*Article*

# Perspectives for Photochemical Leaching Processes of Chalcopyrite: A Solar Radical-Leaching Process

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**Abstract:** This paper review presents a comparison between conventional leaching and advanced photochemical leaching processes and their potential for use in chalcopyrite leaching. Likewise, it presents an analysis of the differences between the advanced leaching processes, photoleaching and radical-leaching, indicating that the photochemical mechanisms (photooxidation/photoreduction and generation of radical oxygen species (ROS) and radical sulfur species (RSS)) would improve the oxidative dissolution of chalcopyrite, taking advantage of the high oxidizing power of free radicals. Initial experimental results of solar-assisted radical-leaching on chalcopyrite are presented, demonstrating that sulfate radicals ($SO_4^-$) allow copper to be leached at a rate 4.7 times higher than in the absence of radicals and sunlight. With these results, a radical-leaching process is presented for the first time, with a perspective toward the future development of a new hydrometallurgical route: solar-assisted radical-leaching.

## 1. Introduction to Metallurgy of Copper Sulfides

Pyrometallurgical methods have traditionally been used to produce metallic copper from sulfide copper ores. This process involves smelting the ore and then subjecting it to successive oxidations to remove impurities, such as iron and sulfur, to obtain copper in metallic form. Although effective, pyrometallurgy, the preferred route for processing sulfide copper ores like chalcopyrite, poses several challenges relating to process dust, gas generation, and slag, among others. Figure 1 outlines the treatment of chalcopyrite through this pyrometallurgical process, with a melting stage generating a matte containing 45% copper and a slag of iron and silica, along with $SO_2$ gases and fine dust. Subsequently, the process produces blister copper with 98% copper, generating $CO_2$, slag, and dust. The process captures and converts $SO_2$ into sulfuric acid, but emissions of metals as particulate matter containing Cu 330 g/t, Pb 2.49 g/t, As 0.97 g/t, Cr 5.92 g/t, and Cd 0.28 g/t have been reported [1]. Smelting copper sulfide ores involves using fossil fuels, which results in the emission of greenhouse gases. According to the report presented by COCHILCO [2], the copper industry reported 416.3 thousand tons of $CO_2$ emissions in 2021, accounting for 6.6% of the total copper industry emissions. Moreover, Chilean smelters have comparatively high direct costs, with the most efficient operation incurring 300 USD/ton of copper produced, while China's operating cost is around 114 USD/ton of Cu produced. As a result, the mining industry needs to adopt new and advanced methodologies to address these issues. In this sense, a very efficient alternative is the roasting sulfide process; roasting serves to convert sulfides into oxides prior to leaching and solvent extraction and electrowinning (SX-EW). In this sense, a very efficient modification is the sulfide roasting process. The

roasting of sulfides corresponds to an exothermic process (reduced energy consumption) that allows for the conversion of refractory sulfides into oxidized species (oxides and mixed minerals) that can be easily leached conventionally. In addition, the recovery of $SO_2$ has also been implemented, allowing the use of gas for the production of $H_2SO_4$ for hydrometallurgical purposes.
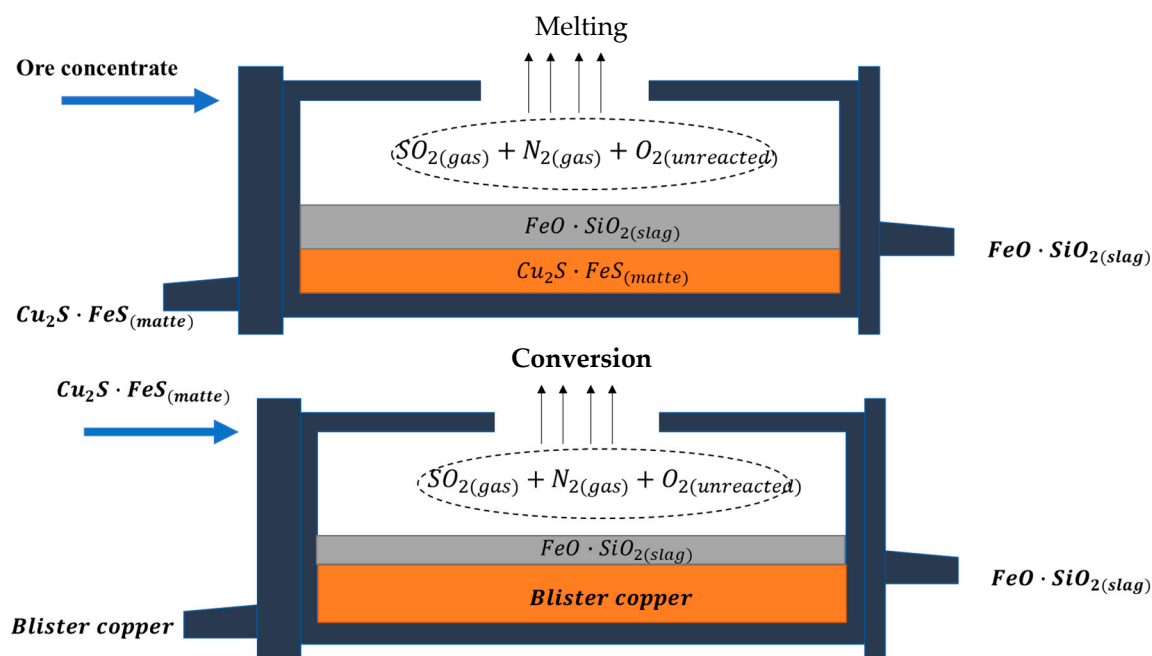


**Figure 1.** Diagram of the smelting and conversion processes for obtaining copper from sulfide ores (Chalcopyrite $CuFeS_2$).

Another promising approach is using hydrometallurgical techniques such as bioleaching and chloride leaching, which offer safe and economically feasible alternatives for metal extraction. These methods have shown substantial potential for widespread application in mining and are becoming increasingly popular in the industry [3].

Hydrometallurgy is an important method for extracting metals that is sustainable and efficient compared to traditional methods. It is becoming increasingly important in the mining industry and effectively addresses the current challenges faced by the sector. In this context, developing new hydrometallurgical production methods or expanding existing operations in this field requires proactive initiatives as there is an imbalance between the abundance of projects to prolong the lifespan of sulfide ore mines and investment in hydrometallurgical production. There has been a noticeable increase in the establishment of new mining operations in the concentrate line, indicating a significant shift in recent years. As a result, the share of hydrometallurgical production is expected to decrease from 27% in 2018 to 11% by 2030 [4]. This decline will increase the dormant capacity of hydrometallurgical plants, resulting in an unused capacity of around 1.3 million tons. Additionally, the production of unrefined concentrates within the country is expected to rise from 71% in 2018 to 75% by 2030. This change involves an increase in the export of about 3 million tons of refined copper in concentrates (equivalent to approximately 10.51 million dry metric tons of concentrates) in 2018 to about 4.74 million tons of refined copper by 2030, which is approximately 16.9 million dry metric tons of concentrates (Figure 2). From an economic perspective, the reported capital cost of a hydrometallurgy plant with a capacity ranging from 40,000 to 200,000 metric tons per year is between USD 400 and USD 5000 per ton of copper cathode [5].
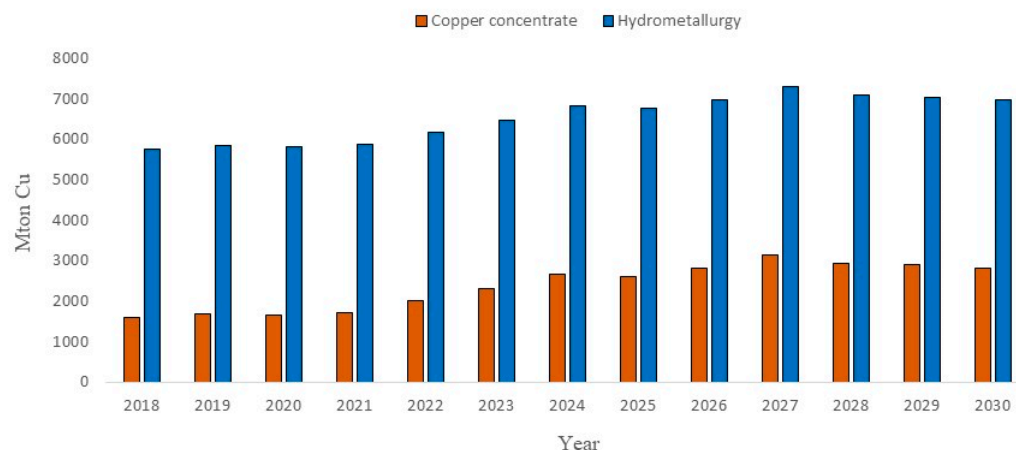
**Figure 2.** Projected copper production for 2030 according to product [6].

It is also important to mention that coincidentally, in specific regions of the copper industry (Chile, Perú, and Australia), the average irradiance level exceeds the established threshold of 2000 kWh m$^{-2}$ per year [7]. This condition indicates that these regions may be optimal for solar energy production, enabling us to reduce our reliance on non-renewable energy sources. It is advisable to consider exploring the potential of solar energy in these areas to promote a shift towards a sustainable future. In addition, this transition to solar energy can significantly benefit mining companies by reducing their carbon footprint, lowering operational costs, and guaranteeing energy availability and accessibility. Taking advantage of the exceptional solar potential in these regions is imperative to create a better future for ourselves and the generations to come. For instance, mining companies operating in copper production sites can leverage their abundant solar energy to reduce dependence on non-renewable energy sources [8]. Solar energy can directly power photochemical processes; photons emitted by sunlight can be absorbed by sulfide and oxide minerals with semiconductor properties, activating photochemical mechanisms contributing to the oxidative dissolution of these minerals (chalcopyrite $CuFeS_2$, pyrite $FeS_2$, covellite $CuS$, chalcocite $Cu_2S$, and others) [9]. Considering the potential of solar energy is pivotal in the mining industry, and an opportunity exists to innovate alternative hydrometallurgical processes for the treatment of sulfide minerals and copper concentrates through a novel solar photoleaching procedure utilizing UV-Vis radiation obtainable from solar energy. Photoleaching and radical-leaching present exciting opportunities for leaching refractory minerals such as chalcopyrite. When subjected to UV-Vis radiation-driven photoleaching, various photochemical mechanisms and processes are activated. These include activating charge carrier pairs ($e^-$ and $h^+$), promoting photochemical reactions of photoreduction and photooxidation, regenerating $Fe^{3+}$ by photolysis, and, most importantly, generating free radicals (ROS: reactive oxygen species; RSS: reactive sulfur species). These free radicals play a crucial role in photobleaching and radical-leaching processes, facilitating the chemical dissolution of sulfide minerals to obtain copper and other metals [10]. In this context, the objective of this paper is to draw a comparison between conventional leaching versus photoleaching and introduce a radical-based leaching process (radical-leaching), in which RSS or ROS free radicals will be responsible for the oxidative dissolution of chalcopyrite and other mineral commodities.

## 2. Materials and Methods

Natural chalcopyrite with a particle size smaller than 100 μm was purchased from Ward Science, Rochester, USA. Type 1 (Ultrapure) water (18.2 MOhm cm$^{-1}$) was used in all experiments (Wasserlab ULTRAMATIC, Wasserlab, Navarra, Spain). $H_2SO_4$ 65% (analytical grade reagent) was provided by Sigma Aldrich, Massachusetts, USA. $H_2O_2$ 30% (Perhydrol® p.a. EMSURE® ISO) was provided by Merck, New Jersey, USA. $S_2O_8^{2-}$ (persulfate: PS) was used as a chemical precursor in radical-leaching (Merck, Branchburg,

NJ, USA). All leaching tests (photoleaching, solar radical-leaching, and control experiments) were carried out using a mineral suspension in a continuously stirred batch reactor (300 mL) at room temperature under atmospheric pressure. The control reaction did not contain chemical precursors and was carried out in the absence of light. After the reaction, all of the samples were filtered using a Millipore (Phillipsburg, NJ, USA) nitrocellulose membrane filter (pore diameter of 0.45 μm; Merck, Branchburg, NJ, USA). The copper released in the leaching tests was determined via flame atomic absorption spectroscopy FAAS (Varian model 280FS, Varian Inc, Mulgrave, Australia) in accordance to the standard protocol [11]. The radiation was measured using a UVA-Vis photo-radiometer (Delta OHM HD 2102, Cambridge, UK).

## 3. Hydrometallurgy of Chalcopyrite

Conventionally, chalcopyrite has been processed to extract copper through pyrometallurgical techniques. Novel techniques, such as photoleaching and radical leaching, are being developed to improve the sustainability and efficiency of metallurgical processes. These innovative approaches offer promising solutions for the extraction of copper from sulfide ores. These innovative approaches utilize light-induced reactions (photoleaching) and radical species (radical-leaching) to improve the leaching kinetics and copper recovery from chalcopyrite. Combining these unconventional methods with conventional leaching techniques can unlock significant advancements and environmental benefits in copper extraction.

### 3.1. Acidic Chalcopyrite Leaching

With the depletion of oxidized minerals, characterized by complex low-grade ores, and the high energy consumption required by conventional extraction pyrometallurgical process for sulfide ores, hydrometallurgical processing is an interesting alternative. By adopting hydrometallurgical methods, we can conserve energy, reduce costs, and positively impact the environment. Due to metallic sulfides thermodynamic stability and insolubility, the limited solubility of sulfide minerals in highly acidic pH conditions is an established occurrence. While metallic sulfides are stable and poorly soluble in water (as shown in Table 1), some of these compounds can undergo decomposition, oxidation, hydration, or carbonation under specific environmental circumstances, according to previous research [12].

**Table 1.** Solubility product of some metal sulfides. Modified from: Alpers and Blower, 1994 [12].

| Metallic Sulfide | Dissolution Reaction | $K_{ps}$/$pK_{ps}$ |
|---|---|---|
| $CuFeS_2$ | $CuFeS_2 + 2H^+ \rightarrow Cu^{2+} + Fe^{2+} + 2HS^-$ | $-35.27$ ($pK_{ps}$) |
| $Cu_2S$ | $Cu_2S \rightarrow 2Cu^+ + S^{2-}$ | $3.16 \times 10^{-49}$ |
| $CuS$ | $CuS \rightarrow Cu^{2+} + S^{2-}$ | $7.9 \times 10^{-37}$ |
| $FeS$ | $FeS \rightarrow Fe^{2+} + S^{2-}$ | $7.9 \times 10^{-19}$ |

Hydrometallurgical techniques have historically been utilized to extract copper from oxidized ores. This process involves sulfuric acid ($H_2SO_4$) in an aqueous solution to dissolve the copper. However, in the case of primary copper sulfides like $CuFeS_2$, the low solubility in water, combined with the formation of a passivating layer, hinders the dissolution rate when in contact with an aqueous solution. Previous studies have found different types of compounds generated on the surface layer, including elemental sulfur ($S^0$), iron compounds (jarosite, iron complexes), mineral intermediates ($Cu_2S$ and $Fe_2O_3$), solid electrolyte interfaces that inhibit electron transfer, as well as metal-deficient sulfides or polysulfides ($S_n^{2-}$), according to the hydrometallurgical route (acid leaching, $Fe^{3+}$, chloride, bioleaching, others) [13]. For acidic leaching, $Cu^{2+}$ is initially released from the surface of chalcopyrite, followed by the release of $Fe^{2+}$, leading to the formation of a sulfur-rich, non-
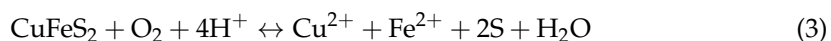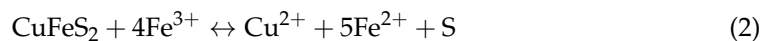
stoichiometric polysulfide layer, effectively passivating the surface of the ore. The chemical reaction proposed below occurs during the formation of the said layer, Equation (1) [14]:

$$CuFeS_2 + 4zH_2O \leftrightarrow Cu_{1-x}Fe_{1-y}S_{2-z} + yFe^{3+} + zSO_4^{2-} + 8zH^+ + (2x + 3y + 6z)e^- \quad (1)$$
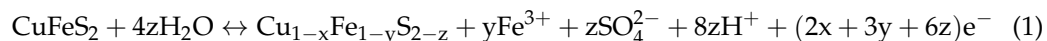
In this equation, coefficient y represents the stoichiometric coefficient for the generation of $Fe^{3+}$, and z represents the stoichiometric coefficient for the generation of $SO_4^{2-}$. The solubility of chalcopyrite is improved by increasing the electrochemical potential while the dissolution process is taking place. This crucial parameter plays a significant role in determining the outcome of the process, where optimal levels of electrochemical potential result in the excellent solubility of chalcopyrite. Additionally, high electrochemical potential values possibly lead to jarosite [$KFe_3(OH)_6(SO_4)_2$] formation on the chalcopyrite surface [15]. Although jarosite is considered an undesirable species in conventional leaching processes, it could possess photoactive properties that may be employed to enhance photoleaching or radical leaching processes [16]. The photoleaching process is a new approach that differs from the traditional method, where species in the passivating layer, like jarosite and $Cu_2S$, among others, limit the leaching of chalcopyrite. If these compounds demonstrate semiconductor properties, the photoleaching process could be improved by utilizing the inherent photochemical properties of such intermediaries formed during the process.

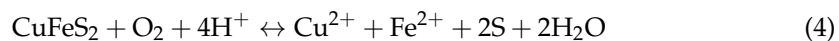*3.2. Ferric Ions (Fe³⁺) on Chalcopyrite Leaching*

The dissolution of copper sulfide minerals is recognized as being limited to strongly acidic conditions due to the insolubility of metal sulfide compounds under alkaline conditions [17,18]. Currently, there are specific hydrometallurgical methods to leach copper sulfides. These methods include biological agents (bacteria) and oxidizing reagents, such as ozone ($O_3$), hydrogen peroxide ($H_2O_2$), and ferric ions ($Fe^{3+}$), including ligands, such as chloride ($Cl^-$) or cyanide ($CN^-$), among others. In the case of chalcopyrite leaching using $Fe^{3+}$ as an oxidizing reagent, elemental sulfur can form due to oxygen, as shown in Equations (2) and (3) [19].

$$CuFeS_2 + 4Fe^{3+} \leftrightarrow Cu^{2+} + 5Fe^{2+} + S \quad (2)$$

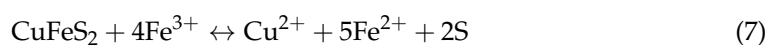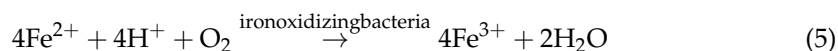$$CuFeS_2 + O_2 + 4H^+ \leftrightarrow Cu^{2+} + Fe^{2+} + 2S + H_2O \quad (3)$$

The dissolution process of chalcopyrite is strongly influenced by its electrochemical potential ($E_h$). Li et al. (2016) found that increasing the electrochemical potential from 650 to 750 mV significantly improved the leaching rate of chalcopyrite [20]. Moreover, Li et al. (2017) suggested that increasing the concentration of $Fe^{3+}$ in the pulp can also enhance the leaching rate of chalcopyrite, indicating the significant role of $Fe^{3+}$ in leaching processes [21]. Similarly, Hirayoshi et al. (2008) proposed that the leaching rate in acidic media using sulfuric acid ($H_2SO_4$) depends on the redox potential of the pulp [22]. Remarkably, the ratio of $Fe^{3+}/Fe^{2+}$ concentration determines the efficiency of the leaching process.

*3.3. Chalcopyrite Bioleaching*

Bioleaching is a hydrometallurgical method that uses bacteria to leach copper from sulfidic minerals. Copper-bearing minerals, such as chalcopyrite, can be effectively leached by bacteria such as acidithiobacillus ferrooxidans. During the bioleaching process, microorganisms oxidize $Fe^{2+}$ to $Fe^{3+}$ (as shown in Equation (5)), regenerating the $Fe^{3+}/Fe^{2+}$ ratio (as shown in Equation (7)). There are two pathways involved in bacterial leaching: direct and indirect. In direct leaching, the electron transfer occurs from metallic sulfide to the cell attached to the mineral surface. In contrast, indirect leaching is enhanced by an oxidizing metallic agent, typically the $Fe^{3+}$ ions derived from the oxidation of $Fe^{2+}$ ions, a byproduct of bacterial activity [23,24].

$$CuFeS_2 + O_2 + 4H^+ \leftrightarrow Cu^{2+} + Fe^{2+} + 2S + 2H_2O \quad (4)$$

$$4Fe^{2+} + 4H^+ + O_2 \xrightarrow{ironoxidizingbacteria} 4Fe^{3+} + 2H_2O \tag{5}$$

$$2S + 3O_2 + 2H_2O \xrightarrow{sulfuroxidizingbacteria} 2SO_4^- + 4H^+ \tag{6}$$

$$CuFeS_2 + 4Fe^{3+} \leftrightarrow Cu^{2+} + 5Fe^{2+} + 2S \tag{7}$$

## 4. Photoleaching: The Use of the Sunlight (UV-Vis) in Chalcopyrite Leaching

Photoleaching is a hydrometallurgical process involving conventional acid–oxidative dissolution of sulfide and oxide minerals in an aqueous medium assisted by UV-Vis radiation to promote the photochemical mechanisms supporting redox dissolution, as shown in Figure 3. This process contributes to dissolving refractory minerals to conventional leaching, such as chalcopyrite, which are typically challenging to dissolve using conventional methods (acidic leaching, oxidant reagents, chlorine, and biological reagents for leaching). In photoleaching, the required UV-Vis radiation can be obtained directly from sunlight, reducing energy costs. This process utilizes photonic energy to induce photochemical mechanisms in the solid and aqueous phases. The aim is to generate highly active oxidative media, including free radicals (radical oxygen species: ROS), through advanced oxidation mechanisms, namely the Fenton and photo-Fenton processes.
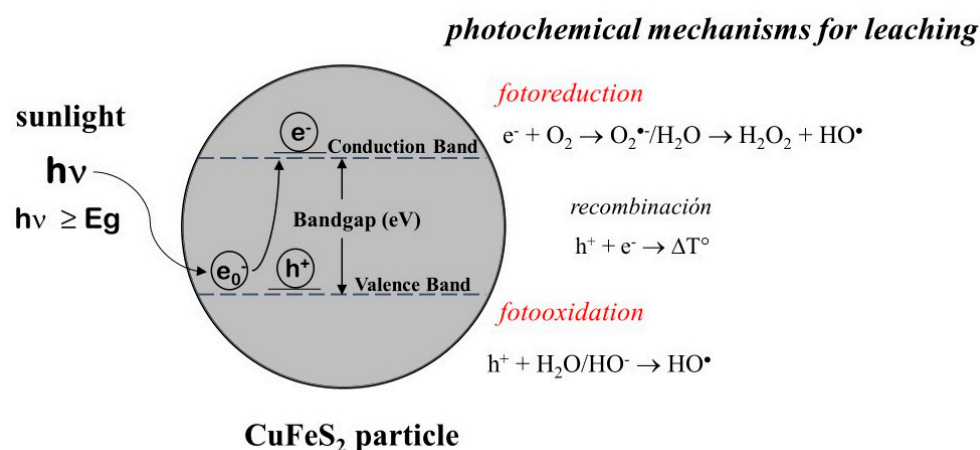


**Figure 3.** Scheme of photoleaching process for chalcopyrite leaching.
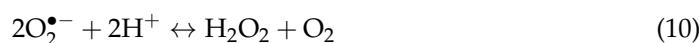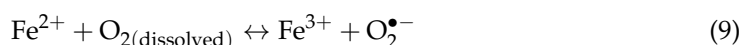
### 4.1. Comparison between Photoleaching and Conventional Acid Leaching of CuFeS$_2$

The impact of sunlight (UV-Vis) extends beyond the surface of minerals, affecting both photoleaching and acid leaching. Additionally, it has a combined effect on the intrinsic semiconductor properties of chalcopyrite minerals and the aqueous solution. According to previous studies, chalcopyrite is classified as an n-type semiconductor, with its band gap (BG) value estimated to be 0.5 eV [25]. However, the BG value of chalcopyrite varies based on the crystal structure and mineralogical associations of the ores. This energy, measured in electron volts (eV), can be associated with a specific wavelength (UV-Vis) using the Planck equation ($\Delta E = h\nu$). In order to comprehend the optical characteristics of chalcopyrite, a major copper ore, it is crucial to conduct an analysis on account of its sulfur composition. Sulfide ores are composed of semiconductor minerals, each characterized by unique chemical and mineralogical properties, each exhibiting distinct chemical and mineralogical characteristics. These minerals include chalcopyrite ($CuFeS_2$), pyrite ($FeS_2$), chalcocite ($Cu_2S$), and covellite ($CuS$), among others [26]. To activate these ores, full-spectrum sunlight (390 to 750 nm) could be used for the photoactivation process. This approach involves using light energy to trigger specific reactions in minerals, potentially providing significant advantages in terms of efficiency and selectivity when compared to conventional acid leaching methods.
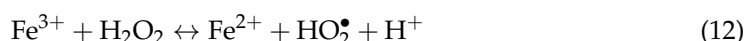
It is important to note that the efficiency of the photoleaching process is influenced by several factors that require careful control during the reaction. These variables include

the pH level (acidic pH < 3), concentration of ionic iron species ($Fe^{3+}$ and $Fe^{2+}$), and the presence of ROS precursor additives, namely hydrogen peroxide ($H_2O_2$). Maintaining optimal conditions for each factor is cruci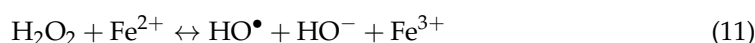al to achieving successful photoleaching outcomes. It is important to note that the efficiency of the photoleaching process is influenced by several factors that require careful control during the reaction. These variables include the pH level (acidic pH < 3), concentration of ionic iron species ($Fe^{3+}$ and $Fe^{2+}$), and the presence of ROS precursor additives, namely $H_2O_2$. Maintaining optimal conditions for each factor is crucial to achieving successful photoleaching outcomes.
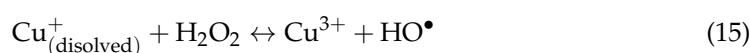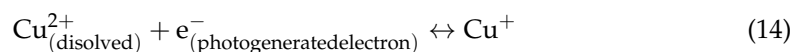
When chalcopyrite, a copper iron sulfide mineral, is exposed to a process called photoleaching in an acidic environment with a pH below 3, using either $H_2SO_4$, $HNO_3$, or HCl, it is photoactivated by UV-Vis radiation. This photoactivation initiates the formation of charge carrier pairs on the mineral's surface, consisting of free electrons ($e^-$) in the conduction band (CB) and holes ($h^+$) in the valence band (VB). When these charge carrier pairs come in contact with an aqueous medium, they trigger a photochemical reaction. The free electrons present in the CB, which correspond to the cathodic zone where photoreduction occurs, can catalyze the production of additional $H_2O_2$. These reactions involve the univalent photoreduction of molecular oxygen to superoxide anion ($O_2^{\bullet-}$) (Equation (8)) [27]. Similarly, superoxide anion ($O_2^{\bullet-}$) can be generated using $O_2$ as the oxidizing agent (Equation (9)) under acidic leaching conditions (in the absence of radiation). Lastly, under acidic conditions, hydrogen peroxide ($H_2O_2$) is produced (Equation (10)). Photoleaching could be a significant process in the mining industry to extract copper from low-grade chalcopyrite ores. A detailed understanding of the photochemical reactions involved in the process can help improve the efficiency of copper extraction while reducing the environmental impact of mining activities.

$$O_{2(\text{dissolved})} + e^-_{(\text{photogeneratedelectron})} \leftrightarrow O_2^{\bullet-} \tag{8}$$

$$Fe^{2+} + O_{2(\text{dissolved})} \leftrightarrow Fe^{3+} + O_2^{\bullet-} \tag{9}$$

$$2O_2^{\bullet-} + 2H^+ \leftrightarrow H_2O_2 + O_2 \tag{10}$$

This supplementary contribution of peroxide is limited (according to laboratory tests); however, it contributes to the generation of hydroxyl radicals through Fenton and photo-Fenton mechanisms (Equations (11)–(13)) [28]. For this reason, the dosage of $H_2O_2$ in the photoleaching process is a fundamental parameter and affects the rate of hydroxyl radical generation.

$$H_2O_2 + Fe^{2+} \leftrightarrow HO^\bullet + HO^- + Fe^{3+} \tag{11}$$

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe^{2+} + HO_2^\bullet + H^+ \tag{12}$$

$$HO_2^\bullet + 2H^+ \leftrightarrow O_2^\bullet + H^+ \tag{13}$$

Additionally, in photoleaching, the photo-excited electrons in the conduction band can reduce the released $Cu^{2+}$ to $Cu^+$. The $Cu^+$ ions then act as catalysts in the photo-Fenton-like process (as depicted in Equations (14) and (15)) [29].

$$Cu^{2+}_{(\text{disolved})} + e^-_{(\text{photogeneratedelectron})} \leftrightarrow Cu^+ \tag{14}$$

$$Cu^+_{(\text{disolved})} + H_2O_2 \leftrightarrow Cu^{3+} + HO^\bullet \tag{15}$$

In the anodic zone of the VB, photooxidation processes can occur, and the interaction with other mineral particles would promote the photooxidation processes through the generated holes ($h^+$) to a lesser degree (Equation (16)).

$$S^-_{(\text{sulfurcomponent})} + h^+_{(\text{photogeneratedhole})} \leftrightarrow S^0 \tag{16}$$
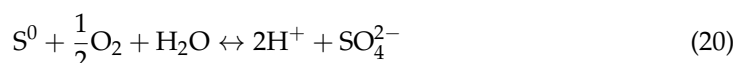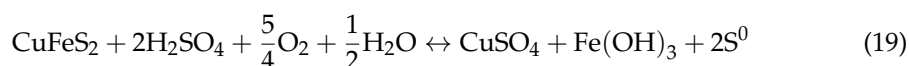
The mechanism discussed is entirely dependent on radiation—without it, there is no way it could occur (as in the case of acid leaching). Notably, minerals with different electrochemical rest potentials, like chalcopyrite and pyrite, produce an oxidation mechanism in the pulp. Further research is required [30].

Recent research has demonstrated that a mineral pulp can lead to a series of chemical reactions that cause a portion of the oxygen in the system to be consumed, producing oxidizing agents as reaction by-products. Nooshabadi and Rao's (2013) investigation found that, in particular, reactions 17 and 18 occur when natural chalcopyrite is wet-grounded with carbon steel balls to create a pulp [31]. These findings indicate that chemical reactions within a mineral pulp have the potential to significantly impact the oxygen levels within the system and produce oxidizing agents, which may have implications for various industrial applications. Reaction 18 shows that the formation of hydrogen peroxide depends on both the superoxide radical and the concentration of protons. Therefore, this chemical reaction would occur in an alkaline environment at the surface level, induced by protons resulting from chalcopyrite oxidation in an alkaline medium.
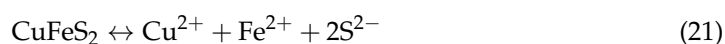
$$Fe^{2+} + O_2 \leftrightarrow Fe^{3+} + (O_2^{\bullet})^- \tag{17}$$

$$Fe^{2+} + (O_2^{\bullet})^- + 2H^+ \leftrightarrow Fe^{3+} + H_2O_2 \tag{18}$$
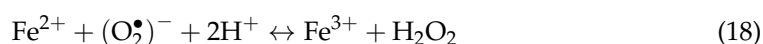
*4.2. Improving Acid Leaching through the Synergistic Action of $H_2O_2$*

Chalcopyrite is known to be a difficult-to-leach mineral. However, adding an oxidizing agent like hydrogen peroxide can enhance the efficiency of acidic leaching. The $H_2O_2$ molecule can react with the ferrous ions in the mineral to produce ferric ions, which are more reactive and can aid in the dissolution of chalcopyrite. Petrovic et al. (2018) reported a significant improvement in the chalcopyrite leaching process when $H_2O_2$ is used as an oxidizing agent [32]. The effectiveness of $H_2O_2$ has been attributed to its ability to promote the formation of elemental sulfur and sulfate ions, which can help dissolve chalcopyrite. As a result, using $H_2O_2$ can be a valuable tool for enhancing the efficiency of chalcopyrite leaching processes (Equations (19) and (20)).
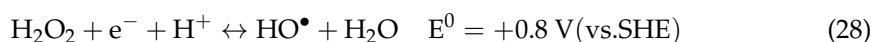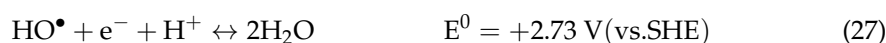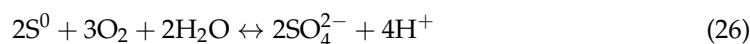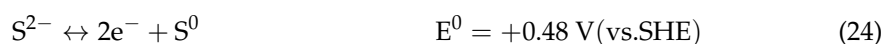
$$CuFeS_2 + 2H_2SO_4 + \frac{5}{4}O_2 + \frac{1}{2}H_2O \leftrightarrow CuSO_4 + Fe(OH)_3 + 2S^0 \tag{19}$$

$$S^0 + \frac{1}{2}O_2 + H_2O \leftrightarrow 2H^+ + SO_4^{2-} \tag{20}$$

In conventional acid leaching techniques for chalcopyrite, $H_2O_2$ is employed as a pulp electrochemical potential modifier and functions primarily as an oxidizing agent ($E^0$ = +1.76 V vs. SHE). The subsequent equations serve to illustrate this redox mechanism (Equations (21) and (23)) [33].

$$CuFeS_2 \leftrightarrow Cu^{2+} + Fe^{2+} + 2S^{2-} \tag{21}$$

$$S^{2-} \leftrightarrow 2e^- + S^0 \tag{22}$$

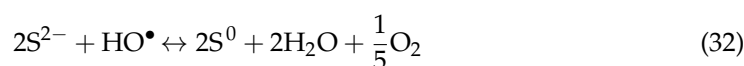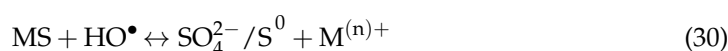$$2H_2O_2 + 4H^+ + 4e^- \leftrightarrow 4H_2O \tag{23}$$

The use of $H_2O_2$ in the process previously described is highly significant, with levels ranging from 2 to 3 mol $L^{-1}$. However, in photoleaching processes, such high concentrations are not necessary; instead, levels similar to those used in Fenton and photo-Fenton processes are used [34]. In addition, through Fenton and photo-Fenton mechanisms, $H_2O_2$ plays a crucial role in photoleaching as a precursor of ROS radicals, particularly the hydroxyl radical ($HO^{\bullet}$). $Fe^{2+}$ released during the oxidative dissolution of a mineral acts as a catalyst for Fenton and photo-Fenton pathways, creating a highly oxidizing leaching environment due to reactive oxygen species, mainly $HO^{\bullet}$, leading to the oxidative dissolution of the mineral. Photoleaching is a unique autocatalytic system. In summary, to fully understand how a metallic sulfide dissolves through oxidation, it is helpful to represent it

as MS, where M represents the cationic metal (such as copper and iron), and S represents the sulfide ion ($S^{2-}$). The sulfide undergoes a chemical transformation from sulfide to oxidized sulfur species, primarily $S^0$ and $SO_4{}^{2-}$ (Equations (24)–(26)) [35].
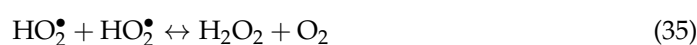
$$S^{2-} \leftrightarrow 2e^- + S^0 \qquad\qquad E^0 = +0.48 \text{ V(vs.SHE)} \tag{24}$$

$$S^0 + 8HO^- \leftrightarrow SO_4^{2-} + 4H_2O + 6e^- \quad E^0 = +0.75 \text{ V(vs.SHE)} \tag{25}$$

$$2S^0 + 3O_2 + 2H_2O \leftrightarrow 2SO_4^{2-} + 4H^+ \tag{26}$$

$$HO^\bullet + e^- + H^+ \leftrightarrow 2H_2O \qquad\qquad E^0 = +2.73 \text{ V(vs.SHE)} \tag{27}$$

$$H_2O_2 + e^- + H^+ \leftrightarrow HO^\bullet + H_2O \quad E^0 = +0.8 \text{ V(vs.SHE)} \tag{28}$$

$$HO_2^\bullet + e^- + H^+ \leftrightarrow H_2O_2 \qquad\qquad E^0 = +1.46 \text{ V(vs.SHE)} \tag{29}$$

Minerals can dissolve in various ways when exposed to free radicals:

$$MS + HO^\bullet \leftrightarrow SO_4^{2-}/S^0 + M^{(n)+} \tag{30}$$

$$S^{2-} + HO^\bullet \leftrightarrow SO_4^{2-} \tag{31}$$

$$2S^{2-} + HO^\bullet \leftrightarrow 2S^0 + 2H_2O + \frac{1}{5}O_2 \tag{32}$$

$$MS + O_2 \leftrightarrow SO_4^{2-} + M^{(n)+} \tag{33}$$

These equations represent general data and provide the most immediate evidence available for initially predicting the oxidative dissolution of sulfide minerals through these routes.
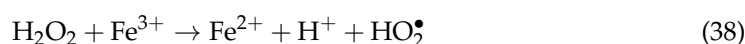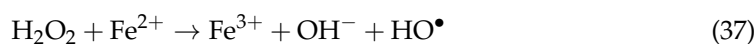
### 4.3. The Role of $H_2O_2$ in Oxidative Acid Leaching v/s in Photo-Assisted Leaching Processes
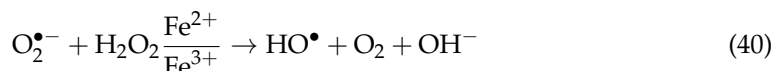
$H_2O_2$ is a chemical that exhibits distinct roles in acid leaching and photoleaching processes, acting as a pure oxidizing agent in acid leaching and undergoing photoactivation to become the hydroxyl radical in photoleaching under UV-Vis radiation. It is important to note that the dose or concentration of $H_2O_2$ is decisive in the leaching of copper, obtaining different degrees of leaching when using different amounts of peroxide [36]. Using an excess of peroxide added to the system, $H_2O_{2(excess)}$ can act as a hydroxyl radical scavenger (Equations (34)–(36)), reducing the oxidative dissolution of the mineral.

$$H_2O_{2(excess)} + HO^\bullet \leftrightarrow HO_2^\bullet + HO^\bullet + H_2O \tag{34}$$

$$HO_2^\bullet + HO_2^\bullet \leftrightarrow H_2O_2 + O_2 \tag{35}$$

$$HO^\bullet + HO^\bullet \leftrightarrow H_2O \tag{36}$$

### 4.4. Acid Mine Drainage and Its Relationship to Oxidative Dissolution Processes Mediated by Free Radicals

It has been reported that pyrite dissolution by acid mine drainage (AMD) and its oxidation mechanism can be explained as a Fenton-like reaction, showing the dependencies between the dissolution of a sulfide mineral (namely $FeS_2$) and the generation of hydroxyl radicals from hydrogen peroxide ($H_2O_2$), stressing the engagement of specific radicals (ROS and RSS) (Equations (37)–(40)) [37]. The AMD is evidence that, under certain conditions, sulfides undergo an oxidative dissolution mediated by free radical intermediates, mainly $HO^\bullet$.

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + HO^\bullet \tag{37}$$

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + H^+ + HO_2^\bullet \tag{38}$$

$$HO_2^\bullet \rightarrow O_2^{\bullet-} + H^+ \tag{39}$$

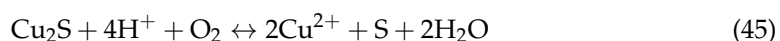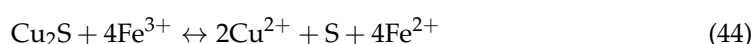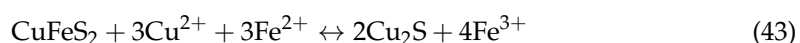$$O_2^{\bullet-} + H_2O_2 \frac{Fe^{2+}}{Fe^{3+}} \rightarrow HO^{\bullet} + O_2 + OH^- \tag{40}$$

Photoleaching and solar radical-leaching processes are based on the possibility of generating various photochemical mechanisms, as well as the generation of highly active intermediates, including free radicals (ROS and RSS), which can be used to contribute to mineral dissolution.

In the AMD, $H_2O_2$ can generate ROS (namely $HO^{\bullet}$) through Fenton-like mechanisms and is catalyzed by $Fe^{2+}$ [38].

Likewise, $Fe^{3+}$ salts have long been employed as oxidizing agents, leveraging a redox mechanism represented by Equations (41) and (42). It is worth noting that the quantity of $Fe^{3+}$ contained in the leaching solution plays a crucial role in forming the products on the mineral surface and the subsequent release of copper into the aqueous medium. Specifically, the concentration of $Fe^{3+}$ directly correlates with the type of products developed on the mineral surface and the extent of copper liberation into the aqueous medium. As such, carefully managing the $Fe^{3+}$ concentration can be instrumental in optimizing the oxidative dissolution process, thereby enhancing its efficiency and efficacy [39].

$$CuFeS_2 \leftrightarrow Cu^{2+} + 5Fe^{2+} + 2S^0 + 4e^- \tag{41}$$

$$Fe^{3+} + e^- \leftrightarrow Fe^{2+} \tag{42}$$
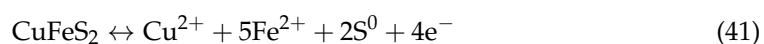
Several researchers have observed that chalcopyrite, a copper iron sulfide mineral, undergoes leaching under certain electrochemical potential conditions. Specifically, this leaching process has been observed to occur within 380 millivolts to 470 millivolts (Ag/AgCl). This information could be valuable for those studying chalcopyrite and its potential applications in various fields. The proposed mechanism to elucidate this phenomenon involves the formation of an intermediate phase, $Cu_2S$, through the reduction of chalcopyrite with $Fe^{2+}$ and $Cu^{2+}$. Subsequently, $Cu_2S$ undergoes oxidation via $Fe^{3+}$ or dissolved oxygen, producing $Cu^{2+}$ and $Fe^{2+}$ as end products [40,41].

$$CuFeS_2 + 3Cu^{2+} + 3Fe^{2+} \leftrightarrow 2Cu_2S + 4Fe^{3+} \tag{43}$$

$$Cu_2S + 4Fe^{3+} \leftrightarrow 2Cu^{2+} + S + 4Fe^{2+} \tag{44}$$

$$Cu_2S + 4H^+ + O_2 \leftrightarrow 2Cu^{2+} + S + 2H_2O \tag{45}$$
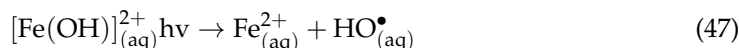
### 4.5. Photochemical Properties of Passivating Layers Compound

Considering that the conventional mechanism of oxidative dissolution of $CuFeS_2$ entails the formation of passivating species on the surface, it is appropriate to evaluate the characteristics of the products formed on the passivating layer in photo-assisted processes (photoleaching and solar radical-leaching). Preliminarily, some of these passivating compounds, such as polysulfides ($S_n^{2-}$), elemental sulfur ($S^{\circ}$), and intermediate species ($Cu_2S$, jarosite-type compounds $KFe^{3+}_3(SO_4)_2(OH)_6$), can be active against UV-Vis radiation [42]. This is a notable difference in relation to leaching processes in the absence of light and requires further study.

### 4.6. The Effect of Radiation in the Iron Cycling $Fe^{3+}/Fe^{2+}$

It is important to note that the performance of the Fenton reaction can be reduced due to the presence of ferric species, particularly $[Fe(OH)]^{2+}$ hydroxy complexes, which can act as scavengers in the process [43]. However, it has been reported that the incidence of UV-Vis photons (irradiation wavelengths of up to 600 nm) can trigger the photolysis of such complexes and, thus, increase the reaction yield. Consequently, UV-Vis irradiation can aid in the regeneration of ferrous ions, which is the limiting step in the iron catalytic cycle of a conventional Fenton process (Equation (46)), resulting in additional $HO^{\bullet}$ (Equation (47)).

Therefore, the regeneration of iron cycling is facilitated by UV-Vis irradiation. This principle is likely to be particularly important for the photoleaching process [44].

$$Fe_{(aq)}^{2+} \rightarrow Fe_{(aq)}^{3+} \rightarrow Fe_{(aq)}^{2+} \tag{46}$$

$$[Fe(OH)]_{(aq)}^{2+} h\nu \rightarrow Fe_{(aq)}^{2+} + HO_{(aq)}^{\bullet} \tag{47}$$

Similar to other leaching studies employing peroxide for potential control, specific data on the amounts of added peroxide were not provided, preventing an assessment of the relative effectiveness of peroxide and $Fe^{3+}$. In another study (Nikoloski et al., 2017 [44]) on ferric leaching of chalcopyritic ore, the potential was controlled at 0.7 V by peroxide addition. In the absence of specific quantities of added peroxide, it is not possible to evaluate the extent to which peroxide-assisted dissolution or the synergistic effect of $Fe^{3+}$ and peroxide were involved [45]. The authors could not explain the unusual observation that the dissolution rate of chalcopyrite was low at silver concentrations below $0.02 \text{ g L}^{-1}$ but increased sharply at a concentration of $0.05 \text{ g L}^{-1}$, which may be related to the previously described phenomenon.

### 4.7. The Effect of UV-Vis Radiation on Bioleaching

One interesting aspect to note is that when a semiconductor is exposed to UV, Vis, and NIR light, the electrons or charge carriers on its surface can participate in various photoreduction reactions, including the photoreduction of ferric by ferrous ions. Zhou et al. (2015) demonstrated this phenomenon in the bioleaching process, where they found that visible light promoted the regeneration of ferrous iron, but its consumption rate was slower than in dark bioleaching [46,47]. As a result, bioleaching under visible light was more effective.

## 5. Radical-Leaching Based on Sulfate Radical ($SO_4^{\bullet-}$) in Chalcopyrite Leaching

The sulfate radical ($SO_4^{\bullet-}$) corresponds to a free radical of the RSS group, with a standard reduction potential ($E^0$) of +2.44 V (vs. SHE) (Equation (48)) [48]. It has been reported that its comparative advantages in oxidation processes are as follows: (i) high standard reduction potential, (ii) long half-life, (iii) it can be produced over a wide pH range, and (iv) it has a high stoichiometric efficiency in terms of the reaction compared to $HO^{\bullet}$ [49].

$$SO_4^{\bullet-} + e^- \rightarrow SO_4^{2-} \quad E^0 = +2.4 \text{ V(vs.SHE)} \tag{48}$$
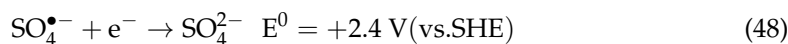
One of the advantages of using the oxidative process based on sulfate radicals is the simplicity of the route; furthermore, the chemical precursors are low cost and include peroxymonosulfate: PMS ($KH_5O_5$ or $H_2SO_5$) or persulfate: PS ($S_2O_8^{2-}$). The photoactivation of PMS or PS can be classified into three groups: (a) catalyst-free, (b) metal catalyst, and (c) metal-free catalyst. We will use the catalyst-free photoactivation method for the radical-leaching process, which corresponds to the direct activation of PS by the action of UV radiation (254 nm) that can be obtained from sunlight to break the O-O bonds of the precursor in a mechanism similar to $H_2O_2$ activation, so hydroxyl radicals are usually produced simultaneously ($HO^{\bullet}$). The general mechanism is described below:

$$S_2O_8^{2-} \xrightarrow{h\gamma} 2SO_4^{\bullet-} \tag{49}$$

$$HSO_5^- \xrightarrow{h\gamma} SO_4^{\bullet-} + HO^{\bullet} \tag{50}$$

$$SO_4^{\bullet-} + H_2O \leftrightarrow SO_4^{2-} + HO^{\bullet} \tag{51}$$

$$SO_4^{\bullet-} + HO^- \leftrightarrow SO_4^{2-} + HO^{\bullet} \tag{52}$$

The conversion into $HO^{\bullet}$ (Equation (52)) depends on the pH of the medium and could eventually compete with the generation of sulfate radicals.

In the radical-leaching or $CuFeS_2$ assisted by solar light, the rate of copper extraction was evaluated. Figure 4 shows the comparison of the kinetic profiles of copper release from chalcopyrite for sunlight-assisted radical-leaching compared to hydrogen peroxide leaching and the control reaction. It can be observed that in the radical leaching process, the release of copper from chalcopyrite increases significantly after 5 h of reaction compared to the reaction with peroxide and control reaction, being about 4.7 times greater than the reaction with peroxide and 25 times greater than the control reaction (Figure 4).
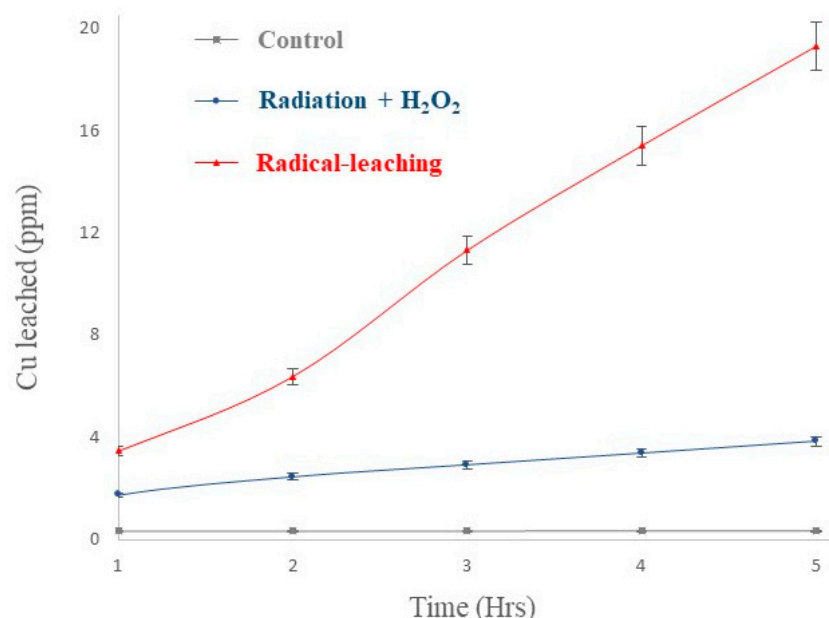


**Figure 4.** Leaching copper extraction from $CuFeS_2$ via solar-assisted radical-leaching in comparison with oxidant reagent ($H_2O_2$) and control reaction. Chalcopyrite 0.5 g $L^{-1}$, pH 6 (radical-leaching), pH 3 (oxidant and control reactions), $[H_2O_2]$ 145 μL/200 mL solution, PS 0.12 g/200 mL, magnetic stirrer (1500 r.p.m.), 1 atm pressure, solar radiation: UVA = 5.22 $Wm^{-2}$, Vis = 361.4 $Wm^{-2}$. Copper released is presented as total Cu concentration released (ppm) in the pregnant leaching solution (PLS).

In the absence of radiation, without an oxidizing agent ($H_2O_2$) or PS at pH 3 and pH 6, copper is not released even after 5 h of reaction, demonstrating that the oxidative dissolution of chalcopyrite is promoted in a radical medium. As demonstrated by the present study, radical leaching solar technology holds great promise for the oxidative leaching of chalcopyrite under soft conditions. The implications of this advancement are far-reaching and have the potential to significantly impact the industry.

## 6. Perspectives and Conclusions

The study compares advanced techniques like photoleaching and radical-leaching compared to conventional chalcopyrite leaching processes. Photo-assisted leaching processes involve photochemical mechanisms that can enhance conventional leaching by generating highly active species (radicals), enhancing the oxidative dissolution of the mineral. Solar radical-leaching, driven by sulfate free radicals ($SO_4^{\bullet-}$), has been introduced for the first time. It is a promising alternative to the conventional hydrometallurgical route for $CuFeS_2$, which can operate using fresh water (pH 6) and under soft conditions (room temperature and 1 atm), achieving outstanding performance using sunlight. These results indicate the proof of concept of a solar radical-leaching process employed in $CuFeS_2$ leaching.

In the photoleaching process, $H_2O_2$ can be photochemically activated to generate ROS, which are necessary in terms of promoting the dissolution of the mineral. Radical leaching could be more efficient than conventional leaching (acid or ferric leaching), but economic, technical, and environmental factors must be considered. Ongoing research seeks to fully utilize the potential advantages of these methods and advance toward more efficient and

sustainable leaching processes in the mining industry. Future studies should consider kinetic parameters, optimize the use of sunlight, and scale to a pilot plant.

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