

Recovery of Copper and DCA from Simulated Micellar Enhanced Ultrafiltration (MEUF) Waste Stream

Chuan-Kun Liu and Chi-Wang Li

Abstract—Simultaneous recovery of copper and DCA from simulated MEUF concentrated stream was investigated. Effects of surfactant (DCA) and metal (copper) concentrations, surfactant to metal molar ratio (S/M ratio), electroplating voltage, EDTA concentration, solution pH, and salt concentration on metal recovery and current efficiency were studied. Electric voltage of -0.5 V was shown to be optimum operation condition in terms of Cu recovery, current efficiency, and surfactant recovery. Increasing Cu recovery and current efficiency were observed with increases of Cu concentration while keeping concentration of DCA constant. However, increasing both Cu and DCA concentration while keeping S/M ratio constant at 2.5 showed detrimental effect on Cu recovery at DCA concentration higher than 15 mM. Cu recovery decreases with increasing pH while current efficiency showed an opposite trend. It is believed that conductivity is the main cause for discrepancy of Cu recovery and current efficiency observed at different pH. Finally, it was shown that EDTA had adverse effect on both Cu recovery and current efficiency while addition of NaCl salt had negative impact on current efficiency at concentration higher than 8000 mg/L.

Keywords—metal recovery, MEUF waste, surfactant, electroplating.

I. INTRODUCTION

RESEARCHES on removing heavy metals or toxic organic compounds using micellar enhanced ultrafiltration (MEUF) processes have been reported in recent years [1-5]. Theory on removing these unwanted metals ions or toxic organic compounds using MEUF process is based on adsorption of small target ions to a large surfactant micelle which only exists at concentration of surfactant higher than its critical micellar concentration, i.e., CMC, followed by subsequent removal of contaminated ion-micelle complexes by ultrafilter. Removal efficiency depends on characteristics and concentrations of targeted contaminated ions and surfactants, solution pH, ionic strength, and parameters related to membrane operation (such as pressure, filtration flow rate, membrane pore size, etc) [5-8].

Choice of surfactants largely depends on the type of contaminated ions to be removed, for example, anionic

surfactants are selected as assistant agent for removing heavy metals in MEUF. Although, different types of surfactants displayed various ability on enhancing metal or organic matter removal efficiency. For example, Huang et al. [7] investigated removal of various heavy metals by MEUF using deoxycholic acid (DCA; $C_{24}H_{40}O_4$), sodium dodecyl sulfate (SDS; $C_{12}H_{25}OSO_3Na$) and other natural surfactants as enhancing agents in ultrafilter. It was found that DCA was more effective for enhancing metal removal than other surfactants investigated and two important parameters, surfactant concentration and surfactant to metal molar ratio (S/M ratio), controlled the removal efficiency of metals. For example, surfactant concentration and surfactant to metal molar ratio (S/M ratio) have to be higher than critical micellar concentration (CMC) of surfactant and critical S/M ratio, respectively, to achieve maximum metal rejection efficiency. When using DCA as enhancing agent, the former is 5.0 mM and is 2.5 for the later.

Multiprotic ligands such as EDTA and NTA are industrially used to enhance the solubility of metals in solution or to remediate soil contaminated with heavy metals. Recovery of metals from wastewater containing ligands using electroplating method has been reported by several researchers [9-13]. Their results indicated that both metal recovery and current efficiency were greatly impaired by the presence of ligands [12] and the extent of influence depends on the overall formation constant of ligands with metals [11]. For example, it has been reported that the metal recovery and current efficiency are in the order of Cu complexes with citrate > NTA > EDTA which is exactly on the opposite order of overall stability constants of Cu with these ligands. Electrolyte pH also played an important role on the recovery of metal and current efficiency due to the presences of different species of ligands at different pH, although in these studies pHs of electrolytes were not constant through the course of electroplating [9,10]. It is believed that two separate reaction steps might involve in the electroplating of metals onto electrode in electrolyte containing ligands. In the first step, chelated ions are destroyed by applied voltage at the location outside of electric double layer of cathode, followed by the second step that metals are deposited on the cathode [9,10]. Therefore, extra electric energy is needed to facilitate the destruction of chelating complex and to migrate the chelated ions away from the cathode resulted in the decreases of Cu recovery and current efficiency with the presence of ligands. Investigation is underway in our lab on the simultaneous recovery of metals and surfactant using process which integrates

Chuan-Kun Liu, Environmental Biotechnology Program, Development Center for Biotechnology, Xizhi City, Taipei County 221, Taiwan, R.O.C. (mail: roko@mail.dcb.org.tw)

Chi-Wang Li, Department of Water Resources and Environmental Engineering, Tam-Kang University, Tamsui 25137, Taiwan, R.O.C.

membrane and electroplating in one single unit. Therefore, effect of EDTA on the recovery of metals and current efficiency were also studied and reported in this communication.

Very few studies focusing on simultaneous recovery of surfactants and metals from concentrated MEUF waste streams has been reported. In this study, electroplating process was employed to recover metal (copper) and surfactant (DCA) from the concentrated stream of MEUF process using DCA as enhancing surfactant. Effects of surfactant (DCA) and metal (copper) concentrations, surfactant to metal molar ratio (S/M ratio), electroplating voltage, EDTA concentration, solution pH, and ionic strength on metal recovery and current efficiency were investigated. Advantages of recovering metals after MEUF treatment as opposed to treating wastewater without MEUF pre-treatment are obvious. First, the amount of wastewater to be treated is drastically reduced by MEUF pre-treatment. Second, the current efficiency of electroplating process would be enhanced due to the concentration of metals has been increased several folds by MEUF. However, several possible effects have to be considered for the recovery process to be useful, such as the effects of surfactants on the recovery of metals and current efficiency and the possible destruction of surfactant during electroplating process.

II. MATERIALS AND EXPERIMENTAL METHODS

All chemicals are reagent grade. Cu(II) solutions were prepared from 1000 mg/L ICP standard (J. T. Baker). DCA (ACROS) was diluted with DI water to pre-determined concentration. Electroplating experiments were performed using potential-stat (model CH 602A, CH instrument Inc.) at constant voltage mode (chronocoulometry). A $3 \times 5 \times 0.01$ cm copper plate (effective area of 30 cm^2) was employed as cathode and $3 \times 5 \times 0.15$ cm graphite was used as anode. All potentials are reported vs. the Ag/AgCl reference electrode (Bioanalytical systems Inc.). Copper plate cathode was polished with sandpaper, immersed in a degreasing agent (prepared by adding 5g NaOH, 30g Na_2CO_3 , and 0.1g Na_3PO_4 in 1 liter of DI water) for 30 minutes, rinsed with DI water and alcohol, and stored in desiccator before used. A 100-ml of Cu-surfactant simulated wastewater was electrochemically treated at pre-defined time in a $6 \times 5.5 \times 5$ cm reactor (length \times width \times height). Samples were taken at the end of electroplating for Cu and surfactant analysis and pH measurement. Cu concentration was analyzed by flame atomic adsorption spectroscopy (Hitachi Z6100). DCA was analyzed using a Thermo Gravimetric analyzer (Perkin-Elmer TGA-7). Figure 1 was change of weight for DCA sample as function of temperature. A slight decrease of weight for temperature from 30 to about 100 °C corresponds to the evaporation of water, followed by a relatively stable region for temperature from 100 to 320 °C (step 1), a rapid decomposition of DCA occurred which was followed a gradual decomposition stage at temperature between 460 to 720 °C (step 2). From Figure 1, one can found that about 89.2% of DCA was thermo-decomposed at 720 °C while 10.8% of DCA was thermo-stable and would not decomposed at temperature above 720 °C. Based on this, following equation was used to calculate DCA concentration in a sample.

$$\text{DCA weight} = \frac{\text{Weight at } 720^\circ\text{C} - \text{Weight at } 320^\circ\text{C}}{0.892} \quad (1)$$

It should be noted that calculation of DCA using the equation (1) was based on the assumption that DCA destroyed in electrochemical cell although not completely mineralized will be thermo-decomposed in TGA analysis at temperature below 320 °C.

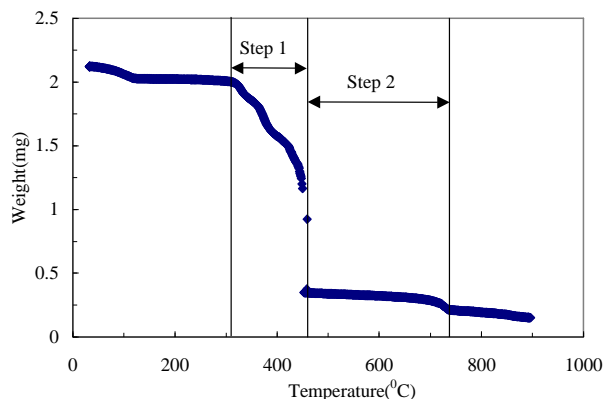


Fig. 1 Weight change versus temperature for DCA. Test temperature form room temperature to 900°C.

III. RESULTS AND DISCUSSIONS

A Effect of applied voltage

Simulated wastewater containing DCA and Cu concentrations of 5 mM and 2 mM, respectively, i.e., S/M of 2.5, was electrolyzed at voltage ranging from -0.9 to -0.1 V vs. Ag/AgCl at pH 2.0. As shown in Table 1, increasing voltage from -0.9 V to -0.3 V (less negative) decreases copper recovery efficiency and increases current efficiency. Cu recovery efficiency and current efficiency are defined using following equations.

$$\text{Cu recovery (\%)} = \frac{\text{Actual amount of Cu removed}}{\text{initial amount of Cu present in the reactor}} \times 100 \quad (2)$$

$$\text{Current efficiency (\%)} = \frac{\text{Actual amount of Cu removed}}{\text{Theoretical amount of Cu removed based on the amount of charge passed}} \times 100 \quad (3)$$

For voltages higher than -0.3 V, concentration of Cu in electrolyte increases due to release of Cu from Cu-cathode resulting in negative recovery efficiency. It is also shown in Table 1 that DCA recovery decreases with increasing applied voltage (more negative). However, it is higher than 90% for voltage above -0.5 V. Other researchers had employed an electrolytic cell with cation-selective membrane to separate anodic and cathodic compartments to avoid the possible anodic destruction of complex ligands such as EDTA and NTA [11]. However, in this study surfactant showed higher resistant than EDTA or NTA for anodic oxidation [12]. Therefore, the separation of anodic and cathodic compartments with cation-selective membrane is not necessary.

At voltage of -0.5 V, copper removal and current efficiency are optimal and the recovery of DCA is above 90.5%. Therefore, the subsequent experiments were conducted at -0.5V.

TABLE I EFFECT OF VOLTAGE ON CU RECOVERY, CURRENT EFFICIENCY, AND SURFACTANT RECOVERY. DCA CONCENTRATION=5 mM; S/M=2.5; pH=2±0.1; ELECTROPLATING TIME=5000 SECONDS

Voltage (vs. Ag/AgCl)	Cu recovery (%)	Current efficiency (%)	DCA recovery (%)
-0.9	76.7	23.7	
-0.5	79.8	60	90.5
-0.3	69.8	58.5	92.8
-0.2	-17.6	NA	NA
-0.1	-22.6	NA	NA

B Effects of surfactant, copper concentrations, and S/M ratio

As mentioned previously, to attain an efficient removal of metals in MEUF process, both surfactant concentration and S/M ratio have to be higher than the CMC of surfactant and a critical S/M ratio, respectively, which are 5 mM and 2.5 for DCA. Under these criteria, two different schemes of MEUF operation would be expected and concentrated waste generated from these two schemes were tested in this study. In type I case, 5 mM of DCA was placed in the MEUF reactor first and waste stream containing metal was continuously pumped into the reactor until system has S/M ratio equal 2.5. By then, solution in reactor has to be disposed and new DCA solution was filled in the reactor again (see Figure A). Therefore, one will have concentrated waste stream with S/M ratio greater than 2.5 while having constant DCA concentration of 5 mM. In the type II case, both DCA and metal were mixed first at S/M ratio equal to 2.5 and DCA concentration higher than 5 mM (in this study, DCA is fixed at 5 mM). Then the mixed solution was directed into the MEUF reactor as shown in Figure 2B. Assuming both surfactant and metal are effectively retained inside the reactor by membrane, concentrations for both surfactant and metal will increase in the same ratio while S/M ratio remains constant, i.e., $nS/nM = 2.5$ where n is a real number.

Figure 3 shows the Cu recovery and current efficiency as function of Cu concentration at fixed pH of 2.0 and DCA concentration of 5 mM, i.e., type I case. It is clear that both current and Cu recovery efficiencies increase with increasing Cu concentration. At Cu concentration of 21.2 mg/L corresponding to S/M ratio of 15, Cu recovery and current efficiency are only 60 and 13.5%, respectively. When increasing Cu concentration to 127 mg/L (at S/M ratio of 2.5), both Cu recovery and current efficiency increase to more than 80 and 60%, respectively. It is due to the increasing concentration gradient of Cu ions between electrode and bulk solution or increasing conductivity of solution with increasing Cu concentration, indicated by the increases of the total amount of charge passed with increasing Cu concentration (see also Figure 3).

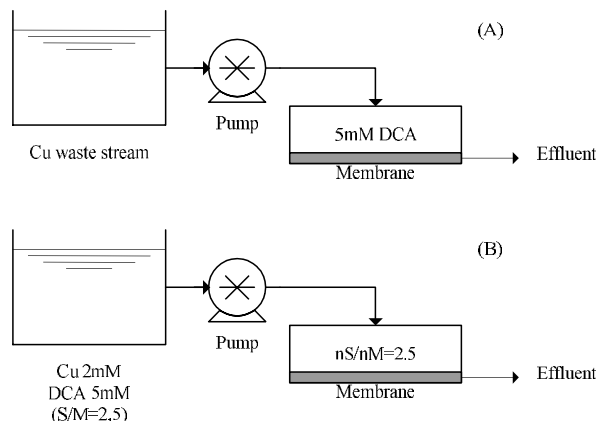


Fig. 2. Schematic representation of concentrated MEUF wastes generated from two operation modes. (A) fixed DCA concentration (B) fixed DCA to Cu molar ratio. n is real number.

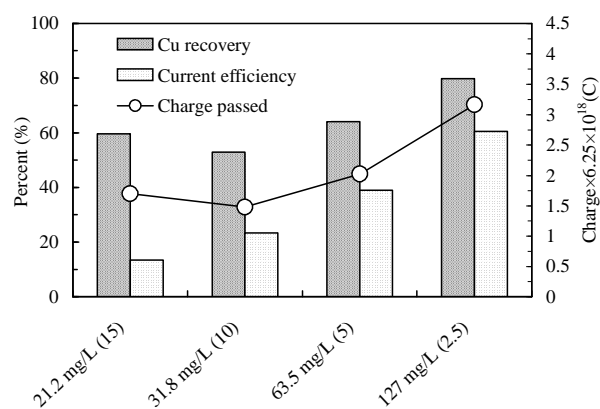


Fig. 3. Cu recovery and current efficiency as function of Cu concentration. DCA concentration of 5 mM, Voltage=-0.5 V (vs. Ag/AgCl). pH=2.0, electroplating time=5000 seconds.

Figure 4 shows Cu recovery and current efficiency as function of DCA and Cu concentrations at fixed S/M ratio of 2.5 at pH 2.0 and electroplating time of 5000 seconds, i.e., type II case. In this test, both surfactant and Cu concentrations are 1.5 to 5 times increases from the baseline case where DCA and Cu concentrations are 5 and 2 mM, respectively, corresponding to S/M ratio of 2.5. As increasing both DCA and Cu concentrations up to 2 times, no significant effect was observed on Cu recovery and current efficiency. Cu recovery decreases from about 80% to less than 60% when the concentrations of DCA and Cu increase to three and five times of those in baseline case, although the amount of charge passed increases with increasing both DCA and Cu concentrations. Several researchers have indicated that increases of surfactant concentration will (1) increase the capacitance between electrode and electrolyte [14] resulted in increase of the energy needed for deposition of Cu ion onto electrode and (2) increase the viscosity of electrolyte resulted in decrease of the mass transfer rate for Cu ions from bulk solution to electrode surface [15]. These two factors might account for the decreases of Cu

recovery when the DCA and Cu concentrations increase three times from the baseline case.

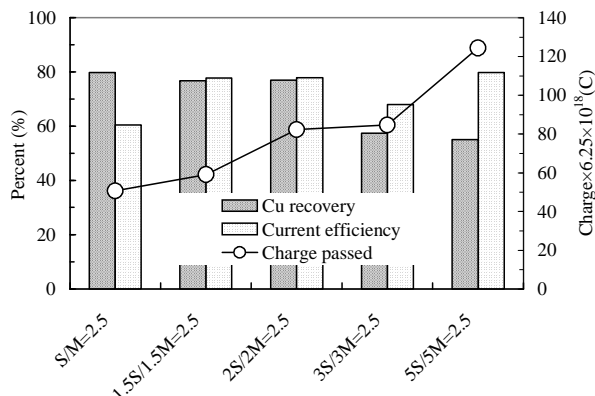


Fig. 4. Cu recovery and current efficiency as function of DCA and Cu concentration at fixed S/M ratio of 2.5. S=5 mM, Voltage=-0.5 V (vs. Ag/AgCl). pH=2 0.1, electroplating time=5000 seconds.

C. Effect of pH

Effect of pH on recovery of Cu and current efficiency were conducted at pH ranging from 1 to 7, DCA concentration of 5 mM (S/M=2.5) and electrical potential of -0.5 V vs. Ag/AgCl. Figure 5 shows both Cu recovery and current efficiency at electrolysis elapsed time of 5000 seconds. Increasing pH from 1 to 7, Cu recovery efficiency decreases from 95 to 13%. In contrast to Cu recovery, current efficiency increases from 40 to 90%. Increasing current efficiency with increasing pH was due to the decrease of hydrogen evolution side reaction at elevated pH. Investigating the recovery of metals and strong complex ligands (e.g., EDTA, NTA, and etc) by electroplating methods, Juang and his co-works [9-11] reported that both current and metal recovery efficiency decreased with increasing pH with maximum at pH ~2. They explained the effect of pH by the presence of different species of metal-ligand complexes at different pH. However, in their experiment, pHs of catholyte are not constant, i.e., drifting during the course of electroplating, and increasing to more than 11.5 at the end of tests regardless of the initial catholyte pHs. In our study, the pH effect could not be explained solely by the different species of metal-ligand complexes at different pH since DCA is not a multiprotic acid and experimental data showed that the electrolyte pHs are very stable during the courses of electroplating (data not shown). Another possible explanation is that the electrolyte conductivity, which changes during pH adjustment, might influence the recovery of Cu at different pH. Indeed, conductivities of electrolytes increase with decreasing pH and the amount of charge passed followed the same trend as shown in Table 2. It is also interested to note the copper recovery efficiency linearly correlates to amount of charge passed except the test at pH 1 (see Figure 6). The low current efficiency at pH 1 indicates the domination of other side reactions (mainly hydrogen evolution) at this pH. The effect of conductivity on Cu recovery is further illustrated in Figure 7.

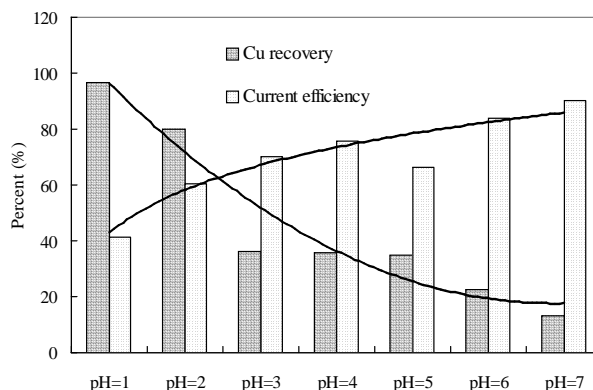


Fig. 5. Effect of pH on Cu recovery and current efficiency. DCA concentration=5 mM (S/M=2.5); Voltage=-0.5 V (vs. Ag/AgCl); Electroplating time=5000 seconds.

It is clear that by adjusting conductivity of electrolytes of pH 4 to the same level as that of pH 2 system, the Cu recovery also increases to the about the same extent as that for pH2 system, where the percentages of Cu removed increase from ~40% to about 80% after adjusting its conductivity at pH 4. The importance of conductivity effect on Cu recovery and current efficiencies signifies the advantage of applying electroplating methods on MEUF concentrated waste stream instead of original waste. Applying MEUF pre-treatment and then electroplating process (or use two processes simultaneously) will drastically reduce the amount of chemicals needed for pH or conductive adjustment and increase metal removal and current efficiencies at the same time.

TABLE II ELECTROLYTES CONDUCTIVITY AND AMOUNT OF CHARGE PASSED AT DIFFERENT pH AT ELECTROPLATING TIME=5000 SECONDS FOR DCA SYSTEM

pH	1	2	3	4	5	6	7
Conductivity(mS)	106	8.71	1.47	1.18	1.13	1.12	1.13
Charge passed (C)	89.9	50.7	20.3	18.5	19.2	9.1	5.7

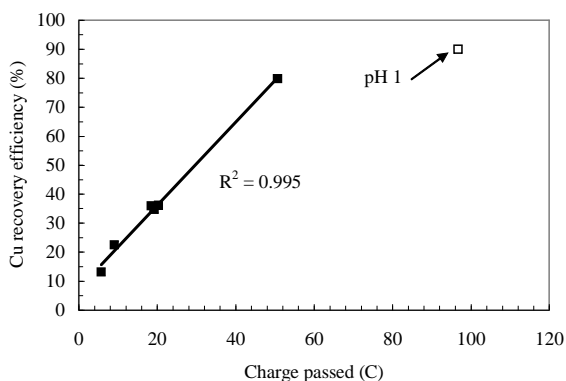


Fig. 6. Cu recovery as function of current passed. DCA concentration=5 mM (S/M=2.5); Voltage=-0.5 V (vs. Ag/AgCl); Electroplating time=5000 seconds; pH 1 to 7.

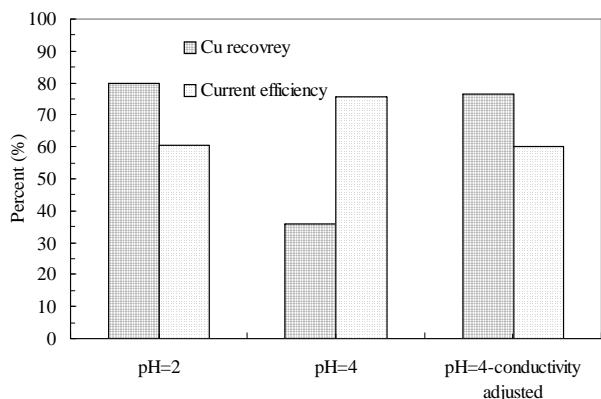


Fig. 7. Effect of ionic strength on Cu recovery and current efficiency. DCA concentration=5 mM (S/M=2.5); Voltage=-0.5 V (vs. Ag/AgCl); Electroplating time=5000 seconds.

D Effect of ionic strength

In MEUF process, surfactant molecules that do not form micelle will inevitably pass membrane, ending up in the permeate side. In MEUF, the highest concentration of surfactant will present in the permeate side is equal to its CMC. One way to ease this flaw is to increase ionic strength of the solution, which decreases CMC of surfactant. It was found that increasing salt concentration to 0.1 M (through NaCl addition) subsequently decreases the surfactant concentration in permeate stream from 1 mM to 0.15 mM [6].

Figure 8 shows that all systems have Cu recovery efficiencies higher than 80% but no clear trend can be drawn. However, current efficiency slightly decreases with NaCl concentration higher than 4000 mg/L, indicating possible side reactions. This is also delineated in the same Figure, which shows that increasing charge passed with increasing NaCl concentration.

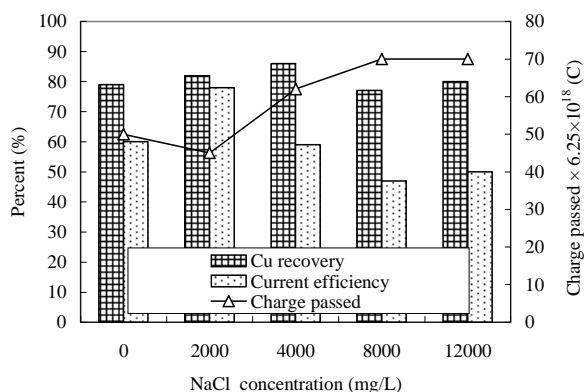


Fig. 8. Effect of ionic strength on Cu recovery and current efficiency. DCA concentration=5 mM; S/M=2.5; Voltage=-0.5 V (vs. Ag/AgCl); pH=2.0; Electroplating time=5000 seconds.

E Effect of EDTA

As previously mentioned, influence of EDTA on the recovery of metal and current efficiency might be interesting while treating metal wastewater using integrated membrane and

electroplating process. In this section, effect of EDTA on the electroplating process was investigated using electrolytes containing varied amount of EDTA (0 to 2 mM), DCA of 5 mM and S/M ratio of 2.5 at pH 2.0 and electric voltage of -0.5 V. Results show that both Cu recovery and current efficiency decrease with increases of EDTA concentration (Figure 9), indicating that an extra electric energy is needed for deposition of Cu onto electrode [9,12].

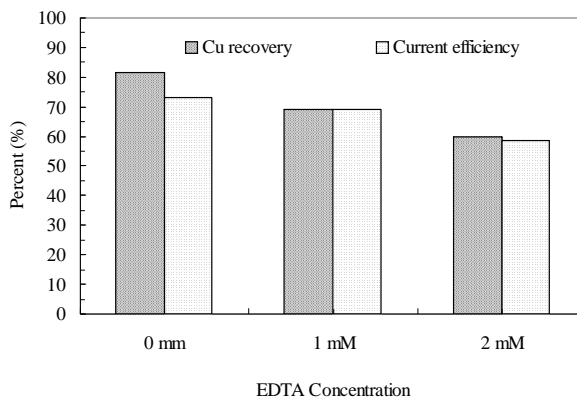


Fig. 9. Effect of EDTA on Cu recovery and current efficiency. DCA concentration=5 mM (S/M=2.5); Voltage=-0.5 V (vs. Ag/AgCl); Electroplating time=5000 seconds; pH=2.0.

As indicated early, pH is also a strong factor influencing the recovery of metals and current efficiency for electroplating process treating wastewater containing both metals and chelating agents. Figure 10 is the effect of pH on the Cu removal and current efficiency for systems containing EDTA (1mM) at pH 2.0 and 5.0. It should be noted that conductivity of electrolyte at pH 5.0 has been adjusted with NaCl to the same level as that of electrolyte for pH 2.0 to account for the conductivity effect. Both Cu recovery and current efficiency decrease with increasing pH from 2.0 to 5.0 which is similar to the results reported by others [9,10]. It is due to at lower pH, more proton ions can compete with Cu ions for EDTA sites resulted in more free Cu ions in the solution.

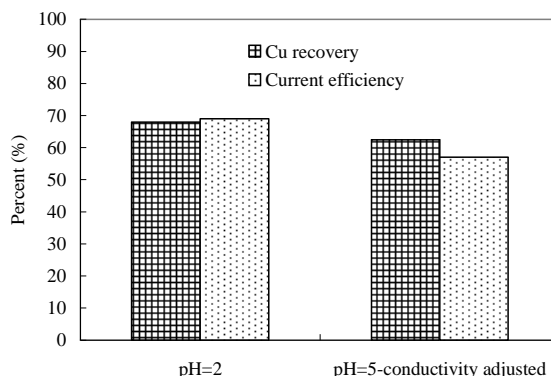


Fig. 10. Cu removal and current efficiency as function of pH for systems containing EDTA (1 mM).

IV. CONCLUSIONS

In this paper, we have investigated electroplating methods for simultaneous recovery of copper and DCA surfactant from simulate MEUF waste stream. The results from this study can be summarized as follows:

- (1) Applied voltage of -0.5 V was the optimum condition considering the amount of Cu and DCA recovered and current efficiency.
- (2) Increasing Cu recovery and current efficiency are observed with increases in Cu concentration while keeping DCA constant. However, increasing both Cu and DCA concentration while keeping S/M ratio constant at 2.5 shows detrimental effect on Cu recovery at DCA concentration higher than 15 mM.
- (3) Cu recovery decreases with increasing pH while current efficiency shows an opposite trend. It is believed that conductivity at different pHs is the main cause for discrepancy of Cu recovery and current efficiency at different pH.
- (4) Addition of NaCl up to 12000 mg/L has minimal effect on Cu recovery but current efficiency decreases slightly. It was due to increasing domination of side reactions at elevated salt concentration.
- (5) Presence of EDTA has adverse effect on both Cu recovery and current efficiency.

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