RESEARCH PAPER

Investigating the Leaching Behavior of Copper from Chalcopyrite Concentrate in $H_2SO_4/CuCl_2$ Media

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Abstract: *The present paper is a detailed investigation of the dissolution behavior of copper from the chalcopyrite concentrate sample using a cupric chloride solution. Response surface modeling (RSM) in combination with d-optimal design (DOD) was utilized for modeling and optimizing the cupric chloride leaching process. Initially, a quadratic polynomial model was developed for the relationship between the recovery of copper and influential factors. The predictions indicated an excellent agreement with the experimental data (with R2 of 0.9399). Then, the effect of main factors including pH (1-4), liquid/solid ratio (2-7 mL/g), temperature (70-90 °C), CuCl2 concentration (6-35 g/L), and leaching time (0.5-16) were determined. The findings demonstrated that the temperature and CuCl2 concentration were the most effective factors on the dissolution rate of copper from chalcopyrite sample, while the liquid/solid ratio had the lowest impact. The recovery of copper increased linearly with an increment in the liquid/solid ratio and the decrease in the pulp pH. Additionally, the recovery enhanced by increasing the temperature and CuCl2 concentration owing to generation of Cu–Cl complexes species and reached a plateau point and then almost remained unchanged. Meanwhile, it was observed that the recovery of copper was independent of the interaction between factors. Moreover, the optimization of leaching process was carried out by Design Expert (version 7) software and desirability function method and the highest recovery of copper was found to be about 86.1% at a pH of ~1.4, temperature of 89 °C, liquid/solid ratio of 6.8 mL/g,* $CuCl_2$ *concentration of 21.79 g/L and leaching time of ~8 h.*

Keywords: *Copper leaching, Chalcopyrite concentrate, HydroCopper® process, Cupric chloride, D-optimal design (DOD).*

1. INTRODUCTION

Chalcopyrite ($CuFeS_2$) is one of the most important and abundant copper minerals due to availability and utilization in nature and occupies nearly 70% of the world's Cu resources [1-4]. Generally, copper ores and concentrates are treated by both pyrometallurgical and hydrometallurgical technologies [5]. It is estimated that about 80-85% of copper in the world is produced through pyrometallurgical processes [6] and nearly 20% of total copper is extracted by hydrometallurgical methods including leaching, followed by SX-EW process [7], mainly from secondary sulfide and copper oxide minerals [8, 9]. In recent years, hydrometallurgical processes have attracted much attention in the treatment of ores, even sulfide minerals, owing to the requirement to avoid SO_2 emissions, the depletion of high-grade (sulfide) deposits, the lower production costs and also more environmentally friendly characteristics [10-12].

A great deal of studies has been carried out on the dissolution of chalcopyrite ores and concentrates, which indicate chalcopyrite is highly refractory mineral to leach in acid media due to the formation of the surface passivation layers during leaching process [4, 5, 13-18]. Hence, in the last two decades, various methods such as adding oxidants or catalysts, grinding chalcopyrite particles to less than 20 µm, exerting pressure and enhancing temperature, adjusting redox potential and using chloride and alkaline mediums have been investigated and reviewed to improve the low dissolution rate [5, 19-31]. These investigations demonstrated the superiority of chloride mediums in chalcopyrite leaching owing to the aggressive nature of the leaching, higher solution redox potentials, and complexation with several elements, such as copper [30]. Also, the higher dissolution rates of copper from chalcopyrite can be because of the formation of copper-chloro complexes (Cu^+, Cu^{2+} complexes with Cl^- ions) [32].

HydroCopper® process is an efficient chloride-based hydrometallurgical technology that economically can extract copper from sulfide (such as chalcopyrite) ores and concentrates at ambient pressure and temperature range of 80-100 °C [25,30, 33-36). Based on the literature, cupric chloride ($CuCl_2$) acts as an oxidant in such processes and the dissolution of chalcopyrite in the leach solutions including H_2SO_4, cupric ions and dissolved oxygen can be performed according to the following reactions [26,28,34]:

$$CuFeS_2 + H_2SO_4 \rightarrow CuS + FeSO_4 + H_2S \quad (1)$$

$$CuFeS_2 + 3CuCl_2 \rightarrow 4CuCl + FeCl_2 + 2S \quad (2)$$

$$CuFeS_2 + CuCl_2 + \frac{3}{4}O_2 \rightarrow 2CuCl + \frac{1}{2}Fe_2O_3 + 2S \quad (3)$$

$$CuFeS_2 + CuCl_2 + \frac{3}{4}O_2 + \frac{1}{2}H_2O \rightarrow 2CuCl + FeOOH + 2S \quad (4)$$

As it is shown in the above reactions, ferrous ions, which are created from chalcopyrite dissolution in the leach liquor, are oxidized to a higher order (i.e. ferric iron) and can be precipitated as hematite or goethite forms by oxygen purging into leach liquor. The sulfur in the concentrate is also released due to dissolution in the leaching medium and ultimately is precipitated.

Literature indicates that there are few reports on the leaching behavior of copper from a concentrate especially using cupric chloride and on the other hand each ore or concentrate has its individual mineralogical and chemical composition and accordingly the optimum extraction conditions of metal from one type of ore or concentrate to another are different, therefore it is required to further attentions. Hence, this study is focused on the use of chloride media to extract copper from a chalcopyrite concentrate. In this work, the dissolution behavior of chalcopyrite in the H_2SO_4-$CuCl_2$ solution is experimentally investigated in detail. Response surface methodology (RSM) combined with d-optimal design (DOD) was employed for this purpose.

2. EXPERIMENTAL SECTION

2.1. Materials

To conduct the leaching experiments, a chalcopyrite concentrate sample was obtained from Miduk copper mine located 42 km northeast of Shahrbabak in Kerman province, Iran. Since the samples were provided from flotation unit concentrate (about 100 kg) and were final product of this circuit, they were not further crushed and milled and only were homogenized and sealed in polyethylene bags. It needs to be pointed out that based on the sieve analysis, about 80% of particles were smaller than 75µm in diameter. Thereafter, the representative sample was chemically analyzed by an X-ray fluorescence spectrometer (XRF Shimadzu-1800, Kyoto, Japan). The results are presented in Table 1.

As it is shown, the content of CuO in the sample studied is about 18.75% and the most important impurities are silica, iron, and calcite. Chemicals used in this work were purchased from Merck and were sulfuric acid (96-98%) and cupric chloride ($CuCl_2$) as lixiviant and sodium hydroxide pellets as pH modifiers. Also, the water used was distilled water.

2.2. Leaching Experiments

All leaching experiments were carried out on the representative concentrate sample in a 250 ml Erlenmeyer glass flask heated on a hot plate, which was equipped with a magnetic stirrer and a thermometer for temperature control within ±2 °C. For each test, leach lixiviant was prepared

Table 1. Chemical analysis of representative sample obtained from Miduk flotation concentrate.

Composition	CuO	PbO	Al_2O_3	Fe_2O_3	ZnO	SiO_2	CaO
Content (wt. %)	18.75	1.98	2.25	28.05	5.58	28.02	12.15
Composition	P_2O_5	MgO	K_2O	MnO	TiO_2	SrO	L.O.I
Content (wt. %)	0.098	1.06	0.49	0.08	0.207	0.64	0.645

by adding 10 mL H_2SO_4 and a predetermined concentration of $CuCl_2$ to distilled water based on the targeted liquid to solid ratios and then was poured into the flask. A 15 g of the concentrated sample was added into the solution and then the liquor was magnetically stirred at 400 rpm at a desired temperature. It needs to be pointed out that the solution pH was adjusted by sodium hydroxide and sulfuric acid for each test at the targeted values. When the leaching process was finished at the targeted times (0.5-16 h), the solution was filtered and analyzed by AAS (Thermo Elemental's SOLAAR S Series atomic absorption, England) for measuring the concentration of copper. Ultimately, the leaching rate of copper (R) was determined using the following formula [37].

$$R = \frac{C_1 \times V}{C_0 \times m} \times 100 \tag{5}$$

where, C_0 is the content of copper in the solid sample studied (%); m is the concentrated sample mass (g); V is the leach solution volume (L) and C_1 represents the concentration of copper in the leach solution (g/L).

Table 2. The main factors influencing the leaching rate of chalcopyrite concentrate associated with their levels based on RSM-DOD technique

Factor	Symbol	Factorial level		
		Low (-1)	Center (0)	High (+1)
pH	A	1	2.5	4
Leaching time (h)	B	0.5	8.25	16
Temperature (°C)	C	70	80	90
$CuCl_2$ concentration (g/L)	D	6	20.5	35
Liquid/solid ratio (mL/g)	E	2	4.5	7

Table 3. HydroCopper® leaching experiments DOD plan and the measured values of copper recoveries

Std	Run	pH	Leaching time (h)	Temperature (°C)	$CuCl_2$ (g/L)	Liquid/Solid ratio	Cu recovery (%)
3	1	2	7	80	16	2	66.08
5	2	4	3	80	16	2	26.3
7	3	1.5	7	90	6	7	50.21
6	4	4	0.5	80	16	2	23.1
21	5	1.5	7	90	16	7	77.12
22	6	3	10	80	16	2	52.25
10	7	2	5	80	16	2	55.16
24	8	1.5	7	90	16	3	63.45
19	9	2	16	90	16	2	49.91
17	10	4	16	90	16	2	42.26
12	11	1.5	7	90	16	5	71.54
9	12	4	1	80	16	2	26.11
16	13	3	16	90	16	2	44.68
13	14	1.5	7	90	16	2	77.57
26	15	2	7	90	16	2	69.38
15	16	3	7	80	16	2	59.91
4	17	4	10	90	16	2	50.76

Table 3. HydroCopper® leaching experiments DOD plan and the measured values of copper recoveries

Std	Run	pH	Leaching time (h)	Temperature (°C)	$CuCl_2$ (g/L)	Liquid/Solid ratio	Cu recovery (%)
18	18	1.5	7	70	16	2	17.31
23	19	1.5	7	90	35	7	85.47
2	20	4	0.5	90	16	2	25.16
11	21	2	16	80	16	2	44.19
25	22	1.5	7	90	10	7	65.66
27	23	2	3	80	16	2	33.82
20	24	3	7	90	16	2	63.59
1	25	1.5	7	90	20	7	79.16
8	26	3	3	90	16	2	40.59
14	27	4	5	90	16	2	48.29

3. RESULTS AND DISCUSSION

3.1. Modeling

In this research response surface modeling (RSM) combined with d-optimal design (DOD) was utilized to characterize the behavior factors affecting the leaching rate of chalcopyrite concentrate and also to determine possible interactive effects between factors. This methodology is a powerful statistical technique for multivariate nonlinear modeling and optimizing the processes even in the presence of complex interactions [38-40]. For this purpose, firstly leaching tests were designed based on RSM-DOD design using Design Expert (Demo v. 7.0.0, Stat-Ease, Inc.) software according to Table 2. Ultimately, a series of 27 experimental runs were randomly selected and implemented as shown in Table 3. Table 3 shows the matrix of leaching tests on chalcopyrite concentrate and the measured values of recovery for each experiment. The range of factors studied was selected based on a series of primary experiments and pervious works published in this field [3,19,29,35;36].

After designing and implementing the experiments, a statistical quadratic model (Eq. 6), which is commonly used for multivariate nonlinear modeling, were fitted to the experimental data presented in Table 3.

$$R = \alpha_0 + \sum_{i=1}^{n} \alpha_i X_i + \sum_{i=1}^{n} \alpha_i X_i^2 + \sum_{1 \le i \le j}^{n} \alpha_j X_i X_j + \varepsilon \quad (6)$$

where, n, α_0, α_i, X_i and X_j, α_{ii}, α_{jj} and ε represent the number of factors, a constant term, the coefficients of the linear terms, the factors, the coefficients of the quadratic terms, the coefficients of the interaction terms and the residual associated with the experiments, respectively [41].

Ultimately, after removing insignificant terms (p-value < 0.05) except main effects, the final equation representing the leaching rate (R) of chalcopyrite concentrate was achieved based on coded factors as functions of pH (A), leaching time (B), temperature concentration (C), $CuCl_2$ concentration (D) and liquid to solid ratio (E):

$$R = 67.94 - 8.95 \times A + 7.55 \times B + 25.91 \times C + 16.551 \times D + 2.91 \times E - 24.32 \times B^2 - 19.57 \times C^2 - 12.68 \times D^2 \quad (7)$$

The factors were codified by Eq. 8 for calculations simplification and uniform comparison of factors.

$$X_i = \frac{x_i - x_0}{\Delta x}, i = 1,2,3,...,n \quad (8)$$

where, X_i is the coded (dimensionless) amount of the *i*th factor, x_i is the actual amount of the factor, x_0 is the amount of x_i at the center point and Δx is the step change amount [42].

Meanwhile, the data were statistically analyzed using analysis of variance (ANOVA) at the 95% confidence level (p-value < 0.05); the results are presented in Table 4. The results presented in Table 4 including R^2 of 0.9399, adjusted R^2 of 0.9133, adequate precision of 21.07, and p-value < 0.0001 indicate the model fitted has a high capability to predict the leaching rate of copper from chalcopyrite concentrate sample. Also, plots of residual normal probability and internally studentized residuals vs. run numbers were utilized to further investigate the reliability of the model as shown in Fig. 1. As observed in Fig. 1, residuals (difference between actual and predicted values) are normally distributed and all data are in the proper range within 95% confidence level, indicating that model developed represents a good fit to the data to predict the dissolution rate of chalcopyrite concentrate. Moreover, ANOVA results in Table 4 indicate that the interaction between factors has no effect on the leaching rate in the system studied.

3.2. Influence of Main Factors

After the selection of the model, the behavior of factors influencing the dissolution of chalcopyrite concentrate in H_2SO_4+$CuCl_2$ media was evaluated by the perturbation and 3D response surface plots as displayed in Figs. 2 and 3.

Fig. 2 displays the perturbation plot of the effects of the main factors on the leaching rate of copper, which is a simulation from Table 3 and Eq. (7). This plot helps us to compare the effect of all the factors at a particular point in the design space [43]. A steep slope or curvature in a factor indicates that the dissolution rate is sensitive to that factor. As observed in Fig. 2, the influence

Table 4. ANOVA of response surface reduced quadratic model based on DOD design for the leaching rate of Cu using HydroCopper® process

Source	Sum of Squares	Degree of freedom (DF)	Mean Square	F value	p-value Prob > F
Model	8770.99	8	1096.37	35.22	< 0.0001
A-pH	454.52	1	454.52	14.6	0.0013
B-Leaching time (h)	368.93	1	368.93	11.85	0.0029
C-Temperature (°C)	2143.13	1	2143.13	68.84	< 0.0001
D-$CuCl_2$ (g/L)	648.88	1	648.88	20.84	0.0002
E-Liquid/solid ratio	50.28	1	50.28	1.62	0.22
B^2	1628.87	1	1628.87	52.32	< 0.0001
C^2	910.25	1	910.25	29.24	< 0.0001
D^2	154.23	1	154.23	4.95	0.039
Residual	560.38	18	31.13		
Cor Total	9331.37	26			
Statistical analysis summary					
R^2	0.9399	Std. Dev.	5.58		
Adjusted R^2	0.9133	Mean	52.19		
Adequate precision	21.069				

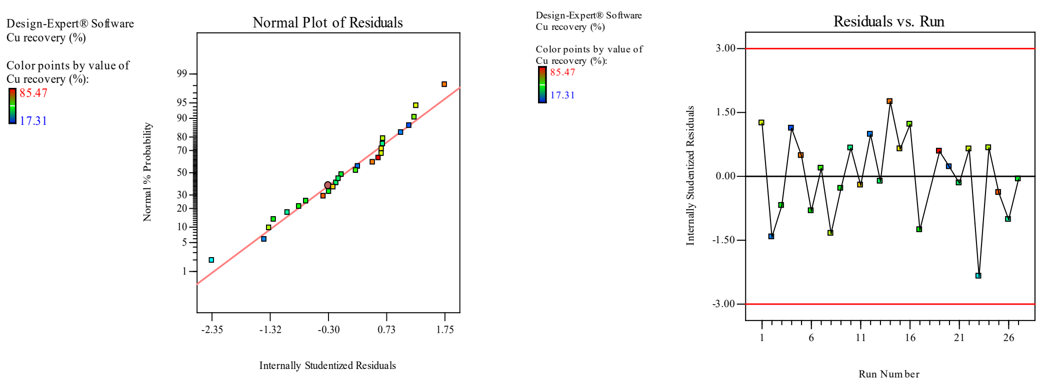

Fig. 1. Plots of residual normal probability (a) and internally studentized residuals vs. run number (b)

degree of important factors is in order of C > D > B > A > E.

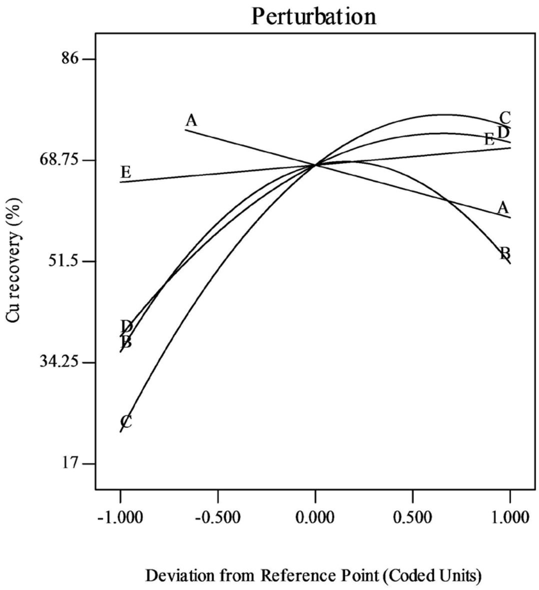

Fig. 2. Perturbation plot indicating the relative significance of factors on the leaching rate of chalcopyrite concentrate.

To obtain a better understanding of the influence of factors on the dissolution rate of copper from chalcopyrite concentrate, the combined effects of factors were evaluated applying the 3D response surface plots (Fig. 3). Fig. 3 demonstrates the effects of two factors on the leaching recovery when other experimental factors are kept constant at their optimal level (these graphs were obtained after optimization).

As can be observed in these graphs, the dissolution process of chalcopyrite concentrate is strongly affected by temperature, leaching time and $CuCl_2$ concentration and recovery of copper is as quadratic polynomial function of these factors.

As seen in Figs. 2 and 3(c, d, f), when temperature increases from 70 to 90C, the recovery significantly increases and reaches a maximum point. It is observed that the leaching rate improves by about 60%. These results were in good agreement with the results reported by Lu et al. [19] and Veloso et al. [29]. Certainly, increasing the leaching rate with an increment in the leaching temperature can be due to the reduction in the pulp viscosity and the increase in the penetration of leach lixiviant into the interior of the particles.

As expressed and seen in Figs. 2 and 3(b, e, f), $CuCl_2$ plays an important role in the dissolution of chalcopyrite sample studied. It can be observed that the leaching rate enhances with an increase in the $CuCl_2$ concentration and reaches a plateau and with further increment remains almost unchanged. This behavior can be described by chemical reactions presented in Eqs. (1) to (4). When copper chloride is reacted with chalcopyrite, cuprous ion (CuCl) is formed and this leads to the breakdown of the sulfide molecular bond and ultimately to the dissolution of copper present in the concentrate. According to Carneiro and Leão [14], Ruiz et al. [44] and Zhong and Li [6], chloride ions can complex and stabilize copper ions and subsequently generate Cu–Cl complexes species.

It is seen from Figs. 2 and 3(a, b, c) that the leaching rate is a linear function of pH and liquid/solid ratio. The dissolution rate increased with increasing the liquid/solid ratio owing to the increase of the volume of acid available for each mineral particle due to the reduction in the suspension density and the viscosity of pulp and accordingly the decrease in the mass transfer resistance [45]. It was also found that the leaching recovery enhanced by decreasing the pulp pH from 4 to 1.5. The low recoveries at the pH values may be due to the formation of Fe hydroxide precipitates species, which can cause the passivation of $CuFeS_2$ dissolution [6]. Lundström et al. [35] reported that low leaching rates at more acidic pH values can be owing to the quick formation of a sulfur layer around chalcopyrite particles. Additionally, Zhong and Li [6] expressed that the dissolution rate of copper enhances normally by increasing H^+ concentration and a reasonable pH value (acid concentration) is necessary for chalcopyrite leaching.

3.3. Optimization

Optimization of the HydroCopper® process of chalcopyrite concentrate sample was performed utilizing the Design Expert software package and desirability function approach to achieve the highest recovery of copper within the experimental range. The results are presented in Figs. 4 and 5 indicate the optimal conditions suggested by DX software and the trend of factors for movement

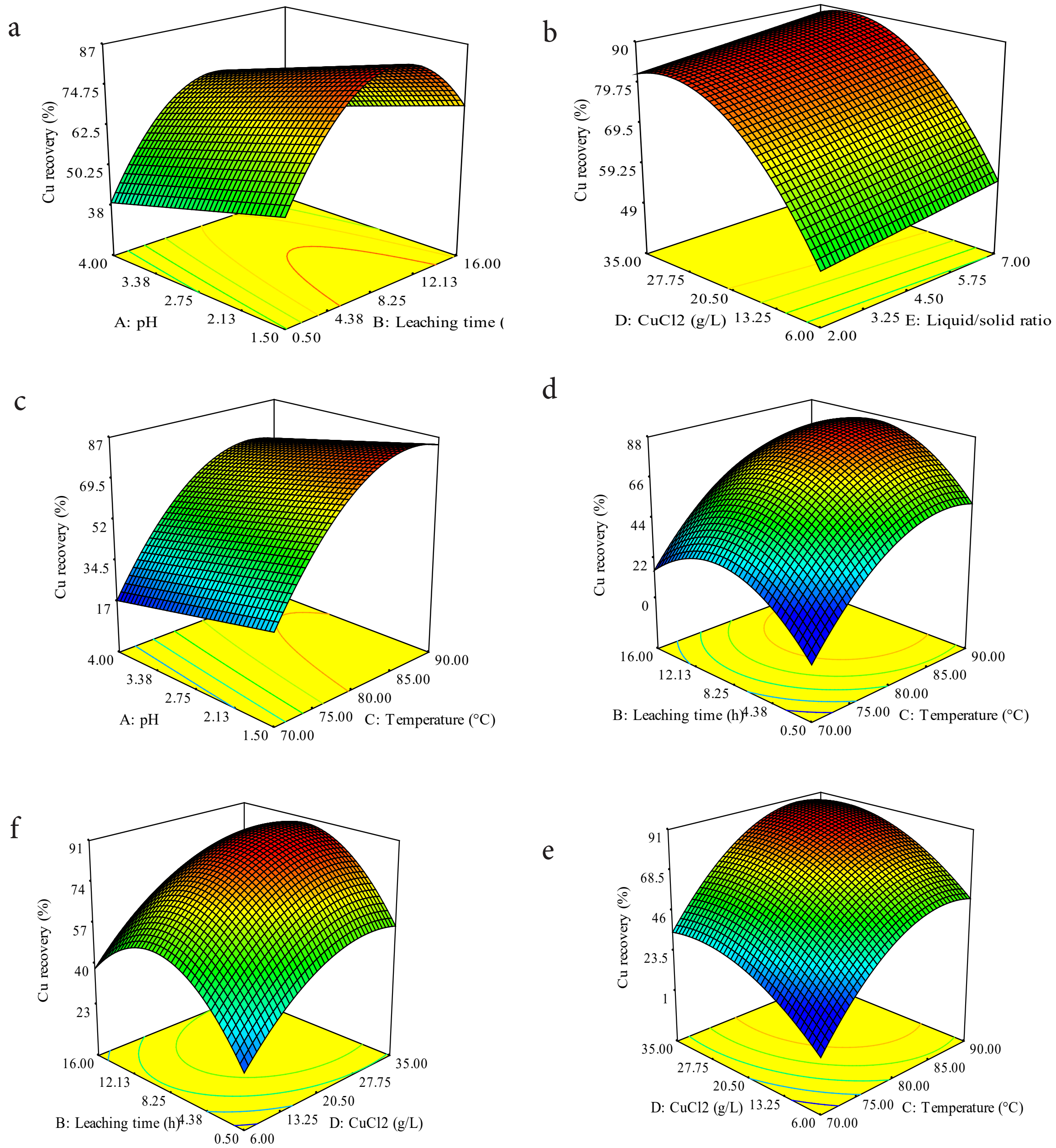

Fig. 3. 3D response surface graphs showing the effects of two factors on the recovery of copper from chalcopyrite concentrate: (a) pH and leaching time, (b) $CuCl_2$ concentration and liquid/solid ratio, (c) pH and temperature, (d) temperature and leaching time, and (e) $CuCl_2$ concentration and leaching time, (f) $CuCl_2$ concentration and temperature.

towards the optimal point, respectively. As can be seen in these figs, the best leaching conditions are obtained at the pH of ~1.4, leaching time of ~8 h, temperature of ~89 °C, $CuCl_2$ concentration of ~21.8 g/L and liquid/solid ratio of ~6.8 mL/g. Under these optimal conditions, the maximum recovery of copper was found to be about 86.1% a desirable value of 100%. Also, one confirmation experiment was conducted at the conditions suggested by DX software, which recovery was determined to be nearly 88%, indicating that there is a good agreement with the value predicted.

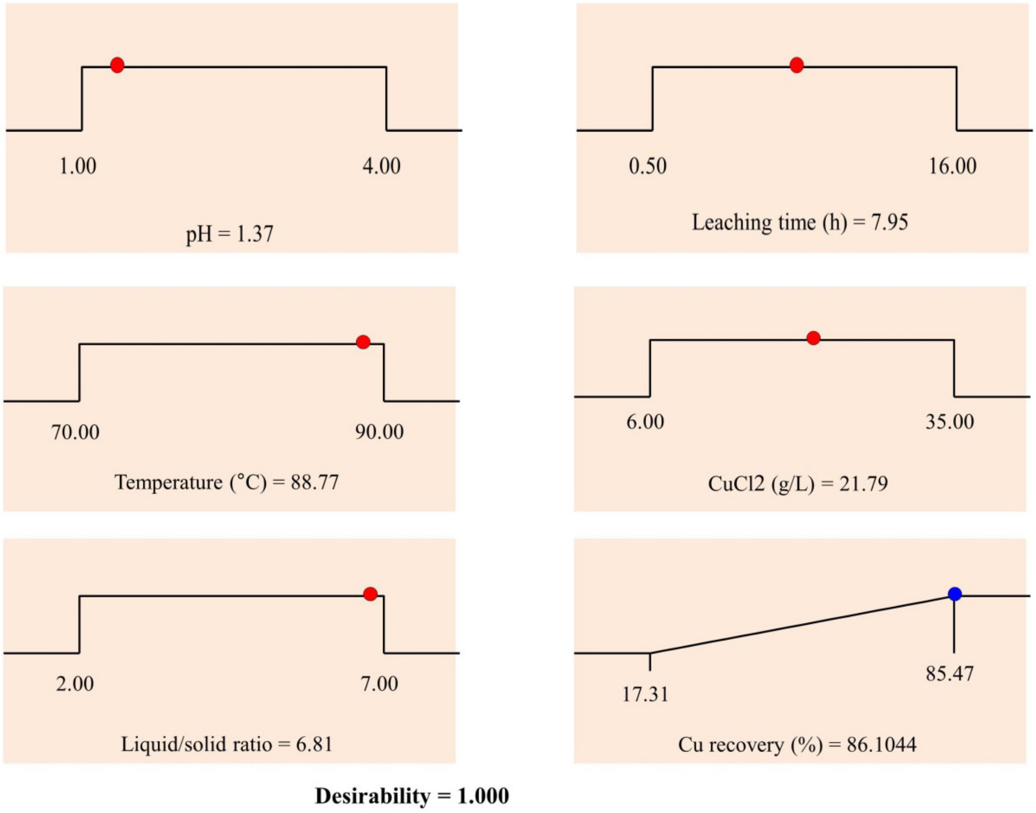

Fig. 4. The operating conditions proposed by DX software to find the maximum recovery of copper from chalcopyrite concentrate.

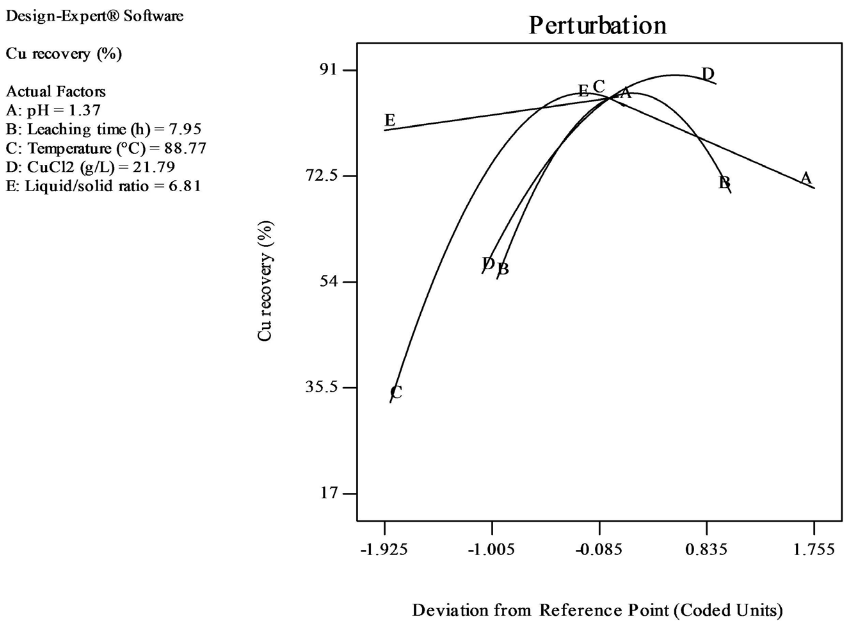

Fig. 5. Trend of factors for movement towards the optimum conditions.

4. CONCLUSION

The present research was focused on the leaching of chalcopyrite concentrate obtained from Miduk copper mine in Iran. In this study, the dissolution behavior of copper from chalcopyrite concentrate sample was investigated in $CuCl_2$ media (HydroCopper® process) using response surface methodology based on d-optimal design. In this regard, the effect of main factors such as pH, leaching time, liquid/solid ratio, temperature, and $CuCl_2$ concentration were evaluated on the leaching recoveries of copper. For this purpose, initially a quadratic mathematical model with an R^2 of 0.9399 was developed and fitted to experimental data. ANOVA technique was employed to determine the influence degree of factors. The results indicated that the recoveries were independent of the interactions between the factors. In addition, the ranking of the important factors was found to be in order of temperature > $CuCl_2$ > leaching time > pH > liquid/solid ratio. The recovery of copper increased with an increment in the temperature and $CuCl_2$ concentration and reached a maximum value and then almost remained constant. Also, the leaching rate was as a linear function of liquid/solid ratio and pH, and increased by increasing the liquid/solid ratio and reducing the pH. Furthermore, the leaching process of copper from chalcopyrite concentrate sample was optimized by applying DX software and the optimum condition was distinguished to be about 1.4 for pH, ~8 h for leaching time, nearly 89 °C for temperature, about 21.8 g/L $CuCl_2$ concentration and ~6.8 mL/g for liquid/solid ratio. Under these conditions, the maximum recovery was determined to be approximately 86.1%. This study demonstrated that the $CuCl_2$ solution (HydroCopper® process) could successfully be applied to recover copper from a chalcopyrite concentrate sample.

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