Optimizing the recovery of copper from electroplating rinse bath solution by hollow fiber membrane

Kürşad Oğuz Oskay and Mehmet Kul

ABSTRACT

This study aimed to recover and remove copper from industrial model wastewater solution by non-dispersive solvent extraction (NDSX). Two mathematical models were developed to simulate the performance of an integrated extraction–stripping process, based on the use of hollow fiber contactors using the response surface method. The models allow one to predict the time dependent efficiencies of the two phases involved in individual extraction or stripping processes. The optimal recovery efficiency parameters were determined as 227 g/L of H_2SO_4 concentration, 1.22 feed/strip ratio, 450 mL/min flow rate (115.9 cm/min. flow velocity) and 15 volume % LIX 84-I concentration in 270 min by central composite design (CCD). At these optimum conditions, the experimental value of recovery efficiency was 95.88%, which was in close agreement with the 97.75% efficiency value predicted by the model. At the end of the process, almost all the copper in the model wastewater solution was removed and recovered as $CuSO_4.5H_2O$ salt, which can be reused in the copper electroplating industry.

Key words | CCD, copper, hollow fiber membrane, NDSX, optimization, recovery

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INTRODUCTION

Copper ore is a finite resource as with many other raw materials. In addition, extracting copper from copper ore by melting requires five to seven times more energy than recovering it from other waste resources using a hydrometallurgical process (Wernick & Themelis 1998). For these reasons, researchers investigated new processes to extract metals from secondary sources. Solvent extraction is one of these processes, which provides efficient removal of toxic heavy metals from industrial effluents to environmentally acceptable levels (Yun et al. 1993; Lin & Juang 2001). In addition, the metals recovered by this process can be reused (Kul & Çetinkaya 2010). Membrane separation processes are increasingly being utilized in many fields because they avoid many of the shortcomings of traditional solvent extraction processes such as solvent loss, emulsion formation, and problems due to flooding and loading (Alonso & Pantelides 1996).

The recovery of metals using hollow fiber membrane (HFM) has been used under different process configurations such as hollow fiber supported liquid membrane (Yang & Kocherginsky 2006; Lothongkum et al. 2009), hollow fiber renewal liquid membrane (HFRLM) (Ren et al. 2010) and non-dispersive solvent extraction (NDSX) (Galán et al. 2006). The main difference between these configurations is

the way of contacting the fluid phases, and the number of hollow fiber contactors used in the separation process (Bringas et al. 2009). Many studies have been carried out using NDSX for the recovery of metal ions (Juang & Huang 2002), phenol (González et al. 2003), anionic pollutants (Ortiz et al. 2006) and various valuable materials in solutions. The common liquid membrane processes have stability problems. The NDSX process has been used to overcome the stability problems of the membrane processes in long-term applications (Baker 2004). In addition, a comparative study was performed by Kumar et al. (2005) to compare NDSX using a single module and the integrated membrane process with two hollow fiber contactors. NDSX of silver cyanide and stripping of silver cyanide from an organic complex were performed simultaneously. The overall mass transfer coefficient obtained in the integrated process was observed to be greater than the values of the mass transfer coefficient for Ag obtained with the single module (no stripping) (Kumar et al. 2005). Therefore, an integrated NDSX membrane process with two hollow fiber contactors was chosen for the recovery of copper from electroplating rinse solution in the present study. NDSX of copper from aqueous ammoniacal/ammonium carbonate medium with LIX 973N using

a microporous hydrophobic polypropylene hollow fiber contactor is reported by Alguacil & Navarro (2002). They indicate that higher organic flow rates are required for near complete copper stripping. However, the studies of NDSX have been carried out with a low concentration feed phase (0.05–0.2 g/L Cu) or at low flow rates (10–48 mL/min.), which do not fulfill industrial expectations (Alguacil & Navarro 2002). It is necessary to operate membrane processes with a high concentration feed phase and flow rates for industrial use. According to the literature search, there are no studies about recovering copper from electroplating rinse bath sulfate solution by NDSX configurations using a statistical optimization technique.

In most experimental studies of concentration processes, conventional methods were used to determine the influence of operational parameters. When using conventional methods to optimize the process, one parameter is changed while others are kept at a constant level. This should be repeated for all influencing parameters, resulting in a great number of experiments (Khataee *et al.* 2010). Its major disadvantage is that it does not include the interactive effects among the variables studied. To overcome this problem, the optimization of analytical procedures has been carried out by using multivariate statistical techniques. Among the most relevant multivariate techniques used in analytical optimization is response surface methodology (RSM) (Bezerra *et al.* 2008). The most popular RSM is the central composite design (CCD) procedure (Hafizi *et al.* 2013).

In the electroplating process, metal is plated in a cell, after that, the plated metal is rinsed in several tanks to clean the electroplating solution from the surface of the metal. The rinsing water has to be replaced when the concentration of the contaminants reach a critical level. Similarly, when the copper content of the second rinsing bath solution reaches ~2.5 g/L in the copper electroplating process, it should be replaced with fresh water. So, the wastewater containing 2.5 g/L is very suitable for recovering copper (Li *et al.* 2011). In this work, the optimum NDSX parameters for recovering copper from an electroplating rinse bath model wastewater solution were determined by CCD. In particular, stripping (recovery) variables were optimized by CCD.

METHODS

Materials

The chemicals used were all analytical grade: copper sulfate pentahydrate (Merck, White House Station, NJ, USA),

sulfuric acid (Merck, White House Station, NJ, USA), sodium carbonate (Merck, White House Station, NJ, USA). The LIX 84-I solvent extraction reagent (kindly supplied by Cognis Ireland Limited, Cork, Ireland), was dissolved in commercially available kerosene, without further purification, in order to prepare the organic phase. The LIX 84-I solvent extraction reagent is a water insoluble 2-hydroxy-5-nonylacetophenone oxime, which is a mixture with a high flash point hydrocarbon diluent. It forms water insoluble complexes with various metallic cations. The stripping phase is prepared by diluting H_2SO_4 in distilled water.

The chemical properties of electroplating rinse bath solutions depend on various factors such as the surface area of the work piece, raw materials used, and their concentration in the plating bath, and the cleaning period of the rinse bath. Therefore, various electroplating rinse bath solution samples were taken from different companies, and their chemical composition and pH values were measured. Thus, ranges of the copper content of the rinse bath solutions were determined. Generally, a large part of the first rinse bath solution was added to the electroplating cell due to its high copper content, but second and subsequent rinse bath solutions were sent for treatment. The second rinse bath solution, which is among the rinse solutions which were sent for treatment, has the greatest copper content. Therefore, the second rinse bath solution was chosen as the most suitable feed solution due to its economic value and high copper content, which is not recovered by any process. The average copper content of the second rinse solutions was determined as approximately 2.5 g/L according to the analyses of the second rinse solutions taken from different companies. Second rinsing bath solutions of a copper electroplating process from MAKEL Group Company (Istanbul, Turkey) were chosen as the most suitable and representative feed solutions for this study because the copper content was 2.513 g/L the chemical analysis and pH are given in Table 1.

Apparatus and procedure

NDSX experiments were carried out at laboratory scale using two HFM contactors, one for extraction and the

Table 1 | Copper electroplating second rinsing bath composition (mg/L) of the MAKEL Group Company

|	Cu	Fe	Cr	Mn	Co	Zn	pH
Rinsing bath	2,513	4.76	ND	0.005	ND	4.214	−0.10

Table 2 | Characteristics of the microporous hollow fiber module used for the extraction and stripping experiments

Type of module	G501 (contactor)
Module length (cm)	28
Module diameter (cm)	7.7
Case inner diameter (cm)	5.55
Center tube diameter (cm)	2.22
Number of fibers	~10,800
Fiber	X50 polypropylene
Effective fiber length (m)	15.6
Inner diameter of the fibers (μm)	214
Outer diameter of the fibers (μm)	300
Pore size (μm)	0.03
Porosity (%)	40
Inner interfacial area (m^2)	1.13
Outer interfacial area (m^2)	1.58
Area per unit volume (cm^2/cm^3)	28

other for the stripping process. The contactors are both Liqui-Cel Extra Flows $2.5' \times 8'$ membrane contactors (Membrana GmbH, Wuppertal, Germany). Additional information about this module is provided in Table 2. The experimental setup was as shown in Figure 1. The feed and stripping solutions were mixed by magnetic stirrer to obtain a homogenous solution, and allowed to circulate through the lumen of each module, while the organic solution was circulated through the shell sides of both modules in series. Thus, the organic solvent wets the membrane pores. The positive static pressure applied to the

aqueous phase prevents dispersion of the organic phase to the feed phase.

Chemical analysis was performed using a BGC Sigma model atomic absorption spectrophotometer (GBC Sigma Avanta AAS, Braeside, Australia). The pH of the solutions was measured by a Hanna HI 221 model pH meter (Hanna Instruments, Woonsocket, RI, USA). NDSX pre-experiment studies were carried out with original electroplating rinse bath solution and synthetic copper sulfate solution. Some precipitation occurred in the original electroplating solution with time or aging; therefore, the copper content decreased with aging. Therefore, pre-experiments were carried out with fresh original and synthetic solutions, which contained the same copper content as the original fresh rinse bath solution to stabilize the feed phase in all experiments. As a result, it was determined that there was no difference between the synthetic solution and electroplating rinse bath solution for recovery from these solutions. After that, the feed phase was prepared by dissolving a weighed amount of $CuSO_4.5H_2O$ in aqueous solutions to stabilize the feed solution and simulate the electroplating wastewater containing copper. In all experiments, the copper concentration and equilibrium pH of the feed solutions were kept constant at 2,500 mg/L and ~ 4.00 mg/L, respectively. The electroplating solution, which was taken from MAKEL, contained very small amounts of Fe and Zn (4.76 mg/L and 4.24 mg/L, respectively). When their concentrations were compared with the copper concentration (2,513 mg/L), they were considered negligible levels. Therefore, the effect of Fe and Zn on the performance of copper extraction and stripping stages was negligible. For this reason, their effect on the performance of copper extraction and stripping was
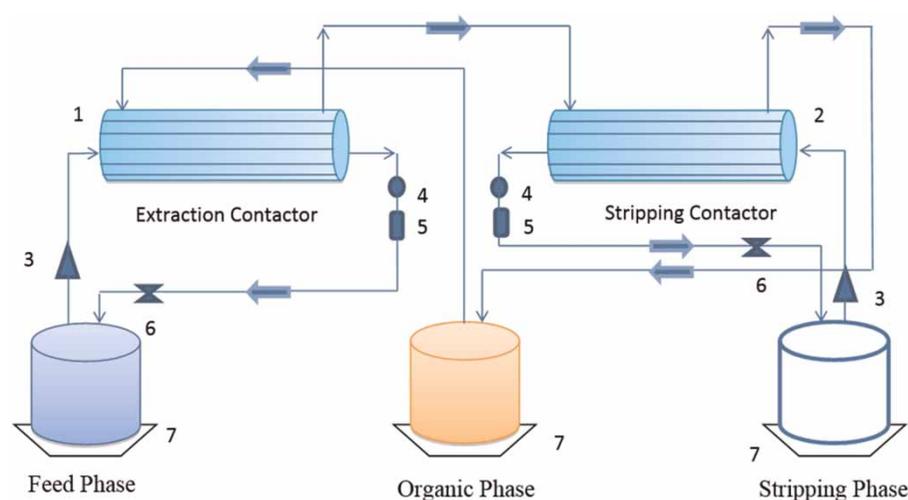
Figure 1 | The experimental setup (1) extraction contactor, (2) stripping contactor, (3) peristaltic pump, (4) pressure gauge, (5) flow meter, (6) valve, (7) magnetic stirrer.

ignored. Finally, synthetic feed solutions were prepared using only $CuSO_4.5H_2O$, making their copper content 2,500 mg/L.

Experimental design

In this study, CCD, which is a widely used form of RSM, was employed optimize the stripping of copper from synthetic rinse bath solution. To evaluate the influence of operating parameters on the extraction and recovery efficiency, five main factors were chosen, which were: H_2SO_4 concentration, extractant concentration, flow rate, volumetric ratio of feed/stripping phases (F/S ratio) and recovery time. Analysis of second rinse solutions showed that their copper concentration was around 2,500 mg/L; therefore, the copper concentration of the feed solutions was kept constant at 2,500 mg/L. The RSM design of the experiment was carried out using JMP 10 trial software (SAS, Marlow, UK) for the analysis and testing parts of this study.

For statistical calculations, the relation between the coded values and actual values are described in Equation (1) (Yin & Dang 2008):

$$X_i = (A_i - A_0)/\Delta A \tag{1}$$

where X_i is a coded value of the variable; A_i the actual value of the variable; A_0 is the actual value of the A_i at the center point; and ΔA is the step change of the variable. The responses of the experiments were measured in terms of extraction efficiency and recovery percentage of copper in the stripping phase, which are defined by Equations (2) and (3):

$$\text{Extraction efficiency} = \frac{C_i - C_f}{C_i} * 100 \tag{2}$$

$$\text{Recovery percentage} = \frac{C_s}{C_i} * 100 \tag{3}$$

where C_i is the initial quantity of copper (g) in the feed phase, C_f and C_s are the copper amounts (g) from the feed and stripping phases at the end of the experiments, respectively. The regression analyses were performed to estimate the response function. Experimental results obtained from the CCD model were described in a form as given in Equation (4):

$$y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{j=1}^{k} b_j x_j^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} b_{ij} x_i x_j \tag{4}$$

where b_i is the linear coefficient, b_j is the quadratic

Table 3 | Variables used in the experimental design

Variables	Coded	−1	0	1
H_2SO_4 concentration (g/L)	X1	150	200	250
Extractant concentration (%v/v)	X2	5	10	15
Flow (mL/min)–(cm/min)	X3	50–10.1	250–64.4	450–115.9
Feed volume/Strip volume	X4	1	2	3
Time (min)	X5	60	180	300

coefficient, b_{ij} is the cross coefficient, k is the number of factors studied in the experiment, x_i, x_j represent the coded value of each factor (X_1, X_2, X_3, X_4, X_5), and y is the predicted response (extraction efficiency or recovery efficiency) (Jiao et al. 2013). A design matrix comprising 28 experimental runs was constructed. The regression analysis was performed to estimate the response function.

Table 3 lists the variable ranges used in RSM with actual and coded values, and Table 4 shows the CCD experimental design for HFM extraction and recovery efficiencies that were developed by JMP 10 trial software. The results were analyzed by the least-squares method and response surfaces were generated with software to find the best region for recovery efficiency.

RESULTS AND DISCUSSION

RSM and analysis

The effect of the process variables on the extraction efficiency for removing copper from electroplating model wastewater solution and recovery efficiency for removing copper from the organic phase were observed using RSM according to CCD design. The design matrix, the results of RSM experiments, and predicted efficiency values obtained using Equations (5) and (6) as given in Table 4:

$$\begin{aligned} Y_1 = &+54.04 + 3.66*X_1 + 6.74*X_2 + 7.60*X_3 - 3.34*X_4 \\ &+ 22.78*X_5 + 2.59*X_1*X_2 + 4.03*X_1*X_3 + 1.38*X_1*X_4 \\ &+ 1.93*X_1*X_5 - 1.33*X_2*X_3 - 2.60*X_2*X_4 + 6.30*X_2*X_5 \\ &- 1.21*X_3*X_4 + 5.16*X_3*X_5 - 4.52*X_4*X_5 - 2.69*X_1^2 \\ &- 0.21*X_2^2 - 9.29*X_3^2 + 1.02*X_4^2 - 15.11*X_5^2 \end{aligned} \tag{5}$$

Table 4 │ CCD design for copper extraction and stripping efficiencies

Exp. No.	X_1	X_2	X_3	X_4	X_5	Extraction efficiency		Recovery efficiency	
						Experimental	Model	Experimental	Model
1	−1	−1	−1	−1	−1	2.94	2.02	6.45	6.93
2	−1	−1	−1	1	1	18.45	18.95	61.58	61.13
3	−1	−1	1	−1	1	51.48	52.41	80.84	81.64
4	−1	−1	1	1	−1	6.85	6.28	8.05	6.60
5	−1	0	0	0	0	48.22	47.67	64.01	66.11
6	−1	1	−1	−1	1	57.89	58.60	55.32	56.25
7	−1	1	−1	1	−1	3.19	2.39	3.08	1.76
8	−1	1	1	−1	−1	2.52	2.16	6.31	6.23
9	−1	1	1	1	1	48.64	49.70	65.26	64.26
10	0	−1	0	0	0	45.86	47.08	78.01	77.01
11	0	0	−1	0	0	35.02	37.14	75.62	74.10
12	0	0	0	−1	0	58.03	58.42	83.02	76.50
13	0	0	0	0	−1	9.74	16.14	19.85	22.35
14	0	0	0	0	0	54.01	54.04	79.01	78.64
15	0	0	0	0	0	58.46	54.04	77.03	78.64
16	0	0	0	0	1	67.01	61.71	88.05	85.23
17	0	0	0	1	0	51.01	51.72	67.56	73.76
18	0	0	1	0	0	53.37	52.35	78.21	79.42
19	0	1	0	0	0	60.69	60.57	79.09	79.78
20	1	−1	−1	−1	1	24.74	25.01	56.37	58.08
21	1	−1	−1	1	−1	3.44	2.20	13.63	13.08
22	1	−1	1	−1	−1	8.3	7.50	10.27	10.97
23	1	−1	1	1	1	52.9	53.52	73.47	73.24
24	1	0	0	0	0	53.37	55.01	78.01	75.60
25	1	1	−1	−1	−1	4.43	3.40	18.27	19.10
26	1	1	−1	1	1	48.03	48.42	85.25	85.15
27	1	1	1	−1	1	96.73	97.56	93.36	94.51
28	1	1	1	1	−1	14.28	13.60	7.67	6.57

X_1 = H$_2$SO$_4$ concentration (g/L); X_2 = Extractant concentration (%v/v); X_3 = Flow (mL/min.); X_4 = feed volume/strip volume; X_5 = time (min.); −1 = low value, 0 = center value, +1 = high value.

$$Y_2 = +78.64 + 4.74*X_1 + 1.38*X_2 + 2.65*X_3 - 1.37*X_4$$
$$+ 31.44*X_5 + 4.86*X_1*X_2 + 1.42*X_1*X_3 - 1.49*X_1*X_4$$
$$+ 0.79*X_1*X_5 - 0.92*X_2*X_3 - 3.96*X_2*X_4 + 1.21*X_2*X_5$$
$$+ 1.87*X_3*X_4 + 3.97*X_3*X_5 + 0.53*X_4*X_5 - 7.79*X_1^2$$
$$- 0.25*X_2^2 - 1.88*X_3^2 - 3.51*X_4^2 - 24.85*X_5^2 \qquad (6)$$

where Y_1 and Y_2 are the extraction and recovery efficiencies of Cu, respectively; X_1, X_2, X_3, X_4 and X_5 are the coded variables for H$_2$SO$_4$ concentration, extractant concentration, flow rate, F/S ratio and time, respectively; X_5 in Equation

(5) is extraction time and X_5 in Equation (6) is stripping time. For the estimation of significance of the model, the analysis of variance (ANOVA) and the *f*-test were applied. The ANOVA of the regression models, which are presented in Tables 5 and 6, demonstrate that the models are highly significant as evident from the calculated *f*-values for extraction and recovery efficiencies, which are 55.83 and 75.23, respectively. These values have a very low probability value $P \leq 0.0001$. If the *p*-value is smaller than 0.05, the model is significant. The results indicated that the model used to fit the response variable was significant and adequate to represent

Table 5 │ ANOVA of the response surface model to predict extraction efficiency

Factor	Degree of freedom	Sum of squares	Mean square	f-value	p-value
Model	20	17,374.493	868.725	55.880	<0.0001
Residual error	7	108.800	15.54		
Lack of fit	6	98.900	16.484	1.664	0.532
Pure error	1	9.900	9.900		
Total	27	17,483.293			

$R^2 = 0.9937$; adjusted $R^2 = 0.9759$.

the relationship between the response and the independent variables (Zhao *et al.* 2012). The lack of fit *p*-value of extraction and recovery efficiencies are 0.51 and 0.22, respectively, which imply that the lack of fits are insignificant. The corresponding variables would be more significant if the absolute *f*-value becomes greater and the *p*-value becomes smaller. The high value of R^2_{adj} indicates that the quadratic equation is capable of representing the system under the given experimental domain (Celep *et al.* 2011). The value of adjusted determination coefficient R^2_{adj} was found to be 0.9759 and 0.9821 for extraction and recovery efficiency, respectively, which means that the calculated model was able to explain 97.59% and 98.21% of the total variations in the system.

The effect of factors on the extraction and recovery efficiencies of copper

Figures 2(a), 2(d), 3(a) and 3(d) illustrate the effects of extractant concentration and the other two factors on extraction and recovery efficiencies, respectively. Extraction and recovery efficiencies increased with increasing extractant and acid concentration. The reason for this observation was believed to be the mass transfer mechanism of the membrane process. The mass transfer mechanism of the NDSX process is a carrier-facilitated transport. It is evident from Figure 2(a) that the extractant concentration has a

positive effect on the recovery of copper from rinse bath solution because the copper extraction capacity of the organic phase increases with the increasing LIX 84-I concentration of the organic phase. However, it is seen that extractant concentration does not affect recovery efficiency as well as it affects extraction efficiency in Figure 3(a).

The viscosity of the organic phase increases at higher extractant concentration, which has a negative effect on the recovery of copper (Parhi *et al.* 2013). Therefore, the upper limit of the extractant concentration was chosen as 15% volume. The transfer of copper from the feed to the stripping solution occurred over a very long time at low extractant concentrations due to the high copper content of the feed solution. Thus, the lower limit of the extractant concentration was taken as 5% volume. In addition, the recovery of copper from wastewater will be more economical at low extractant concentration. Therefore, a high extractant concentration was not chosen.

It is apparent from the response surface plots in Figures 2(b), 2(c), 3(b) and 3(c) that extraction and recovery efficiencies increase with the increasing H_2SO_4 concentration of the stripping phase. In other words, the increment of H_2SO_4 concentration to ~230 g/L in the stripping phase resulted in an increase of the extraction and recovery efficiencies. To maximize the recovery efficiency of copper, the H_2SO_4 concentration of the stripping phase should be in the range of 200–230 g/L at the zero levels of the other factors as shown in Figures 3(b) and 3(c).

The flow rates or lumen flow velocities (υ), which were calculated from the flow rates of the liquid phases, were chosen as 50 mL/min (10.1 cm/min)–250 mL/min (64.4 cm/min)–450 mL/min (115.9 cm/min), respectively. Extraction and recovery efficiencies increase with the increase of flow rates as seen in Figures 2(a), 2(b), 3(a) and 3(b). However, too high flow rates result in lower residence time for the solutions or lower contact time for the relevant ions in the reaction shown in Equation (7) (Lothongkum *et al.* 2009). As shown in Figures 2(a), 2(b), 3(a) and 3(b), the extraction efficiency increases to a

Table 6 │ ANOVA of the response surface model to predict recovery efficiency

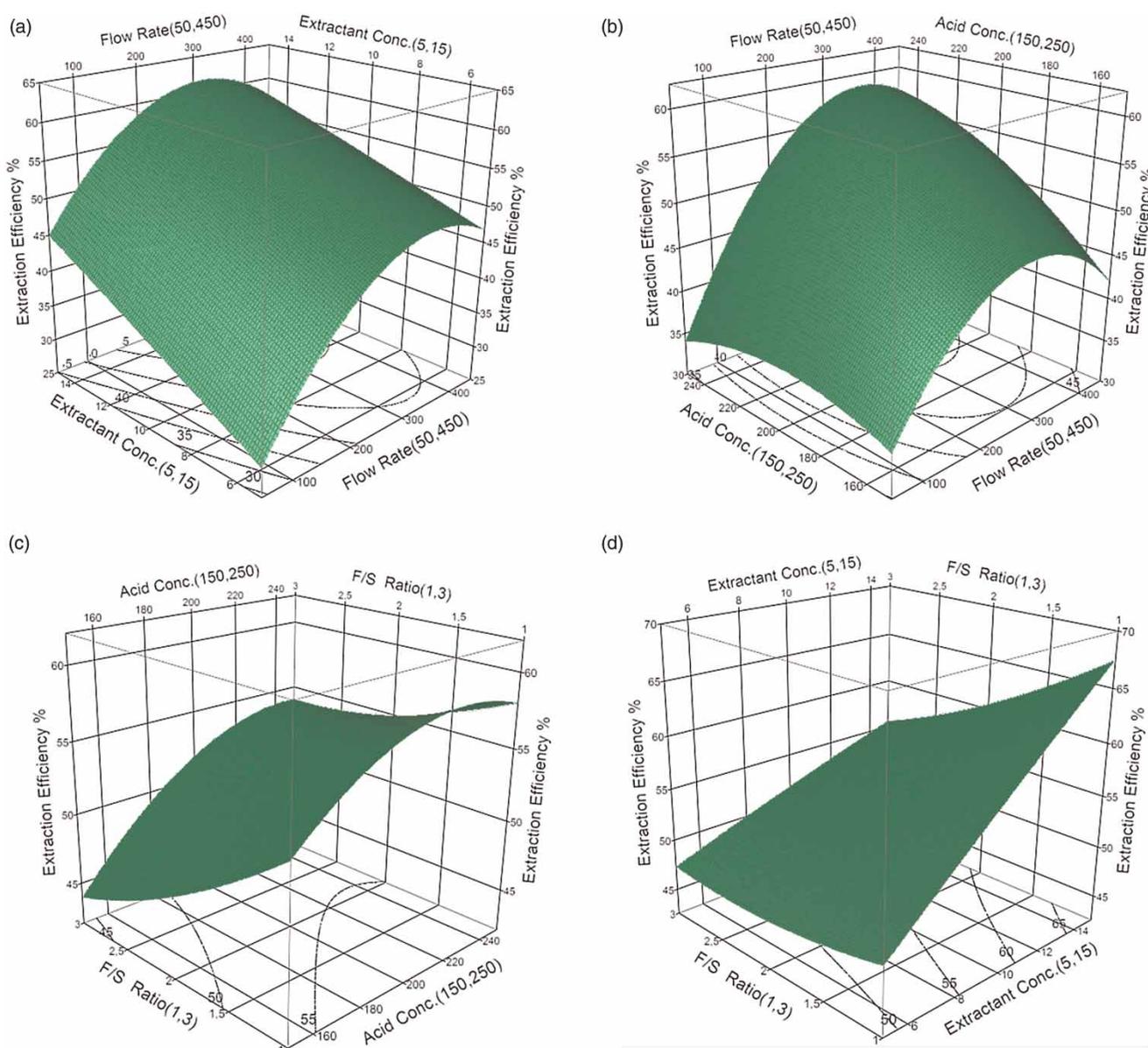| Factor	Degree of freedom	Sum of squares	Mean square	f-value	p-value
Model	20	27,338.148	1,366.910	75.238	<0.0001
Residual error	7	127.174	18.170		
Lack of fit	6	125.214	20.860	10.646	0.230
Pure error	1	1.960	1.960		
Total	27	27,465.322			

$R^2 = 0.9950$; adjusted $R^2 = 0.9809$.

Figure 2 | Response surface plots showing the effect of two variables on extraction efficiency (the other two variables are held at center level). (a) Flow rate or υ (range; 50 mL/min = 10.1 cm/min–450 mL/min = 115.9 cm/min) and extractant concentration. (b) Flow rate and acid concentration. (c) Acid concentration and F/S ratio. (d) Extractant concentration and F/S ratio.

maximum value and then decreases with increasing flow rate. Generally, flow rate has a positive effect on the recovery efficiency. As seen in Figures 3(a) and 3(b), recovery efficiency increases with the increase of flow rate.

Figures 2(d) and 3(d) show the combined effect of F/S ratio and extractant concentration on the extraction and recovery efficiencies. It can be observed that a decrease in F/S ratio increases the extraction and recovery efficiencies. At low extractant concentration, F/S ratio does not affect the extraction efficiency as a result of the decreasing extraction capacity of the organic phase due to low extractant

concentration. With the increase of extractant concentration, the effect of the F/S ratio becomes more significant. Therefore, it is desirable to select a higher F/S ratio to increase the copper recovery capacity of the process.

The amount of H^+ ions in the stripping phase depends on the acidity of the phase and also the volume of the stripping phase. Extraction and stripping reactions occur according to Equation (7). According to this reaction, the transformation of Cu from wastewater to the stripping phase is very dependent on the H^+ concentration of the stripping phase. Copper was separated from a synthetic leach solution using
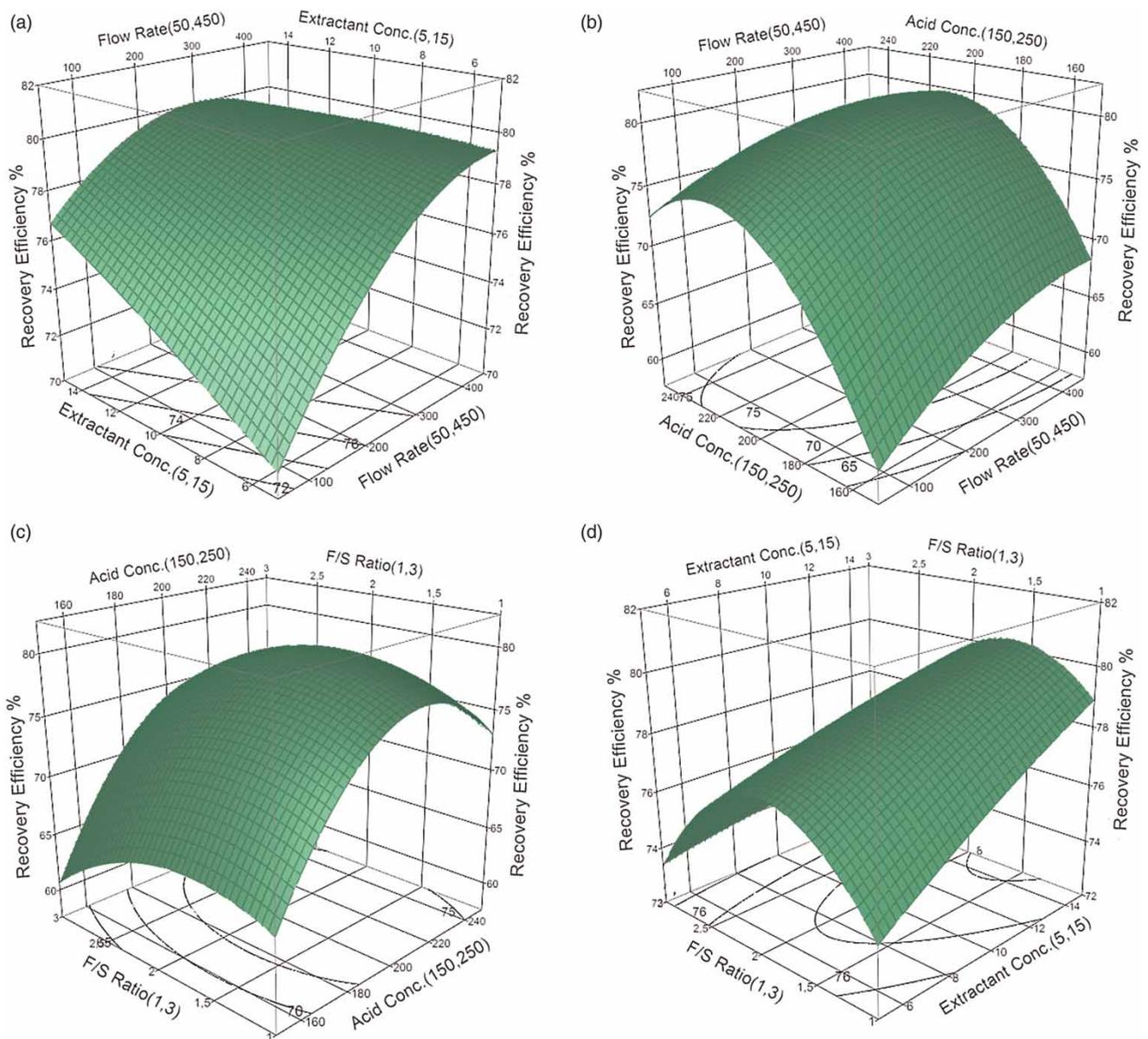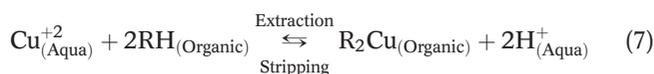
Figure 3 | Response surface plots showing the effect of two variables on recovery efficiency (the other two variables are held at center level). (a) Flow rate or υ (range; 50 mL/min = 10.1 cm/min–450 mL/min = 115.9 cm/min) and extractant concentration. (b) Flow rate and acid concentration. (c) Acid concentration and F/S ratio. (d) Extractant concentration and F/S ratio.

a supported liquid membrane according to Parhi & Sarangi (2008). Copper was recovered using 10% LIX 84-I at pH 4.5 and 900 mol/m³ (88.2 g/L) H_2SO_4 in strip solution (Parhi & Sarangi 2008). The optimum NDSX parameters in our study were determined as 15% LIX 84-I at pH 4.0 and 227 g/L the H_2SO_4 in strip solution. The main difference between these two studies was the H_2SO_4 concentration of the strip solution, but Parhi and Sarangi kept a constant H_2SO_4 concentration of the strip solution at 900 mol/m³ (88.2 g/L); if its effect was researched, a higher H_2SO_4

concentration would be determined to increase the recovery efficiency. A solvent extraction flow sheet for the separation and recovery of Cu(II), Ni(II) and Zn(II) using LIX 84-I as an extractant from sulfate solutions was developed by Reddy & Priya (2005). According to this study, optimum solvent extraction parameters are: a 0.05 M LIX 84-I concentration in the organic phase; an aqueous to organic phase ratio of 5 and an equilibrium pH of 4.0 for extraction; a 2 M (196 g/L) H_2SO_4 concentration in the stripping phase; and an aqueous to organic phase ratio of two-thirds

for stripping. As previously mentioned, the H_2SO_4 concentration of the stripping phase was determined at 227 g/L in our study, which is a little higher than 2 M (196 g/L), which is due to the advantage of the CCD. Because determination of the optimum H_2SO_4 concentration for the stripping phase at 227 g/L is very difficult or impossible to attain by conventional methods. Ren *et al.* (2007) used the HFRLM process for the simultaneous extraction and stripping of copper(II) from wastewater by DEHPA extractant (Ren *et al.* 2007). In addition, they compared HFRLM with NDSX; their studies showed that the overall mass transfer coefficient of the HFRLM process was higher than that of the NDSX process. This was mainly because the renewal effect of the HFRLM process could greatly reduce the resistance of mass transfer in the lumen side, which was the main part of the total mass transfer resistance. Therefore, the presented study might be repeated using the HFRLM process to decrease recovery time in the future. In addition, the volume of the stripping phase affects the extraction and recovery efficiencies. If the volume of the stripping phase is high, the driving force for extraction and stripping will be high. According to Equation (7), the increase in the number of H^+ ions forwards the Cu recovery (Lothongkum

et al. 2009). Therefore, the stripping phase volume is also an important parameter for the NDSX process. Conversely, the increment of the stripping phase volume decreases the copper concentration of the stripping phase, which is not desirable. As shown in Figures 2(c) and 2(d), the extraction efficiency decreases with the increase of the F/S volumetric ratio.

$$Cu^{+2}_{(Aqua)} + 2RH_{(Organic)} \overset{\text{Extraction}}{\underset{\text{Stripping}}{\leftrightarrows}} R_2Cu_{(Organic)} + 2H^+_{(Aqua)} \qquad (7)$$

Optimization study and confirmation studies

The main object of the study was to optimize the stripping stage. To maximize recovery efficiency, the optimization studies were carried out using RSM software for regression analysis. The software generated the optimum values of factors as shown in Table 7. The confirmation test was carried out to clarify the results at these optimum NDSX conditions, and the results of this test are presented in Table 7. This table shows that the predicted value was very close to the experimental results.

Table 7 │ Optimized extraction and recovery efficiency with model validation

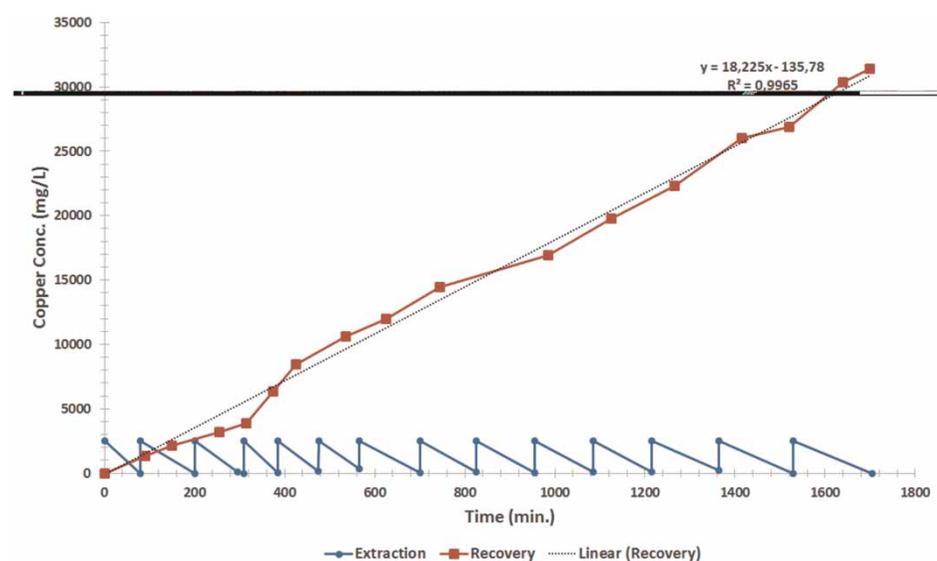|	H_2SO_4 conc. (g/L)	Extractant conc. (v/v)	Flow rate (mL/min)	F/S ratio	Time (min)	Experimental	Model
Recovery	227	15	450	1.22	270	95.88	97.75
Extraction	227	15	450	1.22	55	90.56	91.15

Figure 4 │ Long-term performance of membrane process.

Long-term performance of the NDSX process

To test the long-term performance of the membrane process, 14 extra experiments were performed under optimized NDSX conditions. The feed tank was replenished with fresh electroplating model wastewater solution just after feed phase treatment. The organic and stripping phases were not replenished with fresh solutions during the experiments. Thus, the copper concentration increased gradually in the stripping phase. In total, the feed phase was replenished 14 times and the experiment was continued for 1,700 min. When copper sulfate crystals occurred in the stripping phase, the experiment was terminated. The organic phase was prepared with 500 mL at the beginning of the experiment. At the end of the experiment, 5 mL of the organic phase had been lost, which might be due to the pumps shutting down for a short time to fill the feed tank. When the peristaltic pumps were turned on, the organic phase mixed the feed phase because of the positive pressure. As seen in Figure 4, at the beginning of the process, the copper transportation rate from the feed phase to the organic phase was faster than the end of the process. The reason for this might be because the copper concentration of the stripping phase increased toward the end of the experiment; therefore, the driving force for the transformation of copper decreased according to Equation (7) because of the difficulty of transporting copper ions from the organic phase to the stripping phase.

CONCLUSIONS

In this paper, the treatment of electroplating with model wastewater solution containing copper by HFM using the NDSX technique was studied. The CCD of RSM was successfully applied to optimize the recovery of copper from electroplating model wastewater solution. The mathematical model equations were derived for extraction and recovery efficiencies by using sets of experimental data. The proposed quadratic model agrees well with the experimental data, with correlation coefficients (R^2) for extraction and recovery efficiencies of 0.9937 and 0.9950, respectively.

As a result of CCD, the optimal stripping conditions for the model wastewater solution were as follows: 227 g/L H_2SO_4 concentration, 15% (v/v) extractant concentration, 450 mL/min flow rate ($v = 115.9$ cm/min), 1.22 F/S ratio, and 270 min time. The recovery efficiency was achieved at 95.88% under optimum conditions. Under optimized conditions, the experimental values were close to the values predicted by the software.

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