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Influences of the operational variables on electrochemical treatment of chelated Cu(II) in alkaline solutions using a membrane cell

Alireza Eivazihollagh,[a*] Joakim Bäckström,[b] Magnus Norgren[a*] and Håkan Edlund[a]

Abstract

BACKGROUND: The electrochemical recovery of copper and chelating agent from their complex solution using a membrane flow cell was investigated. The parameters electrolysis time, solution pH, current density, and temperature were investigated.

RESULTS: Electrochemical investigation indicated that chelating ligands can be recovered by the electrodeposition of copper ions on the cathode. For copper and EDTA recovery, the results indicated that recovery efficiency was affected by time, current density, and temperature. The recovery process was not influenced by pH in the range studied (pH 8–12), which can be explained by the low variation in the conditional stability constant, i.e. $\Delta \log_{10} K' \leq 0.7$, over the pH range. However, when NTA, EDTA, and DTPA were compared, the results indicated that the recovery efficiency decreased as the conditional stability constant of the chelating agent–Cu(II) complex increased. The maximum current efficiency of copper and EDTA recovery after 5 h of treatment was approximately 85%, whereas the recovery was 80% of the initial concentration (0.05 mol L^{-1}) at a current density of 1 A dm^{-2}, temperature of 333 K, and pH of 10.

CONCLUSION: Relatively high recovery efficiency makes the process fairly sustainable and hinders the discharge of copper ions and chelating ligands as pollutants into the environment.
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Supporting information may be found in the online version of this article.

Keywords: electrochemistry; heavy metals; recovery; waste-water; hydrometallurgy

INTRODUCTION

Recent developments in the metal, chemical, paper, textile, and oil industries have led to high freshwater consumption and the environmental discharge of huge volumes of effluents with high contents of organic and inorganic pollutants. Heavy metals and chelating agents are considered the most important contaminants in these effluents, given their toxicity and non-biodegradability.[1] Moreover, the strong tendency for interaction between chelating agents and metal ions has led to increasing amounts of chelated heavy metals distributed in natural water systems. Chelating agents and heavy metals should therefore be removed from industrial effluents to meet legal discharge limits before release into the environment.[2,3] To this end, several treatment methods have been proposed to immobilize heavy metals and degrade chelating agents.[2–8] According to a European Commission report,[3] these methods are currently being used in certain industries in Europe. One disadvantage of these methods is that they all generate a product, still consisting of metals,[9] that requires storage and further reprocessing. Another disadvantage is the cost of chelating agent disposal.

To reduce the problems associated with the separation of chelated heavy metals and the degradation of the resulting chelating agents, the substitution of either biodegradable[10,11] or functionally modified alternatives[12,13] for conventional ones such as ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and nitrilotriacetic acid (NTA) has been considered a viable option. In addition, using alternative treatment techniques to minimize the loss of chelating agents and recycle them from industrial effluents has been recommended for economic and practical reasons.[3]

Electrochemical methods[5–9,14–18] to treat effluents containing chelated metal complexes have attracted increasing attention as promising ways to resolve the difficulties caused by the very high stability of chelated metals.[19] Of these methods, membrane electrolysis has proven to be technically efficient, cost-effective, and environmentally compatible.[9,14–17]

Several studies of this process, using a batch membrane cell to treat the metal-laden chelating agent solution, are summarized in Table 1. The membrane electrolysis process has been successfully employed to electrodeposit metal ions onto the cathode and

* *Correspondence to: A Eivazihollagh or M Norgren, FSCN, Surface and Colloid Engineering, Mid Sweden University, SE-851 70 Sundsvall, Sweden. Email: alireza.eivazi@miun.se (Eivazihollagh); magnus.norgren@miun.se (Norgren)*

a *FSCN, Surface and Colloid Engineering, Mid Sweden University, SE-851 70 Sundsvall, Sweden*

b *FSCN, Materials Physics, Mid Sweden University, SE-851 70 Sundsvall, Sweden*

Table 1. Electrolysis in a membrane batch cell for the treatment of synthetic solutions containing metals and chelating agents (T = 298 K)

Species in solution				
Metal ions	Chelating agent	Test conditions	Highlights	References
Single M(II); M = Pb(II), Cd(II), or Cu(II)	EDTA	Catholyte volume: 0.25 L Concentration: 0.01 mol L^{-1} M(II) – 0.01 mol L^{-1} EDTA For Cu(II)-EDTA: initial pH, 3.27; duration, 3.68 h; current density, ~2.88 A dm^{-2} For Pb(II)-EDTA: initial pH, 2.17; duration, 3 h; current density, ~0.96 A dm^{-2}	Cu(II)-EDTA: recovery, ~98%; current efficiency, 3.1% Pb(II) – EDTA: recovery, ~99%; current efficiency, 18.4% Cd(II) – EDTA: no apparent deposition at current density of ~3.85 A dm^{-2}	9
Cu(II)	Citric acid, NTA, or EDTA	Catholyte volume: 0.25 L Concentration: 0.01 mol L^{-1} Cu(II) – 0.01 mol L^{-1} chelating ligand Initial pH, 2.2; duration, 0.66 h; current density, 1.39 A dm^{-2}	Cu(II) – Citrate: recovery, 100%; current efficiency, 30% Cu(II) – NTA: recovery, 98%; current efficiency, 30% Cu(II) – EDTA: recovery, 93%; current efficiency, 25%	14
Single M(II); M = Cu(II), Ni(II), Zn(II), Co(II), Mn(II), Cd(II), Pb(II), or Hg(II)	EDTA	Catholyte volume: 0.25 L Concentration: 0.01 mol L^{-1} Cu(II) – 0.01 mol L^{-1} EDTA Initial catholyte pH, 2.27; duration, 0.83 h; current density, 1.39 A dm^{-2}	Cu(II) – EDTA: recovery, ~95%; current efficiency, 19% M(II) – EDTA: possible electrodeposition of Pb, Hg, and Cd, but no apparent deposition of Co, Ni, Zn, and Mn	15
Cu(II)	Citric acid	Catholyte volume: 0.25 L Concentration: 0.01 mol L^{-1} Cu(II) – 0.01 mol L^{-1} citric acid Initial catholyte pH, 2.2; duration, 0.83 h; current density, 1.39 A dm^{-2}	Recovery, ~95%; current efficiency, ~28%	16
Cu(II)	EDTA	Catholyte solution: 5 g $Cu_2EDTA.4H_2O$ in 0.08 L Acidic suspension: current, 0.1 A; duration, 5.2 h Water suspension: current, 0.005 A; duration, 3.6 h Alkaline suspension: current, 0.025 A; duration, 4 h	Current efficiency of Cu(II): 85% in acidic suspension, 89% in water suspension, and 94% in alkaline suspension	17

to recover chelating agents in a membrane cell where the anode and cathode chambers are separated by an ion-exchange membrane to prevent the anodic oxidation of chelating agents during treatment.[9,14–17] The recovered chelating agents can then be reused, making the process more economical and environmentally friendly. However, this approach must be studied with a view to improving the current efficiency to make the process more feasible for industrial use. According to the studies reviewed in Table 1,[9,14–16] > 90% recovery can be achieved by treating 0.25 L of copper-laden chelating agent solution having an initial pH of approximately 2–3 in a membrane batch cell under studied experimental conditions, whereas the maximum current efficiency is approximately 30%. Researchers have tried to improve the current efficiency of a membrane batch cell process by optimizing various experimental parameters. In their studies, the pH of a catholyte solution is adjusted at the beginning of an experiment and is not controlled during the process, resulting in changes in the conditional stability constant of the Cu(II) – EDTA complex in the catholyte solution. The copper ions are therefore recovered from various species of Cu(II) – EDTA complex.

This study aimed to investigate the simultaneous electrochemical recovery of copper and EDTA from an alkaline solution using a membrane flow cell operating in recycle mode as a function of operation time, solution pH, applied current density, and temperature at a constant flow rate. In addition, the recovery of copper from its complex solution with DTPA and NTA was studied at constant pH during electrolysis and compared with the complex solution with EDTA regarding differences in conditional stability constants with copper. The effects of operating parameters on current efficiency and electricity consumption were evaluated. Overall, the effects of different parameters on the recovery of copper and chelating agents from alkaline solutions were examined on a theoretical and practical basis.

Membrane electrolysis treatment

During membrane electrolysis, Na^+ ions from the anolyte solution diffuse and carry the current through the cation-exchange membrane into the catholyte solution. Increasing the anolyte Na^+ concentration should therefore lead to improved current efficiency and recovery. However, increasing anolyte Na^+ concentration has been demonstrated to result in only a slight increase in current efficiency and recovery.[14] With the application of the electric field, water molecules are reduced at the cathode with the evolution of H_2 gas and formation of OH^- ions, leading to an increase in the pH of the catholyte solution. This reaction is obviously the side reaction at the cathode that decreases the current efficiency of the process.[9,14] In addition, water molecules are oxidized at the

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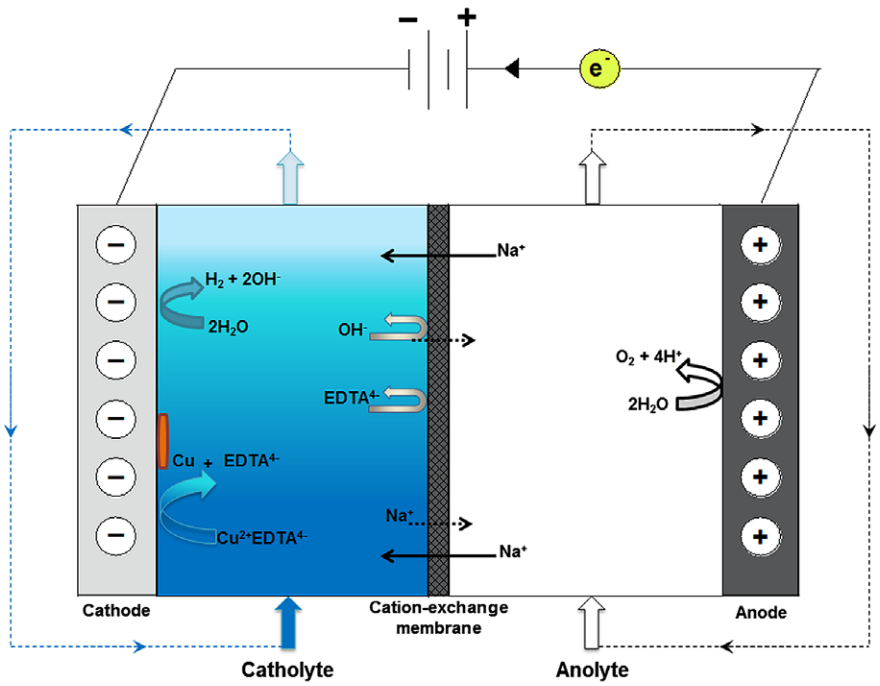

Figure 1. Schematic illustration of copper and EDTA recovery (Equation (2)) in a membrane cell at alkaline pH.

anode with the evolution of O_2 and the production of H^+ ions, reducing the pH of the anolyte solution (Fig. 1). The oxidation reaction of water (Equation (1))[20] is the main anodic reaction in this process.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad E° = -1.23\ V \qquad (1)$$

In catholyte solution containing copper and chelating agent, free copper ions and chelated copper complexes can be reduced to Cu and Cu_2O at the cathode. The possible cathodic reactions of copper complexed with chelating agent (L^{m-}), for example, CuL^{2-m} complex can be described by following reactions:

$$CuL^{2-m} + 2e^- \rightarrow Cu + L^{m-} \qquad (2)$$

$$2CuL^{2-m} + 2OH^- + 2e^- \rightarrow Cu_2O + 2L^{m-} + H_2O \qquad (3)$$

Also, the following cathodic reactions, Equations (4–7, 9, 10)[20] and Equation (8),[21] may occur at the cathode:

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E° = +0.34\ V \qquad (4)$$

$$Cu^{2+} + e^- \rightarrow Cu^+ \qquad E° = +0.15\ V \qquad (5)$$

$$Cu^+ + e^- \rightarrow Cu \qquad E° = +0.52\ V \qquad (6)$$

$$Cu_2O + H_2O + 2e^- \rightarrow 2Cu + 2OH^- \qquad E° = -0.36\ V \qquad (7)$$

$$2Cu^{2+} + 2OH^- + 2e^- \rightarrow Cu_2O + H_2O \qquad E° = +0.17\ V \qquad (8)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad E° = 0\ V \qquad (9)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad E° = -0.83\ V \qquad (10)$$

where all the standard potentials (E°) are reported versus standard hydrogen electrode (SHE).

To investigate the performance of the membrane electrolysis process, the overall current efficiency (η) and specific electricity consumption (E_{cell}) were calculated, as given by Equation (11) and (12), respectively:

$$\eta = \frac{\Delta CvnF}{\Delta tI} \qquad (11)$$

where ΔC is the change in concentration of copper (mol L^{-1}) in Δt (s), v is the volume of the catholyte solution (L), n is the number of electrons transferred in reaction, I is the applied electrical current (A), and F is the Faraday constant (96485 C mol^{-1});

$$E_{cell} = \frac{VIt}{N} \qquad (12)$$

where V is the average cell voltage during the process (V), t is the duration of electrolysis (h), and N is the amount of Cu deposited onto the cathode (mol); E_{cell} is expressed in Wh mol^{-1}. To calculate η and E_{cell} for electrochemical copper recovery from a complex solution containing chelating agent, the change in copper concentration in catholyte solution needs to be considered due to the possible presence of copper oxides in electrodeposits. To estimate more accurately the amount of electrochemically recovered copper, the effects of change in solution volume and loss of copper from solution due to sampling during electrolysis were taken into account.

Copper speciation in electrolyte containing chelating agent

In order to investigate the electrochemical treatment of Cu(II)–chelating ligand, it is important to determine the distribution of various soluble complexed copper species in the electrolyte.[22] In this study, copper species distribution in solution containing chelating ligand (i.e. NTA, EDTA, and DTPA) are calculated and plotted as a function of pH (Fig. 2) using the software MEDUSA[23] and the stability constants of various complexed copper species with studied chelating ligands.[24] As can

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be seen in Fig. 2, at pH > 8, the predominant soluble Cu(II)–NTA complexes are $CuNTA^-$, $Cu(NTA)OH^{2-}$, and $CuNTA_2^{4-}$. In alkaline Cu(II)–DTPA solution, formation of $CuDTPA^{3-}$ complex predominates. For Cu(II)–EDTA solution at pH 8, $CuEDTA^{2-}$ is the most stable copper complexes in solution. While, at pH between 10 and 12, both $CuEDTA^{2-}$ and $Cu(EDTA)OH^{3-}$ are the predominant soluble complexes.

MATERIALS AND METHODS

Preparation of electrolyte solution

The volumes of catholyte and anolyte solutions were 2 L. The catholyte Cu(II)–EDTA solution was prepared as follows: 0.1 mol $CuSO_4 \cdot 5H_2O$ was dissolved in 1 L of 0.94 mol L^{-1} sulphuric acid; 0.1 mol EDTA was dissolved in 1 L of 3 mol L^{-1} sodium hydroxide. The EDTA solution was then carefully added to the copper sulphate solution. In this equimolar solution of copper ions and EDTA, chelating agents form a stable chelating complex with copper ions.[25] The preparation of Cu(II)–NTA and Cu(II)–DTPA solutions was exactly the same as the preparation of Cu(II)–EDTA solution. The initial catholyte pH was determined and it was adjusted by adding 96% sulphuric acid and sodium hydroxide pellets during the experiment. The anolyte solution was prepared by dissolving 0.3 mol Na_2SO_4 in 2 L of distilled water. All the pure acids of chelating agents (purity ≥99%) used for solution preparation were supplied by either Sigma-Aldrich or Fluka. Analytical-grade $CuSO_4 \cdot 5H_2O$ and Na_2SO_4 were obtained from VWR International and were used as received.

Experimental apparatus and procedures

The experimental setup consisted of a membrane flow cell, catholyte and anolyte storage tanks, magnet pumps, and flexible pipes. The Electro MP-Cell membrane flow cell was designed and delivered by ElectroCell A/S, Denmark. This cell is composed of a cathode and anode separated by a Nafion N324 cation-exchange membrane (DuPont), surface area 100 cm^2 (10 × 10 cm), to hinder anion transport between the electrolytes. In all experiments, the distance between electrode and membrane was maintained at approximately 6 mm by positioning a polytetrafluoroethylene (PTFE) flow frame and an ethylene propylene diene monomer (EPDM) gasket. The cathode was made of Ti, whereas the anode was a dimensionally stable anode designed for oxygen evolution ($DSA^® O_2$).

Electrolysis was carried out with constant current supplied by a DC power supply (model KXN-1560D; ZHAOXIN), which was also used to measure the cell voltage. The reference electrode Ag/AgCl 3 mol L^{-1} KCl (Metrohm), was connected to the cathodic half-cell via plastic piping through the flow frame, acting as a salt bridge. The cathode potential was determined using a voltmeter to measure the potential between the cathode and the reference electrode.

Magnet pumps circulated the anolyte and catholyte between the storage tanks and the anode and cathode compartments of the electrolysis cell, respectively. The circulation rate was kept at approximately 1.5 L min^{-1}. Before starting electrolysis, the pH and temperatures of these tanks were adjusted to specified values (±2%) and initial samples were taken from circulation tanks for analysis. At specified intervals, 10 mL samples were taken from the electrolytes during the electrolysis.

In this cell, electrolysis conditions were studied with respect to time, pH (i.e. 8, 10, and 12), current density (i.e. 1, 2, and 3 A dm^{-2}), and temperature (i.e. 295, 313, and 333 K). The values of the studied parameters were kept constant during the electrolysis experiments.

A Versa STAT 4 potentiostat (Princeton Applied Research) equipped with VersaStudio software was used to obtain voltammetric curves. The working electrode was Ti with a rectangular

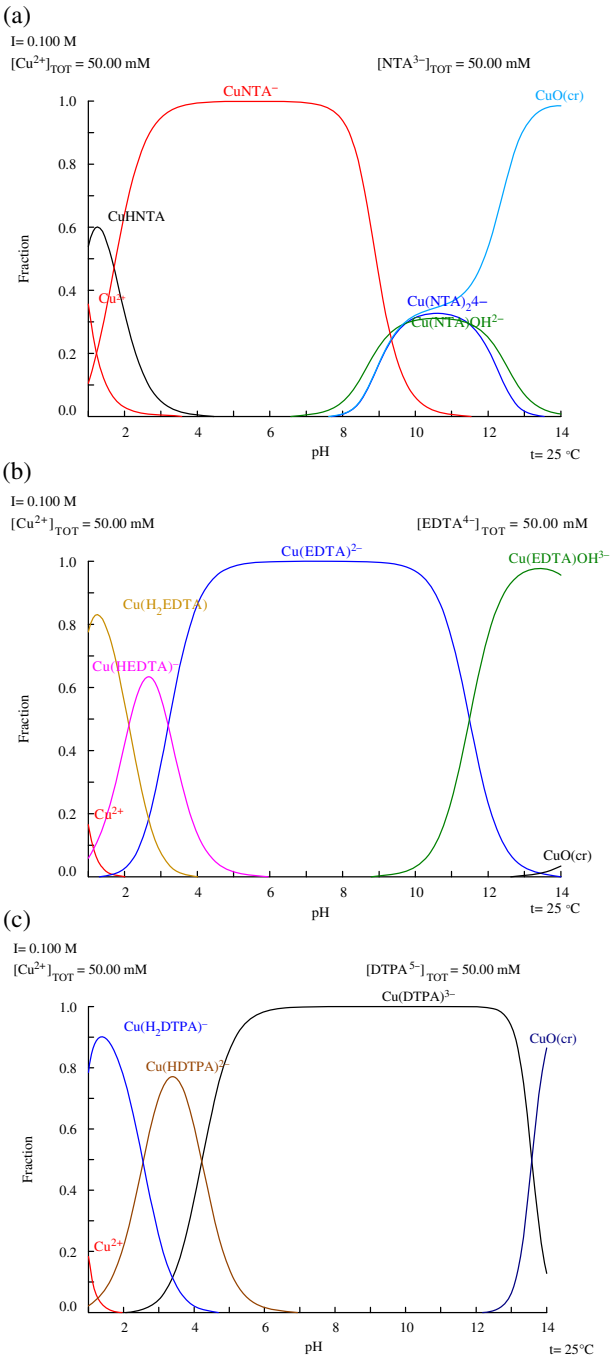

Figure 2. Distribution plots of copper, complexed with equimolar NTA (a), EDTA (b), and DTPA (c), as a function of pH, at 298 K, and I = 0.1 mol L^{-1}. The plots were obtained using the software MEDUSA[23], and the curves for Cu(II)–NTA (a) and Cu(II)–EDTA (b) were calculated from thermodynamic data set included in the program. The thermodynamic data for Cu(II)–DTPA[24] was added to the software to plot distribution diagram of Cu(II)–DTPA (c) (precipitation of crystalline CuO (cr) is also possible in studied complex solutions at alkaline conditions).

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cross-section (approximately 2 cm^2). A Pt cage and an Ag/AgCl 3 mol L^{-1} KCl electrode were used as counter and reference electrodes, respectively. Three different complex solutions were used: 0.05 mol L^{-1} $CuSO_4 \cdot 5H_2O$:0.05 mol L^{-1} chelating ligand (NTA, EDTA, and DTPA). The pH of each complex solution was adjusted to 10 with 1 mol L^{-1} NaOH before conducting the experiments. All experiments were performed at ambient temperature using a scanning rate of 0.01 V s^{-1}. The curves were started at 1.8 $V_{Ag/AgCl}$, swept up to −1.2 $V_{Ag/AgCl}$, and returned to 1.8 $V_{Ag/AgCl}$.

Analytical methods

The copper ion content of the catholyte was analysed on an ICP-OES 720 inductively coupled plasma spectrometer (ICP) (Varian) and used to calculate the recovery percentage of copper. Assuming that EDTA tends to form complexes of a 1:1 molar ratio (ligand:metal) with copper ions, the concentration of free EDTA as recovered was determined by titration with a cupric standard solution. The end point of titration was detected using a perfectION™ combination cupric electrode (Mettler Toledo) calibrated for solutions with a concentration of less than 10×10^{-6} mol L^{-1} cupric (low-level calibration). The catholyte pH values were determined using an MP 225 pH meter (Mettler Toledo) calibrated for alkaline solutions.

The copper electrodeposits were collected for further analysis. An Evo® 50 scanning electron microscope (SEM) (Zeiss), equipped with energy-dispersive X-ray (EDX) analysis capability, was used to investigate the deposit. The X-ray diffraction (XRD) of electrodeposited copper was carried out at room temperature using a D2 Phaser diffractometer (Bruker) with Cu Kα radiation.

RESULTS AND DISCUSSION

Dependence of Cu(II) recovery on complex stability

The stability constant ($\log_{10} K$) of a metal ion-chelating agent complex plays a vital role in the recovery of copper from solution. The stability constants of various complexed copper species with the studied chelating ligands (i.e. NTA, EDTA, and DTPA) can be found for certain temperatures and ionic strengths.[10,24,26] For example, at T = 298 K and I = 0.1 mol L^{-1}, the stability constant ($\log_{10} K$) values for $CuNTA^-$, $Cu(NTA)OH^{2-}$, and $CuNTA_2^{4-}$ are 13.0, 9.2, and 17.4, respectively. Under the same conditions, $\log_{10} K$ values for $CuEDTA^{2-}$, $Cu(EDTA)OH^{3-}$ complexes are 18.8 and 11.4, respectively. The stability constant for $CuDTPA^{3-}$complex is 21.2.[24] In addition, the conditional stability constant ($\log_{10} K'$) of a metal ion-chelating agent complex is introduced as a practical expression of chelate strength as a function of pH by taking into account acidic–basic reactions occurring simultaneously with chelation reactions. Over the entire pH range, the conditional stability constants of the aminopolycarboxylate chelating agents investigated here are increased dramatically by raising the pH of the complex solution from acidic to slightly alkaline, due to the dissociation of the acidic groups in the chelating agent, and varies with either different chelating agent or metal ion.[10,18,26] For example, at pH 4, $\log_{10} K' = 10.2$ for EDTA; however, at pH 8–12, comparably small changes in the logarithmic values of the conditional stability constants can be noted for EDTA, i.e. pH 8, 10, and 12 give $\log_{10} K'$ values of 16.3, 16.6, and pH 15.7, respectively.[26] At the same pH values, the $\log_{10} K'$ values for NTA are 11.0, 11.9, and 12.0 and for DTPA are 17.6, 18.7, and 17.4, respectively.[26] To investigate the effect of copper complex stability on the recovery process, a set of experiments was performed in which the pH and chelating agent were varied.

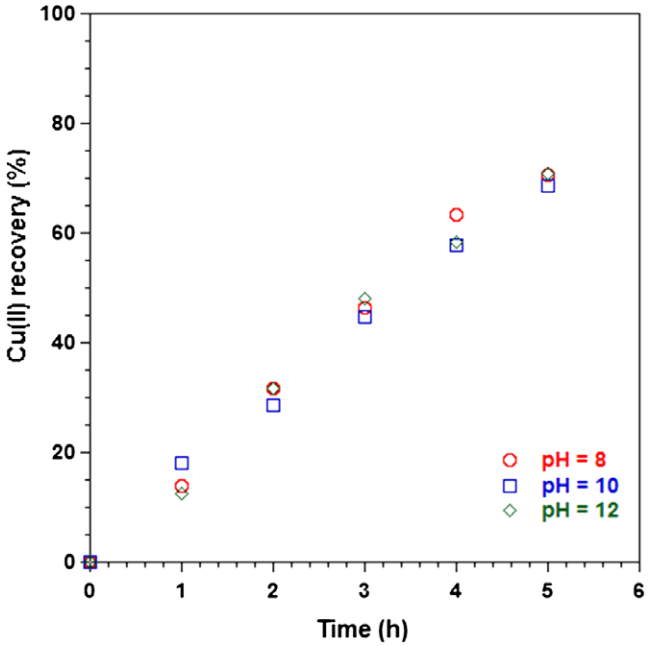

Figure 3. Effect of catholyte bulk pH on copper recovery versus time (current density, 1 A dm^{-2}; T, 295 K).

In practice, the electrolysis of the catholyte solution under weakly acidic conditions led to the formation of white and slightly blue EDTA precipitates covering the membrane and suspended in the catholyte, even though the pH of the catholyte solution increased into the alkaline range during treatment. The operating pH range chosen to be studied was alkaline, based on the results of initial experiments and on a fundamental basis given, for example, the conditional stability constant as a function of pH,[10,26] distribution diagrams,[10,18] and potential–pH diagrams[27] for an aqueous solution of Cu(II) and EDTA. The alkaline pH scale allows us to investigate copper recovery from the most stable complexes in comparison with acidic conditions. In addition, studying the copper recovery at constant pH during electrolysis makes it possible to identify the effect of the conditional stability constant. However, in the pH range1–9, the highest copper recovery from a complex solution with EDTA is reportedly determined at an initial catholyte solution pH of approximately 2.2,[14,15] where $\log_{10} K' \approx 6.5$[26] and predominant species may be free copper ions and protonated copper complexes, $Cu(HEDTA)^-$and $Cu(H_2EDTA)$, see Fig. 2(b). In addition, it was previously proved that the presence of EDTA in solutions extends the copper solubility over a wider (alkaline) pH range, due to the higher stability of the Cu(II)–EDTA complex in comparison with copper hydroxide(s).[28]

As seen in Fig. 3, varying the catholyte pH between 8 and 12 had a minor effect on the observed copper recovery rate. This may be expected as there was no notable change in the conditional stability constant ($\log_{10} K'$) of Cu(II)–EDTA within the pH 8–12 interval, as discussed earlier. This can also be explained by almost constant values of calculated cathodic potentials required to reduce Cu(II)–EDTA complexes to Cu and Cu_2O within the pH 8–12 range. In the alkaline Cu(II)–citrate complex solution, it has been shown that layered deposits of Cu and Cu_2O can be obtained under controlled-current conditions.[29] The cathodic potential for reduction of Cu(II)–EDTA complexes to Cu and Cu_2O can be calculated based on the modified Nernst equation (see Supporting information) taking into account the distribution of Cu(II)–EDTA

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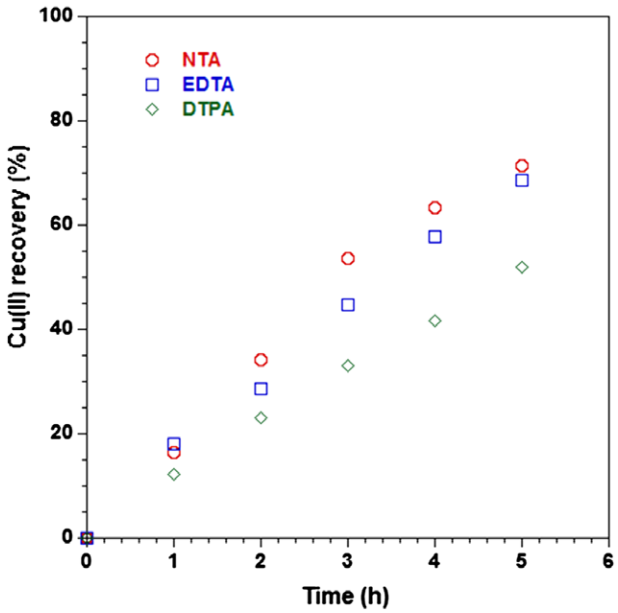

Figure 4. Copper recovery from different complex solutions versus time (current density, 1 A dm^{-2}; pH, 10; T, 295 K).

complexes at certain pH (Fig. 2(b)) and their stability constants. For example, at pH 8, cathodic potentials of $CuEDTA^{2-}$ complex to Cu and Cu_2O, calculated using modified Nernst equation, were −0.18, and −0.99 $V_{Ag/AgCl}$, respectively. At pH 10, the copper ions exist mainly as $CuEDTA^{2-}$ complex (≈98%) and partly as $Cu(EDTA)OH^{3-}$ complex (≈2%), see Fig. 2(b). At this pH, the cathodic potentials of $CuEDTA^{2-}$ complex to Cu and Cu_2O were −0.18, and −0.88 $V_{Ag/AgCl}$, respectively. The cathodic potentials of $Cu(EDTA)OH^{3-}$ complex to Cu and Cu_2O were −0.18, and −0.89 $V_{Ag/AgCl}$, respectively. Additionally, $CuEDTA^{2-}$ complex (≈30%) and $Cu(EDTA)OH^{3-}$ complex (≈70%) are formed at pH 12, see Fig. 2(b). The cathodic potentials of copper complexes to Cu and Cu_2O, for $CuEDTA^{2-}$ were −0.18, and −0.78 and for $Cu(EDTA)OH^{3-}$ were −0.19, and −0.78 $V_{Ag/AgCl}$, respectively.

However, for the initial Cu(II) concentration of 0.05 mol L^{-1} without chelating agent, the cathodic potentials of copper ions to Cu (Equation (4)) was 0.08 $V_{Ag/AgCl}$ within the pH range 8–12. Under the same conditions, the cathodic potentials of copper ions to Cu_2O (Equation (8)) at pH 8, 10, and 12 were −0.48, −0.36, and −0.24 $V_{Ag/AgCl}$, respectively. This indicates that the presence of chelating agent in copper solution decreases the potential for the half-reaction (Equations (4) and (8)), making it thermodynamically less favourable.

It can be also seen in Fig. 3 that the copper recovery was almost linear with increasing electrolysis time at a current density of 1 A dm^{-2} and at ambient temperature. The maximum recovery of copper was approximately 70% after 5 h of experiment. The average current efficiency was calculated to be 68% for the recovery of copper at different operating catholyte bulk pH values and the average specific electricity consumption was 0.27 kWh mol^{-1}. In addition, the average cathodic potential and the average cell voltage of experiments at varying operating pH values were −1.32 $V_{Ag/AgCl}$ and 3.38 V, respectively. Moreover, the solution pH reportedly influences the recovered copper composition and morphology.[30]

Figure 4 shows the copper recovery percentage from complex solutions of Cu(II)–NTA, Cu(II)–EDTA, and Cu(II)–DTPA at a current density of 1 A dm^{-2} and ambient temperature, where the catholyte pH was kept constant at 10. As shown in Fig. 4, the maximum recovery of copper from NTA, EDTA, and DTPA in 5 h of treatment was approximately 71%, 69%, and 52%, respectively. The recovery trends display relatively clear dependencies on their conditional stability constants with copper at a constant pH 10. This is not surprising, since here the differences between the conditional stability constants of the copper complexes with NTA, EDTA, and DTPA are considerably larger than was the case in the pH study of EDTA ($\log_{10} K'_{Cu(II)\text{-}DTPA} > \log_{10} K'_{Cu(II)\text{-}EDTA} >> \log_{10} K'_{Cu(II)\text{-}NTA}$). This effect is even more obvious for the Cu(II)–NTA and Cu(II)–EDTA complex solutions when the amounts of copper recovered within the first 3 h of treatment are compared. As seen in Fig. 4, the recoveries of copper from NTA and EDTA complex solutions after 3 h of treatment were approximately 55% and 45%, respectively. Then, beyond the first 3 h of treatment, the rate of copper recovery from the NTA complex solution gradually decreased due to the depletion of Cu(II) in the catholyte solution and reached almost the same recovery percentage of copper from the EDTA complex solution at the end of the experiment. One might have expected to find even larger differences, especially between NTA and EDTA/DTPA, due to the obvious differences in conditional stability constants.

The recovery trends of copper complexed with the equimolar chelating ligands studied (i.e. NTA, EDTA, and DTPA) can also be explained by the cathodic potentials required to reduce Cu(II)–chelating ligands complexes to Cu and Cu_2O. For example, at pH 10 and a Cu(II) concentration of 0.05 mol L^{-1}, complexed with equimolar NTA, the cathodic potentials for $CuNTA^{-}$, $Cu(NTA)OH^{2-}$, and $CuNTA_2^{4-}$ complexes to Cu were −0.11, −0.11, and −0.07, and to Cu_2O were −0.53, −0.75, and −0.66 $V_{Ag/AgCl}$, respectively. In addition, for Cu(II)–EDTA solution at the same pH, the cathodic potentials for reduction of $CuEDTA^{2-}$, $Cu(EDTA)OH^{3-}$ complexes to Cu were −0.18, and −0.18, and to Cu_2O were −0.88, and −0.89 $V_{Ag/AgCl}$, respectively. For Cu(II)–DTPA solution at pH 10, the cathodic potentials of $CuDTPA^{3-}$ complex to Cu and Cu_2O were −0.21, and −0.95 $V_{Ag/AgCl}$, respectively (see Supporting information). This indicates that the reduction of Cu(II)–studied chelating ligands complexes to Cu and Cu_2O at a constant pH of 10 becomes less favourable as complex stability increases.

Based on the above explanation, a considerably higher complex stability should lead to the need for a higher overpotential in order to electrodeposit copper from an alkaline Cu(II) complex-based electrolyte. Consequently, the higher complex stability should lower the current efficiency (as the rate of side reactions increases) and increase the specific electricity consumption. The current efficiencies (η) of copper deposition from NTA, EDTA, and DTPA complex solutions after 5 h were approximately 70%, 65%, and 50%, whereas the specific electricity consumptions (E_{cell}) were 0.26, 0.29, and 0.36 kWh mol^{-1}, respectively.

The effect of the difference in conditional stability constants on the electrodeposition of copper was also observed using cyclic voltammetry. The voltammograms obtained in the studied copper complex solutions showed that a higher reduction potential is required to reach a certain reduction current in the following order of the complex solutions: Cu(II)–DTPA > Cu(II)–EDTA >> Cu(II)–NTA (see Fig. 5). As discussed earlier, the results can be correlated with their conditional stability constants, which vary in the same order. The reduction of copper complexed with studied chelating ligands can therefore be expected to increase in the following order of the complex solutions, i.e. Cu(II)–NTA >> Cu(II)–EDTA > Cu(II)–DTPA, under comparable conditions. In addition, we observed that the voltammograms obtained in Cu(II)–NTA, Cu(II)–EDTA, and Cu(II)–DTPA complex

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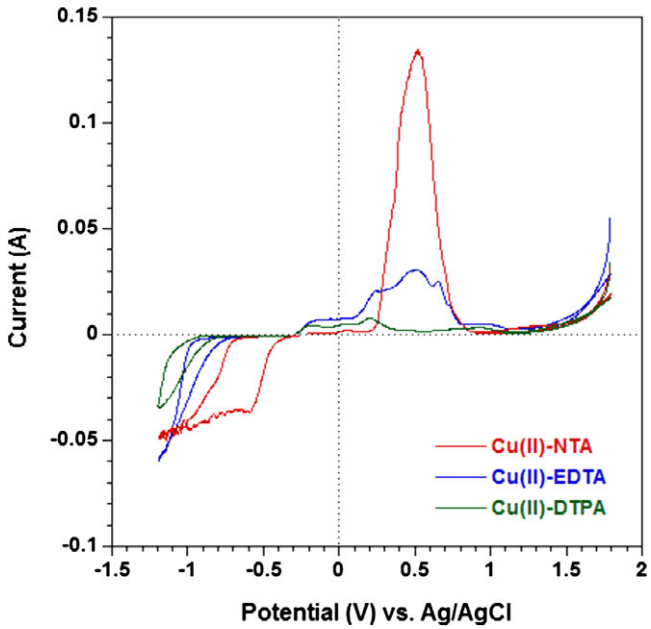

Figure 5. Cyclic voltammetry of complex solutions of 0.05 mol L^{-1} $CuSO_4 \cdot 5H_2O$:0.05 mol L^{-1} chelating ligand (NTA, EDTA, and DTPA) in the range of 1.8 $V_{Ag/AgCl}$ to −1.2 $V_{Ag/AgCl}$ (complex solution pH, 10; T, 298 K; working electrode, Ti; scan rate, 0.01 V s^{-1}).

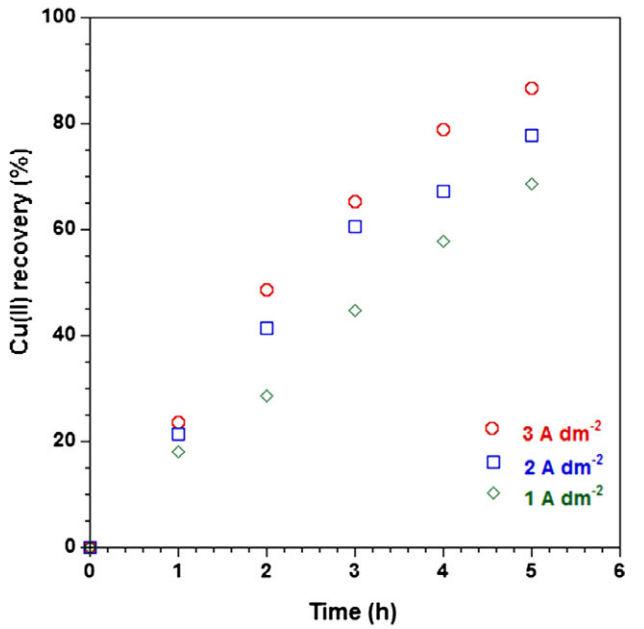

Figure 6. Effect of applied current density on copper recovery at various times (pH, 10; T, 295 K).

solutions presented a main anodic peak (at the potential around 0.5 $V_{Ag/AgCl}$) related to the electrodeposit oxidation followed by the water oxidation reaction (Fig. 5). In another study, the voltammograms obtained in an alkaline complex solution, i.e. Cu(II)–HEDP (1-hydroxyethane-1,1-diphosphonic acid), showed that the anodic peak corresponds to the oxidation reactions of copper deposits followed by the oxidation of water molecules.[31] The results allowed us to conclude that an increase in the anodic current of electrodeposit dissolution is a strong indication that the lower the stability constant of the copper complex, the more copper is deposited on the electrode during cathodic sweep and thereafter dissolved from the electrode during anodic sweep. Other peaks were not discussed in detail, as the objective is to illustrate briefly the effect of the copper complex stability on electrochemical copper behaviour in different copper complex solutions using the cyclic voltammetry technique.

Dependence of Cu(II) recovery on current density

To study the effect of current density on copper recovery, a series of experiments was carried out on solutions of copper and EDTA. Figure 6 shows the recovery of copper as a function of electrolysis time with current density being changed from 1 to 3 A dm^{-2} while the catholyte pH was kept constant at 10. As expected, this figure indicates that increased current results in faster recovery. In addition, it was previously reported that an increase in current density develops the mass transfer coefficient by increasing the hydrogen gas liberation rate, which is known to cause local turbulence near the cathode.[32] However, hydrogen gas generation is an electron-consuming side reaction to copper reduction and leads to lower current efficiency,[9,14] in good agreement with previous findings.[6,7,9,14–16,18] Because of the increased H_2 evolution, the recovery rate does not display direct proportionality to the applied current density. The highest applied current (3 A dm^{-2}) gave the highest recovery rate, with a maximum recovery of 87% occurring after 5 h of treatment.

Applied current density is a major operating factor that directly influences the performance and operating cost of the electrolysis process.[6] The effects of current density on the current efficiency (η) and specific electricity consumption (E_{cell}) are presented in Table 2. With increasing current density, the current efficiency drops[9,14–16] and the specific electricity consumption increases[6,7] as does cell voltage (Table 2). This expected finding is mainly attributable to the increased reduction of water molecules, which leads to greater hydrogen gas generation.[9,14] In addition, the changes in current density noticeably affect the morphology,[33] quality,[34] and composition[31] of copper electrodeposits.

Dependence of Cu(II) recovery on temperature

Experiments were performed to investigate the temperature dependence of the electrolysis in relation to the amount of copper recovered. Figure 7(a) indicates that increasing the temperature from 295 to 333 K improved the copper recovery under constant applied current density and pH. The improvement is attributable mostly to the increased diffusion of species in electrolyte with increasing temperature. Another reason for the improvement could be the lower stability constant of the copper complex with chelating agent due to increasing temperature, as each 38 °C increase in temperature reportedly lowers the stability constant on the order of only one log unit.[26] In addition, it was previously reported that increasing the temperature leads to decreased viscosity and surface tension of solution and increased hydrogen evolution.[35]

For the experiment at the highest studied temperature (333 K), the amounts of EDTA recovered as a result of copper electrodeposition were determined by analysing the concentration of free EDTA in catholyte solution (Fig. 7(b)). As expected, the results indicated that the EDTA recovery was nearly identical to the copper recovery, although the electrolysis was performed at high temperature. The recovery percentages of copper and EDTA were previously determined for experiments performed at ambient temperature and with different values of parameters

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Table 2. Effects of applied current density on current efficiency (η), specific electricity consumption (E_{cell}), average cell voltage, and cathodic potential of experiments (pH, 10; T, 298 K; t, 5 h)

Current density (A dm^{-2})	Average cathodic potential ($V_{Ag/AgCl}$)	Average cell voltage (V)	Current efficiency η (%)	Specific electricity consumption E_{cell} (kWh mol^{-1})
1	−1.38	3.52	65	0.29
2	−1.49	4.10	37	0.59
3	−1.58	5.12	27	1.02

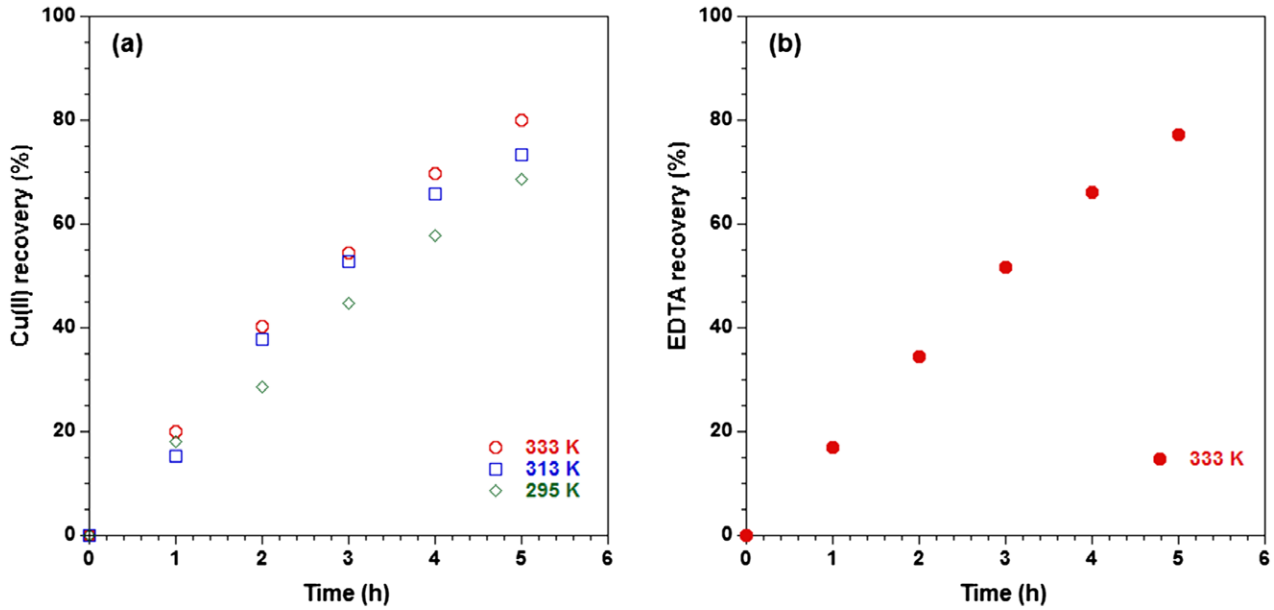

Figure 7. (a) Effect of operating temperature on copper recovery for various electrolysis times (pH, 10; current density, 1 A dm^{-2}). (b) EDTA recovery for various electrolysis times (T, 333 K; pH, 10; current density, 1 A dm^{-2}).

such as anolyte Na^+ concentration, current, and electrolysis time. These percentages indicate that the copper and EDTA recovery are almost the same, differing by a maximum of 3%. However, a close look at these results reveals that an increase in anolyte Na^+ concentration leads to a decrease in the difference between copper and EDTA recoveries.[15]

The results indicate that increasing the temperature from 295 to 333 K increased the current efficiency from 65% to 85% and consequently decreased the specific electricity consumption from 0.29 to 0.18 kWh mol^{-1}. This is attributable to increased ion mass transport through the electrolyte and to the electrolyte conductivity, resulting in reduced cell voltage and energy demand (Table 3). The morphology[35] and quality of copper electrodeposits may be influenced by varying the operating temperature.

Figure 8 shows SEM images and the XRD pattern of copper electrodeposits for the experiment at the highest studied temperature (333 K). The SEM images show that copper was electrodeposited, forming a layer almost 20 μm thick, and that a cauliflower-like structure formed on the cathode during electrolysis. According to the XRD pattern, copper was recovered mainly as pure copper (Cu) and partly as cuprous oxide (Cu_2O) and cupric oxide (CuO). The electrodeposition of cuprous oxide is expected to take place in copper and chelating agent-containing solutions[29,30] based on reaction Equation (3). This can be explained by the higher OH^- concentration near the electrode[29] and by the stability region of the cuprous oxide[27] for an aqueous solution comprising Cu(II) and EDTA. Furthermore, based on the stability region of the cupric oxide,[27] the occurrence of cupric oxide in the recovered material seemed not to be due to the studied operating conditions, since cupric oxide can be precipitated in Cu(II)–EDTA complex solution (Fig. 2(b)) and in solution at higher OH^- concentrations.[36]

Table 3. Effect of operating temperature on current efficiency (η), specific electricity consumption (E_{cell}), average cell voltage, and cathodic potential of experiments (pH, 10; current density, 1 A dm^{-2}; t, 5 h)

Temperature (K)	Average cathodic potential ($V_{Ag/AgCl}$)	Average cell voltage (V)	Current efficiency η (%)	Specific electricity consumption E_{cell} (kWh mol^{-1})
295	−1.38	3.52	65	0.29
313	−1.24	3.28	73	0.24
333	−1.14	2.94	85	0.18

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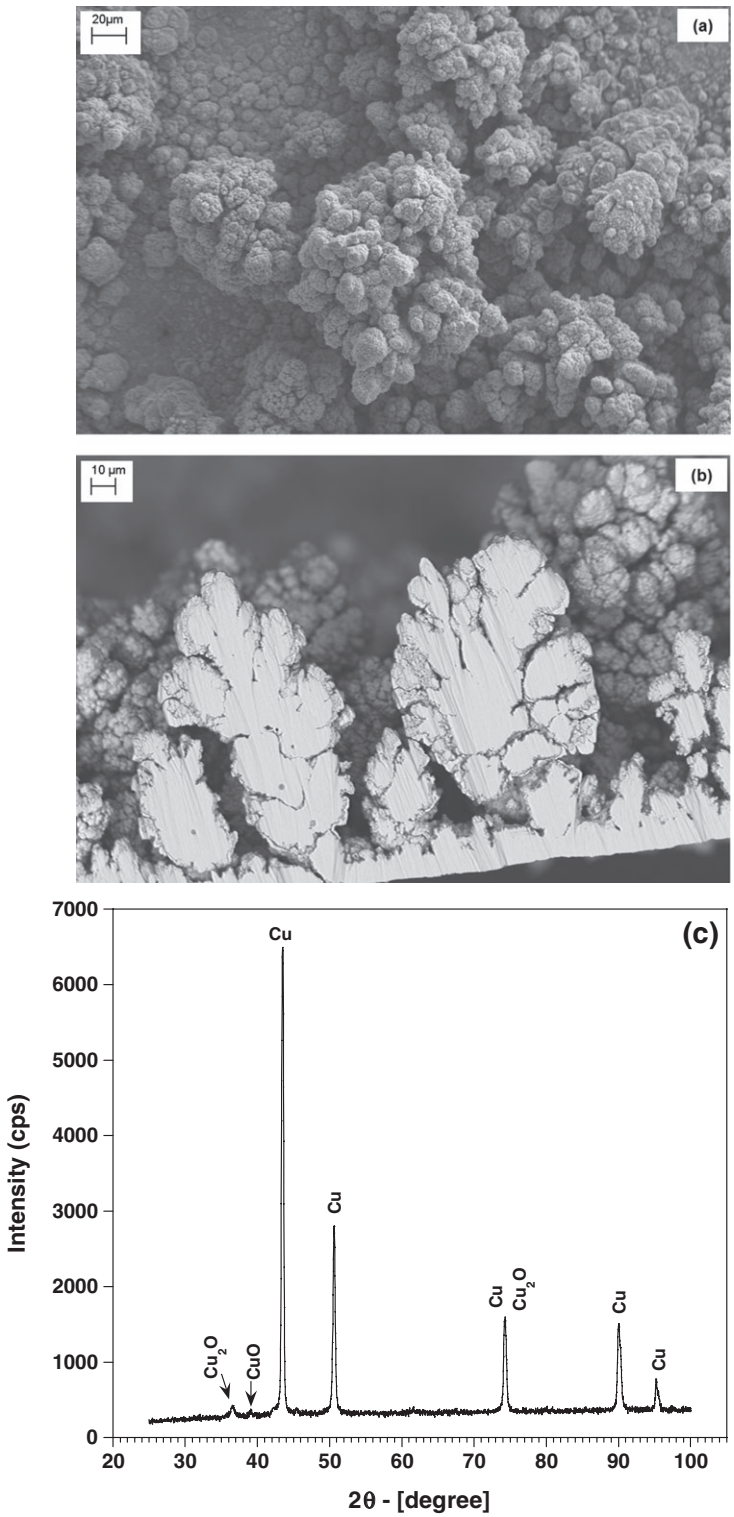

Figure 8. (a) SEM image of recovered copper. (b) SEM cross-sectional image of recovered copper (c) XRD pattern of recovered copper. Conditions: pH, 10; current density, 1 A dm^{-2}; T, 333 K; *t*, 5 h.

CONCLUSION

This study investigated the simultaneous recovery of Cu(II) and EDTA from alkaline solution using a divided electrochemical cell with a cation-exchange membrane. The results indicate that this method can be applied effectively to a complex solution to prevent the discharge of copper ions and chelating agents as contaminants into the environment. According to the experimental results, in the pH 8–12 interval, the recovery efficiency moderately decreased when the magnitude of the conditional stability constants increased significantly, i.e. $\Delta \log_{10} K' > 2$. For copper and EDTA complex solutions, varying the pH between 8 and 12 did not significantly affect the recovery

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process, which was explained by comparably small variation in the conditional stability constant over the pH range, i.e. $\Delta \log_{10} K' \leq 0.7$. Under comparable conditions, the copper recovery efficiency increased in the following order of the complex solutions, i.e. Cu(II)–NTA >> Cu(II)–EDTA > Cu(II)–DTPA, opposite to the magnitudes of their conditional stability constants. Increasing the current density somewhat improved the recovery rate but decreased the current efficiency. The temperature dependency studies demonstrated an increase in current efficiency and recovery when increasing the operating temperature from 295 to 333 K.

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Supporting Information

Supporting information may be found in the online version of this article.

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