Leaching Kinetics of Chalcopyrite Concentrate by Ionic Liquids

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Abstract: Ionic liquids as green solvents with high thermal stability, recyclability, low flash point, and low vapor pressure, have been considered as a viable alternative in hydrometallurgical processes. In this study the leaching kinetics of chalcopyrite concentrate was investigated using 1-Butyl-3-methylimidazolium hydrogen sulfate (BmimHSO₄) as an acidic ionic liquid. The Effect of operational parameters, including temperature, BmimHSO₄ concentration, H_2O_2 concentration, stirring speed, solid-to-liquid ratio, and particle size on the rate of copper dissolution of $CuFeS_2$ were examined systematically. The highest Cu efficiency (ca. 97%) was achieved using 40% (w/v) BmimHSO4, 30 %v/v H_2O_2, and 10 g.L^{-1} solid to liquid ratio for particle sizes less than 37 μm at 300 rpm and 45°C after 180 min leaching time. Kinetics study using Shrinking Core Model (SCM) revealed that $CuFeS_2$ leaching process using BmimHSO₄ follows chemical reaction-controlled process. Under these circumstances, the calculated activation energy was 46.66 KJ/mol. Moreover, the orders of reaction with respect to BmimHSO₄ and H2O2 concentration, solid to liquid ratio and particle size were estimated to be 0.539, 0.933, −0.676 and −1.101 respectively. The obtained Arrhenius constant was found to be 0.26×10^6. The calculation of apparent activation energy using "time given to a fraction method" revealed that the leaching mechanism remains the same over the course of time.

Keywords: Cu extraction, Chalcopyrite, Leaching, BmimHSO₄, Ionic liquid, Kinetic.

1. INTRODUCTION

Chalcopyrite, with the chemical formula of $CuFeS_2$, is the most important and the most common copper mineral found on the Earth [1]. This mineral which comprises 70% of the world's copper resources [2-4], is highly resistant to dissolution mainly due to its chemical structure, variations on the surface of mineral, and formation of passive layer with substantial porosity on its surface [5, 6]. Accordingly, more than 80 to 85% of the world's copper is produced by pyrometallurgy [7]. However, there are problematic issues regarding pyrometallurgy such as environmental pollution as a result of SO_2 emission, high investment and operational costs, decrease in purity of produced mineral over the course of time, and low efficiency of small particles processing. These issues have led to the application of hydrometallurgy methods in copper industry in recent years [7-10]. Therefore, there have been numerous studies on leaching of copper from $CuFeS_2$. Due to low dissolution rate of this mineral, several processes including chloride leaching [11], ammonia leaching [12], bio-leaching [13], and pressure sulfate leaching [14, 15], have been developed for Cu extraction from $CuFeS_2$. However, due to the issues

regarding solvent extraction from the product, incomplete extraction, safety, toxicity, environmental pollution, and high expenses for solvent management, there are some controversies about the applicability of solvent-based leaching of Cu from $CuFeS_2$ [16, 17]. Therefore, novel hydrometallurgical processes are necessary for the green and sustainable development of metallurgy industry for efficient Cu production with low energy consumption, minimal acid requirement, and less pollution under ambient conditions. As a result, ionic liquids have been considered as a viable alternative in metallurgic processes, due to their higher solubility in organic/inorganic compounds, non-volatile nature, and thermal stability [18].

Ionic liquids can be considered as a new branch of chemical compounds with extraordinary properties, creating green chemical environments for chemical processes. These compounds are considered as a suitable alternative to organic/inorganic solvents which provide a non-aquatic organic liquid environment for conduction of numerous chemical reactions. Nowadays, ionic liquids are considered as organic compounds with melting point below 100°C [19-22].

Recently, ionic liquids have been used in

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hydrometallurgy in which they are applied for leaching of gold and silver [17, 23, 24], precious metals [25, 26], and metal oxides [22, 27-29]. The promising ability of ionic liquids for dissolution of metal and metal oxides has been demonstrated in several publications. They also can be used for processing and enrichment of metals via ionometallurgical method [18, 27].

In recent years, several studies on leaching of Cu from $CuFeS_2$ with ionic liquids as solvent have been conducted successfully. Early studies on the dissolution of chalcopyrite concentrate were conducted by McCloskey et al. [30] using 1-Butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4) and iron tetrafluoroborate hexahydrate (Fe(BF_4)$_3$) as oxidative agent. Their results revealed that more than 90% Cu extraction is achievable at 100°C for 8 h. Moreover, in another study, Cu extraction from chalcopyrite concentrate comprised of 20% Cu and 34% Fe was reported using 1-Butyl-3-methylimidazolium hydrogen sulfate (BmimHSO$_4$) and Fe (III) as oxidative agent [17]. Results demonstrated that increasing the BmimHSO$_4$ concentration from 10 to 100% leads to the increase of Cu extraction from 55 to 87% at 70°C. In addition, Fe extraction was 8%. Dong et al. [31] conducted studies on dissolution of $CuFeS_2$ using BmimHSO$_4$ and O_2 gas as oxidative agent. It was found that the copper dissolution increases from 52 to 88% after 24 h at 70°C by increasing the concentration of BmimHSO$_4$ from 10 to 100%. Moreover, the mechanism of chalcopyrite concentrate dissolution using BmimHSO$_4$ and oxygen is controlled by surface electrochemistry due to the high activation energy (ca. 69.4 KJ/mol). Carlesi et al. [18] investigated chalcopyrite leaching from sulfidic ore using BmimHSO$_4$ and 1-h-3-methylimidazolium hydrogen sulfate (HmimHSO$_4$). Similar to the previous studies [17, 31], results demonstrated that copper extraction increases by increasing the ionic liquid concentration and temperature. Moreover, HmimHSO$_4$ is superior to BmimHSO$_4$, and in combination with sulfuric acid, chalcopyrite dissolution yield increases to 70% after 20 h. Aguirre et al. [32] studied chalcopyrite leaching using BmimHSO$_4$, sulfuric acid, and chloride as oxidative agents. The investigated sample contained 96.6% $CuFeS_2$. Results revealed that Cu extraction efficiency at 90°C for 24 h using 20% (v/v) BmimHSO$_4$ and 100 g.L^{-1} chlorine ion

reached 80%. In addition, they concluded that increasing the chlorine concentration and temperature leads to an increase in Cu extraction from chalcopyrite. Kinetic mechanism of chalcopyrite dissolution was also investigated. According to the results, chalcopyrite dissolution with BmimHSO$_4$ and chlorine ion follows chemical reaction with activation energy of 60.4 KJ/mol. 1-ethyl-3-methylimidazolium hydrogen sulfate (EmimHSO$_4$) and potassium dichromate as oxidative agent were used by Hu et al. [33] for Cu extraction from chalcopyrite. They concluded that EmimHSO$_4$ concentration, oxidant concentration, temperature, and particle size have significant effect on Cu extraction, so that 90.2% Cu extraction was achieved after 90 min. Investigation of dissolution kinetic mechanism revealed that chalcopyrite dissolution follows diffusion through a protect layer of elemental sulfur and pyrite mechanism with activation energy of 36.26 KJ/mol.

All of the work done in this field reveals the significant effect of ionic liquids during chalcopyrite leaching. In addition, achievement of considerable efficiency using ionic liquid requires utilization of oxidative agent. The main oxidative agents are KNO_3, $NaClO_3$, $(NH_4)_2S_2O_8$, $K_2Cr_2O_7$, H_2O_2, and Fe^{3+} which have been used in $CuFeS_2$ leaching [33]. Among them, H_2O_2 is known to be a strong oxidant and has been frequently used for the leaching of chalcopyrite [34-36], molybdenite [37] and other minerals[38]. Therefore, in this study, H_2O_2 was chosen as oxidant.

The literature review shows there are few studies on the utilization of main models such as shrinking core model (SCM), to describe the kinetic of chalcopyrite dissolution with BmimHSO$_4$. Also, no study has been reported on the effect of leaching parameters on the dissolution kinetics of chalcopyrite using BmimHSO$_4$. Therefore, in the current study, kinetics of chalcopyrite concentrate leaching using BmimHSO$_4$ at low temperature in the presence of H_2O_2 was investigated using SCM. The effect of operational parameters such as temperature, BmimHSO$_4$ and H_2O_2 concentration, stirring speed, solid-to-liquid ratio, and particle size on the kinetic of chalcopyrite dissolution has been also investigated. In addition, the changes of activation energy during leaching were investigated using the "time given to a fraction method".

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2. EXPERIMENTAL PROCEDURES

2.1. Materials

$CuFeS_2$ concentrate was supplied from the flotation unit of Taknar Copper Mines Complex (Razavi Khorasan, Iran). X-ray diffraction (XRD) analysis (D8-Advance, Bruker axs, USA) was carried out in order to identify the minerals (Figure 1). Accordingly, the main mineral in the sample was $CuFeS_2$ along with trace amounts of Pyrite. Microscopic mineralogy revealed less than 5% Cu with trace amounts of Cu oxide minerals, chalcocite, and bornite which were not detectable by XRD analysis.
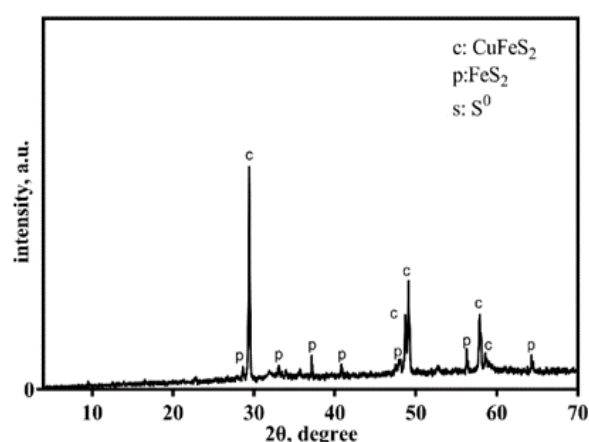

Fig. 1. XRD pattern of $CuFeS_2$ concentrate as leaching feed.

The sample was divided into four size fractions, i.e. <37, 37-53, 53-74, and 74-88 μm, using wet sieving method. The results of X-ray fluorescence (PW1410, Philips, Netherlands) analysis are shown in Table 1.

Table 1. Chemical composition of different size fractions of feed $CuFeS_2$ concentrate

Particle size (μm)	Content (%)		
	Fe	S	Cu
-37	27.58	32.63	30.66
(-53, +37)	30.20	32.49	29.13
(-74, +53)	30.74	31.51	27.84
(-88, +74)	28.48	30.60	29.04

$BmimHSO_4$ (≥94.5% purity) was used as ionic liquid due to its satisfactory performance, water solubility, low price, and availability (Sigma Aldrich, Germany). H_2O_2 (30 wt%) was acquired from Sigma Aldrich (Germany). De-ionized water was used throughout the experiments.

2.2. Procedure

The leaching solution was prepared in a 50 ml Erlenmeyer flask using digital magnetic stirrer-hot plate at 0, 100, 200, 300, 400, and 500 rpm. For this purpose, calculated amounts of $BmimHSO_4$ (10, 20, 30, and 40 % w/v) and H_2O_2 (7.5, 15, 22.5, and 30 %v/v) were placed in flask and heated up to the operation temperature (i.e. 30, 35, 40, and 45°C). After achieving the desired temperature, specific amounts of the $CuFeS_2$ particles (10, 20, 30, and 40 g.L^{-1}) with the aforementioned size fractions were added to the solution. Aliquot samples from solution were drawn and filtered at certain times from start of each experiment. The amount of leached Cu was analyzed using Atomic Absorption Spectrophotometer (Varian, AA240, USA). In order to compensate the errors resulted from sampling, Equation 1 was used for the calculation of Cu extraction [39].

$$X_i = \frac{\left(V_0 - \Sigma_{i=1}^{i-1} v_i\right)C_i + \Sigma_{i=1}^{i-1} v_i C_i}{M(C_M/100)} \quad (1)$$

where X_i is the Cu extraction percent from i^{th} sample, V_0 is the volume of leaching solution in Erlenmeyer (mL), v_i is the volume of ith sample drawn from the solution (mL), C_i is the Cu concentration in i^{th} sample (g mL^{-1}), M is the weight of $CuFeS_2$ in leaching solution (g), and C_M is the Cu concentration in $CuFeS_2$ concentrate.
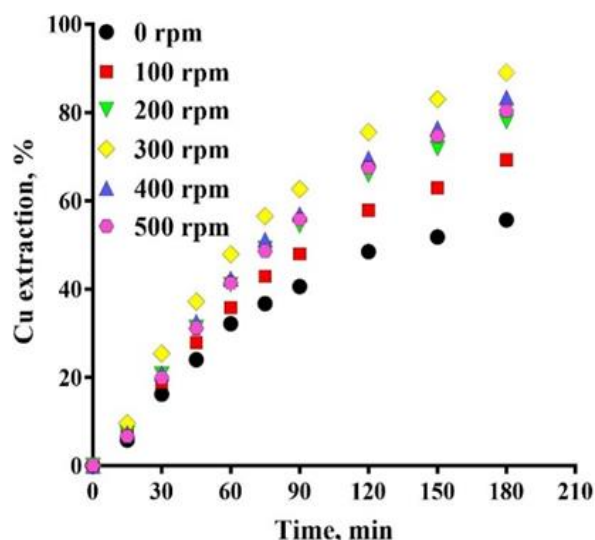
3. RESULTS AND DISCUSSION

3.1. Effect of Stirring Speed

Effect of stirring speed on leaching efficiency was studied under the following operational conditions: 40% $BmimHSO_4$, 30% H_2O_2, 40°C, 10 g.L^{-1} solid to liquid ratio, particle size of less than 37 μm, and leaching time of 180 min. The results are presented in Figure 2.

By increasing the stirring speed to 300 rpm, the dissolution of $CuFeS_2$ increased to 89.1%. However, further increase in stirring speed led to a slight decrease in $CuFeS_2$ dissolution (80.4% Cu extraction at 500 rpm). The same result was obtained by other researchers during chalcopyrite leaching with hydrogen peroxide [36]. The reason for this phenomenon is that the increase of steering speed presumably accelerates the decomposition of the hydrogen peroxide and interferes with the adsorption of hydrogen peroxide on the surface of chalcopyrite and sulfur,

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resulting in significant decrease in the dissolution rate [40]. Sokić et al [34], also observed an increased in the H_2O_2 decomposition at higher stirring speeds leadings to the absorption of more generated O_2 molecules onto the $CuFeS_2$ surface. Therefore, the optimal stirring speed of 300 rpm was used in the subsequent experiments.

Fig. 2. Effect of stirring speed on leaching efficiency (40% BmimHSO₄, 30% H_2O_2, 40°C, 10 g.L⁻¹ solid to liquid ratio, particle size of less than 37 μm, and leaching time of 180 min).
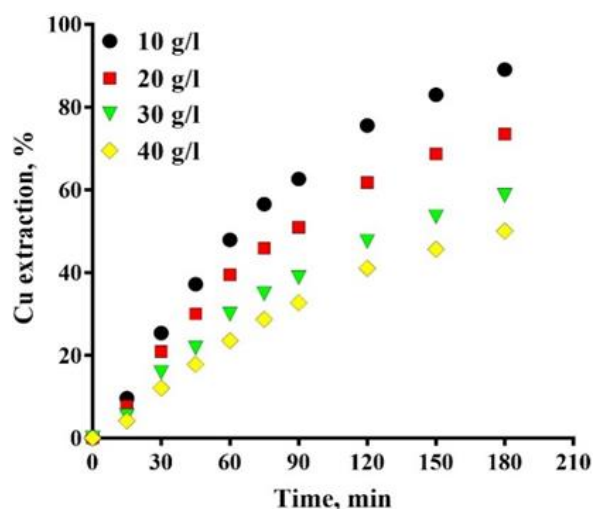
3.2. Effect of Solid to Liquid Ratio

Effect of solid to liquid ratio was investigated under the following operational conditions: 40% BmimHSO₄, 30% H_2O_2, particle size of less than 37 μm, stirring speed of 300 rpm, 40°C, and leaching time of 180 min. The results are displayed in Figure 3. It can be seen that, by increasing the solid to liquid ratio, Cu extraction decreased; after 180 min, increasing the ratio from 10 to 40 g.L⁻¹ led to the decrease in Cu extraction from 89.1 to 50%. From the results, it can be concluded that increasing the solid-to-liquid ratio cannot increase the leaching efficiency.
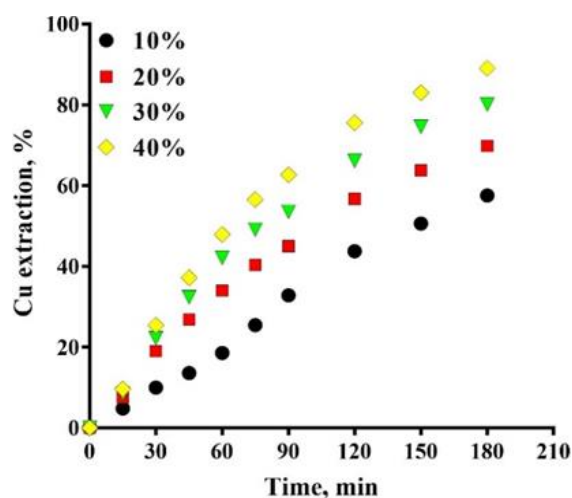
This may be related to the presence of less leaching solution available per unit mass of solids [41, 42], and increase in mass transfer resistance due to increased viscosity[43]. Hence, the optimum solid-to-liquid ratio for leaching reaction in the subsequent experiments was 10 g.L⁻¹.

3.3. Effect of BmimHSO₄ Concentration

Effect of BmimHSO₄ concentration on $CuFeS_2$ dissolution during leaching process was investigated under the following operational conditions: 30% H_2O_2, 40°C, 10 g.L⁻¹ solid to liquid ratio, particle size of less than 37 μm, stirring speed of 300 rpm, and leaching time of 180 min. As can be seen in Figure 4, by increasing the BmimHSO₄ concentration from 10 to 40% w/v, Cu extraction increases from 57.6 to 89.1% after 3 h of leaching which is in accordance with the results of previous studies [17, 18, 31].

Fig. 3. Effect of solid to liquid ratio on leaching efficiency (40% BmimHSO₄, 30% H_2O_2, particle size of less than 37 μm, stirring speed of 300 rpm, 40°C, and leaching time of 180 min).

Fig. 4. Effect of BmimHSO₄ concentration on leaching efficiency (30% H_2O_2, 40°C, 10 g.L⁻¹ solid to liquid ratio, particle size of less than 37 μm, stirring speed of 300 rpm, and leaching time of 180 min).

This may be related to the higher acidity of the

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solution and higher concentration of dissolved oxygen in the presence of higher concentration of BmimHSO$_4$. In addition, the reason for insignificant increase in dissolution of CuFeS$_2$ by further increasing the concentration of BmimHSO$_4$ could be the increased solution viscosity which eventually restricts the diffusion phenomenon [17, 31]. As a result the optimal concentration of 40 % w/v BmimHSO$_4$ was used in the subsequent experiments.

3.4. Effect of H$_2$O$_2$ Concentration

Effect of H$_2$O$_2$ concentration on CuFeS$_2$ dissolution was investigated under the following operational conditions: 40% BmimHSO$_4$, 40°C, 10 g.L^{-1} solid to liquid ratio, stirring speed of 300 rpm, particle size of less than 37 μm, and leaching time of 180 min. Ganbari et al [37] observed with increasing the amount of H$_2$O$_2$ in the solution, the rate of dissolution is increased. As can be seen in Figure 5, increasing H$_2$O$_2$ concentration led to significant change in dissolution rate of CuFeS$_2$. So that, after leaching for 3 h, increasing the H$_2$O$_2$ concentration from 7.5 to 30% led to an increase in Cu extraction from 37 to 89.1%. The increase in dissolution rate could be related to the increased solubility of oxygen and/or the high oxidation potential of hydrogen peroxide [44].

Fig. 5. Effect of H$_2$O$_2$ concentration on leaching efficiency (40% BmimHSO$_4$, 40°C, 10 g.L^{-1} solid to liquid ratio, stirring speed of 300 rpm, particle size of less than 37 μm, and leaching time of 180 min).

Also, according to Figure 5, it can be seen that the improvement of CuFeS$_2$ dissolution by increasing H$_2$O$_2$ concentration in the range of 7.5 to 15% was more significant than that in the range of 15 to 30%. This may be due to the direct

relationship between H$_2$O$_2$ decomposition and its concentration; higher H$_2$O$_2$ concentration leads to higher H$_2$O$_2$ decomposition rate [34-36]. Therefore, the optimal H$_2$O$_2$ concentration of 30% was used in the subsequent experiments.

3.5. Effect of Particle size

Since economic efficiency is highly dependent on the grinding costs, the feed particle size required for leaching process is considered as an effective parameter. In general, smaller particle size leads to more surface area available for leaching, enhancing the leaching rate [45]. Effect of particle size was evaluated under the following operational conditions: 40% BmimHSO$_4$, 30% H$_2$O$_2$, 10 g.L^{-1} solid to liquid ratio, stirring speed of 300 rpm, 40°C, and leaching time of 180 min. As can be seen in Figure 6, the Cu extraction efficiency increased from 45.8 to 89.1% by decreasing the particle size from 74-88 μm to less than 37 μm.
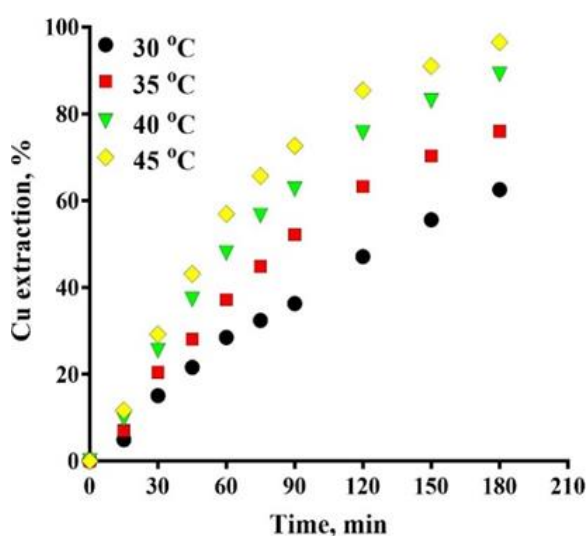

Fig. 6. Effect of particle size on leaching efficiency (40% BmimHSO$_4$, 30% H$_2$O$_2$, 10 g.L^{-1} solid to liquid ratio, stirring speed of 300 rpm, 40°C, and leaching time of 180 min).

This is due to the increase in contact area between the particles and the leaching solution. In addition, porosities and natural cracks on the surface of smaller CuFeS$_2$ particles further increase the dissolution rate [46-48]. Hence, the optimum particle size less than 37 μm was used in the subsequent experiments.

3.6. Effect of Temperature

Temperature is one of the main factors that significantly affects on the leaching rate of

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chalcopyrite More precisely, at low temperatures the dissolution rate of chalcopyrite is very slow [49]. Effect of temperature on $CuFeS_2$ dissolution was studied under the following operational conditions: 40% $BmimHSO_4$, 30% H_2O_2, 10 g.L^{-1} solid to liquid ratio, stirring speed of 300 rpm, particle size of less than 37 μm, and leaching time of 180 min. In general, the dissolution rate of $CuFeS_2$ improved by increasing the temperature. As can be seen in Fugure 7, by increasing the temperature from 30 to 45°C, $CuFeS_2$ dissolution rate increased from 62.5 to 96.5%. This revealed the significant temperature dependence of Cu dissolution which is in good accordance with the previous studies [17, 18, 31, 32].

Fig. 7. Effect of temperature on leaching efficiency (40% $BmimHSO_4$, 30% H_2O_2, 10 g.L^{-1} solid to liquid ratio, stirring speed of 300 rpm, particle size of less than 37 μm, and leaching time of 180 min).

Also, according to Figure 7, it can be seen that the improvement of $CuFeS_2$ dissolution by increasing the temperature in the range of 30 to 40°C was more significant than that in the range of 40 to 45°C because, as confirmed by other researchers, at temperatures above 40°C, the dissolution rate of chalcopyrite slows down, due to the decrease in the amount of H_2O_2 in the solution [40, 50].

3.7. Kinetic Analysis
3.7.1. *Kinetics Model of CuFeS₂ Leaching*
The reaction that occurs between chalcopyrite concentrate particles and $BmimHSO_4$ solution during the leaching process is a typical example of liquid and solid heterogeneous reaction. For

this reaction system, depending on the nature of the solid marterials and the type of the products, the reaction rate is usually controlled by one of the following steps [51-54]:
Diffusion through the liquid film, diffusion through the ash/product layer, chemical reaction at the surface of the solid particles or a mixed state of diffusion and chemical reaction. The shrinking core model (SCM) determines which of these steps controls the leaching process [29, 53, 54].
In order to determine the kinetic parameters and rate controlling step of leaching process, the data obtained in the leaching experiments were analyzed based on shrinking core model. Equations describing different rate-limiting steps of SCM are defined in Table 2 [51, 54]. Coefficient of determination (R^2) for each equation is also presented in this. The step with the greatest resistance toward reaction is considered as the rate-limiting step [51, 54].
According to Table 2 Eq. T5 resulted in higher R^2 values in the studied temperature range in comparison with the other equations, which shows the leaching is mainly controlled by chemical reaction. As a result, the experimental data of the $CuFeS_2$ dissolution can be well described by equation related to this mechanism.

3.7.2. *Determination of Activation Energies*
The temperature dependence of the rate constant for most chemical reactions is defined by the Arrhenius equation (Equations 2 and 3) [54].

$$K_p=A \exp\left(\frac{-E_a}{RT}\right) \qquad (2)$$

$$\ln K_p=\ln A - \left(\frac{-E_a}{RT}\right) \qquad (3)$$

Where k_p is the rate constant, A is the frequency factor, E_a is the activation energy (KJ/mol), R is the universal gas constant, and T is the absolute temperature (K).
To obtain rate constant (k_p) for each temperature, $1-(1-x)^{1/3}$ was plotted vs. reaction time according to data collected in the leaching experiments (Figure 8a). The slope of the fitted straight lines was considered as the rate constant.
Using the apparent rate constants derived from Equation 3 along with the Arrhenius plot ($\ln(k_p)$ vs. 1/T) (Figure 8b), the value of E_a was calculated to be 46.63 KJ/mol.
Large activation energy values (>40 KJ/mol) imply that chemical reaction is the limiting step.

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Table 2. Coefficient of determination (R^2) for different SCM equations

Eq. NO.	Limiting Step	Equation	R^2			
			30°C	35°C	40°C	45°C
T1	Diffusion through the product layer (sp)	$1 - 3(1-x)^{\frac{2}{3}} + 2(1-x) = kt$	0.9485	0.9725	0.9743	0.9776
T2	Diffusion through the product layer (cp)	$x + (1-x)\ln(1-x) = kt$	0.9432	0.9738	0.9827	0.986
T3	Diffusion through the liquid film (sp and cp)	$x = kt$	0.9787	0.9545	0.9325	0.9069
T4	Surface chemical reactions (cp)	$1 - (1-x)^{\frac{1}{2}} = kt$	0.9907	0.9764	0.9733	0.9642
T5	Surface chemical reactions (sp)	$1 - (1-x)^{\frac{1}{3}} = kt$	0.9966	0.9913	0.9955	0.9965

sp—spherical particles, cp—cylinder particles, k—a chemical constant, X—the degree of copper recovery into the solution, and t—the leaching time
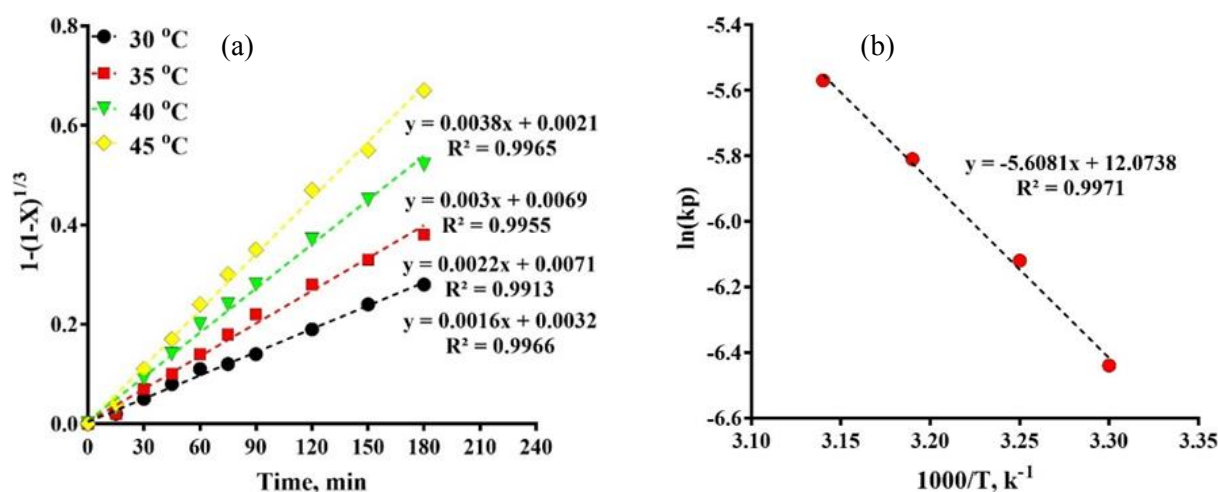
Fig. 8. (a) Plot of $1 - (1-x)^{\frac{1}{3}} = kt$ vs. time for dissolution of $CuFeS_2$ at different temperatures, (b) Arrhenius plot obtained for chalcopyrite dissolution.

Meanwhile, small activation energy values (<40 KJ/mol) are related to the case where diffusion is rate-limiting step [47]. However, different values, 12-26 KJ/mol [55], are reported for activation energy required for diffusion step. Moreover, different values (40-80 KJ/mol) are reported for activation energy where chemical reaction is the controlling factor [56]. According to the results, the activation energy values higher than 40 KJ/mol, and also values reported in the literature, it can be concluded that $CuFeS_2$ leaching using BmimHSO$_4$ does not follow diffusion-controlled kinetics. Instead it is well presented by kinetics controlled by chemical reaction. Although, Arrhenius equation is used for determination of activation energy as well as analysis of mechanism during chemical reactions, this method has two main drawbacks. First, the calculated value of rate constant depends highly on experimental selection of rate equation. For a given reaction, various rate equations present good fit with experimental data. So, several rate constants and subsequently various activation energies might be calculated. Second, activation energy is calculated on average basis. In most chemical reactions, however, especially complex fluid-solid reactions, rate constant and activation energy vary as reaction progresses due to the changes in the reaction mechanism. In order to overcome this problem, "time to a given fraction method" is suggested [57]. Various researchers have used this method in their reports [58-60]. This method is based on the relation of fractional conversion (x) with time (t) according to Equation 4. In this method, time is considered as a dependent variable (Equation 5). Continuity between initial, mean, and final fractional conversions is evaluated using Equation 6-8.

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$$\frac{dx}{xt} = k_c.f(x) \tag{4}$$

$$dt = k_c^{-1}.f^{-1}(x)dx \tag{5}$$

$$t_x = k_c^{-1} \int_{x=0}^{x=x_1} f^{-1}(x)dx \tag{6}$$

$$t_x \propto A^{-1} \exp\left(\frac{-E_a}{RT}\right) \text{ if } t_x \propto k_c^{-1} \tag{7}$$

$$\ln t_x = const - \ln A + \frac{E_a}{R}\left(\frac{1}{T}\right) \tag{8}$$

Where E_a is the apparent activation energy required for the progress of certain reaction in specific time. According to Equation 8 the slope of $\ln(t_x)$ plot vs. $1/T$ is E_a/R. When multiplied by R, the value of activation energy is obtained for a given fractional conversion. Calculation of Ea for different fractional conversions provides full monitoring of possible changes in reaction mechanism. Graphical representation of the calculated activation energy for specific fractional extraction efficiency of Cu is shown in Figure 9.
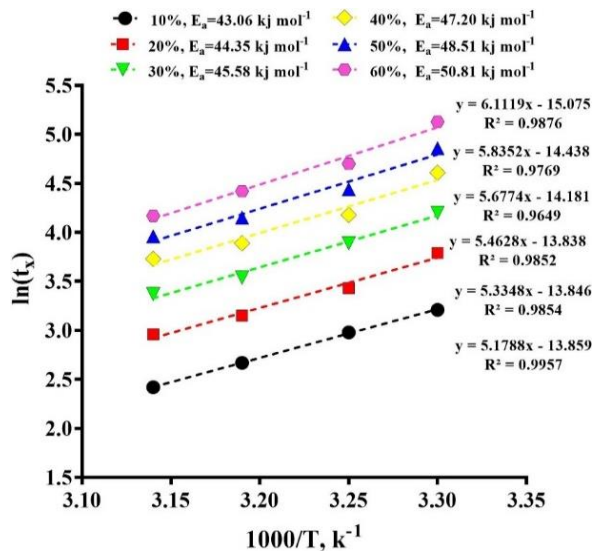

Fig. 9. Plot of $\ln(t_x)$ vs. $1/T$ for different Cu extraction fractions.

The activation energy calculated using time given to a fraction method for Cu extraction of 10 to 60% varies in the range of 43.1-50.8 KJ/mol. These values are in accordance with those obtained by SCM and Arrhenius equation. Therefore, it can be concluded that the mechanism of leaching is remained unchanged overtime. According to Figure 9, the increasing trend for activation energy may be related to the reaction with elemental sulfur (Figure 10), which may warp $CuFeS_2$ particles and prevent the complete leaching of Cu. Value of Gibbs free energy is calculated using the values of ΔS^{++} and ΔH^{++} according to Equation 9.
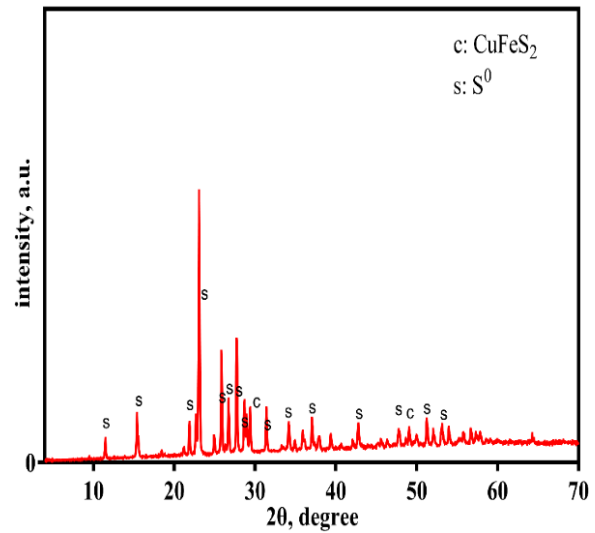
$$\Delta G^{++} = \Delta H^{++} - T\Delta S^{++} \tag{9}$$

Fig. 10. XRD pattern of leached sample (40% $BmimHSO_4$, 30% H_2O_2, 10 $g.L^{-1}$ solid to liquid ratio, stirring speed of 300 rpm, 45°C, particle size of under 37μm, and leaching time of 180 min).

According to Equation 10, by plotting $T \times \ln\frac{k_p}{T}$ vs. T, activation parameters, namely enthalpy and entropy, are calculated to be 48.98 KJ/mol and -153.40 J mol^{-1} K^{-1}, respectively. In addition, according to Equation 11, the slight difference in enthalpy and activation energy at room temperature is acceptable.
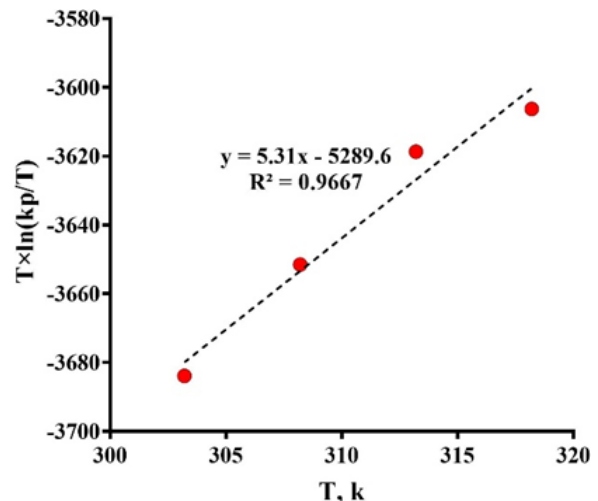
$$E_a = \Delta H^{++} + RT \tag{10}$$

Fig. 11. Eyring equation for $CuFeS_2$ dissolution using experimental data.

3.7.3. Effect of Operational Parameters on the Kinetics of Leaching

In order to further evaluate the leaching kinetics, the effect of experimental parameters (i.e., BmimHSO$_4$ and H$_2$O$_2$ concentration, solid to liquid ratio and particle size (R$_o$)) and the role of each of these parameters on the leaching kinetics was investigated. The effect of these parameters is expressed according to Equation 11.

$$k_p = k_o[\text{BmimHSO}_4]^a[\text{H}_2\text{O}_2]^b\left[\frac{s}{l}\right]^c [R_o]^d \times \exp\left(\frac{-E_a}{RT}\right) \quad (11)$$

Where k$_0$ is the Arrhenius constant. Constants a, b, c, and d are the order of reaction according with BmimHSO$_4$ and H$_2$O$_2$ concentration, solid to liquid ratio, and particle size, respectively. In order to determine the order of reaction of each parameter, 1-(1-x)$^{1/3}$ was plotted versus time at different levels of each operational parameter to obtain the corresponding kp for each parameter (Table 3). Then, ln(k$_p$) was plotted versus ln(variable value) (Figure 12).

The slope of the straight line (k$_c$) indicates the "calculated" order of reaction for each parameter. Which was 0.5386, 0.933, −0.676 and −1.1078 for BmimHSO$_4$ and H$_2$O$_2$ concentration, solid to liquid ratio and particle size, respectively. Negative values of k$_c$ for each parameter reveal that the dissolution rate decreases with increasing the parameter value. Substituting Equation 11 and the values for the order of reaction into 1-(1-x)$^{1/3}$ gives Equation 12 for leaching of CuFeS$_2$ using BmimHSO$_4$ and H$_2$O$_2$ as oxidative agent.

$$1-(1-x)^{\frac{1}{3}} = k_o[\text{BmimHSO}_4]^{0.54}[\text{H}_2\text{O}_2]^{0.93} \times$$
$$\left[\frac{s}{l}\right]^{-0.68} [R_o]^{-1.11} \exp\left(\frac{-46625.74}{RT}\right)t \quad (12)$$

By plotting left side versus the right side expressions of Equation 12, a line is obtained (Figure 13), the slope of which is the Arrhenius constant (k$_0$= 0.2595×10^6).

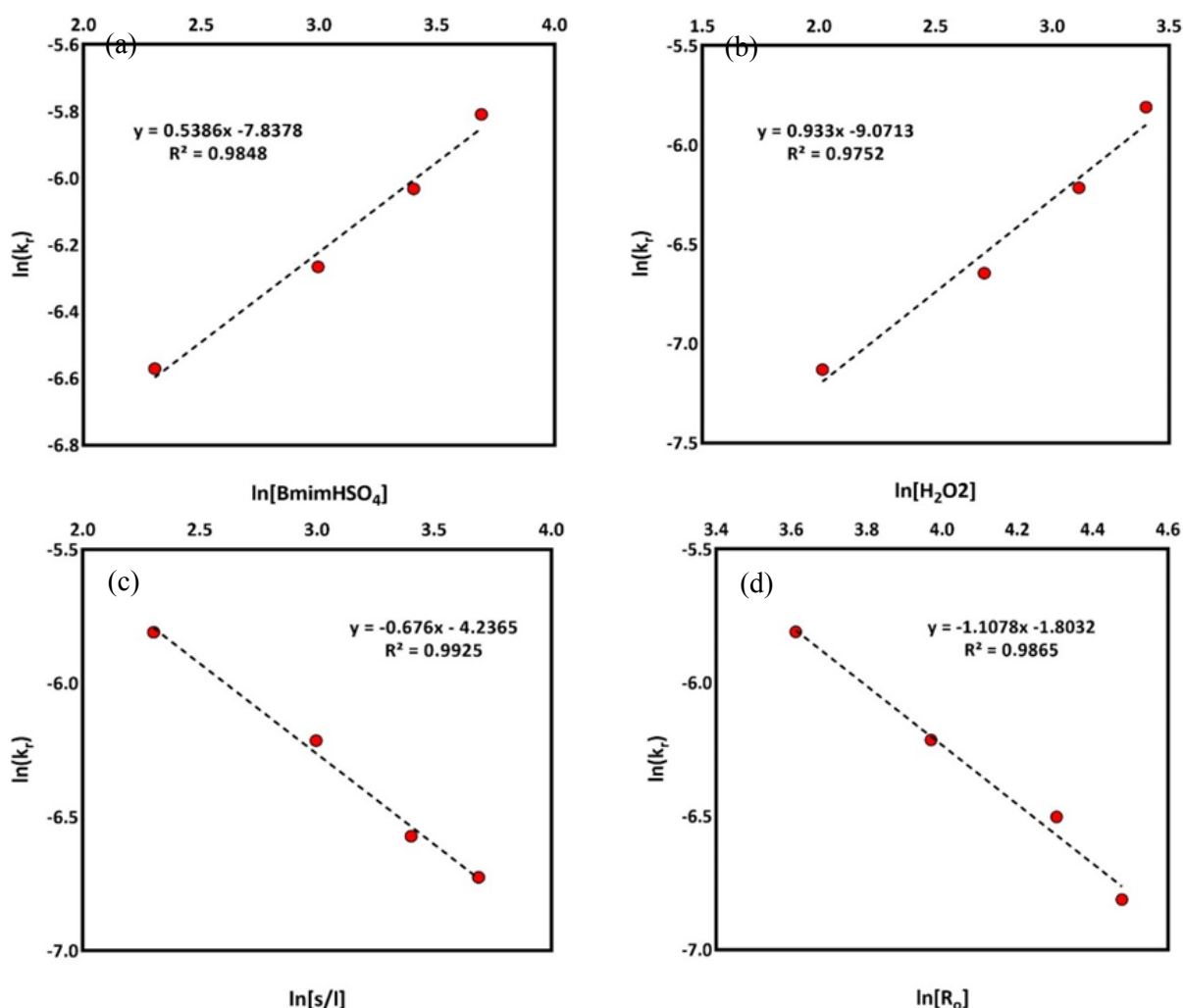**Fig. 12.** Plot of ln kd vs: (a) ln[BmimHSO$_4$], (b) ln [H$_2$O$_2$], (c) ln [S/L] and (d) ln [R$_o$]

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Table 3. Results of order of reaction calculation relative to each operational parameter

parameter BmimHSO$_4$ (%w/v)	K_p (h^{-1})	R^2	$\ln(k_p)$
10	0.0014	0.993	-6.57
20	0.0019	0.993	-6.27
30	0.0024	0.993	-6.03
40	0.0030	0.996	-5.81
H$_2$O$_2$ (%v/v)			
7.5	0.0008	0.988	-7.13
15	0.0013	0.995	-6.65
22.5	0.0020	0.981	-6.21
30	0.0030	0.996	-5.81
Particle size (μm)			
37	0.0030	0.996	-5.81
53	0.0020	0.981	-6.21
74	0.0015	0.989	-6.50
88	0.0011	0.998	-6.81
s/l (g/l)			
10	0.0030	0.996	-5.81
20	0.0020	0.984	-6.21
30	0.0014	0.982	-6.57
40	0.0012	0.983	-6.73

Moreover, R^2 value is 0.9836 which confirms the acceptable agreement with the experimental data. Finally, the kinetic model for CuFeS$_2$ leaching using BmimHSO$_4$ in the presence of H$_2$O$_2$ oxidative agent is obtained as Equation 13

$$1-(1-x)^{\frac{1}{3}}=0.26 \times 10^6[BmimHSO_4]^{0.54} \times [H_2O_2]^{0.93} \left[\frac{s}{l}\right]^{-0.68} [R_o]^{-1.11} \exp\left(\frac{-46625.74}{RT}\right) t \qquad (13)$$

y = 0.2595x + 0.0051
R^2 = 0.9836
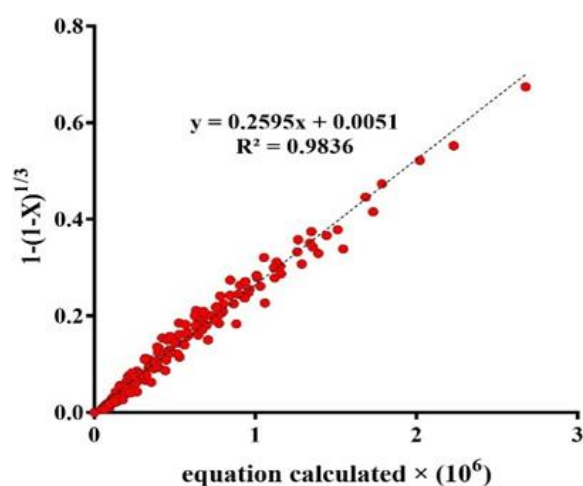
Fig. 13. Plot of Arrhenius constant (k_0).

4. CONCLUSIONS

The effect of leaching operational parameters, i.e. BmimHSO$_4$ concentration, H$_2$O$_2$ concentration, solid to liquid ratio, stirring speed, temperature, and particle size on leaching of CuFeS$_2$ concentrate was investigated. The results are summarized as follows:

- The highest Cu extraction was achieved using 40% BmimHSO$_4$, 30% H$_2$O$_2$, and 10 g.L^{-1} solid to liquid ratio for particle sizes less than 37 μm at 300 rpm and 45°C for leaching time of 180 min. It was found that the increase in BmimHSO$_4$ and H$_2$O$_2$ concentration, and temperature, as well as the decrease in solid to liquid ratio and particle size, contributed to the dissolution of chalcopyrite.

- Investigation of kinetic models showed that dissolution of CuFeS$_2$ using BmimHSO$_4$ can be well described by SCM, which demonstrated that the leaching process using BmimHSO$_4$ does not follow the diffusion-controlled reaction and the results better fit with chemical reaction-controlled mechanism.

- The calculated activation energy was 46.63 KJ/mol and calculation of apparent activation energy using time given to a fraction method revealed that the leaching mechanism remains unchanged overtime.

- The orders of reaction with respect to BmimHSO$_4$ and H$_2$O$_2$ concentration, solid to liquid ratio and particle size were estimated to be 0.539, 0.933, −0.676 and −1.108, respectively. Under these circumstances, the

calculated Arrhenius constant was 0.2596×10^6.

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