Photoelectrocatalytic oxidation of metal-EDTA and recovery of metals by electrodeposition with a rotating cathode

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HIGHLIGHTS

- A photoelectro-reactor with a rotating cathode was designed for metal recovery.
- The cathodic rotation was beneficial for recovery of various metal-EDTA complexes.
- Recovery ratio of Cu was increased by 36.56% at the rotation speed of 100 rpm.

GRAPHICAL ABSTRACT

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ABSTRACT

In this work, a photoelectrocatalytic reactor with a rotating cathode was designed for the destruction of metal complexes and recovery of liberated metal ions. The effects of rotating speed, current density, initial pH and initial Cu-EDTA concentration on the recovery of Cu and destruction of Cu complexes were investigated. At cathode rotation speed of 100 rpm, initial pH of 3.18 and current density of 0.5 mA/cm², the recovery percentage of Cu and destruction of the Cu complexes were increased to be 75.54% and 74.18% from 38.98% and 37.92% at 0 rpm rotation speed within 120 min, respectively. Furthermore, the destruction of Co-EDTA, Ni-EDTA and Zn-EDTA complexes using the rotating cathode were investigated. The Co²⁺, Ni²⁺ and Zn²⁺ recovery percentage was increased by 29%, 19% and 18% with the optimal speed of cathode, respectively. The recovered product from the cathodic electroreduction was all crystallized. The treatment performance of the reactor for the first 5 cycles had a slight downward trend, and then the capability of the reactor tended to be stable. The photoelectrocatalytic reactor with the rotating cathode exhibited the high efficiency for the recovery of liberated metal ions and destruction of metal-EDTA complexes.

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1. Introduction

Heavy metal wastewater has been a major concern in the field of water pollution. The conventional precipitation processes are limited for the removal of metal ions in the presence of chelating agents such as tartrate, citrate and ethylenediaminetetracetic acid (EDTA) [1]. In recent years, advanced oxidation processes (AOPs)

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including photocatalysis [2,3], electrochemical membrane [4] and UV/H₂O₂ [5] have been reported for the treatment of the organic metal complexes. Not only destruction of metal complexes, efficient metal recovery was desired.

Photoelectrocatalytic (PEC) oxidation process in which a diminutive positive potential is applied on the semiconductor photoanode has proven to be more efficient than single photocatalytic (PC) process [6]. In PEC systems, the application of a small external bias decreases the recombination rate of photogenerated electron-hole pairs and thus increasing the photocatalytic activity of the semiconductor photocatalyst [7]. In our previous works, the destruction of Cu-EDTA, Cu(CN)₃²⁻ and Ni-EDTA has been achieved at the semiconductor photoanode in PEC process, and the simultaneous recovery of the liberated metal ions at the cathode was reported [8,9]. Through the experiments, it was exhibited that the mass transfer rate near the cathode was low and the recovery efficiencies of metals were desired to be increased.

The design of efficient electrolytic cell has been guided toward the optimization of the excellent dynamic structure, the large mass transport coefficient and the space time yield [10–13]. For wastewater treatment, there was an electro-Fenton process reactor with a rotating disk electrode as cathode in which hydrogen peroxide was in situ generated [14]. In order to relieve the adverse effect of the low utilization rate arisen from the high recombination of the photon-electron and photo-induced pairs, Buttetfield et al. recommended a large-scale vortex reactor [15]. The results represented a proof-of-concept of the electric field enhancement approach in large scale PEC reactors. The photocatalytic reactor with the rotating disk has been detailedly explained in mixing studies, where the mass transfer efficiency of the rotating disk, light intensity of the rotating and degradation mechanism of organic contaminants were studied [16,17]. A systematic electrochemical research was carried out to permit the selective silver electroseparation with minimum interference from the actual leaching solution by a rotating cylinder electrode reactor [18]. The mass transport of the rotating cylinder electrode reactor for the metal ions recovery from simulated wastewater was investigated [19]. Meanwhile, it was analyzed that the electrochemical recovery of nickel from synthetic solutions simulating plating rinsing discharges [20]. However, there is no mention on the removal of pollutants at photoanode with simultaneous recovery of metal ions at the rotating electrode yet.

Herein, a PEC reactor with a rotating tubular cathode was designed in order to improve the mass transfer and the cathodic metal recovery efficiency. The PEC reactor was comprised of a UV lamp which was in the center of the tubular TiO₂/Ti mesh anode, and a concentrically rotating cylinder cathode driven by a motor in order to promote turbulence to enhance mass transfer. The effects of the rotating speed of the cathode, current density, pH values and aeration were investigated. The capacity of this PEC system was also checked based on the recovery of different heavy metals from their EDTA complexes. In the meantime, the recovery products of metal ions were investigated.

2. Experimental section

2.1. Chemicals

Ethylenediaminetetraacetic acid disodium salt dehydrate (Na₂-EDTA), nickel (II) chloride hexahydrate (NiCl₂·6H₂O), cobalt (II) sulfate heptahydrate (CoSO₄·7H₂O), zinc sulfate heptahydrate (ZnSO₄·7H₂O), sodium sulfate anhydrous (Na₂SO₄), Copper sulfate (CuSO₄), and 5, 5-dimethyl-pyrroline-N-oxide (DMPO) were all purchased commercially and without any purification. Simulated wastewater was prepared by mixing the divalent metal salts and

Na₂EDTA with a mixed molar ratio of 1:1. 1 mM NaOH or H₂SO₄ was used to adjust the pH value of solutions. H₂SO₄ and NaOH were often used to control the pH as a common acid-base regulator [21]. Other reagents of analytical grade were obtained from Beijing Chemical Company (PR China) and used as received. Deionized water was used to prepare and dilute solutions.

2.2. Experimental apparatus

The diagrammatic sketch of the reactor that used in this research was shown in Fig. 1. The PEC experiments with the rotating cathode were performed in the tailor-made cell of 600 mL capacity, 94 mm internal diameter and 145 mm high. The tubular mesh TiO₂/Ti (50 mm diameter, 100 mm high) was used as anode. A tubular reticulated titanium (100 mm diameter, 65 mm high) was used as cathode. The actual area of the cathode was determined to be 136.1 cm² by the calculation area of cathode minus the value of the mesh total area. The actual current in the experiment was obtained by multiplying the current density by the actual working area of the electrode. Before being used, the titanium mesh was rinsed using 0.1 M HCl solution. The distance between the titanium cathode and the TiO₂/Ti anode was 7.5 mm. TiO₂ was deposited onto Ti substrate by the dip-coating method. A certain amount of Ti(OC₄H₉)₄ was dropwise added into 160 mL ethanol, then a small amount of NH(OC₂H₅)₂ was added to this mixed solution. A light-yellow transparent solution was formed after being stirred with an ultrasonic horn for 15 min. The ethanol solution (160 mL) was mixed with the precursor solution with 48 h gelatinized [22]. A viscosity solution was obtained after 72 h sealed and gelatinized, which was coated onto titanium mesh by dip-coating method followed by calcination at 500 °C for 2 h [23].

The UV lamp (wavelength 254 nm; 9 W) was purchased from Nanjing Ziguang Company, China. In the experiment, the UV lamp was protected by a quartz tube. The UV lamp and quartz tube were fixed in the groove of the reactor. Meanwhile, the UV lamp was in concentric with the tubular TiO₂/Ti mesh electrode. The motor supplies various steady state speeds (OS20-Pro, Dragon Laboratory

Fig. 1. The schematic view of the PEC system (1-Motor; 2-DC power; 3-Carbon body; 4-UV lamp; 5-Quartz tube; 6-Anode; 7-Cathode; 8-Reactor cell; 9-AC power; 10-Base; 11-Switch).

Instruments Limited, Beijing, China). There was a carbon body as a link medium, which can connected the direct-current (DC) power and the rotating electrode of cathode. The power used in this study was provided by the DC power supply (DH1718E-6, Dahua Electronic, Co., Ltd., Beijing, China). To adjust the dissolved oxygen content in the solution, purging N_2 ($\geq 99.5\%$) and O_2 ($\geq 99.999\%$) into the system were performed before the experiment. The aeration duration was 30 min and the gas flow rate was 100 mL/min.

2.3. Analytic procedures

The concentration of Cu complexes was tested using a high performance liquid chromatograph (HPLC, 1260, Agilent Technology) with the Hypersil Gold (Thermo Scientific) analytical column, the elution comprised of 8% acetonitrile (v/v)/92% oxalic acid (15 mM) (at pH 3.0, flow rate: 1 mL/min, 25 °C, 254 nm) [24]. The total metal ions concentrations in the solution were measured by ICP-OES (700 series Agilent Technology, U.S.A). Total organic carbon (TOC) was tested by a Shimadzu TOC analyzer (TOC-VCPH, Shimadzu, Japan). The recovery ratio of metal ions ($R_{\text{metal},\%}$) and TOC removal ratio ($R_{\text{TOC},\%}$) were defined by Eqs. (1) and (2):

$$R_{\text{metal}} = \frac{(C_{\text{metal},0} - C_{\text{metal},t})}{C_{\text{metal},0}} \times 100\% \quad (1)$$

$$R_{\text{TOC}} = \frac{(C_{\text{TOC},0} - C_{\text{TOC},t})}{C_{\text{TOC},0}} \times 100\% \quad (2)$$

The C_{metal} ($\text{mg}\cdot\text{L}^{-1}$) is the metal ions concentration in the solution; C_{TOC} ($\text{mg}\cdot\text{L}^{-1}$) is the TOC concentration of the simulated wastewater. The subscript 0 and t respectively represent the initial and the sampling time.

Hydroxyl radicals were tested on a Bruker ESP-300E electron spin resonance (ESR) detector. The surface morphology of the recovered metal on the cathode was observed by the scanning electron microscope (SEM, model 6700F, Tokyo, Japan); the components of the cathode were analyzed by energy dispersive X-ray (EDX, JEOL, Japan). The pH value was tested by the Orion-828 (Beverly, MA) pH analyzer connected with a 9165 BN pH electrode.

3. Results and discussion

3.1. Performance comparison of photodegradation, photocatalysis, electrolysis and PEC process

Firstly, the recovery of Cu^{2+} ions and destruction of Cu complexes by different processes including photodegradation (UV), photocatalysis (PC), electrolysis (EC) and PEC process under the same Cu-EDTA concentration, cathode rotation speed, initial pH and current density were estimated in the reactor. According to Fig. 2(a), it can be seen that 74.18% Cu complexes was degraded and 75.54% Cu^{2+} ions was recovered in the PEC process at 120 min. By contrast, the recovery percentages of Cu^{2+} ions in individual EC and PC processes are 39.45% and 0.8%, respectively. There was almost no degradation of Cu complexes and no recovery of Cu in the UV process. The kinetics constants of the recovery rate of Cu^{2+} ions were calculated by first-order reaction equation, which were 0.004 ($R^2 = 0.967$), 0.191 ($R^2 = 0.997$) and 0.380 h^{-1} ($R^2 = 0.995$), in PC, EC and PEC process. For the removal of Cu complexes, the kinetics constants were 0.029 ($R^2 = 0.946$), 0.188 ($R^2 = 0.999$) and 0.369 h^{-1} ($R^2 = 0.996$) respectively in PC, EC and PEC process. Evidently, the PEC process could achieve a much higher copper recovery compared to the individual PC and EC process.

As shown in Fig. 2(b), the variation of TOC was furthermore compared under the same experiment conditions. It can be seen

Fig. 2. (a) Recovery of Cu^{2+} ions and removal of Cu complexes via UV, PC, EC and PEC processes; (b) The removal efficiency of total organic carbon (inset DMPO spin-trapping ESR spectra at ambient temperature) (initial concentration of Cu-EDTA 0.5 mM, rotating speed = 100 rpm, initial pH = 3.18, current density = 0.5 mA/cm^2).

that after 120 min, TOC removal efficiencies are 2.67%, 5.40% and 22.28% for PC, EC and PEC process, respectively. And the results show that there is no TOC removal by individual photodegradation process. In addition, the peak intensity of DMPO-OH in these processes were given in the inset of Fig. 2(b). The results indicate that the characteristic peak of DMPO-OH is the largest in the PEC process, which can effectively destroy the Cu-EDTA complexes [25]. So it can be proved that the TOC removal efficiency is significantly higher than that of PC and EC in the PEC process.

3.2. Effect of rotating speed

Generally, stir is one of the important methods to boost the relative concentration and mass transfer. The rotating speeds of the cathode were controlled at 0, 50, 100, 150 and 200 rpm to examine its effect on the recovery of Cu^{2+} ions and the degradation of Cu complexes. The rates of Cu^{2+} ions recovery and destruction of Cu complexes were strongly influenced by the rotating speed, as shown in Fig. 3. At 100 rpm cathode rotation speed, initial pH of 3.18 and current density of 0.5 mA/cm^2 , the recovery percentage of Cu and destruction of the Cu complexes were respectively 75.54% and 74.18% within 120 min (Fig. 3(a)). The recovery effect was obviously improved compared with the cathode with 0 rpm. Moreover, the degradation of Cu complexes in this rotation speed range was also enhanced. However, when the rotating speed of

Fig. 3. Effect of the rotation speeds on the Cu recovery and the degradation of Cu complexes in PEC process (a-1) and EC process (b-1); Recovery percentage of Cu under various rotating rate in PEC process (a-2) and EC process (b-2). (initial Cu-EDTA concentration 0.5 mM, current density = 0.5 mA/cm², initial pH = 3.18).

cathode reached 200 rpm, the Cu²⁺ ions recovery rate and Cu complexes destruction rate was decreased.

At the relatively low rotating speed operation, the mass transfer of the solution was enhanced by the rotation of the cathode. The contact probability was greatly increased between metal ions and cathode surface. Therefore, the amount of metal ions on the cathode surface was increased. When the rotating speed of the cathode was too high, the contact area decreased between the inner surface of the cathode plate and the solution in the reactor under the action of centrifugal force. At the same time, it also hindered the stable reduction process of metal ions on the cathode surface with the high stirring speed [26]. Similar results were also observed in the EC process, as shown in Fig. 3(b). Taking into account the above results, the optimal stirring speed was selected as 100 rpm in this system.

3.3. Effect of the current density

The effect of current density on the Cu²⁺ recovery and destruction of Cu complexes was investigated with 0.5 mM Cu-EDTA under initial pH 3.18 and the rotation speed of 100 rpm in PEC process. As shown in Fig. 4(a) and (b), when the current density was 0.25 mA/cm², the recovery percentage of Cu²⁺ ions and destruction of Cu complexes were 24% and 22%, respectively. Nevertheless, recovery percentage of Cu²⁺ ions was nearly 100% and the destruc-

tion rate of Cu complexes can be as high as 98% when the current density was 1.0 mA/cm². The recovery ratios of Cu²⁺ ions and removal rates of Cu complexes were increased with the current density evidently. With the increase of current density, the separation efficiency of photo-generated electrons and holes was increased. And the cathodic reduction efficiency of liberated copper ions was enhanced at the same time. A similar trend was reported in our previous work [27].

In the actual wastewater treatment, both of the efficient recovery of metals and low energy consumption were needed to be taken into account. In this PEC process, the energy consumption mainly derived from the electricity consumption of electrochemical reaction and UV lamp. The electricity consumption was evaluated with a standard of 1 g Cu recovery under different current densities, and according to the equation as follows (3):

$$W(\text{kWh} \cdot \text{g}^{-1}) = \frac{(U \times I + P) \times t}{\Delta x \times 1000} \quad (3)$$

The $W(\text{kWh} \cdot \text{g}^{-1})$ is the electricity consumption of the reaction process. U and I respectively indicate the actual voltage and the actual current during operation, and the corresponding units are volt (V) and ampere (A). The P stands for ultraviolet lamp power, and the unit is watt (W). The t represents the reaction time, and the unit is hour (h). The Δx indicate the recovery quality of copper ion, and the unit is milligramma (mg).

Fig. 4. Effect of current density on the Cu recovery and the degradation of Cu complexes in PEC process (a); Recovery percentage of Cu under various current density in PEC process (b) (initial Cu-EDTA concentration 0.5 mM, rotating speed = 100 rpm, initial pH = 3.18).

Table 1

The energy consumption for recovery of 1 g Cu under different current density.

Current Density (mA/cm ²)	Current (I)	Voltage (V)	Energy (Kwh·g ⁻¹)
0.25	0.034	4.55	3812×10^{-3}
0.50	0.068	6.59	1303×10^{-3}
0.75	0.102	8.32	1145×10^{-3}
1.00	0.136	9.52	1087×10^{-3}

Under the current density of 0.25, 0.50, 0.75, and 1.00 mA/cm², the measured operating voltage was 6.59, 8.32, 4.55, 9.52 V, respectively. The UV lamp power kept at a constant value of 9 W for all the experiments. As shown in Table 1, the energy consumption was reduced with the increase of the current density. Considering the energy cost and the recovery efficiency, the current density was chosen as 5 mA/cm² in the present experiment.

3.4. Effect of the initial pH

The effect of solution pH on the removal of Cu complexes and recovery of Cu²⁺ ions at the rotating speed of 100 rpm in PEC process was investigated. The initial pH of the Cu-EDTA solution without any adjustment is 3.18. As shown in Fig. 5, the recovery efficiency of Cu²⁺ ions at the initial pH 3.18, 5.00, 7.00, and 9.00 were 75.54%, 13.31%, 13.68%, and 16.89%. And the kinetic constants of Cu²⁺ recovery in the PEC process were 0.0105, 0.0009, 0.0009,

Fig. 5. Effect of initial pH on the Cu recovery and the degradation of Cu complexes in PEC process (a); Recovery percentage of Cu under various initial pH in PEC process (b) (initial concentration of Cu-EDTA = 0.5 mM, rotating speed = 100 rpm, current density = 0.5 mA/cm²).

and 0.0012 h⁻¹, respectively. The kinetic constants decreased with the pH increasing. Meantime, the removal of Cu-EDTA decreased with the pH increasing. Moreover, the degradation of Cu complexes and the recovery efficiency of Cu were decreased when the pH value was 2.00.

It was reported that in the case of photocatalysis of Cd-EDTA by TiO₂, at low pH values, a large portion of the complex was adsorbed; under high pH conditions, the complex existed mostly in solution [28]. In our previous work, it was found that Cu-EDTA species depended upon the solution pH value, such as (CuEDTA)²⁻, CuH₂EDTA, (CuHEDTA)⁻, and CuOHEDTA₃. At pH 5.0, 7.0, and 9.0, the major species of the Cu-EDTA complexes in the solution were the fully deprotonated form of (CuEDTA)²⁻. At pH 3.18, the major species were (CuHEDTA)⁻ and (CuEDTA)²⁻, as well as a small amount of possible existing CuH₂EDTA in the solution. It is possible that ·OH radicals can react with (CuHEDTA)⁻ better than with (CuEDTA)²⁻ [29]. On the other hand, the liberated Cu²⁺ may precipitate as CuO or Cu₂O when the pH was higher than 5.0, which were not available for the electrochemical reduction [9]. Herein, the reaction rate was higher at pH 3.18 than pH 5.00, 7.00, and 9.00. In addition, at pH 2.00, the major species were Cu²⁺, CuH₂EDTA and a small ratio of H₄EDTA, which was not beneficial for the degradation by ·OH oxidation, resulting in a low degradation efficiency of Cu complexes as well as low recovery efficiency of Cu at pH 2.00 due to H₂ evolution.

Fig. 6. Effect of initial concentrations on the Cu recovery and the degradation of Cu complexes in PEC process (a); Recovery percentage of Cu under various initial concentrations in PEC process (b) (rotating speed = 100 rpm, current density = 0.5 mA/cm², initial pH = 3.18).

3.5. Effect of the initial concentration of Cu-EDTA

The performance of Cu²⁺ ions recovery and Cu complexes destruction with various initial Cu-EDTA concentrations was evaluated. As shown in Fig. 6, the proportion of Cu²⁺ ions recovery and Cu complexes destruction increases with the decrease of initial Cu-EDTA concentration. The recovery rate of Cu²⁺ ions reached 83% at initial 0.25 mM Cu-EDTA. By contrast, when the initial concentration of Cu-EDTA was 2.00 mM, the recovery rate of Cu²⁺ ions was only 30% at 120 min. The destruction of Cu complexes was followed by the Cu²⁺ electrodeposition according to our previous results [8]. On one hand, the amount of the same electron transfer may electrodeposit equivalent quantity Cu²⁺ ions on the cathode under the same conditions of PEC process. On the other hand, the competitive adsorption onto the active site occurred between Cu-EDTA and its intermediates at high initial concentration of Cu-EDTA [9].

3.6. Aeration condition

The effect of aeration on the PEC process in the reactor was also investigated. In order to avoid the influence of aeration on mass transfer efficiency, purging N₂ (≥99.5%) and O₂ (≥99.999%) into the system were performed before the experiment. The aeration duration was 30 min and the gas flow rate was 100 mL/min. The best performance in the Cu²⁺ ions recovery process was obtained

Fig. 7. Effect of aeration condition on the Cu recovery and the degradation of Cu complexes in PEC process (a); Recovery percentage of Cu under aeration condition in PEC process (b) (initial concentration of Cu-EDTA = 0.5 mM, rotating speed = 100 rpm, initial pH = 3.18, current density = 0.5 mA/cm², gas flow = 100 mL/min).

when the solution was purged with N₂ before. As shown in Fig. 7, the recovery percentage of Cu reaches 97.47% at 90 min by the aeration of N₂. However, the recovery ratio of Cu²⁺ after 120 min is diminished by about 14.51% after purging with O₂. The degradation trend of Cu complexes is almost the same with that of Cu²⁺ recovery.

There was a competitive relationship between the Cu²⁺ ions and O₂. The dissolved oxygen in the solutions can occupy the active sites on the cathode and inhibit the cathodic reduction of the liberated Cu²⁺ ions. When N₂ was pumped into the PEC reactor, and the dissolved oxygen was excluded, thereby improving the efficiency of Cu²⁺ ions recovery.

3.7. Performance for various metal-EDTA complexes

To gain an insight into the ability of the recovery of metal ions and removal of metal-EDTA within the reactor, several metal-EDTA complexes were tested including Co-EDTA, Ni-EDTA, and Zn-EDTA. The initial pH of these metal-EDTA solutions were 3.20, 3.18, and 3.22, respectively. In the section, the initial concentrations of all the metal-EDTA were 0.5 mM. As seen in Fig. 8, it is obvious that the recovery efficiency of the various divalent metals increased significantly through the PEC reactor. The recovery of Co²⁺ ions was determined to be 14% and 60% at the rotation speed of 0 rpm and 50 rpm; the recovery of Ni²⁺ ions was determined to be 10%

Fig. 8. Recovery of metal ions (a) Co-EDTA; (b) Ni-EDTA; (c) Zn-EDTA (initial metals-EDTA concentration = 0.5 mM, current density = 0.5 mA/cm²).

and 29% at the rotation speed of 0 rpm and 100 rpm; and the recovery of Zn²⁺ ions was determined to be 3% and 21% at 0 rpm and 100 rpm under the same current density of 0.5 mA/cm², at the reaction time of 120 min, respectively. The standard reduction potentials of these divalent metal cations were −0.34 V (Cu), −0.28 V (Co), −0.23 V (Ni), −0.763 V (Zn) at 298 K. It was proposed that the reduction potentials influenced the recovery capacity of liberated metal ions in the cathodic reduction.

3.8. Surface morphology analyses of the rotating cathode

Furthermore, the surface morphology of the rotating cathode in treating various metal-EDTA complexes in the PEC process was characterized by SEM and EDX analyses. It can be seen from Fig. 9 that a large amount of metal of a single element was electrodeposited onto the cathode of Ti and the rotating cathode was nearly covered completely. It can also be seen from the EDX analysis in Fig. 9 that the material composition of the rotating cathode after reaction was consisted of Ti and metal elements. The atomic percentage of metals with Ti on the cathode followed the order of Cu > Co > Ni > Zn. This result was consistent with the recovery ratio of metals ions as shown in Fig. 8.

3.9. Stability of the PEC system

The stability of the PEC reactor for the recovery ratio of metal ions and the removal percentage of metal-EDTA was studied by the duplicate use of the same TiO₂/Ti anode and the same rotating cathode for ten successive cycles. In this part, 0.5 mM Cu-EDTA and the rotating speed of 100 rpm was selected. As shown in Fig. 10, in the first cycle, the recovery of Cu²⁺ ions and destruction of Cu complexes were close to 100%. And there was a certain downward trend along with the increase of the reaction cycle in the first five cycles. It remains nearly constant, in which the recovery percentages of Cu²⁺ ions are determined to be 76%, 80%, 77%, 75%, 76% and 78%, respectively. In the meantime, the same change trend was also observed for Cu complexes degradation. The experimental results show that the reactor had better treatment performance in the earlier period. Finally, it tended to be a relatively favorable and stable state after a downward trend in several cycles.

4. Conclusions

The PEC reactor with the rotating cathode can achieve an efficient recovery of liberated metal ions onto the rotating cathode surface and destruction of metal complexes. The UV photodegradation, PC, EC, and PEC processes were used to compare the degradation of Cu complexes. Results showed that the PEC process exhibited a synergistic effect on the Cu recovery and Cu complexes destruction. The recovery percentage of Cu and destruction of the Cu complexes were increased to 75.54% and 74.18% when the cathode rotation speed was 100 rpm at initial pH of 3.18 and current density of 0.5 mA/cm² within 120 min. Before the start of the reaction, purging N₂ into the system can obviously promote the recovery of Cu on the cathode, and thus improved the degradation of Cu complexes. Meanwhile, the capacity of the reactor was investigated by the recovery of different metals. Such as Co-EDTA, Ni-EDTA and Zn-EDTA complexes, the Co²⁺, Ni²⁺ and Zn²⁺ recovery rate increased by 29%, 19% and 18% in the adjustment speed for the optimal parameters of cathode. And the recovery product from the cathodic electroreduction was all elemental crystal. Thus, it can

Fig. 9. SEM analysis of the cathode electrodeposition with the (a-1) Cu-EDTA, (b-1) Co-EDTA, (c-1) Ni-EDTA and (d-1) Zn-EDTA solutions in the PEC process; EDX analysis of the cathode electrodeposition with the (a-2) Cu-EDTA, (b-2) Co-EDTA, (c-2) Ni-EDTA and (d-2) Zn-EDTA solutions in the PEC process.

Fig. 10. The stability analysis of the PEC system reactor. (initial concentration of Cu-EDTA = 0.5 mM, rotating speed = 100 rpm, initial pH = 3.18, current density = 0.5 mA/cm²).

be concluded that the electrodeposition of metal ions could be significantly enhanced by the rotation of the cathode in the PEC reactor.

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