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Investigation into the Biological Leaching of Copper from Chalcopyrite Concentrates Using Moderate Thermophilic Bacteria

M.R. Izadpanah[1,*], A. Sarrafi[2], M.H. Fazaelipoor[2] and M. Mosalmanzadeh[1]

Abstract. *Biological leaching is a process in which metals are dissolved from sulfide ores into aqueous solutions using bacteria as catalysts. Biological leaching is currently gaining acceptance as a viable alternative to pyrometallurgical smelting, due to decreasing ore grades and legislated limits on sulfur dioxide gas emission into the environment. In this research, the feasibility of copper bioleaching from chalcopyrite concentrates by three chemotropic strains was investigated. The strains, coded MS1, MS2 and TSB, were moderate thermophilic bacteria. MS1 and MS2 were indigenous to the site of the mine but TSB had been isolated elsewhere from an acidic hot spring. The bioleaching experiments were done on two types of chalcopyrite concentrate with different compositions. The strains had similar performances. The copper recovery increased from about 15% to about 30% when they were grown on a concentrate with a total initial copper content of 30.16%. When grown on a concentrate with an initial copper content of 43.35%, the copper recovery increased from about 5% to about 35%. The time period for all experiments was 22 days. The effect of pH on the strain performance was also investigated. All the strains performed better when the pH was kept constant at 1.5 compared to 2.2.*

Keywords: *Biological leaching; Moderate thermophilic bacteria; Chalcopyrite*

INTRODUCTION

The application of metabolic reactions of microorganisms could be used to speed up the slow oxidation of copper sulfide ores, which occurs under ambient temperature and pressure. The use of the catalytic action of bacteria seems to be one of the most promising technologies in the future extraction of metals from ores.

Bioleaching has been evaluated for the recovery of copper from sulfidic ores in different regions. Since mineralogical and geochemical characteristics of ores greatly influence the yield of bioleaching, the suitability of each ore for bioleaching should be evaluated separately [1].

1. *Department of Materials Science and Engineering, College of Engineering, Shahid Bahonar University of Kerman, Kerman, P.O. Box 76169-133, Iran.*
2. *Department of Chemical Engineering, College of Engineering, Shahid Bahonar University of Kerman, Kerman, P.O. Box 76169-133, Iran.*
*. *Corresponding author. E-mail: mizadpanah@yahoo.com*

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Although many reports exist on the bioleaching of chalcocite (Cu_2S), covellite (CuS) and bornite (Cu_5FeS_4), information on the bioleaching of chalcopyrite ($CuFeS_2$) is scarce in the literature. Chalcopyrite is the most abundant sulfidic copper ore in the earth's crust and the least reactive to biological activities. The recovery of copper from chalcopyrite is currently done almost entirely by smelting. Using smelting for copper recovery is harmful to the environment due to the emission of sulfur dioxide into the atmosphere. Therefore, in recent years, attention has been focused on bio-hydrometallurgy as an alternative to existing extraction methods.

A number of studies have been reported on the bioleaching of chalcopyrite. The recovery rates using different microorganisms have been claimed to be within 10-25% of ferrous iron and sulphur before the passivation starts [2]. Mesophilic bacteria in the bioleaching of chalcopyrite have had little success, but thermophilic bacteria have shown a promising capability for copper extraction from chalcopyrite. Harvey et al. using thermophilic bacteria, obtained 97% copper recovery in 140 days from a chalcopyrite concentrate with the initial copper content of 26.8% [3]. Yagmae et al. reported 80% copper recovery from a chalcopyrite concentrate with the initial copper content of 24.74% in 30 days. They also used a thermophilic bacterium [4].

The major reactions that take place during the biological leaching of chalcopyrite are as follows [5]:

$$CuFeS_2 + 4O_2 \xrightarrow{\text{Bacteria}} Cu^{2+} + Fe^{2+} + 2SO^{4-},$$

$$2Fe^{2+} + 1/2O_2 + 2H^+ \xrightarrow{\text{Bacteria}} 2Fe^{3+} + H_2O,$$

$$CuFeS_2 + 4Fe^{3+} \longrightarrow Cu^{2+} + 5Fe^{2+} + 2S^0,$$

$$S^0 + 3/2O_2 + H_2 \xrightarrow{\text{Bacteria}} H_2SO_4.$$

Despite the long standing research practice of bioleaching copper ores in Sarcheshmeh, the site of the largest copper mine in Iran, few studies have been carried out on the bioleaching of chalcopyrite samples. The current work presents a bench scale evaluation of the bioleaching of chalcopyrite concentrates produced by the ore dressing plant using moderate thermophilic bacteria.

Materials and Methods

Bacterial Strains

Three different bacterial strains, coded MS1, MS2 and TSB, were used in the experiments. MS1 and MS2 had been previously isolated from the site of the mine in Sarcheshmeh, and TSB had been isolated from an acidic hot spring in another place.

Mineral Media

Two different mineral media were used for bacterial growth. The composition of the media, which are coded 9K and L, are presented in Table 1.

Ore

Chalcopyrite concentrates were sampled from the Sarcheshmeh ore dressing plant at two different time periods. The chemical analysis and the total copper content of the concentrates are given in Table 2. Eighty percent of the particles were less than 325 micrometers in diameter.

Adaptation Experiments

For initial microbial growth, the strains were grown in medium 9K, supplemented with sulfur and $FeSO_4.2H_2O$. The pH of the medium was adjusted to 1.5 and the flasks incubated under 50°C in a shaker incubator. The incubation continued until the number of bacteria in the solution was 5×10^8 cells per ml. The strains were adapted to chalcopyrite as the sole source of energy by replacing $FeSO_4.2H_2O$ and S by chalcopyrite concentrate. The adaptation time was about three weeks.

Bioleaching Experiments

Bioleaching experiments were done on the two types of concentrate A and B. Tables 3 and 4 list the conditions for all experiment. The experiments on concentrate A are coded from A1 to A9, and the experiments on concentrate B are coded from B1 to B6. All bioleaching experiments were carried out in 500 ml shake flasks. Each flask contained 100 ml pulp. All samples were inoculated with 5 ml of the bacterial cells, which after passing through a microbiological filter with 0.2 μm size, were added to the samples. Flasks were then placed on a rotary shaker incubator, rotating at 150 rpm at 50°C. Samples were taken at specified time intervals and the amount of copper released in the solution was determined using an Atomic Absorption Spectroscopy (Varian, A-A1275).

RESULTS AND DISCUSSION

Selection of the Mineral Medium

To select the better mineral medium between 9K and L, strains MS1 and MS2 were grown on pulp A in both of the media (experiments A2, A4, A7 and A9). The results have been summarized in Tables 5 and 6.

Using the data in Table 5 and a paired t-test, the 99% confidence interval for the mean difference in recoveries is 0.23 ± 0.51, which from the existing data, indicates that no significant difference can be observed between the effects of the two media. Using the data in Table 6 and a paired t-test, the 99% confidence interval

Table 1. Mineral media.

Components (gr/l)	KCl	K_2HPO_4	$Ca(NO_3)_2$	$(NH_4)_2SO_4$	$MgSO_4.7H_2O$
9K	0.1	0.5	0.01	3	0.5
L	0.05	0.5	0.01	0.05	0.5

Table 2. Chalcopyrite concentrate analysis.

Constituents (%)	Cu	CuO	Fe	Mo	Total Cu
Concentrate (A)	28	2.7	25.7	0.144	30.16
Concentrate (B)	40	4.2	18.4	0.309	43.35

Table 3. Experiments on concentrate A.

Experiment No.	Bacteria	Culture Medium	pH	Pulp Density (%w/v)
A1	MS2	9K	2.2	3
A2	MS2	9K	1.5	3
A3	MS2	L	2.2	3
A4	MS2	L	1.5	3
A5	TSB	9K	1.5	3
A6	MS1	9K	2.2	3
A7	MS1	9K	1.5	3
A8	MS1	L	2.2	3
A9	MS1	L	1.5	3

Table 4. Experiments on concentrate B.

Experiment No.	Bacteria	Culture Medium	Temp. (°C)	pH	Pulp Density (%w/v)
B1	MS2	9K	50	2.2	1.5
B2	MS2	9K	50	1.5	1.5
B3	TSB	9K	50	2.2	1.5
B4	TSB	9K	50	1.5	1.5
B5	MS1	9K	50	2.2	1.5
B6	MS1	9K	50	1.5	1.5

Table 5. Results of MS2 growth in media 9K and L (pH = 1.5).

Time (h)	Percent Recovery in 9K	Percent Recovery in L	Recovery in L-Recovery in 9K
0	16.02	16.02	0.00
48	19.63	19.62	-0.01
96	22.64	22.68	0.04
168	25.43	26.24	0.81
264	29.03	29.26	0.23
336	28.49	28.15	-0.34
360	29.3	29.3	0.00
432	29.2	30.34	1.14
528	30.36	30.59	0.23

for the mean difference in recoveries is -2.2 ± 0.99, which indicates that for MS1 the recovery in medium L is significantly lower than the recovery in medium 9K. Using the same procedure, it was shown that the copper recoveries in medium 9K, for MS1 and MS2, do not differ significantly (data not presented). Figure 1 shows the copper recovery as a function of time for MS1 and MS2 in media 9K and L graphically. For the strain TSB, it was previously shown by Bagheri et al. that medium 9K is better than medium L [6].

Table 6. Results of MS1 growth in media 9K and L (pH = 1.5).

Time (h)	Percent Recovery in 9K	Percent Recovery in L	Recovery in L-Recovery in 9K
0	16.02	16.02	0.00
48	20.40	17.96	-2.44
96	22.75	20.94	-1.81
168	26.3	23.80	-2.5
264	28.53	25.62	-2.91
336	26.38	24.06	-2.32
360	28.57	26.07	-2.50
432	29.43	26.52	-2.91
528	30.46	28.00	-2.46

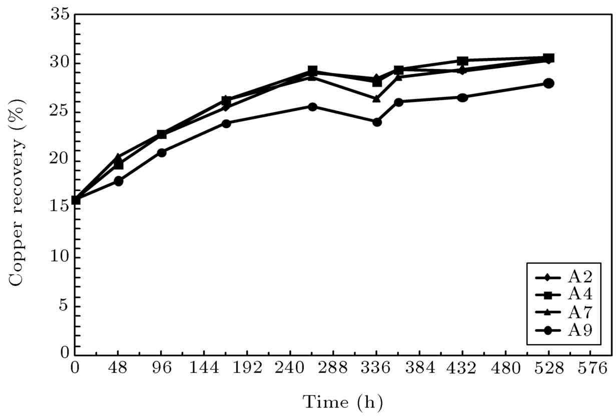

Figure 1. Percent recovery of copper as a function of time for pH = 1.5.

The same experiments were repeated when the pH of the media was kept constant at 2.2 (experiments A1, A3, A6 and A8). The results are presented in Tables 7 and 8. Using the data in Table 7 and a paired t-test, the 95% confidence interval for the mean difference in recoveries is -3.08 ± 1.88, which indicates that for MS2 the recovery in medium L is significantly lower than the recovery in medium 9K. Similarly, using the data in Table 8 and a paired t-test, the 95% confidence interval for the difference in recoveries is -0.88 ± 0.60, which indicates that for MS1 the recovery in L is lower than the recovery in medium 9K. The results are presented graphically in Figure 2. From the above experiments, we selected medium 9K for later experiments.

The Effect of pH on Copper Recovery

The effect of pH on the copper recovery from concentrate A was investigated for MS1 and MS2 in medium 9K. The results are in Tables 9 and 10.

Using the data in Table 9 and performing a paired t-test, it was shown that the mean difference between the MS1 performance at pH 1.5 and pH 2.2 is 1.54 ± 1.106, which indicates that the performance at pH 1.5 is better than the performance at pH 2.2. Similarly, using the data in Table 10 and performing a paired t-test, it can be concluded that the mean difference between the MS1 performance at pH 1.5 and pH 2.2 is 3.88 ± 1.106, which indicates that the performance at pH 1.5 is considerably better than the performance at pH 2.2.

Table 7. Results of MS2 growth in media 9K and L (pH = 2.2).

Time (h)	Percent Recovery in 9K	Percent Recovery in L	Recovery in L-Recovery in 9K
0	14.37	14.37	0.00
96	17.88	15.28	-2.6
168	22.4	18.62	-3.78
264	26.33	23.09	-3.24
336	26.22	22.09	-4.13
360	27.7	23.38	-4.32
432	27.95	25.92	-2.03
528	31.74	27.16	-4.58

Table 8. Results of MS1 growth in media 9K and L (pH = 2.2).

Time (h)	Percent Recovery in 9K	Percent Recovery in L	Recovery in L-Recovery in 9K
0	14.37	14.37	0.00
168	19.94	19.04	-0.90
264	23.41	22.96	-0.45
336	21.88	21.30	-0.58
360	23.62	22.87	-0.75
432	24.30	22.58	-1.72

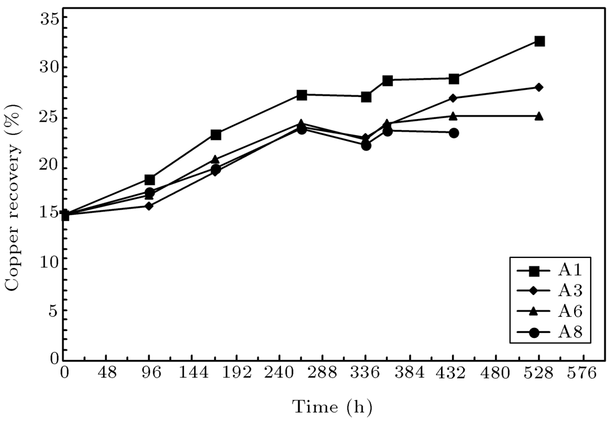

Figure 2. Percent recovery of copper as a function of time for pH = 2.2.

Comparison of MS1, MS2 and TSB in Copper Recovery

The activities of strains on pulp A were compared with each other. They were grown in medium 9K at pH 1.5 and the results are presented in Figure 3. MS1 and MS2 show similar activities, but the activity of TSB is lower than the others. It should be noted that, unlike MS1 and MS2, strain TSB had not been taken under the adaptation procedure at this stage. So, the lower activity of TSB might be attributed to this fact.

Experiments on Concentrate B

To check the reproducibility of the strains' capability to extract copper from chalcopyrite, the experiments were repeated on another concentrate (concentrate B). The activity of all strains in medium 9K at pH 1.5 and 2.2 was monitored as a function of time. Figures 4 and

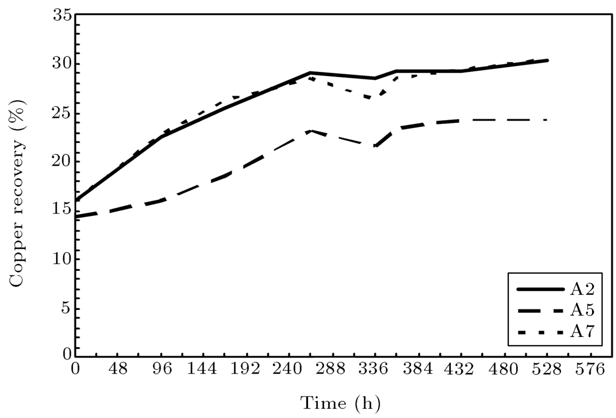

Figure 3. Copper recovery rate by different strains at pH = 1.5.

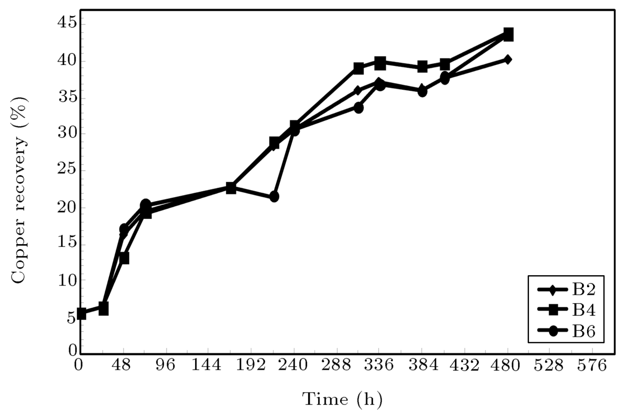

Figure 4. Percent recovery of copper as a function of time for pH = 1.5.

Table 9. Effect of pH on the copper recovery from concentrate A for MS2 performance in 9K.

Time (h)	% Recovery Increase Due to Microbial Activity at pH 1.5	% Recovery Increase Due to Microbial Activity at pH 2.2	%(Recovery at pH 1.5 − Recovery at 2.2)
96	6.62	3.51	3.11
168	9.41	8.03	1.38
264	13.01	11.96	1.05
336	12.47	11.85	0.62
360	13.28	13.33	-0.05
432	13.18	13.58	-0.4

Table 10. Effect of pH on the copper recovery from concentrate A from MS1 performance in 9K.

Time (h)	% Recovery Increase Due to Microbial Activity at pH 1.5	% Recovery Increase Due to Microbial Activity at pH 2.2	%(Recovery at pH 1.5 − Recovery at 2.2)
96	6.73	1.89	4.48
168	10.28	5.57	4.71
264	12.51	9.04	3.47
336	10.36	7.51	2.85
360	12.55	9.25	3.30
432	13.41	9.93	3.48
528	14.44	9.92	4.52

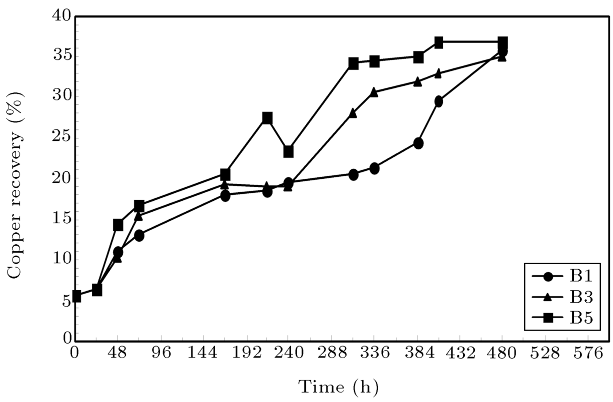

Figure 5. Percent recovery of copper as a function of time for pH = 2.2.

5 show the results. All strains are able to leach copper from concentrate B. Analysis of the variance showed no significant difference between performances of the strains at each pH. In these experiments, all stains had been taken under an adaptation procedure. This shows that strain TSB can leach copper from chalcopyrite, as well as other strains, provided that it goes under an adaptation procedure. The results emphasize the importance of adaptation in bioleaching experiments.

The effect of pH on the activity of each strain was also investigated. Table 11 shows the effect of pH on MS2 activity. Using the data in Table 11, it can be shown that the 95% confidence interval for the mean difference between the MS2 performance at pH 1.5 and pH 2.2 is 8.46±3.29, indicating that the performance at pH 1.5 is considerably better than at pH 2.2. Similarly, using the data in Table 12, it can be shown that the 95% confidence interval for the mean difference between the MS1 performance at pH 1.5 and at pH 2.2 is 2.56 ± 1.85, indicating that the performance at pH 1.5 is better than at pH 2.2.

Using the data in Table 13, it can be shown that the 95% confidence interval for the mean difference between the TSB performance at pH 1.5 and at pH 2.2 is 17.39 ± 1.85, indicating that the performance at pH 1.5 is considerably better than at pH 2.2.

CONCLUSIONS

The results of this research show that the bioleaching of chalcopyrite, using moderate thermophilic bacteria, is feasible. Indigenous as well as non-indigenous bacteria can leach copper from chalcopyrite concentrates, provided that they undergo adaptation. The mineral composition and pH of the culture medium influence the bioleaching rate. Although the bacteria examined here showed to be promising in copper bioleaching, more research is needed to understand all effective

Table 11. Effect of pH on MS2 performance in 9K.

Time (h)	% Recovery Increase Due to Microbial Activity at pH 1.5	% Recovery Increase Due to Microbial Activity at pH 2.2	%(Recovery at pH 1.5 − Recovery at 2.2)
24	0.78	0.92	-0.14
48	10.86	5.51	5.35
72	13.94	7.51	6.43
168	17.16	12.43	4.73
216	22.88	12.94	9.94
240	25.19	14.01	11.18
312	30.57	14.98	15.59
336	31.56	15.82	15.74
384	30.61	18.96	11.65
408	32.27	23.98	8.29
480	34.62	30.34	4.28

Table 12. Effect of pH on MS1 performance in 9K.

Time (h)	% Recovery Increase Due to Microbial Activity at pH 1.5	% Recovery Increase Due to Microbial Activity at pH 2.2	%(Recovery at pH 1.5 − Recovery at 2.2)
24	0.78	0.92	-0.14
48	11.64	8.92	2.72
72	14.83	11.14	3.69
168	17.16	15.22	1.94
240	25.11	18.05	7.06
312	28.23	28.79	-0.56
336	31.37	28.98	2.39
384	30.54	29.5	1.04
408	32.31	31.27	1.04
480	38.01	31.31	6.7

Table 13. Effect of pH on TSB performance in 9K.

Time (h)	% Recovery Increase Due to Microbial Activity at pH 1.5	% Recovery Increase Due to Microbial Activity at pH 2.2	%(Recovery at pH 1.5 − Recovery at 2.2)
24	0.78	0.92	-0.14
48	7.76	4.74	3.02
72	13.71	9.97	3.74
168	17.27	13.72	3.55
240	25.74	13.65	12.09
312	33.62	22.43	11.19
336	34.32	25.18	9.14
384	33.73	26.36	7.37
408	34.16	27.31	6.85
480	38.26	29.64	8.62

factors in the bioleaching of chalcopyrite. Pulp density, particle size and aeration using CO_2 enriched air are among the factors that should be investigated to exploit the full capacity of the bacteria in copper bioleaching from chalcopyrite concentrates.

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