IMPROVING CHALCOPYRITE BIODISSOLUTION FROM LOW GRADE INDIAN COPPER ORE BY MICROBIAL CONSORTIA

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Abstract

Using a consortium of bacteria such as Acidithiobacillus ferrooxidans (A.ferrooxidans) and Acidithiobacillus thiooxidans (A.thiooxidans), isolated in Silverman and Lundgren Media from the source mine water, the biodissolution of copper from untapped lean ores of Malanjhkhand Copper Project (MCP), India was investigated. Inocula of both iron-oxidizing and sulfur-oxidizing bacteria in the ratio of 4:1 (A.ferrooxidans to A.thiooxidans) were used as such (without adaptation on the ore) for the bio-leaching of copper from the low grade chalcopyrite ore (0.27% Cu) of granite origin. In general, the efficiency of the microbiological process is often low because this mineral is one of the most refractory ores of copper for bacterial attack. A maximum copper recovery of 69.4% was obtained in 30 days at 1.5 pH, 35°C temperature, 10% (w/v) pulp density with particles of <50 μm size. High copper recovery at 1.5 pH may be correlated with an increase in redox potential from 340-642 mV and increase in bacterial population from $3x10^7$ to $6.07x10^8$ cells/mL in 30 days. This research has shown the possibility to enhance the leachability of chalcopyrite to achieve high copper extraction in the presence of a consortium of mesophiles. Importance of using A.thiooxidans as a part of consortium in facilitating copper solubilization is also highlighted in the paper.

Keywords: - low grade ore, copper, bioleaching, microbial consortia

Introduction

Fairly large stock of lean grade and complex ores remains untapped for extraction of metals using conventional techniques because of high energy and capital inputs required. Further, fines generated during mining, milling and other metallurgical operations are to be processed not only to recover the values but also to comply with the stringent environmental issues[1]. In order to recover values from these low-grade ores and fines, an appropriate processing technology is required. Production of base metals from lean and off-grade ores using bioleaching has been widely used all over the world[2]. Bioleaching is an emerging technology with significant potential to add value to the mining industries to deliver attractive environmental and economic benefits. Chalcopyrite ($CuFeS_2$), which constitutes the largest portion of the world's known copper reserves is known to be recalcitrant to hydrometallurgical processes. The main hindrance to the commercial application of biohydrometallurgical processing of chalcopyrite is its slow rate of dissolution[3]. Researchers have been striving for decades to accelerate the speed of biological leaching reactions for chalcopyrite. The successful processing of chalcopyrite has been achieved in agitated tank bioreactor using certain thermophilic archaea on relatively pure chalcopyrite concentrates.

Commercial application of bacterial leaching began in the late 1950s at the Kennecott Copper Company's Bingham Canyon Mine[4]. Since then, most use of these and other microorganisms has expanded worldwide applications particularly in copper dump and heap-leaching applications[5-7]. Various researchers have exploited the complex sulfide ore/bulk concentrates using single/mixed culture(s) of mesophilic micro-organisms (*Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans, Leptospirillum ferrooxidans*, etc) in recent past[8-10]. Implications of acidophilic thermophile-*Acidianus brierleyi, Sulfolobus* etc. has off late gained importance for the recovery of copper from chalcopyrite mineral[11-12]. In India, attempts were earlier made to treat MCP ores, particularly the overburden material which were essentially a mixed copper oxide-sulphide (chalcopyrite) and lean grade ore[13-15]. The bio-leaching of lean grade MCP ore was also investigated to a limited extent with 75% recovery in 40 days in shake flasks from the quartzitic ore[16].

The bio-leaching process is often governed by the proper contact of ore with the leach liquor which determines the fluxes of reactants and products, such as bacteria, dissolved gases (O_2 and CO_2), solubilized metals, and sulfur species[17]. Ferric iron has a special role as oxidizing agent in the bacterial leaching of sulfide minerals. Soluble iron species contribute significantly to the high values of redox potential with active iron-oxidizing bacteria, resulting in high Fe^{3+}/Fe^{2+} ratio. Precipitation of ferric iron in the leaching system may suppress the metal solubilizaton by preventing the contact between the leaching agent and the mineral[18]. The bacterial leaching process involving mesophiles requires acidic conditions, the acidity being produced by the oxidation of pyrite and hydrolysis of ferric iron. While the exact mechanism of ferric leaching of chalcopyrite (in both the presence and the absence of microorganisms) is still under much debate, a clear explanation why certain microorganisms appear more successful than others has not yet emerged. In general, bioleaching of copper is considered to follow both direct and indirect routes.

As such, Malanjkhand Copper Project (MCP), an only open pit copper mine in the country (16.5 million tonnes of ~1% Cu) will not last long. Therefore, extracting copper from the low grade ores (2.5 million tonnes) found adjacent to the rich grades requires attention[19]. The aim of this investigation was to examine the behaviour of copper bioleaching from this low grade chalcopyrite ore using a mixed culture of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*.

Experimental Procedure

1. Copper Ore: - Lean grade copper ore (containing 0.27%Cu) was collected in the form of lumps from Malanjkhand copper mine (located in Balaghat, Madhya Pradesh, India). The ore was crushed, ground and passed through 150µm sieve. The resultant sieve fractions were further used for bioleaching experiments. The low grade ore is a granitic rock with disseminated sulfides. As regards morphology, sporadic bright patches were seen on the surface of the feldspar matrix of the bulk ore and the preliminary mineralogical study indicated the presence of mineral chalcopyrite in the cracks and fissures in quartz vein. The bulk ore is slightly pink in appearance; this is due to the high percentage of granite in the ore body. Silica is very high (38%) in the ore. Phase identified by XRD showed major phases as chalcopyrite ($CuFeS_2$), pyrite (FeS_2) and silica (SiO_2) whereas bornite was the minor phase.

2. Isolation of Micro-organism and Bio-leaching experiments: - The source of bacteria was the mine water, which contained *Acidithiobacillus ferrooxidans (At.f)* and *Acidithiobacillus*

thiooxidans (At.t). The bacterium was isolated in 9K and 9K' (*Silverman and Lundgren*) media respectively which provided sufficient nutrients for the growth. *Acidithiobacillus ferrooxidans* required ferrous sulfate as an energy source for its growth, whereas sulfur was the energy source for *At.t.* The fully grown strain of *Acidithiobacillus ferrooxidans* contained 1.5×10^8 cells/mL and *Acidithiobacillus thiooxidans contained* 3.75×10^8 cells/mL after three times sub-culturing. The enriched cultures thus derived from the source mine water were used as such for inoculation in subsequent bioleaching experiments.

Bioleaching experiments were performed in 500 mL Erlenmeyer conical flasks, fitted in an orbital motion incubator shaker[16]. Leaching solutions were inoculated with 10% (v/v) of active and non-adapted *At.f* and *At.t* in the ratio 4:1 in all cases, except in sterile/control experimental sets, where mercuric chloride (0.2 g/L) was used as bactericide. General conditions like 35°C temperature, pH 2 and 10% (w/v) pulp density with shaking at 120 rpm were used unless otherwise stated. Sterilized distilled water was used for the experiments. The pH of the solution was maintained by using 10N sulfuric acid and 2N NaOH. Along with the pH adjustment, redox potential (E) was measured against SCE and reported as such in the text which was mainly governed by the concentration of ferrous and ferric ions in the solution. During bioleaching experiments, cell counts were also obtained by Petroff Hauser Counter. Ferrous ion was estimated by titrating the sample against potassium dichromate with barium diphenylamine sulfonate as indicator. Samples were mostly taken at the interval of the five days unless stated otherwise to analyze metals and to compute the metal recovery by analyzing the solution by AAS. Solution losses due to titration and cell counting were made up by using distilled water. Upon termination of the leaching experiments, the solid residues were dried and samples were taken for chemical analysis and XRD phase identification. The solid residues were dissolved in $HCl\text{-}HNO_3$ mixture and analyzed by AAS.

Results and Discussion

For biodissolution of copper, a mesophilic consortium of *At.f* and *At.t* was inoculated in a ratio of 4:1 with the ore and the process parameters, viz., pH, pulp density, particle size and temperature were optimised. The details are presented in this section.

Effect of pH

Bioleaching of copper was investigated at different pH in the range 1.5-2.5 at a pulp density (PD) of 10% (w/v) and a temperature of 35°C while shaking at 120 rpm. The pH is one of the important factors affecting the bacterial growth as well as its leachability. *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* are reported to thrive at an environmental pH in the range 1.5 to 2.5. Data given in Table-1 show that biorecovery of copper was maximum (69.4%) at pH 1.5 in 30 days, whereas recoveries were 63.8% and 57.6% at pH 2.0 and pH 2.5 respectively. Increased copper recovery at pH 1.5 may be correlated with the increase in redox potential (Table-2) from 340-642 mV and increase in bacterial population from $3\text{x}10^7$ to $6.07\text{x}10^8$ cells/mL The recoveries of copper at different pH in chemical leaching were 24.1%, 21.9% and 17.5% at pH 1.5, 2.0 and 2.5 respectively (Table-1).

Effect of Pulp Density (PD)

Biodissolution of copper was investigated at varying pulp densities in the range 5-20%(w/v) at pH 2.0 and 35°C with 150-75 µm size particles using 10% (v/v) enriched culture of *At.f:At.t* as consortium in the ratio 4:1. The data in Table-3 showed that biorecovery of copper was relatively high (i.e., 37.6 %) at 5%(w/v) PD in 30 days as compared to 10.6 % metal dissolution in chemical leaching. In general, copper dissolution was not very different at varying pulp densities for 25 days of leaching, although the recoveries were high for low pulp density in 30 days. This may be attributed to the deficiency of oxygen and CO_2 availability which was essential for *At.f* and *At.t* growth and increased concentration of metal ions causing toxicity to bacterial growth at higher pulp densities, on prolonging the leaching.

At 5%(w/v) PD, redox potential (E) rose to 589mV for bioleaching in 30 days whereas it was found to be 402mV in chemical leaching at this pulp density. At higher pulp densities viz. 10, 15 and 20% (w/v), there was marginal change in the E values from 570-595mV in 30 days of bio-leaching, with corresponding copper recoveries of 25.9, 18.4 and 19.2%.

Table-1: - Effect of pH on copper recovery [35°C, 10% (w/v) PD, <50 µm particles]

Days	Copper Recovery (%)					
	Control Leaching			Bio-leaching		
	1.5pH	2.0pH	2.5pH	1.5pH	2.0pH	2.5pH
5	**7.2**	**6.6**	**6.28**	**32.64**	**26.14**	**19.84**
10	**15.8**	**14.2**	**13.7**	**49.52**	**37.6**	**28.42**
20	**21**	**19**	**15.7**	**55.67**	**46.6**	**33.47**
30	**24.11**	**21.97**	**17.57**	**69.46**	**63.81**	**57.6**

Table-2: - Effect of redox potential on copper recovery [35°C, 10% (w/v) PD, <50 µm particles]

Redox Potential (mV)					
Control Leaching			Bioleaching		
1.5pH	2.0pH	2.5pH	1.5pH	2.0pH	2.5pH
314	**253**	**246**	**345**	**469**	**318**
373	**349**	**298**	**423**	**582**	**512**
390	**375**	**347**	**567**	**632**	**595**
490	**398**	**372**	**642**	**640**	**560**

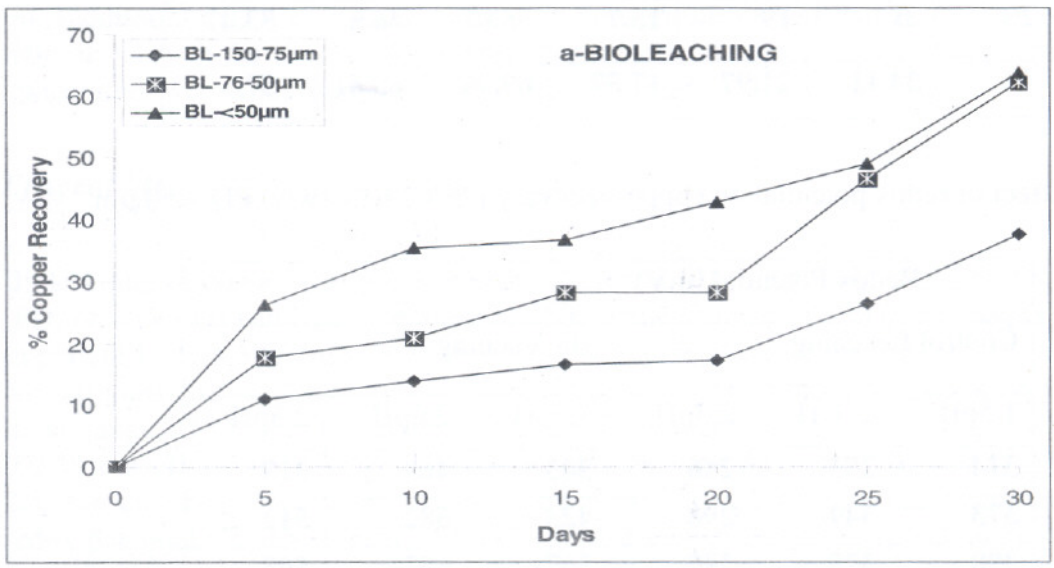
Table-3:

Effect of pulp densities on copper recovery [Particle size: 150-75µm, 35°C, pH 2.0]

Days	Copper Recovery (%)							
	Control Leaching				Bio-leaching			
	5%PD	10%PD	15%PD	20%PD	5%PD	10%PD	15%PD	20%PD
5	**6.44**	**5.91**	**5.68**	**5.63**	**7.625**	**7.61**	**7.59**	**7.33**
10	**6.78**	**6.58**	**5.96**	**7.625**	**8.53**	**8.86**	**8.98**	**9.32**
20	**8.65**	**9.45**	**8.3**	**7.46**	**17.78**	**18.72**	**18.01**	**18.94**
30	**10.75**	**11.83**	**9.44**	**8.11**	**37.6**	**26.05**	**24.7**	**27.62**

Effect of particle size

Results plotted in Fig.1 indicate that the particle size had significant effect on biorecovery of copper when the particle size varied from 150-75µm to <50 µm resulting in increased recovery from 37.6% to 63.8% Cu at 2.0 pH in 30 days. This could be mainly due to better permeation of the leachant to oxidize the copper sulfide present in the ore and increased surface area. Finer particles were increasingly exposed to lixiviant that dissolved copper from the chalcopyrite phase. It was also clear that with coarser particles of 150-75µm size, copper biorecovery (Fig.1-a) was 37.6% with corresponding control/chemical leaching (Fig.1-b) of 10.6% Cu in 30 days.



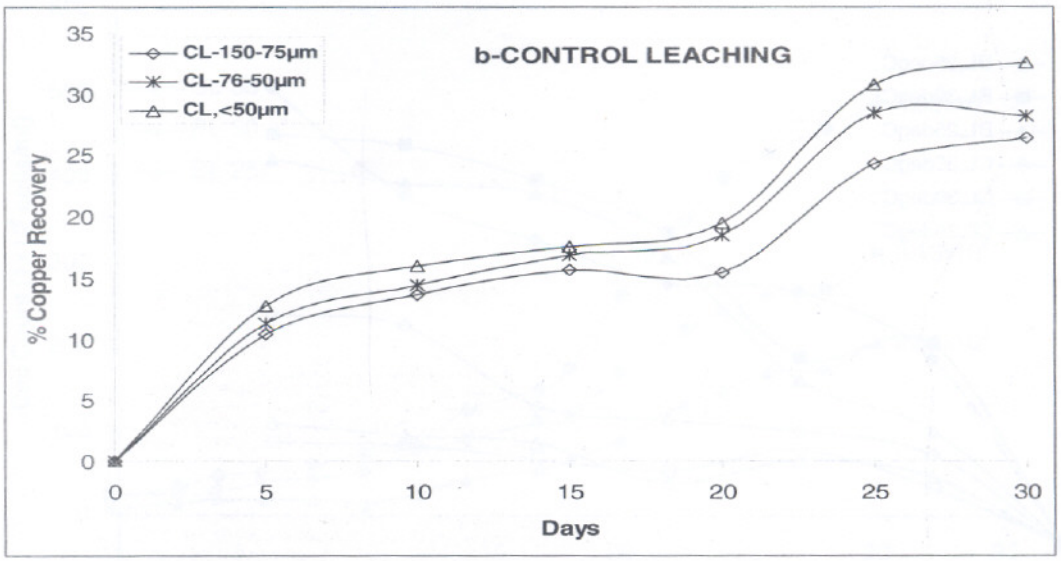


Fig.1:- Effect of particle size on copper recovery [10% (w/v) PD, 35°C, pH 2.0, Particle size: 150-75µm, 75-50µm, <50µm]

Effect of Temperature

As the bacterial strains in the consortium are mesophilic in nature, therefore temperature was varied from 20-35°C in this work. Effect of temperature at 10% (w/v) PD using10% (v/v) enriched culture of *At.f:At.t* mixed in the ratio 4:1 at pH 2 with <50µm ore particles were studied. The maximum copper biorecovery was found to be 63.8% at 35°C whereas it was 57.3% at 30°C and 54.1% at 25°C in 30 days as shown in Fig.2. The corresponding chemical leaching was found to be and 21.9%, 14.66% and 17.35% (Fig.2). The variation in Fe (II) concentrations and E_h (mV) values in 30 days at 35°C are reported in Table-3. It may be seen that Fe (II) was stable for longer period at lower temperatures viz. 25 & 30°C in bioleaching experiments with low redox potentials of 570 and 635mV respectively. The higher redox potential (640 mV) was associated with faster oxidation of Fe (II) to ferric state resulting in high metal dissolution in bioleaching at 35°C. The cell count (Fig.3) was found higher (4.88×10^8 cells/mL) at 35°C as compared to that of 30°C which may be correlated with high recovery of copper at 35°C.

The higher rate of copper dissolution at 35°C may be correlated with the Fe(III) concentration in solution. The lower recovery in 5 days was accompanied by high concentration (0.3351 g/L) of Fe(II) in the solution (Table-4) which showed decreasing trend as the leaching prolonged with corresponding increase in Fe(III) concentration (0.3022 g/L) in 30 days. The conversion of iron(II) to iron(III) may be attributed to bacterial oxidation. The Fe(III) so formed might be involved in oxidation of chalcopyrite as reaction-1.

$$CuFeS_2 + 2O_2 + Fe_2(SO_4)_3 \longrightarrow CuSO_4 + 3\,FeSO_4 + S^o \quad \ldots\ldots\ldots\ldots (1)$$

These observations confirm the involvement of indirect bioleaching for chalcopyrite, although an initial direct leaching mechanism is also operational as reported elsewhere[13,18].

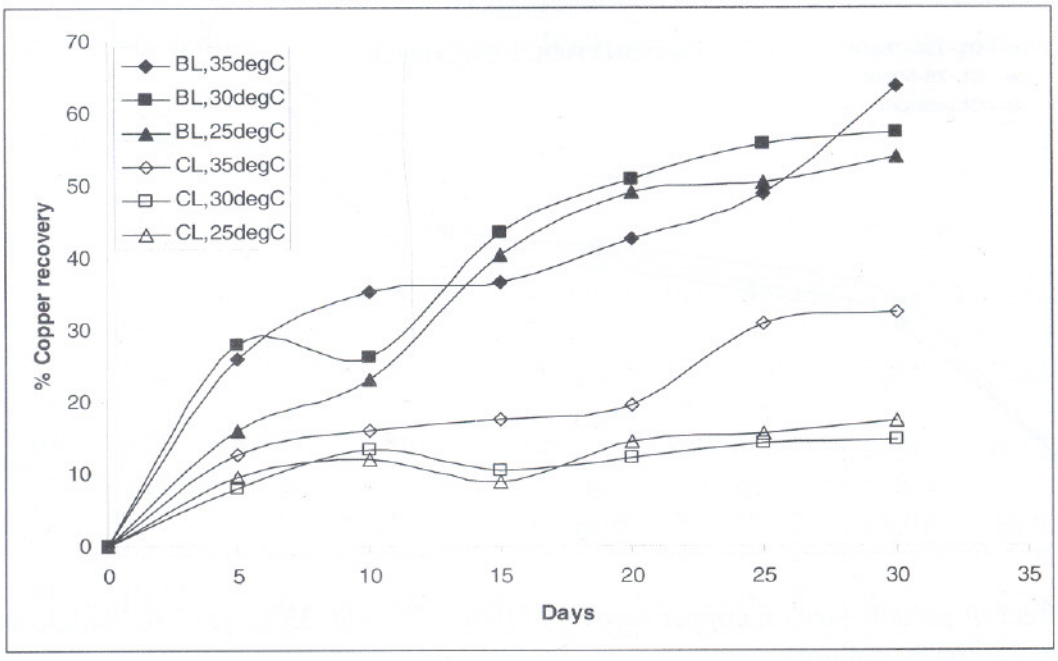


Fig.2:- Effect of temperature on copper recovery [10% (w/v) PD, pH 2.0, particle size: <50µm]

Table-4:- Change in Fe(II) and Fe(III) concentration with redox potential during copper bioleaching at various temperatures [10% (w/v) PD, pH 2.0, particle size: <50µm]

Temp (°C)	Days	Fe(II) in g/L	Fe(III) in g/L	Redox Potential (mV)
25	**5**	**0.3351**	**0.0661**	**365**
	10	**0.3351**	**0.0661**	**458**
	15	**0.2234**	**0.1984**	**514**
	20	**0.1117**	**0.2041**	**529**
	30	***Traces***	**0.2355**	**570**
30	**5**	**0.4468**	**0.0255**	**380**
	10	**0.3351**	**0.0661**	**548**
	15	**0.2234**	**0.1989**	**623**
	20	**0.05585**	**0.2176**	**632**
	30	***Traces***	**0.2486**	**638**
35	**5**	**0.3351**	**0.0661**	**469**
	10	**0.2234**	**0.1989**	**582**
	15	**0.1117**	**0.2041**	**628**
	20	**0.025**	**0.2977**	**632**
	30	***Traces***	**0.3022**	**640**

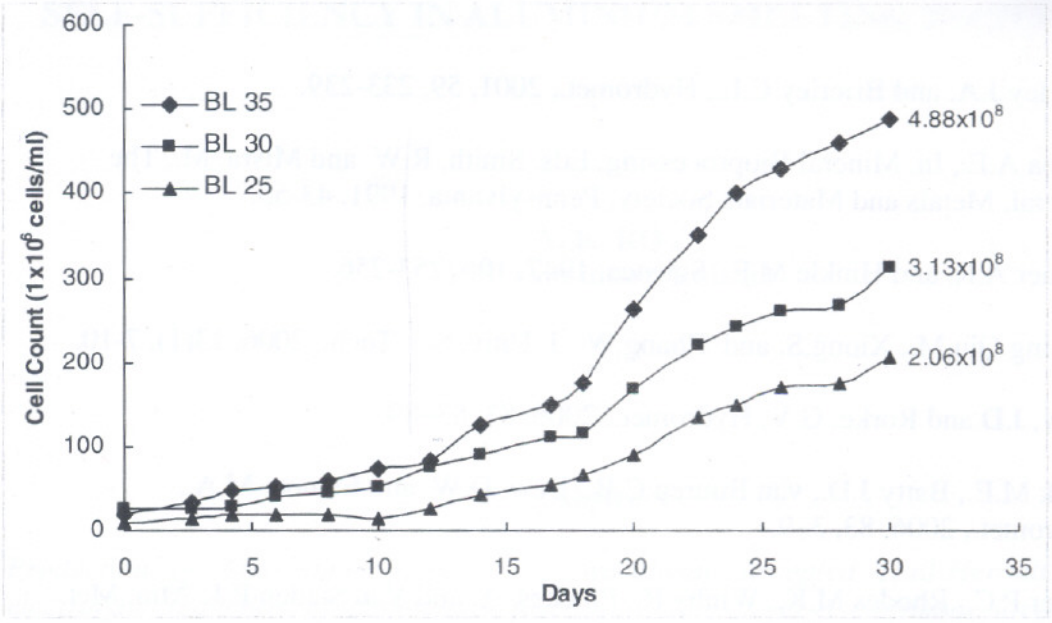


Fig.3:- Change in bacterial cell count/mL at various temperatures on <50µm particles [Conditions: - 10% (w/v) PD, pH 2.0, particle size: <50µm]

Conclusions

Following conclusions may be derived from the present investigation on the bioleaching of copper:

1. The mesophilic bacteria namely, *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* were isolated from the mine water of MCP in Silverman and Lundgren (9K) media. Use of enriched microbial culture in the ratio of 4:1(*Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*) improves the biodissolution of copper with rise in temperature from 25-35°C and increase in fineness of the ore particles.

2. Increase in pH from 1.5-2.5 and pulp density from 5-20% (w/v) has decreased the copper biorecovery.

3. Maximum copper recovery of 69.4% is obtained in 30 days with the unadapted/native mixed microbial culture at pH 1.5, 35°C temperature at 10% (w/v) pulp density with the ore particles of < 50 µm size.

4. Higher redox potential is indicative of improved oxidation conditions in presence of the microbial strains. The metal recovery is also correlated with the degree of oxidation of Fe (II) with time in presence and in absence of bacteria.

Acknowledgements

The authors are thankful to the Director, NML Jamshedpur for giving permission to publish the paper. Thanks are also due to the Hindustan Copper Limited for providing the sample and mine water for investigation.

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