Co$_3$O$_4$–CuO bimetallic catalyst activated PMS to degrade LEV in wastewater: the existence of dual degradation mechanisms†

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In this study a Co$_3$O$_4$–CuO bimetallic catalyst (referred to as CCO) was synthesized using the co-precipitation method. The structure of the catalyst was determined and analyzed using scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, and X-ray photoelectron spectroscopy (XPS). The results provide evidence that the CCO bimetallic catalyst has been successfully prepared, and the surface was rich in oxygen vacancies (Ov). The effects of different factors on the removal of levofloxacin (LEV) by the CCO activated peroxymonosulfate (PMS) system were compared. In the CCO/PMS reaction system, LEV degradation was observed at 85% within 10 minutes and reached a total of 97% within an hour when the CCO dosage was maintained at 0.2 g L$^{-1}$, the PMS dosage was at 0.8 g L$^{-1}$, and the pH level was kept constant at 7. It was also proven that CCO could efficiently degrade LEV (degradation rate over 83%) within a wide pH range (pH = 3–11). Quenching studies demonstrated the predominant role of singlet oxygen (1O$_2$) in LEV degradation, alongside contributions from sulfate (SO$_4$$^-$) and hydroxyl (•OH) radicals. The catalyst could stably and efficiently degrade LEV and most common antibiotics, demonstrating great potential for practical wastewater treatment.

1 Introduction

Fluoroquinolones, as a class of highly effective antibiotics, are prevalent in treating bacterial infections in humans and other animal species.$^{1,2}$ LEV, as a widely used member of the fluoroquinolone class, is commonly prescribed for respiratory infections and other diseases.$^4$ However, LEV is not metabolized in a timely manner$^4$ and enters groundwater directly or indirectly through excretion by organisms.$^5$ Humans and other animals might be exposed to LEV again through their diet, as it can be passed through the food chain. The scenario of LEV resistance growing via the food chain presents a critical challenge to the wellbeing of humans and the preservation of the ecological environment.$^6$ Microorganisms in nature, as well as traditional water treatment technologies, are not effective in removing LEV from water bodies.$^7$ Therefore, developing effective methods to control LEV pollution has become an urgent issue.$^8$

Advanced oxidation processes (AOPs) utilize chemical oxidants to generate oxidative radicals that are effective in degrading pollutants.$^9$ In the organic pollutant breakdown process, sulfate radicals (SO$_4$$^-$) present several advantages when compared to hydroxyl radicals (•OH), notably featuring a superior reduction potential ranging from 2.5 to 3.1 volts, as opposed to the 1.8 to 2.7 volts associated with hydroxyl radicals,$^{10,11}$ a broader pH application range,$^{14,15}$ a longer lifetime of 30–40 µs (10–30 µs for •OH)$^{16}$ and higher oxidation selectivity.$^{17}$ The burgeoning interest in sulfate radical-based advanced oxidation processes (SR-AOPs) stems from their array of advantages,$^{18,20}$ and activated peroxymonosulfate (PMS) can generate highly oxidative sulfate radical (SO$_4$$^-$) species.$^{21}$ Numerous studies have shown that transition metal ions are widely used as activators for PMS, given their economic feasibility, low toxicity, and environmental friendliness.$^{22,23}$ Catalysts containing cobalt metal have shown better performance in the activation of PMS.$^{24,25}$ An upward trend in studies on PMS activation via cobalt-based catalysts is noticeable of late, such as MIL101-derived Fe/Co@C, Co–Fe/NC, Co/CoO, Co$_3$O$_4$/CPANI, and others.$^{26–30}$ It is noteworthy that most of the currently reported single-metal cobalt-based catalysts commonly have issues with ion leaching.$^{31}$ Therefore, it is necessary to find a feasible method to reduce the Co$^{2+}$ leaching from cobalt-based catalysts. Bimetallic oxides, with their distinct structure and pronounced metal-to-metal interactions, are...
known to not only improve the efficacy of PMS activation but also to mitigate metal ion leaching.\(^{32}\)

The degradation of organic pollutants through Co-based catalysts’ activation of PMS has seen continual advancements in research, but the existing Co-based catalysts have various shortcomings. The loading of cobalt on copper oxide (CoO\(_x\)) with oxygen vacancies (O\(_{x}\)) was found to significantly enhance the activation of PMS, but the catalyst only reached optimal degradation efficiency at pH = 7, with degradation being inhibited at pH levels below or above 7.\(^{38,34}\) Moreover, doping iron (Fe) into cobalt-based catalysts had led to the formation of magnetic Co–Fe catalysts.\(^{32}\) Synthesized through this technique, the catalysts’ effectiveness was notably reduced by inorganic anions, achieving just 50% pollutant degradation at 20 mM Cl\(^{-}\), and operated within a limited pH spectrum, peaking at pH = 7, with diminished performance in acidic or alkaline environments.\(^{34}\) Moreover, bimetallic or trinmetallic catalysts like CuFeO\(_x\), CuO/FeO\(_x\), CoO/Fe-CO-GO, and Cu–Co–Fe-LDH have shown effectiveness in activating PMS for organic pollutant degradation, but they still have limitations concerning the pH range.\(^{35}\) Therefore, achieving pollutant degradation over a wide pH range while ensuring low ion leaching had become a development direction for metal catalysts.

In this research, the synthesis of CCO with abundant O\(_x\) was carried out by co-precipitation, and their effectiveness in activating PMS for LEV degradation was demonstrated. This study involved characterizing the morphology, crystal structure, and physical and chemical properties of CCO. In addition, the effects of varying dosages of PMS and catalysts, different pH conditions, and the presence of coexisting anions on the efficiency at which LEV was decomposed were systematically analyzed. The degradation pathway of LEV in the CCO/PMS system was hypothesized through the analysis of intermediates. Radical quenching trials were carried out to reveal the active agents in the system assisting pollutant degradation. Subsequently, the stability, reusability, general applicability, and resistance to interference of the CCO catalyst were assessed through cyclic degradation experiments and by testing its effectiveness in diverse water matrices.

## 2 Materials and methods

### 2.1 Materials

Levofloxacin (C\(_{18}\)H\(_{20}\)FN\(_3\)O\(_4\), 98%) and ciprofloxacin (C\(_{17}\)H\(_{18}\)FN\(_2\)O\(_3\), 98%) were both acquired from Macklin Biochemical Co, Ltd. in Shanghai, China. Ofloxacin (C\(_{22}\)H\(_{24}\)N\(_2\)O\(_8\)) were both sourced from Macklin Biochemical Technology Co, Ltd. in Shanghai. Copper nitrate trihydrate (Cu(NO\(_3\))\(_2\)-3H\(_2\)O, 99%), cobalt nitrate hexahydrate (Co(NO\(_3\))\(_2\)-6H\(_2\)O, 98.5%), sodium hydroxide (NaOH, 98.5%), anhydrous ethanol (EtOH, ≥99.7%), tert-butyl alcohol (TBA, ≥95%), and methanol (MeOH, ≥99.5%) were all purchased from Guang Fu Fine Chemical Research Institute in Tianjin, China. No further purification steps were undertaken for the reagents, which were used as obtained.

### 2.2 Catalyst preparation

CCO catalysts, with O\(_x\), were synthesized using a straightforward co-precipitation technique (refer to Fig. S1, ESI).\(^{36,37}\) The preparation of the desired solution often entails diluting 0.03 mol Co(NO\(_3\))\(_2\)-6H\(_2\)O and 0.03 mol Cu(NO\(_3\))\(_2\)-3H\(_2\)O in 100 ml deionized water. The molar ratios of Co to Cu were varied as follows: 0 : 1, 1 : 4, 1 : 2, 1 : 1, 2 : 1, 4 : 1, and 1 : 0. The solution was continuously stirred magnetically, and was treated with an excess of 60 ml NaOH (4 M) dropwise, then stirred for 2 hours at 363.15 ± 1 K. Once it cooled to room temperature, the precipitate was centrifuged and subjected to five wash cycles using deionized water and ethanol. Finally, the precipitate was left to dry under vacuum conditions at 353.15 ± 1 K overnight. The resulting gray-brown solid was moved to an alumina boat and then positioned in a muffle furnace, where it endured a temperature setting of 673.15 ± 5 K for two hours, heated at a rate of 274.15 K min\(^{-1}\).

### 2.3 Experimental procedures

The experiment was carried out at a constant temperature representing room conditions, specifically 25 °C. The reaction solution was then transferred to a 100 ml beaker and placed on a magnetic stirrer (JOANLAB-MS5, Joan Lab Instruments, China). The foundational reaction system comprised the following parameters: LEV was used at a 20 mg L\(^{-1}\) concentration, accompanied by a catalyst at 0.2 g L\(^{-1}\) and PMS at 0.8 g L\(^{-1}\) for the procedure. 1 M solutions of H\(_2\)SO\(_4\) or NaOH were utilized to change the LEV solution’s initial pH to the predetermined level. After incorporating the catalyst and allowing it to stir for 30 minutes, the sample was withdrawn, and PMS was added to the reaction. The reaction was monitored by taking 3 ml of samples at set intervals, which were then mixed with the same volume of 0.2 M Na\(_2\)S\(_2\)O\(_3\) to effectively stop the reaction.\(^{38}\) After the precipitate was centrifuged down, the supernatant was taken off and filtered using an aqueous 0.45 μm membrane filter for the next stages of analysis. The concentration of LEV was tracked at its peak absorption wavelength using a UV spectrophotometer (UV-2800A, manufactured by UNICO in China). A dissolved oxygen meter (HQ40d, HACH, USA) with a sensitivity range from 0.01 to 20 mg L\(^{-1}\) was utilized to measure the level of dissolved oxygen (DO) in the solution. To hypothesize on LEV’s degradation mechanisms, LC-MS (Ultimate 3000 UHPLC - Q) analysis was undertaken. Reaction rate constants for the degradation process were derived using the Behnajady–Modirshahla–Ghanbery kinetic model (BMGKM)\(^{39,40}\) (eqn (1)). In this context, \(k_0\) and \(k_1\) represent the concentration of LEV at time \(t\) and at the initial time, respectively. The term \(m\) denotes the y-intercept, while \(b\) represents the slope of the line. The reciprocal (1/m), signifies the initial rate of degradation of the reaction

\[
t(1 - C_t/C_0) = m + bt. \tag{1}
\]

### 2.4 Material characterization

Within this experiment, the surface structure of the Co\(_3\)O\(_4\)-CuO materials was studied and described using SEM (Zeiss Sigma300, Germany) technology. The crystallinity of CuO, Co\(_3\)O\(_4\), and the
bimetallic Co$_3$O$_4$–CuO was determined using XRD, with the Bruker D8 Advance diffractometer from Germany. FT-IR with the Thermo Scientific Nicolet iS20 from the USA was employed to identify the main functional groups in Co$_3$O$_4$–CuO. XPS with the PHI5000 VersaprobeIII from Japan was used to verify the main elements and the valence state changes in Co$_3$O$_4$–CuO. Total organic carbon (TOC) was analyzed using a Multi C/N 3100 analyzer from Germany. Quenching experiments were conducted to identify the active species in the CCO/PMS system.

3 Results and discussion
3.1 Structure of the V$_o$-containing Co$_3$O$_4$–CuO

3.1.1 SEM analysis. The morphology of the synthesized CCO catalyst was scrutinized at multiple magnifications via SEM, and as shown in Fig. 1(a)–(c), it featured a resemblance to coral, which suggests that it provides ample sites for the activation of PMS. Additionally, Fig. 1(d)–(f) displays the even dispersal of Co, Cu, and O elements in the CCO, as verified by the corresponding elemental mapping spectral analysis. Analysis with energy-dispersive X-ray spectroscopy (EDS) as part of the SEM procedure confirmed that Co, Cu, and O constitute the main elements of CCO.

3.1.2 FTIR analysis. The chemical bonding and functional groups within CCO were analyzed using FT-IR. The peak appearing at 3775 cm$^{-1}$, shown in Fig. 2(a), is attributed to the O–H bond vibrations of water molecules in their gaseous state, as detected in the analysis. The pronounced and expansive peak located at 3437 cm$^{-1}$ corresponds to the stretching vibrational movements of water molecules in the liquid state on the surface of CCO. The stretching vibrations of the O–H bond in water molecules adsorbed on CCO, which were observed at 1623 cm$^{-1}$, are known to play a significant role in activating PMS. A discernible peak close to 1398 cm$^{-1}$ emerged from the spectrum, associated with the stretching vibrations of C–C bonds. The peaks at 653 cm$^{-1}$ and 565 cm$^{-1}$ are characteristic of Co–O bonds, and the peak at 502 cm$^{-1}$ is characteristic of the Cu–O bond. Compared to the FT-IR spectra of Co$_3$O$_4$ and CuO, both Co–O and Cu–O bonds in CCO exhibit a blue shift. This indicates the presence of copper oxide and cobalt oxide in CCO.

3.1.3 XRD analysis. The CCO material underwent XRD analysis, which was conducted to discern its compositional elements and crystal configuration. The results of the XRD analysis on CuO, Co$_3$O$_4$, and Co$_3$O$_4$–CuO are shown in Fig. 2(b), where the characteristic peaks located at 32.5°, 35.5°, 38.7°, 48.7°, 53.5°, 58.3°, 61.5°, 68.1°, 72.4°, and 75.2° correspond to different crystal planes of CuO, and the peaks at 19.0°, 31.3°, 36.9°, 44.8°, 59.4°, and 65.2° correspond to different crystal planes of Co$_3$O$_4$. In the CCO sample, the characteristic peak of the (311) plane of Co$_3$O$_4$ at 36.9° and the peaks belonging to the (002) and (111) planes of CuO at 35.5° and 38.7° were also observed. These results provide additional evidence confirming the primary composition of the synthesized CCO material as Co$_3$O$_4$ and CuO.

3.1.4 XPS analysis. As shown in Fig. 3(a), elements Co, Cu, and O were detected in CCO using the XPS analysis technique, which further indicates the successful synthesis of CCO. Fig. 3(b) reveals the characteristic peak for Co 2p$_{3/2}$ at a binding energy of $E_b[\text{Co } 2p] = 781.9$ eV. The peak of Co 2p$_{1/2}$ was positioned at a binding energy $E_b[\text{Co } 2p] = 795.8$ eV. Observation of two satellite peaks was made at the binding energies of $E_b[\text{Co } 2p] = 794.5$ eV and 803.7 eV, while the peaks at $E_b[\text{Co } 2p] = 780.9$ eV and $E_b[\text{Co } 2p] = 779.9$ eV correspond to the oxidation states of Co$^{2+}$ and Co$^{3+}$, with their relative proportions being 84.3% and 15.7%, respectively. Fig. 3(c) displays the characteristic peaks of Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ situated at binding energies of $E_b[\text{Cu } 2p] = 933.5$ eV and $E_b[\text{Cu } 2p] = 935.5$ eV, respectively. A satellite peak at $E_b[\text{Cu } 2p] = 961.0$ eV was identified, and a separate satellite peak was divided into two distinct peaks at energies $E_b[\text{Cu } 2p] = 943.46$ eV and $E_b[\text{Cu } 2p] = 940.8$ eV. Additionally, Fig. 3(c) indicates that the Cu element predominantly existed in the form of Cu(0). The XPS analysis in Fig. 3(d) shows the characteristic peaks of O 1s at 529.32 eV.
530.99 eV, and 533.00 eV, which are attributed to lattice oxygen (O_L), adsorbed oxygen (O_A), and adsorbed molecular water in CCO,\textsuperscript{33} with their relative proportions being 46.53\%, 42.62\%, and 10.85\%, respectively. The solid-state EPR characterization of CCO reveals oxygen vacancies (O_v) ($g = 2.004$ 41) (Fig. S5(c), ESI\textsuperscript{†}), which aligns with the oxygen vacancy analysis results obtained from CCO’s XPS measurements. Research findings suggest that the extent of oxygen adhesion to the catalyst’s surface can be a marker of the catalyst’s oxygen vacancy (O_v) levels,\textsuperscript{33} suggesting that the CCO catalyst surface was rich in oxygen vacancies. In addition, in order to verify the XPS analysis results of CCO, we conducted separate XPS analyses of Co$_3$O$_4$ and CuO (Fig. S3, ESI\textsuperscript{†}). It was found that the peak positions of the Co, Cu, and O elements in CCO corresponded with those in Co$_3$O$_4$ and CuO. This indicates that the elemental analysis results of CCO are reasonable.

### 3.2 Impact of operational parameters

#### 3.2.1 Impact of diverse reaction systems

A variety of reaction systems were designed and employed to evaluate the effectiveness of the catalysts’ catalytic performance. As presented in Fig. 4(a), the degradation impact of LEV under the sole action of the CCO catalyst within 1 hour was almost nonexistent. When PMS was used alone, the degradation efficiency of LEV reached 60\% within 1 hour. The CuO/PMS and Co$_3$O$_4$/PMS systems achieved degradation efficiencies of 90\% and 70\% for LEV within 1 hour, respectively. In addition, the degradation efficiency of total organic carbon (TOC) reached 57\%
By adjusting the molar ratios of the two metals, catalysts with different ratios were synthesized (Co : Cu = 4 : 1, 2 : 1, 1 : 1, 1 : 2, 1 : 4). The degradation efficiency of LEV by CCO/PMS showed an initial increase and subsequent decrease with increasing Co ratios, reaching a maximum of 97% at a Co : Cu ratio of 1 : 1. A comprehensive analysis of the reaction efficiency for various systems can be achieved by calculating the BMGKM constants, thus allowing for the selection of the optimal system. The calculated BMGKM constant for LEV degradation by CCO/PMS is 2.0851 min⁻¹ when the Co : Cu ratio is 1. In addition, as detailed in Table S1 (ESI†), the CCO/PMS system demonstrates a higher degradation efficiency for LEV when compared to alternative systems.

3.2.2 Impact of different doses of CCO and PMS. An increase in the catalyst leads to a higher efficiency in degrading LEV up to a threshold, after which the efficiency exhibits a decreasing pattern (Fig. 5(a)). At the beginning, the catalyst was concentrated at 0.1 g L⁻¹ and LEV degradation operated at 83% efficiency. By intensifying the catalyst to 0.2 g L⁻¹, the degradation efficiency correspondingly increased, hitting 96%. With the catalyst amount rising from 0.2 g L⁻¹, there was a gradual decrease in LEV degradation efficiency. Once the catalyst concentration hit
0.8 g L\(^{-1}\), the efficiency plateaued, consistently staying near 85%. Even with an increase in catalyst to 0.8 g L\(^{-1}\), the degradation efficiency did not vary, remaining steady at that percentage. As the catalyst dose was increased, the uplift in LEV degradation efficiency was observed, which might be due to more reactive locations being provided by the added catalyst, therefore, potentially quickening PMS activation. The drop in the degradation efficiency of LEV after the initial rise could be caused by the excessive and rapid reaction between the additional catalyst and PMS, which creates a large number of free radicals in a short period. However, due to the transient presence of free radicals and insufficient contact with LEV, the degradation efficiency of LEV not only failed to increase but actually decreased with the excessive addition of the catalyst. As depicted in Fig. 5(b), with the increment in PMS dosage, LEV degradation efficiency slowly escalated at first, eventually plateauing after reaching a certain point. At the onset, with 0.2 g L\(^{-1}\) PMS, the degradation efficiency of LEV was recorded at 75%. With the progressive increase in the PMS dosage, there is a corresponding improvement in degradation efficiency. At a PMS concentration of 0.8 g L\(^{-1}\), the degradation efficiency peaks at 96%. Subsequently, even with higher PMS dosages, the degradation efficiency of LEV remained essentially static at 96%, showing no substantial increment. Two reasons account for this phenomenon: firstly, the reactive sites on the catalyst become saturated and cannot react with additional PMS; secondly, according to previous studies, excess PMS can undergo self-quenching reactions with SO\(_4^{*}\), ultimately leading to no further increase in the degradation efficiency of LEV.

3.2.3 Analysis of the effects of humic acid (HA) and initial solution pH. Fig. 5(c) presents the changes in catalytic performance with varying humic acid (HA) concentrations. When the HA concentration gradually increased from 0 to 20 mg L\(^{-1}\), the degradation efficiency of LEV dropped from an initial 96% to 77%. The phenomenon might have been caused by the hyaluronic acid molecules, which contain an abundance of carboxyl and hydroxyl groups, forming intermolecular and intramolecular hydrogen bonds in aqueous solutions, thus exhibiting strong water retention capacity, capable of absorbing more than 400 times their weight in water. The possible reason is that HA could compete for and take away the adsorbed water on the catalyst surface, which may reduce the participation of adsorbed water in PMS activation and ultimately lead to a decrease in LEV degradation efficiency. Fig. 5(d) indicates that as the pH of the reaction environment increased from 3 to 11, the degradation efficiency of LEV steadily increased from 83% at pH 3 to 97% at pH 11. This phenomenon is probably caused by the reactions between a large amount of H\(^+\) and free radicals (SO\(_4^{*}\) and *OH) in the reaction system under acidic conditions, which led to a decrease in degradation efficiency. The inhibitory effect of H\(^+\) on the aforementioned free radicals is reduced under neutral and alkaline conditions, making CCO/PMS more efficient at degrading LEV in alkaline environments.

3.2.4 Impact of coexisting inorganic anions at different concentrations. In this research, the impact of different concentrations of coexisting inorganic anions on the degradation efficiency of the CCO/PMS system was analyzed, including Cl\(^-\), H\(_2\)PO\(_4^{-}\), HCO\(_3^{-}\) and NO\(_3^{-}\), with the results depicted in Fig. 6(a)–(d). Fig. 6(a) shows that the degradation efficiency of LEV decreased to 82% when the concentration of Cl\(^-\) reached 20 mM. This could be due to the reaction between Cl\(^-\) and the free radicals (SO\(_4^{*}\) and *OH), which produced chlorine radicals (Cl\(^*\)) (eqn (2) and (3)) with lower oxidation capacity, thus inhibiting the degradation of LEV. As presented in Fig. 6(b), the degradation of LEV seems to be minimally affected by H\(_2\)PO\(_4^{-}\). An increase in HCO\(_3^{-}\) concentration to 5 mM results in a decline in LEV degradation efficiency to 86% (Fig. 6(c)). However, additional increases in the concentration of HCO\(_3^{-}\) do not entail further diminishing of the degradation efficiency of LEV. This phenomenon occurs because HCO\(_3^{-}\) combines with SO\(_4^{*}\) and *OH radicals to form CO\(_3^{*}\) (eqn (4)), a radical species with a less robust oxidation capacity, having potentials of \(E(\text{Cl}^*/\text{Cl}^-)\) at +2.5 V and \(E(\text{CO}_3^{*}/\text{CO}_2^-)\) at +1.63 V, ultimate leading to a decrease in LEV degradation efficiency. However, as HCO\(_3^{-}\) acts as a buffer, it will hydrolyze in water to produce hydroxide ions, and according to the research results shown in Section 3.2.3, alkaline environments are conducive to the degradation of LEV, so further increases in HCO\(_3^{-}\) no longer enhance the inhibitory impact on LEV degradation. Fig. 6(d) shows that as more NO\(_3^{-}\) is added, the efficiency with which LEV is degraded diminishes, with a 20 mM concentration of NO\(_3^{-}\) bringing the efficiency down to 86%, possibly due to NO\(_3^{-}\) inhibiting the reactive SO\(_4^{*}\) and *OH species (eqn (5)).

\[
\text{SO}_4^{*^-} + \text{Cl}^- \rightarrow \text{SO}_4^{2-} + \text{Cl}^* \\
\text{*OH} + \text{Cl}^- \rightarrow \text{Cl}^* + \text{OH}^- \\
\text{HCO}_3^- + \text{*OH} \rightarrow \text{CO}_3^{*^-} + \text{H}_2\text{O} \\
\text{NO}_3^- + \text{*OH} \rightarrow \text{NO}_3^* + \text{H}_2\text{O} 
\]

3.3 Radical identification

Based on the research findings in Section 3.2.1, the following conjecture was made: The degradation of LEV by using CCO alone was almost imperceptible, and even when PMS was used alone, the efficiency of LEV degradation was only 41%. Consequently, it was deduced that other active substances must have been the principal agents in the degradation process. In previous studies, when PMS was activated by metal catalysts, the key reactive species were typically SO\(_4^{*}\) and *OH. Moreover, several studies have identified singlet oxygen (\(\text{O}_2^*\)) as a potent oxidizing reactive intermediate within advanced oxidation processes that utilize PMS. Consequently, to investigate the likely reactive agents in the CCO/PMS system, an experiment was conducted using three distinct scavengers aimed at capturing reactive oxygen species. For the quenching experiments conducted within the study, tert-butanol (TBA), methanol (MeOH), and furfuryl alcohol (FFA) were chosen as the quenching agents. Besides, using PMSO as a quencher for high...
valence metals. The degradation of LEV within the CCO/PMS system was found to be impeded to varying extents by the addition of three distinct quenching agents, according to the experimental data shown in Fig. 7(a)–(d). A 200 mM concentration of MeOH decreased the degradation efficiency to 64%, while 200 mM TBA yielded an 83% degradation efficiency. Additionally, the use of 1 mM FFA led to a substantial inhibition, with only 13% degradation efficiency. After the addition of 20 mM PMSO, it was found that the degradation of LEV was hardly affected, indicating the negligible presence of high-valent metal-oxo species in the CCO/PMS system. Fig. 7(b) demonstrates that the application of FFA caused a profound inhibition of LEV degradation, culminating in a reduced BMGKM constant of 0.0299 min⁻¹/C₀, representing just 2.9% of the rate obtained without quenchers. Overall, TBA exhibited the least inhibition on LEV degradation, followed by MeOH, with FFA having the strongest inhibitory effect. To eliminate the potential impact of quencher dosage on the outcomes, experiments were conducted with varying amounts of the relatively less inhibitory quenchers MeOH and TBA, as presented in Fig. 7(c) and (d). At 400 mM and 800 mM TBA, degradation efficiencies were 81% and 79%, respectively, showing a negligible change compared to 83% with 200 mM TBA. Similarly, at 400 mM and 800 mM MeOH, degradation efficiencies were 61% and 56%, remaining close to 64% at 200 mM. In the CCO/PMS system, the contribution to the degradation of LEV, in descending order, is *OH, SO₄²⁻, and *O₂. The EPR detection of reactive oxygen species that may be generated in the CCO/PMS degradation of LEV system. The detection results revealed the presence of *OH, SO₄²⁻, and *O₂ during the CCO/PMS degradation of LEV (Fig. S5(a) and (b)). These findings are consistent with the results of quenching experiments.

3.4 Stability test experiment of CCO

Five cyclic degradation experiments were conducted. Fig. 8(a) displays the pertinent experimental data, demonstrating that the efficacy of LEV’s degradation by CCO/PMS was diminished after multiple sequential reactions, reaching a reduction rate of 89% by the fifth round. This suggests that the synthesized CCO catalyst has good usage stability. To further investigate the stability of the catalyst in actual wastewater treatment processes, LEV degradation experiments were conducted using four distinct water samples. In these experiments, the catalyst was subjected to different water matrices to evaluate its performance and stability in real-world conditions. The four water samples included deionized water, tap water, lake water, and Yellow River water. Water quality attributes across multiple water bodies are outlined in Table S2 (ESI†). The findings, as portrayed in Fig. 8(b), show that deionized water had the highest degradation efficiency at 96%, followed by Yellow River water at 94%, then tap water at 92%, and lake water at 89%. The CCO catalysts still possessed high degradation efficiency in these water environments, maintaining above 89%. Additionally, to assess the adaptability of the CCO catalysts, degradation
tests of various antibiotics, including LEV, ofloxacin, ciprofloxacin, and tetracycline, were conducted. The degradation efficiencies of ciprofloxacin, ofloxacin, and LEV in the CCO/PMS system were all above 95%, and tetracycline reached complete degradation at 100% within a short span of 10 minutes, as evidenced by Fig. 8(c). This underscores the wide applicability and effective antibiotic degradation capabilities of the CCO/PMS system. A comprehensive analysis of these results shows that the CCO catalyst exhibits commendable recyclability, satisfactory anti-interference properties, and general applicability for degrading multiple pollutants. Post-use characterizations of CCO by FT-IR, compared with pre-reaction characterizations, were presented in Fig. 8(d). According to the FT-IR spectra, there was a noticeable presence of well-defined and intense characteristic peaks at 3437 cm$^{-1}$ and 1623 cm$^{-1}$, suggesting an increase in surface OH groups. In addition, the Fourier transform infrared (FT-IR) spectra of the used CCO and the fresh CCO remain largely consistent, further corroborating the stability of the CCO catalyst. The amount of metal ion leaching is an important parameter for assessing the stability and performance of metal catalysts. Throughout the series of cyclic experiments, the determination of metal ion leaching concentrations was conducted, with the findings illustrated in Fig. S2 (ESI†). During the premiere cycle of degradation, the concentrations of cobalt and copper were measured and found to be 0.350 mg L$^{-1}$ and 0.401 mg L$^{-1}$, respectively. As the cyclic degradation experiments progressed, both concentrations followed a decreasing trajectory. Ultimately, in the fifth cycle of the experiment, the ion concentrations of Co and Cu were reduced to 0.050 mg L$^{-1}$ and 0.090 mg L$^{-1}$, respectively. Experimental data indicate that the levels of metal ion leaching in the CCO/PMS system are significantly lower than the regulatory limits set by relevant standards and guidelines (Co: 1 mg L$^{-1}$ and Cu: 2 mg L$^{-1}$). This suggests that the CCO/PMS system is effective in minimizing metal ion leaching and maintaining the stability of the metal catalyst.

3.5 The possible routes of degradation of LEV

The XPS analysis results of the CCO catalyst before and after use, as presented in Fig. 9(a)–(d), provide a comparative analysis of the different elemental compositions. In Fig. 9(a), it is evident that Co, Cu, O, and C elements are still present in the used CCO, with the metal characteristic peaks showing minimal change. This further substantiates the high stability of the CCO catalyst. As indicated in the depiction of Fig. 9(b), the surface cobalt in fresh CCO was largely in the form of Co(II) and Co(III), accounting for 84.3% and 15.7% of the total cobalt, respectively. The proportion of Co(II) on the used CCO surface decreased from 84.3% to 77.06%, while that of Co(III) increased from 15.7% to 22.94%. This statement suggests that a redox process occurred within the CCO/PMS system involving Co(II) and Co(III). As presented in Fig. 9(c), the copper found on the pristine CCO surface existed as Cu(II), with a near-total ratio of approximately 100%. A considerable shift in the oxidation state
of Cu on the CCO surface was observed, shifting from Cu(II) to Cu(I) following utilization. The proportion of Cu(II) fell from its original 100% to 46.81%, while that of Cu(I) increased to 53.19%, validating a Cu(II)/Cu(I) redox reaction in the CCO/PMS system. The reduction in Cu(II) was attributed to its reaction as a high-valence metal ion with $\text{HSO}_5^-$, forming $\text{SO}_5^{2-}$ (eqn (6)). The reactive species $\text{SO}_5^{2-}$ interacted with Cu(I) and Co(III) to form $1\text{O}_2$ (eqn (7)). Simultaneously, Cu(II) was reduced to Cu(I) and Co(III) was reduced to Co(II). The decomposition of PMS resulted in the formation of $\text{O}_2$ (eqn (8)), which further catalyzed the production of $\text{SO}_4^{2-}$ and $1\text{O}_2$ (eqn (9) and (10)). Some $\text{SO}_4^{2-}$ reacted with $\text{H}_2\text{O}$ or $\text{OH}^-$ to yield $\text{HO}_2$ (eqn (11)). An exchange of electrons from Co(III) to Cu(I) is possible because the reduction potential of $\text{E}_{\text{Cu(III)/Cu(I)}}$ is significantly more positive than $\text{E}_{\text{Co(III)/Co(II)}}$ (eqn (12)).

Experimental conditions: 20 mg L$^{-1}$ pollutant, 0.8 g L$^{-1}$ PMS, 0.2 g L$^{-1}$ catalyst, temperature = 298 K and pH = 7.

$$R_{\text{Cu(II)/Co(III)}} \rightarrow R_{\text{Cu(I)/Co(II)}}$$

$$R_{\text{Cu(I)/Co(II)}} + 2\text{SO}_5^{2-} \rightarrow 2R_{\text{Cu(II)/Co(III)}} + 2\text{SO}_4^{2-} + 1\text{O}_2$$

$$3\text{HSO}_5^- + \text{H}_2\text{O} \rightarrow 3\text{SO}_4^{2-} + 2\text{O}_2^{2-} + 5\text{H}^+$$

$$\text{O}_2 + \text{e}^- \rightarrow \text{O}_2^{2-}$$

$$\text{O}_2^{2-} + \text{H}_2\text{O} \rightarrow \text{O}_2^{3-} + \text{H}_2\text{O} + \text{OH}^-$$

$$\text{HSO}_5^- + \text{SO}_5^{2-} \rightarrow \text{HSO}_4^- + \text{SO}_4^{2-} + 1\text{O}_2$$

Fig. 8 (a) Cycling test for CCO, (b) the impact of different types of water bodies, (c) degradation of different pollutants by the CCO/PMS system, and (d) comparison of AIR-FTIR spectra of fresh and used CCO material. (Inset: corresponding kinetic constants for the experimental conditions).
3.6 Degradation pathways

This examination revealed that the degradation process involves a dual mechanism, including both non-radical and radical pathways. Water samples were collected from the reaction system at various reaction time points and subsequently analyzed using liquid chromatography-mass spectrometry to investigate the degradation pathways of LEV. Within the reaction system degrading LEV using CCO/PMS, 15 intermediate products were detected. Fig. 10 illustrates that four distinct degradation pathways were recognized. In pathway 1, P_1 (m/z = 309) was generated by substituting –OH for –F, dehydrogenating piperazine, and partially decarboxylating it. Next, the p1 piperazine bond undergoes a demethylation reaction to form P_2 (m/z = 309). Pathway 2 described the interaction of LEV with reactive species, which resulted in the removal of the methyl group from the piperazine bond and the opening of the ring to generate P_3 (m/z = 322). The piperazine bond of P_3 further cleaved to form P_4, while the formation of P_5 was mainly due to the demethylation, decarboxylation, and defluorination of P_4. In pathway 3, the piperazine ring of LEV opened and lost a fluorine atom to yield P_6 (m/z = 318), with P_7 (m/z = 273) being the result of further decarboxylation of P_6. In pathway 4, LEV underwent hydroxylation and deamination to produce P_8 (m/z = 364), followed by a series of decarboxylation, dehydroxylation, and piperazine ring-opening reactions, which eventually led to the creation of P_9 (m/z = 265). The intermediate products arising from these four pathways were further attacked by strong oxidants present in the system, transforming into small molecular substances such as P_10–P_15 (Fig. 11) (the LC-MS spectrum is provided in Table S3, ESI†). These small molecules were then subjected to further oxidative breakdown, ultimately being converted into inorganic ions, CO_2, and H_2O.\(^{53}\)

4 Conclusions

In this investigation a CCO catalyst with plentiful oxygen vacancies was synthesized through co-precipitation, which
was used for the degradation of LEV. The combined action of Co and Cu in the bimetallic CCO/PMS system resulted in an impressive 97% degradation efficiency for LEV. The CCO/PMS system maintained good degradation efficiency across a broad range of pH conditions, addressing the issue of low degradation efficiency at high pH commonly encountered with conventional metal catalysts. The robust interaction between Co$_3$O$_4$ and CuO endowed the CCO catalyst with exceptional resistance to interference and long-lasting durability. It was found that singlet oxygen ($^1$O$_2$) played a dominant role in the degradation of LEV as the primary active agent. SO$_4$•$^-$ and •OH radicals also participated in the degradation, but their contribution was smaller than that of singlet oxygen. LC-MS detection of the intermediate products in the CCO/PMS degradation system for LEV was conducted, and a reasonable pathway for LEV degradation was analyzed. The experimental results indicated that the CCO/PMS system exhibited outstanding degradation performance across various pollutant and aquatic environments. Even after five consecutive degradation cycles, the CCO/PMS system maintained a degradation efficiency above 89%, underscoring the practical applicability of the CCO catalyst. Combined with its simple synthesis method and readily available raw materials, CCO is expected to be applied in the treatment of antibiotic wastewater in practice. However, there are also some limitations in our research. For instance, the TOC removal rate of the CCO/PMS system is only 57%, indicating that there is significant room for improvement in the mineralization efficiency of LEV. Although the metal ion leaching rate of the CCO catalyst meets the relevant standard limits, further research on methods to reduce ion leaching remains a worthwhile direction to explore.

Author contributions
Conceptualization, X. J. and H. H.; methodology, X. J. and H. H.; validation, C. W., Y. Y. and J. W.; formal analysis, Y. L.; data curation, H. H.; writing – original draft preparation, H. H.; writing – review and editing, X. J. and X. Z.; visualization, H. H.; supervision, X. J.; project administration, X. Z.; funding acquisition, X. Z. and X. J.; all authors have read and agreed to the published version of the manuscript.

Data availability
The data supporting this article are included in the article and the ESI.

Conflicts of interest
There are no conflicts of interest to declare.

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