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# A comprehensive study of the leaching behavior and dissolution kinetics of copper oxide ore in sulfuric acid lixiviant

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Optimization.

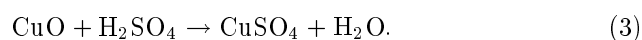
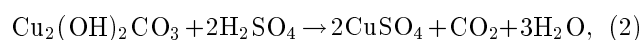
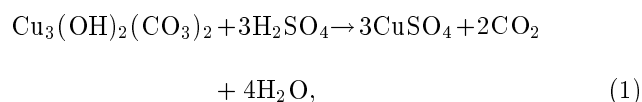
**Abstract.** The leaching behavior of an Iranian copper oxide ore in sulphuric acid was investigated in detail to evaluate the influence of various factors, to optimize the dissolution conditions, and to determine the kinetics of the leaching. The results indicated that the increase in the leaching time and temperature enhanced the leaching rate of copper. The leaching rate increased up to a certain value with increasing the agitation rate, acid concentration, and liquid/solid ratio and, then, reduced with a further increment. Agitation rate had the highest influence on the dissolution of copper. The 3D response surface graphs confirmed the interactive effects of sulphuric acid concentration, agitation speed, and liquid/solid ratio with temperature. About 91% copper content was leached in ~ 13% sulphuric acid concentration, stirring rate of 600 rpm, liquid/solid ratio of 10 mL/g, and 50°C after 80 min leaching. The dissolution kinetics was examined according to heterogeneous models. The shrinking core model, which considers the rate control by diffusion through the product layer, was found appropriate enough to describe the dissolution of copper in sulphuric acid solution. The activation energy was obtained to be 26.699 kJ/mol, and the equation representing the leaching kinetics of copper based on the diffusion-controlled model was found to be  $1 - 3(1 - x)^{2/3} + 2(1 - x) = 161.97 \times \exp(-26.699 \times 10^3 / 8.314 \times T) \times t$ .

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## 1. Introduction

Copper, as one of the most common and valuable metals applied in industrial fields and every aspects of life, is found mainly in nature in the form of sulfide and oxide minerals such as chalcopyrite, chalcocite, malachite, bornite, azurite, chrysocolla, etc. [1-5]. The copper produced from sulfide and oxide copper ores is extracted through pyrometallurgical and hydrometallurgical processes, respectively. Leaching is typically the first step of any hydrometallurgical process [6]. During the leach-

ing process of copper oxidized ores, sulfuric acid leaching is viewed as the most viable and versatile process. The most common copper oxide minerals, such as azurite ( $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ ), malachite ( $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ), and copper oxide ( $\text{CuO}$ ), can be dissolved by sulphuric acid according to the reactions given below [7]:



The dissolution of sulfide and oxide minerals is important in a wide range of fields, including minerals

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**Table 1.** Results of the XRF analysis; chemical composition of the ore sample (mass fraction, %).

Composition	K <sub>2</sub> O	Na <sub>2</sub> O	MnO	MgO	CaO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
w/w (%)	2.41	2.03	0.14	4.46	24.25	6.96	8.59	37.04
Composition	TiO <sub>2</sub>	SrO	ZnO	CuO	SO <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	
w/w (%)	0.66	2.26	0.19	5.89	4.40	0.05	0.35	

processing, hydrometallurgy, geochemistry, and materials science. Knowledge of the mechanism of dissolution can be of assistance in the design, optimization, and intensification of processes for the extraction of copper [8]. For this reason, a great deal of attention has been focused on the study of the behavior and kinetics of leaching. Researches on leaching behavior and kinetics of copper oxide ores have been extensively conducted by different lixiviants including mineral acids, such as HCl, H<sub>2</sub>SO<sub>4</sub>, and HNO<sub>3</sub> [7,9-11]; organic acids, such as citric acid and lactic acid [11-13]; chlorine [14]; ammonium hydroxide or ammonium salts including ammonium chloride, ammonium sulfate, ammonium nitrate, ammonium citrate, ammonium acetate, etc. [2,15-24]; and alkaline glycine solutions [25]. In addition, Deng et al. [26] investigated extraction and dissolution kinetics of copper from a malachite ore by Sulfamic Acid (SA). They indicated that the leaching rate increased with decreasing particle size and increasing concentration, reaction temperature, and stirring speed. In addition, the dissolution kinetics follows a shrinking core model with three-dimensional diffusion as the rate-controlling step. Sun et al. [27] investigated the leaching kinetic behavior of copper from low-grade copper oxide ore. They reported that the leaching process by H<sub>2</sub>SO<sub>4</sub> can be described with a reaction model of shrinking core, and the leaching process can be divided into three stages in the system investigated. Moreover, the leaching efficiency of copper can reach up to a level higher than 90%.

Although many experimental studies have been performed to gain a better understanding of the leaching process and its operation, there are still few researches concerned with the aim of optimizing the process and kinetics modelling. An accurate understanding of the leaching kinetics helps to interpret the complex behavior of leaching process. Thus, this study aims to investigate and discuss the leaching kinetics and dissolution parameters of oxide copper ore in sulphate solution. In this study, the dissolution kinetics is examined according to the shrinking core models, and the best kinetics model is chosen to describe the leaching process of copper oxide ore. Moreover, an experimental design technique, Response Surface Method (RSM), is employed to model, optimize, and evaluate the effects and interactions of the influential parameters on recovery of copper.

## 2. Experimental descriptions

### 2.1. Materials

Copper oxide ore was collected from the Fariman copper mine in Khorasan-e-Razavi province, Iran. The samples were prepared after two stages of laboratory comminution including crushing (jaw crusher) and milling (ball mill). Thereafter, representative samples were analyzed to characterize the main chemical compositions by X-Ray Fluorescence (XRF), in which the results are presented in Table 1. In addition, the phases of sample were characterized by XRD, in which the main phases identified from the XRD pattern for oxide copper included malachite and azurite.

### 2.2. Leaching experiments

Leaching experiments were carried out in a beaker of 500 mL which was heated on a hot plate equipped with a digitally controlled magnetic stirrer and a thermometer for temperature control under different conditions. A representative sample (3g) was selected for each leaching test. The leaching liquor was prepared using distilled water and the analytical grade H<sub>2</sub>SO<sub>4</sub> reagent in predetermined concentrations. Then, based on the desired liquid-to-solid ratio, a definite volume of the solution was poured into the beaker at the required temperature. When the solution reached the desired temperature, sample was added into the beaker and the contents of the beaker were stirred at a certain speed. A 5-mL sample was accurately withdrawn at regular intervals during the reaction and was immediately filtered. Then, the solution was analyzed using a unicam Atomic Absorption Spectrometry (AAS) [28,29]. The amounts of copper leached were calculated via the following equation:

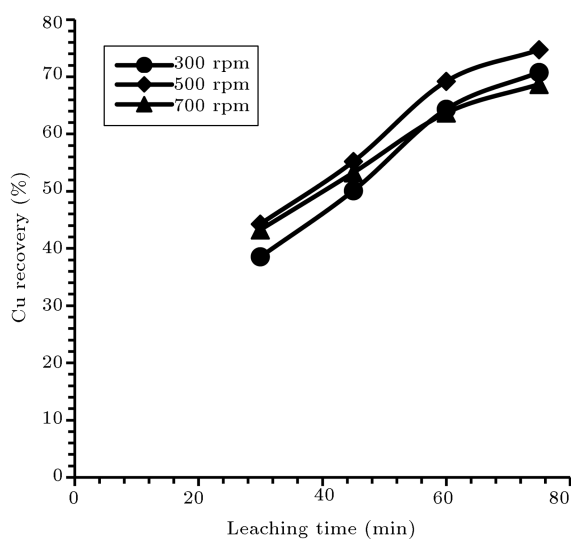
$$R = \frac{M_1}{M_0} \times 100, \quad (4)$$

where  $R$  is the recovery percentage of copper and  $M_0$  and  $M_1$  are the mass of copper passing to the solution and mass of copper in the ore sample, respectively.

## 3. Results and discussion

### 3.1. Effect of stirring speed

The effect of stirring rate on the leaching of copper was investigated using different agitation speeds that

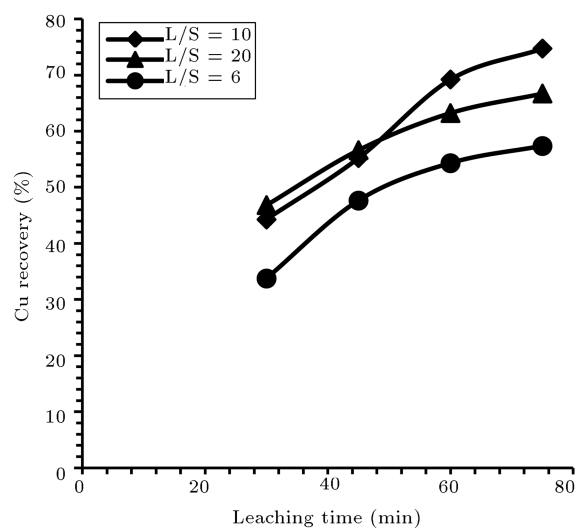


**Figure 1.** Effect of stirring speed on the dissolution of copper oxide ore.

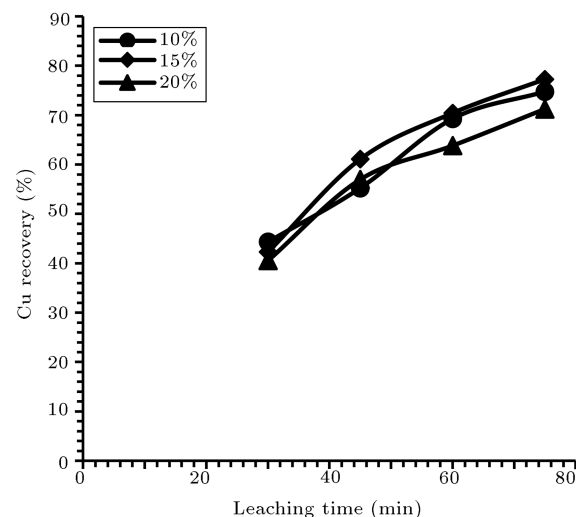
ranged from 200 to 700 rpm. While conducting experiments, the values of other experimental parameters were kept constant at 30°C, liquid/solid ratio of 10 mL/g, and acid concentration of 10%. The results obtained are plotted in Figure 1. The results indicate that the agitation has a more pronounced effect on the dissolution of copper with  $H_2SO_4$ . As shown in Figure 1, the maximum copper leaching rate (74.43%) was obtained at stirring speed of 500 rpm after 75 min of dissolution. An increase in stirring speed usually increases the leaching rate of copper due to the suspension of the mineral particles and decreases the thickness of the mass transfer boundary layer on the surface of the particle [30]. Based on this behavior, leaching can be also influenced by a specific range of stirring speeds. In kinetic terms, a higher stirring speed accelerates diffusion and enables homogeneous mixing of the liquid and solid phases in the reactor, which can promote the reaction [13]. Thus, a stirring speed of 500 rpm was used thereafter to assure that the leaching reaction was not under external diffusion control. However, the diffusion as the controlling step cannot be eliminated, and the leaching process can be controlled by the surface reaction, or the solid internal diffusion, or both of them.

### 3.2. Effect of Liquid-to-Solid (L/S) ratio

To study the effect of pulp density or Liquid-to-Solid (L/S) ratio on the dissolution rate, experiments were performed with three different ratios (6, 10, and 20 mL/g). During the experiments, the leaching temperature, sulphuric acid concentration, and agitation rate were kept constant at 30°C, 10%, and 500 rpm, respectively. Data shown in Figure 2 indicate that the dissolution rate of copper increases with increasing L/S ratio to a certain amount and, then, reduces with a further increment; moreover, a Liquid/Solid (L/S)



**Figure 2.** Effect of liquid-to-solid (L/S) ratio on the dissolution of copper oxide ore.



**Figure 3.** Effect of sulphuric acid concentration on the dissolution of copper oxide ore.

ratio of 10 mL/g is found to be optimal for leaching of copper using  $H_2SO_4$ . This can be explained in a way that the leaching agent is in excess of the calculated amount for the extraction of copper. After 75 min of dissolution, the amounts of copper extracted from the oxide ore were 57.37, 74.73, and 66.71% at L/S ratios of 6, 10, and 20 mL/g, respectively.

### 3.3. Effect of acid concentration

To investigate the effect of acid concentration on the leaching rate of copper, experiments were performed with  $H_2SO_4$  at a temperature of 30°C, stirring rate of 500 rpm, L/S of 10 mL/g, and contact time of 75 min. In this study, the effect of acid concentration was evaluated by regulating the concentration to 10, 15, and 20%, in which the results are given in Figure 3 as a fraction of leached copper versus leaching time. It was observed that the dissolution rate of copper increased

meaningfully by increasing the  $\text{H}_2\text{SO}_4$  concentration up to a certain value and, thereafter, reduced. This behavior takes place due to certain variations in the leaching mechanism and varying acid concentrations (for example, mechanism varying from surface chemical reaction to diffusion). The maximum dissolution of copper was obtained as 77.25% with acid concentration of 15%. In addition, this could be because copper particles exposed to sulphuric acid reduced after a certain time and in a certain concentration (75 min and 15% in this experiment), and, finally, decreased the recovery of copper. On the other hand, there are a lot of  $\text{CaO}$  and  $\text{SiO}_2$  in the copper oxide ore in this work; consequently, the silica gel can be produced in a sulfuric acid leaching system, which may increase acid consumption.

### 3.4. Effect of temperature

The effect of leaching temperature on copper leaching yield was evaluated in an acid concentration of 15%, L/S ratio of 10 mL/g, and stirring speed of 500 rpm. The result shown in Figure 4 indicates that the dissolution rate increases with an increase in leaching temperature from 74.73% at  $30^\circ\text{C}$  to 87.02% at  $50^\circ\text{C}$  in 75 min, for example. As expected, the leaching temperature played an important role in dissolution. However, the impact of temperature on the copper leaching rate is not very large during contact time of 75 min (from 40 to  $50^\circ\text{C}$ ), suggesting that the dissolution process may be controlled by diffusion reaction. In fact, it is observed that with a further increase of the temperature and time, the leaching rate of copper increases intermediately.

### 3.5. Identification of the leaching mechanism

The reaction occurring between copper oxide ore particles and sulphate solution during the leaching process is a typical example of heterogeneous liquid-solid

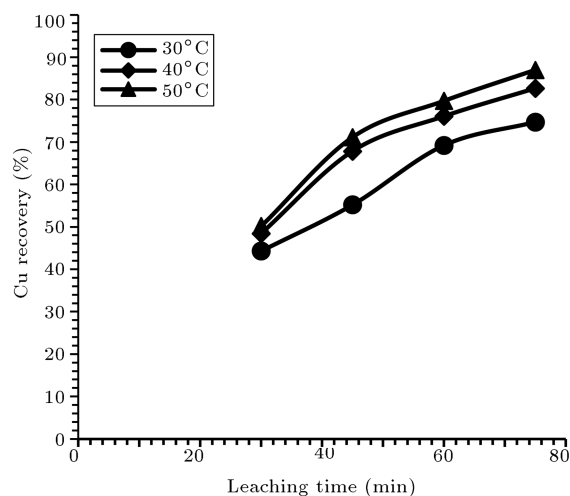


Figure 4. Effect of leaching temperature on the dissolution of copper oxide ore.

reactions. In heterogeneous reaction systems, most reactions follow a Shrinking Core Model (SCM) which approximates the dissolution of real particles [31]. According to this model, it can be concluded that the leaching process in  $\text{H}_2\text{SO}_4$  solution involves:

- (i) Transport of  $\text{H}_2\text{SO}_4$  from the bulk solution to the particle surface;
- (ii) Diffusion of  $\text{H}_2\text{SO}_4$  through the solid residual layer from the particle surface to the surface of unreacted core;
- (iii) Reaction between  $\text{H}_2\text{SO}_4$  and oxide ore on the surface of the unreacted core;
- (iv) Diffusion of the resultants through the solid residual layer from the reaction interface to the particle surface;
- (v) Transport of the resultants from the particle surface to the bulk solution [28,29,32].

Generally, this model expressed below described equations [11,19,31]. This model assumes that the reaction between solid and liquid reactants occurs on the outer surface of the solid particle, and the reacting particles are spherical whose size does not change during reaction [23].

If the leaching rate of the particle is controlled by liquid film diffusion, the kinetic equation can be expressed as in Eq. (5):

$$1 - (1 - x)^{\frac{2}{3}} = k \times t. \quad (5)$$

If the leaching rate is controlled by diffusion through a product layer, the kinetic equation is:

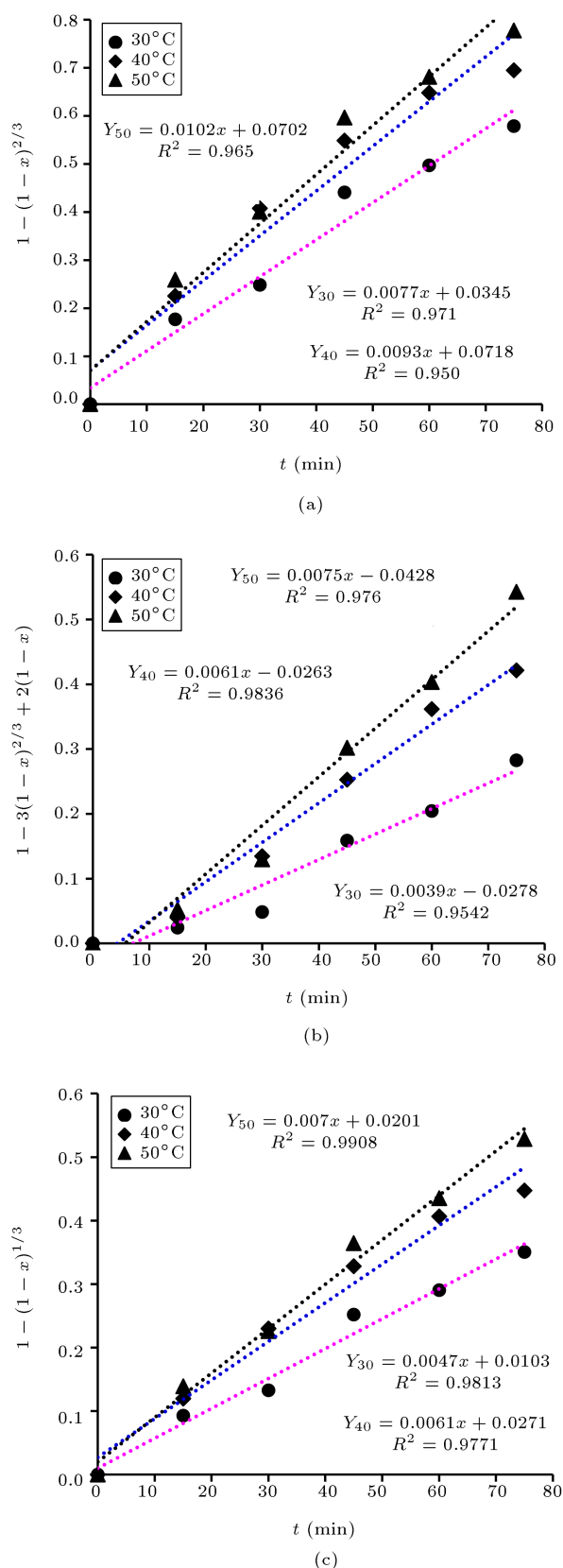
$$1 - 3(1 - x)^{\frac{2}{3}} + 2(1 - x) = k \times t. \quad (6)$$

If the leaching rate is controlled by a surface chemical reaction, the kinetic equation is:

$$1 - (1 - x)^{\frac{1}{3}} = k \times t, \quad (7)$$

where  $x$  is the fraction of lead reacted,  $t$  is the reaction time (min or h), and  $k$  is the apparent rate constant ( $\text{min}^{-1}$  or  $\text{h}^{-1}$ ). The rate of the process is controlled by the slowest sequential steps.

To determine the kinetic parameters and rate-controlling step of copper leaching in the sulphuric acid solution, the data obtained in the leaching experiments were analyzed based on the shrinking core model equations. By applying the rate expression in Eqs. (5)-(7) to the experimental data obtained, the apparent rate constants were calculated. To obtain the apparent rate constants of each step, the left sides of Eqs. (5) to (7) were plotted against time, whose results are shown in Figure 5. From the slopes of the straight lines, the apparent rate constants (Figure 5(a)-(c)),  $k$ ,



**Figure 5.** Plot of the shrinking core models versus leaching time ( $t$ ) for the dissolution of copper with  $\text{H}_2\text{SO}_4$ : (a) Liquid film diffusion, (b) film diffusion through the ash or product layer, and (c) surface chemical reaction.

were evaluated, and the rate constants calculated from the slopes of the straight lines and their correlation coefficients are given in Figure 5.

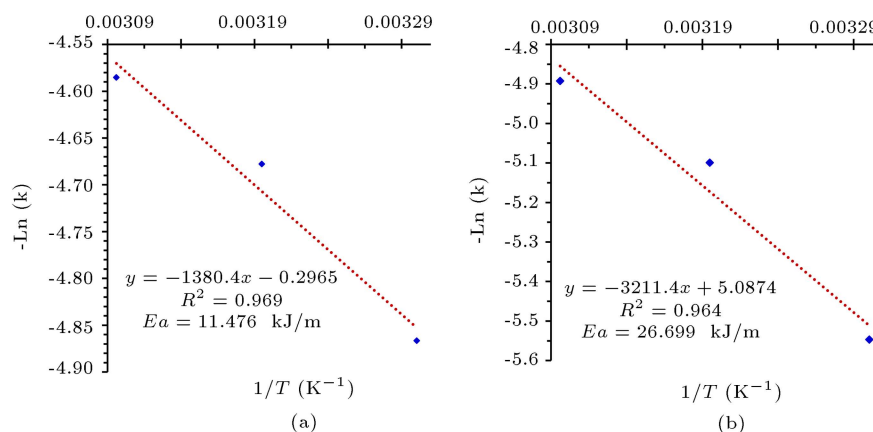
As observed, all three models have good linear fits and their  $R^2$  values are close to each other. Therefore, it is difficult to distinguish between these reaction models. Another important parameter that can be used to justify the rate-determining step in hydrometallurgical process is activation energy [33]. Hence, the activation energy describing the temperature dependence of the reaction rate constant was employed to investigate the dissolution kinetics of copper and determine the rate-controlling step of leaching rate. The activation energy was calculated based on the Arrhenius equation:

$$k = A \times e^{\frac{-Ea}{R \times T}} \Rightarrow \text{Ln}(k) = \text{Ln}(A) - \frac{Ea}{R} \cdot \frac{1}{T}, \quad (8)$$

where  $k$  is the reaction rate constant ( $\text{min}^{-1}$ ),  $A$  is the frequency factor ( $\text{min}^{-1}$ ),  $Ea$  is the activation energy of the reaction ( $\text{J} \cdot \text{mol}^{-1}$ ),  $R$  is the universal gas constant ( $8.314 \cdot \text{JK}^{-1} \cdot \text{mol}^{-1}$ ), and  $T$  is the leaching temperature in Kelvin (K).

Arrhenius equation was plotted as  $\text{Ln}(k)$  versus ( $1/T$ ) for each temperature, and the activation energies were calculated from the slopes of straight lines where the slope is  $-Ea/R$ . For example, the Arrhenius plot ( $\text{Ln}(k)$  versus  $1/T$ ) of copper dissolution in  $\text{H}_2\text{SO}_4$  solution based on the diffusion models is shown in Figure 6. The values of activation energies and frequency factor calculated from Arrhenius equation and reaction rate constants are presented in Table 2.

As considered in Table 2, the activation energies calculated for dissolution of copper in sulphuric acid solution based on fluid film diffusion, diffusion through a product layer, and surface chemical reaction are 11.47, 26.69, and 16.25 kJ/mol, respectively. These small values indicate that the leaching rate is controlled by diffusion process [29,30,34]. In addition, the effects of stirring rate and temperature confirm that a diffusion process controls the dissolution reaction. However, it does not imply that the rate of process is definitely controlled by diffusion through the fluid film or through the product layer. However, the agitation speed had the pronounced effect on the dissolution of copper, and the leachability increased with increasing agitation rate up to 500 rpm; in contrast, at stirring speeds exceeding 500 rpm, the agitation rate showed a decreasing effect. This indicates that the dissolution process does not seem to be controlled by mass transfer through the liquid film; however, the possible change in solution viscosity may be brought about by silica gel formation in the sulfuric acid leaching system due to the presence of high values of CaO (24.25%) and  $\text{SiO}_2$  (37.04%) in the copper oxide ore investigated. Consequently, the equations representing the kinetics of leaching process of copper oxide ore can be expressed



**Figure 6.** Arrhenius plot for the dissolution of copper with  $H_2SO_4$  based on (a) the liquid film diffusion model and (b) diffusion through the product layer.

**Table 2.** Arrhenius parameters (activation energy and frequency factor) values and reaction rate constants calculated for the leaching of copper oxide ore in sulphuric solution.

Shrinking core model	Temperature ( $^{\circ}C$ )	Apparent rate constants ( $k$ ), $min^{-1}$	Frequency factor ( $A$ ), $min^{-1}$	Activation energy ( $Ea$ ), $kJ/mol$
Diffusion through liquid film	30	0.0077	0.7434	11.476
	40	0.0093		
	50	0.0102		
Diffusion through product layer	30	0.0039	161.97	26.699
	40	0.0061		
	50	0.0075		
Surface chemical reaction	30	0.0047	3.034	16.25
	40	0.0061		
	50	0.007		

by internal diffusion through the ash layer/solid residue product according to Eq. (9):

$$1 - 3(1 - x)^{\frac{2}{3}} + 2(1 - x) = 161.97 \times e^{-\frac{26.699 \times 10^3}{8.314 \times T}} \times t. \quad (9)$$

### 3.6. Effect of interaction between factors and RSM

To investigate the interactive effects and optimize the important factor affecting the copper leaching process, a series of experiments (29 runs including 10 axial points, 16 fractional factorial points, and 3 replicates at the center;  $N = 2^{(5-1)} + 2 \times 5 + 3 = 29$ ) were designed according to Central Composite Design (CCD) implemented with Response Surface Methodology (RSM). Table 3 shows the experimental data and the responses measured for each experiment in CCD matrix selected.

In order to describe the behavior of factors in the leaching process, it is first necessary to choose a suitable model. Hence, a quadratic polynomial model (Eq. (10)) was developed [35], following the removal of insignificant terms, to predict the leaching rate

of copper ( $R_{Cu}$ ) and determine the important terms. The analysis of variance (ANOVA) was also used to determine the adequacy of the model and predict the main interaction and quadratic effects of all factors as shown in Table 4. Based on the ANOVA of the quadratic regression model (Table 4), Eq. (10) which was suggested for the real relationship between the dissolution rate of copper and the significant variables is a highly significant model at a 95% confidence level ( $P < 0.0001$ ):

$$\begin{aligned} R_{Cu} = & 360.3896 + 3.75072 \times A - 0.13615 \times B \\ & - 5.24442 \times C - 8.63208 \times D - 1.84265 \\ & \times E - 0.06218 \times A \times D + 0.000363 \times B \\ & \times D + 0.09285 \times C \times D - 0.03701 \times A^2 \\ & + 0.078741 \times D^2 + 0.013898 \times E^2, \quad (10) \end{aligned}$$

where  $A$  is sulphuric acid concentration (%),  $B$  denotes

**Table 3.** Experimental factors and data in CCD matrix and measured and predicted values of copper leaching rate.

Runs	Sulphuric acid concentration <i>A</i> (%)	Stirring speed <i>B</i> (rpm)	Liquid/solid ratio <i>C</i> (ml/g)	Temperature <i>D</i> (°C)	Leaching time <i>E</i> (min)	Cu recovery (%)
1	20	600	15	50	80	82.89
2	10	400	15	50	80	77.34
3	10	600	15	50	60	86.79
4	10	600	10	40	60	80.61
5	10	400	10	40	80	81.93
6	10	600	15	40	80	73.21
7	10	400	15	40	60	70.28
8	15	500	12.5	35	70	77.72
9	20	400	10	50	80	75.91
10	10	400	10	50	60	80.47
11	10	600	10	50	80	90.62
12	15	500	12.5	45	90	85.48
13	15	500	12.5	45	70	77.36
14	15	500	7.5	45	70	81.4
15	15	500	12.5	45	50	78.32
16	20	400	10	40	60	77.84
17	5	500	12.5	45	70	73.77
18	15	500	12.5	45	70	76.13
19	25	500	12.5	45	70	71.51
20	15	500	12.5	55	70	90.71
21	15	700	12.5	45	70	81.78
22	20	400	15	40	80	73.95
23	15	500	17.5	45	70	70.42
24	15	500	12.5	45	70	75.75
25	15	300	12.5	45	70	73.16
26	20	600	10	50	60	84.27
27	20	600	15	40	60	76.07
28	20	400	15	50	60	72.53
29	20	600	10	40	80	83.42

**Table 4.** Analysis of variance (ANOVA) results of quadratic model to predict the leaching rate of copper.

Source	Sum of squares	DF	Mean square	<i>F</i> value	<i>p</i> -value	prob > <i>F</i>
Model	836.81	11	76.07	33.86	< 0.0001	Significant
<i>A</i>	14.87	1	14.87	6.62	0.0198	
<i>B</i>	175.34	1	175.34	78.05	< 0.0001	
<i>C</i>	170.51	1	170.51	75.9	< 0.0001	
<i>D</i>	147.46	1	147.46	65.64	< 0.0001	
<i>E</i>	25.48	1	25.48	11.34	0.0037	
<i>AD</i>	38.66	1	38.66	17.21	0.0007	
<i>BD</i>	52.6	1	52.6	23.41	0.0002	
<i>CD</i>	21.55	1	21.55	9.59	0.0065	
<i>A</i> <sup>2</sup>	23.04	1	23.04	10.25	0.0052	
<i>D</i> <sup>2</sup>	104.28	1	104.28	46.42	< 0.0001	
<i>E</i> <sup>2</sup>	51.97	1	51.97	23.14	0.0002	
Residual	38.19	17	2.25			
Lack of Fit	36.77	15	2.45	3.46	0.2468	Not significant
Pure Error	1.42	2	0.71			
Cor Total	874.99	28				
Std. Dev.	1.5	R-Squared	0.9564			
Mean	78.68	Adj R-Squared	0.9281			
C.V. %	1.9	Pred R-Squared	0.8451			
PRESS	135.52	Adeq Precision	21.64			

agitation speed (rpm),  $C$  depicts liquid-to-solid (L/S) ratio (mL/g),  $D$  represents temperature ( $^{\circ}\text{C}$ ), and  $E$  is leaching time (min).

In order to gain the interactive effects and a better understanding of the main effects of factors on the dissolution of copper, three-dimensional response surface and interaction plots were constructed based on the suggested regression model (Eq. (10)) as shown in Figures 7 and 8. Figure 7(a)-(c) indicate the 3D response surface graphs for the relationship between two factors when the other three factors were held at their center levels.

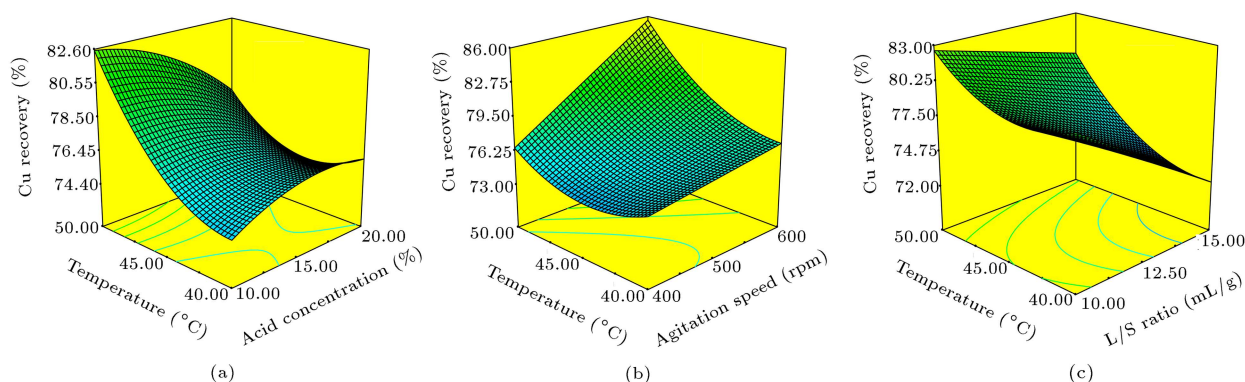
Based on Table 4, the ranking of the significant terms is as follows:  $B > C > D > D^2 > BD > E^2 > AD > E > A^2$ . Thus, it is also observed that agitation speed and L/S ratio are the most influential factors and have a major role in the copper dissolution process. This confirms the previous results and that the transport (diffusion) process may be the rate-controlling step in the leaching system investigated.

According to Figures 7 and 8, temperature has the most interactive effect on copper recovery. As can be seen, at high levels of temperature ( $50^{\circ}\text{C}$ ), increasing the sulphuric acid concentration and L/S ratio results in reducing the copper leaching rate

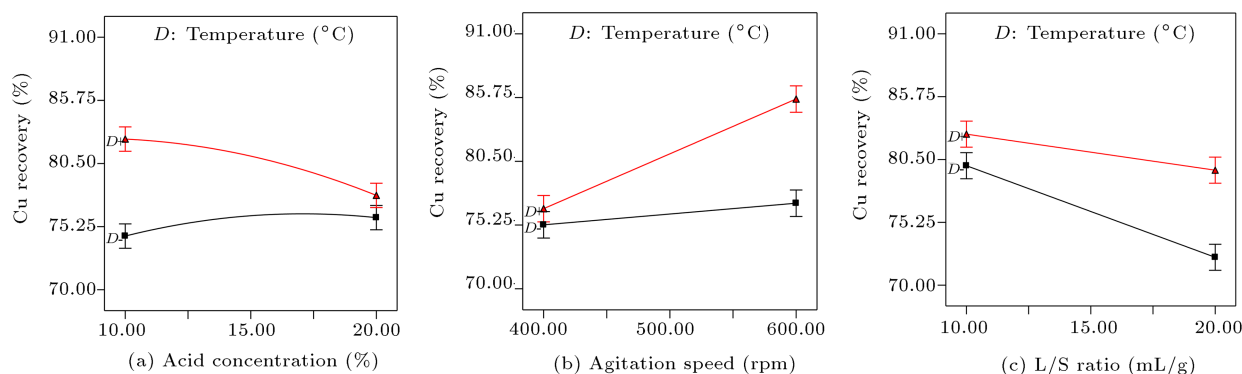
(Figures 7(a) and 8(a)), whereas, at low levels ( $30^{\circ}\text{C}$ ), the increment in the acid concentration and L/S ratio, respectively, leads to a slight increase and a sharp decline of copper recovery (Figures 7(c) and 8(c)). The influence of agitation speed became more apparent when the temperature (Figures 7(b) and 8(b)) was also high. Therefore, it can be generally concluded from the presented model and response surface plots that the copper leaching recovery depends strongly on the interaction among factors with temperature. These findings are consistent with the conclusions obtained previously.

### 3.7. Optimization

The leaching process of copper oxide ore investigated was optimized using Design Expert (DX) software (Demo v. 7.0.0, Stat-Ease, Inc.) within the experimental range studied. Table 5 implies optimum conditions suggested by Design Expert software. Three confirmation experiments were also conducted in the predicted optimum conditions to maximize copper leaching recovery, in which the average of three extra tests is reported in Table 5. The confirmatory experiments indicate the suitability and accuracy of the model. As considered, the optimal point is found to be  $\sim 13\%$



**Figure 7.** 3D response surface graphs: (a) Temperature and acid concentration, (b) temperature and agitation speed, and (c) temperature and liquid/solid (L/S) ratio.



**Figure 8.** Interaction effect plot on Cu recovery between (a) Temperature and acid concentration, (b) temperature and agitation speed, and (c) temperature and liquid/solid (L/S) ratio.



**Table 5.** The proposed levels of factors investigated to maximize the leaching rate of copper and validation of laboratory experiments.

Factors	Sulphuric acid concentration (%)	Stirring speed (rpm)	Liquid/solid ratio (mL/g)	Temperature (°C)	Leaching time (min)	Cu leaching rate (%)
Model projections	12.92	600	10	50	78.98	90.36
Model validation	13	600	10	50	80	91.09

for sulphuric acid concentration, 600 rpm for stirring speed, 10 mL/g for liquid/solid ratio, and 50°C for duration of ~80 min. Under these conditions, the recovery of copper was achieved to be about 91%.

#### 4. Conclusions

The leaching process behavior of an Iranian copper oxide ore was investigated in three phases within the current work. In the first and second phases, the influence of various factors was investigated in detail by a classical approach of one variable at a time; subsequently, the optimal conditions for the dissolution and the interactive effects among factors were exactly determined using response surface methodology combined with a central composite design. The results indicated that agitation speed and L/S ratio were the most influential factors and had a major role in the copper dissolution; moreover, it was also an indication of the diffusion-controlled process. The dissolution rate of copper increased with increasing the temperature and leaching time, while, with increasing the agitation rate, acid concentration and liquid/solid ratio enhanced up to a certain amount and, then, decreased with a further increment. The ANOVA and 3D response surface plots were employed to determine the interactive effects between factors, and it was found that temperature had the most interactive effect on copper leaching rate. The findings confirmed the interaction among the sulphuric acid concentration, agitation speed, and liquid/solid ratio with temperature. In addition, the results showed that the maximum copper recovery (~91%) could be obtained in ~13% sulphuric acid concentration, stirring rate of 600 rpm, liquid/solid ratio of 10 mL/g, temperature of 50°C, and leaching time of 80 min. In the third phase, the dissolution kinetics of copper oxide ore was examined according to heterogeneous model, and it was found that the dissolution rate was controlled by a diffusion process with the activation energy of 26.86 kJ/mol. A closer look indicated that the diffusion through the product layer was the rate-controlling step during the dissolution, and the leaching kinetics can be described by the following equation:

$$1 - 3(1 - x)^{2/3} + 2(1 - x) = 161.97 \times \exp(-26.699 \times 10^3 / 8.314 \times T) \times t.$$

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