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Kinetic modeling of copper bioleaching from low-grade ore from the Shahrbabak Copper Complex

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Abstract: The copper recovery from low-grade copper sulfide ore was investigated using microbial leaching. Several parameters substantially affect the bioleaching of copper; among them, pulp density and nutrient media were selected for investigation. The optimum conditions for copper recovery were a pulp density of 5 g/mL, a mixed-mineral salt medium of *Acidithiobacillus thiooxidans* (70vol%) and *Acidithiobacillus ferrooxidans* (30vol%), and 10vol% of inoculum. Under these conditions, the maximum bioleaching capacity of the medium for copper recovery was determined to be approximately 99%. The effect of pulp density on the kinetics of the bioleaching process was surveyed using both da Silva's method and constrained multilinear regression analysis. The kinetics of copper dissolution followed the shrinking core model, and the process was diffusion controlled at a pulp density of 5 g/mL. Nevertheless, at higher pulp densities, the process was controlled by chemical reaction.

Keywords: bioleaching; kinetics; modeling; copper; mesophilic bacteria

1. Introduction

In recent years, researchers have focused on the recovery of metals from low-grade ores, waste production processes, catalyst residues, slags, dusts, and gases. The recovery process is especially attractive for low-grade minerals and low-grade metals in secondary resources. Traditional metal recovery processes based on pyrometallurgy have become less favored because of environmental protection requirements; consequently, the use of hydrometallurgical methods has been increasing [1–3].

Currently, the poor solubility and low concentrations of metals in ores and the large amount of available low-grade ores have drawn the attention of researchers to methods such as the microbial-assisted recovery of base metals [4]. The attractiveness of this procedure is related to its cost effectiveness, simple operation, lack of specialized equipment, lack of residuals, avoidance of hazardous acid wastes, and ability to recover metals present at low concentrations [5]. The effective dissolution of microorganisms and the microbial efficiency largely depend on the chemical composition and mineralogy of the ore, where bioleaching processes are commercially used especially for the recovery of copper and are strongly favored for secondary copper sulfide ores such as chalcocite (Cu_2S), digenite (Cu_9S_5), bornite (Cu_5FeS_4), and covellite (CuS). These recovery procedures are carried out using acidophilic microorganisms that grow at pH levels less than 3 and oxidize sulfur compounds and ferrous ions to generate solutions with relatively high oxidation–reduction potential (ORP) values [6–7]. During the bioleaching process, ferric ions are chemically reduced by reaction with the sulfide mineral matrix, and iron-oxidizing bacteria re-oxidize the ferrous ions to ferric ions. In most acidic bioleaching systems, the ORP predominantly reflects the Fe^{3+}/Fe^{2+} ratio and, thus, the activity of the iron-oxidizing bacteria [8]. *Acidithiobacillus thiooxidans* (*T.t*) can oxidize sparingly soluble sulfides such as wurtzite, but not sulfides that are totally insoluble (e.g., covellite), except when iron is present [9].

Heap bioleaching is a special method used in the copper mining industry [10]. Common mesophilic bacteria in copper sulfide leaching are *Acidithiobacillus ferrooxidans* (*T.f*),

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T.t, and *Leptospirillum ferrooxidans* (*L.f*) [11]. Several important parameters, including the temperature, pH values, nutrient availability, pulp density, the presence of sulfide minerals, the culture media used, the presence of oxygen (O_2) and carbon dioxide (CO_2), and metal toxicity, affect the bioleaching of copper [12]. These parameters affect the recovery process, the ability of bacteria to recover metals, and the process kinetics. Researchers have successfully applied the shrinking core model (SCM) to the bioleaching process as a result of different kinetic studies [13–17]. Copper dissolution has been shown to be diffusion controlled at a relatively low pH level [18–20]. In addition, the rate-controlling step in the bioleaching of copper from copper smelter dusts has been demonstrated to change at different pulp densities [21].

Various methods have been proposed to study leaching kinetics, and different approaches may result in different outcomes. In some recently published papers [20–22], bioleaching of low-grade sulfide minerals in the presence of various microorganisms was modeled using a conventional method [23]. Nazemi *et al.* [24] proposed an alternative approach to determine the rate-controlling step by applying a constrained multilinear regression analysis using the least squares technique. The bioleaching process is affected by various parameters, and the results vary for different ores with different mineralogical compositions and for different processing conditions. Thus, in the present study, the bioleaching of low-grade copper sulfide ore from the Shahrbabak Copper Complex in Iran was studied using mesophilic microorganisms. The aim of the present research was to assess the influence of two different mesophilic microorganisms, *T.f* and *T.t*, and three mixed cultures at different pulp densities on the kinetics of bioleaching. The kinetics of bioleaching were compared using two different kinetic methods proposed in previous studies [16,24]. The determination of reliable kinetic parameters and the acquisition of valuable complementary information are critical for enabling control of industrial bioleaching operations under defined conditions.

2. Theory

Knowledge of both the mechanism and the kinetics of bioleaching allows the copper recovery under different leaching conditions to be predicted. Kinetic models can be used for plant design, optimization of operating conditions of an existing plant, and real-time optimization, including automatic control and maximization of the metallurgical efficiency [25]. With respect to the bioleaching data, various kinetic models such as chemical reaction, diffusion through the product layer, and liquid-film mass transfer have been examined. In the present work, we used the SCM to determine whether the leaching process was chemically controlled or diffusion controlled. The aim of the kinetic analysis was to acquire the best kinetic model and to deduce reliable kinetic parameters. In the conventional method of kinetic studies, changes in copper recovery with leaching time at different pulp densities are fitted to the three following rate equations and the mechanism whose formula fits best the experimental data is selected as the controlling step [23].

Liquid film mass transfer control:

$$\frac{t}{\tau}=X \tag{1}$$

Product film diffusion control:

$$\frac{t}{\tau}=1-3(1-X)^{\frac{2}{3}}+2(1-X) \tag{2}$$

Chemical reaction control:

$$\frac{t}{\tau}=1-(1-X)^{\frac{1}{3}} \tag{3}$$

where τ is the time for complete conversion of the reactant particle to product, t is the time of recovery, and X is the metal recovery. Previous studies [22,26] on bioleaching demonstrate that, at higher pulp density, the culture may interfere with the mass transfer of O_2 and CO_2. Consequently, the kinetic model may be a combination of diffusion and reaction mechanisms. The conventional method cannot detect cases where more than one mechanism is involved in the overall rate equation or where the correlation coefficients of bioleaching data fit to these equations are too similar to distinguish the controlling mechanism. Hence, in a new method proposed by Nazemi *et al.* [24], the rate is determined by applying a multilinear regression analysis using the constrained least squares technique based on the following equation:

$$\tau=\tau_{\mathrm{F}}X+\tau_{\mathrm{P}}\left[1-3(1-X)^{\frac{2}{3}}+2(1-X)\right]+\tau_{\mathrm{R}}\left[1-(1-X)^{\frac{1}{3}}\right] \tag{4}$$

$$\tau_{\mathrm{F}}=\frac{\rho_{\mathrm{s}}R_0}{3K_1C_{\mathrm{ab}}} \tag{5}$$

$$\tau_{\mathrm{P}}=\frac{\rho_{\mathrm{s}}R_0^2}{6D_{\mathrm{e}}C_{\mathrm{ab}}} \tag{6}$$

$$\tau_{\mathrm{R}}=\frac{\rho_{\mathrm{s}}R_0}{K_{\mathrm{s}}C_{\mathrm{ab}}} \tag{7}$$

where ρ_{s} is the density, kg/m^3; R_0 is the initial radius of the particle, m; K_1 is the mass transfer coefficient of the liquid film, m^3/(m^2·s); C_{ab} is the concentration of sulfuric acid, kg/m^3; D_{e} is the effective diffusion coefficient in porous structures, $m^3/(m^2\cdot s)$; and K_s is the reaction rate constant at the particle surface, s^{-1}.

This technique takes into account all three possible rate-controlling mechanisms for leaching processes: τ_R for chemical reaction, τ_P for diffusion through product layer, and τ_F for liquid film mass transfer; simultaneously, detecting all the mechanisms involved in the leaching process in a single step.

The method developed by da Silva [16] was also used. This method is based on the following mixed-control mechanism equation:

$$t-t_{\text{lag}}=\frac{1}{D}\left\{\left[1-3(1-X)^{\frac{2}{3}}+2(1-X)\right]-\left[1-3(1-X_{\text{lag}})^{\frac{2}{3}})+2(1-X_{\text{lag}})\right]\right\}+\frac{1}{k}\left\{\left[1-(1-X)^{\frac{1}{3}}\right]-\left[1-(1-X_{\text{lag}})^{\frac{1}{3}}\right]\right\} \tag{8}$$

where D is the diffusion coefficient, k is the reaction rate constant, and the subscript "lag" refers to the time point to begin modeling the recovery kinetics. At $t = t_{\text{lag}}$ and $X = X_{\text{lag}}$, the k/D ratio reveals the relative contribution of diffusion and reaction effects. In fact, a k/D ratio greater than 1 would indicate that diffusion control dominates, whereas a ratio of less than 1 would indicate that reaction control dominates. Thus, the calculation of the k/D ratio obtained under different bioleaching conditions would be a proper criterion to determine the reaction mechanism.

3. Experimental procedure

A complex sulfide ore used in this study was obtained from Shahrbabak copper mine (Kerman, Iran). The ore was ground into particles with a size finer than 75 μm. Chemical analysis of the ore by X-ray fluorescence (XRF) (ARL Optimax) showed that the ore contained 0.24wt% copper, mostly as secondary copper sulfide minerals. The sulfide minerals were pyrite (6.53wt%), chalcocite (0.15wt%), covellite (0.078wt%), and chalcopyrite (0.091wt%), and the predominant gangue minerals were quartz (SiO_2), anorthite ($CaO\cdot Al_2O_3\cdot 2SiO_2$), and muscovite ($H_2KAl_3(SiO_4)_3$). The utilized bacteria types for the experiments were *T.t* 1692, *T.t* 1717, and *T.f* 1646, which were obtained from the Microorganisms Collection Research Center (University of Tehran).

Adaptation was carried out at 30°C in Erlenmeyer flasks (500 mL) using a shaker incubator (180 r/min). The volume of the solution was 100 mL with 10vol% inoculum, and the solid-to-liquid (S/L) ratio changed from 1 to 16 g/mL. The microorganisms were separately grown in different culture media: *T.f* in 9K, *T.t* 1692 in A, and *T.t* 1717 in B. In addition, a mixture of 50vol% *T.f* and 50vol% *T.t* 1692 were grown in a mixed culture (Mix). The mineral salt compositions of the media are shown in Table 1. As an indicator of bacterial growth during the sub-culturing processes, the pH and Eh values were measured every 2 d. Serial phases were used to adapt the bacteria. When the pH and Eh values of the solution were in the range required for bacteria growth, which was considered as the stationary phase of adapted bacteria, they were inoculated into another flask containing additional powder, up to a pulp density of 16 g/mL. Also, the time for each stage was varied, e.g., 15 d for 1 to 4 g/mL, 40 d for 4 to 8 g/mL, and 17 d for 8 to 16 g/mL.

Table 1. Mineral salt compositions of the media g/L

Composition	9K	A	B	Mix
$(NH_4)_2SO_4$	3	—	2	4
KCl	0.1	—	0.1	0.1
K_2HPO_4	0.5	—	0.1	0.5
$MgSO_4\cdot 7H_2O$	0.50	—	0.25	0.50
$Ca(NO_3)_2$	0.01	—	—	0.01
$FeSO_4\cdot 7H_2O$	44.2	—	—	22.1
S	—	10	5	5
$CaCl_2\cdot 2H_2O$	—	0.14	—	0.13
$MgCl_2\cdot 6H_2O$	—	0.1	—	—
KH_2PO_4	—	3	—	—
NH_4Cl	—	0.1	—	—

After adaptation, bioleaching tests were performed in 500-mL Erlenmeyer flasks containing 250 mL of nutrient and 10vol% of inoculum bacterial solutions incubated in an orbital shaker at 150 r/min in six different cultures. Copper dissolution was analyzed using an atomic absorption spectrometer (AA spectrometer, UNICAM939). The kinetics of reactions were studied for different pulp densities of 5, 10, and 15 g/mL. Copper dissolutions in six different cultures of 9k, A, B, Mix (50vol% *T.t*–50vol% *T.f*), Mix1 (70vol% *T.t*–30vol% *T.f*), and Mix2 (30vol% *T.t*–70vol% *T.f*) were observed every 2 d to determine the relation between the pulp density and the metal recovery.

4. Results and discussion

4.1. Adaptation results

The bioleaching process of low-grade copper ore was initially performed to study the feasibility of the process for different pulp densities of 1, 2, and 4 g/mL. The pH value of cultures was observed during the process to evaluate the growth of bacteria. Fig. 1 shows the results for cultures in different media of 9K, A, B, and Mix. Bacterial growth is observed at a pulp density of 1 g/mL in Fig. 1(a). Figs. 1(b) and 1(c) compares the results at a pulp density of 4 g/mL before and after adaptation. Fig. 1(b) shows that, before adaptation, the pH value is greater than 3, which indicates that the bacteria are not active. We concluded that higher concentrations of copper ore likely deactivate the microorganisms. However, Fig. 1(c) demonstrates that the pH value was less than 1.5 in all of the cultures studied after the adaptation process. Thus, when larger quantities of copper ore are used, the adaptation of bacteria is critical.

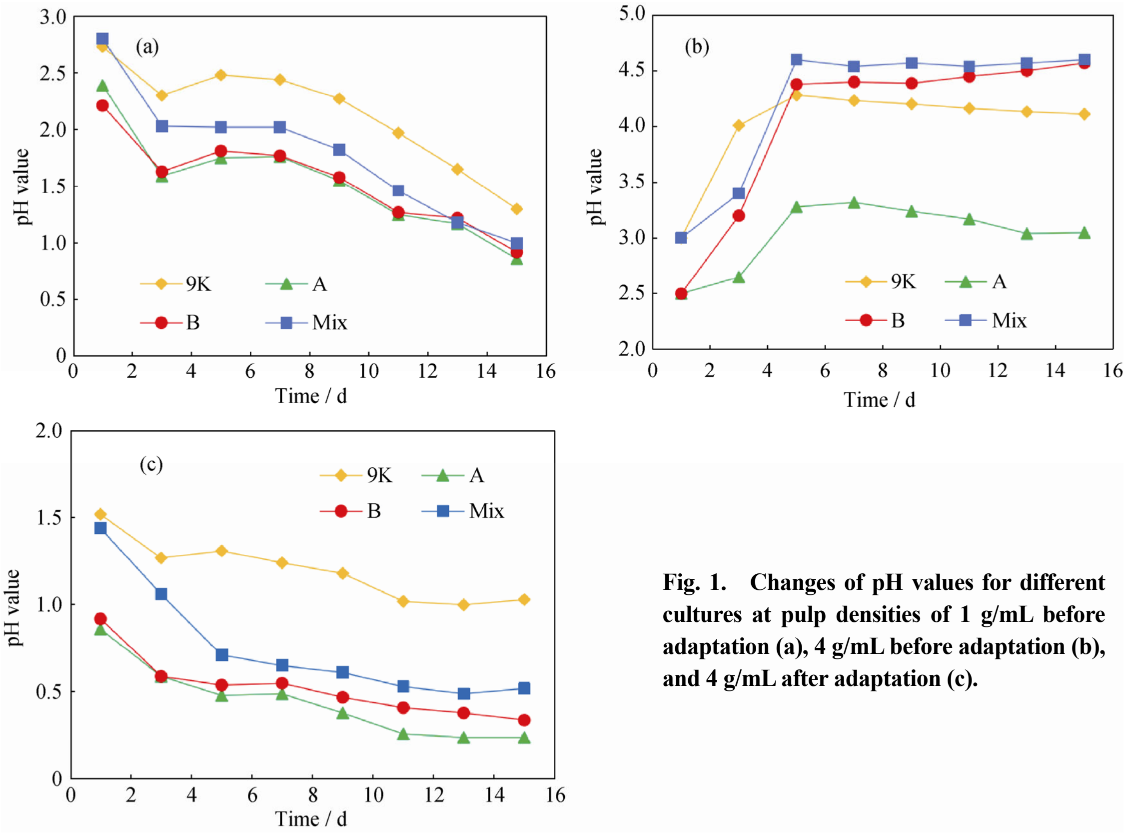

Fig. 1. Changes of pH values for different cultures at pulp densities of 1 g/mL before adaptation (a), 4 g/mL before adaptation (b), and 4 g/mL after adaptation (c).

4.2. Bioleaching results

The Eh and pH values of the different media of the ore samples at different pulp densities were periodically analyzed. As evident in Fig. 2, at the beginning of the process (0–4 d), the pH values in all of the cultures increased for 2 main reasons. Firstly, the oxidation of Fe^{2+} would consume protons in the solution as it can be seen in Eq. (9):

$$Fe^{2+} + O_2 + H^+ \xrightarrow{\text{Bacteria}} Fe^{3+} + H_2O \qquad (9)$$

Secondly, the toxicity of the metal ions results in acidic resistance in the presence of the dissolved inorganic samples [27].

After 4 d, the pH value decreased because of the acid production; this process is related to the mechanism of bacterial activity that converts sulfur to sulfuric acid [4]. Notably, the pH values of the 9K medium containing *T.f* bacteria were higher than the pH values of the other cultures. The conversion kinetics of sulfur to sulfuric acid is known to slower in the presence of *T.f* bacteria than in the presence of *T.t* bacteria. Then again, the medium cultures containing *T.t* bacteria (*A* and *B*) exhibit lower pH values, indicating that the kinetics of sulfuric acid production is faster [11,28].

Fig. 3 shows the changes in Eh at different pulp densities. Regarding the indirect mechanism of dissolution with the help of microorganisms, bacteria gain their energy in the culture from oxidation of Fe^{2+} to Fe^{3+}. The microbial oxidation of Fe^{2+} increases the Fe^{3+}/Fe^{2+} ratio and, thus, the Eh. Depending on the ratio of Fe^{3+} to Fe^{2+} ions, the oxidation potential will change [5]. An increase of the pulp density resulted in a sharp increase in the duration of the lag phase of bacterial growth as well as increases in acid consumption, toxicity of metal ions, and copper concentration. These changes, in turn, resulted in a reduction of the oxidation reduction potential (ORP). When the oxidation reduction potential is low and the majority of Fe ions in the solution are Fe^{2+} ions, *T.f* will predominate because this microorganism has a faster growth rate and will build up a larger number of cells in the system [11,28]. As a result, this kind of microorganisms increases the Fe^{3+}/Fe^{2+} ratio and, thus, the redox potential.

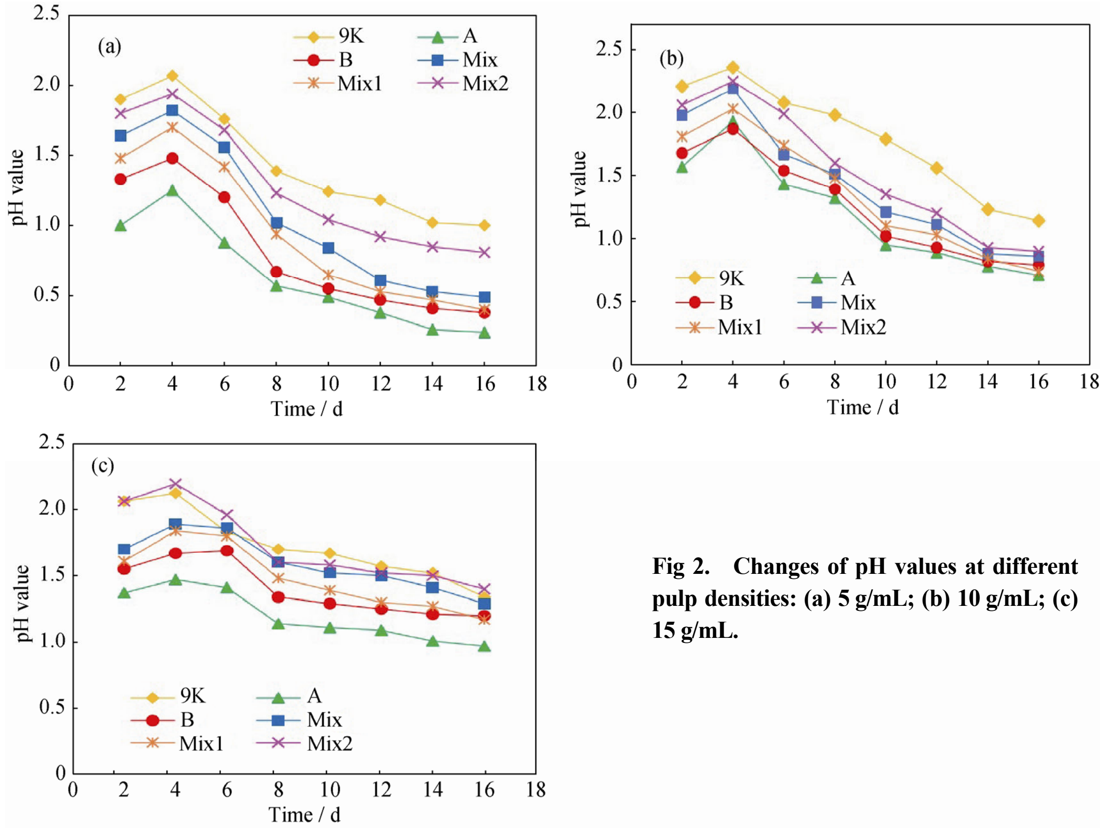

Fig 2. Changes of pH values at different pulp densities: (a) 5 g/mL; (b) 10 g/mL; (c) 15 g/mL.

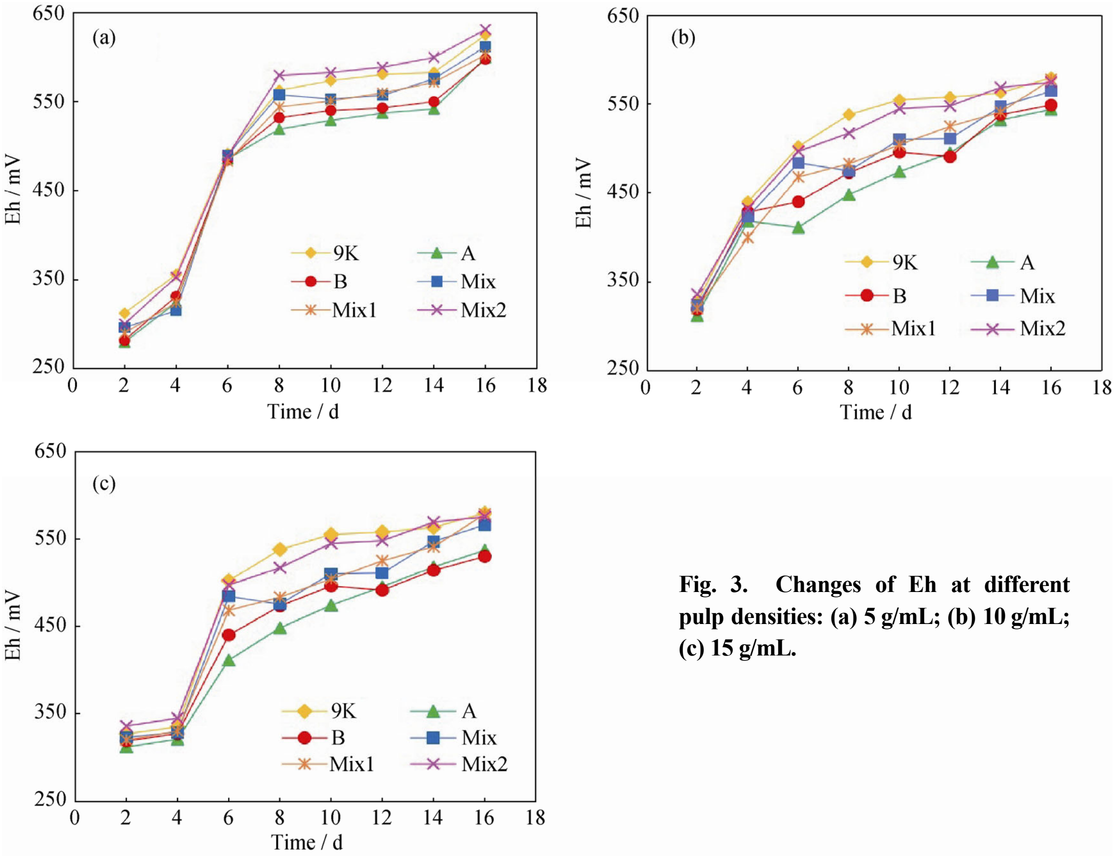

Fig. 3. Changes of Eh at different pulp densities: (a) 5 g/mL; (b) 10 g/mL; (c) 15 g/mL.

Figs. 2 and 3 reveal that pulp density plays a critical role in the leaching process. Actually, small pH changes and large Eh changes are associated with a higher pulp density of 15 g/mL. This behavior can be explained by the decrease in microorganism activity. As a result, the amounts of sulfuric acid and Fe^{3+} ions are reduced. This result is attributable to the limitation of air distribution and oxygen mass transfer at higher pulp densities [29–30]. In addition, the greatest reduction in pH value and the greatest increase in Eh occurred between the 4th and the 8th days, which means that the maximum activity of microorganisms was achieved during this interval.

Fig. 4 shows the copper recovery in different cultures. Increasing pulp density in all media led to a decrease in copper recovery. A copper recovery of 99% at day 16 was achievable at a low pulp density of 5 g/mL. The mineralogy of sulfide ore and the complete adaptation of bacteria to the culture enable such a high copper recovery. This copper recovery over 16 d is comparable to the values of 91% [8] and 94% [31] reported in previous studies. However, in the present work, the copper recovery was 87% and 76% at higher pulp densities of 10 and 15 g/mL, respectively. As explained previously, this behavior is likely related to the decrease in microorganism activity with increasing pulp density. Altogether, the optimum recovery of copper was achieved at a low pulp density of 5 g/mL with the mixed culture containing 70vol% *T.t*.

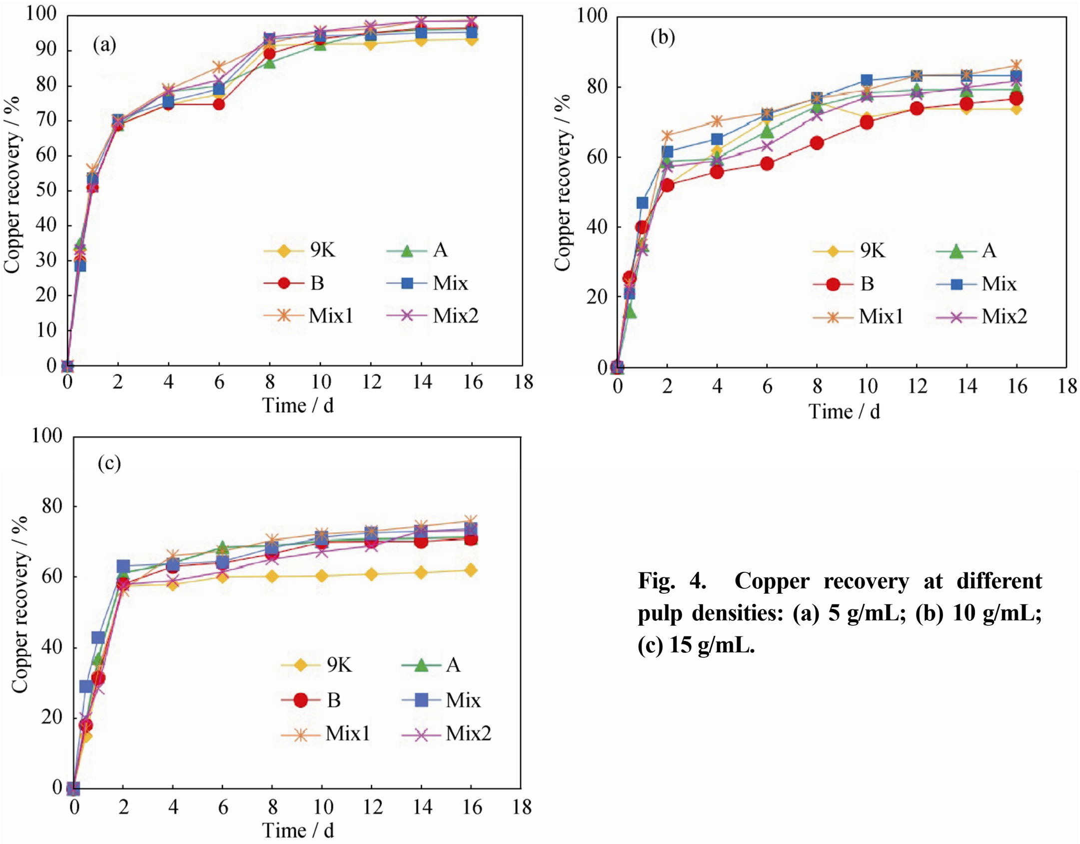

Fig. 4. Copper recovery at different pulp densities: (a) 5 g/mL; (b) 10 g/mL; (c) 15 g/mL.

As observed in Fig. 4, higher copper recovery was achieved with the A, B, and Mix1 cultures. According to the ability of the *T.t* bacteria [6,12], the main mechanism for copper recovery from Shahrbabak ore is based on the percentage of sulfuric acid in the culture. The recovery of copper occurs according to the following reactions [32]:

$$Cu_2S + 2Fe^{3+} = CuS + Cu^{2+} + 2Fe^{2+} \quad (10)$$

$$CuS + 2Fe^{3+} = S^o + Cu^{2+} + 2Fe^{2+} \quad (11)$$

$$Cu_2S + 0.5O_2 + 2H^+ = CuS + Cu^{2+} + H_2O \quad (12)$$

$$2S^o + 3O_2 + 2H_2O = 2H_2SO_4 \quad (13)$$

$$2Cu_2S + 2H_2SO_4 + O_2 = 2CuS + 2CuSO_4 + 2H_2O \quad (14)$$

We therefore concluded that both sulfuric acid and Fe^{3+} ions lead to the dissolution of copper.

4.3. Kinetic study

A kinetic study is a significant step toward understanding the nature and the mechanism of a leaching process. According to Fig. 4, the leaching process includes two stages: in a short period after 2 d, the copper recovery rapidly increases to a value greater than 60%; thereafter, the leaching progresses moderately to copper recoveries approaching

100%. This trend suggests the existence of two mechanisms of leaching at low and high copper recoveries because of the existence of different copper compounds with various leaching solubilities in the copper ore. To study the kinetics of the first stage of leaching, we used the low-recovery (less than 60%) data.

The results were fitted to Eq. (4), and constants τ_F, τ_P, and τ_R were calculated by a constrained multilinear regression analysis using the least squares technique. The calculated fitting results of experimental data are shown in Table 2. Initially, the controlling step clearly does not vary among different cultures. We also concluded from the results in Table 2 that, at recovery values less than 60%, the rate of bioleaching was controlled by product film diffusion at pulp densities of 5 and 10 g/mL because precipitates such as jarosite are constantly produced in bioleaching processes [22]. By contrast, the constant τ_F, which refers to liquid film mass transfer control, was zero in most of the cultures at different pulp densities because of the high rotation speed. The higher values of τ_R at a higher pulp density of 15 g/mL show that the controlling mechanism of copper recovery was chemical reaction. This result can be explained by the observation that increasing the pulp density decreased the concentrations of chemical reactants and consequently reduced the efficient exposure of the pulp to the reactants. In addition, increasing the pulp density led to a limitation in air distribution and oxygen mass transfer. Therefore, at higher pulp densities, chemical reaction plays a key role in the kinetics of the process.

Table 2. Data obtained from Eq. (4) for the first stage of bioleaching with different cultures at different pulp densities

Pulp density / (g·mL^{-1})	Culture medium	τ_F / min	τ_P / min	τ_R / min	R^2
5	9K	0	91.12	0	0.9967
	Mix	0	74.70	0	0.9735
	A	0	160.50	0	0.9921
	Mix1	0	136.60	0	0.9845
	B	0	121.78	0	0.9932
	Mix2	0	102.32	0	0.9896
10	9K	0	362.65	0	0.9903
	Mix	0	184.65	0	0.9946
	A	0	160.17	0	0.9827
	Mix1	0	157.40	0	0.9933
	B	0	134.20	0	0.9746
	Mix2	0	186.93	0	0.9912
15	9K	0	0	149.50	0.9978
	Mix	0	0	120.54	0.9854
	A	0	0	190.96	0.9617
	Mix1	0	0	155.74	0.9667
	B	0	0	197.25	0.9926
	Mix2	0	0	164.32	0.9942

The same type of data processing was applied for the second stage of leaching (recoveries greater than 60%). Eq. (4) cannot be directly applied to the data in this stage because the boundary condition for this stage was not zero. In fact, the recovery of copper at the beginning of the second leaching stage (t_1) was not zero ($X_1 \neq 0$). In this case, the following formula should be used instead [33]:

$$t - t_1 = \tau_F (X - X_1) + \tau_P \left\{ 1 - 3\left[1 - \frac{X}{1 - X_1}\right]^{\frac{2}{3}} + 2\left[1 - (1 - X_1)^{\frac{1}{3}} (X - X_1)\right] \right\} + \tau_R \left[1 - \left(\frac{1 - X}{X - X_1}\right)^{\frac{1}{3}}\right] \qquad (15)$$

where

$$\tau_F = \frac{\rho_s R_0 (1 - X_1)^{\frac{1}{3}}}{3 K_1 C_{ab}} \qquad (16)$$

$$\tau_P = \frac{\rho_s R_0^2 (1 - X_1)^{\frac{2}{3}}}{6 D_e C_{ab}} \qquad (17)$$

$$\tau_R = \frac{\rho_s R_0 (1 - X_1)^{\frac{1}{3}}}{K_s C_{ab}} \qquad (18)$$

The calculated results obtained using the experimental data for recovery values greater than 60% are shown in Table 3. The following conclusions were drawn for the second stage. First, similar to the finding reported for the first stage, the constant τ_F was zero at different pulp densities. This result is most likely related to the bioleaching experiments being carried out in shaken flasks at a high rotation speed. Hence, the liquid film mass transfer control did not play a key role in the kinetics of bioleaching. Second, the rate-controlling mechanism changed from product film diffusion at a lower pulp density of 5 g/mL to chemical reaction at higher pulp densities of 10 and 15 g/mL. A comparison of the results in Tables 2 and 3 reveals that, at a pulp density of 10 g/mL, the controlling mechanism changed as bioleaching progressed. Product film diffusion apparently controlled the process at the first stage, whereas chemical reaction controlled the process at the second stage. The reason for this change is likely related to the rapid acid leaching of oxidized surface material and, hence, rapid chemical reaction [34].

To examine the model proposed by da Silva [16], we obtained the parameters *k* and *D*. The *k*/*D* ratio for copper dissolution in different cultures and pulp densities are presented in Table 4. A *k*/*D* ratio greater than 1 in the case of 5 g/mL

Table 3. Data obtained from Eq. (15) for the second stage of bioleaching with different cultures at different pulp densities

Pulp density / (g·mL^{-1})	Culture medium	τ_F / min	τ_P / min	τ_R / min	R^2
5	9K	0	470.23	0	0.9467
	Mix	0	450.65	0	0.9843
	A	0	432.89	0	0.9712
	Mix1	0	605.91	0	0.9698
	B	0	560.90	0	0.9574
	Mix2	0	514.97	0	0.9502
10	9K	0	0	1164.51	0.9798
	Mix	0	0	1248.03	0.9542
	A	0	0	976.26	0.9869
	Mix1	0	0	1980.75	0.9312
	B	0	0	1143.81	0.9493
	Mix2	0	0	1285.84	0.9079
15	9K	0	0	660.17	0.9391
	Mix	0	0	586.30	0.9867
	A	0	0	403.85	0.8258
	Mix1	0	0	592.34	0.9209
	B	0	0	2096.40	0.9634
	Mix2	0	0	657.86	0.8937

Table 4. Kinetic parameters for bioleaching tests based on Eq. (8) with different cultures at different pulp densities

Pulp density / (g·mL^{-1})	Culture medium	k	D	k/D	R^2
5	9K	255.1600	0.005014	2.8×10^{6}	0.8967
	Mix	14285.71	0.005026	2.9×10^{6}	0.9762
	A	3333.340	0.005010	6.6×10^{5}	0.8694
	Mix1	522537.3	0.005039	1.0×10^{8}	0.9421
	B	153.8400	0.005006	3.0×10^{4}	0.8967
	Mix2	8130.080	0.005020	1.6×10^{6}	0.9023
10	9K	0.003784	323904.9	1.2×10^{-8}	0.9550
	Mix	0.003852	1763.668	2.1×10^{-6}	0.8912
	A	0.004003	813.0121	4.9×10^{-6}	0.8311
	Mix1	0.003876	1763.669	2.2×10^{-6}	0.9247
	B	0.004029	5.010000	0.1×10^{-5}	0.9489
	Mix2	0.003911	1000.006	3.9×10^{-7}	0.8988
15	9K	0.003919	250.0000	1.5×10^{-5}	0.8190
	Mix	0.003754	50000.00	7.5×10^{-8}	0.8243
	A	0.003864	184.0943	2.1×10^{-5}	0.9339
	Mix1	0.003850	794.9128	4.8×10^{-6}	0.8856
	B	0.003644	167834.3	2.1×10^{-8}	0.9243
	Mix2	0.003878	33333.33	1.1×10^{-7}	0.8212

pulp density indicates that the kinetics of bioleaching at low pulp density was controlled by diffusion through the product. However, at a higher pulp density of 15 g/mL, all the leaching experiments exhibited a relatively low *k*/*D* ratio, indicating that the process was controlled by chemical reaction. These results are consistent with the results of constrained multilinear regression analysis. However, a comparison of kinetic study results at a pulp density of 10 g/mL using da Silva's method and constrained multilinear regression analysis indicates that the process was completely controlled by chemical reaction. This result can be explained by the fact that da Silva's model considers the effect of the lag period and/or an initial period of rapid acid leaching of the oxidized surface material encountered in bioleaching processes [16].

5. Conclusions

In this research, the influence of two different mesophilic microorganisms, *T.f* and *T.t*, and three mixed cultures at different pulp densities on the kinetics of copper bioleaching from Shahrbabak low-grade ore was investigated. The results led to the following conclusions. (1) The adaptation of bacteria is necessary in the presence of larger quantities of copper ore. (2) At higher pulp densities, culture Mix1 (70vol% *T.t*–30vol% *T.f*) resulted in the best recovery among the investigated cultures. (3) The highest recoveries of copper after 16 d at pulp densities of 5, 10, and 15 g/mL for the Mix1 culture with 10vol% of inoculum were 99%, 87%, and 76%, respectively. (4) The main mechanism for copper recovery from Shahrbabak ore was based on the production of sulfuric acid by *T.t* bacteria in the culture because of the faster kinetics observed. (5) Kinetic study results revealed that copper dissolution was diffusion controlled at a relatively low pulp density of 5 g/mL. However, at higher pulp densities, chemical reaction control was dominant. (6) A comparison of the results obtained using da Silva's method and using the constrained multilinear regression analysis illustrated that da Silva's model provided more reliable results because it considers the effect of the lag period and an initial period of rapid acid leaching of the oxidized surface material encountered in the bioleaching process.

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