

The behavior of organic components in copper recovery from electroless plating bath effluents using 3D electrode systems

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Received 17 November 2003; received in revised form 11 May 2004; accepted 13 May 2004

Available online 2 July 2004

Abstract

An electrochemical method was applied for the recovery of copper both from the spent solutions and from the rinse waters of electroless copper plating baths, containing copper sulfate, formaldehyde, quadrol, and NaOH. Experiments were conducted in a rotating packed cell (Rollschichtzelle[®]) to investigate the effects of current density, electrolyte composition, temperature, and pH on the copper recovery. All the copper (final $C_{Cu} = 0.1$ ppm) was recovered from the waste and rinse waters of chemical copper plating plants with 70% current efficiency by the electrochemical treatment in a rotating packed cell at 130 A/m² current density, room temperature, with 5 mm diameter cathode granules, with the presence of formaldehyde, and with a specific energy consumption of 3.2–3.5 kW h/kg Cu. On the other hand, final copper concentrations of 5 ppm were reached with 62% current efficiency and 5.5–5.8 kW h/kg Cu specific energy consumption, with electrolytes containing no formaldehyde.

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Keywords: Electroless copper plating; Copper recovery; Copper reduction electrolysis; Quadrol; Formaldehyde

1. Introduction

Electroless copper plating has numerous areas of application in materials and products, such as, thermoplastics, thermosets, printed circuit boards, etc., in parallel to its increasing industrial usage within the last decades, especially in the fields of communication, informatics, automotive, and electronics, where, savings in weight and material are demanded. These plating baths typically contain an inorganic copper salt (copper sulfate), an alkaline reagent (NaOH), a reducing substance (i.e., formaldehyde (HCHO)), and a complexing agent (i.e., EDTA, quadrol, etc.), to prevent copper from precipitating in the form of hydroxide under the chemical copper plating conditions (pH 11–13) [1,2]. Chemical reduction mechanism and anodic reaction could not exactly be defined yet, even though electroless copper plating baths are extensively used and the individual effects of bath components on the reaction rate have been thoroughly investigated.

Bath composition weakens, in terms of copper and formaldehyde concentrations as the plating operation pro-

gresses. The process eventually halts, when the copper concentration reaches 500 ppm [3,4]. Thus, it is essential to control the concentration of these ions and to make up from time to time. However, the bath must inevitably be replenished after a few additions. Spent electrolytes, as they contain quadrol and copper, are even more difficult to process than the rinse waters, form during the washing of plated material. Process streams coming from the chemical copper plating baths (rinse waters and spent electrolytes that lost their plating capabilities), are treated by various methods, such as chemical precipitation, electrolysis, ozone treatment, etc. The main and side reactions that occur during the electrochemical treatment of these solutions are as follows [1,5–10].

1.1. Main reactions

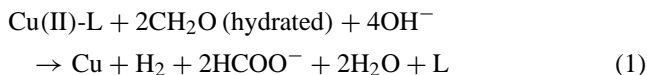
The advantage of electrolysis over the other solution purification methods is that the simultaneous elimination of both copper that exists in rinse waters or spent electrolyte via cathodic reduction, and organics, such as formaldehyde and quadrol by anodic reaction.

In the case of the conventional alkaline formaldehyde containing solutions, the total process of auto catalytic Cu(II)

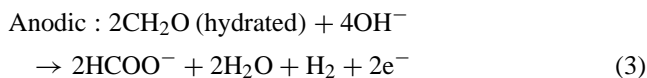
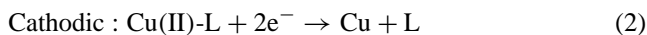
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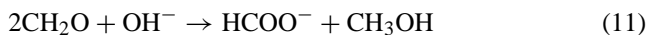
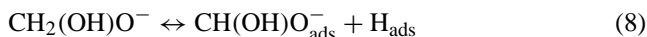
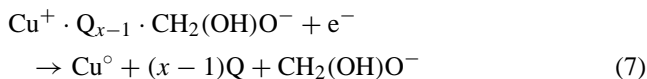
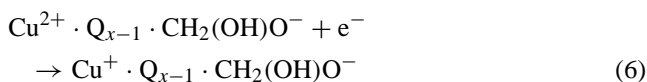
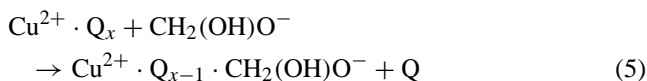
reduction occurs as follows [7,9]:



1.2. Partial reactions



1.2.1. Some important side reactions



where L: ligand, Q: Quadrol, and E: EDTA.

The structure of the complex that *N,N,N',N'*-tetrakis(2-hydroxypropyl)ethylenediamine (THPED) (commercially known as “quadrol”), forms with Cu^{2+} , changes with the solution pH. Norkus et al. have shown that pCu increases within the pH range 6–8, whereas, complex formation with quadrol starts when pH reaches 8 [8]. They have also indicated that the polarographic measurements increase enormously for pH values of >10, which can be explained by the exponential decrease of free Cu^{2+} in the solution [8].

Elimination of metals from electroless copper plating spent electrolytes, is investigated in an earlier study by Müller [11], where EDTA was disintegrated in a packed bed electrolysis cell. The electrolyte, containing 5 g/L EDTA and 1 g/L Cu^{2+} was electrolyzed for 14 h, and the final EDTA concentration decreased to 0.2 g/L. Juang and Shioh-Wen [12], electrochemically recovered more than 96% of the Cu(II) and Pb(II) ion couple, complexed with EDTA, with higher than 30% current efficiency in a membrane cell at 139 A/m² current density and catholyte pH of 2.08, in 50 min of electrolysis time.

2. Experimental

2.1. Equipment—rotating packed cell

The electrolysis of dilute solutions is diffusion controlled. Diffusion limiting current density decreases as the ion concentration in the solution diminishes. The practical meaning of this is that the current efficiency remarkably decreases due to the secondary reactions that occur on the cathode surface (i.e., hydrogen evolution). Therefore, the classical electrolysis cells are not suitable for the electrolysis of dilute solutions and accelerated electrolysis conditions (the highest possible current per unit area) must exist in a unit volume while residing within the economic limits of current efficiency. Cells with cathodes having large or extended surfaces can thus, be appropriately used for this purpose. A rotating packed cell is used in this study where copper granules with different diameters served as cathode with enlarged surface area. The schematic of the experimental cell is displayed in Fig. 1, while the experimental setup is shown in Fig. 2.

2.2. Investigated parameters

The effects of the cathodic current density (130–325 A/m²); current (2–5 A), electrolyte temperature (20–50 °C), electrolyte pH (8–12), and formaldehyde addition (0–2.2 g/L) on copper recovery were investigated. Cathode granule diameters of 5 mm and cell rotation of 4 min⁻¹ were kept constant in all experiments.

2.3. Electrolyte

The solution used in this study contained: 2–3.5 g/L Cu^{2+} , 8–15 g/L NaOH, 2.2–4.8 g/L formaldehyde, and 25–30 g/L quadrol. It was originally produced by Enthone OMI GmbH (Germany) under the trade name of ENPLATE Cu 872 and was kindly supplied by Saxonia Edelmetalle

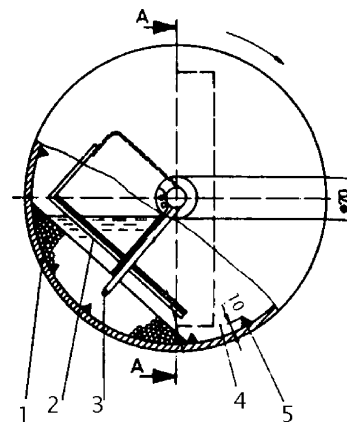


Fig. 1. Cross-sectional view of the rotating packed cell ((1) cathode granules; (2) anode plate; (3) cathodic contact; (4) electrolyte; and (5) cathode carrier). (Rotating disk diameter, 38.5 cm; disk width, 6 cm; cathode area, 153.8 cm²; anode area, 80 cm²).

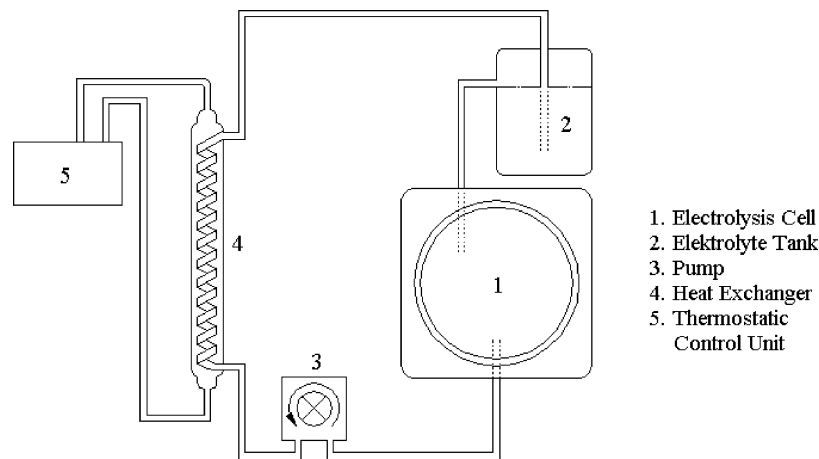


Fig. 2. Schematics of the experimental setup (cell volume, 2 L; reservoir volume, 1.6 L).

GmbH (Germany). Electrolyte volume used in the experiments was 3.6 l. Elemental analyses of the solutions were carried out by the Atomic Absorption Spectrophotometer (Perkin–Elmer, 1100B), whereas, those of formaldehyde, quadrol, and NaOH were conducted gravimetrically.

3. Results and discussions

3.1. Effect of current density

In the first part of experimental study, the effect of current density on copper recovery was investigated. A solution containing 2.3 g/L Cu^{2+} , 2.5 g/L HCOH, and 30 g/L quadrol was electrolyzed in Rollschichtzelle by using copper granules with 5 mm in diameter as the cathode, at 20 °C, 4 min⁻¹ rotational speed, and at different current densities (130 and 325 A/m²) to see the change in copper concentration (Fig. 3).

As seen in Fig. 3, not only the electrolytic reduction (reaction 3) but also the formaldehyde, behaving catalytically at

Table 1

The change in electrolysis parameters depending on the current density (20 °C; ϕ 5 mm; 4 min⁻¹; final Cu^{2+} concentration 0.1 ppm)

Cathodic current density (A/m ²)	η (%)	E_c (V)	W_s (kWh/kg Cu)
130 (=2 A)	70.5	2.2	3.5
325 (=5 A)	43.9	3.0	6.2

130 A/m², affects the chemical reduction (reaction 4) mechanism. Thus, the reduction of copper ions exceeds the theoretically possible values and current efficiencies of over 100% were reached.

It is apparent from Fig. 3 that the reaction rate changes after the second-hour of the experiments, run at 325 A/m². After the second-hour, strong side reactions start to occur in the solution with 120 ppm Cu^{2+} . At 130 A/m² however, this type of a break is observed at 60–80 ppm Cu^{2+} . Table 1 displays, the mentioned quantities for both current densities and electrolyses lasted until the final copper concentrations of 0.1 ppm.

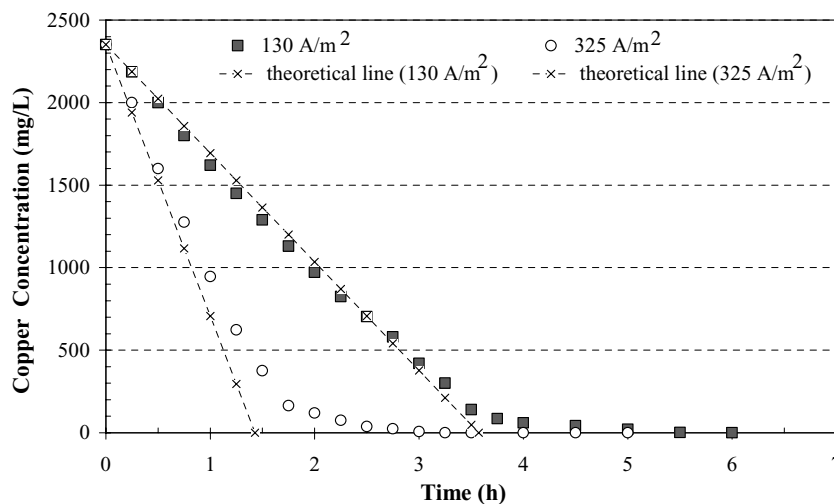


Fig. 3. Effect of current density on copper recovery (20 °C; ϕ 5 mm; 4 min⁻¹).

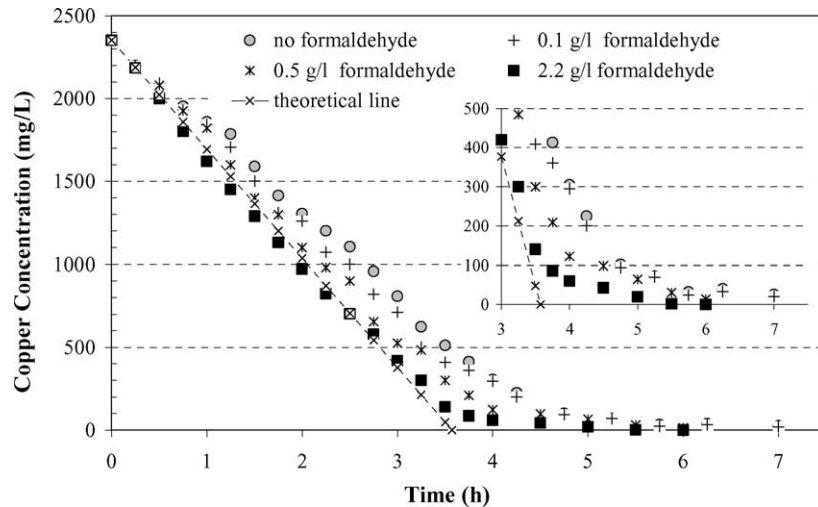


Fig. 4. Effect of formaldehyde on copper removal (130 A/m^2 ; 20°C ; $\phi 5 \text{ mm}$; 4 min^{-1}).

As seen from Table 1, the same amount of copper was recovered 99.99% more economically at 130 A/m^2 , while, the other electrolysis parameters were constant.

3.2. Effect of formaldehyde concentration

Fig. 4 displays, the results of experiments conducted at 130 A/m^2 and 20°C , to investigate the effect of formaldehyde concentration, while keeping the rest of the electrolysis parameters constant. Copper concentration versus time curves are shown for various formaldehyde contents of the solution. The change in copper concentration exhibits a linear relationship with the initial formaldehyde concentration. A similar trend is observed on all the curves below 150 ppm Cu^{2+} concentration, indicating that the copper removal rate solely depends on the current passing through the circuit and the electrolysis time. The amount of copper, reduced by the formaldehyde, varies depending on the experimental condi-

tion. Chemical analyses were carried out at the third-hour of the experiment, run at 130 A/m^2 and 20°C , to determine how the retardation of the chemical reaction was related with the copper-formaldehyde concentration. As a result of the analysis, it was found that 420 ppm Cu existed in the solution, whereas, the formaldehyde concentration was 1.15 g/L . These values were: Cu^{2+} 140 ppm , and HCOH 0.95 g/L , at the end of three and half hours. In other words, the reducing substance, which exists in the waste solution of high concentrations ($>500 \text{ ppm Cu}^{2+}$), becomes inefficient during the final steps of copper removal as the catalytic activation process ceases.

Considering these analytical results and the data available in the literature about the utilization limits of electroless plating baths, it is evident that the chemical reduction rate is restricted by the copper concentration of the solution. Therefore, it is essential to apply processes, such as electrolysis or chemical salt production (oxidative complex decomposi-

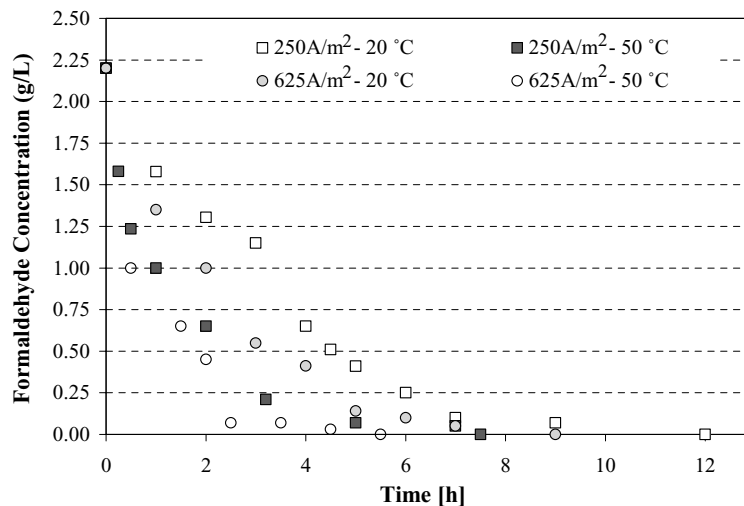


Fig. 5. The change in formaldehyde concentration at different anodic current densities and temperatures ($\phi 5 \text{ mm}$; 4 min^{-1}).

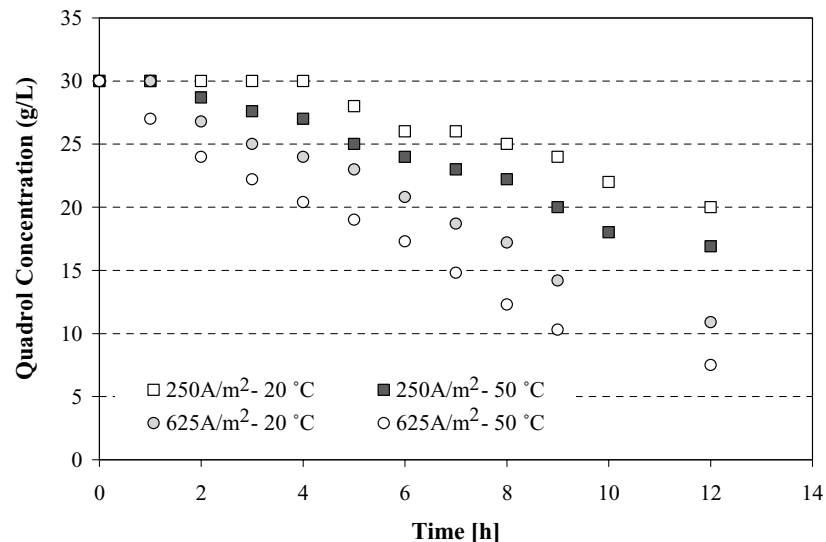


Fig. 6. The change in quadrol content of the electrolyte at different anodic current densities and temperatures (ϕ 5 mm; 4 min^{-1}).

tion + neutralization, or insoluble salt precipitation) for the standardization of ionic concentration values of these types of solutions.

In the experiment, where only electrochemical reduction takes place (electrolyte with no formaldehyde) a current efficiency of 62% is reached at 5 ppm final copper concentration, and with 5.6 kWh/kg Cu specific energy consumption. Adding 2.2 g/L formaldehyde to electrolyte, while keeping the rest of the electrolysis conditions constant and for the same final copper concentration, causes the current efficiency to reach 75% with a corresponding decrease in energy consumption (3.25 kWh/kg Cu). Formaldehyde addition causes chemical reduction of the copper in the solution, instigating an additional 20% increase in current efficiency.

3.3. Anodic decomposition of formaldehyde and quadrol

The effects of some organic components were also tested while determining the conditions of optimum copper recovery from the spent electrolytes and rinse waters of electroless copper plating baths. Fig. 5 shows the change observed in formaldehyde concentrations of the solutions utilized in copper recovery experiments conducted at various anodic current densities and temperatures. As seen, the effective parameter in formaldehyde decomposition was the temperature, rather than the current density. Since, the chemical reduction rates and the rate of Canizzaro reaction (reaction (11), one of the important side reactions in this type of baths) increase with increasing electrolysis temperature, formaldehyde is also consumed as indicated by the side reactions (4) and (11), along with anodic oxidation.

Experiments conducted under the same conditions revealed that quadrol behaved relatively different than formal-

dehyde (Fig. 6). The change in quadrol concentration is negligible, especially for the first two-hours of electrolysis, where the formaldehyde concentration is above 0.5 g/L. However, anodic decomposition of quadrol accelerates after the second-hour of the experiment, which corresponds to a formaldehyde concentration of <0.5 g/L. As seen from Fig. 6, although, the quadrol decomposition rises with increasing temperature and current density, the amount of quadrol which, nevertheless, remains in the electrolyte, is much higher than the acceptable limits set by the environmental regulations. As well known, there exists a maximum "Chemical Oxygen Demand" (COD) value for the solutions with organic additions, depending on their origins. Table 2 lists these COD values of the major organic components exist in the solutions of electroless copper plating baths.

COD value represents the oxygen equivalent of the organic component that can be oxidized. For instance, an electrolyte containing 5 g/L of quadrol is about 18 times above the allowable limits of safe disposal (600 mg/L). On the other hand, it is techno-economically meaningless to keep on the electrolysis operation until these limits for quadrol are reached. Instead, for spent electrolytes with high quadrol contents, a conventional chemical precipitation operation, following the copper removal operation would be more appropriate though some quadrol losses are inevitable.

Table 2
COD values of the major organic components of electroless copper plating baths

Organics	Mol. Wt.	COD	
		Mol ⁻¹	g ⁻¹
Quadrol	292	640	2.19
Formaldehyde	30	32	1.07

Table 3
Behavior of quadrol under various electrolysis conditions and COD values

Anodic current density (A/m ²)	Temperature (°C)	Electrolysis duration (h)	Final quadrol concentration (mg/l)	COD (mg/l)
250 (= 2 A)	20	7.25	35	92
	50	6.5	30	70
625 (= 5 A)	20	6	33	84
	50	5.5	27	68

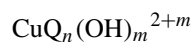
Series of electrolysis experiments were conducted with the rinse waters of plating plants containing 3 g/L quadrol, under the same conditions of copper removal experiments, to determine the lowest level to which COD values can be dropped. The copper content of the electrolyte must be removed prior to the decomposition of a powerful complexing agent, such as quadrol. Thus, the electrolysis operation is kept on even after copper concentrations were below 0.1–0.5 ppm. Table 3 tabulates the electrolysis conditions and the final quadrol concentrations. For all the electrolysis conditions investigated, there was no formaldehyde left in the electrolyte when the electrolysis was over, indicating that all the COD values of electrolyte must either belong to quadrol that remained intact and/or some other decomposed organic products of quadrol.

The COD analyses given in Table 3 were carried out according to ISO standards 6060-1986 [13].

3.4. Effect of pH

In this part of the study, two different electrolytes representing the main baths but with no plating capability (pH 12), and final rinse waters (pH 8) were utilized. It is well known that the pH is an effective parameter in electroless plating systems. Moreover, it is recognized in this research

that the electrolyte's formaldehyde content is an important factor in copper recovery. The results of the experiments conducted at 130 A/m² to examine the effects of pH and the electrolyte's formaldehyde content are given in Fig. 7 (formaldehyde concentration: 0–2.2 g/L, pH 8 and 12). As seen, copper recoveries at pH 12 are faster, as compared to those of at pH 8, independently from the formaldehyde content of the electrolyte. This effect is probably, due to the new components that the complexing agents form through the side reactions, and the reaction properties of complexed copper at that pH. The general formula of the complex compounds, expected to form in copper sulfate solutions with quadrol, depending on the pH, are:



where $n = 1$ or 2 $m = 0-4$

Moreover, depending on solution pH and quadrol concentration, hydroxy- or oxy-radicals (such as OH^- , OH^\bullet , O^- , O^\bullet , $\text{O}^{\bullet-}$, etc., which are capable of forming ligand in the form of either adsorbed or labile molecules in the inner Helmholtz layer) can possibly form complexes with copper ions. Numerous complex structures, such as $\text{Cu}^{2+} \cdot \text{Q}_x \cdot \text{O}^-$, $\text{Cu}^{2+} \cdot \text{Q}_x(\text{OH})^-$, $\text{Cu}_2\text{O} \cdot \text{Q}^+$, $\text{Cu} \cdot \text{Q}_{x-1} \cdot (\text{OH})^+$, and $\text{Cu}^{2+} \cdot \text{Q}_{x-1} \cdot \text{O}(\text{OH})^-$, may form by the combined effect of these, when active radicals were joined into the ligand of copper that is linked to the quadrol. Norkus et al. have conducted researches aimed at determining the structures of these complexes and found that they were directly related with the pH of the solution; CuQ^{2+} structure was dominant when pH 5–6, whereas CuQ_2^{2+} was the leading formation when pH 7–8, and $\text{CuQ}_2(\text{OH})_2$ complex was the principal structure when pH > 10 [8].

It is not an easy task to explain the effective mechanism of pH on copper recovery though, experimentally measurable, as it is related with the numerous parameters and their combined interactions.

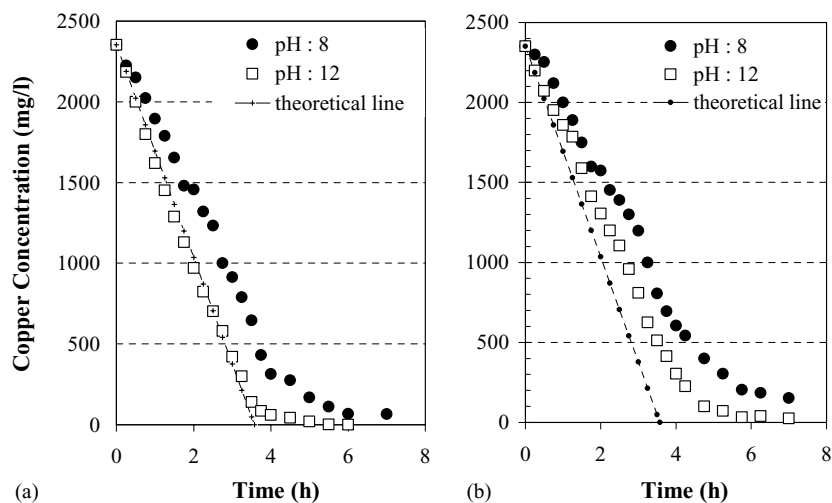


Fig. 7. (a) Copper removal in solutions with 2.2 g/L formaldehyde and (b) copper removal in solutions with no formaldehyde (130 A/m²; 20 °C; ϕ 5 mm; 4 min⁻¹).

4. Conclusions

In this study, a rotating packed cathode cell was used for the treatment of spent solutions and rinse waters of chemical copper plating plants. The optimum copper recovery conditions found to be: 130 A/m² current density and 20 °C, while keeping cathode granules of 5 mm in diameter, and cell rotation of 4 min⁻¹ constant. Under these conditions, 70% copper recovery was obtained with 3.2–3.5 kW h/kg Cu specific energy consumption in an electrolyte containing formaldehyde and for a final copper concentration of 0.1 ppm. On the other hand, the current efficiency and the specific energy consumption values were 62% and 5.5–5.8 kW h/kg Cu, respectively, for the case, where no formaldehyde was utilized and the final Cu concentration was 5 ppm. Plating bath reagents, such as formaldehyde, and complexing agents, such as quadrol decompose anodically during the period of copper recovery. Total elimination of the formaldehyde from the system, is technically and economically possible in such an electrolysis operation. The required energy for the decomposition of 1 g formaldehyde is 2–2.2 A h, under the optimum copper recovery conditions. However, it is somewhat different for quadrol and economically irrational (though

technically possible) to decrease the quadrol concentrations to desired values if the treated electrolyte's quadrol content is around 30 g/L. Only the rinse waters contain low amounts of quadrol, 3–5 g/L. Experiments carried out at various current densities (the same temperature), and at different temperatures (the same current density) revealed that it was possible to eliminate quadrol from this type of effluents to the COD levels permitted by the environmental standards.

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