lower cost, while offering higher activation efficiency and selectivity than traditional iron-based activators [18,19]. Consequently, Ru catalysts have been widely employed in fields such as hydrogenation catalysis [20] and the degradation of organic pollutants [21]. Moreover, homogeneous Ru species are difficult to recover from aqueous systems, leading to high operational costs and the risk of secondary water contamination, thereby restricting their large-scale application in PMS-based processes. Although a few studies have investigated the performance of Ru-based catalysts for PMS activation, their large-scale application is still limited by issues such as catalyst stability and cost. Therefore, it is necessary to develop Ru-based heterogeneous catalysts that are more stable and cost-effective.

To overcome this challenge, various materials have been employed as supports for ruthenium (Ru), including carbon-based materials [22,23], graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) [24], and metal oxides [25]. Among these, manganese dioxide (MnO_2)—the most common manganese oxide compound—occurs widely in natural environments and has attracted significant attention due to its low toxicity and high chemical stability. Its large specific surface area and diverse pore structures enable efficient dispersion and anchoring

of active components [26]. Moreover, MnO_2 , owing to its outstanding electron-shuttling capability, is frequently utilized as a support or co-catalyst for transition metals to facilitate effective electron transfer; such interactions can act synergistically with other supports, thereby enhancing PMS activation and pollutant degradation efficiency [27,28]. MnO_2 exists in various crystalline polymorphs, including α -, β -, γ -, and δ - MnO_2 , which are constructed from different microstructural units [29]. Among them, α - MnO_2 has been reported to exhibit superior PMS activation performance compared with β -, γ -, and δ - MnO_2 , owing to its unique tunnel structure, abundant mixed-valence Mn sites, and high density of oxygen vacancies [30]. Consequently, α - MnO_2 has demonstrated excellent performance as a doped or supported material in PMS-based systems. For instance, α - MnO_2 nanorods supported on palygorskite (α - MnO_2 /Pal) achieved nearly 100% degradation of Rhodamine B within 180 min in the PMS system [31]; similarly, a novel MnO_2 /UiO-66 composite synthesized via an oil-bath heating method efficiently activated PMS under UV irradiation for the degradation of oxytetracycline (OTC) [26]. However, the development of heterogeneous Ru/ α - MnO_2 composite catalysts and the systematic investigation of their catalytic performance in PMS activation remain scarce in the literature.

Considering the above aspects, this study designed and synthesized a heterogeneous catalyst (Ru/ α - MnO_2) by loading catalytically active Ru onto α - MnO_2 . The prepared activator was systematically characterized, and a series of experiments was conducted to evaluate its performance and applicability in the degradation of carbamazepine (CBZ) in aqueous systems. The objectives of this work are as follows: (1) to synthesize and characterize the heterogeneous activator Ru/ α - MnO_2 ; (2) to investigate the CBZ degradation performance of PMS activation by Ru/ α - MnO_2 and evaluate the effects of various operating parameters; (3) to elucidate the activation mechanism of PMS by Ru/ α - MnO_2 and identify the possible degradation pathways of CBZ; and (4) to assess the reusability and practical applicability of Ru/ α - MnO_2 in real wastewater treatment.

2. Results and Discussion

2.1. Catalyst Characterization

The surface morphology and structural characteristics of the catalysts play a critical role in their PMS activation efficiency. Field-emission scanning electron microscopy (FE-SEM) was employed to examine the morphology and microstructure of pristine α - MnO_2 and the Ru-doped α - MnO_2 composites prepared by two different methods. As shown in Figure 1a, α - MnO_2 exhibits a uniform nanorod structure; the incorporation of Ru did not alter the overall morphology of α - MnO_2 . Energy-dispersive X-ray spectroscopy (EDS) mapping was further performed to analyze the elemental distribution of O, Mn, and Ru within selected regions of the composites (Figure S1a,b). The results confirm a homogeneous dispersion of Ru on the surface of both composites, with O, Mn, and Ru elements clearly detected in the mapped areas. The Ru contents in the as-prepared Ru_{latt}/ α - MnO_2 and Ru_{surf}/ α - MnO_2 were quantified as 1.43 wt% and 1.02 wt%, respectively. However, due to the difficulty of directly visualizing Ru species on the α - MnO_2 support by SEM-EDS, transmission electron microscopy (TEM) was employed for further investigation. As shown in Figure 1b, Ru_{latt}/ α - MnO_2 retained the distinct nanorod morphology of α - MnO_2 without observable surface nanoparticles, consistent with the SEM results. In contrast, the TEM images of Ru_{surf}/ α - MnO_2 surface revealed numerous nanoparticles on the MnO_2 surface. This observation is likely attributed to the hydrolysis of RuCl_3 during the impregnation process, followed by decomposition to form Ru-based oxides or hydroxides. Therefore, it is reasonable to infer that the nanoparticles observed on the surface of α - MnO_2 in Ru_{surf}/ α - MnO_2 are composed of Ru oxides and hydroxides [32].

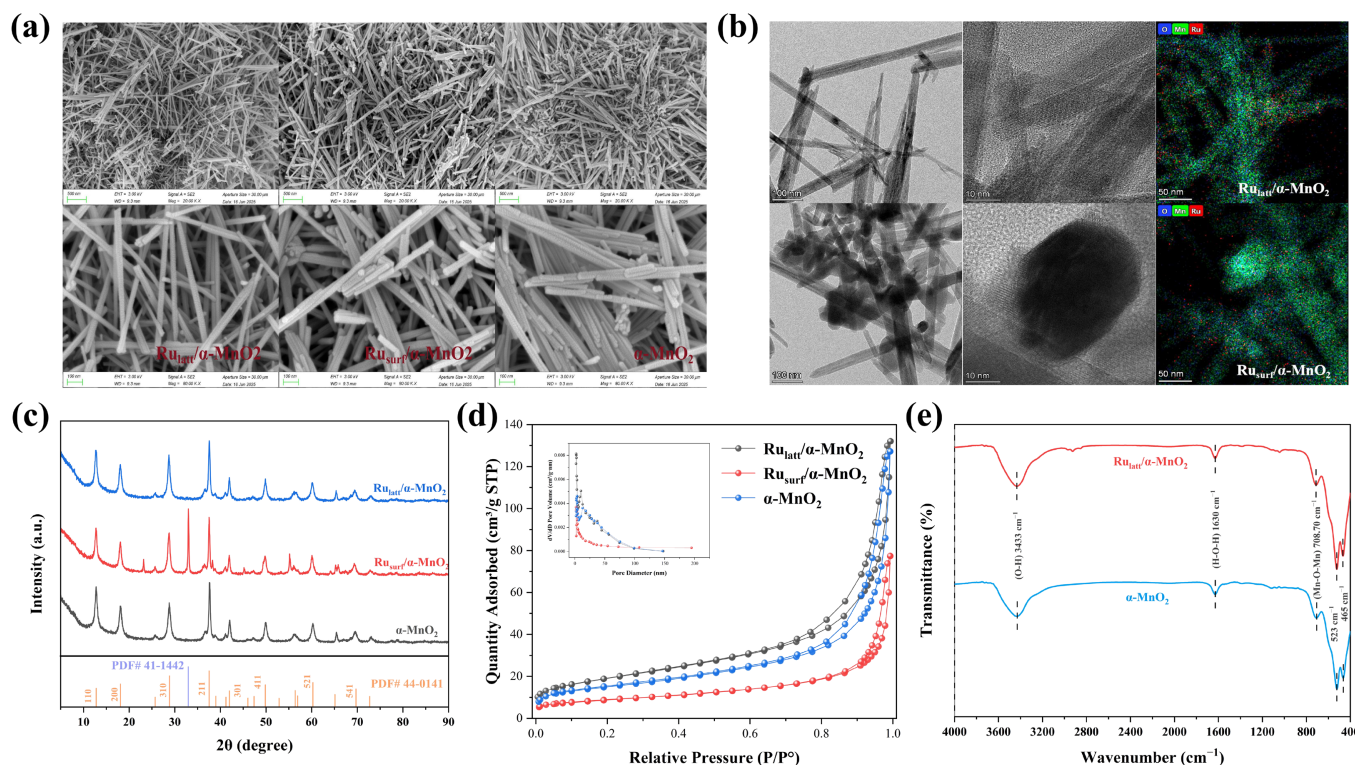


Figure 1. Material Results Characterisation Chart. (a) SEM, (b) EDS mapping and TEM images of Ru/ α -MnO₂, (c) XRD, (d) BET, and (e) FT-IR analysis of α -MnO₂ and Ru/ α -MnO₂.

The crystal phase structures of the three catalysts were characterized by X-ray diffraction (XRD). As shown in Figure 1c, the diffraction patterns of all samples exhibit prominent peaks at 12.8°, 18.1°, 28.8°, 37.5°, 41.9°, 49.9°, 60.3°, and 69.7°, corresponding to the (110), (200), (310), (211), (301), (411), (521), and (541) planes of α -MnO₂, respectively. These reflections are in good agreement with the standard pattern of α -MnO₂ (PDF# 44-0141) [26]. In addition, Ru_{surf}/ α -MnO₂ displays an additional diffraction peak at 32.9°, which matches the characteristic peak of Mn₂O₃ (PDF# 41-1442) [31]. This result indicates that α -MnO₂ and Ru_{latt}/ α -MnO₂ retain the pure α -MnO₂ phase, whereas the calcination process during the preparation of Ru_{surf}/ α -MnO₂ partially transformed α -MnO₂ into Mn₂O₃. All three samples show sharp and intense diffraction peaks, suggesting good crystallinity of the synthesized materials. Notably, the diffraction pattern of Ru_{latt}/ α -MnO₂ is almost indistinguishable from that of pristine α -MnO₂, and no characteristic peaks of Ru or other Ru-based phases are detected. The absence of Ru-related reflections may be attributed to the fact that Ru was successfully incorporated into the α -MnO₂ lattice [33]. These findings are consistent with the TEM and EDS observations.

The specific surface area (SSA) of catalysts plays a crucial role in the heterogeneous activation of PMS. To evaluate the catalytic activity of α -MnO₂ with different exposed crystal facets, it is essential to first measure the SSA of each sample and normalize the catalytic performance accordingly. The Brunauer–Emmett–Teller (BET) surface areas of the three materials were analyzed (Figure 1d), and the SSA values of Ru_{latt}/ α -MnO₂, Ru_{surf}/ α -MnO₂, and pristine α -MnO₂ were determined to be 68.74, 31.86, and 53.48 m²/g, respectively. The results indicate that Ru_{latt}/ α -MnO₂ possesses the largest BET surface area, which can expose more active sites during the reaction, thereby increasing the probability of effective collisions between active sites and target molecules and facilitating the catalytic process. Fourier transform infrared (FT-IR) spectroscopy was further employed to investigate the surface functional groups of Ru_{latt}/ α -MnO₂ and pristine α -MnO₂ (Figure 1e). The

characteristic peaks at 472 and 522 cm^{-1} are assigned to the stretching vibrations of Mn–O bonds [34], while the peak at 717 cm^{-1} corresponds to the vibration of bridging Mn–O–Mn bonds. The band observed at 1625 cm^{-1} is attributed to the bending vibration of adsorbed H_2O molecules (H–O–H), and the broad absorption at 3420 cm^{-1} is associated with the stretching vibration of surface hydroxyl groups on $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2$ [34,35]. Notably, no distinct new functional groups were detected on the surface of $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2$, suggesting that Ru species were successfully incorporated into the $\alpha\text{-MnO}_2$ lattice rather than forming separate surface-bound species.

2.2. Evaluation of CBZ Degradation Efficiency Across Different Systems

The CBZ removal performance of PMS, $\alpha\text{-MnO}_2/\text{PMS}$, $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2/\text{PMS}$, and $\text{Ru}_{\text{surf}}/\alpha\text{-MnO}_2/\text{PMS}$ systems was compared under identical conditions, with both PMS and activators dosages fixed at 200 mg/L. As shown in Figure 2, the PMS-only system achieved less than 3% CBZ removal, indicating that although PMS possesses strong intrinsic oxidizing capability, it generates few reactive species at ambient temperature and thus has negligible direct oxidation capacity toward CBZ under the tested conditions. In contrast, the introduction of $\alpha\text{-MnO}_2$, $\text{Ru}_{\text{surf}}/\alpha\text{-MnO}_2/\text{PMS}$, and $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2/\text{PMS}$ markedly enhanced PMS activation and CBZ degradation. Within 5 min, CBZ removal reached 16.74% in the $\alpha\text{-MnO}_2/\text{PMS}$ system, 50% in the $\text{Ru}_{\text{surf}}/\alpha\text{-MnO}_2/\text{PMS}$ system, and up to 70% in the $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2/\text{PMS}$ system. These results clearly demonstrate that $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2$ exhibits superior catalytic performance for PMS activation and CBZ degradation compared with the other systems. This enhanced activity can be attributed to the excellent structural stability of $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2$ and the synergistic interaction between Ru species and the $\alpha\text{-MnO}_2$ framework, where Ru is incorporated in different forms, thus facilitating more efficient PMS activation. The degradation efficiency, underlying mechanism, and practical applicability of the $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2/\text{PMS}$ system for CBZ removal will be further discussed in the following sections.

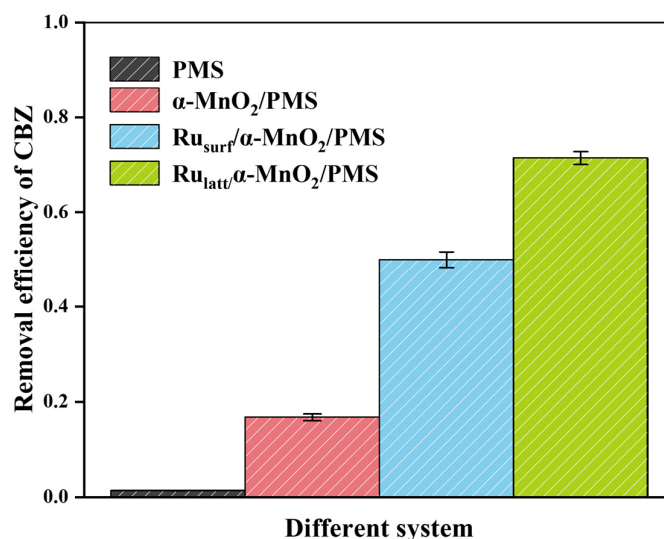


Figure 2. The removal efficiency of CBZ by different AOPS systems. Conditions: $[\text{CBZ}]_0 = 10 \text{ mg/L}$, $[\text{PMS}]_0 = 200 \text{ mg/L} = [\alpha\text{-MnO}_2]_0 = [\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2]_0 = [\text{Ru}_{\text{surf}}/\alpha\text{-MnO}_2]_0 = 200 \text{ mg/L}$, time = 5 min, pH = 3.

2.3. The Influence of Several Reaction Parameters on the Degradation of Carbamazepine

The initial pH of the solution exhibited a pronounced influence on CBZ degradation. As shown in Figure 3, the highest catalytic efficiency was achieved under strongly acidic conditions (pH = 3), where complete CBZ removal was accomplished within 8 min, and the

observed rate constant (K_{obs}) reached 0.33502 min^{-1} . As the pH increased from 5 to 11, the 10 min removal efficiencies decreased to 64.3%, 65.8%, 62%, and 20.4%, respectively. These results indicate that the system maintains high degradation efficiency under acidic to near-neutral conditions, exhibiting a broad operational pH range (pH 3–9). However, when the pH increased from 9 to 11, the CBZ removal efficiency dropped sharply from 62% to 20.4%. K_{obs} progressively declined with increasing pH, reaching a minimum of 0.0223 min^{-1} at pH 11—approximately 15-fold lower than that observed at pH 3. This decline can be explained by the acid–base speciation of PMS, a diprotic weak acid whose protonation state varies with pH [36]. Under acidic conditions, PMS predominantly exists as the monovalent anion HSO_5^- , which is more readily activated to generate sulfate radicals ($\text{SO}_4^{\bullet-}$). $\text{SO}_4^{\bullet-}$ possesses a longer half-life and a higher redox potential than hydroxyl radicals ($\cdot\text{OH}$) [37], resulting in enhanced CBZ degradation in acidic media. In alkaline conditions, however, $\text{SO}_4^{\bullet-}$ tends to react with H_2O or OH^- to yield $\cdot\text{OH}$ and SO_4^{2-} , while deprotonation of HSO_5^- leads to SO_5^{2-} , whose oxidative potential is lower than that of $\text{SO}_4^{\bullet-}$ [38]. Moreover, an excessively high pH promotes $\cdot\text{OH}$ self-quenching reactions, further reducing the concentration of reactive radicals and thus the overall degradation efficiency.

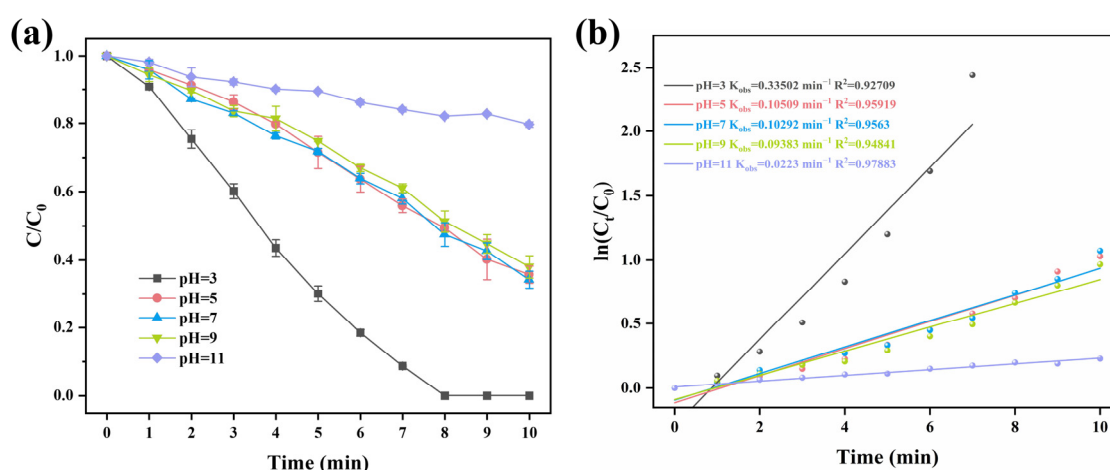


Figure 3. (a) Effect of pH on CBZ degradation of $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2/\text{PMS}$ system; (b) The corresponding fitted kinetics curves. Conditions: $[\text{CBZ}]_0 = 10 \text{ mg/L}$, $[\text{PMS}]_0 = 200 \text{ mg/L}$, $[\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2]_0 = 200 \text{ mg/L}$.

The dosage of the activator directly influences the total number of active sites available in the system. In this study, the effect of $\text{Ru}_{\text{latt}}/\text{MnO}_2$ dosage on CBZ removal was investigated (Figure 4). When the catalyst loading was 100 mg/L , CBZ removal reached 99.91% after 10 min, with an observed rate constant K_{obs} of 0.2342 min^{-1} . Increasing the dosage to 200 mg/L dramatically accelerated the reaction, achieving complete CBZ removal within 8 min and increasing K_{obs} to 0.33502 min^{-1} . Further increasing the catalyst loading to 300, 400, and 500 mg/L enabled nearly complete CBZ degradation within only 3 min, with K_{obs} rising to 0.69548, 0.67915, and 0.74015 min^{-1} , respectively. These results reveal a positive correlation between $\text{Ru}_{\text{latt}}/\text{MnO}_2$ dosage and CBZ degradation efficiency (and reaction kinetics) within a certain range, demonstrating the excellent PMS activation capability of this catalyst. With PMS concentration fixed, increasing the amount of $\text{Ru}_{\text{latt}}/\text{MnO}_2$ introduces more $\alpha\text{-MnO}_2$ and Ru active species, thereby providing additional reactive sites that can interact with PMS to generate more reactive oxygen species (ROS), which in turn accelerate CBZ degradation. For consistency and comparability in subsequent experiments, a catalyst dosage of 200 mg/L was selected.

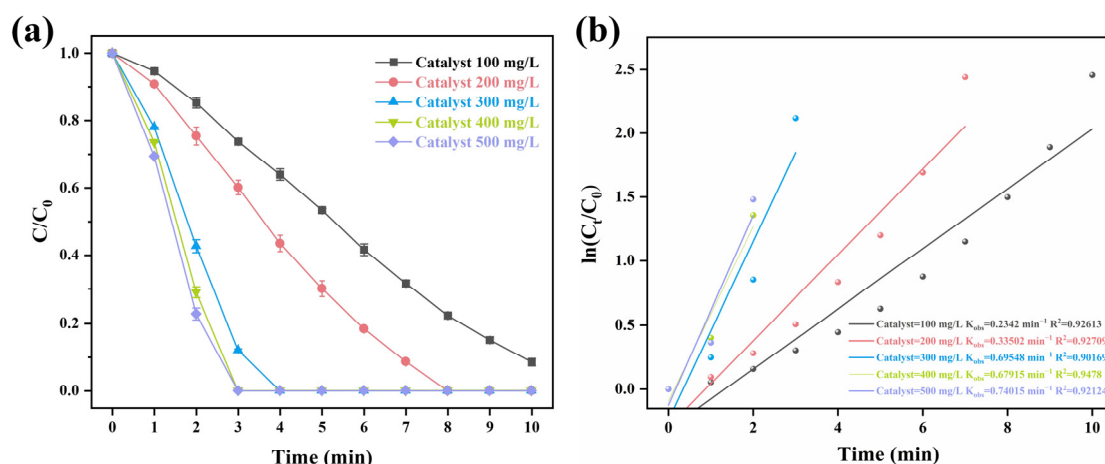


Figure 4. (a) Effect of $\text{Ru}_{\text{lat}}/\alpha\text{-MnO}_2$ dosage on CBZ degradation of $\text{Ru}_{\text{lat}}/\alpha\text{-MnO}_2/\text{PMS}$ system; (b) The corresponding fitted kinetics curves. Conditions: $[\text{CBZ}]_0 = 10 \text{ mg/L}$, $[\text{PMS}]_0 = 200 \text{ mg/L}$, $\text{pH} = 3$.

The effect of PMS dosage on CBZ removal was investigated by varying the PMS concentration from 100 to 500 mg/L (Figure 5). As shown in the figure, the reaction rate gradually increased with increasing PMS concentration, achieving complete CBZ removal within 10, 8, 4, and 3 min, respectively. Meanwhile, the apparent rate constant (K_{obs}) also progressively increased with PMS concentration. Specifically, K_{obs} rose from 0.20686 min^{-1} at 100 mg/L PMS to 0.80676 min^{-1} at 500 mg/L PMS—approximately 3.9 times higher than that observed at 100 mg/L. This trend indicates that a higher PMS dosage enhances the contact between PMS molecules and the active sites of $\text{Ru}_{\text{lat}}/\alpha\text{-MnO}_2$, thereby accelerating the degradation of CBZ. When PMS is supplied in sufficient amounts, it can rapidly occupy the available active sites on $\text{Ru}_{\text{lat}}/\alpha\text{-MnO}_2$, generating more reactive species to effectively oxidize CBZ. Considering both cost efficiency and operational practicality, a PMS concentration of 200 mg/L was selected for subsequent experiments.

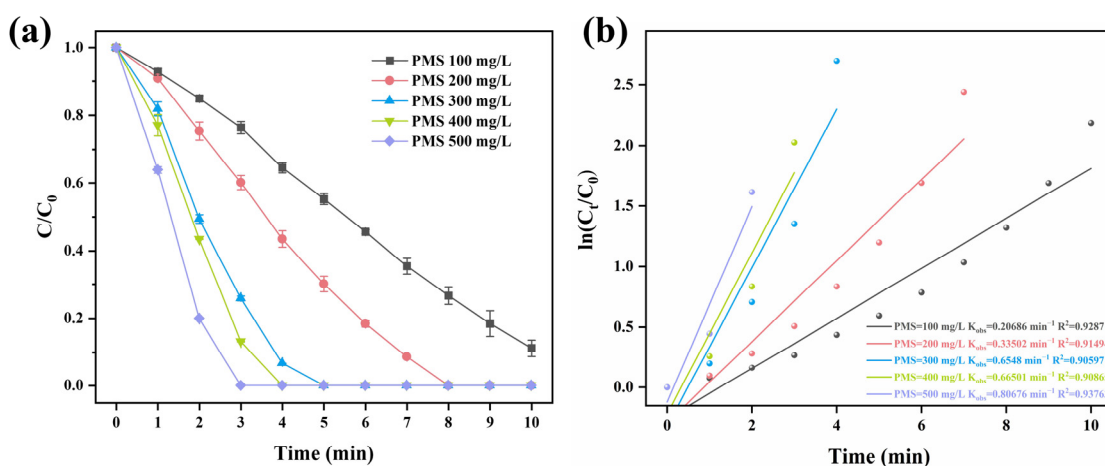


Figure 5. (a) Effect of PMS dosage on CBZ degradation of $\text{Ru}_{\text{lat}}/\alpha\text{-MnO}_2/\text{PMS}$ system; (b) The corresponding fitted kinetics curves. Conditions: $[\text{CBZ}]_0 = 10 \text{ mg/L}$, $[\text{Ru}_{\text{lat}}/\alpha\text{-MnO}_2]_0 = 200 \text{ mg/L}$, $\text{pH} = 3$.

2.4. Catalytic Mechanism of $\text{Ru}_{\text{lat}}/\alpha\text{-MnO}_2$

Identification of Reactive Species

It has been reported that both radical species and singlet oxygen ($^1\text{O}_2$) are commonly generated in PMS activation systems, contributing to the degradation of organic pollutants in $\text{Ru}/\text{MnOx}/\text{PMS}$ systems [15,27]. Therefore, quenching experiments were

conducted to identify the dominant reactive species involved in the $\text{Ru}_{\text{latt}}/\text{MnO}_2/\text{PMS}$ system (Figure 6a). *tert*-Butyl alcohol (TBA) was employed as a scavenger for hydroxyl radicals ($\cdot\text{OH}$), while methanol (MeOH) was used to quench both sulfate radicals ($\text{SO}_4^{\bullet-}$) and $\cdot\text{OH}$. Furfuryl alcohol (FFA) was applied as a selective scavenger for singlet oxygen ($^1\text{O}_2$) to evaluate its contribution [39], and *p*-benzoquinone (*p*-BQ) was used to capture superoxide radicals ($\text{O}_2^{\bullet-}$) [40]. As shown in Figure 6a, the addition of *p*-BQ almost completely suppressed CBZ degradation since the apparent rate constant (K_{obs}) sharply decreased, dropping to a value 26-fold lower than that of the blank group. This result indicates a critical role of $\text{O}_2^{\bullet-}$ in the reaction system. In addition to radical pathways, nonradical processes were also investigated. The introduction of FFA exhibited a nearly complete inhibition effect, with CBZ removal dropping to only 0.12% within 3 min; the apparent rate constant (K_{obs}) decreased to 46.5 times lower than that of the blank group. Suggesting that CBZ degradation was almost entirely suppressed. These findings indicate that $^1\text{O}_2$ is the predominant reactive oxygen species responsible for CBZ degradation in the $\text{Ru}_{\text{latt}}/\text{MnO}_2/\text{PMS}$ system, while $\text{O}_2^{\bullet-}$ also contributes significantly to the overall oxidation process.

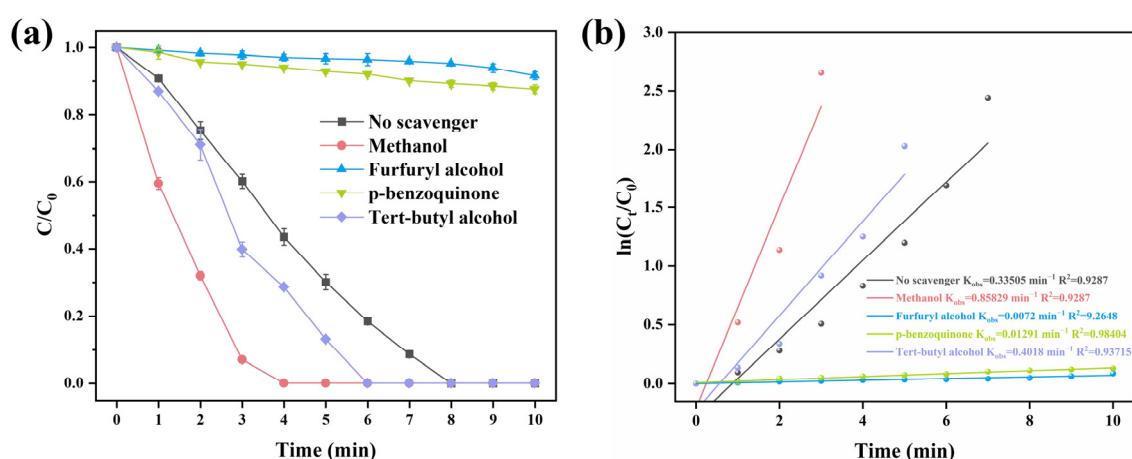


Figure 6. (a) Effects of different scavengers on CBZ degradation via $\text{Ru}_{\text{latt}}/\text{MnO}_2/\text{PMS}$ system; (b) The corresponding fitted kinetics curves. Conditions: $[\text{CBZ}]_0 = 10 \text{ mg/L}$, $[\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2]_0 = 200 \text{ mg/L}$, $[\text{PMS}]_0 = 200 \text{ mg/L}$ pH = 3, $[\text{extinguishing agent}]_0 = 50 \text{ mmol/L}$.

Interestingly, the addition of MeOH or TBA did not lead to the expected decrease in CBZ removal; the apparent rate constant (K_{obs}) increased by 2.6-fold with MeOH and 1.2-fold with TBA, indicating a significant enhancement in the reaction kinetics. In other words, their presence promoted CBZ degradation. According to previous studies, this phenomenon may be attributed to the inherently short lifetime and low reactivity of superoxide radicals ($\text{O}_2^{\bullet-}$) in pure water. In the presence of less polar protic solvents such as methanol, the solvation environment of $\text{O}_2^{\bullet-}$ is altered, resulting in significantly enhanced stability and reactivity [41]. In addition, TBA can react with $\text{O}_2^{\bullet-}$ to generate peroxy radicals ($\text{ROO}\cdot$), which are capable of directly oxidizing Mn^{2+} in aqueous solution to form manganese oxides (e.g., MnO_2). In the presence of TBA, the average oxidation state of manganese species shifts from trivalent to more tetravalent forms, potentially enhancing PMS activation. Taken together, the quenching experiments suggest that the $\text{Ru}_{\text{latt}}/\text{MnO}_2/\text{PMS}$ system predominantly follows a nonradical pathway for CBZ degradation. Based on the above discussion, it can be inferred that $^1\text{O}_2$ and $\text{O}_2^{\bullet-}$ are the primary reactive species responsible for PMS activation in the $\text{Ru}_{\text{latt}}/\text{MnO}_2/\text{PMS}$ system. Previous reports have suggested that $\text{O}_2^{\bullet-}$ often serves as a precursor or auxiliary oxidant for $^1\text{O}_2$ formation [42,43]; specifically, $\text{O}_2^{\bullet-}$ and SO_5^- can be consumed by water molecules to generate $^1\text{O}_2$ [44]. The introduction

of a low concentration of methanol improves the stability and reactivity of $\text{O}_2^{\bullet-}$, thereby promoting $^1\text{O}_2$ generation and accelerating CBZ degradation.

Electron paramagnetic resonance (EPR) spectroscopy was further employed to investigate the generation of reactive oxygen species (ROS) during PMS activation by $\text{Ru}_{\text{latt}}/\text{MnO}_2/\text{PMS}$ (Figure 7). As shown in Figure 7a, the EPR spectra exhibited a characteristic 1:1:1 triplet signal of $\text{TEMP-}^1\text{O}_2$ adducts, confirming the production of singlet oxygen ($^1\text{O}_2$) [10], with the signal intensity increasing progressively over time. In addition, distinct signals assigned to the $\text{DMPO-O}_2^{\bullet-}$ adduct were observed [45], and their intensity also increased with reaction time, further verifying the presence of $\text{O}_2^{\bullet-}$ in the system. In contrast, no characteristic peaks corresponding to $\text{DMPO-SO}_4^{\bullet-}$ or $\text{DMPO-}\cdot\text{OH}$ were detected, indicating that sulfate radicals ($\text{SO}_4^{\bullet-}$) and hydroxyl radicals ($\cdot\text{OH}$) were not generated in significant amounts. These findings demonstrate that CBZ degradation in the $\text{Ru}_{\text{latt}}/\text{MnO}_2/\text{PMS}$ system is primarily governed by a nonradical pathway, dominated by $^1\text{O}_2$, with $\text{O}_2^{\bullet-}$ either serving as a precursor for $^1\text{O}_2$ formation or participating as an auxiliary oxidant. The EPR results, combined with the quenching experiments, provide strong evidence that the PMS activation and CBZ degradation process is mainly driven by $^1\text{O}_2$ and $\text{O}_2^{\bullet-}$.

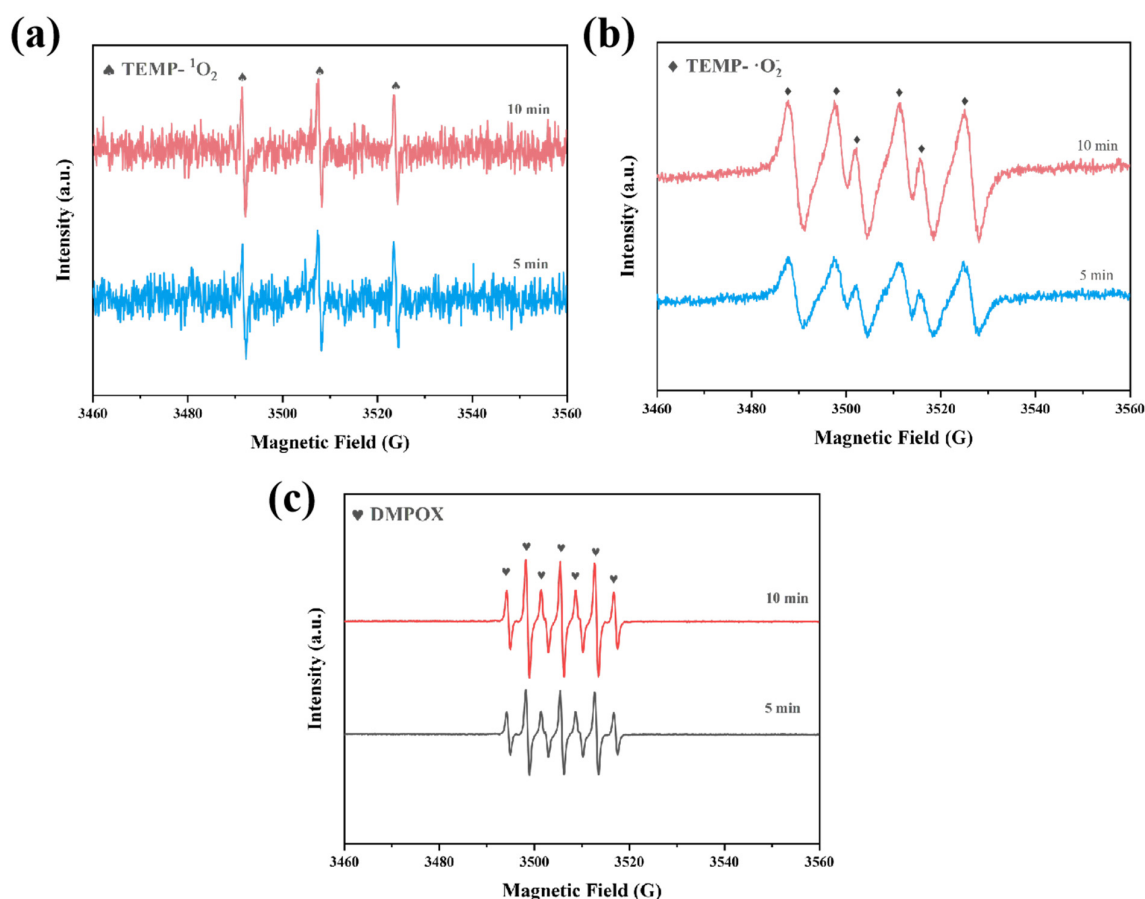


Figure 7. EPR Characterization Results. (a) $\text{TEMP-}^1\text{O}_2$, (b) $\text{DMPO-O}_2^{\bullet-}$, (c) $\text{DMPO-SO}_4^{\bullet-}$ and $\text{DMPO-}\cdot\text{OH}$.

Manganese oxides are generally considered capable of reacting with PMS to generate sulfate radicals ($\text{SO}_4^{\bullet-}$) and hydroxyl radicals ($\cdot\text{OH}$), as described in previous studies [46,47]. However, the quenching experiments and EPR results in this work revealed that neither $\text{SO}_4^{\bullet-}$ nor $\cdot\text{OH}$ was detected in the $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2/\text{PMS}$ system. Therefore, it is necessary to further elucidate the actual role of manganese oxides in this catalytic process. To achieve this, phosphate (H_2PO_4^-) was introduced as a blocking agent for the Mn active sites.

Previous studies have shown that H_2PO_4^- can form stable complexes with Mn (III) [48], allowing us to distinguish whether Mn (III) participates in an alternative degradation pathway rather than directly activating PMS to generate radicals. Using this strategy, we aimed to clarify whether manganese oxides contribute through a nonradical pathway and to provide stronger evidence regarding the mechanistic role of Mn in PMS activation. As shown in the results (Figure 8), the addition of H_2PO_4^- significantly suppressed the CBZ removal efficiency, with only 4% degradation observed after 10 min. This strong inhibition suggests that Mn (III) plays a crucial role in the degradation process of the $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2/\text{PMS}$ system, rather than simply catalyzing PMS to produce free radicals. To further clarify the involvement of Mn (III) and its valence-state changes during the reaction, X-ray photoelectron spectroscopy (XPS) analysis was performed.

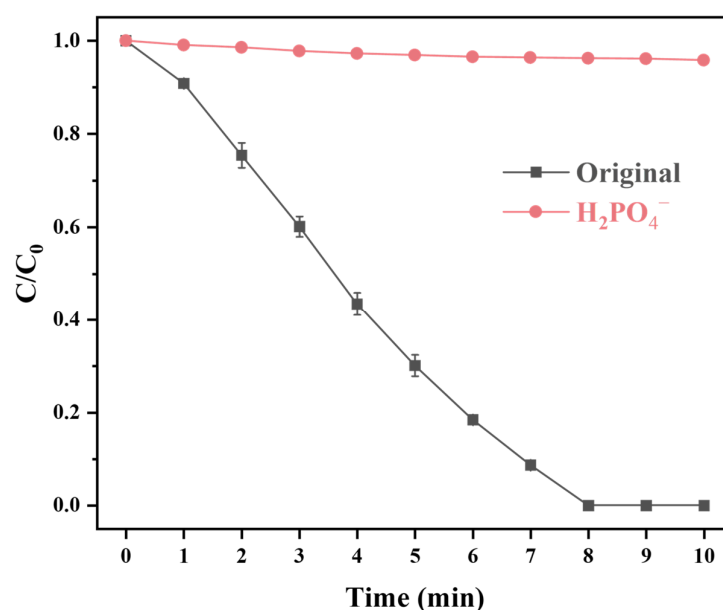


Figure 8. Effects of H_2PO_4^- on CBZ degradation via $\text{Ru}_{\text{latt}}\text{-MnO}_2/\text{PMS}$ system. Conditions: $[\text{CBZ}]_0 = 10 \text{ mg/L}$, $[\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2]_0 = 200 \text{ mg/L}$, $[\text{PMS}]_0 = 200 \text{ mg/L}$ pH = 3, $[\text{H}_2\text{PO}_4^-]_0 = 10 \text{ mmol/L}$.

To further elucidate the activation mechanism of the $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2/\text{PMS}$ system, X-ray photoelectron spectroscopy (XPS) was employed to analyze the valence states of the metal elements. The oxygen species of pristine $\alpha\text{-MnO}_2$ and $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2/\text{PMS}$ were examined, as shown in Figure S2. The O 1s spectra of both materials could be deconvoluted into three peaks located at 533.3, 531.8, and 530.4 eV, corresponding to chemisorbed water or hydroxyl oxygen (O_{latt}), surface-adsorbed oxygen species near oxygen vacancies (O_{ads}), and lattice oxygen (O_{surf}), respectively [49]. Generally, the content of O_{ads} can reflect the abundance of oxygen vacancies (O_v), as O_{ads} is typically formed by oxygen molecules adsorbing at O_v sites [41]. It can be observed that the relative proportion of O_{ads} is similar between $\alpha\text{-MnO}_2$ and $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2/\text{PMS}$, suggesting that the introduction of Ru did not significantly alter the structural framework of $\alpha\text{-MnO}_2$ and that both materials possess abundant surface-active sites capable of participating in the reaction. However, despite their comparable O_{ads} content, the two catalysts show markedly different PMS activation efficiencies, implying that the oxygen vacancies exposed on the crystal facets are not the dominant factor governing catalytic activity in PMS activation. Previous studies have reported that Mn (II) and Mn (III) species serve as key active sites, with Mn (III) playing a particularly critical role in PMS activation [50]. As shown in the Mn 2p_{3/2} spectra (Figure S2), the peaks at 640.7, 642.2, and 643.2 eV correspond to the binding energies of Mn (II), Mn (III), and Mn (IV), respectively [50]. Quantitative analysis revealed that

the proportion of Mn (III) in Ru_{latt}/α-MnO₂/PMS is slightly higher than that in pristine α-MnO₂, indicating that the incorporation of Ru increased the Mn (III) content in the α-MnO₂ framework, thereby enhancing its intrinsic PMS activation capability.

X-ray photoelectron spectroscopy (XPS) was further conducted to examine the valence-state changes in O, Mn, and Ru in Ru_{latt}/α-MnO₂/PMS before and after reaction in order to elucidate the fundamental activation mechanism. As shown in Figure 9a, the proportion of surface-adsorbed oxygen species (O_{ads}) markedly decreased from 34.3% to 19.0%, accompanied by a relative increase in chemisorbed water/hydroxyl oxygen (O_{latt}) from 55.0% to 72.8%. This observation is consistent with previous reports, where O_{ads} is typically consumed or transformed during PMS activation dominated by nonradical pathways (e.g., ¹O₂ generation), leading to a decrease in O_{ads} content and a relative enrichment of O_{latt} [51]. Therefore, these results indirectly indicate that singlet oxygen (¹O₂) generation plays a predominant role in PMS activation within this system, which is in good agreement with the quenching and EPR analyses.

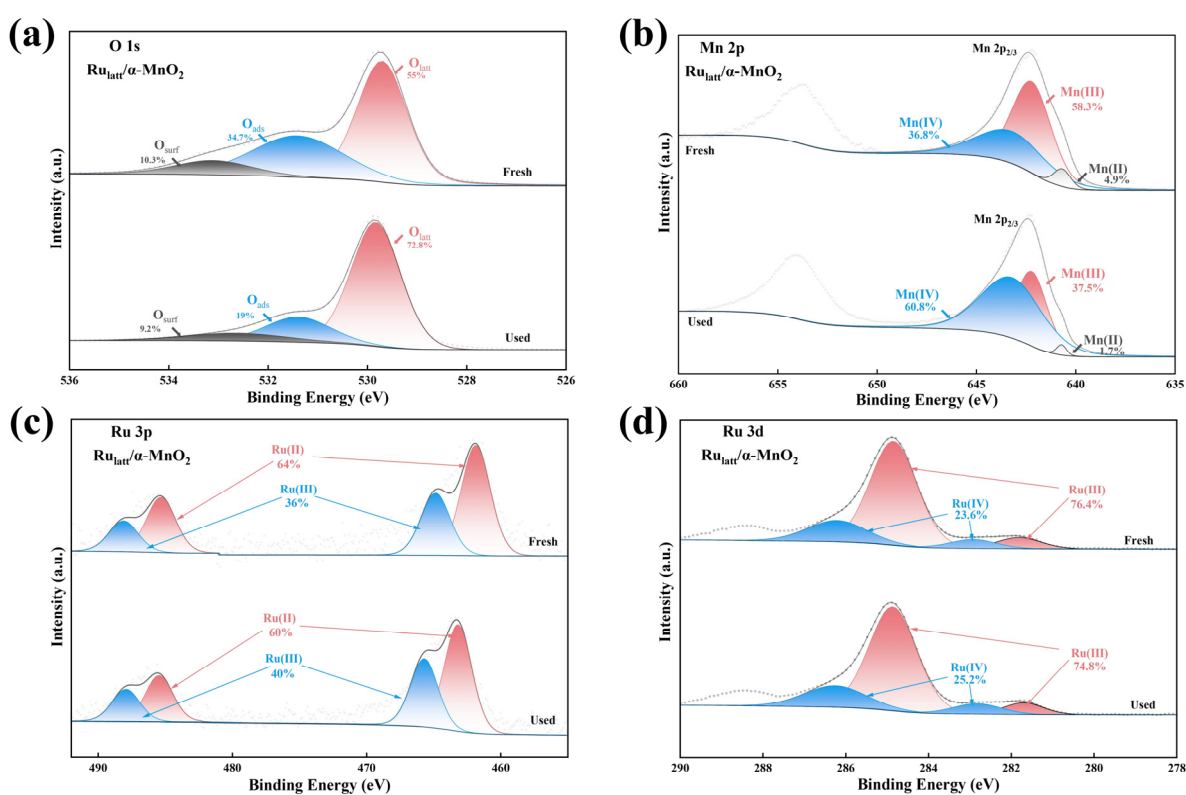
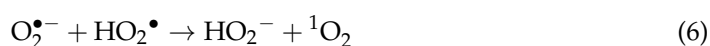
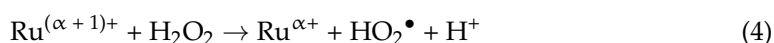
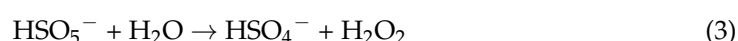


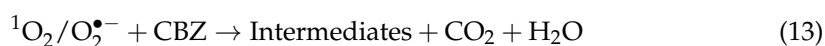
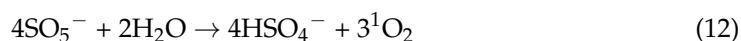
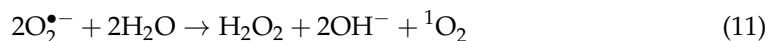
Figure 9. XPS spectra of (a) of O 1s, (b) Mn 2p, (c) Ru 3p, and (d) Ru 3d of the fresh and used Ru_{latt}/α-MnO₂/PMS.

The Mn 2p XPS spectra revealed a pronounced decrease in the proportion of Mn (III) from 58.0% to 37.5% after reaction, accompanied by a corresponding increase in Mn (IV). Although previous studies have widely reported that Mn (III) plays a key role in PMS activation, the combined results of the present work indicate that the valence transition of Mn is not associated with radical generation from PMS. Together with the phosphate blocking experiments, it can be inferred that Mn participates in the reaction via an alternative pathway. Similar phenomena have been reported in earlier studies, in which Mn acted as an electron reservoir to facilitate the redox cycling of Ru, while Ru sites dominated PMS activation and drove contaminant degradation through a nonradical pathway. As shown in Figure 9c,d, the evolution of Ru oxidation states further supports this hypothesis. The Ru 3p spectra show a relative decrease in Ru (II) and a corresponding increase in Ru (III) after reaction. Meanwhile, in the Ru 3d spectra, the fraction of Ru (III)

slightly decreased relative to Ru (IV), with a modest enrichment of Ru (IV) [52]. Overall, Ru tends to be oxidized to higher valence states under PMS exposure, while a reversible redox transition between Ru (III) and Ru (IV) occurs during the catalytic process. Based on these results and the previous evidence, a plausible degradation mechanism for the Ru_{latt}/α-MnO₂/PMS system can be proposed: (1) PMS is activated at the Ru sites, where low-valent Ru is oxidized to higher oxidation states, concurrently generating singlet oxygen (¹O₂) that initiates CBZ degradation [53]; (2) Mn(III) in α-MnO₂ is converted to Mn(IV), releasing electrons to reduce the high-valent Ru species and thus sustain the reversible Ru redox cycle [53]; (3) during this process, Mn(IV) does not generate SO₄^{•−} or ·OH upon interaction with PMS but is instead reduced back to Mn(III), establishing a Mn(III)/Mn(IV) redox loop [54]. Collectively, these findings suggest that Ru primarily governs PMS activation through a nonradical pathway, while α-MnO₂ functions as an electron reservoir that supports the reversible Ru valence cycling and enhances the overall catalytic stability.

In summary, the degradation of carbamazepine (CBZ) in this catalytic system is predominantly governed by a singlet oxygen (¹O₂)-driven pathway rather than the widely reported sulfate radical (SO₄^{•−}) or hydroxyl radical (·OH) routes. This conclusion is strongly supported by radical quenching experiments and EPR analysis. In particular, EPR spectra clearly revealed the presence of O₂^{•−} and ¹O₂ signals but showed no detectable SO₄^{•−} or ·OH, confirming that nonradical pathways dominate the PMS activation process [8]. It is noteworthy that O₂^{•−} is commonly considered a precursor or auxiliary oxidant for ¹O₂ formation; it can be generated through surface electron-transfer reactions or via SO₅^{2−} decomposition, subsequently promoting the continuous production of ¹O₂ [55], thereby synergistically contributing to CBZ oxidation. Furthermore, combined evidence from quenching tests, EPR detection of reactive oxygen species, Mn (III) blocking experiments, and XPS analysis elucidated the evolution of surface valence states and oxygen species during PMS activation. Mn (III) content decreased significantly with a concomitant enrichment of Mn (IV), indicating that Mn acts as an electron reservoir undergoing progressive oxidation. Meanwhile, Ru (II) was partially consumed, and the fraction of Ru (III)/Ru (IV) slightly increased, reflecting a reversible Ru (II) → Ru (III) → Ru (IV) redox cycle. In this cycle, Ru sites serve as redox mediators to activate PMS [25], while interfacial electron transfer from Mn to Ru sustains the Ru turnover and enhances its catalytic stability [56]. Simultaneously, the marked decrease in surface-adsorbed oxygen species (O_{ads}) and the relative enrichment of chemisorbed water/hydroxyl oxygen (O_{latt}) indicate that O_{ads} is consumed or transformed during the generation of O₂^{•−} and ¹O₂, indirectly validating the nonradical pathway. Collectively, the synergistic coupling of the Mn (IV)/Mn (III) redox cycle with the reversible Ru (II)/Ru (III)/Ru (IV) transition facilitates efficient PMS activation and CBZ degradation. The overall process is dominated by ¹O₂, with O₂^{•−} acting as a precursor and auxiliary oxidant, while Ru–Mn interfacial electron transfer and the dynamic reconstruction of surface oxygen species further enhance catalytic performance (Equations (1)–(13)) [25,57–61].





2.5. The Influence of Coexisting Anions and Natural Organic Matter

In real aquatic environments, the presence of coexisting anions and natural organic matter (NOM) can interfere with the degradation of target pollutants. Therefore, the effects of common coexisting anions (NO_3^- , Cl^- , and HCO_3^-) as well as humic acid (HA) on CBZ removal were investigated. As shown in Figure 10, the presence of Cl^- remarkably accelerated CBZ degradation, achieving nearly 100% removal within 5 min. Similar promoting effects of chloride have also been observed in other studies [62,63], which can be attributed to the fact that Cl^- , as an electron-rich anion, can act as an electron donor during PMS activation, thereby enhancing CBZ oxidation. The NO_3^- containing system also showed a slight improvement in CBZ removal compared with the control, reaching 99.95% degradation within 5 min. Compared with the control, the presence of HCO_3^- exhibited a modest promoting effect on CBZ degradation. This could be associated with its ability to modulate deprotonation of functional groups and facilitate PMS decomposition toward nonradical pathways; under certain conditions, HCO_3^- may also generate carbonate radicals ($\text{CO}_3^{\bullet-}$) that contribute to pollutant oxidation [64]. Considering that wastewater typically contains a substantial amount of organic matter, humic acid (HA) was employed as a representative model to evaluate the effect of NOM on CBZ degradation in the $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2/\text{PMS}$ system. The addition of HA significantly inhibited CBZ degradation, reducing the removal efficiency to only 63% after 10 min, likely due to the competitive consumption of reactive oxygen species (ROS) by both HA and CBZ [47].

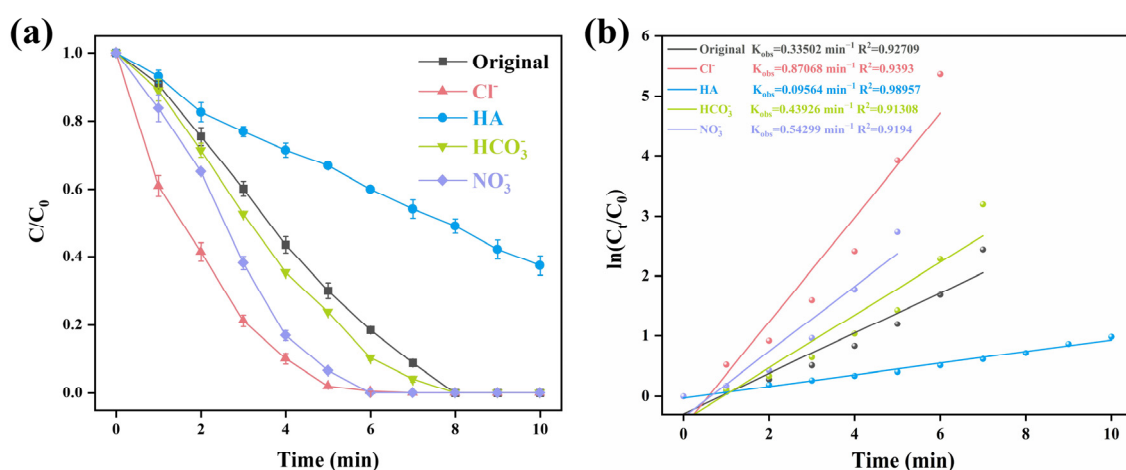


Figure 10. (a) Effects of interfering ions on CBZ degradation via $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2/\text{PMS}$ system; (b) The corresponding fitted kinetics curves. Conditions: $[\text{CBZ}]_0 = 10 \text{ mg/L}$, $[\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2]_0 = 200 \text{ mg/L}$, $[\text{PMS}]_0 = 200 \text{ mg/L}$ pH = 3, $[\text{interfering ions}]_0 = 10 \text{ mmol/L}$.

3. Materials and Methods

3.1. Chemicals

All reagents were of analytical grade and used without further purification. Potassium permanganate (KMnO_4), manganese(II) sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), ruthenium(III) chloride hydrate ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$), and potassium peroxydisulfate ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$, 47%) were purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). Carbamazepine (CBZ) was obtained from Macklin and stored at 4 °C before use. tert-Butyl alcohol (TBA), p-benzoquinone (p-BQ), methanol (MeOH), and furfuryl alcohol (FFA) were also supplied by Macklin. All solutions were prepared using high-purity deionized (DI) water.

3.2. Preparation of Materials

A total of 1.26427 g potassium permanganate (KMnO_4), 1.35208 g manganese(II) sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), and 0.136 g ruthenium(III) chloride hydrate ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$) were dissolved in 50 mL deionized (DI) water and stirred for 30 min to obtain a deep purple–black precursor solution. The mixture was then transferred to a Teflon-lined stainless steel autoclave and subjected to hydrothermal treatment at 140 °C for 6 h. After cooling to room temperature, the resulting solid was washed three times with ultrapure water, dried at 100 °C, and ground into a fine powder to obtain the catalyst denoted as $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2$. For comparison, $\alpha\text{-MnO}_2$ was prepared following the same procedure but without the addition of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$; specifically, 1.26427 g KMnO_4 and 1.35208 g $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ were dissolved in 50 mL DI water, stirred for 30 min, and then treated under identical hydrothermal, washing, drying, and grinding conditions. The surface-loaded $\text{Ru}_{\text{surf}}/\alpha\text{-MnO}_2$ catalyst was synthesized by an impregnation method: a $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ aqueous solution was mixed with the as-prepared $\alpha\text{-MnO}_2$, followed by solvent evaporation at 100 °C, washing three times with DI water, drying at 100 °C, and calcination at 500 °C for 2 h with a heating rate of 2 °C min^{-1} . Finally, the product was naturally cooled to room temperature to obtain the desired $\text{Ru}_{\text{surf}}/\alpha\text{-MnO}_2$ catalyst.

3.3. Sample Characterizations

The surface morphologies of $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2$ and $\text{Ru}_{\text{surf}}/\alpha\text{-MnO}_2$ were examined using scanning electron microscopy (SEM, ZEISS GeminiSEM 300, Freiburg, Germany) operated at an accelerating voltage of 30 kV. The nanostructures were further observed by transmission electron microscopy (TEM, Talos F200 S, Thermo Fisher Scientific, Waltham, MA, USA) at 200 kV. The internal structure, phase composition, and crystallinity of the materials were analyzed by X-ray diffraction (XRD, PANalytical X'Pert Powder, Spectris, Almelo, The Netherlands) with $\text{Cu K}\alpha$ radiation over a 2θ range of 5–90° at a scanning rate of 5° min^{-1} . The Brunauer–Emmett–Teller (BET) specific surface areas were determined using a surface area analyzer (ASAP 2460, Micromeritics, Norcross, GA, USA). The surface elemental compositions and oxidation states of Mn and Ru were characterized by X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific, Waltham, MA, USA), and the spectra were deconvoluted using XPSPEAK41 software. Surface functional groups were identified by Fourier transform infrared spectroscopy (FT-IR, Nicolet iS20, Thermo Fisher Scientific, Waltham, MA, USA). Electron paramagnetic resonance (EPR, EMXplus-6/1, Bruker, Karlsruhe, Germany) was employed to detect reactive oxygen species (ROS), with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and 2,2,6,6-tetramethyl-4-piperidinol (TEMP) used as spin-trapping agents.

3.4. Test Apparatus and Analytical Methods

The catalytic degradation performance of $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2$ and $\text{Ru}_{\text{surf}}/\alpha\text{-MnO}_2$ toward CBZ was evaluated in a 100 mL beaker under continuous stirring at 800 rpm at room

temperature. Briefly, a predetermined amount of $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2$ was ultrasonically dispersed in 50 mL deionized (DI) water for 30 s, followed by the addition of 50 mL CBZ stock solution (10 mg L^{-1}). The pH of the mixed solution was adjusted to 7.0 using 0.1M H_2SO_4 and 0.1M NaOH as needed. Subsequently, 50 mg of peroxymonosulfate (PMS) was added to initiate the degradation reaction. At predetermined time intervals, 2.4 mL of the reaction solution was withdrawn and immediately quenched with 0.6 mL anhydrous methanol to stop further reaction. The quenched samples were filtered through a $0.22 \mu\text{m}$ PTFE membrane, and 1 mL of the filtrate was transferred to an HPLC vial for organic contaminant analysis using high-performance liquid chromatography (HPLC, Agilent 1260, Waltham, MA, USA). Degradation experiments using $\text{Ru}_{\text{surf}}/\alpha\text{-MnO}_2$ were performed under identical conditions. The apparent reaction rate constants (k) were determined using a pseudo-first-order kinetic model.

$$\ln(C_0/C) = kt \quad (14)$$

The reaction rate constant is determined by a first-order kinetic model, where C_0 , C , k , and t denote the initial concentration ($\text{mg}\cdot\text{L}^{-1}$), concentration at time t ($\text{mg}\cdot\text{L}^{-1}$), reaction rate constant (min^{-1}), and reaction time (min), respectively.

4. Conclusions

In this study, a simple strategy was employed to prepare heterogeneous Ru-based catalysts ($\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2$ and $\text{Ru}_{\text{surf}}/\alpha\text{-MnO}_2$) by introducing Ru into the $\alpha\text{-MnO}_2$ through two different incorporation methods, and their ability to activate PMS for the degradation of CBZ was systematically investigated. Structural characterization revealed that both $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2$ and $\text{Ru}_{\text{surf}}/\alpha\text{-MnO}_2$ possessed larger specific surface areas and superior structural stability compared with pristine $\alpha\text{-MnO}_2$. Catalytic degradation experiments demonstrated that $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2$ exhibited significantly enhanced PMS activation and CBZ removal, particularly under acidic conditions, outperforming both $\text{Ru}_{\text{surf}}/\alpha\text{-MnO}_2$ and $\alpha\text{-MnO}_2$. The resulting Ru-doped $\alpha\text{-MnO}_2$ overcomes the recovery and leaching problems of homogeneous Ru catalysts, enhances the catalytic performance compared with pristine $\alpha\text{-MnO}_2$, and fills a research gap by providing a routinely synthesizable $\text{Ru}/\alpha\text{-MnO}_2$ heterogeneous material and a systematic evaluation of its performance for PMS activation. Operational parameters, including catalyst dosage, PMS concentration, and solution pH, were found to influence CBZ degradation efficiency. Mechanistic investigations revealed that Ru sites dominate the nonradical PMS activation pathway. As shown in Figure 11, where Ru undergoes reversible valence transitions and generates singlet oxygen ($^1\text{O}_2$) as the primary reactive species responsible for CBZ oxidation. Meanwhile, the Mn (III)/Mn (IV) redox cycle within $\alpha\text{-MnO}_2$ functions as an electron reservoir, sustaining Ru valence cycling and enhancing the catalyst's stability and long-term reactivity. Multiple characterizations confirmed the structural robustness of $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2$ during PMS activation. The $\text{Ru}_{\text{latt}}/\alpha\text{-MnO}_2$ maintained excellent performance in batch experiments under acidic conditions and in the presence of interfering anions, indicating promising potential for practical application in the remediation of CBZ-contaminated acidic water environments.

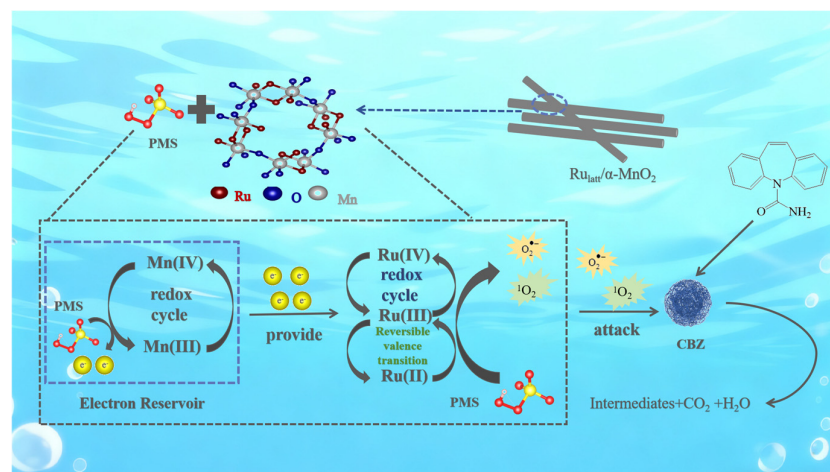


Figure 11. Schematic diagram of the removal CBZ by $\text{Ru}_{\text{lat}}/\alpha\text{-MnO}_2/\text{PMS}$.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal15111085/s1>, Figure S1: EDS mapping of (a) $\text{Ru}_{\text{lat}}/\alpha\text{-MnO}_2$, (b) $\text{Ru}_{\text{surf}}/\alpha\text{-MnO}_2$, and (c) $\alpha\text{-MnO}_2$; Figure S2: XPS of (a) O 1s and (b) Mn 2p.

Author Contributions: P.H.: Formal analysis, Data curation, Methodology, Writing—review and editing. L.Q.: Investigation, Formal analysis, Data curation. M.F.: Supervision, Investigation, Writing—review and editing. Y.C.: Investigation, Formal analysis, Data curation. P.T.: Methodology, Formal analysis, Investigation. B.X.: Investigation, Data curation. W.S.: Methodology, Investigation. Q.W.: Writing—original draft, Resources, Investigation, Funding acquisition, Project administration. J.Z.: Methodology, Investigation. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding author(s).

Conflicts of Interest: Authors Panfeng Hu, Long Qin, Yuanling Cheng, Pan Tang, Beibei Xin, and Wei Song were employed by Sichuan Changning Natural Gas Development Co., Ltd., Author Manman Feng was employed by Sichuan Jiacheng Petroleum and Natural Gas Pipeline Quality Inspection Testing Co., Ltd., Quanfeng Wang and Jujiao Zhao declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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