

RECOVERY OF COPPER FROM A CHALCOPYRITE ORE USING NATURAL DEEP EUTECTIC SOLVENTS (NADES) OF CHOLINE CHLORIDE-UREA AS A LEACHING AGENT

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Abstract

Due to the environmental impact caused by using strong acids as leaching agents, research on more environmentally friendly leaching agents has increased over the past decade. In this study, a natural deep eutectic solvent (NADES) called Reline (ChCl;2Urea) was used as a leaching agent to recover copper from sulfide ore. Variables such as NADES/water weight ratio, pH, and temperature were analyzed to determine the optimal recovery conditions over 4 hours and to allow extrapolation to longer durations. The ores used were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray fluorescence (XRF), while the NADES was analyzed using infrared spectroscopy (FTIR). The results showed that at 25°C, pH = 7, and stirring at 300 rpm, significant copper recovery begins with a 20% NADES-to-water ratio, demonstrating high selectivity for copper over iron. The efficiency of the organic leaching process improves as the values of the three analyzed variables increase, with temperature having the most significant effect. The best recovery conditions were pH = 12, T = 100°C, w = 300 rpm, and 30% NADES, achieving an 11.68% recovery rate. The kinetic data of the leaching process fit the Kröger-Ziegler model, with an activation energy value of 5.8 kcal/mol, demonstrating that the process is controlled by the transport stage. It was observed that at 100°C, from t = 160 min onwards, the process rate increases. This copper recovery process proposal could pave the way for further research into mineral extraction processes using environmentally friendly systems, particularly biodegradable green solvents.

Keywords: leaching, NADES, waste minimization, copper recovery

1. INTRODUCTION

The increasing demand for copper (Cu) in the industry to meet human needs has placed greatly emphasized on its recovery through hydrometallurgical, pyrometallurgical, and recycling processes. However, these processes require large amounts of energy and involve significant quantities of harmful substances that negatively impact the ecosystem, making them costly and leading to severe environmental issues. Therefore, it is necessary to propose new methods for obtaining copper. Recycling and recovering copper from various sources using novel recovery methods aims to reduce greenhouse gas emissions and contribute to environmental preservation. Currently, different studies have shown that deep eutectic solvents (DES) are promising for recovering various metallic species by dissolving them due to their components (hydrogen bond donors and hydrogen bond acceptors, HBD-HBA) [1]. Recently, among the wide variety of DES, natural deep eutectic solvents (NADES) have emerged as the most attractive alternative to conventional solvents due to their environmentally friendly qualities, such as biodegradability, ease of synthesis, and low cost [2]. Thus, their apparent dissolving power and ecological characteristics make NADES one of the best options for metal recovery while avoiding soil and

water contamination caused by current methods. NADES exhibit biodegradability, biocompatibility, and high selectivity in metal extraction [1]. For this reason, the main objective of this research is to recover copper using a NADES solution and determine the optimal operating conditions, including temperature, agitation, NADES/water ratio, and recovery time. The present study hypothesizes that using deep eutectic solvents (NADES) will promote the selective recovery of copper through the dissolution of oxide and sulfide compounds found in the analyzed minerals. Therefore, the goal is to recover copper from a mineral containing copper, iron, zinc, and manganese through an organic leaching process using choline chloride-urea as the leaching agent. The study evaluates the effect of temperature, pH, and water/solvent ratio to determine the optimal parameters in the leaching process to achieve the highest copper recovery. A kinetic study was carried out to evaluate the leaching reaction.

2. EXPERIMENTAL

For the development of the experiments, two variables were considered: temperature and the amount of NADES in the organic leaching process. Experiments were conducted by varying these two parameters. The first parameter is the amount of NADES in the solution, which was tested within a range of 5 to 30 g in the solution. The temperature variation was carried out to determine the optimal temperature at which the mineral is leached with the highest efficiency. Similarly, the variation in the NADES/water ratio was performed to identify the best extraction/time relationship. The temperature varied within a range of 25 to 100 °C to determine the optimal NADES/water ratio. The total contact time was kept constant at 4 hours of leaching. Finally, the optimal pH for copper recovery was determined by varying this parameter at values of 3, 7, and 12

3. RESULTS AND DISCUSSION

Ore characterization was carried out by X-ray Diffraction Figure 1, and the quantitative results obtained through X-ray Diffraction are shown in Table 1.

Table 7. DRX ore composition results

Species	Formula	Content [%]
Calcite	CaCO ₃	1.6
Quartz	SiO ₂	19.1
Chalcopyrite	CuFeS ₂	1
Muscovite	H ₂ Al _{2.43} K _{0.77} O ₁₂ Si _{3.5}	70.3
Periclase	MgO	0.9
Covellite	CuS	7.1

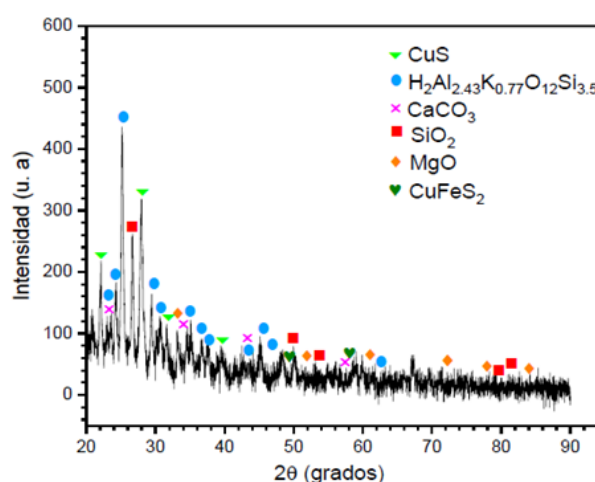


Figure 4. XDR ore analysis.

Table 2 shows the chemical analysis of the copper ore developed by X-ray fluorescence analysis.

Table 8. X-ray fluorescence copper ore analysis.

Sample	Wt. %							
	Cu	Fe	Si	Ca	Zn	Mn	Al	Mg
1	0.239	9.305	21.979	7.779	0.0171	0.154	10.682	4.28
2	0.237	9.156	21.942	7.217	0.0148	0.147	10.783	4.47
3	0.222	8.491	20.418	6.748	0.0137	0.135	9.895	4.182
4	0.239	9.765	21.874	7.324	0.0185	0.155	11.011	4.465
Average	0.234	9.179	21.553	7.267	0.0160	0.148	10.593	4.352

The average copper content in the ore is 0.23%, while the average iron content is 9.17%. A high content of silicon, aluminum, and calcium is observed, which is consistent with the results obtained through X-ray diffraction regarding the presence of aluminosilicates.

The leaching process was carried out at different pH and the results are shown in Figure 2.

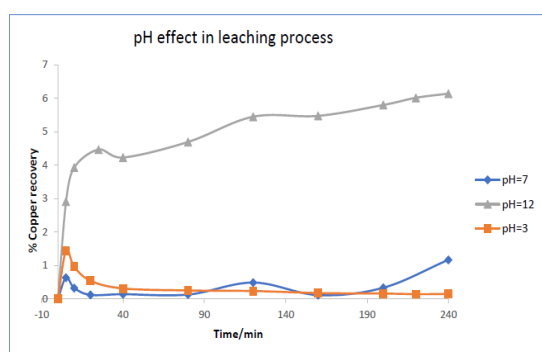


Figure 5. pH effect in the leaching process.

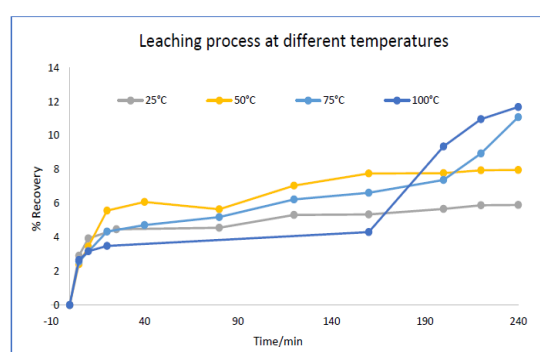


Figure 6. Leaching process at different temperatures.

It can be observed that at a pH of 3, the maximum copper recovery reaches 1.4% at minute 5; however, the recovery decreases to 0.14% at minute 240. On the other hand, at a pH of 7, the recovery increases to 1.16% at minute 240. Finally, at a pH of 12, a recovery of 3.79% is achieved at minute 25, and although the recovery decreases by minute 40, it continues to increase, reaching a final recovery of 6.13% at minute 240. Under basic conditions, the system exhibits the best recoveries. The reason for this effect is likely related to the species formed by the dissolution of NADES in water. Experiments were conducted under the best pH conditions and NADES content, varying the temperature. The results are shown in Figure 3. It is worth highlighting that at higher temperatures, a greater amount of copper is recovered, starting with a 5.9% recovery at 25°C and reaching an 11.68% recovery at 100°C. This represents an almost twofold increase in recovery compared to that obtained at 25°C over 240 minutes. However, the kinetics indicate that longer reaction times will lead to higher recoveries, given that the current recoveries are still low.

With the results shown in Figure 3, kinetic analysis was carried out by evaluating the 29 models compiled by C.F. Dickson and G.R. Heal [3]. Once the modeling was performed for all the mentioned equations, it was found that the best fit corresponds to the Zhuravlev, Leksohin, and Templeman (ZLT) model:

$$kt = \left(\frac{1}{(1 - \alpha)^{1/3}} - 1 \right)^2 \quad (1)$$

And for the Krogler and Zieger (KZ) equation:

$$k \ln t = \left[1 - (1 - \alpha)^{1/3} \right]^2 \quad (2)$$

These two models assume that diffusion is the rate-controlling step in the kinetics [4]. Based on the correlation coefficient results, the D7 model of Kröger-Ziegler was selected. This model assumes that the diffusion coefficient is not constant but instead is inversely proportional to the reaction time. Unlike the ZLT model, the Kröger-Ziegler model suggests that the diffusion coefficient decreases over time [4]. The Kröger-Ziegler model assumes that, during the initial stage of the reaction, rapid surface diffusion covers the particles with a continuous product layer [5]. This means that the applicability of this model implies that, during the leaching process with NADES, a layer of by-products forms on the mineral surface, leading to a decrease in the diffusion coefficient over time. This explains why recovery is low for many systems. In other words, as the reaction progresses, this by-product layer makes it increasingly difficult for fresh NADES to reach the particle. The exact nature of these by-products must be determined in future studies to enhance process efficiency. Moreover, this kinetic behavior also explains the trend observed in Figure 3. As the temperature increases, it is expected that these by-products will become less stable, allowing better diffusion of NADES to the particle, which accounts for the increased recovery. Additionally, at higher temperatures (75°C and 100°C), there is a moment in time when the dissolution rate increases sharply (at minute 160 and minute 200 for 75°C and 100°C, respectively). It is therefore plausible that, at this point, the combined effect of agitation and temperature enhances NADES diffusion in the system, accelerating the reaction rate.

4. CONCLUSION

Given the fit to the Kröger-Ziegler model, it can be concluded that during the leaching process with NADES, a layer of by-products likely forms on the mineral surface, causing a decrease in the diffusion coefficient over time. This explains why recoveries are low in many systems, as the by-product layer progressively hinders the access of fresh NADES to the particle. The activation energy (E_a) is 5.8 kcal/mol, indicating that the process is transport-controlled, further confirming the observations that the system depends on diffusion.

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