

# The influence of adding a supplementary constituent to choline chloride and p-toluenesulfonic acid based deep eutectic solvents on the dissolution of chalcopyrite

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## ABSTRACT

The conventional techniques of pyrometallurgy and hydrometallurgy used to produce copper involve high energy consumption, substantial costs, and pose environmental challenges. Leaching in biocompatible solvents such as deep eutectic solvents (DESs) can be considered a suitable alternative to conventional production methods. In this study, Sungun copper concentrate (SCC), with the primary phases of chalcopyrite, and pyrite, was used to evaluate the leaching of copper, and iron in various DESs with a solid-to-liquid ratio of 20 g/L, at a temperature of 100 °C, and a time of 24 h. Three-component DES based on choline chloride (ChCl) as hydrogen acceptor, and p-toluene sulfonic acid (PTSA), and various third phases as hydrogen donors were used as solvents. The third components are oxalic acid (OA), ethylene glycol (EG), sucrose (S), malonic acid (MOA), fructose (F), urea (U), maleic acid (MA), citric acid (CA), glucose (G). According to the results of the leaching of copper, and iron, selective dissolution wasn't achieved in any of the ternary DESs. Among these DESs, the ChCl:PTSA:MOA with a leaching efficiency of 89% of copper had the highest leaching efficiency, and at the same time, it dissolved less iron. By adding a small amount of water to sugar-based DES (*i.e.*, ChCl:PTSA:S, ChCl:PTSA:F, and ChCl:PTSA:G), the synthesis was successfully performed by changing the physical, and chemical properties, but the dissolution of chalcopyrite in sugar-based DES was significantly reduced.

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## 1. Introduction

Copper is known as the second most used non-ferrous element after aluminum. Currently, 80 % of the world's copper production is extracted from sulfide minerals by pyrometallurgical processes, and the rest is obtained from oxide minerals by hydrometallurgical processes [1,2]. Chalcopyrite is the most abundant copper mineral, and accounts for approximately 70% of the world's copper reserves, and has tough leaching conditions. Its dissolution rate is slow due to the formation of a passive layer on the mineral surface during the leaching process. For this reason, currently the primary method for producing copper from chalcopyrite is pyrometallurgy. However, the pyrometallurgical method is economical only for high-grade minerals. The hydrometallurgical

method seems to be a more suitable alternative due to the low costs, and the possibility of using minerals with a lower grade than the pyrometallurgical method [3,4]. Currently, the different chalcopyrite leaching methods are mainly: the direct leaching method (materials are not pre-treated, and strong oxidants are added directly to destroy the chalcopyrite structure, and dissolve copper), and electroleaching method. Although the copper hydrometallurgical method has made significant progress, most of the existing technologies, and processes deal with oxidized ore and waste rock, and there are still serious problems such as corrosion, high energy consumption, high acid consumption, long leaching time, and poor selective leaching [5]. Therefore, the development of new theories, and methods of hydrometallurgy of chalcopyrite with strong compatibility with minerals, low energy consumption, low gas

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emission, and operation at low temperature, and low pressure, and environmentally friendly is necessary for copper production [6]. Therefore, scientists in this field are looking for leaching agents with the lowest level of environmental pollution, among which solvometallurgy is one of the alternative options. Conceptually, solvometallurgy is similar to hydrometallurgy in terms of unit operations, and operating conditions, with the only difference being the use of non-aqueous solvents such as molecular organic solvents, ionic liquids (ILs), and deep eutectic solvents (DESs) instead of aqueous, acidic or alkaline solutions [7]. Among these solvents, DESs have been considered due to their more accessible synthesis, and more excellent biodegradability. These solvents are a mixture of a stoichiometric substance with a ratio of hydrogen bond acceptors (HBA) to hydrogen bond donors (HBD) with a freezing point significantly lower than the melting point of each component. Hydrogen bond acceptors mainly include quaternary ammonium or phosphonium salts, while the most common hydrogen bond donors are amides, alcohols, and carboxylic acids [8–11].

Charge transfer through hydrogen bonding between a halide ion, and the hydrogen donor is the reason for the lowering of the melting point of the mixture relative to the melting point of the individual components [1]. DESs are known as green solvents due to their wide liquid temperature range, good solubility, high thermal, and chemical stability, almost non-volatile, and low toxicity. Due to the mentioned advantages, DESs are potentially used for the treatment of low-grade minerals as well [5]. Some research has been done to investigate the leaching of copper sulfide compounds in DESs [12,13].

Anggara et al. [12], investigated the leaching of covellite (CuS), chalcocite (Cu<sub>2</sub>S), and chalcopyrite (CuFeS<sub>2</sub>) using two different DESs (ChCl:U, and ChCl:EG). They found that three sulfide ores in DESs can recover high-purity copper by electrochemical dissolution, and electrodeposition. The primary copper species present after dissolution is CuCl<sub>4</sub><sup>2-</sup>, while chalcopyrite forms a mixture of Cu(I), and Cu(II) species. Interestingly, there was no sign of production of gases such as SO<sub>2</sub>, and H<sub>2</sub>S. It is expected that SO<sub>2</sub> or H<sub>2</sub>S was oxidized to sulfate in the leaching process in DES. An optimum copper efficiency of 99% was obtained using

mixed DESs of 80 wt.% ChCl:EG, and 20 wt.% ChCl:OA [12]. In another study, Li et al.[13], investigated copper extraction from copper sulfide ore minerals (bornite (Cu<sub>5</sub>FeS<sub>4</sub>), chalcopyrite, and chalcocite) in different DESs. All solvents could extract copper, but the EG/FeCl<sub>3</sub> system had the best leaching efficiency. The leaching products of chalcopyrite in the EG/FeCl<sub>3</sub> system are: CuCl, FeCl<sub>2</sub>, and solid elemental sulfur. The kinetics of sulfide leaching is determined by the chemical reaction on the mineral surface [13]. In another study, Carlesi et al.[14], studied the leaching of chalcopyrite in ChCl:EG with a liquid to solid ratio (1:2) at ambient pressure, and moderate temperature. Iron and copper dissolve without changing the pH of the solvent, and their oxidation state, forming a stable chloride complex, and the system shows no signs of passivation. It was found that the rate-controlling step of the dissolution process is the diffusion of species in the solvent.

In this study, Sungun copper concentrate (SCC) was used to evaluate the leaching of copper, and iron in DESs with a solid-to-liquid ratio of 20 g/L, at a temperature of 100 °C for 24 h. Three-component DES based on choline chloride (ChCl) as hydrogen acceptor, p-toluene sulfonic acid (PTSA), and various third phases as hydrogen donors were used as solvents. The third component is oxalic acid (OA), ethylene glycol (EG), sucrose (S), malonic acid (MOA), fructose (F), urea (U), maleic acid (MA), citric acid (CA), and glucose (G). DESs include ChCl:PTSA:OA, ChCl:PTSA:EG, ChCl:PTSA:S, ChCl:PTSA:MOA, ChCl:PTSA:F, CHCl:PTSA:U, ChCl:PTSA:MA, ChCl:PTSA:CA, ChCl:PTSA:G.

## 2. Materials and Methods

### 2.1. Characterization of chalcopyrite concentrate

Copper sulfide concentrate (chalcopyrite) was used as the primary material in this study. X-ray diffraction (XRD) analysis and X-ray fluorescence (XRF), Scanning electron microscopy (SEM), Atomic absorption spectroscopy (AAS), and Inductively coupled plasma spectroscopy (ICP) were performed to analyze the chemical composition of this concentrate. XRD analysis was carried out using an XRD (Advance D8 model manufactured by Bruker, Germany) with a Cu lamp. SEM analysis was carried out using an SEM (EM8000F model manufactured by Kyky, China).

To determine the amounts of copper, and iron in the concentrate, the copper concentrate was first dissolved in aqua regia, and then analyzed using AAS (Varian 240A). Additionally, a sample of concentrate was analyzed using ICP to determine the low-grade elemental values. Furthermore, 100 g of the homogenized concentrate was subjected to particle size distribution analysis using a particle size analyzer.

## 2.2. DES synthesis

At first, a two-component eutectic solvent was synthesized with a 1:1 molar combination of choline chloride, and toluene sulfonic acid. In addition, three-component DES was synthesized by mixing of two fixed components: choline chloride (ChCl) ((CH<sub>3</sub>)<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>OH)Cl (>98%, Merck) as the hydrogen bond acceptor, and p-toluene sulfonic acid (PTSA) (Merck, <98%, C<sub>7</sub>H<sub>8</sub>O<sub>3</sub>S) as the hydrogen bond donor, along with a third variable component including: oxalic acid (OA) (C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>, >95%, Merck), ethylene glycol (EG) (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>, >99%, Merck), sucrose (S) (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>, >99%, Merck), malonic acid (MOA) (C<sub>3</sub>H<sub>4</sub>O<sub>4</sub>, >99%, Merck), fructose (F) (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, >98%, Merck), urea (U) (CH<sub>4</sub>N<sub>2</sub>O, >99%, Merck), maleic acid (MA) (C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>, >99%, Merck), citric acid (CA) (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>, >99.5%, Merck), and glucose (G) (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, >97.5%, Merck), with a 1:1:1, and 2:1:1 molar ratio. This mixture was heated at 70 °C for one hour in a glass vial within an oil bath. To obtain a completely transparent mixture, the temperature was increased to 80 °C, and continuously stirred with a magnet. It is worth mentioning that, in order to reduce experimental error due to the significant moisture absorption by these substances, especially in the case of ChCl, the materials were thoroughly dried in an oven at 70 °C for 3 h before the synthesis.

## 2.3. Leaching procedure

After synthesizing the three-component mixture, the temperature of solvent was increased to 100 °C within an oil bath using a heater. Then, 0.1 grams of the concentrate was added to the synthesized DES to prepare a pulp with a solid-to-liquid ratio of 20 g/L. Other parameters such as stirring speed, and time were set at 400 rpm, and 24 h, respectively. Finally, after the leaching operation, the resulting solution was immediately

filtered. The efficiency of copper and iron leaching was calculated using the following equation (1) and (2), respectively:

$$R_{Cu}(\%) = \frac{M_{Cu} \times V}{m \times S_{Cu}} \times 100 \quad (1)$$

$$R_{Fe}(\%) = \frac{M_{Fe} \times V}{m \times S_{Fe}} \times 100 \quad (2)$$

In these formulas, respectively, M<sub>Cu</sub> is the concentration of copper in the solution and M<sub>Fe</sub> is the concentration of iron in the solution in g/L, V is the volume of the leaching solution in L, m is the mass of chalcopyrite concentrate in gram (g), and S<sub>Cu</sub> is the copper grade of the concentrate and S<sub>Fe</sub> is the iron grade of the concentrate in percentage (%).

## 3. Results and Discussion

### 3.1. characterization result

The results of the XRD analysis are presented in Fig. 1, which shows that the primary components of the copper concentrate are chalcopyrite (JCPDF 13-201-611), pyrite (JCPDF 14-211-211), and silica (00-016-1157). The results of XRF analysis are shown in Table 1, which confirms the presence of the chemical composition of silica in the copper concentrate. Additionally, the results of the AAS indicate the presence of 25% copper, and 27% iron in the copper concentrate. The results of the ICP analysis for identifying elements with lower values are presented in Table 2.

Furthermore, Fig. 2 shows the particle size distribution of the concentrate obtained from the particle size analyzer. The particle size of the concentrate is in the range of 40 to 180 μm. It can be observed that the d<sub>80</sub> value is also 118 μm. Fig.3 shows SEM image and map analysis obtained from EDX analysis of chalcopyrite concentrate powder. As the SEM image shown, the particles of chalcopyrite concentrate are completely angular and sharp, which were polished by performing grinding operations and become spherical with softer corners. According to map images obtained from EDX analysis, the presence of oxygen, silicon, sulfur, iron and copper elements in chalcopyrite, pyrite and silica phases is confirmed.

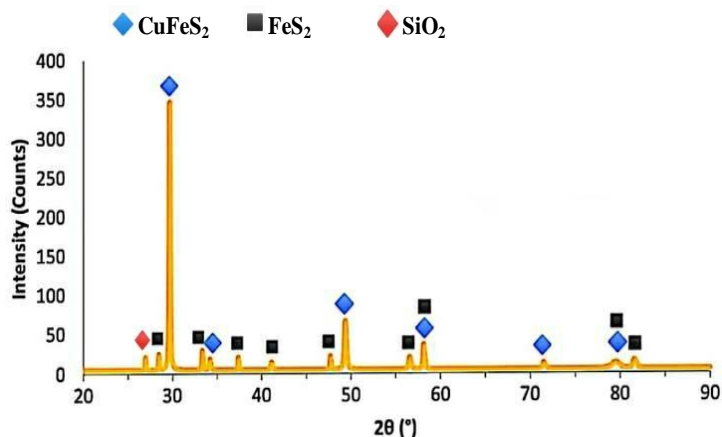


Fig. 1. X-ray diffraction pattern of the copper concentrate sample.

Table 1. Chemical analysis of copper concentrate by XRF

Combinations	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	CaO	MgO	Na <sub>2</sub> O	Pb <sub>2</sub> O <sub>5</sub>
wt. %	31.88	9.299	2.518	0.614	0.528	0.312	0.219	0.088

Table 2. Elemental analysis of copper concentrate by ICP

Elements	As	Pb	Sb	Al	Ca	Na	Zn	Mg	Mo
wt. %	0.22	0.21	0.073	0.13	0.38	0.17	0.61	0.096	0.094

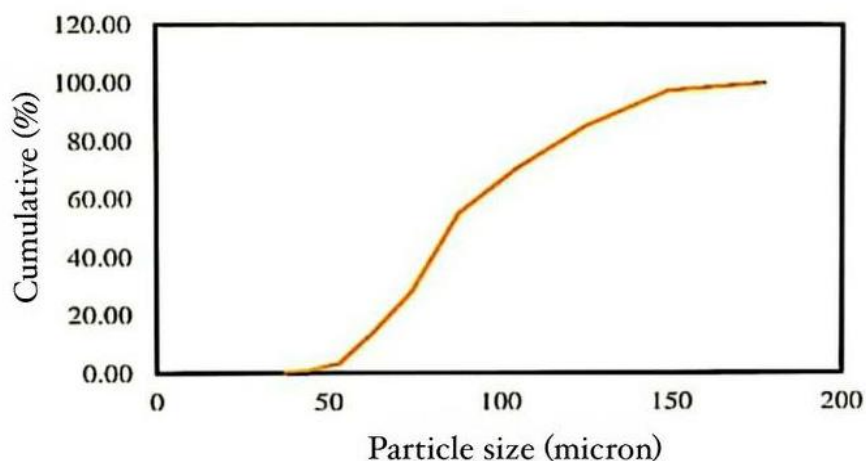


Fig. 2. Particle size distribution of copper concentrate (µm).

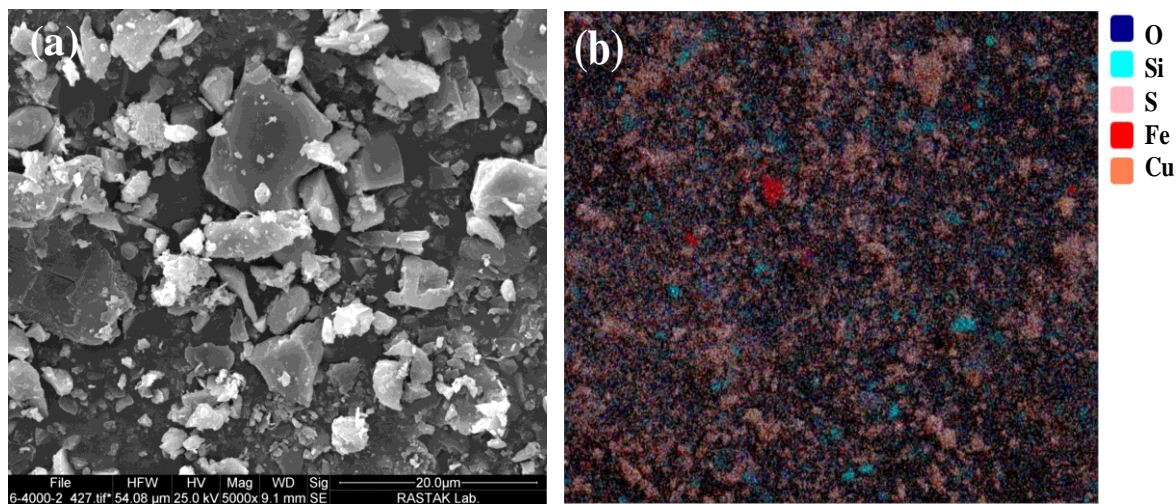


Fig. 3. (a) SEM image and, (b) map analysis obtained from EDX analysis of chalcopyrite concentrate powder.

Table 3. Different conditions for sugar-based DES synthesis

DESs	Molar Ratio	Temp. (°C)	time (h)	Result*
ChCl:PTSA:S	1:1:1	80	0.5	×
ChCl:PTSA:F	1:1:1	80	0.5	×
ChCl:PTSA:G	1:1:1	80	0.5	×
ChCl:PTSA:S	1:1:1	50	0.5	×
ChCl:PTSA:F	1:1:1	50	0.5	×
ChCl:PTSA:G	1:1:1	50	0.5	×
ChCl:PTSA:S	2:1:1	80	0.5	×
ChCl:PTSA:F	2:1:1	80	0.5	×
ChCl:PTSA:G	2:1:1	80	0.5	×
ChCl:PTSA:S	2:1:1	50	0.5	×
ChCl:PTSA:F	2:1:1	50	0.5	×
ChCl:PTSA:G	2:1:1	50	0.5	×

\*«×» it means the desired synthesis was not failed.

### 3.2. Synthesis three-component DES

First, we examine the results of the synthesis of three-component DES. three components containing sugar in two molar ratios 1:1:1, and 2:1:1 (ChCl:PTSA:Sugers) were examined to evaluate the synthesis. Table 3 shows the synthesis of various compounds of ChCl, PTSA, and sugars including G, S, and F at temperatures of 50, and 80 °C. Three-component DESs, including ChCl:PTSA:S, ChCl:PTSA:F, ChCl:PTSA:G, after 0.5 h of the synthesis at 80 °C, due to the decomposition of its components, it was removed from the liquid state. This indicates that the molar ratio is disturbed after the decomposition of the components. In other words, in these solvents, the ratio of hydrogen bond acceptor and donor has been changed, and as a result, the lack of supply of the hydrogen bond chain by each other causes disruption of solvents. With the idea that high synthesis temperature causes the decomposition of sugar compounds, we reduced the synthesis temperature up to 50 °C. In the ratios of 1:1:1, and 2:1:1 with the synthesis temperature of 50 °C, with over time, the compounds were completely unmixed and decomposed. In other words, lowering the temperature did not create a homogeneous solvent for three-component DES based on the sugar.

According to the research by El-Achkar et al.[15], water can be added to some DESs to modify their physical, and chemical properties, such as viscosity, and ionic conductivity. However, due to its high polarity, water may gradually weaken the molecular bonds between the components of the DESs, and eventually destroy them. Due to the effects of water on the molecular bonds of different DES; Therefore, a small amount of water was added to the solvents containing the sugar compound. By adding 0.1 mL H<sub>2</sub>O, the homogeneous liquids from three compounds containing sugar were created. The synthesis of the three-component deep eutectic solvents at a 1:1:1 molar ratio was carried out at 80 °C, except for sugar-based DESs. The sugar-based DESs were synthesized at 50 °C by adding 0.1 mL H<sub>2</sub>O. The results are shown in Table 4.

#### 3.2.1. FTIR

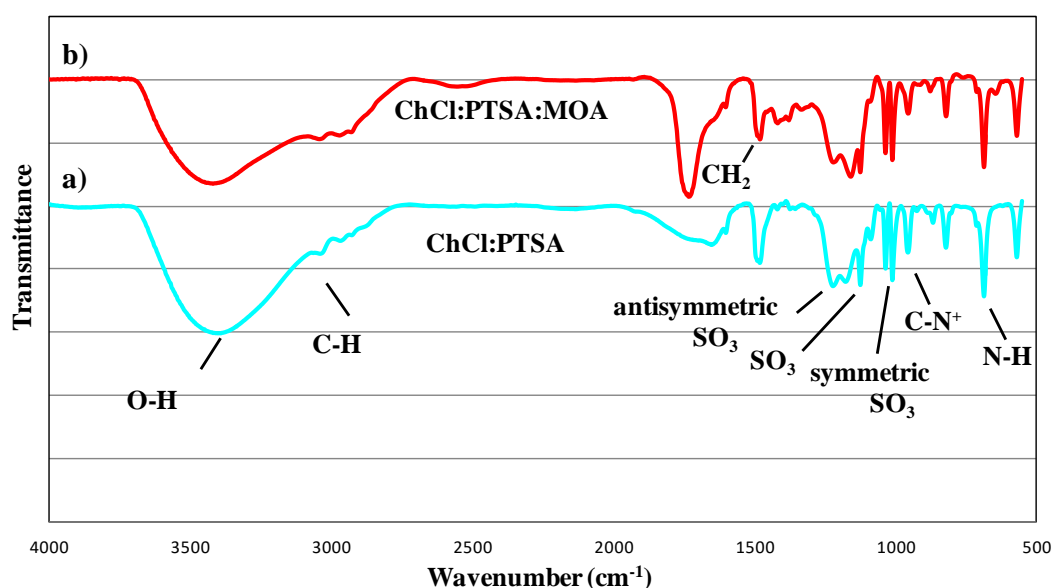
Fig.4 shown the results of FTIR: (a) DES two-component (ChCl:PTSA) and (b) DES three-component (ChCl:PTSA:MOA). According to the FT-IR spectrum, the broad band between 3030 and 3650 cm<sup>-1</sup> for both DES is related to the stretching vibration of the O-H group. The formation of O-H bond in two and three components' solutions is due to the bond formed between the components of the solution. A characteristic band is observed at 955cm<sup>-1</sup>, which is related to the C-N<sup>+</sup> bond, which

originates from the ChCl compound. Longer and sharper peak indicates order and higher percentage of bonding in the structure. On the other hand, the shorter peak indicates a lower percentage of bond presence in the structure, which is the result of breaking bonds and converting to other bonds. The characteristic band at 1723  $\text{cm}^{-1}$  in ChCl:PTSA:MOA compounds refers to the bending of C=O. Also, The characteristic band at 1652  $\text{cm}^{-1}$  in ChCl:PTSA compounds refers to the bending of NH<sub>2</sub>. The characteristic band at 1479

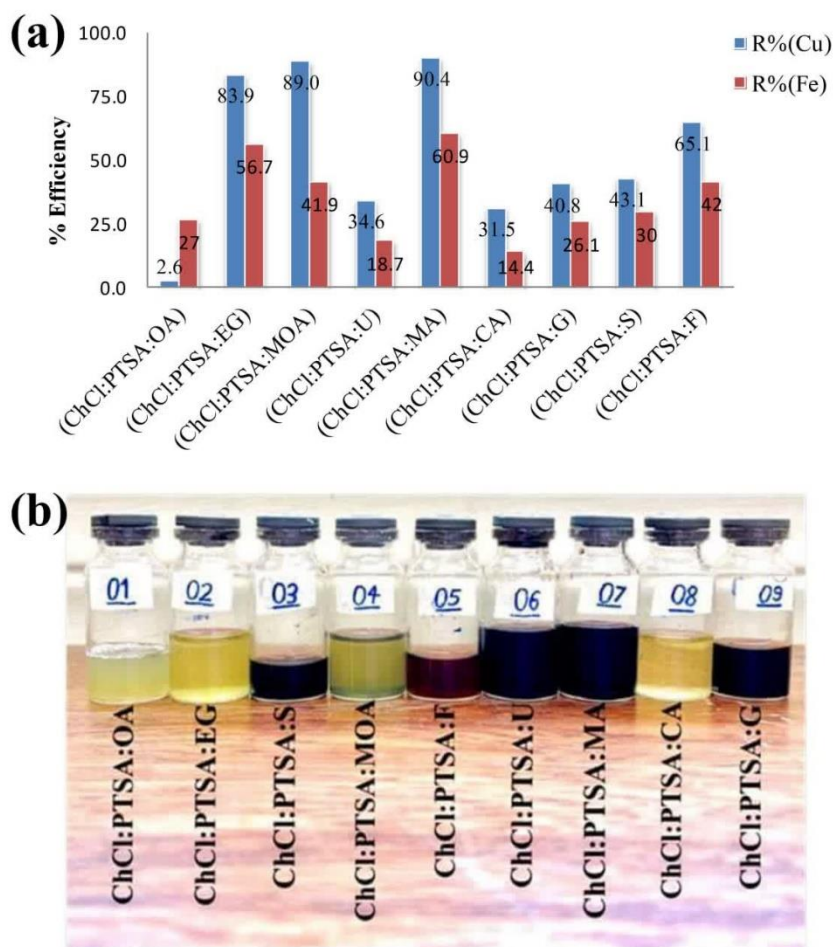
$\text{cm}^{-1}$  in both compounds refers to the bending of CH<sub>2</sub>, an alkyl group that creates its ChCl component. In both DES, asymmetric stretching vibrations of SO<sub>3</sub> are seen in the range of 1203 to 1167  $\text{cm}^{-1}$  and symmetric stretching vibrations of SO<sub>3</sub> are seen in the range of 1009 to 1035  $\text{cm}^{-1}$ . In two-component DES, we will have N-H amino group in the characteristic band of 684  $\text{cm}^{-1}$ . For a more comprehensive analysis of the FT-IR peaks, more details can be found in other sources [16].

**Table 4.** Three-component DESs, and their synthesis condition

DES	Molar Ratio	Temp. (°C)	Synthesis time (h)	Final volume (mL)
ChCl:PTSA:OA	1:1:1	80	1	1.4
ChCl:PTSA:EG	1:1:1	80	1	4.35
ChCl:PTSA:MOA	1:1:1	80	1	4.5
ChCl:PTSA:U	1:1:1	80	1	4.7
ChCl:PTSA:MA	1:1:1	80	1	4.8
ChCl:PTSA:CA	1:1:1	80	1	4.1
ChCl:PTSA:S	2:1:1+0.1mL H <sub>2</sub> O	50	1	4.65
ChCl:PTSA:F	2:1:1+0.1mL H <sub>2</sub> O	50	1	4.6
ChCl:PTSA:G	2:1:1+0.1mL H <sub>2</sub> O	50	1	5



**Fig. 4.** FTIR analysis results: (a) ChCl:PTSA, (b) ChCl:PTSA:MOA.



**Fig. 5.** (a) The leaching efficiency of copper, and iron in different DESs, and (b) their variation in color after leaching

### 3.3. Leachability of chalcopyrite in different DES

In the subsequent experiments, after initial heating of the synthesized solvents, 0.1 g of copper concentrate was added to the solvent, and the mixture was subjected to leaching at 100 °C for 24 h. To observe the effect of the third factor on the dissolution of chalcopyrite, first, the efficiency of copper, and iron was evaluated in a binary solution of ChCl, and PTSA with a molar ratio of 1:1. According to the dissolution result, the efficiency in ChCl:PTSA solvent for copper, and iron was 90.5%, and 69.1%, respectively. In addition, the leaching efficiencies for Cu, and Fe in three-component solvents are presented in Fig. 5a. Furthermore, the color changes of the solution after leaching for different DESs are shown in Fig. 5b. The highest efficiency of copper dissolution has been established in solvents ChCl:PTSA:EG, ChCl:PTSA:MOA, and ChCl:PTSA:MA with efficiency of 83.9, 89.0, and 90.4 %, respectively. In contrast, the lowest efficiency of copper dissolution is observed in the solvent containing oxalic acid with a rate of 2.6%. The interesting

point here is that the three-component combination based on choline, and toluene containing glucose, sucrose, and fructose could not result to proper efficiency for copper, and iron dissolution. Since iron is dissolved as an impurity in the chalcopyrite leaching process, a solvent with the lowest iron dissolution efficiency, and the highest copper efficiency at the same time will be a better option for leaching. Therefore, the ChCl:PTSA:MOA solvent was considered suitable for dissolving the copper concentrate.

## 4. Conclusions

The In this study, the dissolution of Sungun copper concentrate (chalcopyrite) in various three-component DESs was investigated. The dissolution efficiency of copper in different DES, including ChCl:PTSA, ChCl:PTSA:OA, ChCl:PTSA:EG, ChCl:PTSA:S, ChCl:PTSA:MOA, ChCl:PTSA:F, ChCl:PTSA:U, ChCl:PTSA:MA, ChCl:PTSA:CA, and ChCl:PTSA:G was found to be 90.5, 2.6, 83.9, 43.1, 89.0, 65.1%, 34.6, 90.4, 31.5, and 40.8%

respectively. Three DES solvents, including ChCl:PTSA:MOA, ChCl:PTSA:EG, and ChCl:PTSA:MA showed good efficiency for copper dissolution. While the dissolution of iron as an impurity is significant in the two solvents ChCl:PTSA:EG, and ChCl:PTSA:MA. Although it was expected that adding water to the DES would reduce leaching efficiency, in the case of DESs containing S, F, and G, adding a small amount of water was able to improve some physical, and chemical properties by providing a hydrogen bonding chain, and modifying the molecular structure of these solvents, while the leaching efficiencies for Cu, and Fe were low in the case of sugar-based DESs (ChCl:PTSA:S, ChCl:PTSA:F, and ChCl:PTSA:G). Therefore, the ChCl:PTSA:MOA with a leaching efficiency of 89.0% for Cu, and 41.9% for Fe was chosen as the suitable solvent for leaching the copper concentrate.

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