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Passivation Layer Reduction of Chalcopyrite for Sustainable Extraction of Copper Using Additives Assisted Bioleaching: A Mini Review

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Abstract

Nowadays, rich copper ore grades have been exploited and thus mining companies have been increasing their interest to liberate or extract copper from low grade copper ores, mainly from chalcopyrite. However, chalcopyrite ore is the future source of copper, its extraction is hindered due to the formation of passivation film, which consequently inhibiting the leaching efficiency of copper. This review paper sheds light on and critically assesses the recent advancements in passivation film reduction strategies to enhance the recovery rate of copper from chalcopyrite using a synergetic effect of bioleaching and external additives. The microorganisms used in bioleaching enhance the surface property of chalcopyrite due to their unique capabilities of biofilm formation, which enhances adhesion properties. Addition of external additives during the bioleaching improve the microbial activities the ore by providing an active surface for microbial attachment, which boosts dissolution of the chalcopyrite and consequently reduces the formation of passivation film. According to their optimum temperature, microorganisms used in bioleaching classify as mesophilic, moderate thermophilic and extremely thermophilic microorganisms. Mesophilic microorganisms are dominated in bioleaching. This review paper aims as a compiled reference material for future studies towards high recovery of copper from chalcopyrite by modifying the surface property of the ore. Recognizing the rapid advancement and importance of bioleaching in the extractive metallurgy industry (mainly in the extraction of copper from low grade copper sulphide ores), this review paper serves for practitioners as a crucial and technically advanced source for future researches in chalcopyrite bioleaching, techniques for passivation layer reduction of chalcopyrite and current advancements in bioleaching.

1. Introduction

Copper is a metallic element having an atomic number of 29, has been one of the key materials mined and utilized by human being since the ancient time for making items such as ornaments and coins during ancient civilizations. Through the history, copper has played a significant role in enhancing societal living standards. Its use in tool-making can be tracked back 10,000 years ago [1]. During the 18th and 19th centuries, the copper industry has been made a significant transformation, driven by new innovations and progresses in electricity and magnetism by many scientists, such as Faraday, Ampere and Ohm. Even today, copper remains integral to human day-to-day activities. Copper is a critical component in modern energy production, including solar cells, wind, thermal, and hydro energy. Additionally, copper is extensively used in construction, power transmission, electrical wiring, anticorrosive coatings, refrigeration, alloying, and heat exchangers [2].

The global demand for copper, both in quantity and quality, is steadily rising due to its widespread use in industrial, energy, electronics, biomedical, ornamental, and domestic applications. Experts predict that by the 2050s, the demand for copper could increase by 275% to 350 % [3].

Copper is mainly occurred in the Earth's crust in the form of sulphide and oxide ores, with sulphide ores accounting for 80 % of the copper resources. From these ores, chalcopyrite constitutes 70 % of the world's copper deposits [4].

Traditional (conventional) copper extraction methods, which are pyrometallurgy and hydrometallurgy, have substantial environmental and health impacts due to the emission of pollutant gases and harmful chemicals. As high-grade mineral ores are becoming depleted, mining companies are increasingly focusing on extracting copper from low-grade ores [5]. Similarly, the exploitation of high-grade copper ores has led to a growing reliance on bioleaching for liberating (extracting) copper metal from low-grade sulphide ores to meet the growing demand for the metal. Although bioleaching is a promising method for copper recovery from chalcopyrite, it faces challenges [6]. The flow sheet of conventional metal extraction (pyrometallurgy) and bioleaching techniques is shown in Fig. 1 [32].

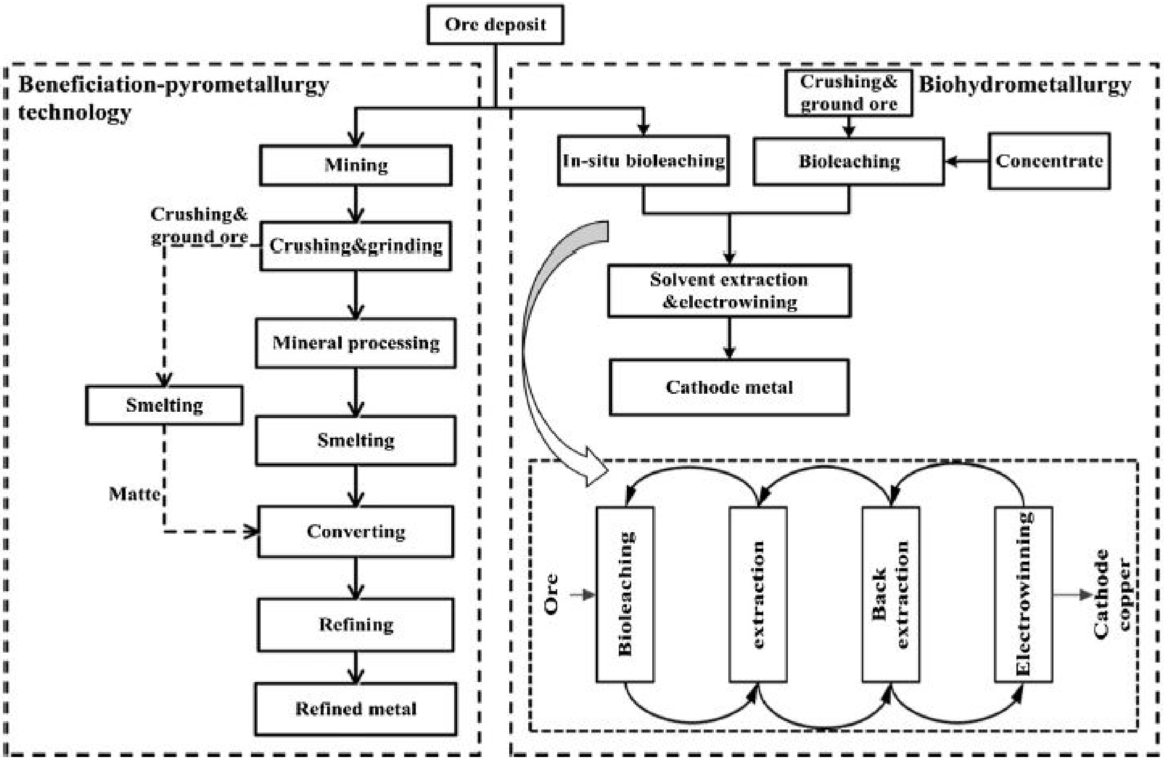

Fig. 1 *Flow sheet of conventional metal extraction (pyrometallurgy) versus bioleaching [32]*

Chalcopyrite tends to form a passivation film under various oxidative leaching conditions, which hinders copper dissolution and leads to low recovery rates [7]. As a result, mineral processing companies are seeking alternative leaching techniques that can enhance copper recovery by reducing passivation films through cost-effective, energy-efficient, and environmentally friendly methods. Currently, the most effective approach to improving chalcopyrite ore recovery is the combined use of bioleaching and external additives [2,4].

Nowadays, several scientists have used microorganisms to liberate (recover) minerals from low grade sulphide ores using bioleaching [8].

Bioleaching is an oxidative solubilization of sulfide minerals through the action of microorganisms. It is a leaching technique in which insoluble minerals convert to soluble (dissolving minerals) with the help of microorganisms. The primary microorganisms involved in bioleaching are chemolithoautotrophs, which utilize inorganic sources of energy and carbon. These organisms derive energy from ferrous iron and/or reduced sulfur compounds, which are typically present in ores. The microbial activity generates ferric ions, which are powerful oxidants that facilitate the dissolution of copper sulfides, releasing copper into the solution. Additionally, the reduced sulfur compounds formed during the oxidation of ferric ions are converted into sulfuric acid by the microorganisms. This process helps maintain a low pH, which is crucial for the survival of the microorganisms and the solubility of ferric iron. Furthermore, the reduced iron produced during the mineral dissolution is subsequently re-oxidized by these microorganisms [9].

Based on the optimum temperature required for their growth, the microorganisms used in bioleaching are classified into three groups: mesophilic microorganisms (which grow in the temperature range of 20 °C to 39 °C), moderately thermophilic microorganisms (which grow in the temperature range of 40 °C to 60 °C) and extremely thermophilic (which grow at the temperature higher than 60 °C) [18]. A detailed explanation of these microorganisms and examples are discussed in part four (4) of this review paper.

Bioleaching is among the promising technologies that is not only environmentally friendly but also very effective in cost. Bioleaching has a significant advantage over the traditional leaching techniques due to its ability of extraction of high value metals from low grade ores, tailings and electronic waste streams in an economical manner and without affecting the ecology. In bioleaching, no hazardous chemicals (such as acids, cyanides and mercury) are used for extraction of metals, unlike in hydrometallurgy. Additionally, there is no emission of pollutant gases, such sulphur dioxide to the environment as seen in pyrometallurgy [2,6,7]. Despite these advantages, bioleaching also has its own drawbacks. Currently, bioleaching is effective for extraction of metals from its sulphide ores. There are no advancements if bioleaching works for extraction of metals from their oxide ores. In addition, bioleaching is also limited to the extraction of few metals, mainly copper, gold, silver, lead and zinc. Another drawback of bioleaching is a slow process often taking time from weeks to months to breakdown the ores and dissolve the metals [57,58].

In this review paper, the bioleaching mechanisms of minerals, microorganisms involved in bioleaching, the attachment between microorganisms and minerals, bioleaching of chalcopyrite, passivation layer reduction of chalcopyrite and enhancement of bioleaching activity of chalcopyrite are discussed.

2. Methodology

A systematic literature review (SLR) was conducted to write this review paper. The methodological style used in this manuscript was based on a search and selecting a recent peer reviewed articles and other literatures. Based on the literature type, 58 literatures are selected. The selection of literature was done based on search engine from scientific journal websites such as Science Direct, Google Scholar and Research Gate. This review paper focused on publication of most relevant articles and covered the area of bioleaching, microbial attachment to the metal ore, passivation film and synergetic effect of bioleaching and external additives for mitigation of passivation film towards high recovery of copper. The keywords used for searching the papers on the scientific websites are biofilm; chalcopyrite recovery; bioleaching of low grade ores; passivation film; synergetic effect of bioleaching and external additives. More than 75 were retrieved and finally only 58 recent and relevant literatures were selected to prepare the manuscript. Recently published, peer reviewed articles and articles which are relevant to bioleaching was the main criteria for the selection of articles used to write this review paper.

3. Bioleaching Mechanisms

In bioleaching, the microbial mobilization of metals occurs by two primary mechanisms: contact and noncontact (or indirect) bioleaching [10,11]. In contact bioleaching, microbes directly interact with the mineral surface, oxidizing the sulphidic sulphur to elemental sulphur and liberating the metal as metal sulphate. The microbes oxidize metal sulphides by directly extracting electrons from the reduced minerals. This mechanism involves a direct interaction between the microorganisms and the mineral surfaces. The oxidation of mineral sulphides to sulphates occurs through several enzymatically catalyzed steps. Contact bioleaching is often preferred because of the direct interaction between microorganisms and minerals [12,13]. Reaction 1 represents the contact bioleaching mechanisms of metal sulphide ores.

$$\mathrm{MS} + \mathrm{H_2SO_4} + 0.5\mathrm{O_2} \xrightarrow{\text{Bacteria}} \mathrm{MSO_4} + \mathrm{S^o} + \mathrm{H_2O} \tag{1}$$

$$\mathrm{S^o} + 1.5\mathrm{O_2} + \mathrm{H_2O} \xrightarrow{\text{Bacteria}} \mathrm{H_2SO_4} \tag{2}$$

M stands for the valuable metal to be recovered from the ore.

Several copper sulphide ores such as chalcocite, covellite can be oxidized by contact bioleaching using *acidithiobacillus ferrooxidans* [12].

In contrast, noncontact bioleaching involves microbes producing a lixiviant by oxidizing ferrous ion present in the minerals. The generated ferric ion then chemically oxidizes the metal-containing ore, reducing itself back to ferrous ion. In this process, the microorganisms do not need to directly contact the metal surface; instead, they generate chemical agents that facilitate the oxidation. The reduced metals are oxidized by ferric ion, which is produced through the microbial oxidation of ferrous ion compounds found in the minerals [14]. The schematic diagram for contact and noncontact bioleaching is shown in Fig. 2 [15].

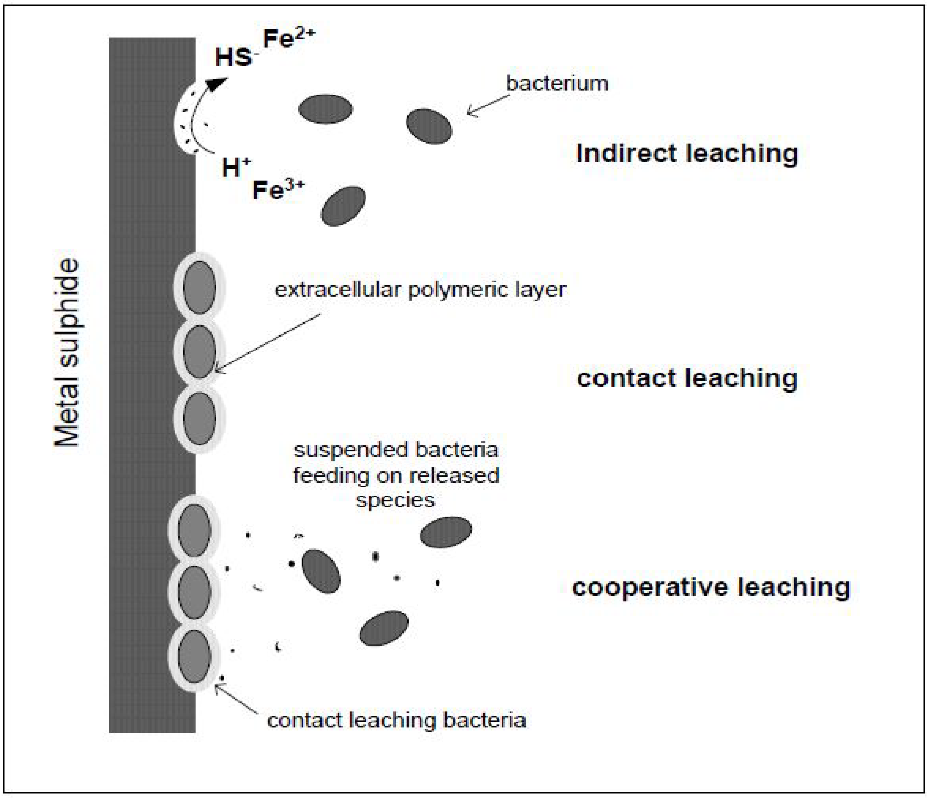

Fig. 2 *Schematic visualization of noncontact/indirect and direct bioleaching of metal sulphide [15]*

Reaction 3 represents the noncontact bioleaching of metal sulphide ores.

$$MS + H_2SO_4 + 0.5O_2 \xrightarrow{\text{Bacteria}} MSO_4 + S^o + H_2O \tag{3}$$

$$S^o + 1.5O_2 + H_2O \xrightarrow{\text{Bacteria}} H_2SO_4 \tag{4}$$

Although contact and noncontact mechanisms are distinct, a complete understanding of metal bioleaching processes has yet to be established. Both methods have been used to extract copper from low-grade copper ores. However, it's been noted that contact metal oxidation occurs more slowly than the noncontact oxidation mechanism [12].

In the bioleaching process, minerals undergo dissolution as a result of being targeted by their constituents, thereby generating energy for microorganisms. This energy generation occurring through oxidation (progresses via an intermediary reaction pathway). Within the scope of noncontact mechanisms, two distinct mechanisms have been projected for the oxidation of metals [16]. The first mechanism is thiosulphate mechanism, encompasses metal sulphides which can be solubilize in acid, such as molybdenite and pyrite. In this particular mechanism, thiosulphate ion serves as intermediary agent facilitating the solubilization of acid-insoluble metal sulphides upon interaction with ferric iron, ultimately yielding sulphate as a final product [8,11]. The thiosulphate bioleaching mechanism is shown in Fig. 3a [13].

An example of breaking reaction of pyrite using thiosulphate mechanisms is presented as follow [13].

$$FeS_2 + 6Fe^{3+} + 3H_2O \rightarrow S_2O_3^{2-} + 7Fe^{2+} + 6H^+ \tag{5}$$

$$S_2O_3^{2-} + 8Fe^{3+} + 5H_2O \rightarrow 2SO_4^{2-} + 8Fe^{2+} + 10H^+ \tag{6}$$

The second mechanism is polysulphide mechanism involves the dissolution of minerals containing acid-soluble metal sulphides, such as chalcopyrite. In this mechanism, the dissolution occurs through the collective attack by ferric ion and protons. Polysulphide mechanism results the solubilization of elemental sulphur as an intermediate. In polysulphide bioleaching mechanisms, the polysulphide ions serves as electron donors for microbial metabolism [17]. The polysulphide bioleaching mechanism is shown in Fig. 3b [13].

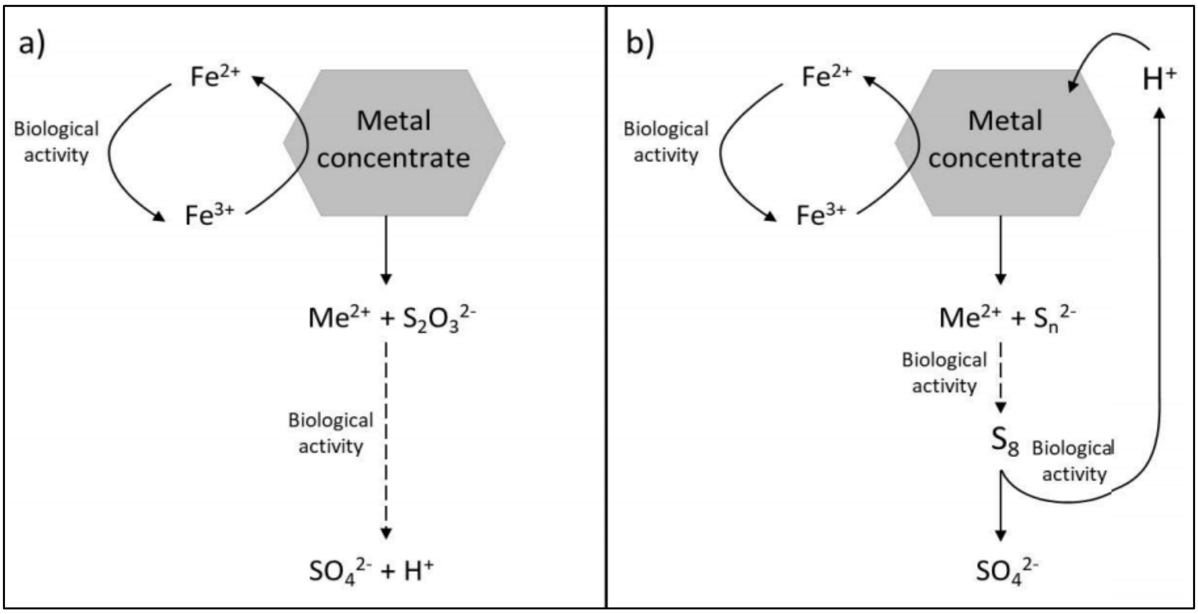

Fig. 3 *Noncontact mechanisms of bioleaching proceed by (a) thiosulphate; (b) polysulphide mechanisms. The dashed lines show the existence of intermediate sulphur compounds [13]*

The reaction for polysulphide mechanism for chalcopyrite is presented in the chemical Equation 7. According to this mechanism, chalcopyrite is initially attacks by the protons that release metallic ions and hydrogen sulphides. Then the hydrogen sulphide is oxidized by ferric ions to produce hydrogen sulphide radicals (H_2S^{*+}) [17].

$$CuFeS_2 + 4H^+ \rightarrow Cu^{2+}\ Fe^{2+} + 2H_2S \tag{7}$$

$$H_2S + Fe^{3+} \rightarrow Fe^{2+} + H_2S^{*+} \tag{8}$$

$$H_2S^{*+} + H_2O \rightarrow H_3O^+ + HS^* \tag{9}$$

$$2HS^* \rightarrow H_2S_2 \tag{10}$$

In bioleaching, the primary role of microorganisms is to speed up the oxidative breakdown of sulphide ores by converting ferrous into ferric ion [18].

When iron oxidizer microorganisms oxidize ferrous to ferric iron, the generated ferric iron is a strong oxidant having 0.77 V reduction potential. Iron (III) is a suitable oxidizing agent to leach copper from low grade ores. The bioleaching activity of these microorganisms can improve by the addition of external iron (II), iron (III) or pyrite [19].

4. Microorganisms Involved in Bioleaching

According to the optimum temperature for their growth, the microorganisms participated in bioleaching are classified into three groups: mesophilic, moderate thermophilic and extremely thermophilic microorganisms [18].

4.1 Mesophilic Microorganisms

Mesophilic microorganisms are the first microorganisms used in the mining industry. They grow at the range of temperature between 20 ^{o}C to 39 ^{o}C. These microorganisms are adapted for leaching of copper ores that have a low grade [18]. Mesophilic microorganisms have the capacity for fixing of carbon dioide by oxidizing the ferrous iron or reduced sulphur to ferric iron and sulphuric acid respectively. Metal sulphide solubilization by ferric iron or sulphuric acid lowers the pH of the solution and accordingly, the solubilization of metals rises. Low pH is a preferable condition for microbial leaching, because it helps to stay the metals in solution. Iron and sulphur oxidizing *Acidithiobacillus ferrooxidans*, iron oxidizing *Leptospirillum ferriphilum* and *Leptospirillum ferrooxidans* and sulphur oxidizing *Acidithiobacillus thiooxidans* are among the most widely used mesophilic metal solubilizing microorganisms involved in bioleaching. These microorganisms have low rate of metal sulphide dissolution capacity compared to thermophilic microorganisms [20].

Acidithiobacillus ferrooxidans (formerly known as *Thiobacillus ferrooxidans*) is the first microorganism used in bioleaching. The use of this microorganism in the hydrometallurgy industry dates back to 1950s when it identified and cultured by Colmer, Hinkle and Temple. *Acidithiobacillus ferrooxidans* is a gram negative chemolithotroph acidophilic bacteria, grows at high acidic environment. *Acidithiobacillus ferrooxidans* gains its energy from the oxidation of ferrous iron and sulphur containing minerals for their growth [18,48]. *Leptospirillum sp.* (*Leptospirillum ferriphilum* and *Leptospirillum ferrooxidans*) are gram-negative and chemolithotrophic microorganisms gain their energy by the oxidation of iron. *Leptospirillum sp.* are acidophilic bacteria (exist in extremely acidic environment). These microorganisms have a potential for solubilisation of metals from their sulphide ores [18,49]. *Acidithiobacillus thiooxidans* (formerly known as *Thiobacillus thiooxidans*) is a gram-negative and rod-shaped bacteria that gets their primary source of energy from sulphur [18,50]. Several mesophilic microorganisms involved in bioleaching with their optimum temperature and optimum pH is given in Table 1.

Table 1 *Mesophilic microorganisms involved in bioleaching [4,18,20,21,48-50]*

Microorganism	Optimum Temperature (°C)	Optimum pH	Microorganism	Optimum Temperature (°C)	Optimum pH
Acidithiobacillus ferrooxidans	28-35	2.0	Alicyclobacillus tolerans	37	2.5
Acidithiobacillus thiooxidans	28-30	2.0-3.0	Acidiferrobacter thiooxydans	38	2.0
Sulfobacillus benefaciens	39	1.5	Acidithiobacillus albertensis	25-30	3.5-4.0
Leptospirillum ferrooxidans	28-30	1.5-3.0	Acidithiobacillus ferrivorans	27	2.5
Leptospirillum ferriphilum	30-37	1.3-1.8	Ferrimicrobium acidiphilum	35	2
Acidiphilium cryptum	35-41	3.0	Alicyclobacillus disulfidooxidans	35	1.5-2.5
Ferroplasma acidiphilium	35	1.7	Thiomonas cuprina	30-36	3.5-4.0

4.2 Moderate Thermophilic Microorganisms

Moderate thermophilic microorganisms are heterotrophic microorganisms play an important role in bioleaching. These microorganisms grow in the temperature ranges from 40 °C to 60 °C [21,22]. They grow in the presence of yeast extract and use ferrous ion as a source of energy. *Acidimicrobium ferrooxidans*, *Acidithiobacillus caldus*, *Sulfobacillus thermosulfidooxidans* and *Sulfobacillus thermotolerans* are some of the most widely used microorganisms used in bioleaching [23].

Acidimicrobium ferrooxidans is authotrophic, gram-positive bacterium. *Acidimicrobium ferrooxidans* is a ferrous iron oxidizing bacterium that survive at lower pH (pH = 2) and moderate temperature (45 °C to 50 °C) environments[23,51]. *Acidithiobacillus caldus* is one of the most commonly used bacterium in bioleaching. It is one of the dominant bacterium has a potential of oxidizing reduced inorganic sulphur. It is acidophilic (exists in acidic environment) and moderately temperature microorganism [23,52]. *Sulfobacillus thermosulfidooxidans* is a genus *Sulfobacillus* bacteria characterize by their rod-shape, gram-positive, non-motile, endospore forming, acidophilic and moderate temperature bacterium. *Sulfobacillus thermosulfidooxidans* is sulphur oxidizing bacterium [23,53]. *Sulfobacillus thermotolerans* is aerobic, endospore forming, gram positive and acidophilic chemolithotrophic bacteria. *Sulfobacillus thermotolerans* gains its energy by the oxidation of ferrous iron [23,54]. Varieties of thermophilic microorganisms involved in bioleaching is given in Table 2.

4.3 Extremely Thermophilic Microorganisms

The extremely thermophilic microorganisms grow above 60 °C temperature. Extremely thermophilic microorganisms have a high rate of metallic dissolution capacity. *Acidianus sulfidivorans* and *Metallosphaera* *sedula* are some of the most widely used of extremely thermophilic microorganisms used in bioleaching [24]. *Acidianus sulfidivorans* is extremely acidophilic (survives up 0.3 pH) and extremely high temperature (up to 83 °C). It classifies in obligately chemolithotrophic in a species of archaeon. It is non-motile, gram negative, irregular shape properties and oxidize sulphur element. It was originally isolated from Solfatara in Lihr Island[24,55]. *Metallosphaera sedula* is extremely thermoacidophilic archaean grouped in the species *Metallosphaera.* It was first isolated from volcanic field located in Italy. *Metallosphaera sedula* is iron oxidizing microorganism [24,56]. Varieties of extremely thermophilic microorganisms involved in bioleaching is given in Table 3.

Table 2 *Moderate thermophilic microorganisms involved in bioleaching [4,21-23,51-54]*

Microorganism	Optimum Temperature (°C)	Optimum pH	Microorganism	Optimum Temperature (°C)	Optimum pH
Acidimicrobium ferrooxidans	45-50	2.0	Picrophilus torridus	60	0.7
Acidiplasma cupricumulans	54	1-1.2	Sulfobacillus sibiricus	55	2.2-2.5
Acidithiobacillus caldus	45	2.0-2.5	Sulfobacillus acidophilus	45-50	2.0
Ferrithrix thermotolerans	43	1.8	Sulfobacillus thermosulfidooxidans	40-48	1.7-2.4
Ferroplasma acidarmanus	42	1.2	Sulfobacillus thermotolerans	40	2.0-2.5
Alicyclobacillus GSM	47	1.8	Thermoplasma acidophilum	59	1.0-2.0
Thermoplasma volcanium	59-60	2.0	Sulfurococcus yellowstonensis	60	2.0-2.6

Table 3 *Extremely thermophilic microorganisms involved in bioleaching [4,22,24,55,56]*

Microorganism	Optimum Temperature (°C)	Optimum pH	Microorganism	Optimum Temperature (°C)	Optimum pH
Metallosphaera prunae	up 75	2.0-3.0	Metallosphaera hakonensis	70	3.0
Thermoplasma volcanium	59-60	2.0	Alicyclobacillus GSM	47	1.8
Acidianus sulfidivorans	74	0.35-3.0	Metallosphaera sedula	75	2.0-3.0
Acidianus infernus	up to 90	2.0	Sulfolobus acidocaldarius	70-75	2.0-3.0
Acidianus brierleyi	up to 70	1.5-2.0	Sulfolobus metallicus	65	2.0-3.0
Sulfolobus tokodaii	80	4.0	Sulfurococcus mirabilis	70-75	2.0-2.6

5. Microorganisms-Mineral Surface Attachment

In bioleaching, the attachment between microorganisms and mineral surface facilitates biooxidation, thereby enhancing the dissolution of metals from the mineral matrix [25,26]. This microbial attachment increases the surface area available for bioleaching reactions, resulting in a higher rate of metal dissolution due to the extensive interaction between microorganisms and minerals [27,28]. These interactions occur on two levels: initially through physical sorption driven by electrostatic forces, and subsequently through chemical sorption involving chemical bonding between the cells and minerals. During chemical sorption, extracellular metabolites are produced and released near the attachment site. Microorganisms tend to adhere selectively to specific sites of crystal imperfections on the mineral surface rather than uniformly across the entire surface. This selective adherence promotes electrochemical reactions that facilitate metal solubilization [29,30]. The schematic diagram for microbial and metal ore attachment during bioleaching is depicted in Fig. 4 [15].

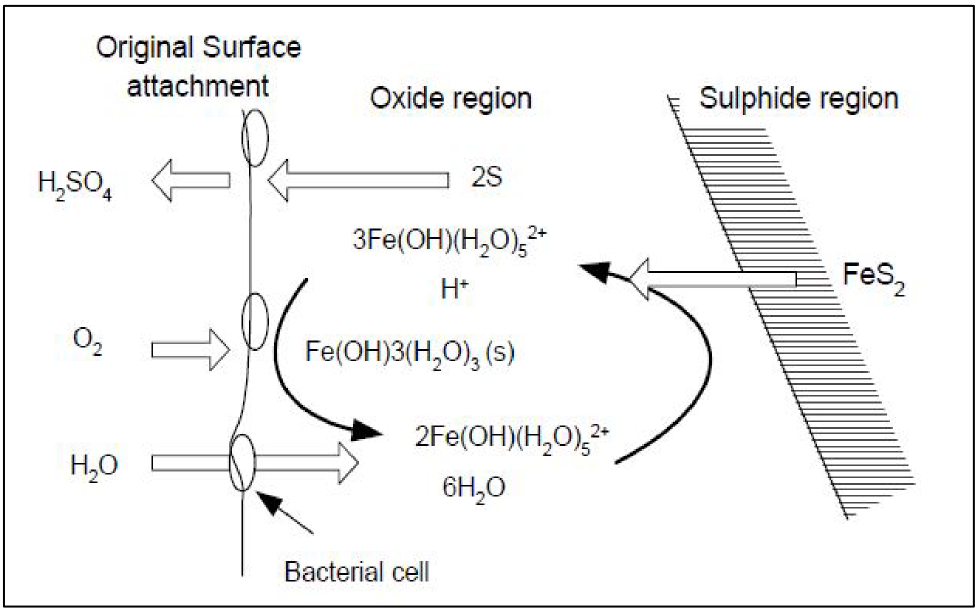

Fig. 4 *Schematic diagram of bacterial and ore attachment during bioleaching [15]*

6. Bioleaching of Chalcopyrite

The bioleaching process of chalcopyrite is fundamentally governed by electrochemical principles [31,32]. Chalcopyrite exhibits very slow dissolution in acidic solutions, primarily due to the creation of a protective passivation film on its surface. This sluggish dissolution can be enhanced through bioleaching and the addition of external additives [33,34]. Chalcopyrite bioleaching involves a series of interconnected biochemical and chemical reactions facilitated by microbial activity. Initially, microbial cells adhere to the surface of chalcopyrite particles, forming biofilms that create a favorable microenvironment for enzymatic reactions [35]. The oxidation of ferrous to ferric ions by microbial iron oxidizers plays a fundamental role in chalcopyrite bioleaching. The generated ferric ions oxidize sulfur in chalcopyrite to water-soluble sulfate ions. This process releases copper ions, which can then be recovered through solvent extraction or ion exchange processes [36,37]. The schematic diagram of chalcopyrite bioleaching process is shown in Fig. 5 [32].

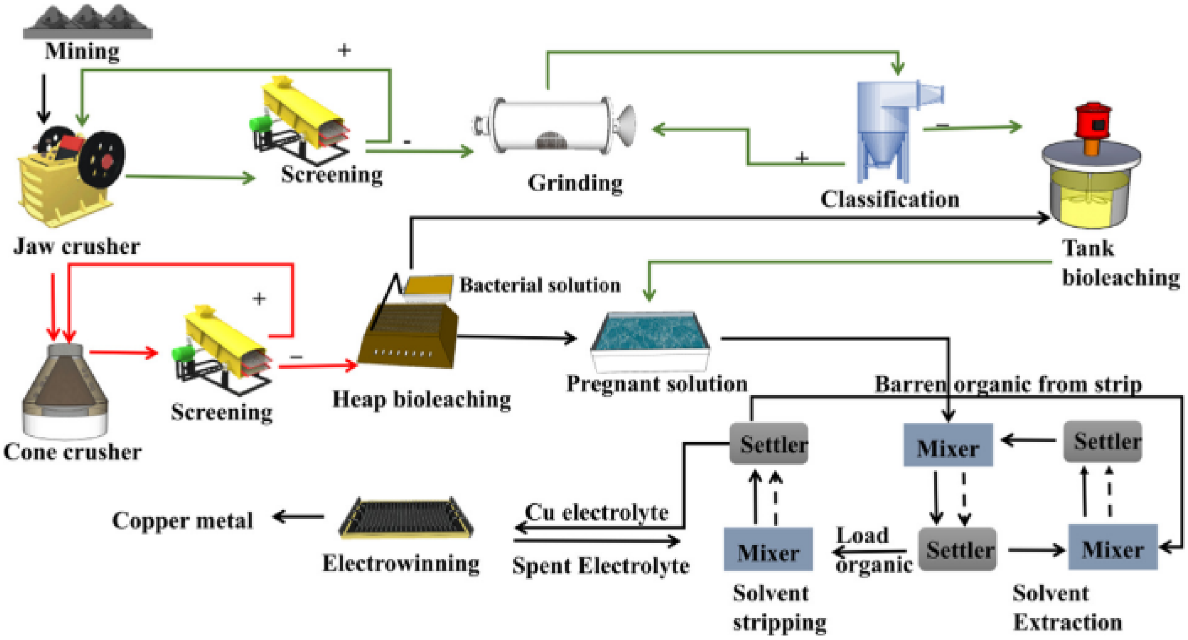

Fig. 5 *Schematic diagram of bioleaching of chalcopyrite [32]*

The overall bioleaching reaction of chalcopyrite is represented as follows:

$$CuFeS_2 + 5O_2 + 4H^+ \xrightarrow{\text{Bacteria}} Cu^{2+} + Fe^{3+} + 2SO_4^{2-} + 2H_2O \tag{11}$$

Additionally, chalcopyrite dissolution involves a concurrent chemical reaction mediated by ferric ions [37].

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 2S + 5Fe^{2+} \tag{12}$$

The dissolution behavior of chalcopyrite has been extensively studied using electrochemical analysis, particularly cyclic voltammetry [38]. In chalcopyrite bioleaching, the redox potential typically reaches an extreme value of around 0.8 V [32]. Cathodic and anodic peaks of chalcopyrite electrodes is shown in Figure 6 [32].

The results show the presence of both cathodic and anodic peaks in the positive and negative scan voltammograms. Five cathodic peaks (C1, C2, and C3 in the positive scan, and C2 and C3 in the negative scan) and nine anodic peaks (A1, A2, A4, A5, and A6 in the positive scan, and A3, A4, A5, and A6 in the negative scan) were detected. The study also showed a decrease in anodic and cathodic current signals due to the development of the passivation film on the surface of chalcopyrite after bioleaching [32].

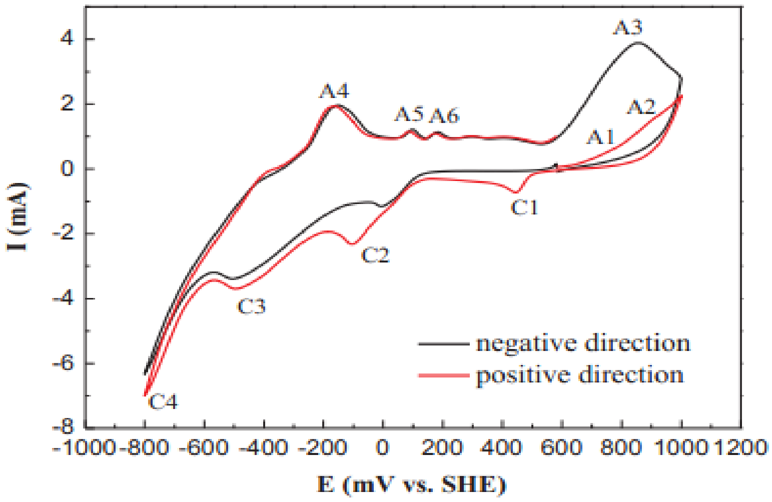

Fig. 6 *Chalcopyrite's cyclic voltammograms in a medium with Leptospirillum ferriphilum [32]*

7. Passivation Film Reduction and Enhancement of Bioleaching Activity of Chalcopyrite

Bioleaching of chalcopyrite is characterized by slow activity, primarily due to the generation of passivation film on the chalcopyrite surface. Passivation film is very thin thickness cover (in the range of micrometer) on the surface a bulk material. This passivation during the dissolution process results in reduced kinetics. Key components of these passivation films include jarosites, polysulfides, insoluble sulfates and elemental sulfur [4,32]. To mitigate passivation and enhance chalcopyrite dissolution, specific additives are incorporated into the bioleaching process. These additives catalyze the activity of mesophilic or thermophilic microorganisms, breaking down the passivation film on chalcopyrite. Often, these additives interact with the passivation film, facilitating its degradation and thus promoting higher copper dissolution. Mechanical agitation can also erode the passivation film. Currently, additives such as activated carbon, silver ions, L-cysteine, quartz, and sodium chloride are employed to enhance chalcopyrite bioleaching and minimize the passivation film [39,40]. Researchers have been explored various techniques to enhance chalcopyrite bioleaching, focusing on increasing microbial attachment and reducing passivation [41].

Addition of pretreated sargassum to bacterial consortia significantly improved microbial and copper ore attachment, resulting in a copper recovery of 82.99 %. The pretreated sargassum acts as a scaffold for biofilm formation by providing a substrate for bacterial consortia, thereby facilitating microbial and copper ore attachment [42].

Arsenopyrite is another additive that significantly influences chalcopyrite dissolution during bioleaching. Addition of arsenopyrite promoted chalcopyrite dissolution and reduced the passivation film. When arsenopyrite and chalcopyrite minerals come into interaction, the higher rest potential of arsenopyrite induces a galvanic interaction, enhancing chalcopyrite dissolution [43].

Quartz addition during chalcopyrite bioleaching has been shown to reduce the passivation film and promote ore dissolution. Addition of 50 g/L of quartz concentration during chalcopyrite bioleaching with *Acidithiobacillus ferrooxidans* increased the rate of dissolution of copper by 20 % compared to leaching of chalcopyrite without quartz. The increment of the dissolution is due to the ability of quartz to decrease the jarosite on the surface of the chalcopyrite by the action of rubbing between the quartz fine particles and the chalcopyrite. Addition of quartz particles during bioleaching of chalcopyrite using *Acidithiobacillus ferrooxidans* helps to enhance the microbial of the microorganism by providing an active surface for microbial attachment and biofilm formation [44].

Silver ions also play a crucial role in improving chalcopyrite bioleaching. Silver-bearing ores, such as silver sulphide and silver sulphate release silver ions (Ag^+) which enhance chalcopyrite bioleaching and reduce the passivation film. Adding of silver bearing ores improves the leaching efficiency of copper from 5.37 % (without silver) to 10.03 %. The silver ions accelerate chalcopyrite dissolution by promoting electron transfer on its surface [45].

Adding of L-cysteine during bioleaching with *Leptospirillum ferrooxidans* reduces passivation film formation on chalcopyrite, enhancing dissolution [41]. Adding of NaCl during bioleaching using extreme thermophile *Acidianus manzaensis* significantly improves chalcopyrite dissolution by eliminating elemental sulfur accumulation on the surface. Elemental sulfur buildup lowers dissolution rates, but adding 0.66 g/L of NaCl reduced elemental sulfur accumulation from 25.4 % to 30.0 %, increasing copper ion concentration from 2.37 g/L to 2.67 g/L [46].

Activated carbon is another effective additive for reducing chalcopyrite passivation during bioleaching. Activated carbon strongly speeded up chalcopyrite dissolution by preventing passivation film formation. This effect is due to the galvanic interaction between activated carbon and chalcopyrite [47].

8. Recommendations

Passivation film reduction of chalcopyrite is a crucial method to enhance the recovery of copper from the uneconomical resources. Many auspicious researches have done to reduce the passivation film from the surface of the minerals in order to enhance the recovery of copper. A combined utilization of bioleaching and external additives is an effective method has been done for reduction of the passivation film. However, many researches have been done to reduce the passivation film from chalcopyrite, several works should be done for the future to strongly reduce the passivation film and optimize the dissolution of copper. Some of the recommendations suggested for the future researchers to reduce the passivation film and enhance dissolution rate of copper are explained as follow:

1. Using thermophilic bacterial consortia and external additives: A mesophilic bacterial consortia have been used in copper bioleaching process in previous works. However, due to the slow kinetics of mesophilic microorganisms, they do not provide high dissolution copper. Using thermophilic bacterial consortia with external additives can increase the dissolution of the copper.
2. Design innovative bioreactors: Exposing the sulphide minerals to the oxidative environment promotes a formation passivation film. So, designing a modern and innovative bioreactor will reduce the passivation film of chalcopyrite by maintaining optimal conditions for microbial activities.
3. Using nanoparticles: Nanoparticles have high surface area to the volume ratio. The nanoparticles interact with large surface area of the chalcopyrite. Hence, using nanoparticles as catalysts or additives enhance the chalcopyrite dissolution by breaking the passivation film. Furthermore, nanoparticles can catalyze reactions involved in chalcopyrite passivation film breakdown, stimulating bioleaching kinetics.

9. Conclusion

In conclusion, this review paper highlights the significant progress made for passivation film reduction to rise the recovery of copper from chalcopyrite ore. Through the combined utilization of bioleaching techniques and external additives, researchers have successfully mitigated passivation film, thereby improving the leaching efficiency of copper. The synergistic effects observed between bioleaching and several additives (catalysts), such as activated carbon, silver ion, L-cysteine, quartz and sodium chloride, have been demonstrated promised outcomes in improving the recovery rate of copper from chalcopyrite. However, many works have been done on passivation film reduction of chalcopyrite, further works should be continued to optimize the recovery of copper from chalcopyrite. Nanoparticles can potentially inhibit the formation of passivation film due to their property of high surface area to volume ratio

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Conflict of Interest

The authors reported no potential conflict of interest.

Author Contribution

Elias Tadesse Fisha: ***conceived and wrote the manuscript****. Daniel Toyin Oloruntoba, Oladunni Oyelola Alabi, Oluwatoyin Adenike Olaseinde and Eba Mala Maldaye:* ***proofread and made edition to the manuscript.***

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