



## Rapid recovery of dilute copper from a simulated Cu–SDS solution with low-cost steel wool cathode reactor

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### ABSTRACT

Copper–surfactant wastewaters are often encountered in electroplating, printed circuit boards manufacturing, and metal finishing industries, as well as in retentates from micellar-enhanced ultrafiltration process. A low-cost three-dimensional steel wool cathode reactor was evaluated for electrolytic recovery of Cu ion from dilute copper solution (0.2 mM) in the presence of sodium dodecyl sulfate (SDS), octylphenol poly (ethyleneglycol) 9.5 ether (TX), nonylphenol poly (oxyethylene) 9 ether (NP9) and polyoxyethylene (20) sorbitan monooleate (TW) and also mixed surfactants (anionic/nonionic). The reactor showed excellent copper recovery ability in comparison to a parallel-plate reactor. The reactor rapidly recovered copper with a reasonable current efficiency. 93% of copper was recovered at current density of  $1 \text{ A m}^{-2}$  and pH 4 in the presence of 8.5 mM SDS. Initial solution pH, cathodic current density, solution mixing condition, SDS concentration, and initial copper concentrations significantly influenced copper recovery. The copper recovery rate increased with an increase in aqueous SDS concentrations between 5 and 8.5 mM. The influences of nonionic surfactants on Cu recovery from SDS–Cu solution depended not only on the type of surfactants used, but also on applied concentrations. From the copper recovery perspective, TX at 0.1 mM or NP should be selected rather than TW, because they did not inhibit copper recovery from SDS–Cu solution.

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### 1. Introduction

Surfactants (anionic/or nonionic types) are often used in Cu-related electroplating, electrowinning, and printed circuit board manufacturing industries to improve plating surface quality or to clean plating surface [1–3], as well as in the micellar-enhanced ultrafiltration process (MEUF) to enhance the separation of metals [4–5]. The presence of heavy metals in wastewater poses risks to human health and the environment.

Many techniques have been developed to remove metals, including chemical precipitation, ion exchange, and the electrolytic process. Chemical precipitation treatment generates a large amount of sludge, leading to sludge disposal problems. Ion exchange can effectively recover metal ions, but the high cost of resin limits its application. The electrolytic process has the advantages of metal recovery without further sequential treatment. A mass transfer rate of metal ions from solution to cathode is critical for metal electrolytic recovery. However, metal ion transfer rates in dilute solution are low.

Three-dimensional electrolytic reactors have large electrode surfaces and short distance for metal ion transport from solution to cathode. These reactors can significantly improve mass transfer rates and significantly increase current efficiency. Many types of three-dimensional electrolytic reactors have been developed, including the fluidized-bed electrolytic cell [6], the rotating packed cell [7], porous graphite, reticulated vitreous carbon [8], and the steel wool cathode reactor [9–11]. The steel wool cathode reactor has many advantages, such as low-cost, simple assembly, and high current efficiency. It has been used for metal recovery from dilute solution including gold [10], cadmium [11], lead [12], and copper [9]. The operating parameters including initial metal concentration, pH, conductivity, current density, mixing condition, and supporting electrolytes have been investigated for their effects on metal recovery by steel wool reactors [9–12].

Since electroplating wastewater and retentate from MEUF often contain copper ion and surfactants, anionic surfactants, which compose the negatively charged hydrophilic parts, can electro-statically attract positively charged metal ions, leading to the interference of electrolytic metal recovery [5,13]. Additionally, if nonionic surfactants coexist with the anionic surfactant in the wastewater, they will attract each other with their hydrophobic tails. The mixed anionic and nonionic surfactants may inhibit the mass transfer of metal ions and reduce current efficiency. Studies on metal

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**Table 1**  
Properties of SDS, Triton X-100, NP9, and Tween 80

Name	Chemical formula	Property	MW (g mol <sup>-1</sup> )	CMC (mM)	Aggregation number
SDS	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> OSO <sub>3</sub> Na	Anionic	288	7.9	55–65
Triton X-100	C <sub>8</sub> H <sub>17</sub> C <sub>6</sub> H <sub>4</sub> O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>9.5</sub> H <sup>a</sup>	Nonionic	625	0.24 <sup>a</sup>	140
NP9	C <sub>9</sub> H <sub>19</sub> C <sub>6</sub> H <sub>4</sub> (OCH <sub>2</sub> CH <sub>2</sub> ) <sub>9</sub> OH	Nonionic	630	0.064	–
Tween 80	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	Nonionic	1300	0.01	59

<sup>a</sup> The number “9.5” represents the average number of ethylene oxide units per Triton X-100 molecule.

recovery from surfactant–metal solution by 3D electrolytic reactor are limited.

In this study, electrolysis experiments were conducted to evaluate the influences of pH, current density, solution mixing, SDS concentration, and copper concentration on copper recovery from a simulated dilute copper solution by steel wool cathode reactor. Effects of mixed surfactants (anionic/nonionic) on copper electrolytic recovery were also investigated. The aims of this study are to provide valuable information on selected optimal operating conditions for copper recovery from electroplating wastewater and retentates from MEUF.

## 2. Materials and methods

### 2.1. Chemicals

CuSO<sub>4</sub> was obtained from Arcos (analytic grade, Panreac Química, E.U.). Four surfactants used in this study included an anionic surfactant, SDS (sodium dodecyl sulfate, purity 90%, Sigma), and three nonionic surfactants, Triton X-100 (octylphenol poly (ethyleneglycol) 9.5 ether, HPLC grade, Merck), NP9 (nonylphenol poly (oxyethylene) 9 ether, purity > 97%, First Chemical, Taiwan), and Tween 80 (polyoxyethylene (20) sorbitan monooleate, purity: 99%, American Biorganics Inc., USA). The properties of surfactants are listed in Table 1.

### 2.2. Electrolysis experiment

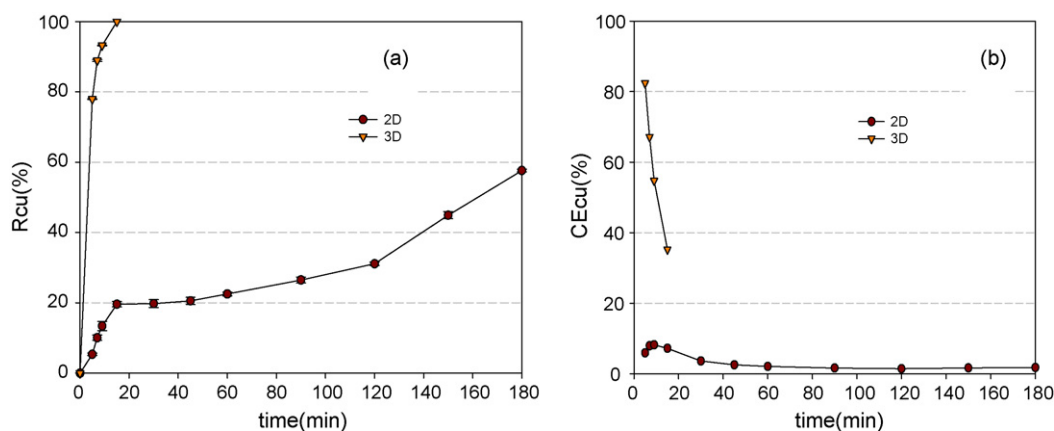
The electrolysis experiment was conducted in a 600 mL beaker containing 500 mL of surfactant–copper solution. For the 2D electrolysis experiment, two parallel stainless plates (3 cm × 7 cm) were used as electrodes. The distance between the two electrodes was 1 cm. For the three-dimensional electrolysis experiment, stainless plate (3 cm × 7 cm) and steel wool (0.5 mm width, total area: 626 cm<sup>2</sup>) were employed as anode and cathode, respectively. The

length and width of a strip of steel wool with known mass was measured under a microscope. Then, the total surface area of the steel wool cathode was calculated from the product of the total mass of the cathode and its specific surface per unit mass. The anode was wrapped with nylon net to separate the two electrodes. The electrodes were rinsed in 30% HNO<sub>3</sub> and washed with distilled water before the experiment. The electrolysis experiment was conducted under galvanostatic conditions using a regulated DC power supply (GP C-3030D, Taiwan). The solution was sufficiently mixed by a magnetic stirrer. Samples were withdrawn at specific time intervals and analyzed for copper with flame atomic-absorption spectrophotometer (PerkinElmer, Model 3300).

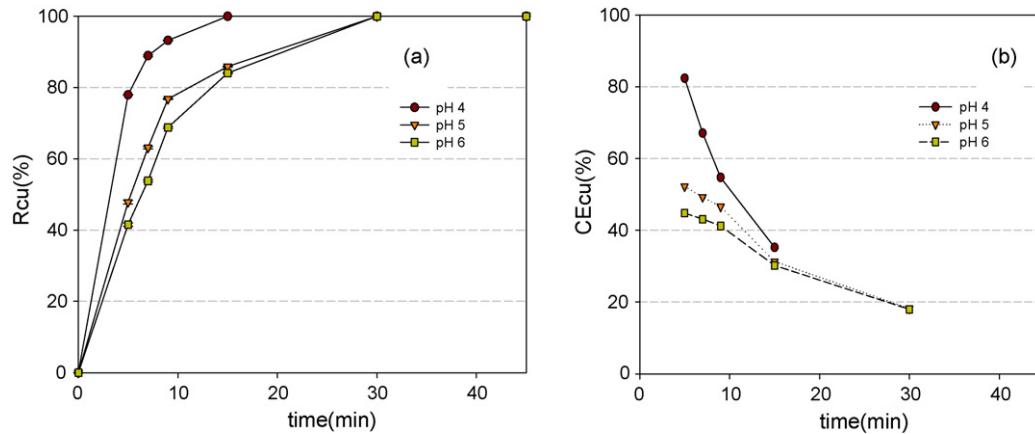
## 3. Results and discussion

### 3.1. Copper recovery by 2D and 3D reactors

First, a comparative study of copper recovery by two-dimensional parallel-plate reactor and three-dimensional steel wool cathode reactor was conducted. The experimental conditions were 8.5 mM SDS, 0.2 mM Cu<sup>2+</sup>, initial solution pH 4, supporting electrolyte of 0.1 M Na<sub>2</sub>SO<sub>4</sub>, stirring speed 1080 rpm, and current density 1 A m<sup>-2</sup>. Fig. 1 shows that 50% of copper recovery was obtained after electrolysis time of 180 min by using the parallel-plate reactor (Fig. 1a). The current efficiency was very low (<1%, Fig. 1b). In contrast, when the steel wool cathode reactor was applied, the Cu recovery rate and current efficiency improved significantly. For example, 93% of copper was recovered within 9 min of electrolytic time and a reasonable current efficiency of 55% was obtained. This indicates that the steel wool cathode reactor was suitable for copper recovery from dilute solution even in the presence of SDS. Copper electrolysis involves three steps: copper ions transfer from the solution to the cathode surface, receive electrons, are reduced to element copper, and form a lattice layer on the cathode surface.



**Fig. 1.** Copper recovery by parallel-plate reactor and steel wool cathode reactor. (a) Copper recovery efficiency, (b) current efficiency. Electrolytic conditions: Cu 0.2 mM, SDS 8.5 mM, pH 4, Na<sub>2</sub>SO<sub>4</sub> 0.1 M, cathodic current density 1 A m<sup>-2</sup>, magnetic stirring speed: 1080 rpm.



**Fig. 2.** Effects of initial solution pH (4, 5, and 6) on copper recovery. (a) Copper recovery efficiency, (b) current efficiency. Electrolytic conditions: Cu 0.2 mM, SDS 8.5 mM, Na<sub>2</sub>SO<sub>4</sub> 0.1 M, cathodic current density: 1 A m<sup>-2</sup>, magnetic stirring speed 1080 rpm.

As is well known, a two-dimensional electrolysis reactor (parallel-plate reactor) is not suitable for recovery of metals in dilute solution because of the low mass transfer of metal ions from solution to cathode and low current efficiency. Three-dimensional electrolytic reactors that have large electrode surface areas and high mass transfer rates are developed to improve the metal recovery and current efficiency. The results of this study indicate that steel wool cathode reactor has certain advantages for copper recovery from a dilute solution, including short electrolytic time needed, high current density, simple structure, low operation and installation cost, and avoidance of the generation of a huge amount of sludge like the chemical precipitation process. Therefore, the application of a steel wool cathode reactor for copper recovery from dilute solution is economically feasible.

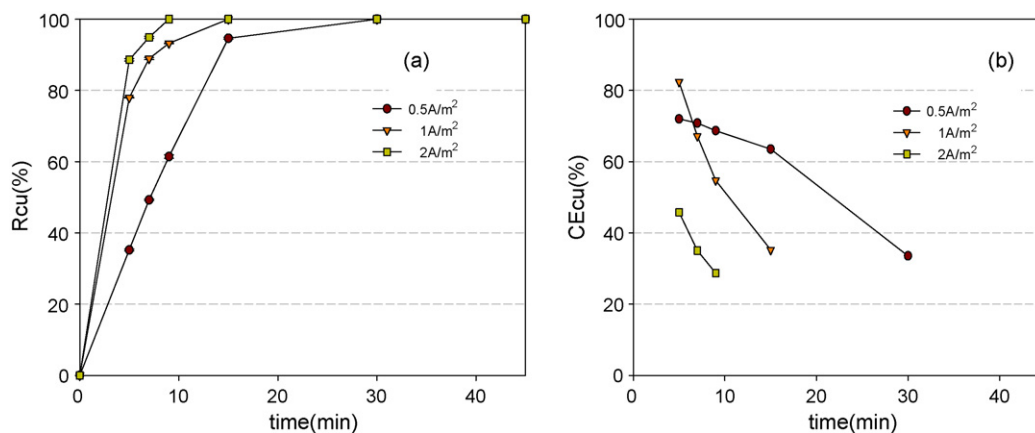
The performance of a spiral wound steel cathode electrolytic reactor for metal recovery from dilute solution has been investigated by Elsherief [11]. He suggests that the polarization curves can be used to realize the relationships between kinetic electrolysis of cadmium recovery and the respective current density. In this study, stainless steel plate was used as the anode because of its low cost and ease to obtain and the short electrolysis time (within 12 min) needed in this study. However, because steel wool cathode reactors operate for a long time in field application, inert materials should be used as anode to avoid anode corrosion.

### 3.2. Effects of solution pH

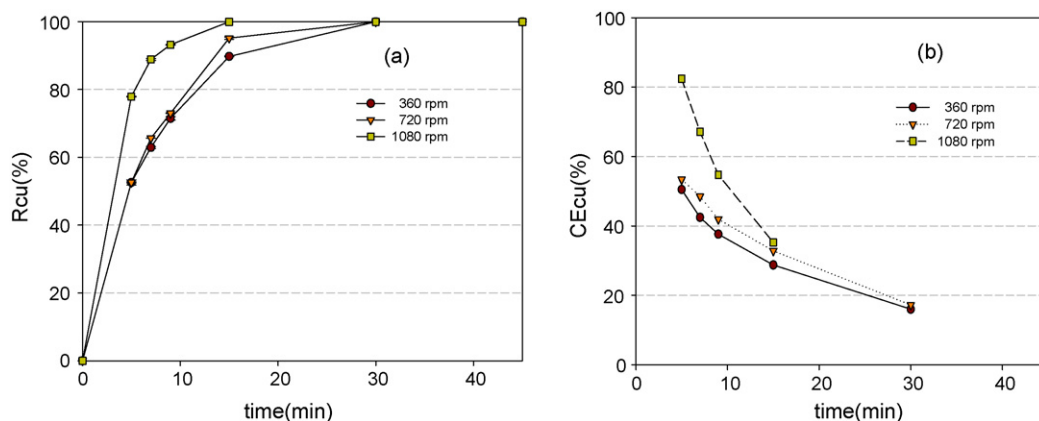
The effect of initial solution pH (4, 5, and 6) on electrolytic copper recovery was investigated. The experimental conditions were 8.5 mM SDS, 0.2 mM Cu<sup>2+</sup>, and cathode current density 1 A m<sup>-2</sup>. Fig. 2 illustrates that the copper recovery efficiency increased with the decrease of initial solution pH. For example, when the initial solution pH was 6, only 67% of copper recovery (current efficiency 31%) was obtained after 9 min electrolysis. As the initial solution pH decreased to 4, the copper recovery significantly increased to 93% at a current efficiency of 55% (Fig. 2b). It is possible that most SDS presented in anionic form at solution pH higher than 1.5 (pK<sub>a</sub> of SDS) [14]. The negatively charged SDS and positively charged Cu<sup>2+</sup> electro-statically attracted each other, leading to inhibition of copper recovery. When the solution decreased to pH 4, hydrogen ions competed with Cu<sup>2+</sup> for SDS, and most Cu<sup>2+</sup> presented in free form. Thus the copper recovery rate was enhanced.

### 3.3. Effects of cathode current density

Fig. 3 shows the effects of cathode current density (0.5, 1 and 2 A m<sup>-2</sup>) on copper recovery. As expected, an increase in cathode current density significantly enhanced the copper recovery rate, and the current efficiency decreased. For example, 62% copper was recovered after 9 min at cathode current density 0.5 A m<sup>-2</sup>. As the cathode current density increased to 2 A m<sup>-2</sup>, >99% copper recovery



**Fig. 3.** Effects of cathodic current density (0.5, 1 and 2 A m<sup>-2</sup>) on copper recovery. (a) Copper recovery efficiency, (b) current efficiency. Electrolytic conditions: Cu 0.2 mM, SDS 8.5 mM, pH 4, Na<sub>2</sub>SO<sub>4</sub> 0.1 M, magnetic stirring speed 1080 rpm.



**Fig. 4.** Effects of magnetic stirring speed (360, 720, and 1080 rpm) on copper recovery. (a) Copper recovery efficiency, (b) current efficiency. Electrolytic conditions: Cu 0.2 mM, SDS 8.5 mM, pH 4,  $\text{Na}_2\text{SO}_4$  0.1 M, cathodic current density  $1 \text{ A m}^{-2}$ .

was obtained, but current efficiency obviously decreased to 28%. This is because the transport rate of copper ions from the solution to the cathode surface was much slower than the reduction rate of  $\text{Cu}^{+2}$  ions on the cathode surface, which was limited in the dilute solution when a higher cathode current density was applied.

#### 3.4. Effects of mixing condition

Three stirring speeds (350, 720, and 1080 rpm) were chosen to evaluate the effects of mixing conditions on copper recovery. Fig. 4 shows that when mixing speeds were reduced from 1080 to 720 rpm, the copper recovery efficiency significantly decreased from 93% (current efficiency 55%) to 73% (current efficiency 42%) after 9 min electrolysis. This suggests that the mixing condition was also an important factor for copper recovery by steel wool cathode reactor. Several studies reported that an increase in mixing conditions reduces the electric double layer thickness of the cathode, resulting in enhanced mass transfer of metal ions to cathode surfaces and improved metal recovery efficiency [8,13].

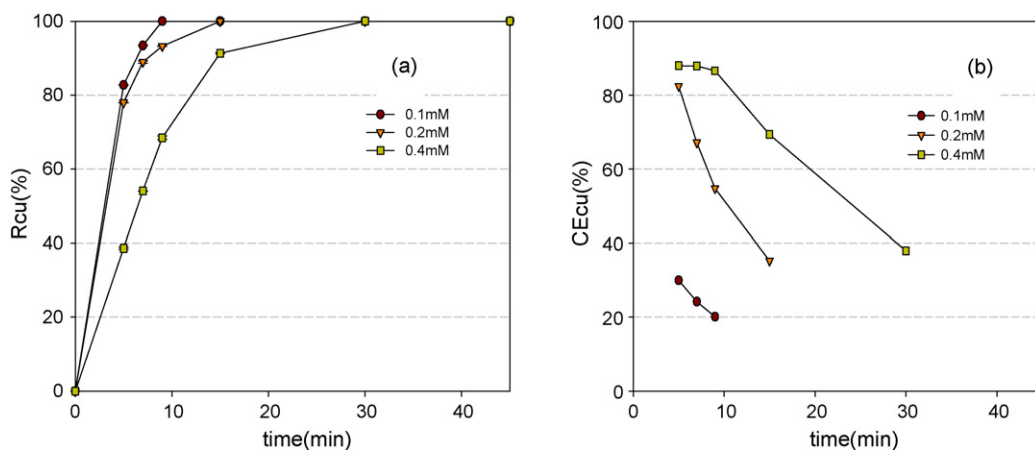
#### 3.5. Effects of initial copper ion concentration

The initial copper ion concentrations (0.1, 0.2, and 0.4 mM) were investigated for their effects on copper recovery at current density of  $1 \text{ A m}^{-2}$  and pH 4. Fig. 5 shows that an increase in the initial copper concentrations reduced copper recovery efficiency. For

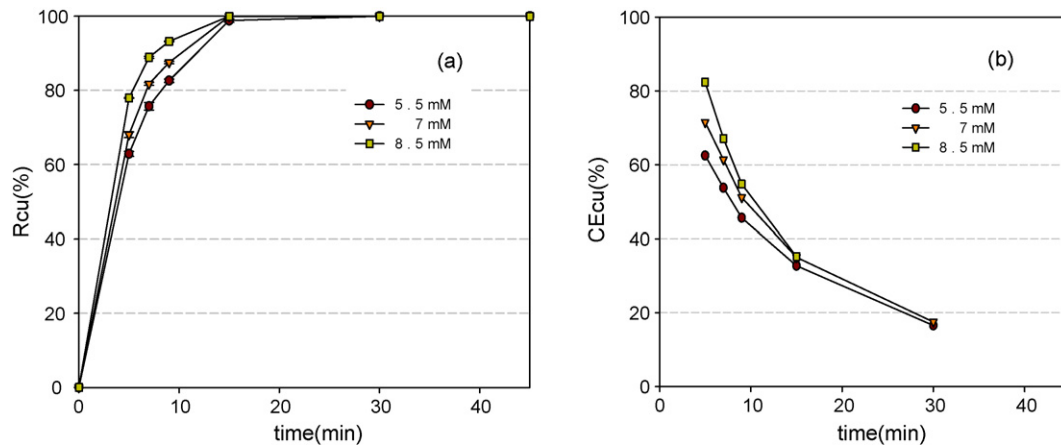
example, 95% copper (current efficiency 24%) was obtained when the initial copper concentration was 0.1 mM at 7 min electrolysis time. When initial copper concentrations increased to 0.4 mM, the electrolysis time needed was 15 min to achieve 95% copper recovery (current efficiency 69%). The phenomenon that high current efficiency was obtained for high initial Cu concentration can be explained by the fact that the transport rate of copper from solution to cathode increased with an increase in the initial copper concentrations, reducing the side effects of hydrogen generation at the cathode.

#### 3.6. Effects of SDS concentrations

Effects of SDS concentrations (5.5, 7, and 8.5 mM) on copper recovery were investigated under the experimental conditions of 0.21 mM  $\text{Cu}^{+2}$ , pH 4, and cathodic current density of  $1 \text{ A m}^{-2}$  (Fig. 6). It was expected that when the SDS concentrations increase, the copper recovery would decrease. However, it is interesting that the copper recovery increased with an increase of SDS concentrations in the applied dose ranges. For example, the copper recoveries were 82% and 93% at SDS concentrations of 5.5 and 8.5 mM, respectively, at electrolysis time of 9 min. Huang [13] indicates that anionic surfactants could reduce electrolytic recovery of copper through the following processes: (1) The surfactants sorb onto the cathode surface and reduce the effective surface of cathode; (2) The long molecular chain-length of the surfactants decreases the mass transfer in solution. However, in this study, the increase in SDS



**Fig. 5.** Effect of initial copper concentrations (0.1, 0.2, and 0.4 mM) on electrolytic copper recovery. (a) Copper recovery efficiency, (b) current efficiency. Electrolytic conditions: SDS 8.5 mM, pH 4,  $\text{Na}_2\text{SO}_4$  0.1 M, cathodic current density  $1 \text{ A m}^{-2}$ , magnetic stirring speed 1080 rpm.

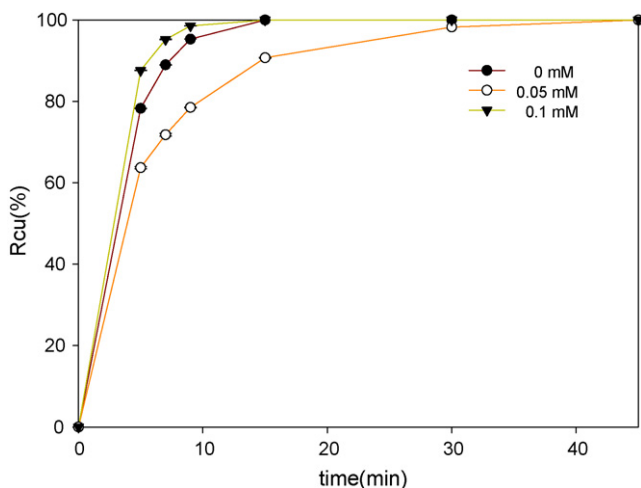


**Fig. 6.** Effects of SDS concentrations (5.5, 7, and 8.5 mM) on electrolytic copper recovery. (a) Copper recovery efficiency, (b) current efficiency. Electrolytic conditions: Cu 0.21 mM, pH 4, Na<sub>2</sub>SO<sub>4</sub> 0.1 M, cathodic current density 1 A m<sup>-2</sup>, magnetic stirring speed 1080 rpm.

concentrations enhanced the copper recovery. It is possible that as SDS concentrations increased above its critical micelle concentrations (7.9 mM, Table 1), SDS micelles were formed. Copper ions that electro-statically absorbed on the negatively charged outer surface of SDS micelles had more opportunity to contact with cathode than copper sorbed on the long-chain head of the SDS monomer at SDS concentrations below its critical micelle concentration (CMC).

### 3.7. Effects of mixture of anionic and nonionic surfactants

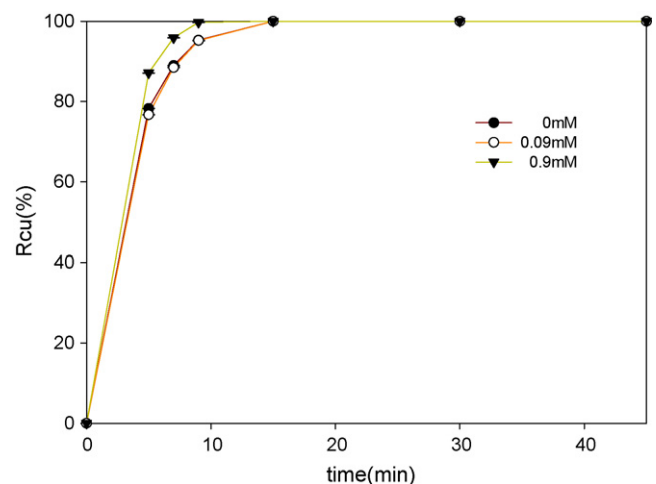
The presence of surfactant mixtures (anionic and nonionic surfactants) is often encountered in metal-surfactant wastewater. Effects of the mixed surfactants on copper recovery were investigated. One anionic surfactant, SDS, and three nonionic surfactants, Triton X-100 (TX), NP9, and Tween 80 (TW), were used. Their properties are listed in Table 1. SDS concentration was fixed at 8.5 mM. The nonionic surfactant concentrations used were chosen because their applied dose did not seriously influence the solution viscosity. The applied nonionic surfactant concentrations were Triton X-100: 0.05 mM (0.2 CMC) and 0.1 mM (0.42 CMC); NP9: 0.09 mM (1.4 CMC) and 0.9 mM (14 CMC); Tween 80 (TW): 0.03 mM (3 CMC) and 0.3 mM (10 CMC). The electrolytic conditions were Cu<sup>2+</sup> of 0.2 mM, cathodic current density of 1 A m<sup>-2</sup>, and pH 4.



**Fig. 7.** Effects of Triton X-100 on copper recovery. Electrolytic conditions: Cu 0.2 mM, SDS 8.5 mM, pH4, cathodic current density 1 A m<sup>-2</sup>, magnetic stirring speed 1080 rpm.

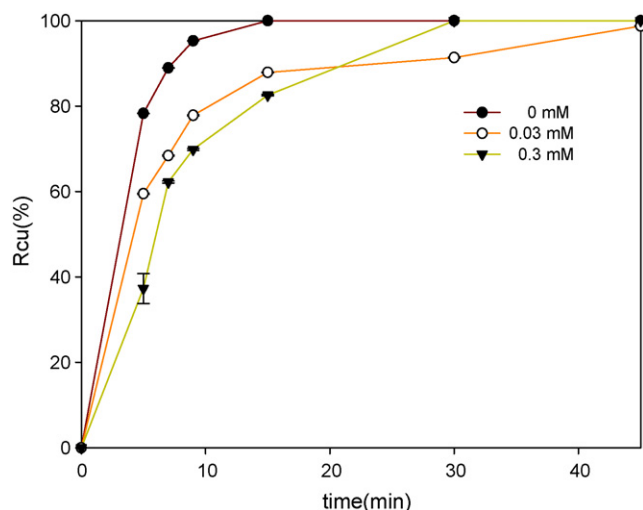
Fig. 7 indicates that the presence of 0.05 mM TX significantly inhibited the copper recovery in comparison to the solution without TX. When the TX concentration increased to 0.1 mM, copper recovery efficiency was enhanced. In contrast, NP9 at 0.09 mM did not significantly influence copper recovery in comparison to the solution without NP (Fig. 8). However, as NP concentrations increased to 0.9 mM, the copper ion recovery efficiency was enhanced. The addition of TW (0.03–0.3 mM) greatly inhibited the copper recovery (Fig. 9). This indicates that the effects of nonionic surfactants on copper recovery depended not only on the types of surfactants but also on their doses.

To further investigate whether effects of nonionic surfactants on copper recovery were related to their concentrations above or below micelle concentrations, the surfactant concentrations were calculated as multiples of micelle concentrations. Table 2 shows that the addition of nonionic surfactant, whether above its CMC or not, did not significantly affect the copper recovery. For example, both TX and NP9 are alkyl phenol ether, and they have similar molecular structures and molecular weight (Table 2). 0.1 mM of TX (0.42 CMC) enhanced the copper recovery; however, 0.09 mM of NP showed no effects. Besides, the applied TW doses of 0.03 mM (3 CMC) and 0.3 mM (10 CMC) seriously inhibited copper recovery. It is possible that the large molecular weight of TW (1300 g mol<sup>-1</sup>) inhibited the mass transfer of copper ions in the solution [13].



**Fig. 8.** Effects of NP9 on copper recovery. Electrolytic conditions: Cu 0.2 mM, SDS 8.5 mM, pH4, cathodic current density 1 A m<sup>-2</sup>, magnetic stirring speed 1080 rpm.





**Fig. 9.** Effects of Tween 80 on copper recovery. Electrolytic conditions: Cu 0.2 mM, SDS 8.5 mM, pH4, cathodic current density  $1 \text{ A m}^{-2}$ , magnetic stirring speed 1080 rpm.

**Table 2**  
Effects of nonionic surfactants on copper recovery from SDS–Cu solution

	0.2 CMC	0.42 CMC	1.4 CMC	3 CMC	14 CMC	30 CMC
TX	– <sup>a</sup>	+ <sup>b</sup>				
NP			0 <sup>c</sup>		+ <sup>b</sup>	
TW				– <sup>a</sup>		– <sup>a</sup>

<sup>a</sup> –: inhibition.

<sup>b</sup> +: enhancement.

<sup>c</sup> 0: no effect.

Therefore, from the copper recovery perspective, if nonionic surfactants should be used, TX at 0.1 mM or NP should be selected rather than TW, because they did not inhibit copper recovery from the SDS–Cu solution.

#### 4. Conclusions

A steel wool cathode reactor could rapidly recover copper from dilute solution with an acceptable current efficiency in comparison to a parallel-plate reactor. The initial solution pH, applied cathodic

current, mixing effects, and initial copper concentrations had significant influences on copper recovery. The copper recovery rate increased with an increase in aqueous SDS concentrations between 5 and 8.5 mM. The effects of nonionic surfactants on Cu recovery from the SDS–Cu solution were significantly influenced by both the types of the applied surfactants used and their applied dose. The addition of either Triton X-100 above 0.1 mM or NP9 did not inhibit copper recovery from the SDS–Cu solution. From the copper recovery perspective, TX at 0.1 mM or NP should be selected rather than TW, because they did not inhibit copper recovery from SDS–Cu solution.

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