

Article

Peroxymonosulfate Activation by Bi-Fe Oxide Co-Doped Graphitic Carbon Nitride for Degradation of Sulfamethoxazole: Performance and Mechanism

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Abstract: Graphite carbon nitride (g-C₃N₄) has been employed as an emerging metal-free catalyst in heterogeneous catalysis. However, the catalyst has a poor activation property for peroxymonosulfate (PMS). In this study, Bi-Fe oxide co-doped g-C₃N₄ (Bi@Fe/CN) was synthesized for PMS activation to degrade sulfamethoxazole (SMX). In particular, Bi@Fe/CN-3 presented remarkable catalytic performance with 99.7% removal of SMX within 60 min in the PMS system. Additionally, Bi@Fe/CN-3 presented good stability and recyclability through the cycling experiments. Moreover, it was shown that free radicals (O₂^{•−}, •OH, and SO₄^{•−}) and non-free radicals (¹O₂) were the primary active species in the Bi@Fe/CN-3/PMS system. Bi, Fe, and surface lattice oxygen were confirmed to be the main contributors to the active species. This work elucidates the mechanism of activation of PMS by Bi@Fe/CN-3, which is beneficial to promote the application of bimetallic oxide-modified g-C₃N₄/PMS systems in wastewater treatment.

Keywords: carbon nitride; peroxymonosulfate; degradation; sulfamethoxazole; Bi₂Fe₄O₉; mechanism



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1. Introduction

In recent years, antibiotics have been used extensively in treating bacterial infections and in the animal husbandry, agriculture, and pharmaceutical industries [1]. Speculatively, the consumption of antibiotics will rise by 200% from 2015 to 2030 [2]. However, the excessive use of antibiotics causes bacterial drug resistance and antibiotic resistance [3]. In addition to the potential harm caused by antibiotic-resistant bacteria, the one-time or continuous intake of antibiotics beyond the maximum dosage for the human body also brings direct adverse effects and even toxicity to the human body [4]. Nowadays, antibiotic residues in the environment have become a global concern. Sulfamethoxazole (SMX), a well-known antibiotic, is used frequently to treat or prevent a wide range of illnesses. A serious hazard to human health and aquatic ecosystems is posed by the widespread use of SMX, which is found in surface water regularly [5]. In recent years, scholars have developed various technologies to remove antibiotic residues, such as membrane separation, physical adsorption, biodegradation, and photocatalytic degradation, etc. [6–9]. However, most of these methods have drawbacks, such as high energy consumption, low mineralization capacity, and ineffective purification [6].

Persulfate-based advanced oxidation processes are gaining attention due to their excellent performance in the removal of pollutants [10]. In comparison to the conventional hydroxyl radicals (•OH), sulfate radicals (SO₄^{•−}) are more efficient for the degradation of refractory pollutants due to their longer half-life, higher oxidation potential, etc. Moreover, due to their asymmetric structure, PMS is easily activated [11]. Various strategies have

been utilized for PMS activation, including thermal treatment, ultrasound, ultraviolet, radiation, alkaline, transition metal, and carbon material activation [12]. Carbon materials are generating more and more interest as catalysts for PMS activation due to their tunable pore structure, larger specific surface area (SSA), lack of secondary pollution, lack of leaching of toxic metal ions, and thermal stability [13]. One of the carbon materials, graphitic carbon nitride (g-C₃N₄), has been reported to be used for PMS activation [14]. However, single g-C₃N₄ has poor catalytic capacity for activating PMS [15]. In order to improve the PMS activation capacity of g-C₃N₄, researchers modified it by heteroatom modification [16]. For example, the PMS activation performance of g-C₃N₄ has been improved by Fe doping, resulting in an increase in phenol degradation rate from 10% (g-C₃N₄) to 35% (Fe-doped g-C₃N₄) within 60 min [17]. Oxygen doping has been found to significantly enhance the PMS activation performance of g-C₃N₄ due to the shift in electron density [18]. Additionally, metal oxide-doped g-C₃N₄ was proved to be effective in activating PMS to degrade pollutants [19–21]. For example, the CoO_x@C/g-C₃N₄/PMS system and the LaCoO₃/g-C₃N₄/PMS system exhibited superior tetracycline degradation performance with removal rates of more than 80% at 60 min and 30 min [19,20]. SMX has been degraded completely in the Fe-Co-O-g-C₃N₄/PMS system within 30 min [21]. Research has shown that Bi₂Fe₄O₉ can activate PMS effectively [22]. It is speculated that g-C₃N₄ co-doped with Bi-Fe oxide may increase the active sites on the surface of g-C₃N₄, thereby improving its catalytic activity. However, the PMS activation ability of Bi-Fe oxide co-doped g-C₃N₄ has not been verified, and the mechanism of Bi-Fe oxide co-doped g-C₃N₄ to activate PMS for pollutant degradation is not clear.

The purpose of this study was to prepare Bi-Fe oxide co-doped g-C₃N₄ and estimate its potential as a PMS activation catalyst, as well as the mechanism of PMS activation by Bi@Fe/CN. This work elucidates the mechanism of activation of PMS by Bi@Fe/CN-3, which is beneficial to promote the application of bimetallic oxide-modified g-C₃N₄/PMS systems in wastewater treatment.

2. Materials and Methods

2.1. Materials and Chemicals

The chemical reagents used in this study were as follows: sodium hydroxide, iron chloride, bismuth nitrate, urea, sulfamethoxazole, potassium peroxydisulfate, sodium thiosulfate pentahydrate, hydrochloric acid, phosphoric acid, sodium nitrate, tert-butanol (TBA), methanol (MeOH), and L-histidine. Every chemical reagent employed was of analytical quality, and only ultrapure water was used for dilution or dissolution.

2.2. Bi@Fe/CN Preparation Method

Bi(NO₃)₃·5H₂O (0.005 mol), Fe(NO₃)₃·9H₂O (0.005 mol), urea (0.05 mol), and nitric acid (2 mL) were added to deionized water to form a 20 mL mixture and stirred for 20 min. Then, a saturated solution of KOH was dropped into the mixture until the concentration of KOH reached 10 M. After that, the mixture was transferred to a 100 mL steel autoclave for hydrothermal reaction. The reactor was heated at a rate of 2 °C/min from room temperature to 120 °C and kept for 800 min. The obtained samples were centrifuged, cleaned three times with deionized water and ethanol, and labeled as Bi@Fe-1. The experiments were repeated with modified conditions to obtain Bi@Fe-2 and Bi@Fe-3, as listed in Table 1.

Table 1. Preparation conditions for Bi@Fe-1, Bi@Fe-2, and Bi@Fe-3.

Sample	Bi@Fe-1	Bi@Fe-2	Bi@Fe-3
KOH concentration (mol)	10	5	5
Hydrothermal temperature (°C)	120	120	160

The preparation process for g-C₃N₄ is as follows: in a muffle furnace, 10 g of melamine was heated at a rate of 5 °C/min from room temperature to 520 °C for 4 h.

Then, Bi@Fe/CN was prepared by mixing Bi@Fe and g-C₃N₄ at a mass ratio of 2:1, shaking well, and placing the mixture in a tube furnace for pyrolysis. Specifically, the mixture was heated to 300 °C under N₂ atmosphere at a heating rate of 10 °C/min, held for 1 h, and labeled as Bi@Fe/CN-1, Bi@Fe/CN-2, and Bi@Fe/CN-3 separately.

2.3. Characterization

The crystalline structure of Bi@Fe/CN was evaluated by X-ray diffraction. The SSA and pore size of samples were identified using an N₂ adsorption-desorption analyzer. The surface morphology was verified by scanning electron microscope (SEM). Fourier transform infrared spectroscopy (FTIR) was employed for functional group analysis with a scanned area of 400–4000 cm^{−1}. X-ray photoelectron spectroscopy (XPS) was employed to analyze surface active sites. The reactive oxidative species (ROS) were detected using an electron paramagnetic resonance (EPR).

2.4. Degradation Experiments and Analytical Methods

The SMX degradation experiments were conducted in 150 mL beakers at room temperature. The initial pH of the solution was adjusted by NaOH and H₂SO₄. Typically, 0.1 g catalyst was mixed into 100 mL SMX solution (15 mg/L) for 30 min. Then, PMS was added to initiate the SMX degradation with concentration of 0.6 mM. Periodically, 1.5 mL of the solution was taken, filtered with a 0.22 µm membrane, and quenched with Na₂SO₃ solution (0.15 mL, 0.5 M). Finally, the sample was measured by high-performance liquid chromatograph (HPLC).

Furthermore, the effect of catalyst dosage (0.025, 0.050, 0.100, and 0.200 g/L, PMS concentration (0.2, 0.4, 0.6, and 0.8 mM), initial pH (3, 5, 7, and 9), inorganic anions (10 and 100 mM chloride (Cl[−]), nitrate (NO₃[−]), bicarbonate (HCO₃[−]), and monohydric phosphate (HPO₄^{2−})) on SMX degradation in Bi@Fe/CN-3 system was explored in this work. L-histidine (100 mM), MeOH (100 mM), and TBA (100 mM) were employed as quenching agents in Bi@Fe/CN-3/PMS system.

3. Results and Discussion

3.1. Characterization of Bi@Fe/CN

SEM images were used to examine the surface morphology of the samples. The samples were irregular block granules with rough surfaces, as seen in Figure 1. It is obvious that there are defects on the surface of Bi@Fe/CN, which may be due to the bismuth iron oxide doped on the surface.

The SSA of Bi@Fe/CN-1, Bi@Fe/CN-2, and Bi@Fe/CN-3 were 19.604, 37.073, and 43.964 m²/g, separately (Figure 2a). Additionally, the average pore diameters of Bi@Fe/CN-1, Bi@Fe/CN-2, and Bi@Fe/CN-3 were 3.72, 3.72, and 5.43 nm, respectively (Figure 2b). Obviously, Bi@Fe/CN-3 showed the largest pore size and SSA due to the higher hydrothermal temperature. This may be attributed to the decrease in the microcrystalline particle size of bismuth ferrite with the increase in hydrothermal temperature [23]. Generally, a larger SSA and favorable pore structure may provide more reaction sites for pollutants and oxidants in the reaction process, thereby increasing the removal efficiency of SMX [24].

The XRD patterns of the different samples are shown in Figure 3a. The presence of Bi₂Fe₄O₉ and g-C₃N₄ was found in Bi@Fe/CN-3 (JCPDS #87-1522 and JCPDS #25-0090). Specifically, the peaks at 2θ = 24.5°, 27.5°, and 47.7° were observed in Bi@Fe/CN-3, which correspond to the (101), (110), and (112) crystal planes of g-C₃N₄, respectively. The result shows that the graphitic structure of g-C₃N₄ remained even after the synthesis of the composite catalyst and subsequent pyrolysis [25]. Additionally, the diffraction peaks at 2θ = 14.8°, 28.2°, 28.9°, 33.7°, and 47.0°, which stood for the crystal faces of Bi₂Fe₄O₉ (001), (121), (211), (130), and (141), respectively, have been found in Bi@Fe/CN-3. Interestingly, the 14.8° peak was not present in Bi@Fe/CN-1 and Bi@Fe/CN-2; instead, the characteristic peaks at 27.7° (310), 30.4° (222), 32.9° (321), 52.4° (530), and 55.6° (611) corresponding to Bi₂₅FeO₄₀ (JCPDS #46-0416) could be observed in Figure S1. This was attributed to the

effect of hydrothermal temperature on the crystal phase and structure of the synthesized bismuth iron oxide. The rise of hydrothermal temperature led to the phase evolution from $\text{Bi}_{25}\text{FeO}_{40}$ to $\text{Bi}_2\text{Fe}_4\text{O}_9$ [26].

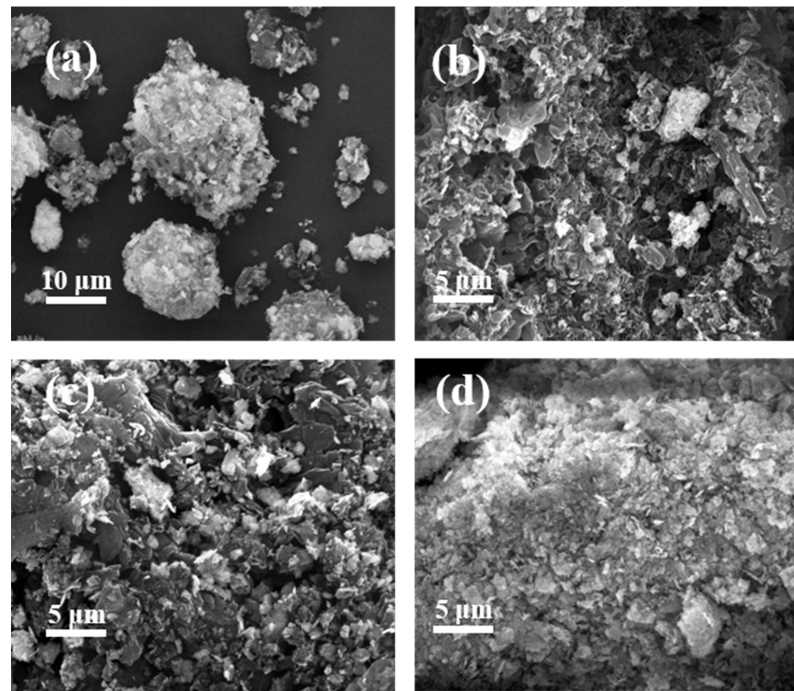


Figure 1. SEM scanning images of the samples (a) and (b) Bi@Fe/CN-1; (c) Bi@Fe/CN-2; (d) Bi@Fe/CN-3.

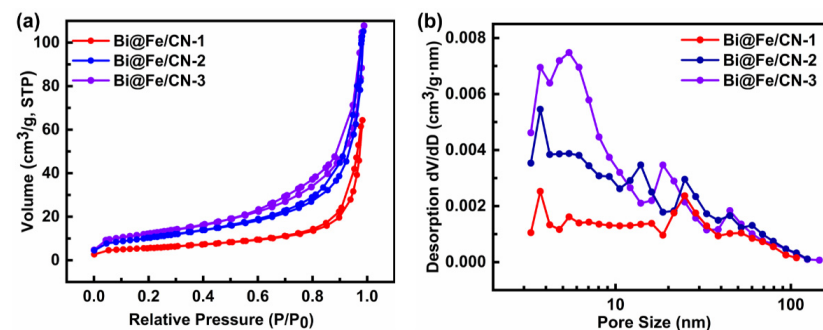


Figure 2. (a) N_2 adsorption-desorption isotherm; (b) pore size distribution of Bi@Fe/CN-1, Bi@Fe/CN-2, and Bi@Fe/CN-3.

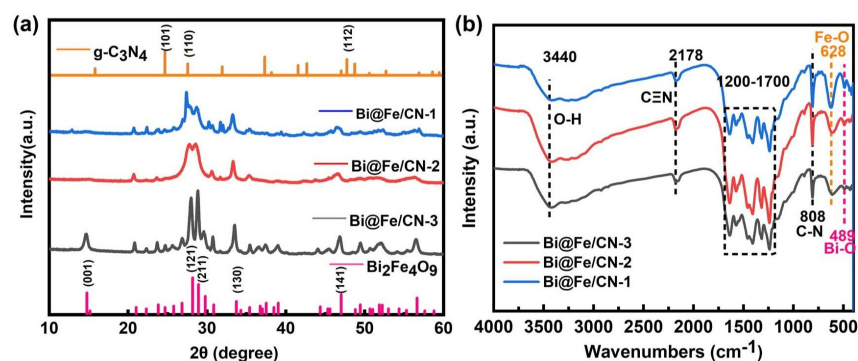


Figure 3. (a) XRD image of Bi@Fe/CN; (b) FTIR image of Bi@Fe/CN (Vertical lines: Different peaks of Bi@Fe/CN).

Furthermore, FTIR was used to study the surface functional groups of each sample. As depicted in Figure 3b, all samples exhibited stretching vibration peaks of the CN conjugated ring in the range of 1200–1700 cm^{-1} [27]. The sharp peak at 808 cm^{-1} represented the out-of-plane stretching vibration peak of the C–N heterocyclic ring [28]. Besides, the peak at 489 cm^{-1} is attributed to the Bi–O stretching vibration in the BiO_6 octahedron, while the peak at 628 cm^{-1} is related to the Fe–O in the FeO_6 octahedron in the system [29]. The presence of the mentioned characteristic peaks indicates that the g- C_3N_4 functional group structure still remains in Bi@Fe/CN.

XPS spectra were used to examine the elemental composition and valence on the surface of Bi@Fe/CN. As shown in XPS surveys of Bi@Fe/CN (Figure 4a), the characteristic peaks of the C, N, O, Fe, and Bi elements were observed. The peaks at the binding energies of 284.7, 285.9, 287.0, and 288.3 eV correspond to C–C/C–C, C–O/C–N, C–O, and N–C–O, respectively (Figure 4b) [30]. The N 1s XPS spectrum (Figure 4c) was deconvoluted into three peaks at the binding energies of 398.8, 399.4, and 401.4 eV, corresponding to pyridinic N, pyrrolic N, and graphitic N, respectively [31]. As shown in Figure 4d, the O 1s XPS spectrum can be fitted with three components: the lattice oxygen of the metal oxide at the binding energies of 529.7 eV [32], C–O (531.3 eV) [33], and C–O (531.9 eV) [34]. The high-resolution Fe 2p XPS spectrum (Figure 4e) shows two spin-orbit centers centered at the binding energies of 711 eV and 725 eV, corresponding to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively. The Fe 2p_{3/2} peak can be decomposed into two peaks at 710.3 eV and 712.2 eV, corresponding to Fe²⁺ and Fe³⁺, respectively, indicating the coexistence of Fe²⁺ and Fe³⁺ in the catalyst [35]. Additionally, as seen in the high-resolution Bi 4f XPS spectrum (Figure 4f), the peaks at 158.8 eV and 164.1 eV are associated with the Bi 4f_{7/2} and Bi 4f_{5/2} orbitals of Bi³⁺, respectively [36].

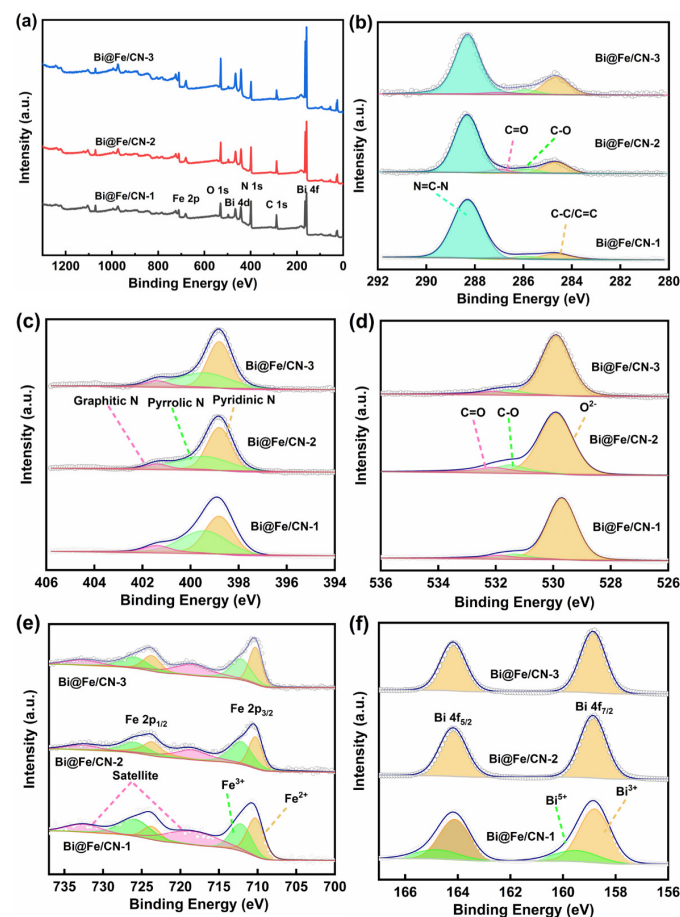


Figure 4. XPS spectra of Bi@Fe/CN, (a) survey XPS spectra, (b) C 1s spectra, (c) N 1s spectra, (d) O 1s spectra, (e) Fe 2p spectra, and (f) Bi 4f spectra.

3.2. Catalytic Degradation of SMX

In the PMS system, the degradation efficiency of SMX by different catalysts is shown in Figure 5. As shown in Figure 5a, the adsorption of SMX was negligible by Bi@Fe/CN-1 and Bi@Fe/CN-2 within 30 min. In comparison, the adsorption efficiency of SMX by Bi@Fe/CN-3 reached 6.6%. The increased adsorption capacity of Bi@Fe/CN-3 was attributed to the large SSA. Only 21.7% of SMX were removed by PMS alone within 60 min. It is worth noting that the addition of Bi@Fe/CN enhanced the degradation of SMX significantly in the PMS system. The degradation of SMX by Bi@Fe/CN/PMS followed the order of Bi@Fe/CN-3/PMS (99.7%) > Bi@Fe/CN-2/PMS (88.4%) > Bi@Fe/CN-1/PMS (62.5%). In addition, the pseudo-first-order kinetic model ($R^2 > 0.97$) was used to fit the reaction rate constant (k), which was found to be in the order of Bi@Fe/CN-3/PMS (0.0911 min^{-1}) > Bi@Fe/CN-2/PMS (0.0340 min^{-1}) > Bi@Fe/CN-1/PMS (0.0156 min^{-1}) > PMS (0.0029 min^{-1}). Thus, it can be derived that Bi@Fe/CN-3 exhibits the best catalytic activity.

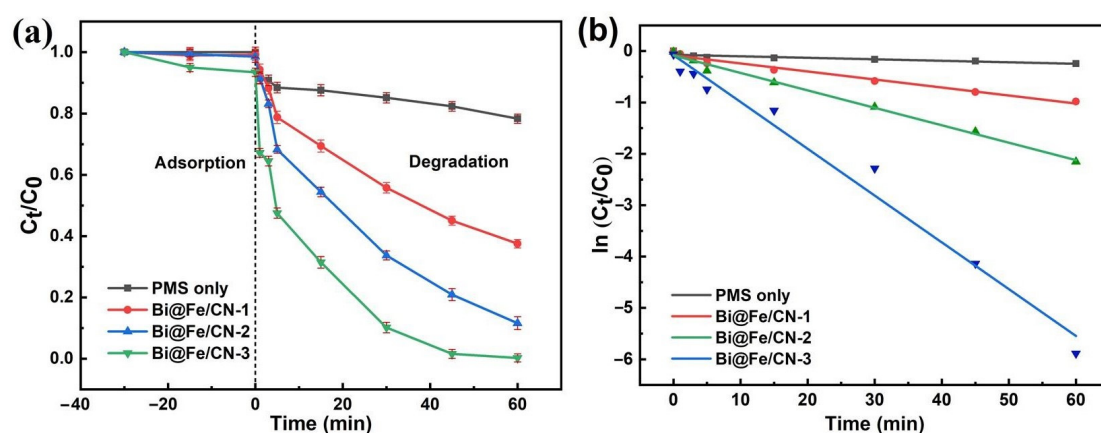


Figure 5. (a) Degradation of SMX in different Bi@Fe/CN/PMS systems; (b) Kinetics curves of different catalytic systems fitted by a pseudo-first-order kinetic model. Reaction conditions: [catalyst] = 0.10 g/L, [PMS] = 0.60 mM, [SMX]₀ = 15.0 mg/L, initial pH = 5.18.

As shown in Table 2, a comparison was made on the normalized degradation rates of SMX in different PMS systems. Compared with g-C₃N₄, the degradation rate of SMX was improved after Bi-Fe oxide co-doped on g-C₃N₄, and the normalized degradation rate of SMX in Bi@Fe/CN-3/PMS system is significantly higher than that of other systems. Hence, Bi@Fe/CN-3 exhibited superior activation properties in the PMS system.

Table 2. Comparison of SMX degradation rates in various PMS activation systems.

PMS Systems	[SMX] (mg·L ⁻¹)	[PMS] (mM)	[Catalyst] (g·L ⁻¹)	Time (min)	Degradation Rate * (%)	Reference
g-C ₃ N ₄ /PMS	5.10	0.15	0.200	60	1.089	[37]
FeO _y /S-g-C ₃ N ₄ /PMS	10.0	0.8	0.500	60	0.417	[38]
FNCCN/PMS	5.00	1.6	0.400	60	0.467	[39]
Fe-Co-O-g-C ₃ N ₄ /PMS	10.1	0.8	0.200	30	2.063	[21]
Fe ₃ O ₄ /β-FeOOH/PMS	5.0	1.3	0.200	30	2.333	[40]
Bi@Fe/CN-3/PMS	15.0	0.6	0.100	45	2.432	This work

* Degradation rate per unit concentration of SMX (mg·L⁻¹), PMS (mM), and catalyst (g·L⁻¹) and per unit time (min).

The effects of Bi@Fe/CN-3 dosage, initial solution pH, PMS concentration, and co-existing anions on the degradation of SMX were studied in Figure 6. The rate constant of SMX removal increased from 0.0046 to 0.194 min⁻¹ with the dosage of Bi@Fe/CN-3 increased from 0.025 to 0.200 g/L (Figure 6a). This is due to the fact that a higher catalyst dosage provides more active sites for PMS activation. A similar pattern was also seen in the degradation of SMX with different PMS doses (Figure 6b). SMX was nearly entirely

degraded with 0.6 mM and 0.8 mM PMS. It is worth noting that the rate constants of SMX degradation were in the order of 0.2 mM (0.0179 min^{-1}) < 0.4 mM (0.0419 min^{-1}) < 0.6 mM (0.0911 min^{-1}) < 0.8 mM (0.0921 min^{-1}). The rate constants were observed to increase with PMS concentration increase from 0.2 to 0.6 mM. However, there was no discernible improvement in the rate constant of SMX removal, with a further increase in PMS concentration from 0.6 to 0.8 mM. At low PMS concentrations, an increase in the PMS concentration makes it easier to produce active species, which speeds up the degradation of SMX. However, at high PMS concentrations, PMS depletes the free radicals produced (Equations (1)–(3)) [41].

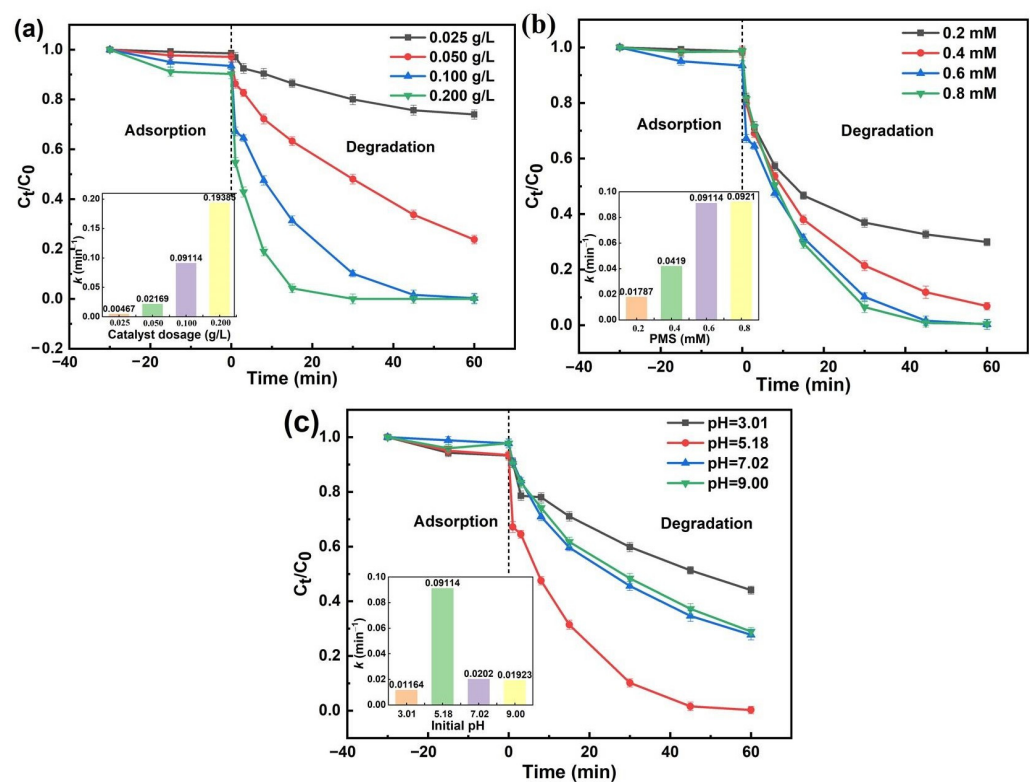
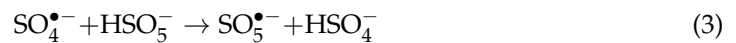
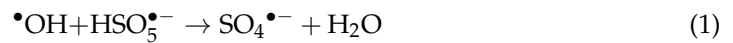


Figure 6. Effect of (a) catalyst dosage, (b) PMS concentration and (c) initial pH on SMX degradation in the Bi@Fe/PMS system (inset: Reaction rate values with different (a) catalyst dosages, (b) PMS concentrations and (c) initial solution pH values). Reaction conditions: [catalyst] = 0.10 g/L, [PMS] = 0.60 mM, [SMX]₀ = 15.0 mg/L, initial pH = 5.18.

The solution pH would affect the degradation of SMX in the Bi@Fe/CN-3/PMS system. Figure 6c demonstrates that the degradation efficiency of SMX in mild acidic conditions was excellent, with nearly complete degradation of SMX (99.7%) and a rate constant of 0.0911 min^{-1} . However, the degradation rate of SMX decreased (<80%) in very neutral, strongly alkaline, or strongly acidic environments. This is due to the fact that at high pH, the O–O bond in PMS will combine with a substantial quantity of H to create strong hydrogen bonds. The phenomenon prevents PMS from being activated by Bi@Fe/CN-3 [42]. Regarding the decrease in the removal rate of SMX at pH > 5.18, the higher pH encourages the conversion of HSO_5^- to SO_5^{2-} , which speeds up the self-decomposition of PMS. On the other hand, the SMX degradation rate decreased at pH 7–9,

due to SMX mostly presenting as an anionic species that electrostatically repels active intermediate free radicals like $\text{SO}_4^{\bullet-}$ [43].

3.3. Influence of the Co-Existing Ions

Typically, various anions in natural water have an impact on the activity of catalysts. Therefore, the effects of different concentrations (10 mM and 100 mM) of H_2PO_4^- , HCO_3^- , Cl^- , and NO_3^- on the degradation of SMX in Bi@Fe/CN-3/PMS system were studied. As shown in Figure 7a, the SMX removal rate dropped from 99.9% to 36.3–44.9% in the presence of H_2PO_4^- (10–100 mM). The inhibitory effect of H_2PO_4^- on the removal of SMX may be attributed to the fact that H_2PO_4^- can react with active species such as $\bullet\text{OH}$ to generate low-oxidizing $\text{H}_2\text{PO}_4^\bullet$ and $\text{HPO}_4^{\bullet-}$ (Equations (4) and (5)) [44].

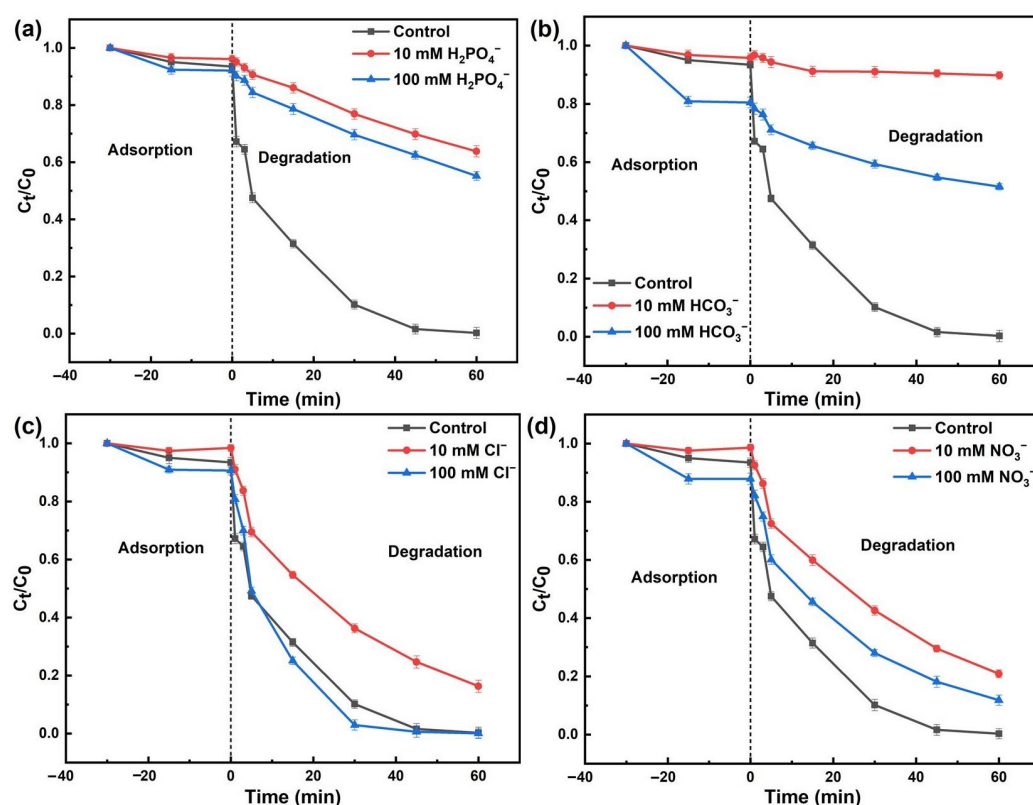
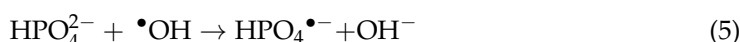
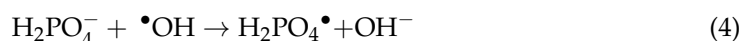
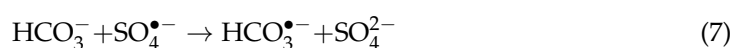
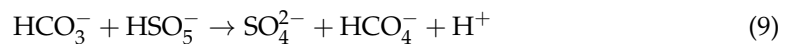
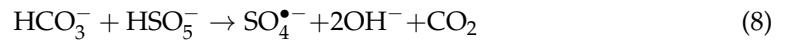


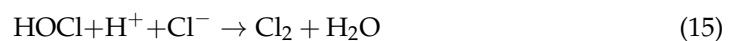
Figure 7. Effect of different anions (a) H_2PO_4^- , (b) HCO_3^- , (c) Cl^- and (d) NO_3^- on SMX removal in the Bi@Fe/CN-3/PMS system. Reaction conditions: [catalyst] = 0.10 g/L, [PMS] = 0.60 mM, $[\text{SMX}]_0 = 15.0$ mg/L, initial pH = 5.18.

As shown in Figure 7b, HCO_3^- has a significant inhibitory effect on the degradation of SMX in Bi@Fe/CN-3/PMS system. The rate of SMX degradation was reduced to 11.2% in the presence of 10 mM HCO_3^- due to HCO_3^- being able to interact with free radicals to produce low-oxidizing $\text{HCO}_3^\bullet$ (Equations (6) and (7)) [45]. However, when the HCO_3^- concentration was further increased to 100 mM, the degradation rate of SMX increased to 48.4% since HCO_3^- can also directly interact with PMS to provide $\text{SO}_4^{\bullet-}$ and HCO_4^- , which further promotes the removal of SMX (Equations (8) and (9)) [46].

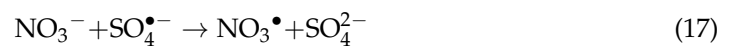
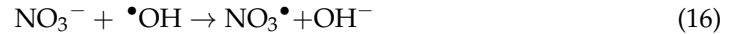




Cl^- exhibits a dual effect on the degradation of SMX in Bi@Fe/CN-3/PMS system (Figure 7c). The degradation rate of SMX in the presence of Cl^- (10 mM) was 83.7% within 60 min. However, the degradation rate of SMX reached 98.1% within 30 min with the addition of 100 mM Cl^- . In comparison, the Bi@Fe/CN-3/PMS system without Cl^- only managed 63.7%. The negative effect of the low concentration of Cl^- on the degradation of SMX is due to its reaction with active free radicals ($\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$), which generates $\text{Cl}^\bullet$ and $\text{Cl}_2^{\bullet-}$ with lower oxidizing abilities (Equations (10)–(13)) [47]. The Cl_2 and HClO with high oxidizing ability will be generated due to a further increase in Cl^- concentration. (Equations (14) and (15)) [48].



In addition, the effect of NO_3^- on the degradation of SMX in the Bi@Fe/CN-3/PMS system was studied (Figure 7d). Similar to H_2PO_4^- and HCO_3^- , NO_3^- can react with $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ in the system to generate less oxidizing $\text{NO}_3^\bullet$ (Equations (16) and (17)) [49]. Therefore, NO_3^- has a negative impact on the degradation of SMX in the Bi@Fe/CN-3/PMS system.



3.4. Stability and Recyclability of Bi@Fe/CN-3

In order to study stability and recyclability of Bi@Fe/CN-3, the SMX degradation was investigated by four-cycle experiments under the same condition. As shown in Figure 8, the SMX removal rates were 99.7%, 97.9%, 94.7% and 93.3%, respectively. The SMX degradation efficiencies declined slightly after four cycles. It was concluded that Bi@Fe/CN-3 showed excellent catalytic stability and recyclability.

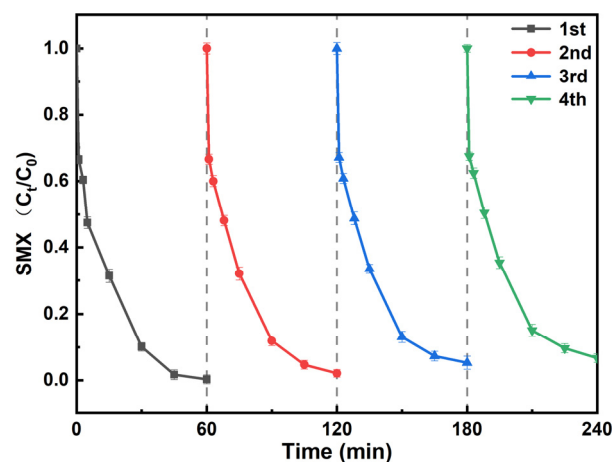


Figure 8. Cycle experiments of Bi@Fe/CN-3 in Bi@Fe/CN-3/PMS system. Reaction conditions: [catalyst] = 0.10 g/L, [PMS] = 0.60 mM, [SMX]₀ = 15.0 mg/L, initial pH = 5.18.

The SEM images of used Bi@Fe/CN-3 were shown in Figure S2. Similar to the fresh Bi@Fe/CN-3, the used Bi@Fe/CN-3 were irregular block granules with rough surfaces too. Besides, the FTIR spectrum of used Bi@Fe/CN-3 was presented in Figure S2c. Obviously, the FTIR spectrum of used Bi@Fe/CN-3 was very similar to that of fresh Bi@Fe/CN-3. This indicates that the composition of surface functional groups did not change with the degradation of SMX in Bi@Fe/CN-3 system.

In addition, the surface chemistry and element content of used Bi@Fe/CN-3 were further clarified by XPS analysis and listed in Table S1. Compared with fresh Bi@Fe/CN-3, there was little change in the content of each element in used Bi@Fe/CN-3, further confirming the good stability of Bi@Fe/CN-3.

3.5. Catalytic Mechanism

TBA, MeOH, and L-histidine were used as scavengers to identify the active species involved in the Bi@Fe/CN-3/PMS system. Figure 9d demonstrates that the degradation rate of SMX in the presence of MeOH, TBA, and L-histidine (100 mM) dropped from 99.8% to 39.2%, 45.3%, and 0.18% within 60 min, respectively. Meanwhile, the rate constants of SMX removal were arranged in the following order: control (0.0911 min^{-1}) > TBA (0.0095 min^{-1}) > MeOH (0.0074 min^{-1}) > L-histidine (0.0001 min^{-1}). The rate constants of the reaction between MeOH and $\bullet\text{OH}$ or $\text{SO}_4^{\bullet-}$ have similar values ($k_{\text{MeOH}/\bullet\text{OH}} = (1.2\text{--}2.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{\text{MeOH}/\text{SO}_4^{\bullet-}} = (1.6\text{--}7.7) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) [50]. In contrast, $k_{\text{TBA}/\bullet\text{OH}} = (3.8\text{--}7.6) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, which is much higher than $k_{\text{TBA}/\text{SO}_4^{\bullet-}} = (4.0\text{--}9.1) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ [51]. As a result, the contributions of $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ can be examined individually by the combination of TBA and MeOH quenching tests. It is worth noting that the degradation rate of SMX was reduced by 54% in the presence of TBA. Meanwhile, in the presence of MeOH, the degradation rate of SMX was reduced by 60%, only 6% less than in the presence of TBA. This indicates that both $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ contribute to the degradation of SMX. The inhibition of SMX degradation in the presence of TBA or MeOH can be attributed to the scavenging of $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ by these species. $^1\text{O}_2$ can be quenched by L-histidine, which prevents $^1\text{O}_2$ contributing to the SMX degradation. In the presence of L-histidine, SMX was essentially undegraded, showing that $^1\text{O}_2$ plays a dominant role in the degradation of SMX. These results indicate that the $\text{SO}_4^{\bullet-}$, $\bullet\text{OH}$, and especially $^1\text{O}_2$ made contributions to the removal of SMX in Bi@Fe/CN-3/PMS system.

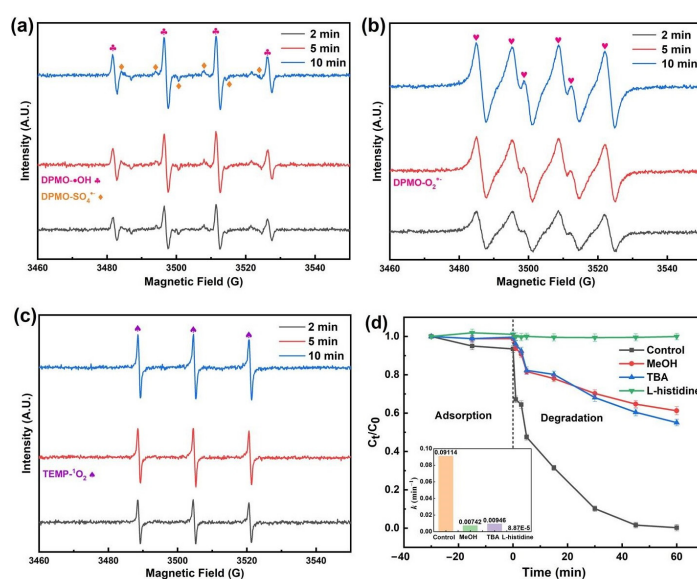


Figure 9. EPR spectra of (a) $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$, (b) $\text{O}_2^{\bullet-}$ and (c) $^1\text{O}_2$ in the Bi@Fe/CN-3/PMS system; (d) Degradation of SMX with different scavengers. Reaction conditions: [catalyst] = 0.10 g/L, [PMS] = 0.60 mM, [SMX]₀ = 15.0 mg/L, initial pH = 5.18.

In this study, the active species in Bi@Fe/CN-3 were further studied by EPR analysis. The active species, including $\text{SO}_4^{\bullet-}$, $\bullet\text{OH}$, and $\text{O}_2^{\bullet-}$, were captured by DMPO, while $^1\text{O}_2$ was captured by TEMP. As shown in Figure 9a,b, the characteristic signals of $\text{DMPO-O}_2^{\bullet-}$, $\text{DMPO-}\bullet\text{OH}$, and $\text{DMPO-SO}_4^{\bullet-}$ were observed, providing further evidence for the presence of $\text{O}_2^{\bullet-}$, $\bullet\text{OH}$, and $\text{SO}_4^{\bullet-}$ in Bi@Fe/CN-3/PMS system.

Clearly, an identifiable 1:1:1 triplet signal peak related to $\text{TEMPO-}^1\text{O}_2$ was observed in the EPR spectrum (Figure 9c), providing evidence for the presence of $^1\text{O}_2$ in Bi@Fe/CN-3/PMS system [52]. The intensity of the $^1\text{O}_2$ signal peak increased sharply from 2 to 10 min, indicating the continuously generation of $^1\text{O}_2$ in Bi@Fe/CN-3/PMS system. In summary, the $\text{O}_2^{\bullet-}$, $\bullet\text{OH}$, $\text{SO}_4^{\bullet-}$, and notably $^1\text{O}_2$ exhibit a major role in the degradation of SMX.

Further investigation of the activation mechanism of PMS was conducted by XPS analysis of fresh and used Bi@Fe/CN-3. As shown in Figure 10a, the ratio of $\text{Fe}^{3+}/\text{Fe}^{2+}$ increased from 1.03 to 1.25 after the degradation of SMX, indicating that Fe(II) was partially converted to Fe(III) during the reaction, as Fe^{2+} can react with HSO_5^- (Equations (18) and (19)). Similar to other bimetallic catalysts, Bi also plays an important role in Bi@Fe/CN/PMS system. As shown in the high-resolution Bi 4f spectrum of fresh and used Bi@Fe/CN-3 (Figure 10b), the peaks at 159.5 eV and 164.8 eV, corresponding to Bi (V) in Bi $4f_{7/2}$ and Bi $4f_{5/2}$, appeared in used Bi@Fe/CN-3 while not being present in fresh Bi@Fe/CN-3 spectrum. The results indicated that Bi^{3+} was partially converted to Bi^{5+} due to the direct reaction between Bi^{3+} and HSO_5^- (Equation (20)), which encourages the production of active free radicals [36].

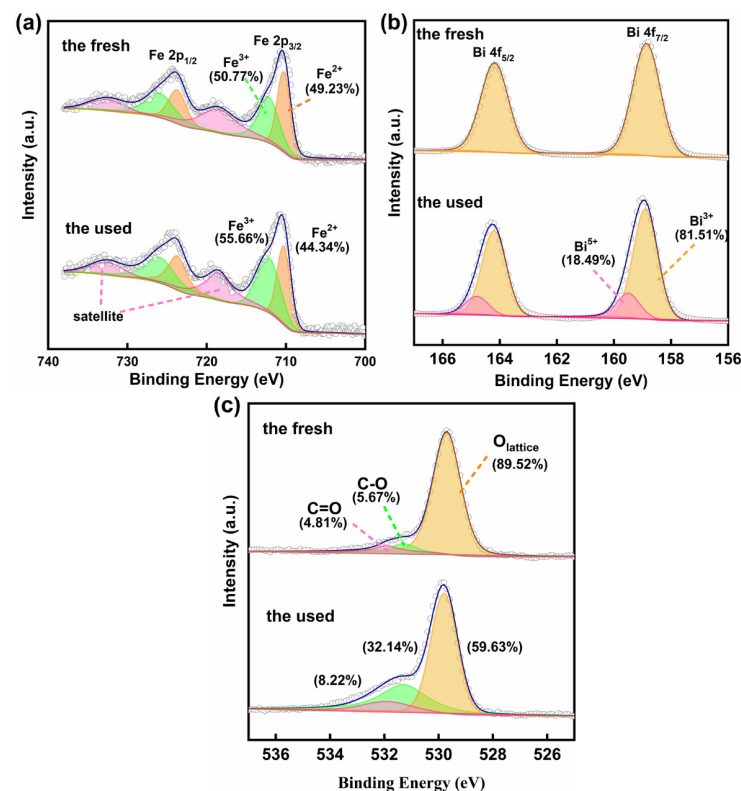
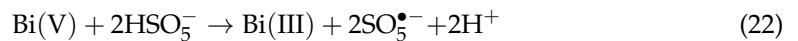
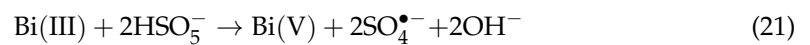
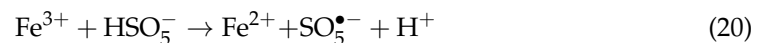
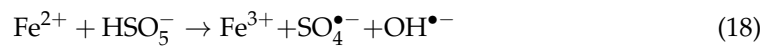


Figure 10. XPS spectra of (a) Fe 2p, (b) Bi 4f and (c) O 1s in fresh and used Bi@Fe/CN-3 samples.

Additionally, previous studies have demonstrated that surface lattice oxygen can be converted to $^1\text{O}_2$ [53]. Compared with fresh Bi@Fe/CN-3, the lattice oxygen of used Bi@Fe/CN-3 dropped significantly from 89.52% to 59.63% (Figure 10c), which suggests that lattice oxygen plays an important role in the degradation of SMX. Due to the conversion of lattice oxygen to reactive oxygen species (O^*) (Equation (23)), $^1\text{O}_2$ was further produced during the reaction with PMS (Equation (24)) [54]. The possible mechanism of PMS activation in Bi@Fe/CN-3/PMS system was proposed and illustrated in Figure 11.

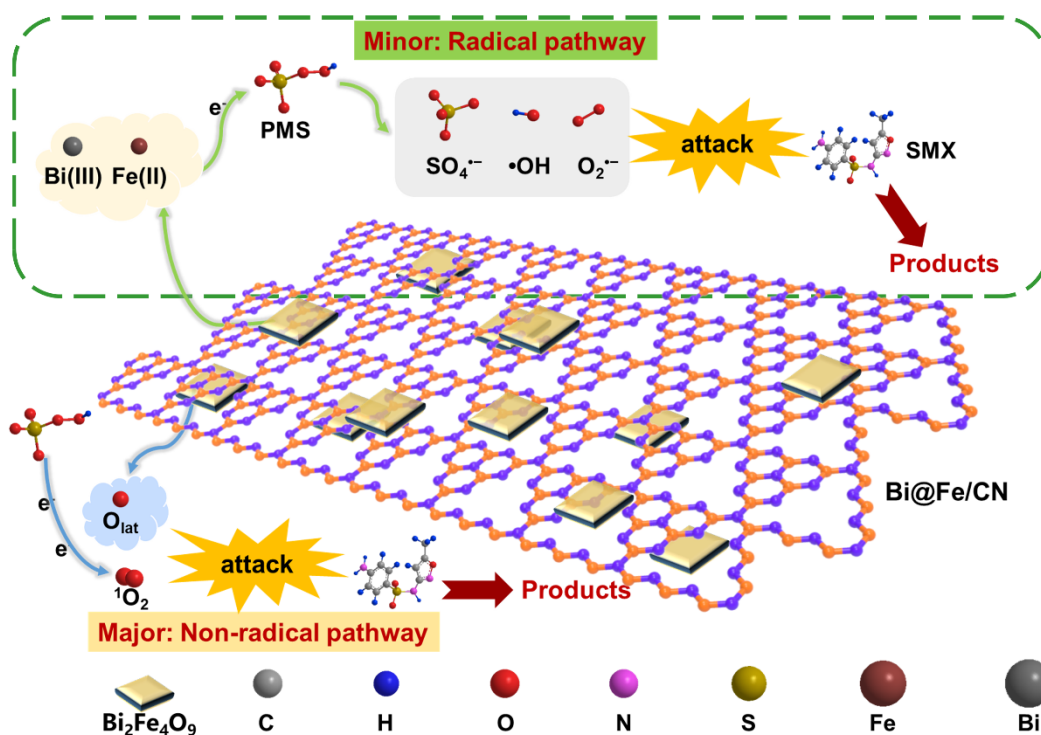
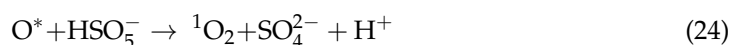


Figure 11. The mechanism of Bi@Fe/CN activating PMS to degrade SMX.

4. Conclusions

Overall, the g-C₃N₄-based composite catalyst Bi@Fe/CN shows excellent activity in activating PMS for the elimination of SMX. The increase in the PMS concentration (0.2–0.8 mM) and catalyst dose (0.025–0.2 g/L) in the Bi@Fe/CN-3/PMS system could improve the degradation of SMX. It was determined through quenching tests and EPR that the Bi@Fe/CN-3/PMS system contributed to the degradation of SMX via a simultaneous radical pathway with $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ and a non-radical pathway dominated by $^1\text{O}_2$. Based on the results of the XPS analysis, Fe, Bi, and surface lattice oxygen activated PMS to generate the active free radicals $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ and the non-free radical $^1\text{O}_2$, leading to SMX removal. However, the relationship between the preparation conditions and active site generation (Fe, Bi, and lattice oxygen) of Bi@Fe/CN is not clear. In the future, the preparation parameters of Bi@Fe/CN, such as pyrolysis temperature and the dopant ratio of Bi-Fe oxide, can be further optimized by researchers. This study provides a new approach for the development of PMS system in water treatment.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app14083181/s1>, Figure S1: The spectrum of JCPDS #46–0416 (Bi₂₅FeO₄₀) and Bi@Fe/CN. Figure S2: SEM of (a) fresh Bi@Fe/CN–3 and (b) used Bi@Fe/CN–3, (c) FTIR of fresh and used Bi@Fe/CN–3 (Vertical lines: Different peaks of Bi@Fe/CN). Table S1: Different

atom contents of fresh and used Bi@Fe/CN-3 catalysts. Table S2: Effect of catalyst dosage on SMX degradation in Bi@Fe/CN-3/PMS system. Table S3: Effect of PMS concentration on SMX degradation in Bi@Fe/CN-3/PMS system. Table S4: Effect of initial pH on SMX degradation in Bi@Fe/CN-3/PMS system. Table S5: Effect of different anions on SMX degradation in Bi@Fe/CN-3/PMS system. Table S6: Degradation of SMX with different scavengers in Bi@Fe/CN-3/PMS system.

Author Contributions: Conceptualization and methodology: Z.W. and N.L.; software: Z.W., L.L. and S.W.; writing, review, and editing: Z.W., L.L., S.W. and N.L.; validation: N.L., G.C., B.Y. and Z.C.; supervision: G.C., B.Y. and Z.C.; funding acquisition: N.L. All authors have read and agreed to the published version of the manuscript.

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Abbreviations

Graphitic carbon nitride (g-C₃N₄); Graphitic carbon nitride co-doped with Bi-Fe oxide (Bi@Fe/CN); Peroxymonosulfate (PMS); Sulfamethoxazole (SMX); Specific surface area (SSA); Sulfate radicals (SO₄•[−]); Tert-butanol (TBA); 5,5-dimethyl-1-pyrrolidine N-oxide (DMPO); 2,2,6,6-tetramethyl-4-piperidinol (TEMP); Methanol (MeOH); X-ray diffractometer (XRD); Scanning electron microscope (SEM); X-ray photoelectron spectroscopy (XPS); Infrared absorption spectrum (FTIR); Reactive oxidative species (ROS); Electron paramagnetic resonance (EPR); High-performance liquid chromatography (HPLC); Chloride (Cl[−]); Nitrate (NO₃[−]); bicarbonate (HCO₃[−]); monohydric phosphate (HPO₄^{2−}); single oxygen (¹O₂); Hydroxyl radicals (•OH).

References

1. Dutta, S.; Mandal, W.; Desai, A.V.; Fajal, S.; Dam, G.K.; Mukherjee, S.; Ghosh, S.K. A luminescent cationic MOF and its polymer composite membrane elicit selective sensing of antibiotics and pesticides in water. *Mol. Syst. Des. Eng.* **2023**, *8*, 1483–1491. [\[CrossRef\]](#)
2. Yu, C.; Huang, H.; Jin, H.; Zhang, W.; Lv, Z.; Zhao, L. Contamination by antibiotics and their degradation and removal methods. *Mar. Freshw. Res.* **2023**, *74*, 766–769. [\[CrossRef\]](#)
3. Mandal, W.; Fajal, S.; Samanta, P.; Dutta, S.; Shirolkar, M.M.; More, Y.D.; Ghosh, S.K. Selective and sensitive recognition of specific types of toxic organic pollutants with a chemically stable highly Luminescent Porous Organic Polymer (POP). *ACS Appl. Polym. Mater.* **2022**, *4*, 8633–8644. [\[CrossRef\]](#)
4. Yang, W.; Li, J.; Yao, Z.; Li, M. A review on the alternatives to antibiotics and the treatment of antibiotic pollution: Current development and future prospects. *Sci. Total Environ.* **2024**, *926*, 171757. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Yan, J.; Li, J.; Peng, J.; Zhang, H.; Zhang, Y.; Lai, B. Efficient degradation of sulfamethoxazole by the CuO@Al₂O₃ (EPC) coupled PMS system: Optimization, degradation pathways and toxicity evaluation. *Chem. Eng. J.* **2019**, *359*, 1097–1110. [\[CrossRef\]](#)
6. Ahmadijokani, F.; Ghaffarkhah, A.; Molavi, H.; Dutta, S.; Lu, Y.; Wuttke, S.; Kamkar, M.; Rojas, O.J.; Arjmand, M. COF and MOF hybrids: Advanced materials for wastewater treatment. *Adv. Funct. Mater.* **2023**, *33*, 2305527. [\[CrossRef\]](#)
7. Wang, L.; Yang, C.; Lu, A.; Liu, S.; Pei, Y.; Luo, X. An easy and unique design strategy for insoluble humic acid/cellulose nanocomposite beads with highly enhanced adsorption performance of low concentration ciprofloxacin in water. *Bioresour. Technol.* **2020**, *302*, 122812. [\[CrossRef\]](#) [\[PubMed\]](#)
8. Ayanda, O.S.; Amoo, M.O.; Aremu, O.H.; Oketayo, O.O.; Nelana, S.M. Ultrasonic degradation of ciprofloxacin in the presence of zinc oxide nanoparticles and zinc oxide/acha waste composite. *Res. J. Chem. Environ.* **2023**, *27*, 22–28. [\[CrossRef\]](#)
9. Khan, P.; Saha, R.; Halder, G. Towards sorptive eradication of pharmaceutical micro-pollutant ciprofloxacin from aquatic environment: A comprehensive review. *Sci. Total Environ.* **2024**, *919*, 170723. [\[CrossRef\]](#)
10. Li, Y.; Zhu, W.; Guo, Q.; Wang, X.; Zhang, L.; Gao, X.; Luo, Y. Highly efficient degradation of sulfamethoxazole (SMX) by activating peroxymonosulfate (PMS) with CoFe₂O₄ in a wide pH range. *Sep. Purif. Technol.* **2021**, *276*, 119403. [\[CrossRef\]](#)
11. Oturan, M.A.; Aaron, J.J. Advanced oxidation processes in water/wastewater treatment: Principles and applications. A review. *Crit. Rev. Environ. Sci. Technol.* **2014**, *44*, 2577–2641. [\[CrossRef\]](#)

12. Oyekunle, D.T.; Zhou, X.; Shahzad, A.; Chen, Z. Review on carbonaceous materials as peroxymonosulfate activators: Structure–performance relationship, mechanism and future perspectives on water treatment. *J. Mater. Chem. A* **2021**, *9*, 8012–8050. [\[CrossRef\]](#)
13. Zhao, Q.; Mao, Q.; Zhou, Y.; Wei, J.; Liu, X.; Yang, J.; Luo, L.; Zhang, J.; Chen, H.; Chen, H.; et al. Metal-free carbon materials-catalyzed sulfate radical-based advanced oxidation processes: A review on heterogeneous catalysts and applications. *Chemosphere* **2017**, *189*, 224–238. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Qin, Q.; Gao, X.; Wu, X.; Liu, Y. NaBH₄-treated cobalt-doped g-C₃N₄ for enhanced activation of peroxymonosulfate. *Mater. Lett.* **2019**, *256*, 126623. [\[CrossRef\]](#)
15. Wang, Y.; Cao, D.; Liu, M.; Zhao, X. Insights into heterogeneous catalytic activation of peroxymonosulfate by Pd/g-C₃N₄: The role of superoxide radical and singlet oxygen. *Catal. Commun.* **2017**, *102*, 85–88. [\[CrossRef\]](#)
16. Jiang, H.; Li, Y.; Wang, D.; Hong, X. Recent advances in heteroatom doped graphitic carbon nitride (g-C₃N₄) and g-C₃N₄/Metal Oxide Composite Photocatalysts. *Curr. Org. Chem.* **2020**, *24*, 673–693. [\[CrossRef\]](#)
17. Hu, J.-Y.; Tian, K.; Jiang, H. Improvement of phenol photodegradation efficiency by a combined g-C₃N₄/Fe(III)/peroxymonosulfate system. *Chemosphere* **2016**, *148*, 34–40. [\[CrossRef\]](#) [\[PubMed\]](#)
18. Li, J.; Shen, B.; Hong, Z.; Lin, B.; Gao, B.; Chen, Y. A facile approach to synthesize novel oxygen-doped g-C₃N₄ with superior visible-light photoreactivity. *Chem. Commun.* **2012**, *48*, 12017–12019. [\[CrossRef\]](#) [\[PubMed\]](#)
19. Yu, X.; Wu, X.; Guo, F.; Liu, J.; Zhao, Q. Visible-light-assisted activation of peroxymonosulfate (PMS) over CoO_x@C/g-C₃N₄ composite for efficient organic pollutant degradation. *J. Alloys Compd.* **2023**, *948*, 169702. [\[CrossRef\]](#)
20. Yuan, X.; Leng, Y.; Fang, C.; Gao, K.; Liu, C.; Song, J.; Guo, Y. The synergistic effect of PMS activation by LaCoO₃/g-C₃N₄ for degradation of tetracycline hydrochloride: Performance, mechanism and phytotoxicity evaluation. *New J. Chem.* **2022**, *46*, 12217–12228. [\[CrossRef\]](#)
21. Wang, S.; Liu, Y.; Wang, J. Peroxymonosulfate activation by Fe–Co–O-Codoped graphite carbon nitride for degradation of sulfamethoxazole. *Environ. Sci. Technol.* **2020**, *54*, 10361–10369. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Oh, W.-D.; Chang, V.W.C.; Lim, T.-T. A comprehensive performance evaluation of heterogeneous Bi₂Fe₄O₉/peroxymonosulfate system for sulfamethoxazole degradation. *Environ. Sci. Pollut. Res. Int.* **2019**, *26*, 1026–1035. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Ponzoni, C.; Rosa, R.; Cannio, M.; Buscaglia, V.; Finocchio, E.; Nanni, P.; Leonelli, C. Optimization of BFO microwave-hydrothermal synthesis: Influence of process parameters. *J. Alloys Compd.* **2013**, *558*, 150–159. [\[CrossRef\]](#)
24. Li, X.; Yan, X.; Hu, X.; Feng, R.; Zhou, M.; Wang, L. Hollow Cu-Co/N-doped carbon spheres derived from ZIFs as an efficient catalyst for peroxymonosulfate activation. *Chem. Eng. J.* **2020**, *397*, 125533. [\[CrossRef\]](#)
25. Dong, H.; Guo, X.; Yang, C.; Ouyang, Z. Synthesis of g-C₃N₄ by different precursors under burning explosion effect and its photocatalytic degradation for tylosin. *Appl. Catal. B Environ.* **2018**, *230*, 65–76. [\[CrossRef\]](#)
26. Tong, T.; Cao, W.; Zhang, H.; Chen, J.; Jin, D.; Cheng, J. Controllable phase evolution of bismuth ferrite oxides by an organic additive modified hydrothermal method. *Ceram. Int.* **2015**, *41*, S106–S110. [\[CrossRef\]](#)
27. Zhang, H.; Zhao, L.; Geng, F.; Guo, L.-H.; Wan, B.; Yang, Y. Carbon dots decorated graphitic carbon nitride as an efficient metal-free photocatalyst for phenol degradation. *Appl. Catal. B Environ.* **2016**, *180*, 656–662. [\[CrossRef\]](#)
28. Tang, R.; Gong, D.; Zhou, Y.; Deng, Y.; Feng, C.; Xiong, S.; Huang, Y.; Peng, G.; Li, L.; Zhou, Z. Unique g-C₃N₄/PDI-g-C₃N₄ homojunction with synergistic piezo-photocatalytic effect for aquatic contaminant control and H₂O₂ generation under visible light. *Appl. Catal. B Environ.* **2022**, *303*, 120929. [\[CrossRef\]](#)
29. Sahoo, A.; Das, M.; Mandal, P.; Bhattacharya, D. Hydrothermal synthesis of Bi₂Fe₄O₉ nanochains and study of their multiferroic coupling. *Mater. Lett.* **2021**, *296*, 129905. [\[CrossRef\]](#)
30. Duan, X.; O'Donnell, K.; Sun, H.; Wang, Y.; Wang, S. Sulfur and nitrogen Co-doped graphene for metal-free catalytic oxidation reactions. *Small* **2015**, *11*, 3036–3044. [\[CrossRef\]](#)
31. Li, N.; Li, R.; Duan, X.; Yan, B.; Liu, W.; Cheng, Z.; Chen, G.; Hou, L.A.; Wang, S. Correlation of active sites to generated reactive species and degradation routes of organics in peroxymonosulfate activation by Co-loaded carbon. *Environ. Sci. Technol.* **2021**, *55*, 16163–16174. [\[CrossRef\]](#) [\[PubMed\]](#)
32. Wang, L.; Wang, L.; Shi, Y.; Zhu, J.; Zhao, B.; Zhang, Z.; Ding, G.; Zhang, H. Fabrication of Co₃O₄-Bi₂O₃-Ti catalytic membrane for efficient degradation of organic pollutants in water by peroxymonosulfate activation. *J. Colloid Interface Sci.* **2022**, *607*, 451–461. [\[CrossRef\]](#) [\[PubMed\]](#)
33. Huang, Z.-F.; Song, J.; Pan, L.; Wang, Z.; Zhang, X.; Zou, J.-J.; Mi, W.; Zhang, X.; Wang, L. Carbon nitride with simultaneous porous network and O-doping for efficient solar-energy-driven hydrogen evolution. *Nano Energy* **2015**, *12*, 646–656. [\[CrossRef\]](#)
34. Li, L.; Zhu, Z.H.; Lu, G.Q.; Yan, Z.F.; Qiao, S.Z. Catalytic ammonia decomposition over CMK-3 supported Ru catalysts: Effects of surface treatments of supports. *Carbon* **2007**, *45*, 11–20. [\[CrossRef\]](#)
35. Chen, L.; Zuo, X.; Yang, S.; Cai, T.; Ding, D. Rational design and synthesis of hollow Co₃O₄@Fe₂O₃ core-shell nanostructure for the catalytic degradation of norfloxacin by coupling with peroxymonosulfate. *Chem. Eng. J.* **2019**, *359*, 373–384. [\[CrossRef\]](#)
36. Zhang, H.; Song, Y.; Nengzi, L.-C.; Gou, J.; Li, B.; Cheng, X. Activation of peroxymonosulfate by a novel magnetic CuFe₂O₄/Bi₂O₃ composite for lomefloxacin degradation. *Chem. Eng. J.* **2020**, *379*, 122362. [\[CrossRef\]](#)
37. Li, Y.; Li, J.; Pan, Y.; Xiong, Z.; Yao, G.; Xie, R.; Lai, B. Peroxymonosulfate activation on FeCo₂S₄ modified g-C₃N₄ (FeCo₂S₄-CN): Mechanism of singlet oxygen evolution for nonradical efficient degradation of sulfamethoxazole. *Chem. Eng. J.* **2020**, *384*, 123361. [\[CrossRef\]](#)

38. Wang, S.; Liu, Y.; Wang, J. Iron and sulfur co-doped graphite carbon nitride (FeO_y/S-g-C₃N₄) for activating peroxymonosulfate to enhance sulfamethoxazole degradation. *Chem. Eng. J.* **2020**, *382*, 122836. [[CrossRef](#)]
39. Zhang, P.; Cao, X.; Gu, L.; Yu, H.; Wu, F.; Liu, Y.; Liu, X.; Gao, Y.; Zhang, H. Embedded iron and nitrogen co-doped carbon quantum dots within g-C₃N₄ as an exceptional PMS photocatalytic activator for sulfamethoxazole degradation: The key role of FeN bridge. *Sep. Purif. Technol.* **2024**, *342*, 126975. [[CrossRef](#)]
40. Wang, S.; Xu, L.; Wang, J. Nitrogen-doped graphene as peroxymonosulfate activator and electron transfer mediator for the enhanced degradation of sulfamethoxazole. *Chem. Eng. J.* **2019**, *375*, 122041. [[CrossRef](#)]
41. Ding, Y.; Wang, X.; Fu, L.; Peng, X.; Pan, C.; Mao, Q.; Wang, C.; Yan, J. Nonradicals induced degradation of organic pollutants by peroxydisulfate (PDS) and peroxymonosulfate (PMS): Recent advances and perspective. *Sci. Total Environ.* **2021**, *765*, 142794. [[CrossRef](#)] [[PubMed](#)]
42. Chen, J.; Zhang, L.; Huang, T.; Li, W.; Wang, Y.; Wang, Z. Decolorization of azo dye by peroxymonosulfate activated by carbon nanotube: Radical versus non-radical mechanism. *J. Hazard. Mater.* **2016**, *320*, 571–580. [[CrossRef](#)] [[PubMed](#)]
43. Peng, Y.; Xie, G.; Shao, P.; Ren, W.; Li, M.; Hu, Y.; Yang, L.; Shi, H.; Luo, X. A comparison of SMX degradation by peroxymonosulfate activated with different nanocarbons: Kinetics, transformation pathways, and toxicity. *Appl. Catal. B Environ.* **2022**, *310*, 121345. [[CrossRef](#)]
44. Wang, J.; Wang, S. Effect of inorganic anions on the performance of advanced oxidation processes for degradation of organic contaminants. *Chem. Eng. J.* **2021**, *411*, 128392. [[CrossRef](#)]
45. Ma, J.; Yang, Y.; Jiang, X.; Xie, Z.; Li, X.; Chen, C.; Chen, H. Impacts of inorganic anions and natural organic matter on thermally activated peroxymonosulfate oxidation of BTEX in water. *Chemosphere* **2018**, *190*, 296–306. [[CrossRef](#)]
46. Lou, X.; Wu, L.; Guo, Y.; Chen, C.; Wang, Z.; Xiao, D.; Fang, C.; Liu, J.; Zhao, J.; Lu, S. Peroxymonosulfate activation by phosphate anion for organics degradation in water. *Chemosphere* **2014**, *117*, 582–585. [[CrossRef](#)] [[PubMed](#)]
47. Yang, Y.; Pignatello, J.J.; Ma, J.; Mitch, W.A. Comparison of halide impacts on the efficiency of contaminant degradation by sulfate and hydroxyl radical-based advanced oxidation processes (AOPs). *Environ. Sci. Technol.* **2014**, *48*, 2344–2351. [[CrossRef](#)]
48. Wang, S.; Wang, J. Treatment of membrane filtration concentrate of coking wastewater using PMS/chloridion oxidation process. *Chem. Eng. J.* **2020**, *379*, 122361. [[CrossRef](#)]
49. Thomas, K.; Volz-Thomas, A.; Mihelcic, D.; Smit, H.G.J.; Kley, D. On the exchange of NO₃ radicals with aqueous solutions: Solubility and sticking coefficient. *J. Atmos. Chem.* **1998**, *29*, 17–43. [[CrossRef](#)]
50. Duan, X.; Su, C.; Miao, J.; Zhong, Y.; Shao, Z.; Wang, S.; Sun, H. Insights into perovskite-catalyzed peroxymonosulfate activation: Maneuverable cobalt sites for promoted evolution of sulfate radicals. *Appl. Catal. B Environ.* **2018**, *220*, 626–634. [[CrossRef](#)]
51. Liang, C.; Su, H.-W. Identification of sulfate and hydroxyl radicals in thermally activated peroxymonosulfate. *Ind. Eng. Chem. Res.* **2009**, *48*, 5558–5562. [[CrossRef](#)]
52. Luo, R.; Li, M.; Wang, C.; Zhang, M.; Nasir Khan, M.A.; Sun, X.; Shen, J.; Han, W.; Wang, L.; Li, J. Singlet oxygen-dominated non-radical oxidation process for efficient degradation of bisphenol A under high salinity condition. *Water Res.* **2019**, *148*, 416–424. [[CrossRef](#)] [[PubMed](#)]
53. Chai, H.; Zhang, Z.; Zhou, Y.; Zhu, L.; Lv, H.; Wang, N. Roles of intrinsic Mn³⁺ sites and lattice oxygen in mechanochemical debromination and mineralization of decabromodiphenyl ether with manganese dioxide. *Chemosphere* **2018**, *207*, 41–49. [[CrossRef](#)]
54. Zhang, T.; Ding, Y.; Tang, H. Generation of singlet oxygen over Bi(V)/Bi(III) composite and its use for oxidative degradation of organic pollutants. *Chem. Eng. J.* **2015**, *264*, 681–689. [[CrossRef](#)]

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