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Cu₂O-Promoted Degradation of Sulfamethoxazole by α-Fe₂O₃-Catalyzed Peroxymonosulfate under Circumneutral Conditions: Synergistic Effect, Cu/Fe Ratios, and Mechanisms

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Abstract: To promote the application of iron oxides in sulfate radical-based advanced oxidation processes, a convenient approach using Cu$_2$O as a catalyst additive was proposed. Composite catalysts based on α-Fe$_2$O$_3$ (CTX%Cu$_2$O, X = 1, 2.5, 5, and 10) were prepared for peroxymonosulfate (PMS) activation, and sulfamethoxazole was used as a model pollutant to probe the catalytic reactivity. The results show that a synergistic catalytic effect exists between Cu$_2$O and α-Fe$_2$O$_3$, which was explained by the promoted reduction of Fe(III) by Cu(I). Iron K-edge X-ray absorption spectroscopy investigations indicated that the promoted reduction probably occurred with PMS acted as a ligand that bridges the redox centers of Cu(I) and Fe(III). The weight ratio between Cu$_2$O and α-Fe$_2$O$_3$ influenced the degradation of sulfamethoxazole, and the optimal ratio depended on the dosage of PMS and catalyst. With 40 mg L$^{-1}$ PMS and 0.6 g L$^{-1}$ catalyst, a pseudo-first-order constant of $\sim$0.019 min$^{-1}$ was achieved for CT2.5%Cu$_2$O, whereas only 0.004 min$^{-1}$ was realized for α-Fe$_2$O$_3$. Nearly complete degradation of the sulfamethoxazole was achieved within 180 min under the conditions of 40 mg L$^{-1}$ PMS, 0.4 g L$^{-1}$ CT2.5%Cu$_2$O, and pH 6.8. In contrast, less than 20% degradation was realized with α-Fe$_2$O$_3$ under similar conditions. The CT2.5%Cu$_2$O catalyst had the best stoichiometric efficiency of PMS (0.317), which was 4.5 and 5.8 times higher than those of Cu$_2$O (0.070) and α-Fe$_2$O$_3$ (0.054), respectively. On the basis of the products identified, the cleavage of the S–N bond was proposed as a major pathway for the degradation of sulfamethoxazole.

Keywords: Peroxymonosulfate; Synergistic effect; α-Fe$_2$O$_3$; Cu$_2$O; Sulfamethoxazole
1. Introduction

Advanced oxidation processes (AOPs) based on sulfate radicals (SO₄⁻) have shown great promise in water and wastewater purification [1, 2, 3]. Compared with the hydroxyl radical (·OH, \( E_{\text{OH/OH}^-}^0 = +(1.9−2.7) \text{ V} \)) [4], \( \text{SO}_4^- \) (\( E_{\text{SO}_4^-/\text{SO}_4^2^-}^0 = +(2.5−3.1) \text{ V} \)) has advantages of stronger oxidizing capability in neutral conditions and longer half-life in aqueous solution [2, 3]. Peroxymonosulfate (HSO₅⁻, PMS), usually available in the commercial form as Oxone (2KHSO₅·KHSO₄·K₂SO₄), has been widely used as an environmentally friendly peroxide source of \( \text{SO}_4^- \) over the past few years [5, 6, 7]. Compared with other peroxides, PMS is generally easier to activate [8, 9] and has higher stability at elevated temperatures [9]. In most previous catalysts tested, Co(II) ions are the best activators for the activation of PMS [10, 11]. However, Co has toxicity and even carcinogenic concerns. Due to these considerations, the potential for the practical application of Co/PMS combination is highly limited.

Iron, with its low toxicity and huge abundance, is an important functional material for environmental remediation and has been intensively investigated as a catalyst in ·OH–based AOPs [12, 13]. Fe(II) ions have also been used to homogeneously activate PMS (Eq. 1) [8, 14]. However, the production of ferric hydroxide sludge, the requirement of strongly acidic conditions, and the scavenger effect from overdose of Fe(II) restrict their application. To improve iron’s reactivity in neutral conditions, Rastogi et al. [15] used citrate as the complexing agent and studied the degradation of polychlorinated biphenyls by iron citrate complexes/PMS at pH 7.0. They found that the degradation of polychlorinated biphenyls was greatly improved by the addition of citrate.

Wang and Chu [16] used an electrochemical approach to generate Fe(II) in situ, which realized high removal of 2,4,5-trichlorophenoxyacetic acid without pH adjustment to strongly acidic conditions. However, extra energy was required to initiate the electrochemical reactions. Similar
to heterogeneous Fenton-like processes [17, 18], in which activation reactions occur on the surface of solid catalysts, using iron oxides as heterogeneous catalysts might be an effective and low-cost method of PMS activation. However, according to the studies from Zou et al. [19] and Wang et al. [16], the regeneration of Fe(II) is the rate-determining step in Fe(III)/PMS oxidation and thereby limits the reactivity of this combination (Eq. 2). Zou et al. [19] added hydroxylamine, a strong reducing agent for Fe(III), to Fe(III)/PMS oxidation and found that target pollutant degradation was greatly improved. This conclusion is consistent with the results from Anipsitakis and Dionysiou [8], in which Fe(III) was significantly less reactive than Fe(II) in the activation of PMS for 2,4-dichlorophenol degradation; after a reaction time of 30 min, around 66% of the 2,4-dichlorophenol was degraded with Fe(II), whereas only 14% was realized with Fe(III). To improve the reactivity of Fe(III) (≡ represents the elements on the surface of the solid catalysts), many transition metals such as Co(II) [20, 21, 22, 23] and Cu(II) [24, 25] have been used as doping metals. In addition to their individual catalytic reactivity, the interactions between iron and doping metals, such as the transfer of surface hydroxyl groups from iron and redox reactions, have also been found to be beneficial for PMS activation.

\[
\begin{align*}
\text{1. } & \text{HSO}_5^- + \text{Fe(II)} \rightarrow \text{SO}_4^{2-} + \text{Fe(III)} + \text{H}^+ \\
\text{2. } & \text{Fe(III)} + \text{HSO}_5^- \rightarrow \text{Fe(II)} + \text{SO}_4^{2-} + \text{H}^+
\end{align*}
\]

Our recent studies revealed that a synergistic catalytic effect exists between ≡ Cu(I) and ≡ Fe(III) when using CuFeO₂ crystals as catalysts for PMS activation [26]. In this study, we report a convenient and innovative method to improve the catalytic reactivity of ≡ Fe(III) by using Cu₂O as a catalyst additive. Four composite catalyst-based on α-Fe₂O₃ with different weight ratios of Cu₂O (CTX%Cu₂O, where X = 1, 2.5, 5, and 10) were prepared and their reactivity was evaluated with sulfamethoxazole (SMX, CAS No. 723-46-6, Fig. S1), one of the most widely used
antibiotics, as a model pollutant. Due to the low biodegradability of SMX, this compound has been
frequently detected in sewage effluents and surface water [27, 28]. X-ray absorption near edge
structure was used to study the solid-state redox reaction between Cu₂O and α-Fe₂O₃. To obtain
the optimal Cu/Fe ratio, the effects of PMS dosage, catalyst loading, and stoichiometric efficiency
of PMS were investigated. Some intermediates that are more toxic than SMX were found during
the degradation of SMX by photo-Fenton [29]. Therefore, the transformation products of SMX
were examined with ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-
MS/MS). On the basis of the degradation products identified, a major pathway via the cleavage of
the S–N bond was proposed for the degradation of SMX.

2. Materials and Methods

2.1. Chemicals and materials

The CTX%Cu₂O catalysts were prepared by mixing different amounts of α-Fe₂O₃ and Cu₂O
together in an agate mortar. To eliminate the potential difference in the surface area induced by
the mixing step, the pure α-Fe₂O₃ used for PMS activation was processed in a similar way. SMX
(≥98%), Cu₂O (≥97%), α-Fe₂O₃ (≥95%), sulfanilic acid (99%), 1,3-dihydroxybenzol (99%),
maleic acid (99%), fumaric acid (99%), and oxalic acid (98%) were provided by Sigma-Aldrich
(St. Louis, MO). PMS in form of Oxone (2KHSO₅·KH₂SO₄·K₂SO₄) and tert-Butanol (99%) were
supplied by J&K Scientific (Hong Kong). Sodium hydroxide (≥97.0%), perchloric acid (~65%),
sodium phosphate, monobasic (reagent grade), hydrochloric acid (~36.5%, ACS grade), and nitric
acid (~69%, ACS grade) were purchased from BDH Chemicals (Poole, UK). Sulfanilamide (99%),
ethanol absolute, and stock solutions of metal ions were supplied by Merck Ltd. (Darmstadt,
Germany). Optima LC-MS grade methanol was obtained from Fisher Scientific (Loughborough,
LC and LC-MS grade formic acid were supplied by Fluka Chemical Corp. (Wisconsin, WI, USA) and Waters Corp. (Milford, MA), respectively. Ultrapure water ($R = 18 \text{ M} \Omega \cdot \text{cm}$) for the preparation of chemical solutions was produced by a Barnstead Easypure UV/UF purification system (Boston, MA).

2.2. Catalyst characterization

The X-ray diffraction (XRD) spectra were obtained on a Bruker D8 powder diffractometer (Karlsruhe, Germany) with a Copper X-ray tube at 40 kV and 40 mA. The XRD results of the fresh catalysts are displayed in Fig. S2. The X-ray absorption near edge structure (XANES) spectra of the iron in the catalysts were collected with a synchrotron radiation light source at beam line 17C of the National Synchrotron Radiation Research Centre in Hsinchu, Taiwan. The samples were held at room temperature and analysed at the Fe K-edge (7112 eV). The ATHENA software was used for standard background correction and edge-height normalization [30]. The oxidation states of copper were investigated with a Thermo ESCALAB 250XI X-ray photoelectron spectroscopy (Waltham, MA, USA) equipped an aluminium K-alpha excitation source. The binding energy was calibrated versus the C 1s peak at 284.8 eV.

2.3. Experimental procedures

Batch catalytic experiments were carried out in 50-mL Nalgene™ Oak Ridge PPCO centrifuge tubes at $23 \pm 2 \degree \text{C}$. In a typical procedure, 20 mL 1.6 mg L$^{-1}$ SMX solution buffered with 10 mM phosphate (sodium phosphate, monobasic) was first added into the tubes. The initial pH value of the SMX solution was adjusted to 6.8 with 1 M NaOH and its variation was within ±0.1 throughout the experiments. Certain amounts of catalysts were then added into the tubes, and the catalytic
degradation was initiated by introducing specified amounts of PMS solution (10 g L\(^{-1}\)). To keep
the catalysts suspended, an orbital shaker was used to rotate the tube reactors and the rotation speed
was fixed at 120 rpm. 1 mL of aliquot from the reactors was sampled at specified time intervals,
and immediately filtered with a 0.22-\(\mu\)m Millipore PVDF filter (Darmstadt, Germany). Control
experiments showed that the filter had no obvious adsorption effect on the SMX. After filtration,
the solution was quenched with 200 \(\mu\)L of pure ethanol. The tubes were sacrificial and duplicate
experiments were conducted. To evaluate the stability of the CT2.5\%Cu\(_2\)O catalyst, the particles
after reactions were recollected by centrifugation at 4000 rpm for 5 min at 10 \(^\circ\)C (Centrifuge 5810R,
Eppendorf, Germany).

2.4. Chemical analysis

The concentration of PMS was analysed with an iodometric method [31]. The SMX concentration
was determined using a Waters Acquity\textsuperscript{TM} UPLC system (Milford, MA, USA) with a PDA
detector at 270 nm. Separation was carried out on a Waters BEH\textsuperscript{TM} C18 column (50 mm \(\times\) 2.1
mm, 1.7-\(\mu\)m particle size) at 50 \(^\circ\)C at a flow rate of 0.4 mL min\(^{-1}\) with an injection volume of 10
\(\mu\)L. The mobile phase was a mixture of methanol and ultrapure water (with 0.1\% (v/v) LC-grade
formic acid as an additive) at a volume ratio of 60\%:40\%. The calibration curve for SMX ranged
from 0.1 mg L\(^{-1}\) to 2 mg L\(^{-1}\) and exhibited good linear correlation \((R^2 = 0.998)\). The detection limit
(S/N = 3) and retention time for SMX were \(~\)60 \(\mu\)g L\(^{-1}\) and 0.44 min, respectively.

The transformation products of SMX was monitored with a Waters Acquity\textsuperscript{TM} tandem
quadrupole mass spectrometer equipped with an electrospray ionization in positive and negative
modes. Chromatographic separation of the degradation products was realized with binary gradient
mobile phases of A (ultrapure water with 0.01\% (v/v) LC-MS grade formic acid as an additive)
and B (methanol) at a volume ratio of 95%:5%. Gradient elution was started with 95% phase A and linearly decreased to 5% within 5 min. Then, phase A was increased to 5% within 0.1 min and held for 1 min. Separation was performed on the same column at 50 °C. A flow rate of 0.4 mL min⁻¹ with an injection volume of 10 µL was used. Possible degradation products were first identified by operating the MS in the full-scan and selective ion recording mode. Multiple reaction monitoring (MRM) methods for these products were then established with their corresponding standard reagents. Parameters such as collision energy and cone voltage were optimized for each compound, with the most abundant daughter ion recorded in each case. Other parameters for MS can be found in our previous publication [26].

To determine the dissolved copper and iron ions, the samples filtered were acidified with nitric acid and analysed with a PerkinElmer Optima 2100 DV inductively coupled plasma optical emission spectrometry (ICP-OES) (Waltham, MA). To quantify the Cu₂O and α-Fe₂O₃ contents in the fresh and used CT2.5%Cu₂O catalysts, an exact amount of the catalysts was dissolved in acid mixtures (nitric acid and hydrochloric acid at a volume ratio of 1:3) at 60 °C. The resulting solutions were then diluted, and used for copper and iron measurements by ICP-OES.

3. Results and discussion

3.1. Synergistic catalytic effect between Cu₂O and α-Fe₂O₃

Figure 1

The degradation of SMX in the presence of different catalysts was compared (Fig. 1a). With 10 mM phosphate buffer, Cu(II) and Fe(III) ions (20 mg L⁻¹) had no obvious reactivity for SMX degradation. When Cu₂O and α-Fe₂O₃ were used to activate PMS, only ~29% and ~18% of the SMX were degraded, respectively, after a degradation time of 60 min, which means that both of
these catalysts had low efficiency for PMS activation and Cu$_2$O had relatively greater reactivity than α-Fe$_2$O$_3$. In contrast, ~42% of the SMX was degraded with CT1%Cu$_2$O. This efficiency was obviously higher than that achieved in the presence of Cu$_2$O or α-Fe$_2$O$_3$. Kinetic investigations (Fig. 1b) showed that the degradation of SMX was governed by pseudo-first-order kinetics when Cu$_2$O ($R^2 = 0.979$) or CT1%Cu$_2$O ($R^2 = 0.987$) was used. In the system with α-Fe$_2$O$_3$, the degradation was also successfully modelled with pseudo-first-order kinetics during the first 20 min ($R^2 = 0.994$, inset in Fig. 1b). However, the fitting result ($R^2 = 0.788$, Fig. 1b) during the entire reaction was not good. This was probably due to the decline in the degradation of SMX in the late reaction stage (from 20 min to 60 min), as can be noticed from Fig. 1a. Both the degradation of SMX and the kinetic constants revealed that of the three catalysts tested, CT1%Cu$_2$O had the greatest reactivity. As the reduction potential of Cu(II)/Cu(I) ($E^{\text{Cu(II)/Cu(I)}}_{\text{red}} = 0.15$ V) is significantly lower than that of Fe(III)/Fe(II) ($E^{\text{Fe(III)/Fe(II)}}_{\text{red}} = 0.77$ V) [32], the redox reactions between ≡Cu(I) and ≡Fe(III) are quite thermodynamically favorable. In fact, previous studies have documented the reduction property of Cu(I) toward transition metals. [33] studied the reduction of cobalt (III) complexes by Cu(I) and found that high second-order rate constants of $4.46 \times 10^5$ M$^{-1}$ s$^{-1}$ and $4.48 \times 10^4$ M$^{-1}$ s$^{-1}$ exist for Co(NH$_3$)$_5$Br$^{2+}$ and Co(NH$_3$)$_5$Cl$^{2+}$ reduction, respectively. [34] proposed that the reduction of Fe(III) complexes by Cu(I) takes place through an outer-sphere mechanism, and the rearrangement of coordination geometries of the two reactants likely occurs before the electron transfer. [35] explored the electron transfer kinetics between the complexes of Fe(III) and Cu(I). The results showed that very fast reactions exist between these complexes, with second-order rate constants determined in the range of $10^6$ to $10^8$ M$^{-1}$ s$^{-1}$. Therefore, the great reactivity of CT1%Cu$_2$O could be explained by the synergistic effect resulting from the ≡Cu(I)-promoted reduction of ≡Fe(III).
The reduction of $\equiv$ Fe(III) by $\equiv$ Cu(I) could occur either in the solid state or in PMS solution. Thus, there was a possibility of generating $\equiv$ Fe(II) in CTX%Cu$_2$O before the catalytic reactions and that the generated $\equiv$ Fe(II) contributed to the high reactivity of the CT2.5%Cu$_2$O.

To evaluate this contribution, XANES, a powerful tool to probe phase transformation, was used to investigate the presence of $\equiv$ Fe(II) in the fresh CT2.5%Cu$_2$O (Fig. 2a). The results showed that based on the comparison with the standard K-edge XANES spectra of FeO and $\alpha$-Fe$_2$O$_3$, no $\equiv$ Fe(II) was present in the fresh CT2.5%Cu$_2$O, which suggests that the redox reactions between $\equiv$ Fe(III) and $\equiv$ Cu(I) mainly occurred in the presence of PMS. Previous studies showed that the reactions of PMS with transition metals such as Fe(II) and Cu(II) probably proceed via an inner-sphere electron-transfer mechanism [24, 26, 36]. Therefore, the PMS in CTX%Cu$_2$O suspensions likely acted as a ligand that bridges the redox centres of $\equiv$ Fe(III) and $\equiv$ Cu(I), and thereby promoted the electron transfer processes (Eqs. 3–5).

$$\equiv$$ Fe(III) + HSO$_5^-$ + $\equiv$ Cu(I) →

$\equiv$ Fe(III) − (HO)OSO$_3^-$ − Cu(I) \hspace{1cm} (3)

$\equiv$ Fe(III) − (HO)OSO$_3^-$ − Cu(I) →

$\equiv$ Fe(II) − (HO)OSO$_5^-$ − Cu(II) \hspace{1cm} (4)

$\equiv$ Fe(II) − (HO)OSO$_3^-$ − Cu(II) →

$\equiv$ Fe(II) + $\equiv$ Cu(II) − (HO)OSO$_3^-$ \hspace{1cm} (5)

3.2. Activation mechanism and radical generation

As displayed in Eq. 1, SO$_4^-$ was produced during $\alpha$-Fe$_2$O$_3$/PMS oxidation. ·OH might be generated by the reaction of SO$_4^-$ with H$_2$O molecules (Eq. 6 [25]). Previous investigations with quenching
agents and electron paramagnetic resonance showed that both $\text{SO}_4^-$ and ·OH radicals are produced during iron-catalyzed PMS oxidation [15, 37, 38]. In addition, it has been reported that ·OH radicals are the reactive species formed in the first stage of Cu$_2$O/PMS oxidation, as illustrated in Eq. 7 [24, 36]. Therefore, both $\text{SO}_4^-$ and ·OH were probably produced during CTX%Cu$_2$O/PMS oxidation. The $\equiv \text{Cu}(\text{II})$ generated then reacted with PMS to produce $\text{SO}_4^-$ and itself was oxidized to $\equiv \text{Cu}(\text{III})$ (Eqs. 8 and 9) [24]. $\equiv \text{Cu}(\text{III})$ was highly unstable and could be easily reduced to $\equiv \text{Cu}(\text{II})$ (Eqs. 10 and 11) [24, 26, 39]. The generation of $\equiv \text{Cu}(\text{II})$ on the surface of Cu$_2$O was confirmed by the X-ray photoelectron spectroscopy spectrum (Fig. 2c).

\[
\text{SO}_4^- + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \cdot \text{OH} + \text{H}^+ \quad (6)
\]

\[
\equiv \text{Cu}(\text{I}) - \text{OH}^- + \text{HSO}_5^- \rightarrow \equiv \text{Cu}(\text{II}) - \text{OH}^- + \cdot \text{OH} + \text{SO}_4^{2-} \quad (7)
\]

\[
\equiv \text{Cu}(\text{II}) - \text{OH}^- + \text{HSO}_5^- \rightarrow \equiv \text{Cu}(\text{II}) - (\text{HO})\text{OSO}_3^- + \text{OH}^- \quad (8)
\]

\[
\equiv \text{Cu}(\text{II}) - (\text{HO})\text{OSO}_3^- \rightarrow \equiv \text{Cu}(\text{III}) - \text{OH}^- + \text{SO}_4^- \quad (9)
\]

\[
\equiv \text{Cu}(\text{III}) - \text{OH}^- + \text{HSO}_5^- \rightarrow \equiv \text{Cu}(\text{II}) - \text{OOSO}_3^- + \text{H}_2\text{O} \quad (10)
\]

\[
2 \equiv \text{Cu}(\text{II}) - \text{OOSO}_3^- + 2\text{H}_2\text{O} \rightarrow 2 \equiv \text{Cu}(\text{II}) - \text{OH}^- + \text{O}_2 + 2\text{SO}_4^- + 2\text{H}^+ \quad (11)
\]

To further determine the contribution of these radicals, the effects of tert-Butanol and ethanol, two alcohols widely used in AOPs for radical identification [10, 25], on the degradation of SMX were studied (Fig. 3). The quenching results show that tert-Butanol had significantly weaker inhibition on the degradation of SMX than ethanol. When 500 mM ethanol was present, around 55% decrease in the SMX degradation occurred, whereas only 14% decrease was noticed with 500 mM tert-Butanol. Because ethanol is an efficient scavenger for both ·OH and $\text{SO}_4^-$ and tert-Butanol is relatively inert toward $\text{SO}_4^-$ [40], the absence of significant inhibition with tert-Butanol suggests that $\text{SO}_4^-$ was mainly responsible for the degradation of SMX in CT2.5%Cu$_2$O/PMS oxidation. As $\equiv \text{Cu}(\text{I})$ reacts with PMS generating ·OH and $\equiv \text{Fe}(\text{II})$ or $\equiv$
Cu(II) reacts with PMS generating $\text{SO}_4^-$, this conclusion is consistent with the increased contribution from $\equiv \text{Fe}(\text{II})$ (Eqs. 1–5) and the catalytic mechanisms of $\equiv \text{Cu}(\text{I})$ and $\equiv \text{Cu}(\text{II})$ (Eqs. 7–11).

3.3. Effect of PMS dosage and catalyst loading

To obtain the optimal ratio between Cu$_2$O and $\alpha$-Fe$_2$O$_3$ for PMS activation, the four catalysts with different contents of Cu$_2$O were tested, and the kinetic constants for SMX degradation were calculated under different PMS dosages and catalyst loadings (Fig. 4). For the constant fitting in systems with $\alpha$-Fe$_2$O$_3$, all of the data points from 0 min to 60 min were used, and the corresponding fitting coefficients are listed in Table S1. An increase in $\alpha$-Fe$_2$O$_3$ loading did not have an obvious effect on the degradation kinetics when the PMS dosage rose from 20 mg L$^{-1}$ to 60 mg L$^{-1}$. In the oxidation systems (20 mg L$^{-1}$ PMS) with mixture catalysts, an increase in the catalyst loading generally had a promotion effect on the kinetic constant with the exception of CT10%Cu$_2$O, in which a slight decrease was observed when its loading was increased from 0.4 g L$^{-1}$ to 0.6 g L$^{-1}$ (Fig. 4a). In addition, a high Cu$_2$O content had a negative effect on the kinetic constant at the high catalyst loading of 0.6 g L$^{-1}$. When 40 mg L$^{-1}$ PMS was used (Fig. 4b), the negative effect of catalyst loading with the CT10%Cu$_2$O was more obvious. In the presence of 0.6 g L$^{-1}$ catalyst, an increase followed by a decrease in the constant after 60 min was observed when the content of Cu$_2$O was increased from 1% to 10%, with the CT2.5%Cu$_2$O having the highest constant of 0.0186 min$^{-1}$. When the PMS dosage was increased to 60 mg L$^{-1}$ (Fig. 4c), the inhibitory effect of the Cu$_2$O increase declined when compared with the system that contained 40 mg L$^{-1}$ PMS. With 60 mg L$^{-1}$ PMS, the CT10%Cu$_2$O had the highest constant, but this value was lower than the highest
value achieved with the CT2.5%Cu2O at 40 mg L−1 PMS, indicating that the CT2.5%Cu2O was
more efficient than the CT10%Cu2O. As Fe(II) has high reactivity toward SO₄⁻ (k = 3 × 10⁸ M⁻¹ s⁻¹,
Eq. 12 [15]) and Cu(I) has greater reducing capability than Fe(II), the relative low efficiency of
the CT10%Cu2O was probably due the scavenging effects of both ≡ Fe(II) (Eq. 12) and ≡ Cu(I)
(Eq. 13). Similar inhibition effect of Fe(II) was also reported by Wang et al. when examining the
degradation of 2,4,5-trichlorophenoxyacetic acid by Fe(II)/PMS [41]. The fast reaction between
Fe(II) and SO₄⁻ was consistent with the absence of Fe(II) in the used CT2.5%Cu2O surface, as
indicated by the Fe K-edge XANES spectra (Fig. 2a). Under the conditions of 40 mg L⁻¹ PMS, 0.4
g L⁻¹ CT2.5%Cu2O, and at pH 6.8, approximately 100% of the SMX was degraded after 180 min
(Fig. 4d).

≡Fe(II) + SO₄⁻ → ≡Fe(III) + SO₄²⁻ \[ k = 3 × 10⁸ \text{ M}⁻¹ \text{s}⁻¹ \] \hspace{1cm} (12)
≡Cu(I) + SO₄⁻ → ≡Cu(II) + SO₄²⁻ \hspace{1cm} (13)

3.4. Stoichiometric efficiency

The stability of PMS in the presence of catalysts is an important factor that governs the practical
feasibility of these oxidation systems. High stability suggests a high stoichiometric efficiency (SE,
Eq. 14) of PMS. However, this factor is usually not reported in the numerous previous publications.
In this work, the SE value of PMS was studied in the presence of different catalysts (Fig. 5). Less
than 15% of the PMS was consumed in all of the oxidation systems tested (Fig. 5a), which suggests
that the PMS was generally stable. The calculated SE values (Fig. 5b) reveal that the CT2.5%Cu₂O
had the highest value of 0.317, which was significantly higher than that of Cu₂O and α-Fe₂O₃. To
reduce a high-valent metal to a lower state, extra peroxide is usually consumed (Eq. 2 [42]). In the
presence of $\equiv \text{Cu(I)}$, $\equiv \text{Fe(III)}$ could be reduced to $\equiv \text{Fe(II)}$ (Eqs. 3–5), which saved the cost of PMS.

$$\text{SE} = \frac{\Delta \text{SMX (\mu mol)}}{\Delta \text{PMS (\mu mol)}}$$  \hspace{1cm} (14)

3.5. Reusability and stability of CT2.5%Cu2O

As demonstrated above, the CT2.5%Cu2O had efficient reactivity for SMX degradation and the highest SE value after a reaction time of 60 min. However, the long-term reactivity of this catalyst is still unknown. Therefore, experiments were conducted to investigate the reusability of the CT2.5%Cu2O (Fig. 6). The results showed that in the first 3 cycles, no obvious difference in the SMX degradation was noticed. However, a sharp decline was observed in the 4th run, followed by a slight decrease in the 5th run. These observations suggest that the reactivity of the CT2.5%Cu2O was highly dependent on its contact time with the PMS.

To investigate the stability of the catalysts, the leachability of metals and the variation in the composition of the catalysts were investigated. Approximately 0.85 mg L$^{-1}$ of dissolved copper was detected after 40 min with Cu2O as the catalyst, and the leached copper from the CT2.5%Cu2O was much lower, with a value of $\sim$0.32 mg L$^{-1}$ (Fig. 7a). It is worth noting that 1.03 mg L$^{-1}$ of Cu(II) was detected in the experiment of CT10%Cu2O use, and this leachability is slightly higher than that obtained with Cu2O. As the Cu2O content in the CT10%Cu2O is just 10 percent of that in the Cu2O catalyst, the accelerated leaching of copper could probably be related to the interactions of $\equiv \text{Cu(I)}$ with $\equiv \text{Fe(III)}$ (Eqs. 3–5). This assumption was further supported by the iron leaching results (Fig. 7b). An increase in the dissolved iron concentration was observed with the increase of Cu2O content in the catalyst.
To further examine the sharp decline in SMX degradation in the 4th run (Fig. 6), the used CT2.5%Cu2O powders after the 3rd run were collected. Their compositions were characterized with XRD and ICP-OES. The XRD results showed that two compositions including α-Fe2O3 and Cu2O were still detected. However, the relative ratio of Cu2O in the catalyst was reduced, as suggested by the decreased intensity of the (111) plane of Cu2O (Fig. 8a). Therefore, both the dissolution and oxidation of Cu2O may contribute to the deactivation. The ICP-OES analyses revealed that the Cu/Fe ratio was decreased from 0.034 to 0.027 (Fig. 8b), indicating that the leachability of copper was much greater than that of iron during the catalytic reactions. This conclusion was consistent with the leaching and XRD results and the unstable property of copper oxides in AOPs [43, 44].

Figure 8

3.6. Possible pathways for SMX degradation

Usually, it is hard to completely mineralize pollutants even with AOPs. Therefore, degradation intermediates are produced, and these compounds may possess higher toxicity than their parent compounds. Due to the environmentally relevant concentration of SMX used, measuring the mineralization efficiency with a total organic carbon analyser is not convenient. Instead, a UPLC-MS system was used to monitor the degradation of SMX, and UPLC-MS/MS operating in the MRM mode was used for further qualification and quantification. As shown in Fig. S4 and Table S1, ten products were determined during the degradation. On the basis of these evidences, two pathways were possibly responsible for the destruction of SMX (Fig. 9). Two intermediates with m/z values of 349 and 270 were detected at 0.36 min and 1.30 min (Fig. S3b), respectively. Based on the mass loss, they were assigned to sulfate SMX (product A) and hydroxyl SMX (product B),
which further proves that radicals were produced in the CT2.5%Cu2O/PMS oxidation. In previous publications, different attacking positions such as the benzene ring [45, 46, 47, 48] and heterocyclic ring [47] have been reported regarding the addition of hydroxyl radicals onto sulfonamides. In addition, various products are formed when hydroxyl radicals are added onto the benzene ring (e.g., 4-hydroxy-sulfadiazine and 5-hydroxy-sulfadiazine [45]). Therefore, the structure of these adducts of SMX is not clear and deserves further study.

Sulfanilic acid (product C) is assumed to be produced when the S–N bond of sulphonamide breaks [49], but its peak intensity at ~1.12 min (confirmed by standard sulfanilic acid) was too low to be quantified (Fig. S3c). The low response of this compound was probably due to its quick transformation into hydroxyl sulfanilic acid (product D), which was present throughout the degradation (Fig. S3d and Fig. S4). The production of this product was also observed by Yan et al. [48] when examining the degradation of sulfamonomethoxine. The S–N bond cleavage is also supported by the production of 3-amino-t-methylisoxazole (product E) that was detected at 0.86 min (Fig. 9e). The quantification of this compound showed that an increase followed by a decrease in its peak area took place, which indicates that this product first accumulated in the oxidation and then degraded into small molecular products as the reaction continued. The cleavage of the C–N bond linking the benzene and heterocyclic rings in sulfonamides has also been reported in the literature [47, 49], and this cleavage probably occurred during the degradation of SMX. As one of the products resulting from the C–N bond cleavage, sulfanilamide with an m/z of 173 > 156 (product F) was determined. However, its concentration was extremely low (~0.3 µg L⁻¹). In addition, no 5-methylisoxazole was detected throughout the degradation. Therefore, the cleavage of the C–N bond might not be the major pathway for the degradation of SMX. Under further attack by SO₄²⁻ and ·OH, product D and product F were oxidized to aniline and phenol [50]. Although
neither of these products were detected in this study, their production was supported by the
generation of 1, 3-dihydroxybenzol (product G) that was determined at 0.43 min with an \( m/z \) of
109 > 56.

Figure 9

4. Conclusions

As the generation of \( \equiv \text{Fe} (\text{II}) \) is the rate-determining step for radical production in AOPs, \( \alpha \)-Fe\(_2\)O\(_3\) is low efficient for PMS activation. With Cu\(_2\)O as the catalyst additive, a synergistic catalytic effect between \( \alpha \)-Fe\(_2\)O\(_3\) and Cu\(_2\)O was found. This finding offers a convenient and innovative approach to improve the reactivity of iron oxides and thereby may facilitate their application in AOPs. In addition, the discovery of the synergistic effect in radical production might be meaningful for anti-oxidation research because copper is second only to iron in terms of its metalloprotein prevalence.

The synergistic effect was explained by the \( \equiv \text{Cu} (\text{I}) \)-promoted reduction of \( \equiv \text{Fe} (\text{III}) \). These processes probably occurred with PMS acted as a ligand that bridges the redox centers of \( \equiv \text{Cu} (\text{I}) \) and \( \equiv \text{Fe} (\text{III}) \). Because \( \equiv \text{Cu} (\text{I}) \) instead of PMS was consumed in the reduction of \( \equiv \text{Fe} (\text{III}) \), a high SE value was achieved with the CT2.5%Cu\(_2\)O catalyst.

The optimal ratio between copper and iron for SMX degradation depended on the PMS dosage and catalyst loading. Under the conditions of 40 mg L\(^{-1}\) PMS and 0.4 g L\(^{-1}\) catalyst loading, the CT2.5%Cu\(_2\)O had efficient reactivity for SMX degradation and the best stoichiometric efficiency of PMS. Under such conditions, nearly complete degradation of SMX was achieved after 180 min.

The CT2.5%Cu\(_2\)O showed high reutilization performance over the first three cycles, but an obvious decline occurred in the fourth cycle, which was due to the unstable property of Cu\(_2\)O. To
use the combination of \( \equiv \text{Fe(III)} \) and \( \equiv \text{Cu(I)} \) as the catalyst, future studies should be carried out to increase the stability of \( \equiv \text{Cu(I)} \).

Finally, a total of ten products were identified via UPLC-MS/MS. On the basis of these products, the cleavage of the S–N bond was found to be the major pathway for the degradation of SMX. This finding may provide some scientific basis for predicting the oxidative transformation of other sulfonamides in AOPs.

**Disclosure statement**

The authors declare no competing financial interest.
References


Figure 1. (a) Degradation of SMX by PMS in the presence of different catalysts. (b) Plot of \(-\ln(C/C_0)\) versus reaction time (apparent degradation constant \(k_{app}\)). Conditions: \([\text{PMS}] = 20 \text{ mg L}^{-1}, [\text{Cu}_2\text{O}] = [\alpha-\text{Fe}_2\text{O}_3] = [\text{CT1}\%\text{Cu}_2\text{O}] = 0.2 \text{ g L}^{-1}, [\text{Cu(II)}] = [\text{Fe(III)}] = 20 \text{ mg L}^{-1}, [\text{SMX}] = 1.6 \text{ mg L}^{-1}, \) and 10 mM phosphate buffer at pH 6.8. Error bars represent the standard deviation of two replicates. The solid lines in (b) represent the linear regression. The inset in (b) displays the plot of \(-\ln(C/C_0)\) versus reaction time in \(\alpha-\text{Fe}_2\text{O}_3/\text{PMS}\) oxidation during the first 20 min.
Figure 2. Normalized Fe K-edge XANES spectra for the fresh and used CT2.5%Cu2O catalysts (a); the standard Fe K-edge XANES spectra for FeO and α-Fe2O3 are shown for comparison. X-ray photoelectron spectroscopy spectra for Cu 2p of the fresh Cu2O (b) and used Cu2O (c). Conditions: [PMS] = 40 mg L–1, [CT2.5%Cu2O] = [Cu2O] = 0.4 g L–1, [SMX] = 1.6 mg L–1, reaction time = 60 min, and 10 mM phosphate buffer at pH 6.8.
Figure 3. Effect of radical scavengers on the degradation of SMX in CT2.5%Cu₂O/PMS oxidation. Conditions: [PMS] = 40 mg L⁻¹, [CT2.5%Cu₂O] = 0.4 g L⁻¹, [SMX] = 1.6 mg L⁻¹, and 10 mM phosphate buffer at pH 6.8. Error bars represent the standard deviation of two replicates.
Figure 4. SMX degradation kinetics with 20 mg L$^{-1}$ (a), 40 mg L$^{-1}$ (b), or 60 mg L$^{-1}$ (c) PMS under different catalyst loadings. Degradation of SMX by PMS in the presence of different catalysts (d). Conditions: [$\alpha$-Fe$_2$O$_3$] = [CT1%Cu$_2$O] = [CT2.5%Cu$_2$O] = 0.4 g L$^{-1}$ (d), [PMS] = 40 mg L$^{-1}$ (d), reaction time = 60 min (a, b, and c), [SMX] = 1.6 mg L$^{-1}$, and 10 mM phosphate buffer at pH 6.8. Error bars represent the standard deviation of two replicates.
Figure 5. Profile of PMS concentration (a) and stoichiometric efficiencies of PMS (b) in the presence of different catalysts. Conditions: [PMS] = 40 mg L$^{-1}$, [Cu$_2$O] = [$\alpha$-Fe$_2$O$_3$] = [CT1%Cu$_2$O] = [CT2.5%Cu$_2$O] = [CT5%Cu$_2$O] = [CT10%Cu$_2$O] = 0.4 g L$^{-1}$, [SMX] = 1.6 mg L$^{-1}$, reaction time = 60 min (b), and 10 mM phosphate buffer at pH 6.8. Error bars represent the standard deviation of two replicates.
Figure 6. Reusability performance of the CT2.5%Cu2O for SMX degradation. Conditions: [PMS] = 40 mg L\(^{-1}\), [CT2.5%Cu2O] = 0.4 g L\(^{-1}\), [SMX] = 1.6 mg L\(^{-1}\), and 10 mM phosphate buffer at pH 6.8. Error bars represent the standard deviation of two replicates.
Figure 7. Leachability of copper (a) and iron (b) from different catalysts. Conditions: [PMS] = 40 mg L$^{-1}$, $[^\alpha$-Fe$_2$O$_3] = [Cu_2O] = [CT2.5\%Cu_2O] = [CT10\%Cu_2O] = 0.4$ g L$^{-1}$, [SMX] = 1.6 mg L$^{-1}$, and 10 mM phosphate buffer at pH 6.8. Error bars represent the standard deviation of two replicates.
Figure 8. XRD patterns (a) and Cu/Fe ratios (b) of the fresh and used CT2.5%Cu$_2$O catalysts. Error bars represent the standard deviation of two replicates.
Figure 9. Proposed pathways for the degradation of SMX during CT2.5%Cu2O/PMS oxidation. Compounds with capital letters were detected by UPLC-MS/MS. Bold names suggest products confirmed by reference standard compounds. Identified products with italic names are shown in Figure S4 with further specifications.