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Silver-catalyzed Bioleaching of a Low Grade Complex Nickel-copper Concentrate: Optimization of Process Variables by Response Surface Methodology

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This study was prompted by the phenomenon of the optimal conditions for nickel and copper extractions were quite different in the bioleaching of a low grade complex nickel-copper concentrate. Response surface methodology (RSM) was firstly utilized to promote chalcopyrite oxidation under optimal condition of nickel recovery. The experiment results showed that a satisfactory second-order polynomial regression equation was achieved with a high coefficient of determination (R^2=0.9522) which demonstrated that the model could be effectively applied for optimization of silver-catalyzed bioleaching process. Based on the model, the term of silver-bearing species and the interaction term of adding time and Ag^+ concentration exhibited high contribution to copper extraction. The different effect of silver-bearing species on bioleaching was revealed by RSM. Besides, the addition time of silver was quite significant in silver-catalyzed bioleaching process, which has never been reported. The high copper extraction reached 0.814 under the optimal conditions of Ag_2SO_4 as silver-bearing species, adding catalyst after 7 d of bioleaching and Ag^+ concentration 1.1 g Ag/kg of ore. Moreover, validation tests were performed and the results were very close to the predicted values.

Key words: Bioleaching, Nickel-copper concentrate, Box-Behnken design, Silver catalysis, Chalcopyrite.

The demand for nickel is growing worldwide, driven by the world stainless steel market which consumes 67% of primary nickel, due to increased demand from China[1]. The increased demand has generated renewed interest in exploration to discover new resources and the development of new processes suited to lower grade or complex ores. In the present, a low grade complex nickel-copper concentrate was subjected to bioleaching. However, the authors found that the best conditions for Ni extraction and Cu extraction were quite different. And it is infeasible to realize the synchronous control of two different conditions for bioleaching a complex nickel-copper ore within a single batch. Therefore, using some active methods, such as catalysis of Ag^+, to promote chalcopyrite oxidation under optimal condition of Ni recovery is alternative. Though there are several reports about the catalytic effect of silver ions on (bio)leaching of metal sulfides[2-6], the effect of silver ion concentration and adding time on metal recovery is never further investigated. Besides, the utilization of silver-bearing species was quite different in the former reports, such as silver sulfate[2,4], silver nitrate and silver sulfide[3]. And there is no report on the relationship between various silver-bearing species and metal recovery. Response surface methodology (RSM) coupled with Box-Behnken design (BBD) is a comprehensive and multi-functional tool for

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designing experiments, building models, and analyzing the effects of multiple factors and their interactions[7,8]. RSM is the most popular technique used to find the optimal conditions by using quadratic polynomial model and is applied as a consequence of a screening or diagnostic experiment[9]. However, very few works have focused on using BBD in silver-catalyzed bioleaching technology. Moreover, the interactions between silver-bearing species, silver ion concentration and adding time still need more investigation to understand the catalytic action.

To simplify the calculations and for uniform comparison, the silver-catalyzed bioleaching process of the low grade complex nickel-copper concentrate was investigated for copper ions extraction via BBD. During the process, three main factors (silver-bearing species, silver ion concentration and adding time) were systematically researched and optimized for high extraction. The experimental results were analyzed statistically by the analysis of variance (ANOVA), model components, 3D response surfaces and optimized studies.

MATERIALS AND METHODS

Concentrate samples and characterization

The low grade complex nickel-copper concentrate obtained from Danba County, Sichuan Province, China, was used in the test. The sample of concentrate contained 5.3% Ni, 2.21% Cu, 35.52% Fe, 16.18% S, 3.71% Mg and 6.55% SiO_2. Using XRD, the major phases in the concentrate were found to be calcopyrite, pentlandite and pyrrhotite, together with lesser amounts violarite, covellite, and calcocite et al. The main minerals, calcopyrite, pentlandite and pyrrhotite were not completely liberated exhibiting very fine and intimately associated grains. The concentrate samples used for flask leaching were screened and further ground to -0.074 mm (≥90%).

Microorganism and medium

A mixed moderate thermophiles was obtained from a mine in Sichuan province and previous biooxidation studies have shown that the bacteria are capable to oxidize ferrous iron and sulfur (Data not shown). The cultural conditions were showed in previous report[10].

Table 1. Box-Behnken design arrangement and responses

Run	Factors (coded)	Cu extraction		Ni extraction		
	X_1[a]	X_2[b]	X_3[c]	Observed	Predicted	Observed
1	$AgNO_3$ (-1)	7^e (0)	0.2 (-1)	0.815	0.817	0.970
2	Ag_2SO_4 (0)	14^f (1)	2.0 (1)	0.705	0.704	0.977
3	Ag_2SO_4 (0)	0^d (-1)	0.2 (-1)	0.705	0.704	0.896
4	Ag_2S (1)	7^e (0)	2.0 (1)	0.795	0.791	0.956
5	Ag_2SO_4 (0)	7^e (0)	1.1 (0)	0.818	0.810	0.958
6	Ag_2SO_4 (0)	7^e (0)	1.1 (0)	0.798	0.810	0.949
7	Ag_2SO_4 (0)	7^e (0)	1.1 (0)	0.831	0.810	0.979
8	Ag_2S (1)	0^d (-1)	1.1 (0)	0.763	0.765	0.904
9	$AgNO_3$ (-1)	14^f (1)	1.1 (0)	0.795	0.791	0.998
10	Ag_2S (1)	7^e (0)	0.2 (-1)	0.772	0.769	0.940
11	$AgNO_3$ (-1)	0^d (-1)	1.1 (0)	0.809	0.805	0.900
12	Ag_2S (1)	14^f (1)	1.1 (0)	0.781	0.783	0.979
13	Ag_2SO_4 (0)	0^d (-1)	2.0 (1)	0.759	0.758	0.864
14	$AgNO_3$ (-1)	7^e (0)	2.0 (1)	0.790	0.791	0.960
15	Ag_2SO_4 (0)	7^e (0)	1.1 (0)	0.795	0.810	0.975
16	Ag_2SO_4 (0)	14^f (1)	0.2 (-1)	0.763	0.762	0.981

[a] Silver-bearing species (/).
[b] Adding time (d).
[c] Adding concentration (g Ag/kg of ore).
[d] The catalyst of silver was added at the beginning of bioleaching.
[e] The catalyst of silver was added after 7 d of bioleaching.
[f] The catalyst of silver was added after 14 d of bioleaching.

Bioleaching experiments

The basal salts medium without ferrous ions, of 85 ml and an amount of concentrate sample (-0.074 mm ≥ 90%) suitable for a pulp density of 10 g solid/100 ml, were added into a 250-ml Erlenmeyer flask before the inoculation. The flasks were placed in an orbital shaker at 200 rpm and 48°C. The pH value of acid leaching in the first 3~5 days was controlled at pH 0.8~1.0 since the ore contained high levels of acidconsuming minerals, then 15 ml of the inoculums with the cell density of about 10^8 cell ml^{-1} was added into the conical flask for bioleaching. The pH was maintained around 1.5 using 6 mol/l H_2SO_4. The catalysts of silver were added in different time of bioleaching process. And the utilization of silver-bearing species, adding time of silver and Ag^+ concentration were controlled according to the experimental design (Table 1). The total bioleaching time was three weeks. Water lost by evaporation was supplemented periodically by adding sterile water until the mass of the flask equaled its initial mass. Samples (3 ml) were removed for analysis and the sample volume was replaced with an equal volume of fresh 9K media.

Analytical techniques

Aqueous metal concentrations (Ni, Cu and total iron) were determined using ICP-AES (a Perkin-Elmer Optima 5300V device). Ore samples were digested in aqua regia (HNO_3: HCl=1:3) analysis by ICP-AES.

Experimental design and evaluation

Based on the results obtained by the classical approach, the factors were selected, and the ranges of these variables were decided (Date not shown). Further, RSM coupled with BBD was employed to optimize the silver-catalyzed bioleaching process and investigate the relative and interactive effects of silver-bearing species, adding time of silver and Ag^+ concentration on the Cu extraction. In brief, BBD was performed with three chosen independent variables at three levels, as shown in Table 1. According to statistical theory, three-factor, three-level BBD requires 16 sets of experiments, which include four replicates at the center point.

Design Expert software (trail Version 8.0.5.0, Stat-Ease Inc., Minneapolis, MN, USA) was used to design the experiments and analyze the data. The experiments were randomized to minimize the effects of uncontrolled factors. The experimental data were fitted to the following quadratic polynomial model via multiple regression analysis:

$$Y = \alpha_0 + \sum_{i=1}^{3} \alpha_i x_i + \sum_{i=1}^{3} \alpha_{ii} x_i^2 + \sum_{i,j=1}^{3} \alpha_{ij} x_i x_j + \varepsilon \quad \text{...(1)}$$

where Y represents the predicted response, α_0 is the model constant, α_i is the linear coefficient, α_{ii} is the quadratic coefficient, α_{ij} is the interaction coefficient, x_i and x_j are the coded variables and could be obtained according to previous report[10], ε is the error.

RESULTS AND DISCUSSION

Regression model and statistical analysis

The multiple regression analysis has been employed to study the relationships between the three effect factors and the responses (Table 1). After regression analysis of the experimental data using Design Expert software, the following second-order polynomial equation in the coded form was obtained, which could give the predicted value of Cu extraction:

$$P = 0.81 - 0.012x_1 + 1.000\times10^{-3}x_2 - 7.500\times10^{-4}x_3 + 8.000\times10^{-3}x_1x_2$$
$$+0.012x_1x_3 - 0.028x_2x_3 + 0.018x_1^2 - 0.042x_2^2 - 0.036x_3^2 \quad \text{...(2)}$$

where P is the response denoted as the predicted Cu extraction. And x_1, x_2 and x_3 are the coded terms for the three independent variables denoted as silver-bearing species, adding time of silver and Ag^+ concentration, respectively. It could be obtained that the predicted Cu extraction from different batches by analyzing Eq. (2). Moreover, from Table 1, a wide variation ranging from a minimum of 0.704 to a maximum of 0.817 occurred for the predicted Cu extraction.

Analysis of variance (ANOVA) and adequacy test of the model

From Table 2, it was demonstrated that Cu extraction was strongly dependent on the choice of the variables in the study. For more detailed explanation in mathematics, ANOVA was applied to generate the sum of squares, degrees of freedom (df), mean squares, F values, and p values by fitting the experimental data in Table 2 to the second-order polynomial Eq. (2). According to the results, the coefficient of determination (R^2) was 0.9522, implying that this response model could explain 95.22% of the variability, and only 4.78% of the total variations cannot be explained by the model. The regression quadratic model and the effect terms (X_1, X_2X_3, X_1^2, X_2^2 and X_3^2) were significant (p value < 0.05). A model can be considered reasonably reproducible if its coefficient of variation (CV) is not greater than 10%. In the present case, the high degree of precision and reliability of the conducted experiments was confirmed by the very low CV (1.60%), which was a cue to the goodness fit of the regression model. Meanwhile, as 'Adeq Precision' measures the signal-to-noise ratio, the adequate signal of this model (ratio 11.482 > 4) indicated that this response model could be used to navigate the design space.

Table 2. ANOVA results of the quadratic regression model [a]

Source	Sum of squares	df	Mean square	*F*-value	*p*-value
Model	0.019	9	2.066×10^{-3}	13.27	0.0026
X_1	1.200×10^{-3}	1	1.200×10^{-3}	7.71	0.0321
X_2	8.000×10^{-6}	1	8.000×10^{-6}	0.051	0.8282
X_3	4.500×10^{-6}	1	4.500×10^{-6}	0.029	0.8706
X_1X_2	2.560×10^{-4}	1	2.560×10^{-4}	1.64	0.2470
X_1X_3	5.760×10^{-4}	1	5.760×10^{-4}	3.70	0.1028
X_2X_3	3.136×10^{-3}	1	3.136×10^{-3}	20.15	0.0042
X_1^2	1.332×10^{-3}	1	1.332×10^{-3}	8.56	0.0264
X_2^2	6.972×10^{-3}	1	6.972×10^{-3}	44.79	0.0005
X_3^2	5.112×10^{-3}	1	5.112×10^{-3}	32.84	0.0012
Residual	9.340×10^{-4}	6	1.557×10^{-4}		
Lack of fit	6.100×10^{-5}	3	2.033×10^{-5}	0.070	0.9722
Pure error	8.730×10^{-4}	3	2.910×10^{-4}		
Total	0.020	15			

[a] R^2=0.9522; Adj. R^2=0.8805; Pred. R^2=0.8706; Adeq Precision=11.482; CV =1.60%.

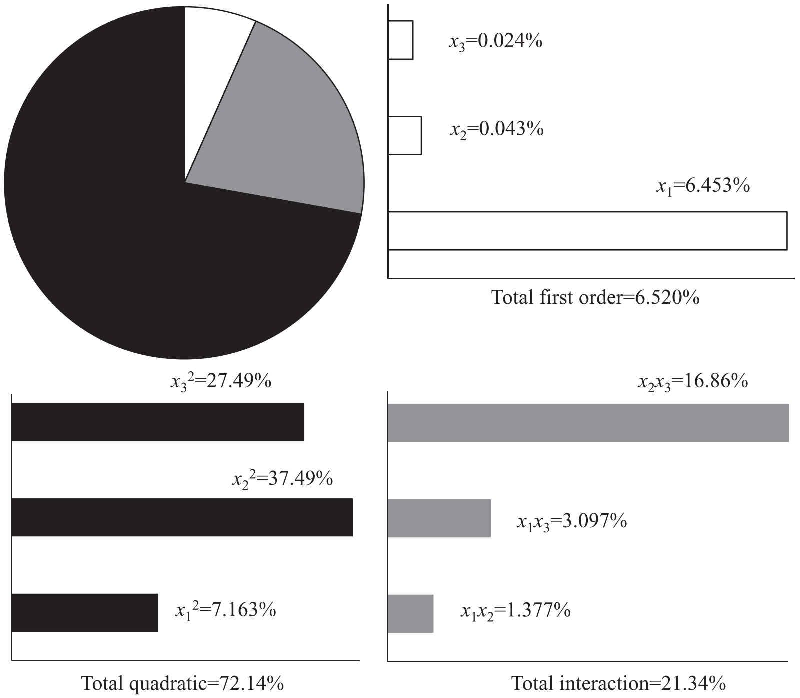

Fig. 1. Percentage contributions of model components from the regression model

In order to elucidate the predictive model, it is necessary to quantify the effect of each variable on the response. In this way, according to ANOVA (Table 2), the percentage contribution (PC) of individual component was calculated from the sum of squares. And similar work was done by Meng's group[8]. Herein, the PC value corresponds quantitatively to the effect degree of variable on the response. According to the standard (Fig. 1), two components that determined the Cu extraction were the term of silver-bearing species and the interaction term of adding time and Ag^+ concentration, which account for 6.453% and 16.86% of total contribution to the response, respectively. Moreover, the sectoral diagram (Fig. 1) showed the percentage contributions for the first-order, quadratic and interaction terms according to the sum of squares. As a result, the quadratic terms exhibited the highest percentage of total contribution of 72.14%. And this result was also consistent with the *F* test mentioned above.

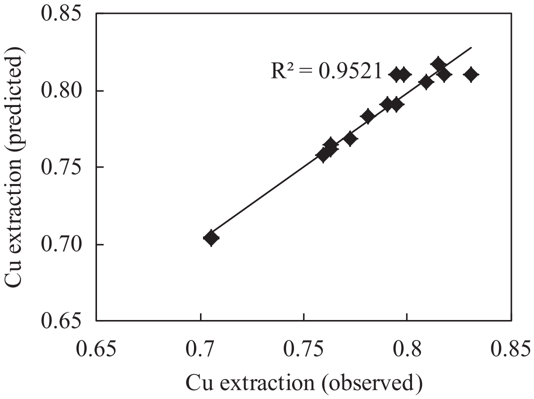

Fig. 2. Comparison between the predicted and actual values of the copper extraction

The predicted values of copper extraction were calculated using the regression model and compared with experimental values in Fig. 2. It can be seen from Fig. 2 that the experimental values were distributed relatively near to a straight line and a satisfactory correlation between these values is observed. This demonstrates that the fitted regression equation showed the fitting is good, and the BBD model with an experimental design can be effectively applied for optimization of silver-catalyzed bioleaching process.

Three-dimensional response surfaces and contour plots

Three-dimension (3D) response surfaces were performed to elucidate the individual and mutual effects of the experimental variables on the response (Fig. 3).

It was clean that the earlier addition time of silver resulted in the lower Cu extraction (Fig. 3A). In the Ag^+-free systems, the cells in logarithmic growth phase grow remarkably at the initial stage of bioleaching process. But, addition of silver catalyst was destructive to most bioleaching microorganisms except few silver-tolerant bacteria[11]. The result of this study was consistent with other investigators[12], who reported that cell densities of systems consisting of silver ion were just slightly raised in the beginning 5 days owing to that silver toxicity to the growth of most bioleaching bacteria. However, many researchers

Table 3. Comparison of operating processes between this study and other previous studied

Main type of ore/leaching	Dominant strains	Condition/lixiviant	Leaching efficiency/d	References
Chalcopyrite bioleaching	*Acidithiobacillus* sp. *Leptospirillus* sp.	0.1~0.5 g of Ag/kg ore, 50°C, 0 d[b]	~1.7%	[6]
Chalcopyrite chemleaching	NA[a]	266 mg AgCl, $CuCl_2^-$, 0 d[b]	3.2%	[14]
Chalcopyrite bioleaching	*Acidithiobacillus* sp.	1.0 mg/L $AgNO_3$, 30°C, 0 d[b]	2.6	[10]
Chalcopyrite bioleaching	*Acidithiobacillus* sp. *Leptospirillus* sp.	1.1 g Ag/kg of ore, Ag_2SO_4, 48°C, 7 d[c]	3.88%	This study

[a]: NA: not applicable.
[b] The catalyst of silver was added at the beginning of bioleaching.
[c] The catalyst of silver was added after 7 d of bioleaching.

commenced that adding silver catalyst into bioleaching process before cells were in stationary growth phase. As they reported, this method of silver catalysis yielded lower cell yields. This probable was the reason of low Cu extraction. Daily stage productivity of copper ion in silver ion systems was showed in Table 3. Thus, earlier addition time of silver reduced productivity of copper ion and adding silver catalysts after cells are in the stationary growth phase was recommended.

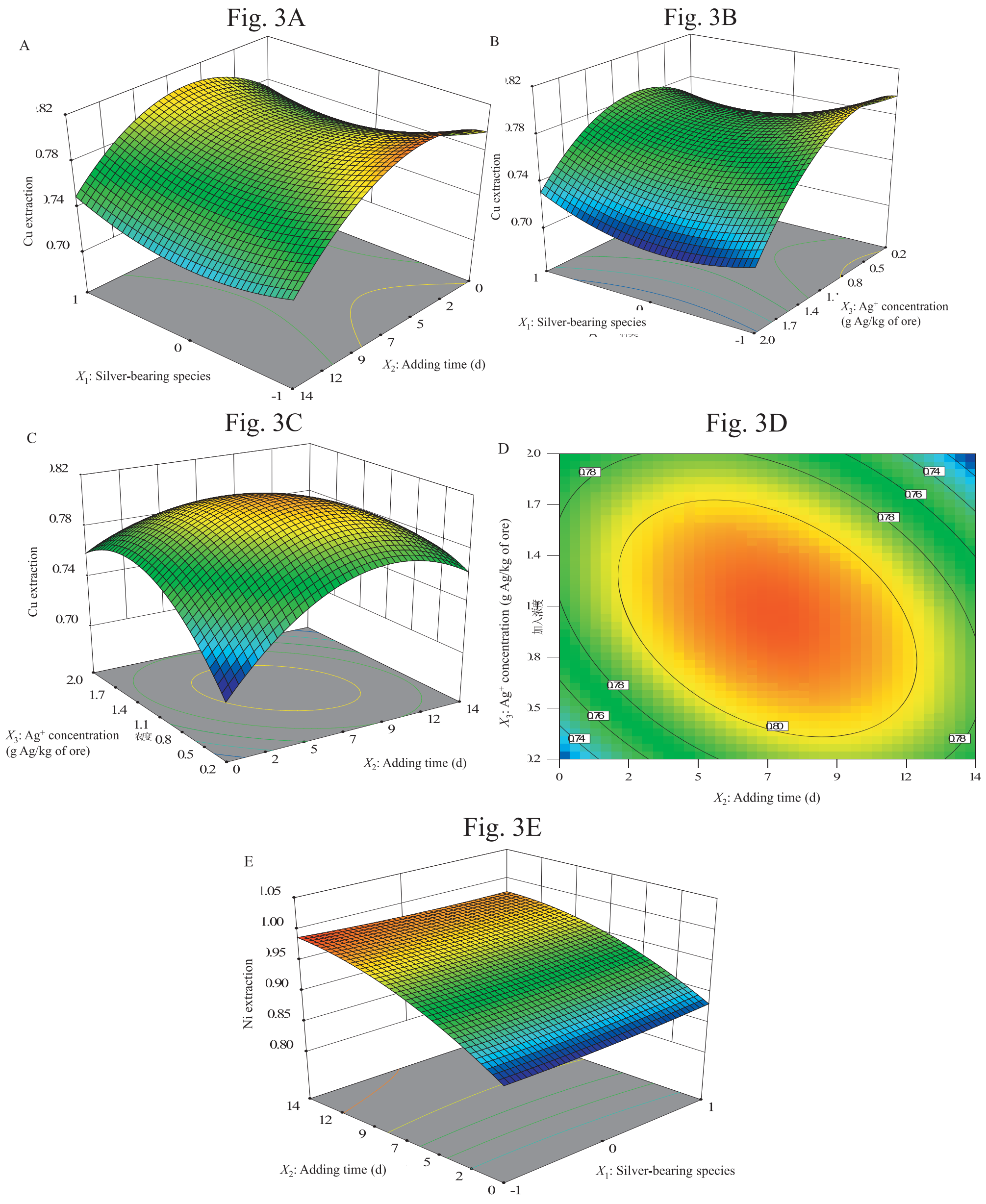
Fig. 3A

Fig. 3B

Fig. 3C

Fig. 3D

Fig. 3E

Fig. 3. Metal extraction in 3D response surfaces and contour plot, respectively: (A) effects of silver-bearing species and adding time on Cu extraction, (B) effects of silver-bearing species and silver concentration on Cu extraction, (C) effects of adding time and silver concentration on Cu extraction, (D) the contour plot of adding time and silver concentration on Cu extraction, (E) effects of silver-bearing species and adding time on Ni extraction

As shown in Fig. 3B, adding more than 1.1 g Ag/kg of ore resulted in undesirable decreased Cu extraction, probably due to silver toxicity to cells at high silver concentration. Moreover, there was some difference between using Ag^+ ion (Ag_2SO_4 and $AgNO_3$) or Ag_2S as catalyst. The bioleaching efficiency of copper was higher in the presence of Ag_2S than other two silver-bearing species. The result was similar to previous report[6].

The mechanism of silver catalysis proposed by Miller et al. indicates that Ag^+ ion rapidly reacts with chalcopyrite according to the following[13]:

$$CuFeS_2+4Ag^+=Cu^{2+}+Fe^{2+}+2Ag_2S \quad ...(3)$$

The Ag^+ ion can be regenerated through the oxidation of Ag_2S by Fe^{3+}:

$$Ag_2S+2Fe^{3+}=2Ag^++S^0+2Fe^{2+} \quad ...(4)$$

Besides, once the film of Ag_2S is formed on the chalcopyrite surface, a chalcopyrite–silver sulfide couple is established [6]. The anodic dissolution of the Ag_2S with lowest rest potential could be:

$$2Ag_2S=4Ag^+ + 2S^0+4\overline{e} \quad ...(5)$$

The cathodic reduction of O_2 on the chalcopyrite with highest potential could be:

$$O_2+4H^++4\overline{e}=2H_2O \quad ...(6)$$

Through reaction (5), Ag^+ ions could again be liberated to the solution to be deposited on the chalcopyrite surface, in turn, liberating more Cu^{2+} ions by reaction (3), which generates a cyclic process leading to the progressive dissolution of chalcopyrite.

As mentioned above, when using Ag^+ ion as catalyst, Cu^{2+} ion was at first dissolved through the surface displacement by reaction (3). Bacteria oxidized Fe^{2+} and elemental S^0 to promote the reaction (4). When using Ag_2S as catalyst, the mechanism mainly involved the galvanic interaction between chalcopyrite/silver sulfide. Reaction (5) preferentially takes place to produce Ag^+ ion. Then, the copper ion was dissolved through reaction (3). Bacteria oxidized elemental S^0 to enhance reaction (5) and then promote reaction (3). However, silver sulfide is more expensive than Ag^+ ion and it is difficult to recover the silver added in the processes. In views of cost effectiveness, utilization of silver ion was well-advised.

As seen in Fig. 3C, it could be observed that the response changed with adding time and silver concentration. The addition of silver after 7 d of bioleaching and adding concentration of about 1.1 g Ag/kg of ore devoted to achieve the maximum Cu extraction. The phenomenon had been explained before. Inappropriate addition time and addition concentration would cause damage to cells and then demote reaction (4). Most importantly, the earlier addition time of silver would also cause decrease of nickel extraction (Fig. 3E and Table 1). The reason of this phenomenon was that the activity of cells was inhibited by the toxicity of silver. This again proved that silver catalysts should be added after cells are in the stationary growth phase. In addition, Cu extraction was also not high when the later addition time was controlled because of insufficient silver-catalyzed time. On the other hand, the contour plot of X_2 (adding time) and X_3 (Ag^+ concentration) exhibited an elliptical morphology (Fig. 3D). A circular of a contour plot indicates that the interaction between the two selected variables possessing little role in predicting the response. So, the morphology of the result indicated a perfect interaction between the adding time and adding concentration, which was also confirmed by the ANOVA (Table 2).

Optimized studies for maximizing copper extraction

One of the main objectives was to optimize the silver-catalyzed bioleaching process to maximize the copper extraction of the low grade complex nickel-copper concentrate. Accordingly, three variables (silver-bearing species, adding time of silver and Ag^+ concentration) have been studied through the regression model obtained by RSM. To confirm the adequacy and the validity of the optimization procedure, validation experiment was performed. And it was found that the experimental value (Cu extraction=0.814) matched well with predictive counterpart (Cu extraction=0.810). It was revealed that the statistical method of RSM was successfully applied to optimize the process parameters of silver catalysis. Furthermore, the optimum conditions of silver-bearing species, adding time of silver and Ag^+ concentration were Ag_2SO_4, adding after 7 d of bioleaching and 1.1 g Ag/kg of ore. And the highest copper extraction reached about 0.814 compared with a recovery of 0.514 in the absence of a catalyst.

CONCLUSION

The different effect of silver-bearing species on bioleaching was revealed by Response surface methodology (RSM) and the regression model was successfully established using Design Expert software to estimate the influence of factors. The results demonstrated that the BBD model could be effectively applied for optimization of silver-catalyzed bioleaching process (R^2=0.9522).

Based on the model, the term of silver-bearing species and the interaction term of adding time and Ag^+ concentration exhibited high contribution to copper extraction. Moreover, the addition time of silver catalyst was quite significant in silver-catalyzed process. An inappropriate addition time would cause decrease of Cu extraction.

The optimum conditions of silver-bearing species, adding time of silver and Ag^+ concentration were Ag_2SO_4, adding after 7 d of bioleaching and 1.1 g Ag/kg of ore while the high copper extraction could reach to 0.814.

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