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Enhanced 2,4,6-Tribromophenol Degradation via Slow-Release S(IV) in Fe(II)-Activated CaSO₃ Advanced Oxidation Process

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Abstract

In this study, insoluble CaSO₃ was applied to replace soluble sulfite/bisulfite salt in the Fe(II)-activated sulfite/bisulfite [S(IV)] process for the efficient 2,4,6-tribromophenol (TBP) degradation. CaSO₃ serves as a low-cost and slow-release source of S(IV), significantly improving S(IV) utilization compared to conventional soluble Na₂SO₃. The Fe(II)/CaSO₃ system generated SO₄^{•−} and HO[•] through Fe(II)/Fe(III) redox cycling. Mechanistic studies confirmed SO₄^{•−} as the dominant reactive species, selectively attacking C-Br bonds and hydroxyl groups in TBP. Process optimization revealed effective performance under acidic conditions (pH 3.5–4.0) with minimal inhibition by common anions (Cl[−], HCO₃[−]). The reactive sites of TBP were identified through Fukui function calculations, and the degradation pathway was elucidated based on LC-MS analysis. Toxicity evaluation indicated reduced ecological risk of degradation intermediates due to debromination and benzene ring cleavage. This work provides a sustainable strategy for efficient TBP removal and detoxification in wastewater treatment with benefiting S(IV) utilization.

Keywords: advanced oxidation processes; CaSO₃; sulfite; 2,4,6-tribromophenol; ferrous



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1. Introduction

With the rapid progress of industrialization, urbanization, and population expansion, discharges of industrial wastewater and municipal sewage have risen substantially. A considerable portion of industrial effluents, agricultural runoff, and insufficiently treated urban wastewater are directly released into water bodies, leading to aggravated water pollution and further intensifying water scarcity concerns [1,2]. Trace contaminants such as halogenated aromatic compounds, pesticide residues, and pharmaceuticals persist in aquatic systems and pose significant long-term risks to human and ecological health due to their bioaccumulative potential, environmental persistence, and ecotoxicity [3,4]. Among

them, 2,4,6-tribromophenol (TBP) is produced in the largest quantities and is frequently detected across various environmental matrices [5,6]. TBP bioaccumulates in organisms and has been increasingly identified in human blood, urine, and tissues [7]. Consequently, it is imperative to develop efficient and safe treatment technologies to mitigate the multifaceted risks that TBP and its transformation products pose to human and ecosystem health.

Among the treatment technologies for TBP, biological treatment methods exhibit relatively poor removal efficiency [8]. Physical adsorption methods face challenges such as limited adsorbent capacity and incomplete regeneration processes [9,10]. Membrane filtration is associated with issues like membrane fouling and clogging, which can lead to reduced treatment efficiency, as well as relatively high costs for membrane replacement and maintenance [11]. Advanced oxidation processes (AOPs) represent a category of environmentally friendly water treatment technologies. They efficiently degrade refractory organic pollutants by generating high reactive species, such as hydroxyl radicals ($\text{HO}^\bullet$), sulfate radicals ($\text{SO}_4^{\bullet-}$), and chlorine radicals ($\text{Cl}^\bullet$) [12,13]. Among various AOPs, $\text{SO}_4^{\bullet-}$ -based AOPs have garnered extensive attention globally. However, the methods for activating persulfate to generate $\text{SO}_4^{\bullet-}$ possess several drawbacks: on one hand, residual persulfate in the reaction system can exhibit certain acute toxicity. On the other hand, when the target pollutant like TBP contains halogen elements, it can lead to the formation of highly carcinogenic halogenated disinfection byproducts [14,15]. Sulfite/bisulfite [S(IV)] is considered a preferable alternative to persulfate, as S(IV)-AOPs offer the following advantages: (1) Residual S(IV) after reaction in water can be removed through aeration [6]; (2) S(IV) is less expensive compared to persulfate; (3) The formation of brominated disinfection byproducts and bromate during the treatment of bromide-containing wastewater by S(IV)-AOPs is significantly minimal due to the strong reducing capacity of S(IV) [5].

While iron-activated S(IV) AOPs offer broad advantages for practical application, this method still presents challenges. When S(IV) was activated to generate free radicals, it also acts as a strong reducing agent [16]. Hence, S(IV) can compete with target pollutants for reactive species in the system, thereby reducing the utilization efficiency of chemicals and increasing treatment costs [17]. Although our previous research has demonstrated that batch dosing of S(IV) can enhance the efficacy of S(IV)-AOPs in degrading TBP [5], the operational process is complex. Thus, there is a need to develop more efficient S(IV) utilization techniques. Calcium sulfite (CaSO_3), a byproduct of flue gas desulfurization, is low-cost and readily available [18,19]. Compared to Na_2SO_3 , CaSO_3 has a relatively low solubility in water (approximately 0.07 g/L H_2O at 25 °C), endowing it with the ability to release S(IV) gradually, which can improve S(IV) utilization efficiency [17]. Based on these advantages, this study employs CaSO_3 as a substitute for Na_2SO_3 to serve as the source of S(IV).

Herein, the primary objective of this study is to develop a method for enhanced S(IV) utilization efficiency in S(IV)-based AOPs, thereby improving the removal effectiveness of TBP. Firstly, the degradation efficiency of TBP in different S(IV)-AOPs was systematically compared to evaluate the feasibility of CaSO_3 as a S(IV) source. The slow-release process of CaSO_3 was elucidated by monitoring Fe(II)/Fe(III) redox cycle dynamics and real-time S(IV) concentration variation during the reaction. Electron paramagnetic resonance (EPR) spectroscopy and chemical probe experiments were employed to identify the radical species (e.g., $\text{SO}_4^{\bullet-}$, $\text{HO}^\bullet$) generated in the Fe(II)/ CaSO_3 system [20]. Quenching experiments were further conducted to quantitatively analyze the oxidative contributions of different radicals and identify the dominant reactive species responsible for TBP degradation [21]. Additionally, the effects of key operational parameters, including chemical dosage, initial TBP concentration, solution pH, and dissolved oxygen, on the reaction kinetics were comprehensively investigated. To assess the practical applicability of the

Fe(II)/CaSO₃ system, the influences of natural organic matter (NOM) and common anions (e.g., Cl[−], HCO₃[−]) on TBP degradation were experimentally evaluated. Finally, liquid chromatography-mass spectrometry (LC-MS) was used to identify intermediate products during TBP degradation, and toxicity evolution was assessed using computational toxicity prediction software Ecological Structure Activity Relationships (ECOSAR, Version 2.2). This study provides an effective strategy to address the low chemical utilization efficiency in S(IV)-AOPs and advances the development of water treatment technologies toward greater efficiency, sustainability, and cost-effectiveness.

2. Materials and Methods

2.1. Chemicals and Reagents

All chemical reagents employed in this study conformed to at least the analytical grade standard to ensure the reliability of experimental results. The specific reagents and their details are as follows: 2,4,6-tribromophenol (TBP), with a purity of no less than 98%, was purchased from Aladdin (Shanghai, China); calcium sulfite (CaSO₃), having a purity of ≥90.0%, was supplied by Sinopharm Chemical Reagent (Wuhan, China); ferric sulfate (Fe₂(SO₄)₃), which had a purity of ≥99%, was obtained from Adamas (Shanghai, China); methyl alcohol, with a purity of ≥99.9%, was sourced from Tedia (Fairfield, OH, USA); acetic acid (CH₃COOH, purity ≥ 99.0%), sodium hydroxide (NaOH, purity ≥ 96.0%), sulfuric acid (H₂SO₄, purity ≥ 96%), and ethyl alcohol (purity ≥ 95.0%) were all provided by Sinopharm Chemical Reagent (Wuhan, China). All experimental stock reagent solutions were prepared with 18.2 MΩ ultrapure water as solvent to avoid impurity introduction and subsequent reaction interference.

2.2. Experimental Procedure

All experiments for treating 2,4,6-tribromophenol (TBP)-contaminated water were performed on a programmable jar tester (TA6-1, Hengling, Wuhan, China), which was equipped with 500 mL beakers, mechanical stirrers, and a circulating water bath system. The experiment followed a two-stage process: oxidation and coagulation. First, 500 mL water samples containing 10 μM TBP were moved to the beakers. They were mechanically stirred to ensure uniformity, and the circulating water bath kept the solution temperature at 25 °C. Next, Fe₂(SO₄)₃ was added, then the solution pH was adjusted. Finally, CaSO₃ was added to start the oxidation reaction. It is important to note that throughout the entire experimental process, 1 M dilute sulfuric acid (H₂SO₄) solution and 1 M sodium hydroxide (NaOH) solution were used for pH adjustment. No buffer solutions were added to the system to avoid potential interference with the reactions between the experimental reagents. To ensure accuracy and reproducibility, all the experiments were performed at least twice, and average values along with the standard deviation were presented in figures as error bars.

2.3. Analytic Methods

Turbidity was directly measured with a turbidimeter (WZB-175, Leici, Shanghai, China). TBP quantification was conducted via high-performance liquid chromatography (LC-15C, Shimadzu, Shanghai, China) equipped with an Agilent HC-C18 column (5 μm, 250 mm × 4.6 mm), under conditions of 25 °C column temperature, 50 μL injection volume, 290 nm detection wavelength, 1.0 mL min^{−1} flow rate, and a mobile phase of methanol, ultrapure water, and glacial acetic acid (85:15:1). The concentrations of Fe(II) and Fe(III) in the system were determined via the 1,10-phenanthroline spectrophotometric method (details in Text S1) [22], while the S(IV) concentration was measured using a colorimetric approach with 5,5-dithiobis (2-nitrobenzoic acid) as the reagent [23]. Solution pH was

analyzed with a pH meter (Model pHs-3C, Lei-ci, Shanghai, China), and dissolved oxygen (DO) content was detected using a DO meter (Model DO2000, YSI, Yellow Springs, OH, USA). For the intermediate products generated during TBP degradation, they were first extracted using a Cleaner S C18 solid-phase extraction (SPE) cartridge, then identified by a Q-Exactive hybrid quadrupole-Orbitrap mass spectrometer coupled with an Ultimate 3000 Complete Ultra High Performance Liquid Chromatography system (U-HPLC-Q-Exactive Orbitrap HRMs, Thermo Fisher Scientific, Waltham, MA, USA). To determine the reaction rate constants of TBP with $\text{SO}_4^{\bullet-}$ and $\text{HO}^{\bullet}$, the relative rate method was adopted, with ethanol (EtOH) and tert-butanol (TBA) used as chemical probes. Density functional theory (DFT) was conducted using Gaussian 09 at B3LYP/6–311G* basis set.

3. Results and Discussion

3.1. Comparison of Different Processes in TBP Degradation

The degradation efficiency of TBP was first evaluated across various S(IV)-AOPs, as summarized in Figure 1. Control experiments including TBP alone, Fe(II) alone, and CaSO_3 alone, all exhibited less than 10% degradation within 10 min, ruling out significant contributions from physical adsorption or volatilization. In the Fe(III)/ CaSO_3 and Fe(II)/ CaSO_3 systems, TBP degradation reached 85.7% and 86.1%, respectively, outperforming the Fe(II)/ Na_2SO_3 system with 67.9% removal. These results indicate that substituting Na_2SO_3 with the slow-release CaSO_3 significantly enhances contaminant removal efficiency in S(IV)-activated AOPs. The primary reactions occurring within the system are illustrated in Equations (1)–(8). It is noteworthy that within the first 30 s, TBP degradation was only 4.8% in the Fe(II)/ CaSO_3 system compared to 46.6% in the Fe(III)/ CaSO_3 system, suggesting a distinct initiation period of approximately 30 s in the Fe(II)/ CaSO_3 system. This delay is likely due to the requirement for Fe^{2+} to first form a complex with HSO_3^- (as FeHSO_3^+), which then reacts with O_2 to generate FeSO_3^+ [24], whereas Fe^{3+} directly reacts with HSO_3^- to form FeSO_3^+ in the Fe(III)/ CaSO_3 system (Equation (3)). After 3 min, the performance of both systems became comparable. Given the similar reaction pathways and the lower cost of FeSO_4 , Fe(II) was selected over Fe(III) for subsequent experiments [25].

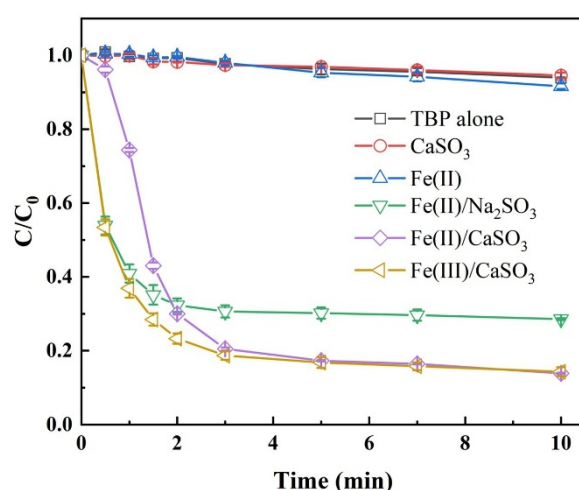
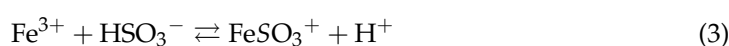
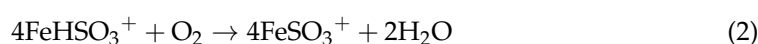
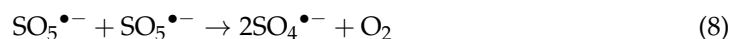
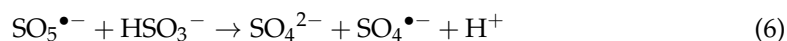


Figure 1. Comparison of TBP degradation in different processes. Conditions: $[\text{TBP}] = 10 \mu\text{M}$, $[\text{Fe(III)}] = [\text{Fe(II)}] = 50 \mu\text{M}$, $[\text{CaSO}_3] = [\text{Na}_2\text{SO}_3] = 400 \mu\text{M}$, initial pH 3.5, temperature 25°C .





3.2. Quantitative Analysis of CaSO_3 Slow-Release Process

During the degradation of TBP in the $\text{Fe(II)}/\text{CaSO}_3$ system, CaSO_3 undergoes sustained release of SO_3^{2-} , which further reacts with H^+ to form HSO_3^- , thereby modulating the solution pH [18]. Since pH significantly influences the species of both Fe and S(IV) in the solution, it is essential to monitor the concentration profiles of Fe(II), Fe(III), and S(IV) throughout the reaction. Simulations performed using MEDUSA software (Version 16) in Figure 2a,b and Figure S1 illustrated the pH-dependent species of Fe(II) and S(IV), indicating that at the initial pH of 3.5, Fe(II) and S(IV) predominantly exist as Fe^{2+} and HSO_3^- , respectively.

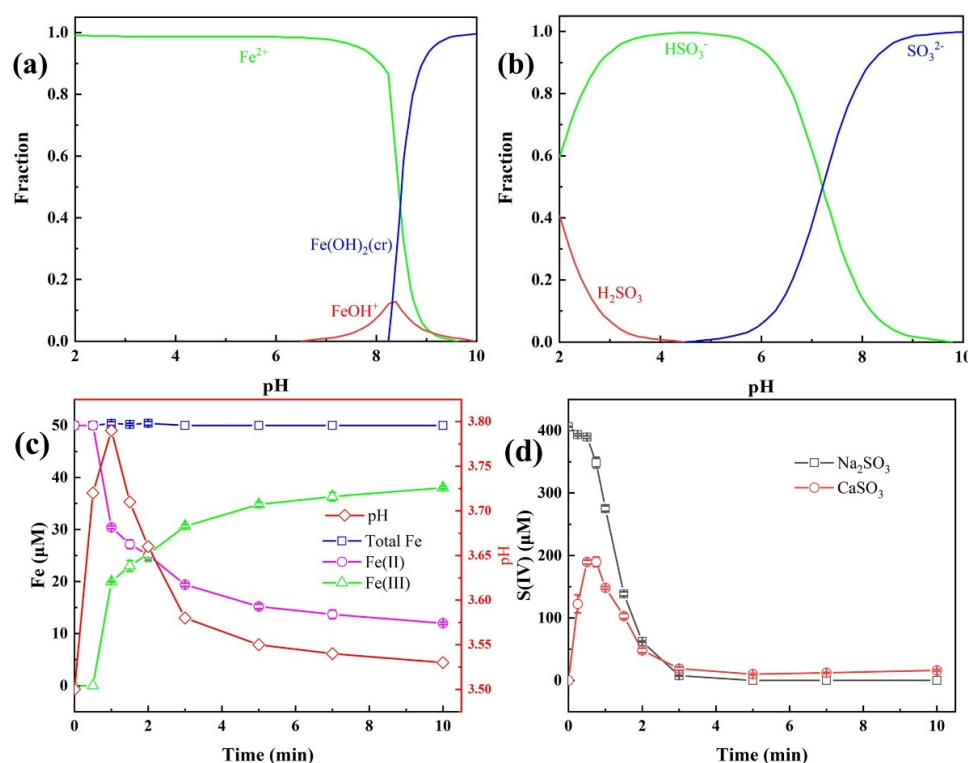


Figure 2. Distribution curves of Fe(II) (a) and S(IV) (b) under different solution pH; Concentration variation in Fe species (c) and S(IV) (d) during the $\text{Fe(II)}/\text{CaSO}_3$ reaction. Conditions: $[\text{TBP}] = 10 \mu\text{M}$, $[\text{Fe(II)}] = 50 \mu\text{M}$, $[\text{CaSO}_3] = 400 \mu\text{M}$, initial pH 3.5, temperature 25°C .

Experimental measurements of pH, Fe(II), Fe(III), and S(IV) concentrations in the $\text{Fe(II)}/\text{CaSO}_3$ system are presented in Figure 2c,d. Upon initiation of the reaction, CaSO_3 released SO_3^{2-} gradually, leading to a rapid increase in both pH and S(IV) concentration within the first 30 s, whereas the concentration of Fe(II) remained largely unchanged. This suggests that the initially low concentration of S(IV) delayed the formation of the FeHSO_3^+ complex via reaction between Fe(II) and HSO_3^- , which aligns with the observed initiation phase in the $\text{Fe(II)}/\text{CaSO}_3$ system (Figure 1). After 1 min, the pH began to decline as the concentration of Fe(III) increased, indicating that the rate of H^+ generation

in the Fe(II)/CaSO₃ system exceeded the consumption rate via reaction with SO₃²⁻ [19]. The S(IV) concentration subsequently decreased, stabilizing around 20 µM after 3 min, thereby prolonging the pollutant degradation process. In contrast, the S(IV) concentration in the Fe(II)/Na₂SO₃ system decreased rapidly and was completely consumed within 3 min, suggesting significant consumption of S(IV) via radical quenching pathways [26]. The sustained and slow release of S(IV) from CaSO₃ effectively enhances the utilization efficiency of S(IV), highlighting the advantage of the CaSO₃ compared to Na₂SO₃ in the previous literature [16,23].

3.3. Generation Pathways and Oxidative Contribution of Reactive Species

The Fe(II)/CaSO₃ system exhibited significantly enhanced degradation efficiency toward TBP compared with the Fe(II)/Na₂SO₃ system, which is presumably attributed to the continuous generation of multiple reactive species, including SO₅^{•-}, SO₄^{•-}, HO[•], and Fe(IV) [21,27]. In this study, 5,5-dimethyl-1-pyrrolineN-oxide (DMPO) was employed as a spin-trapping agent to identify radical species generated in the Fe(II)/CaSO₃ system [28]. As shown in Figure 3a, the intensity of DMPO–SO₃^{•-} adducts in EPR spectroscopy initially increased and then decreased over the reaction process. The increase in signal intensity at 3 min indicates continuous generation of SO₃^{•-} in the solution. While after 8 min reaction, the decreasing intensity suggests that the formation rate of DMPO–SO₃^{•-} adducts was lower than their oxidative degradation rate. This observation implies the formation of higher reactivity radicals via Equations (5) and (6) in the system [24].

To elucidate the potential formation of Fe(IV) in the Fe(II)/CaSO₃ system during the reaction, PMSO was employed as a probe compound for the identification of Fe(IV), which oxidizes PMSO to PMSO₂ [27]. As shown in Figure S2, approximately 4.7 µM of PMSO was degraded, accounting for 23.5% of the initial dosage (100 µM). However, no PMSO₂ was detected after the reaction for 10 min. These results indicate that the degradation of PMSO was attributable to the strong oxidative activity of radical species such as SO₄^{•-}, thereby excluding the possible contribution of Fe(IV) to TBP degradation under optimal experimental conditions [29].

To further quantitatively evaluate the contributions of various radical species to the TBP degradation, the effects of EtOH and TBA, acting as quenching agents, on the degradation efficiency of TBP in the Fe(II)/CaSO₃ system were investigated. TBA is an effective quencher for HO[•] ($k = 6 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$) but exhibits limited reactivity toward SO₄^{•-} [30]. In contrast, EtOH reacts rapidly with both SO₄^{•-} ($k = 7.7 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$) and HO[•] ($k = 1.9 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$), but only slowly with SO₅^{•-} ($k < 1 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$) [6]. By comparing the TBP removal after the addition of different quenchers, the relative contributions of each radical species to TBP degradation could be assessed. In the absence of any quencher, the degradation rate of TBP reached 86.1%. Upon addition of 10 mM TBA, the degradation rate decreased to 73.9%, representing a reduction of 12.2%. In contrast, when 10 mM EtOH was introduced, the degradation rate declined markedly to 36.9%. These results indicate that SO₄^{•-}, SO₅^{•-}, and HO[•] all participate in the oxidative degradation of TBP in the Fe(II)/CaSO₃ system, with SO₄^{•-} playing the dominant role.

Based on the above analysis, the reaction mechanism of the Fe(II)/CaSO₃ system is summarized in Figure 3c. Fe(II) activates S(IV) that was sustainably released from CaSO₃. This activation generates a series of reactive species including SO₃^{•-}, SO₄^{•-}, SO₅^{•-}, and HO[•]. Among these radicals, SO₄^{•-}, SO₅^{•-}, and HO[•] all contribute to the TBP degradation, with SO₄^{•-} being the primary reactive species responsible for TBP decomposition [31]. During this process, Fe(II) is oxidized to Fe(III), which further reacts with S(IV) to produce radicals and is subsequently reduced back to Fe(II), establishing a Fe(II)/Fe(III) redox cycle.

Concurrently, Ca^{2+} released from the dissolution of CaSO_3 react with SO_4^{2-} to form CaSO_4 precipitate, thereby reducing the potential impact on effluent water quality [32,33].

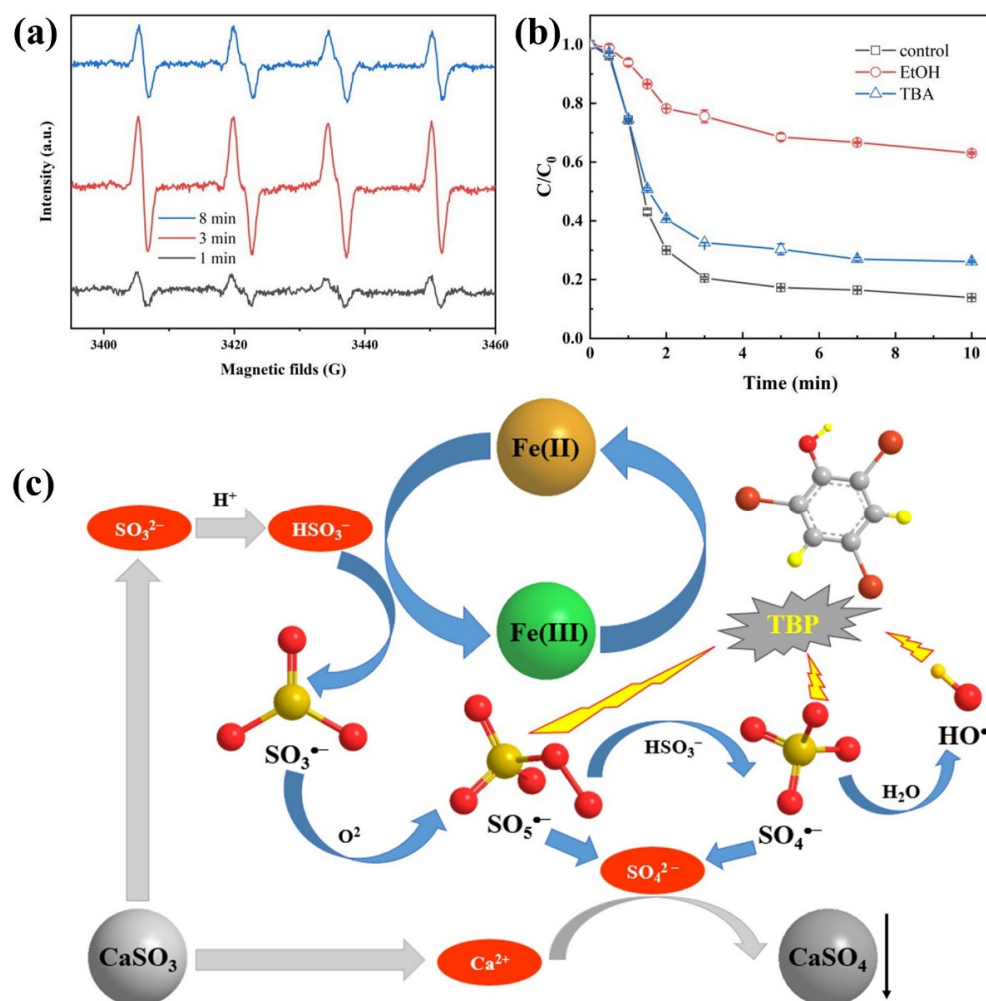


Figure 3. EPR spectrum using DMPO as trap agent (a) and quenching experiments (b) in the Fe(II)/ CaSO_3 system; The proposed reaction mechanism (c) of radical generation pathways. Conditions: [DMPO] = 50 mM in (a), [TBP] = 10 μM , [Fe(II)] = 50 μM , [CaSO_3] = 400 μM , initial pH 3.5, temperature 25 $^{\circ}\text{C}$.

3.4. Effects of Operating Parameters

Under the condition of an initial CaSO_3 dosage of 400 μM , the effect of Fe(II) dosage on the degradation efficiency of TBP in the Fe(II)/ CaSO_3 system was investigated in Figure 4a. As the Fe(II) dosage increased from 10 μM to 100 μM , the removal efficiency of TBP gradually improved from 57.8% to 86.1%. This enhancement can be attributed to the increased generation of reactive species through Fe(II)-activated S(IV), thereby promoting TBP degradation [34]. However, when the Fe(II) concentration exceeded 100 μM , the excess Fe(II) scavenged the reactive radicals owing to its reducing nature, resulting in a decline in TBP degradation efficiency [35].

The dosage of CaSO_3 also exhibited a trend of initial increase followed by a decrease in TBP degradation. As shown in Figure 4b, when the CaSO_3 dosage increased from 100 μM to 700 μM , the removal rate of TBP gradually rose from 42.2% to 89.4%. However, as the dosage was further elevated to 1000 μM , the TBP removal rate significantly decreased to 34.9%. As the source of S(IV), the dosage of CaSO_3 directly determines the concentration of S(IV) during the reaction process [36]. According to Figure S2, with increasing initial CaSO_3 dosage, the concentration of released S(IV) increased rapidly, promoting the

generation of more radical species and thereby significantly enhancing TBP degradation. However, SO_3^{2-} is also a strong reducing agent that can compete with TBP for reactive radicals such as $\text{SO}_4^{\bullet-}$, $\text{SO}_5^{\bullet-}$, and $\text{HO}^\bullet$. Therefore, excessive addition of CaSO_3 led to an obvious inhibition.

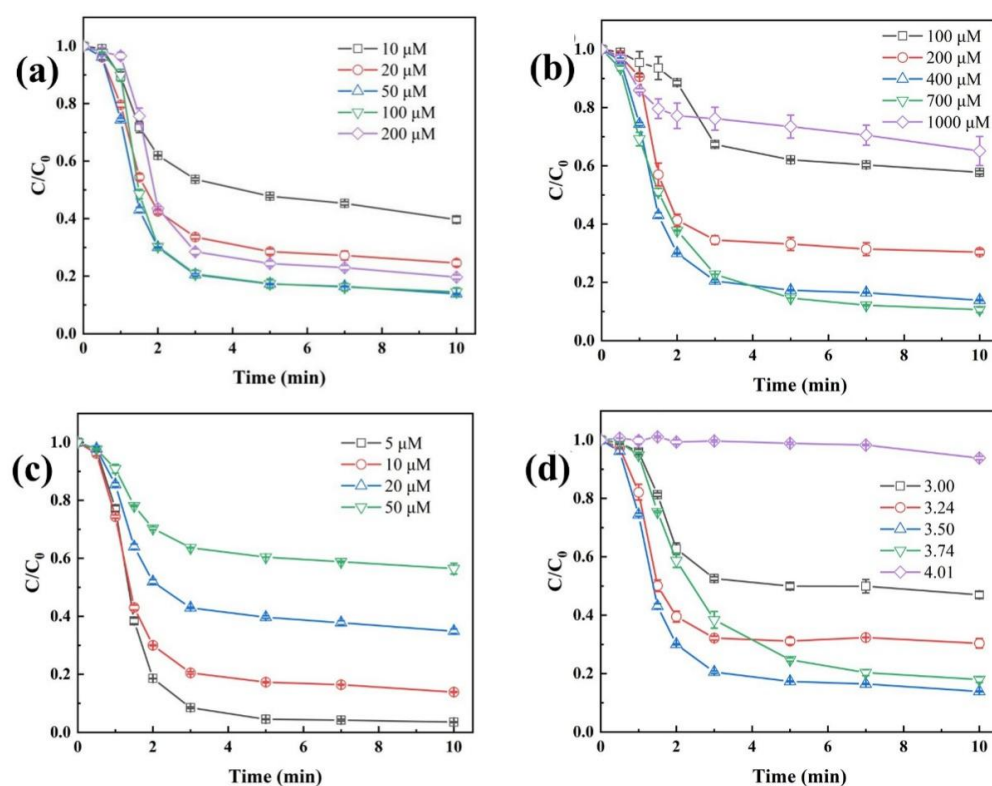


Figure 4. Effects of operating parameters including Fe(II) (a) and CaSO_3 (b) dosage, TBP concentration (c) and initial solution pH (d). Conditions: $[\text{Fe(II)}] = 50 \mu\text{M}$ except (a), $[\text{CaSO}_3] = 400 \mu\text{M}$ except (b), $[\text{TBP}] = 10 \mu\text{M}$ except (c), initial pH 3.5 except (d), temperature 25°C .

Figure 4c illustrates the effect of initial TBP concentration on the degradation efficiency in the Fe(II)/ CaSO_3 system. The results indicated that as the concentration increased from 5 μM to 50 μM , the removal efficiency decreased from 96.5% to 43.6%. Given that typical environmental concentrations of TBP generally fall within the ng/L to $\mu\text{g/L}$ range under realistic pollution scenarios [15,37], the Fe(II)/ CaSO_3 system demonstrates highly effective removal performance. Further analysis of the absolute amount of degraded TBP in Figure S3 revealed that at initial TBP concentrations of 5, 10, 20, and 50 μM , the total degradation amounts were 4.82, 8.61, 13.03, and 21.78 μM , respectively. This trend can be attributed to the fact that higher TBP concentration competes for more available radicals.

Considering the significant influence of solution pH on the species of S(IV) and Fe, experiments were conducted to evaluate the removal efficiency of TBP by the Fe(II)/ CaSO_3 system under different pH conditions (Figure 4d). At pH 3.0, part of S(IV) exists as H_2SO_3 , which exhibits low reactivity toward both Fe(II) and Fe(III), resulting in limited TBP removal [18]. As the initial pH increased from 3.0 to 3.5, the proportion of HSO_3^- rose gradually, promoting the formation of FeHSO_3^+ and FeSO_3^+ complexes. Consequently, the TBP removal efficiency increased from 53.0% to 86.1%. However, when the initial pH exceeded 4.0, the H^+ concentration decreased markedly, and the subsequent release of S(IV) induced a rapid increase in solution pH (Figure S4). Under such conditions, Fe(III) undergoes complete hydrolysis and precipitation, preventing its participation in the radical chain propagation process. As a result, TBP degradation was nearly completely inhibited.

3.5. Impacts of Water Quality Conditions

Figure 5a illustrates the influence of dissolved oxygen (DO) concentration on the degradation efficiency of TBP in the Fe(II)/CaSO₃ system. Under both non-purged and air-purged conditions, the degradation efficiency of TBP after 10 min reaction showed no significant difference. In contrast, when N₂ gas was introduced, the degradation efficiency of TBP decreased markedly to 22.1%. To elucidate the reason for this inhibition, variations in DO concentration during the reaction were monitored, as shown in Figure S5. Under non-purged and air-purged conditions, the DO concentration decreased rapidly within the first 3 min, reaching a minimum before gradually recovering. Since sufficient DO was available in both scenarios to sustain the reaction, the TBP removal rates were nearly identical. This result indicates that mechanical stirring alone can provide adequate oxygen replenishment for the system. However, when nitrogen was purged, DO was completely depleted, preventing the conversion of SO₃^{•−} to SO₅^{•−} via Equation (5). Consequently, the pathway for generating highly oxidative SO₄^{•−} was disrupted, leading to significant inhibition of TBP degradation [38].

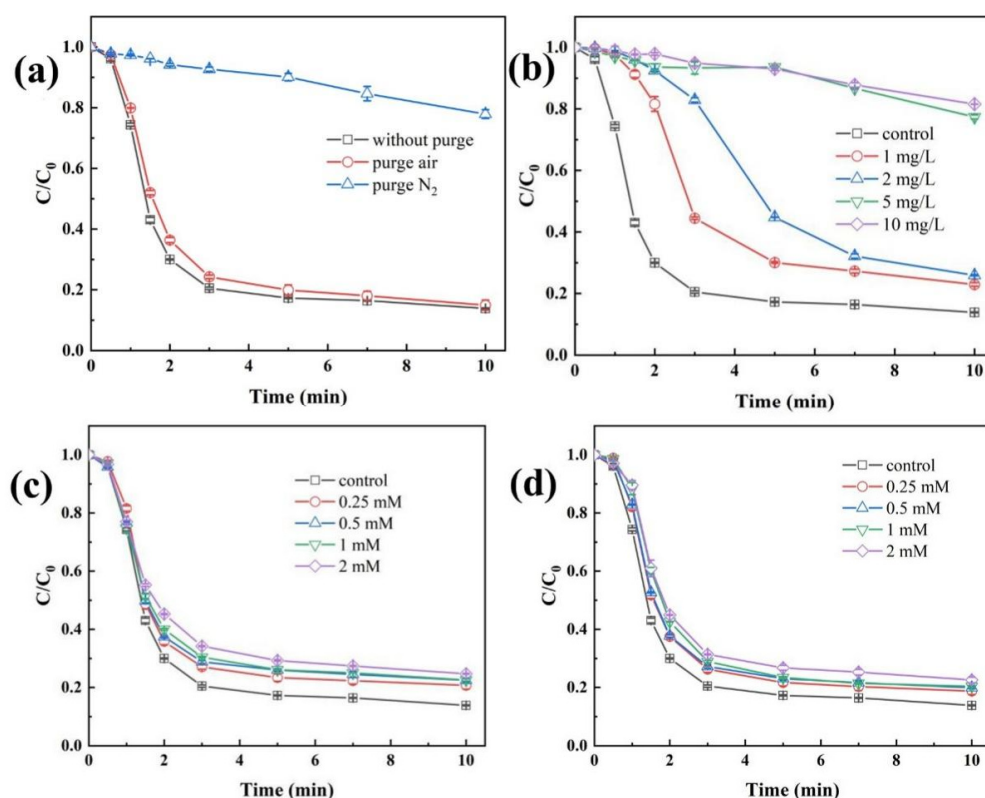


Figure 5. Impacts of water quality conditions, including aeration (a), NOM (b), Cl[−] (c) and HCO₃[−] (d). Conditions: [TBP] = 10 μM, [Fe(II)] = 50 μM, [CaSO₃] = 400 μM, initial pH 3.5, temperature 25 °C.

Natural organic matter (NOM) is widely present in natural water bodies and can significantly influence the degradation efficiency of pollutants in AOPs. Humic acid (HA), a major constituent of NOM, was thus selected as a representative model compound in this study [39]. Under fixed experimental conditions (50 μM Fe(II) and 400 μM CaSO₃), the effect of HA concentration on the oxidative degradation of TBP in the Fe(II)/CaSO₃ system was investigated. The results are presented in Figure 5b. At HA concentrations of 1 mg/L and 2 mg/L, the TBP degradation was only slightly inhibited, with removal efficiencies decreasing to 77.1% and 74.1%, respectively. However, when the HA concentration increased to 5 mg/L, the TBP removal dropped markedly to 22.6%. A further increase to 10 mg/L

HA resulted in a removal efficiency of only 18.5%. The inhibition of TBP degradation is attributed to the ability of NOM to rapidly react with $\text{HO}^\bullet$ and $\text{SO}_4^{\bullet-}$, thereby competing with TBP for reactive radicals [40]. In addition, the abundant carboxylic groups in HA may complex with Fe(III), hindering the formation of the key intermediate FeSO_3^+ , which is essential for radical generation.

The influence of common anions in water, including Cl^- and HCO_3^- , on the removal efficiency of TBP by the Fe(II)/ CaSO_3 system was further investigated. When the concentration of Cl^- was increased from 0 mM to 2 mM, the removal efficiency of TBP decreased from 86.1% to 75.3% (Figure 5c), indicating a moderate inhibitory effect. This can be attributed to the fact that Cl^- reacts with $\text{SO}_4^{\bullet-}$ and $\text{HO}^\bullet$ in the system to form $\text{Cl}^\bullet$ and $\text{Cl}_2^{\bullet-}$, which can also rapidly react with TBP [18]. As shown in Figure 5d, when the concentration of HCO_3^- was raised from 0 mM to 2 mM, the removal efficiency of TBP only declined from 86.1% to 77.4%. Using the chemical equilibrium software MEDUSA, the species distribution of HCO_3^- under different pH conditions was simulated. Throughout the reaction in the Fe(II)/ CaSO_3 system, the pH remained between 3.5 and 3.8. Under these conditions, HCO_3^- predominantly exists as $\text{CO}_2(\text{aq})$ or H_2CO_3 , while the concentration of the HCO_3^- species capable of rapidly scavenging radicals is relatively low [6]. Thus, its inhibitory effect on TBP degradation remains limited. In addition, the performance of Fe(III)/ CaSO_3 in treating actual water bodies spiked with TBP was examined in Figure S7, and a significant enhancement in the removal of DOC, TBP, and UV254 was observed compared to Fe(III) coagulation alone, demonstrating its excellent practical feasibility.

3.6. Intermediate Products Identification and Toxicity Prediction

To elucidate the attack process of free radicals on the TBP molecule, DFT calculations were employed to determine the reactive sites of TBP. The optimized molecular structure of TBP and the computed natural bond orbital (NBO) charges for each atom are presented in Figure S6 and Table S1. Here, N represents the ground state of the molecule, N-1 denotes the state after losing one electron, and N+1 corresponds to the state after gaining one electron [41]. The results of the Fukui index indicated that the C2 and C6 positions are more susceptible to substitution reactions, whereas the C4–O12 and O12–H13 bonds are more prone to cleavage. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of a molecule largely dictate its chemical reactivity. A lower energy LUMO facilitates easier electron acceptance, while a higher energy HOMO indicates that electrons in this orbital experience less nuclear attraction, making them more likely to be donated [41]. Molecular orbital analysis (Figure S7) reveals that the HOMO of TBP is primarily localized on the C–Br bonds. Consequently, these sites are prone to donate electrons, leading to the oxidative debromination of TBP. To elucidate the degradation mechanism of TBP in the Fe(III)/ CaSO_3 system, the oxidation products were qualitatively analyzed using HR-LC-MS by comparing m/z values. The results are summarized in Table S2 and Figure S10, and a detailed degradation pathway for TBP in the Fe(III)/ CaSO_3 system is proposed in Figure 6a. The formation of P2 indicates that $\text{SO}_4^{\bullet-}$ exhibits high reactivity toward the -OH of TBP, oxidizing it to a carbonyl group. $\text{SO}_4^{\bullet-}$ can selectively attack C-Br bonds via electron transfer, generating P3, P5, and P6. These intermediate products can be further oxidized by $\text{SO}_{50}^{\bullet-}$ and $\text{HO}^\bullet$ at the carbonyl group, followed by sequential debromination and cleavage of the benzene ring [42].

To assess changes in toxicity during TBP degradation, an ECOSAR model was employed to evaluate the toxicity of intermediate products (Figure 6b). Toxicity endpoints included acute and chronic effects on three aquatic organisms (fish, daphnid, and green algae) [27]. In the resulting heatmap, darker blue colors and lower numerical values indicate higher toxicity, while red colors and higher values indicate lower toxicity. The results

revealed that TBP exhibited the highest toxicity, with the lowest acute and chronic toxicity values for all three aquatic species. The high ecological risk indicated that developing efficient water treatment technologies for TBP is critically necessary. The oxidation of the carbonyl group led to the destruction of the benzene ring structure, significantly reducing the toxicity of P2 and P4. Moreover, debrominated products P3, P5, and P6 also showed decreased toxicity, suggesting that both the benzene ring and C-Br bonds are key structural features contributing to high toxicity. Given that all degradation products demonstrated reduced toxicity, the Fe(III)/CaSO₃ system not only efficiently degrades TBP but also effectively detoxifies contaminated water. Luminescent bacteria toxicity test was further conducted in Figure S11. The initial reaction solution exhibited an inhibition rate of 27.3% toward photobacterium phosphoreum, indicating considerable acute toxicity attributable to the parent compound TBP. However, after 1 min treatment in the Fe(III)/CaSO₃ system, the inhibition rate decreased significantly to 17.6%. It further declined to 4.6% in 5 min. These experimental data clearly demonstrate that the Fe(III)/CaSO₃ process can effectively and rapidly reduce the acute toxicity of TBP.

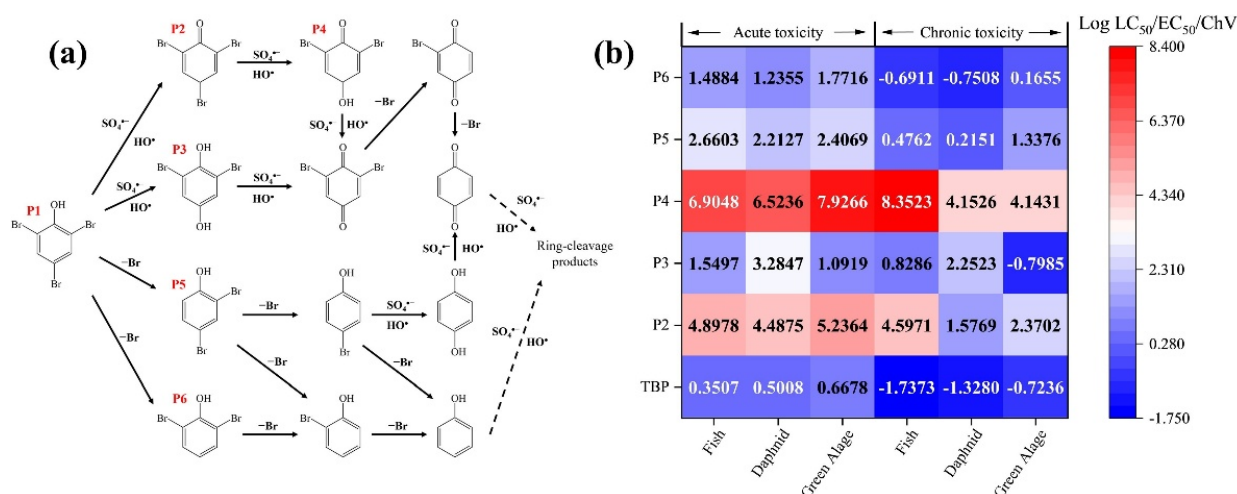


Figure 6. Degradation pathway (a) and toxicity evaluation (b) of immediate products in the Fe(III)/CaSO₃ system.

4. Conclusions

The reducing property of S(IV) leads to nonproductive consumption of free radicals, which significantly inhibits the pollutant degradation efficiency of conventional S(IV)-based AOPs. This study demonstrates that the Fe(II)/CaSO₃ system significantly enhances S(IV) utilization efficiency and achieves effective degradation and detoxification of TBP. The slow-release process of CaSO₃ enables sustained generation of reactive species (mainly SO₄•⁻), overcoming the limitations of soluble S(IV) sources. Mechanistic studies confirm the dominance of radical-induced pathways, including debromination and benzene ring cleavage, leading to markedly reduced ecological toxicity of intermediate products. The system maintains robust performance under acidic conditions and shows strong resilience to common water matrix components. By integrating cost-effective CaSO₃ with efficient radical generation, this work provides a practical and sustainable strategy for treating halogenated aromatic compound-contaminated wastewater, highlighting the potential of slow-release oxidant sources in advancing green water treatment technologies.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w17213100/s1>.

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