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Review article

A Review on Microorganisms' Assisted Leaching of Copper from Electronic Waste and Low Grade Copper Ore

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ABSTRACT

Since the dawn of civilization, copper has significantly contributed to societal advancements. The current global demand for copper, driven by its extensive use in energy, electronics, and biomedical applications, has surpassed all historical precedents. With the exploitation of high-grade copper ore reserves, mining companies turn their attention to the extraction of copper from low-grade ores and electronic waste. The most significant of these low-grade sources is chalcopyrite, which poses challenges due to its tendency of passivation formation under oxidative leaching conditions. Bioleaching has emerged as a cost-effective, energy-efficient, and environmentally sustainable method for extracting copper from low-grade ores and electronic waste. Microorganisms play a pivotal role in this process due to their ability to form biofilms, enhancing the surface properties and adhesion necessary for mitigating the passivation film and effective copper recovery. This review highlights recent advancements in bioleaching methodologies and mechanisms, the role of specific microorganisms in the process, factors influencing bioleaching efficiency, isolation of microorganisms, bacterial attachment to the ores and current applications of bioleaching in copper recovery. By consolidating these cutting-edge developments, this paper aims to provide a comprehensive overview of microorganisms' assisted copper leaching to revolutionize copper extraction from low-grade ores and electronic waste.

1. INTRODUCTION

Copper (Cu) is one of the primary metals mined and used by human being for making items such as ornaments and coins. From the beginning of civilization, copper metal has made a great contribution to improve the life of the society. The use of copper for making of tools dates back to 10,000 years ago. In the modern Iraq, a copper pendant which dates back to before 8700 B.C. was discovered. In 18th and 19th centuries, the copper industry has been flourished to new era with the development of new discoveries and innovations in electricity and magnetism by many scientists such as Ampere, Faraday and Ohm. Nowadays, copper is still one of the main materials used in our day-to-day activities [1]. According to Joathan Ward [2], "Without the presence of copper, the human civilization would still be stuck in an era reminiscent of the Stone Age". Copper is one of the primary metals used as modern energy material to generate energy from solar cells, wind, thermal and hydro energies. It is also highly utilizing in construction industry, power transmission lines, electrical wires, anticorrosive coatings, refrigeration tubing, alloying and heat exchangers [1].

Our globe has practiced fast economic progress and amazing increment in its rate of urbanization. Copper is one of the foremost metals used in the expansion of urbanization. Nowadays, the global demand of copper in terms of quantity and quality greatly exceeds the previous demand for industrial, energy, electronics, biomedical, ornamental and domestic applications. Researchers put their prediction that the demand of copper will rise by 275 to 350% by 2050s [3]. Copper is commonly exist in the earth crust as sulphide ore, such as $CuFeS_2$ (chalcopyrite), Cu_2S (chalcocite), Cu_5FeS_4 (bornite), CuS (covellite), Cu_9S_5 (degenite) and as oxide ores such as Cu_2O (cuprite), $CuCO_3.Cu(OH)_2$ (malachite) and $2CuCO_3.Cu(OH)_2$ (azurite). It also exists as polymetallic ore with silver, gold, zinc and iron ores. Copper sulphide ores are the major source of metallic copper. Copper sulphide ores account for 80% of the copper resource. $CuFeS_2$ is the most common copper ores accounts around 70% of the copper deposit in the globe. It is also the most enduring copper mineral having a lattice structure of face centered tetragonal [4]. Nowadays, there are three basic methods of copper mining. These are surface mining, underground mining and leaching. At this time, copper is predominantly mined using open-pit mining [5]. Because of the rich grade of sulphide deposits, the old copper processing techniques were quite easy. However, we have left now with low grade sulphide ore deposits and oxide or mixed deposits due to their continuous exploration and excavation of the deposits. It is so, bioleaching or biomining is the best extraction method for such deposits [6].

Under standard environmental circumstances and the effect of weak acids, copper sulphide ores respond weakly to leaching compared to oxide copper ores [1,4]. The mining industry is extremely faced many challenges, mainly the need to extract low-grade copper sulphide ores like chalcopyrite and covellite and from tailings and electronic waste. Nowadays, rich copper ore grades have been exploited and thus, the interest of mining companies have been increasing to use lower grade ores and to recover from metallic wastes. Low grade sulphide minerals of copper, in particular chalcopyrite, which is the most important copper-bearing ore has been found to undergo passivation under various oxidative leaching conditions [7,8]. Today, mineral processing companies are highly concentrated on the finding of an alternative leaching technique which are inexpensive, less energy demand, environmentally friendly and most advanced processing technique for the use of uneconomic grade ores and industrial waste, tailings and e-waste (electronic waste). Several mining industries and global researchers have been driven their attention to innovate more advanced leaching techniques [4]**.** Leaching of copper using an acid solvent can be old-fashioned to the twenty century and causes a pollution and health problems and needs a revolutionized technique for its extraction [9].

Bioleaching is the best technique to leach copper ores which have small concentration [2]**.** The efficiency of copper recovery varies from one bacterial consortia to another. Romo et al., 2013 [10] reported that 70% of copper was recovered from sulphide ore mainly, chalcopyrite by integrated consortium composed of Acidithiobacillus ferooxidans and Acidithiobacillus thiooxidans in 35 days and only 35% of copper was recovered by another bacterial consortium composed of Leptospirillum ferooxidans and Acidithiobacilus thiooxidans in the same days.

Singh et al., 2011 [11] used thermophilic heterotrophic bacterium, Bacillus stearothermophilus to recover copper from chalcopyrite ore at neutral pH 6.8 by varying the parameters of pulp density and temperature at residence time of 30 days. He found that 10% of pulp density solubilizes 73.34% of copper, 15% of pulp density solubilizes 63.67%, 20% of pulp density solubilize 50.25% and 30% of pulp density solubilizes 39.88% of copper. And a maximum of 81.25% copper was recovered at 60 ^{o}C, 56.92% at 40 ^{o}C, 60.37% at 50 ^{o}C and 78.92% at 60 ^{o}C. The dissolution of copper was higher at higher temperature due to the rising temperature of reaction medium, which results an increment of activation energy of the reacting molecules and this leads to increment of reaction kinetics.

2. BACKGROUND TO BIOLEACHING AND ITS PROGRESS

Bioleaching was started during the ancient era, but without knowing the contribution of the microbes in the process. The Romans, and Greeks extracted copper from mine water 2000 years ago. Scientists proved that microbes have been actively engaged in the formation and breakdown of minerals since the earth's formation [12-14]. In 1752, the Rio Tinto Mine, located in the South Western Spain is generally considered as a foundation of bioleaching. In the beginning of 1890s, efforts had been undertaken to establish bioleaching. At that time, a heap with 10 meters of height was built for natural decomposition of a low grade copper ore having 0.75% of copper. The heap left for decomposition for 1-3 years and 20 to 25% of copper were recovered annually from the heaps. Even though industrial-scale leaching processes were carried out at the Rio Tinto mines for many decades, the role of microbes to metal solubilization confirmed in 1961 when Acidithiobacillus ferrooxidans was identified in the leachates [15,16]. The gram negative chemolithotroph bacteria, Acidithiobacillus ferrooxidans was identified and cultured in the early 1950s by Colmer, Hinkle and Temple as part of microbial species found in the acidic mine drainage and granted the patent for the first time in 1958. Since then, Acidithiobacillus ferrooxidans has gained a popularity in the field of biohydrometallurgy for the leaching of sulphide copper ores and bioleaching attracts many researchers and industries. In 1950s, a dump bioleaching was commercialized for the first time to leach copper from copper sulphide ores. Since then, the bioleaching has grown faster and started copper oxide heap leaching and industrial bio-heap leaching processes for chalcopyrite and covellite. In 1970s, the largest plant of bioleaching (dump bioleaching) was established by Kennecott Copper Corporation at Bingham, USA. 200 tons/day were recovered by bioleaching from a dump content of 3.6×10^{9} tons. At that time, 25% of the USA's copper metal production was recovered by bioleaching. In 1980s, Chile established an industrial-scale copper bioleaching plant using Acidithiobacillus bacteria at Lo Aguirre Mine, which processed 16,000 tons/year of ore at the initial establishment [17].

In the 1990s, the rising prices of copper, the reduction of rich-grade ores, high cost of traditional processes and the growing concern of the environment, resulted for discovering of new technologies for recovery of copper. In the late of 20th century and early of 21st century, several mines shut down because of the exhaustion of the higher grade ores and caused for the birth of an extraction of low-grade ores using a bioleaching [16].

Bioleaching is among the promising technologies that is not only environmentally friendly but also very effective in cost. Bioleaching is the extraction of metals by biological process using appropriate strains that perform as biological catalysts. During bioleaching process, the microorganisms help for solubilizing of metal solutions of leach liquor encompassing metals followed by a solvent extraction and electrowinning to obtain the pure metal [11,18].

Bioleaching has a great advantage over the traditional leaching due to its ability of extraction of high value metals from tailings and low-grade ore deposits with the support of microbes/microorganisms such as archaea and bacteria [19]. In bioleaching, the microorganisms alter the solid ore in to water soluble compound and the target elements remain in the solution during the oxidation process[1,20,21]. In the aspect of sulphide minerals extraction, bioleaching involved an electrochemical process in which a metal sulphide mineral oxidized to Fe(III), sulphur and sulphate involving the transfer of electron[22].

3. BIOLEACHING MECHANISMS

In bioleaching, there are two main mechanisms in which the microbial mobilization of metals are involved. These two mechanisms are direct and indirect bioleaching [15,23-26]. In direct bioleaching mechanisms, the mineral is directly solubilize by the microbes to oxidize the sulphidic sulphur to elementary sulphur, releasing the metal as metal sulphate. The microbes oxidize the metal sulphides by gaining electrons from the reduced minerals directly. In this mechanism there is a direct contact between the surface of the minerals and the microbes. The oxidation the mineral sulphide to sulphate takes place via several enzymatically catalyzed steps [23]. In many cases, direct mechanisms are the most widely used mechanisms due to the direct contact of the microorganisms to the minerals, but it has slower rate compare to indirect bioleaching [27].

Investigations shows that many copper sulphide ores such as chalcocite, covellite can be oxidized by direct leaching using Acidithiobacillus ferrooxidans [28].

On the other hand, in the indirect bioleaching mechanism, the microbes produce a lixiviate (ferric ion) by the oxidation of ferrous iron present in the minerals. The generated ferric ion chemically oxidizes the metal-containing ore and reduced itself to ferrous ion. The microorganisms only generate chemical agents and do not necessary to contact to the metal surface. In this mechanism, the oxidation of the reduced metals is mediated by ferric iron/Fe^{3+}, which is originates from the microorganisms oxidation of ferrous iron/Fe^{2+} compounds existing in the minerals.

The primary sulphur (S^o) may be oxidized to sulphuric acid by Acidithiobacillus ferrooxidans. Much faster oxidation of the primary sulphur occurs by the mixed culture (consortia) of Acidithiobacillus thiooxidans and Acidithiobacillus ferrooxidans.

In spite of the explanation of direct versus indirect mechanisms, a universal theory about the mechanisms of leaching of metals is still to be discovered. Lilova et al. 2007 [29] confirmed that both direct and indirect oxidation have been used in the oxidation of e-waste. However, they found that the direct metal oxidation is slow compare to the indirect oxidation mechanism.

In the bioleaching process, minerals are dissolved due to the attack to their constituents that leads to the production of energy for the microorganisms. The energy production (oxidation) passes through an intermediate reaction process. There are two mechanisms that have been proposed for oxidation of metals using the indirect mechanism [23]. The first mechanism is thiosulphate mechanism, which includes acid-insoluble metal sulphides, such as pyrite (FeS_2) and molybdenite (MoS_2). In this mechanism, thiosulphate ion ($S_2O_3^{2-}$) is an intermediate for the solubilization of acid insoluble metal sulphides by the attack of ferric iron, and results sulphate as an end product [20].

The second mechanism is polysulphide mechanism, in which a collective attack of ferric ion and protons of acid-soluble metal sulphides, such as chalcopyrite ($CuFeS_2$). Polysulphide mechanism results the solubilization of elemental sulphur as an intermediate. In polysulphide bioleaching mechanisms, the polysulphide ions (S_n^{2-}) serves as electron donors for microbial metabolism [1, 20].

The microorganisms in bioleaching accelerate the oxidative dissolution of sulphide ores [30]. The microorganisms participate for copper oxidative dissolution have the characteristic of extremely acidophilic, grow at a pH of 3 or less. The main function of microorganisms in bioleaching process is to catalyze the regeneration of ferric ion from ferrous ion and proton by sulphur oxidation [31]. The iron oxidizer microorganisms, oxidize Fe (II) to Fe (III). The generated Fe(III) is a strong oxidant having 0.77 V reduction potential. Fe (III), ferric iron is a suitable oxidizing agent to leach copper from wastes and low grade ore. The bioleaching activity of these microorganisms can improve by the addition of external Fe (II), Fe (III), pyrite and quartz particles [22,32-35].

4. MICROORGANISMS INVOLVED IN BIOLEACHING

Bioleaching commenced in 1960s when Acidithiobacillus ferrooxidans was patented for extraction of copper by Kennecott Mining Company [4]. The bioleaching microorganisms are all chemolithoaoutotrophic. Bioleaching microorganisms use reduced inorganic sulphur or ferrous iron as electron donors. Most of the bioleaching microorganisms grow in an acidic environment (pH of 1.5 -3.0), because of the formation of the sulphuric acid as a byproduct of the sulphur oxidation [19]. The standard nucleic acid based molecular method used to study the diversity of microbes are PCR (polymerase chain reaction) based randomly amplified polymorphic DNA (RAPD), terminal restriction fragment length polymorphism (TRFLP) and amplified ribosomal DNA restriction enzyme analysis (ARDREA). For quantification of bioleaching microbes, the real time PCR (RT-PCR) and fluorescence in situ hybridization (FISH) have been used [6].

4.1. Chemolithotrophic Microorganisms

Chemolithotrophic Microorganisms have an efficiency from 75 to 100% recovery of copper from low-grade ores, e-waste, coal fly ash, municipal wastes and tailings. Examples of Chemolithotrophic microorganisms used in bioleaching include Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans, Leptospirillum ferrooxidans, Sulfobacillus thermosulfidooxidans, Leptospirillum ferriphilum and Thermoplasma acidophilum [4,36,37].

4.2. Heterotrophic Microorganisms

Hetrotrophic microorganisms consume water and organic carbon sources as both energy and electron sources. Solubilization of the metal is due to the enzymatic reduction of strong oxidized metal compounds. Hetrotrophic microorganisms are used in the treatment of moderate alkaline waste materials due to their tolerance in a wider pH range and complex metals. Hetrotrophic microorganisms are classified as heterotrophic cyanogenic bacteria and heterotrophic fungi [36].

a. Heterotrophic bacteria

Heterotrophic Bacteria produce byproducts that assist the mobilization of metals from the minerals. Heterotrophic Bacteria that have the ability of leaching copper ores include: Bacillus licheniformis, bacillus plomyxa, Chromobacterium violaceum, Pseudomonas chlororaphilis, Bacillus megaterium, Pseudomonas putida and Bacillus foraminis [36].

b. Heterotrophic fungi

Heterotrophic Fungi secrete a large amount of organic acid, which participate in the mobilization of metal from the minerals. Fungi has the ability of tolerance and adaptation for environmental stress and thus they are one of the best and candidates microorganisms for bioleaching. Fungi, such as Aspergillus, Penicillium, Candida, Trichoderma, Saccharomyces, and Phanerochaete are the most widely used microorganisms for the solubilization of metals [20,36]. Studies show that Aspergillus Niger has more than 60% leaching rate for cobalt and nickel bioleaching. These species are also used to leach nickel and zinc silicates. A combination of Aspergillus and penicillium used to leach low grade laterite ores, low grade nickel-cobalt oxide ores and aluminosilicates [20].

5. OPTIMUM TEMPERATURE-BASED BIOLEACHING MICROORGANISM CLASSIFICATION

Based on the optimum temperature for their growth, microorganisms are classified into three groups: mesophilic (20-39 ^oC), moderately thermophilic (40-60 ^oC) and extremely thermophilic (60-80 ^oC) microorganisms [38-40].

a. Mesophilic microorganisms

Mesophilic microorganisms are the first microorganisms used in the mining industry. These microorganisms are adapted for leaching of copper ores that have low grade. Mesophilic microorganisms have the capacity for fixing of CO_2 by oxidizing the ferrous iron or reduced sulphur to ferric iron and H_2SO_4 respectively. Metal sulphide solubilization by ferric iron or H_2SO_4 lowers the pH of the solution and consequently, the solubilization of metals increased. Low pH is a preferable condition for microbial leaching, since it helps to stay the metals in solution. Sulphur and iron 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. There are also other genus of microorganisms involved in bioleaching categorized under mesophilic microorganisms, such as Sulfobacillus benefaciens, Acidiphilium cryptum, Ferroplasma acidiphilium and Alicyclobacillus disulfidooxidans. Mesophilic microorganisms are the most widely used microorganisms used for industrial-scale heap bioleaching of chalcopyrite due to the normal operating atmospheric temperature [4,6,28,41].

b. Moderate thermophilic microorganisms

Moderate thermophilic microorganisms are heterotrophic microorganisms play a significant role in bioleaching. These microorganisms grow on chalcopyrite in the temperature ranges from 40-60 °C. They grow in the presence of yeast extract and use ferrous ion as a source of energy [28,38]. Thermoplasma acidophilum, Thermoplasma volcanium, and Picrophilus torridus are some of the microorganisms that fall under this category [4,42,43].

c. Extremely thermophilic microorganisms

The extremely thermophilic bacteria grow above 60 °C temperature. Such microorganisms were isolated by Brierley, Karavaico and Norris. Thermophilic microorganisms have a high rate of metal sulphide oxidation. Thermoplasma volcanium, Acidianus sulfidivorans, Acidianus infernus, Sulfolobus acidocaldarius and Sulfolobus metallicus are some of the examples of extremely thermophilic microorganisms used in bioleaching [4,6,28,44].

6. MICROBIAL ISOLATION, CULTURING AND GROWTH

Microbial isolation is the separation of genetic variants (strains) from a natural environment or from an environment with a mixed population of living microbes, such as soil, food, air, water and from living beings. Microbial isolation is an attempt to grow and separate microbes outside of their natural environment using selective media such as nutrient broth and nutrient agar media. A Small number of cells are inoculated in the media, which has a relatively large volume and expansive area. Target microbe isolation starts with choosing the right targeted environment, as it will help to increase the probability of finding the targeted microbe [45-47].

6.1. Steps to Isolate Microbes

In the microbial isolation process, the first step is collection of a sample from the targeted site. After the sample collection is carried out, the collected mineral ore sample is ground and changes into small size powder particles. Next, the weighted soil sample will be dissolved in distilled water to prepare soil extracted media and then a serial dilution will be performed. After that, a spread plate or streak plate method with a high dilution factor is used to easily count and isolate the microorganisms in the sample. The spread plate/streak plate technique helps to obtain isolated colonies and the dilution helps to prevent the crowding of colonies [48,49].

An optimum temperature, which depends on the type of microorganism to be isolated is required to incubate the spread plate in an incubator. Agar plate with a selective media will be prepared to grow the bacteria in an incubator for a specified period of time at a given pH. After the microorganism is incubated, a colony with the desired microorganism will form. A colony counter is used to identify the colony morphology and count individual colonies on the agar plate [45,47,50].

Microorganisms have the ability to adapt to extreme temperatures (either in a freezing environment or hot environment) and acidic or basic environment. The adaptation of microorganisms is mediated by a spectrum of processes like horizontal gene transfer, genetic recombination, natural selection, DNA damage repair and pleiotropy-like events. Microorganisms are adapted for the purpose of improving microbial performance for a specific application, to enhance the utilization of non-preferred substrate and to improve the stress tolerance. To adapt microbes for different pH, temperature or contaminated environment, we use different mechanisms, such as long retention protein and epigenetic modification methods [51-53]. Rakhshani et al., 2023 [54] used 9K liquid media and 2:2 solid media for enrichment and isolation of *Acidithiobacillus* strains. The compounds of 9K media and 2:2 solid media were briefly explained and listed in their study [54,55].

7. BIOLEACHING TECHNIQUES

Bioleaching is an easiest and effective technique for processing of sulphide ores, low-grade ores, e-waste and tailings. The efficiency of bioleaching depends on the microbial activities, mineralogical and chemical composition of the ore. Hence, a technique works for one type of ore may not work for another ore. In commercial scale bioleaching, there are two main types of processes, i.e irrigation type process and stirred tank process [56, 57].

7.1. Stirred Tank Processes

Stirred tank processes are extremely aerated stirred tank reactors employed in a sequence of stages that have a lot of tanks connected in parallel used in mineral concentrate feeds. Since, the cost of operation and construction of stirred tank reactors is high, their application is restricted to high worth ores. Stirred tank bioreactors mostly used as pretreatment processes for the recovery of gold from recalcitrant aresenopyrite concentrates. The bioreactor tanks in the first stage are lined in parallel to give enough retention time for the microorganisms to reach high steady state levels without being washed out [19,20,28,57].

7.2. Irrigation Type Bioleaching Processes

The irrigation process includes the infiltration of leaching solutions over the crushed ore that has been arranged in heaps, columns, or dumps. The irrigation system also includes the percolation of ore body without bringing the metal ore to the surface.

a. Heap bioleaching

Heap bioleaching is the highly advanced and preferred environmentally friendly leaching technology for recovery of uneconomic copper ores. The ore is crushed, acidified with sulphuric acid and agglomeration takes place in rotating drum to bind the fine ore particles to coarse particles. Heap bioleaching reaction being finalized in months rather than years. Nowadays, several studies show that heap bioleaching contributes to about 7% of the 17 million tons of the global copper supply. This technique of bioleaching is mainly used to extract copper from secondary copper sulphide ores [20,31].

b. Dump bioleaching

Dump bioleaching is the leaching of run of mine, contains ores having low grade and uncrushed waste rock. The size of the dump may be in the range of several hundred thousand to more than 10 million tons of ore and up to 60 meters depth [19,20,28]. Dump leaching was started in the end of 1960s. One of the well-known dump bioleaching is Kennecott Copper Mine located in Bingham. The size of the dump of this mine is four billion tons of copper ore waste. Escondida Mine located in Chile, is the biggest bio-dump in the world [20,58]. Dump leaching of copper is like heap leaching technique, except the dump leaching is less efficient than the heap leaching in some circumstances [57].

c. In situ bioleaching

In situ techniques are used for the recovery of metals from low-grade ores, which are uneconomical to remove from the ground and difficult to transport to the surface. The solutions having the appropriate microorganisms is injected into the boreholes in the fractured ore body. The in situ technique of bioleaching requires adequate permeability of the ore body and the gangue rock should be impermeable to prevent any discharge of the pregnant leaching solution. One of the copper recovery processes that uses in situ bioleaching process is San Manuel Mine in Arizona and Queensland in Australia [19,20,28,59,60].

8. FACTORS INFLUENCING THE BIOLEACHING OF COPPER

There are several factors which affect the bioleaching of metals. The rates and efficiencies of the leaching environment is affected by physicochemical, microbiological, the characteristics of the solid mineral to be leached and the processing of the bioleaching. Pulp density, pH, particle size, mineralogical composition, temperature and bacterial activities are the main parameters for bioleaching [15,16,61-66].

Metal oxidation intermediated by acidophilic microbes can be repressed by several factors such as solvents, organic compounds, surfactants and specific metals. Certain metals that exist in bioleaching environments can hinder microbial growth and thus, they reducing the leaching efficiencies. Quartz particles at pulp densities of 80 g/L almost totally repressed the oxidation of covellite by Acidithiobacillus ferrooxidans especially in the presence of iron(II). The bioleaching efficiencies can also reduce by the coprecipitation of metals with mineral phases. Flotation agents such as isopropylxanthate and solvent extraction agents such as LIX 984 also cause inhibition problems. These agents prevented the oxidation of chalcopyrite by Acidithiobacillus ferrooxidans. On the other hand, metabolites excreted by Acidithiobacillus enhance the efficiency of metals [15].

9. BACTERIAL ATTACHMENT ON THE MINERAL SURFACES

Interactions between the microbial and mineral surfaces happen on two levels. The first level is physical sorption due to the result of electrostatic forces and the second level is chemical sorption, in which the cells and minerals are chemically bonded. In the second level, extracellular metabolites are formed and excreted in the near vicinity of the attachment site. The microorganisms do not attach to the entire mineral surface, instead they prefer particular sites of crystal imperfection and the electrochemical reactions lead to metal solubilization [67-69].

10. CURRENT BIOLEACHING APPLICATIONS OF COPPER RECOVERY

10.1. Bioleaching of Chalcopyrite

Chalcopyrite has very slow dissolution in an acidic solution. The very slow dissolution of chalcopyrite can be enhance using bioleaching microorganisms [70,71]. Chalcopyrite bioleaching occurs through a series of interconnected biochemical and chemical reactions mediated by microbial activity. Initially microbial, microbial cells adhered to the surface of chalcopyrite particle and forms biofilms that provides a favorable microenvironment for enzymatic reactions. The oxidation of ferrous ions to ferric ions by microbial iron oxidizer, plays a crucial role in chalcopyrite bioleaching, as it generates ferric ions that oxidize sulphur in the chalcopyrite to water soluble sulphate ions. The resulting release of copper ions enables their solubilization and subsequent recovery through solvent extraction or ion exchange processes.

The bioleaching of chalcopyrite under mesophilic microorganisms is still slow due to the passivation of chalcopyrite during the dissolution process. The main factor for the slow chalcopyrite dissolution is the elemental sulphur and jarosites [4]. The passivation of chalcopyrite during the dissolution process leads to slow kinetics. The passivation of chalcopyrite can be reduced by using thermophilic microorganisms. The critical review by Panda et al., 2015 [4] has been suggested that the passivation of chalcopyrite can be overcome by operating the bioleaching system under controlled redox potential. Many researchers have attempted to discover a best method to enhance the bioleaching efficiency of chalcopyrite by limiting the passivation [72]. Researchers have proposed a novel integrated bioleaching system to increase the leaching efficiency of chalcopyrite. Feng et al., 2013 [73] proposed an integrated bioleaching system with a stable silver ion-chloride ion to improve the bioleaching efficiency of the chalcopyrite using mixed strains of acidithiobacillus. In this integrated system, the formation of elementary sulphur (s^o) and jarosite precipitation has been greatly minimized. In 2014, Feng et al., 2014 [74] proposed another three-stage pH controlled fed batch bioleaching system. Their study showed improved copper extraction by weakening the jarosite deposition, causing passivation of chalcopyrite. The same researcher has proposed a direct-step-wise microbial community regulation strategy for enhancing of the bioleaching efficiency of chalcopyrite using *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans*. The study showed an increase of the copper concentration from 57.1 mg/L to 93.2 mg/L. Another study by Panda et al., 2013 [75] proposed a bioleaching system for improving of chalcopyrite leaching by direct removal of surface passivation layers.

10.2. Bioleaching of Copper from Electronic Wastes (e-waste)

Nowadays, a large quantity of electronic waste is accumulated when electronic devices end their service life. Studies showed that in 2019, about 50 million metric tons of electronic waste was generated. However, only 9.3 metric tons of the electronic waste (17.4%) have been gathered and reused. Electronic waste contains several metals, such as Al, Cu, Ag, Au, Ni and Zn. Several physicochemical techniques, such as hydrometallurgy and pyrometallurgy have been used for mobilization of metals from electronic waste in the past years. The extraction of copper using pyrometallurgy demands high energy and causes environmental pollution due to the emission of hazardous gases such as CO_2 and SO_2 during the operation. At this time, hydrometallurgy covers 25% of the global copper production nevertheless of losing its popularity because of the using of acids during leaching. Pyrometallurgy and hydrometallurgy are not preferable recently due to a high operational and investment costs associated to the huge amount of energy demand, high chemical and material losses, and generate of secondary byproducts [4]. Currently, biohydrometallurgy, also known as bioleaching, is considered the most advanced type of leaching with the immense interest of mining industries and researchers for recovery of electronic waste. This technique is a green and sustainable technology that solubilize metals from electronic waste using the help of microbes. Microbial solubilization of metals is the combination of biological (the microbes are responsible for generating of the leaching agents) and chemical (metals are recovered by the action of Fe^{3+} or acid) processes [15,36,76,77].

11. CONCLUSION

In conclusion, bioleaching stands out as an environmentally sustainable and cost-effective technology for metal extraction. This process leverages microorganisms to solubilize metals from ores and electronic waste, offering a greener alternative to traditional hydrometallurgical and pyrometallurgical methods. Key mechanisms of bioleaching involve direct microbial action on minerals or indirect oxidation mediated by microbial generated ferric ions. Notably, enhancing bioleaching efficiency through additives like silver ions, quartz, and mixed microbial cultures has shown significant promise, particularly in the recovery of metals from chalcopyrite and e-waste. Despite its slower rates compared to conventional methods, bioleaching brings high potential to reduce environmental concerns and operational costs. These advantages makes it a compelling option for the future of sustainable mining and metal recovery. Ongoing research and development in optimizing microbial consortia and process conditions will further enhance its effectiveness and application scope of bioleaching.

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