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Synthetic Cu(III) from copper plating wastewater for onsite decomplexation of Cu(II)- and Ni(II)-organic complexes

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ABSTRACT

Herein, the Cu(III) synthesized from copper plating effluent was developed for the first time to evaluate the onsite degradation performance of heavy metal complexes in the wastewater, thus achieving the purpose of "treating waste with waste". The results indicated that synthetic Cu(III) presented the excellent decomplexation performance for Cu(II)/Ni(II)-organic complexes. The removal efficiency of Cu(II)/Ni(II)-EDTA significantly increased with increasing Cu(III) dosage, and the degradation of Cu(II)/Ni(II)-EDTA by synthetic Cu(III) system displayed highly pH-dependent reactivity. The radical quencher experiments confirmed that Cu(III) direct oxidation were mainly involved in the degradation of Cu(II)-EDTA. Additionally, the continuous decarboxylation process was proven to be the main degradation pathway of Cu(II)-EDTA in Cu(III) system. The coexisting substances (SO_4^{2-}, Cl^- and fulvic acids) showed little impacts at low level for the removal of Cu(II)/Ni(II)-EDTA, while retarded the degradation of Cu(II)-EDTA slightly at high level, which features high selective oxidation. Encouragingly, it was also effective to remove Cu(II)/Ni(II)-EDTA from in treating actual Cu/Ni-containing wastewater through synthetic Cu(III) treatment.

A considerable portion of heavy metals present as complexed species in heavy metal industrial effluents such as smelting, electroplating, and manufacturing due to the wide employment of complexing agents (*e.g.*, ethylenediaminetetraacetic acid (EDTA), citric acid, and tartaric acid) [1–3]. Complexed heavy metals exhibit more stable structure and higher water solubility than free species, which are resistant to the conventional methods such as precipitation, adsorption, and ion exchange, and thus posing potential risks to the environment and human health [4,5]. Therefore, in the context of strict emission standards, developing new technologies for efficient treatment of complexed heavy metal wastewater have become an urgent problem to be solved.

Most of advanced oxidation processes (AOPs), mainly including Fenton oxidation [6,7], photocatalytic oxidation [8–10], ozone oxidation [11,12], electrochemical oxidation [13–16], are able to eliminating heavy metal complexes because of their ability to produce strong oxidizing radicals such as hydroxyl radical ($HO^•$). Non-selective $HO^•$ can destroy the strong bonds between heavy metals and atoms such as N and O in the ligand into free species, which thereby was removed by the following conventional methods such as chemical precipitation [17,18]. However, the coexistence of a large amount of organic compounds such as stabilizers and high concentrations of inorganic anions including Cl^-, NO_3^-, and SO_4^{2-} in wastewater consume a large amount of $HO^•$, resulting in low decomplexation efficiency and high reagent dosage [19–22]. Thus, the alternative AOPs that can degrade heavy metal complexes selectively in complex water matrices will be the key to solving the above bottleneck.

In recent years, high-valent metals such as Cu(III) and Fe(VI) have been extensively studied as a result of their oxidation properties comparable to $HO^•$ and sulfate radicals ($SO_4^{•-}$), capable of chelating with ligands to accelerate electron transfer [23–25]. Among them, Cu(III), a single-electron strong oxidant, possesses higher substrate selectivity than $HO^•$, which is considered to be one of the effective methods to remove refractory pollutants in wastewater [26–28]. It is worth noting that the redox potential of solid Cu(III) reaches up to 2.3 V, slightly higher than Fe(VI) (2.2 V), and its oxidation capacity is comparable to Fe(VI) [29]. Therefore, preparing solid Cu(III) for selective oxidation of various pollutants will be an effective and promising way. There have been many studies [29–31] on the preparation of Cu(III) compounds which

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in general were prepared using the potassium persulfate oxidation method, and the prepared Cu(III) has high removal efficiency for common pollutants such as phenols and antibiotics in water. Unfortunately, to date, the synthesis of Cu(III) was still based on the preparation of traditional copper compounds, which required a large amount of additional copper reagents and leaded to high processing costs. In addition, Cu itself with high toxicity, is the main element causing heavy metal pollution [32,33], so the addition of Cu(III) in the wastewater treatment is bound to be accompanied by secondary pollution of heavy metals. The activation of coexisting Cu(II) *per se* in wastewater to produce Cu(III) will be an alternative approach of "using waste to treat waste" to avoid extra input of Cu chemical reagent and secondary pollution. The coordination regulation can promote Cu(II) activation to generate Cu(III), such as Cu(II) complexation with phosphonate and beta-lactam antibiotic [27,30]. Recently, we demonstrated ultraviolet (UV) can be capable of accelerating the activation of Cu(II) complexation with (amino)carboxylate to produce the endogenous Cu(III) species for self-catalytic decomplexation of Cu(II) complexes during UV/peroxymonosulfate (PMS) [34]. However, due to the scenario limitation of particular ligand and the unclear and complicate electron transfer between Cu(II) and ligand, the controllable generation and efficient utilization of Cu(III) from complexed Cu(II) are still challenging.

The employment of inherent Cu(II) to synthesize Cu(III) is a controllable process of resource utilization. Acidic copper plating wastewater is also one of the heavy metal wastewater in electroplating industry, accompanying with the complexed heavy metal wastewater such as Cu and Ni [35]. In contrast to the complexed Cu/Ni wastewater, Cu is in the form of free state in acidic copper plating effluent, and its concentration reaches tens to hundreds of mg/L [36]. Clearly, these abundant Cu ions can be used as the raw material for the preparation of Cu(III). Moreover, Cu(III) exhibited the fast and high reactivity with carboxylic metal complexes such as Cu(II)-glycine and Cu(II)-nitrilotriacetic acid (NTA) [37,38]. Thus, the *in-situ* utilization of synthetic Cu(III) from copper plating effluent will be a very promising strategy for the destruction of Cu(II)/Ni(II)-organic complexes in the electroplating wastewater. We believe this strategy of "waste controlled by waste" could realize resourceful utilization of copper plating wastewater and simultaneous efficient elimination of refractory Cu(II)/Ni(II) complexes.

From the perspective of "treating waste with waste", this study prepared Cu(III) from a large amount of Cu ions contained in copper plating wastewater, and its structural property was characterized. The carboxylic Cu(II)/Ni(II) complexes were selected as targeted contaminants to explore the removal of heavy metal complexes by synthesized Cu(III). Consequently, the main purposes in the study were to: (1) characterize Cu(III) prepared from copper plating wastewater; (2) investigate the performance and internal mechanism of synthetic Cu(III) for destroying complexed heavy metals; (3) validate the feasibility of its treatment of actual wastewater.

All reagents were of analytic grade and the solutions were prepared with ultrapure water (Millipore, 18.2 MΩ cm) in this study. Copper sulfate (98%), potassium persulfate (99%), potassium hydroxide (98%), sodium nitrate (98%), sulfuric acid (98%), sodium hydroxide (99.5%), sodium chloride (98%), sodium sulfate (98%), sodium formate (98.5%), fulvic acid (98%), NTA (98%), disodium ethylenediaminetetraacetate (98%), sodiumcitrate (98%), sodium tartrate (98%) and nickel sulfate (99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium periodate (98%), methanol (98%) and *tert*-butanol (TBA, 99.5%) were obtained from Aladdin Reagent Co., Ltd. Nitrobenzene (NB, 99%) was purchased from Sigma-Aldrich.

Conventional Cu(III)-periodate was synthesized by oxidizing Cu ions with potassium persulfate in the presence of sodium periodate. The large amount of Cu contained in the copper plating wastewater was used to replace copper sulfate. The copper wastewater, sodium periodate, potassium persulfate and potassium hydroxide were added to a 250 mL round-bottomed flask containing 100 mL ultrapure water in a typical procedure. After dissolution, the solution was refluxed for 30 min and cooled to ambient temperature. The resulting mixture was filtered through a glass funnel and the filtrate was cooled in an ice bath to remove potassium sulfate. The resulting mixture was filtered again through a glass funnel. The filtrate was then dripped with sodium nitrate solution (5 mol/L) until crystals began to form, and the system was allowed to stand for 12 h to allow crystals to settle completely. The resulting dark brown crystals were filtered, washed with ultra-pure water to remove remaining potassium hydroxide, and dried in a lyophilizer for 12 h.

Unless otherwise stated, all experiments were performed at room temperature (25 ± 1 °C) in a 200 mL glass beaker under magnetic agitation. Carboxylic Cu(II)/Ni(II) complexes solution was prepared by dissolving copper/nickel sulfate and ligands including EDTA, NTA, citric acid, tartaric acid at the molar ratio of 1:1. In a typical procedure, a certain concentration of Cu(II)/Ni(II) complexes was placed in a 200 mL volumetric flask and then transferred to a glass beaker. The synthesized Cu(III)-periodate was then added to the resulting complexed Cu(II)/Ni(II) solution to initiate the degradation reaction. Samples drawn at the predetermined time were quenched with sodium sulfite solution (1 mol/L) to prevent further degradation of Cu(II)/Ni(II) complexes, and filtered through 0.45 μm membrane. All the experiments were repeated at least three times.

The solution pH was determined using a precision pH meter (PB-10, Cedolys). The concentration of Cu(II)-EDTA and its degradation products were analyzed by high performance liquid chromatography (HPLC, E2695, Waters) at the detection wavelength of 258 nm [39]. The mobile phase was methanol/formic acid-sodium formate-tetrabutylammonium bromide buffer solution (15 mmol/L formic acid, 5 mmol/L sodium formate and 1 mmol/L tetrabutylammonium bromide) at the volume ratio of 45:55 and the flow rate of 1 mL/min. Cu/Ni content was determined using an atomic absorption spectrometer (AA800, PE). The synthesized Cu(III)-periodate species were identified by laser Raman spectroscopy (inVia Qontor, Renishaw, UK). The chemical state of elemental Cu of the synthetic Cu(III) were analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe, Japan). The characteristic peak of Cu(III)-periodate was detected by UV–vis spectrophotometer (TU-1901, Persee, China). The functional groups of Cu(III)-periodate were obtained using Fourier transform infrared spectroscopy (FT-IR) (Nicolet iN10 MX, Thermo Scientific, USA).

A dark brown and powder-like Cu(III) solid was sucessfully synthesized using copper plating wastewater instead of copper sulfate reagent (Fig. 1a). The preparation conditions of PDS dosage and the Cu concentration in copper wastewater were optimized. The yield of Cu(III) production increased with the increase of PDS dosage and Cu concentration, and the highest yield was achieved at the PDS dosage of 15 g/L and Cu concentration of 3.99 g/L (Figs. S1 and S2 in Supporting information).

The synthetic Cu(III) power was characterized with laser Raman spectrometer, and an obvious characteristic peak of Cu(III) was observed near 603 cm^{-1} (Fig. 1a) [40,41]. Furthermore, the X-ray photoelectron spectrometer was used to determine the valence state of Cu(III) power. The results indicated that the binding energies of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ were 934.2 eV and 953.7 eV, respectively (Fig. 1b) [29,42]. The satellite peaks were also observed on the high binding energy side of the main peaks of Cu $2p_{3/2}$ (943.2 eV) and Cu $2p_{1/2}$ (962.2 eV). These X-ray photoelectron parameters were also generally consistent with the previously reported Cu(III) complexes. The absorbances of Cu(III) complex, Cu^{2+}

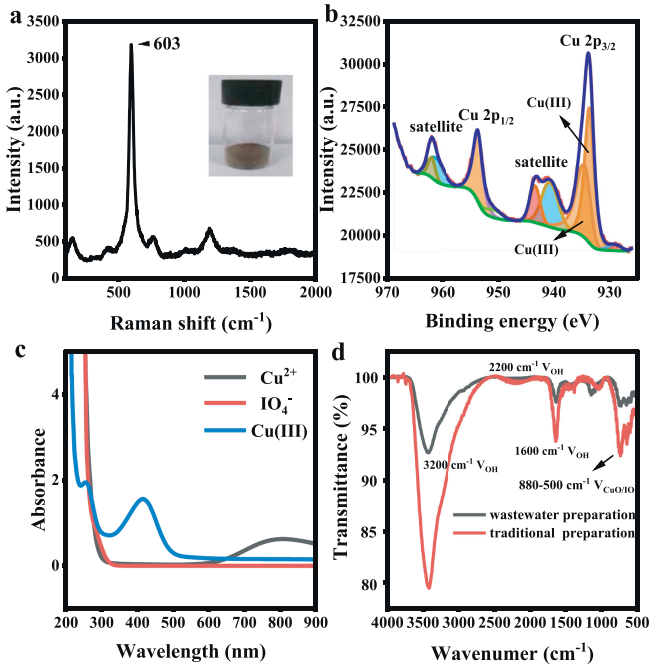

Fig. 1. (a) Laser Raman spectra of Cu(III). (b) X-ray photoelectron spectroscopy of Cu(III). (c) UV–vis spectra of Cu^{2+}, IO_4^- and Cu(III) in aqueous solution at 200–900 nm. (d) Fourier transform infrared spectroscopy of Cu(III). Conditions: $[Cu^{2+}] = 50$ mmol/L, $[IO_4^-] = 50$ mmol/L.

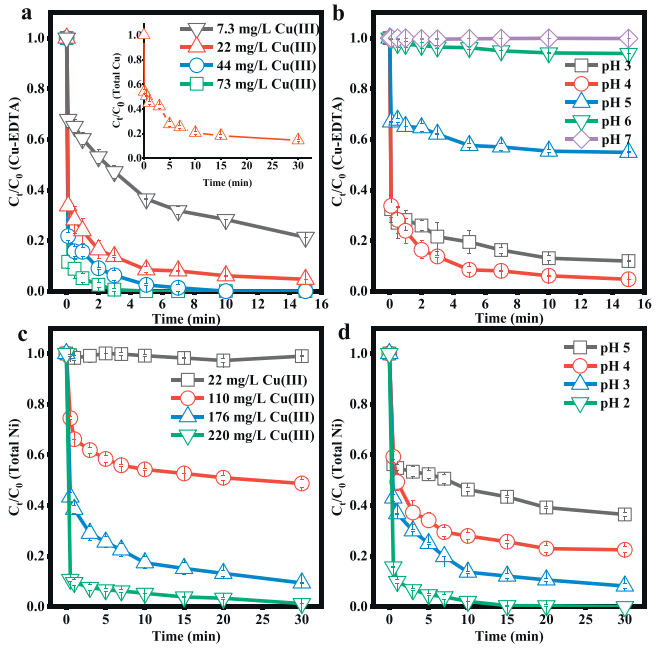

Fig. 2. Effects of different Cu(III) concentrations (a, c) and pH (b, d) on Cu(II)-EDTA and Ni(II)-EDTA degradation. Conditions: [Cu(II)-EDTA] = 0.1 mmol/L, pH 4.0 (a), [Cu(III)] = 22 mg/L (b); [Ni(II)-EDTA] = 0.1 mmol/L, pH 3.0 (c), [Cu(III)] = 176 mg/L (d), 25 °C.

and IO_4^- in the UV–vis spectrophotometer were also detected to verify Cu(III) formed (Fig. 1c). The Cu(III) complex presented an obvious characteristic peak at about 420 nm, while the characteristic peak of Cu^{2+} in the non-UV region was about 800 nm, and IO_4^- exhibited no obvious characteristic peak when the wavelength was greater than 300 nm. Wang *et al.* [43] found that the stable copper periodate complex formed by the complexation of periodate with Cu(III) exhibited obvious characteristic peaks about 415–420 nm in the UV visible spectrum. Therefore, it can be inferred that the absorption peak near 420 nm was the characteristic peak of Cu(III) [44]. Finally, Fourier infrared microspectroscopy (FT-IR) was used to identify the molecular structure and chemical composition of the Cu(III) complex. As shown in Fig. 1d, the FT-IR spectrum of the Cu(III) complex showed Cu-I-O stretching vibration band in the wavenumber range of 550–800 cm^{-1}, which was the characteristic peak of Cu(III) [29]. In addition, the trend of infrared spectrum of Cu(III) samples prepared from wastewater was consistent with that of traditional pharmaceutical products [31]. At the same time, the peak value around 3200 cm^{-1} represents the presence of water molecules, indicating that the presence of a certain amount of water in the sample, which was generally consistent with the composition of $Na_5[Cu(IO_5(OH))_2]\cdot 14H_2O$ reported previously [29,31,45].

The synthetic Cu(III) from Cu(II) wastewater exhibited the same excellent efficiency for Cu(II)-EDTA removal as that using Cu(II) salt, with more than 95.0% of Cu(II)-EDTA degradation within 15 min (Fig. S3 in Supporting information). In order to further explore its capacity for the decomplexation of the complexed heavy metals, the effects of Cu(III) dosage and pH on the degradation of Cu(II)-EDTA and Ni(II)-EDTA were examined. As presented in Fig. 2a, as Cu(III) dosage increased from 7.3 mg/L to 44 mg/L, the degradation efficiency of Cu(II)-EDTA significantly increased from about 78.0% to 100.0%. Moreover, when the dosage of Cu(III) was set to 44 mg/L, approximately 80.0% of Cu(II)-EDTA was oxidized within 10 s, achieving "instant kill" effect, which was related to the ultra-high oxidation of Cu(III). The dosage of 22 mg/L Cu(III) was selected to facilitate subsequent experimental exploration due to its moderate degradation kinetic of Cu(II)-EDTA. As shown in Fig. 2b, the degradation of Cu(II)-EDTA presented a significant pH dependence. The degradation of Cu(II)-EDTA was negligible at pH 7 and pH 6, while significantly increased with decreasing pH. The best degradation performance of Cu(II)-EDTA was achieved at pH 4 with 96.0% of removal efficiency, and the residual Cu of less than 0.081 mg/L (Fig. 2a). However, the degradation of Cu(II)-EDTA was slightly inhibited as pH further reduced to 3, which may be possibly attributed to the self-decomposition of partial Cu(III) under strong acidic conditions. In addition, Cu(III) also showed a similar trend on Ni(II)-EDTA degradation, that was, the degradation efficiency of Ni(II)-EDTA increased with the increase of Cu(III) dosage and the decrease of pH (Figs. 2c and d). A complete removal of Ni(II)-EDTA was obtained within 20 min at the Cu(III) dosage of 176 mg/L and pH 2, with the residual Ni of less than 0.1 mg/L. Considering the potential secondary pollution that may be introduced by the addition of Cu(III), the experiment was further conducted to analyze the residual Cu after the Cu(III) oxidation of Ni(II)-organic complexes followed by alkali precipitation. The result showed that no Cu was detected after precipitation treatment, which suggested that the generated Cu from Cu(III) reaction with heavy metal complexes can be easily removed by alkali precipitation.

There are often various organic ligands in real water bodies, which complex with free heavy metal ions to form more stable heavy metal complexes [39]. Therefore, in this study, other organic complexes composed of citric acid (CA), tartaric acid (TA), and NTA with Cu and Ni were used as typical pollutants to further demonstrate the degradation performance of Cu(III) oxidation system. As shown in Fig. 3a, Cu(III) also presented a good decomplexation effect on Cu(II)-citrate and Cu(II)-tartrate with Cu removal of 94.4% and 98.5% within 15 min, respectively. This may be ascribed to the strong oxidizing ability of Cu(III) for β-hydroxyl groups in citric acid ligands and tartaric acid ligands [46]. Although the degradation performance of Cu(II)-NTA was slightly poor in Cu(III) oxidation, the removal efficiency of Cu(II)-NTA also reached 84.1% within 15 min.

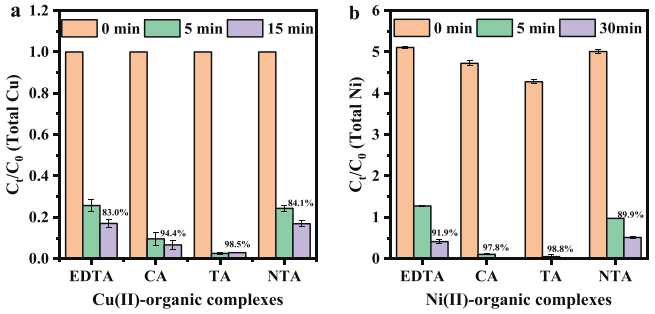

Fig. 3. The removal efficiency of Cu(II)-organic complexes (a) and Ni(II)-organic complexes (b) by Cu(III) system. Conditions: [Cu(II)-EDTA] = [Cu(II)-CA] = [Cu(II)-TA] = [Cu(II)-NTA] = 0.1 mmol/L, [Cu(III)] = 22 mg/L, pH 4.0, 25 °C (a); [Ni(II)-EDTA] = [Ni(II)-CA] = [Ni(II)-TA] = [Ni(II)-NTA] = 0.1 mmol/L, [Cu(III)] = 176 mg/L, pH 3.0, 25 °C (b).

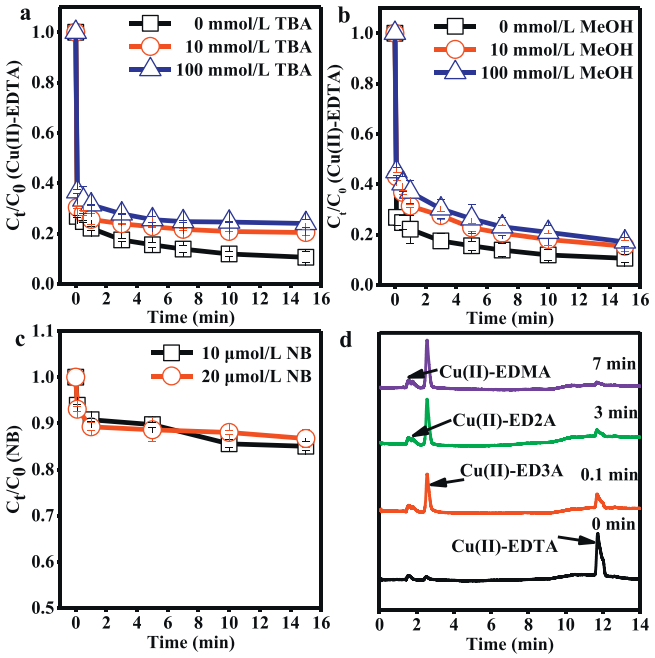

Fig. 4. (a) The effect of different TBA concentrations on Cu(II)-EDTA degradation. (b) The effect of different concentrations of MeOH on Cu(II)-EDTA degradation. (c) The degradation effect of NB on Cu(II)-EDTA degradation in Cu(III) system. (d) The evolution of the HPLC spectra during Cu(II)-EDTA degradation by Cu(III) system. Conditions: [Cu(II)-EDTA] = 0.1 mmol/L, [Cu(III)] = 22 mg/L, pH 4.0, 25 °C.

Besides, the Cu(III) oxidation system also possessed excellent decomposition effect on different ligand complexes with Ni(II) (Fig. 3b). Cu(III) showed significant decomplexation effect for Ni(II)-citrate and Ni(II)-tartrate with Ni removal of 97.8% and 98.8% within 5 min, respectively. The decomplexation effect on Ni(II)-NTA was relatively slow, but the removal efficiency of Ni still reached about 90.0% within 30 min. It was worth noting that the degradation of Ni(II) complexes required more Cu(III) compared to Cu(II) complexes. Taken together, the Cu(III) system also presented excellent degradation performance on the heavy metal complexes, further verifying the high oxidation ability of Cu(III) system.

Previous studies have reported that Cu^{3+} and its hydrolyzed form $Cu(OH)^{2+}$ may decompose to produce HO•, which may also cause the degradation of heavy metal complexes. In order to identify the main active species and their contributions in Cu(III) system, *tert*-butanol (TBA) and methanol were used as different radical quencher to conduct the degradation experiments of Cu(II)-EDTA by Cu(III) system. As is well known, TBA and methanol can act as effective scavengers for HO•. As shown in Figs. 4a and b, the addition of 10–100 mmol/L TBA and methanol only slight inhibited the degradation of Cu(II)-EDTA, indicating that HO• was not the main active substance in Cu(III) oxidation. Accordingly, nitrobenzene (NB) was used as radical probe to further confirm the relative contribution of HO• and Cu(III) direct oxidation due to the high reactivity of NB with HO• only ($K_{HO\cdot,\ NB} = 3.9 \times 10^9$). As exhibited in Fig. 4c, less than 15% of Cu(III) was conversed to HO• in the process, indicating the main Cu(III) direct oxidation of Cu(II)-EDTA.

The degradation intermediates of Cu(II)-EDTA during Cu(III) oxidation was identified by HPLC and high resolution mass spectrometry (HRMS). As shown in Fig. 4d, with the increase of reaction time, the characteristic peak of Cu(II)-EDTA at a retention time of approximately 12 min gradually decreased. Concurrently, new characteristic peaks appeared, corresponding to Cu(II)-ED3A, Cu(II)-ED2A, and Cu(II)-EDMA. HRMS analysis further confirmed the formation of decarboxylation intermediates, including Cu(II)-EDTA (*m/z* 352), Cu(II)-ED3A (*m/z* 294), Cu(II)-ED2A (*m/z* 237) and Cu(II)-EDMA (*m/z* 180) (Table S1 in Supporting information). The results of HPLC and HRMS suggested Cu(II)-EDTA degradation *via* Cu(III) oxidation followed by the stepwise decarboxylated process, and the possible pathway was proposed in Fig. S4 (Supporting information). Similar to HO•, Cu(III) preferentially attacked the N-C bond in Cu(II)-EDTA and its decarboxylation intermediates [9,47], and then the decarboxyalted intermediates such as Cu(II)-ED3A, Cu(II)-ED2A, Cu(II)-EDMA were gradually produced. Ultimately, Cu(II)-EDMA was mineralized into CO_2, H_2O, and small organic acids. Besides, the possible reactions of Cu(III) reaction with Cu(II)-EDTA and its intermediates were presented in Table S2 (Supporting information) [34].

The impacts of coexisting anions and natural organic matter (NOM) on the Cu(III) oxidation of Cu(II)/Ni(II)-EDTA were thoroughly investigated to assess its selectivity. Unlike the commonly reported inhibitory effects of inorganic anions on traditional oxidation processes [19–21], the concentrations of coexisting substances such as chloride (Cl^-), sulfate (SO_4^{2-}), and fulvic acids (FA) (simulation of natural organic matter (NOM)) up to 10 mmol/L or 5 mg/L showed negligible influence on the degradation of Cu(II)/Ni(II)-EDTA (Figs. 5a–e). Furthermore, the presence of coexisting substances up to 100 mmol/L or 10 mg/L, also exerted only a marginal adverse effect on the degradation of Cu(II)-EDTA, thus demonstrating the high selectivity of the Cu(III) oxidation process. However, when the concentration of FA increased to 5 mg/L or 10 mg/L, it significantly inhibited the degradation of Ni(II)-EDTA (Fig. 5f). The inhibition at high concentrations of coexisting NOM could be due to their competitive consumption of oxidative Cu(III) species, reducing Cu(III) interactions with the target pollutant [21]. The selectivity of Cu(III) in the oxidation process can withstand the interference of the coexisting ions and relatively low concentration of NOM, but more precise control of conditions were required to maintain oxidation efficiency and selectivity of Cu(III) at relatively high concentration of NOM, such as the increase of Cu(III) dosage. These findings are crucial for understanding and optimizing the application of Cu(III) in water treatment, particularly in complex water quality conditions.

In order to verify its feasibility in actual wastewater treatment, authentic Cu or Ni industrial wastewaters were sampled from an electroplating plant in Wenzhou city (Main parameters in Table S3 in Supporting information) to investigate the decomplexation effect of the Cu(III) system on heavy metal complexes, and the results were presented in Fig. 6. The degradation efficiency of Cu(II)-EDTA significantly improved from 52.0% to 96.0% with increasing Cu(III) dosage from 15 mg/L to 37 mg/L, while the removal rate of Ni(II) increased from 50.0% to 100% with increasing Cu(III) dosage from 110 mg/L to 220 mg/L. The results indicated that the Cu(III) oxidation was quite effective in treating actual heavy metal complexed wastewater, also suggested the high selectivity of Cu(III)

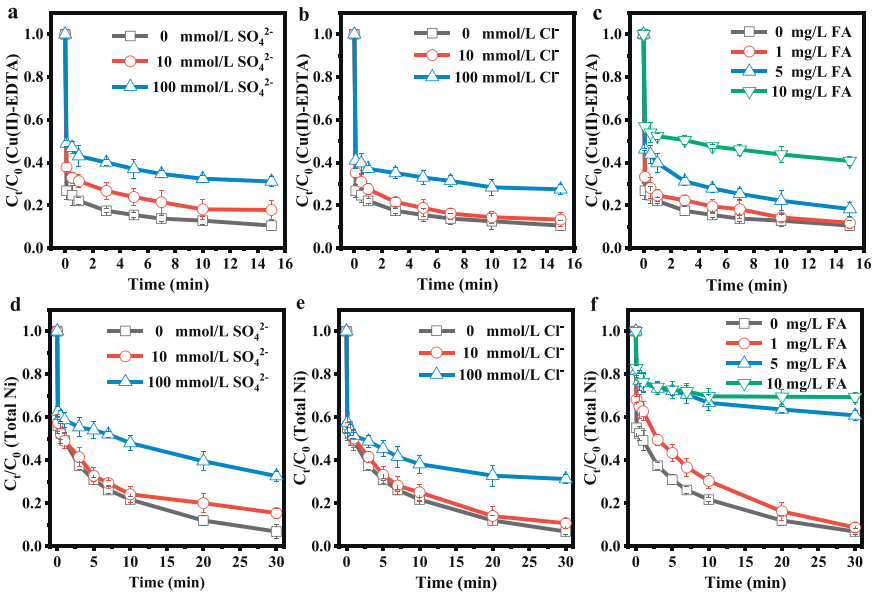

Fig. 5. Effects of SO_4^{2-} (a, d), Cl^- (b, e) and FA (c, f) on the decomposition of Cu(II)-EDTA and Ni(II)-EDTA. Conditions: [Cu(II)-EDTA] = 0.1 mmol/L, [Cu(III)] = 22 mg/L, pH 4.0, 25 °C (a–c); [Ni(II)-EDTA] = 0.1 mmol/L, [Cu(III)] = 176 mg/L, pH 3.0, 25 °C (d–f).

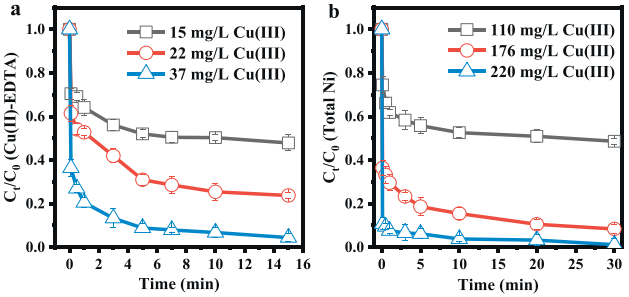

Fig. 6. Effects of different Cu(III) dosages on Cu(II)-EDTA (a) and Ni(II)-EDTA (b) degradation in real industrial wastewater. Conditions: [Cu(II)-EDTA] = 0.1 mmol/L, pH 4.0, 25 °C (a); [Ni(II)-EDTA] = 0.1 mmol/L, pH 3.0, 25 °C (b).

in complex water matrices. In addition, satisfactory COD removal was obtained after the treatment of the complexed wastewater by Cu(III) oxidation, with the removal efficiency of 61.0%–88.0% (Tables S4 and S5 in Supporting information). Besides, the ammonia nitrogen increased accordingly after the treatment of actual wastewater by Cu(III) system, with its concentration of 67.8–171.6 mg/L, which was derived from the Cu(III) oxidation of organic ligands such as EDTA. In summary, synthetic Cu(III) from copper plating wastewater presented excellent degradation performance in treatment of actual Cu/Ni-containing wastewater, verifying its feasibility in treating actual wastewater and achieving the expectation of "treating waste with waste". Furthermore, the total cost per gram Cu(II)-EDTA decomplexation was calculated using Eqs. S1 and S2 (Supporting information), respectively (Text S1 in Supporting information) [34,48]. As shown in Table S6 (Supporting information), the total cost of Cu(II)-EDTA decomplexation by Cu(III) oxidation was 0.013 USD/g, which was significantly lower than other technologies such as UV/chlorine and UV/PMS. The results confirmed that synthetic Cu(III) oxidation possessed superior economic efficiency.

It was found that copper plating wastewater could be used to synthesize stable Cu(III)-periodate instead of copper sulfate, and the yield could be increased by optimizing the preparation conditions. The synthetic Cu(III) can effectively degrade carboxylic Cu(II)/Ni(II) complexes with EDTA, citric acid, tartaric acid, and NTA under acidic pH conditions. HPLC and HRMS analysis evidenced that the main degradation pathway of Cu(II)-EDTA by Cu(III) direct oxidation was gradual decarboxylation process. In the treatment of actual electroplating wastewater, Cu(III) oxidation showed satisfactory removal of both Cu(II)-EDTA and Ni(II)-EDTA, with total Cu and Ni removal of more than 96.0%. Therefore, the *in-situ* utilization of a synthetic Cu(III) from copper plating wastewater is regarded as a promising technology for treating heavy metal complexing wastewater.

Declaration of competing interest

The authors declare that they have no known competing financial interests.

CRediT authorship contribution statement

Junyi Yu: Data curation, Investigation, Methodology, Writing – original draft. **Yin Cheng:** Data curation, Investigation, Methodology. **Anhong Cai:** Formal analysis, Investigation, Methodology, Software, Validation. **Xianfeng Huang:** Conceptualization, Funding acquisition, Methodology, Supervision, Validation, Writing – original draft, Writing – review & editing. **Qingrui Zhang:** Funding acquisition, Supervision, Validation, Writing – review & editing.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2024.110549.

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