

Article

Activation of Peroxymonosulfate by Carbon Nanofiber Supported Fe/Co Bimetallic MOFs for Efficient Degradation of Ceftiofur Sodium

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Abstract

With the rapid development of the pharmaceutical industry and animal husbandry, conventional wastewater treatment plants have difficulty effectively degrading the widely occurring ceftiofur sodium (CEF) in aquatic environments. To address this issue, this study successfully loaded Fe/Co-ZIF onto carbon nanofibers (CNF), thereby preparing Fe/Co-ZIF@CNF composites with well-dispersed supported materials and a stable structure. The as-prepared Fe/Co-ZIF@CNF was further applied in a persulfate-based advanced oxidation system (SR-AOPs) for CEF degradation and exhibited good catalytic performance. When the Fe/Co molar ratio was 1.25:1, the Fe/Co-ZIF_{1.25} material achieved a CEF degradation efficiency, k_{obs} value, and TOC removal rate of 94.0%, 0.135 min⁻¹, and 43.8%, respectively. Radical quenching experiments preliminarily indicated that SO₄^{•-} played a dominant role in the reaction system, while •OH and ¹O₂ also made non-negligible contributions to CEF degradation. This work provides a new strategy for constructing composite catalysts based on carbon nanofiber-supported polymetallic MOFs.

Keywords: carbon nanofibers; MOFs; peroxymonosulfate; ceftiofur sodium; SR-AOPs

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1. Introduction

In recent years, with the rapid development of the pharmaceutical industry and animal husbandry, antibiotic residues have become a major challenge in global water environmental governance [1,2]. As a broad-spectrum cephalosporin antibiotic, CEF has been widely used in livestock farming and aquaculture because of its excellent antibacterial performance [3,4]. However, due to its poor biodegradability and environmental persistence, CEF has frequently been detected in the environment, posing potential threats to ecosystems and human health [5,6]. Consequently, there is a pressing need to explore highly effective and economically viable strategies for CEF degradation.

Traditional wastewater treatment processes are generally ineffective for the removal of residual CEF. Owing to the strong oxidation capacity, wide applicability, and

environmental friendliness, advanced oxidation processes (SR-AOPs) have shown great potential for degrading refractory organic pollutants [7–9]. The core of this technology lies in the activation of PMS through multiple pathways to generate various reactive oxygen species (ROS), which can rapidly degrade or even completely mineralize organic pollutants. Among the many PMS activation strategies, activation by transition metal-based heterogeneous catalysts has demonstrated strong application potential [10–12]. Metal–organic frameworks (MOFs) are porous crystalline architectures constructed through the coordination of inorganic metallic nodes and organic linkers. Their large specific surface area and highly tunable microstructure provide an excellent foundation for the construction of high-performance catalysts [13–15]. Recently, many studies have focused on the degradation of antibiotics through MOF-driven peroxymonosulfate (PMS) self-decomposition [16–19]. Notably, Co-based MOFs exhibit superior catalytic performance for PMS activation. Driven by the dynamic $\text{Co}^{2+}/\text{Co}^{3+}$ redox cycle, they can trigger massive production of reactive oxygen species (ROS), thereby facilitating the rapid elimination of target contaminants.

Owing to their rich redox properties and the cooperative interactions between diverse metal centers, bimetallic and mixed-metal MOFs have recently emerged as a focal point in catalytic PMS activation [20]. For example, Gu et al. prepared Fe/Co bimetallic core–shell MOFs via an epitaxial growth strategy, in which the synergistic interaction between Co and Fe promoted the generation of ROS for the rapid degradation of chlorophenol. Catalytic performance experiments showed that the reaction system could remove 83.68% of chlorophenol within 15 min, with a corresponding reaction rate constant as high as 0.241 min^{-1} [21]. Tang et al. synthesized Co and Cu bimetallic ZIFs via a one-step hydrothermal method and subsequently obtained the bimetallic/carbon composite catalyst $\text{Co}_x\text{Cu}_{10-x}\text{-CNP}$ through high-temperature pyrolysis. Catalytic experiments showed that at pH 6.5, $\text{Co}_x\text{Cu}_{10-x}\text{-CNP}$ achieved 98% chloramphenicol removal within 60 min, with a mineralization rate of 62.5% and a corresponding reaction rate constant of 0.13 min^{-1} [22]. As a typical transition metal, Fe not only exhibits excellent PMS activation ability itself, but also has the advantages of low cost and environmental friendliness. Introducing Fe into Co-based MOFs is expected to accelerate the redox cycling of $\text{Co}^{2+}/\text{Co}^{3+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ through the synergistic interaction between Fe and Co, thereby simultaneously enhancing catalytic performance and suppressing metal ion leaching [23].

However, powdered MOFs still face several challenges in practical water treatment, including easy agglomeration leading to insufficient exposure of active sites, difficulty in solid–liquid separation, and low catalyst recovery efficiency [24]. Immobilizing powdered catalysts on suitable supports is an effective way to overcome these drawbacks. Endowed with superior electrical conductivity, remarkable chemical robustness, and rich surface functionalities, CNFs serve as an optimal substrate for anchoring MOFs [25–27]. The in situ growth or loading of Fe/Co bimetallic MOFs onto the surface of CNF can not only effectively prevent MOF agglomeration and improve their stability and recyclability but also enhance catalytic performance by facilitating electron transfer through the conductivity of the carbon fibers.

Based on this, this study designed a carbon fiber-supported Fe/Co bimetallic MOF composite catalyst, denoted as Fe/Co-ZIF@CNF, and applied it to PMS activation for the efficient degradation of CEF in water. The microstructure, crystal structure, and surface chemical properties of the composite were systematically characterized, and the degradation performance of Fe/Co-ZIF@CNF toward CEF under different reaction parameters was comprehensively evaluated. To comprehensively decipher the underlying PMS activation mechanism, quenching assays were performed to evaluate the specific involvement of both radical and non-radical routes in CEF decomposition. This

work is expected to provide useful insights into the efficient removal of antibiotics and offer a theoretical basis as well as experimental reference for the development of high-performance composite catalysts.

2. Experimental

2.1. Chemicals

Wos1009 carbon cloth, Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), iron chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), 2-methylimidazole (2-MeIm) and acetone were produced by Aladdin Co., Ltd., (Shanghai, China) and used without further purification.

2.2. Pre-Activation of CNF

CNF was obtained by splitting Wos1009 carbon cloth. To activate the material, the isolated CNFs were immersed in 200 mL of acetone and subjected to oil-bath refluxing at 70 °C for 48 h. Following this treatment, the solid was sequentially rinsed three times with ethanol and deionized water, prior to being dried under vacuum at 60 °C overnight.

2.3. Preparation of Fe/Co-ZIF_x@CNF

Initially, Solution A was formulated by dissolving NaOH (0.2 g) and 2-methylimidazole (1.38 g) into 10 mL of deionized water, which was subsequently sonicated for 5 min. Then, 0.116 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.108 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 6 mL of water to prepare solution B. After that, 100 mg of carbon fiber was added to solution B, and the mixture was stirred on a thermostatic magnetic stirrer for 5 h until the solution completely infiltrated the carbon fiber. Subsequently, solution B was slowly added dropwise into solution A under ultrasonic treatment. Following the introduction of all reagents, the mixture was subjected to magnetic stirring for 3 h and subsequently left undisturbed for an equal duration. After standing, the supernatant was removed, and the purplish-red carbon fiber material was taken out with tweezers and transferred into a beaker containing ethanol for repeated washing. This washing step was repeated three times. Subsequently, the collected purple fibers were vacuum-dried at 60 °C for 24 h, yielding the Fe-doped ZIF-67/carbon nanofiber composite. The obtained products were designated as Fe/Co-ZIF_x@CNF, where X represents the feeding molar ratio of Fe/Co during the material synthesis ($X = 0.5, 0.75, 1.0, 1.25, 1.5, 2.0$), and the total amount of Fe and Co salts was 0.8 mmol. Finally, it was placed in a 5 mL centrifuge tube, sealed with parafilm, and stored for later use.

3. Results and Discussion

3.1. Characterization of Fe/Co-ZIF_x@CNF

As shown in Figure 1, the microscopic morphology of the Fe/Co-ZIF@CNF composite was observed and analyzed by scanning electron microscopy (SEM). Figure 1a presents the SEM image of the Fe/Co-ZIF@CNF composite, in which the Fe/Co bimetallic ZIF constructed on the carbon fibers still exhibits a rhombic dodecahedral morphology similar to that of ZIF-67. It can be clearly observed that, after loading onto the nanocarbon fibers, the Fe/Co-ZIF crystals are uniformly distributed over the surface of the nanocarbon fibers. Compared with the Fe/Co-ZIF material, the Fe/Co-ZIF@CNF composite shows better dispersion and a more uniform distribution of the Fe/Co bimetallic ZIF. As shown in Figure 1b, pure CNF consists of fine carbon fibers with a diameter of about 15 µm. During the preparation of the Fe/Co-ZIF material, the crystal size of the ZIF-67-based material increases significantly with increasing Fe/Co ratio. When the Fe/Co doping ratio is 1:1, the diameter of Fe/Co-ZIF is about 0.9 µm, which is larger than that of ZIF-67 at about 0.4 µm. However, after Fe/Co-ZIF is grown on the carbon fibers, the nanocarbon fibers appear to

restrict the growth and agglomeration of MOF microcrystals. As a result, the diameter of the bimetallic ZIF-67 in Fe/Co-ZIF@CNF decreases to about 0.7 μm , indicating that the carbon matrix has a significant effect on the size and distribution of the MOFs.

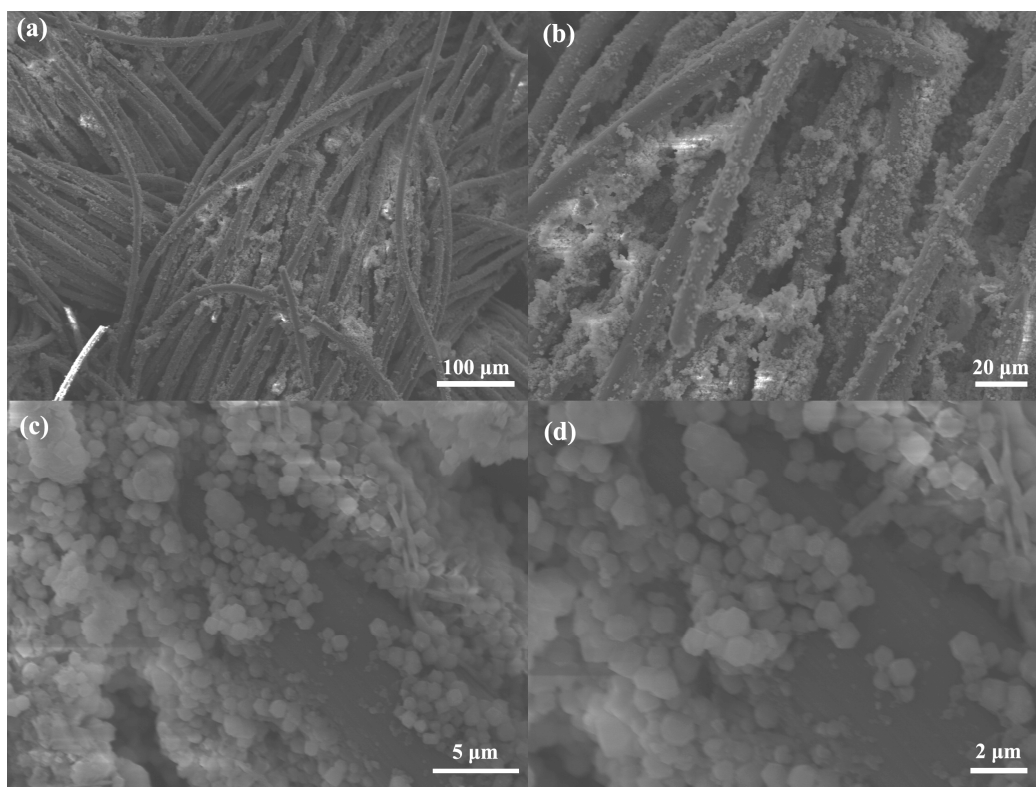


Figure 1. SEM image of bimetallic Fe/Co-ZIF@CNF composites with different scale bars (a) 100 μm , (b) 20 μm , (c) 5 μm , (d) 2 μm .

To investigate the phase composition of the composites after constructing Fe/Co bimetallic ZIF on nanocarbon fibers, as well as the differences from the previously prepared samples, XRD patterns were collected for Fe/Co-ZIF@CNF composites with Fe/Co molar ratios of 1:1 and 2:1, together with nanocarbon fibers. As shown in Figure 2, the Fe/Co-ZIF@CNF composites with different Fe doping ratios all exhibit good crystallinity. For the unmodified CNF sample, the diffractogram displays two distinct broad maxima located at approximately 26° and 43° . These signals are assigned to the (002) and (101) reflection planes of carbon, demonstrating a highly crystallized graphitic framework [28,29]. Independent ZIF-67 synthesized without CNF or Fe exhibits its main characteristic diffraction peaks near 6° , 11° , 16° and 18° , along with several other minor peaks, which is consistent with previously reported results. After Fe doping and growth on CNF, the characteristic peaks of ZIF-67 remain well preserved, indicating that the nanocarbon fibers do not hinder the formation of coordination between $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2-methylimidazole.

In contrast, the characteristic X-ray diffraction peaks of ZIF-67-derived materials, including those from Fe/Co-ZIF to Fe/Co-ZIF@CNF, all shift slightly toward lower angles after preparation. This reflects the influence of lattice constant changes caused by the incorporation of Fe^{3+} , which has a larger ionic size and longer coordination bonds, replacing Co^{2+} in ZIF-67. In addition, after the Fe/Co bimetallic ZIF-67 was successfully prepared on the nanocarbon fiber matrix, a very obvious broad peak corresponding to CNF appeared among the characteristic peaks of Fe/Co-ZIF@CNF. Combined with the

previous SEM images, this further confirms that uniform Fe/Co-ZIF nanoparticles were successfully loaded onto the CNF support.

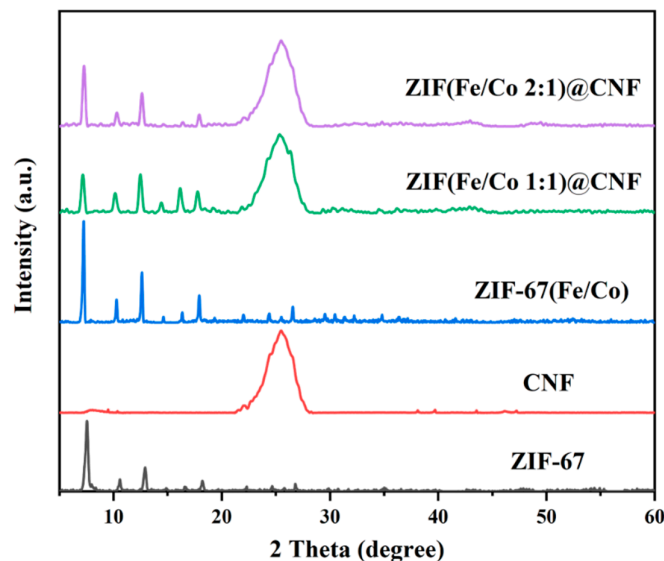


Figure 2. XRD patterns of Fe-Co-ZIF and Fe/Co-ZIF@CNF materials.

The composite was characterized by FT-IR spectroscopy. FT-IR spectra were collected over the range of 500 to 4000 cm^{-1} to confirm the coordination of Co and Fe with the organic ligands as well as the presence of functional groups in the MOFs. As shown in Figure 3, the characteristic peaks in the infrared spectrum of Fe/Co-ZIF@CNF are almost identical to those of ZIF-67 and Fe/Co-ZIF, strongly supporting the successful integration of Fe/Co-ZIF with the carbon fibers. For Fe/Co-ZIF@CNF, the symmetric and asymmetric stretching vibrations of the imidazole ring are observed in the ranges of 650–1300 cm^{-1} and 1300–1550 cm^{-1} , respectively. Peaks located at 1409 cm^{-1} and 1307 cm^{-1} are assigned to the in-plane vibrations of the imidazole ring. The aliphatic C-H stretching band at 929 cm^{-1} indicates that 2-methylimidazole is the main ligand of ZIF-67. This result suggests that, after ZIF-67 is combined with the carbon fibers, the linker based on 2-methylimidazole remains unchanged.

According to previous studies, compared with untreated CNF, some characteristic peaks similar to those of the untreated CNF can still be observed at 3430 cm^{-1} , corresponding to O–H stretching vibrations. However, the peak appearing at 1730 cm^{-1} is attributed to the C=O stretching vibration, which is clearly absent in unmodified CNF [30]. The C=C stretching mode of the benzene ring and the C–N stretching vibration within the 2-methylimidazole framework are responsible for the absorption bands located at 1500 cm^{-1} and 2942 cm^{-1} , respectively. Some studies have also suggested that C–H bonds formed during the synthesis of ZIF-67, owing to the disruption of C–N bonds by Co, may also contribute in this region [31]. The intense signal at approximately 750 cm^{-1} is ascribed to the out-of-plane C–H bending of the benzene ring. Collectively, these spectral findings confirm the effective complexation between the metal centers and organic linkers, verifying the assembly of the MOF and its subsequent immobilization on the CNF support.

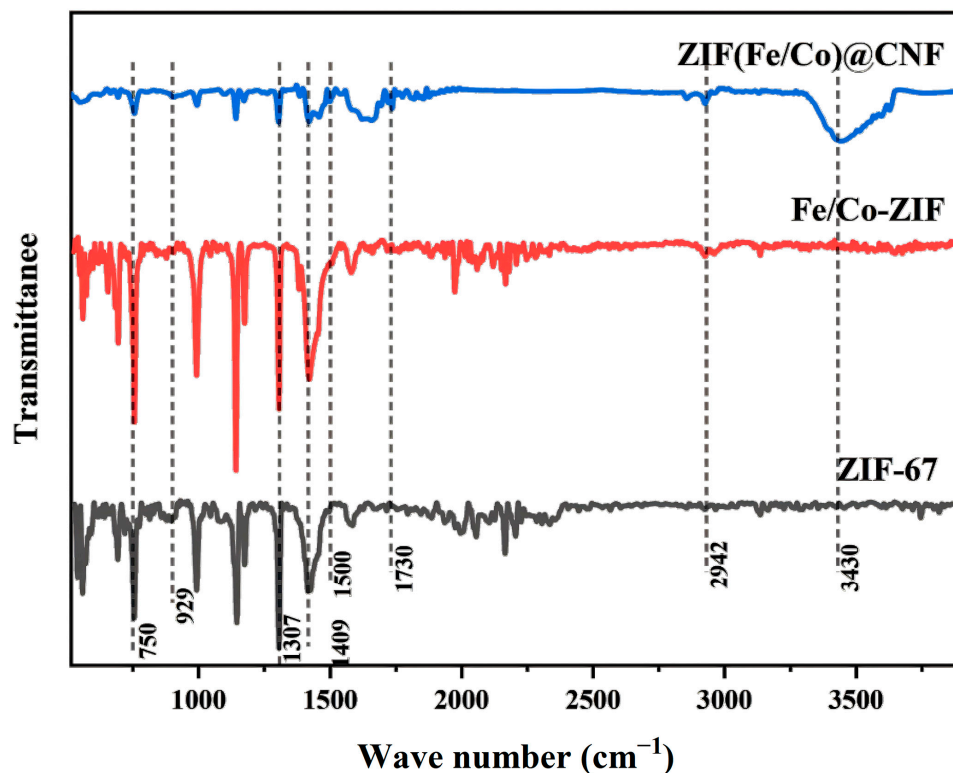


Figure 3. FT-IR spectra of ZIF-67, Fe/Co-ZIF and Fe/Co-ZIF@CNF composites.

To ensure the correctness of the elemental composition of the synthesized Fe/Co-ZIF@CNF composite and to investigate the changes in the valence states of different elements and the molecular structure of the material, XPS analysis was performed on the prepared samples. The XPS survey spectra of the Fe/Co-ZIF@CNF composite are shown in Figure 4a. No significant change in elemental composition was observed for the Fe/Co-ZIF@CNF composite before and after participation in the advanced oxidation reaction; in both cases, characteristic peaks corresponding to C 1s, N 1s, O 1s, Fe 2p, and Co 2p were detected, indicating that Fe/Co-ZIF@CNF is mainly composed of C, N, O, Fe, and Co. Compared with the freshly prepared Fe/Co-ZIF@CNF composite, the N 1s characteristic peak decreased slightly after the reaction, which may be attributed to changes in the framework structure of the composite during the reaction process. The high-resolution C 1s spectrum of the Fe/Co-ZIF@CNF composite is shown in Figure 4b. Three characteristic peaks assigned to C 1s appear at binding energies of 284.6 eV, 286.0 eV, and 288.5 eV. The C–C and C=C linkages within the imidazole framework of Fe/Co-ZIF@CNF contribute to the dominant binding energy signal observed at 284.6 eV [32,33]. The peaks at 286.0 eV and 288.5 eV are assigned to C=N and C–N bonds in the composite, respectively, indicating that the framework of Fe/Co-ZIF@CNF contains a large amount of nitrogen.

As depicted in Figure 4c, the high-resolution Fe 2p spectrum reveals the coexistence of iron in various oxidation states, which can be resolved into eight constituent peaks through curve-fitting. The two characteristic peaks located at 710.5 eV and 724.0 eV correspond to Fe²⁺, while the peaks at 712.4 eV and 726.2 eV are assigned to Fe³⁺. The satellite peaks corresponding to Fe²⁺ and Fe³⁺ are located at 714.1 eV, 718.6 eV, 732.1 eV, and 733.8 eV, respectively. The fitting results of these characteristic peaks strongly confirm that the major valence states of Fe in the Fe/Co-ZIF@CNF composite are divalent and trivalent. Figure 4d shows the high-resolution Co 2p spectrum. In the Co 2p region, the signals at 781.3 eV and 796.8 eV are identified as Co 2p 3/2 and Co 2p 1/2, respectively, with each being accompanied by its corresponding shake-up satellite at 785.9 eV and 802.5

eV. These results indicate that Co exists in the divalent state in the freshly prepared Fe/Co-ZIF@CNF composite.

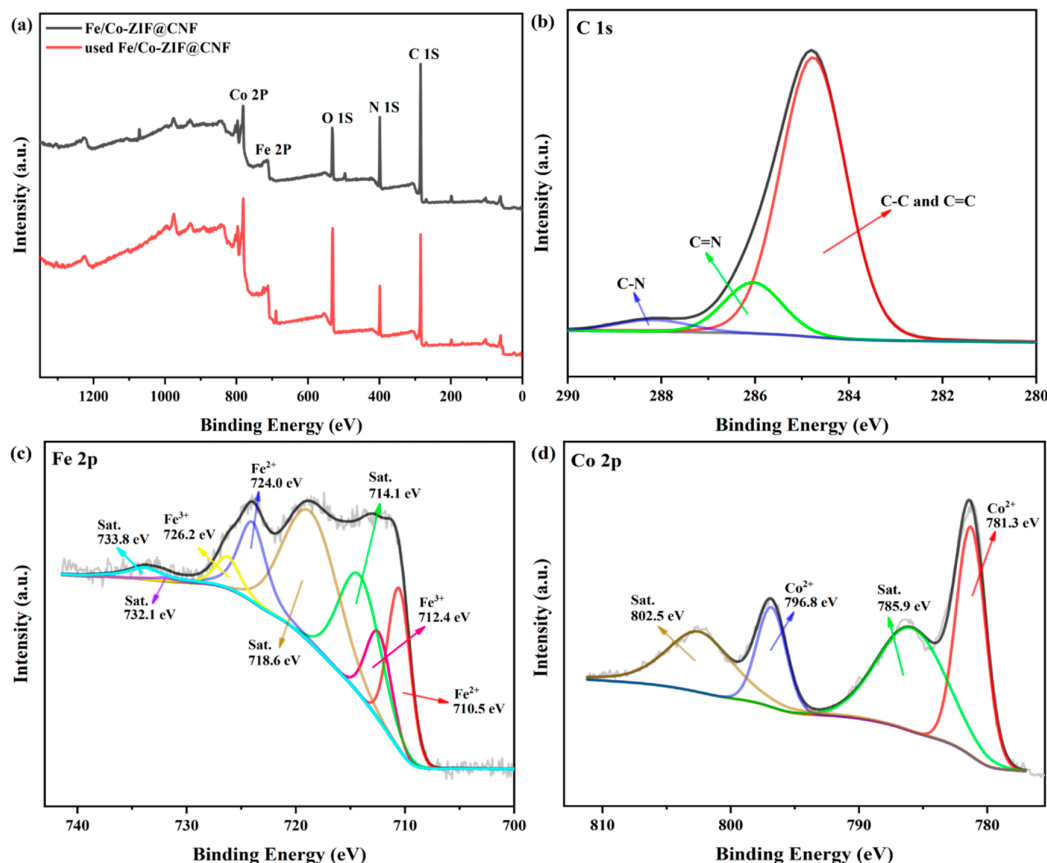


Figure 4. (a) XPS spectra of Fe/Co-ZIF@CNF before and after the reaction; (b) XPS spectra of C 1s; (c) XPS spectra of Fe 2p; (d) XPS spectra of Co 2p.

3.2. Catalytic Performance of Fe/Co-ZIF@CNF

During the experiments, in order to eliminate the influence of adsorption on the evaluation of the advanced oxidation performance of the Fe/Co-ZIF@CNF/PMS system, a pre-adsorption test lasting 30 min was carried out. During the pre-adsorption process, we found that, unlike ZIF-based materials reported in many studies, which usually exhibit high adsorption performance for various pollutants due to their ultrahigh specific surface area and unique pore structure, the Fe/Co-ZIF@CNF composite showed only weak adsorption capacity toward ceftiofur sodium. After the 30 min pre-adsorption experiment, the concentration of ceftiofur sodium in the reaction system did not decrease significantly. After the pre-adsorption experiment, PMS was added and activated through contact with the active sites on the surface of the Fe/Co-ZIF@CNF composite in solution. As shown in Figure 5, when the Fe/Co molar ratio was 0.5:1, the degradation rate of the Fe/Co-ZIF@CNF/PMS system was relatively slow, and only 84.5% of ceftiofur sodium was degraded after 20 min of reaction. With the gradual increase in the Fe/Co ratio in the composite, the degradation rate of the reaction system also increased correspondingly. When the Fe/Co ratios were 0.75:1 and 1:1, the Fe/Co-ZIF@CNF/PMS system achieved CEF degradation efficiencies of 89.9% and 93.3% within 20 min, respectively. When the Fe/Co molar ratio in the composite reached 1.25:1, the degradation performance of Fe/Co-ZIF@CNF toward CEF reached its maximum, and the degradation efficiency of the reaction system reached 94.0%.

These experimental data strongly demonstrate that Fe doping promotes the catalytic performance of the Fe/Co-ZIF@CNF composite. However, with a further increase in the Fe/Co ratio, the advanced oxidation performance of the system declined. As shown in Table 1, when the Fe doping ratios were 1.5:1 and 2:1, the degradation efficiencies of CEF within 20 min decreased to 85.8% and 87.6%, respectively. Combined with the previous characterization results and the specific preparation process of the composite, it is speculated that when the amount of Fe introduced exceeds a certain level, the Fe/Co bimetallic ZIF-67 can no longer be stably synthesized, and the loading amount on the nanocarbon fibers also decreases. This indicates that although doping an appropriate amount of Fe into Co-based ZIF-67 can effectively enhance the catalytic performance of Fe/Co-ZIF@CNF, the incorporation of Fe has a definite limit. Furthermore, despite the limited number of studies on the degradation of CEF by MOF-derived materials reported to date, the material fabricated in this study demonstrated favorable catalytic performance (Table S1).

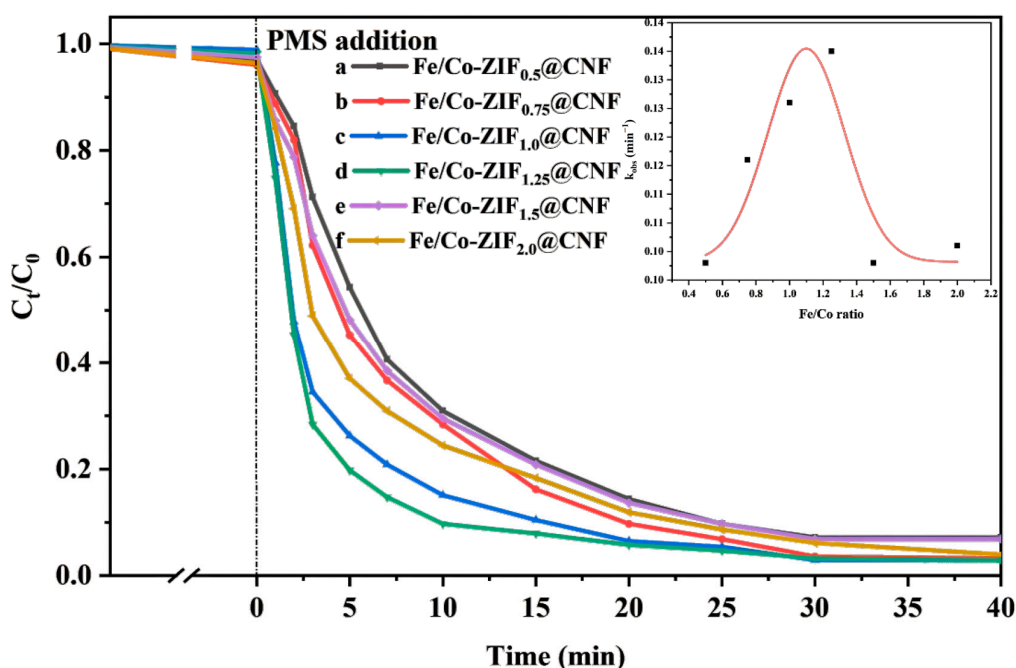


Figure 5. Catalytic properties of Fe/Co-ZIF@CNF composites with different Fe/Co ratios. C_0 (CEF) = 30 mg/L, Co-ZIF@CNF = 0.1 g/L, C_0 (PMS) = 0.3 g/L, and pH = 7 (without adjustment).

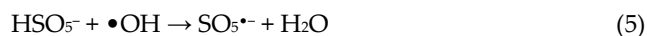
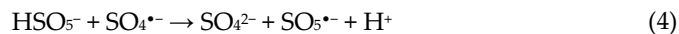
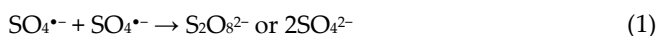
Table 1. Catalytic properties of materials with different Fe/Co molar ratios.

Catalysts	Removal Rate (%)	k_{obs} (min ⁻¹)
Fe/Co-ZIF _{0.5} @CNF	84.5	0.098
Fe/Co-ZIF _{0.75} @CNF	89.9	0.116
Fe/Co-ZIF _{1.0} @CNF	93.3	0.126
Fe/Co-ZIF _{1.25} @CNF	94.0	0.135
Fe/Co-ZIF _{1.5} @CNF	85.8	0.098
Fe/Co-ZIF _{2.0} @CNF	87.6	0.101

The dosage of PMS has a significant impact on the catalytic performance of the catalyst. Figure 6 and Table 2 show the effect of different PMS dosages on CEF degradation, and the inset presents the apparent rate constants under different PMS conditions. As shown in Figure 6a, with the dosage of Fe/Co-ZIF@CNF fixed at 0.1 g/L, the performance of the Fe/Co-ZIF@CNF composite in catalytic degradation of ceftiofur

sodium by activating PMS was investigated. During the experiment, it was found that CEF was hardly degraded when PMS was used alone, indicating that PMS by itself has weak catalytic capability and must be activated by the active sites on the surface of Fe/Co-ZIF@CNF as a catalyst. To evaluate the impact of oxidant concentration, the influence of varying PMS dosages on CEF degradation was investigated while maintaining a constant Fe/Co-ZIF@CNF loading. Elevating the PMS dosage from 10 mg to 20 mg led to a modest improvement in CEF removal efficiency from 91.6% to 93.9%, with a corresponding rise in the k_{obs} value from 0.093 min^{-1} to 0.101 min^{-1} . This phenomenon can be attributed to the improved contact between PMS and the surface of the composite as the PMS dosage increases, allowing more active sites on the material surface to be utilized. As a result, more ROS can be generated in the Fe/Co-ZIF@CNF/PMS system during the reaction, accelerating the oxidative degradation of CEF.

When the PMS dosage was 25 mg, the CEF degradation efficiency of the Fe/Co-ZIF@CNF/PMS system reached 94.0%, with a corresponding k_{obs} value of 0.116 min^{-1} . With a further increase in PMS dosage to 30 mg, the degradation efficiency of CEF increased to 94.4%, and the k_{obs} value reached 0.121 min^{-1} . However, when the PMS dosage was further increased to 40 mg and 50 mg, the degradation efficiency of the reaction system decreased instead, with degradation rates within 20 min dropping to 92.5% and 75.1%, respectively, and the k_{obs} values decreasing to 0.108 min^{-1} and 0.053 min^{-1} , respectively. This may be because excessive $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ can be consumed by themselves, leading to PMS self-quenching reactions (Equations (1)–(3)) [34], thereby weakening the degradation performance of the Fe/Co-ZIF@CNF/PMS system toward CEF. Some low-oxidation-activity species can also be generated through the reaction of $\text{SO}_4^{\bullet-}$ or $\bullet\text{OH}$ with excess PMS (HSO_5^-) (Equations (4)–(6)). In addition, as the PMS dosage increases, the insufficient number of active sites on Fe/Co-ZIF@CNF can also lead to a decrease in catalytic activity. It is worth noting that, according to previous studies, it can be inferred that nanocarbon fibers, as the matrix structure, may facilitate rapid electron transfer and promote PMS activation. Considering both pollutant degradation efficiency and catalytic reaction cost, a PMS dosage of 0.3 g/L was selected as the appropriate concentration.



The solution pH plays a pivotal role in governing the chemical speciation of PMS, modulating the surface physicochemical properties of the composite, and ultimately determining the yield of reactive radicals. The pK_a of PMS is 9.4. When $\text{pH} < 9.4$, PMS activation mainly produces HSO_5^- with strong catalytic activity, whereas when $\text{pH} > 9.4$, SO_5^{2-} with lower catalytic activity is formed. Compared with SO_5^{2-} , HSO_5^- has stronger oxidation ability and is more favorable for generating $\text{SO}_4^{\bullet-}$. As shown in Figure 6b, when the pH ranged from 5 to 8, the degradation efficiency of CEF in the reaction system exceeded 93% within 20 min. However, in a solution with $\text{pH} = 3$, the CEF degradation efficiency dropped to 83.1%. This is because excess H^+ can scavenge $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ radicals, thereby inhibiting CEF degradation [35,36]. In addition, under lower pH conditions, PMS exists mainly in the form of H_2SO_5 , which has lower catalytic activity and

hinders the generation of $\text{SO}_4^{\bullet-}$. Moreover, although it can still be activated for oxidation during the reaction, the Fe/Co-ZIF@CNF composite may also suffer severe metal leaching and structural damage [37]. Some studies have suggested that H^+ adsorbed on the O–O group of PMS can also increase interfacial repulsion between PMS and the catalyst, thereby affecting the catalytic reaction [38]. The hydrolysis product (CoOH^+) formed under acidic conditions may also limit the conversion of Co^{3+} to Co^{2+} in the system, thereby suppressing subsequent reactions. Therefore, under lower pH conditions, the overall catalytic oxidation efficiency of the Fe/Co-ZIF@CNF/PMS system is significantly reduced.

However, when the pH of the reaction system gradually increased to 10 and 11, the degradation efficiency decreased to 50.3% and 59.2%, respectively. This phenomenon may be because, in a strongly alkaline environment, $\bullet\text{OH}$ plays a greater role than $\text{SO}_4^{\bullet-}$ in the Fe/Co-ZIF@CNF/PMS system, and changes in the dominant reactive radicals lead to changes in the degradation performance of the system. PMS is unstable under alkaline conditions and can undergo self-quenching through a non-radical pathway, thereby reducing the removal efficiency of the reaction system (Equation (7)). A large amount of $\bullet\text{OH}$ can also form polyhydroxy surface complexes during the reaction, which attach to the catalyst surface and hinder contact between the catalyst and PMS, and this may be another reason for the reduced degradation efficiency of the Fe/Co-ZIF@CNF/PMS system. Furthermore, the reaction system exhibited strong resistance to interference from various common coexisting anions and natural macromolecular organic matter (humic acid), with only HCO_3^- showing a noticeable inhibitory effect on the catalytic performance (Figures S2 and S3).

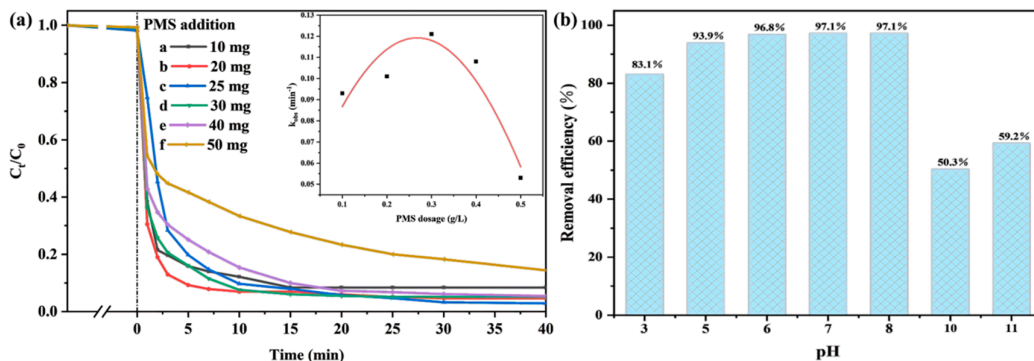
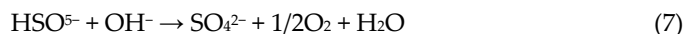


Figure 6. (a) Effects of different PMS dosages on CEF degradation; (b) effect of different pHs on catalytic performance of Fe/Co-ZIF@CNF composites. C_0 (CEF) = 30 mg/L, Co-ZIF@CNF = 0.1 g/L, C_0 (PMS) = 0.3 g/L, and pH = 7 (without adjustment).

Table 2. Catalytic properties of materials with different PMS dosages.

PMS Concentration	Removal Rate (%)	k_{obs} (min ⁻¹)
10 ppm	91.6	0.093
20 ppm	93.9	0.101
25 ppm	94.0	0.116
30 ppm	94.4	0.121
40 ppm	92.5	0.108
50 ppm	75.1	0.053

Although Fe/Co-ZIF@CNF exhibited high catalytic performance and application potential in the above experiments, its reusability is of great importance in practical wastewater treatment. Therefore, batch-wise continuous degradation experiments of

ceftiofur sodium using Fe/Co-ZIF@CNF were conducted, and the degradation efficiency data over multiple cycles were collected. As shown in Figure 7, in the second cycling experiment, the degradation efficiency of CEF within 20 min decreased from 97.0% to 93.8%. In the third cycle, the degradation efficiency of Fe/Co-ZIF@CNF toward CEF dropped significantly to 83.3% and further decreased to 74.0% in the fourth cycle. The deactivation of the Fe/Co-ZIF@CNF composite may be due to the adsorption of CEF or related intermediates on the catalyst surface during the reaction process, which reduces the number of active sites available for reaction and thus affects the reaction progress. In addition, insufficiently tight coupling between Fe/Co-ZIF and the nanocarbon fibers during the preparation process may have caused partial detachment of Fe/Co-ZIF during the reaction and subsequent regeneration. ICP-MS characterization revealed that after the fourth reaction, the concentrations of Fe ions and Co ions in the solution were 1.37 mg/L and 0.41 mg/L, respectively. This result further confirms that ion leaching and active site detachment are among the primary reasons for the decline in catalytic performance.

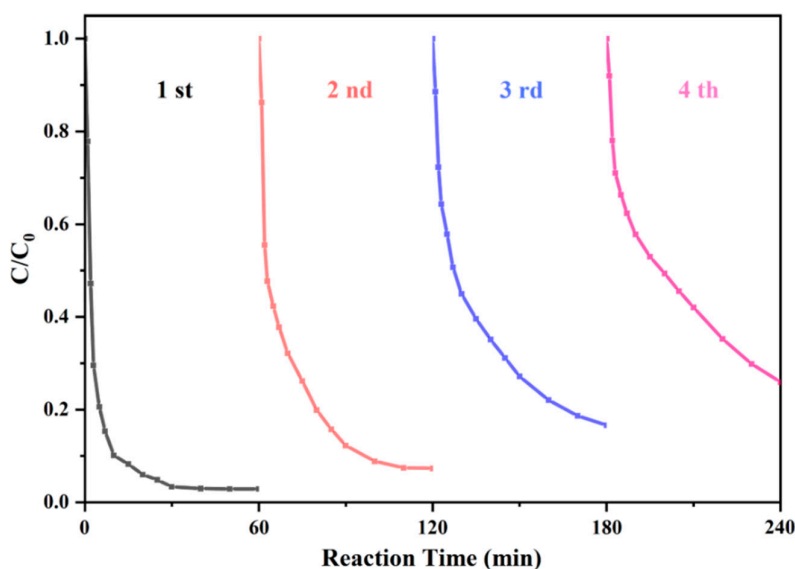


Figure 7. The reusability of Fe/Co-ZIF@CNF for the CEF degradation. C_0 (CEF) = 30 mg/L, Co-ZIF@CNF = 0.1 g/L, C_0 (PMS) = 0.3 g/L, and pH = 7 (without adjustment).

In practical wastewater treatment, ceftiofur sodium may be removed through multiple pathways such as adsorption or degradation. Therefore, the mineralization efficiency of the reaction needs to be determined to evaluate the extent to which CEF is completely degraded. The mineralization of CEF was evaluated by quantifying the residual organic carbon via TOC analysis (Figure 8). For the Fe/Co-ZIF@CNF/PMS system, the TOC removal efficiencies reached 40.1% and 41.9% at Fe/Co molar ratios of 0.5:1 and 0.75:1, respectively. When Fe/Co-ZIF@CNF composites with Fe/Co ratios of 1:1 and 1.25:1, which exhibited better catalytic performance, were used, the TOC removal efficiencies of the Fe/Co-ZIF@CNF/PMS system toward CEF increased to 43.2% and 43.8%, respectively. This indicates that, with an appropriate Fe loading, more than 43% of CEF can be completely removed. Moreover, compared with the TOC removal efficiency of Fe/Co-ZIF materials, the TOC removal efficiencies of the nanocarbon-fiber-supported Fe/Co-ZIF_{1.0}@CNF and Fe/Co-ZIF_{1.25}@CNF composites toward CEF were improved by more than 5%. However, when the Fe/Co molar ratio was increased to 1.5:1 and 2:1, the TOC removal efficiencies of the Fe/Co-ZIF@CNF/PMS system were 43.4% and 41.1%, respectively. This suggests that more Fe is not necessarily better, and selecting an appropriate Fe loading is crucial for improving the catalytic performance of Fe/Co-ZIF.

To benchmark the enhanced advanced oxidation performance of the Fe/Co-ZIF@CNF composites, Table 3 compiles key catalytic metrics, namely, the CEF removal efficiency, k_{obs} , and TOC reduction rate. This allows for a systematic comparison across formulations with varying Fe/Co ratios, alongside the pristine ZIF-67 and Fe/Co-ZIF materials. As shown in Table 3, Fe/Co-ZIF@CNF, prepared by loading Fe/Co-ZIF onto nanocarbon fibers, exhibited higher CEF degradation efficiency and reaction rate, as well as higher TOC removal efficiency, than conventional ZIF-67 and Fe/Co-ZIF materials. The catalytic performance was markedly optimized as the Fe/Co molar ratio reached 1.25:1. The degradation efficiency, k_{obs} value, and TOC removal efficiency of Fe/Co-ZIF_{1.25} reached 94.0%, 0.135 min⁻¹, and 43.8%, respectively, showing a marked improvement compared with Fe/Co-ZIF.

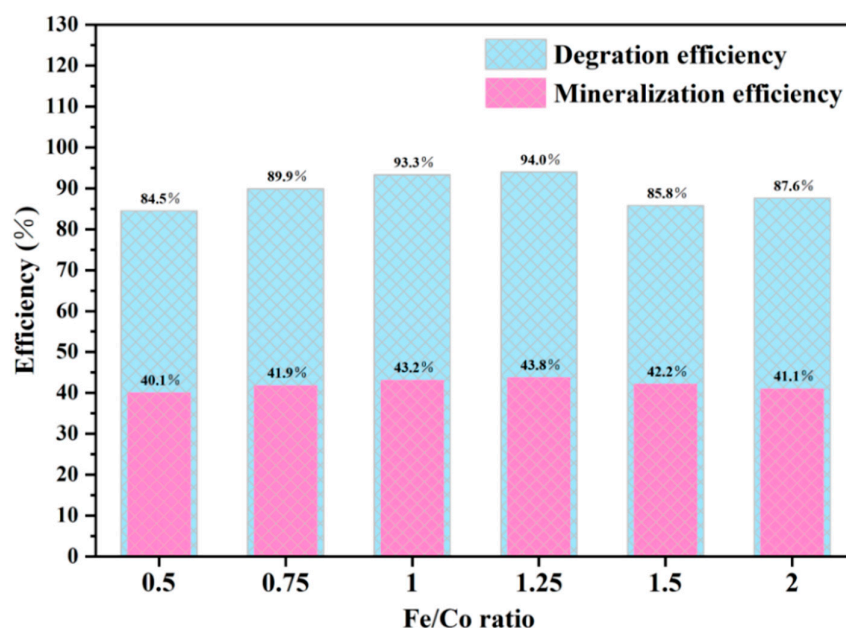


Figure 8. Mineralization rate of CEF degraded by Fe/Co-ZIF@CNF with different Fe/Co ratios. C_0 (CEF) = 30 mg/L, Co-ZIF@CNF = 0.1 g/L, C_0 (PMS) = 0.3 g/L, and pH = 7 (without adjustment).

Table 3. Catalytic properties of different materials.

Catalysts	Removal Rate (%)	k_{obs} (min ⁻¹)	TOC Removal (%)
ZIF-67	81.3	0.085	32.1
Fe/Co-ZIF _{1.0}	91.4	0.101	37.6
Fe/Co-ZIF _{1.25}	91.4	0.105	38.4
Fe/Co-ZIF _{1.5}	88.7	0.091	32.9
Fe/Co-ZIF _{1.0} @CNF	93.3	0.126	43.2
Fe/Co-ZIF _{1.25} @CNF	94.0	0.135	43.8
Fe/Co-ZIF _{1.5} @CNF	85.8	0.098	42.2

3.3. Catalytic Mechanisms

After the introduction of Fe, in order to distinguish the dominant role of specific radicals in pollutant degradation in the Fe/Co-ZIF@CNF/PMS system, methanol (1000 mM, Meth), tert-butanol (1000 mM, TBA), and furfuryl alcohol (1000 mM, FFA) were used in this chapter to quench $\bullet\text{OH}$, $\text{SO}_4^{\bullet-}$ and $^1\text{O}_2$ that may be generated during the reaction in the Fe/Co-ZIF@CNF/PMS system. Previous studies have extensively documented the reactive radicals generated by the redox reaction involving peroxide bond cleavage of PMS initiated by catalytic materials [39–41]. Within the ZIF-67/PMS framework, the

intrinsic cobalt sites act as the primary catalytic centers for peroxymonosulfate activation. Specifically, the continuous redox cycling between Co^{2+} and Co^{3+} facilitates the decomposition of HSO_5^- , thereby yielding highly reactive $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$. The strongly oxidative $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ can effectively degrade pollutants into reaction intermediates and further transform them into nontoxic small molecules.

Meth is a selective radical scavenger, with rate constants of 3.2×10^7 and $9.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$, respectively [21]. As shown in Figure 9, the degradation of CEF was significantly inhibited after the addition of methanol. Compared with the condition without methanol, the degradation efficiency of CEF in the reaction system decreased from 92.7% to 37.4%, indicating incomplete quenching during the removal process and suggesting that $\bullet\text{OH}$ and $\text{SO}_4^{\bullet-}$ may both participate to some extent in the degradation of CEF. To further identify the ROS in the reaction system, tert-butanol was selected as the scavenger for $\bullet\text{OH}$. Its rate constant with $\bullet\text{OH}$ is $3.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, while its rate constant with $\text{SO}_4^{\bullet-}$ is $4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. Therefore, it is regarded as a scavenger for $\bullet\text{OH}$. After adding 1000 mM TBA, the degradation efficiency of the Fe/Co-ZIF@CNF/PMS system decreased from 92.7% to 84.3%, showing only a slight inhibitory effect on CEF degradation. This indicates that $\bullet\text{OH}$ is not the main reactive radical in the system, while $\text{SO}_4^{\bullet-}$ plays the dominant role during the reaction, and $\bullet\text{OH}$ contributes as a secondary radical to CEF degradation. In addition, when TBA was added to the CEF solution containing PMS, the degradation performance of the Fe/Co-ZIF@CNF/PMS system was not greatly affected. In contrast, when 1000 mM methanol was added, the degradation performance of the reaction system was strongly affected. This may be attributed to the complexity and stability of the CEF structure. Compared with the less oxidative $\bullet\text{OH}$, $\text{SO}_4^{\bullet-}$ exhibited stronger oxidation capability to decompose CEF, thereby achieving its degradation.

During the reaction, PMS may also be activated to form $^1\text{O}_2$ to promote CEF degradation, and many studies regard $^1\text{O}_2$ as an important ROS formed during PMS activation. Therefore, FFA was added at a concentration of 1000 mM as a quencher to remove any $^1\text{O}_2$ that may be generated in the reaction system. It can be observed that after adding 1000 mM FFA, the degradation efficiency of CEF decreased only slightly from 92.7% to 90.3%, indicating that only a small amount of $^1\text{O}_2$ may have been produced in the reaction system. Thus, $^1\text{O}_2$ is not the dominant ROS in the system.

EPR characterization was used to further characterize the reactive oxygen species generated in the system during the reaction. As shown in Figure S4, DMPO was employed to capture $\text{SO}_4^{\bullet-}/\bullet\text{OH}$ and $\text{O}_2^{\bullet-}$, while TEMP was used to trap $^1\text{O}_2$. It can be observed that no characteristic signals corresponding to DMPO- $\text{SO}_4^{\bullet-}$ or DMPO- $\bullet\text{OH}$ adducts appeared in the EPR spectra; instead, high-intensity characteristic peaks of DMPO-X, a product of DMPO oxidation exhibiting hyperfine splitting, were detected. This suggests that the DMPO- $\text{SO}_4^{\bullet-}$ or DMPO- $\bullet\text{OH}$ adducts generated in the system may have been further oxidized by some non-radical reactive oxygen species. Furthermore, upon the addition of TEMP, the typical characteristic signal of TEMP- $^1\text{O}_2$ was observed, but its signal intensity was evidently lower than that of DMPO-X, indicating that the contribution of $^1\text{O}_2$ to CEF degradation is likely lower than that of $\text{SO}_4^{\bullet-}/\bullet\text{OH}$. Meanwhile, characteristic signals attributable to DMPO- $\text{O}_2^{\bullet-}$ were also detected in the reaction system. Given the relatively low reactivity of $\text{O}_2^{\bullet-}$, it is more likely to participate in the reaction process as one of the sources of $^1\text{O}_2$. In summary, it is preliminarily inferred that $\text{SO}_4^{\bullet-}$ is the main reactive species in the Fe/Co-ZIF@CNF/PMS system, and the contribution of ROS to CEF degradation follows the order $\text{SO}_4^{\bullet-} > \bullet\text{OH} > ^1\text{O}_2$.

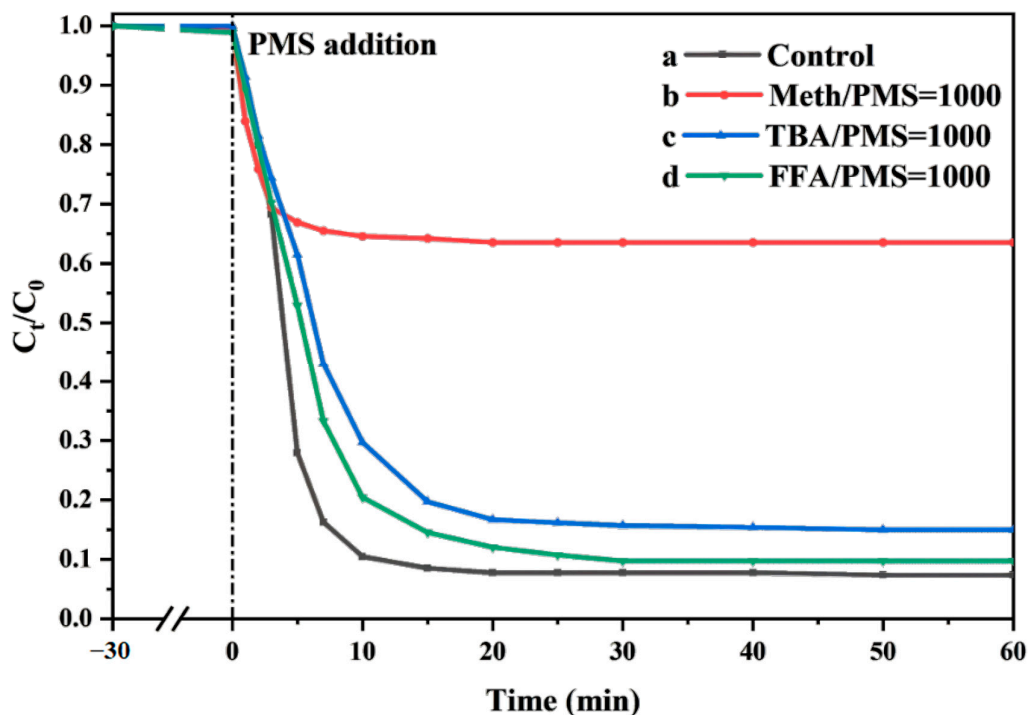


Figure 9. Effect of different scavengers on CEF degradation efficiency in Fe/Co-ZIF@CNF/PMS system. C_0 (CEF) = 30 mg/L, Co-ZIF@CNF = 0.1 g/L, C_0 (PMS) = 0.3 g/L, and pH = 7 (without adjustment).

Although the XPS survey spectra did not show any obvious change in the elemental composition of the Fe/Co-ZIF@CNF composite before and after the reaction, the elements and valence states in the material may still change during the reaction. Therefore, XPS was used to analyze the valence-state changes in Fe and Co in the Fe/Co-ZIF@CNF composite before and after CEF degradation. As shown in Figure 10, the valence states of both Fe and Co in the Fe/Co-ZIF@CNF composite changed to some extent before and after the reaction. The Fe 2p spectrum of the material is shown in Figure 10a. The Fe 2p $3/2$ peak can be fitted into two peaks at 710.5 eV and 712.4 eV, corresponding to Fe^{2+} and Fe^{3+} , respectively. According to curve integration, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in the freshly prepared Fe/Co-ZIF@CNF composite was 1.90. After the reaction, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio decreased to 1.63, indicating that Fe^{2+} participated in PMS activation during the advanced oxidation process and was partially consumed and converted into Fe^{3+} . Similar transformation from Fe^{2+} to Fe^{3+} has also been reported in related studies [42].

To elucidate the dynamic valence shifts in Co during the catalytic process, the core-level Co 2p spectrum of the spent composite was analyzed (Figure 10b). In stark contrast to the pristine sample, the post-reaction spectrum can be deconvoluted into six distinct sub-peaks. Specifically, the binding energies at 781.5 eV and 796.9 eV are assigned to the Co 2p $3/2$ and Co 2p $1/2$ orbitals of Co^{2+} . Concurrently, the emergence of new peaks at 780.5 eV and 796.0 eV signifies the presence of Co^{3+} species, with their associated shake-up satellites identified at 786.0 eV and 802.7 eV. This indicates that Co^{2+} was converted to Co^{3+} after participating in PMS activation during the Fe/Co-ZIF@CNF/PMS reaction. The above XPS results show that both $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Co}^{2+}/\text{Co}^{3+}$ participated to some extent in the PMS activation process for CEF degradation. In addition, due to differences in redox potential, electron transfer reactions may also occur between Fe^{2+} and Co^{3+} during CEF degradation.

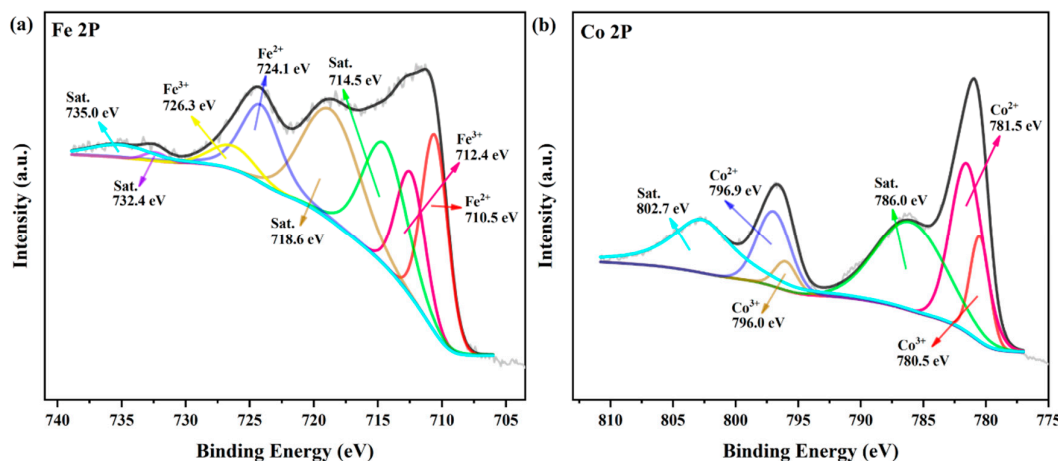


Figure 10. (a) XPS spectra of Fe 2p in used Fe/Co-ZIF@CNF; (b) XPS spectra of Co 2p in used Fe/Co-ZIF.

4. Conclusions

In this study, to improve the catalytic performance and recyclability of the material, a Fe/Co-ZIF@CNF composite with well-dispersed supported species and a stable structure was successfully prepared by loading Fe/Co-ZIF onto CNF. The morphology, elemental composition, and surface functional group changes in the obtained material were comprehensively characterized using SEM, XRD, FT-IR, XPS, and other techniques. The catalytic performance tests showed that when the Fe/Co molar ratio was 1.25:1, the Fe/Co-ZIF@CNF composite exhibited good degradation performance toward CEF, achieving 94% CEF degradation within 20 min. Systematic physicochemical characterization and radical quenching experiments demonstrated that the dominant ROS in the reaction system was the $\text{SO}_4^{\bullet-}$, while $\bullet\text{OH}$ and $^1\text{O}_2$ played auxiliary roles in the degradation of CEF. The synergistic effect between Fe and Co, as well as the confinement and dispersion effect of the CNF support on the MOFs, were the main reasons for the high catalytic performance of the composite. In addition, the Fe/Co-ZIF@CNF composite was applicable over a relatively wide pH range, indicating potential for practical applications. However, the poor reusability still needs to be further improved in subsequent experiments. In summary, this study provides new insights into the development of MOF-based composite catalysts with efficient removal of CEF.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/pr14132150/s1>, Text S1. Characterization, Text S2. Catalytic degradation experiment, Figure S1. Removal efficiency of different reaction systems for CEF; Figure S2. Effect of inorganic anions on CEF removal; Figure S3. Effect of HA on CEF removal. Removal efficiency of different reaction systems for CEF; Figure S4. EPR spectra of PMS activation on Fe/Co-ZIF@CNF with TEMP and DMPO as the trapping agent; Table S1. Comparison of catalytic activity of Fe/Co-ZIF@CNF with previous reported metal based catalysts.

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Data Availability Statement: Due to privacy concerns, the data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

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