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ScienceDirect
Trans. Nonferrous Met. Soc. China 32(2022) 1301−1313
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Optimization of process parameters and kinetic modelling for leaching of copper from oxidized copper ore in nitric acid solutions

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Received 16 January 2021; accepted 1 September 2021

Abstract: The leaching behavior of Tunceli malachite mineral was investigated in nitric acid solutions by two steps to evaluate the effect of various experimental parameters. In the first step, the optimal conditions for the leaching process were determined, while in the second step, a kinetic evaluation for the process was performed. In the optimization experiments, the concentration of nitric acid, temperature, stirring speed, and solid-to-liquid ratio were selected as the independent variables, and the central composite design method (CCD) was applied to the experimental data. At the end of the experiments, the optimal values for the concentration of nitric acid, temperature, solid-to-liquid ratio and stirring speed were determined to be 0.5 mol/L, 50 °C, 0.004 g/mL and 500 r/min, respectively. Under the optimal conditions, the leaching rate was found to be 99% for 120 min of reaction time. In the kinetic evaluation tests, the effects of the concentration of nitric acid, temperature, stirring speed, solid-to-liquid ratio and particle size on the leaching rate of copper from malachite were investigated. In these tests, it was determined that the leaching rate increased with the increase in the temperature, acid concentration and stirring speed, and with the decrease in the particle size and solid-to-liquid ratio. In consequence of the kinetic analysis, it was observed that the leaching kinetics followed the mixed kinetic model, and a mathematical model for the leaching process was introduced. The activation energy for this process was calculated to be 36.23 kJ/mol.

Key words: leaching; copper; recovery; central composite design; shrinking core model

1 Introduction

Copper and copper alloys are widely used in the domestic and industrial areas because of their unique properties such as excellent ductility, thermal and electrical conductivity, and resistance to corrosion [1]. The production of metallic copper from copper sources such as ore, concentrate and secondary sources is carried out by pyrometallurgical or hydrometallurgical methods. In consequence of the increased demand for the metals and gradual reduction of high grade ores, low-grade copper ores have also been processed to produce metallic copper [2,3]. Pyrometallurgical methods can be effectively utilized for high-grade sulfide copper minerals because oxidized copper minerals cannot be enriched by flotation. They are evaluated via hydrometallurgical method to produce copper and its compounds [4]. The most known copper minerals are mainly malachite, azurite, chrysocolla, brochantite, chalcopyrite, enargite, chalcocite, covellite and bornite [5,6]. Malachite, an oxidized copper mineral, can be used to produce

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DOI: 10.1016/S1003-6326(22)65875-8

copper. Because malachite minerals are generally low-grade, hydrometallurgical route is applied to producing copper from them [6,7].

The leaching and kinetics of copper from malachite minerals have been widely studied by various researchers using different lixiviants [8]. Sulfuric acid and ammonia-containing solutions have been mostly used as the lixiviants to leach copper oxide minerals. Sulfuric acid [2,6,8], ammonia [7], ammonium chloride [9], ammonium sulfate [9], ammonium carbonate [9], NH_3-saturated water [5], ammonia/ammonium carbonate [10], ammonia−ammonium chloride [11], ammonium nitrate [12], alkaline glycine [13], ammonium acetate [14], citric acid [15], acetic acid [16], lactic acid [17], 5-sulfosalicylic acid [4], sulfamic acid [18], sulfuric acid [19], perchloric acid [20], and phosphoric acid [21] have been used as the reagents in the leaching of malachite provided by different locations. In practice, H_2SO_4 is preferred generally as the lixiviant for the leaching of the oxidized copper ores, like azurite, malachite, tenorite, and chrysocolla. In addition to this, the other strong acids, such as HCl, and HNO_3, can be also used as the leaching reagents [22]. In the leaching process the H^+ ions are basically responsible from the dissolution treatment. Besides, anions arising from lixiviant can be also effective on the leaching rate. HNO_3 has some advantages in the leaching systems. It has less corrosive properties for the equipment. HNO_3 is also effective in removing flotation reagent on mineral surfaces due to its strong oxidation properties. It ionizes completely in an aqueous medium. NO_3^- ions produced by ionization of an oxidizing agent are capable of entering various oxidation−reduction reactions. Nitrate species can oxidize minerals due to a progression of complex reactions, and nitric acid could be regenerated [23]. HNO_3 is often used to produce fertilizers, ammonium nitrate, and calcium ammonium nitrate. As a result, HNO_3 left over from the leaching process can be precipitated as hydroxide as manure grade NH_4NO_3 using NH_4OH.

The aims of this study are to determine the optimal conditions and the leaching kinetics of malachite leaching in HNO_3 solutions. Thus, the four-factor optimization method was chosen as the five-level central composite design (CCD) to obtain the optimal values of the experimental parameters. Afterwards, the leaching kinetics of malachite mineral in HNO_3 solutions using the optimal conditions was investigated to analyze the effects of the experimental parameters.

2 Experimental

2.1 Materials

Malachite ore used in this study was provided from Ovacık, region of Tunceli, Turkey. The ore was crushed, ground, and then sieved through ASTM standard sieves to give fractions of average sizes 115, 137, 164, 214, and 335 μm. The mineralogical analysis of the ore sample was performed using Rigaku RadB-DMX II model X-ray diffractometer (Rigaku Corporation, The Woodlands, TX). Figure 1 indicates that the sample contains mainly malachite ($CuCO_3Cu(OH)_2$), quartz (SiO_2), smithsonite ($ZnCO_3$), siderite ($FeCO_3$), and berlinite ($AlPO_4$). The chemical analysis result of the sample is given in Table 1.

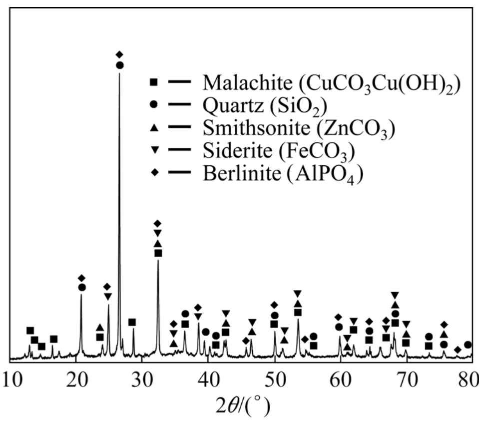

Fig. 1 XRD pattern of malachite ore used in this study

Table 1 Chemical analysis of malachite ore used in this study (wt.%)

SiO_2	ZnO	CuO	Fe_2O_3	Al_2O_3	Ignition loss	Other oxides (Na, Ca, K, and Mg oxides)
45.62	21.27	6.3	12.05	3.42	10.25	1.09

2.2 Experimental procedure

The leaching experiments were performed in a 1 L cylindrical glass reactor equipped with a mechanical agitator, a temperature control unit, and a cooler to avoid loss of solution by evaporation. The experimental procedure was initiated by putting 500 mL of nitric acid solution into the glass reactor, bringing it to the working temperature.

After then a given amount of ore sample was added to the solution, and the stirring speed was set. Aliquots of 5 mL of sample were taken from the solution at regular intervals during the leaching and filtered. The amount of Cu(II) in the leach solutions was determined complexometrically using Titriplex III solution as the titrant, and murexide was used as indicator for Cu(II). The fraction of the leached copper (X_{Cu}) was calculated as Eq. (1). Each analysis was repeated twice, and the arithmetic average of the results was used to calculate the conversion fraction.

$$X_{Cu}=\frac{m_1}{m_2} \quad (1)$$

where m_1 is the mass of copper passing to the solution, and m_2 is the mass of copper in the ore sample.

2.3 Experimental design and analysis

Response surface methodology (RSM) is a combination of mathematical and statistical techniques that are useful for designing experiments, modelling, and analyzing the effects of variables, and optimization of engineering problems. The careful design of the experiments aims this technique, and the main objective is to optimize the response surfaces influenced by various process parameters. An experiment is a series of tests, where the input variables are made to identify the cause of change in the output response [24−29]. RSM was applied according to a central composite design experiments in order to examine the performance of copper leaching reaction and to determine the optimum working conditions. This method assists in analyzing the interaction effect between these parameters, as well as optimizing the effective parameters with a minimum number of experiments. The CCD was carried out to optimize the yield of copper by leaching of malachite mineral by using the nitric acid solution. Four factors were taken into consideration in the experimental planning: temperature (A), nitric acid concentration (B), stirring speed (C), and solid-to-liquid ratio (D), as given in Table 2. The experiments were designed by using the design expert 10.0.0 (State Ease, Inc., Minneapolis, MN) and performed in duplicate. The chosen independent variables used in process optimization were coded according to Eq. (2), where X_i was the dimensionless coded value of the ith independent variable, x_0 was the value of x_i at the center point, and Δx was the step change value. The conversion fraction factors of copper, zinc, and iron were the response variables of the experimental conditions in the design of experiments. The leaching time and particle size were constant at 90 min and 164 μm, respectively. A total of 30 experiments consisting of 16 factorial points, 8 axial points and 6 replicates at the central points were performed.

$$X_i=\frac{x_i-x_0}{\Delta x} \quad (2)$$

Table 2 Factors and levels for CCD

Factor	Notation	Range of level				
		−2	−1	0	+1	+2
Temperature/°C	A	20	30	40	50	60
Concentration/(mol·L^{-1})	B	0.05	0.2	0.35	0.5	0.65
Stirring speed/(r·min^{-1})	C	225	350	475	600	725
Solid-to-liquid ratio/(g·mL^{-1})	D	0.001	0.004	0.007	0.01	0.013

An empirical model has been developed to relate the response to the leaching process and is based on a second-order quadratic model for leaching of malachite mineral in nitric acid solution by Eq. (3) to analyze the effect of parameter interactions.

$$Y=\beta_0+\sum_{i=1}^{k}\beta_i x_i+\sum_{i=1}^{k}\sum_{j=1}^{k}\beta_{ij}x_i x_j+\sum_{i=1}^{k}\beta_{ii}x_i^2+\varepsilon \quad (3)$$

where Y is the measured response; β_0 is the intercept; β_i, β_{ij} and β_{ii} are the coefficients of the linear effect and double interactions; x_i and x_j are the independent variables or factors; ε is the error.

3 Results and discussion

3.1 Results of experimental design

Before the effects of the experimental parameters on the leaching rate of copper (Y_{Cu}) from malachite were determined, the optimal values of the parameters were found using CCD that is one of the most commonly utilized methods of RSM. The experimental results relating to CCD experiments and predicted values of copper are given in Table 3.

According to the analysis of variance (ANOVA) the leaching of copper from malachite mineral using nitric acid solution was used to validate the model, as given in Table 4. The second-order polynomial analysis and quadratic model were employed to find out the relationship between variables and responses. The *F*-value of the model should be greater than the tabulated value of the *F*-distribution for a certain number of degrees of freedom (df) at a level of significance, α=5%. *F*-value of the leaching of copper from malachite mineral using nitric acid solution was reported as 9.98 which is significant. *p*-value of the model for recovery of copper was significant. The insignificant lack of fit, the *p*-value of 0.0763 (more than 0.05) for the leaching of copper from malachite minerals

Table 3 Design matrix and results of experiments

Run	Factor 1 (A)	Factor 2 (B)	Factor 3 (C)	Factor 4 (D)	Response
	Temperature/°C	Concentration/($mol\cdot L^{-1}$)	Stirring speed/($r\cdot min^{-1}$)	Solid-to-liquid ratio/($g\cdot mL^{-1}$)	Y_{Cu}/%
1	50	0.20	350	0.004	80
2	50	0.50	350	0.010	65
3	20	0.35	475	0.007	77
4	50	0.50	600	0.004	98
5	30	0.20	350	0.004	65
6	50	0.50	350	0.004	95
7	40	0.35	475	0.007	76
8	30	0.50	600	0.004	92
9	40	0.35	475	0.013	60
10	30	0.50	350	0.010	72
11	40	0.35	725	0.007	82
12	40	0.35	475	0.007	79
13	30	0.20	600	0.004	69
14	40	0.35	475	0.001	98
15	50	0.20	600	0.010	68
16	40	0.35	225	0.007	72
17	50	0.20	350	0.010	66
18	50	0.20	600	0.004	86
19	30	0.50	350	0.004	83
20	60	0.35	475	0.007	92
21	40	0.35	475	0.007	77
22	30	0.20	350	0.010	60
23	50	0.50	600	0.010	74
24	30	0.20	600	0.010	63
25	40	0.05	475	0.007	42
26	40	0.35	475	0.007	79
27	40	0.65	475	0.007	85
28	40	0.35	475	0.007	79
29	30	0.50	600	0.010	72
30	40	0.35	475	0.007	74

Table 4 Fit summary for leaching of copper from malachite mineral using nitric acid solution

Model	Source	Sum of squares	df	Mean square	F-value	p-value (prob>F)	
Sequential model	Mean vs total	1.734×10^5	1	1.734×10^5			
	Linear vs mean	3566.83	4	891.71	22.79	< 0.0001	
	2FI vs linear	304.37	6	50.73	1.43	0.2546	
	Quadratic vs 2FI	489.67	4	122.42	9.98	0.0004	Suggested
	Cubic vs quadratic	143.67	8	17.96	3.11	0.0763	Aliased
	Residual	40.42	7	5.77			
	Total	1.780×10^5	30	5932.57			

Model	Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Summary statistics model	Linear	6.26	0.7848	0.7504	0.6671	1512.84	
	2FI	5.95	0.8518	0.7737	0.7059	1336.61	
	Quadratic	3.50	0.9595	0.9217	0.7870	968.16	Suggested
	Cubic	2.40	0.9911	0.9632	0.3886	2778.72	Aliased

using a nitric acid solution, indicated that the quadratic model was valid for the present study. The regression equation obtained after the ANOVA showed that the correlation coefficient (R^2) was 0.9595 for the leaching of copper from malachite mineral using a nitric acid solution. However, in this case, R^2 value of 0.9595 implied a sample variation of 95.95% attributed to the variable, the model could not explain only 4.05% of the total variance. It corrects the R^2 value for the sample size and the number of terms in the model by using the degree of freedom on its computations. So, if there are many terms in a model and not a very large sample size, adjusted R^2 may be visibly smaller than R^2 values [27]. Hence, the R^2 values were in reasonable agreement with the adjusted R^2 value of 0.9217 for nitric acid leaching. The model also investigated the amount of variation in predicted data as the predicted R^2 values. It was observed that the predicted R^2 was 0.7872 for nitric acid leaching. Thus, predicted R^2 values agree with the adjusted R^2 values and according to Refs. [27,28], adjusted R^2 and predicted R^2 values should be within 20% to be in good agreement. These results indicated a high correlation between the observed and predicted values. The high value of R^2 indicates that the quadratic equations are capable of representing the system under the given experimental domain. This is also evident from the plot of predicted versus observed values for Y_{Cu} in Fig. 2. Predicted and actual Y_{Cu} data confirm the fitted results, as shown in Fig. 2.

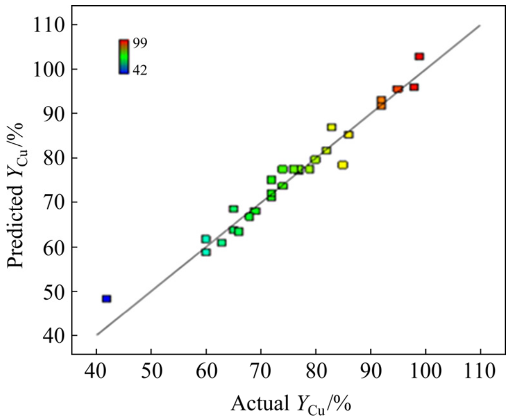

Fig. 2 Plot of predicted vs actual Y_{Cu} for nitric acid leaching of malachite

The ANOVA of leaching was performed to evaluate the significant level of parameters. The second-order response surface model fitting ANOVA is given in Table 5. Considering Table 5, the positioning of the significant terms is as per D, B, B^2, A, C, AD, BD, A^2 and AB which were insignificant to the response. Thus, it is also seen that nitric acid concentration, solid-to-liquid ratio and square of solid-to-liquid ratio (B^2) are the most compelling parameters and have a significant role in the malachite leaching process. The significant correlation between input variables and response(output) for leaching of copper was expressed by

$$Y_{\text{Cu}}=77.33+3.62A+7.54B+2.37C-8.54D-1.81AB+0.31AC-2.81AD+0.44BC-2.69BD-0.56CD+1.72A^2-3.53B^2-0.16C^2+0.34D^2 \quad (4)$$

Table 5 Analysis of variance (ANOVA) for leaching of copper from malachite mineral using nitric acid solution

Source	Sum of squares	df	Mean square	F-value	p-value (prob>F)	Significance
Model	4360.88	14	311.49	25.38	< 0.0001	Significant
A	315.37	1	315.37	25.7	0.0001	
B	1365.04	1	1365.04	111.23	< 0.0001	
C	135.37	1	135.37	11.03	0.0047	
D	1751.04	1	1751.04	142.68	< 0.0001	
AB	52.56	1	52.56	4.28	0.0562	
AC	1.56	1	1.56	0.13	0.7262	
AD	126.56	1	126.56	10.31	0.0058	
BC	3.06	1	3.06	0.25	0.6246	
BD	115.56	1	115.56	9.42	0.0078	
CD	5.06	1	5.06	0.41	0.5304	
A^2	81.03	1	81.03	6.6	0.0214	
B^2	342.03	1	342.03	27.87	< 0.0001	
C^2	0.67	1	0.67	0.055	0.8185	
D^2	3.24	1	3.24	0.26	0.6148	
Residual	184.08	15	12.27			
Lack of fit	162.75	10	16.28	3.81	0.0763	Not significant
Pure error	21.33	5	4.27			
Corrected total	4544.97	29	−	−	−	
R^2	0.9595	−	−	−	−	
Adjusted R^2	0.9217	−	−	−	−	
Predicted R^2	0.787	−	−	−	−	

The analysis of variance indicated that the quadratic model significantly explained the variables and variables interaction responses. Values of prob>F less than 0.0500 imply that the model terms are significant while values greater than 0.1 are insignificant for the regression model. The high F-value (25.38 for copper) and probability p-value<0.0001 ensure that the quadratic model is highly significant. The not-significant lack of fit test (low F-value (3.81) and p-value >0.05) was confirmed and quadratic model well justified the present leaching of malachite mineral.

Figure 3 shows the three-dimensional response surfaces plots and contours plots constructed to show the effects of malachite leaching using nitric acid solution variables (temperature, concentration, stirring speed, and solid-to-liquid ratio) on the recovery of copper. It indicated a significant relationship between independent variables and their optimum response. The effects of temperature and concentration were studied as they were found to have significant effects on the response. As shown from Fig. 3(a), copper recovery increases with the increase of temperature and concentration. The highest recovery of copper was obtained when both the variables were at the maximum point within the range studied. Figure 3(b) shows the effects of stirring speed and temperature on the recovery of copper. It can be seen from Figs. 3(b) and (d) that the recovery of copper slightly increases with an increasing stirring speed. As shown in Figs. 3(c) and (f), recovery of copper decreases with an increasing solid-to-liquid ratio. It can be seen from Fig. 3 that the acid concentration, temperature, and solid-to-liquid ratio on the dissolution of copper from the ore matrix are effective parameters.

3.2 Results of leaching experiments

The optimal values of the temperature, acid

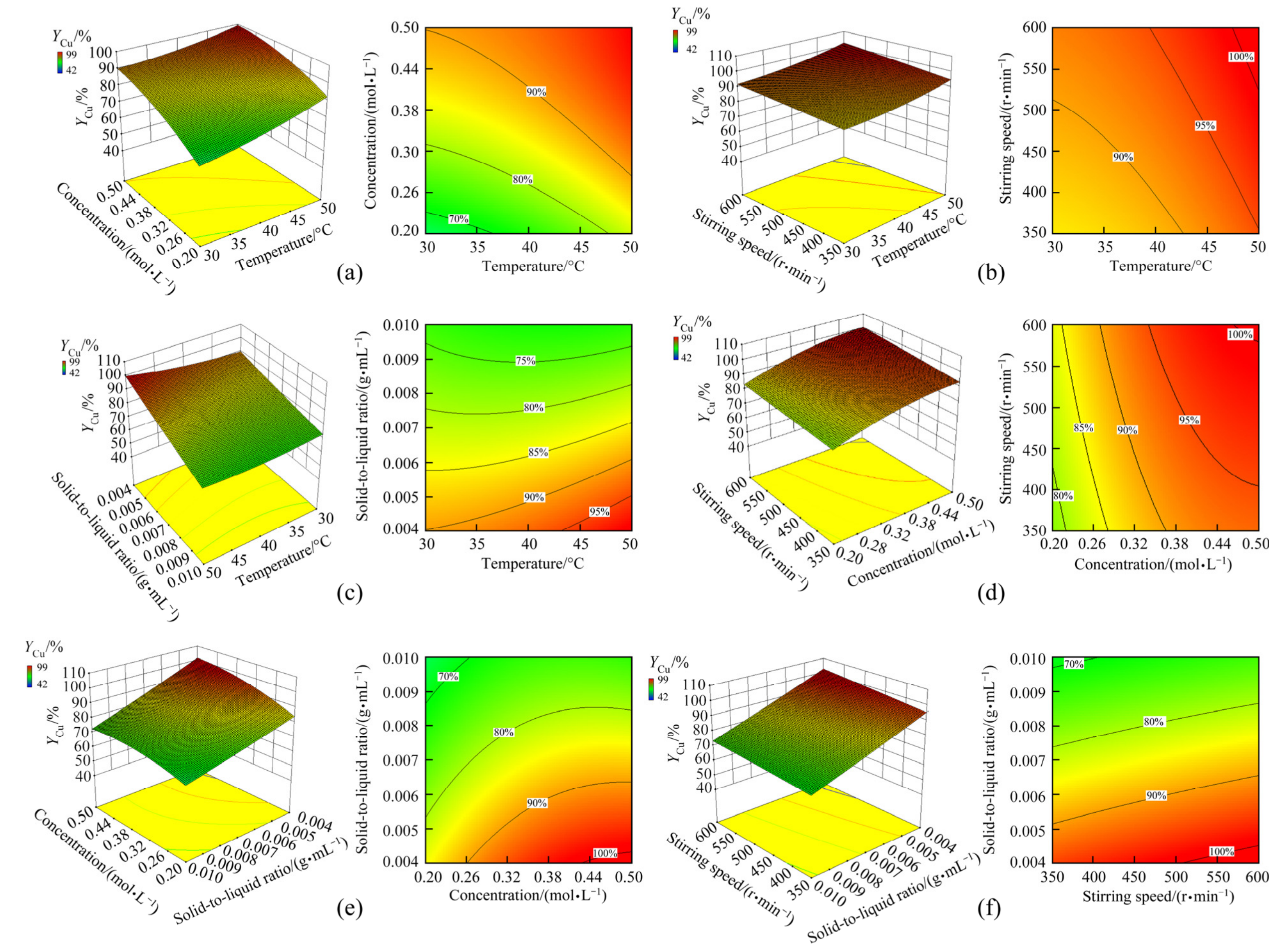

Fig. 3 Response surface graphs (left) and corresponding contour plots (right) showing effects of interaction: (a) Concentration and temperature; (b) Stirring speed and temperature; (c) Solid-to-liquid ratio and temperature; (d) Concentration and stirring speed; (e) Concentration and solid-to-liquid ratio; (f) Stirring speed and solid-to-liquid ratio on copper recovery

concentration, stirring speed, solid-to-liquid ratio, and reaction time for the leaching of malachite in nitric acid solution were determined to be 50 °C, 0.5 mol/L, 500 r/min, solid-to-liquid ratio 0.004 g/mL, and 120 min, respectively. In consequence of these experiments, it was observed that there was a logical connection between experimental and statistical analysis data. After the optimization tests, the second step experiments were performed to determine the leaching rate of malachite in nitric acid solutions. In these group experiments, the effects of the concentration of nitric acid, temperature, particle size, stirring speed, and solid-to-liquid ratio on the leaching rate were examined. Copper, zinc, and iron are found in the form of malachite, smithsonite, and siderite minerals in the ore matrix. Thus, the overall dissolution reactions of the minerals in nitric acid solutions can be written as follows:

$$CuCO_3\cdot Cu(OH)_2+4HNO_3\rightarrow 2Cu^{2+}+4NO_3^-+CO_2\uparrow+3H_2O \quad (5)$$

$$ZnCO_3+2HNO_3\rightarrow Zn^{2+}+2NO_3^-+CO_2\uparrow+H_2O \quad (6)$$

$$FeCO_3+2HNO_3\rightarrow Fe^{2+}+2NO_3^-+CO_2\uparrow+H_2O \quad (7)$$

Determining the amount of copper ions passing to the solution, the progress of the leaching reaction was monitored according to Reaction (5).

3.2.1 Effect of concentration

The effect of the nitric acid concentration on the leaching rate was studied at concentrations of 0.1, 0.2, 0.3, 0.4 and 0.5 mol/L. In these experiments, the reaction temperature, stirring speed, solid-to-liquid ratio, and particle size were kept constant at 50 °C, 500 r/min, 0.004 g/mL, and 164 μm, respectively. After 120 min of the leaching, it was found that the extent of dissolved copper was

61%, 76%, 88%, and 95% for the acid concentration of 0.1, 0.2, 0.3, and 0.4 mol/L, respectively. At a concentration of 0.5 mol/L, the extent of dissolved copper was 99% for 120 min of the reaction time. The dissolved copper is given for different concentrations in Fig. 4. As shown from the results given in Fig. 4, the leaching rate increases with an increase in the solution concentration.

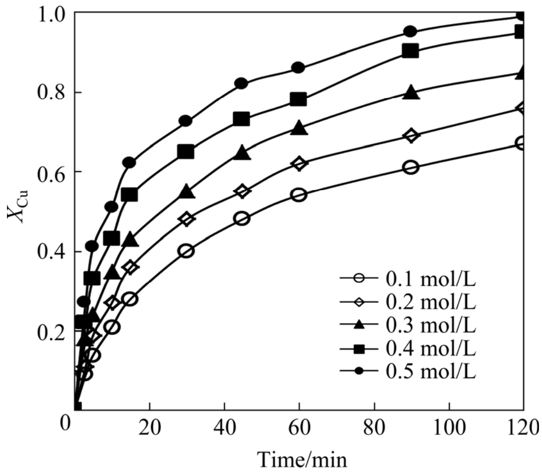

Fig. 4 Effect of nitric acid concentration on leaching of malachite mineral

3.2.2 Effect of particle size

To examine the effect of particle size on the leaching of malachite mineral, the experiments were carried out using the ore with an average particle size of 335, 214, 164, 137, and 115 μm, while the nitric acid concentration, solid-to-liquid ratio, temperature, and stirring speed were kept constant at 0.5 mol/L, 0.004 g/mL, 50 °C, and 500 r/min, respectively. Figure 5 shows that the dissolution rate decreases with increasing particle size. The leaching rate generally increases with the particle size reduction because the contact surface between the solid and liquid reactants grows with particle size reduction. At a particle size of 335 μm, 85% of copper in the ore was extracted after 120 min, whereas at a particle size of 115 μm, 99% of the copper was leached only after 90 min of leaching time. These results indicate that the average particle size of ore has a considerable effect on the leaching of malachite in nitric acid solutions.

3.2.3 Effect of stirring speed

The effect of the stirring speed on the leaching rate was identified at speeds of 200, 300, 400, 500, and 600 r/min. During the experiments, the concentration of nitric acid, temperature, solid-to-liquid ratio, and particle size were constant at 0.5 mol/L, 50 °C, 0.004 g/mL, and 164 μm, respectively. As seen from the result in Fig. 6, the leaching rate increases as the stirring speed increases. At a stirring rate of 200 r/min, 81% of copper in the ore was extracted after 10 min of leaching time, whereas at a stirring speed of 600 r/min, 98.5% of the copper was leached only after 90 min. The agitation of the reactants content is an essential factor in the leaching process because it facilitates the diffusion of the leaching reagent towards the outer surface of the solid particle, providing a reduction in the thickness of the diffusion layer formed around the particle. Therefore, the leaching rate of the metal species generally increased from the ore by an increase in the stirring speed. In addition, the solid particles are

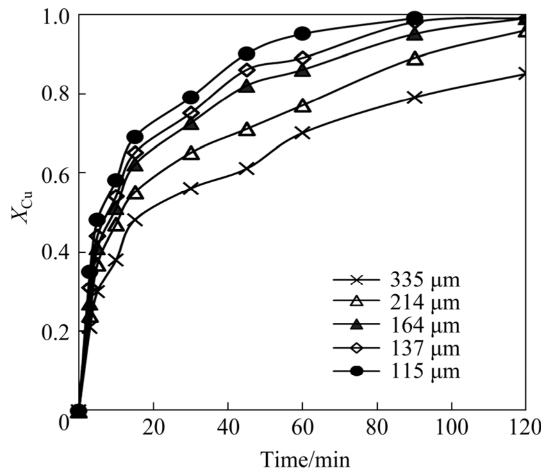

Fig. 5 Effect of particle size on leaching of malachite mineral

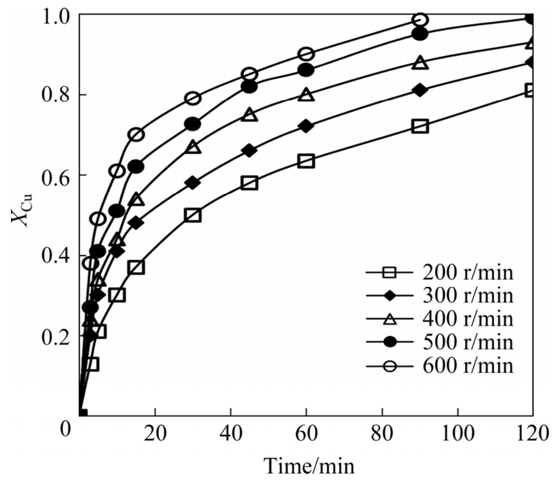

Fig. 6 Effect of stirring speed on leaching of malachite mineral

suspended in the solution with increasing stirring speed and exhibit a good distribution in the reaction mixture. As a result, it provides better contact between the solid particles and the leach reagent, and the efficiency of leaching increases.

3.2.4 Effect of solid-to-liquid ratio

The effect of the solid-to-liquid ratio on the leaching of the malachite mineral was examined at solid-to-liquid ratios of 0.002, 0.004, 0.006, 0.008, and 0.010 g/mL. These experiments kept the concentration of nitric acid, temperature, stirring speed, and particle size constant at 0.5 mol/L, 50 °C, 500 r/min, and 164 μm, respectively. Figure 7 shows that the dissolution rate increases with decreasing solid-to-liquid ratio. Because the amount of solid per unit amount of liquid reagent increases with increasing solid-to-liquid ratio, a decrease in the leaching rate is expected. At a solid-to-liquid ratio of 0.010 g/mL, 76% of copper in the ore was dissolved in 120 min of leaching time, whereas at a solid-to-liquid ratio of 0.002 g/mL, 91% of copper was dissolved after only 60 min of leaching time.

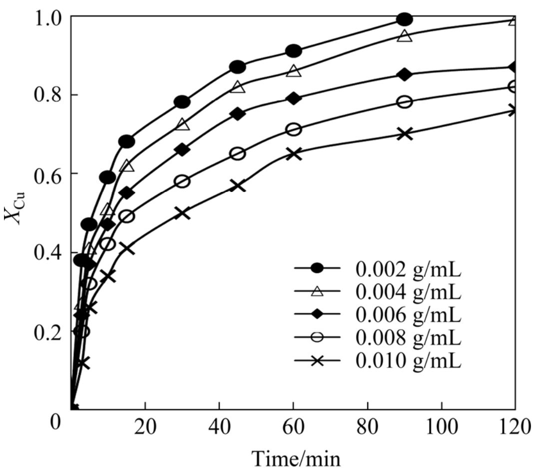

Fig. 7 Effect of solid-to-liquid ratio on leaching of malachite mineral

3.2.5 Effect of temperature

To see the effect of the temperature on the leaching of the malachite mineral, the experiments were conducted at 20, 30, 40, 50, and 60 °C, while the nitric acid concentration, solid-to-liquid ratio, stirring speed, and particle size were kept at constant of 0.5 mol/L, 0.004 g/mL, 500 r/min, and 164 μm, respectively. As can be seen from the results given in Fig. 8, the leaching rate increases with increasing temperature. It can be seen that the temperature has a significant effect on the dissolution of copper. It was found that 75% of copper at a temperature of 20 °C was dissolved after 120 min of reaction time, whereas 99% of copper at a temperature of 60 °C was dissolved after only 90 min. Determining the effect of reaction temperature on the dissolution rate is an important issue because the activation energy calculated from the Arrhenius equation may give an idea about the rate-controlling step of the dissolution process.

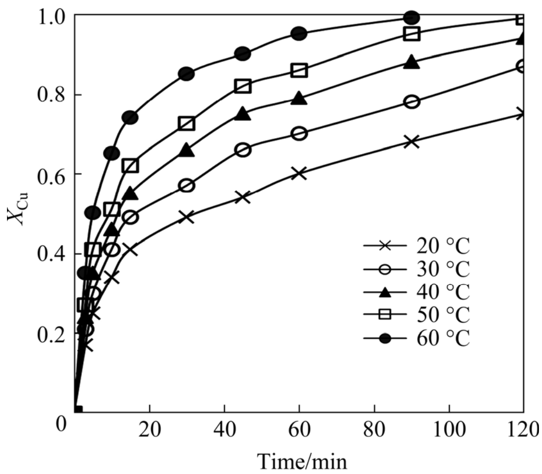

Fig. 8 Effect of temperature on leaching of malachite mineral

3.3 Leaching kinetics

The non-catalytic solid−liquid heterogeneous reaction systems have many applications in chemical and hydrometallurgical processes. A suitable reactor design for these processes is mainly dependent on the kinetics data. A heterogeneous and homogeneous reaction model can be performed by analyzing the data obtained from experiments. Among the non-catalytic heterogeneous reaction models, to create the rate expressions of these reactions, the most common model applied to leach reactions is the shrinking core model. In such systems, reaction rate can generally be controlled by one of the following steps: diffusion through the fluid film, diffusion through the ash or product layer, or the chemical reaction on the surface of the core of unreacted materials [30,31].

The reaction between solid and fluid can be written as

$$A(fluid)+bB(solid) \rightarrow Products \tag{8}$$

where A and B represent the fluid reactant and the solid undergoing leaching, and b is the stoichiometric coefficient. According to the shrinking core model, the reaction between the solid and liquid reactants is thought to occur on the outer surface of the solid material. The solid reactant was initially surrounded by a fluid film, where mass transfer between solid and bulk liquid occurred. As the reaction proceeds, the unreacted core of the solids shrinks to the center of the solid and a porous product layer is formed around the unreacted core. However, it is considered that the initial outer radius of the solid material does not change as the leach reaction continues. The integrated rate equations can be written as Eqs. (9)−(11) [30−32]:

$$x=k_l t \text{ (for diffusion through the fluid film)} \quad (9)$$

$$1-(1-x)^{1/3}=k_r t \text{ (for surface chemical reaction)} \quad (10)$$

$$1-3(1-x)^{2/3}+2(1-x)=k_d t \text{ (for diffusion through the product layer)} \quad (11)$$

where x is the fractional conversion, t is the reaction time, and k_l, k_r and k_d are the apparent rate constants for the diffusion through the fluid film, for the surface chemical reaction, and for the diffusion through the product layer, respectively. Generally, the kinetics of any leaching reaction fits one of the above models. In addition to these models, the mixed kinetic models can determine the rate expressions of leaching reactions. The rate equations for the mixed kinetic models are given in the literatures [30−32].

To find the rate-controlling step of the leaching of malachite, the kinetic parameters in nitric acid solutions were analyzed based on the shrinking core model using the rate expressions given in Eqs. (9)−(11) and the mixed kinetic models introduced in the literature [30−32]. In consequence of the kinetic analysis, it was determined that the model in Eq. (12) could be more appropriate to demonstrate the kinetics of this leaching system.

$$[1-(1-x)^{1/3}]^2=k_m t \quad (12)$$

where k_m is the apparent rate constant for the mixed kinetic model. To determine the validity of the model in Eq. (12), the left side of Eq. (12) vs time was plotted for the concentration, particle size, stirring speed, solid-to-liquid ratio, and temperature. From the graphs obtained, it was observed that the straight lines with high correlation coefficients were obtained for all experimental parameters. The apparent rate constants calculated from the slopes of the straight lines and their correlation coefficients are given in Table 6.

Table 6 Apparent rate constant and correlation coefficient for kinetic model $[1-(1-X_{Cu})^{1/3}]^2=k_m t$

Parameter		k_m/min^{-1}	R^2
Concentration/ (mol·L^{-1})	0.1	0.0008	0.9969
	0.2	0.0012	0.9978
	0.3	0.0019	0.9988
	0.4	0.0031	0.9884
	0.5	0.0049	0.9916
Temperature/ °C	20	0.0011	0.9913
	30	0.0018	0.9914
	40	0.0030	0.9952
	50	0.0049	0.9916
	60	0.0068	0.9941
Stirring speed/ (r·min^{-1})	200	0.0014	0.9938
	300	0.0021	0.9967
	400	0.0029	0.9982
	500	0.0049	0.9916
	600	0.0065	0.9911
Particle size/μm	335	0.0018	0.9950
	214	0.0028	0.9891
	164	0.0047	0.9938
	137	0.0057	0.9916
	115	0.0066	0.9950
Solid-to-liquid ratio/(g·mL^{-1})	0.002	0.0066	0.9958
	0.004	0.0049	0.9916
	0.006	0.0028	0.9943
	0.008	0.0019	0.9905
	0.010	0.0014	0.9943

To determine the effects of the reaction parameters on the apparent rate constant, the following mathematical model can be suggested:

$$k_m = k_o C^d S^e V^f n^g \exp\left(\frac{-E_a}{RT}\right) \quad (13)$$

where C, S, V, n, E_a, R, and T represent the solution concentration, particle size, stirring speed, solid-to-liquid ratio, activation energy, the molar gas constant, and reaction temperature, respectively. The constants d, e, f, and g represent the dependence of the reaction rate to the relevant parameters, and k_o is the frequency factor.

Combining Eqs. (12) and (13), the following equation can be written as

$$[1-(1-X_{\mathrm{Cu}})^{1/3}]^2 = k_{\mathrm{o}} C^{1.27} S^{-1.28} V^{1.40} n^{-0.94} \cdot \exp\left(\frac{4358}{T}\right) t \quad (14)$$

The values of constants d, e, f, and g can be estimated using the apparent rate constants given in Table 6. To estimate these constants, the plots of $\ln k_{\mathrm{m}}$ versus $\ln C$, $\ln k_{\mathrm{m}}$ versus $\ln S$, $\ln k_{\mathrm{m}}$ versus $\ln V$, $\ln k_{\mathrm{m}}$ versus $\ln n$ must be constructed. When these plots are constructed, the values of the mentioned constants can be found from the slopes of the straight lines formed on the plots. The constants d, e, f, and g were estimated to be 1.27, −1.28, 1.40, and −0.94 for the concentration, particle size, stirring speed and solid-to-liquid ratio, respectively. The activation energy for the leaching process was determined from the Arrhenius plot constructed in Fig. 9. From the straight-line slope shown in Fig. 9, the activation energy was calculated to be 36.23 kJ/mol. The intercept was determined to be 9.005 s^{-1}.

The overall rate of the non-catalytic solid−liquid reactions generally depends on the chemical reaction and the mass transfer properties. In the case where the chemical reaction controls the overall rate, the diffusion of the liquid reactant from the solid reactant becomes rapid, where diffusion of the liquid reactant occurs slowly, the chemical reaction step is fast, and the overall rate is governed by the mass transfer of the liquid reactant. The mixed kinetic model can control the reaction rate if both chemical kinetics and diffusion events have a certain role on the overall process rate. The leaching rate of copper from malachite minerals is susceptible to particle size, stirring speed, acid concentration, and reaction temperature. Therefore, these observations may suggest that the mixed kinetic model controls the rate of this process. The activation energy indicates that the dissolution of malachite mineral in nitric acid solutions followed the mixed kinetic control model. The activation energy of a diffusion-controlled process is generally below 40 kJ/mol while this value for a chemically controlled process is usually greater than 40 kJ/mol [31]. Figure 10 shows a very good agreement between experimental and theoretical values. Similar graphs were obtained for the other experimental values.

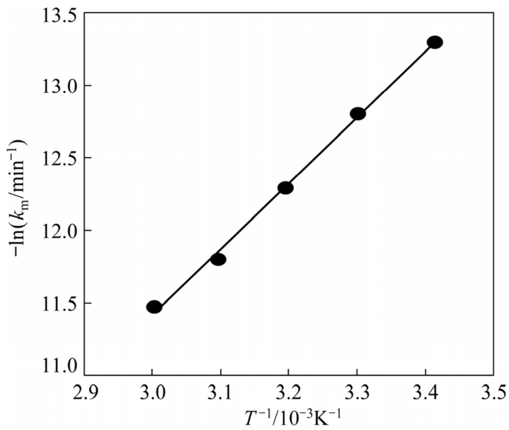

Fig. 9 Arrhenius plot for leaching process

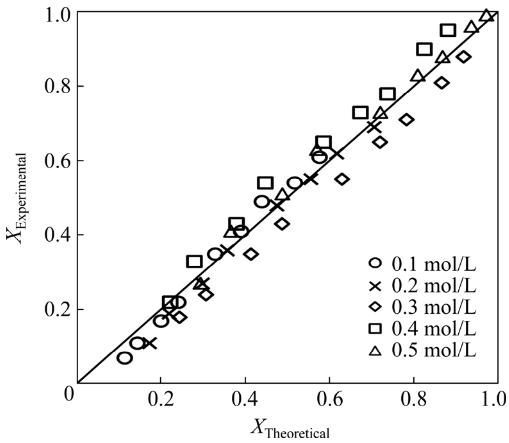

Fig. 10 Agreement between experimental and theoretical conversion values

4 Conclusions

(1) The optimal values of the concentration of nitric acid, temperature, solid-to-liquid ratio, and stirring speed to maximize the recovery of copper from malachite were determined to be 0.5 mol/L, 50 °C, 0.004 g/mL, and 500 r/min, respectively.

(2) It was resolved that the request for the significant terms on the dissolution of copper is as solid-to-liquid ratio > acid concentration > square of acid concentration > temperature > stirring speed > the interaction between temperature and solid-to-liquid ratio > the interaction between acid concentration and solid-to-liquid ratio. ANOVA and 3D response surface plots were applied to understanding parameter interaction and individual impacts. It was determined that the solid-to-liquid ratio, concentration, and square of acid concentration had the most intuitive impact on the dissolution of copper.

(3) The lack of fit for the model was significant and indicated that the quadratic model fitted the data well.

(4) In consequence of the kinetic analysis, it was found that the mixed kinetic control model was the best model to represent the leaching kinetics. According to this model, it could be said that the overall rate of the present leaching process was governed by both chemical reaction and diffusion events. The activation energy of the leaching process was calculated to be 36.23 kJ/mol.

Acknowledgment

This work was supported by Munzur University Scientific Investigations Project Unit (PPMUB018-13).

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硝酸溶液中氧化铜矿浸出工艺参数优化及动力学模拟

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摘　要：研究 Tunceli 孔雀石矿物在硝酸溶液中的溶出行为，以评估各种实验参数的影响。研究为分两个阶段。在第一步中，确定浸出过程的最佳条件，而在第二步中，对该过程进行动力学评估。在优化实验中，以硝酸浓度、温度、搅拌速度和固液比为自变量，采用中心组合设计法(CCD)获得实验数据。确定硝酸浓度、温度、固液比和搅拌速度的最佳值分别为 0.5 mol/L、50 ℃、0.004 g/mL 和 500 r/min。在最佳条件下，120 min 反应时间的浸出率为 99%。在动力学评价测试中，研究硝酸浓度、温度、搅拌速度、固液比和粒度对孔雀石中铜浸出率的影响。在这些试验中，确定浸出率随着温度、酸浓度和搅拌速度的增加以及粒度和固液比的降低而增加。通过动力学分析，观察到浸出动力学遵循混合动力学模型，并引入浸出过程的数学模型。经计算，该过程的活化能为 36.23 kJ/mol。

关键词：浸出；铜；回收；中心组合设计；收缩核模型

(Edited by Xiang-qun LI)