Copper Recovery from Chalcopyrite Concentrate by an Indigenous *Acidithiobacillus ferrooxidans* in an Air-Lift Bioreactor

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ABSTRACT: *In this study, effects of solid concentration, temperature, and initial Fe^{2+} concentration on bioleaching of sulfide mineral (chalcopyrite) obtained from Sarcheshmeh Copper Mine in the region of Kerman located in the south of Iran were investigated. A mesophilic iron oxidizing bacterium, Acidithiobacillus ferrooxidans has been isolated from a typical chalcopyrite copper concentrate of the mentioned mine. Bioleaching experiments were carried out in two batch air-lift bioreactors with recycling stream. One reactor contained 2 liters of medium and 10% (v/v) inoculum while in the other reactor, control bioleaching tests were carried out with sterilized concentrate without inoculum by the addition of 40 ml of 0.5% (v/v) formaline in ethanol. The results indicate that the efficiency of copper extraction is dependent on all of the aforementioned variables. In addition, results show that the effects of solid concentration and temperature had more effect compared to the initial Fe^{2+} concentration. Maximum copper recovery was achieved 70% at pH=1.5, initial Fe^{2+} concentration=7g/L and pulp density = 10% (w/v) in bioreactor, after 10 days.*

KEY WORDS: *Bioleaching, Acidithiobacillus ferrooxidans, Air-lift bioreactor, Sulfide mineral, Copper extraction.*

INTRODUCTION

The supply of high grade ores in the world is becoming more and more scarce making the processing of more complex ores necessary. Conventional mineral possessing on complex sulfides ores carried out by differential flotation often produce high-grade concentrates but causes environmental pollutions and accompanying penalties, which make its marketing and pyrometallurgical processing difficult. Therefore, a lot of effort has been made to develope hydrometallurgical process suitable for ores treatment, but most of the proposed methods are

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complex and expensive [1].

Among the hydrometallurgical processes, biohydrometallurgical techniques seem to be one of the best alternatives for treatment of these type of ores. These methods, which were applied industrially in copper and uranium productions, using bioassisted heap, dump and in situ technologies, are successfully used today in extraction of gold from refractory sulfide-bearing ores and concentrates [2-7]. However, for other metal concentrates, this technology remains as a promising alternative against conventional pyrometallurgical extraction processes. This is the case of the treatment of chalcopiritic concentrates, which represent a more complicated situation, due to the natural refractivity of chalcopyrite.

Bioleaching is an attractive means of extraction of metals from the sulfide minerals. During bioleaching, acidophilic micro-organisms attack the iron sulfide and use the oxygen of air to oxidize the sulfide to sulfuric acid. In industrial mineral ore treatment, bioleaching of sulfides is usually implemented in very large mechanically agitated reactors. Suspension of the finely ground concentrate particles and aeration to ensure the gas-liquid mass transfer rates allowing bioleaching to take place, require considerable amounts of mechanical energy. In addition, in this type of reactors, generally a maximum solid loading of 20% is used, since several factors such as oxygen requirements, nutrient availability and effect of shear and turbulence generated by agitation; limit the bioleaching efficiency as reported by [8-9]. The use of air-lift bioreactors may be an alternative to overcome this limitation and have more efficiency [10]. In fact, in such reactors, shear and turbulence are usually smaller than in agitated tank reactors, while the gas-liquid mass transfer is satisfactory. However, choosing a proper type of bioreactor is a key step in achieving successful bioleaching. Hence, the selection of reactor is an important subject. The propose of this study is to investigate the applicability of air-lift bioreactors in bioleaching processes, which was found to be a suitable subject for research work, that least attention has been paid to it.

MATERIALS AND METHODS

Ore concentrates

A copper sulfide concentrate supplied by Sarcheshmeh Copper Mine (Kerman, Iran) was used. Chemical analysis of the sample revealed: 24.74% Cu; 26.39% Fe; 0.68% Mo; and 35% S. X-ray diffraction analysis of the ore showed chalcopyrite ($CuFeS_2$) as the major component (57.1%), pyrite (FeS_2)(19.3%) as the minor one, and small amounts of chalcocite (Cu_2S), covellite (CuS) and molybdenite (MoS_2). Over 90% of the ore had a size less than 45 μm.

Microorganism and Media

The strain used in this study has been isolated from the heap of Sarcheshmeh Copper Mine and it was identified by the department of microbiology in IROST (Iranian Research Organization of Science and Technology). According to the report of IROST the strain was identified as *Acidithiobacillus ferrooxidans*.

The bacteria were grown on a medium containing $FeSO_4.7H_2O$: 33.4g/L, $(NH_4)_2SO_4$: 0.4g/L, $MgSO_4.7H_2O$: 0.4 g/L, and K_2HPO_4: 0.4g/L [11]. The cultures of *Acidithiobacillus ferrooxidans* were incubated in 500 ml Erlenmeyer flasks each containing of 200 ml of the medium and 10% (v/v) inoculum, at a constant temperature of 33°C on a rotary shaker at 180 rpm. The initial pH of the cultures was adjusted to 1.5 using 1N H_2SO_4. The stock and pre-inoculum cultures were maintained in the same medium under similar conditions. The stock cultures were subcultured every two weeks.

Bioleaching Experiments

In air-lift bioreactors, both mixing and suspension of solids is induced by aeration only. The reactor itself does not contain any moving parts in contact with the process water. In this study bioleaching experiments were carried out in two batch air-lift bioreactors with recycling stream consisting of three parts: top part, main column with water jacket and bottom part with an air diffuser. The main column consisted of an internal tube of 3.5 cm internal diameter, an external tube of 7 cm diameter and 55 cm height and a total working volume of 2 l. Compressed air was sparged from the bottom of the column into the internal tube, and the air bubbles move to the top of the reactor, where they can escape. As a consequence of the induced density difference, a recirculation flow pattern of the concentrate slurry in the column will occur. The top part of the reactor had a 10 cm diameter and 20 cm height and was employed to prevent the overflow of slurry from the

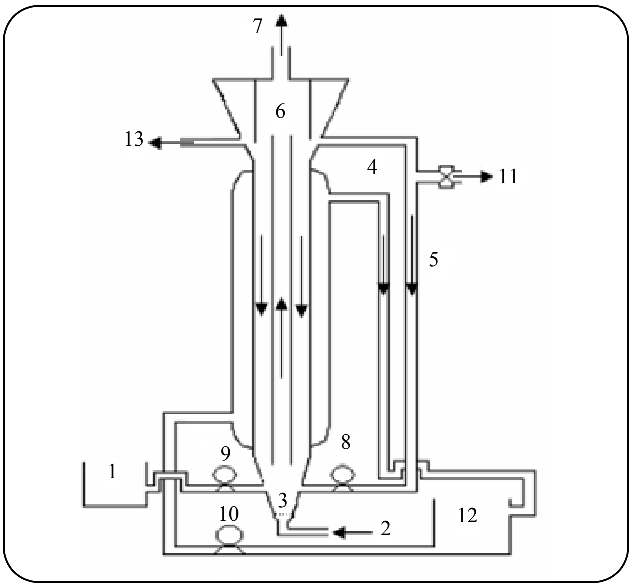

Fig. 1: Schematic diagram of air-lift bioreactor (1: fresh feed; 2: input air; 3: air sparger; 4: circulation of water in jacket; 5: recycling stream; 6: draft tube; 7: output air; 8,9,10: peristaltic pump; 11: sampling port; 12: thermostatic bath; 13: effluent solution)

reactor. Fig. 1 shows a schematic diagram of the experimental setup. Temperature was adjusted using a water jacket. One of the reactors contained 2 liters of medium and 10% (v/v) inoculum. At beginning, various amounts of concentrate were added to the medium. Other reactor used as control, using sterilized concentrate by autoclaving at 121 ºC for 30 min under 1 atm pressure, without inoculum and 40 ml of 0.5% (v/v) formaline in ethanol was added to keep sterile control experiment after start-up.

For investigation of effect of the initial Fe^{2+} concentration some medium with various amounts of $FeSO_4$ were made. During the experiments, the pH was kept at 1.5 (except one test for investigation of variations of pH versus time in presence of bacteria) by addition of 1N H_2SO_4 when were necessary. Cell number, pH, amounts of copper and total iron in solution, ferrous and ferric ion concentrations were measured every day. Water was added to the reactors to compensate for evaporation losses.

Analysis

Quantity of free bacteria in the solution was determined by direct counting, using a Thoma chamber of 0.1 mm depth and 0.0025 mm^2 area with an optical microscope ($\times$1000). Copper and total iron concentration in solution were measured by atomic absorption spectrophotometer (model AAS 5EA). The ferric ion concentrations in the solution were determined by sulfosalicylic acid spectroscopy method (Varian Techtron UV-VIS spectrophotometer, model 635) [12] and the ferrous ion concentration was analyzed by a volumetric method by titration with potassium dichromate [13]. The pH of the supernatant at room temperature was also measured with a pH meter (Metrohm, model 691).

RESULTS AND DISCUSSION

The main mechanism of bacterial catalysis in the dissolution of sulfide minerals is based on the bacterial oxidation of ferrous ion, with oxygen as electron acceptor, according to the reaction:

$$2FeSO_4 + H_2SO_4 + 1/2\,O_2 \xrightarrow{\text{bacteria}} Fe_2(SO_4)_3 + H_2O$$

It is known that ferrous ion oxidation by *Acidithiobacillus ferrooxidans* rapidly decreases at pH greater than 2.5 and therefore control of pH is an important factor in the dissolution of sulfide minerals [14]. Fig. 2 indicates that the pH decreased to 2.2 initially due to the consumption of acid during the protonic attack of the chalcopyrite according to the following reaction:

$$CuFeS_2 + O_2 + 4H^+ \rightarrow Cu^{2+} + Fe^{2+} + 2S^0 + 2H_2O$$

Later, acidity increased and pH reached to 1.3, because of the oxidation of elemental sulfur by sulfur-oxidizing microorganisms.

Fig. 3 illustrates the percentage copper recovery at different pulp densities as a function of time. As it can be observed, the results show that at low pulp densities (1% and 5% w/v) almost all of the copper was extracted (about 94% and 90% respectively) from chalcopyrite (in 5 and 8 days respectively).

In these range of pulp densities, the oxygen transfer coefficient in the solution was not a limiting factor. At the highest pulp density (20% w/v) copper extraction reached 65% after 15 days. The main reason for inefficient bioleaching at high pulp densities is that the rate of oxygen demand outstrips the oxygen supply limited by gas-liquid mass transfer rates. For this reason 10% (w/v) of pulp density was selected as the best level. Control is the medium containing chalcopyrite without micro-organism and it has these conditions, namely pH=1.5;

initial Fe^{2+} concentration = 7 g/L; T=33ºC and pulp density =10% (w/v).

Fig. 4 indicates that 33ºC is the best temperature for the bioleaching of chalcopyrite. Most growth of *Acidithiobacillus ferrooxidans* take place in 33ºC and it is the optimum temperature for this microorganism. In 20ºC and 40ºC the rate of bioleaching according to this figure decreased because in these temperatures the activity of bacteria decreased. At higher temperature than 33ºC the solubility of Cu in solution increases but the growth of microorganism would be slowed.

Fig. 5 shows comparison of copper extraction in presence and absence of bacteria. At same conditions, namely pH=1.5; initial Fe^{2+} concentration =7g/L; T=33ºC and pulp density =10% (w/v) in case of absence of bacteria, value of Cu extraction reached only to 10%, while Cu extraction in bioleaching was achieved to 70%.

Variation of Fe^{2+} and Fe^{3+} concentrations vs. time at pulp density of 10% (w/v) and T=33ºC has been shown in Fig. 6. The changing of the values of Fe^{2+} and Fe^{3+} concentrations in solution indicates a microbial activity. As it can be seen in this figure while initial Fe^{2+} concentration decreases, Fe^{3+} concentration increases with respect to time.

The effect of the initial ferrous ion concentration on the bioleaching kinetics was investigated. Seven different media containing different quantities of Fe^{2+} as ferrous sulfate (0, 2, 4, 5.5, 7, 9 and 11.5 g/L) were used.

According to the Fig. 7, at the same conditions, copper extraction reached to 14%, 35%, and 70% for media containing 7 g/L of initial Fe^{2+} after 2, 6 and 10 days respectively.

Using initial Fe^{2+} concentration higher than 7 g/L, efficiencies were achieved to a little more than previous efficiencies. These results indicate that increase in the ferrous ion leads to enhanced activity and growth by the bacteria, but this activity is not very considerable, so the initial Fe^{2+} concentration=7 g/L has been chosen as the optimum initial ferrous ion concentration.

CONCLUSIONS

The bioleaching ability of indigenous microorganism which was isolated from the soil of Sarcheshmeh Copper Mine near the city of Kerman in the south of Iran has been studied in an air-lift bioreactor. The experimental results show that among three variables (temperature,

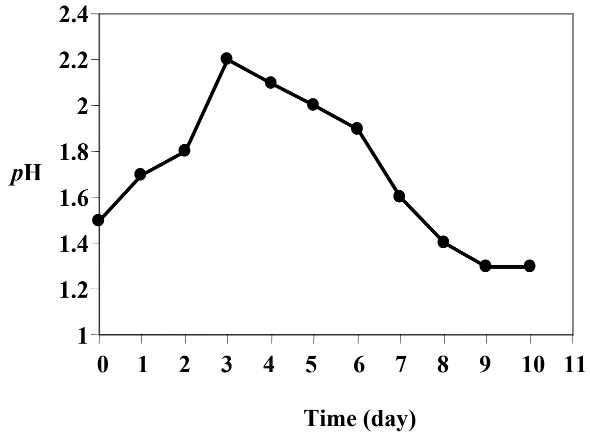

Fig. 2: Variation of pH vs. Time in air-lift bioreactor; pulp density = 10% (w/v),T=33 °C; initial Fe^{2+} concentration = 7 g/L.

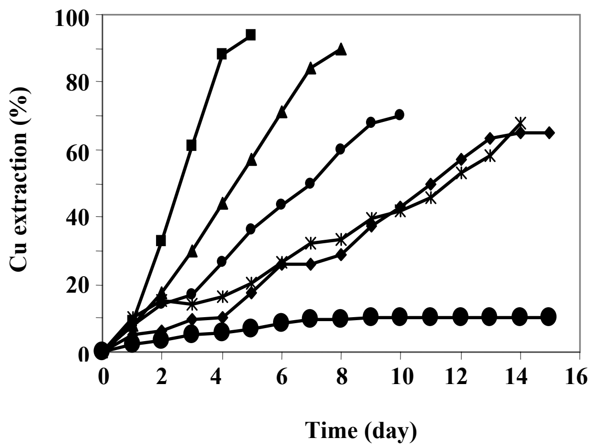

Fig. 3: Effect of pulp density on Cu extraction; pH=1.5; initial Fe^{2+} concentration = 7 g/L; T=33 °C.

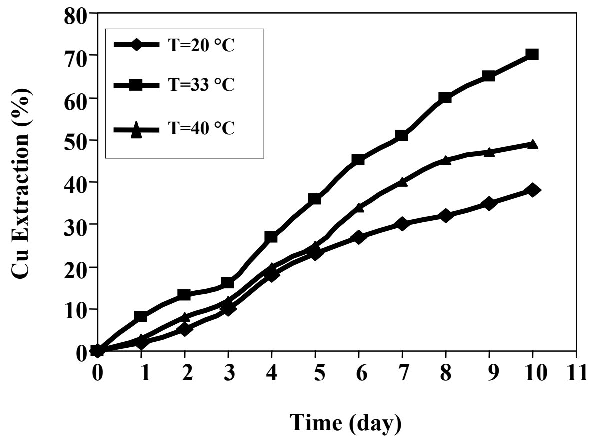

Fig. 4: Cu extraction at different temperatures in air-lift bioreactor; pH=1.5; initial Fe^{2+} concentration=7 g/L; pulp density = 10% (w/v).

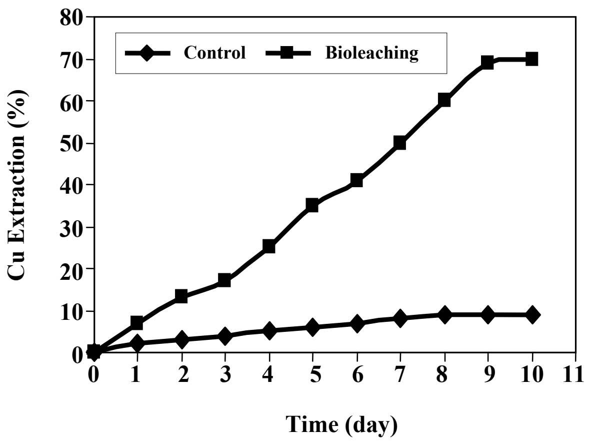

Fig. 5: Cu extraction in presence and absence of bacteria in air-lift bioreactor; pH=1.5; initial Fe^{2+} concentration=7 g/L; pulp density = 10% (w/v); T=33 °C.

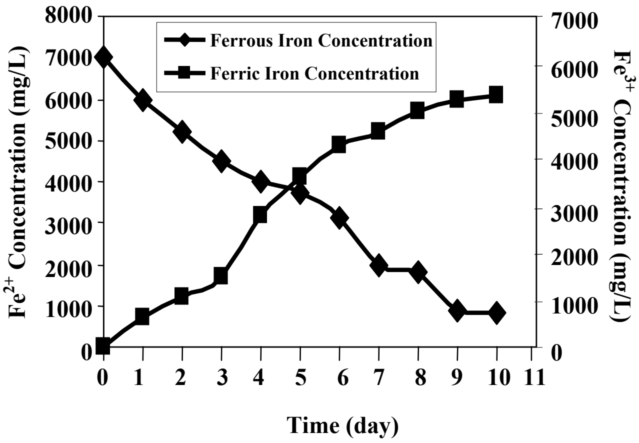

Fig. 6: Variation of ferrous and ferric ion concentration vs. Time in air-lift bioreactor; pH=1.5; pulp density = 10% (w/v); T=33 °C.

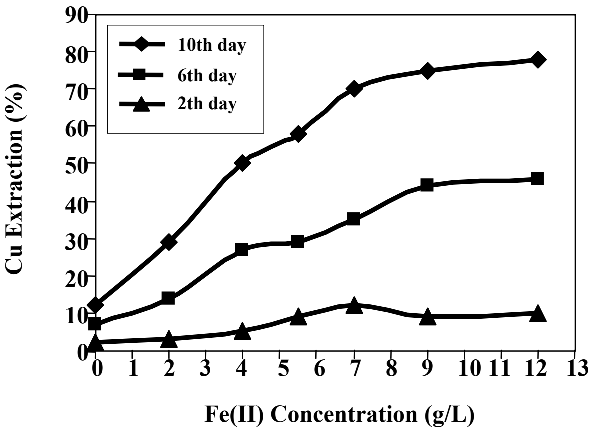

Fig. 7: Effect of initial Fe^{2+} concentration on Cu extraction; pH=1.5; pulp density =10% (w/v); T=33 °C.

solid concentration and initial Fe^{2+} concentration), temperature and solid concentration are more significant compared to initial Fe^{2+} concentration. The results indicate that increasing the ferrous ion leads to enhance activity and growth by the bacteria, but this activity is not very considerable, so the initial Fe^{2+} concentration=7 g/L has been chosen as the optimum initial ferrous ion concentration.

The main reason for inefficient bioleaching at high pulp densities is that the rate of oxygen demand outstrips the oxygen supply limited by gas-liquid mass transfer rates; therefore 10% (w/v) of pulp density was selected as the best level. The optimum temperature has been determined 33°C and in this temperature the bacteria has the highest activity to copper recovery from chalcopyrite.

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