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Selective extraction of Zinc and Lead from oxidized flotation wastes using $C_6H_8O_7$: A green and sustainable approach

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Abstract

This study investigates the selective extraction of zinc and lead from oxidized Pb/Zn flotation wastes using $C_6H_8O_7$. The flotation waste primarily consists of goethite (FeO(OH)) with minor amounts of quartz, calcite, and dolomite. Experimental results showed extraction rates of 64.27% Zn (35.4 kg/ton ore) and 29.82% Pb (7.4 kg/ton ore), with iron exhibiting minimal extraction. Extraction efficiencies improved with higher temperatures (368 K), increased acid concentrations (192 g/L), prolonged leaching times (2 h), and reduced solid-to-liquid ratios (1/19 w/w). FT-IR analysis confirmed the dissolution of smithsonite and other carbonate bonds, while XRD Rietveld analysis indicated an increase in goethite and gangue minerals post-leaching. FESEM-EDS analyses revealed that iron oxy/oxyhydroxide structures and gangue minerals remained consistent before and post-leaching. Unlike conventional inorganic acids, the use of citric acid, an inexpensive and easily degradable organic acid, minimizes environmental impact by reducing secondary pollution risks during metal extraction processes. These findings highlight the potential for industrial application, particularly with further optimization for large-scale processing, while promoting a greener and more sustainable approach to waste management.

Keywords

Oxidized flotation waste, Organic acid, $C_6H_8O_7$, Extraction, Pb/Zn

Introduction

Pb/Zn ores are primarily found in nature as oxide, sulfide, and mixed types such as smithsonite, cerussite, and galena (Gilg et al., 2006); (Koski, 2010); (Moradi & Monhemius, 2011). Metal production can be derived from these ores and many secondary sources (mining, metallurgy, automotive, electronic waste, etc.) (P. Liu, 2018); (Halli et al., 2020). In addition, although the concentration is high in primary sources, secondary sources are more abundant (Williamson et al., 2021), and comminution costs are lower, especially in the recovery of processed small grain size content such as mine wastes (Yoğurtcuoğlu, 2023c).

Mine wastes containing these metals typically originate from lead-zinc plants (such as flotation, gravity) (Tang et al., 2020); (Nayak et al., 2021); (Yoğurtcuoğlu, 2022a) as well as wastes from other precious metal production (such as gold, silver, copper) (Chepushtanova et al., 2022); (Yoğurtcuoğlu, 2023a). These tailing wastes are among the most hazardous mining wastes due to their environmental impact and valuable metal content (Hussaini et al., 2023).

Depending on their composition, these wastes can accumulate in tailings ponds for many years or be sold. From an environmental perspective, they are particularly significant, as water presence and rainfall in these ponds accentuate the importance of recycling these metals. Flotation/leaching chemicals are recycled and/or subjected to neutralization processes in plants (Aylmore, 2016); (Yang et al., 2018); (Miettinen et al., 2019); (Zhang et al., 2021). However, as changes occur in the structures of metals during chemical processes, the presence of water in pools and/or rainwater emphasizes the importance of recycling these metals.

Additionally, recycling these wastes before natural resources are depleted not only contributes to the economy but also represents a fundamental step in sustainable environmental and waste management practices worldwide (Şahin & Erdem, 2015); (Doğan-Sağlamtimur et al., 2019).

For these reasons, numerous studies have been conducted on recycling secondary wastes and low-grade ores. These are classical and new technologies, such as gravity, flotation, pyrometallurgy, and hydrometallurgical methods, and the processes in which these methods are carried out together.

Jian et al. (2019) studied the separation of gangue by biconical dense media cyclone (BDMC) before flotation from a low-grade Pb-Zn sulfide ore with 11.34% precious content. As a result of the application, 7.92% Pb and 12.50% Zn extraction were obtained, with a recovery of 51.22% (Jian et al., 2019).

Many studies have been carried out on the extraction of these metals through hydrometallurgical processes using three different types of agents and their combinations. Alkaline solutions and salt solutions are low-cost, selective reagents. However, zinc can be extracted from solutions such as ammonia solutions, while metals such as lead precipitate as hydroxide under the same conditions without forming a complex (Yin et al., 2010).

Ehsani et al. (2019) examined lead and zinc extraction of smithsonite ores (23.43% Zn) in an alkaline medium. While 4-71% Zn and 18-47% Pb extractions were obtained at 1-4 M NaOH concentrations, it was determined that these extractions decreased in the leaching time range of 1800-14400 s (Ehsani et al., 2019).

When Pb extraction from Zn oxide was investigated by alkali leaching, optimum test conditions were liquid-to-solid ratio 5:1 mL/g, stirring speed 650 r/min, Na_2EDTA concentration 0.12M, initial NaOH concentration 0.5M, leaching temperature 70°C, and the leaching time was 120 min. Under these conditions, lead, zinc, fluoride, and chloride were extracted at approximately 90%, 1%, 63%, and 90%, respectively (Q. Liu et al., 2014).

Although inorganic acids, especially strong acids such as H_2SO_4, HCl, HNO_3, and HF, are generally successful in the recovery of metals, since they affect all metals, they have disadvantages such as removing unwanted metals, especially iron, and high corrosion and environmental degradation difficulties (Yin et al., 2010). A few examples of these dissolution methods can be given as follows.

Sulfuric acid and ferric sulfate leaching were applied to mixed Pb-Zn flotation wastes from the Bama processing plant (Isfahan-Iran). The optimum conditions of the model were approximately 320 rpm stirring speed, 1.14 M sulfuric acid concentration, 2.49 acid/ferric sulfate ratio, 10.10 ml/g liquid/solid ratio, and 80 °C temperature; zinc extraction was obtained with approximately 94% (Asadi et al., 2017).

In addition to classical roasting processes, microwave heating processes have also been found to have applications in pyrometallurgical processes. A study was carried out in which the extraction of zinc from blast furnace slag with different inorganic acids in a microwave environment was investigated. This study determined that, especially in the dissolution of sulfuric acid, zinc was extracted at high levels, and iron remained at very low levels (Vereš et al., 2011).

Organic acids, including citric (Schwab et al., 2008); (Ke et al., 2020); (W. Hu et al., 2021), oxalic (Lee et al., 2006); (Lee et al., 2007); (Kursunoglu et al., 2021); (Wang et al., 2022), and acetic (Nagib & Inoue, 2000); (Kuramochi et al., 2005); (Aydoğan et al., 2007); (Jakmunee & Junsomboon, 2008); (G. Hu et al., 2022)), offered an environmentally friendly and sustainable alternative to traditional mining methods. These acids provide several benefits, including post-process decomposition and selective metal extraction. This use of reagents aligned with the increasing global push for greener, less resource-intensive extraction technologies. However, their metal extraction capabilities can sometimes be limited due to their relatively weak acidity. Citric acid, in particular, has been shown to support zinc solubility more effectively than other metals, leading to higher zinc extraction compared to formic acid, succinic acid, and oxalic acid (Burckhard et al., 1995); (Halli et al., 2020). While citric acid also dissolves a small amount of iron, it is particularly effective in extracting higher levels of lead (Hamuyuni et al., 2018).

The efficiency of citric acid for multi-metal recovery was a significant advantage, as it allows for the extraction of several valuable metals simultaneously. This method is not only economically attractive but also reduces the environmental burden associated with separate extraction processes. For example, Irannajad et al. (2013) investigated the recovery of zinc from Angoran Pb/Zn wastes, characterized by high zinc oxide content (16.1%) alongside significant amounts of CaO (21.3%), SiO_2 (21.2%), and Al_2O_3 (8.0%), with minimal Fe_2O_3 (3.59%). Their study examined particle size (50-350 microns), solid-to-liquid ratio (1:30-1:5), acid concentration (0.05-1.5 M), leaching duration (30-150 minutes), and temperature (25-80°C) parameters, achieving zinc recoveries of 42-70% and up to 82% in optimized conditions (Irannajad et al., 2013). Such results demonstrated the potential of citric acid in extracting multiple metals from complex ore bodies.

In this context, the solubility of citric acid and its effectiveness in degrading metal oxides, including zinc, lead, and iron, are of significant importance. The dissolution reactions of citric (Eq. 1) (Cavus & Kuslu, 2005); (Yoğurtcuoğlu, 2023c) acid in water are as follows:

$$C_6H_8O_{7(s)} + 3H_2O_{(aq)} \leftrightarrow C_6H_5O_7^{3-}{}_{(aq)} + 3H_3O^+{}_{(aq)} \qquad (1)$$

When reacting with metal oxides, citric acid forms soluble metal citrate complexes, as seen in the reactions for zinc (Eq. 2) (Larba et al., 2013), lead (Eq. 3) (Halli et al., 2018), and iron (Eq. 4) (Yoğurtcuoğlu, 2023b).

$$1.5ZnO + C_6H_8O_7 = 1.5Zn^{2+} + C_6H_5O_7^{3-} + 1.5H_2O \qquad (2)$$

$$1.5PbO + C_6H_8O_7 = 1.5Pb^{2+} + C_6H_5O_7^{3-} + 1.5H_2O \qquad (3)$$

$$Fe_3O_4 + C_6H_8O_7 + 2e^- = 3FeO + C_6H_5O_7^{3-} + H_2O + H^+ \qquad (4)$$

With all this information, this study focuses on the extraction of zinc, lead, and iron from oxidized flotation tailings of the Kayseri-Yahyali region using citric acid ($C_6H_8O_7$), a sustainable and eco-friendly leaching reagent (Padh et al., 2023). Unlike previous studies that focus solely on zinc extraction, this research investigates the recovery of zinc, lead, and iron, with special emphasis on the structural transformations of the waste materials. This broader scope of multi-metal recovery not only enhances the economic viability of the process but also reduces the environmental footprint by minimizing the need for separate leaching processes for each metal.

Characterization analyses, including FT-IR, XRD Rietveld, and FESEM-EDX, were conducted to assess the post-leaching state of the waste materials. These methods provide valuable insights into the structural and chemical changes that occur during the leaching process, confirming the effectiveness of citric acid in metal extraction while maintaining the integrity of the surrounding environment.

This integrative approach underscores the originality of the current study, highlighting the potential of citric acid as a versatile and sustainable agent for multi-metal extraction. By demonstrating its efficacy in extracting multiple valuable metals, this research advances sustainable metal extraction technologies and has significant implications for industrial-scale applications, contributing to the growing demand for greener mining practices.

Material and Methods

A sample (approximately 30kg) of oxidized lead-zinc flotation wastes obtained from the Kayseri/Yahyali (Turkiye) region was first dried in an oven at 378 K to remove moisture. The dried sample was divided using sample splitting techniques and packaged into portions of approximately 100g. Since approximately 25-30g of sample was used in each experiment, the packaged samples were further repartitioned prior to the experiments. Experiments were conducted under controlled temperature and steam conditions with a stirring speed of 750-1000 rpm using magnetic stirrers (within a fume hood).

The experimental conditions are summarized in Table 1. The parameters include $C_6H_8O_7$ (citric) acid concentrations (24-192 g/L), leaching temperatures (298-368 K), leaching times (0.25-2.0 hours), and solid-to-ratios (1/19 to 2/3 w/w).

Table 1. Experimental parameters determined for the dissolution of oxidized flotation waste in citric acid media

Parameters	Value
Leaching time (hour)	0.25-0.50-0.75-1.0-2.0
Leaching temperature (K)	298-333-368
Solid-to-liquid ratios (w/w)	1/19-1/9-1/4-3/7-2/3
Acid concentration (g/L)	24-48-96-144-192

When evaluated in terms of sample weight loss due to dissolution with $C_6H_8O_7$ acid, weight losses were determined to be in the range of 13-33%.

AAS (Atomic absorption spectroscopy) analyses of zinc, lead, and iron in the liquid solutions obtained at the end of the experiments were performed using the PerkinElmer PinAAcle 500 AAS device, with results based on the average of three measurements.

Previously conducted XRF (X-ray fluorescence) analysis using a Panalytical/Zetium brand instrument revealed the presence of 6.28% ZnO, 55.48% Fe_2O_3, and 2.46% PbO were found (Yoğurtcuoğlu, 2024). Plant analysis results (Table 2) also identified Zn, Pb, and Fe concentrations as 5.51%, 2.49%, and 31.37%, respectively.

Table 2. Metal Analysis of the Flotation Waste Sample Conducted at the Plant

%	Element
31.37	Fe
5.51	Zn
2.49	Pb

According to the particle size analysis results conducted on a similar flotation waste sample, the d_{80} value was found to be 78 µm, and the d_{90} value was 112 µm (Yoğurtcuoğlu, 2023b); (Yoğurtcuoğlu, 2024).

Fourier Transform Infrared Spectroscopy (FT-IR) analysis of the leaching waste sample was performed using the Bruker-Vortex 70 device in the measurement range of 4000 to 400 cm^{-1} at Niğde Ömer Halisdemir University (NOHU) Central Research Laboratories (CRS) to identify changes in the bond structures post-leaching process.

This analysis of the waste sample revealed that the waste sample possesses an oxidized, carbonated, silicate structure. It contained valuable minerals such as smithsonite, hydrozincite, plumbojarosite, and goethite, along with gangue minerals including dolomite, calcite, and quartz (Yoğurtcuoğlu, 2022b).

XRD (X-ray diffraction) Rietveld analysis was conducted to determine the percentage of mineral content in the waste sample post-leaching. This analysis was performed using the Panalytical Empyrean instrument with the following settings: a current of 45 mA, a voltage of 40 kV, and a scanning range of 5-90 degrees.

FESEM (Field Emission Scanning Electron Microscope) images were taken at Kayseri Erciyes University Technology Research and Application Center (Gemini Zeiss 500) for the main waste and the leaching waste samples. The main waste (secondary waste) was obtained from the flotation process, while the leaching waste (tertiary waste) was collected after a 1-hour leaching process at 333 K, with a solid-to-liquid ratio of 1/9 (w/w) and a citric acid concentration of 96 g/L. EDS analyses were performed at two different points on these images.

Results and Discussion

Metal extractions, according to the experimental processes

Preliminary evaluation leaching was carried out at the beginning of the experimental processes. This process was tried to be chosen from the most appropriate point of all experiments. As experimental conditions, citric acid concentration was chosen as 96 g/L, leaching temperature 333K, leaching process time 1.0 hour, and 1/9 solid ratio (S/L, w/w). One of these determined parameter values was changed in all parameter processes, and the others were kept constant. Therefore, the effectiveness of the parameters was examined in this context as a result of preliminary evaluation experiments. Metal extractions were obtained around 24-26% of lead, 54-56% of zinc, and 17-19% of iron. In the experiments where the difference in citric acid concentration values (between 24-48-96-144-192g/L) was examined (Figure 1), other parameters were kept constant and determined as 1.0 hour leaching time, 333K leaching temperature, and 1/9 (w/w) solid-to-liquid ratio. As a result of the experiments, lead extraction efficiencies increased from 16.42% to 29.82%. With the increase in concentration, zinc extraction efficiencies increased between 35.39-61.18%. Iron extraction efficiencies (20.29% to 12.64%) did not increase and even decreased by about 7-8% with increasing acid concentration. The highest extractions in this parameter were determined for zinc metal. The metal extraction shows a positive correlation with the increase in citric acid concentration. Furthermore, the amounts of extracted metals increase within the ranges of 19.50-33.71 kg/ton ore for zinc and 4.09-7.43 kg/ton ore for lead, while iron, in contrast, decreases from a maximum of 63.66 kg/ton ore to 39.67 kg/ton ore. According to this graph, it is concluded that the increase in citric acid concentration is a critical factor for Pb and Zn extraction. However, the inverse effect observed for Fe suggests that higher concentrations of citric acid may negatively impact its extraction. This discrepancy could be attributed to differences in the complexation kinetics of Fe in a citric acid medium. While 15% Pb was extracted in brine leaching experiments at 60 °C for 1.0 hours with similar samples, no zinc extraction was realized. In experiments with the same conditions except for acid, 85% Zn and 70% Pb were obtained from the hydrochloric acid experiment in the salt medium. In the sulfuric acid salt leaching experiment, 80% Zn and 29% Pb were dissolved (Yoğurtcuoğlu, 2022a). The highest extraction was 67% Zn, 57% Pb, and 28% Fe in citric acid leaching experiments in the salt medium (200 g/L NaCl, 1 hour, 60°C, and 10% solids) (Yoğurtcuoğlu, 2022b). In the studies where the experiments with organic and inorganic acids were compared in terms of selective metal extraction, it was determined that zinc extraction of citric acid is higher than lead and that iron has lower extraction in organic acids (Hamuyuni et al., 2018); (Kaya et al., 2020); (Ke et al., 2020); (Hussaini et al., 2021). In this study, the extraction of zinc was 20-30% higher than lead and 30-40% higher than iron. The extraction of zinc, lead, and iron from electric arc furnace (EAF) dust using 27 different leaching media was investigated. After dissolution with 0.94 M and 0.09 M citric acid, approximately 77-37% Zn, 19-17% Fe, and 50-1% Pb were extracted, respectively (Halli et al., 2017).

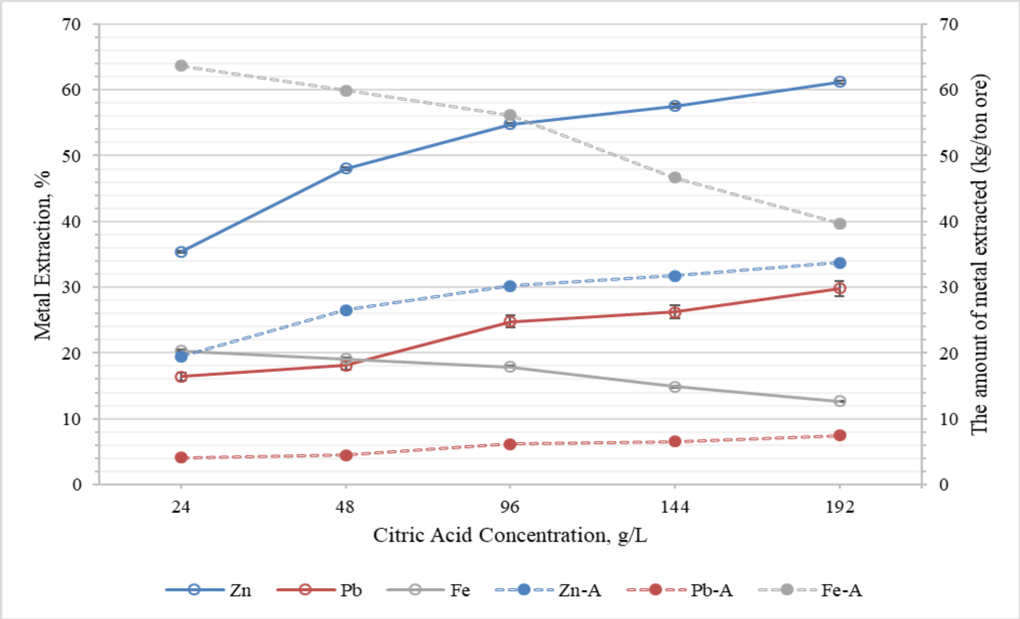


Figure 1. Metal extractions as a function of citric acid concentrations (24, 48, 96, 144, and 192 g/L) at a leaching temperature of 333K, leaching time of 1.00 hour, and a solid-to-liquid ratio of 1/9 (w/w).

In the experiments investigating the effect of temperature differences (Figure 2), the leaching was performed at temperatures of 298K, 333K, and 368K, with a citric acid concentration of 96 g/L, a leaching time of 1.0 hour, and a solid-to-liquid ratio of 1/9 (w/w). The lead extraction efficiency at 298K was approximately 18%, and with increasing temperature, there was a trend of about a 7% increase, reaching approximately 25%. Zinc extraction at 368K leaching temperature reached 64.27%, and the leaching difference between 298K and 368K was 41.82%. Similarly, iron extraction increased from 14.08% to 21% with a 7% rise, following a trend similar to zinc. Metal extraction amounts followed similar trends, with zinc increasing from 12.37 kg/ton ore at 298K to 35.41 kg/ton ore at 368K. Lead extraction increased with temperature from 4.52 kg/ton ore to 6.27 kg/ton ore. Iron, benefiting positively from temperature, was recovered as 44.16 kg/ton ore at 298K and approximately 66.09 kg/ton ore at 368K. In terms of citric acid concentration, lead exhibited a higher extraction, while iron showed a lower extraction. However, in the case of temperature increase, both zinc and iron showed higher metal extraction amounts. The Electric Arc Furnace (EAF) dust primarily contains Fe, Mn, Zn, Pb, and Cr, with the Zn and Pb content negatively affecting the steel production process. Therefore, an alternative alkaline (NaOH) roasting process was investigated as a substitute for citric acid leaching. In the direct citric acid leaching process, at a concentration of 0.4 M citric acid and a leaching time of 120 minutes, the extraction of Zn, Pb, and Fe was conducted at temperatures of 30°C, 40°C, and 50°C, resulting in approximately 62%, 80%, and 40% Zn, 39%, 62%, and 37% Pb, and 10% Fe at all temperatures, respectively (Halli et al., 2018).

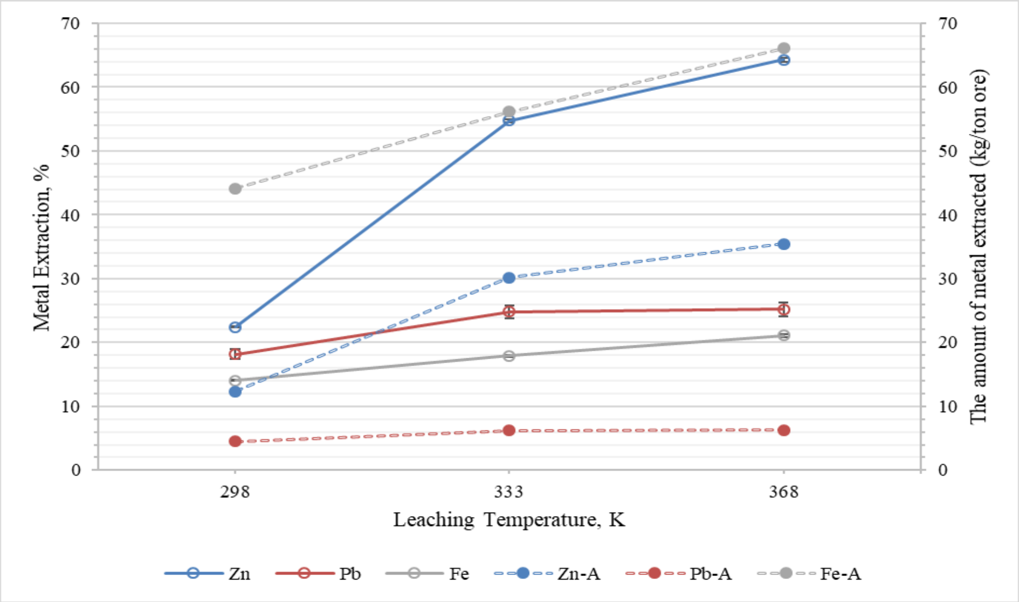


Figure 2. Metal extractions as a function of leaching temperatures (298-333-368K) at a citric acid concentration of 96 g/L, leaching time of 1.00 hour, and a solid-to-liquid ratio of 1/9 (w/w).

In Figure 3, leaching times were set at 0.25, 0.5, 0.75, 1.0, and 2.0 hours, while other experimental conditions, including a citric acid concentration of 96 g/L, a leaching temperature of 333K and a solid-to-liquid ratio of 1/9 (w/w), were kept constant. As the leaching time increased, the metal extraction efficiencies exhibited an increasing trend. At 15 minutes, the dissolution was 20.87%, and after 2.0 hours, the increase was approximately 7.94%, reaching a final value of 28.81%. Zinc extraction increased from 37.93% to 63.2% after 2.0 hours. Iron extraction also showed a time-dependent increase, rising from 10.57% to 18.12%, with a 7.55% increase. Parallel to these efficiencies, the lead metal recovery ranged from 5.20 to 7.17 kg/ton ore, zinc metal recovery ranged from 20.90 to 34.82 kg/ton ore, and iron metal recovery ranged from 33.15 to 56.83 kg/ton ore. In the study on flotation wastes, it was stated that zinc dissolved 90-91% and lead dissolved 9-10% at 1M citric acid concentration, 3 hours, 80 °C leaching temperature, and 20% solid/liquid ratio (Hussaini et al., 2021). In the direct citric acid leaching of EAF dust, the variations in leaching time and citric acid concentration were investigated. At acid concentrations of 0.05 M, 0.1 M, and 0.2 M, the extraction efficiencies of zinc remained around 35% over the 0-120 minute range. However, at acid concentrations of 0.4 M and 0.8 M, the extraction of zinc increased from 50% to 70-80% with increasing leaching time, showing a positive effect of time on extraction. Iron, however, did not exceed 10% extraction under all time and acid concentration conditions. Lead exhibited a similar trend to zinc, reaching up to 50% extraction at 0.4 M acid concentration. At 0.8 M citric acid, lead extraction increased from 70% to 90% with the extension of leaching time (Halli et al., 2018). In this study, an increase in metal extraction efficiencies with respect to time is observed for both zinc and lead, while iron extraction remains at lower efficiencies. However, although the lack of significant increases in extraction efficiencies for these two metals can be related to the acid concentration, it is evident from Figure 3 that these efficiencies were not achieved even at higher acid concentrations. Furthermore, it is anticipated that the waste sample's structure, composition, and particle size could influence the extraction efficiencies. Moreover, in the subsequent phase of the study conducted by Halli et al. (2018), it was demonstrated that Zn and Pb extraction efficiencies reached 100% and 88%, respectively, through alkaline roasting. Therefore, it appears that the effectiveness of citric acid could be further enhanced by integrating it with an alternative process.

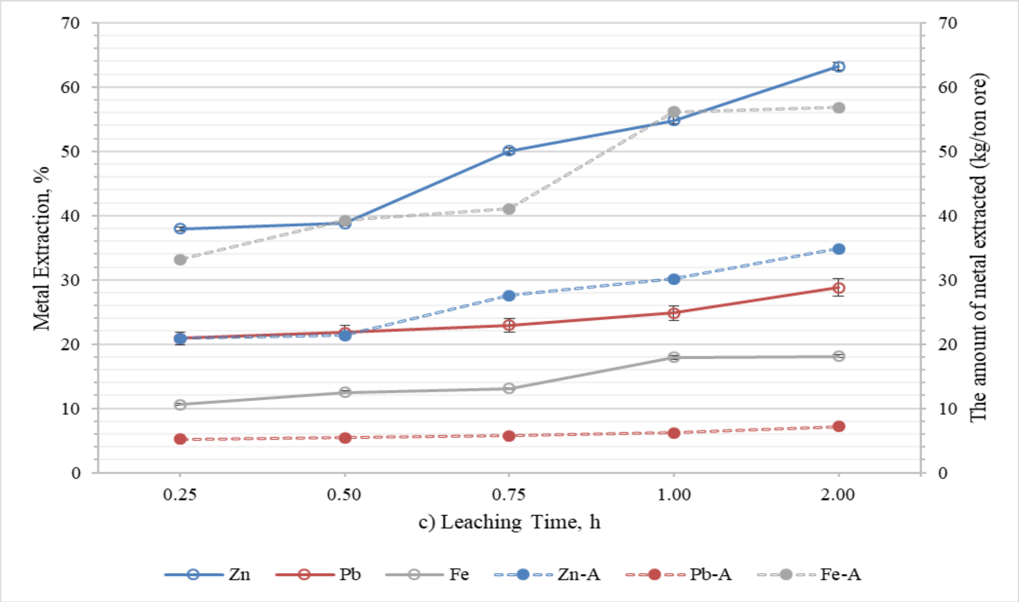


Figure 3. Metal extractions as a function of leaching times (0.25-0.50-0.75-1.00-2.00) at a citric acid concentration of 96 g/L, leaching temperature of 333K, and a solid-to-liquid ratio of 1/9 (w/w).

According to Figure 4, the solid-to-liquid ratio was varied between 1/19, 1/9, 1/4, 3/7, and 2/3 (w/w), with the other experimental conditions fixed at a citric acid concentration of 96 g/L, a leaching temperature of 298K, and a leaching time of 1.0 hour. As a result, the lead dissolution showed a decrease of 16.73% (from 6.57 kg/ton ore to 2.41 kg/ton ore), with values ranging from 26.4% at a 1/19 (w/w) ratio to 9.67% at a 2/3 (w/w) ratio. Zinc dissolution decreased from 60.26% to 12.73%, and the metal extraction dropped from 33.20 kg/ton ore to 7.01 kg/ton ore. Iron dissolution decreased from 22.07% to 8.36%, with metal extraction also dropping from 69.23 kg/ton ore to 26.23 kg/ton ore. In conclusion, the increase in the solid-to-liquid ratio is inversely proportional to the dissolution rate and, consequently, to the metal extraction amounts.

Among all experiments, the highest zinc recovery efficiency was observed at 368K, with 64.27% (35.41 kg/ton ore), while the highest lead extraction of 29.82% (7.43 kg/ton ore) was achieved in the citric acid concentration increase experiment at 192 g/L. The highest iron extraction of 22.07% to 69.23 kg/ton ore was obtained in the experiment investigating the effect of the solid-to-liquid ratio, specifically at a ratio of 1/19 (w/w). It is possible to extract 82-83% zinc and dissolve <0.5% iron after a 2-hour test at pH 2, 40°C temperature, 20% liquid-to-solid ratio, in a sulfuric acid environment created by lead-zinc dissolution from non-sulfurous ore wastes, with lead extraction greater than 60% was achieved in the presence of potassium sodium tartrate (40-80°C) (Kursunoglu et al., 2020). In a study demonstrating that citric acid (CA) is an effective washing agent for zinc (Zn) extraction from contaminated soils, Zn extraction efficiency increased with the liquid-to-solid (L/S) ratio, rising from 17.47% at 10 mL/g to 51.26% at 30 mL/g. However, increasing the L/S ratio from 20 mL/g to 30 mL/g resulted in less than a 10% improvement in extraction efficiency. At lower L/S ratios, incomplete dispersion of soil particles limited contact between Zn and the citric acid solution, reducing efficiency. Higher L/S ratios improved soil dispersion and enhanced interactions between Zn ions and citric acid molecules. However, excessively high L/S ratios increased costs, energy and water consumption, generating larger volumes of metal-containing wastewater (W. Hu et al., 2021). Similarly, this study observed that increasing the L/S ratio negatively affected the extraction efficiency of zinc and other metals.

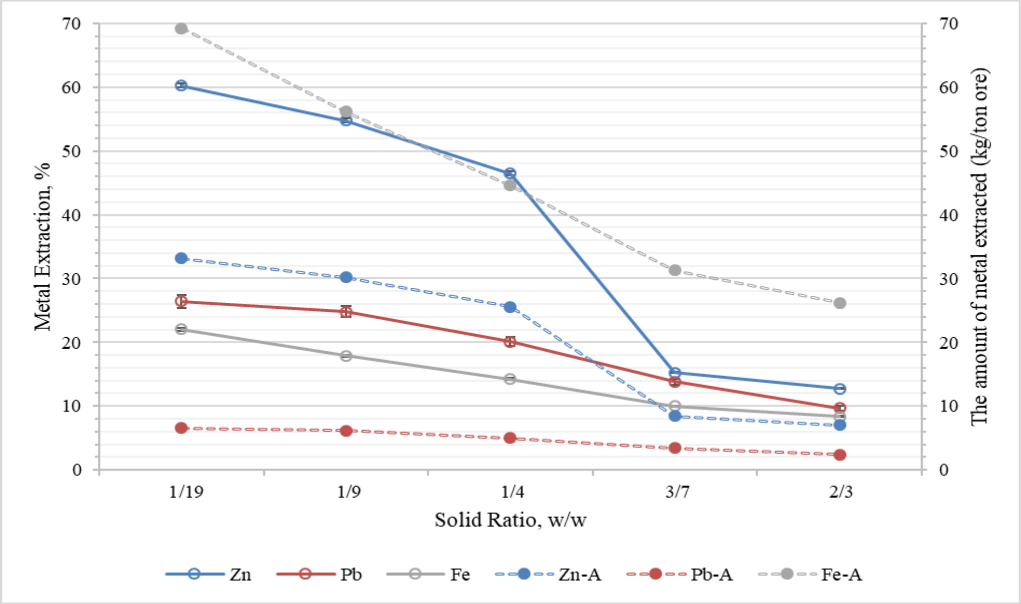


Figure 4. Metal extractions as a function of solid-to-liquid ratios (1/19-1/9-1/4-3/7-2/3 (w/w)) at a citric acid concentration of 96 192 g/L, leaching temperature of 333K, leaching time of 1.00 hour.

Characterization studies

In the XRD analysis of the waste sample used in the experiment, previous studies have determined that Pb/Zn/Fe minerals had an oxide and carbonate structure (Yoğurtcuoğlu, 2022a). The results of the chemical analysis revealed that iron, zinc, and lead were the most abundant elements, respectively.

Figure 5 presents the FTIR analysis of the leaching waste sample, also called the tertiary waste sample. The peaks observed in the leaching process waste are 3625, 3128, 2113, 1633, 1416, 1006, 908, 797, and 524 cm^{-1}. When these peaks are compared with the main waste sample (Yoğurtcuoğlu, 2024), it is evident that especially the 2349 cm^{-1} (shallow) and 1416 cm^{-1} (deep) peaks diminish significantly after the process. In addition to the C=O (or O=C=O) bonds of these two peaks (Chuprov et al., 2006), (Kauffman et al., 2011), (Yoğurtcuoğlu & Alp, 2023), the 1435 cm^{-1} peak is also related to the zinc oxide structure (Hosseini & Forssberg, 2006). This change is thought to be related to the dissolution of zinc in the waste sample after the citric acid leaching process.

Figure 5. FT-IR Analyses of leaching waste

In the XRD Rietveld analysis of the post-leaching waste sample (Figure 3), 8.0% dolomite ($CaMg(CO_3)_2$), 68.9% goethite ($FeO(OH)$), 19.3% quartz (SiO_2), 0.3% calcite ($CaCO_3$), 0.9% smithsonite ($ZnCO_3$), 1.2% hydrozincite ($Zn_5(CO_3)_2(OH)_6$), and 1.4% plumbojarosite ($PbFe^{3+}{}_6(SO_4)_4(OH)_{12}$) minerals were identified. These results showed that lead and zinc minerals remain around 3-4% of the entire content, and the remaining content primarily consists of iron oxy/oxy hydroxide-containing minerals and other gangue minerals. These analysis results further supported the conclusion that the valuable content dissolved during the extraction process remained in low amounts. Compared to the analysis of a similar sample, the primary waste sample contained lower amounts of gangue minerals (approximately 8% dolomite, 14% quartz, and 42% goethite). However, post-citric acid leaching, the waste sample exhibited an approximate 45% increase in gangue mineral content. Additionally, similar proportions of gangue minerals were identified in the leach residues from acetic acid, with no calcite detected. The amounts of smithsonite, hydrozincite, and plumbojarosite were found to be approximately 4.6% higher compared to those in the citric acid leach residue (Yoğurtcuoğlu, 2024). This observation aligns with the XRD Rietveld analysis, which corroborates the similar extraction trends for zinc and lead, both of which are abundantly present in the main waste.

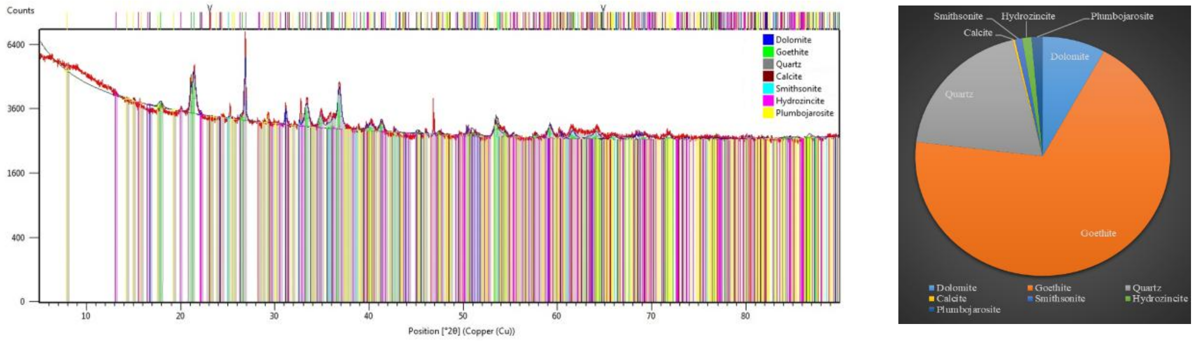
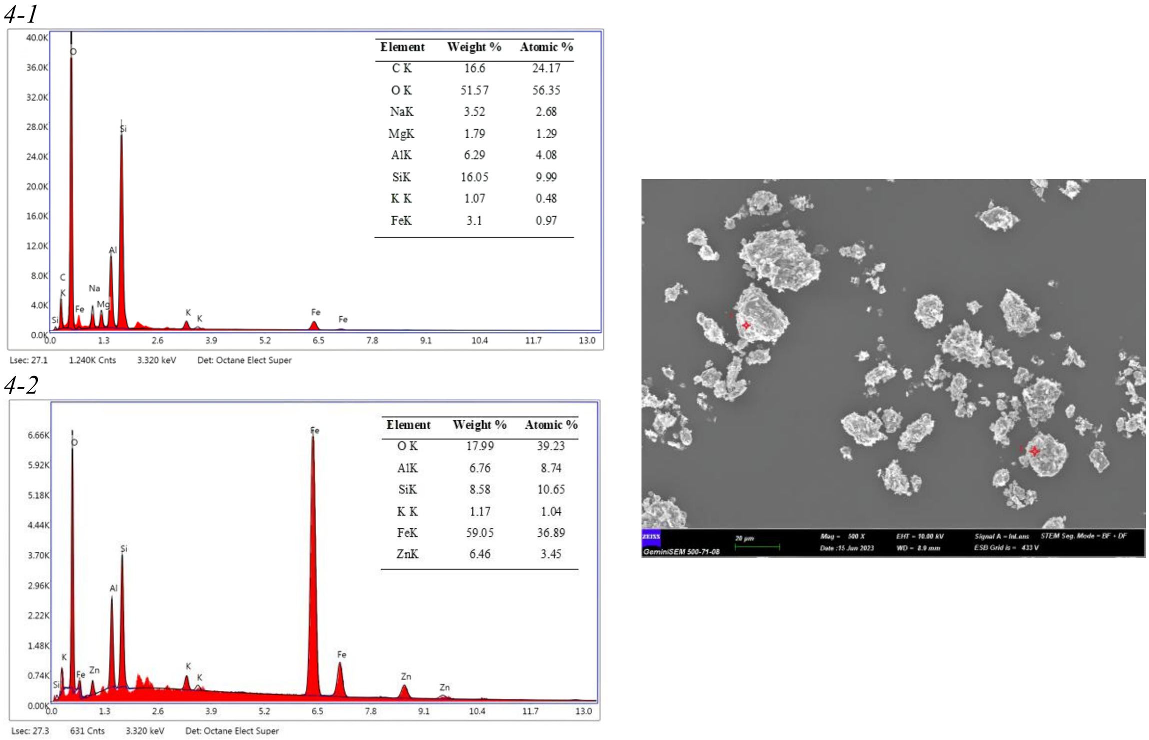


Figure 6. XRD Rietveld analysis of leaching waste

It was determined that O, C, and Si elements were particularly concentrated in the FESEM analysis image of the main waste sample (Figure 6) and at the EDS-1 point (Fig. 6-1). This indicates that the imaging was taken from a point where silicate/carbonate structures containing quartz, calcite, dolomite, and clay structures with aluminium silicate (feldspar). Additionally, the Fe element suggests the presence of an iron oxy/oxyhydroxide. At the EDS-2 point (Fig. 6-2), this oxidized iron mineral also reveals the presence of quartz and oxidized zinc minerals.

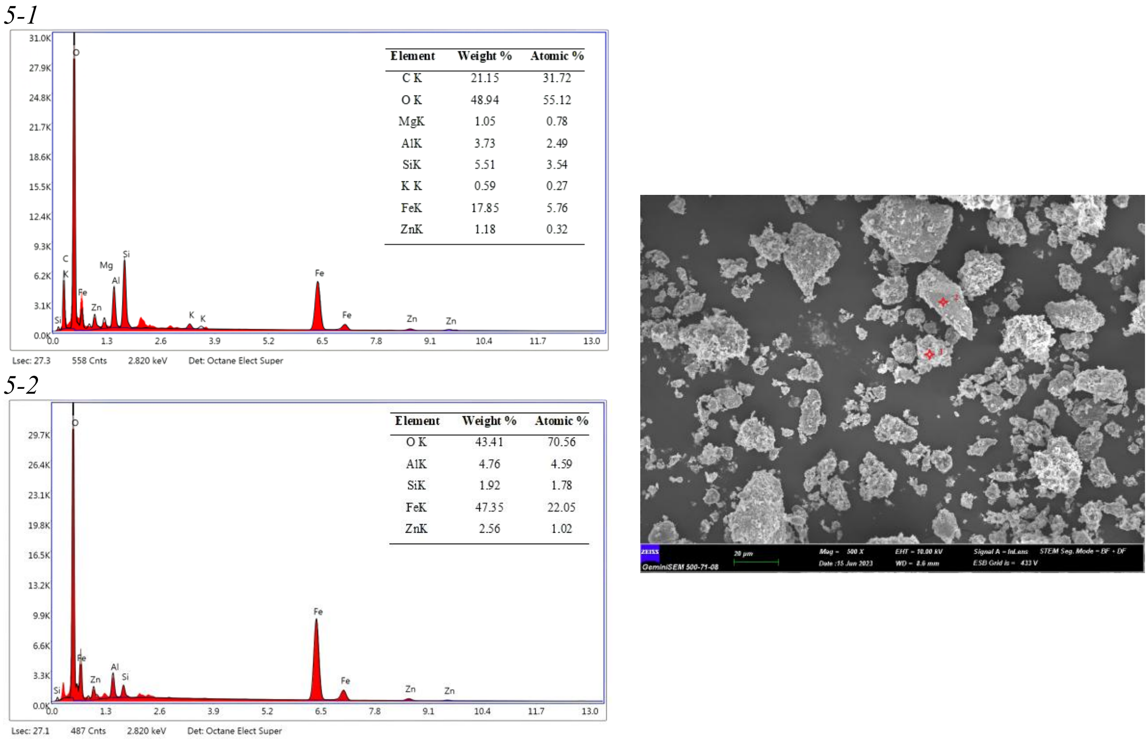


Element	Weight %	Atomic %
C K	16.6	24.17
O K	51.57	56.35
NaK	3.52	2.68
MgK	1.79	1.29
AlK	6.29	4.08
SiK	16.05	9.99
K K	1.07	0.48
FeK	3.1	0.97

Element	Weight %	Atomic %
O K	17.99	39.23
AlK	6.76	8.74
SiK	8.58	10.65
K K	1.17	1.04
FeK	59.05	36.89
ZnK	6.46	3.45

Figure 7. FESEM image of main waste (right), 7-1. the image of EDS-1 point (left top image), and 7-2. EDS-2 point (left bottom image)

FESEM images of the waste sample post-leaching are shown in Figure 7. Silicate, oxide, and carbonate structures were predominantly detected at the EDS-1 point (Fig. 7-1) taken from this image. Additionally, significant iron content and small amounts of zinc were identified. Minerals with increased iron oxide content were observed at the EDS-2 point (Fig. 7-2), which corresponds to the goethite mineral identified in the XRD Rietveld results.



5-1

Element	Weight %	Atomic %
C K	21.15	31.72
O K	48.94	55.12
MgK	1.05	0.78
AlK	3.73	2.49
SiK	5.51	3.54
K K	0.59	0.27
FeK	17.85	5.76
ZnK	1.18	0.32

5-2

Element	Weight %	Atomic %
O K	43.41	70.56
AlK	4.76	4.59
SiK	1.92	1.78
FeK	47.35	22.05
ZnK	2.56	1.02

Figure 8. FESEM image of leaching waste (right), 8-1. the image of EDS-1 point (left top image), and 8-2. EDS-2 point (left bottom image)

The zinc contents determined in the waste sample can be attributed to the successful extraction of these valuable metals through citric acid leaching, as the remaining zinc post-leaching process corresponds to an extraction rate of approximately 60–65%. Therefore, both the leaching parameters and characterization studies indicate that valuable metals can be efficiently extracted using this environmentally friendly organic acid while the iron content selectively increases in the solution.

These findings collectively demonstrate the effectiveness of the citric acid dissolution process in extracting valuable metal contents, particularly zinc, as confirmed by the characterization studies.

Conclusions

Oxidized flotation wastes contain valuable, unextracted metals. This study investigated the extraction of lead, zinc, and iron from these wastes using citric acid ($C_6H_8O_7$) as a leaching agent. In addition to extraction processes, comprehensive characterization analyses were conducted, particularly for the leached residues.

Preliminary leaching tests were performed with 96 g/L citric acid concentration, at 333 K, for 1 hour and with a solid-to-liquid ratio of 1/9 (w/w). These initial conditions resulted in metal extractions of 54.8% Zn (30.2 kg/ton ore), 24.8% Pb (6.2 kg/ton ore), and 17.9% Fe (56.2 kg/ton ore).

Experiments examining citric acid concentrations revealed that increasing the concentration improved metal extractions, achieving extraction rates of 61% Zn (33.7 kg/ton ore), 30% Pb (7.4 kg/ton ore), and 13% Fe (39.7 kg/ton ore). Lead exhibited the highest extraction efficiency and amount in this set of experiments. Similarly, higher leaching temperature and time also enhanced extractions, with the maximum zinc extraction (64%-35.4 kg/ton ore) observed at 368 K. The variation in the solid-liquid ratio demonstrated that reducing the solid content from 2/3 (w/w) to 1/19 (w/w) enhanced the extraction efficiency. The highest iron extraction rate, 22% Fe (69.2 kg/ton ore), was achieved under the 1/19 (w/w) condition.

Characterization analyses supported these findings. FT-IR analysis indicated reductions or disappearance of zinc oxide and carbon-related bonds in the leached residues. XRD Rietveld analysis identified dominant waste components as goethite, quartz, and dolomite. SEM-EDS analysis further confirmed that zinc oxide structures diminished post-leaching, leaving gangue minerals more prominent.

In conclusion, citric acid was demonstrated to be an effective and environmentally friendly leaching agent for zinc extraction. This study highlights the potential for utilizing oxidized flotation wastes, particularly for zinc extraction, while offering advantages such as low corrosion and reduced iron dissolution.

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