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Modified Hydrometallurgical Approach for the Beneficiation of Copper from Its Low-Grade Ore

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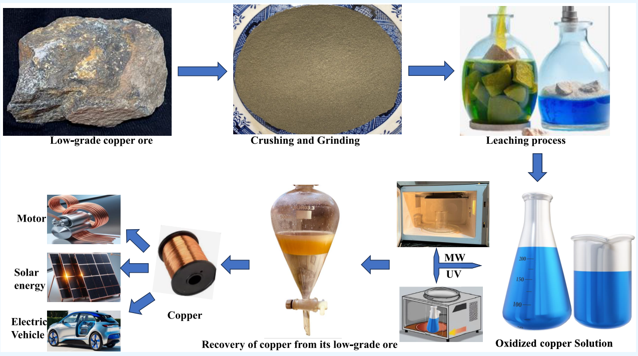
ABSTRACT: This study describes a novel hydrometallurgical approach for efficient copper recovery from low-grade ores. Improvement in the copper extraction efficiency was explored by employing blends of acids (sulfuric acid and nitric acid) and an oxidizing agent along with exposure to microwave and ultraviolet radiation. Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX), X-ray diffraction (XRD), and optical microscopy (OM) were used to characterize the ores' elemental composition, morphology, and mineralogy, revealing the presence of wroewolfeite, chalcopyrite, and other mineral phases. Thermogravimetric analysis (TGA) investigated the thermal stability of the ore samples. Under optimal leaching conditions (liquid−solid ratio of 15:1 mL g^{-1}, copper ore particle size of 55−65 μm, and stirring for 30 min at 300 rpm), the method demonstrated an outstanding copper leaching efficiency of 96.8%. Solvent extraction was performed efficiently with the pregnant leach solution, further enhancing copper extraction to 97.9% within less than a minute of loading time. These results underscore the effectiveness of the modified hydrometallurgical approach for extracting copper from low-grade ores and hint at its potential for extracting other metals. Such versatility of this approach makes a significant contribution to the field of hydrometallurgy.



1. INTRODUCTION

Copper holds enormous significance in achieving sustainable development, as it is essential for numerous industries like housing, transportation, electrification, and appliances and serves as a fundamental element for global economic growth and the betterment of mankind.[1] Solar energy, known as photovoltaics, requires 11−40 times more copper per unit of electricity produced than traditionally deployed power generation methods, mainly from fossil fuels.[2] Thus, switching toward solar energy will result in a substantial demand for copper not only in PV solar cells but also its broader applications in solar energy systems. The final global copper demand is expected to rise from 24.3 Mt recorded in 2015 to 44.4 Mt in 2050.[3] As the demand for copper continues to increase, the world is facing a decline in reserves of high-quality copper ores.[4] This dilemma has dramatically stressed on the development of innovative approaches for efficiently extracting copper from its low-grade ore deposits.[5]

Currently, copper extraction from its ores is achieved through various techniques such as bioleaching, gravity separation, flotation, pyrometallurgy, solvometallurgy, and hydrometallurgy.[6] Undoubtedly, bioleaching, gravity separation, and flotation are useful mineral processing techniques, but they are often not as widely used as pyrometallurgy, solvometallurgy, and hydrometallurgy due to several reasons in terms of complex processes requiring precise monitoring of various factors like temperature, pH, and reagent concentrations.[7] Consequently, these approaches result in longer processing times and higher operational costs contrasting well-established methods such as pyrometallurgy, solvometallurgy, and hydrometallurgy. Pyrometallurgy is considered a predominant technique, especially for beneficiating copper from chalcopyrite-bearing ores.[8] However, it is only economically feasible for chalcopyrite ores with a high copper content and requires elevated temperatures, which makes it energy-intensive. Additionally, the release of SO_2 during pyrometallurgical beneficiation of copper can cause serious environmental concerns.[9] At the same time, solvometallurgy uses organic solvents either entirely or partially and has proven to be effective for extracting (solvoleaching) and recovering metals (nonaqueous solvent extraction and nonaqueous electrodeposition).[10] However, this technique necessitates the use of expensive and volatile organic solvents that are challenging to handle, and the reaction process must be conducted in an

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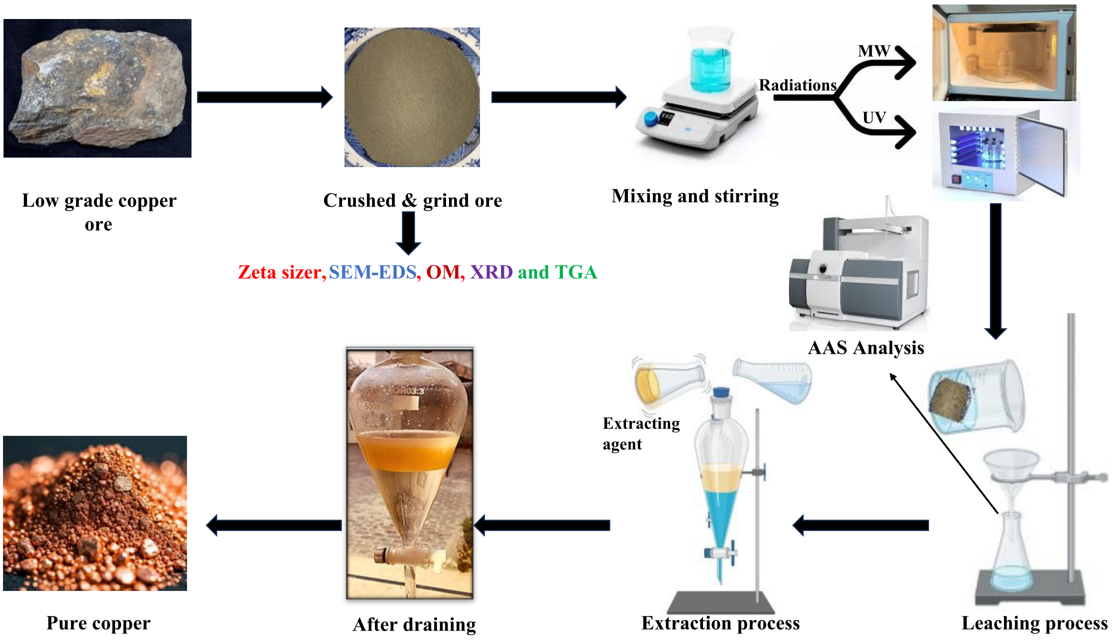

Figure 1. Schematic of the modified hydrometallurgical approach for copper leaching from its low-grade ore and its recovery through solvent extraction.

enclosed chamber to avoid hazardous vapors.[11] Contrasting with the above-mentioned copper beneficiation approaches, hydrometallurgical methods are highly valued for their instant construction, affordable price, simple operation, excellent efficacy, and positive environmental impact.[12] Hydrometallurgical approaches involve leaching of desired metals from their ores by utilizing different chemicals termed lixiviants (primarily inorganic) and then recovering the leached metals from the mother solutions.[13] Noteworthily, the success of a leaching process for a specific metal extraction is significantly controlled by several factors, including ore characteristics (i.e., mineral composition, chemical properties, type, particle size, and source of ore), lixiviant properties (concentration and nature of leaching agent), and other experimental parameters such as stirring time and speed and liquid-to-solid (L/S) ratio.[14] Among these experimental parameters, the nature and concentration of lixiviant is recognized as the dominating parameter as it significantly impacts the leaching process efficiency.[15] To this end, the use of mixed inorganic acids is widespread; however, adding an oxidizing agent such as H_2O_2 could further enhance the overall leaching efficiency for the successful beneficiation of a specific metal.[16]

A study was carried out to leach different forms of low-grade copper ore in sulfuric acid and recovered a maximum of 93% from its leached solution through solvent extraction.[14c] Another group of researchers deployed HCl solution as a lixiviant for the leaching of copper. It deployed a commercial solvent extractant (SX) called CYANEX 921 in kerosene and obtained significant copper recoveries (69−87%).[17] In another study, mixed sulfate/chloride leach using tributyl phosphate (TBP) as a leaching agent and LIX 841 and CYANEX 923 in kerosene as extractants were also deployed for the beneficiation of copper(II) from printed circuit boards (PCB).[18]

Interestingly, metal extraction efficiencies could be enhanced significantly when sample solutions were exposed to microwave (MW) radiation.[19] It is important to mention that microwave-sensitive materials on exposure to MW radiation undergo internal heating, creating thermal stress and cracks between different components, leading to dissociation of minerals into their monomeric forms.[20]

Recently, photoleaching of sulfide minerals and copper concentrates using ultraviolet−visible (UV−vis) radiation has been published and has opened new avenues in hydrometallurgical processes for treating low-grade ores.[21] This process helps break down difficult-to-dissolve minerals, like chalcopyrite, using sunlight instead of conventional methods like acid leaching, chemicals, and microorganisms. Photoleaching uses UV and visible light from the sun to trigger chemical reactions that create highly reactive moieties, including free radicals, which can assist in the mineral's dissolution. Furthermore, this approach can reduce the energy costs compared to other leaching techniques.[21,22] Owing to the above-mentioned reasons, the deployment of MW and ultraviolet (UV) radiation has become a popular and cost-effective approach in recent years in the mineral processing industry.[23] Previous research studies mainly focused on leaching of copper from high-grade ores, especially copper sulfide ores, and appreciable extraction efficiencies were achieved. To date, no study has been conducted to explore the potential of blends of acids and oxidizing agents, along with the assistance of MW and UV radiation, to extract copper from low-grade ores and achieve maximum extraction efficiencies.

This study addresses this gap by investigating a novel hydrometallurgical route assisted by MW and UV radiation for extracting copper from low-grade ores. We hypothesize that this combined approach can achieve superior extraction efficiencies compared to conventional methods. The optimized process will be established through the evaluation of various experimental parameters, including the ore and leaching characteristics. Figure 1 provides a schematic illustration depicting the copper leaching process.

2. EXPERIMENTAL SECTION

2.1. Chemicals. Following standard sampling protocols, copper ore samples were obtained from Khawazakhela, Swat, Khyber Pakhtunkhwa, Pakistan. The collected samples underwent a meticulous cleaning process. Subsequently, they were crushed using a jaw crusher and ground in a ball mill. Finally, the crushed and ground material was pulverized into a fine powder using a steel mortar and pestle. To achieve a consistent particle size distribution, 200 g of the powdered copper sample was sieved through a series of five mechanical sieves with mesh numbers 100 to 325, conforming to American National Standards.[24] Table 1 illustrates details of the obtained particle size fractions and their corresponding weights. Approximately 73% of the sieved material corresponds to the particle size range less than 132 μm, and the remaining sample did not pass-through the sieve due to the large particle size. High-purity chemicals, including 98% H_2SO_4, 30% H_2O_2, 68% HNO_3, and ≥97.0% NaOH, were utilized throughout the experimental work. All of the aforementioned chemicals were procured from Sigma-Aldrich. The extractant ACORGA M5640 was purchased from Haihang Industry Sanqing Fengrun, Jinan City, Shandong Province, China. Deionized water was utilized to prepare stock solutions and further dilutions.

Table 1. Particle Size Sieve Analysis of Low-Grade Copper Ore

#	particle size (μm) (±7 μm)	weight (%)
1	<55	1.61
2	55−65	42.14
3	65−75	13.72
4	75−96	16.21
5	>132	26.32

2.2. Characterization Techniques. Various analytical techniques were employed to characterize the copper ore samples and monitor the leaching process. An atomic absorption spectrophotometer (AAS, Aurora Biomed ICR8000) was employed to quantify copper in leached and spent lixiviant solution using a hollow cathode lamp as an excitation source and a fuel-air ratio of 2:10 L min^{-1}. Morphological and elemental details of the low-grade copper ore were obtained using a scanning electron microscope equipped with an energy-dispersive X-ray (EDX) spectrometer (Zeiss EVO LS10, Germany). Standard laboratory equipment facilitated the experiments, including an analytical balance for precise weight measurements (Aczet CX 320, USA) and a hot plate with a magnetic stirrer (CJJ78-1, Pakistan) for controlled heating and mixing. Adhering to American standards, sieve analysis was done to separate the copper ore samples into different particle size fractions. The mineralogical composition of the ore was investigated using an optical microscope (AmScope digital, LED-1444A) for initial observations, and an X-ray diffractometer (Bruker D8) was used for more precise identification and quantification of mineral phases. X-ray diffraction (XRD) scan was performed at 2θ from 4 to 80°, with Cu kα radiation. The thermal behavior of the copper ore was explored using a thermogravimetric analyzer (Linseis PT-1600 simultaneous thermal analyzer). Finally, microwave and ultraviolet radiation treatments were administered using a Dawlance microwave oven (DW 180G, Korea) with a power source of 220 V-50 Hz. Additionally, a B1450 UV Clave chamber with an intensity of +500 μW cm^{-2} (at the center of the chamber) was utilized for UV radiation. The steps performed during the current investigation are given in Figure S1.

2.3. Leaching Process. The copper leaching process commenced after analyzing the copper ore samples. To achieve optimal extraction efficiency, various particle size fractions (Table 1) were tested. The particle sizes obtained from the sieve analyzer were verified using a Zetasizer ZS90 (Malvern Instruments, U.K.), confirming that the selected particle size was accurate, as given in Figure S2. A fresh lixiviant mixture was prepared by combining 5 mL each of 30% hydrogen peroxide solution, 0.25 M sulfuric acid, and 0.25 M nitric acid. Experiments were conducted using different solid-to-liquid (L/S) ratios to determine the most effective leaching conditions. The optimal conditions were identified as follows: 1 g of copper ore powder leached in 15 mL of lixiviant at 40 °C for

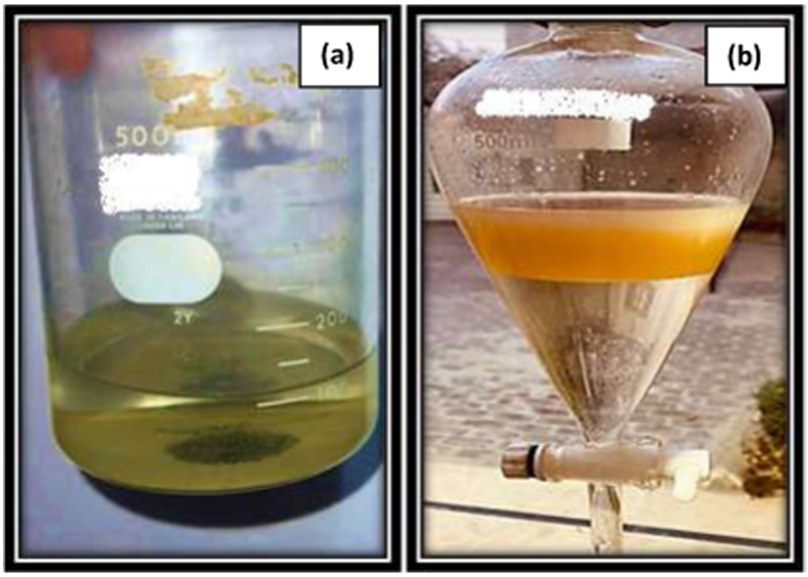

Figure 2. (a) Pre- and (b) post-extraction of copper from its low-grade ore.

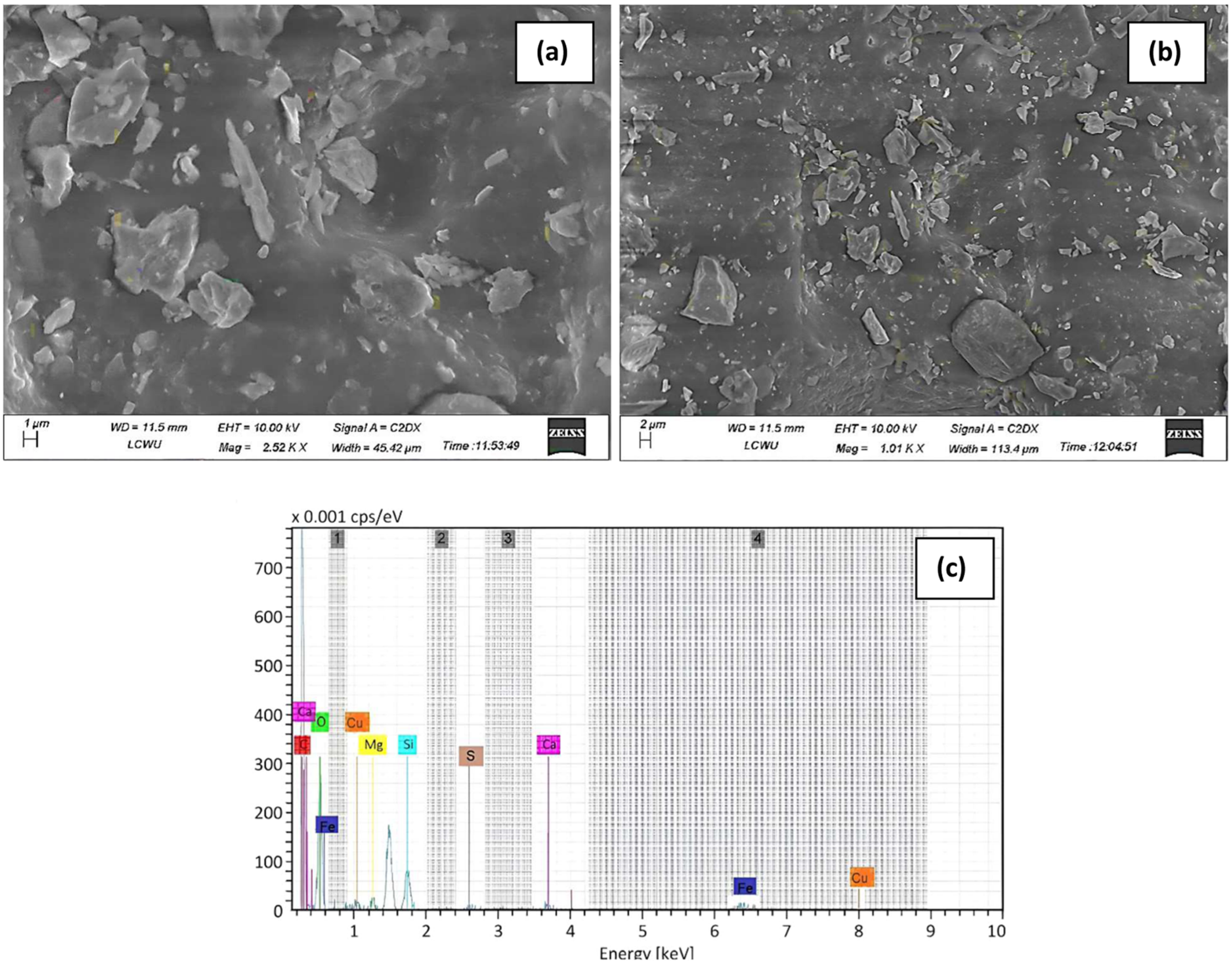

Figure 3. SEM images of the low-grade copper ore sample at two different magnifications (a) and (b). EDX analysis of the low-grade copper ore (c).

30 min by using a magnetic hot plate, achieving most significant copper oxidation.[14c,25] Following the leaching step, filtration was done to separate the green-colored filtrate (mother liquor) from the solids. Finally, this filtrate was irradiated in a microwave oven and a UV chamber for 1.5 min.[26] It is pertinent to mention that UV irradiation of leached solution was executed in a quartz vessel to ensure effective UV transmission to the leached solution.

2.4. Extraction Process. Copper extraction was conducted using a 250 mL separating funnel following the leaching process. An organic solvent extractant (SX) called ACORGA M5640 OPT series, prediluted at a 1:10 ratio with *n*-decane, was used for this step.[27] To thoroughly evaluate the effectiveness of the SX in selectively capturing copper, a 400 mL pregnant leach solution (PLS) containing a known amount of copper was prepared under optimal leaching conditions. The pH of PLS was adjusted to the desired level for efficient SX operation using dilute solutions of NaOH and H_2SO_4.

Approximately 20 mL of prediluted SX was added to 100 mL of PLS within the separating funnel. The mixture was then shaken for 10 min to maximize copper extraction. After shaking, the mixture settled into two distinct layers, as shown in Figure 2, an upper dark organic phase containing the extracted copper and a lower aqueous phase. The aqueous phase was cautiously taken out in a beaker by gradually opening the tap of the separating funnel and observing the drop-by-drop extraction, leaving behind the copper-loaded organic phase.

The copper concentration in the spent lixiviant (aqueous phase) was then determined using atomic absorption spectroscopy (AAS). This procedure was repeated with the remaining 300 mL of PLS. The final clear aqueous solution was collected, and its copper content was again measured using AAS. The efficiency and selectivity were determined by comparing the initial and final copper concentrations in the PLS, providing essential insights into the process efficacy.

3. RESULTS AND DISCUSSION

3.1. SEM-EDX Analysis. A low-grade copper ore sample (with a particle size fraction of 55−65 μm) was examined using SEM-EDX to investigate the surface structure and elemental composition. The SEM images in Figure 3(a,b) display the uneven distribution of irregularly shaped copper ore particles. The particle size was measured using software (ImageJ 1.52v/java 1.8.0_112 64 bit) and found to be within the range of 55−65 μm. The EDX spectrum of the copper ore sample in the chosen area shows the elemental composition, as illustrated in

Figure 3c. Additionally, Table 2 displays the semiquantitative data of the chemical components present in the copper ore sample.

Table 2. Semiquantitative Analysis of the Low-Grade Copper Ore Sample

element	at. no.	mass [%]	mass norm [%]	atom [%]	rel. error [%] (1 σ)
sulfur	16	4.46	4.46	3.97	15.45
oxygen	8	44.24	44.24	57.89	19.79
silicon	14	13.73	13.73	12.85	6.62
copper	29	2.08	2.08	0.72	11.52
calcium	20	15.86	15.86	9.50	13.99
magnesium	12	2.62	2.62	2.17	12.86
iron	26	13.78	13.78	7.31	12.34
manganese	25	3.23	3.23	0.98	7.67

3.2. Optical Microscopy Analysis. Optical microscopy investigation of low-grade copper ore samples, revealed the presence of copper in the form of sulfide mineral phases, including chalcopyrite and wroewolfeite, and iron sulfide minerals. Quartz, calcite, chlorite, and amphibole are the main gangue minerals contained in the copper ore sample. Figure 4 illustrates that the chalcopyrite and iron sulfide minerals exist in gangue minerals as disseminations, stringers, brecciated, and fracture-filled forms. Subsequent XRD analysis corroborated the presence of both gangue and copper-bearing mineral phases.

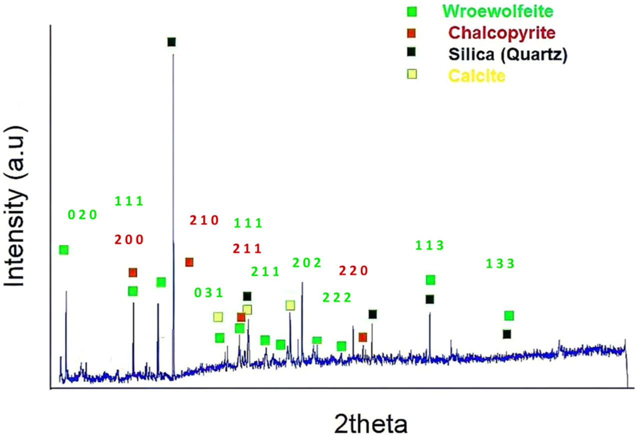

Figure 5. XRD pattern of the low-grade copper ore sample.

3.3. XRD Analysis. The X-ray diffraction pattern (XRD) of the low-grade copper ore sample (Figure 5) confirms the presence of wroewolfeite (CODB no. 9000979) and chalcopyrite (CODB no. 2104753) as the dominant copper-bearing mineral phases. The XRD graph suggests that the low-grade copper ore sample contains copper-bearing minerals such as wroewolfeite and chalcopyrite with obscured signals due to their low concentrations. The presence of wroewolfeite is indicated by peaks at 2θ angles of 16, 23, 26, 29, 34, 35, 38, 49, 52, 56, and 62°, while the peaks around 30, 50, and 58°confirm the presence of copper in chalcopyrite. The XRD graph also indicates the prominent peaks for gangue minerals like quartz and calcite.

3.4. Thermogravimetric Analysis. Thermogravimeteric analysis (TGA) of a copper low-grade ore sample was executed in the air atmosphere with a heating rate of 5 °C min^{-1}. The TGA curve (Figures 6 and S3) for the low-grade copper samples shows three decomposition stages; The thermal decomposition copper ore occurs in three stages. The first stage involves the evaporation of a small amount of water molecules between 27.9 and 167 °C.[28] The second stage involves the reactions at lower temperatures (167.2–526 °C), leading to the formation of copper sulfide, iron sulfide, sulfates, and copper oxysulfate, depending on the heating rate.[29] The third stage consists of the dissociation of iron sulfate and copper oxysulfate at higher temperatures (526–924 °C). These changes occurred primarily due to the direct oxidation of Cu_2S/CuS and FeS, which were formed after the decomposition of chalcopyrite. Furthermore, the oxidation process resulted in the production of $CuSO_4$, iron sulfate, and their relevant oxides. Different chemical reactions occurring during the oxidation and sulfonation steps can be described as follows:[14c]

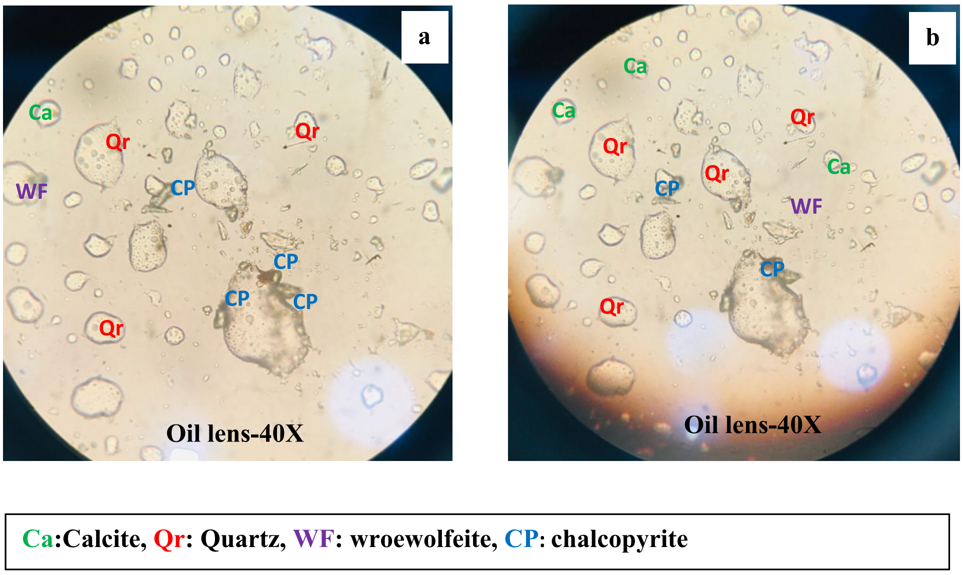

Figure 4. Optical microscopy analysis of low-grade copper ore (a, b).

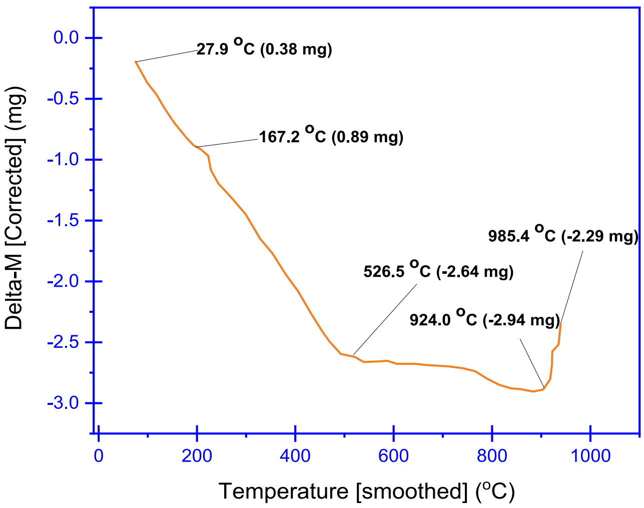

Figure 6. Thermogravimetric analysis of the low-grade copper ore.

$$2CuFeS_2 + O_2(g) \rightarrow Cu_2S + 2FeS + SO_2(g) \tag{1}$$

$$2FeS_2 + 2O_2(g) \rightarrow 2FeS + 2SO_2(g) \tag{2}$$

$$FeS + 2O_2(g) \rightarrow FeSO_4 \tag{3}$$

$$Cu_2S + SO_2(g) + 3O_2(g) \rightarrow 2CuSO_4 \tag{4}$$

$$2Cu_2S + 5O_2(g) \rightarrow 2CuO\cdot CuSO_4 \tag{5}$$

$$CuSO_4 \rightarrow Cu + SO_3 \tag{6}$$

$$2CuO\cdot CuSO_4 \rightarrow 2CuO + SO_3 \tag{7}$$

3.5. Optimization of Experimental Parameters. The effectiveness of the leaching process for specific metal extraction is governed by several factors, including the particle size, L/S ratio, agitation time, lixiviant concentration, oxidizing agent, and others.[30] Below is a detailed discussion of the aforementioned experimental parameters affecting the leaching and recovery processes of copper from its low-grade ore.

3.5.1. Effect of Cu Ore Particle Size. To investigate the impact of particle size on the copper leaching efficiency, different copper ore size fractions (<55, 55–65, 65–75, 75–96, and >132.30 μm) were examined. 1 g of each copper ore size fraction was dissolved in a leaching mixture of 7.5 mL, each in 0.25 M H_2SO_4 and 0.25 M HNO_3 solutions with stirring at 300 rpm for 30 min. As generally observed, the leaching efficiency tends to increase with decreasing particle size due to the greater particle surface area exposed to the leachant. The results confirm this trend as fine particle distributions exhibit higher copper leaching rates (Figure 7a). The 55–65 μm size fraction achieved the highest leaching efficiency (32.3%) due to its larger surface area, facilitating more interactions between the reactants.[31] However, as the particle size increased beyond 65 μm, recovery declined from 32.3 to 29.50% (Figure 7a). Larger ore particles (>132.30 μm) exhibiting a less surface area exposed to the leachants reduce the contact between the leaching agents and the metal in the ore and result in reduced dissolution rates.[32] Interestingly, particle sizes smaller than 55 μm also display a decrease in the leaching efficiency. This can be attributed to the formation of slimes that coat the copper mineral particles, hindering their dissolution.[14c] Based on these findings, the 55–65 μm fraction was determined to be the optimal particle size and was chosen for further investigation.

3.5.2. Effect of Liquid-to-Solid Ratio. The influence of L/S ratio on copper leaching from low-grade ore was studied using various ratios (5:1, 15:1, 25:1, 35:1, and 45:1 mL g^{-1}) under constant conditions (300 rpm stirring, 30 min, 55–65 μm particles, 0.25 M H_2SO_4/HNO_3 lixiviant). As expected (Figure 7b), the lowest copper dissolution occurred at a 5:1 L/S ratio due to insufficient lixiviant volume to leach all copper particles within the leaching time. A lower lixiviant volume with a constant solid mass increases the solution viscosity and hinders the particle contact, reducing the leaching rate.[33] Conversely, the leaching efficiency increased with increasing L/S ratio due to a greater lixiviant volume per unit solid.[34] However, beyond 15:1 mL g^{-1}, there was no significant increase in copper dissolution. Therefore, 15:1 mL g^{-1} was chosen as the optimal L/S ratio. These findings highlight the importance of sufficient lixiviant volume for effective copper leaching. The study achieved 34.64% copper leaching rate at this L/S ratio. Increasing the lixiviant volume to 25 or 35 mL g^{-1} did not significantly improve extraction (Figure 7b), posing challenges for separating the leached products from the excess acid.

3.5.3. Effect of Lixiviant Concentration. The effect of lixiviant concentration on the copper leaching process was investigated using various concentrations of H_2SO_4 and HNO_3 (0.12, 0.25, 0.5, and 0.75 M) while maintaining constant leaching conditions (55–65 μm particles, 15:1 mL g^{-1} L/S ratio, 300 rpm stirring, 30 min).[32,35] As shown in Figure 7c, both acids achieved the highest copper leaching percentage (31.94%) at a lixiviant concentration of 0.25 M. Increasing the concentration beyond 0.25 M did not significantly improve. Therefore, 0.25 M was chosen as the optimal value for further experiments.

3.5.4. Effect of Stirring Time. The impact of agitation time on copper leaching was studied by varying the agitation time from 10 to 40 min (10 min increments) under constant conditions (1 g, 55–65 μm particles, 0.25 M H_2SO_4/HNO_3 lixiviant, 15:1 mL g^{-1} L/S, 300 rpm). As shown in Figure 7d, the maximum copper dissolution (34.52%) occurred at 30 min. Extending the agitation time beyond 30 min did not significantly improve the leaching efficiency (Figure 7d).[36] Therefore, 30 min was chosen as the optimal agitation time for further studies.

During the dissolution of copper ore particles in lixiviant, the following reaction represents the overall leaching procedure of the copper-bearing sulfide material.[37]

$$\begin{aligned} &CuFeS_2 + 2H_2SO_4 + HNO_3 + O_2 \\ &\quad \rightarrow CuSO_4 + FeSO_4 + Cu(NO_3)_2 + Fe(NO_3)_2 + 2S \\ &\quad + 2H_2O \end{aligned} \tag{8}$$

3.5.5. Effect of the Nature of Lixiviant Mixture. By using different ratios of oxidizing agent (H_2O_2) with sulfuric acid and nitric acid, different lixiviant mixtures were prepared to explore the relative role of H_2O_2. Various ratios of H_2O_2 with H_2SO_4 and HNO_3 (mL/mL; 1:14, 2:13, 3:12, 4:11, and 5:10) were used as a lixiviant mixture to obtain the final volume of the lixiviant mixture as 15 mL to ensure the optimized L/S ratio. From Figure 7e, it can be seen that a noticeable increase in copper dissolution occurs when the ratio of hydrogen peroxide and a mixture of sulfuric acid and nitric acid is adjusted to 5:10 mL/mL. In addition, the combination of sulfuric acid, nitric

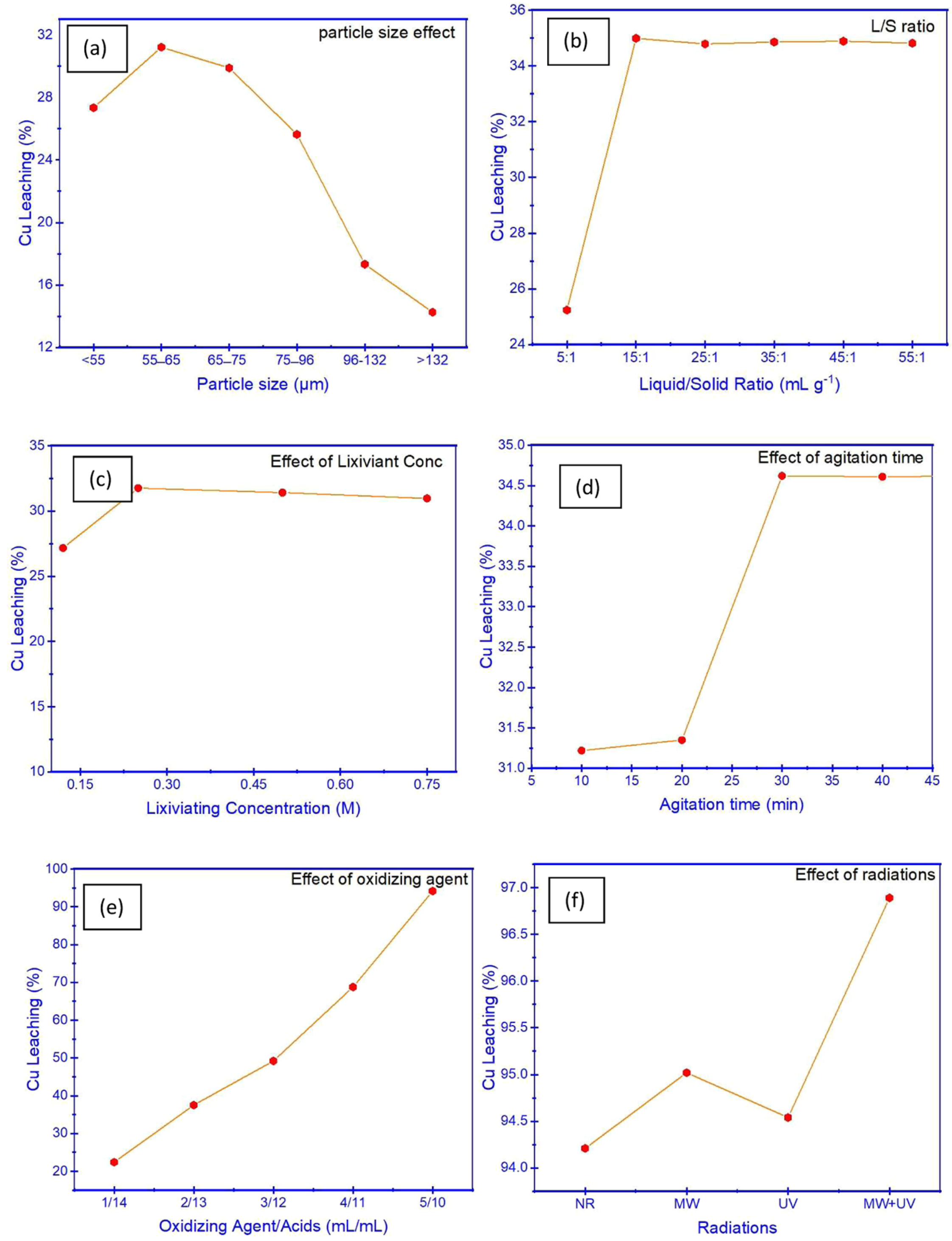

Figure 7. Effect of different experimental parameters on copper dissolution: (a) particle size, (b) liquid–solid ratio, (c) lixiviant concentration, (d) agitation time, (e) volume of the oxidizing agent, and (f) radiation.

acid, and hydrogen peroxide produces heat through an exothermic process, which speeds up the dissolution reaction and allows for a substantial increase in copper dissolution (94.2%).

3.5.6. Effect of Radiation. To investigate the effect of irradiation on the leaching percentage of copper, four leaching experiments were conducted: first with no radiation (NR), second in the presence of microwaves (MW) only, third under ultraviolet (UV) light only, and fourth under both MW first and then UV radiation. In the absence of radiation, copper leaching was found to be 94.2% under optimized conditions of other leaching parameters. However, when the leached solution was placed in the MW chamber, copper leaching slightly increased from 94.2 to 95.2%, as shown in Figure 7f. The effect of UV irradiation was minimal, with copper leaching increasing from 94.2 to 94.5%. However, in the fourth experiment, where the copper-leached solution was irradiated with MW and UV, copper leaching significantly increased to

96.8%, confirming the significant impact of combined MW and UV radiation on copper leaching. MW and UV radiation trigger the chemical processes that produce heat and highly reactive moieties such as free radicals that can enhance the overall mineral's dissolution process.[21] The aforementioned experiment was conducted in triplicate, and the average Cu extraction efficiency was taken with a standard deviation of 0.23515.

3.6. Solvent Extraction. The solvent extraction process is described in detail in Section 2.3. Table 3 displays the results of AAS analysis for the SX reagent's performance in *n*-decane. A 1:10 dilution was carried out, and the pH was kept within the parameters of the product (ACORGA M5640). In a 250 mL separating funnel, 20 mL of extractant (SX) was mixed with 100 mL of pregnant leach solution (PLS) at a controlled pH. At pH 3.5, three extraction values (63.07, 63.12, and 63.41 mg/mL) from PLS yielded an average copper extraction efficiency of 97.9%. At this pH, the iron absorption in the loaded organic phase was measured at 1%. Nonetheless, it was found that the overall effectiveness of copper extraction % using solvent extraction and adjusted leaching parameters was 97.9%. Increasing the pH resulted in a slight decrease in copper extraction.

Table 3. Extraction Efficiency of Copper Load

#	copper in PLS solution (mg/mL)	copper in raffinate (mg/mL)	extraction efficiency (%)
1	64.53	1.46	97.77
2	64.53	1.41	97.81
3	64.53	1.12	98.26

CONCLUSIONS

In this study, we successfully developed a radiation-assisted hydrometallurgical method for efficient copper extraction from low-grade ore. Comprehensive characterization using SEM, XRD, TGA, and chemical analysis provided valuable insights into the ore composition. XRD confirmed the presence of wroewolfeite and chalcopyrite as the primary copper-bearing minerals.

The study optimized various parameters influencing copper leaching and its extraction, thus maximizing the overall recovery. Under optimized conditions (liquid-to-solid ratio: 15:1 mL g^{-1}; lixiviant composition: 0.25 M H_2SO_4, 0.25 M HNO_3, and 30% H_2O_2; particle size: 55−65 μm; stirring at 300 rpm for 30 min; exposure to microwave and UV radiation), a remarkable copper leaching efficiency of 96.8% was achieved. Finally, the ACORGA M5640 OPT series extractant achieved a high extraction efficiency of 97.9% within a short loading time (less than 1 min).

These findings demonstrate the exceptional performance of the modified hydrometallurgical approach for copper recovery from low-grade ores. This approach has the potential to be successfully applied to extract other metals from their respective low-grade ores, promoting efficient utilization of valuable resources. However, assessment of precise cost incurred on the installation and operational costs will be helpful prior to the commercialization of this approach for extraction of copper and other metals from their low-grade ores.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c09656.

> Schematic steps performed during extraction of copper from its low-grade ore; particle size of copper ore after crushing and grinding obtained from a Zetasizer; and TGA analysis of low-grade copper ore (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Doebrich, J. *Copper: A Metal for the Ages*; US Geological Survey, 2009; pp 2327−6932.

(2) Hertwich, E. G.; Gibon, T.; Bouman, E. A.; Arvesen, A.; Suh, S.; Heath, G. A.; Bergesen, J. D.; Ramirez, A.; Vega, M. I.; Shi, L. Integrated life-cycle assessment of electricity-supply scenarios confirms global environmental benefit of low-carbon technologies. *Proc. Natl. Acad. Sci. U.S.A.* **2015**, *112* (20), 6277−6282.

(3) Klose, S.; Pauliuk, S. Sector-level estimates for global future copper demand and the potential for resource efficiency. *Resour., Conserv. Recycl.* **2023**, *193*, No. 106941.

(4) Vidal, O.; Le Boulzec, H.; Andrieu, B.; Verzier, F. Modelling the demand and access of mineral resources in a changing world. *Sustainability* **2022**, *14* (1), No. 11.

(5) Canpolat, G.; Ziyadanoğullari, R. Recovery of copper from complex copper oxide ore by flotation and leaching methods. *Adv. Phys. Res.* **2023**, *5* (2), 103−116.

(6) Whitworth, A. J.; Vaughan, J.; Southam, G.; van der Ent, A.; Nkrumah, P. N.; Ma, X.; Parbhakar-Fox, A. Review on metal extraction technologies suitable for critical metal recovery from mining and processing wastes. *Miner. Eng.* **2022**, *182*, No. 107537.

(7) Nkuna, R.; Ijoma, G. N.; Matambo, T. S.; Chimwani, N. Accessing metals from low-grade ores and the environmental impact considerations: a review of the perspectives of conventional versus bioleaching strategies. *Minerals* **2022**, *12* (5), No. 506.

(8) Souza, R.; Queiroz, C.; Brant, J.; Brocchi, E. Pyrometallurgical processing of a low copper content concentrate based on a thermodynamic assessment. *Miner. Eng.* **2019**, *130*, 156−164.

(9) Baba, A. A.; Ayinla, K. I.; Adekola, F. A.; Ghosh, M. K.; Ayanda, O. S.; Bale, R. B.; Sheik, A. R.; Pradhan, S. R. A review on novel techniques for chalcopyrite ore processing. *Int. J. Min. Eng. Miner. Process.* **2012**, *1*, 1−16.

(10) (a) Peeters, N. Solvometallurgy for recovering metals from secondary resources. 2022. (b) Li, Z.; Dewulf, B.; Binnemans, K. Nonaqueous solvent extraction for enhanced metal separations: concept, systems, and mechanisms. *Ind. Eng. Chem. Res.* **2021**, *60* (48), 17285−17302.

(11) Kumar, R.; Chakrabortty, S.; Chakrabortty, P.; Nayak, J.; Liu, C.; Khan, M. A.; Ha, G.-S.; Kim, K. H.; Son, M.; Roh, H.-S.; et al. Sustainable recovery of high-valued resources from spent lithium-ion batteries: A review of the membrane-integrated hybrid approach. *Chem. Eng. J.* **2023**, *470*, No. 144169.

(12) (a) Li, Y.; Kawashima, N.; Li, J.; Chandra, A.; Gerson, A. R. A review of the structure, and fundamental mechanisms and kinetics of the leaching of chalcopyrite. *Adv. Colloid Interface Sci.* **2013**, *197−198*, 1−32. (b) Lambiel, F.; Dold, B.; Spangenberg, J. E.; Fontboté, L. Neoformation of exotic copper minerals from gel-like precursors at the Exótica deposit, Chuquicamata, Chile. *Miner. Deposita* **2023**, *58* (4), 661−680.

(13) (a) Perez, J. P. H.; Folens, K.; Leus, K.; Vanhaecke, F.; Van Der Voort, P.; Du Laing, G. Progress in hydrometallurgical technologies to recover critical raw materials and precious metals from low-concentrated streams. *Resour., Conserv. Recycl.* **2019**, *142*, 177−188. (b) Raza, N.; Raza, W.; Zafar, Z. I.; Kumar, R. Beneficiation of zinc from electric arc furnace dust using hydrometallurgical approach. *Russ. J. Appl. Chem.* **2016**, *89*, 836−845.

(14) (a) Tian, H.; Guo, Z.; Pan, J.; Zhu, D.; Yang, C.; Xue, Y.; Li, S.; Wang, D. Comprehensive review on metallurgical recycling and cleaning of copper slag. *Resour., Conserv. Recycl.* **2021**, *168*, No. 105366. (b) Romero, R.; Mazuelos, A.; Palencia, I.; Carranza, F. Copper recovery from chalcopyrite concentrates by the BRISA process. *Hydrometallurgy* **2003**, *70* (1−3), 205−215. (c) Mohanraj, G.; Rahman, M.; Arya, S.; Barman, R.; Krishnendu, P.; Meena, S. S. Characterization study and recovery of copper from low grade copper ore through hydrometallurgical route. *Adv. Powder Technol.* **2022**, *33* (1), No. 103382.

(15) (a) Raza, N.; Raza, W.; Asif, M. Reaction Kinetics of magnesite ore in dilute ethanoic acid. *Russ. J. Non-Ferrous Met.* **2016**, *57*, 308−315. (b) Raza, N.; Zafar, Z. I.; Najam-ul-Haq. An analytical model approach for the dissolution kinetics of magnesite ore using ascorbic acid as leaching agent. *Int. J. Met.* **2013**, *2013*, No. 352496.

(16) Nicol, M. J. The role and use of hydrogen peroxide as an oxidant in the leaching of minerals. 1. acid solutions. *Hydrometallurgy* **2020**, *193*, No. 105328.

(17) Tang, J.; Steenari, B.-M. Solvent extraction separation of copper and zinc from MSWI fly ash leachates. *Waste Manage.* **2015**, *44*, 147−154.

(18) Choubey, P. K.; Panda, R.; Jha, M. K.; Lee, J.-c.; Pathak, D. Recovery of copper and recycling of acid from the leach liquor of discarded Printed Circuit Boards (PCBs). *Sep. Purif. Technol.* **2015**, *156*, 269−275.

(19) Al-Ghouti, M. A.; Khan, M.; Nasser, M. S.; Al Saad, K.; Heng, O. E. A novel method for metals extraction from municipal solid waste using a microwave-assisted acid extraction. *J. Cleaner Prod.* **2021**, *287*, No. 125039.

(20) (a) Huang, W.; Liu, Y. Study on microwave-assisted grinding and liberation characteristics for Ludwigite. *J. Microwave Power Electromagn. Energy* **2021**, *55* (1), 28−44. (b) Sun, J.; Wang, W.; Liu, Z.; Ma, Q.; Zhao, C.; Ma, C. Kinetic study of the pyrolysis of waste printed circuit boards subject to conventional and microwave heating. *Energies* **2012**, *5* (9), 3295−3306.

(21) Yepsen, O.; Cornejo-Ponce, L.; Yepsen, R. Perspectives for Photochemical Leaching Processes of Chalcopyrite: A Solar Radical-Leaching Process. *Mining* **2024**, *4* (2), 352−366.

(22) Yepsen, O.; Yáñez, J.; Mansilla, H. D. Photocorrosion of copper sulfides: Toward a solar mining industry. *Sol. Energy* **2018**, *171*, 106−111.

(23) Wu, Z. H.; Hu, Y. J.; Lee, D. J.; Mujumdar, A. S.; Li, Z. Y. Dewatering and drying in mineral processing industry: Potential for innovation. *Drying Technol.* **2010**, *28* (7), 834−842.

(24) Azizi, A.; Masdarian, M.; Hassanzadeh, A.; Bahri, Z.; Niedoba, T.; Surowiak, A. Parametric optimization in rougher flotation performance of a sulfidized mixed copper ore. *Minerals* **2020**, *10* (8), No. 660.

(25) Kumari, R.; Prabhakar, R.; Samadder, S. R. Enhanced copper extraction from waste printed circuit boards using glycine after supercritical methanol pre-treatment: Process optimization, leaching kinetics, and thermodynamic analysis. *Waste Manage.* **2025**, *193*, 551−560.

(26) Gyimah, K. O. *An Investigation on the Chemical and Microwave-assisted Approaches for the Reclamation of Metallic values from Computer Printed Circuit Boards (PCB) Wastes*, University of Leeds2018.

(27) (a) Djokić, J.; Radovanović, D.; Nikolovski, Z.; Andjić, Z.; Kamberović, Ž. Influence of Electrolyte Impurities from E-Waste Electrorefining on Copper Extraction Recovery. *Metals* **2021**, *11* (9), No. 1383. (b) Gotfryd, L.; Pietek, G. Contaminants of post-leaching copper solutions and their behavior during extraction with industrial extractants *Physicochem. Probl. Miner. Process.* 2013; Vol. *49*.

(28) Deraz, N. Production and characterization of pure and doped copper ferrite nanoparticles. *J. Anal. Appl. Pyrolysis* **2008**, *82* (2), 212−222.

(29) Prasad, S.; Pandey, B. Thermoanalytical studies on copper—iron sulphides. *J. Therm. Anal. Calorim.* **1999**, *58*, 625−637.

(30) Barton, I. F.; Hiskey, J. B. Chalcopyrite leaching in novel lixiviants. *Hydrometallurgy* **2022**, *207*, No. 105775.

(31) Chetty, D. Acid-gangue interactions in heap leach operations: A review of the role of mineralogy for predicting ore behaviour. *Minerals* **2018**, *8* (2), No. 47.

(32) Olubambi, P.; Borode, J. O.; Ndlovu, S. Sulphuric acid leaching of zinc and copper from Nigerian complex sulphide ore in the presence of hydrogen peroxide. *J. South. Afr. Inst. Min. Metall.* **2006**, *106* (11), 765−770.

(33) Ntengwe, F. W. The leaching of dolomitic-copper ore using sulphuric acid under controlled conditions. *Open Miner. Process. J.* **2010**, *3* (1), 60−67.

(34) Li, M.; Li, B.; Chen, J.; Shen, X.; Cui, S.; Liu, K.; Han, Q. A novel green method for copper recovery from cuprous thiocyanate-containing acidified sediments in the gold industry. *J. Cleaner Prod.* **2021**, *329*, No. 129729.

(35) Ajiboye, E.; Panda, P.; Adebayo, A.; Ajayi, O.; Tripathy, B.; Ghosh, M.; Basu, S. Leaching kinetics of Cu, Ni and Zn from waste silica rich integrated circuits using mild nitric acid. *Hydrometallurgy* **2019**, *188*, 161−168.

(36) (a) Gülfen, M.; Aydin, A. O. Dissolution kinetics of calcined chalcopyrite ore in sulphuric acid solution. 2008. (b) Ekmekyapar, A.; Demirkıran, N.; Künkül, A.; Aktaş, E. Leaching of malachite ore in ammonium sulfate solutions and production of copper oxide. *Braz. J. Chem. Eng.* **2015**, *32*, 155−165.

(37) (a) Turkmen, Y.; Kaya, E. Leaching of chalcopyrite concentrate in sulphuric acid with the aid of mechanical activation and microwave energy. *Asian J. Chem.* **2010**, *22* (10), No. 8107. (b) Cháidez, J.; Parga, J.; Valenzuela, J.; Carrillo, R.; Almaguer, I. Leaching chalcopyrite concentrate with oxygen and sulfuric acid using a low-pressure reactor. *Metals* **2019**, *9* (2), No. 189.