Chinese Chemical Letters 35 (2024) 109185

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Complexes of cupric ion and tartaric acid enhanced calcium peroxide Fenton-like reaction for metronidazole degradation

Shiyu Pan, Bo Cao, Deling Yuan*, Tifeng Jiao, Qingrui Zhang, Shoufeng Tang*

State Key Laboratory of Metastable Materials Science and Technology, Hebei Key Laboratory of Heavy Metal Deep-Remediation in Water and Resource Reuse, School of Environmental and Chemical Engineering, Yanshan University, Qinhuangdao 066004, China

ARTICLE INFO

Article history:
Received 14 June 2023
Revised 7 September 2023
Accepted 9 October 2023
Available online 10 October 2023

Keywords:
Cupric ion
Tartaric acid
Complexation
Calcium peroxide
Metronidazole removal

ABSTRACT

To surmount the obstacles of traditional Fenton method and synchronously utilize Cu^{2+} and polyphenol in water, an improved Fenton-like reaction applying calcium peroxide (CaO_2) as H_2O_2 source and regulating by the complex of Cu^{2+}-tartaric acid (TA, a representative of polyphenol) was constructed. A typical antibiotic, metronidazole (MTZ) could be effectively eliminated by the Cu^{2+}/TA/CaO_2 system, and the optimized parameters were as follows: 0.1 mmol/L Cu^{2+}, 2 mmol/L TA, 2 mmol/L CaO_2, and initial pH 5. UV spectrum confirmed the formation of Cu^{2+}-TA complex, which promoted the Cu^{2+}/Cu^{+} circulation through decreasing the Cu^{2+}/Cu^{+} couple redox potential, which further enhanced the H_2O_2 decomposition and the formation of reactive species. Hydroxyl radical was dominant for MTZ degradation, followed by oxygen and superoxide radical. The degradation intermediates of MTZ were detected and their evolution way was speculated. Furthermore, the ternary process showed a wide pH tolerance (3–8) for removing MTZ and broad applicability for eliminating other dyes and antibiotics. This work provided a reference for Cu-based Fenton-like strategy for organic wastewater settlement.

Advanced oxidation processes (AOPs) have been universally recognized strategy for the treatment of organic contaminants [1]. The traditional Fenton can non-selectively remove the organics by hydroxyl radical ($HO^{\bullet}$), which is generated from the ferrous ion (Fe^{2+}) activated hydrogen peroxide (H_2O_2) process at acidic conditions (Eqs. 1–3) [2]. Nevertheless, there are a few inherent limitations for the Fenton reaction, including the narrow application range of pH [3,4], the slow ferric ion (Fe^{3+})/Fe^{2+} circulation rate [5,6], and the instability of H_2O_2 [7]. As a solid oxidant, calcium peroxide (CaO_2) is easier to store and transport, which can slowly release H_2O_2 (Eq. 4) [8]. The decomposition rate of CaO_2 could be controlled by adjusting pH, which could avoid the disproportionation of H_2O_2 [9]. Therefore, CaO_2 is considered as an effective substitute for H_2O_2 [10].

On the other side, as another common transition metal, cupric ion (Cu^{2+}) is ubiquitous in multiple waterbodies [11,12]. Cu^{2+} has a larger solubility ($K_{sp\ Cu(OH)2} = 4.8 \times 10^{-20}$) than that of Fe^{3+} ($K_{sp\ Fe(OH)_3} = 2.8 \times 10^{-39}$) [13], and the circulation of Cu^{2+}/cuprous ion (Cu^{+}) is easier than that of Fe^{3+}/Fe^{2+} due to the lower standard potential (E^0 (Fe^{3+}/Fe^{2+}) = 0.77 V *vs.* SHE, E^0 (Cu^{2+}/Cu^{+}) = 0.17 V *vs.* SHE) [14], which means the Cu-based Fenton process is superior with a greater pH tolerance and better catalytic activity (Eqs. 5 and 6) than the Fe-based Fenton method [11]. Therefore, if the Cu^{2+} existed in water matrix can be *in-situ* used to activate Fenton/Fenton-like reactions, which could put forward to the practicality of the homogeneous Cu-based Fenton-like system. However, similar to the conventional Fenton reaction, the slow reduction of Cu^{2+} to Cu^{+} ($k = 1$ L mol^{-1} s^{-1}) remains the rate-limiting step [15,16]. Thus, exploring a skill to accelerate the Cu^{2+}/Cu^{+} circulation is imperative for promoting this Fenton-like reaction.

$$H_2O_2 + Fe^{2+} \rightarrow HO^{\bullet} + OH^{-} + Fe^{3+}, k_1 = 63\ \text{L mol}^{-1}\ \text{s}^{-1} \quad (1)$$

$$H_2O_2 + Fe^{3+} \rightarrow HO_2^{\bullet} + H^{+} + Fe^{2+}, k_2 = 2.7 \times 10^{-3}\ \text{L mol}^{-1}\ \text{s}^{-1} \quad (2)$$

$$HO_2^{\bullet} + Fe^{3+} \rightarrow O_2 + H^{+} + Fe^{2+}, k_3 = 1.8 \times 10^{3}\ \text{L mol}^{-1}\ \text{s}^{-1} \quad (3)$$

$$CaO_2 + 2H_2O \rightarrow H_2O_2 + Ca(OH)_2 \quad (4)$$

$$H_2O_2 + Cu^{+} \rightarrow Cu^{2+} + HO^{\bullet} + OH^{-}, k_4 = 4 \times 10^{5}\ \text{L mol}^{-1}\ \text{s}^{-1} \quad (5)$$

$$H_2O_2 + Cu^{2+} \rightarrow HO_2^{\bullet} + H^{+} + Cu^{+}, k_5 = 1\ \text{L mol}^{-1}\ \text{s}^{-1} \quad (6)$$

* Corresponding authors.
E-mail addresses: yuandl@ysu.edu.cn (D. Yuan), tangshf@ysu.edu.cn (S. Tang).

https://doi.org/10.1016/j.cclet.2023.109185
1001-8417/

$$Cu^{+} + O_2 \rightarrow Cu^{2+} + O_2^{\bullet -} \quad (7)$$

$$Cu^{+} + O_2^{\bullet -} + 2H^{+} \rightarrow Cu^{2+} + H_2O_2 \quad (8)$$

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \quad (9)$$

$$HO_2^{\bullet} \rightarrow H^{+} + O_2^{\bullet -} \quad (10)$$

$$O_2^{\bullet -} + H_2O_2 \rightarrow OH^{-} + HO^{\bullet} + {}^1O_2 \quad (11)$$

The complexation of Cu^{2+} with organic ligands could alter the activity of Cu^{2+}/Cu^{+} couple, and stabilize Cu ions in terms of electronic property and steric effect [12]. Moreover, some Cu^{2+} complexes could efficiently trigger H_2O_2 or persulfates to produce radicals, for degrading diverse organic pollutants [17]. However, some organic ligands, such as ethylenediaminetetraacetic acid [18,19], pyridine [17], and ethylenediamine [20], they are themselves contaminants, which not only increase the amount of organic matter and bring secondary pollution, but also quench free radicals by their self-degradation effect [21]. Hence, searching an environmentally friendly organic ligand is the key for improving homogeneous Cu-based Fenton-like system.

Plant-derived polyphenols belong to natural organic matter (NOM) and also low-molecular-weight organic acids, which are commonly found in the natural environments, including water [11,22]. The hydroxyl groups of polyphenols have the property of strong electron donor [23], which could mediate the Cu^{2+}/Cu^{+} cycle and then reduce Cu^{2+} to Cu^{+} [11,24], triggering a series of chain reactions (Eqs. 5-11) to generate $HO^{\bullet}$, superoxide ($O_2^{\bullet -}$), and singlet oxygen ($^1O_2$) [25,26]. Tartaric acid (TA) is a typical polyphenol, comes from grape and tamarind [10,27], which could be strongly complexed with Fe ions and regulate their redox cycling [28,29]. Nevertheless, there has been an obvious knowledge gap in the function of TA complexed with Cu ions for Fenton/Fenton-like processes.

Based on above, the *in-situ* simultaneous utilizations of Cu^{2+} and NOM in water might realize the most efficient implementation for Fenton/Fenton-like reactions [30]. Thus, in this study, the effectiveness of Cu^{2+}-TA complex for catalyzing CaO_2-based Fenton-like system was verified for metronidazole (MTZ) elimination. The systematical study centered around the followings: (1) Determine the influences of key factors (the dosages of Cu^{2+}, TA, and CaO_2, and pH) of the ternary processes; (2) investigate the catalytic function of Cu^{2+}-TA complex; (3) explore the evolution and contribution of reactive oxygen species (ROS) during this Cu-based Fenton-like reaction.

The specific chemicals of the work were recorded in Text S1 (Supporting information). The batch experiment was conducted in a 150 mL glass vessel under electromagnetic stirring at room-temperature. The desired concentration of MTZ was configured with phosphate buffer, which fixed the initial pH of the reaction solution. TA and cupric chloride ($CuCl_2$) were successively added into 100 mL of MTZ solution, the experiment was triggered once added the desired concentration of CaO_2. All the tests were conducted at least in twice. MTZ concentration was detected through UV spectroscopy at 320 nm [13,31]. *Tert*-butyl alcohol (TBA), L-Histidine (L-His), and *p*-benzoquinone (*p*-BQ) were selected as the ROS scavenger, and the generation of ROS was detected by electron spin resonance technique (ESR). The concentration of H_2O_2 was determined by potassium titanium oxalate colorimetry [13]. The content of Cu ions was measured by neocuproine spectrophotometry [32]. Electro-chemical workstation was applied to conduct the cyclic voltammetry measurement [13].

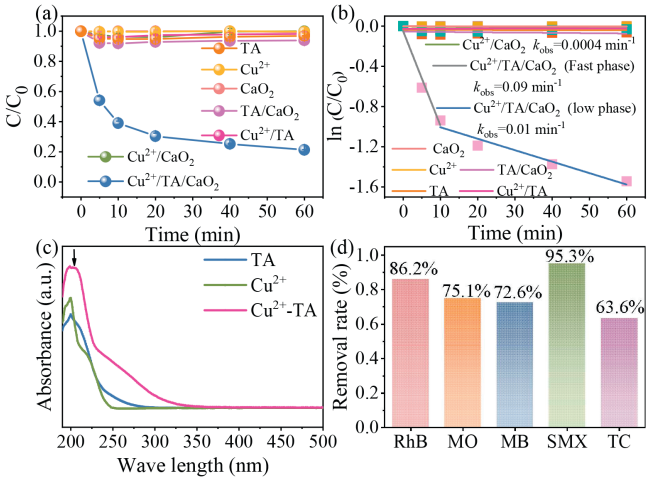

Fig. 1. (a) Elimination for MTZ in different systems and (b) corresponding pseudo-first-order kinetic rate constant. (c) UV–vis absorption spectra of Cu^{2+}, TA, and Cu^{2+}-TA. (d) Degradation of different organic contaminants in $Cu^{2+}/TA/CaO_2$ system. Experimental condition: $[Cu^{2+}]_0 = 0.1$ mmol/L, $[TA]_0 = 2$ mmol/L, $[CaO_2]_0 = 2$ mmol/L, pH_0 5, [MTZ] = [MB] = [MO] = [RhB] = [SMX] = [TC] = 5 mg/L.

MTZ decomposed intermediates were determined by high performance liquid chromatography-mass spectrometry (HPLC-MS). The detailed analysis and operation were listed in Text S2 (Supporting information).

The enhancement effect of TA on Cu^{2+}/CaO_2 was evaluated by comparing the degradation efficiencies of MTZ in diverse processes. Fig. 1a shows the removal of MTZ was negligible in Cu^{2+}/CaO_2 after 60 min. Nevertheless, the elimination of MTZ augmented to 78.7% in the $Cu^{2+}/TA/CaO_2$ system. The apparent rate constant (k_{obs}) of MTZ degradation in $Cu^{2+}/TA/CaO_2$ process was 225 times higher than that in Cu^{2+}/CaO_2 in the first 10 min, and 25 times higher in the following 50 min reaction (Fig. 1b). The decrease of k_{obs} during the following 50 min might be ascribed to the quickly falling H_2O_2. Furthermore, the insignificant degradation of MTZ was observed in TA/CaO_2 and Cu^{2+}/TA systems, which indicated that TA could not activate CaO_2 directly, and CaO_2 was the motivity of MTZ removal [33]. UV–vis spectrum was employed to verify the formation of Cu^{2+}-TA complex. As depicted in Fig. 1c, compared with the spectra of Cu^{2+} and sole TA, an emerging absorption peak was appeared around 213 nm in the mixed sample of Cu^{2+} and TA, which testified the production of Cu^{2+}-TA metal organic ligand. TA might serve as the chelating agent to mediate the redox potential of Cu ions and promote the generation of ROS [18], therefore enhancing the performance of the Cu^{2+}/CaO_2 system.

Besides, Fig. 1d shows the $Cu^{2+}/TA/CaO_2$ process also had the remarkable capability for other contaminants removal, including rhodamine b (RhB), sulfamethoxazole (SMX), methyl orange (MO), tetracycline (TC), and methylene blue (MB). Furthermore, Fig. S1 (Supporting information) shows that 34.6% of chemical oxygen demand (COD) removal ratio was reached for domestic sewage by the synergistic process after 180 min reaction. Besides, the total organic carbon (TOC) removal achieved 20.2% after 180 min (Fig. S2 in Supporting information). Thus, the ternary system possessed an extensive applicability and actual potential for removing organic pollutants in wastewater.

The influences of specific reaction parameters on the elimination of MTZ in the $Cu^{2+}/TA/CaO_2$ system were systematically investigated, including Cu^{2+} dosage (Fig. 2a), TA dosage (Fig. 2b), and CaO_2 concentration (Fig. 2c). The results manifested that Cu^{2+}, TA, and CaO_2 were all indispensable factors, the absence of any one of them would seriously affect the degradation of MTZ. Furthermore, the higher dosages of Cu^{2+} and CaO_2 would accelerate the

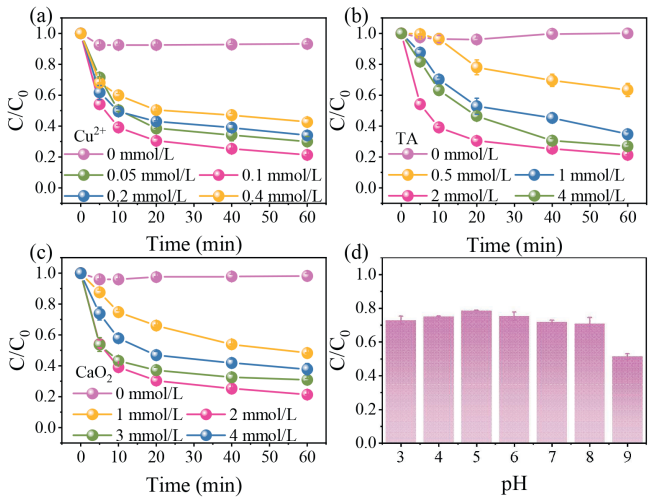

Fig. 2. Influences of (a) Cu^{2+}, (b) TA, (c) CaO_2, and (d) pH on MTZ degradation in Cu^{2+}/TA/CaO_2 system. Experimental condition: $[Cu^{2+}]_0 = 0.05–0.4$ mmol/L, $[TA]_0 = 0.5–4$ mmol/L, $[CaO_2]_0 = 1–4$ mmol/L, pH_0 3–9, [MTZ] = 5 mg/L.

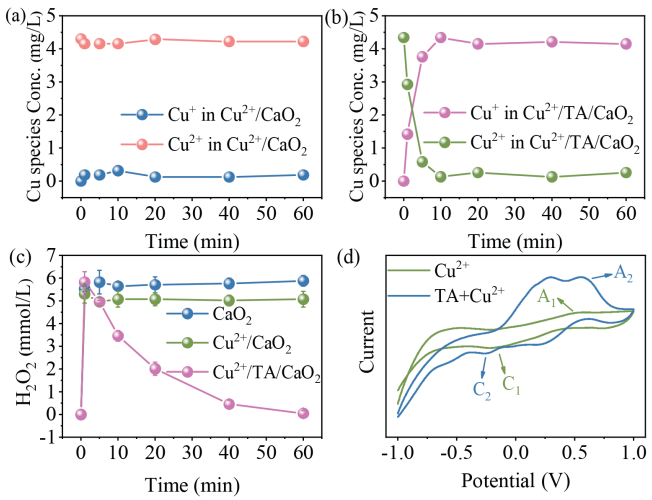

Fig. 3. Variation of Cu^{2+} and Cu^{+} concentration in Cu^{2+}/CaO_2 (a) and Cu^{2+}/TA/CaO_2 systems (b). (c) Change of H_2O_2 concentration in different systems. (d) CV of Cu^{2+}-TA. Experimental condition: $[Cu^{2+}]_0 = 0.1$ mmol/L, $[TA]_0 = 2$ mmol/L, $[CaO_2]_0 = 2$ mmol/L, pH_0 5, [MTZ] = 5 mg/L.

generation of HO• to trigger the self-quenching reaction (Eq. 9) to restrain the elimination of MTZ. TA as an organic compound would compete HO• with MTZ, hence the excess TA also hindered the removal of MTZ. Therefore, after the comprehensive investigation, the optimal experimental dosages were as follows: 0.1 mmol/L Cu^{2+}, 2 mmol/L TA, and 2 mmol/L CaO_2. Moreover, the ternary process indicated a wide pH tolerance, as described in Fig. 2d, MTZ could be eliminated efficiently as the pH values increased from 3 to 8. Above results proved the benign catalytic ability of Cu^{2+}-TA complex.

Moreover, the resistant ability for common anions (chloridion (Cl^-), sulfate ion (SO_4^{2-}), nitrate ion (NO_3^-), and bicarbonate ion (HCO_3^-)) on the Cu^{2+}/TA/CaO_2 system was investigated (Fig. S3 in Supporting information). The complexing system represented a great resistant ability for different anions expect HCO_3^-. Carbonate radical anion ($CO_3^{\bullet-}$) with lower redox potential (1.59 V) would be generated by HCO_3^- quenching HO• (Eqs. 12–14), which would inhibit the degradation of MTZ [34,35].

$$HCO_3^- + HO^\bullet \rightarrow CO_3^{2-} + H_2O \quad (12)$$

$$HCO_3^- \rightarrow CO_3^{2-} + H^+ \quad (13)$$

$$CO_3^{2-} + O_2^{\bullet-} \rightarrow CO_3^{\bullet-} + O_2^{2-} \quad (14)$$

To investigate the role of TA in the enhanced Cu^{2+}/CaO_2 process, the change of Cu^{2+}/Cu^+ cycle and H_2O_2 concentration during the reaction were compared in Cu^{2+}/CaO_2 and Cu^{2+}/TA/CaO_2. As displayed in Fig. 3a. 0.19 mg/L of Cu^+ was produced in Cu^{2+}/CaO_2 system, the weak reduction of Cu^{2+} to Cu^+ might be the reason for hindering MTZ degradation. However, the Cu^{2+} was almost completely converted into Cu^+ in the present of TA (Fig. 3b), which testified that the Cu^{2+}-TA complex could effectually accelerate the reduction of Cu^{2+}. In addition, the consumption of H_2O_2 in different systems was also investigated (Fig. 3c). Firstly, 5.88 mmol/L H_2O_2 could be released by CaO_2 alone, and only 0.2 mmol/L of H_2O_2 was decomposed in Cu^{2+}/CaO_2. In Cu^{2+}/TA/CaO_2 system, H_2O_2 could be consumed rapidly, and the concentration of H_2O_2 was declined from 5.82 mmol/L to 0.05 mmol/L after 60 min. These results proved that the Cu^{2+}-TA complex could availably promote the disintegration of H_2O_2.

To demonstrate the redox ability of Cu^{2+}-TA complex, the cyclic voltammetry (CV) was conducted in the Cu^{2+} system with or without TA. As shown in Fig. 3d, the peaks of A_1 and A_2 were owed to the oxidation of Cu^+ to Cu^{2+}, while C_1 and C_2 were the reducing peaks of Cu^{2+} to Cu^+ [13]. The higher peak potential in the mixed Cu^{2+} and TA solution (A_2, C_2) than that in the without TA (A_1, C_1) indicated that the Cu^{2+}-TA complex had the greater redox capacity. Hence, TA chelated with Cu^{2+} in the Cu^{2+}/TA/CaO_2 could reduce the Cu^{2+}/Cu^+ redox potential to improve the Cu^{2+}/Cu^+ cycle, enhancing the H_2O_2 disintegration and the ROS production [13].

The primary ROS in the Cu^{2+}/TA/CaO_2 were clarified firstly by quenching experiment. TBA was applied to quench HO• ($k_{HO^\bullet, TBA} = 6 \times 10^8$ L mol^{-1} s^{-1}) [36,37]. As described in Fig. 4a, MTZ removal efficiency significantly declined to 24.2% under 2 mmol/L TBA, indicating that HO• played the dominant role for MTZ elimination. Moreover, *p*-BQ and L-His were selected to suppress $O_2^{\bullet-}$ and $^1O_2$ ($k_{O_2^{\bullet-}, p\text{-BQ}} = (0.9–1) \times 10^9$ L mol^{-1} s^{-1}, $k_{^1O_2, \text{L-His}} = 3.2 \times 10^7$ L mol^{-1} s^{-1}), separately [38–40]. As shown in Figs. 4b and c, the slight quenching effect of *p*-BQ and L-His illustrated that $O_2^{\bullet-}$ and $^1O_2$ both played the minor role in this system. Ulteriorly, ESR was employed to confirm the existence of ROS. 5,5-dimethyl-1-pyrrolidine-*N*-oxide (DMPO) was used to trap HO• and $O_2^{\bullet-}$, 2,2,6,6-tetramethylpiperidine (TEMP) was employed to capture $^1O_2$ [38,41]. As presented in Figs. 4d– f, the typical signals of DMPO-HO•, DMPO-$O_2^{\bullet-}$, and TEMP-$^1O_2$ adducts were detected in both processes with and without TA. Of note, the signal intensity of Cu^{2+}/TA/CaO_2 was obviously stronger than that of Cu^{2+}/CaO_2, which affirmed the role of TA on the enhancement of ROS generation in this Cu-based Fenton-like reaction.

The generated HO• exhibited triple roles in this system: (1) contributing to the degradation of MTZ; (2) reacting with the excess H_2O_2 to generate the secondary $O_2^{\bullet-}$ and $^1O_2$ (Eqs. 9–11); (3) attacking the electrophilic TA into the small molecule. Furthermore, Cu^+-TA also reacted with O_2 to promote the production of $O_2^{\bullet-}$ (Eq. (15)), and the generated Cu^{2+}-TA reacted with the excess H_2O_2 to sustain the Cu^{2+}/Cu^+ cycle (Eq. 16) [42]. However, $O_2^{\bullet-}$ and $^1O_2$ could not effectively remove MTZ due to the low oxidation capacity ($k_{O_2^{\bullet-}, MTZ} = 0$ L mol^{-1} s^{-1}, $k_{^1O_2, MTZ} = 1.5 \times 10^8$ L mol^{-1} s^{-1}), so HO• was the dominant ROS for MTZ elimination ($k_{HO^\bullet, MTZ} = 6 \times 10^9$ L mol^{-1} s^{-1}) in the ternary system, followed by $^1O_2$ and $O_2^{\bullet-}$ [43,44].

$$Cu^+–TA + O_2 \rightarrow Cu^{2+}–TA + O_2^{\bullet-} \quad (15)$$

$$Cu^{2+}–TA + H_2O_2 \rightarrow Cu^+–TA + HO_2^\bullet + H^+ \quad (16)$$

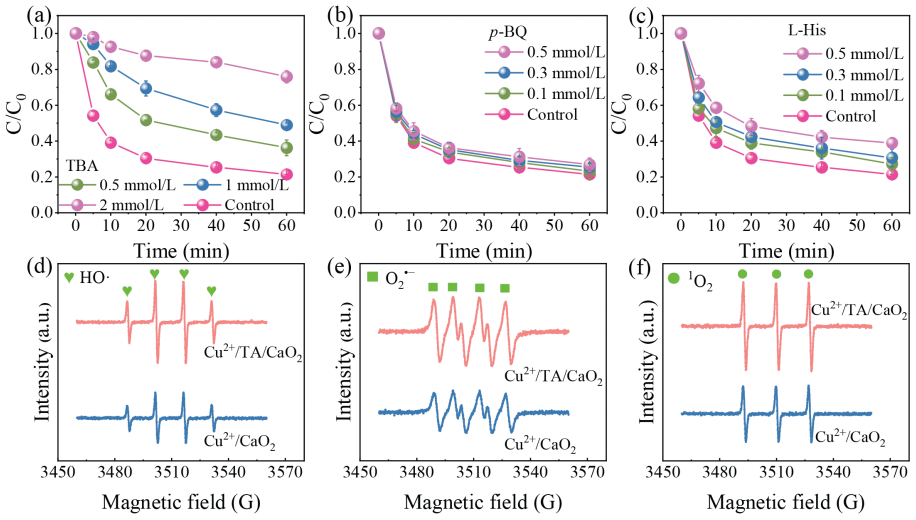

Fig. 4. Influences of (a) TBA, (b) *p*-BQ, and (c) L-His on MTZ degradation in Cu^{2+}/TA/CaO_2 system. EPR spectra of (d) DMPO-HO· adduct, (e) DMPO-$O_2^{\bullet-}$ adduct, and (f) TEMP-$^1O_2$ adduct in both systems. Experimental condition: $[Cu^{2+}]_0 = 0.1$ mmol/L, $[TA]_0 = 2$ mmol/L, $[CaO_2]_0 = 2$ mmol/L, $[TBA]_0 = 0.5–2$ mmol/L, $[p\text{-BQ}]_0 = [\text{L-His}]_0 = 0.1–0.5$ mmol/L, pH_0 5, [MTZ] = 5 mg/L.

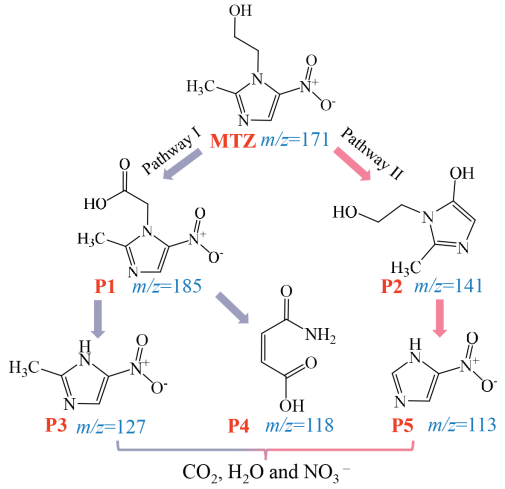

Fig. 5. Speculated decomposition pathways of MTZ.

According to the result of HPLC-MS, the possible degradation pathways of MTZ during Cu^{2+}/TA/CaO_2 were proposed. As revealed in Fig. 5, firstly, (2-methyl-5-nitroimidazol-1-yl) acetic acid (**P1**, $m/z = 185$) might be produced by the *N*-ethanol group oxidation of MTZ [45,46]. Next, HO· attacked the *N*-acetic acid group of **P1** and generated 2-methyl-5-nitro-1*H*-imidazole (**P3**, $m/z = 127$) [45,47], or **P1** underwent hydroxylation and ring opening reaction to form 3-carbonyl propylene glycol 2-oleic acid (**P4**, $m/z = 118$) [45,48]. In another pathway, 3-(2-hydroxy-ethyl)-2-methyl-3*H*-imidazole-4-ol (**P2**, $m/z = 141$) was formed by the direct hydroxylation of nitro group [45,49]. The crack of *N*-acetic acid group and nitration reaction were occurred on **P2** to form byproduct **P5** ($m/z = 113$) [50]. In addition, the biotoxicity of MTZ and its elimination byproducts was evaluated by toxicity assessment software, the results demonstrated that the oral rat LD50 (Fig. S4a in Supporting information) and the developmental toxicity (Fig. S4c in Supporting information) of part intermediates were higher than that of MTZ. However, the bioaccumulation factor (Fig. S4b in Supporting information) and the mutagenicity (Fig. S4d in Supporting information) of the intermediates were all decreased after the treatment of the synergic process. Therefore, the Cu^{2+}/TA/CaO_2 process could decrease the biotoxicity of MTZ to some extent, and appropriate prolongation of reaction might be required to minimize toxicity in practical treatment.

To sum up, the conceivable mechanism of TA enhanced Cu^{2+}/CaO_2 system can be summarized as follows. In the Cu^{2+}/CaO_2 system, the sluggish Cu^{2+}/Cu^{+} cycle hindered the activation of H_2O_2 (Eqs. 5 and 6), then hampered the elimination of MTZ (Fig. 1a). Upon the TA addition, Cu^{2+} was rapidly complexed with the two hydroxyl groups of TA to form a soluble Cu^{2+}-TA complex (Eq. 17, Fig. 1c), which could decrease the redox potential of Cu^{2+}/Cu^{+} (Fig. 3d). The Cu^{2+}-TA could be reduced by H_2O_2 to form the reductive Cu^{+}-TA, which could improve the reduction of Cu^{2+} (Eq. 16, Fig. 3b) and the activation of H_2O_2 (Eq. 18, Fig. 3c) [42]. Next, the production of various ROS was enhanced by the complexation, such as HO·, $O_2^{\bullet-}$, and $^1O_2$ (Figs. 4d–f), and the removal of MTZ was also promoted. Overall, Cu^{+}-TA was the critical species to manipulate this ternary system, and TA severed as the electron donor to promote the electron transfer in metal-ligand and enhance the generation of ROS.

$$Cu^{2+} + TA \rightarrow Cu^{2+}\text{–}TA \quad (17)$$

$$Cu^{+}\text{–}TA + H_2O_2 \rightarrow Cu^{2+}\text{–}TA + HO^{\bullet} + OH^{-} \quad (18)$$

In summary, the complexation of Cu^{2+} and TA could efficaciously catalyze CaO_2 oxidation of MTZ in the pH extent of 3–8. The addition of TA could accelerate the regeneration of Cu^{+}, which was driven from the formed ligand of Cu^{2+} and TA. Furthermore, the Cu^{2+}-TA complex could motivate the H_2O_2 disintegration and the ROS production. HO· was proved to be the main ROS for MTZ degradation, followed by $^1O_2$ and $O_2^{\bullet-}$. MTZ decomposition pathways mainly included hydroxylation, ring opening, attack on specific group, and nitration reactions. This work proved that TA could be a potential chelating agent to promote Fenton-like reaction for degrading different organic contaminants, which provided a referable method for improving the performance of Cu-based Fenton-like system.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

We thank the supports from the National Natural Science Foundation of China (No. 51908485), the Central Guidance on Local Science and Technology Development Fund of Hebei Province (No. 226Z3603G), Hebei Province Foundation for Returnees (No. C20210502).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2023.109185.

References

[1] H. Weng, Y. Yang, C. Zhang, et al., Chem. Eng. J. 453 (2023) 139812.
[2] S. Pan, Z. Zhai, K. Yang, et al., Sep. Purif. Technol. 289 (2022) 120806.
[3] C. Wang, B. Wei, H. Zhu, et al., Chin. Chem. Lett. 33 (2022) 3073–3077.
[4] W. Zheng, Y. Liu, F. Liu, et al., Water Res. 223 (2022) 118994.
[5] W. Hu, M. Yang, Q. Yan, et al., Chin. Chem. Lett. 34 (2023) 108109.
[6] Q. Zhao, C. Wang, P. Wang, Chin. Chem. Lett. 33 (2022) 4828–4833.
[7] S. Tang, E. Zhu, Z. Zhai, et al., Chemosphere 319 (2023) 138025.
[8] D. Yuan, C. Zhang, S. Tang, et al., Chin. Chem. Lett. 32 (2021) 3387–3392.
[9] Y. Zhou, X. Fang, T. Wang, Y. Hu, J. Lu, Chem. Eng. J. 313 (2017) 638–645.
[10] S. Tang, Z. Wang, D. Yuan, et al., J. Clean. Prod. 268 (2020) 122253.
[11] Y. Wang, Y. Wu, Y. Yu, et al., Water Res. 186 (2020) 116326.
[12] J. Chen, X. Zhou, P. Sun, Y. Zhang, C. Huang, Environ. Sci. Technol. 53 (2019) 11774–11782.
[13] Q. Ye, H. Xu, Q. Wang, et al., J. Hazard. Mater. 407 (2021) 124351.
[14] G. Pan, Z. Sun, Chemosphere 283 (2021) 131257.
[15] N. Li, T. Liu, S. Xiao, et al., J. Hazard. Mater. 445 (2023) 130536.
[16] L. Jin, S. You, N. Ren, B. Ding, Y. Liu, Environ. Sci. Technol. 56 (2022) 11750–11759.
[17] J. Li, A.N. Pham, R. Dai, Z. Wang, T.D. Waite, J. Hazard. Mater. 392 (2020) 122261.
[18] A. De Luca, R.F. Dantas, S. Esplugas, Water Res. 61 (2014) 232–242.
[19] A. Gabet, C. Guy, A. Fazli, et al., Sep. Purif. Technol. 317 (2023) 123877.
[20] A. Rastogi, S.R. Al-Abed, D.D. Dionysiou, Water Res. 43 (2009) 684–694.
[21] Y. Xiang, K. Yang, Z. Zhai, et al., Chem. Eng. J. 438 (2022) 135656.
[22] H. Zhou, H. Zhang, Y. He, et al., Appl. Catal. B. 286 (2021) 119900.
[23] Q. Ouyang, F. Kou, N. Zhang, et al., Chem. Eng. J. 366 (2019) 514–522.
[24] Y. Bai, D. Wu, W. Wang, et al., Environ. Res. 192 (2021) 110242.
[25] X. Li, Y. Jia, J. Zhang, et al., Chin. Chem. Lett. 33 (2022) 2105–2110.
[26] D. Yuan, C. Zhang, S. Tang, et al., Water Res. 163 (2019) 114861.
[27] M. Rashidipour, Z. Derikvand, A. Shokrollahi, Z. Mohammadpour, A. Azadbakht, Arab. J. Chem. 10 (2017) S3167–S3175.
[28] P. Villegas-Guzman, S. Giannakis, R.A. Torres-Palma, C. Pulgarin, Appl. Catal. B. 205 (2017) 219–227.
[29] Z. Ouyang, C. Yang, J. He, et al., Chem. Eng. J. 402 (2020) 126122.
[30] T. Pan, Y. Wang, X. Yang, X. Huang, R. Qiu, Chem. Eng. J. 384 (2020) 123248.
[31] Y. Xiang, H. Liu, E. Zhu, et al., Sep. Purif. Technol. 295 (2022) 121293.
[32] X. Zhou, H. Luo, B. Sheng, et al., J. Hazard. Mater. 411 (2021) 125050.
[33] M. Zhao, Y. Xiang, X. Jiao, et al., Sep. Purif. Technol. 276 (2021) 119289.
[34] S. Pan, T. Zhao, H. Liu, et al., Chem. Eng. J. 452 (2023) 139245.
[35] Y. Huang, L. Bu, Y. Wu, et al., Chem. Eng. J. 442 (2022) 135995.
[36] F. Ye, W. Sun, K. Pang, et al., Chin. Chem. Lett. 34 (2023) 107755.
[37] M. Wang, M. Fu, J. Li, et al., Chin. Chem. Lett. 35 (2024) 108442.
[38] Y. Li, H. Dong, J. Xiao, et al., Chem. Eng. J. 455 (2023) 140773.
[39] L. Yang, W. Chen, C. Sheng, et al., Appl. Surf. Sci. 549 (2021) 149300.
[40] Z. Yang, Z. Wang, G. Liang, X. Zhang, X. Xie, Chem. Eng. J. 426 (2021) 131777.
[41] P. Yang, A. Shen, Z. Zhu, et al., Chem. Eng. J. 464 (2023) 142724.
[42] J. Guo, X. Chen, Y. Shi, Y. Lan, C. Qin, PLoS One 10 (2015) e0134298.
[43] L. Gao, Y. Guo, J. Zhan, G. Yu, Y. Wang, Water Res. 221 (2022) 118730.
[44] Y. Guo, J. Long, J. Huang, G. Yu, Y. Wang, Water Res. 215 (2022) 118275.
[45] H. Ren, H. Liu, T. Cui, et al., Chem. Eng. J. 431 (2022) 133803.
[46] S. Tang, H. Liu, E. Zhu, et al., Sep. Purif. Technol. 301 (2022) 122056.
[47] J. Cao, J. Li, W. Chu, W. Cen, Chem. Eng. J. 400 (2020) 125813.
[48] X. Guo, B. Hu, K. Wang, et al., Chem. Eng. J. 435 (2022) 132910.
[49] J. Zeng, J. Liu, W. Su, et al., J. Water Process. Eng. 53 (2023) 103733.
[50] X. Tian, T. Luo, Y. Nie, et al., Environ. Sci. Technol. 56 (2022) 5542–5551.