

Article

Catalytic Ozonation of Sulfachloropyridazine Sodium by Diatomite-Modified Fe₂O₃: Mechanism and Pathway

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Abstract: A diatomite-modified Fe₂O₃ (Fe₂O₃/Dia) catalyst was prepared to catalyze the ozonation degradation of sulfachloropyridazine sodium (SPDZ). The chemical oxygen demand (COD) was used as the index of pollutant degradation. The catalytic ozonation experiment showed that the COD removal rate of SPDZ was 87% under Fe₂O₃/Dia catalysis, which was much higher than that obtained when using Fe₂O₃ as the catalyst. The characteristics of the Fe₂O₃/Dia catalyst were investigated, and the successful synthesis of the Fe₂O₃/Dia composite catalyst was proved by XRD, XPS, SEM, FTIR, BET and other characterization methods. The catalytic mechanism of degradation by ozone with Fe₂O₃/Dia was analyzed. According to free-radical trapping experiments and an in situ electron paramagnetic spectrometer characterization analysis, the main oxidizing species in the catalytic Fe₂O₃/Dia ozone system is ·OH. The intermediates in the degradation process of SPDZ were detected and analyzed in detail by liquid chromatography-coupled mass spectrometry. The degradation mechanism and three degradation paths of SPDZ were proposed.

Keywords: diatomite-modified Fe₂O₃ (Fe₂O₃/Dia); catalytic ozonation; sulfachloropyridazine sodium (SPDZ); mechanisms; degradation pathways



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1. Introduction

Sulfonamides are one of the most common antimicrobial antibiotics available [1]. Common sulfonamides include sulfamethoxazole and sulfadiazine [2]. Due to the structure of sulfonamide antibiotics, which prevents their absorption by humans and animals, antibiotic wastewater accumulates in natural water bodies, leading to environmental pollution and potential health risks [3–6]. Sulfonamides themselves are potentially harmful to humans and the environment, and the harmful substances they produce affect the overall carbon cycle environment [7], so they need to be removed by suitable methods. Among these methods are the biological method [8], the physical method [9], the chemical treatment method [10] and the advanced oxidation method. As advanced oxidation has the advantages of a simple process and a strong oxidizing capacity, this method has gradually become prominent in sulfonamide antibiotic wastewater treatment [11].

Heterogeneous catalytic ozonation can produce reactive oxygen species (ROSs), which have an excellent degradation effect on refractory organic pollutants [12–15]. The performance of the catalyst is critical to the efficiency of heterogeneous catalytic ozone oxidation. Many studies have concentrated on the design of new catalysts to improve the efficiency of heterogeneous catalytic ozonation [16–18]. Metal oxides are the most widely used

substances for designing catalysts, among which Fe_2O_3 is a non-noble metal oxide with abundant surface active centers and the ability to transfer electrons [19]. Due to its high catalytic activity and wide availability, Fe_2O_3 is often used as an active material [20,21]. Its surface is usually covered by hydroxyl groups, which typically are Lewis acid sites and are active sites for ozone adsorption and further decomposition [22]. Fe_2O_3 exhibits various states, which enhance ozone decomposition and ROS generation through electron transfer at the active sites during catalytic ozonation. However, pure Fe_2O_3 displays low surface area and catalytic activity, primarily due to changes in morphology and aggregation occurring during the preparation process [23]. The existing approaches, to address this issue, usually adopt the method of preparing catalysts by loading Fe_2O_3 on carriers or synthesizing composites of Fe_2O_3 and other substances. The commonly used carriers are zeolites [24], ceramics [25], and activated carbon [26,27], but in the process of catalytic ozonation, the catalyst is unstable, easy to deactivate, and exhibits low utilization rates [28,29]. The effective surface area and catalytic activity of iron oxides are influenced by their morphological variability, which can lead to agglomeration or chain formation during preparation. Current materials and methods involve modifying or loading iron oxides to enhance the activity of iron-based catalysts. In summary, loading techniques address agglomeration issues, increase specific surface area, and improve catalytic performance. For example, $\text{Fe}_2\text{O}_3/\text{SiO}_2$ catalysts are used for the continuous treatment of phenol aqueous solutions in a fixed bed reactor [30]. For example, Wang [31] used a $\gamma\text{-Al}_2\text{O}_3/\text{TiO}_2/\gamma\text{-Fe}_2\text{O}_3$ micrometer catalyst to catalyze ozone treatment of ibuprofen wastewater. An analysis of the treated water samples by gas chromatography-coupled mass spectrometry showed that the types of organic matter in the water were significantly reduced, among which nine pollutants with originally high content, such as bisphenol A and sulfamethoxazole, were not detected after treatment. To solve the above problem, this paper uses diatomite-modified Fe_2O_3 for the catalytic ozone oxidation of pollutants.

Diatomite is often used as a catalyst or adsorbent carrier due to its natural porous structure [32,33]. Compared with other silica materials, the better affinity of diatomite for alkaline substances is due to a large number of hydroxyl groups and acidic sites, such as Lewis and Brønsted acidic sites [34,35]. Recent studies have shown that diatomaceous earth-modified iron trioxide composite catalysts have superior adsorption effects on pollutants [36]. However, its role in multiphase catalytic ozone oxidation has not been systematically investigated.

This study aims to develop a catalytic ozone oxidation method for organic pollutants using diatomite-modified Fe_2O_3 . Sulfonamides, a common component of antibiotic wastewater, dissolve readily in water and migrate into the ecosystem [37–40]. Sulfamethoxazole sodium (SPDZ) is a type of organic pollutant that does not degrade easily and is harmful to water and soil in the environment [41]. So far, many systems (adsorption [42,43], mycelial carriers [44,45], and biochar [46]) have been used to treat SPDZ-containing wastewater. However, there is a strong need for other useful and capable SPDZ removal techniques. In this study, SPDZ was selected as a simulated organic pollutant to estimate the efficiency and investigate the mechanism of the catalytic ozone oxidation system. The catalytic properties of $\text{Fe}_2\text{O}_3/\text{Dia}$ for the ozonation of SPDZ, including the decomposition mechanism and pathway, were studied. The main ROSs were determined, and the catalytic ozonation mechanism of $\text{Fe}_2\text{O}_3/\text{Dia}$ was discussed. This research provides new insights into the catalytic ozone oxidation of SPDZ, which will help in the subsequent further analysis of the sulfachloropyridazine sodium degradation pathway and the methods.

2. Results and Discussion

2.1. Factors on the Catalytic Ozone Efficiency of $\text{Fe}_2\text{O}_3/\text{Dia}$

2.1.1. Catalyst Dosage

Catalytic ozonation is primarily facilitated by active sites on the catalyst's surface, which promote the decomposition of ozone into reactive oxygen species, such as $\cdot\text{OH}$ [47]. Increasing the quantity of catalysts enhances the frequency of contact between catalysts

and O_3 in the reaction system, leading to a greater utilization of O_3 within the same timeframe. Consequently, more potent oxidizing $\cdot OH$ species are generated for pollutant degradation [48]. Notably, when the catalyst dosage is $1\text{ g}\cdot\text{L}^{-1}$, the removal efficiency is at its lowest (Figure 1a). However, excessive catalyst amounts can agglomerate the catalyst, resulting in a reduction in the specific surface area or the masking of active sites, thereby impeding the decomposition of ozone into $\cdot OH$ and other reactive oxygen species. Alternatively, it is possible that the effective active sites on the catalyst surface have reached their maximum capacity [49].

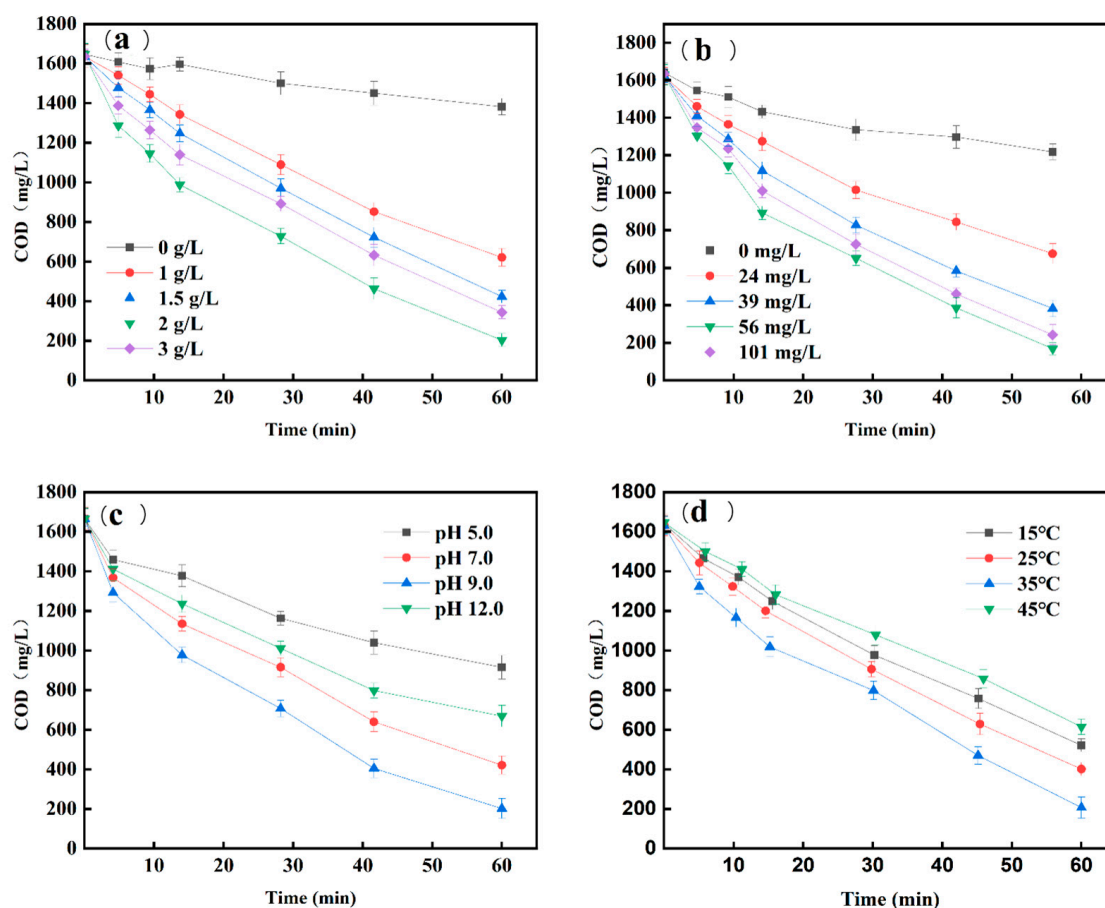


Figure 1. Effect of (a) catalyst dosage, (b) ozone dosages, (c) pH and (d) temperature on COD degradation of sulfonamide chlordazine sodium catalyzed by Fe_2O_3/Dia .

2.1.2. Ozone Dosage

As illustrated in Figure 1b, the COD decreases as the ozone dosage increases. This phenomenon arises because the increase in ozone dosage correlates with an escalation in the COD removal rate, which rises from 64% to 87% after 60 min of reaction time. Fe_2O_3/Dia catalyzes ozone more effectively, facilitating its decomposition into various active substances and thereby augmenting the removal rate. However, when the ozone dosage escalates from $56\text{ mg}\cdot\text{L}^{-1}$ to $101\text{ mg}\cdot\text{L}^{-1}$, and the COD removal rate diminishes after 60 min. This decline is primarily attributed to excessive ozone levels and the limited capacity of the catalyst's active sites to decompose ozone [50].

2.1.3. pH

During the catalytic ozone oxidation reaction, pH significantly influences the degradation rate, thereby determining the catalytic activity of the catalyst to a certain extent [51,52]. The pH value of the Fe_2O_3/Dia system increased gradually with increasing reaction

time [53]. Increasing the pH by one unit doubles the rate of ozone decomposition, leading to a higher concentration of $\cdot\text{OH}$ in the system. Alkaline conditions significantly enhance the formation of strong oxidizing $\cdot\text{OH}$, whereas under acidic conditions, ozone mainly participates in oxidation as a molecular species. In alkaline environments with OH^- present, ozone reacts with OH^- on the catalyst surface to produce strong oxidizing species. Additionally, chemical reactions occur between ozone and water, and the surface structure of the catalyst changes with varying pH levels, affecting its catalytic performance [54]. As depicted in Figure 1c, the removal effect of COD initially increases and then decreases with the continuous rise in pH. At pH = 9, the degradation effect is optimal, with the COD of sulfachlordazine sodium reduced from $1643 \text{ mg}\cdot\text{L}^{-1}$ to $213 \text{ mg}\cdot\text{L}^{-1}$, achieving a degradation efficiency of 87%. The degradation efficiency at pH = 7 ranks second only to that at pH = 9. While the alkaline environment facilitates the decomposition of O_3 into more $\cdot\text{OH}$, the solubility of ozone is limited, and excessively high pH levels can degrade $\cdot\text{OH}$, thereby reducing the quantity available for sulfachlordazine sodium degradation in the solution and consequently lowering degradation efficiency.

2.1.4. Temperature

As depicted in Figure 1d, the variation in COD during catalytic ozone degradation of sulfamethoxazole sodium exhibits significant differences at various temperatures. The highest COD removal efficiency was observed at 35°C , followed by 25°C , 15°C , and 45°C , respectively. At 35°C , COD was reduced from $1643 \text{ mg}\cdot\text{L}^{-1}$ to $213 \text{ mg}\cdot\text{L}^{-1}$, achieving an 87% removal rate. The degradation effect at 25°C was second only to that at 35°C , while the removal efficiency was lowest at 45°C . These results indicate that increasing the temperature during catalytic ozone oxidation accelerates the reaction rate, enhances the forward progression of the catalytic reaction, and generates more active oxygen species during ozone decomposition. However, at higher temperatures, the solubility of ozone decreases, resulting in reduced COD removal efficiency. At excessively low temperatures, minimal activation energy and increased water viscosity hinder mass transfer in the gas–solid–liquid system, negatively impacting the catalytic ozone oxidation process [55].

2.2. Ozone Oxidation of SPDZ Catalyzed by Catalyst before and after Modification

O_3 is often applied as an oxidant in wastewater, but the direct oxidation of aromatic complexes by ozone is difficult [56]. To remove organic compounds that are difficult to degrade, adding catalysts to the ozone oxidation system can significantly promote the decomposition of O_3 molecules to produce ROSs, such as $\cdot\text{OH}$, $\text{O}_2\cdot^-$, and $^1\text{O}_2$ [57], which is beneficial to the removal of aromatic compounds [58]. In this paper, ozone alone, $\text{Fe}_2\text{O}_3/\text{Dia}$ alone, and $\text{O}_3/\text{Fe}_2\text{O}_3$ and $\text{O}_3/\text{Fe}_2\text{O}_3/\text{Dia}$ are compared. The COD removal curves for SPDZ are displayed in Figure 2. For systems using ozone or $\text{Fe}_2\text{O}_3/\text{Dia}$ alone, the COD removal rates were 15% and 25%, respectively. After 60 min, COD removal rates of 73% and 87% were achieved with ozone in the presence of Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{Dia}$, respectively.

In the absence of a catalyst, O_3 can degrade SPDZ, indicating that O_3 itself may produce some ROSs. However, the ability of ozonation and SPDZ degradation was enhanced when Fe_2O_3 was introduced into the reaction because of the synergistic interaction between the catalyst and ozone, which created more free radicals in the system to degrade pollutants. $\text{Fe}_2\text{O}_3/\text{Dia}$ was more efficient than Fe_2O_3 during catalysis under the same conditions. In the ozone and $\text{Fe}_2\text{O}_3/\text{Dia}$ systems, the COD removal rate of SPDZ was much higher than in O_3 and Fe_2O_3 , because silica increased the surface adsorption capacity for Fe_2O_3 on ozone and produced more hydroxyl radicals, thus improving the surface ozone mass transfer process [59]. In conclusion, the $\text{Fe}_2\text{O}_3/\text{Dia}$ catalyst has a high degradation ability.

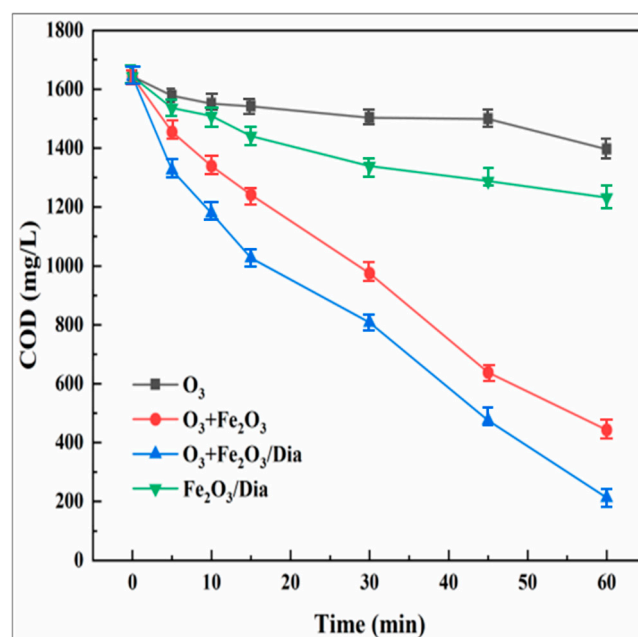


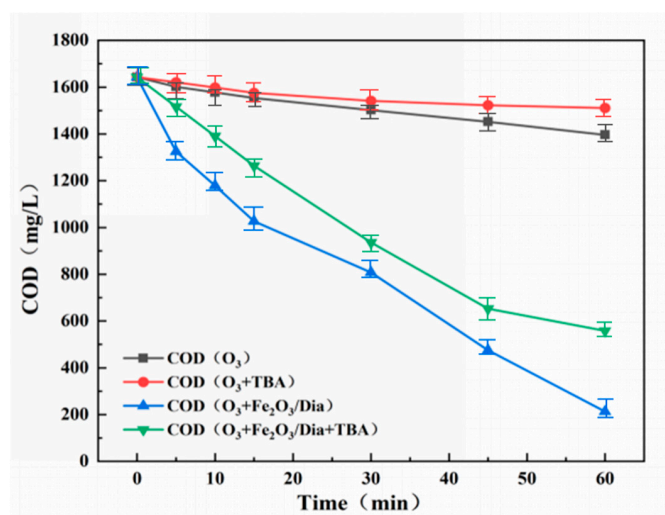
Figure 2. COD degradation curve for various systems. Reaction conditions: $[\text{SPDZ}]_0 = 2 \text{ g}\cdot\text{L}^{-1}$, catalyst dosage = $2 \text{ g}\cdot\text{L}^{-1}$.

2.3. Identification of Major ROSs

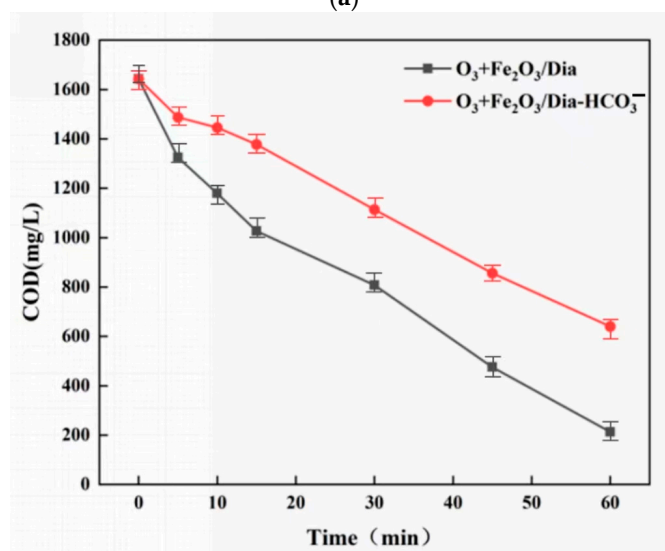
Hydroxyl radicals are common ROSs in heterogeneous ozone oxidation, and relevant experiments were conducted to investigate whether hydroxyl radicals are the major ROSs in this work. TBA [60,61] and bicarbonate (HCO_3^-) can be used as hydroxyl radical scavengers [36]. After the addition of TBA, the oxidation rate of SPDZ decreased to 8%, and 45% in the ozone, and ozone and $\text{Fe}_2\text{O}_3/\text{Dia}$, respectively (Figure 3a). Thus, $\cdot\text{OH}$ may be the main oxides species in heterogeneous solutions. However, except for a small amount of pollutants adsorbed by the catalyst, the COD removal rate of SPDZ in the catalytic ozone oxidation system was still higher than that in the pure ozone system with TBA. As a possible reason, TBA scavenged free hydroxyl radicals in water, while the free hydroxyl radicals on the catalyst surface were not removed [62–64]. Additionally, a small number of other ROSs were present [65,66]. In the research on degradation processes, findings indicate that although superoxide radicals ($\text{O}_2^{\cdot-}$) and hydrogen peroxide (H_2O_2) are involved in pollutant degradation, they are not the predominant reactive species. This conclusion was supported by ESR measurements and radical quenching experiments [67].

HCO_3^- can react with hydroxyl radicals on the surface of the catalyst to form dicarbonate radicals (Equations (1) and (2)) [68]. In the presence of HCO_3^- , the COD removal rates of SPDZ decreased to 15% and 63% in ozone and ozone/ $\text{Fe}_2\text{O}_3/\text{Dia}$, respectively (Figure 3b). The results showed that $\cdot\text{OH}$ was consumed by HCO_3^- to decrease the degradation of SPDZ. In the catalytic ozone oxidation reaction, $\cdot\text{OH}$ was the main ROS.

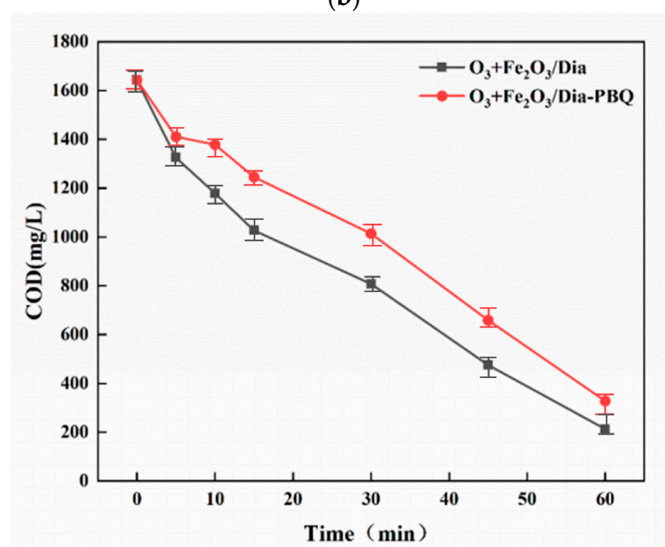
PBQ can be used as a scavenger of $\text{O}_2^{\cdot-}$ [69,70] and does not interfere with other ROSs. With the addition of PBQ, the oxidation rate of SPDZ decreased to 75% in the ozone and $\text{Fe}_2\text{O}_3/\text{Dia}$ systems (Figure 3c). The results show that in the catalytic ozone oxidation system, in addition to $\cdot\text{OH}$ as the main ROS, $\text{O}_2^{\cdot-}$ also contributes to the oxidation capacity. $\text{O}_2^{\cdot-}$ is the intermediate radical in the process of ozonolysis radical chain, which is responsible for the $\cdot\text{OH}$ generation (Equations (3)–(8)) [71]. In summary, it can be concluded that the main ROS in the catalytic ozone system is $\cdot\text{OH}$, but there are other ROSs present in the system that contribute to oxidation to some extent.



(a)

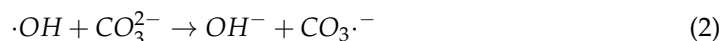
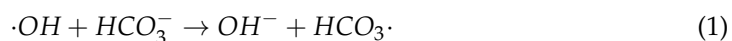


(b)



(c)

Figure 3. Effect of (a) TBA, (b) HCO₃⁻, and (c) PBQ on the catalytic ozonation of SPDZ. Reaction conditions: [SPDZ]₀ = 2 g·L⁻¹, catalyst dosage = 2 g·L⁻¹.



It can be seen from the free radical masking experiment that $\cdot\text{OH}$ plays a major role in the system. In order to further verify the reactive oxygen species in the system, experiments were conducted using the EPR technique and 5,5-dimethyl-1-pyrrolidone-N-oxide (DMPO) as a trapping agent for $\cdot\text{OH}$ and $\text{O}_2\cdot^-$ [72]. DMPO can react with free radicals to generate stable substances. The $\cdot\text{OH}$ is detected in an ultrapure water system and $\text{O}_2\cdot^-$ is detected in a methanol solution. As shown in Figure 4, the DMPO- $\cdot\text{OH}$ and DMPO- $\text{O}_2\cdot^-$ spin signals were observed after a reaction time of 10 min.

According to Figure 4, the DMPO- $\cdot\text{OH}$ spin signal was not observed in the system of the $\text{Fe}_2\text{O}_3/\text{Dia}$ catalyst alone, but it was observed in the $\text{Fe}_2\text{O}_3/\text{Dia}$ -catalyzed ozone oxidation system, showing a 1:2:2:1 spin signal. The $\text{Fe}_2\text{O}_3/\text{Dia}$ -catalyzed ozone oxidation system also exhibited the characteristic DMPO- $\text{O}_2\cdot^-$ sextet spin signal. The results demonstrated that $\cdot\text{OH}$ and $\text{O}_2\cdot^-$ can be produced in the $\text{Fe}_2\text{O}_3/\text{Dia}$ -catalyzed ozone oxidation of SPDZ.

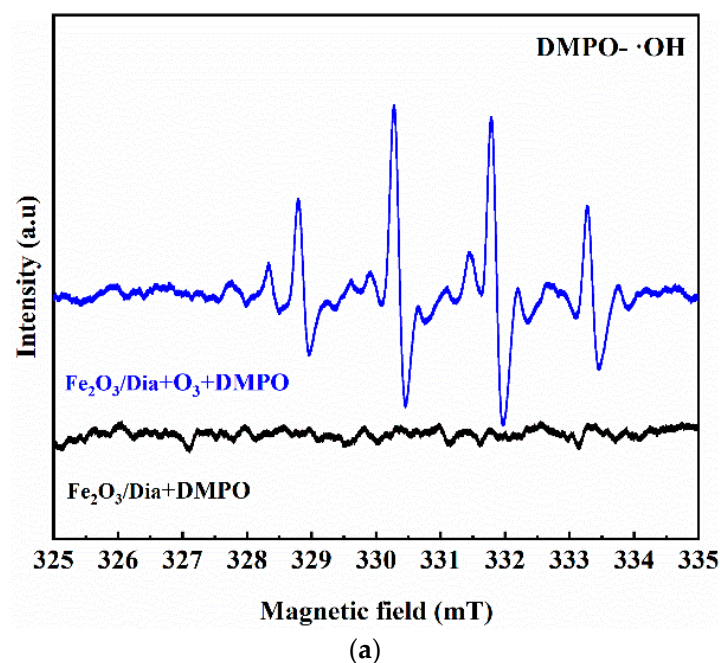


Figure 4. Cont.

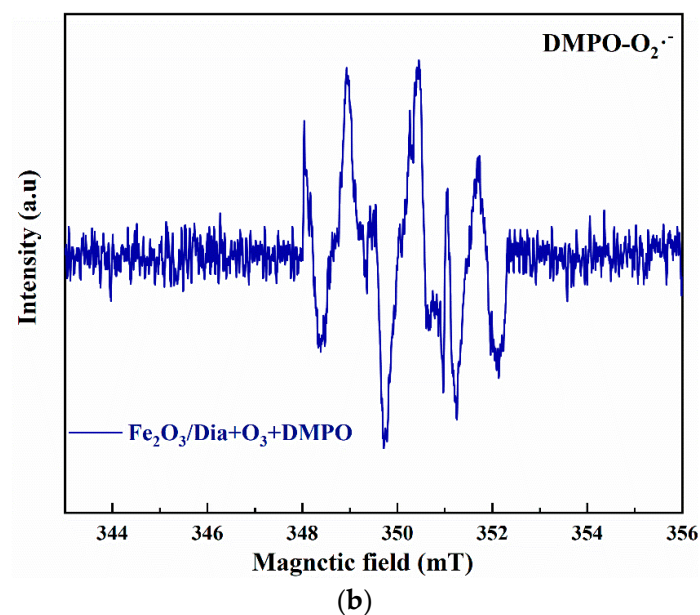
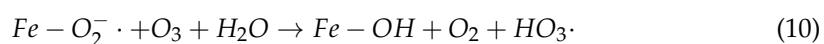


Figure 4. EPR signal of reactive oxygen species. (a) DMPO- $\cdot$ OH, (b) DMPO- $O_2^{\cdot-}$.

2.4. Reaction Mechanism

Lewis acid sites have an affinity for Lewis bases, such as ozone, and participate in the process of ozone decomposition [14]. Further verification is required to ascertain whether Lewis acidic sites contribute to ozonolysis in this system. Phosphate, being a strong Lewis base, may interact with Lewis acids on the catalyst surface, potentially impeding the interaction between ozone and the substrate, and thus inhibiting ozone decomposition [73]. The inhibitory effect of different concentrations of phosphate on ozone decomposition is negligible [74]. As shown in Figure 5, phosphate reduces ozone adsorption and decomposition on the catalyst surface, possibly because it blocks the Lewis acid sites on the catalyst surface, preventing ozone adsorption and subsequent ROSs, resulting in reduced catalytic activity. Fe₂O₃/Dia contains abundant active sites and promotes the generation of hydroxyl radicals. These results confirm that the Lewis acid site on the surface of Fe₂O₃/Dia significantly contribute to the catalytic ozonation process. The process of Fe₂O₃/Dia-catalyzed ozonation is shown in Equations (9)–(11). Ozone decomposes on the surface of iron-based catalysts, generating hydroxyl radicals and superoxide radicals. The ozone undergoes a series of reactions on the catalyst surface to form $\cdot$ OH.



In recent advancements, the optimization of electronic properties of Fe₂O₃-modified diatomite has shown significant improvement in catalytic ozonation reactions. The uniform distribution of iron oxide on the silicate ore's surface and the presence of surface hydroxyl groups were identified as key factors contributing to this improved catalytic performance [75,76]. The main component of diatomite is SiO₂. In recent advancements, the optimization of electronic properties of Fe₂O₃-modified diatomite has shown significant improvement in catalytic ozonation reactions. Fe₂O₃ is modified by diatomite, and the Fe₂O₃ is loaded on the diatomite. The surface morphology of diatomite and Fe₂O₃/Dia was studied by SEM. As shown in Figure 6a,b, the micropores of the original diatomite were narrow and small, and the pores were blocked [77]. It can be noted from Figure 6c,d that the modified diatomite shell was clean, smooth, and had a clear surface structure and significantly larger pore size. It shows that after the thermal and acid modification,

part of the impurities in the holes was removed, the pore size channel was opened, and the surface of the diatomite was improved, which was conducive to the loading of Fe^{3+} . According to Figure 6e,f, the structure of diatomite itself did not change, but a layer of dense material was attached to the surface of diatomite, which is presumed to be loaded Fe_2O_3 ; Fe_2O_3 particles were evenly distributed around the pore, and no pore blockage was found, and the number of active site was increased. This iron oxide reduced the smoothness of the pore size, increased the surface roughness, and improved the pore structure of $\text{Fe}_2\text{O}_3/\text{Dia}$.

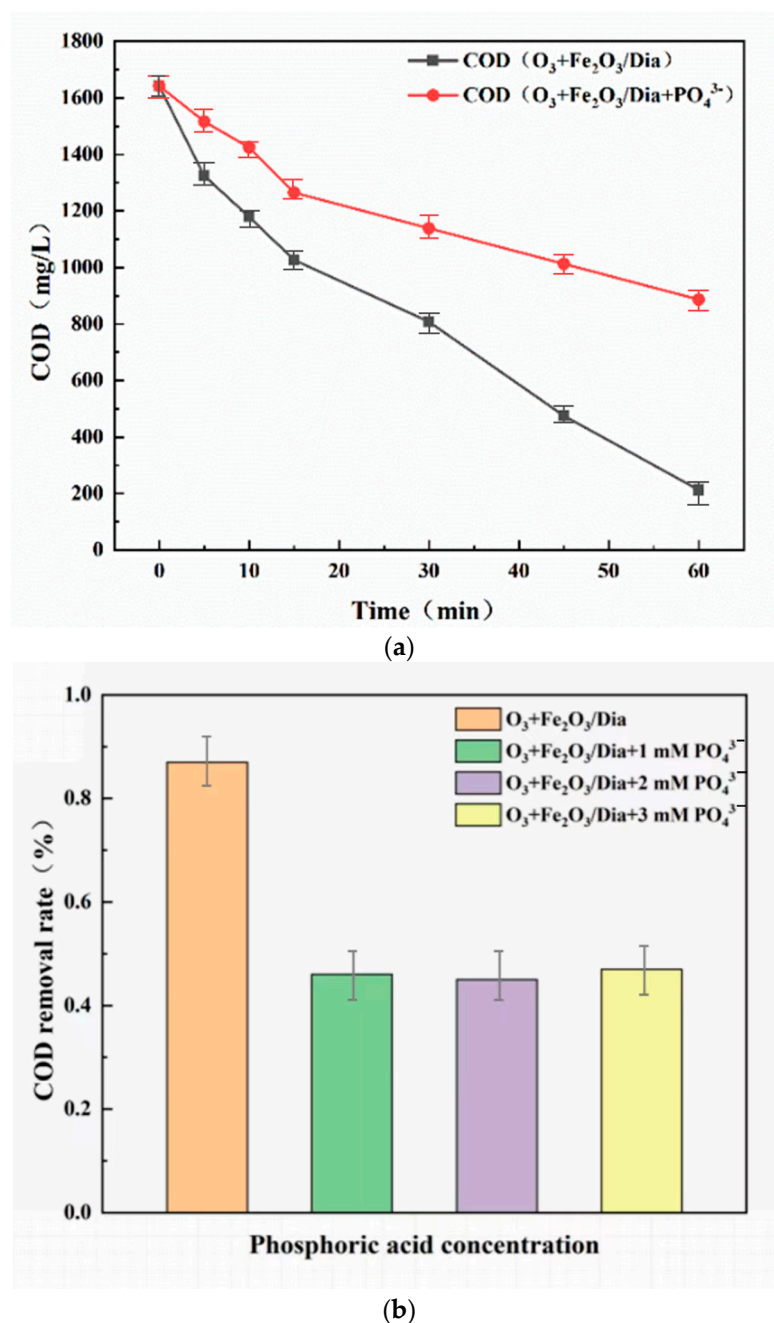


Figure 5. (a) Effect of PO_4^{3-} on the catalytic ozonation of SPDZ with $\text{Fe}_2\text{O}_3/\text{Dia}$. (b) Effect of various PO_4^{3-} concentrations on the catalytic ozonation of SPDZ with $\text{Fe}_2\text{O}_3/\text{Dia}$. Reaction conditions: $[\text{SPDZ}]_0 = 2 \text{ g} \cdot \text{L}^{-1}$, catalyst dosage = $2 \text{ g} \cdot \text{L}^{-1}$.

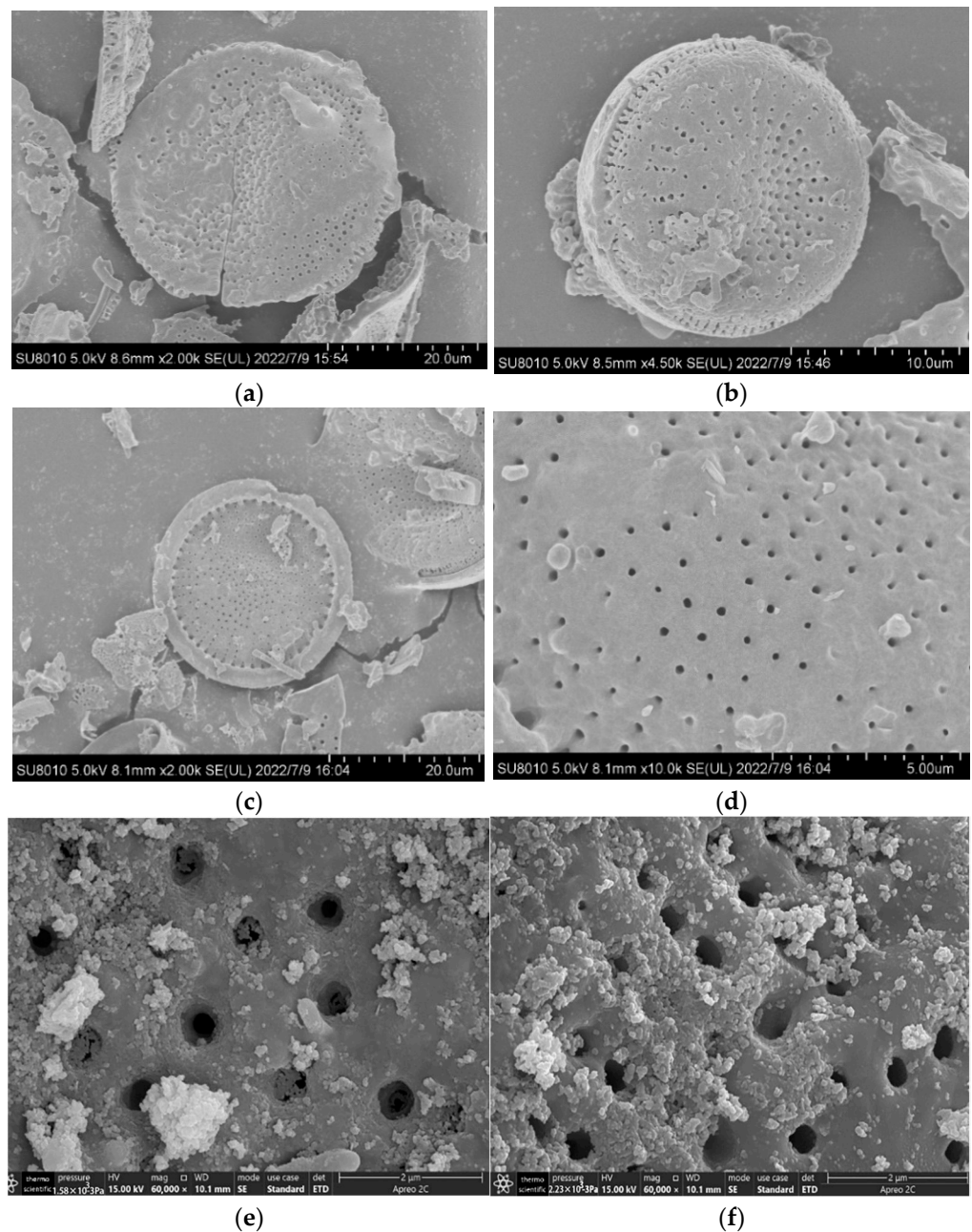


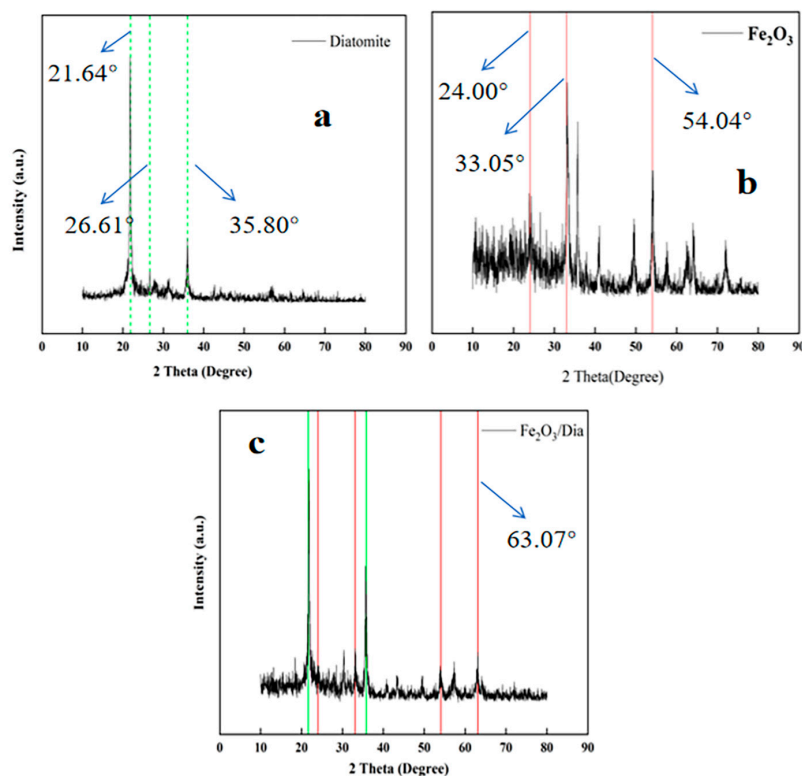
Figure 6. (a,b) SEM of diatomite before modification. (c,d) SEM of diatomite after modification. (e,f) SEM of diatomite-modified Fe_2O_3 .

In this paper, a specific surface area (BET) analysis of the materials before and after modification was conducted, and the results are shown in Table 1. The BET of pure Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{Dia}$ were $19.70 \text{ m}^2 \cdot \text{g}^{-1}$ and $22.36 \text{ m}^2 \cdot \text{g}^{-1}$, respectively, which is essential to improving the active surface of the iron oxide composites. The above results show that the $\text{Fe}_2\text{O}_3/\text{Dia}$ has a certain adsorption effect. Although the catalytic capacity of Fe_2O_3 alone was low, the addition of diatomaceous earth could improve the COD removal of SPDZ by ozone oxidation, demonstrating that the larger surface area had better catalytic capacity for ozone conversion and showed better degradation of organic components.

Table 1. Specific surface area and pore characteristics of pure Fe₂O₃ and Fe₂O₃/Dia catalysts.

Samples	Specific Surface Area/ m ² ·g ^{−1}	Total Pore Capacity/cm ³ ·g ^{−1}	Average Pore Size/nm
Fe ₂ O ₃	19.70	0.1540	24.75
Fe ₂ O ₃ /Dia	22.36	0.1909	30.28

An analysis of the XRD patterns was performed to identify the crystal structure of diatomite before and after modification. In the XRD spectrum of diatomite (Figure 7a), distinct peaks were observed at $2\theta = 21.64^\circ$, 26.61° , and 35.80° , which correspond to the characteristic peaks of SiO₂ as identified from the PDF standard card (PDF#46-1045). This result is consistent with the expectation that SiO₂ is the primary component of the diatomite catalyst support. A comparison with standard cards revealed that neither the original nor the modified diatomite exhibited characteristic peaks of Fe₂O₃, indicating the absence of Fe₂O₃ in the diatomite and confirming that its interference can be excluded [78]. After the modification of diatomite by Fe₂O₃ (Figure 7c), the characteristic peaks at $2\theta = 33.05^\circ$ increased, and some characteristic peaks also appeared at $2\theta = 24.00^\circ$, 54.04° , and 63.07° . A comparison with the standard card revealed (PDF#33-0664) that the characteristic peak can be assigned to Fe₂O₃, and it can be concluded that Fe₂O₃ was successfully loaded onto diatomite.

**Figure 7.** XRD spectra of (a) diatomaceous earth, (b) Fe₂O₃, and (c) Fe₂O₃/Dia.

To investigate the changes in Fe valence within Fe₂O₃/Dia, XPS reduction analysis was performed on the catalyst. Figure 8a–c illustrate the survey spectrum, Fe 2p XPS spectrum, and Si 2p XPS spectrum of the Fe₂O₃/Dia composite, respectively. Elements O and C were detected in the catalyst, along with peaks corresponding to Fe and Si elements. The Fe 2p spectrum displayed two peaks: Fe 2p_{3/2} and Fe 2p_{1/2}. Following deconvolution, peaks centered at binding energies of 711.4 eV and 725.2 eV were attributed to Fe (III), while peaks at 709.9 eV and 722.9 eV were assigned to Fe (II). The binding energy of the satellite peak at 720.3 eV was associated with Fe 2p_{3/2} and was attributed to charge transfer, confirming the presence of Fe³⁺. The binding energy of Fe 2p_{3/2} in pure Fe₂O₃ is 710.59 eV [79], and

that of Fe 2p_{3/2} in Fe₂O₃/Dia is 711.4 eV. The reason for the increase in binding energy is that Si is more electronegative than Fe, which results in a shift of the lone electron pair of Fe towards Si, and therefore in a decrease in the electron density of Fe atoms. The binding energy of the Fe element is increased due to the enhanced ability of the Fe nucleus to hold electrons outside the nucleus. The characteristic peak position of the Si element is 103 eV, which belongs to the 2p_{3/2} and 2p_{1/2} orbitals of Si element, and is the characteristic peak of Si-O bonds. It originates from the oxide form of Si, which proves that the Si element exists in the form of SiO₂. While the Si 2p_{3/2} binding energy of pure diatomite is 102.78 eV [80], that Fe₂O₃/Dia was reduced, and the Si element corresponded to the Fe element. Therefore, it is speculated that Fe₂O₃ particles are bound together by Si-O-Fe bonds on the surface of diatomite. The results above demonstrate that the Fe₂O₃/Dia composite catalyst was successfully synthesized, contained abundant active sites, and had good catalytic effect. Figure 9 shows the catalytic mechanism of ozonation catalyzed by the Fe₂O₃/Dia composite catalyst. Fe₂O₃, loaded onto diatomaceous earth, decomposes ozone into ROS on the surface active sites of Fe₂O₃/Dia.

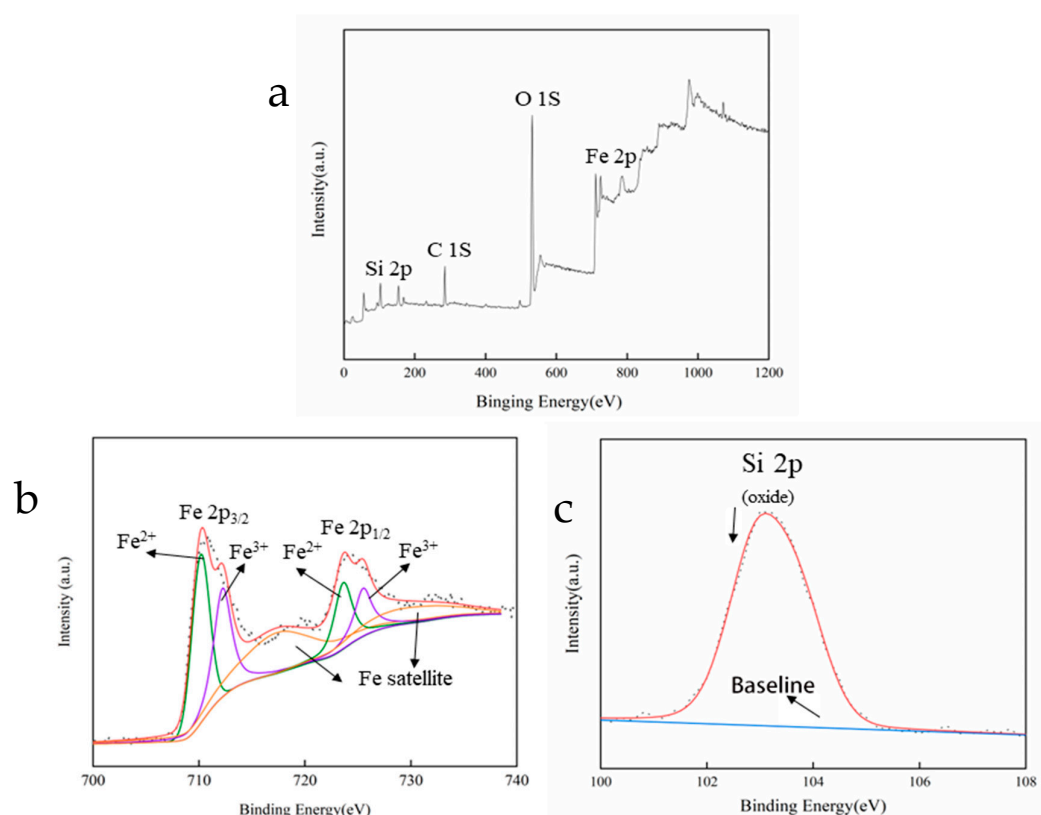


Figure 8. XPS spectra of Fe₂O₃/Dia: (a) survey spectrum, (b) Fe 2p spectrum, (c) Si 2p spectrum.

FTIR spectroscopy was used to analyze the functional groups before and after modification. Characteristic peaks of Si-O were present at 442 cm⁻¹ and 791 cm⁻¹ in the spectrum of diatomite, as well as the anti-symmetric stretching vibration peaks of Si-O-Si at 1093 cm⁻¹ (Figure 10). For Fe₂O₃, the characteristic absorption peak of the Fe-O bond in the Fe₂O₃ crystal was observed at 528 cm⁻¹. In the Fe₂O₃/Dia materials, characteristic absorption peaks for Fe-O bonds were observed at 525 cm⁻¹ and 474 cm⁻¹. Compared to the Fe-O bond in Fe₂O₃, these absorption peaks were weaker and shifted towards shorter wavelengths. This indicates that Fe₂O₃ molecules interacted with the surface of the diatomaceous earth, leading to some cooperative bonding between the Fe-O and Si-O bonds. The oscillation and stretching vibration peaks of Si-O bonds were observed at 791 cm⁻¹, corresponding to the characteristic absorption peak of diatomite. These results suggest that the chemical composition of the surface was altered, resulting in different ozone affinities

and a reduced lifetime of hydroxyl radicals, which hinders their migration from the catalyst surface to the aqueous phase [81]. Therefore, the special chemical bonds in $\text{Fe}_2\text{O}_3/\text{Dia}$ catalyst increase the ozone affinity of the surface and the number of hydroxyl radicals, resulting in the faster generation of ROSs. The transfer from catalyst surface to water allows for the more efficient degradation of pollutants.

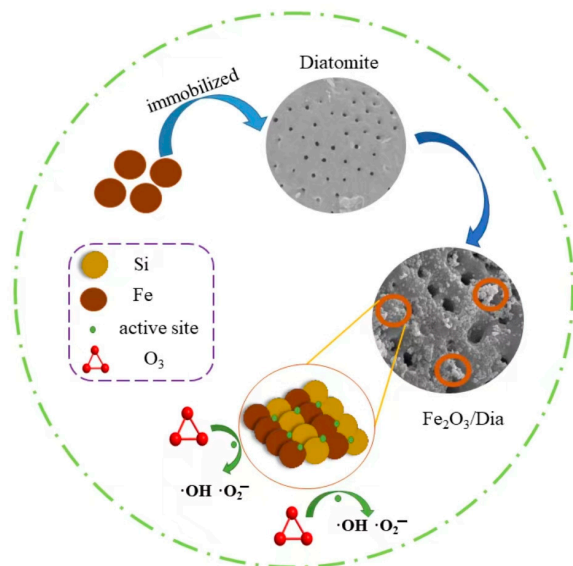


Figure 9. Mechanism diagram of ROS formation from ozone catalyzed by the $\text{Fe}_2\text{O}_3/\text{Dia}$ composite catalyst.

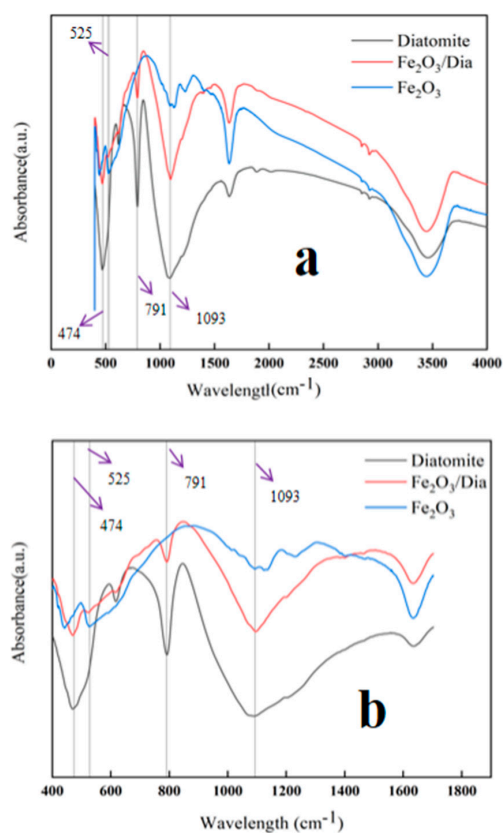


Figure 10. FTIR spectra of $\text{Fe}_2\text{O}_3/\text{Dia}$: (a) full spectrum, (b) selected range.

2.5. Mechanism and Pathway of SPDZ Degradation

The parent of SPDZ is sulfachlorpyridazine (SCP). When sodium sulfadiazine is dissolved in water, sodium ions are dissociated from the molecule, and the sulfadiazine compound is the main pollutant [82]. Based on the product intermediates, three potential degradation pathways are proposed for the catalytic ozonation of SPDZ (Figure 11). In the first pathway, the smallest electrostatic interactions on the SPDZ molecule surface occur near the N atom of the pyridine ring and the sulfa group, making these N atoms the most likely sites for electrophilic reactions. The cleavage of the S-N bond in SPDZ may be facilitated by attack from $\cdot\text{OH}$ radicals and $\text{O}_2^{\cdot-}$, resulting in the formation of two products: 3-amino-6-chloropyridine ($m/z = 130.01$) and 4-amino-3-hydroxybenzenesulfonic acid ($m/z = 190.01$) [83]. The N-N bond of 3-amino-6-chloropyridine ($m/z = 130.01$) is further broken to form the product 1-chloro-4-aminopyridine ($m/z = 132.01$), and the amino group of the product 4-amino-3-hydroxybenzenesulfonic acid ($m/z = 190.01$) is oxidized to nitro group to form 4-nitrobenzenesulfonamide ($m/z = 202.00$). In a second pathway, a single electron is transferred to form free radical aniline cations, which undergo intermolecular Smiles rearrangement to form SO_2 to form the products 1-amino-4-(3-chloro-6-aminopyridine)-aniline ($m/z = 221.057$) [84,85]. Under the attack of $\cdot\text{OH}$, 1-amino-4-(3-chloro-6-aminopyridine)-aniline ($m/z = 221.057$) decomposes to Cl and 1-amino-4-(6-aminopyridine)-aniline ($m/z = 185.99$), which is then hydroxylated to 1-amino-4-(6-aminopyridine)-6-hydroxyaniline ($m/z = 201.9$) [84]. However, 1-amino-4-(6-aminopyridine)-aniline ($m/z = 185.99$) was not detected in this study, which might be explained by the rapid conversion of 1-amino-4-(6-aminopyridine)-aniline ($m/z = 185.99$) to 1-amino-4-(6-aminopyridine)-6-hydroxyaniline ($m/z = 201.9$) after oxidation. This sequence is promoted by the orientation effect of the amino group and the spatial site blocking of the sulfonamide chain, and the hydroxylation which occurs in the neighboring position of the amino group [84,86]. In the third route, SPDZ is directly oxidized by the hydroxylation of the aniline ring to generate N-(6-chloropyrimidine-4-yl)-3-nitrobenzenesulfonamide ($m/z = 314.99$), which then undergoes intermolecular Smiles rearrangement under the release of SO_2 , producing 4-chloro-6-(3-nitrophenyl)-pyrimidine amine ($m/z = 251.03$) [87]. Finally, organic pollutants of low molecular weight will be oxidized by $\cdot\text{OH}$ radicals to form simple small molecular organic matter, and will be finally mineralized to CO_2 and H_2O [83].

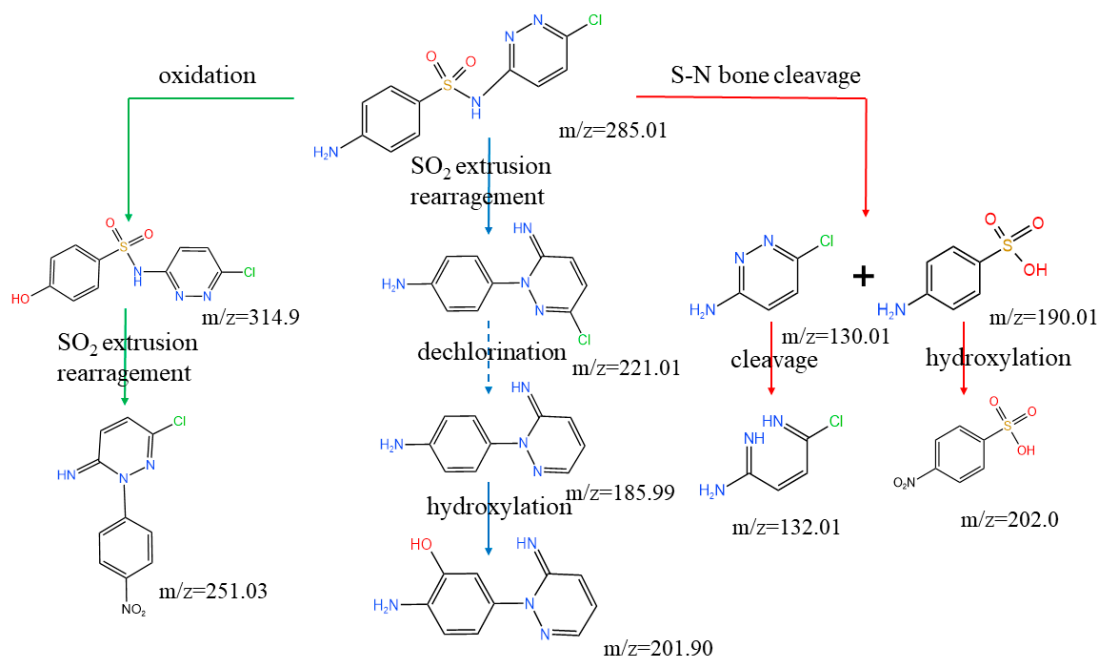


Figure 11. The catalytic ozonation pathway of SPDZ was proposed.

2.6. Reuse of $\text{Fe}_2\text{O}_3/\text{Dia}$

The stability and reuse of $\text{Fe}_2\text{O}_3/\text{Dia}$ in catalytic ozone oxidation reactions were studied. As shown in Figure 12, the recovered $\text{Fe}_2\text{O}_3/\text{Dia}$ material demonstrated its best catalytic property in the initial two catalytic cycles, while the subsequent reuse led to a gradual reduction in the catalytic productivity of SPDZ ozonation, but still maintained an excellent catalytic activity. In the catalytic $\text{Fe}_2\text{O}_3/\text{Dia}$ system, the degradation rate of SPDZ in the first run was 87%, while the removal rate of SPDZ in the fifth run was 80%. The catalytic performance of recycled $\text{Fe}_2\text{O}_3/\text{Dia}$ decreased because of the accumulation of SPDZ degradation intermediates on the catalyst surface during repeated reactions, which impeded the adsorption and reaction of ozone on the active centers [74]. In conclusion, the $\text{Fe}_2\text{O}_3/\text{Dia}$ composite catalyst has good stability.

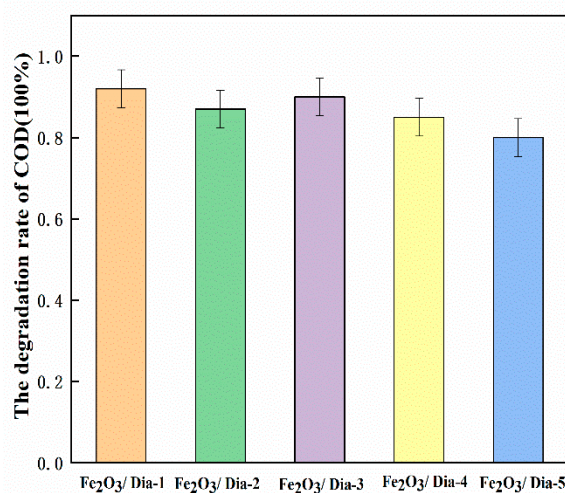


Figure 12. Recycling tests of SPDZ degradation by $\text{Fe}_2\text{O}_3/\text{Dia}$ -catalyzed ozonation.

3. Materials and Methods

3.1. Materials

The ozone generator was obtained from Sansan Technology, Rizhao, China. Diatomite and FeCl_3 were purchased from Maclean, and SPDZ ($\text{C}_{10}\text{H}_8\text{ClN}_4\text{NaO}_2\text{S}$), dipotassium hydrogen phosphate, and sodium bicarbonate were acquired from Macklin (Shanghai, China). Furfuryl alcohol was purchased from Runyou Chemical Co., Ltd. (Nanjing, China). *Tert*-butyl alcohol was bought from Macklin.

3.2. Catalysts Preparation

Li Jun's investigation into the stability and synergistic effects of nanobubbles in microsilica flotation provides valuable insights that can be extended to catalytic systems. Applying these concepts to $\text{Fe}_2\text{O}_3/\text{Dia}$ systems can provide a new perspective on optimizing catalyst design [88]. Fe_2O_3 was prepared by a chemical method. $\text{Fe}_2\text{O}_3/\text{Dia}$ was prepared by a precipitation method [20], as follows: (1) Diatomite was thermally acid modified; the appropriate amount of diatomite powder was placed in a ceramic crucible, which was subsequently heated to 450 °C in a muffle furnace, followed by calcination for 2 h. After the diatomite powder was cooled to room temperature, the thermally modified diatomite powder was placed in a dry beaker. Then, 50% mass fraction of concentrated sulfuric acid was added at a solid–liquid ratio of 1:10, and the reaction was stirred in a water bath with a magnetic stirrer at 95 °C for 4 h. After cooling, the diatomite powder was filtered, and then rinsed repeatedly with ultrapure water until the supernatant was neutral. The rinsed diatomite was dried in a far-infrared constant temperature drying oven at 105 °C for 10 h to obtain the hot acid-modified diatomite. (2) $\text{Fe}_2\text{O}_3/\text{Dia}$: a mixture of 2 g modified diatomite and 500 mL deionized water was stirred in a beaker, and 6 g FeCl_3 was added. After thorough mixing, the mixture was gradually added to an appropriate

volume of 3 mol·L⁻¹ NaOH solution. Stirring was maintained for 5 h, followed by a 3 h standing period before filtering the supernatant. The filtered sample was rinsed repeatedly with ultrapure water until a neutral pH was achieved. The sample was then dried in a far-infrared constant temperature drying oven at 105 °C for 5 h. Subsequently, the dried sample was calcined in a muffle furnace at 450 °C for 2 h and allowed to cool to room temperature to yield the Fe₂O₃/Dia composite catalyst.

3.3. Catalytic Ozone Oxidation

Catalytic ozone oxidation experiments were performed in 1 L three-necked flasks. A volume of 1 L simulated wastewater, containing 2 g·L⁻¹ SPDZ, and 2 g catalyst were added to a three-necked flask, and ozone, produced in situ from pure oxygen (3 L·min⁻¹) by the ozone generator, was added in a dosage of 56 mg; the reaction time was 60 min.

3.4. Analysis Methods

The ozone concentration was controlled by adjusting the oxygen intake, while the degree of pollutant mineralization was assessed by measuring the COD at various times. Contaminant degradation pathways were proposed based on liquid chromatography-coupled mass spectrometry (LC-MS) through the identification of intermediates in the degradation process. Catalyst properties were analyzed using XPS, XRD, SEM, FTIR, and EPR. Hydroxyl radicals and other free radicals were identified by monitoring the effects of specific trapping agents, with ·OH detected using tert-butanol (TBA) and carbonate ion (HCO₃⁻), and superoxide anions (O₂^{·-}) identified with p-benzoquinone (PBQ).

4. Conclusions

In this paper, the catalytic potential of Fe₂O₃/Dia for the ozonation of SPDZ was investigated. The results indicated that the COD degradation of SPDZ by Fe₂O₃/Dia reached approximately 87% in the presence of ozone, which was significantly higher compared to the 15% degradation achieved through ozonation without a catalyst. Hydroxyl radical trapping experiments and EPR spectroscopy confirmed that ·OH is the predominant oxidant in the catalytic ozonation system. The incorporation of Fe₂O₃/Dia enhanced the SPDZ removal rate and notably reduced the toxicity of the oxidation products. Intermediates in the SPDZ degradation process were detected and identified using LC-MS. The first degradation pathway involves the cleavage of the S-N bond, the second pathway entails the rearrangement of the SPDZ radical with SO₂ release, and the third pathway involves the direct oxidation of SPDZ. Ultimately, these pathways lead to the formation of low-molecular-weight organic pollutants, which are converted into CO₂ and H₂O. The findings suggest that Fe₂O₃ modification by diatomite holds considerable promise for enhancing SPDZ ozonation.

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