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# Microwave-assisted leaching for copper recovery from the chalcopyrite concentrate of Sarcheshmeh copper complex

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## ABSTRACT

Microwave applications in mining and process metallurgy have been the subject of many studies over the past two decades. This paper reviews the microwave-assisted leaching of copper from high-grade sulfide concentrate of the Sarcheshmeh copper complex. Response surface methodology (RSM) is used to optimize the leaching process. In this research, leaching experiments were carried out in a multi-mode cavity, and times in the presence of varying concentrations of $H_2O_2$ with microwave assistance after the leaching process parameters including type and concentration of the oxidizing agent, NaCl concentration, and leaching temperature, were optimized using Taguchi orthogonal array design method. Conventional leaching experiments were also performed to evaluate the influence of microwave radiation. It has been recognized that microwave technology has great potential to improve the extraction efficiency of metals in terms of both reductions in required leaching time and the recovery of valuable metals. Under the optimized conditions, the leaching efficiencies of copper were 75.3% and 42.5% in 3 hours by microwave assistance and conventional leaching methods, respectively.

**Keywords:** *Sarcheshmeh; Microwave leaching; Taguchi; RSM; Optimization.*

## 1. Introduction

Sarcheshmeh Copper Mine is considered as one of the largest complexes of the mining industry in the world and is the largest copper producer in Iran. The geological reserve of the mine is over 1,200 billion tons of sulfide ore with an average assay of 0.7% [1]. Amongst the sulfide ores of copper, chalcopyrite is the most common and important mineral from which copper is extracted. Presently, chalcopyrite ores are concentrated by the froth flotation process and processed using pyrometallurgical techniques of smelting and converting [1].

In recent years, hydrometallurgical processes are more considered and they have become more attractive mainly due to their low air pollution, lower energy demands, and wide adaptability to the different grades of the ore [2-4]. Much effort has been directed toward the development of hydrometallurgical processes [3, 5, 6]. Whereas, the limited leaching rate of chalcopyrite is an obvious defect of hydrometallurgy, due to the generation of the passivation layer [7]. Nakazawa mentioned that passivation prevented the transfer of $Cu^{2+}$ from the chalcopyrite [8]. Therefore, many techniques have been explored to weaken the effect of the passivation layer and increase the copper recovery from chalcopyrite, such as bioleaching, organic extractant additions, sulfidizing chalcopyrite, mechanical activation, the use of ozone as an oxidant, and catalyst addition (like Silver ions, surfactants, Carbon particles, Iron powder, chloride ions or Hematite) [9, 10].

Microwave-assisted heating is a new processing technology and has been employed to recover copper from chalcopyrite by leaching[11-13]. A microwave is a form of electromagnetic radiation with frequencies ranging from 300 MHz to 300 GHz [14]. The most commonly used frequencies for heating purposes are 915 MHz and 2.45 GHz. These frequencies were chosen by an international agreement to minimize the interference with microwave communication signals [15]. The electric field of the microwave interacts with polar materials while the magnetic field of the microwave reacts with charged materials [16].

Selective heating leads to the different temperatures of different materials in the microwave system. Many studies have reported that the microwave is an effective method for accelerating the leaching rate of chalcopyrite [11, 17, 18]. However, the mechanisms of high recovery in microwave systems are still vague and controversial [18, 19].

In Behera's research (2020), the microwave-assisted leaching of Cu and Cr from Cu-Cr spent catalyst was investigated. The optimum condition; was 900 W power, 2 min treatment time, 10% $H_2O_2$ (v/v), and 1 M sulphuric acid during microwave irradiation followed by leaching with a very low concentration of $H_2SO_4$ (1% (w/w)) was suitable for quantitative extraction of both metals from the spent catalyst phase. The XRD and EDAX characteristics pattern of residue samples resulted in optimum leaching conditions further ascertained on substantial extraction of copper (99.99%) and chromium (98.56%) from the spent catalyst phase[11].

In another research by Ma (2017), the decomposition of copper anode slime heated by microwave energy in a sulfuric acid medium was investigated. Leaching experiments were carried out in a multi-mode cavity with microwave assistance. The leaching process parameters were optimized using response surface methodology (RSM). Under the optimized conditions, the leaching efficiencies of copper and tellurium were 99.56% ± 0.16% and 98.68% ± 0.12%, respectively. In the results, microwave technology is demonstrated to have a great potential to improve the leaching efficiency and reduce the leaching time. The enhanced recoveries of copper and tellurium are believed to result from the presence of a temperature gradient due to the shallow microwave penetration depth and the superheating at the solid-liquid interface [18].

Baghurst and Mingos (1992) [18] have reported that the boiling point

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of various solutions in microwave systems is higher than that in the conventional heating system. A higher boiling point can effectively improve the temperature of a reactive layer to accelerate the rate of leaching reaction. Additionally, it has been investigated that the energy input from the surrounding can improve the surface energy [11].

The present research aims to investigate the influence of microwave irradiation on the oxidative leaching of sulfide concentrate of the Sarcheshmeh copper complex. In addition, the optimum leaching conditions were obtained by Taguchi Orthogonal Array (OA) design and response surface methodology (RSM), respectively. In detail, the leaching efficiencies of Cu obtained by the conventional and microwave radiation heating methods were compared and interpreted.

## 2. Materials and methods

### *2.1. Materials*

The high-grade sulfide concentrate of the Sarcheshmeh copper complex in Iran was used as the raw material for all experiments. The samples of concentrates were sieved into $d_{80}$ = 75 microns. The chemical and mineralogical analyses of samples were determined using ICP and XRD methods, respectively. The results were shown in Table 1 and Figure 1. All chemical materials used in this study were of Merck laboratory grade. In this study, two different types of leaching methods, including conventional acid leaching and microwave leaching, were used separately.

**Table 1.** Results of the chalcopyrite concentrate sample assay.

| Chemical analysis | | Mineralogical analysis | |
|---|---|---|---|
| Element | % | Mineral, XRD | % |
| S | 36.64 | $CuFeS_2$ | 60 |
| Fe | 31.22 | $FeS_2$ | 17 |
| Cu | 20.93 | $Cu_2S$ | 2.5 |
| $SiO_2$ | 4.99 | CuS | 1.9 |
| Zn | 0.72 | $Fe_2O_3$ | 1.9 |
| $K_2O$ | 0.38 | | |
| MgO | 0.23 | | |
| $TiO_2$ | 0.20 | | |
| $P_2O_5$ | 0.15 | | |
| CaO | 0.15 | | |

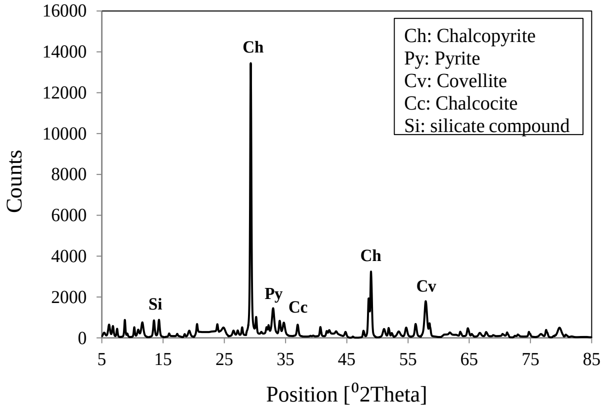

**Figure 1.** XRD pattern of Sarcheshmeh Copper Concentrate.

### *2.2. Methods*

A sample of 1 g mixed with the configured leaching solution in 80 ml Erlenmeyer flasks. The leaching solution contained a 50 ml mixed solution of $H_2SO_4$ (0.5M) and various concentrations of different oxidizing agents and NaCl promoters, at the desired temperature designed by $L_9$ orthogonal array of Taguchi and the solid-liquid ratio of 5%, which stirred for 3 h at 300 rpm.

The microwave-assisted leaching is carried out in the (2.45 GHz, multimode cavity, 1000 W) microwave chemical reactor of 300 W. The temperature and time are controllable and an incorporated temperature sensor into the system is monitored and controlled the set temperature. Subsequently, the microwave-assisted leaching was performed under the same conditions as conventional experiments (designed by $L_9$ orthogonal array of Taguchi) in a clear and chemically resistant Polytetrafluoroethylene (PTFE) vessel as a leaching vessel. After leaching, the residues were collected from suspension by filtering, and then separated solutions were analyzed using ICP-OES to determine copper extraction efficiency. The independent parameters, their levels, and experimental condition of both experimental methods used for Taguchi orthogonal arrays of $L_9$ ($3^4$) are shown in Tables 2 and 3.

Then a statistical variance analysis (ANOVA) was performed to determine effective parameters and their confidence levels. Also, the effect of each controlling factor at a given level can be estimated using an analysis of the mean (ANOM), and subsequently, the optimum levels can be found [20]. Finally, a verification test was carried out to verify the optimum parameters [21].

After the parameters were optimized, to develop the models for copper leaching efficiencies, three input parameters (Microwave power, Reaction time, and $H_2O_2$ concentration) were considered. The solid-to-liquid ratio and $H_2SO_4$ concentration were kept constant at 5% and 0.5 mol. $L^{-1}$, respectively. The parameters and their levels are shown in Tables 4 and 5.

### *2.3. Material characterization*

The crystalline structure of the sulfide concentrate was determined by X-ray phase analysis (XRD, PHILIPS, X' pert MPD system, λ=1.54 Å) with Kα Cu radiation. Also, the inductively coupled plasma optical emission spectrometry (ICP, VARIAN OES) was used for the determination of leachate $Cu^{2+}$ concentrations.

## 3. Results and Discussion

The results of the matrix experiment, conducted under conditions presented in Table 3, are illustrated in Table 6. The maximum efficiency of copper extraction in conventional and microwave leaching was about 39.7% and 40.9%, respectively. Similarly, Tables 7a and 7b show the results of variance analysis (ANOVA) in conventional and microwave leaching. In these tables, the sum of squares ($SS_{Factor}$), degrees of freedom ($d_f$) and mean of squares ($V_{Factor} = SS_{Factor} / d_f$), were represented, respectively. Subsequently, the F-value ($F_{Factor}=V_{Factor}/V_{Error}$), and P-value were calculated.

As illustrated in Tables 7a and 7b, the F-values of some factors were greater than the extracted F-value of the table for $\alpha$ =0.05. It means that the variance of those factors is significant compared to the variance of error and all of them have a significant effect on the response. The significance of each coefficient was also determined by p-values, which are listed in this Table. P-values less than 0.05 indicate that model terms are significant with a 95% confidence level.

Finally, the contribution of each factor to leaching efficiency is shown in Figures 2a and 2b. These analyses reveal that all three parameters including temperature, oxidizing agent, and concentration have a significant contribution to leaching efficiency. However, NaCl concentration has no involvement in the results.

Accordingly, the effect of each parameter level on the response variable is shown in Figures 3a and 3b. It demonstrates that the best efficiency was obtained when all parameters were set at the third level. The optimum condition of each variable is briefly shown in Table 8.

**Table 2.** Main controlling factors and their levels.

| Factors | Levels | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| Oxidizing Agent | $Fe_2(SO_4)_3$ | $FeCl_3$ | $H_2O_2$ |
| Oxidant Concentration (M) | 0.05 | 0.15 | 0.25 |
| NaCl Concentration (M) | 0 | 1 | 2 |
| Leaching Temperature ($^0$C) | 50 | 75 | 90 |

**Table 3.** Experimental condition based on Taguchi $L_9(3^4)$ standard orthogonal array.

| Exp. No | oxidizing agent | Oxidant Concentration (M) | NaCl Concentration (M) | Leaching Temperature (⁰C) |
|---|---|---|---|---|
| 1 | $Fe_2(SO_4)_3$ | 0.05 | 0 | 50 |
| 2 | $Fe_2(SO_4)_3$ | 0.15 | 1 | 75 |
| 3 | $Fe_2(SO_4)_3$ | 0.25 | 2 | 90 |
| 4 | $FeCl_3$ | 0.05 | 1 | 90 |
| 5 | $FeCl_3$ | 0.15 | 2 | 50 |
| 6 | $FeCl_3$ | 0.25 | 0 | 75 |
| 7 | $H_2O_2$ | 0.05 | 2 | 75 |
| 8 | $H_2O_2$ | 0.15 | 0 | 90 |
| 9 | $H_2O_2$ | 0.25 | 1 | 50 |

**Table 4.** Independent variables and their levels for response surface methodology.

| Factors | Levels | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| Microwave power (W) | 300 | 600 | 900 |
| Reaction time (h) | 1 | 2 | 3 |
| $H_2O_2$ concentration (M) | 0.2 | 0.3 | 0.4 |

**Table 5.** Experimental design matrix.

| Exp. No | Microwave power (W) | Reaction time (h) | $H_2O_2$ concentration (M) |
|---|---|---|---|
| 1 | 600 | 2 | 0.3 |
| 2 | 600 | 2 | 0.3 |
| 3 | 300 | 2 | 0.4 |
| 4 | 300 | 3 | 0.3 |
| 5 | 600 | 3 | 0.2 |
| 6 | 600 | 1 | 0.2 |
| 7 | 900 | 2 | 0.4 |
| 8 | 600 | 2 | 0.3 |
| 9 | 600 | 2 | 0.3 |
| 10 | 900 | 3 | 0.3 |
| 11 | 900 | 1 | 0.3 |
| 12 | 600 | 1 | 0.4 |
| 13 | 300 | 2 | 0.2 |
| 14 | 900 | 2 | 0.2 |
| 15 | 600 | 2 | 0.3 |
| 16 | 600 | 3 | 0.4 |
| 17 | 300 | 1 | 0.3 |

**Table 6.** Results of leaching efficiency from the Taguchi method.
a: Conventional leaching
b: Microwave leaching

| Run a | R% | Run b | R% |
|---|---|---|---|
| 1 | 5.71 | 1 | 8.37 |
| 2 | 14.35 | 2 | 17.44 |
| 3 | 39.67 | 3 | 40.59 |
| 4 | 16.51 | 4 | 18.06 |
| 5 | 9.72 | 5 | 12.66 |
| 6 | 18.98 | 6 | 20.84 |
| 7 | 14.66 | 7 | 22.38 |
| 8 | 34.42 | 8 | 40.90 |
| 9 | 29.79 | 9 | 36.89 |

**Table 7a.** Analysis of variance (ANOVA) in conventional leaching.
F (0.05, 2, 2) =19

| Source | $SS_{Factor}$ | $d_f$ | $V_{Factor}$ | F-value | p-value |
|---|---|---|---|---|---|
| Model | 1068.36 | 6 | 178.06 | 83.61 | 0.0119 |
| Oxidizing Agent | 190.02 | 2 | 95.01 | 44.61 | 0.0219 |
| Oxidizing Concentration (M) | 446.94 | 2 | 223.47 | 104.93 | 0.0094 |
| NaCl Concentration (M) | 4.26 | 2 | 2.13 | Error Factor | - |
| Temperature (⁰C) | 431.40 | 2 | 215.70 | 101.28 | 0.0098 |
| $V_{Error}$ | 4.26 | 2 | 2.13 | - | - |
| Total | 1072.62 | 8 | - | - | - |

It was found that the rate of copper extraction from the solution was highly temperature-dependent. As illustrated in Figures 3a and 3b, at a temperature of 50 ºC and after 3 hours, 15.1% and 19.3% of copper were extracted from both conventional and microwave leaching respectively, whereas 30.2% and 33.2% were recovered at a temperature of 90 ºC after the same time.

### *3.1. Effect of temperature*

The reaction rate of chalcopyrite dissolution is highly dependent on temperature [22, 23]. So that the increase in temperature led to an increase in reaction rate. Generally, a double increase in the reaction rates is reported for every 10°C rises in temperature [24]. In another research, increasing temperature from 70°C to 90°C increased the leaching efficiency from 28% to 70% after 2 h in a sulfate media [23].

The temperature effect can be quantified by measuring the activation energies at high and low temperatures, respectively. Based on the published data, the activation energy during the initial stages of the reaction was calculated to be 48 $kJ.mol^{-1}$ at low temperature and 20 $kJ.mol^{-1}$ at high temperature [22]. It is, also, reasonable to compare directly the results of microwave and conventional leaching. Figures 3a and 3b show a comparison between the rate of copper leaching from Sarcheshmeh concentrate in different solutions at different temperatures, with and without the influence of microwaves. It demonstrates the positive influence of microwave energy on copper recovery over the range of temperatures used. However, this positive influence is not great (Figures 3a and 3b). As shown, after 3 h, the amount of copper extracted at 90°C is 33.2% under microwave conditions while 30.2% under conventional conditions. The mechanisms by which microwaves interact with a chemically reactive system are still a matter of controversy.

**Table 7b.** Analysis of variance (ANOVA) in microwave leaching.
F (0.05, 2, 2) =19

| Source | $SS_{Factor}$ | $d_f$ | $V_{Factor}$ | F -Value | p-value |
|---|---|---|---|---|---|
| Model | 1185.18 | 6 | 197.53 | 77.02 | 0.0129 |
| Oxidizing Agent | 413.73 | 2 | 206.87 | 80.66 | 0.0122 |
| Oxidizing Concentration (M) | 410 | 2 | 2.56 | 79.93 | 0.0124 |
| NaCl Concentration (M) | 5.13 | 2 | 2.13 | Error Factor | - |
| Temperature (⁰C) | 361.44 | 2 | 180.72 | 70.46 | 0.0140 |
| $V_{Error}$ | 5.13 | 2 | 2.56 | - | - |
| Total | 1190.31 | 8 | - | - | - |

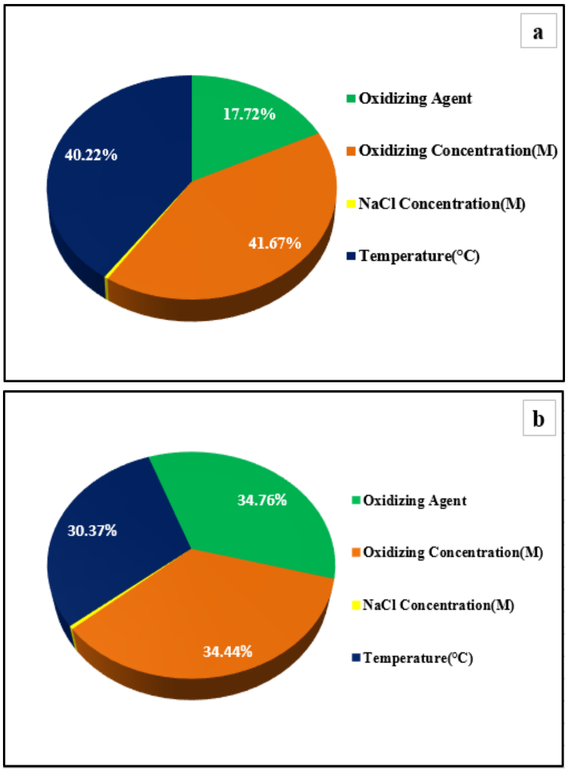

**Figure 2.** Contribution of affecting factors to the response.
a: Conventional leaching, b: Microwave leaching.

**Table 8.** The optimum levels of each parameter.

| Levels | Leaching temperature (⁰C) | NaCl concentration (M) | Oxidant concentration (M) | Oxidizing agent |
|---|---|---|---|---|
| Optimum | 90 | 2 | 0.25 | $H_2O_2$ |

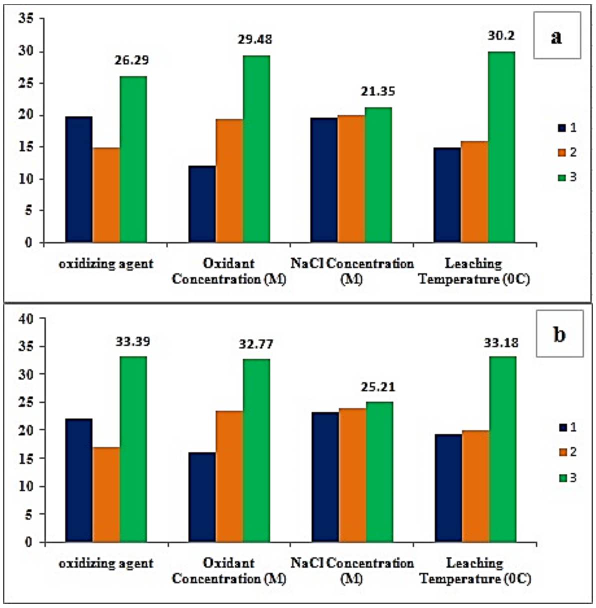

**Figure 3.** Effect of each parameter level on the response variable.

a: Conventional leaching, b: Microwave leaching

Considering this, some researchers claim the existence of a non-thermal microwave effect by which the activation energy can be significantly reduced. Others, explain the remarkable acceleration of reaction rate by microwave-induced thermal effects or the so-called superheating effect [25]. However, it is predictable that the activation energy determined for microwave leaching is lower than conventional leaching.

### *3.2. Effect of oxidizing agent*

Similarly, according to the results shown in Figures 3a and 3b, the effect of ferric sulfate and ferric chloride in copper extraction is lower than $H_2O_2$ also higher concentrations of oxidant agents led to an increase in copper extraction. The effects of ferric sulfate and ferric chloride on copper sulfide minerals have been investigated by many researchers [4, 9, 22]. The main reaction, which describes the leaching of chalcopyrite in ferric sulfate, was proposed in the reaction (1) [4, 22, 26]:

$$CuFeS_2 + 2Fe_2(SO_4)_3 \rightarrow CuSO_4 + 5FeSO_4 + 2S^\circ \tag{1}$$

However, reaction (2) may also take place thermodynamically [26]:

$$CuFeS_2 + 8Fe_2(SO_4)_3 + 8H_2O \rightarrow CuSO_4 + 17FeSO_4 + 8H_2SO_4 \tag{2}$$

Despite all benefits of leaching by ferric sulfate, the principal disadvantage is its slower reaction rate compared to leaching by ferric chloride and $H_2O_2$. This is probably due to the formation of a passive layer (elemental sulfur) on the surface of the particles, which retards the reaction rate and the transport of reactants[4]. The formation of about 94% sulfide sulfur during acid leaching of chalcopyrite in ferric sulfate solution has been proven by some researchers [4, 27].

Generally, it would be expected that as $Fe^{+3}$ concentration increases an increase in the reaction rate will follow. But, the reaction rate of chalcopyrite dissolution in ferric sulfate is independent of the ferric ion concentration. It became clear that the rate-limiting step is the transport of electrons through the elemental sulfur layer [26]. The leaching reaction of chalcopyrite with ferric chloride is [9]:

$$CuFeS_2 + 4FeCl_3 \rightarrow CuCl_2 + 5FeCl_2 + 2S^\circ \tag{3}$$

The reaction in below, although thermodynamically less likely, could also occur [9]:

$$CuFeS_2 + 3FeCl_3 \rightarrow CuCl + 4FeCl_2 + 2S^\circ \tag{4}$$

Similar to the leaching of chalcopyrite by ferric sulfate, in the ferric chloride medium, $S0_4^{2-}$ could be generated in quantities of less than 5% [28].

The reaction rate of chalcopyrite dissolution in ferric chloride increases considerably by increasing the concentration of $FeC1_3$ (from 0.001-0.2 M) [29]. Unlike the ferric sulfate system, the leaching rate is more dependent on ferric chloride concentration [22]. It is reported that the amount of extracted copper was doubled when the ferric chloride concentration was increased from 0.1 to 2 M [30]. Also, it is proved that the addition of sulfate ions to a mixed solution of 0.1M $FeC1_3$ in 0.3M HCl at 90°C reduced the amount of dissolved copper [22].

Hydrogen peroxide was used as a relatively cheap and strong oxidizing agent, with a redox potential of +1.77 mV in the acidic medium. The application of hydrogen peroxide for the leaching of chalcopyrite in sulfuric acid solution has previously been examined by several authors [31-34].

Oxidative activity of the hydrogen peroxide is based on its dissociation to the reactive hydroxyl anion group (OH−) and hydroxyl radical (•OH), dissociation is catalyzed by ferric ion, this reaction occurs according to the chemical equation (5) [31]:

$$H_2O_2 + Fe^{2+} \rightarrow {\bullet}OH + OH^- + Fe^{3+} \tag{5}$$

A dominant mechanism of chalcopyrite dissolution by the hydrogen peroxide in acidic solution is given by the equation (6) [35]:

$$2CuFeS_2 + 17H_2O_2 + 2H^+ \rightarrow 2Cu^{2+} + 2Fe^{3+} + 4SO_4^{\ 2-} + 18H_2O \tag{6}$$

At the same time, a small part of sulfide sulfur is oxidized to its elemental form, this is confirmed by XRD analysis of the leach residue and a leaching degree of 55%, the reaction is presented by equation (7):

$$2CuFeS_2 + 5H_2O_2 + 10H^+ \rightarrow 2\,Cu^{2+} + 2Fe^{3+} + 4S^0 + 10\,H_2O \tag{7}$$

Agacayak et al. obtained similar results [32]. They did not confirm the formation of elemental sulfur in the leaching process, as confirmed by the XRD analysis of the leach residues. Simultaneously, they found a pH decrease in the solution, which confirms that sulfide sulfur transforms to sulfate during the leaching. On the other hand, Misra and Fuerstenau [36] have shown that most of the sulfide sulfur was transformed into its elemental form. Adebayo et al. [37] examined the leaching kinetics of chalcopyrite and found that increasing the concentration of sulfuric acid and hydrogen peroxide could increase the copper leaching rate; also, the chalcopyrite dissolution reaction takes place by a shrinking-core model with the surface reaction as the rate-controlling step with an activation energy of 39 kJ/mol. In the leaching process of sulfide minerals, hydrogen peroxide is unstable and quickly decomposes in the presence of iron and copper ions, mineral particles, and different impurities. Intensive depletion of hydrogen peroxide by metal cations and discontinuation of chalcopyrite leaching after 60 min were confirmed by Olubambi and Potgieter [31], and Agacayak et al. [32]. They also confirmed the decomposition of hydrogen peroxide at elevated temperatures.

Therefore these results are in agreement with the earlier results that the decomposition rate of peroxide was proportional to its concentration [37, 38]. Because of that, the different concentration of hydrogen peroxide was used for parameter optimization by RSM.

### *3.3. Taguchi prediction and verification test*

Prediction of the leaching efficiency at the optimized conditions was the last objective of the Taguchi statistical design and one of the important goals of this research. By determining the optimized factors and their levels, the optimized leaching will be predicted by equations (8) and (9) [39, 40].

$$\bar{Y} = \frac{\sum_{i=1}^{n} y_i}{n} = 20.42 \text{ (for conventional l) and } 24.23 \text{ (for microwave l)} \quad (8)$$

$$Y_{opt} - \bar{Y} + (A_3 - \bar{Y}) + (B_3 - \bar{Y}) + (C_3 - \bar{Y}) + (D_3 - \bar{Y}) = 46.05 \text{ (conventional l) and } 51.84 \text{(microwave l)} \quad (9)$$

In equation (8), $\bar{Y}$ is the grand average of the responses and in equation (9) $Y_{Opt}$, $A_3$, $B_3$, $C_3$, and $D_3$ are the predicted surface area in the optimum condition, and each of the four defined variables in the third level, respectively. After prediction, a verification test should be conducted. This experiment was conducted under optimum conditions presented in Table 8. The leaching efficiency reached 42.5% and 50.5% for conventional and microwave leaching, respectively. The best result formed under optimum conditions and the difference between the predicted (46.05% for conventional leaching and 51.84% for microwave leaching) and the achieved values (42.5% for conventional and 50.5% for microwave) is not significant and the error of 7.7% for conventional and 2.58% for microwave leaching confirms the predictability of the process and accuracy of the experimental results.

Briefly, the results showed that microwaves had a positive influence on the leaching kinetics of chalcopyrite in all oxidative systems. The increase in copper extraction during microwave leaching probably referred to a combination of two factors. Primarily, the limitation of microwave penetration through a high loss leaching solution causes a temperature difference between the outer shell of the leaching solution and the bulk temperature measured, and the actual temperature. Secondly, the selective heating to chalcopyrite in such a high loss leaching solution potentially explains the higher copper recovery under microwave conditions, which is demonstrated by the higher recovery of copper [41].

For this reason, investigation of the other effective parameters including microwave power, reaction time, and $H_2O_2$ concentration were conducted by response surface methodology (RSM).

### *3.4. Parameter optimization by RSM*

The results of the matrix experiment, conducted under conditions presented in Table 5, are illustrated in Table 9.

According to the regression coefficients, the leaching efficiency model for copper is calculated by:

$$\text{Copper extraction} = 46.73 - 0.014048\times A - 1.73200\times B + 22.77\times C + 8.05\times10^{-3}\times A\times B - 0.0175\times A\times C - 3.75\times B\times C + 2.70889\times10^{-5}\times A^2 + 0.433\times B^2 + 0.8\times C^2 \quad (10)$$

Where A, B, and C are the parameter values of the microwave power, reaction time, and $H_2O_2$ concentration, respectively. According to the analysis, the quadratic model provided the best fit for the experimental data. The result of the variance analysis is shown in Table 10. The significance of each coefficient is determined by the p-value listed in Table 10. The lower p-value indicates that the coefficient is more significant; in general, any variable for a $p\text{-value} < 0.05$ is significant. The model has a p-value of less than 0.0001, indicating that the model is suitable for this experiment. The respective value of $R^2$ for the copper leaching model is 0.9971, demonstrating the accuracy of the prediction models [42]. “Adequate precision” refers to the signal-to-noise ratio; for copper leaching efficiency is 57.916, confirming the adequate significance of the model.

Figure 4 demonstrates the relationship between the predicted and actual leaching efficiencies. The fact that the predicted value is closer to the actual value implies that equation 1 is accurate.

**Table 9.** Results of leaching efficiency from RSM methodology.

| Ex. | Leaching efficiency % | Ex. | Leaching efficiency % |
|---|---|---|---|
| 1 | 58 | 10 | 75.42 |
| 2 | 57.61 | 11 | 63.62 |
| 3 | 52.76 | 12 | 54.7 |
| 4 | 52.26 | 13 | 50.26 |
| 5 | 61.9 | 14 | 68.15 |
| 6 | 53.3 | 15 | 57.24 |
| 7 | 68.55 | 16 | 61.8 |
| 8 | 57.21 | 17 | 50.12 |
| 9 | 57.36 | | |

### *3.5. Interactions among key Parameters*

Figures 5–7 show the effects of the three variables on leaching efficiency using a 3D response surface methodology under the optimal leaching conditions and complex interaction between the two variables in this condition. Figure 5 shows that the leaching efficiency increases from 50.12% to 75.42% when the microwave power is increased from 300 to 900 W for an $H_2O_2$ concentration of 0.3 M (zero level). Reaction time has also a significant effect on the leaching efficiency at the microwave power considered. If the microwave power and the reaction time reach 900 W and 3 h, respectively, then leaching will occur at a favorable rate. In Figure 6, if the reaction time is 2 h (zero level), as the microwave power increases, the leaching efficiency grows rapidly before eventually stabilizing. Changes in the $H_2O_2$ concentration do not affect the leaching efficiency compared to changes in the microwave power, indicating that the reaction is mainly due to the microwave power and reaction time.

**Table 10.** Analysis of variance for response surface quadratic model.

| Source | Sum of Squares | df | Mean Square | F-value | p-value Prob > F | |
|---|---|---|---|---|---|---|
| Model | 781.96 | 9 | 86.88 | 270.38 | < 0.0001 | significant |
| A-Microwave Power | 618.46 | 1 | 618.46 | 1924.65 | < 0.0001 | |
| B-Reaction Time | 109.82 | 1 | 109.82 | 341.75 | < 0.0001 | |
| C- $H_2O_2$ Concentration (M) | 2.20 | 1 | 2.20 | 6.86 | 0.0344 | |
| AB | 23.33 | 1 | 23.33 | 72.60 | < 0.0001 | |
| AC | 1.10 | 1 | 1.10 | 3.43 | 0.1064 | |
| BC | 0.56 | 1 | 0.56 | 1.75 | 0.2274 | |
| $A^2$ | 25.03 | 1 | 25.03 | 77.88 | < 0.0001 | |
| $B^2$ | 0.79 | 1 | 0.79 | 2.46 | 0.1610 | |
| $C^2$ | 2.695E-004 | 1 | 2.695E-004 | 8.386E-004 | 0.9777 | |
| Residual | 2.25 | 7 | 0.32 | | | |
| Lack of Fit | 1.82 | 3 | 0.61 | 5.61 | 0.0646 | not significant |
| Pure Error | 0.43 | 4 | 0.11 | | | |
| Cor Total | 784.20 | 16 | | | | |

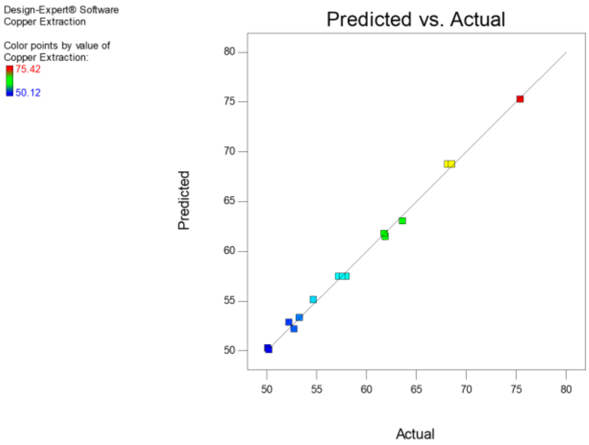

**Figure 4.** Experimental and predicted leaching efficiency.

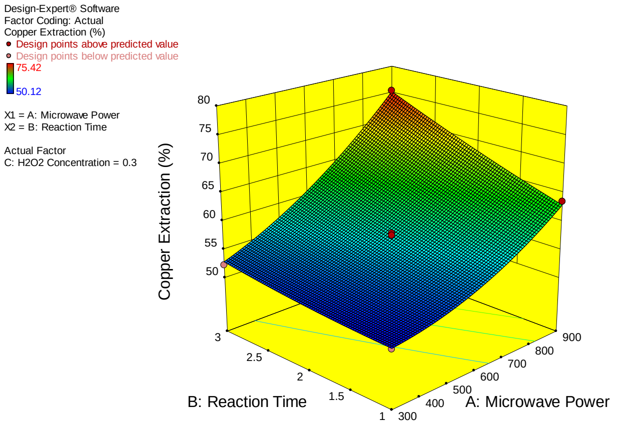

**Figure 5.** Three-dimensional response surface map of the microwave power vs. reaction time at an $H_2O_2$ concentration of 0.3 M.

Figure 7 illustrates that the leaching efficiency increases when the reaction time is increased from 1 to 3 h, and while the microwave power is 600 W (zero level). Also, we can conclude that the $H_2O_2$ concentration has no significant effect on the leaching efficiency at the reaction time considered.

### *3.6. Process Optimization*

Response surface software gives several different leaching solutions, which can then be compared by their economic costs. Table 11 summarizes the optimum leaching conditions. In the optimum leaching conditions, the actual leaching efficiency reaches 75.3% and the predicted leaching efficiency is 75.44%. The best result formed under optimum conditions and the difference between the predicted (75.44%) and the achieved values (75.3%) is negligible and the low error of (0.18%) confirms the predictability of the process and accuracy of the experimental results. So, the actual measured value is consistent with the model prediction.

### *3.7. Effect of microwave irradiation*

The recovery of copper under microwave irradiation was much higher than those obtained by conventional leaching. The effect of microwave heating on better leaching of complex copper sulfide concentrates probably refers to the creation of large convection thermal currents, which agitated the surface of the particles and swept away the formed sulfur layer. It was observed that the elemental sulfur formed during the first stage of leaching of chalcopyrite was dissolved after 8 minutes of microwave treatment, probably via reaction (11) [43].

$$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O \qquad (11)$$

As mentioned, this observation could be attributed to the presence of a superheated layer close to the periphery of the reactor and the selective heating of the mineral particles [44]. In conventional leaching, the reaction product could cover the mineral surface; in contrast, in microwave-assisted leaching, the thermal currents created by the temperature gradient between liquid and solid might sweep away the reaction product layer on the surface of particles, reducing the diffusion-limiting effect [43]. On the other hand, most of the microwave energy was dissipated within the thin outer layer of the reactor.

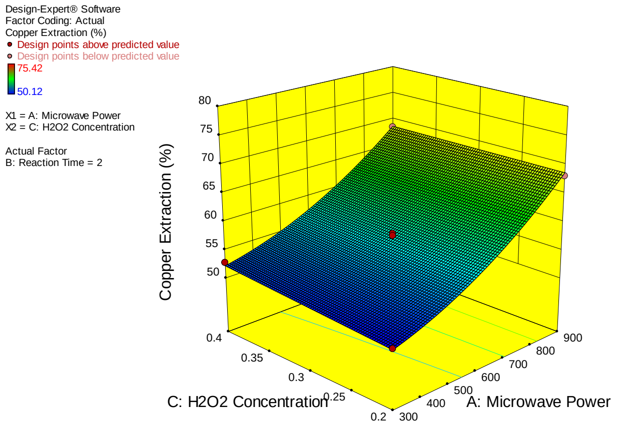

**Figure 6.** Three-dimensional response surface map of the microwave power vs $H_2O_2$ concentration at a reaction time of 2 h.

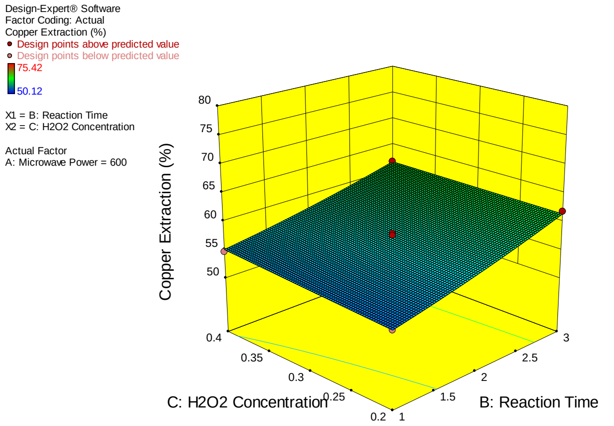

**Figure 7.** Three-dimensional response surface map of the reaction time vs $H_2O_2$ concentration at a microwave power of 600 W.

Thus, a temperature gradient existed between the outer layer and the central area of the reactor due to the shallow microwave penetration depth. If the surface of the solid particles heated up faster than the liquid, a temperature gradient would arise between the liquid and solid. The two temperature gradients mentioned above would create thermal currents that could improve the recovery of valuable metals [41].

In conclusion, a possible explanation for the increased copper recovery under higher microwave irradiation is the presence of the temperature gradients due to the shallow microwave penetration depth and the superheating occurring at the solid-liquid interface.

### *3.8. Effect of time*

The sample temperature increases obviously with increasing microwave-heating time. Temperature initially increases from the environment (28°C) to more than 200°C at 2.5 min, which may result

**Table 11.** Predicted and experimental values of the responses at optimum conditions.

| Number | Microwave Power | Reaction Time | $H_2O_2$ Concentration | Copper Extraction | Desirability |
|---|---|---|---|---|---|
| Optimum | 900 | 3 | 0.244 | 75.437 | 1.000 |
| Modified | 900 | 3 | 0.244 | 75.3 | |

from the microwave absorption properties of the copper concentrate. Indeed, the sample temperature is significantly higher than the solution temperature (90°C at 2.5 min). This fact further supports the presence of a temperature gradient between the liquid and solid[43].

### *3.9. Effect of oxidizing agent concentration*

The leaching efficiency is maximized at an $H_2O_2$ concentration of 0.0.25 mol·L$^{-1}$. This might be explained by the fact that the active species of hydroxyl radicals (•OH) could be generated from $H_2O_2$ under microwave-$H_2O_2$ conditions, as shown in equation (12). The oxidation-reduction potential of •OH (2.8 eV) was higher than that of $H_2O_2$ (1.8 eV), which might be beneficial for the destruction of metal-binding structures [45, 46]. $H_2O_2$ had a negative effect on the leaching efficiency of copper at concentrations greater than 0.25 mol·L$^{-1}$. This fact could be attributed to the consumption of •OH radical, resulting in the production of the less reactive •$HO_2$ radical, as shown in equations (13) and (14). This meant that the excess $H_2O_2$ might inhibit •OH radical formation, suppressing the oxidizing ability of $H_2O_2$ [46]:

$$H_2O_2 \rightarrow 2{\bullet}OH \quad (12)$$

$$\bullet OH + H_2O_2 \rightarrow 2{\bullet}HO_2 + H_2O \quad (13)$$

$$2{\bullet}HO_2 \rightarrow H_2O_2 + O_2 \quad (14)$$

## 4. Conclusion

In this research, the application of conventional and microwave leaching of the Sarcheshmeh copper complex was studied. Taguchi $L_9$ orthogonal array and response surface methodology (RSM) were used to optimize experimental conditions for access to maximum copper extraction. Temperature, NaCl concentration, oxidizing agent, and concentration were chosen as the main parameters in the Taguchi $L_9$ orthogonal array method. The optimum condition was created in the presence of 0.25 M $H_2O_2$ and a NaCl concentration of 2 M at 90 °C.

After parameter optimization by this method (Taguchi $L_9$ orthogonal array), RSM is used to estimate and optimize three key parameters including microwave power, reaction time, and $H_2O_2$ concentration. ANOVA and ANOM analyses were applied to evaluate the relative importance of the effects of various factors. The optimal conditions of the microwave-assisted leaching process are created under microwave power = 900 W; reaction time = 3 h, and $H_2O_2$ concentration = 0.224 mol.L$^{-1}$ while temperature and $H_2O_2$ as an oxidizing agent were selected as optimized variables in the previous stage.

Under these conditions at 90 ºC temperature, the experimental leaching efficiencies of copper by conventional and microwave leaching conditions were 42.5% and 75.43%, respectively. The recovery of copper under microwave conditions is higher than those for conventional leaching in the same temperature range. The enhancement seems to occur as a result of the presence of a temperature gradient and superheating at the solid-liquid interface. The temperature variations in the sample and solution are compared. The sample temperature is higher than that of the solution. This fact further supports the presence of a temperature gradient between the liquid and solid.

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