Photo-assisted electrolytic decomplexation of Cu-EDTA and Cu recovery enhanced by H_2O_2 and electro-generated active chlorine

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HIGHLIGHTS

- H_2O_2 or Cl^- enhanced Cu-EDTA decomplexation and Cu cathodic recovery.
- $\text{OH}^\cdot$ generated from H_2O_2 with UV irradiation enhanced Cu-EDTA decomplexation.
- Active chlorine and $\text{Cl}^\cdot$ enhanced Cu-EDTA decomplexation with Cl^- addition.
- Different decomplexation pathway of Cu-EDTA by H_2O_2 or Cl^- was proposed.

GRAPHICAL ABSTRACT

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ABSTRACT

The performance of Cu-EDTA decomplexation and copper recovery by photo-assisted electrolysis (UPE) process using TiO_2/Ti as anode and stainless-steel as cathode was explored by adding $\text{H}_2\text{O}_2/\text{Cl}^-$. The Cu-EDTA decomplexation and Cu recovery were well fitted with a pseudo-first-order reaction model. The results indicated that with the addition of H_2O_2 into the UPE process (H_2O_2 -UPE process), the kinetic constant of Cu-EDTA decomplexation was increased from 0.0677 min^{-1} to 0.0880 min^{-1} , and the kinetic constant of Cu recovery was increased from 0.0607 min^{-1} to 0.0749 min^{-1} . Similar enhancement was observed by adding Cl^- into the UPE process (EC-UPE process), where the kinetic constant of Cu-EDTA decomplexation was increased from 0.0272 min^{-1} to 0.0632 min^{-1} . Correspondingly, the kinetic constant of Cu recovery was increased from 0.0249 min^{-1} to 0.0565 min^{-1} . In the H_2O_2 -UPE process, the efficiency of Cu-EDTA decomplexation and Cu recovery was optimal at the initial solution pH of 2.5–3.5; in the EC-UPE process, an optimum current density of 1.00 mA/cm^2 was obtained. Intermediates were detected in H_2O_2 -UPE process and a decomplexation pathway was proposed. A different degradation pathway was concluded in the EC-UPE process.

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1. Introduction

Copper was extensively used in many fields such as electroplating, construction, transportation equipment and electrical industry

Abbreviations: UPE, photo-assisted electrolysis; H_2O_2 -UPE, UPE process with addition of H_2O_2 ; EC-UPE, UPE process with addition of Cl^- .

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[1]. In the effluent from above fields, copper ions were usually combined with chelating agents, such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA) and citrate. The application of conventional precipitation and biological process for the removal of the copper complexes was limited [2,3]. Recently, advanced oxidation processes (AOPs) including Fenton oxidation process and UV/ H_2O_2 process have been investigated in treating metal-binding EDTA [4,5]. In these processes, the complexing agents were efficiently oxidized by the active radicals and metal ions were liberated, which were needed to be further-

more treated. Recovery of the metal ions such as copper, nickel, and zinc et al. was desired.

The oxidation of Cu-EDTA by TiO_2 photocatalysis with a simultaneous reduction of copper ions was reported [6,7]. The liberated copper ions were deposited on the catalyst via reduction by photo-generated electrons. In comparison with the decomplexation of Cu-EDTA, the removal efficiency of copper ions remained relatively low, and separation of the TiO_2 powder and the deposited Cu was needed. Our previous work indicated that the combination of photocatalysis and electrochemical oxidation process can achieve a simultaneous decomplexation of Cu-EDTA complexes and copper recovery by the cathodic reduction process [8]. Cu-EDTA complexes were destroyed at the photoanode, and the liberated copper ions were electrodeposited on the cathode. In this process, destruction of Cu-EDTA mainly occurred near the photoanode with a relatively low efficiency. Efforts on enhancing the photoelectrocatalytic efficiency were performed to optimize the configuration of the photoelectrocatalytic cell, including the distance between the UV source, the working electrode and the electrode structure [9].

In the last two decades, Many researches have demonstrated that AOPs employing H_2O_2 with ultraviolet ($\text{UV}/\text{H}_2\text{O}_2$) were effective in the rapid degradation of organics [5,10–12]. It was indicated that high degradation efficiency of Pb-EDTA was achieved in 10 min [5]. In comparison with the $\text{UV}/\text{H}_2\text{O}_2$ process or the individual photocatalysis, the combination of TiO_2 photocatalysis with $\text{UV}/\text{H}_2\text{O}_2$ process increased the degradation efficiency ofalachlor and Procion H-exl dyes [13,14]. It was concluded that the large amount of hydroxyl radicals produced by heterogeneous photocatalysis and homogenous oxidation in the combined process may be responsible for the efficient degradation of targeted pollutants. Therefore, addition of H_2O_2 into the PEC system was desired for efficient oxidation of Cu-EDTA complexes.

It was reported that the addition of chloride ions in the electrolyte can increase the electrooxidation removal efficiency of many pollutants such as 2-naphthol, urea and microcystins [15–17]. In the case of EDTA, it was reported that *in situ* generated active chlorine allowed the decomplexation of metal-EDTA, which was beneficial to the metal recovery [18]. Furthermore, the combination of UV and chlorination was proved to be an improved oxidation technology in the aspect of some organics like metoprolol compared with pure chlorination due to the photogenerated hydroxyl radicals and chlorine radicals [19]. It's conceivable that the in the photoelectrocatalytic process assisted by Cl^- the degradation efficiency of the targeted pollutants may be improved [20,21].

Herein, the enhancement of decomplexation of Cu-EDTA using the TiO_2 film photoanode and recovery of copper ions at the stainless-steel cathode by electrodeposition was exhibited under high current density by adding $\text{H}_2\text{O}_2/\text{Cl}^-$ into the photo-assisted electrolytic (UPE) reactor. In the case of H_2O_2 addition, a large amount of active $\text{OH}\cdot$ radicals were produced for UV activation of H_2O_2 . In the case of Cl^- addition, generated radicals including active chlorine, $\text{Cl}\cdot$ and $\text{OH}\cdot$ were responsible for the enhanced oxidation of Cu-EDTA. The different degradation pathways of Cu-EDTA with the addition of H_2O_2 or Cl^- were also proposed.

2. Experimental section

2.1. Chemicals

Copper sulfate (CuSO_4) was purchased from Acros. Sodium sulfate (Na_2SO_4), sodium chloride (NaCl), Ethylenediaminetetraacetic acid disodium salt (Na_2EDTA) and hydrogen peroxide (H_2O_2) were

purchased from Sinopharm Chemical Reagent Co., Ltd. China. Iminodiacetic acid (IDA) and nitrilotriacetic acid (NTA) were purchased from Alfa Aesar. Ethylenediamine diacetate (EDDA) was purchased from Tokyo chemical industry Co., Ltd.

Cu-EDTA solution was prepared by mixing a solution of CuSO_4 and Na_2EDTA to obtain a 1:1 M percentage of copper ions to EDTA. Solution pH regulation was performed using either 100 mM NaOH or 50 mM H_2SO_4 . Deionized water was used for the preparation and dilution of the solutions.

2.2. Setup and experiment

The UPE experiments were performed in a single-compartment photo-assisted electrolytic cell with a working volume of 450 mL in galvanostatic mode. As shown in Fig. 1, the cell was connected to a power supplier, the tubular TiO_2/Ti mesh electrode (50 mm diameter) was used as anode, and the TiO_2 film was deposited onto the Ti plate via a dip-coating method as described by Shang et al. [22]. A tubular stainless-steel was used as cathode. The gap between the anode and cathode was 3 mm. A UV lamp (main wavelength 254 nm; 15 W) in a quartz tube was put in the center of the tubular TiO_2/Ti mesh electrode. The UV fluence rate at the wavelength of 254 nm in the same position as photoanode in the reactor have been performed by an irradiatometer (UVB254, Beijing Normal University Photo-Electric Equipment Factory), which was determined as $7.0 \text{ mW}/\text{cm}^2$. The photon flux into the solution from the UV lamp was $2.59 \times 10^{-3} \text{ Einstein}/\text{min}$ according to the calculation. Untreated water containing given concentration of Cu-EDTA was pumped into the reactor from bottom by a peristaltic pump (BT100-2L, Longer pump).

2.3. Analytical method

The concentration of Cu-EDTA was measured by a high-performance liquid chromatography (HPLC, 1260, Agilent Technology) with a C18 column and ultraviolet detector. The elution was comprised of 92% oxalic acid (concentration, 15 mM; pH, 3.0)/8% acetonitrile (v/v) at a temperature of 25°C . The flow rate was set as 1 mL/min and the detection wavelength was set as 254 nm.

Concentrations of total copper ions were measured using 700 series inductively coupled plasma-optical emission spectrometry

Fig. 1. The schematics view of photo-assisted electrolytic reactor.

(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 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 7.12) according to the procedure [8]. Cu-EDDA, Cu-IDA, Cu-NTA (1:1 M ratio) were prepared according to the procedure of Cu-EDTA solution. The intermediates were identified by a comparison of the retention time to those of the prepared standards. Acetic acid, formic acid, oxalic acid and nitrate were detected by ion chromatography (IC) analysis (ICS-2000, DIONEX, USA). Dichloroacetic acid and trichloroacetic acid were detected by the GC-ECD analysis (Agilent technologies, USA).

3. Results and discussion

3.1. Effect of H_2O_2 and Cl^- addition on the UPE performance

The effect of H_2O_2 addition on the UPE process was examined. Decomplexation of Cu-EDTA complexes and recovery of copper ions via individual H_2O_2 oxidation, electrooxidation (EO), photocatalysis (PC), UPE process, and UPE process with H_2O_2 addition (H_2O_2 -UPE process) were investigated with the constant concentration of Cu-EDTA, initial solution pH, and current density. The variation of Cu-EDTA residual ratio (C_t/C_0) was used as a probe of the Cu-EDTA decomplexation. And the decomplexation ratio of Cu-EDTA can be calculated by the following equation:

$$\text{Decomplexation ratio} = 1 - \text{Residual ratio}$$

The recovery percentage of copper ions (R_{Cu}) in the reactor was calculated as following:

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

As shown in Fig. 2(a), no Cu-EDTA decomplexation and Cu recovery occurs in the individual UV photolysis. By contrast, obvious decomplexation of Cu-EDTA and Cu recovery are obtained in the photocatalytic process. Furthermore, an increase of the performance in UPE process can be observed in comparison with EO process and PC process. At 60 min, the decomplexation ratios of Cu-EDTA in the EO process, PC process and UPE process are 89.99%, 39.33% and 97.63%, and the Cu recovery percentages are 89.98%, 43.86% and 97.66%, respectively. The decomplexation rate of Cu-EDTA and the recovery rate of Cu in Fig. 2(a) were simulated using a first-order reaction equation and results are shown in Fig. 2(c). The kinetic constants of UPE process (0.0677 min^{-1} , $R^2 = 0.966$; 0.0607 min^{-1} , $R^2 = 0.976$) are higher than the sum of the kinetic constants of single EO process (0.0361 min^{-1} , $R^2 = 0.974$; 0.0343 min^{-1} , $R^2 = 0.968$) and single PC process (0.0078 min^{-1} , $R^2 = 0.954$; 0.0081 min^{-1} , $R^2 = 0.921$), not only in the decomplexation process but also in the recovery process.

According to the work reported by Frontistis et al. [23], a synergy index (S) was used to assess the synergy effect of UPE process on the decomplexation of Cu-EDTA and Cu recovery.

$$\%S = 100 \times \frac{(k_{\text{UPE}} - k_{\text{EO}} - k_{\text{PC}})}{k_{\text{UPE}}}$$

In this case, the S in the decomplexation process of Cu-EDTA and recovery process of Cu were calculated as 35.16% and 30.15%, indicating that the individual EO and PC process does not

Fig. 2. (a) Decomplexation of Cu-EDTA and Cu recovery via the photolysis, EO process, PC process and UPE process; (b) decomplexation of Cu-EDTA and Cu recovery via H_2O_2 oxidation process, UPE process and UPE process with H_2O_2 addition; (c) first-order kinetic constants in the Cu-EDTA decomplexation process and Cu recovery process via H_2O_2 oxidation process, EO process, PC process, UPE process and UPE process with H_2O_2 addition. ([Cu-EDTA], 0.05 mM; initial pH, 4.6; [H_2O_2], 50 mM; current density, 0.50 mA/cm²).

simply add up (*i.e.* $S = 0$) but a synergistic effect toward both the decomplexation of Cu-EDTA and recovery of Cu was exhibited. Similar results under the low current density were observed and explained in our previous study [8].

It can be seen from Fig. 2(b) that the half-life time of Cu-EDTA decomplexation is increased from 8 min in the H_2O_2 -UPE process to 15 min in the UPE process. Correspondingly, the kinetic constant of Cu-EDTA decomplexation is also increased from 0.0677 min^{-1}

($R^2 = 0.966$) to 0.0880 min^{-1} ($R^2 = 0.968$) (Fig. 2(c)). It was obvious that the performance of Cu-EDTA decomplexation by UPE oxidation was enhanced with addition of H_2O_2 . In this case, the S of the decomplexation process in the combination of UPE process and H_2O_2 oxidation process was calculated as 21.13%.

In individual UPE process, the heterogeneous electrooxidation or hydroxyl radicals oxidation of the pollutants may be restricted by low $\text{OH}\cdot$ radicals concentration. By contrast, AOPs employing H_2O_2 with UV irradiation, as reported in previous literatures, were effective in the degradation of organics by producing a multitude of hydroxyl radicals [10,12]. Therefore, the decomplexation of Cu-EDTA was enhanced via the homogeneous and heterogeneous oxidation process with addition of H_2O_2 . The recovery process followed the decomplexation process of Cu-EDTA, consequently, the enhancement in the copper recovery process is also observed (Fig. 2(b) and (c)).

The feasibility of the UPE process enhanced by Cl^- addition was investigated at a Cu-EDTA concentration of 0.50 mM. The EO process in the presence of Cl^- (EC process), UPE process in the absence of Cl^- and UPE process in the presence of Cl^- (EC-UPE process) were studied with a constant initial solution pH and current density. As shown in Fig. 3, the rate of Cu-EDTA decomplexation in the EC-UPE process is higher than that of EC process and UPE process in the absence of Cl^- . The first-order kinetic constant in Cu-EDTA decomplexation process is increased from 0.0474 min^{-1} (EC process, $R^2 = 0.983$) and 0.0272 min^{-1} (UPE process, $R^2 = 0.987$) to 0.0632 min^{-1} (EC-UPE process, $R^2 = 0.987$).

In the UPE oxidation process, active chlorine was generated through the following reactions (1–3). The generated active chlorine was transferred into the bulk solution in the form of chlorine, hypochlorous acid and hypochlorite [16]. It was proved that with the addition of Cl^- into the electrochemical process using non-photoactive dimensionally stable anode combined with UV light irradiation, the performance for the pollutant removal was improved [24,25].

It was reported that hydroxyl radicals and chlorine radicals were generated via reaction (4) [26]. In our case, the above active radicals may produce, which were responsible for the enhanced oxidation of Cu-EDTA with the addition of Cl^- ions into the UPE system.

3.2. Effect of the concentration of H_2O_2 and Cl^- ions

As shown in Fig. 4(a), a rapid decomplexation of Cu-EDTA accompanied with the recovery of Cu is observed in the H_2O_2 -UPE process in comparison with the UPE process in the absence of H_2O_2 . Corresponding to the H_2O_2 concentration of 0.5 mM, 5 mM and 50 mM, the decomplexation ratios of Cu-EDTA are 34.67%, 43.77% and 69.87% at 10 min, and the recovery percentages of Cu are 29.76%, 44.47% and 67.12%, respectively. After 20 min, the enhancement becomes weak. The kinetic constants in the processes of both Cu-EDTA decomplexation and Cu recovery are also increased with the increase of H_2O_2 concentration (Fig. 4(b)). A similar result that high concentration of H_2O_2 benefited the UV/ H_2O_2 process was also obtained by Jiraroj [5]. The consistency of decomplexation efficiency with H_2O_2 concentration may be

Fig. 3. (a) Decomplexation of Cu-EDTA and Cu recovery via EO process in the presence of Cl^- , UPE process in the absence of Cl^- and UPE process in the presence of Cl^- ; (b) first-order kinetic constants in the Cu-EDTA decomplexation and Cu recovery via EO process in the presence of Cl^- , UPE process in the absence of Cl^- and UPE process in the presence of Cl^- . ([Cu-EDTA], 0.50 mM; initial pH, 4.6; $[\text{Cl}^-]$, 0.20 M; current density, 1.00 mA/cm^2).

ascribed to the increased amount of hydroxyl radicals generated from the UV irradiation of H_2O_2 .

With respect to the effect of chloride ions on the UPE process, different amounts of chloride ions ranging from 0 to 0.20 M were added into the UPE system at a constant current density of 1.00 mA/cm^2 and initial pH of 4.6. As shown in Fig. 5(a), in the UPE process, the decomplexation ratio of Cu-EDTA in 60 min is increased from 80.47% at a NaCl concentration of 0.02 mM to 90.48% with the addition of 0.20 M NaCl, and the recovery percentage is also improved. With the increase of Cl^- concentration from 0.02 M to 0.20 M, the kinetic constants are increased from 0.0351 min^{-1} ($R^2 = 0.990$) and 0.0367 min^{-1} ($R^2 = 0.994$) to 0.0445 min^{-1} ($R^2 = 0.969$) and 0.0453 min^{-1} ($R^2 = 0.995$) in the processes of Cu-EDTA decomplexation and Cu recovery (Fig. 5(b)). It was reported that high concentration of Cl^- was recommended for the production of active chlorine [15,27]. As a result, a large amount of chlorine radicals and hydroxyl radicals were produced under UV irradiation via the reaction (4) [25,26], which can accelerate the decomplexation of Cu-EDTA and Cu recovery.

3.3. Effect of the initial solution pH

As shown in Fig. 6, under the constant Cu-EDTA concentration of 0.05 mM and current density of 0.50 mA/cm^2 , the largest kinetic constants of Cu-EDTA decomplexation and copper recovery are obtained at the initial solution pH of 3.5 and 2.5.

Fig. 4. (a) Effect of concentration of H_2O_2 on decomplexation of Cu-EDTA and Cu recovery; (b) first-order kinetic constant in the decomplexation process and recovery process as a function of H_2O_2 concentration in H_2O_2 -UPE process. ([Cu-EDTA], 0.05 mM; initial pH, 4.6; current density, 0.50 mA/cm^2).

In acidic condition, a large portion of Cu-EDTA was adsorbed onto TiO_2 photoanode, and the adsorption was favorable to the electrooxidation and photocatalytic oxidation process. By contrast, in less acidic condition, the copper ions liberated from Cu-EDTA were inclined to be adsorbed onto TiO_2 , and the oxidation was weakened because active sites were occupied or the generation of the oxidant ($\text{OH}^\cdot$) by photocatalysis was restrained [28]. In different solution pH, the species of Cu-EDTA varied, such as $(\text{CuOHEDTA})^{3-}$, $(\text{CuEDTA})^{2-}$, $(\text{CuHEDTA})^-$, $\text{Cu-H}_2\text{EDTA}$ and $(\text{CuH}_3\text{-EDTA})^+$. At low pH, the major species ($(\text{Cu-EDTA})^{2-}$, $(\text{CuHEDTA})^-$) existed in the solution, which can react with hydroxyl radicals more easily than other species [8]. Therefore, low solution pH value was beneficial to UPE oxidation process.

The influence of solution pH on the UV/ H_2O_2 process demonstrated a different trend. Under UV irradiation, a molar of H_2O_2 was transferred into two molar of hydroxyl radicals by reaction (5) [10,12]. While the pH variation from 1 to 3 increased the oxidation ability, further increase of pH from 3.0 to 5.0 decreased the rate of H_2O_2 production by reaction (5). Under less acidic condition, H_2O_2 underwent photodecomposition to water and oxygen (reaction (6)) rather than production of hydroxyl radicals (reaction (5)) [10]. Therefore, oxidation of Cu-EDTA by the UV/ H_2O_2 process was weakened.

Fig. 5. (a) Effect of concentration of Cl^- on decomplexation of Cu-EDTA and Cu recovery; (b) first-order kinetic constant in the decomplexation process and recovery process as a function of Cl^- concentration in EC-UPE process. ([Cu-EDTA], 0.50 mM; initial pH, 4.6; current density, 1.00 mA/cm^2).

In the case of Cl^- ions, the performance of EC-UPE process at solution pH varied from 2.0 to 5.5 was investigated at the Cu-EDTA concentration of 0.50 mM, current density of 1.00 mA/cm^2 and Cl^- concentration of 0.02 M. It should be pointed out here that, although pH was left uncontrolled, only slight pH increase occurred (Fig. S2). It's obvious that when the initial solution pH changed from 2.0 to 5.5, the kinetic constants of both Cu-EDTA decomplexation and Cu recovery decrease rapidly in EC-UPE process (Fig. 7(b)). As suggested by literatures [15,25], the low solution pH had a slight negative effect on the electrochemical generation of active chlorine but a positive effect on the UV/chlorination oxidation process. In our cases, low pH condition benefited the decomplexation of Cu-EDTA and Cu recovery in EC-UPE process. Therefore, it was proposed that the UV/chlorination mechanism (reaction (4)) played a dominant role in our system.

3.4. Effect of the current density

Effect of current density on the decomplexation of Cu-EDTA and recovery of Cu in the H_2O_2 -UPE process was investigated. With the increase of current density from 0.25 mA/cm^2 to 2.50 mA/cm^2 , decomplexation of Cu-EDTA and Cu recovery are slightly improved (Fig. 8(a)), the first-order kinetic constant is increased from 0.0501 min^{-1} ($R^2 = 0.959$) to 0.0747 min^{-1} ($R^2 = 0.963$) in the decomplexation process of Cu-EDTA, a similar trend of the kinetic constant in the Cu recovery process is obtained (Fig. 8(b)). When the current density was higher than a certain value, the indirect electrooxidation and photocatalysis played a predominant role in

Fig. 6. (a) Effect of initial solution pH on decomplexation of Cu-EDTA and Cu recovery; (b) first-order kinetic constant in the decomplexation process and recovery process as a function of initial solution pH in H_2O_2 -UPE process. ([Cu-EDTA], 0.05 mM; $[\text{H}_2\text{O}_2]$, 50 mM; current density, 0.50 mA/cm^2).

the UPE process, and the photocatalysis cannot be improved by further increase of current density [8,29]. Furthermore, there was no effect of current density on the production of hydroxyl radicals in the $\text{UV}/\text{H}_2\text{O}_2$ oxidation process. Hence, it was concluded that the increase of Cu-EDTA decomplexation at high current density in the H_2O_2 -UPE process may be induced by the indirect electrooxidation of the Cu-EDTA.

In the case of Cl^- ions, the effect of current density on the decomplexation of Cu-EDTA and copper recovery of EC-UPE process is illustrated in Fig. 9(a) and (b). With an increase of the current density from 0.25 mA/cm^2 to 1.00 mA/cm^2 , the kinetic constant of the decomplexation process is improved from 0.0029 min^{-1} ($R^2 = 0.918$) to 0.0780 min^{-1} ($R^2 = 0.960$), and the kinetic constant of Cu recovery is increased from 0.0023 min^{-1} ($R^2 = 0.937$) to 0.0760 min^{-1} ($R^2 = 0.964$). The performance of main oxidation processes including electro-enhanced photocatalysis, direct electrooxidation and electrochlorination in the EC-UPE process were highly in accordance with the current density. However, when the current density is higher than 1.00 mA/cm^2 , the first-order kinetic constants of decomplexation and recovery doesn't increase. Both the UPE process and electrochlorination process (reaction (1–4)) reached the maximum rate. Under a current density of 1.00 mA/cm^2 , the electro-enhanced photocatalytic oxidation obtained its best performance due to the total disappearance of recombination between photogenerated electrons and hole. Moreover, the electrochlorination rate was also limited because the highest mass transfer velocity of Cl^- induced

Fig. 7. (a) Effect of initial solution pH on decomplexation of Cu-EDTA and Cu recovery; (b) first-order kinetic constant in the decomplexation process and recovery process as a function of initial solution pH in EC-UPE process. ([Cu-EDTA], 0.50 mM; $[\text{Cl}^-]$, 0.02 M; current density, 1.00 mA/cm^2).

by a concentration gradient was reached and most of the chloride ions that transfer to the anode surface were efficiently utilized.

3.5. Intermediates and proposed pathways

In order to explore the Cu-EDTA oxidation pathway in the UPE process with the addition of H_2O_2 or Cl^- , CE, IC and GC-ECD techniques were used to analyze the samples taken from various UPE process with the initial solution of 1.00 mM Cu-EDTA at pH 3.0. In the H_2O_2 -UPE process, as shown in Fig. 10(a), Cu-EDTA is detected at the reaction time of 10 min with the peak intensity decrease of Cu-EDTA until the disappearance at 30 min; the peaks assigned to Cu-NTA and Cu-IDA are also observed at 10 min. Acetic acid was detected by IC analysis in the sample at reaction time of 10 min.

Based on the above results, it can be concluded that an acetic group was removed from Cu-EDTA, and then a Cu-EDDA and acetic acid were formed following reaction (7). Another possible pathway followed the reaction (8) or reaction (9), Cu-EDTA was broken from the C–N bond, forming Cu-NTA and IDA or Cu-IDA and NTA.

Fig. 8. (a) Effect of current density on decomplexation of Cu-EDTA and Cu recovery in H_2O_2 -UPE process; (b) first-order kinetic constant in the decomplexation process and recovery process as a function of current density in H_2O_2 -UPE process. ([Cu-EDTA], 0.05 mM; initial pH, 4.6; $[\text{H}_2\text{O}_2]$, 50 mM).

With the reaction evolution, the above intermediates are furthermore degraded. According to the TOC removal in Fig. 10(c), in the H_2O_2 -UPE process, a dramatic TOC removal of 55.69 mg/L happens within reaction time of 60 min, which means some organics were thoroughly mineralized. The remained TOC was ascribed to some small molecular acids such as acetic acid, formic acid, and oxalic acid [8].

In the case of Cl^- addition, no intermediate peaks of NTA, Cu-NTA, IDA, Cu-IDA, EDDA and Cu-EDDA are observed. Instead, only one peak appears at 10 min (Fig. 10(b)). Similarly, oxalic acid was detected by the IC analysis; dichloroacetic acid and trichloroacetic acid were detected by GC-ECD analysis. It can be concluded that a different removal pathway of Cu-EDTA occurred in the presence of Cl^- .

With respect to the mineralization degree, as shown in Fig. 10(c), only about 11% TOC removal in both UPE and EC-UPE processes is observed. As mentioned in other studies, UV/ H_2O_2 system had an impressive performance in the TOC removal [30]. The effluent in the H_2O_2 -UPE process was more beneficial to the environment not only due to high mineralization degree of organics in the H_2O_2 -UPE process but also to avoid the generation of chlorinated products.

3.6. Comparison of various UPE processes

The comparison of UPE process and two enhanced UPE processes was carried out at a Cu-EDTA concentration of 0.50 mM.

Fig. 9. (a) Effect of current density on decomplexation of Cu-EDTA and recovery of Cu in EC-UPE process; (b) first-order kinetic constants in the decomplexation process and recovery process as a function of current density in EC-UPE process. ([Cu-EDTA], 0.50 mM; initial pH, 4.6; $[\text{Cl}^-]$, 0.02 M).

The initial solution pH and current density were adjusted as 3.0 and 1.00 mA/cm². The concentration of NaCl and H_2O_2 was adjusted as 0.20 M and 50 mM, respectively. As shown in Fig. 11, the decomplexation ratio in the UPE process is determined as 75.27%. With the addition of H_2O_2 and NaCl, the decomplexation ratios are increased to 87.32% and 99.99%, respectively. In the Cu recovery process, the recovery percentages are also increased from 77.26% (UPE process) to 87.32% (H_2O_2 -UPE process) and 99.89% (EC-UPE process). Under the optimum condition, the performance improvement in two enhanced UPE processes was impressive. Among them, the best enhancement can be obtained in the EC-UPE process.

4. Conclusions

The UPE process enhanced by adding $\text{H}_2\text{O}_2/\text{Cl}^-$ was possible from the view of Cu-EDTA decomplexation and simultaneous Cu recovery. The rate of Cu-EDTA decomplexation and Cu deposition for H_2O_2 -UPE process and EC-UPE process were higher than that of the individual UPE process. In the H_2O_2 -UPE system, the treatment of Cu-EDTA complexes at high concentration of H_2O_2 , high current density and initial solution pH 2.5–3.5 could provide a high rate of Cu-EDTA decomplexation and Cu recovery. And, in the EC-UPE process, the process condition of high initial concentration of Cl^- , low solution pH and current density of 1.00 mA/cm² benefits Cu-EDTA decomplexation and Cu recovery. Interme-

Fig. 10. Electropherograms of Cu-EDTA solution treated at various times in the H₂O₂-UPE process (a) and EC-UPE process (b): 50 phosphate buffer and 0.50 mM TTAB (pH 6.8), 195 nm, 20 kV, and 25 °C. A.u. = absorbance units; (c) TOC changes in UPE process, H₂O₂-UPE process, EC-UPE process. ([Cu-EDTA], 1 mM; Initial solution pH, 3.0; Current density, 0.25 mA/cm²; [Cl⁻], 0.20 M; [H₂O₂], 50 mM).

diates such as Cu-EDDA, Cu-NTA, Cu-IDA, EDDA, NTA and IDA and by-products like acetic acid, formic acid, oxalic acid and nitrate were identified in the H₂O₂-UPE process. By contrast, oxalic acid, dichloroacetic acid and trichloroacetic acid were detected in the EC-UPE process. The enhancement performance in the EC-UPE process was better than that in the H₂O₂-UPE process; the effluent of H₂O₂-UPE process was more environmental-friendly due to its higher mineralization degree and less generation of the by-products.

Fig. 11. The comparison of the UPE process and two enhanced UPE process. ([Cu-EDTA], 0.50 mM; initial solution pH, 3.0; current density, 1.00 mA/cm²; [Cl⁻], 0.20 M; [H₂O₂], 50 mM).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2016.04.006>.

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