Photoelectrocatalytic Oxidation of Cu^{II}–EDTA at the TiO₂ Electrode and Simultaneous Recovery of Cu^{II} by Electrodeposition

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S Supporting Information

ABSTRACT: The simultaneous decomplexation of Cu–EDTA and electrodeposition recovery of Cu²⁺ ions was attempted in a photoelectrocatalytic (PEC) system using TiO₂/Ti as the anode and stainless steel as the cathode. At a current density of 0.5 mA/cm², removal efficiencies of 0.05 mM Cu–EDTA by photocatalysis, electrooxidation, and PEC processes were determined to be 15, 43, and 72% at 3 h, respectively. Recovery percentages of Cu²⁺ ions were determined to be 10, 33, and 67%, respectively. These results indicated that a synergetic effect in the decomplexation of Cu–EDTA and recovery of Cu²⁺ ions occurred in the PEC process, which favored acid conditions and increased with the current densities. The removal of Cu–EDTA and Cu²⁺ ions can be described by a pseudo-first-order kinetics model. Ca²⁺ ions significantly increase the removal of Cu–EDTA and recovery of Cu²⁺ ions. Intermediates, including Cu–NTA, Cu–EDDA, acetic acid, formic acid, and oxalic acid, were identified, and a decomplexation pathway of Cu–EDTA was proposed. The Cu–EDTA decomplexation at the anode via oxidation of hydroxyl radicals was revealed. On the basis of X-ray photoelectron spectra analysis, a reduction pathway of Cu²⁺ ions at the cathode was discussed. The present study may provide a promising alternative for destruction of the metal complex and recovery of metal ions.

INTRODUCTION

Heavy metal wastewater is a major concern that is toxic to the environment. The presence of chelating agents, such as citrate, tartrate, and ethylenediaminetetracetic acid (EDTA), make the conventional precipitation process ineffective for the removal of metal ions from the wastewater.¹ Recently, advanced oxidation processes (AOPs) have been largely investigated in the treatment of refractory organics and organic complexes.² Application of photocatalysis, sonochemical process, H₂O₂/ultraviolet (UV) process in the treatment of metal-binding EDTA has been studied.^{3–5}

It is generally known that EDTA forms a stable complex having an octahedron structure of hexacoordination with cupric. To achieve an effective treatment of Cu–EDTA complexes, not only the oxidation of EDTA groups but the recovery of cupric ions would also be desirable. Previous studies have investigated the removal of the organic contaminants and recovery of dissolved metal ions from wastewater by the TiO₂ photocatalytic process, in which the reduction of metal ions by photogenerated electrons and subsequent deposition of metals onto the semiconductor surface was involved, followed by their extraction through chemical acid extraction.^{6–9} Because of the fast recombination of the photogenerated electron/hole, practical exploitation of the TiO₂ photocatalytic process in the oxidation of organic contaminants and reduction of metal ions is still restricted.

Application of the electrochemical process in removing heavy metals and organic contaminants was largely reported.¹⁰ In an electrochemical reactor with a Ti/Pt anode, the simultaneous electrooxidation of cyanides and recovery of copper as a metallic deposition on the cathode from weak-concentration rinse wastewater were investigated.¹¹ In a cylindrical spouted electrochemical reactor, co-electrodeposition of copper and nickel from acidic solution mixtures was investigated.¹² Generally, the oxygen evolution and chloride evolution occur at the anode readily in the electrolysis process, which lead to the low current efficiency. Electrolysis is cost-effective only for solutions with a high concentration. Simultaneous recovery of metals and complexing agents from complexed solutions by an electrochemical membrane process has been investigated. In a two-chamber electrolysis cell that was separated by a cation-exchange membrane, electrolytic recovery of metals, such as Cu²⁺, and strong chelating agents, such as EDTA, was achieved.^{13,14} In this process, the low pH value was needed and heavy side reactions (the evolution of O₂ and H₂ gases) readily occur. Recently, a hybrid ion-exchange electrodialysis, in which a conventional ion exchange is combined with

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electrodialysis to intensify mass transfer and to increase the limiting current density, was used for the removal of heavy metals from moderately acidified copper sulfate solutions simulating rinsing water of copper-plating lines.¹⁵ However, the organic complex metals cannot be removed via this system.

A combination of photocatalysis and electrolysis in removing pollutants has been shown to be more efficient than individual photocatalysis and electrolysis processes. In a photoelectrochemical cell, a photocatalyst immobilized onto a conductive substrate was used as the anode and an external voltage cell was applied to drive the photogenerated electrons to the cathode, consequently minimizing the rate of electron/hole recombination. This process, which is also referred to as photoelectrocatalysis (PEC), has been recently demonstrated for the degradation of organics^{16–18} and the inactivation of bacteria.^{19,20} The above studies on the PEC process mainly focus on the oxidation process occurring at the anode, and reactions occurring at the cathode were generally ignored.²¹ Wang et al. reported the efficient PEC reduction of Cr^{VI} using TiO₂ nanotube as the photoanode and a large-area Ti mesh as the photocathode.²² Photocatalytic degradation of organic contaminants, including acid red 151, anionic surfactant, and tamol, using TiO₂ film as the photoanode and reduction of Cr^{VI} to the less toxic Cr^{III} at the Pt gauze cathode was investigated.²³ Both above studies focus on the reduction of Cr^{VI} into less toxic Cr^{III} by the photogenerated electrons driven to the cathode by the applied bias potential.

Herein, the simultaneous PEC oxidation of Cu–EDTA at a TiO₂ film electrode and recovery of Cu²⁺ ions at a stainless-steel cathode by electrodeposition was investigated in a PEC system. The removal of Cu–EDTA and recovery of Cu²⁺ in the PEC process is significantly increased in comparisons to individual photocatalysis and electrolysis processes. The generated active •OH radicals were revealed to be responsible for the oxidation of Cu–EDTA; simultaneously, recovery of Cu²⁺ ions occurred at the cathode by the photogenerated electrons. The effect of the current density, pH, and coexisting ions was investigated in detail. The oxidation of Cu–EDTA and the reduction process of Cu²⁺ ions occurring at the anode and cathode were discussed.

■ EXPERIMENTAL SECTION

Chemicals. Copper sulfate and ethylenediaminetetraacetic acid disodium salt dehydrate (Na₂EDTA) were purchased from Merck. Iminodiacetic acid (IDA), nitrilotriacetic acid (NTA), and Na₂EDTA were obtained from Sigma. The solution of Cu–EDTA was prepared by mixing a solution of CuSO₄ and Na₂EDTA to obtain a 1:1 molar ratio of Cu²⁺/EDTA. pH regulation was performed using either 1 mM NaOH or HNO₃. Deionized water was used for the preparation and dilution of the solutions.

Setup and Experiment. Photocatalysis, electrooxidation, and the PEC experiments with a batch mode were performed in a single-compartment cell (600 mL) with a 3.5 cm diameter quartz tube placed in the center and used as the UV bulb housing. The UV lamp with the UV housing was put in the middle between the anode and cathode with a distance of 5 cm. UV irradiation was provided by a 10 W mercury lamp (main wavelength of 254 nm), and the light intensity at the center of the compartment was 8 mW/cm², as measured with a UV radiometer (Light and Electric Instruments Factory of Beijing Normal University).

The TiO₂/Ti film electrode (70 × 50 mm) was selected as the anode with an active area of 35 cm². TiO₂ film was deposited onto the Ti plate via a dip-coating method as described by Shang et al.²⁴ The stainless steel with the same active area was used as the cathode. The power was provided by a direct-current (DC) power supply source DH1718E-4 (Dahua Instrument Corporation of Beijing). NaClO₄ (0.5 mM) was used as electrolyte solution. The reaction solution (400 mL) was put in the reaction cell, and a 5 mL sample was taken at a given time for analysis. All of these experiments were at least performed twice.

Analytical Method. The concentration of Cu–EDTA was determined by high-performance liquid chromatography (HPLC, 1260, Agilent Technology). A Hypersil Gold (Thermo Scientific) analytical column was used along with the elution comprised of 92% oxalic acid (15 mM)/8% acetonitrile (v/v) at a temperature of 25 °C. The solvent was adjusted to pH 3.0, and the flow rate was set as 1 mL/min. The detection wavelength was set as 254 nm. Nitrate, formate, and acetate were measured using ion chromatography (IC, ICS-2000, Dionex, Sunnyvale, CA) equipped with an AS-11 anion column. The analytic procedure with a gradient elution model was as follows: 0–18 min, 0.8 mM KOH; 18–33 min, 50 mM KOH; and 33–58 min, 0.8 mM KOH. The flow rate was set as 1 mL/min. Ammonia was determined by an UV spectrophotometer (Hitachi U-3010). Concentrations of total cupric ions were measured using 700 series inductively coupled plasma–optical emission spectrometry (ICP–OES, Agilent Technology). Total organic carbon (TOC) was measured using a Shimadzu TOC analyzer (TOC-VCPH, Shimadzu, Japan). The pH was measured using a 9165 BN pH electrode connected to an Orion-828 pH analyzer (Orion Research, Inc., Beverly, MA). The chemical equilibrium model for the calculation of Cu–EDTA at various pH values was calculated via Visual MINTEQ, version 3.0. Data and graphs from MINTEQ calculations were illustrated for discussion purposes.

The intermediates were identified by capillary electrophoresis (P/ACETM MDQ series capillary electrophoresis system). An uncoated fused silica capillary, 50 cm in length (to the detector) and 75 μm in diameter, was used with UV detection at 185 nm. The carrier electrolyte was 50 mM phosphate and 0.5 mM tetradecyltrimethylammonium bromide (TTAB, pH 6.8) according to the procedure.²⁵ Cu–IDA, Cu–NTA, and Cu–ethylenediamine-*N,N'*-diacetic acid (EDDA) (1:1 molar ratio) were prepared. The byproducts were identified by a comparison of the retention time to those of the prepared standards. Ultra-performance liquid chromatography–mass spectrometry (UPLC–MS) was also performed to identify the intermediates. UPLC analyses were performed using a Waters Acquity Ultra Performance LC system (Waters, Milford, MA). Identification was performed using a Waters Micromass Quattro Premier XE tandem quadrupole mass spectrometer (Waters, Manchester, U.K.) with negative electrospray ionization. The analytic conditions were given in the Supporting Information.

The morphology of the anode and cathode was characterized using JSM 6301 scanning electron microscopy (SEM). X-ray diffraction (XRD) of the TiO₂ film was recorded on a Scintag-XDS-2000 diffract meter with Cu Kα radiation. XRD and SEM results of the TiO₂/Ti film and Ti substrate were given in Figure SM-1 of the Supporting Information. The peak of 2θ appearing at 25.3 was attributed to the anatase. X-ray photoelectron spectra (XPS) were used to analyze the surface variation of the electrode using a PHI Quantera SXM (PHI-

5300/ESCA, ULVAC-PHI, Inc.). Prior to the measurement, the electrode was washed with water to remove electrolyte. The electron spin resonance (ESR) signals of radicals spin trapped by spin-trap reagent 5,5'-dimethyl-1-pyrroline-*N*-oxide (DMPO, purchased from Sigma Chemical Co.) were detected on a Bruker model ESR 300E spectrometer equipped with a quanta-Ray Nd:YAG laser system as the irradiation source. The $\bullet\text{OH}$ radical spin adduct of DMPO was prepared by instantaneously sampling the solution during electrooxidation, photocatalysis, and the PEC reaction with a syringe containing a constant volume of 30 mM DMPO.

The acute toxicity of the Cu–EDTA solution treated at various times in the PEC oxidation was performed according to the procedure.²⁶ Briefly, the bioluminescence inhibition of luminescent marine bacteria *Vibrio qinghaiensis* sp. Q67 exposed to diluted Cu–EDTA solution for 20 min was measured using an infinite M200 luminometer (TECAN, Switzerland), and the results were compared to an aqueous control. The acute toxicity of the sample on Q67 was expressed as the inhibition value in percent (%).

RESULTS AND DISCUSSION

Removal of Cu–EDTA and Recovery of Cu^{2+} . First, removal of the Cu–EDTA complex and recovery of Cu^{2+} ions via photocatalysis, electrooxidation, and PEC processes were investigated with the constant Cu–EDTA concentration, pH, and current density. It can be seen from Figure 1 that 15 and

Figure 1. Removal of Cu–EDTA and recovery of Cu^{2+} ions via photocatalysis (PC), electrooxidation (EO), and PEC processes ($C_{(\text{Cu-EDTA})}$, 0.05 mM; pH, 6.6; and current density, 0.5 mA/cm²).

43% Cu–EDTA can be removed via photocatalysis and the electrooxidation process at 3 h, respectively. The removal percentage is increased to 72% in the PEC process. The kinetics constants (k_1) of Cu–EDTA removal, obtained using a first-order reaction rate to simulate the data in Figure 1, are 0.052, 0.173, and 0.377 h^{−1} for photocatalysis, electrooxidation, and PEC processes, respectively ($R^2 = 0.949$, 0.949, and 0.930).

The recovery percentages of Cu^{2+} ions in photocatalysis, electrooxidation, and PEC processes are determined to be 10, 33, and 67%, respectively (Figure 1). Herein, the recovery percentage of Cu^{2+} ions is defined as R_{Cu} (%) shown in the following equation:

$$R_{\text{Cu}} (\%) = 100 \times \left(\frac{\text{initial amount of Cu ions} - \text{remaining amount of Cu ions}}{\text{initial amount of Cu ions in the reaction cell}} \right)$$

It is obvious that R_{Cu} (%) in the PEC process is higher than that in photocatalysis and electrooxidation processes. Meanwhile, the removal rate of total Cu^{2+} ions from reaction solution in Figure 1 is also simulated using a first-order reaction equation. The kinetics constants (k_2) are 0.048, 0.167, and 0.392 h^{−1} for photocatalysis, electrooxidation, and PEC processes, respectively ($R^2 = 0.921$, 0.942, and 0.971). The above results indicate that an efficient removal of Cu–EDTA proceeds via the PEC oxidation at the TiO_2 film anode accompanied with electrodeposition of Cu^{2+} ions at the cathode in comparison to the single photocatalysis and electrooxidation processes. The complexation may occur between the Cu^{2+} ions with the intermediates in the Cu–EDTA oxidation because of the strong Cu^{2+} affinity for organic complexation ligands. Thus, the precipitation and co-precipitation of Cu^{2+} ions does not readily occur.

TOC variation under the same experiment conditions was furthermore compared. As shown in Figure SM-2 of the Supporting Information, TOC removal efficiencies increase with the reaction time in all of the processes. At 3 h, TOC removal efficiencies are 12, 11, and 40% for the photocatalysis, electrooxidation, and PEC processes, respectively. HPLC spectra variation in the PEC reaction process is given in the inset of Figure SM-2 of the Supporting Information. It can be seen that the peak intensity of Cu–EDTA decreases with the reaction time, which indicates that Cu–EDTA is efficiently removed. Variation of UV–vis spectrum for the Cu–EDTA solution in various processes with reaction time was checked. As shown in Figure SM-3 of the Supporting Information, the UV–vis spectrum for the untreated Cu–EDTA solution exhibits the peak at the broad absorption bands in the range of 210–320 nm that are centered at 260 nm; the decrease of the absorbance value of the peak in the PEC process is larger than that in electrooxidation and photocatalytic processes, which furthermore confirms that Cu–EDTA is destroyed in the PEC process efficiently.

It can be seen from Figure SM-4 of the Supporting Information that the inhibition to *V. qinghaiensis* sp. Q67 of Cu–EDTA solution samples collected at 1, 2, and 3 h for the PEC oxidation process was less than 6%, being recorded at 20 mg/L. Nearly no toxicity of the above sample may be due to the complexation between Cu^{2+} and the generated intermediates in the overall PEC process.

Effect of the Applied Current Density. The removal kinetic constants of Cu–EDTA and total Cu^{2+} ions with the current density in the PEC and electrooxidation processes at the Cu–EDTA concentration of 0.05 mM and pH 6.6 are given in Figure 2. The degradation kinetics of Cu–EDTA was in the range of 0.05–0.45 h^{−1}, which is lower than the results reported by Yang and Davis.²⁷ In their studies about the effect of pH on the oxidation of Cu^{II} –EDTA, first-order reaction kinetics was simply used to analyze the degradation data of Cu–EDTA at various pH conditions, which range from about 0.12 to 0.02 min^{−1}. With respect to the electrochemical process, the electrolysis longer than 500 h was necessary for the full oxidation of Cu–EDTA complexes to CO_2 with the boron-

Figure 2. Kinetic constants (k) of Cu–EDTA and total Cu^{2+} ions removal via current density in the electrooxidation (EO) and PEC processes ($C_{(\text{Cu-EDTA})}$, 0.05 mM; pH, 6.6; and current density, 0.5 mA/cm^2).

doped diamond (BDD) electrode in the study reported by Yamaguchi et al.²⁸ Generally, the kinetic constants depend upon the experimental conditions, such as the initial concentration of Cu–EDTA, current density, initial pH, value of V/S (volume of the reaction solution/surface of the electrode), etc.

As shown in Figure 2, the removal kinetics constant of Cu–EDTA and total Cu^{2+} ions are significantly increased when the current density is increased from 0 to 0.05 mA/cm^2 in the PEC process. Then, a plateau is observed when the current density is less than 0.3 mA/cm^2 . After that, the kinetics constants are largely increased. In the individual electrochemical process, the removal constants of Cu–EDTA and total Cu^{2+} ions increase slightly when the current density is less than 0.3 mA/cm^2 . After that, a significant increase is also observed.

With a low current density (less than 0.05 mA/cm^2), the applied bias potential increases the photocatalytic degradation rate by promoting the separation of photogenerated electron and hole. Individual electrooxidation of Cu–EDTA is slight. When the current density is larger than 0.3 mA/cm^2 , the electrooxidation and photocatalysis occur simultaneously and contribute to the synergetic removal of Cu–EDTA and total Cu ions; when the current density is up to 0.4 mA/cm^2 , indirect electrooxidation and photocatalysis of Cu–EDTA occur, which contributes to the high removal rate constant of Cu–EDTA and total Cu^{2+} ions. A similar trend was observed in our previous research work.²⁹ Nearly the same variation trend for total Cu^{2+} ion and Cu–EDTA in the PEC process confirms that destroying of Cu–EDTA is preferred to deposition of Cu^{2+} ions. Then, Cu^{2+} ions are liberated from Cu–EDTA, which can be deposited at the cathode quickly.

Effect of pH. Effect of solution pH on the removal of Cu–EDTA and recovery of Cu^{2+} ions in electrooxidation and PEC processes was investigated. As shown in Figure 3a, the kinetics constants of Cu–EDTA removal in the PEC process at pH 3.5, 6.6, and 8.5 are 0.374, 0.200, and 0.240 h^{-1} , respectively. The constants decrease with the pH increase. Meantime, R_{Cu} (%) at the cathode decreases with the pH increase. A similar trend is observed in the electrooxidation process (Figure 3b). It should be pointed out here that, although pH was left uncontrolled during the reactions, it did not change more than 0.1–0.2 units.

In the case of photocatalysis of Cd–EDTA by TiO_2 , it was reported that, at low pH values, a large portion of the complex is adsorbed; at high pH, the complex exists mostly in solution.³⁰ Therefore, it is concluded that a large portion of Cu–EDTA is

Figure 3. Effect of pH on the removal of Cu–EDTA and recovery of Cu^{2+} ions: (a) PEC process and (b) electrooxidation (EO) ($C_{(\text{Cu-EDTA})}$, 0.05 mM; current density, 0.5 mA/cm^2).

adsorbed at acid conditions, which is beneficial to the PEC reaction. Another reason is that, at a high pH value, liberated Cu^{2+} ions become easily adsorbed onto TiO_2 , occupying active sites or otherwise causing adverse effects on the generation of the oxidant.³¹

Cu–EDTA occurs in various species, which depends upon the pH of the solution, i.e., $(\text{CuEDTA})^{2-}$, CuH_2EDTA , $(\text{CuHEDTA})^-$, and CuOHEDTA^{3-} . As shown in Figure SM-5 of the Supporting Information, at pH 6.6 and 8.5, the major species of the Cu–EDTA complex in the solution is the fully deprotonated form of $(\text{CuEDTA})^{2-}$. At pH 3.5, the major species in the solution is $(\text{CuEDTA})^{2-}$ and $(\text{CuHEDTA})^-$, and a slight ratio of CuH_2EDTA may also be present. It is possible that $\bullet\text{OH}$ radicals can react with $(\text{CuHEDTA})^-$ better than with $(\text{CuEDTA})^{2-}$. Herein, Cu–EDTA is removed more rapidly at pH 3.5 than at pH 6.6 and 8.5. With respect to the electrodeposition occurring at the cathode, a portion of $(\text{CuOHEDTA})^{2-}$ present in the solution increases with the solution pH, which may lead to the low recovery percentage of Cu^{2+} ions.

Promoted Effect of Ca^{2+} Ions on Cu–EDTA Decomplexation and Cu^{2+} Recovery. Under the constant conditions of $C_{(\text{Cu-EDTA})}$ = 0.05 mM, current density = 0.3 mA/cm^2 , and pH 6.6, removal of Cu–EDTA and R_{Cu} (%) via the PEC process in the presence of NaNO_3 and $\text{Ca}(\text{NO}_3)_2$ with the same NO_3^- concentrations are given in panels a and b of Figure 4, respectively. It can be seen that the presence of $\text{Ca}(\text{NO}_3)_2$ significantly increases the removal of Cu–EDTA and R_{Cu} (%), which is more than those in the presence of NaNO_3 .

The above results indicate that Ca^{2+} ions promote the decomplexation process of Cu–EDTA in the electrooxidation and PEC processes. It has been reported that the $\text{Ca}(\text{OH})_2$ -based replacement–precipitation process can efficiently remove the EDTA-chelated copper.³² Accordingly, a complex reaction between Ca^{2+} and EDTA or its intermediates occurs, which

Figure 4. Removal of Cu–EDTA and recovery of Cu^{2+} ions by the PEC process in the presence of (a) NaNO_3 and (b) $\text{Ca}(\text{NO}_3)_2$ ($C_{\text{Cu-EDTA}}$, 0.05 mM; current density, 0.3 mA/cm^2 ; and pH, 6.6).

may promote the decomplexation of Cu–EDTA and the electrodeposition process of Cu^{2+} ions at the cathode. Meantime, the increase in the PEC process is larger than that in the electrooxidation process (see Figure SM-6 of the Supporting Information). In the PEC process, active species, such as NO_2^- and $\bullet\text{OH}$, can be generated under NO_3^- photolysis, which may contribute to the decomplexation of Cu–EDTA in the PEC process to some extent.

Involved Active Radicals and Electrodeposition Analysis. Four characteristic peaks of DMPO– $\bullet\text{OH}$ are observed in the photocatalysis, electrooxidation, and PEC processes; no such signals are detected in the dark (Figure 5a). The peak intensity for the PEC process is larger than that in individual electrooxidation and photocatalysis processes. The above results indicate that a large amount of $\bullet\text{OH}$ radicals are generated in the PEC process. Furthermore, the effect of the Na_2CO_3 concentration on Cu–EDTA degradation and Cu^{2+} recovery in the PEC and electrooxidation processes was investigated. As shown in Figure 5b, the removal rate of Cu–EDTA and R_{Cu} (%) decrease with the increase of the Na_2CO_3 concentration. It is known that CO_3^{2-} ions act as radical scavengers and react with $\bullet\text{OH}$ quickly. A similar inhibition trend is observed in the electrochemical process (see Figure SM-7 of the Supporting Information). The above results indicate that the PEC degradation of Cu–EDTA mainly proceeds via the $\bullet\text{OH}$ radical oxidation.

Electrodeposition of Cu^{2+} ions at the cathode was first checked by SEM–energy-dispersive X-ray (EDX) analysis. As shown in Figure SM-8 of the Supporting Information, the granular deposition of copper and the oxide formation near the edges of the electrode surface are observed after 3 h of PEC reaction. Furthermore, XPS analysis of the cathode surface before and after the PEC reaction was performed. As shown in Figure 6a, the peaks of Fe 2p, Fe 3p, Cr 2p, O 1s, O KLL, Na 1s, Si 2s, Si 2p, and C 1s are observed for the cathode before the PEC reaction. With the reaction proceeding, the peaks of

Figure 5. (a) DMPO spin-trapping ESR spectra recorded at ambient temperature under photocatalysis, electrooxidation, and PEC processes. (b) Effect of the Na_2CO_3 concentration on Cu–EDTA removal and recovery of Cu^{2+} ions in the PEC process ($C_{\text{Cu-EDTA}}$, 0.05 mM; current density, 0.3 mA/cm^2 ; and pH, 6.6).

Fe 2p and Cr 2p disappear. In contrast, the peaks of Cu 2p and Cu 3p appear, and their intensity increases with the reaction evolution obviously. Furthermore, the high-resolution XPS spectrum of the Cu $2p_{3/2}$ peak for the cathode in the PEC reaction for 3 h is given in panels b and c of Figure 6. The signals are present at 932.0 and 951.7 eV, which are assignable to the emissions from the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ levels, respectively.³³ As shown in Figure 6c, the peak is split into two components with binding energies of 934.50 and 932.47 eV, which correspond to the binding energies of Cu^{2+} and Cu^0 , respectively.³⁴ The satellite structures observed on the high binding energy of 943.87 and 941.48 eV of the copper core line $2p_{3/2}$ are due to the multiplet splitting in the $2p^53d^9$ final state, which is directly related to the presence of Cu^{2+} species.³⁵ These results confirm that Cu^{2+} ions are efficiently deposited onto the cathode followed by the electroreduction to Cu^0 .

Identified Intermediates and a Proposed Degradation Pathway. Capillary electrophoresis (CE) results are shown in Figure 7a. It is seen that Cu–NTA is generated at 0.5 h with the decrease of Cu–EDTA in the PEC process. Peak intensity of Cu–NTA increases with the reaction time up to 4 h. After that, it begins to weaken. Intermediates of EDDA and Cu–EDDA are generated at 0.5 and 3 h through removal of the acetate groups. Acetate acid is also observed at 1 h by ion chromatography (IC) analysis. Furthermore, the UPLC–MS result confirms that the IDA group was removed from Cu–EDTA at 1 h, leading to the generation of Cu–NTA (see Figure SM-9 of the Supporting Information). Using IC analysis, intermediates, including acetic acid, formic acid, oxalic acid, and NO_3^- , are identified (Figure 7b). The concentration of acetic

Figure 6. XPS spectrum of the cathode in the PEC process: (a) full spectra analysis, (b) Cu spectra analysis, and (c) high-resolution XPS spectrum of the Cu 2p_{3/2} peak at 3 h of reaction ($C_{\text{(Cu-EDTA)}}$, 0.05 mM; current density, 0.3 mA/cm²; and pH, 6.6).

Figure 7. (a) Electropherograms of Cu-EDTA solution treated at various times in the PEC oxidation conditions: 50 mM phosphate buffer and 0.5 mM TTAB (pH 6.8), 195 nm, 20 kV, and 25 °C. AU = absorbance units. (b) Generation and concentration variation of acetic acid, formic acid, oxalic acid, and NO₃[−] in the PEC process ($C_{\text{(Cu-EDTA)}}$, 0.05 mM; current density, 0.3 mA/cm²; and pH, 6.6).

acid, formic acid, and oxalic acid increases with the reaction time. A difference for oxalic acid is that its concentration begins to decrease after 4 h. NO₃[−] appears at 4 h. In addition, NH₄⁺ is also detected; the percentage of NH₄⁺ to total N increases with

the reaction time (see Figure SM-10 of the Supporting Information).

On the basis of the above results, a degradation pathway of Cu-EDTA was proposed in Scheme 1. Cleavage at the N-CH₂ bond of the [(HOOC-CH₂)₂-(N-CH₂)-CH₂-] group on Cu-EDTA occurs with a removal of the IDA [(HOOCCH₂)₂NH] group. Cu-EDDA/EDDA and acetic acid are generated by the removal of the acetic acid group from Cu-EDTA. The remaining Cu-NTA {Cu-[CH₂-CH₂-N-(CH₂COOH)₂]} and Cu-EDDA were furthermore decomposed into some molecular acids. NH₄⁺ and NO₃[−] were finally generated. Intermediates, such as glycine, nitrilotriacetic acid, and ethylenediamine, have been identified in the photocatalytic oxidation of Cu-EDTA.³⁶ Similar intermediates were also identified in the electrochemical oxidation of Cu-EDTA.^{37,38} In the current work, oxidation of Cu-EDTA by the PEC process was mainly through active hydroxyl radicals or photogenerated holes. It is concluded that the degradation of Cu-EDTA mainly proceeds through the cleavage of the amine group with a slight removal of the acetic group from Cu-EDTA first. Furthermore, oxidation of generated organic acids leads to the production of NO₃[−] and NH₄⁺ ions.

Potential Application. In the current work, the simultaneous oxidation of Cu-EDTA at the TiO₂ film electrode and recovery of Cu²⁺ ions by electrodeposition was achieved in the PEC system. In the case of single photocatalysis of Cu-EDTA, the liberated Cu²⁺ ions will be adsorbed onto TiO₂, which need to be removed by an acid extraction step.⁹ The waste solution containing Cu²⁺ ions needs to be treated via conventional metal treatment methods. The TiO₂ photocatalyst need to be reused following separation. In the PEC process, TiO₂ was deposited onto the Ti substrate and used as a photoanode. Thus, the separation and recovery of TiO₂ was avoided. The photocatalytic efficiency was increased by the applied bias potential. The electrons driven into the cathode can be used to reduce Cu²⁺ ions. With respect to electrolysis recovery of Cu²⁺ ions

Scheme 1. Proposed Destruction Pathway of Cu–EDTA in the PEC Process

with high current density, the oxygen evolution reaction becomes strong in the high potential region, which will lead to low current efficiency.²⁸ In the PEC process, the bias potential applied to the photoanode is low, which can inhibit the oxygen evolution reaction efficiently at the oxidation process of Cu–EDTA at the anode; meantime, photogenerated electrons are used to reduce the metal ions at the cathode. All of the above processes can increase the current efficiency.

Power consumption is one of the basic parameters considering the applicability of the PEC process to water treatment. It appears more meaningful to calculate energy consumption with reference to the recovery of copper rather than the destruction of Cu–EDTA, considering the fate of different organic compounds, which may be formed during the

EDTA destruction. As shown in the Figure SM-11 of the Supporting Information, electric energy consumptions for the PEC process are larger than those for the electrooxidation process. If the energy consumption of the UV lamp was not included, the energy cost for the PEC process is determined to be 0.36 against 0.83 kWh/g for the EC process at the current density of 0.5 mA cm^{−2} (shown in the inset). It is clear that the energy consumption was largely influenced by the UV power of the used lamp, which will be carefully considered as specific to the experimental setup in our further work.

Meantime, the degradation of EDTA and the recovery of Cu²⁺ ions are incomplete. It is known that PEC oxidation is a heterogeneous reaction occurring at the electrode surface, and the region for the reaction is confined to the area near the

electrode surface. Moreover, it takes time to transport Cu–EDTA from the bulk solution to the electrode surface. The methods for improvement of the treatment efficiency are to increase the ratio of the electrode surface area/volume (S/V) and transport parameters, to shorten the distance between the anode and cathode, to optimize the UV lamp intensity, to improve the frequency of the contact between the target species and the electrode surface using a porous electrode, etc. The optimization of the PEC system is being performed.

■ ASSOCIATED CONTENT

■ Supporting Information

Additional information about characteristics of the TiO_2 film and the cathode, removal of Cu–EDTA and recovery of Cu^{2+} ions under various conditions, toxicity results, analytic procedure and results of EC and UPLC–MS, and the generation of NO_3^- and NH_4^+ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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