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RECOVERY OF COPPER FROM COMPLEX COPPER OXIDE ORE BY FLOTATION AND LEACHING METHODS

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Abstract. The objective of this study is to achieve economic-scale copper extraction from complex copper oxide ore obtained from mining site in Diyarbakir, Turkey through the application of flotation and leaching enrichment experiments. Prior to the flotation process, the ore crystal structure was modified by sulfidation. In this context, the effect of particle size, Na_2S, H_2S, and $Ca(OH)_2$ amount on the sulfidation process was investigated. The optimum recovery was achieved by processing 220 g of -100 mesh ore with $Ca(OH)_2$ at a solid-liquid ratio of 1:1, followed by sulfidation with 4.16 g of $H_2S(g)$. Under optimal flotation conditions using MIBC (Methyl Isobutyl Carbinol) (1%, 0.5 mL) as frother, Aerophine 3418A (1%, 12 mL) as collector, and $CuSO_4$ (5 mg/mL, 3 mL) as activator at pH 9, the newly-formed crystalline ore was enriched with copper to a yield of 81.9%. As a second method, the ore was leached with sulfuric acid for high copper extraction, and various parameters (acid concentration, time, temperature, solid/liquid ratio, HNO_3, H_2O_2, NaOH) were examined. Under optimal leaching conditions, 96% of the copper was successfully extracted into the solution (1.0 M H_2SO_4, time: 90 min, solid-liquid ratio: 1/1 g/mL, temperature: room temperature, NaOH: 1M).

Keywords: *Copper oxide ore, H_2S, flotation, leaching.*

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1. Introduction

Copper is an important metal used in many industrial areas such as electronics, construction, transportation, etc. Due to its unique properties such as high electrical conductivity, ductility, and corrosion resistance, the demand for copper is constantly increasing (Northey *et al.*, 2014; Zhang *et al.*, 2022). With the global economy consistently growing, there has been a substantial increase in the demand for copper, leading to a heightened necessity for copper production (Zhang *et al.*, 2015). Consequently, there has been a lot of interest in the extraction of copper from its natural resources as well as in the effective use of these resources. Copper sulfide and copper oxide are the two most common forms of copper ore. Copper recovery from low-grade oxide ores has become increasingly practical and desirable as a result of the decline of high-grade copper sulfide sources (Zhang *et al.*, 2022; Razavizadeh & Afshar, 2008). Copper oxide deposits are formed after the long-term oxidation of shallow copper sulfide deposits, and these deposits are widely distributed worldwide and are rich in reserves (Razavizadeh & Afshar, 2008; Feng *et al.*, 2022). Copper oxide ores often exhibit certain characteristics that can make their processing challenging, including high

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surface hydrophilicity, a high concentration ratio, small particle size, difficult mud-related problems, and a complex mineral composition (Gu *et al.*, 2019; Han *et al.*, 2017; Paquot & Ngulube, 2015). Therefore, it is difficult to effectively recover copper oxide sources using conventional techniques for separating copper sulfide ore (Feng *et al.*, 2022).

Flotation is one of the common methods used for the extraction of copper oxide minerals (Zhang *et al.*, 2022; Cao *et al.*, 2009). Flotation methods consist of two main approaches: direct flotation and sulfidization flotation (Zhang *et al.*, 2022). In direct flotation, collectors and frothing reagents are added directly to the mineral mixture, without using activating agents or depressants. However, this method is limited in its ability to selectively separate target minerals from non-target minerals, which makes it unsuitable for large-scale separation (Han *et al.*, 2021). Sulphidization, first developed for industrial applications on Pb-Zn oxide ores in Australia, is the standard method for the flotation of copper oxide (Crozier, 1992). The method involves using a sulfidization reagent before adding a collector to alter the surface properties of minerals. Through sulfidization, a copper-sulfide layer is produced on the hydrophilic copper-oxide mineral surface, leading to an improvement in its floatability. As a result, the mineral surface becomes hydrophobic and effectively solves the problem of insufficient selectivity exhibited by conventional collectors (Jia *et al.*, 2017; Jia *et al.*, 2018). There are many parameters that can affect the efficiency of sulfidization. These include the type and amount of sulfidizing reagent, the structure of the mineral surface, time, temperature, pH, stirring method, and speed (Feng *et al.*, 2022; Castro *et al.*, 1974a; 1974b).). In the sulfidization, Na_2S (Zhang *et al.*, 2022; Cao *et al.*, 2009; Park *et al.*, 2016) and NaHS (Kongolo *et al.*, 2003; Zhou & Chander, 1993) as sulfidizing reagents are widely used in the processing of low-grade copper oxide ores. The disadvantage of using these reagents is that the optimal dosage of them depends on various variables, leading to poor repeatability. Insufficient addition of the sulfidizing reagent results in low recoveries, while an excess can lead to the precipitation of copper oxide minerals (Han *et al.*, 2017). According to Ziyadanoğullar and his team, a successful sulfidization procedure was carried out by directly interacting H_2S gas with the ore in a closed system (Ziyadanogullari, 1992; Aydin *et al.*, 1998; Ziyadanoğullari *et al.*, 1999; Ziyadanogullari & Aydin, 2005; Ziyadanoğullari & Aydın, 2004; Dolak *et al.*, 2007; Teğin & Ziyadanoğullari, 2008; Tegin & Ziyadanoğulları, 2018; Dolak & Ziyadanoğullari, 2019; Aydın *et al.*, 2005; Dolak, 2021; Dolak & Keçili, 2023). The process involves a direct interaction between the solid ore and the H_2S gas produced in the autoclave by the reaction of FeS and H_2SO_4.

In recent years, the economic viability of hydrometallurgical methods for copper extraction has led to an increase in the scientific and engineering importance of direct leaching of copper oxide ores (Emmanuel *et al.*, 2019). This technique is advantageous due to its minimal energy consumption, uncomplicated hardware requirements, and compliance with the environment (Razavizadeh & Afshar, 2008). Typically, strong acids like H_2SO_4, HCl veya HNO_3 are used as lixiviant. However, when leaching gangue minerals containing silicon, silicic acid is formed which can further react to form three-dimensional poly-silicic acid, silica sol, and hydrogel through the condensation of SiOH molecules. This can create significant difficulties during the filtration process. Therefore, a more selective reagent is required for these ores (Han *et al.*, 2017).

In this study, sulphidization flotation and leaching methods were applied for the recovery of copper from complex copper oxide ore (paramelaconite) containing approximately 57% quartz gangue mineral. The method includes an innovative step whereby the complex ore is activated using saturated lime solution before the sulfidization with H_2S. In the second part of the study, the sulfuric acid leaching process was successfully applied and the results were examined in detail.

2. Materials and Methods

2.1. Sample preparation and used equipment

The complex copper oxide ore used in this study was obtained from a mining area in Diyarbakir, Turkey and has a wide distribution. Ore samples were crushed, ground and sieved (Table 1). Resulting in particles that had a size of -100 mesh. The copper content of the ore sample (%1.63±0.05) was measured using atomic absorption spectroscopy (AAS; Perkin Elmer 200), while other chemical components were determined by X-ray fluorescence spectroscopy (Table 2). The results show that the ore contains only 2.58% CuO and primarily consists of SiO_2, Al_2O_3, Fe_2O_3, Na_2O, CaO, and MgO. The crystal phase composition was analyzed by X-ray powder diffraction (XRD) method (Figure 1), revealing that the ore mainly contains quartz, paramelaconite (Cu_4O_3), magnesium copper oxide, and aluminum phosphate. In addition, a 1.3 L autoclave made of 2 cm thick steel, capable of withstanding 350 °C temperature and 250 atm pressure, was used for sulfidation processes. In a Carbolite Company tunnel furnace, raw pyrite was exposed to roasting procedures. Mettler Toledo pH meters were used for pH measurements, and purified water was produced by a Milipore Direct-Q pure water device.

Table 1. Sieve analysis of the ore

Particle size (mesh)	w.t. (%)
-100-150	18.5
-150-200	13.1
-200	68.4
Total	100

Table 2. Chemical analysis of copper oxide ore

Constituent	(%)
SiO_2	57.47
Al_2O_3	16.01
TiO_2	0.36
Fe_2O_3	9.32
CaO	1.58
MgO	4.73
K_2O	0.07
Na_2O	7.149
CuO	2.58
P_2O_5	0.12
MnO	0.4

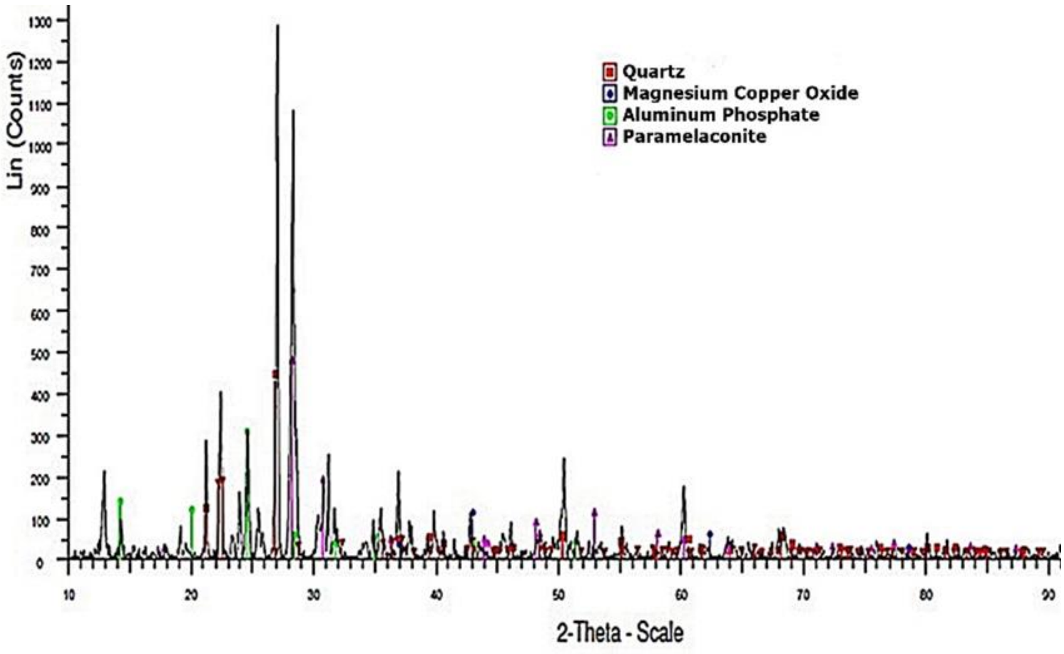

Fig. 1. X-ray diffraction patterns of copper oxide ore

2.2. Production method of H_2S

The general process for the production of $H_2S_{(g)}$ as sulfidizing reagent is as follows (Canpolat, 2017): A raw sample of pyrite (Fe_2S) sourced from Küre Copper Plant was initially processed via roasting for two hours at 725°C in a closed system. This resulted in the following reaction (1);

$$FeS_2 \rightarrow FeS + S \tag{1}$$

In order to sulfurize the ore sample, an autoclave shown in Figure 2 was used. Initially, treated pyrite and a beaker containing 6M H_2SO_4 that had been frozen using liquid nitrogen was placed into the autoclave. Subsequently, 220 g of copper oxide ore that had been wrapped in filter paper was positioned atop the beaker, taking care not to fall into it. The autoclave was then rapidly closed. As a result of this process, $H_2S_{(g)}$ was produced by the following reaction (2):

$$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S(g) \tag{2}$$

The sulfidization process were conducted for a total of 2 hours, with the first hour carried out at 100 °C, and the second hour at 150 °C. Following the completion of the sulfidization process, the samples were subjected to a flotation.

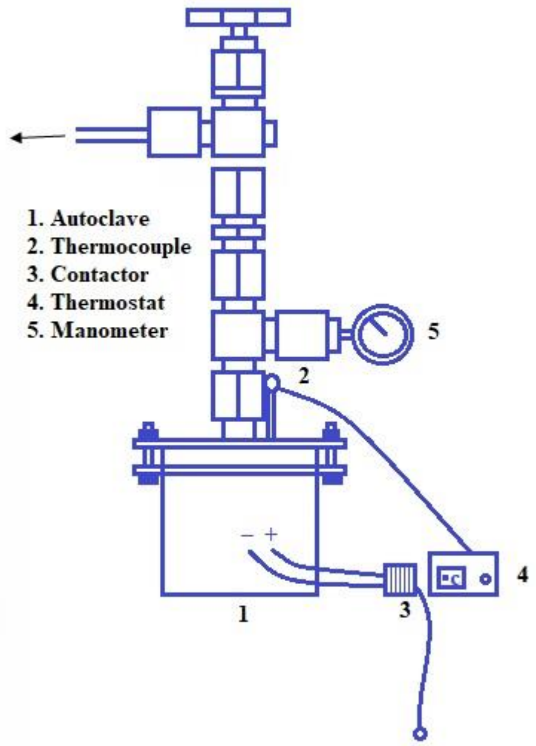

Fig. 2. Autoclave used for sulfidization process

2.3. Flotation process

The Denver flotation device was used to conduct copper oxide ore flotation experiments under constant conditions (as shown in Table 3) such as a 10% solid-liquid ratio, a stirring speed of 900 rpm, and a pH value of 9. During the flotation experiments, lime was utilized to adjust the pH level, $CuSO_4$ was used as an activator, Aerophine 3418A acted as a collector, and Methyl Isobutyl Carbinol (MIBC) served as a foaming agent. Aerophine 3418A is a sulfide mineral collector based on P-type sodium isobutyl dithiophosphine, with its chemical composition illustrated in Figure 3.

Following the flotation process, the concentrated (floated) and the non-floated tailing phases were filtered separately and subsequently dried at a temperature of 120ºC. After cooling in a desiccator, 0.50 grams of each sample were dissolved using a mixture of HNO_3 and HCI. The solutions were then diluted and prepared for AAS analysis.

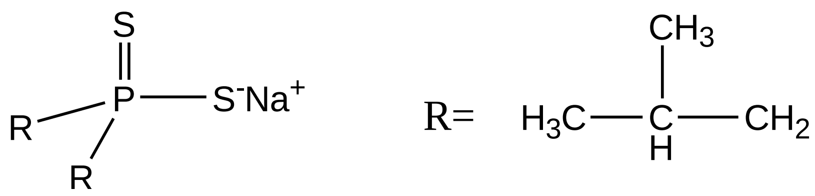

Fig. 3. Chemical structure of Aerophine 3418A

Table 3. Conditions of flotation

Amount of ore	: 100 g
Particle size (mesh)	: -100 mesh
Solid-liquid ratio	: 100 g/L
pH	: 9.0 (CaO)
Activator	: 3 mL $CuSO_4$ (5 mg/mL) mixing for 10 min.
Collector	: 12 mL 3418A(% 1'lik) mixing for 3 min.
Frother	: 0.5 mL MIBK (%1'lik) mixing for 2 min.
Stirring speed	: 900 rpm

3. Results and Discussion

3.1. Sulfidization flotation technique

The study initially focused on direct flotation of oxidized copper ore, but flotation yielded adverse outcomes. Aydın et al. (Aydın *et al.*, 2005) observed a similar result in the direct flotation of asphaltite ash, the primary components of which are quartz, calcite, gypsum, and metal oxide. Therefore, it has been suggested to utilize surface activation techniques using Na_2S and H_2S as sulfurizing chemicals.

3.1.2. Sulfidization with Na_2S

In this experiment, three different doses of $Na_2S.xH_2O$ solutions 5g/200 mL, 7.5g/200 mL, and 10g/200 mL were used to react a 100 g ore sample overnight at 50°C. Optimum flotation conditions were then employed to float the sulfurized samples. The floated and tailing samples were analyzed to determine the copper content, and these findings are presented in Figure 4. The obtained data confirmed that the use of Na_2S does not provide sufficient effect on the flotation performance of the ore and that the increase in the amount of Na_2S reduces the floatability. These results suggest that Na_2S is inappropriate for the sulfidization process and that alternative chemicals are necessary. Therefore, a sulfidization based on H_2S was carried out.

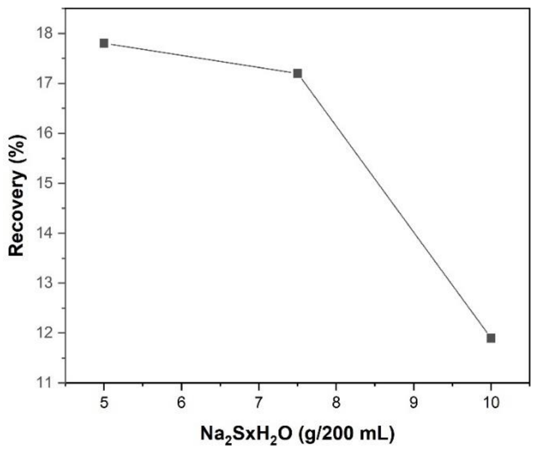

Fig. 4. Effect of Na_2S as sulfurizing chemical

3.1.3. Sulfidization with H_2S

In order to determine the effect of H_2S amount on flotation, 220 g of oxidized copper ore was treated with 2.08 g of H_2S in autoclave. Also, the same process was repeated for 3.12 g, 3.64 g, 4.16 g, 4.68 g, and 5.2 g of H_2S. Study results are summarized in Figure 5.

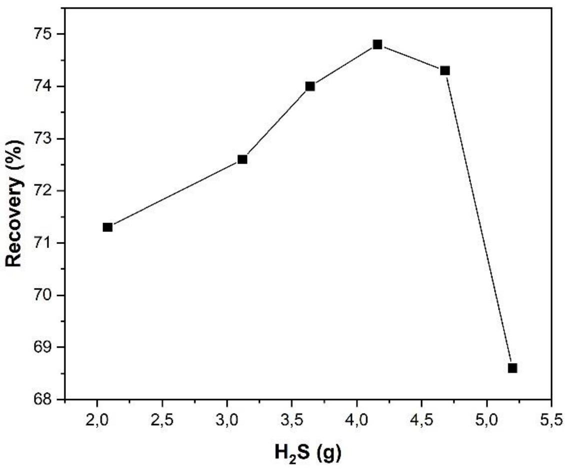

Fig. 5. Effect of amount H_2S

The results indicate that the floatability efficacy increases as the amount of H_2S used increases but decreases after 4.16 g. It has been observed that the use of 4.16 g H_2S gives optimum results and provides the highest concentrated copper with 74.8% recovery.

3.1.4. Effect of particle size on sulfidization flotation

In order to investigate the effect of particle size on flotation efficiency, 220 grams of ores with -100, -120, -150 and -200 mesh sizes were sulfured using 4.16 grams of H_2S. The test results obtained by working the sulphurized sample under optimum flotation conditions are shown in Figure 6.

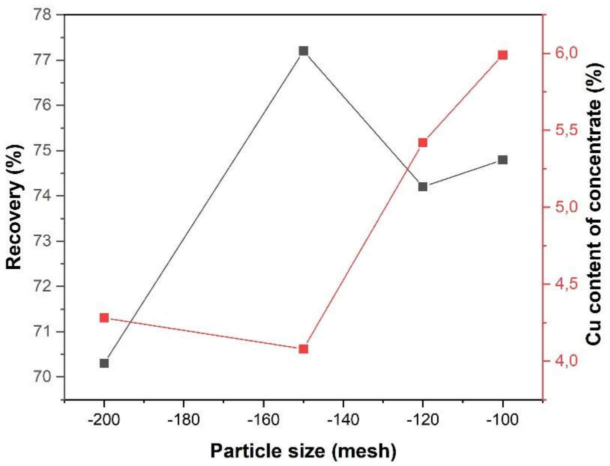

Fig. 6. Effect of particle size

The results show that although the flotation efficiency is higher for the sample with -150 mesh particle size compared to the others, the copper content of the concentrated sample is significantly reduced. Therefore, we concluded that the sample with a particle size of -100 mesh had the best copper recovery.

3.1.5. Effect of $Ca(OH)_2$ on sulfidization flotation

To examine the impact of lime, the copper oxide ore was treated with a lime solution that was saturated in a 1:1 ratio at room temperature prior to the sulfidation process. A series of studies were carried out by adding 0, 0.5, 1.0, and 2.0 grams of lime, respectively, to raise the basicity of the medium. After filtering and washing the resultant slurry mixture until the pH level reached 8, it was dried at 120 °C. The ore that underwent sulfidation under the most optimal conditions was subsequently utilized in the flotation process, and the data acquired from the experiments are shown in Figure 7.

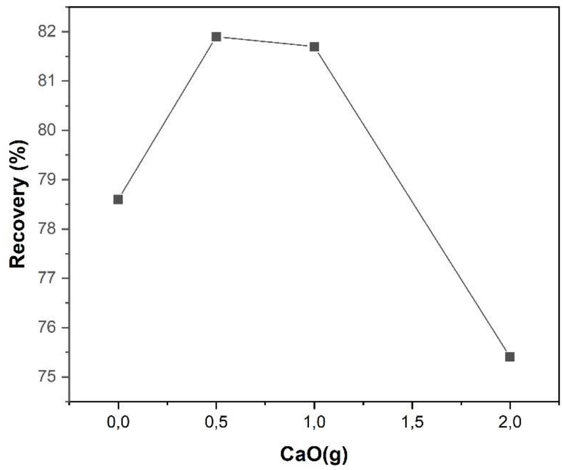

Fig. 7. Effect of $Ca(OH)_2$

The results show that treatment with saturated lime solution has a significant effect on the efficiency of the sulfidization process, and with the addition of 0.1 g of CaO, the yield reached 81.9%. However, the addition of an excessive amount of CaO negatively affected the flotation efficiency.

3.2. Leaching technique

The second part of the research focused on exploring the use of H_2SO_4 leaching as an alternative method to sulfidization flotation for copper ore processing. Various factors, such as acid concentration (ranging from 0.5 M to 2.5 M), leaching time (ranging from 30 min to 120 min), leaching temperature (ranging from 23°C to 50°C), and solid-to-liquid ratio (ranging from 1:1 to 1:1.75 g/mL), were investigated to determine their effects. Additionally, the study assessed the impact of other chemicals, such as HNO_3, H_2O_2, and NaOH. The leaching experiments were carried out using a 100-mL glass beaker on a magnetically stirred hot plate that was temperature-controlled and set to 500 rpm.

3.2.1. Effect of acid concentration

Various acid concentrations (0.50M, 1.0M, 2.0M, and 2.50M H_2SO_4) were used in the experiment to assess the impact of acid concentration on copper recovery. The experiment was performed at a temperature of 23°C, with a particle size of -100 mesh, a solid-to-liquid ratio of 5.0 g:5.0 mL, and a leaching time of 120 minutes. The recovery of copper was found to be strongly influenced by the concentration of acid used in the leaching process. It was observed that an increase in acid concentration led to a corresponding increase in leaching recovery (%), as illustrated in Figure 8(a). This trend had been previously observed in a study that employed sulfuric acid media (Sahu *et al.*, 2012). The copper recovery rate was increased to 86.5% with an acidity level of 1.0 M. Although the highest copper recovery was achieved at a concentration of 2.5M H_2SO_4, extraction recovery beyond 1.0 M sulfuric acid concentrations was only slightly increased. Due to the fact that higher acid concentrations resulted in greater acid consumption, the optimal value for minimizing acid usage was determined to be the lower concentration of 1.0 M, rather than 2.5 M.

3.2.2. Effect of leaching time

The effect of leaching time was studied under the conditions that H_2SO_4 concentration was 1.0 M, leaching temperature was 23 ˚C, ore particle size was -100 mesh and the ratio of solid to liquid was 1:1. The results are shown in Figure 8 (b). When the leaching time increased from 90 to 120 minutes, copper extraction (%) increased from 86.1% to 87.1%. It was seen that copper extraction (%) was not affected much by increasing the leaching time after 90 min.

3.2.3. Effect of leaching temperature

In this experiment, the effect of temperature on copper leaching efficiency was investigated over a temperature range of 23 to 50 °C. The experiment was conducted under the following conditions: a solid-to-liquid ratio of 1:1, a particle size of -100 mesh, a leaching time of 90 minutes, and a concentration of 1.0 M H_2SO_4. The results, as depicted in Figure 8(c), indicate that copper recovery (%) was not influenced by increasing the temperature, as the rate of recovery remained almost constant. Similarly, according to the research results of Özlem & Çakir, (2019) the leaching temperature has no effect on the percentage of zinc extracted from zinc oxide using sulfuric acid. Based on experimental results the leaching temperature of 23 °C was chosen as the most suitable leaching temperature.

3.2.4. Effect of solid/liquid ratio

In order to study the effect of the solid-to-liquid ratio (w/v) on the leaching process, the ratio was varied from 1/1 to 1/1.75 under optimum conditions. The effect of the solid-to-liquid ratio on copper extraction is given in Figure 8(d). When the ratio increased from 1:1 to 1:1.75, copper extraction (%) increased from 86.8% to 89.0%. It was seen that copper extraction (%) was not affected much by increasing the solid/liquid ratio. Hence, in this case, the 1:1 ratio was taken as the optimal solid-to-liquid ratio for optimal copper recovery.

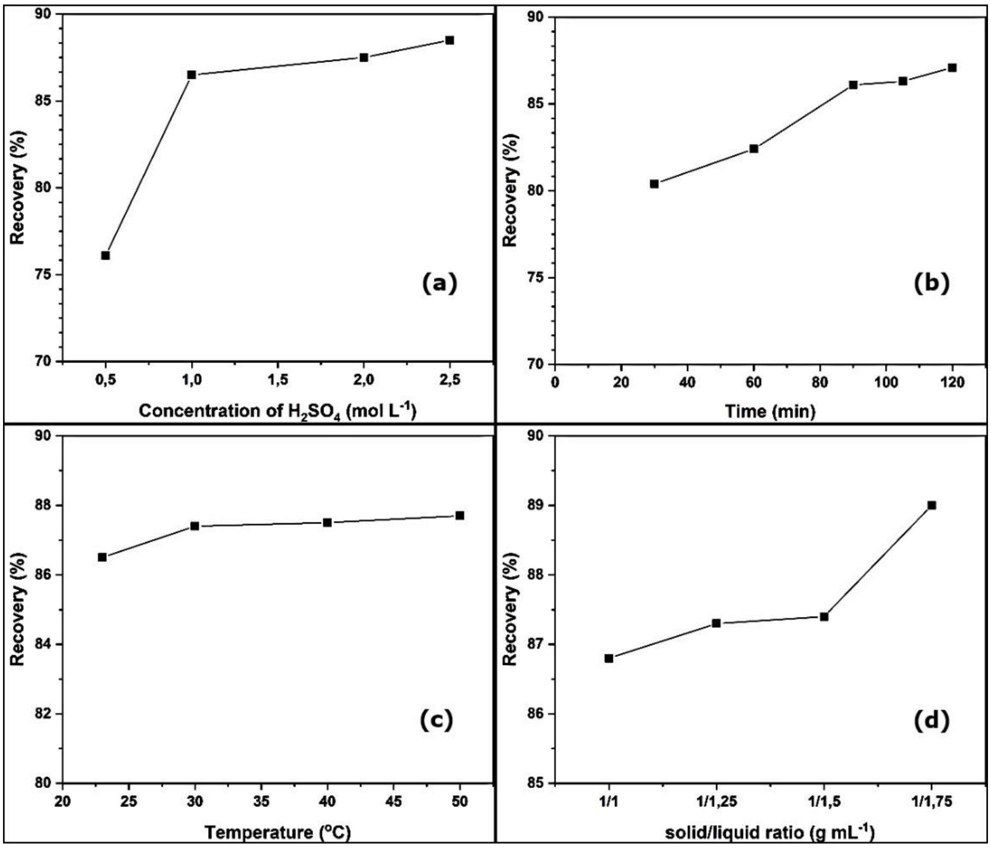

Figure 8. Copper leaching in different conditions; (a) effect of acid concentration, (b) effect of time, (c) effect of temperature, (d) effect of solid/liquid ratio

3.2.5. Effect of HNO_3 and H_2O_2 as oxidants

The purpose of this study was to examine the effect of using HNO_3 and H_2O_2 separately as oxidants to improve sulfuric acid leaching. To conduct the experiment, 5.0 g of ore was mixed with 5.0 mL of a solution containing 1.0 M H_2SO_4 and various concentrations (0.2-0.5 M) of the oxidizing reagent for 90 minutes at room temperature. The leaching efficiency data obtained from the experiments is shown in Figure 9.

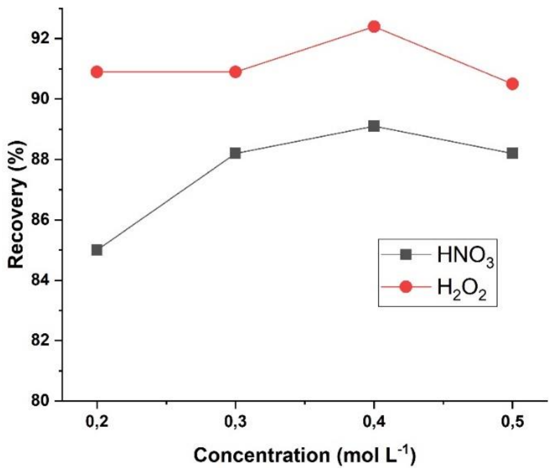

Fig. 9. Effect of HNO_3 and H_2O_2 as oxidants

Based on the results, it was found that the combination of HNO_3 and H_2O_2 at a concentration of 0.4 M with 1.0 M H_2SO_4 provided the highest leaching recovery, with values of 89.1% and 92.4%, respectively.

3.2.6. Effect of NaOH

The complex copper oxide ore studied in this study has a high concentration of gangue minerals, specifically SiO_2 and Al_2O_3, with referring content ratios of 57% and 16% (Table 2). Sodium hydroxide can be used to selectively target these gangue material. This results in the formation of soluble sodium silicate and aluminate (reaction (3) and (4)), while minimizing the dissolution of metal oxides (Sarkar, 2011).

$$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O \quad (3)$$

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_2 + 2H_2O \quad (4)$$

The leaching of copper oxide trapped in silica lattice units was investigated at three distinct NaOH concentrations: 0.2, 0.5, and 1.0 M. The resulting samples were then subjected to leaching with a 1.0M H_2SO_4 solution at a 1:1 solids-to-liquids ratio for 90 minutes at room temperature. The experimental findings obtained from these procedures are presented in the Figure 10.

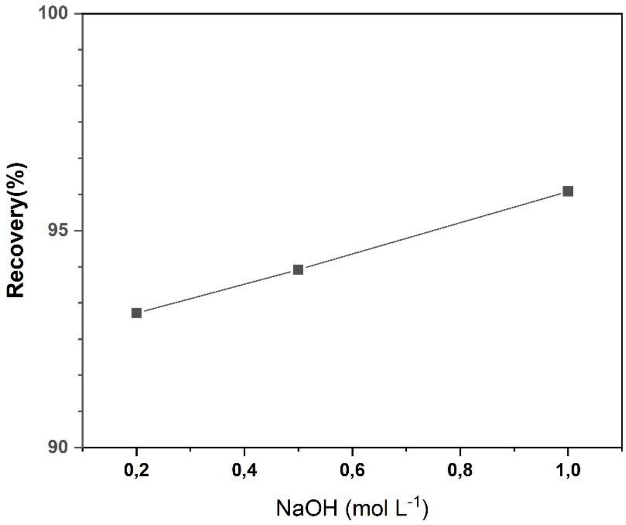

Fig. 10. Effect of NaOH on leaching

The experimental results indicated that the use of NaOH solution was effective in extracting the trapped copper from the silica structure. In particular, it was found that 1.0 M NaOH achieved a remarkable copper recovery rate of 96%.

5. Conclusions

In this study, it was aimed to concentrate low copper from copper oxide ore by flotation and leaching processes. Direct flotation applications could not, however, concentrate the copper in the ore because of its presence in various mineralogical structures. For this reason, the sulfurization flotation method was applied. The sulfurization process was carried out with two different methods: the process with Na_2S available in the literature and the sulfurization process with H_2S, which was applied in our previous studies, using a closed system. Although sulfuring with Na_2S is suitable for azurite, malachite, and similar copper-oxide ores, it has not been successful in complex copper-containing ores. For this reason, sulfurization with H_2S was carried out in an autoclave.

With this method, the copper recovery was increased up to 74%, and the copper ratio in the obtained copper concentrate was increased 3.5 times. In addition, as one of the novelties of the study, the sulphurization process after the interaction of the ore with saturated lime increased the flotation efficiency up to 81.9%.

In the second stage of the study, H_2SO_4 leaching studies were carried out. Under optimum conditions (0.1M H_2SO_4, 90 min, 1:1 solid-liquid ratio, room temperature), copper was recovered with an efficiency of 86.5%. The synergistic effects of oxidants such as HNO_3 and H_2O_2 were also investigated, and it was determined that the leaching efficiency of the 0.1M H_2SO_4+0.4M H_2O_2 mixture increased to 92.4%. Based on the results obtained, it is advisable to assess the feasibility of utilizing HNO_3 and H_2O_2 as oxidizing agents in terms of their cost-effectiveness, as they have been found to significantly enhance leaching efficiency. Additionally, due to the mineral structure's high silica content, a pre-treatment step involving NaOH was employed to facilitate the liberation of copper in the ore. This process yielded a remarkable leaching efficiency of approximately 96%.

The results of this study present a promising alternative technique for achieving efficient copper production from complex copper oxide ores. The findings furnish valuable insights that could be employed in industrial applications and serve as a guide for those looking innovative solutions for the mining industry.

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