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Hydrometallurgical Recovery of Copper Tailing Waste by Bioleaching at Hindustan Copper Limited, India

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Abstract - **The conventional methods of refining cannot be implemented for recovery of copper from tailing waste collected from Hindustan Copper Limited, Khetri, India as it contains low copper and higher iron along with other metals present. Hence bioleaching was tested as an alternative approach for the recovery of copper from the waste. The study investigated the feasibility of using a bioleaching process for the treatment of copper tailing waste. The XRD and ED-XRF analysis confirmed that the waste contained 0.13% *w/w* copper, which is present in different forms including chalcopyrite ($CuFeS_2$). Shake flask studies optimized with tailing concentration, optimum temperature, and pH showed 94.03 % *w/w* recovery of copper at 2 % *w/v* waste concentration after 40 days of exposure at pH 2.0. The study was extended to a pilot-scale glass column filled with raw copper tailing mixed with *Acidithiobacillus ferrooxidans* at a flow rate of 3 L h^{-1}. A recovery of 54.71% *w/w* of copper was obtained by this setup. The mix-proportion clay bricks were cast with the tailing waste after bioleaching. The bricks showed better compressive strength as compared to normal bricks. A pilot scale heap leaching study with 5 kg of tailing waste mixed with *Acidithiobacillus ferrooxidans* showed a 64.28% *w/w* copper tailing in 40 days.**
Keywords: **Bioleaching, Copper Recovery, *Acidithiobacillus ferrooxidans,* Column Leaching, Heap Leaching**

I. INTRODUCTION

Rapid growth in the requirement of heavy metals for numerous industries has increased the pace of recovery of various metals from their ores. The traditional mineral sources have been utilized for centuries and are falling short in the fulfillment of the industrial needs of developing as well as developed countries. The increased consumption and exploitation of the mineral ores have urged the exploration of low-grade ores and thereof recovery of metals from these ores. The tailing waste generated at Hindustan Copper Limited, Khetri, India, has been collected in a huge dam at the site.

The Khetri copper mines are over a hundred-year-old and are currently the second largest copper-producing mines in India [1]. As the ore is processed, the remaining tailing waste has built up posing contamination and seepage threats to nearby areas. The traditional hydro- and pyro-metallurgy techniques are not a viable option for this low-grade ore due to their lower efficiency in terms of energy and resource input. [2]. In addition to these, the metal leaches out slowly into the nearby lands and water bodies causing environmental concerns. The mine tailing waste treatment has gained attention after several reports of adverse effects of seepage from tailing dams in different parts of the world [3-5].

In the last three decades, bioleaching has emerged as a frontier technology for mineral ore processing in general and low metal-containing ores in particular [6]. The strategy has been applied for the extraction of nickel, zinc, gold, uranium, copper, and many other metals from low-grade ores or tailings [7, 8]. Over 10% of total copper production worldwide is obtained through bioleaching processes [9].

Among the vast number of prokaryotes capable of sulfur oxidation-reduction and iron oxidation, the *Acidithiobacillus ferrooxidans* has been exploited because of its ore-dissolution kinetics, bioleaching capability, survival under leaching conditions, and resource usage [10]. The bioleaching capability of microorganisms is adversely affected by changes in ore composition, pH, nutrients, aeration, and temperature. The successful scale-up requires the optimization of various parameters such as changes in ore composition, pH, nutrients, aeration, and temperature.

The slow reaction of the bioleaching process is the major challenge in the adoption of this technology. The batch culture reaction depends mainly on the ratio of biomass to ore and microbe-mineral ore interaction [11, 12]. The optimum growth of bacteria depends on the availability of nutrients and the maintenance of optimum conditions. Column leaching can provide a continuous culture mode, but the reaction time becomes the limiting factor. In column and heap leaching, percolation of leachate and nutrients into the deeper layers of the leach bed can create problems [2]. Improved reaction kinetics, mass transfer of nutrients, and intense mixing conditions can overcome the mentioned limitations [13]. Since the ore composition is different in different regions, the same methodology cannot be used for all bioleaching operations. The present study aims to development of a copper bioleaching and recovery technique and its further optimization for the recovery of copper from tailing waste at Hindustan Copper Limited, Khetri. This study also provides the option of immobilizing the waste generated after the bioleaching process and conversion of leaching waste.

II. MATERIALS AND METHODS

A. Collection Site and Sample Analysis

The copper tailing waste was collected from Hindustan Copper Limited, Khetri, India which is situated at the foothills of the Aravalli Range, and hosts copper ores stretching across 80 km long metallogenetic province from Singhana in the north to Raghunathgarh in the south which is popularly known as Khetri Copper Belt. The region is characterized by the presence of tightly folded Proterozoic metasediments where mineral exploration started with the advent of the 20th century and later mining activities were expanded after the 1960s.

The tailing samples were first characterized for metal composition by Energy Dispersive X-ray fluorescence (ED-XRF). EDXRF analysis was carried out using Panalytical Epsilon 5 Energy Dispersive X-ray Fluorescence Spectrometer.

X-ray diffraction (XRD) patterns were obtained for qualitative analysis which revealed the ore composition of the waste. X-Ray powder diffraction patterns were acquired using Rikagu MiniFlex II Desktop X-ray Diffractometer. The sample was analyzed with 2θ (2 theta) value ranging from 20° to 80° with a step size of 2θ value 0.005° and a scan rate of 2° per minute. Match! software version 3.2.1 [14] was used for peak analysis and compound characterization of diffraction patterns. Different compound peaks were identified using fundamental principles of Rietveld analysis [15, 16] with the help of Match! software version 3.2.1.

B. Microorganisms and Growth Media

Two commercially available bacterial stains i.e., *Thiobacillus novellus* and *Acidithiobacillus ferrooxidans* (ATCC® 23270™), were used in the present study. While *Thiobacillus novellus* was procured from the National Chemical Laboratory Culture Collection, Pune, India, and grown in an inorganic medium as described by Santer et. al., 1959 [17], *Acidithiobacillus ferrooxidans* was obtained from ATCC, and grown in ATCC 2039 media as specified by supplier [18].

C. Bioleaching Potential of Different Bacteria Against the Tailing Waste

The leaching reaction involving *Thiobacillus novellus* was set up with 50 ml of described medium containing bacteria with varying concentrations of tailing waste.

The leaching experiments with *Acidithiobacillus ferrooxidans* were conducted in two components; solution A [3.0 g $(NH_4)_2SO_4$, 0.1g KCl, 0.5 g K_2HPO_4, 0.5 g $MgSO_4.7H_2O$, 0.01 g $Ca(NO_3)_2$, 700 ml of distilled water] and the solution B (44.22 g $FeSO_4.7H_2O$, 10 ml 1 N H_2SO_4 in 300 ml of distilled water) [19] supplemented with varying concentration of tailing waste. The supernatant collected after leaching was analyzed for copper content by Atomic Absorption Spectrometry.

D. Shake Flask Leaching Studies

1. Effect of Waste Concentration on Bioleaching

The experiment was carried out in 500 ml Erlenmeyer flasks containing 200 ml of 9K medium with different concentrations of tailing ranging from 2% to 15% (*w/v)*, 1% *v/v* inoculum of *Acidithiobacillus ferrooxidans* containing 2 x 10^9 cells ml^{-1}. The flasks were incubated at 30 °C and a constant stirring speed was kept at 130 rpm throughout the study. The copper concentration in the leachate was measured after collecting two ml of leachate at definite time intervals. The concentration was measured with AAS. The percentage recovery of copper after bioleaching (% *w/w*) was calculated on the 40^{th} day.

2. Effect of pH on Bioleaching of Tailing Waste

100 ml of 9k medium with different pH values *viz.* pH 2, 3, 4, 5, and 6 were prepared and inoculated with 1% *v/v* inoculum containing 2 x 10^9 cells ml^{-1} of *Acidithiobacillus ferrooxidans* culture. The copper tailing waste concentration added was 2% *w/v* into each flask. The reaction conditions were maintained with the addition of base (0.4 M NaOH) when the pH of the media deviated, and all the flasks were kept at 30 ℃ temperature with 130 rpm rotation in an incubator shaker. The study was conducted for 40 days. The samples were collected at defined time intervals and the concentration of copper in the solution was measured using the standard technique of AAS. The same parameters were also chosen to study the effects of pH at higher concentrations (10% *w/v* of tailing waste). This study was conducted for 40 days. All other parameters were kept identical except tailing waste concentration. The copper concentration in the media was measured using AAS.

3. Effect of Temperature on Bioleaching

The effect of temperature was evaluated by studying leaching capabilities at different temperatures ranging from 8 °C to 50 °C. The reaction was set up in 100 ml of 9K media with 2% *w/v* tailing waste concentration. *Acidithiobacillus ferrooxidans,* as 1% *v/v* inoculum containing 2 x 10^9 cells ml^{-1}, was added to the reaction mixture. The copper concentration was measured in the media as stated earlier. The percentage recovery of copper in leachate was calculated on the 40^{th} day.

E. Designing of Column and bioleaching operations

The bioleaching column was fabricated for carrying out bioleaching in continuous culture mode. The system was equipped with two parallel glass columns, two pumps, and two leachate collection trays along with a central control panel for maintaining liquid and air flow rates into the columns. The schematics of column designing and the column used in the study are shown in fig. 1a and 1b. Each column was made up of five individual glass tubing, each of length 30 cm, for adjusting the height of the column, connected longitudinally with sealed rubber clamps which bear valves for sample collection at different heights in the column. The column parameters are a height of 170 cm with an outer diameter of 12 cm and an inner diameter of 10 cm, which makes the total volume of the column 53 liter. The sample collection ports/valves are fitted at regular intervals at every foot. The column had a leachate/media intake port on the top while the exit port for leachate opens in the leachate collection tray at the lowermost glass tubing. The lowermost tubing also has an intake port for air. The dimensions of the leachate collection tray are 40 cm*36 cm*30 cm with a volume capacity of over 40 Liter.

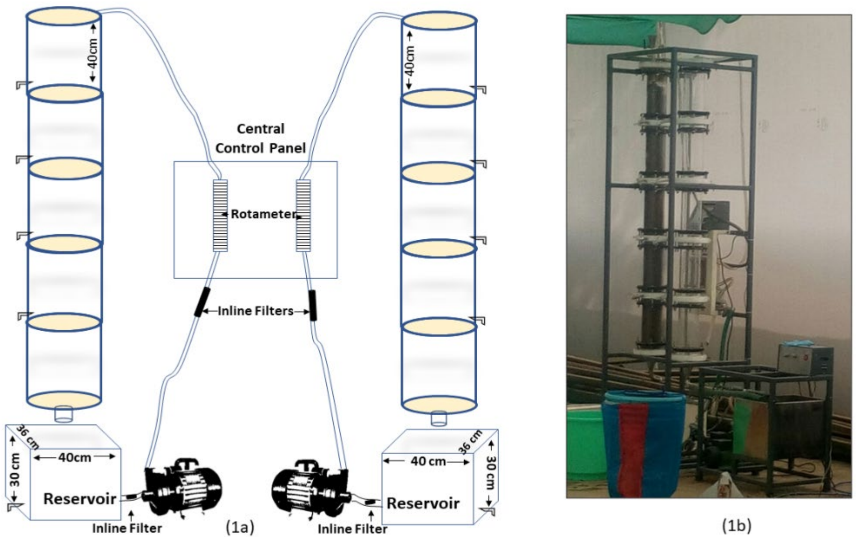


Fig. 1 Schematics of column designing (1a), The actual column setup used for the study (1b)

The flow of liquid and air into the column is controlled by pumps, rotameters, and inline ball valves connected by a central control panel. The leachate collected in the collection tray is recirculated in the column with the help of a pump and inline valves. The media/leachate slowly percolates through the column and gets collected in the collection tank, which is further recirculated, and samples are collected for copper concentration measurement in the leachate. The system can operate both columns simultaneously.

1. Packing of the Column

The column was packed with 6.880 kg of tailing waste with 5.880 kg of glass rings as filling material. Prior to the commencement of the experiment, the reactor was circulated with the 9K medium for acclimatization of the reactor bed for *Acidithiobacillus ferrooxidans* inoculation. After a pre-run of 7 days, the column was inoculated with *Acidithiobacillus ferrooxidans* (1% *v/v* inoculum containing 2 x 10^9 cells ml^{-1}) in a total of 10 L of 9K medium, pH 2. Fresh media and distilled water were regularly added to the column to ensure that enough bacterial culture/9K media is available for recirculation in the column. The leachate samples were collected every 24 hours and copper concentration in leachate was measured by the standard technique of AAS. The leaching operations were continued for 40 days, and later the column was disassembled, 5g of solid samples were oven dried and analyzed by ED-XRF to measure residual copper.

F. Pilot Scale Heap Bioleaching Operations

Pilot scale studies were performed with a pilot plant of 20 kg capacity. The column contained a slanting tray equipped with a spray system attached to pipes with inline valves for controlled leachate/media flow (Fig. 2).


Fig. 2 The heap leaching setup used in the heap leaching study

The leachate collection chamber collects the leachate and recirculates it onto the top of the heap with the help of a pump and sprinklers. The bioleaching study was conducted with 5 kg of finely ground representative copper tailing waste, which formed the leaching bed. The leaching bed was sprayed with 3 liters of *Acidithiobacillus ferrooxidans* for colonization of the leaching bed. 9K medium, pH 2 was sprinkled over the leaching bed every 12 hours. Leached was collected every 12 hours and copper concentration in the leachate was measured by AAS. The study was carried out for 40 days. The samples were oven-dried and ED-XRF analysis was performed to measure residual copper in the heap.

G. Mass Balance Calculations and Percentage Recovery after Bioleaching

The percentage recovery of copper in all experiments was calculated by mass balance equations, where percentage copper recoveries were obtained by calculating copper remaining in tailing waste after treatment or the amount of copper recovered in leachate.

III. RESULTS AND DISCUSSION

A. Characterization of Copper Tailing Waste

The tailing waste is an inevitable by-product of metal extraction industries which is usually stored at the site of extraction. After the successful processing of mineral ores by pyrometallurgical techniques, the storage of tailing waste has been a challenging issue from an environmental perspective.

ED-XRF analysis of copper tailing samples collected from Khetri revealed 0.13% w/w copper in tailing waste. The major fraction of waste was silica, iron oxide, and aluminum oxide having 73.54% w/w, 16.96 % w/w, and 4.53 % w/w concentrations respectively. The various elements/oxides identified in copper tailing along with their percentage composition are displayed in Fig. 3.

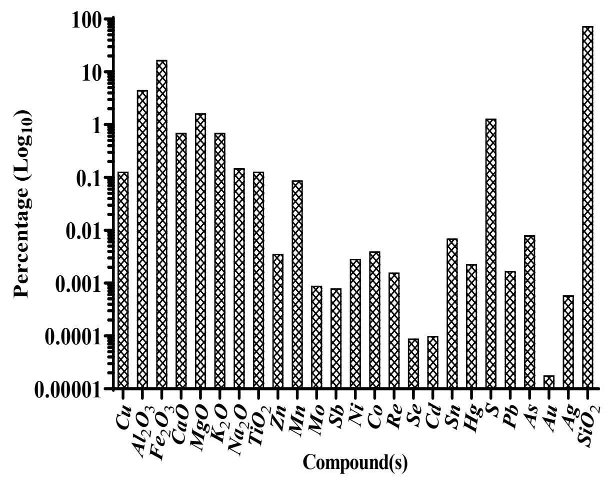


Fig. 3 Energy Dispersive –X-Ray Fluorescence analysis of copper tailing waste. The samples were collected from the tailing dam of Hindustan Copper Ltd., Khetri, India

Various other elements were also present in trace quantities. The different minerals/compounds present in the tailing waste were revealed after X-ray diffraction analysis and it indicated the presence of discrete peaks corresponding to chalcopyrite, yoderite, and zangboite along with many other ores as shown in Fig. 4.

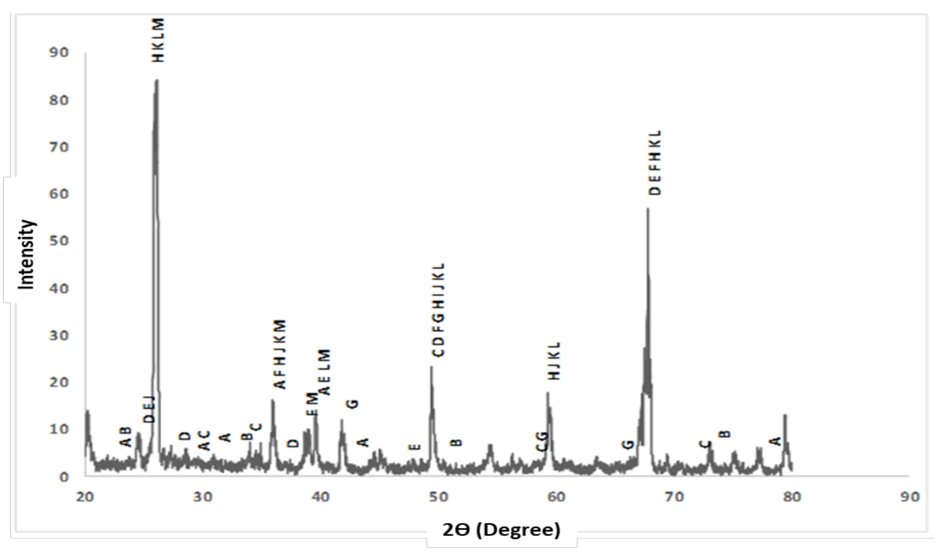


Fig. 4 X-Ray Diffraction analysis of copper tailing waste

Relative peak intensity is shown on the y-axis against the diffraction angle (2Θ) on the x-axis. Different peaks owing to various ores have been identified and labeled- A: Calcite ($CaCO_3$), B: Ferrous Sulfa-e, C: Chalcopyrite ($CuFeS_2$), D: Yoderite ($Mg_2Al_{5.6}Fe^{3+}_{0.3}Mn^{3+}_{0.1}Si_4O_{18}(OH)_2$), E: Zangboite ($TiFeSi_2$) F: Fayalite ($Fe_2SiO_4$), G: Chromium Nickel Arsenide (AsCrNi), H: Quartz (SiO_2), J: Copper Manganese Molybdenum oxide ($Cu_{2.86}Mn_{0.8}Mo_3O_{12}$), K: Copper Iron Molybdenum, L: Dibarium Copper dioxide iodide (Ba_2CuIO_2), M: Pellouxite ($Ag_{0.26}C_{10.5}Cu_{0.68}O_{0.5}Pb_{10.44}S_{27}.5Sb_{11.56}$)

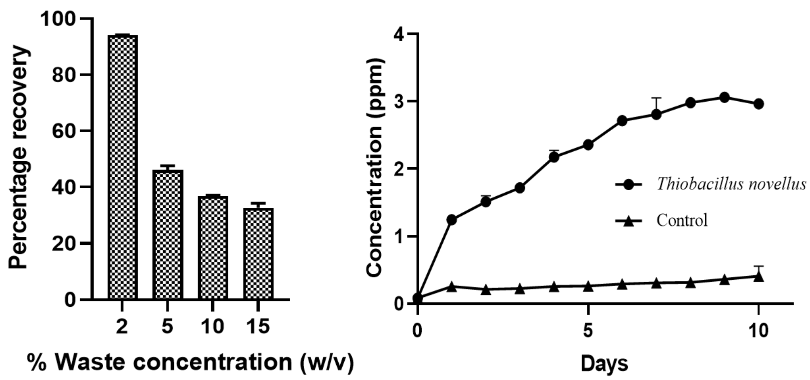
The successful application of bioleaching in batch culture depends on different parameters i.e., chemical, biological and physical properties of the tailing waste and leaching media used [20].

The iron oxide present in tailing waste can assist in the better growth of iron oxidizers in the waste. Ferric ions can break the metal sulfur bonds in metal sulfur ores like chalcopyrite [21].

Hence the composition of the tailing waste can provide essential nutrients required for the proliferation of *Acidithiobacillus ferrooxidans.*

B. Bioleaching Potential of Different Bacteria Against the Tailing Waste

The experiment employing varying concentrations of tailing waste has shown the maximum copper recovery at 2% *w/v* waste concentration which was 94.03% *w/w* in the case of *Acidithiobacillus ferrooxidans* and less than 1% for *Thiobacillus novellus* after 40 days of incubation suggesting a clear choice of the organism for further studies. The copper recovery gradually declined from 94.03% *w/w* to 33.85% *w/w* at copper tailing concentrations ranging from 2% *w/v* to 15% *w/v* (fig. 5).



(5a) (5b)

Fig. 5 The effect of copper tailing waste concentration on bioleaching. The percentage copper recovery has been shown at different percentages of waste (5a). Fig. 5b shows the copper bioleaching using a different bacterium *T. novellus*

A varying concentration of tailing waste was dissolved in 100 ml of 9K media. 1% *v/v* culture of *Acidithiobacillus ferrooxidans* containing 2 x 10^9 cells ml^{-1}, was added to the reaction mixture and incubated at 30° C for 40 days. The recovery of copper after bioleaching was calculated and presented as a percentage of initial metal concentration (*w/w*) after 40 days of incubation (5a). The bioleaching potential of *Thiobacillus novellus* was checked at 1% (*w/v*) copper tailing waste concentration. The study was conducted in 50 ml of media containing *Thiobacillus novellus* at 2 x 10^9 cells ml^{-1} concentration at 30° C for 10 days. The y-axis shows bioleached copper concentration (in ppm) at different time intervals (5b).

Further, *Acidithiobacillus ferrooxidans* has been well characterized for oxidation of iron-rich ores and successful dissolution via indirect leaching method [10, 22-24]. Enhanced leaching capabilities have been reported with adapted cultures of *Acidithiobacillus ferrooxidans* in several cases due to changes in the cellular components of the adapted culture [25].

We observed a decline in the copper recovery at higher tailing waste concentrations as seen in Fig. 5a. The plausible explanations could be the low solubility of tailing at high concentrations and higher toxicity of copper along with other dissolved elements when elevated tailing waste concentrations were used.

C. Effect of Tailing Waste Concentration and pH on Bioleaching

The various parameters like waste concentration, nature of the tailing, composition of the tailing waste and growth medium, the toxicity of the waste, temperature, pH, bacterial strain, cell number, etc. can alter the bioleaching efficiency in both a positive and negative manner [26]. The leaching efficiency is further inhibited by the formation of passivation layers. Wang et al have proposed a mechanism for the formation of Polysulfide, Chalcocite, and Jarosite layer formation in bioleaching which decreases the reduction of the ore. This layer passivates the surface hence reducing the bioleaching efficiency of microbes at higher waste concentrations [27]. Other studies have demonstrated the hindrances caused by the establishment of metal deficient layer, Jarosite precipitates, elemental sulfur films, and hence, decelerating the bioleaching process [28, 29]. Iron and sulfur-rich environments have been shown to form relatively inert layers which hinder bioleaching and metal recovery declines sharply thereafter [30, 31].

The growth and bioleaching capability of *A. ferrooxidans* heavily depends on the pH of the reaction mix. The bioleaching, expressed as copper recovery at different pH values ranging from 2.0 to pH 6.0 under the varying time of incubation is shown in Fig. 6. The inset figure shows the percent copper recovery at different pH after 40 days of incubation. Maximum (93.89% *w/w*) recovery of copper could be achieved at pH 2.0 at 2% *w/v* waste concentration. This finding confirms the earlier report by Mishra *et al.,* 2008, suggesting that the acidic pH range, usually pH values below 2, favors high metal recovery. The inverse relationship of percentage copper recovery and pH value is expected as the leaching is inhibited at higher pH due to the acidophilic nature and requirements of low pH for the bioleaching process by *A. ferrooxidans* [32].

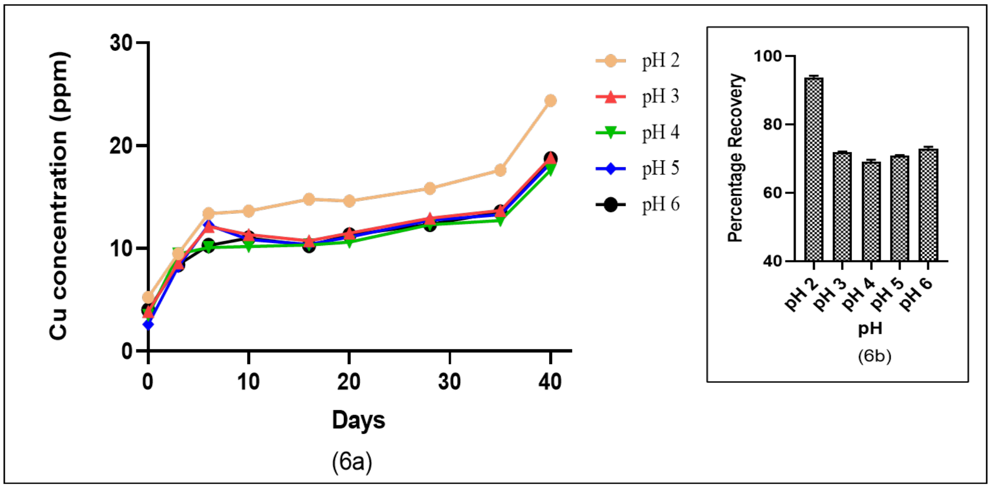


Fig. 6 The Effect of pH on bioleaching at 2% (*w/v*) copper tailing waste concentration in shake flask study. The copper concentration obtained at different periods (6a). The percentage recovery at different pH after 40 days (6b)

The study was conducted in 100 ml of 9K medium. 1% *v/v* culture of *Acidithiobacillus ferrooxidans* containing 2 x 10^9 cells ml^{-1}, was used as inoculum, and incubated at 30° C for 40 days (6a). Inset figure (6b) shows the % Copper recovery after 40 days at different pH values.

D. Effect of Temperature on Bioleaching

The incubation temperature along with other environmental conditions is known to influence the growth of prokaryotic organisms. To optimize the bioleaching process, the reaction mixture was incubated at different temperatures. We obtained a continuous increase in the copper recovery from 8 °C to 37 °C followed by a decrease at 50 °C. Fig. 7 represents the percentage recovery of copper at different temperatures. The highest percentage recovery of copper (72% *w/w*) was found at 37 °C on the 40^{th} day of incubation indicating the optimum temperature requirements for mineral dissolution and growth of *A. ferrooxidans.* The mesophilic nature of *A. ferrooxidans* has also been reported to exhibit high iron oxidation in a temperature range of 30°C to 40°C [33]. Mixed consortia of different mesophiles have also shown maximum iron and sulfur-oxidizing activity for bioleaching in a range of around 35 °C [34].

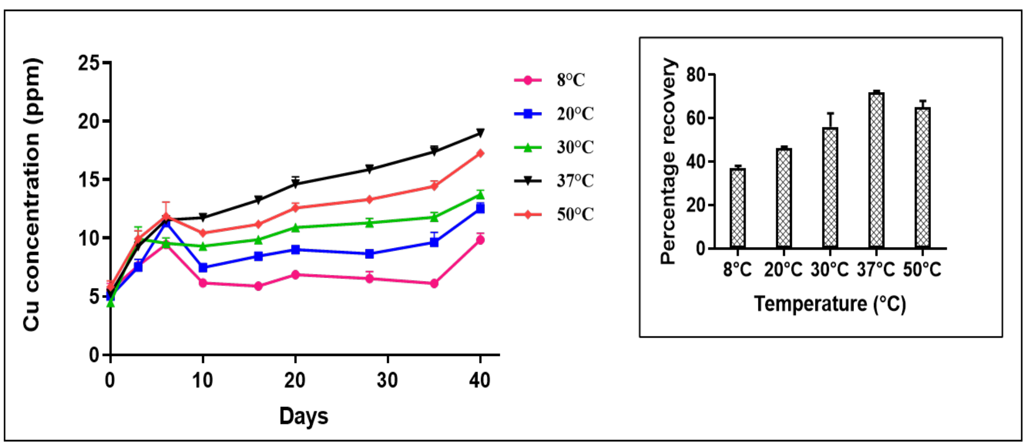


Fig. 7 The effect of the temperature on the bioleaching of tailing waste by *A. ferrooxidans.* The copper concentration in the leachate at different temperatures. The inset figure shows the calculated percentage recovery on the 40^{th} day

At 2% (*w/v*) copper tailing waste concentration in 100 ml of 9K medium, pH 2. 1% *v/v* culture of *A. ferrooxidans* containing 2 x 10^9 cells ml^{-1}, was added and incubated for 40 days. The bioleaching is represented as the copper concentration in media at specific time points shown in ppm on *the* vertical axis. The copper recovery is expressed in terms of percentage recovery (*w/w)* after 40 days [Inset].

E. Column Leaching

The parameters obtained during the lab studies were utilized for scale-up leaching operation by constructing a glass column which is already described in the materials and methods section. The column was filled with tailing waste and added with *A. ferrooxidans* to achieve 2.0 x 10^9 cells m^{-1} concentration. The flow rate of leachate and media was maintained at 3 L h^{-1}. The concentration of copper in the outflow obtained after leaching increased initially up to 66 ppm after 22 days of column running followed by a decline till the end of the study *i.e.,* 40^{th} day (fig. 8). The residual copper content present in the tailing waste was measured at different time points and a decrease in the residual copper in the column was indicated by ED-XRF analysis (Fig. 8 inset).

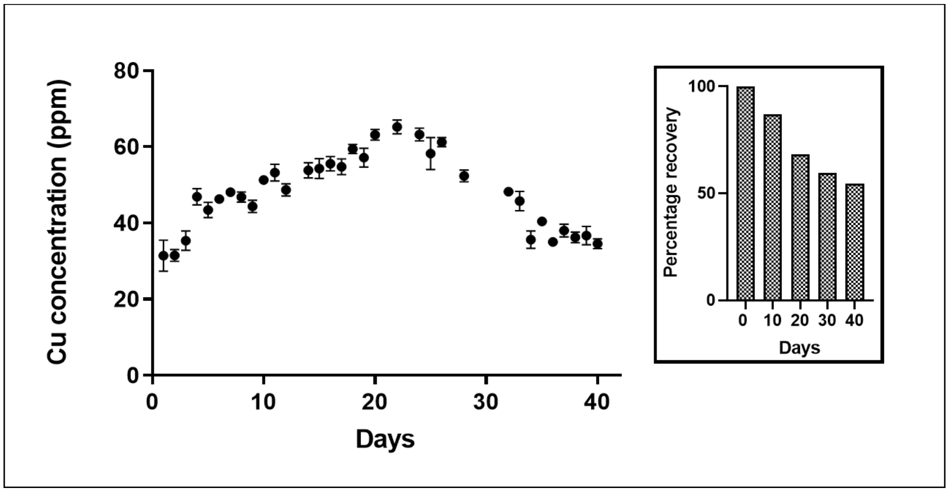


Fig. 8 Copper leaching in glass column. Copper concentration in the leachate collected. The Inset figure shows the percentage of copper remained in the tailing waste as measured by XRF analysis

The column was filled with 9K medium, pH 2, and run under ambient temperature conditions. The reaction mix was inoculated with 1% *v/v Acidithiobacillus ferrooxidans* of concentration 2 x 10^9 cells ml^{-1}. The flow rate was maintained at 3 L h^{-1}. The concentration of bioleached copper (ppm) in the leachate at different time points is shown on the vertical axis. The inset figure shows the percentage of residual copper calculated as a percentage of copper amount present at time t= 0 days.

The pulp density and particle size play a huge role in the microbial oxidation of minerals. At lower pulp densities the recoveries are good as seen in the flask leaching studies (fig. 5, 6, and 7). At similar conditions more than 80% of the copper has been recovered in different independent reports such as Rouchalova *et al.,* 2020 and ConiĆ *et al.,* 2014 [24, 35]. Similar copper recoveries have also been obtained in this study. Though lower pulp densities are not economically viable as these would require larger volumes of media and hence maintaining the optimal growth conditions at such a scale is always difficult. The glass rings were used to enhance the flow of media and optimal growth conditions in the column. The fine particle size has been linked to damage to the cellular structure of *A. ferrooxidans* and other microbes commonly used in bioleaching. Nemati et al. have demonstrated loss of microorganisms at particle sizes < 25 µm [24, 36]. Here the glass rings used as a filling matrix helped in easier percolation of leachate down the leaching bed in the column.

The chemistry of *A. ferrooxidans* is thoroughly studied and the leaching mechanism involved in *A. ferrooxidans*-mediated pyrite and chalcopyrite dissolution can be summarized as –

$CuFeS_2$ (Chalcopyrite) + O_2 + 2 H_2SO_4 → $CuSO_4$ + $FeSO_4$ + 2 H_2O + 2 S
2 FeS_2 (Pyrite) + 7 O_2 + 2 H_2O → 2 $FeSO_4$ + 2 H_2SO_4 [37, 38]

After bioleaching, copper recovery on the 40^{th} day was found to be *54.71% w/w* of initial copper present in tailing waste (fig. 8, inset). The percentage recovery of copper was calculated by studies of the copper tailing waste before and after bioleaching.

The previous studies of copper leaching of sulfur and oxide ores of copper have obtained leaching of copper up to 80% in various ores utilizing high concentrations of acids [39], high temperature [13], lower pulp densities [24], use of geopolymers/binders to increase the agglomerate size and percolation [40]. These practices can compromise the commercial use of technology despite good recoveries. The use of a filling matrix has been shown here to improve the column bioleaching recoveries at high pulp densities i.e., 68 % and it can improve the bioleaching rates making the process suitable for handling higher pulp density operations.

F. Pilot Scale Heap Bioleaching Operations

In the initial phase of the heap bioleaching, the concentration of copper in the leachate showed a continuous increase over time, where the pattern is comparable to column leaching.

The efficiency of the heap leaching operations by *A. ferrooxidans* is affected by multiple factors *viz.*, the geometry of the heap, particle size, porosity, air supply, iron content, the acidity of the media used, liquid supply system, etc. [41]. The iron-oxidizing bacteria such as *A. ferrooxidans* interact with copper sulfide ores and colonize the heap bed. The colonization and growth of microbes result in the leaching of metals via an indirect mechanism. The reactive species generated migrate to the different layers of the heap-bed [42]. Hence proper aeration and irrigation of the bed at regular intervals ensure a regular supply of nutrients for microbes in the different layers of the leaching bed.

The bulk migration of reactive species and dissolved metal ions through the bed is high in initial irrigation cycles when the heap is not channelized. With time, the microbes colonize the bed and percolation channels are formed [43], hence a surge in the recovery of the copper in the initial days is obtained (fig. 9).

The heat produced in the bed can affect microbial growth and colonization and the temperature inside the bed can have a substantial effect on the leaching capabilities of the bed. Since many of the reactions occurring in the heap bed require oxygen, the air unavailability directly affects the leaching and indirectly as the aeration has been linked to the escape of heat [44]. The height and width of the column at smaller scales do not require aeration as heat and air can be trapped and released from the sides.

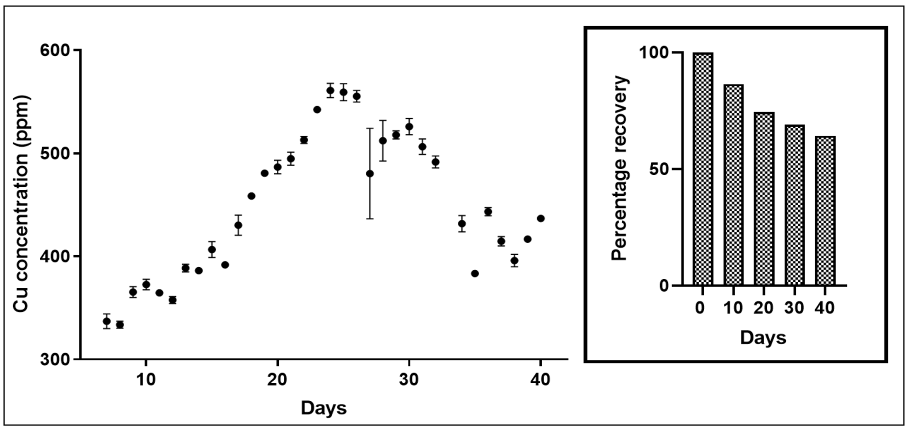


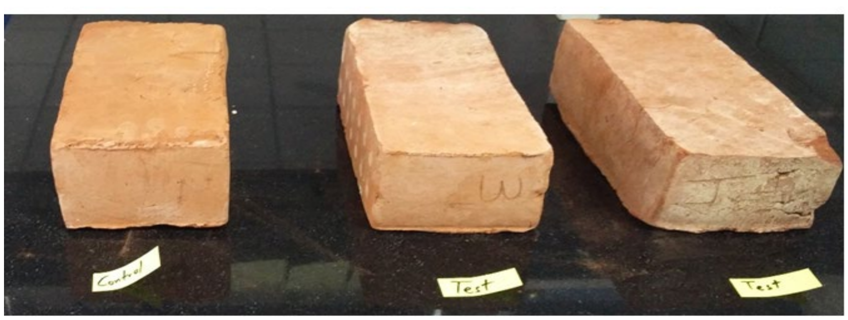
Fig. 9 Copper concentration in heap leaching study. Copper concentration in the leachate collected. The Inset figure shows the percentage of copper remained in the tailing waste as measured by XRF analysis

The study was conducted in 9K medium, pH 2, and ambient temperature conditions. The initial inoculum size used was 1% *v/v* culture of *Acidithiobacillus ferrooxidans* containing 2 x 10^9 cells ml^{-1}. The dots show copper concentration (on the vertical axis) at definite time points. Fig. 9, inset shows residual copper content in the tailing waste in heap at different time points.

The maximum copper concentration in leachate was found on day 24^{th} and later it declined gradually. The copper concentration in the leachate at various time points is depicted in fig. 9. The residual concentration of copper in the heap was calculated at different time points and measured by ED-XRF study, after bioleaching, was used for calculating percentage copper recovery. After 40 days of the study, the copper recovery from the treated copper tailing waste was found to be 64.28% *w/w* (fig. 9, inset).

G. Use of Tailing Waste to Cast Clay Bricks

Clay bricks were cast according to BIS (Bureau of Indian Standards) size recommendations. A ten percent mixed proportion of treated tailing was taken. The bricks were oven dried at 55°C for 3 days. The bricks were then burnt in a furnace for 24 hours at 950°C.



A B C

Fig. 10 Clay bricks were cast according to BIS (Bureau of Indian Standards) size recommendations

The normal clay bricks and the bricks with untreated tailing waste were also cast in similar ways to act as a control in the experiment (fig. 10). To study the possible leaching of metals the bricks were dipped in water for 24 hours followed by sample collection for release of any metal. A comparison of the test brick and the control brick suggests that the compressive strength of the test brick was comparable to those of the normal brick. It also shows no traces of copper in the leachate (Table I). This study suggests that it could be a viable strategy to dispose of the waste generated after bioleaching of copper tailing.

Ten percent mixed proportion of treated tailing from the column was taken. The bricks were then burnt in a furnace for 24 hours at 950℃. The different bricks cast are Brick A – Normal clay brick, Brick B – clay + tailing waste, and Brick C – Clay + treated tailing waste.

TABLE I COMPARISON OF COMPRESSIVE STRENGTH OF CLAY: TAILING WASTE MIXED PROPORTION BRICKS

Type of Brick	**Compressive strength (kg/cm^2)**	**Cu concentration in leachate (mg/l)**
100 % clay	35.1	Nil
Clay + tailing waste (90:10)	36.2	0.2
Clay + bioleached waste (90:10)	34.6	Nil

The bricks were oven dried for 72 hours and burnt for 24 hours at 950℃ for 24 hours before measurement of compressive strength and leaching of copper.

IV. CONCLUSION

The study investigated the use of bioleaching technology for the recovery of copper from low-grade copper tailing waste present in the tailing pond of the Khetri copper mine area. The study concludes that high waste concentration adversely affects the solubilization and recovery of copper thereof. A copper recovery of >94% from tailing waste can be obtained by *A. ferrooxidans* mixed with a 2% (w/v) concentration of tailing waste solution prepared with K9 culture media.at pH2.0. Further, the waste generated after the bioleaching can be successfully utilized in casting clay bricks with better compressive strength, hence disposing of the treated waste in an eco-friendly way.

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