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PJBS

ISSN 1028-8880

Pakistan Journal of Biological Sciences

ANSI*net*

Asian Network for Scientific Information
308 Lasani Town, Sargodha Road, Faisalabad - Pakistan

Biorecovery of Copper from Chalcopyrite Ore Using *Thiobacillus ferrooxidans*

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Abstract: Studies on the solubilisation of copper from chalcopyrite by 'direct (contact)' and 'indirect leaching' using *Thiobacillus ferrooxidans* were carried out. *Thiobacillus ferrooxidans* produced up to 2380 ppm acidic Fe³⁺ solution of pH 1.5 in 480 h. The direct leaching method was slow for the solubilisation of copper from the ore and only 28.52% of copper leached in 70 days. While on the other hand 87.57% of copper was brought in to solution in 192 h by indirect leaching technique utilizing biologically oxidized acidic Fe³⁺ solution at 30°C. The increase in temperature of the indirect leaching process, shorten the metal recovery time. At 60°C maximum leaching (88.30%) was obtained in 8 hrs only.

Key words: Chalcopyrite, copper, leaching, direct, indirect, *Thiobacillus ferrooxidans*, Fe³⁺, temperature

Introduction

Microbial leaching processes are getting importance in the recovery of metals from sulphide ores, because of low energy requirement, minimum pollution and maximum yield. Copper, zinc, gold etc., can be recovered from their sulphide ores by microbial leaching. Three groups of microorganisms are used for leaching process: autotrophic bacteria (Troma and Bosecker, 1982), heterotrophic bacteria (Keil and Schwartz, 1980; Munier-Lamy and Berthelin, 1987) and fungi (Keil and Schwartz, 1980; Siegel, 1973). Chemoautotrophic iron and sulphur oxidizing bacteria actively participate in leaching of sulphide minerals. Among iron oxidizing microorganisms belonging to the genus *Thiobacillus*, cultures of *T. ferrooxidans* and *T. thiooxidans* are of great importance in biometallurgy and related processes. A lot of information has been reported on the vital role of *T. ferrooxidans* and *T. thiooxidans* in leaching of copper and other metals from low grade ores (Brierley, 1978, Rahman and Gul, 1999; Rahman and Gul, 2001; Kelly *et al.*, 1977), wastes (Lundergren and Malouf, 1983), desulfurisation of petroleum (Devis, 1967) and coal (Dugan and Apel, 1978, Chandra *et al.*, 1980; Kwang and Yen, 1990; Mannivannan *et al.*, 1994). *T. ferrooxidans* is the most widely used organism in microbial leaching. Metals can be recovered from their sulphide ores by 'direct (contact) leaching' and 'indirect leaching' by acidic ferric (Fe³⁺) iron that is generated by bacterial oxidation from ferrous (Fe²⁺) iron. The studies presented here deals with the comparison of direct and indirect leaching of copper from the chalcopyrite ore of saindak by using *Thiobacillus ferrooxidans*. The effects of temperature on copper leaching in 2-stage process were also carried out.

Materials and Methods

Substrate: The chalcopyrite ore supplied by Saindak Metals Limited was used for these studies. This ore contained chalcopyrite (CuFeS₂), copper oxide (CuO), Pyrite (Fe₂S₃) and silica (SiO₂) as major constituents. The ore used in these studies contained 0.45% copper including 0.038% copper as copper oxide. The ore was grinded and # -100, +150 was used through out the studies.

Organism: The strain *Thiobacillus ferrooxidans* of Rahman and Gul (1999) was used through out the studies. The strain was maintained in a medium containing (g l⁻¹) ammonium sulphate 3.0, potassium chloride 0.1, dipotassium hydrogen phosphate 0.5, magnesium sulphate 0.5 calcium nitrate 0.01 and ferrous sulphate 4.0. The pH of the medium was adjusted at 2.5 with 10 N H₂SO₄. The strain was sub cultured after every 20 days.

Inoculum preparation: The inoculum was prepared by growing *Thiobacillus ferrooxidans* in conical flasks having sterilized 9K medium for 15 days at 35±1°C. The bacterial cells were harvested by centrifugation and resuspended in 0.005 M H₂SO₄. The final concentration of inoculum was ~5X 10⁵ bacteria ml⁻¹.

Preparation of acidic ferric sulphate solution: The acidic ferric sulphate solution was prepared by using mineral salt solution (g l⁻¹) ammonium sulphate 3.0, Potassium chloride 0.1, Magnesium sulphate 0.5 and Fe²⁺ iron 3000 pm as ferrous sulphate. The pH of the solution was adjusted at 2.5 by 10 N H₂SO₄. 2.5 L mineral salt solution was inoculated by 10% v/v inoculum and incubated at 35±1°C. The aeration of the medium was started after 24 h

and continued up to 432 h of incubation. After than the medium was kept standing for further 48 h. The medium containing acidic ferric sulphate was centrifuged and supernatant used as copper leachant.

Microbial leaching technique: Direct leaching of copper was carried out in 250 ml conical flasks containing 10 g ore and 100 mL medium containing (g l^{-1}) ammonium sulphate 3.0, potassium chloride 0.1, dipotassium hydrogen phosphate 0.5, magnesium sulphate 0.5 and calcium nitrate 0.01. The pH of the medium was adjusted at 2.5 with 10 N sulphuric acid. The medium and ore were sterilized at 121°C for 15 minutes and inoculated. The flasks were incubated at 35°C on rotatory shaker at an operating speed of 150 rpm.

The indirect leaching was carried out in 250 mL conical flasks containing 40 g ore and 100 mL biologically oxidized acidic ferric sulphate solution in presence of sodium azide 10 mM, to inhibit microbial growth. The flasks were incubated at 30°C on rotatory shaker, adjusted at a speed of 150 rpm. After regular intervals samples were withdrawn and analyzed for copper and iron contents. Studies on the effects of temperature on leaching of copper were carried out at 30, 40, 50 and 60°C .

Analytical methods: The analyses of the leached solution was done after filtration through $2\text{ }\mu\text{m}$ -pore size membrane to remove bacterial mass and other insoluble materials. The copper contents in the leached solution and ore residue were determined by atomic absorption spectrophotometer AAS 2380, Perkin Elmer, USA, using standard conditions.

The Fe^{2+} , Fe^{3+} and total iron contents were analyzed by o-phenanthroline method (Herrera *et al.*, 1989).

Results and Discussion

Direct leaching of copper: Fig. 1 show the results of leaching of copper from chalcopyrite ore in presence of *Thiobacillus ferrooxidans*. The dissolution of iron, its oxidation and leaching of copper were started after 24 h of incubation. The initial dissolution of copper was a chemical reaction in which copper oxide present in the ore was solubilized with the action of sulfuric acid in the medium. The dissolution of iron in Fe^{2+} form was quite high than the other two processes. The higher leached concentration of Fe^{2+} in the medium may be due to the presence of iron in forms other than pyrite (Fe_2S_3) i.e., pyrrhotite Fe_{1-x}S , that dissolved with the action of sulfuric acid. The concentration of ferrous iron in the medium increased up to 40 days and then decreased gradually. The decrease in Fe^{2+} contents could be attributed to increased rate of oxidation by the

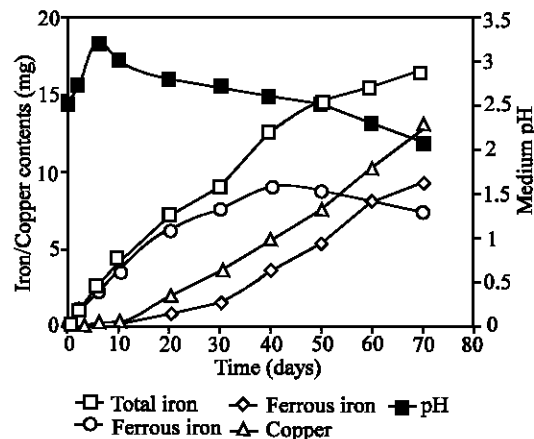


Fig. 1: Direct 'intact' leaching of copper from chalcopyrite by *Thiobacillus ferrooxidans*

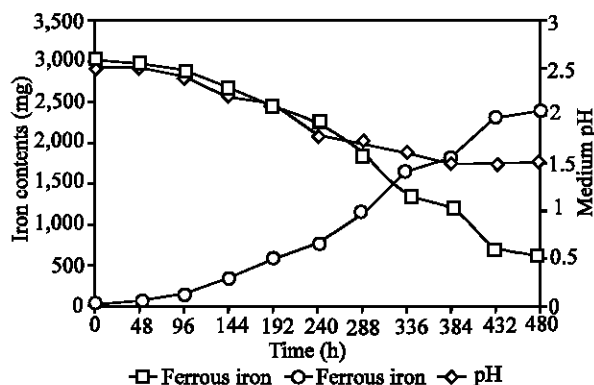


Fig. 2: Course of Fe^{2+} Oxidation by *Thiobacillus ferrooxidans*

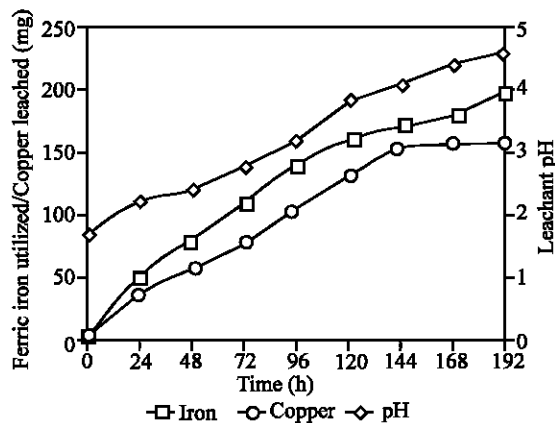


Fig. 3: Leaching of copper by biologically oxidized ferrous sulfate solution from chalcopyrite

establishment of *Thiobacillus ferrooxidans* in the medium. The rate of oxidation Fe^{2+} almost doubled after 40 days of incubation i.e., from 0.089 mg to 0.187 mg per

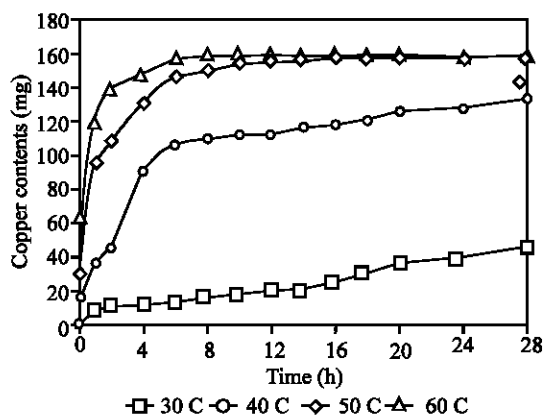


Fig. 4: Effects of temperature on copper leached by biologically oxidized ferrous sulfate solution from chalcopyrite

day. Niemela *et al.* (1994) have also reported the initial solubilization of Fe^{2+} iron from Black Schist ore and subsequent oxidation to Fe^{3+} iron. They described the dissolution of iron as chemical reaction with some enhancement by bacteria whereas the oxidation of Fe^{2+} to Fe^{3+} iron was bacterial mediated with negligible concentration from chemical reaction.

The pattern of leaching of copper and oxidation of Fe^{2+} iron were more or less the same except the rate of copper leaching was little high. The results show two phases of copper leaching and iron oxidation. The 1st phase lasted up to 30 days and 2nd from 31st to 70th day. The 1st phase was slow in respect of copper leaching and Fe^{2+} iron oxidation, which show the establishment of *Thiobacillus ferrooxidans* in the medium. In the next i.e., 2nd phase, the rate of both the processes i.e., leaching of copper and Fe^{2+} oxidation, increased and reached to as high as 2.33 and 0.192 mg per day in last 40 days, respectively. The rates of Fe^{2+} oxidation and leaching of copper were statistically the same during the 50th to 60th day of the experiment i.e., Fe^{2+} oxidation 0.263 mg and copper leaching 0.270 mg per day. This phase of bacterial Fe^{2+} oxidation show that *Thiobacillus ferrooxidans* had established itself and fully functional. At the end of experiment the medium contained 12.835 mg copper and 16.539 mg iron (9.211 mg Fe^{3+} and 7.328 mg Fe^{2+}). Our results are much better than reported by Choi and Hopkin (1987) who achieved 30% dissolution of copper contained in the ore in over 21 months by direct leaching whereas in present studies 28.52% leaching of copper was obtained in only 70 days. An increase in the pH of the medium to 3.2 was also observed in the initial phases of the experiment, this may be because of the chemical reaction of H_2SO_4 on the ore which solubilised the copper from

copper oxide and iron from the ore. However, the pH of the medium later on decreased to 2.1 because of the production of H_2SO_4 by *Thiobacillus ferrooxidans*.

Oxidation of Fe^{2+} iron: Data regarding oxidation of iron by *T. ferrooxidans* (Fig. 2) show three distinct phases of iron oxidation. The first lag phase of bacterial growth lasts up to 96 h where the rate of oxidation was quite slow, the 2nd log phase between 96 to 432 h where the rate of oxidation was as high as 6.4 mg h^{-1} . The oxidation of Fe^{2+} was statistically non significant in 3rd and last stationary phase from 432 to 480 h of incubation. The slow rate of oxidation in 3rd phase may be due to the toxicity of high concentration of Fe^{3+} ions to *Thiobacillus*, which retard the metabolism. Pakinkar and Agate (1987) have also reported the intolerance of metal ion in *Thiobacillus sp.* The changes in pH were more or less inversely proportional to the growth of bacteria and oxidation of Fe^{2+} iron. After 480 h the oxidized Fe^{3+} contents of the medium reached to 2379 mg with pH 1.5.

Indirect leaching of copper: Acidic ferric sulfate is an important oxidizing agent and lixiviant for sulphide minerals of copper. The oxidized acidic iron solution plays an important role in dump and situ leaching. 40 gm ore was subjected to leaching with 100 mL biologically oxidized acidic ferric sulfate solution. The results regarding leaching of copper, utilization of Fe^{3+} and changes in pH of the leachant are depicted in fig. 3. The rate of indirect copper leaching was quite high as compared to direct leaching. In this process Fe^{3+} iron attacked the copper compounds of the ore. Fe^{3+} iron oxidized monovalent copper ion (Cu^+) to create a divalent copper ion (Cu^{2+}), which then combined with SO_4^{2-} ion with the contribution of sulfuric acid to form copper sulfate. By this process maximum of 87.57% of copper present in the ore was recovered in 192 h. The utilization of Fe^{3+} iron was more or less directly proportional to the leached copper. The pH of the ferric sulfate solution was changed from 1.5 to 4.6 during the leaching of copper from the ore.

Effects of temperature on indirect leaching of copper: Temperature, play an important role in chemical reactions. The rate of copper leaching was increased with the increase in temperature. At 30°C maximum leaching of copper was achieved in 192 h (Fig. 3), while at 40 and 50°C in 48 and 20 h, respectively (Fig. 4). The fastest rate of leaching was observed at 60°C, where the maximum leaching was observed after 8 h. After than, although there was an increase in copper contents of leaching solution but it was not significant. The average rate of

copper dissolution in initial 2 h was 5.4 mgh^{-1} at 30°C , 22.62 mgh^{-1} at 40°C , 53.65 mgh^{-1} at 50°C and 69.11 mgh^{-1} at 60°C . It was also observed that the leaching process slow down after 86% leaching of copper. This probably may be due to the accumulation of Fe^{2+} iron around the chalcopyrite particles and leaving small sites of attack for the attack of Fe^{3+} iron.

From the results of the studies presented here, it can be safely concluded:

- I) That indirect leaching method is efficient than direct (contact) leaching.
- ii) That indirect leaching permits the advantage of separate enhancement of each the two processes involved in the bio-recovery of copper.
- iii) That in indirect leaching chemical attack of Fe^{+3} to release copper from the ore can be performed at higher temperatures for enhanced recovery rate, in order to reduce the processing time.

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