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BIOLEACHING OF COPPER FROM COPPER SULFIDE MINERALS OF REKO DIQ DEPOSITS IN CHAGAI, BALOCHISTAN

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Abstract:
Chagai, District of Balochistan, Pakistan is rich in minerals and has great diversity of mineral resources such as copper, Gold, Silver, molybdenum etc. Copper sulfide ore sample was obtained from Reko Diq deposit (Chagai District, Balochistan) Diq H- 4 Tanjeel area for experimental leaching studies. Concentration of copper by froth floatation or any other beneficiation technique is costly, very expensive, harmful to environment and not so efficient.

Bioleaching concentration used in this study is considered one of the green methods adopting by many countries worldwide. During bioleaching process, mesophilic bacterial culture used in laboratory tests was sourced from the acid mine drainage of sulfur deposit collected from Koh-i-Sultan, Chagai District (Balochistan) and bioleaching was carried out by shake flasks at 30ºC. Optimum growth occurs at pH 2.0-2.5 and 28-35 °C. Pyrite (FeS_2) was also present in the ore simple. Calcite ($CaCO_3$) was present as acid consuming gangue mineral in the ore. The presence of acidophilic bacteria in the acid mine water was observed under phase contrast microscope. Copper became soluble from ore owing to sulfuric acid in leaching process. Chemically controlled leach solution displayed 125.22 ppm copper during the similar leaching time. Leaching data exhibited that 87% copper became soluble from the ore owing to 30-days of acidophilic bacterial leaching. The rate of solubilization of copper from ore enhances due to the biological production of sulphuric acid by utilizing indigenous acidophilic bacteria present in pyrite, during leaching experiments.

Keywords: *Copper sulfide ore, acidophilic bacteria, bioleaching, metal extraction.*

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INTRODUCTION:

Copper porphyry belt extends nearly 300 km along with Chagai Hills and adjacent ranges of Balochistan plateau near northwest Afghanistan and Iran Border, in Chagai District, Balochistan, Pakistan. There are approximately 48 porphyry Copper deposits in this belt and prospected mostly porphyry Copper (Chalcocite, Chalcopyrite. covellite, muscovite) from sulfide, small manto-type copper, Kuroko-type of volcanogenic massive sulfide and magnetite-rich contact metasomatic formation [1-3]. Reko Diq copper and gold deposits are economically beneficial and recently being explored and defined at H-14, H-15, and Tanjeel H-4 site [4].

Extraction of metals is being carried out by using living organisms. In Bio hydro metallurgy methods, bioleaching is considered one of the key methods to recover metals including cobalt [5], copper, gold, silver etc. There is a dramatic increase in utilization of Biotechnological principles in mineral industries. [6] This growing interest is due to interdisciplinary studies that are now available at many universities involved in mineral and biotechnological education. The numerous related national and international congresses, symposia, and workshops are also part of this education system [7].

In the dissolution and formation of minerals, microorganisms play a vital role in this regard, since geological eras. Recently, the biological methods show great alertness regarding to sedimentary [8] and mineral searching [9]. According to mineral processing industries, the utilization of microorganisms in hydrometallurgical operations enhances a significant resolution for the complications which have aroused in the countries owing to constant depletion of ore deposits that cannot be controlled by conventional hydrometallurgical procedures [10,11].

It has been estimated that the 25% of copper production is being produced by bacterial leaching [12] The leaching reaction of chalcopyrite is

$$2CuFeS_2 + H_2SO_4 + 8½.5\ O_2 \rightarrow FeSO_4 + 2CuSO_4 + H_2O$$

Utilization of microorganism in hydrometallurgical processes has been recognized a major solution of problems which many countries are facing due to depletion of high quality ore deposits. There is a growing interest to develop cheap and environmentally green methods to recover metals from low grade ores but it seems difficult with conventional methods [10, 13, 14].

Chemical and biochemical reactions, such as biosorption, bio-corrosion, chelation, oxidation and reduction possibly take place simultaneously in bioleaching process under the catalytic influence of acidophilic autotroph and heterotroph microorganisms in symbiotic growth. Recently, bioleaching is being used to recover uranium and other costly metals on a large scale [15].

Copper (Latin: cuprum) is a ductile, malleable and soft metal with very good electrical and thermal conductivity. A reddish-orange colour is appeared when a freshly cut surface is exposed. Copper is the main constituent of various alloys including sterling silver, cupronickel, coins and thermocouple detectors.

Copper is one of the metals like gold that exists in native state in some regions where it does not need extraction [16]. It is the key constituent of cytochromec oxidase enzyme of respiratory system. The blood pigment hemocyanin in crustaceans and molluscs, is comprised of copper. Copper is found mainly in bones, muscles and liver in human beings. In adults, 1.4 and 2.1 mg of copper is required per kilogram of body weight [17].

MATERIALS AND METHODS:

Copper sulfide ore sample

Copper sulfide core sample was obtained from Reko Diq deposit (Chaghi District, Balochistan) at the depth of 41-43 meters at coordinate 29°32'20.47N; 61°41'27.97E for present experimental leaching studies. The core sample was crushed, well mixed and homogenized and subsequently, it was passed through a sample divider to make a representative ore sample. Finally, the ore sample was ground to fine particle size by using vibrating cup mill. The ore sample was passed through 200 mesh particle size (-74 µm) to use for mineralogical, chemical and leaching studies.

Indigenous acidophilic iron- and sulfur-oxidizing bacteria

Mesophilic bacteria to be cultured, was obtained and collected from acid mine drainage of sulfur deposit located in Koh-i-Sultan, Chagai District (Balochistan) at coordinate 29°07'17.49 N; 62°47'26.75E in plastic bottles. The optimum pH and temperature ranges at which suitable growth of the bacteria has been observed, are 2.0–2.5 and 28–35 °C respectively. While, low pH over the range 0.9–1.2, can be tolerated by the culture after adaptation. This acid mine drainage was used as a mixed bacterial culture of acidophilic Fe- and S-oxidizing bacteria for bioleaching studies of copper ore in shake flasks at 30 ºC. The presence of acidophilic bacteria in the acid mine water was observed under phase contrast microscope.

Bacterial oxidation of elemental sulfur

Research-grade powder elemental sulfur (S^0) was used in this study. For inoculation, 1-ltr acid mine drainage water was centrifuged at 10,000 rpm in a refrigerated centrifuge machine at 4 °C for 15 minutes to get a bacterial pellet biomass. Washing of cell pellet (twice) was accomplished with pre-sterilized deionized water and further re-suspended in deionized water for use as an inoculum. Finely ground sulfur (1g) was dispensed in 100 ml 9K mineral salts medium (initial pH 2.5) pre-sterilized mineral salts medium. Powder sulfur was sterilized by tyndalization. Cultures were grown in shake flasks at 30 °C. For sterile control of chemicals, thymol (0.08% concentration) dissolved in ethanol will be added in respective experiments. Periodically, samples were taken aseptically for measurement of pH and acidity analysis of the solid residues. Titratable acidity was determined by standard acid-base titration using phenolphthalein as a pH-indicator.

RESULTS:

Shake flasks bioleaching studies of Reko Diq copper ore

Reko Diq copper ore contained acid consuming calcite ($CaCO_3$) as a gangue mineral during leaching process. As the optimum pH for acidophilic S- and Fe-oxidizing bacterial growth in the leach slurry ranges over 2.5-3.0. For this purpose, the H_2SO_4 consumed due to chemical reaction between calcite and sulfuric acid was added to acquire the optimum pH. During this chemical reaction, gypsum ($CaSO_4.2H_2O$) was produced according to the following equation:

$$\mathbf{CaCO_3 + H_2SO_4 \rightarrow CaSO_4.2H_2O + CO_2}$$

Gypsum ($CaSO_4.2H_2O$) is precipitated as calcium sulfate dihydrate during the reaction while carbon dioxide produces in gaseous state. Carbonate contents directly adjust the amount of H_2SO_4 required during the biological or chemical leaching process. The pH of leach solution was initially maintained with 5M H_2SO_4 at pH 2.5.

Shake flasks leaching experiments were performed to extract Cu from copper ore by using indigenous mixed culture of acidophilic bacteria present in the acid mine water at 30 °C. In the leaching process, 5%wt/ vol. ore pulp density was investigated at 150 rpm shaking condition. A drastic change in the initial pH of leach solutions inoculated with indigenous strains of acidophilic present in the acid mine water was observed during leaching process. The oxidation of pyrite through bacteria and copper sulfide minerals produced sulfuric acid which results decrease in pH of the leach solutions. Acid is generated during the bacterial oxidation of pyrite (FeS_2) and further biochemical reactions have been elaborated in the chemical equations given below:

$$FeS_2 + 3½O_2 + H_2O \rightarrow FeSO_4 + H_2SO_4$$
(Bacterial oxidation)

$$2FeSO_4 + H_2SO_4 + ½\ O_2 \rightarrow Fe_2(SO_4)_3 + H_2O$$
(Bacterial oxidation)

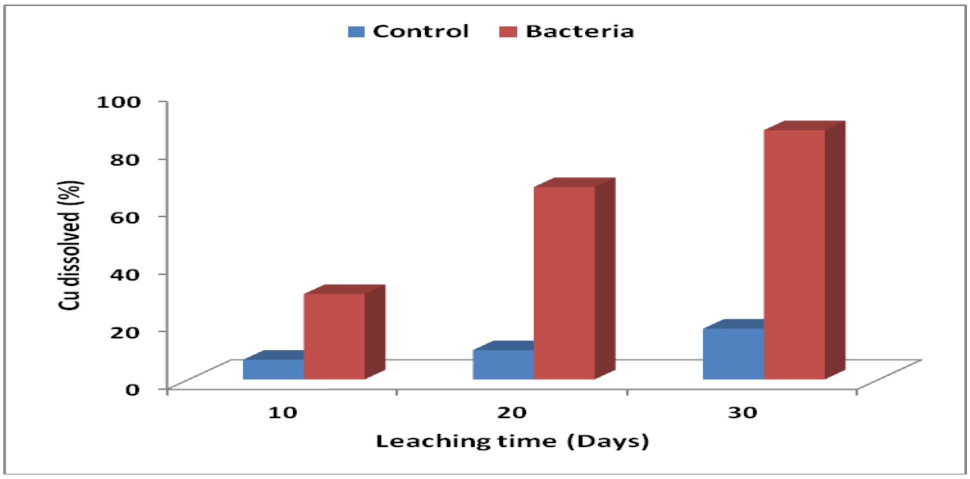
$$FeS_2 + 6Fe^{3+} + 3\ H_2O \rightarrow S_2O_3^{2-} + Fe^{2+} + 6\ H^+$$
(Chemical oxidation)

$$S_2O_3^{2-} + 8Fe^{3+} + 5\ H_2O \rightarrow 2SO_4^{-2} + 8\ Fe^{2+} + 10\ H^+$$
(Chemical oxidation)

As a result, the generation of H_2SO_4 due to bacterial activity shown in the above reactions, the pH of the medium decreases continuously. The studies performed on the solubilization of Cu from the Reko Diq copper ore during the shake flask leaching experiments has been shown in Table 1. During 30-days of leaching, the inoculated leach solution with strain of acidophilic mesophile bacteria was observed at pH 1.54. In the samples controlled by sterilizaiton, the pH of solution sustained in the range 2.42-2.52 throughout the studies. No acid produced in chemically controlled reactors.

Table 1: Shake flask leaching studies for Cu solubilization from Reko Diq copper ore sample at 30 °C

Leaching time (Days)	Treatment solution	pH of leach solution	Cu in leach (ppm)	Cu solubilized (%)
10	Control	2.52	48.50	6.83
	Bacteria	2.30	210.80	29.70
20	Control	2.48	72.50	10.21
	Bacteria	1.83	475.32	66.95
30	Control	2.42	125.22	17.64
	Bacteria	1.54	615.90	86.75



Graph 1: Copper dissolved (%) from ore by using indigenous acidophilic bacteria

Copper became soluble from ore owing to sulfuric acid in leaching process. Copper solubilization leached data are given in Table 1. Bacterial leach solution resulting from iron-oxidizing bacteria exhibited 615.90 ppm at pH soluble copper concentration after 30 days of leaching. Chemically controlled leach solution displayed 125.22 ppm copper during the similar leaching time. Leaching data exhibited that 87% copper became soluble from the ore because 30-days of acidophilic bacterial leaching (Table 1 and Graph 1).

Leaching data indicated that the copper recovery was optimum at pH 1.54 which displayed the enhanced activity due to bacterial activity. Copper solubilization from chalcocite (Cu_2S) and covellite (CuFeS) are shown below in chemical equations.

$$Cu_2S + 2\frac{1}{2}O_2 + H_2SO_4 \rightarrow 2CuSO_4 + H_2O$$

This reaction proceeds in two steps :

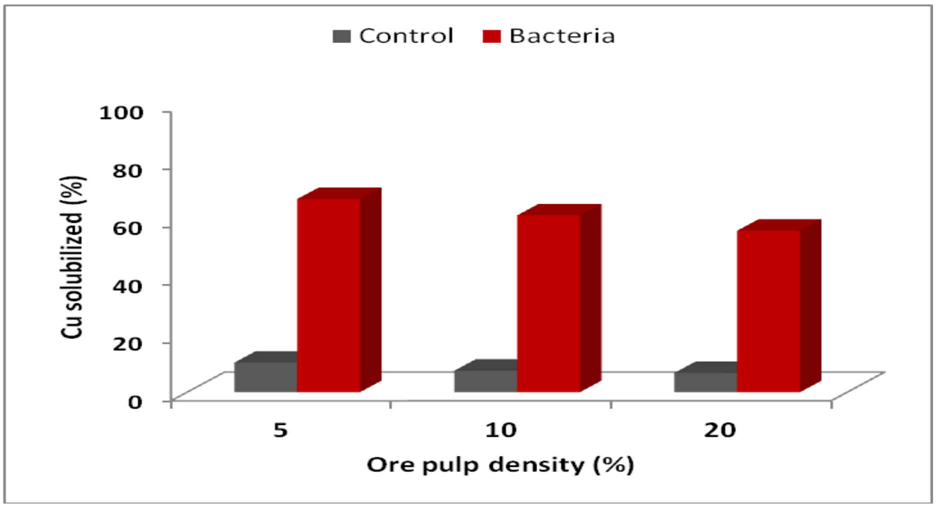
Step 1: $Cu_2S + \frac{1}{2}O_2 + H_2SO_4 \rightarrow CuS + CuSO_4 + H_2O$

Step 2: $CuS + 2O_2 + H_2SO_4 \rightarrow CuSO_4 + H_2O$

The oxidative leaching is highly dependent on the redox potential, for example, higher dissolution of copper has been observed at redox potential of 450-650 mV [18]. Copper dissolution from ore was mainly attributed to the concentration of sulfuric acid and ferric sulfate in the leaching process.

Effect of pulp density on copper bioleaching from ore

To investigate the effect of pulp solid to liquid ratio (pulp density) on the extraction of Cu from ore, shake flasks leaching tests were assayes at 5, 10 and 20% ore pulp densities using indigenous acidophilic bacteria present in the acid mine water at 30 ^oC. The leaching experiments were performed for 20 days leaching at 150 rpm. It was observed that that there was a drastic decrease in pH of the leach suspensions enriched with acidophilic mesophile culture during leaching process (Table 2). This decrease in pH is associated with biological generation of H_2SO_4 in inoculated media due to the bacterial oxidation of pyrite and copper sulfide minerals present in the ore sample.



Graph 2: Cu dissolution from copper ore at various pulp density with and without bacteria

Tab.2 Effect of pulp density (% wt / vol) on copper solubilization from Reko Diq ore with indigenous acidophilic bacteria at 30°C and 150 rpm in shake flasks
Leaching time = 20-day

Pulp density (%wt/ vol)	Treatment	pH of leach liquor	Physical appearance	Cu in leach solution (ppm)	Cu solubilized (%)
5	Control	2.60	Colorless	72.50	10.23
	Bacteria	1.72	Very light blue	475.32	66.95
10	Control	2.64	Colorless	105.60	7.44
	Bacteria	1.56	Light blue	870.52	61.30
20	Control	2.43	Colorless	189.50	6.67
	Bacteria	1.32	Light blue	1590.20	55.99

It was observed that increase in pulp density inversely affects the pH which is responsible for drastic decrease in pH. The pH 1.72, pH 1.56 and pH 1.32 were found for 5, 10 and 20% (w/v) leach suspensions, respectively after leaching with indigenous mesophile for 20 days. It indicates much production of sulphuric acid owing to increase in solid liquid ratio and it may be attributed to much pyrite availability in the process of leaching. Whereas, abiotically controlled pH suspensions showed pH in range 2.47-2.67 with increase in pulp density keeping identical experimental conditions.
It is observed in this study that the rate of solubalization of copper from ore enhances due to the biological production of sulphuric acid by utilizing indigenous acidophilic bacteria present in pyrite, during leaching experiments. This indicates that the role of sulphuric acid is pdomiment in solubalization of copper from ore. The results of Table 2 indicate that soluble copper concentration enhances during leaching owing to increase in pulp density with onoculated S- and Fe-oxidizing mesophiles. The concentration of soluble copper is found 475.32, 870.52 and 1590.20 ppm for 5, 10 and 20% (wt/vol) pulp density, respectively after 20 days leaching.

After 20 days of leaching, maximum 66.95% copper was produced from 5% (wt/vol) solid liquid ratio as shown in (Fig. 4.4). It was revealed that pulp density is inversely proportional to copper extraction. Subsequent continuous laboratory testing exhibited that it might be owing to inadequate biological adaptation or insufficient nutrient. But an economic recovery of copper form ores having low pulp density would not feasible technically on industrial scale.

DISCUSSION:

Economical extraction of copper from ores of low grade is the dream of mining industry [14]. Bacterial species which are mainly involved in the bioleaching of chalcocite ore are (*Acidithiobacillus ferrooxidans Leptospirillum ferriphilum, Leptospirillum ferrooxidans* and *Acidithiobacillus thiooxidans*) [19, 20]. These species were isolated and experiments were assayed in combination of *At. thiooxidans* and individual bacteria [21,22].
In conclusion, it was observed that the group of bacteria integrated by *At. thiooxidans* and *At. Ferrooxidans* extracted 70% in 35 days of leaching from ore, exhibiting wide differences with other consortia, which extracted only 35% of copper in 35 days of bioleaching [19, 23]. For validation of experiments, an escalation column was also performed, in which a higher percentage of copper was achieved by bacterial consortium concerning to control. However, oxidation of sulfur to sulfuric acid increased at lower pH values.

CONCLUSION:

Current studies were carried out on Cu-sulfide minerals at Reko Diq ore samples. Concentration of copper by froth floatation or any other beneficiation technique is costly, very expensive, harmful to environment and not so efficient. Present method of bioleaching of copper secondary minerals by indigenous acidophilic bacteria produced 63-87% copper concentrate is found significant. Moreover, we propose bioleaching method adaptation for concentration of copper at Reko Diq, Chagai Balochistan for industrial purposes.

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