Recovery of copper by LIX 984N-C from electroplating rinse bath solution

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ABSTRACT

Development of a complete hydrometallurgical process at the laboratory scale for recovering copper from the copper electroplating second rinse bath solution containing ~2.5 g/L copper (CESRBS) by solvent extraction route using LIX 984N-C dissolved in commercial kerosene was investigated. By using LIX 984N-C, an electrolyte from CESRBS with ~97 g/L copper content, which was addable to the copper electroplating bath, was generated by 30 vol.% LIX 984N-C in commercial kerosene at the O/A ratio of 1/8 and equilibrium pH value of 2 with two-stage counter-current extraction, and stripping of loaded organic by copper electroplating first rinse bath solution (7.8 g/L Cu) with 550 g/L sulfuric acid addition and with the O/A ratio of 2 at two-stage counter-current stripping process. The copper in stripping solution precipitated as $CuSO_4 \cdot 3H_2O$ salt. If the copper sulfate is produced without contaminated with organic phase, it could be recycled to the copper electroplating bath. A complete flow sheet of 30 vol.% LIX 984N-C process for the recovery of copper from CESRBS was demonstrated.

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1. Introduction

The application of the solvent extraction (SX) process is considered as an attractive option for the removal and recovery of metals from electroplating rinse bath solutions. Because currently, the spent baths are treated by alkaline precipitation, but this process generates a large amount of hazardous plating sludge and thus requires dumping sites the regulations for which are quite stringent in Turkey. Ion exchange and electrodialysis were studied in order to remove and recover each component in the baths in order to extend the bath life; however, many problems still remain unsolved, such as the low exchange capacity for the ion exchange, and the low durability and unsatisfactory selectivity of the electrodialysis membrane. From the standpoints of environmental protection and resource recycling, it is urgent to develop an effective technique to treat the electroplating copper plating bath without sludge generation and recover copper (Huang and Tanaka, 2008). But numbers of studies are scarce on the SX process for the removal and recovery of metals from electroplating rinse bath solutions (Priya et al., 2008; Kalidhasan et al., 2008; Agrawal et al., 2008).

Heavy metals are present in the wastewater as either cations or anions. Cations are usually extracted into an organic diluent by acidic or chelating extractants. Thus, for example, aromatic oxime molecules, known commercially as LIX 84, LIX 984N, LIX 860 (Cognis) and Acorga P50 (Avecia), may be used as extractants to remove Cu(II) or Au(I) whereas organophosphates, such as 2-ethylhexylphosphonic acid mono-ethylhexyl ester (HEH(EHP)), mono(2-ethylhexyl) phosphoric acid (H2MEHP), di(2-ethylhexyl) phosphoric acid (D2EHPA) or di(2-ethylhexyl) di thiophosphoric acid (DTPA) may be used as extractants to remove Pb, Cd, Zn(II), Ni, Co, Cr(III), Ag(I) and rare earth metal species (Kentish and Stevens, 2001; Khwaja et al., 2000; Raghuraman et al., 1995; Youn et al., 1997; Lee et al., 1999; Chilyumova and Thöming, 2007).

Metal anions can be extracted by ion-pair formation with long chain alkyl amines in an organic diluent, as long as salts or acids are present in the aqueous feed (Ritcey and Ashbrook, 1984). Suitable metal complexing agents include tri-*n*-octylamine (TOA) for the removal of Cr (VI) and Hg (II) (Yun et al., 1993) and methyl tricaprylyl ammonium choride (Aliquat 336) for Cr (VI) removal (Alonso and Pantelides, 1996).

Other instances where solvent extraction processes can be applied to wastewater treatment include the use of a tertiary amine, tris (2-ethylhexyl) amine (TEHA) or a phosphine oxide mixture (CYANEX 923) for the recovery of mineral acids from hydrometallurgical process waste streams (Rickleton 1993; Eyal and Baniel, 1991).

During many plating operations, a substantial amount of bath solution adheres to the plated workpiece as they leave the plating tank. In this manner, valuable materials are lost as "drag-out" into the subsequent cascade rinse tanks (Papadopoulos et al., 2004). This contaminated rinse solutions can be treated in a solvent extraction system, where these escaping materials can be recovered and returned to the plating tank. Comparing the technology of SX with others, it has the advantage that a large volume of wastewater can be treated which can directly recycle the metals to the plating bath. It has more than 97% recovery efficiency. For this reason, determination of optimum copper

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	Cu	Fe	Cr	Mn	Co	Zn	pH
1st rinsing bath	7762	9.49	ND	ND	ND	8.92	0.45
2nd rinsing bath	2513	4.76	ND	0.005	ND	4.214	−0.10

ND: Below detection limit.

recovery parameters from CESRBS by SX using LIX 984N-C, which might be considered as a new extractant developed by Cognis, was studied in this work. The obtained results have been presented systematically and discussed in detail as well.

2. Experimental

2.1. Solutions, reagents and materials

Chemical properties of electroplating rinse bath solutions depend on various factors such as the surface area of workpiece, used raw materials and their concentration in the plating bath and the cleaning period of rinse bath. Therefore, various electroplating rinse bath solution samples were taken from different companies, and their chemical composition and pH values were measured. According to these analysis, the second (as feed solution) and the first (as stripping solution) rinsing bath solutions of a copper electroplating process from the MAKEL Group company were chosen as the most suitable and representative feed and stripping solutions for this study. Chemical analysis and pH of them are given in Table 1. Chemical analysis was performed using a BGC Sigma model atomic absorption spectrophotometer (AAS). pH of the solutions was measured by Hanna HI 221 model pH meter.

LIX 984N-C solvent extraction reagent, supplied by Cognis Ireland, was dissolved in a commercially available kerosene without further purification in order to prepare the organic phase. LIX 984N-C reagent, a 1:1 volume blend of LIX 860N-IC and LIX 84-IC, is a mixture of 5-nonylsalicylaldoxime and 2-hydroxy-5-nonylacetophenone oxime in a high flash point hydrocarbon diluent and easily forms water insoluble complexes with various metallic cations. It is a more concentrated form of LIX 984N. Therefore, it might be considered as a new SX reagent developed by Cognis. For this reason, there is not any copper SX data about it in the public domain. Only, Sengupta et al. (2006) published a paper about LIX 984N-C, but they used emulsion liquid membranes for extraction of copper. Analytical grade Na_2CO_3 and dilute H_2SO_4 solutions were used to adjust the pH of CESRBS.

Generally, some parts of the first rinse water bath were recycled to the plating bath, in order to properly recover some copper. However, the wastewater from the second rinse bath contains the most important copper source to be recovered as seen Table 1, unfortunately it is lost completely. Therefore, the copper electroplating second rinsing bath solution (CESRBS) from the MAKEL company was chosen as the potential copper resource to be recovered. Thirty-five liters CESRBS wastewater of MAKEL was taken to carry out the all of the extraction experiments.

2.2. Procedure of solvent extraction

Each one of the experiment, unless otherwise stated, was done at room temperature by mixing a 25 ml of organic mixture with a 25 ml of aqueous phase in a 100 mL separatory funnel at a constant shaking speed of 300 rpm for 15 min by using a mechanical shaker (IKA yellow line RS 10 control). The organic phase to aqueous phase (O/A) ratio was taken as unity, unless stated otherwise. At the end of each experiment, the separated and filtrated aqueous phase was analyzed by AAS to determine the metal concentration in the aqueous phase, and the metal concentration in the organic phase was calculated by

subtracting it from the total. Percent extraction and stripping efficiency of copper were calculated from these results. The variation in multiple readings from the same sample was generally within 4%, while that of the duplicated experiments was from 2% to 5%.

3. Results and discussion

Analytic grade NaOH and Na_2CO_3 reagents were employed in order to increase the pH of rinse bath solution. In pretests, it was found that the use of Na_2CO_3 solution resulted in more clear aqueous phase with no precipitate formation at high pH. Also, Na_2CO_3 is one of the cheapest chemicals that can be used for this purpose. Therefore, Na_2CO_3 reagent was chosen as pH adjusting agent.

3.1. Variation of equilibrium pH and extractant concentration

Equilibrium pH of CESRBS was adjusted to different values ranging from −0.20 to 2.31, and extraction experiments were done by using 5, 10 and 15 vol.% LIX 984N-C organic phases in order to improve the recovery of copper from CESRBS. The results of these tests are presented graphically in Fig. 1. As expected, the percent copper extraction increased with the rising of equilibrium pH in all organic phases as shown in these graphs. Greater than 99% copper recovery for 5, 10 and 15 vol.% LIX 984N-C organic phases was achieved at equilibrium pH values of 2.31, 1.85 and 1.69, respectively. These results indicate that higher pH values significantly improved the recovery of copper from CESRBS. LIX 984N-C extractant could extract copper at very low equilibrium pH values as shown in this graph. The other well known extractants such as DEHPA, Cyanex 272, etc. cannot extract the copper from CESRBS at these low equilibrium pH values. The most important advantage of LIX 984N-C was that little amount of pH adjusting agent (Na_2CO_3) was required at these SX conditions.

For original CESRBS, pH, and phase ratio, the amount of copper extracted increased with increasing extractant concentration, as a result of which the distribution curves shifted to lower pH values as shown in Fig. 1. An increase in the extractant concentration resulted in higher copper extraction efficiency at low equilibrium pH values, therefore 15 vol.% LIX 984N-C organic phases were chosen as suitable organic solutions, because the aim of this study was the production of an aqueous solution with high copper content which could be recycled to copper electroplating bath. Also, the optimum equilibrium pH range for 15 vol.% LIX 984N-C organic phase was chosen as 1.69–2.30, according to Fig. 1.

3.2. Solvent loading capacity

By itself, % extraction metal versus pH curve has really no meaning, simply because it is dependent on the O/A ratio, loading capacity etc. There are two methods to determine the loading capacity of a solvent, in the first method the O/A ratio is studied and in the other, the organic
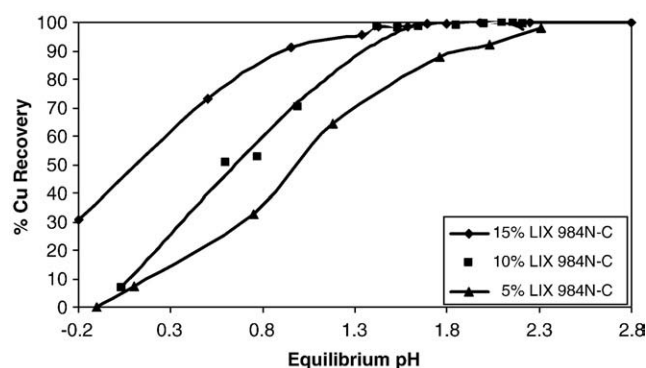

Fig. 1. Effect of LIX 984N-C concentration on % Cu recovery vs. equilibrium pH curve.

phase is loaded several times with fresh aqueous at previously determined constant SX conditions. The latter process was carried on until the saturation of the solvent with the metal was obtained. Loading capacity of 10 vol.% LIX 984NC organic phase was determined by the second method. Organic phase (containing 10 vol.% LIX 984N-C) was loaded 7 times with fresh CESRBS at the O/A ratio of unity and at equilibrium pH range of 1.7–2.1. The results of these studies are presented graphically in Fig. 2. As a result, the copper extraction capacity of 10 vol.% LIX 984N-C from CESRBS was determined as 7.4 g/L at the equilibrium pH range of 1.7–2.3 and at the O/A ratio of unity, at 300 rpm shaking speed for 15 min of extraction time. Also McCabe–Thiele diagram of 10 vol.% LIX 984N-C was drawn from results of these loading experiments as seen in the small graphic in Fig. 2. The shape of extraction isotherm indicates high distribution coefficients. It is apparent from the McCabe–Thiele plot that the raffinate would be left with very little copper after two extraction stages at the O/A ratio of 2.75, which is very suitable for the aim of this research.

3.3. Effect of O/A ratio on copper extraction and McCabe–Thiele diagrams

The O/A ratio studies were done to find out the theoretical number of extraction stages and the enrichment of copper in loaded organic phase during extraction. Extraction of copper by using 10, 15 and 30 vol.% LIX 984NC organic phases from CESRBS was carried out by varying the O/A ratio from 1/30 to 10 at the equilibrium pH of 2.10 ± 0.20. McCabe–Thiele diagram of organic solvents is presented in Fig. 3 which was obtained for the same O/A ratio. The shape of extraction isotherms indicated high distribution coefficients. The plots of them indicated that <0.1 g/L Cu in the raffinate after 2 extraction stages at the O/A ratio of 4 for 15 vol.% and 8 for 30 vol.%. The number of theoretical counter-current stages required for the copper extraction of 10, 15 and 30 vol.% LIX 984NC systems were determined as two stages for all of them. The possibility of enriching the copper concentration in the loaded organic phases containing 10, 15 and 30 vol.% LIX 984NC were predicted as 2.75, 4 and 8 times, respectively, at two counter-current extraction stages. Also, copper loading capacities of 10, 15 and 30 vol.% LIX 984N-C organic phases were determined as 7.3, 11.5 and 22.5 g/L, respectively. As a result, organic phase containing 30 vol.% LIX 984N-C seems more convenient than the others for the aim of this research. Because, an organic solution with high copper content (22 g/L) could be produced by using it. Then, an aqueous solution with high copper content could be obtained by stripping of it, and the resulting solution could be recycled to the copper electroplating bath. But the problem in the using 30 vol.% LIX 984N-C is that; a reagent concentration that the industry recognizes as being too viscous to operate smoothly. Therefore it might not be suggested in the industrial applications, however any
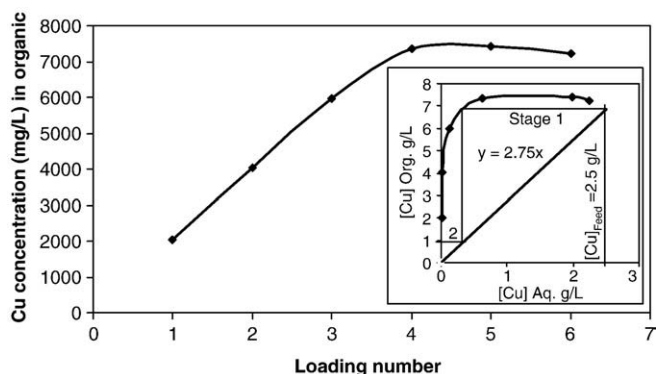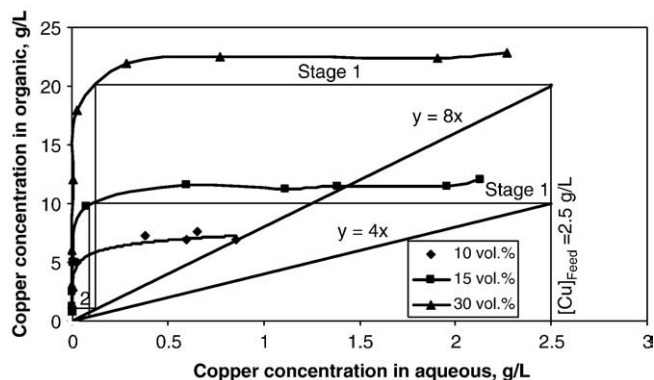

Fig. 3. McCabe–Thiele diagrams of 10, 15 and 30 vol.% LIX 984N-C organic phases.

problem didn't occur in this laboratory scale work due to a bit larger viscosity of organic phase containing 30 vol.% LIX 984N-C.

3.4. Counter-current batch simulation tests for copper extraction

A two-stage counter-current extraction simulation (CCES) was done at the O/A ratio of 1/4 and 1/8 by using 15 and 30 vol.% LIX 984NC according to the results of McCabe–Thiele diagrams. First of all, organic phases were loaded with copper by using CESRBS, and then they were stripped by the aqueous phase containing 600 g/L H_2SO_4 at the O/A ratio of unity for 45 min. Only one time loaded and stripped organics were used in CCES studies. The results of these studies are presented in Table 2. When 15 vol.% LIX 984N-C was loaded twice with CESRBS at the O/A ratio of 1/4 and at an equilibrium pH of 2.0–2.7, a loaded organic containing 10.51 g/L copper was produced (Table 2). Also, by using 15 vol.% LIX 984N-C in two-stage CCES studies under same conditions resulted in a raffinate containing 1.21 mg/L copper corresponding to an extraction of 99.72% (Table 2). Not only the percent copper extraction but also the copper content of the loaded organic is important for this study. Therefore, 15 vol.% LIX 984NC extractant concentration doesn't seem to be a suitable organic content due to its low copper content. If the LO (15 vol.% LIX 984NC) containing 10.5 g/L Cu was stripped in the O/A ratio of 2, the strip solution would contain

Table 2
Analysis results of input and output streams during C. C. extraction simulation of Cu.

Stream	Eqm. pH	15 vol.% LIX 984NC 2 stage C. C. extraction		Eqm. pH	30 vol.% LIX 984NC 2 stage C. C. extraction	
		[Cu], mg/L	% Cu extraction		[Cu], mg/L	% Cu extraction
CESRBS	–	2526	–	–	2518	–
Organic phase	–	–	–	–	–	–
Stage 1 raffinate	2.10	47.75	98.12	2.05	320	87.30
Raffinate	2.42	1.21	99.72	2.28	0.0	100
Loaded Organic[a]	–	9913	–	–	17,584	–
Loaded Organic[b]	–	10,511	–	–	19,896	–
Raffinate[c]	2.7	2376	5.92	2.5	2229	11.5
Loaded Organic[d]	–	–	–	–	16,998	
Raffinate[e]	–	–	–	2.37	104	95.86
Loaded Organic[f]	–	–	–	–	21,054	
Raffinate[g]	–	–	–	2.59	2011	20.14

Loaded Organic[a]: LO in the first extraction.
Loaded Organic[b]: Loading of organic in the first stage with fresh CESRBS.
Raffinate[c]: raffinate coming from Loaded Organic[b].
Loaded Organic[d]: aquouese = Raffinate[c], organic = coming from Raffinate experiment.
Raffinate[e]: raffinate coming from Loaded Organic[d].
Loaded Organic[f]: Loading of Loaded Organic[d] with fresh CESRBS.
Raffinate[g]: Raffinate of Loaded Organic[f].

Fig. 2. Extraction capacity of 10 vol.% LIX 984N-C = 7.4 g/L Cu (equilibrium pH; 1.7–2.1).

maximum 21 g/L Cu. The strip solution containing 21 g/L Cu would not be recycled to plating thank due to low copper content. By using 30 vol.% LIX 984N-C, at two-stage CCES studies under similar conditions (except the O/A ratio of 1/8) resulted in a raffinate containing 0.0 mg/l copper corresponding to an extraction of 100%. Furthermore, a loaded organic phase containing 19.90 g/L copper was produced (Table 2). These results are very good, because both percent copper extraction and copper content of the loaded organic phase are high. So a strip solution with high copper content would be achieved easily by stripping of it, which can be recycled to plating bath. Also a few extra experiments were done in order to determine the extractability behaviors of second stage raffinate (Raffinate[c]) by using fresh organic (Loaded Organic[d]), and results of these studies are presented in Table 2. 95.86% of copper in the second stage raffinate (Raffinate[c]) could be extracted with a fresh organic (Loaded Organic[d]). A second loading of the loaded organic phase (Loaded Organic[d]) with fresh CESRBS, the copper enrichment reached to 21,054 mg/L meaning that for a 30 vol.% LIX 984N-C organic (Loaded Organic[f]) almost theoretical loading capacity (solubility limit) it was reached. As a result, a two-stage counter-current extraction with organic phase containing 30 vol.% LIX 984N-C extractant is optimum at the O/A ratio of 1/8 and at an equilibrium pH of 2.0–2.5. The viscosity of the organic phase containing 30 vol.% LIX 984N-C did not create any problem in these laboratory scale studies.

3.5. Effect of sulfuric acid concentration on copper stripping efficiency

The quantity of loaded organic (LO) phase (Cu = 21,880 mg/L for 30 vol.% LIX 984NC) was produced by carrying out the copper stripping studies with a copper electroplating first rinse bath solution containing 7762 mg/L Cu. Since the aim was to produce a pregnant electrolyte containing >30 g/L copper (which could be recycled to electroplating bath) suitable for the copper electroplating bath with a copper depletion of 20 g/L. However, the pretests showed that 15 min stripping duration was not sufficient for the stripping of 99% of the copper in the LO. Indeed, 80–90% of the stripping reaction completed in a few minutes. Therefore, stripping duration was taken as 45 min in order to be sure stripping reaction reached to equilibrium. Stripping tests were done using the copper electroplating first rinse bath solution containing 7.8 g/L Cu and different concentrations of sulfuric acid ranging from 50 to 550 g/L for 30 vol.% LIX 984N-C LO. The O/A ratio was unity, and also the stripping duration was kept constant at 45 min in these studies. The results are presented graphically in Fig. 4. 550 g/L sulfuric acid concentration was ideal at these conditions as shown in the figure. Also, three extra experiments were carried out in order to determine the effect of stripping temperature on the percent copper stripping efficiency, and the results are given in the same graph. There was no net effect of temperature on the stripping efficiency as seen in the figure. Furthermore, second stripping studies were done by using the first stripping solutions. In other words, fresh LO was stripped again by the stripping solutions that were used in the first one. Naturally, percent
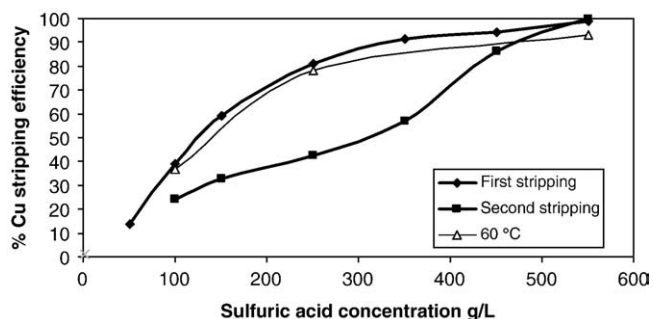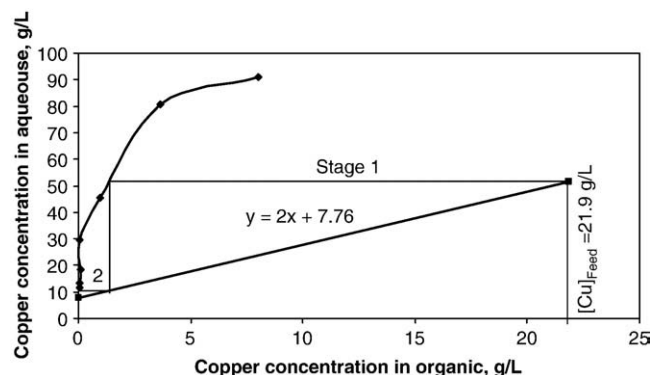

Fig. 5. Stripping McCabe–Thiele diagram of 30 vol.% LIX 984N-C loaded organic.

copper stripping efficiency of the second trial was lower than the first one. The interesting point was that copper in the aqueous phase precipitated as copper sulfate salt during the stripping at 550 g/L sulfuric acid concentration due to the high Cu^{++} and SO_4^- concentrations in the stripping solution. This is a very good result, because copper sulfate is one of the raw materials of copper electroplating bath solution. Thus, it can be added directly into the copper electroplating bath. But the copper sulfate product may be contaminated with organic phase. If copper sulfate contaminated with organic phase is recycled to a copper electroplating bath it could get poor quality copper plating.

3.6. Effect of A/O ratio on copper stripping efficiency and McCabe–Thiele diagram

The last group of experiments was carried out by keeping the acid concentration constant at 550 g/L for 30 vol.% LIX 984NC LO and the stripping duration was 45 min while the O/A ratio was changed between 6 and 1/6. A stripping McCabe–Thiele diagram for 30 vol.% LIX 984N-C LO are plotted in Fig. 5 from the results which were obtained for these O/A ratio studies. The graph indicates that about 2-stages of stripping were necessary to theoretically strip more than 99% copper from LO using 550 g/L sulfuric acid at the O/A phase ratio of 2. Strip solution contained approximately 50 g/L copper at these conditions. Besides, the stripped copper in the aqueous phase started to precipitate as copper sulfate salt at the O/A ratio of 2, and the amount of precipitation increased with the increasing of O/A ratio. The XRD pattern of precipitate showed that copper precipitated as $CuSO_4 \cdot 3H_2O$ salt.

According to the results of O/A ratio tests and McCabe–Thiele diagram, a two-stage counter-current stripping simulation of copper was carried out at the O/A ratio of 2, and the results are given in Table 3. An electrolyte containing ~97 g/L Cu was generated by two-stage

Fig. 4. Effect of acid concentration on % Cu stripping efficiency.

Table 3
Analysis results of input and output streams during C. C. stripping simulation of Cu.

Stream	[H₂SO₄], g/L	30 vol.% LIX 984NC 2 stage C. C. stripping	
		[Cu], mg/L	% Cu stripping
Strip solution	–	7762.3	–
Loaded Organic	–	22,765	–
Stage 1 spent Org.	–	581.1	–
Spent Org.	–	0.0	100
Stage 1 Pregnant strip	500	52,130	97.45
Pregnant strip soln.[a]	500	97,070	98.70
Spent Org.[b]	–	295	–

Pregnant strip soln.[a]: Stripping of fresh LO by stage 1 pregnant strip.
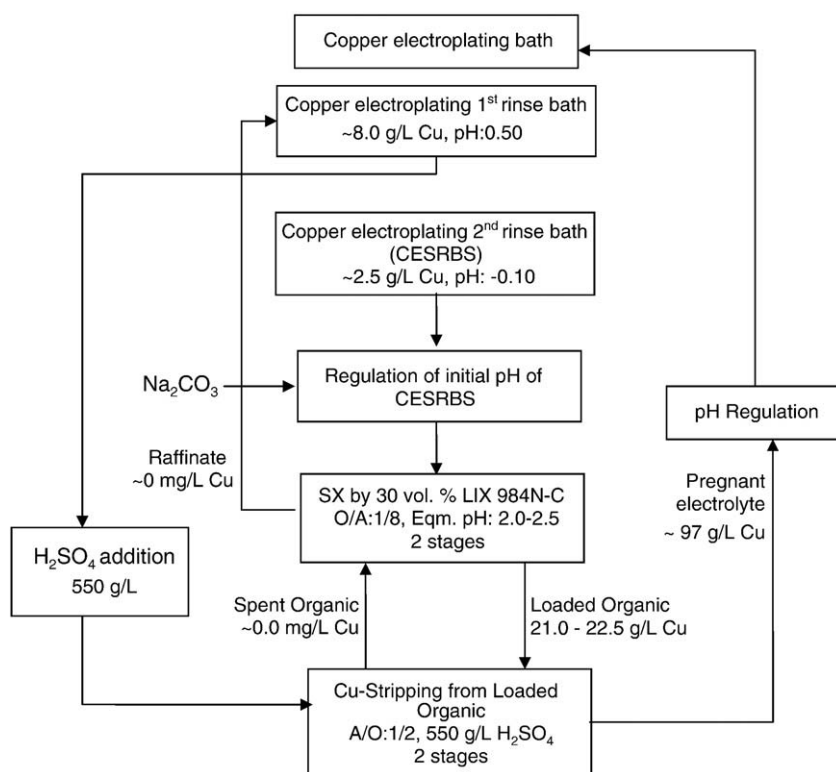Spent Org.[b]: Spent organic coming from pregnant strip[a].

Fig. 6. Working flow sheet of the process for recovery of copper from CESRBS.

counter-current stripping of loaded organic containing 30 vol.% LIX 984N-C with 100% stripping efficiency. Actually, the stripping solutions didn't contain so much Cu^{++} ion, most of the copper precipitated as sulfate in the aqueous phase. For example, the Pregnant strip soln.[a] had 25570 mg/L copper, and it also contained 2.4 g. copper sulfate at same time, therefore, its total copper content was 97,070 mg/L. As a result, copper in the CESRBS was recovered as copper sulfate which was in the form of the raw material added to the electroplating bath.

3.7. Working flowsheet

The laboratory scale solvent extraction by 30 vol.% LIX 984N-C dissolved in commercial kerosene and stripping of LO by the copper electroplating first rinse bath solution containing 550 g/L sulfuric acid experiments were performed in order to produce an electrolyte from CESRBS with a high copper content which could be recycled to the copper electroplating bath. So, the spent rinses were successfully treated and recycled, both the rinsing water and the utilizable raw material (copper sulfate and pregnant electrolyte) were recovered, which can in turn be looped back to the rinsing and process baths, respectively, as long as sufficient concentrations are attained as shown in the working flow sheet (Fig. 6).

4. Conclusions

A complete hydrometallurgical process was developed at the laboratory scale for recovering copper from CESRBS by solvent extraction route using LIX 984N-C dissolved in a commercially available kerosene. An electrolyte from CESRBS with ~97 g/L copper content (copper sulfate salt + pregnant electrolyte), which could be recycled to the copper electroplating bath, was generated by 30 vol.% LIX 984N-C in a commercial kerosene at the O/A ratio of 1/8 and equilibrium pH value of 2.0–2.5 with two-stage counter-current extraction, and stripping of loaded organic at the O/A ratio of 2 by copper electroplating first rinse bath solution with 550 g/L sulfuric acid addition at two-stage counter-current stripping process. Further-

more, a copper sulfate salt was produced as $CuSO_4$ $3H_2O$ salt at the end of stripping, which could be added to copper electroplating bath as raw material. The other conclusions might be summarized as:

- The percent copper extraction increased with the rising of equilibrium pH in all organic phases. Greater than 99% copper recovery for 5, 10 and 15 vol.% LIX 984NC organic phases was obtained at equilibrium pH values of 2.31, 1.85 and 1.69, respectively.
- Increment in the extractant concentration of organic phase caused shifting of the distribution curves to lower pH values.
- The copper extraction capacity of 10 vol.% LIX 984N-C from CESRBS was determined as 7.4 g/L
- The possibility of enriching the copper concentration in the loaded organic phases containing 10, 15 and 30 vol.% LIX 984NC were predicted as 2.75, 4 and 8 times, respectively, at two counter-current extraction stages.
- A two-stage counter-current extraction with organic phase containing 30 vol.% LIX 984N-C extractant is optimum for the recovery of copper from CESRBS at the O/A ratio of 1/8 and at an equilibrium pH of 2.0–2.5 to achieve high copper content.
- The optimum sulfuric acid concentration was determined as 500 g/L due to advantage of $CuSO_4.3H_2O$ salt formation.
- 2-stages of stripping were necessary to successfully strip more than 99% copper from LO using 550 g/L sulfuric acid at the O/A phase ratio of 2.

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