

## Article

# The Extraction of Copper from Chalcopyrite Concentrate with Hydrogen Peroxide in Sulfuric Acid Solution

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**Abstract:** Research on chalcopyrite leaching represents a great challenge, given its importance as one of the most abundant copper minerals and its significant role in global copper extraction. This study aimed to evaluate the effects of different parameters on chalcopyrite leaching by hydrogen peroxide as a strong oxidizing reagent in sulfuric acid solution. A series of leaching tests were carried out to investigate the effect of the solid/liquid ratio, stirring speed, temperature, oxidant and acid concentrations, and lixiviant dosing method on copper extraction from chalcopyrite concentrate. The catalytic decomposition of hydrogen peroxide occurred in the investigated leaching system, as reflected in the obtained metal extraction values. Copper extraction was increased in the first 60 min of the reaction, after which it essentially ceased. The maximum final copper extraction of 64.5% was attained with 3.0 mol/L H<sub>2</sub>O<sub>2</sub> in 3.0 mol/L H<sub>2</sub>SO<sub>4</sub> at a temperature of 40 °C after 120 min of reaction. Due to the catalytic decomposition of hydrogen peroxide in the examined leaching system, the leaching experiment was performed with the periodic addition of lixiviant at specific time intervals as well. The dissolution process was described by the first-order kinetics equation with an apparent activation energy of ~39 kJ/mol. Finally, XRD and SEM-EDS analyses were used to characterize the leached residue, and the results showed that the formation of elemental sulfur on the chalcopyrite surface affected the dissolution process.

**Keywords:** chalcopyrite; leaching; hydrogen peroxide; sulfuric acid; kinetics; XRD; SEM-EDS; sulfur



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## 1. Introduction

Chalcopyrite is of great economic importance since approximately 70% of global copper reserves are present in this mineral [1]. Traditionally, the main technology for copper extraction from its ores and concentrates was pyrometallurgy, but the gradual depletion of rich ore deposits and growing environmental concerns over pyrometallurgical processing have made the search for hydrometallurgical processes more attractive [2]. In particular, in recent years, extensive research has been carried out to identify hydrometallurgical processes that can be used for the treatment of low-grade ores and sulfide concentrates [3–5] as well as for the treatment of tailings and secondary raw materials [6–8].

Hydrometallurgical methods offer a wide range of benefits. One crucial aspect is that they enable the effective extraction of precious components from raw materials through complex processing methods. These methods also involve selective chemical reactions and operate at lower temperatures, making them exceptionally effective and environmentally friendly. As a result, hydrometallurgical metal extraction is increasingly outshining high-temperature methods in terms of competitiveness [9].

Chalcopyrite, as one of the most widely found copper minerals in nature, exhibits slow dissolution kinetics due to surface passivation phenomena [10–12]. Specifically, the

passivation layer covering the chalcopyrite mineral surface during leaching prevents further dissolution of this mineral. Consequently, knowing that this mineral is one of the most poorly soluble minerals, the main goal of most research is to identify appropriate conditions to achieve efficient copper extraction [13–15].

A number of scientific studies have been performed on chalcopyrite leaching in sulfuric acid with different oxidizing agents [16–20]. Sulfuric acid is the most common and important leaching reagent for many minerals; it is considerably less corrosive than hydrochloric acid and chlorides, and sulfates can be formed directly through sulfide oxidation. However, under atmospheric leaching conditions in a sulfate solution with Fe(III) ions and/or dissolved oxygen as an oxidizing agent, the chalcopyrite dissolution rate is low, resulting in inefficient copper extraction [19]. To dissolve copper from chalcopyrite, the oxidants applied for chalcopyrite leaching need to have a high potential to oxidize sulfide sulfur from chalcopyrite to elemental sulfur or sulfate. Therefore, investigations of chalcopyrite oxidation in sulfuric acid have been carried out with stronger oxidizing agents that can affect the dissolution kinetics. Hydrogen peroxide, one of the agents in the leaching of sulfide minerals, stands out as a relatively inexpensive and strong oxidizing agent, with a redox potential of +1.77 mV in acidic media [21]. Hydrogen peroxide is very unstable at higher temperatures or in the presence of a catalyst and decomposes rapidly to yield only oxygen and water; thus, it is considered an environmentally friendly reagent [22].

The results of chalcopyrite oxidation in the presence of hydrogen peroxide show that by increasing the concentration of peroxide, the rate of reaction in sulfuric acid solution is increased [23–25]. Sokić et al. [20] examined the kinetics and mechanism of dissolution of chalcopyrite by hydrogen peroxide in a sulfuric acid solution. The authors showed that the copper extraction yield increased with temperature up to 40 °C; after that, the yield began to decline due to the decomposition of hydrogen peroxide at higher temperatures. The highest yield of copper (97.69%) was achieved under the following conditions: particle size, 37 µm; solid phase concentration, 2 g/L; leaching time, 240 min; stirring speed, 100 min<sup>-1</sup>; temperature, 40 °C; concentration of H<sub>2</sub>SO<sub>4</sub>, 1.5 mol/L; and concentration of H<sub>2</sub>O<sub>2</sub>, 2.0 mol/L. A comparative analysis of chalcopyrite concentrate leaching from different Serbia mines has revealed distinct differences in behavior, including the kinetics and mechanisms of the leaching process [20,24].

Agacayak et al. [25] showed that in a pure H<sub>2</sub>O<sub>2</sub> solution, copper extraction from chalcopyrite is directly proportional to the hydrogen peroxide concentration, but the extraction decreases at temperatures above 60 °C. Turan and Altundogan [26] showed that 76% of Cu and 9% of Fe can be leached from chalcopyrite concentrate under elevated temperature and pressure. In particular, in oxidative leaching systems, the presence of iron or copper in the solution results in relatively rapid decomposition of hydrogen peroxide [27].

To minimize the decomposition of hydrogen peroxide during the dissolution process, stabilizers such as polar organic solvents are employed [28–30]. For example, the addition of acetone and ethylene glycol to sulfuric acid solutions significantly affects the leaching of copper from chalcopyrite under atmospheric leaching conditions [28]. Ruiz-Sánchez and Lapidus [29] found that 99% of the initial hydrogen peroxide decomposed within 24 h in the absence of ethylene glycol. In contrast, in the presence of ethylene glycol, the hydrogen peroxide consumption was minimal (~16%) in the same time period. However, it is important to consider the potential risks associated with the presence of additives during the copper refining process [31].

In general, variations in the mineralogy of natural ores can greatly influence the leaching process. Pure samples of chalcopyrite may contain other types of copper minerals or associated phases. These diverse mineralogical variations have a profound impact on the leaching process, resulting in a wide range of outcomes [32].

Although numerous studies on the leaching of chalcopyrite in sulfuric acid have been performed, issues related to the parameters affecting oxidation processes still persist, and these parameters are closely related to the mineralogical and chemical composition

of chalcopyrite ore/concentrate used in certain research studies. Extensive research conducted on leaching frequently leads to contradictory findings in terms of the mechanism and kinetics of leaching and the efficiency of the leaching process, even when the same combinations of leaching agent and oxidant are used. The primary focus lies in uncovering the optimal conditions for oxidation, which will facilitate the dissolution of chalcopyrite. Simultaneously, this undertaking provides vital data that will drive the advancement of the copper extraction process. Given the aforementioned facts, the analysis in this study includes investigating the mechanisms and kinetics of chalcopyrite concentrate leaching by hydrogen peroxide as a strong oxidizing agent in sulfuric acid solution. This investigation is a continuation of a previous study, where the same sample of chalcopyrite concentrate was leached with hydrogen peroxide in a hydrochloric acid solution [33]. The goal was to investigate the mechanism and kinetics of leaching the identical sample of chalcopyrite concentrate by hydrogen peroxide as an oxidizing agent in a different medium, without any hydrogen peroxide stabilizers. As a result, sulfuric acid was selected.

## 2. Materials and Methods

### 2.1. Material

The chalcopyrite sample used in the present study was obtained by refloating the chalcopyrite concentrate from the Veliki Krivelj Copper Mine, Serbia. The detailed chemical composition is presented in Table 1. The particle size  $-75 + 0 \mu\text{m}$  was used for all experiments.

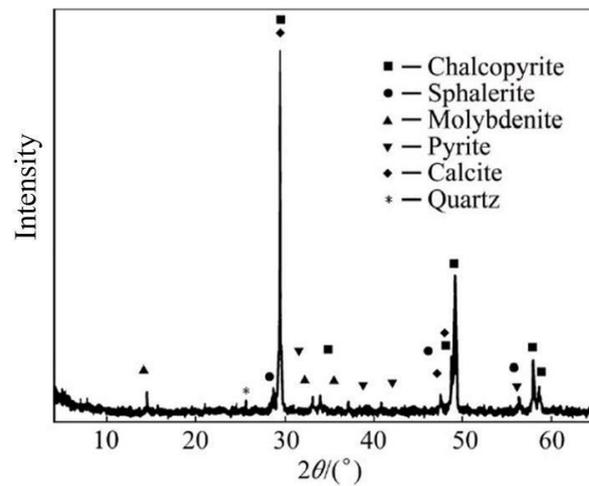
**Table 1.** Chemical composition of chalcopyrite concentrate. Reproduced with permission from ref. [33]. Copyright Elsevier, 2018).

Element	Content (wt %)
Cu	24.84
Fe	29.52
S	32.92
Mo	0.57
Zn	0.60
Pb	0.076
SiO <sub>2</sub>	2.67
Al <sub>2</sub> O <sub>3</sub>	1.06
Fe <sub>3</sub> O <sub>4</sub>	<0.03
CaO	3.23
MgO	0.29
K <sub>2</sub> O	0.18

The mineralogical composition of the chalcopyrite concentrate was determined using a Philips PW-1710 X-ray diffractometer (Cu K $\alpha$  radiation 0.154178 nm; 40 kV; 30 mA). The XRD pattern presented in Figure 1 indicates the presence of chalcopyrite (CuFeS<sub>2</sub>) as the predominant mineral and then pyrite (FeS<sub>2</sub>), sphalerite (ZnS), molybdenite (MoS<sub>2</sub>), and gangue minerals—calcite (CaCO<sub>3</sub>) and quartz (SiO<sub>2</sub>) [33].

The quantitative mineralogical composition of chalcopyrite concentrate indicated that the major crystalline phases were chalcopyrite (64.79%) and pyrite (18.78%). The gangue minerals predominantly consist of carbonates, mainly calcite and quartz, and significantly less silicate. Detailed quantitative mineralogical analysis of the chalcopyrite concentrate is shown in Table 2.

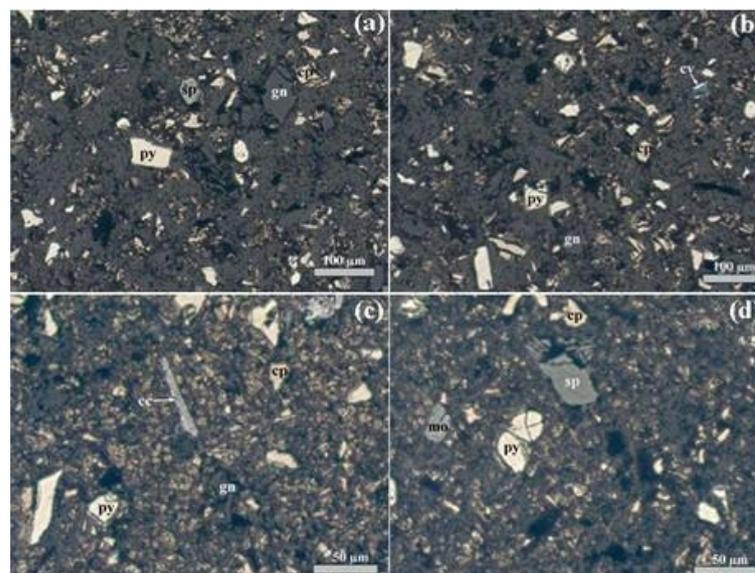
The qualitative mineralogical analysis was carried out by polarizing reflected light microscopy (Carl Zeiss JENAPOL-U microscope, Jena, Germany). The microscopic photograph of the initial chalcopyrite sample presented in Figure 2 shows chalcopyrite as the main mineral phase, pyrite, gangue minerals, and grains of covellite, chalcocite, sphalerite, and molybdenite.



**Figure 1.** XRD pattern of initial chalcopyrite concentrate (Reproduced with permission from ref. [33]. Copyright Elsevier, 2018).

**Table 2.** Mineralogical composition of the chalcopyrite sample (Data adapted from ref. [33]).

Mineral	Chemical Formula	Content, %
Chalcopyrite	CuFeS <sub>2</sub>	64.79
Pyrite	FeS <sub>2</sub>	18.78
Covellite	CuS	0.86
Chalcocite	Cu <sub>2</sub> S	0.37
Bornite	Cu <sub>5</sub> FeS <sub>4</sub>	0.08
Sphalerite	ZnS	0.91
Galena	PbS	0.09
Molybdenite	MoS <sub>2</sub>	0.88
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	0.07
Rutile	TiO <sub>2</sub>	0.02
Cassiterite	SnO <sub>2</sub>	0.03
Gangue	CaCO <sub>3</sub> , SiO <sub>2</sub>	13.12
Total		100.00



**Figure 2.** Photomicrographs of the initial chalcopyrite sample (reflected light, air, II N): (a) chalcopyrite (cp), pyrite (py), sphalerite (sp), and gangue minerals (gn); (b) chalcopyrite (cp), pyrite (py), covellite (cv), and gangue minerals (gn); (c) chalcopyrite (cp), pyrite (py), chalcocite (cc), and gangue minerals (gn); and (d) chalcopyrite (cp), pyrite (py), molybdenite (mo), and sphalerite (sp).

## 2.2. Reagents and Experimental Procedure

Analytical grade chemicals (sulfuric acid  $\text{H}_2\text{SO}_4$ —1.84 g/cm<sup>3</sup>, 96%; hydrogen peroxide  $\text{H}_2\text{O}_2$ —1.11 g/cm<sup>3</sup>, 30%) and distilled water were used for the leaching solution preparation. All leaching experiments were carried out in a 600 mL five-necked glass tempering beaker. The experimental setup for performing the leaching tests was described in detail in a previous study [33]. The standard leaching experiments involved leaching with 200 mL of freshly prepared sulfuric acid–hydrogen peroxide solution heated to the defined temperature. After reaching the desired temperature, 2 g of the chalcopyrite concentrate sample was added to the reactor, and then mixing started. The reaction time was 120 min. Sampling was performed at regular time intervals by taking 1 mL of the leach liquor. The leach liquor sample was filtered and the filtrate was transferred and filled with distilled water to the 50 mL volumetric flask. The diluted solution was analyzed by atomic absorption spectrophotometry (atomic absorption spectrophotometer, Perkin Elmer (Waltham, MA, USA) model 403).

The influence of the solid/liquid ratio (1:100 to 1:10), stirring speed (0–600 min<sup>−1</sup>), temperature (from room temperature to 60 °C), hydrogen peroxide concentration (0.5–3.0 mol/L), sulfuric acid concentration (0.3–3.0 mol/L), and the periodic addition of lixiviant at specific time intervals were investigated.

The copper extraction degree (Equation (1)) was determined by calculating the ratio between the copper content in the analyzed leach solutions  $[\text{Cu}]_2$  (g/L) and the total copper content in the powdered sample of a specific mass of concentrate  $[\text{Cu}]_1$  that undergoes leaching (g/L). In order to accurately calculate the leaching degree, it is important to consider the dilution of the solution (R).

$$\text{Cu}_{\text{extraction degree}} = \frac{[\text{Cu}]_2 \cdot R}{[\text{Cu}]_1} \cdot 100, \quad \% \quad (1)$$

## 2.3. Leach Residue Characterization

The solid residues obtained by leaching were washed, dried, and analyzed by an X-ray diffractometer (PHILIPS (Eindhoven, The Netherlands), model PW-1710) with  $\text{CuK}\alpha$  radiation ( $\lambda = 0.154178$  nm, 40 kV, 30 mA), and by a scanning electron microscope (Tescan (Brno, Czech Republic) VEGA 3 LM) with energy-dispersive X-ray spectrometry (EDS) (Oxford Instruments (Abingdon, UK) X-act) with an accelerating voltage of 30 kV. Prior to imaging on the electron microscope, each sample was subjected to a well-defined and detailed preparation process. This process involves several critical steps to ensure the sample is suitable for analysis. Among these steps, the samples are coated with carbon to provide a conductive surface. This conductive surface is essential for high-quality electron microscopy imaging. A Quorum Technologies Sputter Coater Q150R ES was employed for sample coating. This step ensures that the sample surface is appropriately prepared and optimized for electron microscopy. The imaging process was carried out in a controlled vacuum environment using a TESCAN VEGA 3 LMU microscope. For elemental analysis, the Oxford Instruments AZtec Standard X-Act EDS system was utilized.

The experimental process diagram is presented in Figure 3.

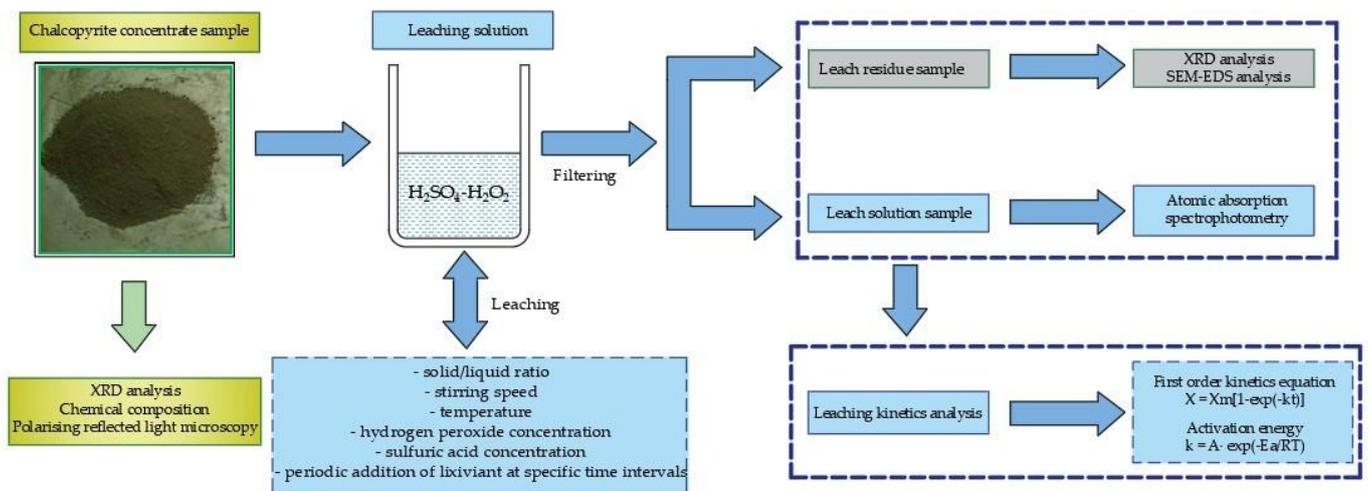


Figure 3. Experimental procedure and methodology diagram.

### 3. Results and Discussion

#### 3.1. Effect of Solid/Liquid Ratio

The effect of the solid/liquid ratio on copper extraction from chalcopyrite concentrate was studied by leaching 2, 4, 8, and 20 g of chalcopyrite concentrate with 200 mL of lixiviant at 40 °C for 120 min, which corresponds to solid/liquid ratios of 1:100, 1:50, 1:25, and 1:10. The results of these experiments are presented in Figure 4.

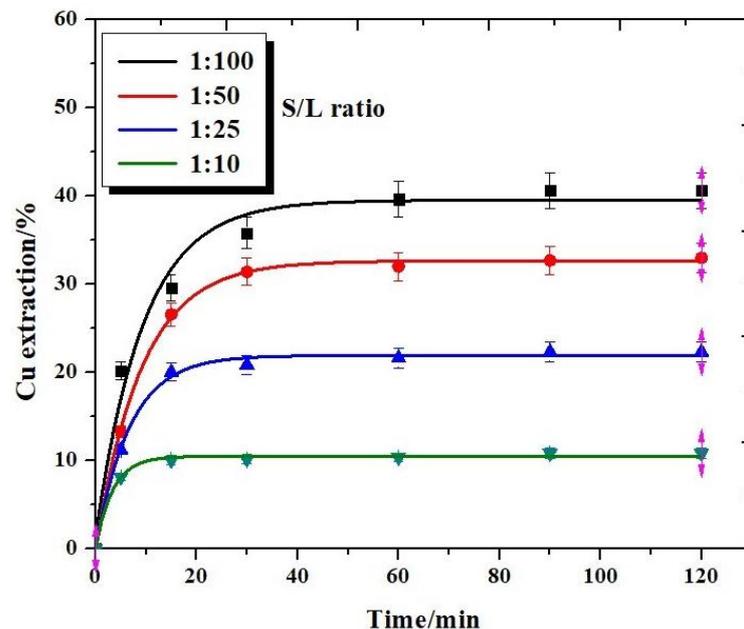


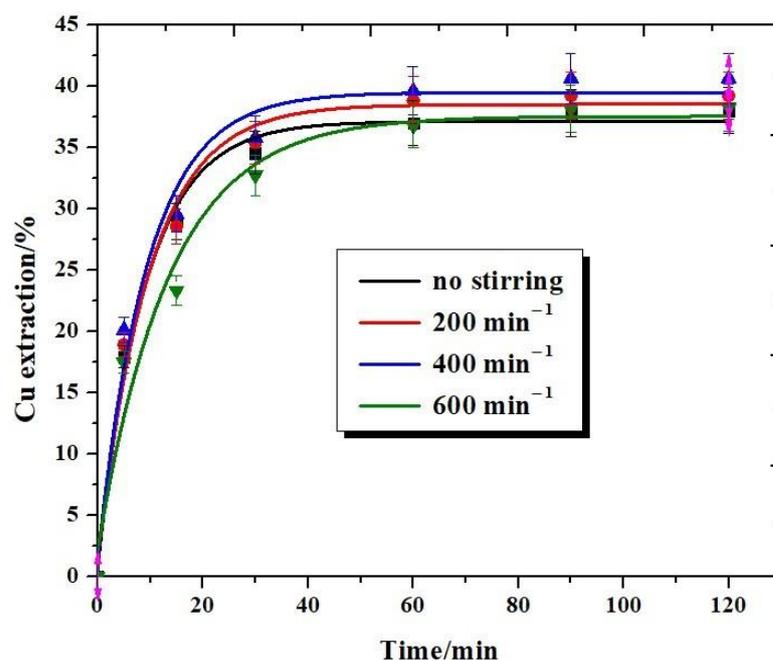
Figure 4. Effect of the solid/liquid ratio on copper extraction from chalcopyrite concentrate (conditions: 3.0 mol/L  $H_2SO_4$ , 2.0 mol/L  $H_2O_2$ , 40 °C, 400  $min^{-1}$ ).

The results shown in Figure 4 indicate that the greatest degree of copper extraction was achieved in the most dilute suspension ( $S/L = 1:100$ ), which corresponds to a concentrate mass of 2 g. Increasing the solid phase content in the solution ( $S/L$  ratio from 1:50 to 1:10) led to a decrease in the copper extraction values. Figure 2 shows that the maximum leaching efficiency of copper was found to be approximately 41% at an  $S/L$  ratio of 1:100. Increasing the suspension solid phase content from 4 g to 20 g decreased the extraction of copper from 33% to ~11%, respectively. With higher solid phase content in the suspension, there was an insufficient hydrogen peroxide concentration and copper extraction decreased.

To achieve high leaching efficiency for copper, a solid/liquid ratio of 1:100 was selected as the most suitable ratio, and changes to other test conditions maintained the solid/liquid ratio at 1:100. Arslanoglu and Yaras [34] found that copper extraction increased from 7.83 to 62.37% as the liquid/solid ratio increased from 2 to 100, respectively. Generally, the liquid/solid ratio is high in most studies with hydrogen peroxide to elucidate the kinetics of the leaching process [24,31].

### 3.2. Effect of Stirring Speed

The effect of the stirring speed (0, 200, 400, and 600  $\text{min}^{-1}$ ) on copper extraction from chalcopyrite concentrate was studied in 3.0 mol/L  $\text{H}_2\text{SO}_4$  and 2.0 mol/L  $\text{H}_2\text{O}_2$  solutions at 40 °C. The results are presented in Figure 5.



**Figure 5.** Effect of stirring speed on copper extraction from chalcopyrite concentrate (conditions: 3.0 mol/L  $\text{H}_2\text{SO}_4$ , 2.0 mol/L  $\text{H}_2\text{O}_2$ , S/L = 1:100, 40 °C).

The results shown in Figure 5 indicate that the copper extraction values increased slightly with stirring speeds up to 400  $\text{min}^{-1}$  and the obtained final copper extraction value was approximately 41%. The decrease in the copper extraction rate at a stirring speed of 600  $\text{min}^{-1}$  is most likely due to the intensified agitation, which speeds up the degradation of hydrogen peroxide. A previous study by Adebayo et al. [16] demonstrated that increasing the stirring speed can significantly accelerate the decomposition of hydrogen peroxide. Therefore, the concentration of hydrogen peroxide decreased due to its decomposition, resulting in a reduction in oxidizing conditions. Leaching in the suspension without stirring showed that the copper extraction value was approximately 38%.

The results obtained may be a consequence of slightly effective contact between mineral particles and the leaching solution achieved by stirring the suspension. Based on the results obtained, a stirring speed of 400  $\text{min}^{-1}$  was selected for further experimental study in the  $\text{H}_2\text{SO}_4$ – $\text{H}_2\text{O}_2$  system.

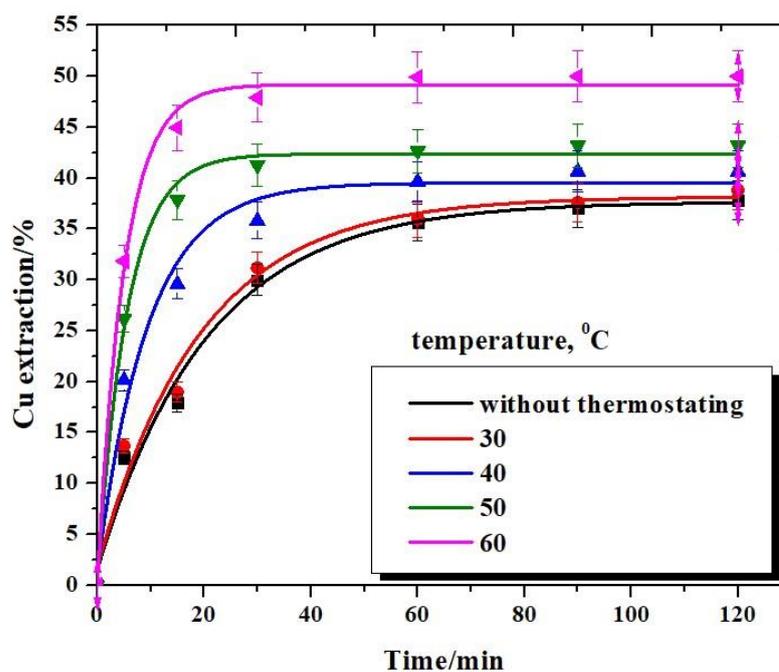
Arslanoglu and Yaras [34] found that the highest leaching yields of copper and iron during chalcopyrite leaching with hydrogen peroxide in formic acid occurred at 500  $\text{min}^{-1}$  as a result of better contact between the chalcopyrite particles and the leach solution at higher stirring speeds. Hu et al. [35] carried out leaching tests on chalcopyrite in a 10% (v/v) [HMIm]HSO<sub>4</sub> aqueous solution at 40 °C with 20%  $\text{H}_2\text{O}_2$  and revealed that the chalcopyrite dissolution rates were not significantly changed when the stirring speed was greater than 200  $\text{min}^{-1}$ . Similar conclusions were drawn by Sokić et al. [20]. On the

other hand, Adebayo et al. [16] reported that the highest dissolution rate of chalcopyrite was observed without mechanical stirring. Similar results have been reported for pyrite oxidation by hydrogen peroxide in sulfuric acid solution [36].

### 3.3. Effect of Reaction Temperature

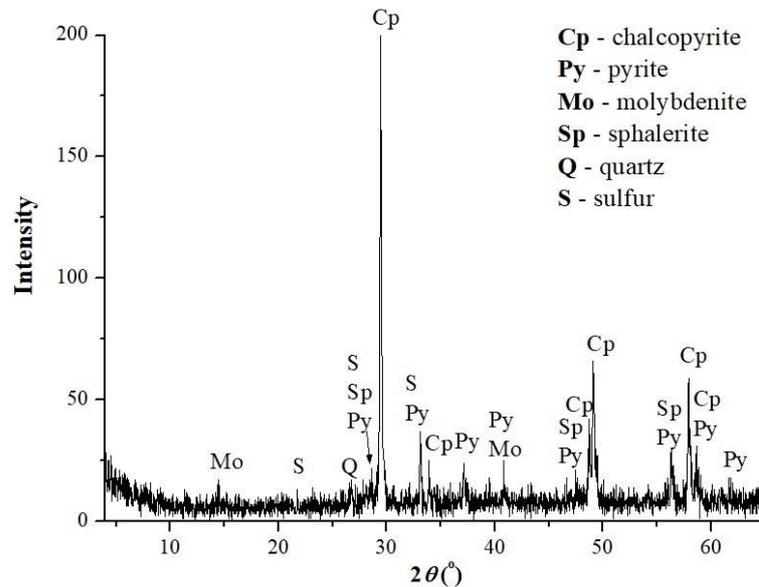
Temperature is a key factor in the leaching process with hydrogen peroxide because it affects the stability of  $H_2O_2$ . Thus, the temperature effect on copper extraction from chalcopyrite concentrate was investigated in the temperature range between room temperature (without thermostating the solution) and 60 °C in a solution containing 3.0 mol/L  $H_2SO_4$  and 2.0 mol/L  $H_2O_2$ .

The results shown in Figure 6 reveal that temperature has a greater influence on the chalcopyrite oxidation rate in the initial leaching stage. The rate of the chalcopyrite oxidation reaction at the beginning was more intense, and after a certain period, the reaction rate decreased. The final copper extraction values varied from approximately 38% to approximately 50% in the studied temperature range. The shape of the dissolution curves from Figure 4 shows that a plateau was reached after 90 min of oxidation at temperatures up to 30 °C, while at 40 °C, the plateau was observed after 60 min of oxidation. At the highest tested temperatures of 50 °C and 60 °C, the plateau was reached much faster and was observed after only 20 min, which means that the oxidation of chalcopyrite occurred up to that time. This phenomenon was attributed to the fact that hydrogen peroxide is unstable in the investigated leaching system due to its decomposition;  $H_2O_2$  decomposition can be catalyzed by solid particles, specifically by chalcopyrite particles, as well as by Fe(III) ions generated by chalcopyrite dissolution and pyrite dissolution (pyrite was present in the tested sample). The concentration of hydrogen peroxide decreased significantly which led to rapid plateau formation in the dissolution curves, especially at temperatures above 40 °C, which is consistent with the results of other researchers [24,25]. Based on the obtained experimental results in this study, a temperature of 40 °C was selected. Adebayo et al. [16] showed that leaching rates were strongly dependent on temperature and that the dissolution curves at 70 °C and 80 °C showed a leveling-off trend at 90 min, indicating that the reaction had almost ceased. This was attributed to increased peroxide decomposition at higher temperatures.



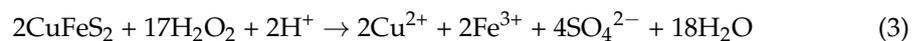
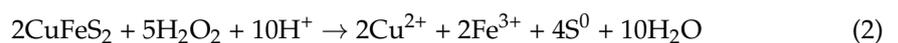
**Figure 6.** Temperature effect on copper extraction from chalcopyrite concentrate (conditions: 3.0 mol/L  $H_2SO_4$ , 2.0 mol/L  $H_2O_2$ , S/L = 1:100, 400  $min^{-1}$ ).

Additionally, active chalcopyrite dissolution during the initial leaching stage led to the surface of chalcopyrite being coated with a product layer which could prevent further oxidation. Thus, the mineralogical composition of the obtained leach residue was examined by XRD. The XRD pattern of the leach residue sample shown in Figure 7, in addition to the detected mineral phases, also shows the appearance of a new peak corresponding to elemental sulfur.



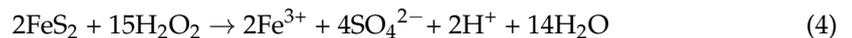
**Figure 7.** X-ray diffraction pattern of the leach residue (leaching conditions: 3.0 mol/L  $\text{H}_2\text{SO}_4$ , 2.0 mol/L  $\text{H}_2\text{O}_2$ , S/L = 1:100, 40 °C, 400  $\text{min}^{-1}$ , reaction time 120 min).

The XRD pattern of the leach residue (Figure 7) revealed elemental sulfur formation without the formation of mineral phases such as copper-rich sulfides, polysulfides, and jarosite, which are often solid reaction products of sulfide mineral leaching. As a result, the reaction mechanism proposed by [21,24] can be accepted here for chalcopyrite leaching in  $\text{H}_2\text{SO}_4$ – $\text{H}_2\text{O}_2$  as follows:

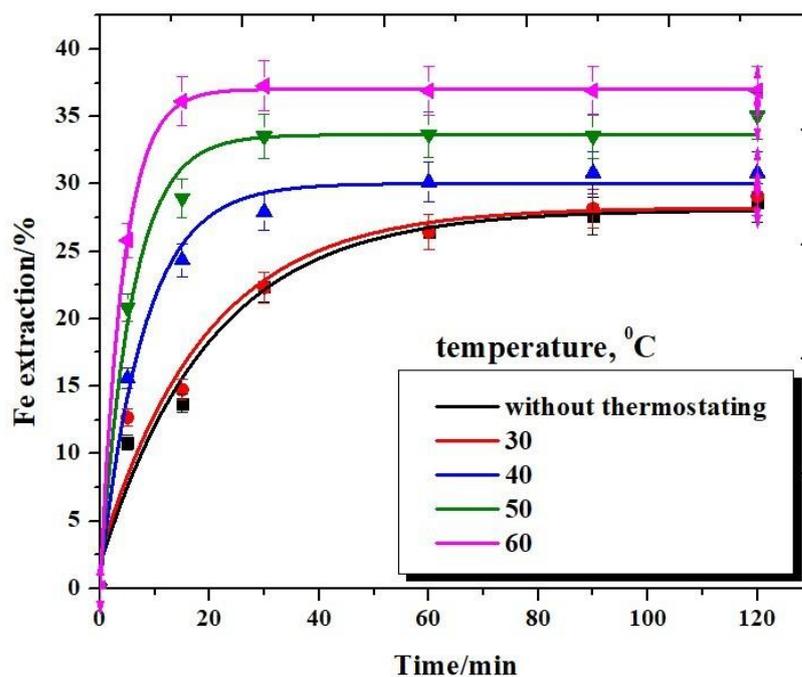


#### Dissolution of Iron

Mineralogical analysis of the tested chalcopyrite concentrate sample revealed the remarkable presence of pyrite mineral. The oxidation of chalcopyrite (reactions (2) and (3)) and pyrite also took place in the acidic hydrogen peroxide solution, resulting in the release of Fe(III) ions into the solution during the leaching process (reactions (4) and (5)) [37]:



Considering this, the dependence of the degree of oxidation of chalcopyrite (via iron) on time at different temperatures is illustrated in Figure 8. The final iron extraction values varied from approximately 28.6% to approximately 37% in the studied temperature range. The shape of the dissolution curves in Figure 8 is similar to the shape of the dissolution curve in Figure 6. It can be said that the rapid formation of a plateau on the dissolution curves indicated that iron extraction was completed after 30 (60) min of reaction as well.



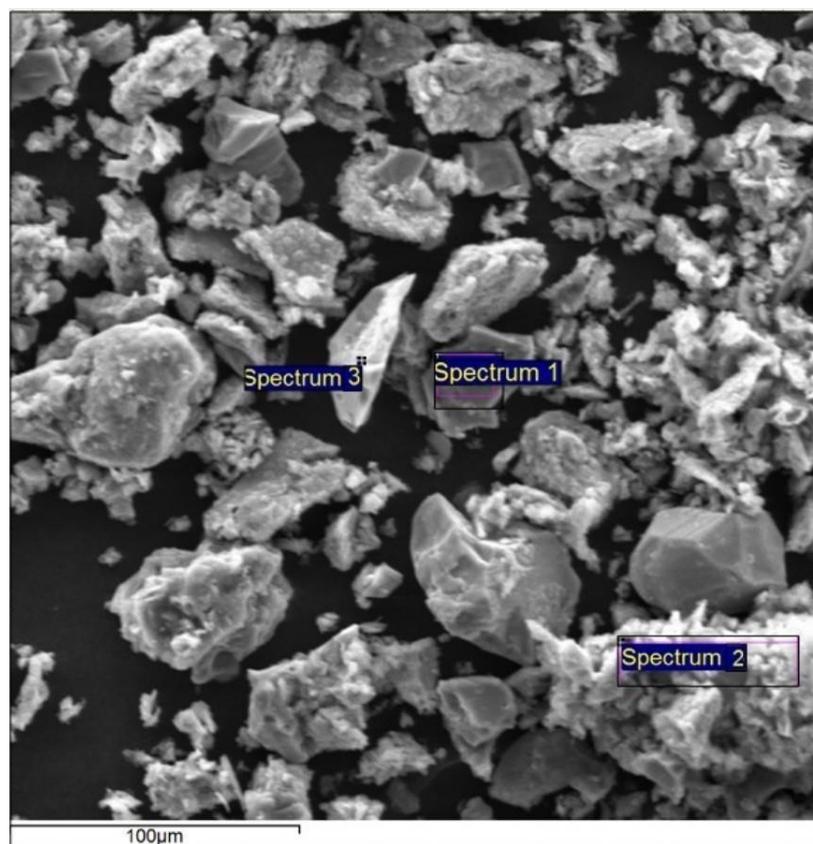
**Figure 8.** Temperature effect on iron extraction from chalcopyrite concentrate (conditions: 3.0 mol/L  $\text{H}_2\text{SO}_4$ , 2.0 mol/L  $\text{H}_2\text{O}_2$ , S/L = 1:100, 400  $\text{min}^{-1}$ ).

Additionally, it was observed that the oxidation reaction was very turbulent, especially in the first 60 min, as a result of intensive peroxide decomposition and oxygen effervescence. This phenomenon was also observed in the previously investigated  $\text{HCl-H}_2\text{O}_2$  leaching system [33] but significantly more intensively. The decomposition of hydrogen peroxide can be catalyzed by solid particles, soluble ions, and impurities [38,39]. Ruiz-Sanchez and Lapidus [29] showed that  $\text{Cu(II)}$  ions themselves did not catalyze the decomposition of hydrogen peroxide but that in the presence of  $\text{Fe(II)}$  or  $\text{Fe(III)}$  ions in solution, as well as in the presence of both  $\text{Fe(II)}$  ions and  $\text{Fe(III)}$  ions, which is the most unfavorable scenario,  $\text{Cu(II)}$  ions led to hydrogen peroxide decomposition, as proposed by Kremer [38]. The products of hydrogen peroxide decomposition are oxygen and water (reaction (6)):



Besides XRD analysis, the leach residue sample was tested by SEM-EDS analysis. Figure 9 shows the scanning electron microscopy image and corresponding energy spectra of the leach residue sample (after 120 min of leaching in the 3.0 mol/L  $\text{H}_2\text{SO}_4$  and 2.0 mol/L  $\text{H}_2\text{O}_2$  solution at 40 °C). The semiquantitative elemental analyses of selected areas listed in Table 3 present slightly oxygenated material of predominantly iron–(copper–)sulfide composition. An intense peak of sulfur with weaker peaks of copper and iron in all three spectra is obvious. The EDS analysis revealed that sulfur is the primary solid product resulting from the leaching process of chalcopyrite with  $\text{H}_2\text{O}_2$  in sulfuric acid solution. The results strongly support the findings of the XRD analysis.

The presence of elemental sulfur on the surface of the leach residue after chalcopyrite leaching with hydrogen peroxide in sulfuric acid solution was confirmed by Olubambi and Potgieter [23]. Hu et al. [35] also found that sulfur is the main solid product for the leaching of chalcopyrite with  $\text{H}_2\text{O}_2$  in an  $[\text{HMIm}]\text{HSO}_4$  ionic liquid aqueous solution. Ahn et al. [40] confirmed by SEM-EDS and XRD analyses that elemental sulfur was the main byproduct of chalcopyrite leaching with methanesulfonic acid and hydrogen peroxide.



**Figure 9.** Scanning electron microscopy image of the leach residue (leaching conditions: 3.0 mol/L  $\text{H}_2\text{SO}_4$ , 2.0 mol/L  $\text{H}_2\text{O}_2$ , 40 °C, S/L = 1:100, time 120 min, 400  $\text{min}^{-1}$ ).

**Table 3.** EDS results of the leach residue.

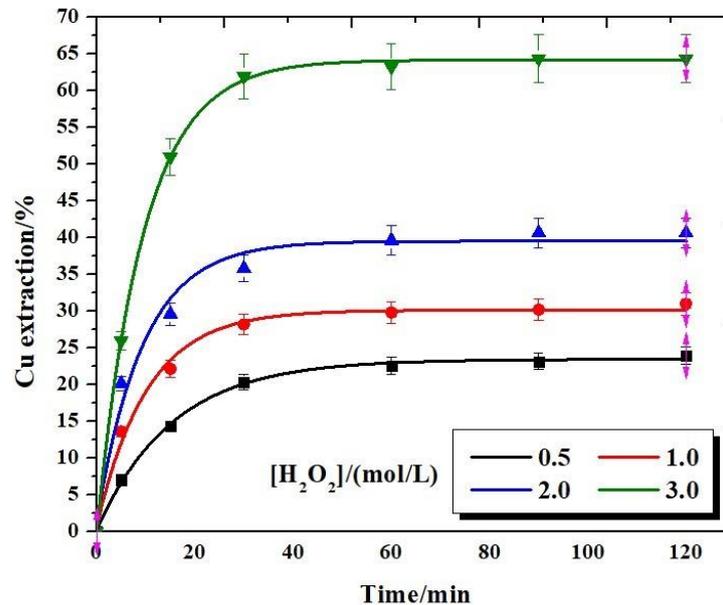
Element	Spectrum 1	Spectrum 2	Spectrum 3
O	4.00	8.84	2.70
Al	/	0.90	/
Si	0.30	5.30	1.70
K	/	1.40	/
Cu	1.25	13.50	6.40
Fe	49.20	24.80	32.85
S	45.25	44.46	53.65
Zn	/	0.80	2.70
$\Sigma$	100.00	100.00	100.00

### 3.4. Effect of Hydrogen Peroxide Concentration

The effect of the hydrogen peroxide concentration on copper extraction from chalcopyrite concentrate was investigated at initial hydrogen peroxide concentrations ranging from 0.5–3.0 mol/L in a 3.0 mol/L  $\text{H}_2\text{SO}_4$  solution at 40 °C. The results are presented in Figure 10.

The results in Figure 10 show that after 120 min of leaching, copper extraction reached ~64.5% when the highest concentration of hydrogen peroxide was used (3.0 mol/L  $\text{H}_2\text{O}_2$ ), whereas the copper extraction value was ~24% for the lowest tested hydrogen peroxide concentration (0.5 mol/L  $\text{H}_2\text{O}_2$ ). As the concentration of  $\text{H}_2\text{O}_2$  increased, the degree of copper extraction increased, and on the other hand, the catalytic decomposition of hydrogen peroxide into oxygen and water was more intensive. After 30 min of reaction, it became evident that there was no substantial enhancement in copper extraction. This implies that molecular oxygen, generated from the decomposition of peroxide within the system,

did not act as an oxidizing agent. This was also attributed to the formation of elemental sulfur distributed around the particles during the leaching process, which could hinder the contact between the chalcopyrite particles and reactants. The copper extraction in the examined system was significantly higher than that of the 3.0 mol/L HCl–2.0 mol/L H<sub>2</sub>O<sub>2</sub> system at 40 °C, where the copper extraction value was ~27% [33].



**Figure 10.** Extraction of copper from chalcopyrite concentrate as a function of time at different H<sub>2</sub>O<sub>2</sub> concentrations (conditions: 3.0 mol/L H<sub>2</sub>SO<sub>4</sub>, S/L = 1:100, 40 °C, 400 min<sup>-1</sup>).

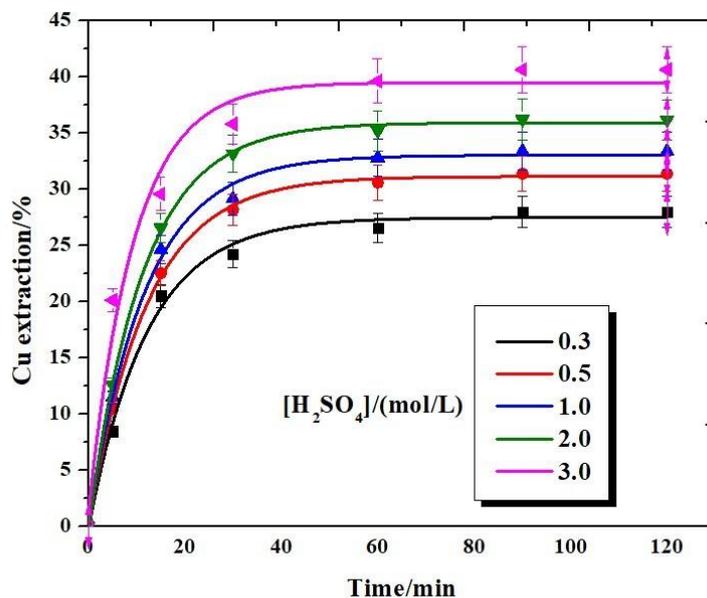
Different results of copper extraction values obtained during chalcopyrite leaching by hydrogen peroxide in sulfuric acid (without hydrogen peroxide stabilizers added) can be found in the research studies [23,24,26]. Olubambi and Potgieter [23] showed that the highest copper extraction of 87% was obtained at a hydrogen peroxide concentration of 3.0 mol/L during the fourth hour of leaching. It should be noted that the difference in the results obtained regarding copper extraction can be explained by the different leaching conditions as well as by the mineralogical and chemical composition of chalcopyrite samples used in certain leaching studies.

### 3.5. Effect of Sulfuric Acid Concentration

The effect of the initial concentration of sulfuric acid (0.1–3.0 mol/L) on chalcopyrite leaching was investigated in a 2.0 mol/L H<sub>2</sub>O<sub>2</sub> solution at 40 °C. As illustrated in Figure 11, at the tested concentrations of H<sub>2</sub>SO<sub>4</sub> from 0.3 to 3.0 mol/L, copper extraction ranged from ~28% to ~41%, respectively.

Under the investigated conditions, the copper extraction rate increased with increasing acid concentration during the early period of leaching. However, a significant decrease in the leaching rate in the final leaching stage was recorded. The formation of a plateau on the dissolution curves indicates that copper extraction ends. It was observed that the chalcopyrite dissolution reaction was vigorous in the first 30 min as a result of the intensive peroxide decomposition, but this phenomenon was less pronounced than that in the previously investigated HCl–H<sub>2</sub>O<sub>2</sub> system [33], where the instability of hydrogen peroxide was very pronounced. Antonijević et al. [24] determined that the sulfuric acid concentration has a positive effect on chalcopyrite oxidation in the H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O<sub>2</sub> system. Similar results have been observed in other studies on the oxidation of sulfide minerals in H<sub>2</sub>SO<sub>4</sub> solutions with H<sub>2</sub>O<sub>2</sub> [17]. On the other hand, different results were obtained during pyrite oxidation by hydrogen peroxide in sulfuric acid [36]. It has been found that an increase in sulfuric acid concentration leads to a decrease in the rate of pyrite dissolution.

The most likely reason for this decrease in the pyrite dissolution rate is that sulfate ions adsorb on the surface of pyrite particles and thus impede the contact surface between peroxide and pyrite particles [36].



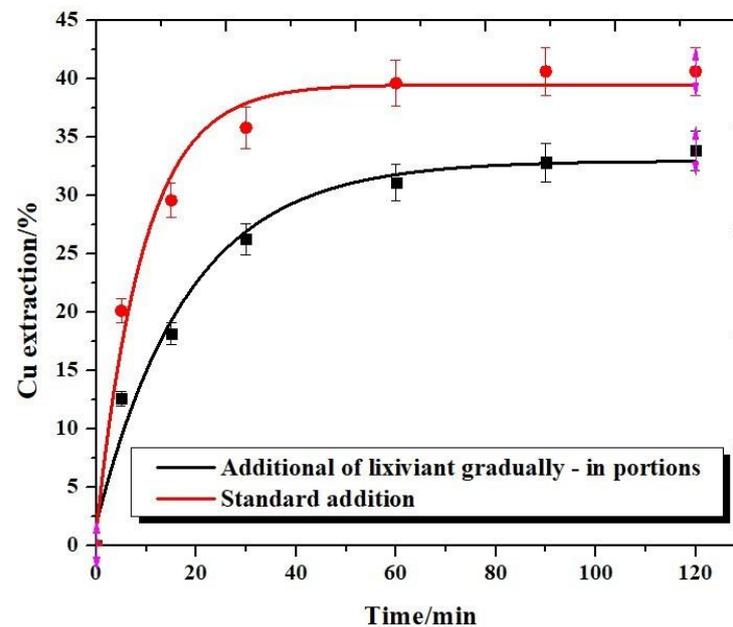
**Figure 11.** Copper extraction from chalcopyrite concentrate as a function of time at different  $\text{H}_2\text{SO}_4$  concentrations (conditions: 2.0 mol/L  $\text{H}_2\text{O}_2$ , S/L = 1:100, 40 °C, 400  $\text{min}^{-1}$ ).

### 3.6. Effect of the Mode of Lixiviant Dosing

In oxidative leaching systems, the presence of iron or copper in solution, mineral solid particles, etc., results in the relatively rapid decomposition of peroxide, which affects the dissolution rate of the minerals. From the shape of the dissolution curves in the present study, a tendency to increase mainly up to 30 (60) min of the reaction can be seen, which means that the oxidation of chalcopyrite occurred until that time. The main challenge that hindered the attainment of higher copper extractions seems to be the catalytic decomposition of hydrogen peroxide upon its interaction with chalcopyrite particles, as well as the subsequent release of Fe(III) ions during the leaching process. For this reason, in addition to a standard procedure of lixiviant addition, the leaching experiments were performed with a modified experimental procedure. In this procedure, 8 mL portions of lixiviant I (17 mL conc.  $\text{H}_2\text{SO}_4$  + 23 mL conc.  $\text{H}_2\text{O}_2$ ) were added at 10, 20, 40, 70, and 100 min of reaction into a glass beaker initially containing 160 mL of lixiviant II (17 mL conc.  $\text{H}_2\text{SO}_4$  + 18 mL conc.  $\text{H}_2\text{O}_2$  + water) and 2 g of chalcopyrite concentrate. The leaching solutions were sampled at 5, 15, 30, 60, 90, and 120 min of reaction. The lixiviant concentration in the experiment was adjusted to correspond to the standard experimental leaching conditions. The results are presented in Figure 12.

The dissolution curves obtained upon standard addition of the leaching solution were similar in shape to the curves obtained upon the addition of the lixiviant in portions (Figure 12). The dissolution curves when lixiviant was added in portions showed a trend of a slight increase up to 90 min of reaction. Nevertheless, the addition of lixiviant in portions did not contribute to greater metal extraction. When  $\text{H}_2\text{O}_2$  was added as an oxidant at the beginning of the leaching test without further additions, the copper extraction after 120 min of reaction reached ~41% upon leaching with 3.0 M  $\text{H}_2\text{SO}_4$ —2.0 M  $\text{H}_2\text{O}_2$ , while the extraction of copper when adding the lixiviant in portions for the same reaction time was 10% lower (i.e., approximately 30% Cu). On the other hand, in a recent study of the kinetics and mechanism of chalcopyrite leaching using organic methanesulfonic acid and hydrogen peroxide, Wu et al. [31] found that periodic addition of  $\text{H}_2\text{O}_2$  provided enough oxidant for chalcopyrite oxidative leaching in methanesulfonic acid solution, which contributed to consumption of the reducing reagent. Copper extraction gradually increased by increasing the hydrogen peroxide concentration from 0.3 vol. % to 0.9 vol. %. A study of copper slag

leaching with hydrogen peroxide in chloride media [41] showed that lixiviant should be added continuously to the leach suspension rather than at once at the beginning of the leaching experiment.



**Figure 12.** Effect of the mode of lixiviant dosing on copper extraction from the chalcopyrite concentrate.

### 3.7. Kinetics of Chalcopyrite Leaching

The main characteristic of heterogeneous reactions is their complexity and their occurrence in multiple stages. Chalcopyrite leaching is a complex heterogeneous process [42]. The rate of dissolution of chalcopyrite in acidic media depends on a large number of parameters, including temperature, the concentration and type of oxidants, acid concentration, agitation rate, etc. To determine the kinetic parameters and the rate-controlling step of the chalcopyrite leaching process, there are a large number of equations on the basis of which the essential characteristics of the investigated process can be defined [43–45].

To illustrate the leaching kinetics, two models are utilized: the shrinking core model (SCM) and the progressive conversion model (PCM). The models emphasized the crucial significance of the transformations taking place at both the physical and chemical levels within the particles themselves [46,47]. In the field of mineral leaching, it is common to employ mathematical models that rely on an inverse exponential function to effectively describe the process. This function is widely known as a first-order rate equation. Considering the above, the study conducted a detailed analysis of the results from a kinetic point of view. It can be seen that the shapes of the dissolution curves in this study showed an exponential dependence. To achieve a linear representation of the experimental data, it is essential to employ a logarithmic function. With a goal to describe the leaching kinetics of chalcopyrite in the investigated  $\text{H}_2\text{SO}_4\text{--H}_2\text{O}_2$  system, the Kazeev-Erofeev equation [48] was selected.

Based on Equation (7):

$$1 - X = \exp(-kt) \quad (7)$$

where  $X$  is the degree of Cu extraction,  $t$  is the leaching time, and  $k$  corresponds to the reaction kinetic constant. Introducing the parameter  $X_m$  related to the maximum extraction of copper in the system (determined from the dissolution curves for  $t \rightarrow \infty$ ), a classical first-order kinetics equation (Equation (8)) was attained:

$$X = X_m [1 - \exp(-kt)] \quad (8)$$

The logarithm of Equation (8) yielded Equation (9):

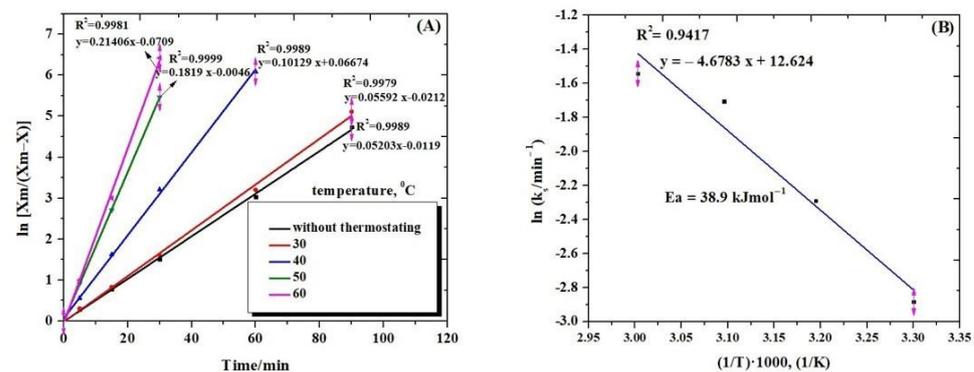
$$\ln [X_m/(X_m - X)] = k \cdot t \quad (9)$$

Equation (9) was selected as the most optimal kinetics model for precisely fitting the experimental data in this study.

By determining the value of the reaction rate constant at different temperatures, it is possible to determine the activation energy for the observed system through calculation or graphics. The value of the activation energy indicates the nature of the reaction itself, i.e., whether the reaction is under chemical control, diffusion control, or mixed process control. An activation energy below 40 kJ/mol generally indicates that diffusion primarily influences the leaching process, resulting in parabolic leaching. Conversely, if the activation energy is greater than 40 kJ/mol, this suggests a chemical reaction is taking place during the leaching process, which is referred to as linear leaching [47,49].

### 3.7.1. Effect of Temperature

To determine the activation energy, Equation (9) was used for the linearization of the kinetic curves shown in Figure 6. A plot of  $\ln [X_m/(X_m - X)]$  versus the leaching time at different leaching temperatures is shown in Figure 13A. The high values of correlation coefficients ( $R^2$ ) imply very good agreement of the experimental data with the selected kinetic model (Equation (9)).



**Figure 13.** Plot of  $\ln [X_m/(X_m - X)]$  vs. time at different temperatures (A) and Arrhenius plot of chalcopyrite dissolution in the H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O<sub>2</sub> system (B).

The relationship between the reaction rate constant and temperature can be described by the Arrhenius law shown by Equation (10):

$$k = A \cdot \exp(-E_a/RT) \quad (10)$$

where  $k$  is the reaction constant ( $\text{min}^{-1}$ ),  $A$  is the frequency factor,  $E_a$  is the apparent activation energy (kJ/mol),  $R$  is the universal gas constant (8.314 J/K/mol), and  $T$  is the absolute temperature (K).

Apparent rate constants  $k_s$  for each temperature were obtained from the slopes of the lines in Figure 13A. From the dependency  $\ln k_s = f(1/T)$  shown in Figure 13B, an activation energy value of 38.9 kJ/mol was determined.

It is important to point out that the calculation of the activation energy of the chalcopyrite leaching process did not take into account the experimental results obtained under non-thermostated conditions. The decision was based on the fluctuating reaction temperature observed during the experiment, highlighting the crucial need to maintain consistent conditions in order to achieve accurate and dependable results. Thus, the activation energy in the H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O<sub>2</sub> system was determined in the tested temperature range of 30–60 °C.

For the studied H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O<sub>2</sub> system, the experimental curves showed an exponential dependence, and the first-order kinetics equation best modelled the examined process.

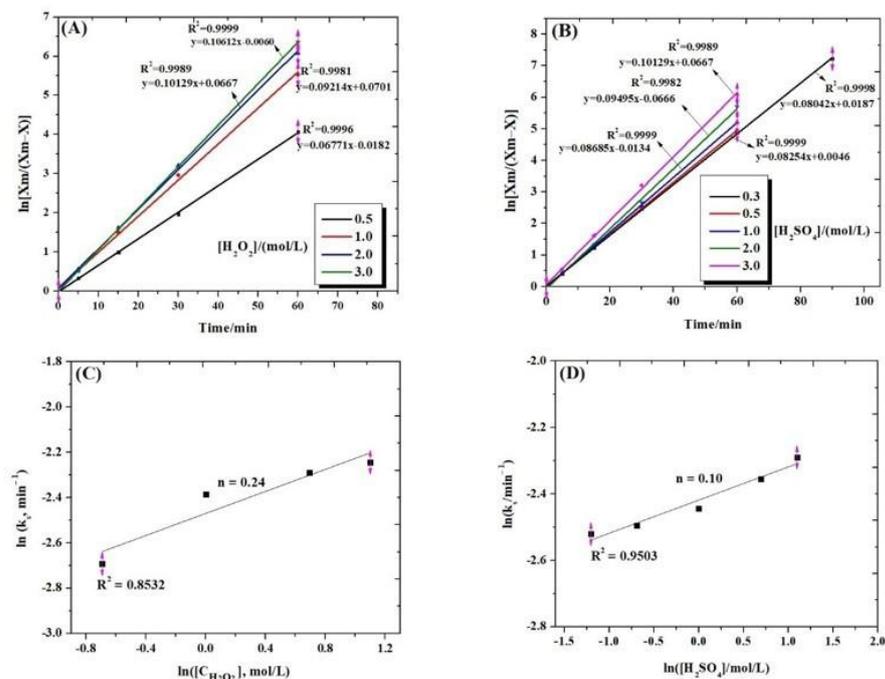
During leaching, elemental sulfur was formed as a reaction product on the mineral particles, decreasing the reaction rate. The activation energy value was  $\sim 39$  kJ/mol. Based on the abovementioned facts, it was concluded that the chalcopyrite dissolution reaction was most likely controlled by the diffusion of reactants through the product layer. The chemical surface reaction mechanism was probably important only throughout the initial leaching stages. The leaching kinetic equation is Equation (11), where the correlation coefficient  $R^2$  is 0.9417 and the apparent activation energy  $E_a$  is approximately 39 kJ/mol.

$$\ln [X_m/(X_m - X)] = 0.10129 \cdot t \quad (11)$$

The activation energy values obtained from kinetic studies of chalcopyrite leaching with hydrogen peroxide in acidic media span a wide range. For example, Antonijević et al. [24] showed that the chalcopyrite oxidation kinetics follow a shrinking core model with the surface chemical reaction as the rate-controlling step, and an activation energy of 60 kJ/mol was determined. Mahajan et al. [21] reported that the activation energy of the chalcopyrite leaching process was 30 kJ/mol and that the leaching reaction follows the surface reaction-controlled model. According to Adebayo et al. [16], dissolution kinetics follow a shrinking-core model controlled by the surface chemical reaction as the rate-determining step, and an activation energy value of 39 kJ/mol was calculated. Sokić et al. [20] reported that the kinetic data for the copper leaching process show a good fit for the model controlled by diffusion, and the calculated activation energy value was 80 kJ/mol. Hu et al. [35] examined the kinetics of the copper extraction process in an [HMIIm]HSO<sub>4</sub> aqueous solution with H<sub>2</sub>O<sub>2</sub> as an oxidizing agent and found that the copper leaching process was controlled by a chemical reaction with an activation energy of 52.06 kJ/mol and with the formation of sulfur as the main leaching product located near unleached chalcopyrite. Ahn et al. [40] calculated the activation energy to be 39.9 kJ/mol and indicated that the rate-determining step was the surface chemical reaction.

### 3.7.2. Effect of Hydrogen Peroxide and Sulfuric Acid Concentrations

The kinetic curves shown in Figures 10 and 11 were linearized by means of Equation (9), as shown in Figure 14A,B, respectively.



**Figure 14.** Plot of  $\ln [X_m/(X_m - X)]$  vs. time at different concentrations of H<sub>2</sub>O<sub>2</sub> (A) and H<sub>2</sub>SO<sub>4</sub> (B); Plot of  $\ln k_s$  vs.  $\ln[H_2O_2]$  (C) and  $\ln[H_2SO_4]$  (D).

The rate constants were calculated from the slopes of the straight lines from Figure 14A,B. Logarithms of these values were plotted as a function of the logarithm of concentrations of  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$  (as shown in Figure 14C,D, respectively). The reaction orders for  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$  were determined to be 0.24 and 0.10, respectively.

Previous studies on chalcopyrite leaching with hydrogen peroxide have shown that an increase in sulfuric acid concentration increased the oxidation of chalcopyrite, where reaction orders of 0.3 (between 0.5 and 3 mol/L  $\text{H}_2\text{SO}_4$ ) [24] and 0.77 (between 0.1 and 6 mol/L  $\text{H}_2\text{SO}_4$ ) [16] were determined in relation to the acid concentration.

The aforementioned research and the obtained results represent a good basis for further research that would be based on the use of modern research concepts using one of the many methods of machine learning [50]. There is a proven application of machine learning concepts in research conducted in the area of material characterization [51], which creates the possibility of application in the area of research considered in this paper. Since the majority of the obtained results presented in the previous considerations are made by different analyses based on the use of time series, there is great potential for the use of predictive methods in order to obtain appropriate forecast values over the data presented by those time series [52,53].

In the case of the application of predictive methods, a special advantage is realized in accordance with the fact that the previous research procedures have already carried out the necessary input processing in terms of historical data that will be used during the realization of forecasts. The data have already been adequately processed in the previous procedures in terms of filtering, adequate representation, the removal of missing values, and other necessary preparatory actions. Also, the data have already been verified by previously obtained results. This means that the probability of model training with data for which we do not have information about their accuracy is reduced to a minimum in this case, which creates good predispositions for high-quality and reliable model training.

#### 4. Conclusions

In this study, the extraction of copper from chalcopyrite concentrate by hydrogen peroxide as a strong oxidizing agent in sulfuric acid solution was investigated.

The investigations conducted on the impact of different leaching parameters have revealed that higher temperatures and increased concentrations of hydrogen peroxide and sulfuric acid have a beneficial effect on the leaching of chalcopyrite. The results obtained clearly demonstrate that copper extraction experienced a substantial increase within the initial 60 min of the reaction. However, as a consequence of the catalytic decomposition of hydrogen peroxide, the dissolution of chalcopyrite ceased thereafter.

The maximum final copper extraction value of 64.5% was obtained under the following conditions: 3.0 mol/L  $\text{H}_2\text{SO}_4$  and 3.0 mol/L  $\text{H}_2\text{O}_2$ , a solid/liquid ratio of 1:100, a particle size of  $-75 \mu\text{m}$ , a temperature of  $40^\circ\text{C}$ , a leaching time of 120 min, and a stirring speed of  $400 \text{ min}^{-1}$ .

The catalytic decomposition of hydrogen peroxide was noticed in the  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2$  system but was less pronounced than that observed in the previously investigated  $\text{HCl-H}_2\text{O}_2$  system for chalcopyrite leaching, which was reflected in the obtained metal extraction values. The sulfate system has proven to be more suitable for leaching chalcopyrite, based on the achieved results in both systems.

Hydrogen peroxide underwent spontaneous decomposition with the evolution of oxygen gas, which was more pronounced in the presence of the Fe(III) ions that were produced by the dissolution process itself and acted as a catalyst for peroxide decomposition.

The dissolution process of chalcopyrite was described by the first-order kinetics equation  $X = X_m [1 - \exp(-kt)]$  with an activation energy of  $\sim 39 \text{ kJ/mol}$ . The rate of reaction was most likely controlled by lixiviant diffusion through the sulfur layer. The reaction orders for  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$  were determined to be 0.24 and 0.10, respectively.

The formation of elemental sulfur as the main product of chalcopyrite leaching by hydrogen peroxide in sulfuric acid solution was confirmed by XRD and SEM-EDS analysis.

The research described above, along with its findings, provides a good basis for conducting further studies in the field presented in the paper in terms of achieving predictions using appropriate procedures and machine learning models.

**Author Contributions:** Conceptualization, S.J.P. and G.D.B.; investigation, S.J.P.; writing—original draft preparation, S.J.P.; writing—review and editing, G.D.B. and M.M.A.; visualization, M.V. and R.K.; supervision, M.M.A. and M.V. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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