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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 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.

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^{-1})	CMC (mM)	Aggregation number
SDS	$CH_3(CH_2)_{11}OSO_3Na$	Anionic	288	7.9	55–65
Triton X-100	$C_8H_{17}C_6H_4O(CH_2CH_2O)_{9.5}H$[a]	Nonionic	625	0.24[a]	140
NP9	$C_9H_{19}C_6H_4(OCH_2CH_2)_9OH$	Nonionic	630	0.064	–
Tween 80	$C_{18}H_{34}O_2$	Nonionic	1300	0.01	59

[a] 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

$CuSO_4$ was obtained from Arcos (analytic grade, Panreac Qulmica, 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^2) 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_3 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^{+2}, initial solution pH 4, supporting electrolyte of 0.1 M Na_2SO_4, stirring speed 1080 rpm, and current density 1 A m^{-2}. 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.

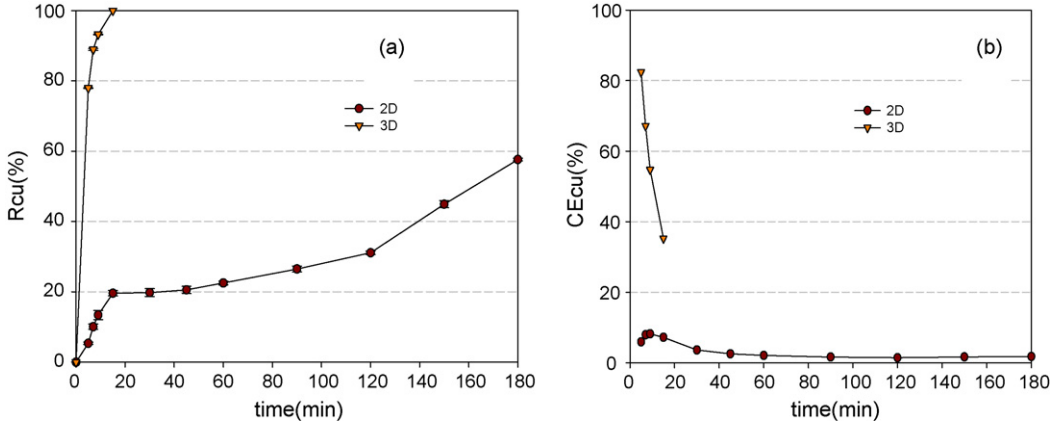

Fig. 1. Copper recovery by parallel-plate reactor and steel wool cathode reactor. (a) Copper recovery efficiency, (b) current efficiency. Electrolytic conditions: Cu 0.2 mM, SDS 8.5 mM, pH 4,Na_2SO_4 0.1 M, cathodic current density 1 A m^{-2}, magnetic stirring speed: 1080 rpm.