Photoelectrocatalytic oxidation of Cu-EDTA complex and electrodeposition recovery of Cu in a continuous tubular photoelectrochemical reactor

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HIGHLIGHTS

- A photoelectro-reactor was designed for Cu-EDTA destruction and Cu^{2+} recovery.
- The percentages of Cu recovery and Cu-EDTA destruction were over 85% and 80%.
- Metal recovery efficiency for various metal-EDTA complexes was compared.

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ABSTRACT

In this paper, a tubular photoelectrocatalytic reactor using the TiO_2/Ti mesh anode was designed for the destruction of Cu-EDTA complex and recovery of liberated Cu^{2+} ions in a continuous mode. Its performance was evaluated in terms of the destruction of the Cu-EDTA and the yield of Cu recovery as a function of the current density, hydraulic residence time, initial pH, and initial Cu-EDTA concentration. The efficiency of Cu recovery and Cu-EDTA destruction were determined to be over 85% and 80% with the current density of 1.13 A m^{-2} and the hydraulic residence time of 60 min at pH 3.5. Energy consumed for copper electrodeposition proved to be inversely proportional to the current density. Electrodeposition recovery of Pb ions from its EDTA solutions was possible, but low deposition recovery of Ni, Cd, and Zn was observed. The tubular photoelectrocatalytic reactor shows a high stability and may be scaled up for the destruction of metal-complexes and recovery of the metal ions.

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1. Introduction

The removal and recovery of heavy metals from industrial effluents has received great attention in recent years. The technologies of precipitation [1], sorption/biosorption [2], ion exchange [3], and membrane filtration [4] are proved to be effective for metal removal. However, recovery of the heavy metals by the above methods was limited.

Electrolytic method has been largely investigated for the recovery of heavy metals from wastewater [5–8]. Generally, the recovery of heavy metals proceeds via the electrodeposition process. In recent years, the combined use of electrochemical (EC) and photocatalytic (PC) processes for the remediation of harmful pollutants has undergone rapid development [9]. It was recognized that the electrical bias potential applied between the anode and cathode largely increased the PC degradation efficiencies of organic pollutants or other toxic substances by means of prohibiting the photo-generated charges recombination in the photoelectrocatalytic

(PEC) process [10–13]. In comparison with the extensive study about the oxidation process occurring at the anode, the role of the cathode was less paid in the PEC process. A PEC-enzymatic hybrid system for hydrogen production is presented; the photogenerated electrons in the TiO_2/Ti anode are transferred to the cathode where the hydrogenase enzyme catalyzes the reduction of the H^+ species to H_2 [14]. Utilization of the photogenerated electrons to react with the oxygen for H_2O_2 production at the carbon cathode was reported in a PEC cell, in which PEC oxidation of chlortetracycline using TiO_2/Ti anode occur simultaneously [9]. With respect to the electrodeposition of metal ions, a combined PEC system using an activated carbon concentrator cathode is described by Grimes et al. that achieves a simultaneous destruction of phthalic acid and recovery of cobalt ions [15]. In their work, TiO_2 photocatalyst was used as powder, which was needed to be separated. Application of the PEC process in the recovery of Cu^{2+} ions onto a stainless steel cathode and PEC degradation of EDTA complex by a TiO_2 film electrode were studied in our previous work with a batch mode [16]. Simultaneous recovery of Cu^{2+} ions and degradation of EDTA was achieved. However, the recovery percentage of Cu^{2+} ions was desired to be increased.

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Many efforts on the PEC studies have been made to improve the photocatalytic capability of TiO_2 including synthesis of new TiO_2 structures or modification of TiO_2 with other elements [17,18]. The actual implementation of the PEC technology is dependent on not only electrode materials but also the configuration of the PEC cell. Efficient electrolytic cell design has been directed towards the optimization of the space time yield, high specific electrode area, and a large mass transport coefficient [19]. In the case of the PEC cell, effectively making use of photons and the photoanode with fast electron transfer, UV lamp position and distance between the UV source and the working electrode, and the electrode structure could also influence the mass transfer coefficient [9,20]. A vertical PEC cylindrical reactor was used for the water disinfection, in which two concentric Pyrex tubes and the UV lamp was located in the internal configuration along the axis of the reactor; the reaction solution occupied the annular volume [20]. With three electrodes, a cylindrical quartz cell has also been used, in which TiO_2/Ti was used as anode and placed at the bottom of the reactor to receive UV light irradiation [21]. Reticulated vitreous carbon or Pt used as a cathode was placed at one side of the cell. A rectangular quartz photoreactor with TiO_2 at the anode and Pt at the cathode was used to decompose the organic contaminants by the PEC process [22]. A three-electrode thin-layer PEC cell with TiO_2 film electrode as anode was also described by Zhao et al. [23]. The distance between the anode and the cathode was 200 μm and the UV lamp was put above the PEC cell. Recently, Xu et al. developed a rotating disc reactor for dye treatment [24]. TiO_2 nanoparticle/Ti electrode was used as the round disk photoanode, and the upper half of the round disk photoanode was coated with a thin layer of wastewater and exposed to UV radiation in air, meanwhile, the other half of the disk electrode was immersed in the bulk wastewater to perform a conventional treatment. The high PEC efficiency was achieved by only half area of the electrode.

Herein, a tubular PEC reactor that consists of a tubular TiO_2/Ti mesh anode and stainless steel cathode was carefully designed in order to increase the A/V ratio (ratio of electrode area and solution volume) and improve the mass transfer of the system. The UV lamp was in the center of the tubular TiO_2/Ti mesh anode along with the axis. Simultaneous Cu-EDTA complex destruction and Cu^{2+} ions recovery by the electrodeposition from a Cu-EDTA solution was realized in the PEC system. The effects of the current density, hydraulic residence time (HRT), and pH values were investigated. The performance of the PEC system was also checked based on the recovery of other heavy metals from their EDTA complexes. Finally, the feasibility of the PEC technology and economy was evaluated.

2. Experimental section

2.1. Experimental apparatus

The PEC experiments were performed in a single-compartment electrochemical flow cell with a net working volume of 450 mL. As shown in Fig. 1(a), the cell is connected to a power supplier. A storage tank and a recirculation pump complete the experimental system. As shown in Fig. 1(b), the tubular TiO_2/Ti mesh electrode (50 mm diameter) is used as anode. A tubular stainless steel (60 mm diameter) is selected as cathode. The gap between the anode and cathode is 3 mm. A UV lamp (main wavelength 254 nm; 5 W) in a quartz tube is put in the center of the tubular TiO_2/Ti mesh electrode.

Tubular titanium mesh was employed as the substrate. Before being used, the titanium mesh was first rinsed by hydrochloric acid (0.1 M) and distilled water. Aliquot $\text{Ti}(\text{OC}_4\text{H}_9)_4$ (A.R., 20 mL) was added dropwise to ethanol (A.R., 160 mL) and then $\text{NH}(\text{OC}_2\text{H}_5)_2$

(3 mL) was added to this solution. After being stirred with an ultrasonic horn for 15 min, a light-yellow transparent solution was formed. After being gelatinized for 15 days, the precursor solution was mixed with ethanol solution (98% (V/V), 160 mL). Sealed and gelatinized for 5 days, a sol with a certain viscosity was obtained, which was coated onto titanium mesh by dip-coating method followed by being calcined at 500 $^\circ\text{C}$ for 1 h. The pictures of the tubular titanium mesh substrate and TiO_2 coated tubular titanium mesh electrode were given in the Supporting information as Fig. S1.

2.2. Experimental procedures

Recovery of heavy metal ions and destruction of EDTA by electrolysis, photocatalysis, and PEC process were performed in the above experiment setup and the experiments of electrolysis and PEC process were performed at a galvanostatic mode. Effects of current density, HRT, initial pH value, and initial concentration of Cu-EDTA were investigated. In the case of current density, destruction of Cu-EDTA and recovery of Cu^{2+} ions with the current densities of 0.29, 0.57, 1.13, and 1.70 A m^{-2} were performed under the constant conditions of HRT = 1 h and pH = 6.6. A thermoregulated water bath was used to maintain a constant temperature.

2.3. Analytical procedures

Concentration of Cu-EDTA complexes was determined using a high performance liquid chromatography (HPLC) (1260, Agilent Technology). Hypersil Gold (Thermo scientific) analytical column was used along with the elution composed of 92% oxalic acid (15 mM)/8% acetonitrile (V/V) at a temperature of 25 $^\circ\text{C}$. The solvent was adjusted to pH 3.0, and the flow rate was set as 1 mL min^{-1} . The detection wavelength was set as 254 nm. Concentrations of metal ions were measured using a 700 series inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent Technology). All the data were measured at least twice.

3. Results and discussion

3.1. Basic reaction processes in the PEC system

There exist some possible reactions in the PEC destruction of Cu-EDTA complexes containing water:

Anode:

Cathode:

Cu-EDTA complexes can be destroyed at the anode of TiO_2/Ti mesh in the PEC process. Liberated Cu^{2+} ions are deposited onto the cathode; the hydrogen evolution is mainly competitive

Fig. 1. (a) The schematic view of the photoelectrocatalytic system; (b) a full numerical scale and capacity of the photoelectrocatalytic reactor (1) outlet; (2) UV lamp; (3) TiO₂/Ti mesh anode; (4) inlet; (5) cathode; and (6) quartz tube.

reaction, which will reduce the current efficiency. On the other hand, oxygen evolution may occur at the anode, which will compete with the oxidation reaction of Cu-EDTA. Therefore, the parameters of the current density, reaction time, initial concentration, and solution pH play the important role in the destruction of Cu-EDTA and Cu recovery.

3.2. Comparison of photocatalysis, electrolysis, and PEC process

Firstly, the destruction of Cu-EDTA and recovery of Cu²⁺ ions in individual photocatalysis, electrolysis, and the PEC process was estimated in the PEC system. Individual electrolysis and the PEC

process were performed under the same current density of 1.13 A m⁻². As shown in Fig. 2(a), the removal percentage of Cu-EDTA by individual electrolysis and photocatalysis process is determined to be about 15% and 20%, respectively. By contrast, it is increased to be nearly 80% in the PEC process. With respect to the Cu recovery, 15% and 18% recovery percentage is observed from Fig. 2(b) for the photocatalysis and electrolysis process, respectively. By contrast, 86% recovery percentage is achieved in the PEC process. And, the cell potentials with the same current density of 1.13 A m⁻² in the electrolysis and PEC process are measured to be 5.5 V and 1.2 V, respectively. The low cell potentials mean low energy cost consumption.

Fig. 2. Comparison of photocatalysis, electrolysis and the photoelectrocatalytic process on the destruction of Cu-EDTA and Cu^{2+} ions recovery (HRT = 1 h, initial concentration of Cu-EDTA = 0.1 mM, current density = 1.13 A m^{-2} , pH = 6.6).

Destruction of metal-EDTA complexes by the TiO_2 photocatalytic process has been largely reported [25,26]. Their results indicated that Cu-EDTA can be destroyed by the photocatalytic process. However, the separation/recovery of TiO_2 powder was needed. In our case, photocatalytic destruction of Cu-EDTA complexes using the TiO_2 film was firstly evaluated. The separation of TiO_2 powder was avoided. It is known that quick recombination of photogenerated electrons and holes occur in the TiO_2 photocatalytic process, which leads to the low rate of Cu-EDTA destruction. And, the recovery percentage of Cu^{2+} ions is about 10%. In the single electrolysis process, the percentage of Cu-EDTA destruction and Cu^{2+} ions recovery was determined to be about 20% at the current density of 1.13 A m^{-2} . It has been reported that a high current density and a long time was needed in order to achieve a high efficiency of Cu-EDTA destruction and Cu^{2+} ions recovery in the electrolysis process [27], which will lead to a high energy cost.

In the PEC process, the photocatalytic oxidation of Cu-EDTA can be enhanced by a low cell potential. With a low cell potential, the photogenerated electrons were driven to the cathode and a recombination of photogenerated electrons and holes were inhibited and oxidation of Cu-EDTA was enhanced at the anode. Besides, electrolysis process can also lead to the destruction of Cu-EDTA to some extent. All above processes are responsible for the efficient destruction of Cu-EDTA. Meantime, the electrons driven onto the cathode can be used to reduce the liberated Cu^{2+} ions. As a result, the electrodeposition recovery of Cu^{2+} can be achieved efficiently. Following, the destruction of Cu-EDTA and recovery of Cu^{2+} ions was checked under various experiment conditions in the PEC system.

3.3. Effect of current densities

Fig. 3(a) and (b) show the profile of Cu-EDTA concentration and Cu^{2+} ions recovery with the reaction time in the PEC process, respectively. The destruction rates of Cu-EDTA and recovery percentage of Cu^{2+} ions increase strongly with the current density. At the current density of 1.70 A m^{-2} , removal rate of Cu-EDTA is nearly 90% and recovery percentage of Cu^{2+} ions can be as high as 85%.

With the current density of 0.29, 0.57, 1.13, and 1.70 A m^{-2} , cell potentials are increased to be 0.22, 0.55, 1.20, 2.31 V, respectively. Therefore, an optimum point should be carefully determined giving a high removal rate and low energy consumption. In addition, an increase in the current density results in more gas evolved at the anode and cathode, which will consume the electro-energy and decrease the current efficiency. In addition, it was reported that vigorous stir of the solution by the generated gas leads to a decrease in the diffusion layer, which will decrease the mass transfer coefficient [28], leading to the low efficiencies of EDTA oxidation and Cu electrodeposition in our case.

3.4. Effect of hydraulic residence time

The effects of the HRT ranging from 30 to 60 min on copper recovery efficiency and the destruction of Cu-EDTA were investigated with the constant current density of 1.13 A m^{-2} and initial Cu-EDTA concentration of 0.1 mM, respectively. As shown in Fig. 4(a) and (b), the increase in the flow rate results in a low destruction rate of Cu-EDTA and percentage of Cu electrodeposition. With the HRT of 30, 45, and 60 min, the destruction percentage

Fig. 3. Effect of current density on the destruction of Cu-EDTA (a) and recovery of Cu^{2+} ions (b) in the photoelectrocatalytic process (HRT = 1 h, initial concentration of Cu-EDTA = 0.1 mM, pH = 6.6).

of Cu-EDTA are determined to be ca 40%, 60%, and 80%, respectively. Correspondingly, the copper recovery percentages are about 30%, 50%, and 60%. It is observed that the differences for HRT 45 min and 60 min are slight.

3.5. Effect of initial pH

The effect of initial pH values on the destruction of Cu-EDTA and recovery of Cu^{2+} ions is presented in Fig. 5(a) and (b). It is observed that the net rate of Cu-EDTA removal decreases with the pH increase over this range. By contrast, the recovery percentage of Cu^{2+} ions favors at acid conditions. EDTA can form complexes with Cu^{2+} ions in the PEC cell in the form of Cu-EDTA, and the precipitation of insoluble products at alkaline pH values is avoided. In the PEC process, Cu-EDA complex was destroyed at the anode. Meantime, liberated Cu^{2+} ions are electrodeposited onto the cathode.

Therefore, a low pH is necessary for the performance of the metal reduction at the cathode. When the pH is larger than 4.5, liberated Cu^{2+} may precipitate as CuO or Cu_2O , which are not available for the electrochemical reduction. Besides, with the increase of pH values, the presence of copper oxides suppresses the adsorption of reactive intermediate for metal deposition, and also inhibits the nucleation and crystal growth of copper.

3.6. Effect of initial Cu-EDTA concentration

The performance of Cu-EDTA destruction and Cu^{2+} ions recovery with various Cu-EDTA concentrations was evaluated. It can be seen from Fig. 6 that the rates of Cu-EDTA destruction and

Fig. 4. Effect of hydraulic residence time on the destruction of Cu-EDTA (a) and recovery of Cu^{2+} ions (b) in the photoelectrocatalytic process (initial concentration of Cu-EDTA = 0.1 mM, current density = 1.13 A m^{-2} , pH = 6.6).

Fig. 5. Effect of initial pH on the destruction of Cu-EDTA (a) and recovery of Cu^{2+} ions (b) in the photoelectrocatalytic process (HRT = 1 h, initial concentration of Cu-EDTA = 0.1 mM, current density = 1.13 A m^{-2}).

Cu^{2+} ions recovery increase with the decrease of initial Cu-EDTA concentration. The similar various trends indicate that the destruction of Cu-EDTA is followed by the Cu^{2+} electrodeposition. The smaller the initial Cu-EDTA concentration, the faster it could be removed from the solution accompanied with the higher Cu recovery percentage in the PEC process. The fact that destruction of Cu-EDTA at higher Cu-EDTA concentrations may be associated with the availability of fewer active sites, thus triggering competitive adsorption between Cu-EDTA and intermediates onto the electrode surface which thereby decreases the concentration of oxidizing species attacking Cu-EDTA.

3.7. Electrical energy consumption

Power consumption is one of the basic parameters considering the applicability of the PEC processes to the wastewater treatment. It is presented in Fig. 7 that an overview of the different specific electric energy consumptions based on copper recovery, calculated from the difference of the total amount of initial copper with residual amount of copper in the reaction solution. It appears more meaningful to calculate energy consumption with reference to the recovery of copper rather than the destruction of Cu-EDTA, considering that the fate of different organic compounds, which may be formed during the EDTA destruction. The unit energy consumptions E , expressed in kWh necessary to recovery of 1 g copper, can be calculated according to $E = 10^{-3} (UI + W) t m^{-1}$. Where U = cell potential (V), I = applied current, W = 5 W, t = reaction time (h), and m = mass of the removed target (g).

As shown in Fig. 7(a), the electric energy consumptions increase with the current density without the calculation of the energy cost

Fig. 6. Effect of initial concentrations of Cu-EDTA on the destruction of Cu-EDTA (a) and recovery of Cu^{2+} ions (b) in the photoelectrocatalytic process (HRT = 1 h, pH = 6.6, current density = 1.13 A m^{-2}).

Fig. 7. Energy cost for Cu^{2+} ions recovery with various current density. (a) Electrochemical process; and (b) photoelectrocatalytic process.

of UV lamp. And, the energy cost is less than 0.12 kWh/g even at the current density of 1.70 A m^{-2} . As shown in Fig. 7(b), the energy cost is increased to be over 1.2 kWh/g when the energy cost of UV lamp was included in the PEC process. In the present study, the energy consumption was largely influenced by UV power of the used lamp, which should be considered as specific to the future experimental setup.

3.8. Treatment of other metal-EDTA complexes

In addition to Cu-EDTA complexes, several EDTA-bearing complexes were tested to study the applicability of the PEC process. As shown in Fig. 8(a), recovery of the divalent metals including Pb and Cu is determined to be over 90% and 70% under the conditions of HRT = 1 h and current density = 1.13 A m^{-2} , respectively. By contrast, a low recovery ratio of Zn, Cd, and Ni from their EDTA solutions is observed. The results indicate that the order for the investigated metals for electrodeposition is as follows: $\text{Pb} > \text{Cu} > \text{Zn} > \text{Co} > \text{Cd} > \text{Ni}$. As shown in Fig. 8(b), the TOC removal efficiency for various metals-EDTA complexes follows the above order. The constant of the 1:1 complexes of divalent metal cations and EDTA anions, are 20.5 (Cu), 20.4 (Ni), 19.8 (Pb), 18.3 (Zn), and 18.2 (Cd) at 298 K and zero ionic strength [29]. The standard reduction potentials of these divalent metal cations are -0.34 (Cu), -0.126 (Pb), -0.23 (Ni), -0.403 (Cd), and -0.763 (Zn) at 298 K [30]. As discussed above, the decomplexation of metal-EDTA occur at the anode was followed by the recovery of metal ions by electroreduction at the cathode. It can be concluded that the recovery percentage of metal ions was influenced by the rates of metals-EDTA complexes decomplexation and electrodeposition of the liberated metals ions. The cell potentials remained nearly constant in each

Fig. 8. (a) Recovery of various metal ions and (b) TOC removal efficiency in the photoelectrocatalytic process (HRT = 1 h, initial concentration of Metal-EDTA complexes = 0.1 mM , pH = 6.6, current density = 1.13 A m^{-2}).

experiment, indicating that appreciable deterioration of the electrode or passivation phenomena did not occur.

4. Conclusions

The PEC oxidation of Cu-EDTA on the tubular TiO₂/Ti mesh anodes with simultaneous copper recovery in the PEC reactor is possible. The rate of Cu-EDTA destruction and copper deposition for the PEC process were higher than that for single photocatalysis and electrolysis process. Considering the results reported here, a comparison of data for the rate constant for Cu-EDTA decomplexation and Cu recovery and the energy consumption as a function of applied current density, initial pH, concentration, and HRT, the PEC treatment of Cu-EDTA complexes at 1.13 A m⁻², pH 3.5, HRT 1 h could provide a good combination of rate constant value and energy consumption. Thus, it can be concluded that reduction of heavy metals in a PEC cell can be effectively applied for the removal of heavy metals containing organic chelates effluent at low pH. The energy cost was largely influenced by UV lamp power, which needed to be optimized. The pilot scale experiments have to be performed to suggest the method's adaptability in practice.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2013.10.088>.

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