https://doi.org/10.53964/jmab.2023004

https://www.innovationforever.com

Journal of
Modern Agriculture and Biotechnology

ISSN 2788-810X (Online)

Open Access

Research Article

Hydrometallurgical Processing of Chalcocite Tailing Sample for Extraction of Copper

Humma Akram Cheema[1,2*], **Samiya Azhar**[1]

[1]Department of Chemistry, University of Agriculture, Faisalabad, Pakistan

[2]Department of Chemistry, University of Education Lahore, Lahore, Pakistan

[*]**Correspondence to: Humma Akram Cheema, PhD, Researcher,** Department of Chemistry, University of Agriculture, C3HG+483 Jail Road Near Al-Khidmat Police Markaz Police Lines, Faisalabad 38000, Pakistan; Email: humcheema242@yahoo.com

Received: August 19, 2022 **Revised:** October 4, 2022 **Accepted:** October 17, 2022 **Published:** January 30, 2023

Abstract

Objective: To recover the copper remained in tailing sample of chalcocite due to its hazardous impact on biota, in addition to the fact that primary sources are becoming scare and they are of high economic values.

Methods: In order to recover copper from tailing, herein, hydrochloric acid leaching followed by the selective precipitation of copper has been studied. The parameters like acid concentration (1.0-2.5M), sodium hypochlorite addition dosage (0.5-5.0M), temperature (25-55°C), time (1-9h), agitation speed (180-360rpm) and pulp density (2-14 wt./vol.%) were varied to determine the optimum condition of leaching.

Results: According to experimental findings, metal-chloro complexes were effectively synthesized by the addition of 0.5M hydrogen peroxide with 1.5M hydrochloric acid solution at 45°C, 3h of leach time and 260rpm that yielded approximately 99% of copper into the leach liquor. Afterward, the leach liquor was treated for recovery of copper salt by adding a 300g/L solution of sodium hydroxide, precipitating Cu $(OH)_2$.

Conclusion: The current research potentially contributes to both ecologically and economically through the hydrometallurgical processing of tailing sample for extraction of copper.

Keywords: hydrometallurgical processing, chalcocite, tailing, chloride leaching

Citation: Cheema HA, Azhar S. Hydrometallurgical Processing of Chalcocite Tailing Sample for Extraction of Copper. *J Mod Agric Biotechnol*, 2023; 2(1): 4. DOI: 10.53964/jmab.2023004.

1 INTRODUCTION

Copper is considered as one of the most economically important metals with demand expected to rise dramatically by 2050[1]. Meanwhile, its mining also poses a detrimental impact on environment because it is usually operated in open pits and produces a huge amount of waste. The dominant causes of contamination in the surface environment include mine and mill activities, consist of grinding, concentrating ores, and dumping of tailings[2]. Typically, ore in excess of 150 tons must be mined, crushed, concentrated using froth flotation, and then extracted using various techniques depending on whether the ore is sulphide or non-sulfide for production of 1-ton copper[3]. The entire process results in massive amounts of tailings, which are the ore residues after the extraction of copper and are highly contaminated with various hazardous metals such as Cd, Fe, Pb, and Zn and metalloids along with Cu[4,5]. These waste minerals (known as tailings) are usually disposed of in massive lagoons, which can also, in time, grow to be drained thereby allowing entrance of oxygen and dissolution of the minerals, a process frequently paralleled by intense acidification[6]. Therefore, tailing sample is considered a point source of copper contamination in food chain.

Copper toxicity, a rare condition that primarily affects the liver, may arise from chronic or long-term exposure to high levels of copper through contaminated water as well as food sources, with its major symptoms of diarrhea, headaches, and in severe cases, kidney failure. As a result of a hereditary tendency to copper accumulation in the liver, serious chronic liver diseases such Wilson's disease and Indian childhood cirrhosis can occur[7,8]. High levels of heavy metals such as copper have been a concern in recent years due to mining activities around mine sites, particularly at mine waste disposal sites[9-11]. In order to mitigate the mine waste dumpsites associated hazards of copper on ecosystems and human health[12-14], appropriate management of tailing sample is urgently required. The chalcocite mining and smelting have led to chronic exposure of copper in soil, water, plants, animals, and humans[15].

Moreover, the extraction of copper from tailing sample also contribute to economic development, as copper is major industrial metal with useful properties include high thermal and electrical conductivity, low corrosion, alloying ability, and malleability. The current increasing industrial demand for copper and the restricted availability of natural minerals make tailings samples a potential alternative resource. The present study was undertaken for processing of chalcocite tailing sample for efficient extraction of copper.

2 MATERIALS AND METHODS

In this study, 5kg sample of chalcocite tailing was collected from Shanxi China. After receiving the samples, they were smoothly homogenized by manual stirring and saved for leaching studies. To confirm the composition of the tailings samples, wet chemical digestion was performed by using aqua regia (hydrochloric acid (HCl) + nitric acid). After digestion, the filtrate was analyze with Atomic absorption spectrometer for determination of chemical composition of tailing sample as given in Table 1.

Table 1. Elemental Analysis of Tailing Sample before Leaching

Elements	% Age Composition
Cu	0.91
Fe	4.34
S	0.035
SiO_2	58.46
Others	36.2

A fixed amount of sample was taken in a glass beaker of 500mL that consist of a predetermined concentration of HCl diluted in deionized water along with maintenance of required pulp density (solid-to-liquid ratio). At a certain temperature, the acid solution was pre-heated on the magnetic hot plate cum stirrer (Robus-RTH-340, United Kingdom) and the tailing sample was charged under the stirring condition as maintained by the batch studies using a magnetic paddle. Once the leaching experiment was completed, the slurry was filter out by using Whatman-40 filter paper and Buckner funnel. After filtration, the residue on the filter paper was washed twice with hot water, and air dried and kept for analysis. In order to analyze the metal ions liberated from the tailing sample during leaching operation, the filtrate (leach liquor) was properly diluted. The leaching efficiency of metals ions (in %) from the chalcocite tailing sample was determined by the reading of atomic absorption spectrometer analysis (SP-IAA4530, China) along with the difference in mass fraction between input metal in sample and output metal in leach liquor, as follows:

$$\%\ leaching = \left(\frac{M_{LL}}{M_{IS}} * 100\right) \quad (1)$$

where MIS and MLL are metals' input from sample and output in leach liquor (on absolute basis in gram), respectively.

For achievement of recovery process, the leach liquor produced at optimum conditions of leaching studies of tailing sample contain (890mg/100mL) was used for the precipitation studies. To keep the mother liquor volume at only 10% of the leach liquor, 1L of leach liquor was initially heated to 190°C for evaporation. Thus, obtained solution enriched with metal ions (890mg/10mL) was used for the succeeding precipitation studies. A 250mL glass beaker was filled with 100mL of mother liquor. After preheating the solution to 40±2°C, 50mL of the desired concentration of sodium hydroxide solution was immediately added while being vigorously stirred by the magnetic paddle. After injecting the precipitant solution, the stirring was given for the next 60min, and the filtrate was then heated. After being dried for a night at 90°C, the precipitate was recovered, cleaned with distilled water, and collected for analysis.

3 RESULTS AND DISCUSSION

3.1 Leaching Studies of Chalcocite Tailing

3.1.1 Effect of Acid Concentration on Leaching Experiment

In order to examine the effect of lixiviant concentration on leaching efficiency of copper from chalcocite ore sample, the leaching experiment was performed at different acid concentrations (1M, 1.5M, 2M, 2.5M) by keeping other parameters constant (1.5% pulp density, 5h, 45°C temperature, 400rpm and 0.5M oxidant concentration). During the leaching experiment, a chlorine gas odor was observed.

$$4HCl \rightarrow 2Cl_2 + 4H^+ \quad (2)$$

This chlorine gas could dissolve chalcocite as shown in equation

$$Cu_2S + 2Cl_2 \rightarrow 2CuCl_2 \quad (3)$$

The acid concentration has an important role in the leaching of copper from chalcocite. The concentration of HCl was varied in the range of 1 to 2.5M by keeping other parameters constant. Figure 1A depicts the increased leaching of dissolved copper from dolomite as the concentration of acid was increased from 1 to 1.5 M. The chlorite ion's oxidation potential rises in proportion to the concentration of hydrogen ions. In the presence of an oxidizing agent, the addition of chloride ions improves the leaching of chalcopyrite and produces a more stable cuprous chloride. Cu^{2+} ions were more stable in acidic media. When the concentration of HCl is further increased, the leaching efficiency of copper decreases because the leaching of copper in highly acidic media leads to an increase of chloride ions in the solution and the formation of a porous layer on the reaction surface, which inhibits further penetration of the reagent in the particles[16].

3.1.2 Effect of Pulp Density on Leaching Experiment

Effect of pulp density on leaching efficiency of copper from chalcocite ore sample was studied. The leaching experiment was performed at various pulp densities (2%, 4%, 6%, 8%, 10%, 12% and 14%) by keeping other parameters constant (1.5M acid concentration, 0.5M oxidant concentration, 400rpm, 5hrs and 45°C temperature) as indicated in Figure 1B. It depicts that when the pulp density was varied from 2 to 10% by keeping other parameters constant, the leaching efficiency of metal was high because the available surface area per unit volume of the solution was higher and 56% copper was leached from chalcocite ore. After the pulp density increased above 10%, the efficiency of copper was decreased because the available surface per unit volume was decreased[17]. More increase in pulp density will cause difficulties for agitation, slurry filtration etc[18].

3.1.3 Effect of Temperature on Leaching Experiment

Effect of temperature on leaching of copper from chalcocite ore was inspected and leaching experiment was performed at different temperatures (25°C, 35°C, 45°C and 55°C) by keeping other parameters unvaried (1.5M acid concentration, 0.5M oxidant concentration, 10% pulp density, 400rpm and 5h contact time). The outcomes revealed in Figure 1C that when temperature was kept constant from 25°C to 45°C, the copper leaching efficiency increased and 56% of copper was leached from the tailing sample. The high copper extraction at high temperature may be attributed to the increase of the mass transfer coefficient and diffusivity as the increase in temperature[19].

3.1.4 Effect of Contact Time on Leaching Experiment

Time has a significant effect on leaching efficiency, hence its effect was examined at different time intervals (1, 3, 5, 7 and 9h) by keeping other parameters constant (1.5M acid concentration, 10% pulp density, 0.5M oxidant concentration, 400rpm and 45°C temperature). The result demonstrated in Figure 1D that when contact time changes from 1 to 3hrs, the leaching efficiency of copper was increased and 64% copper was leached out. These results corroborated with a direct consequence of the prolonged exposure of the mineral surface to the acid medium. After that leaching efficiency of copper was gradually decrease, which may be due to decrease of available surface area of ore[20].

3.1.5 Effect of Agitation on Leaching Experiment

For a heterogeneous reaction, proper mixing is vital for complete transfer of solid mass into liquid. Hence, the effect of agitation speed was examined at various stirring speed (180, 220, 260, 300 and 340rpm) by keeping other parameters constant (10% pulp density, 0.5M oxidant concentration, 1.5M acid concentration, 45°C temperature and 3hrs contact time). The result revealed that the dissolution rate increased when the agitation speed was varied from 180 to 360rpm and 77% copper was leached from chalcocite ore as shown in Figure 1E. This may be attributed to the fact that agitation of the leaching solutions improved the mass transfer and accelerated the leaching of copper. The agitation reduces the liquid film thickness formed around the ore particles, the diffusion through the boundary layer of the leach reagent toward the external surface of the particle[21]. Hence, the agitation speed of 260rpm was optimized and kept constant throughout the experimental sets.

3.1.6 Effect of Oxidant on Leaching Experiment

Sodium hypochlorite (NaOCl) concentration has prominent effect on leaching of copper from chalcocite. In order to explore the effect of oxidant concentration on leaching efficiency, an experiment was carried out at different concentrations (0.5M, 1.5M, 2.5M, 3.5M,

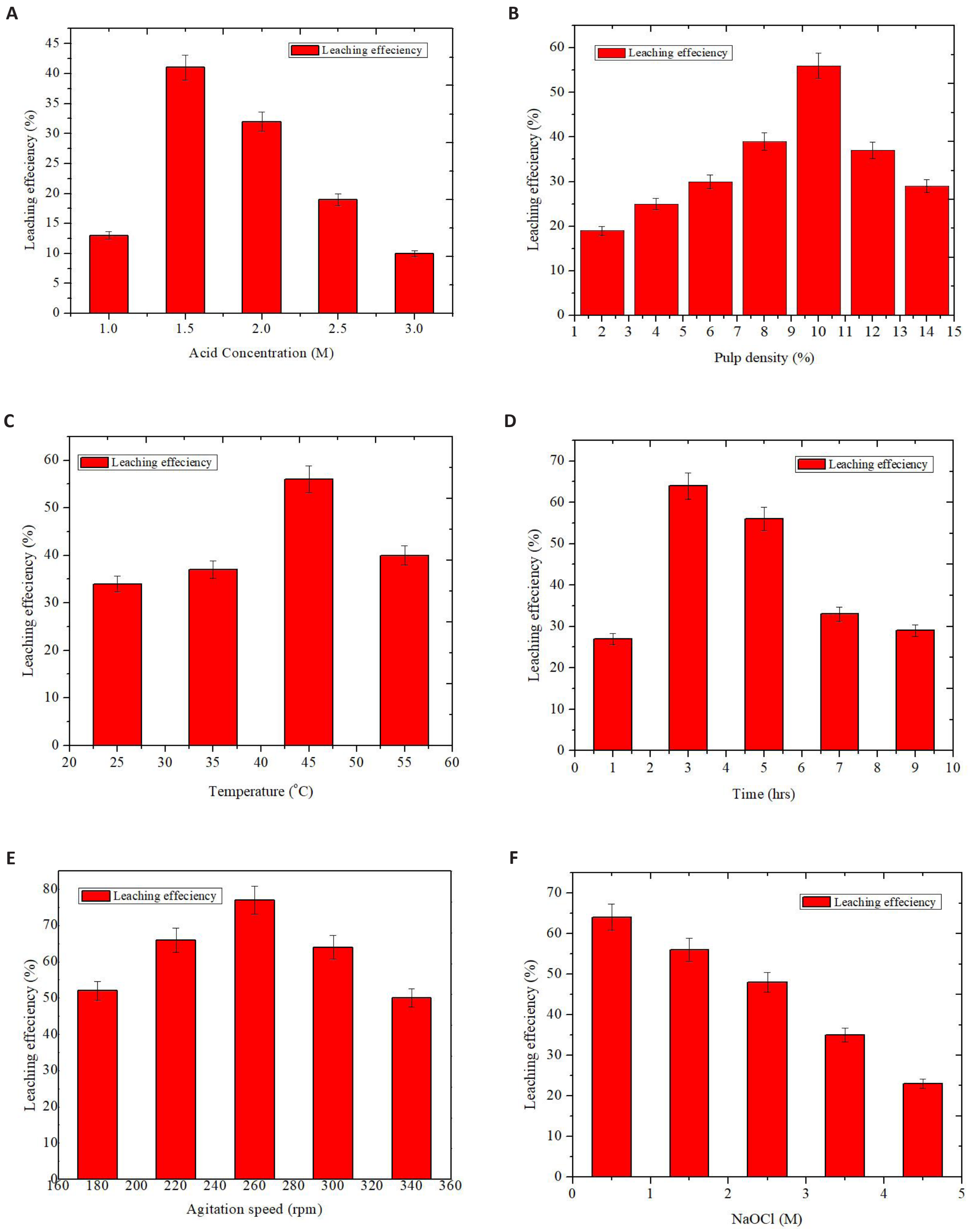

Figure 1. Effects of acid concentration (A), pulp density (B), temperature (C), time (D), agitation speed (E) and oxidant concentration (F) on % extraction of copper.

4.5M) by keeping other parameters constant (1.5M acid concentration, 10% pulp density, 400rpm, 3h and 45°C temperature) as indicated in Figure 1F.

Figure 1F depicts that leaching efficiency of copper was maximum at 0.5M due to production of chlorine gas that readily dissolve copper according to following equations:

$$NaOCl + 4HCl \rightarrow 2Cl_2 + 2NaCl + 2H_2O \quad (4)$$

This chlorine gas could dissolve chalcocite as shown in Equation (5):

$$Cu_2S + 2Cl_2 \rightarrow 2CuCl_2 \quad (5)$$

Overall reaction of dissolution of chalcocite can be represented as in Equation (6):

$$Cu_2S + 2NaOCl + 4HCl \rightarrow 2CuCl_2 + 2NaCl + 2H_2O + S \quad (6)$$

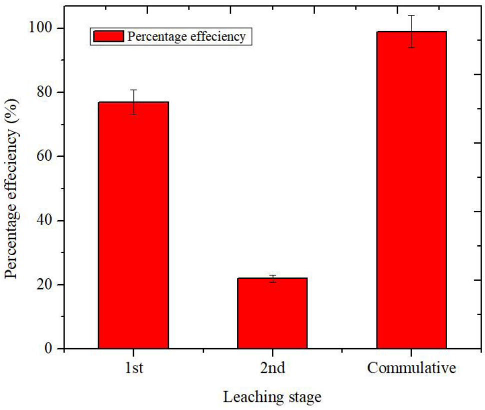

Figure 2. Multistage leaching of copper on % extraction of copper.

A further increase in oxidant concentration, on the other hand, leads to a decrease in leaching efficiency, as more chloride ions are present in the solution and form a porous layer on the reaction surface, thus inhibiting further penetration of the oxidant in the particles[16].

3.2 Multistage Leaching Experiments

After the optimization of leaching parameters, multistage leaching experiments were performed for the maximum recovery of copper. The residue from multistage leaching was used multiple times and all the experiments were performed in one flask. The first experiment was performed at optimum conditions, i.e., 1.5M acid concentration, 10% pulp density, 0.5M NaOCl for 3h with 260rpm at 45°C. After leaching, the solution was filtered and the remaining residue was washed with water. Thereafter, the residue was subjected to a second leaching under optimized parameter conditions. The cumulative leaching of copper was 99% as shown in Figure 2.

3.3 Chemical Precipitation

Before adding the precipitant solution of various concentrations, the mother liquor, which comprised of copper (890mg/100mL), was heated to a preset temperature of 40±2°C. The mother liquor was exposed to a solution of sodium chloride at a concentration of 50g/L to 300g/L while stirring vigorously for a contact time of 60min. The outcomes depicted in Figure 3 show that by increasing concentration of sodium hydroxide in the solution, the precipitation of bluish green copper compounds also increased. It was found that copper could be quantitatively precipitated out as $Cu(OH)_2$ (>98%) from the leach liquor using a solution of 300g/L sodium hydroxide as shown in Figure 3. Before drying, the precipitates were filtered and cleaned with distilled water. The following reactions can be used to describe synthesis of end product[22]:

$$CuCl_2 + 2NaOH \leftrightarrow Cu(OH)_2 + 2NaCl \quad (7)$$

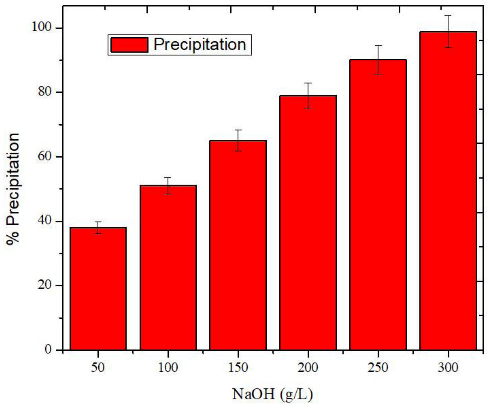

Figure 3. Effect of sodium hydroxide concentration on % precipitation of copper.

The composition of leach liquor after precipitation is shown in Table 2.

Table 2. Elemental Analysis after Precipitation

Elements	% Age Composition
Cu	0.125
Fe	3.87
S	0.035
SiO_2	61.01
Others	36.1

The entire flowsheet of process is decorated in Figure 4.

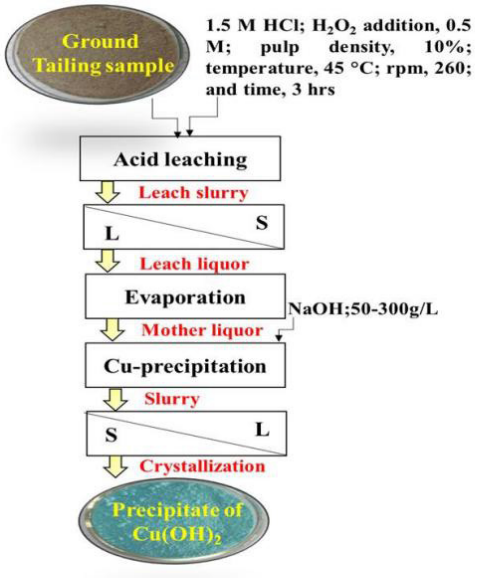

Figure 4. Flowsheet for processing of chalcocite tailing sample.

4 CONCLUSION

The potential for extraction of copper from chalcocite tailing sample has been determined using the acidic leaching process. With 1.5M HCl, copper leaching was found to be more than 45%; however, when 0.5M

NaOCl was introduced to the solution, the leaching of copper considerably increased to 77%. The optimal conditions for leaching were: acid concentration of 1.5M HCl, hydrogen peroxide addition of 0.5M, pulp density of 10%, temperature of 45°C, speed of 260 and time of 3h, which make it possible to leach 98% of copper into the HCl solution in two stages. For the recovery process, leach liquor was treated with sodium hydroxide for precipitation of copper. At 40°C and a range of precipitant concentrations (50-300g/L sodium hydroxide), more than 98% of the copper was produced as $Cu(OH)_2$.

Acknowledgements
Not applicable.

Conflicts of Interest
The authors declared no conflict of interest.

Author Contribution
Cheema HA performed conceptualization, original draft preparation, review and editing; and Azhar S made efforts in methodology and formal analysis.

Abbreviation List
HCl, Hydrochloric acid
NaOCl, Sodium hypochlorite

References

[1] Elshkaki A, Graedel TE, Ciacci L et al. Copper demand, supply, and associated energy use to 2050. *Glob Environ Chang*, 2016; 39: 305-315. DOI: 10.1016/j.gloenvcha.2016.06.006

[2] Abraham MR, Susan TB. Water contamination with heavy metals and trace elements from Kilembe copper mine and tailing sites in Western Uganda; implications for domestic water quality. *Chemosphere*, 2017; 169: 281-287. DOI: 10.1016/j.chemosphere.2016.11.077

[3] Wills BA, Napier-Munn T. Wills' mineral processing technology (Seventh Edition): An introduction to the practical aspects of ore treatment and mineral recovery. Butterworth-Heinemann: Oxford, UK, 2006. DOI: 10.1016/B978-075064450-1/50003-5

[4] Courtney R. Mine tailings composition in a historic site: implications for ecological restoration. *Environ Geochem Health*, 2013; 35: 79-88. DOI: 10.1007/s10653-012-9465-z

[5] Wang P, Liu Y, Menzies NW et al. Ferric minerals and organic matter change arsenic speciation in copper mine tailings. *Environ Pollut*, 2016; 218: 835-843. DOI: 10.1016/j.envpol.2016.08.007

[6] Rzymski P, Klimaszyk P, Marszelewski W et al. The chemistry and toxicity of discharge waters from copper mine tailing impoundment in the valley of the Apuseni Mountains in Romania. *Environ Sci Pollut Res*, 2017; 24: 21445-21458. DOI: 10.1007/s11356-017-9782-y

[7] Schilsky M. Wilson disease: Genetic basis of copper toxicity and natural history. *Semin Liver Dis*, 1996; 16: 83-95. DOI: 10.1055/s-2007-1007221

[8] Barceloux DG, Barceloux D. Copper. *Clin Toxicol*, 1999; 37: 217-230. DOI: 10.1081/CLT-100102421

[9] Sracek O. Formation of secondary hematite and its role in attenuation of contaminants at mine tailings: Review and comparison of sites in Zambia and Namibia. *Front Environ Sci*, 2015; 2: 1-11. DOI: 10.3389/fenvs.2014.00064

[10] Kayika P, Siachoono S, Kalinda C et al. An investigation of concentrations of copper, cobalt and cadmium minerals in soils and mango fruits growing on Konkola copper mine tailings dam in Chingola, Zambia. *Arch Sci*, 2017; 1: 2-5.

[11] Chileshe MN, Syampungani S, Festin ES et al. Physico-chemical characteristics and heavy metal concentrations of copper mine wastes in Zambia: Implications for pollution risk and restoration. *J For Res*, 2020; 31: 1283-1293. DOI: 10.1007/s11676-019-00921-0

[12] Nazir R. Accumulation of heavy metals (Ni, Cu, Cd, Cr, Pb, Zn, Fe) in the soil, water and plants and analysis of physico-chemical parameters of soil and water collected from Tanda Dam Kohat. *J Pharm Sci Res*, 2015; 7: 89-97.

[13] Nguyen Van T, Ozaki A, Nguyen Tho H et al. Arsenic and heavy metal contamination in soils under different land use in an estuary in northern Vietnam. *Int J Environ Res Public Health*, 2016; 13: 1091. DOI: 10.3390/ijerph13111091

[14] Surbakti EP, Iswantari A, Effendi H. Distribution of dissolved heavy metals Hg, Pb, Cd, and As in Bojonegara Coastal Waters, Banten Bay. *IOP Conf Ser Earth Environ Sci*, 2021; 744: 012085. DOI: 10.1088/1755-1315/744/1/012085

[15] Salem MA, Bedade DK, Al-ethawi L et al. Assessment of physiochemical properties and concentration of heavy metals in agricultural soils fertilized with chemical fertilizers. *Heliyon*, 2020; 6: 05224. DOI: 10.1016/j.heliyon.2020.e05224

[16] Xian YJ, Wen SM, Deng JS et al. Leaching chalcopyrite with sodium chlorate in hydrochloric acid solution. *Can Metall Q*, 2013; 51: 133-140. DOI: 10.1179/1879139512Y.0000000001

[17] Cheema HA, Bhatti IA, Srivastava RR et al. Dissolution of molybdenite roasting flue dust in sulfuric acid: Kinetics and mechanism for molybdenum and rhenium leaching. *Chem Pap*, 2022; 76: 4049-4058. DOI: 10.1007/s11696-022-02145-9

[18] Jha MK, Kumari A, Jha AK et al. Recovery of lithium and cobalt from waste lithium ion batteries of mobile phone. *J Waste Manag*, 2013; 33: 1890-1897. DOI: 10.1016/j.wasman.2013.05.008

[19] Wang Z, Guo S, Ye C. Leaching of copper from metal powders mechanically separated from waste printed circuit boards in chloride media using hydrogen peroxide as oxidant. *Procedia Environ Sci*, 2016; 31: 917-924. DOI: 10.1016/j.proenv.2016.02.110

[20] Kim EY, Kim MS, Lee JC et al. Leaching kinetics of copper from waste printed circuit boards by electro-generated chlorine in HCl solution. *Hydrometallurgy*, 2011;

107: 124-132. DOI: 10.1016/j.hydromet.2011.02.009

[21] Ekmekyapar A, Demirkiran N, Kunkuln A et al. Leaching of Malachite ore in Ammonium Sulfate solutions and production of copper oxide. *Braz J Chem Eng*, 2015; 32: 155-165. DOI: 10.1590/0104-6632.20150321s00003211

[22] Cudennec Y, Lecerf A, Gerault Y. Synthesis of Cu $(OH)_2$ and CuO by soft chemistry. *Eur J Solid State Inorg Chem*, 1995; 32: 1013-1022.