

## INVESTIGATION OF THE EFFECT OF SOME POLAR ORGANIC SOLVENTS ON THE LEACHING AND DISSOLUTION KINETICS OF CHALCOPYRITE IN HYDROGEN PEROXIDE AND SULFURIC ACID SOLUTION

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(Received October 27, 2022; Revised December 5, 2022; Accepted December 27, 2022)

**ABSTRACT.** The effect of acetic acid and ethanol as polar aqueous solvents on sulfuric acid with hydrogen peroxide as an oxidant was studied. A small amount of these polar aqueous solvents significantly improved the copper leaching recovery. The leaching parameters such as temperature, stirring speed, H<sub>2</sub>O<sub>2</sub> concentration, solid/liquid ratio, H<sub>2</sub>SO<sub>4</sub> concentration and particle size were examined. About 76.33% as highest Cu extraction was gained with 2 M H<sub>2</sub>O<sub>2</sub>, 600 rpm stirring speed, 50 °C temperature, 1 M H<sub>2</sub>SO<sub>4</sub>, 240 min of the reaction and 75 x 53 μm particle size fraction. Further experimental tests were carried out when the stirring speed, solid-to-liquid ratio (S/L), particle size, H<sub>2</sub>O<sub>2</sub> concentration, temperature and H<sub>2</sub>SO<sub>4</sub> concentration were kept constant to investigate the effect of ethanol and acetic acid concentration in the range of 0–2 M. The experimental results proved that the copper extraction recovery reached to 99.03% in 180 min of the reaction with 2 M acetic acid. While 2 M of ethanol increased copper extraction recovery up to 100% in 90 min of the leaching time. The dissolution reaction found to be described by mixed kinetic model and activation energy of 54.37 kJ/mol. Addition of acetic acid and ethanol suggested reaction controlled by diffusion across product layer.

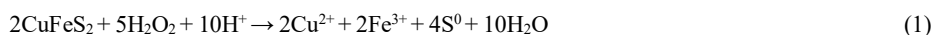
**KEY WORDS:** Hydrogen peroxide, Sulfuric acid, Activation energy, Leaching, Chalcopyrite

### INTRODUCTION

Chalcopyrite (CuFeS<sub>2</sub>) is one of the most abundant and important minerals in nature, representing approximately 70% of the copper-containing mineral reserves [1, 2]. Approximately 80-85% of the total world copper is processed by pyrometallurgical methods [3, 4]. However, smelting is only economical for high grade concentrates and causes pollution problems due to SO<sub>2</sub> emission [5]. Nowadays, hydrometallurgical processes have received considerable attention as an applicable alternative method to extract copper from low grade sulfide ores [6, 7].

Copper extraction from chalcopyrite demands existence of the oxidants in an acidic media; such as: the dichromate ions [8, 9], the cupric ions [10-12], the ferric ions [13–18], the nitrate ions [19, 20], some acidophilic bacteria [21, 22], the chlorate ions [23], the oxygen ions [24], ozone [25], and the presence of hydrogen peroxide [26].

From all these oxidation agents, hydrogen peroxide is widely used as environmentally safe and powerful oxidizing agent. Oxidative leaching of chalcopyrite in hydrogen peroxide and acid medium can be summarized in Eq. (1) and Eq. (2) [27]:



According to this mechanism of chalcopyrite dissolution, sulfide sulfur can be oxidized by hydrogen peroxide to the elemental sulfur (S<sup>0</sup>) (Eq. 1) and/or SO<sub>4</sub><sup>2-</sup> ions (Eq. 2).

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Organic solvents are very advantageous in enhancing leaching recovery of chalcopyrite, since the creation of by-products like jarosites, metal sulfides and elemental sulfur during extraction of copper from chalcopyrite will cause surface passivation of chalcopyrite [28-30].

Researchers have investigated the influence of polar solvents on chalcopyrite dissolution and reported enhancement in leaching after adding acetone [31], methanol [32] and ethylene glycol [33]. These solvents have very low sulfur solubility, and their impact in promoting chalcopyrite leaching has been referred to their role in inhibiting the hydrogen peroxide decomposition [33].

The purpose of this work is to study the effect of ethanol and acetic acid on leaching and dissolution kinetics of chalcopyrite, using sulfuric acid as the leaching solution and hydrogen peroxide as an oxidant. We carried out a comparison of kinetic and leaching experimental tests conducted under terms with and without ethanol and acetic acid.

## EXPERIMENTAL

### *Materials*

The chalcopyrite concentrate used in this work was taken from ETI Bakir flotation plant (Siirt, Turkey). Different size fractions samples were provided by wet sieving into 212 x 106, 106 x 75, 75 x 53, 53 x 38  $\mu\text{m}$ . Atomic absorption spectrometer (GBC SensAA model) analysis of each size fraction has achieved and the percentage of copper found as 14.50%, 16.20%, 16.45%, and 17.12 %, respectively.

### *Methods*

All tests were conducted in 1 dm<sup>3</sup> glass reactor equipped with the Heidolph RZR 2021 model mechanic stirrer placed into a variable temperature water bath. The 500 mL sulfuric acid-hydrogen peroxide solution was poured into the glass reactor and heated to the temperature changed from 30–60 °C. The amount of chalcopyrite sample was added in the range of 1 to 5 g when the desired temperature was reached. In the leaching experiments, the effect of the stirring speed in the range of 0 to 600 rpm, the H<sub>2</sub>SO<sub>4</sub> concentration in the range of 0.1–1.0 M, the concentration of hydrogen peroxide up to 2.0 M, acetic acid and ethanol in the range of 0-2 M and the particle size range was 212 x 106, 106 x 75, 75 x 53 and 53 x 38  $\mu\text{m}$  were investigated. Atomic absorption spectrometer was used to define the amount of Cu in all leaching tests. Distilled water was used in all experimental tests.

## RESULTS AND DISCUSSION

### *Effect of stirring speed*

The experiments were conducted on solutions containing 2.0 M H<sub>2</sub>O<sub>2</sub> to assess the influence of the stirring speed on the chalcopyrite dissolution in the range of 0-600 rpm, solid/liquid ratio of 2/1000 g/mL, particle size of 106 x 75  $\mu\text{m}$  and H<sub>2</sub>SO<sub>4</sub> concentration of 0.5 M at 50 °C temperature. The test results as shown in Figure 1 indicate that the increase in stirring rate increases the dissolution rate of chalcopyrite (at 600 rpm/min copper recovery was 73.10%). Because high stirring speed provides better contact between leaching solution and chalcopyrite particles. So, the stirring speed of 600 rpm was selected as stirring speed to investigate the influence of other leaching parameters on dissolution of chalcopyrite. Petrović *et al.* [34] confirmed that the Cu dissolution is proportional to stirring speed up to 400 rpm.

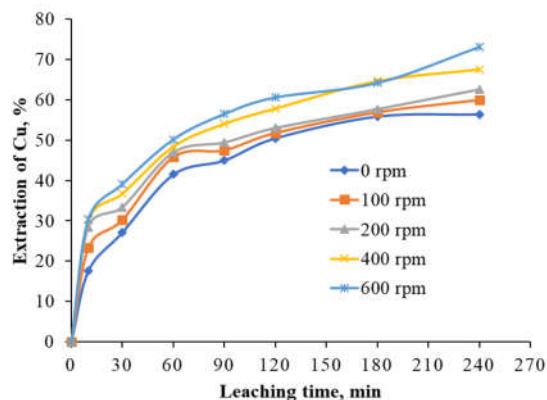


Figure 1. Influence of stirring speed on copper dissolution from chalcopyrite concentrate sample (Conditions: 2 g/L solid liquid ratio, 0.5 M  $\text{H}_2\text{SO}_4$ , 2.0 M  $\text{H}_2\text{O}_2$ , 50 °C, particle size 106 x 75  $\mu\text{m}$ ).

#### Effect of $\text{H}_2\text{O}_2$ concentration

The experimental tests were performed in solutions containing various  $\text{H}_2\text{O}_2$  concentrations in the range of 0.5–2.0 M at 50 °C temperature in 0.5 M sulfuric acid concentration. After 4 h of reaction time, the Cu recoveries were 17.88%, 34.41%, 41.62% and 73.10% with 0.5, 1, 1.5 and 2 M respectively. As shown in Figure 2, Cu extraction was noted to reach up 73.10% with 2 M  $\text{H}_2\text{O}_2$  concentration. For this reason, concentration of 2 M  $\text{H}_2\text{O}_2$  was chosen for the study of other tests. Agacayak *et al.* [35] reported that Cu extraction from chalcopyrite increased with increasing hydrogen peroxide concentration because the oxidation effect of the hydrogen peroxide will be strong.

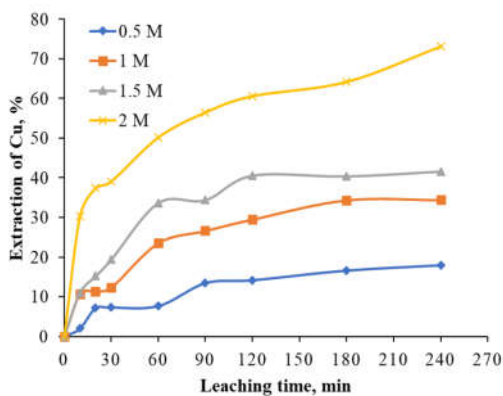


Figure 2. Influence of  $\text{H}_2\text{O}_2$  concentration on copper dissolution from chalcopyrite concentrate sample (Conditions: 2g/L solid liquid ratio, 0.5 M  $\text{H}_2\text{SO}_4$ , 600 rpm, 2 M  $\text{H}_2\text{O}_2$ , 50 °C, particle size 106 x 75  $\mu\text{m}$ ).

### *Influence of temperature*

The experimental tests on the influence of reaction temperature were performed in solution temperature varied from 30 to 60 °C. In these experimental tests, the H<sub>2</sub>O<sub>2</sub> concentration was kept constant as 2 M, particle size as 106 x 75 μm, H<sub>2</sub>SO<sub>4</sub> as 0.5 M and stirring speed as 600 rpm. As seen in Figure 3, it is clear that increase in temperature from 30 to 50 °C has a positive influence in Cu extraction. At 50 °C, 73.10% Cu dissolution was obtained after 4 h. However, at temperature of 60 °C Cu extraction decreased. This is attributed to decomposition of hydrogen peroxide occurs at higher temperatures [35, 36]. For this reason, a 50 °C reaction temperature was chosen for investigation of all subsequent experiments.

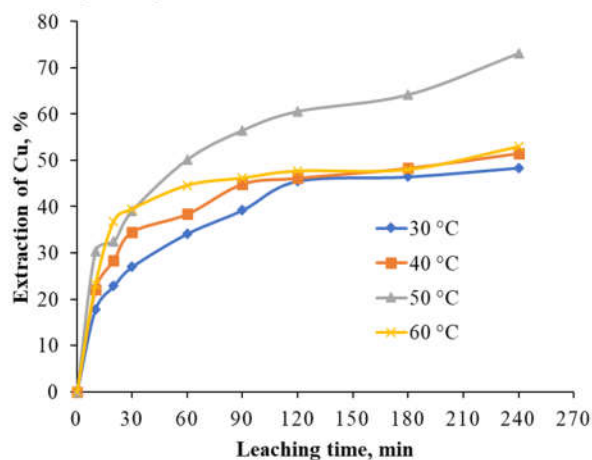


Figure 3. Effect of temperature on Cu dissolution from chalcopyrite concentrate sample (Conditions: 2 g/L solid liquid ratio, 0.5 M H<sub>2</sub>SO<sub>4</sub>, 600 rpm, 2 M H<sub>2</sub>O<sub>2</sub>, particle size 106 x 75 μm).

### *Influence of sulfuric acid concentration*

The influence of sulfuric acid concentration (0.1–1.0 M) on dissolution of chalcopyrite was studied using solutions containing 2.0 M H<sub>2</sub>O<sub>2</sub> concentration at 50 °C temperature. As seen in Figure 4, when the sulfuric acid concentration was increased, it had considerable influence on chalcopyrite dissolution. It could be said that the oxidation influence of the hydrogen peroxide will be stronger in the acidic environment (0.1–1.0 M H<sub>2</sub>SO<sub>4</sub>). At the end of 240 min leaching time, 39.61%, 52.34%, 73.10% and 74.79% Cu recoveries were obtained with 0.1, 0.3, 0.5 and 1 M H<sub>2</sub>SO<sub>4</sub>, respectively. For the investigation of other parameters, 1 M H<sub>2</sub>SO<sub>4</sub> concentration was chosen.

### *Influence of particle size and solid/liquid ratio*

The leaching tests were conducted using several particle size fractions in the leaching solutions containing 2.0 M H<sub>2</sub>O<sub>2</sub> concentration at temperature of 50 °C. As shown in Figure 5(a), Cu dissolution increased with decreasing particle size due to the increase in surface area at unit weight. At the end of 4 h leaching time, 70.50%, 74.79%, 76.33% and 76.91% Cu recoveries were achieved with particle size of 212 x 106, 106 x 75, 75 x 53 and 53 x 38 μm, respectively. The test results revealed that there is no noticeable change on Cu recovery at the particle size of finer than 75 x 53 μm. A particle size of 75 x 53 μm was chosen for the other experimental tests.

To determine influence of solid/liquid ratio more experimental tests were carried out in the solution of 2 M  $\text{H}_2\text{O}_2$  concentration, 1 M  $\text{H}_2\text{SO}_4$  concentration, 75 x 53  $\mu\text{m}$  at leaching temperature of 50 °C and solid/liquid ratio in the range of (1/500-5/500 g/mL). The test results are presented in Figure 5(b). The Cu leaching recovery decreased with increase in the solid amount. Because the viscosity of suspension increases as the solid amount increases, which affected the efficiency of the dissolution rate of the mineral. The Cu recoveries were 76.33%, 44.46% and 30.78% after 240 min leaching time.

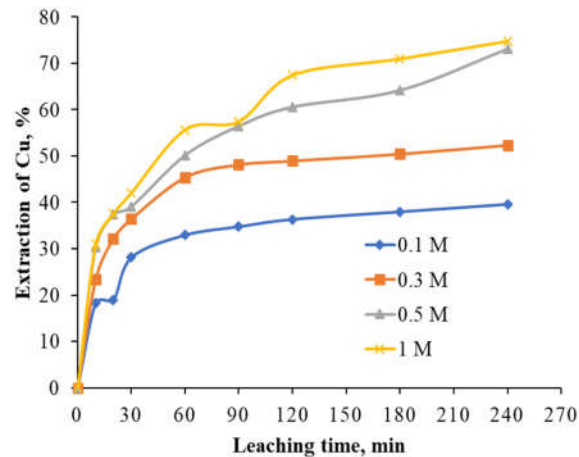


Figure 4. Influence of  $\text{H}_2\text{SO}_4$  concentrations on Cu extraction recovery from chalcopyrite concentrate sample (Conditions: 2 g/L solid liquid ratio, 50 °C, 600 rpm, 2 M  $\text{H}_2\text{O}_2$ , particle size 106 x 75  $\mu\text{m}$ ).

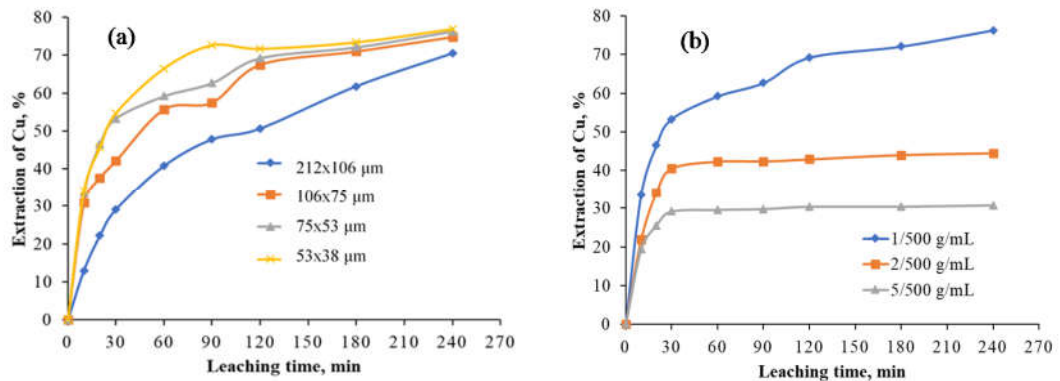


Figure 5. (a) Influence of particle size on dissolution of chalcopyrite concentrate sample (Conditions: 2 g/L solid liquid ratio, 50 °C, 600 rpm, 1 M  $\text{H}_2\text{SO}_4$ , 2 M  $\text{H}_2\text{O}_2$ ) and (b) Effect of solid/liquid ratio on Cu extraction from chalcopyrite concentrate sample (Conditions: 1 M  $\text{H}_2\text{SO}_4$ , 600 rpm, 2 M  $\text{H}_2\text{O}_2$ , particle size 75 x 53  $\mu\text{m}$ , 50 °C).

### Influence of acetic acid concentration and ethanol concentration

To study the influence of the addition of acetic acid concentration (0-2 M) on chalcopyrite dissolution, experiments were performed at the following terms: H<sub>2</sub>O<sub>2</sub> concentration as 2 M, 50 °C of leaching temperature, 1/500 g/mL of solid/ liquid ratio, 600 rpm stirring speed and particle size of 75 x 53 μm. The experimental test results are reported in Figure 6(a). As shown in Figure 6(a), the Cu extraction recoveries after only 3 h leaching reaction increased from 72.12% without acetic acid to 97.92% and 99.03% at 1 M and 2 M acetic acid, respectively.

Further experimental tests were conducted to investigate the effect of ethanol concentration on the extraction of chalcopyrite leaching in the range of 0-2 M when the H<sub>2</sub>SO<sub>4</sub> concentration, stirring speed, solid-to-liquid ratio (S/L), temperature and H<sub>2</sub>O<sub>2</sub> concentration were kept constant. As seen in Figure 6(b), the addition of 2 M ethanol led to obtain complete Cu dissolution in only 90 min of leaching time. Cu extraction recovery increases from 62.68% without ethanol to 100% with 2 M of ethanol concentration. It is clear that the existence of alcohol has a good influence in the chalcopyrite leaching.

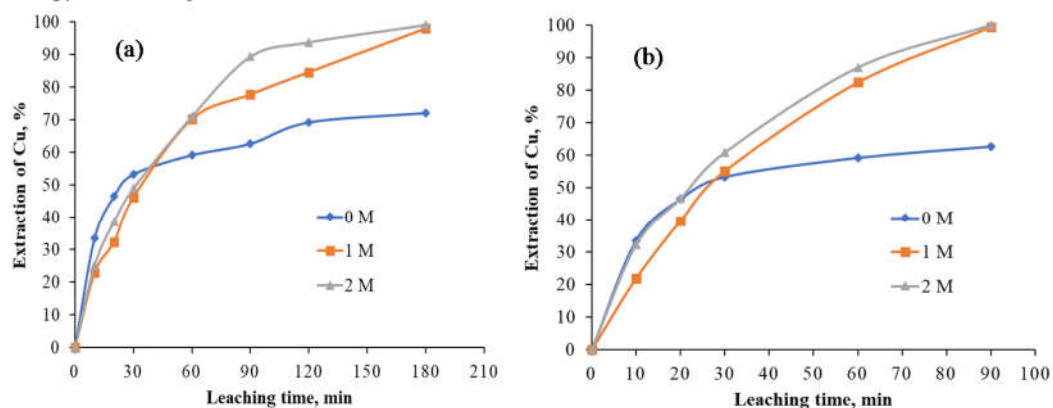


Figure 6. (a) Influence of acetic acid concentrations and (b) influence of ethanol concentration on Cu extraction from chalcopyrite concentrate sample (Conditions: 2 g/L solid liquid ratio, 1 M H<sub>2</sub>SO<sub>4</sub>, 50 °C, 600 rpm, 2 M H<sub>2</sub>O<sub>2</sub>, particle size of 75 x 53 μm).

### Leaching kinetics

The dissolution kinetics of chalcopyrite involved three types of kinetic models such as surface reaction model, diffusion model and mixed kinetic model of dissolution containing chemical control and diffusion model [37].

In case of a reaction controlled by surface reaction, the following equation can be used [38],

$$1-(1-\alpha)^{1/3} = k_s t \quad (3)$$

In case of reaction controlled by film diffusion [38],

$$1-(1-\alpha)^{2/3} = k_{diff} t \quad (4)$$

In case of a reaction controlled by diffusion across the product layer control model Eq. (5) is used [39].

$$1-3(1-\alpha)^{2/3}+2(1-\alpha) = k_p t \quad (5)$$

In case of reaction controlled by combination of both interface transfer and diffusion through the product layer [40],

$$(1/3)\ln(1-\alpha)-[1-(1-\alpha)^{-1/3}] = k_{mt} \quad (6)$$

where  $\alpha$  is the fraction reacted,  $t$  is the reaction time,  $k_{diff}$ ,  $k_s$ ,  $k_p$  and  $k_m$  are the rate constants. Equations (5) and (6) were used to the tests results and the correlation coefficient values for each leaching temperature were given in Table 1. As seen in Table 1, evaluation of reaction kinetics of chalcopyrite leaching in sulfuric acid medium shows that the chosen kinetics model (Eq. 6) was the most suitable model to fit leaching tests results. Because the correlation coefficient values of this model are higher than the correlation coefficient values of the other model.

Table 1. Apparent rate constants and correlation coefficients values for various temperatures.

Temperature (°C)	Product layer diffusion control $1-3(1-\alpha)^{2/3}+2(1-\alpha)$		Mixed kinetic control model $(1/3)\ln(1-\alpha)-[1-(1-\alpha)^{-1/3}]$	
	R <sup>2</sup>	$k_p$	R <sup>2</sup>	$k_m$
30	0.896	0.40841	0.916	0.10996
40	0.890	0.40773	0.922	0.11608
50	0.973	1.05761	0.974	0.42436

The graph of leaching time,  $t$  versus Eq. (6), for various reaction temperatures is shown in Figure 7(a). The test results from Figure 7(a) showed that this model fits all experiments with very good correlation coefficients values, R<sup>2</sup>. For this reason, this model can describe the kinetics of the dissolution of chalcopyrite in sulfuric acid media. The correlation coefficients and apparent rate constants for each reaction temperature were given in Table 1. The Arrhenius curve for the chalcopyrite dissolution is plotted using the  $k$  values gained by applying Eq. 6 (Figure 7(b)). The activation energy of leaching calculated as 54.37 kJ/mol.

Table 2. Apparent rate constants and correlation coefficients values for various acetic acid and ethanol concentrations

Concentration (M)	Product layer diffusion control $1-3(1-\alpha)^{2/3}+2(1-\alpha)$				Mixed kinetic control model $(1/3)\ln(1-\alpha)-[1-(1-\alpha)^{-1/3}]$			
	Acetic acid		Ethanol		Acetic acid		Ethanol	
	R <sup>2</sup>	$k_p$	R <sup>2</sup>	$k_p$	R <sup>2</sup>	$k_m$	R <sup>2</sup>	$k_m$
1	0.987	4.55340	0.962	11.18738	0.755	6.82626	0.728	34.36807
2	0.980	5.36550	0.974	11.91982	0.832	1.48004	0.708	76.00608

As shown in Table 2, after addition of acetic acid and ethanol as polar aqueous solvents to the H<sub>2</sub>O<sub>2</sub> - H<sub>2</sub>SO<sub>4</sub> system the reaction kinetics indicates that the leaching reactions are not appropriate with Eq. (6).

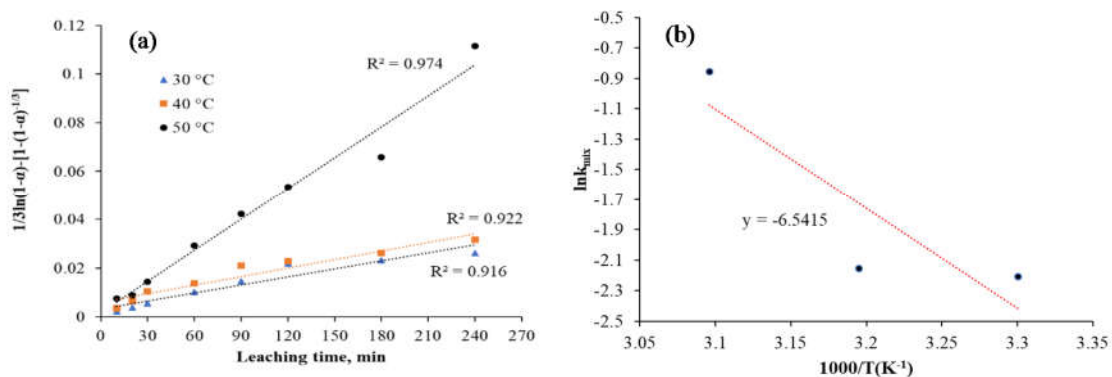


Figure 7. Plot of leaching time vs. Eq. (6) for different leaching temperatures (a) and (b) Arrhenius plot for chalcopyrite dissolution.

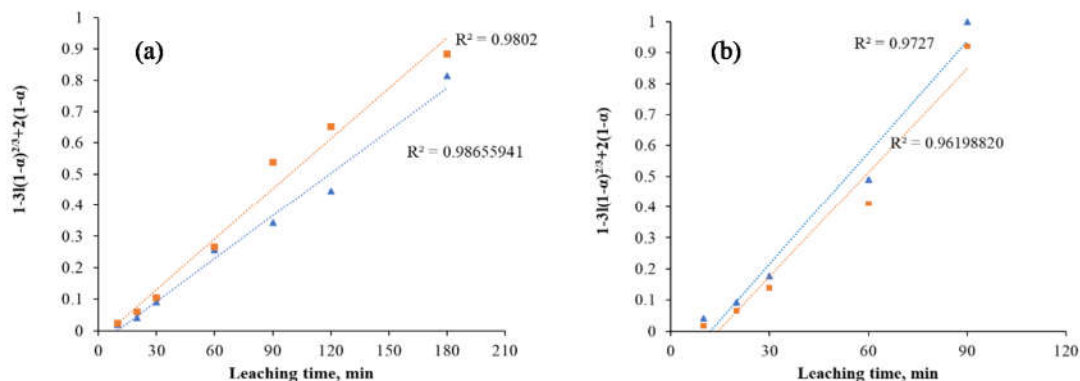


Figure 8. (a) Plot of leaching time vs. Eq. (5) for different acetic acid concentrations and (b) plot of leaching time vs. Eq. (5) for different ethanol concentrations (b).

As seen in Figure 8 (a,b), after addition of acetic acid and ethanol as polar aqueous solvents to the  $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}_2$  system the reaction kinetics indicates that the leaching reactions are fitted diffusion across the product layer control model Eq. (5) with good correlation coefficients values,  $R^2$ .

### CONCLUSION

In this study, the influence of the addition of acetic acid and ethanol as polar aqueous solvents on the leaching of chalcopyrite concentrate sample in sulfuric acid–hydrogen peroxide media was investigated. The highest Cu extraction recovery of 76.33% is gained under optimum leaching test conditions as 1 M  $\text{H}_2\text{SO}_4$  concentration, 2 M  $\text{H}_2\text{O}_2$  concentration, stirring speed of 600 rpm, temperature of 50 °C, reaction time of 4 h and solid liquid ratio of 2/1000 g/mL. The chalcopyrite dissolution in sulfuric acid with  $\text{H}_2\text{O}_2$  could be described by the mixed kinetic control model equation,  $(1/3)\ln(1-\alpha)-[1-(1-\alpha)^{1/3}] = k_m t$ . The activation energy of chalcopyrite leaching in hydrogen peroxide–sulfuric acid system is calculated as 54.37 kJ/mol. With these constant conditions, the experimental tests were carried out at different acetic acid and ethanol concentrations ranging from 0 to 2 M to define their influence on the leaching Cu extraction. It can be seen that the addition of acetic acid increased the Cu extraction recovery up to 99.11%. In case of addition of ethanol, Cu extraction recovery reached 100%. The dissolution of chalcopyrite concentrate in hydrogen peroxide–sulfuric acid system with addition of acetic acid and ethanol can be described by diffusion across product layer equation,  $1-3(1-\alpha)^2+2(1-\alpha) = k_p t$ .

### ACKNOWLEDGMENTS

The authors would also like to thank the Konya Technical University for guidance and providing information.



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