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PROCESS INTENSIFICATION IN HYDRO- AND ELECTROMETALLURGY

Recovery of Lead and Zinc from a Citric Leach Solution of a Non-sulfide Type Ore Flotation Tailing via Precipitation Followed by Solvent Extraction

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The recovery of zinc (Zn) and lead (Pb) from a citric leach solution of a non-sulfide type ore flotation tailing was examined utilizing sulfuric acid precipitation followed by solvent extraction using di(2-ethylhexyl) phosphoric acid (D2EHPA) as the extractant. Following lead precipitation (98.9%) with sulfuric acid, the pregnant leach solution was sent to solvent extraction stage with D2EHPA for the separation of zinc from the other impurities such as Ca, Mg and Fe. The best solvent extraction conditions were determined to be a concentration of 20% D2EHPA, temperature of 25 °C, contact time of 10 min and phase ratio of unity. Under the optimum conditions, 98.3% Zn was extracted into the organic phase in a single contact at a pH of 3.6, along with a significant amount of Ca (79%) and minor amounts of Mg (14.7%) and Fe (8.6%). At pH 4.5, the loaded organic solution was carried to the scrubbing stage, where 20 g/L zinc solution was used to remove approximately 91% Ca and 34% Mg from the organic solution. At a pH of 0.25, the loaded organic solution was almost completely stripped of zinc and 27% of calcium in two steps.

INTRODUCTION

Mining wastes are produced in massive quantities by the mining industry. Tailings are one of the most hazardous of these mine discharges because of their very fine particle sizes and the chemicals required to treat the ore. Concerns such as acid mine drainage (AMD) arise due to oxidation of some of these wastes.[1] Over the years, the interest in treating mine tailings to recover valuable metals has been on the rise. The processing of the low-grade ore has resulted in an increase in the tailings amount produced by the extractive industry. This issue has the potential to cause environmental destruction and will necessitate significant investment to control tailings disposal. Tailings are produced during the crushing, grinding, flotation, cycloning and drying processes in the processing of zinc. These tailings are stored in dams, which have a direct impact on the environment. The poisoning of watercourses by toxic metals found in the tailings is one of the main concerns associated with this method of disposal.[2] Lead and zinc recovery from flotation tailings is one of the focused topics in this field.[3] This is because using these tailings to recover the two metals at the same time reduces the volume of harmful and toxic mine wastes, while simultaneously producing more Pb and Zn to meet the increasing Pb-Zn demands without going through conventional mining and deteriorating the land.[4,5] For instance, an estimated 4 billion tons of bauxite residue is stored worldwide.[6] Zinc is a significant non-ferrous metal that is widely used,

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after aluminum and copper.[4,7] Zinc ores are classified as sulfide minerals or oxide minerals in nature. Since sulfide mineral resources are becoming increasingly exhausted, zinc oxide minerals have emerged as viable replacements to sulfurous ores. Zinc extraction techniques from oxide ores are still evolving.[8] The recovery of Zn from secondary resources has been extensively studied in recent years because of the anticipated rise in the demand for zinc in the near future.[4,7,9,10]

The two widely used methods for zinc recovery are pyrometallurgy and hydrometallurgy but hydrometallurgy is preferred.[11,12] In the first stage of hydrometallurgy, which is leaching, inorganic acids such as sulfuric acid,[10,13–18] hydrochloric acid[13,16] and nitric acid[19] were extensively used as a lixiviant in the literature. Also, alkaline lixiviants such as $NaOH$[20,21] and NH_3[22] were demonstrated in the literature. Alkaline leaching has been extensively considered in research because of its ability to dissolve zinc without dissolving iron, freeing the solid residue of hazardous waste.[21] In recent years, the use of organic acids as lixiviants has been studied in detail[23,24] as these organic acids are biodegradable.[9,24–26] Organic acids, such as malic, citric, formic, oxalic, tartaric and ascorbic, were tested for the recovery of zinc and lead from such a specific flotation tailing. The authors made a comparison with inorganic acids and concluded that inorganic acids were more Zn dissolving than organic acids, but organic acids were more environmentally friendly. Their research showed that malic and citric acids were the organic acids with the best leaching performance of $>$ 90% Zn dissolution.[27]

The use of solvent extraction in hydrometallurgical processes has grown in importance because of rising demand for metals with high purity, environmental issues, the desire to reduce costs of production and the continued degradation of high-grade ores.[28] Pb is typically found in Zn-bearing materials' leach solutions, and some researchers have investigated different methods of completely and selectively removing Pb from the leach solution. Halli et al. (2020) used precipitation with sulfuric acid at room temperature to completely remove Pb from an organic leach solution of electric arc furnace (EAF) dust. After these precipitation steps, solvent extraction was carried out to separate zinc from other impurities. The researchers found that higher pHs are required for high zinc extraction in organic leach solutions.[29] Organophosphorus extractants, namely bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272), di (2- ethylhexyl) phosphoric acid (D2EHPA) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC88A), were the most commonly used extractants for this purpose. D2EHPA is the most popular of these extractants since it is the cheapest of the three, as demonstrated by its use in most zinc refineries.[29–31] The chemical structure of D2EHPA is given in the online supplementary material (see supplementary Fig. S1). Solvent extraction is an equilibrium process, and the equilibrium between the ions in the raffinate phase and extract phase is nonlinear. The equilibrium process is given as (Eq. 1):

$$M^{n+}_{\mathrm{aq}} + \mathrm{nHR} \rightleftharpoons \mathrm{MR_n} + \mathrm{nH}^{+}_{\mathrm{aq}} \tag{1}$$

HR: Extractant (organic).
MR_n: Metal–organic extracted species.
H^+: proton released by extractant to be exchanged with metal species M^{n+}

The metal ion distribution between the aqueous and organic phases is influenced by a number of variables, which include extraction/equilibrium pH, aqueous to organic (A/O) volume ratio, extractant concentration and type, solution composition and, in some cases, the diluent employed.[28] For specifically zinc extraction, D2EHPA is used as extractant dissolved in an aliphatic diluent. Equations 2 and 3 might represent the extraction of zinc.

$$Zn^{2+}_{(\mathrm{aq})} + 1.5(\mathrm{HR})_{2(\mathrm{org})} \rightleftharpoons \mathrm{ZnR.2HR}_{(\mathrm{org})} + 2\mathrm{H}^{+}_{(\mathrm{org})}\ \text{at the liquid} - \text{liquidinterface} \tag{2}$$

$$\mathrm{2ZnR.2HR}_{(\mathrm{org})} \rightleftharpoons \mathrm{2ZnR}_{2(\mathrm{org})} + (\mathrm{HR})_{2(\mathrm{org})}\ \text{in the extract phase} \tag{3}$$

Equations 2 and 3 show that the extraction of zinc using D2EHPA as extractant involves both heterogeneous and homogeneous complex reactions occurring concurrently in both liquids, resulting in two metal-complex species in the extract phase.

Numerous studies have been carried out on zinc solvent extraction from inorganic pregnant leach solution (PLS) using D2EHPA as extractant.[32–39] More than 95% of Zn extraction with D2EHPA was reported between 25 and 40 °C at very low pH between 1 and 3 for most of the researchers. The solvent extraction of zinc from organic leach solutions using D2EHPA, on the other hand, has not been extensively reported compared to inorganic acids. The recovery of lead and zinc from a malic acid leach solutions of a non-sulfide Pb-Zn flotation tailing by means of precipitation followed by solvent extraction was studied in our previous work.[4] It is obvious that the extraction mechanism that occurs in inorganic acids differs from that of organic acids since metal ion extraction behaves differently. Therefore, the present study focused on the separation of lead and zinc from a citric acid leach solution of non-sulfide Pb-Zn flotation tailing, using precipitation, solvent extraction, scrubbing and stripping as purification methods. In addition, a recycling process of the extractant was introduced using HCl such that D2EHPA extractant was used in a closed loop to ensure environmental and economic benefits.

MATERIALS AND METHOD

Materials

The Pb-Zn tailing sample provided by Orex Mining Co. in Turkey was used for the experiments. All the required information regarding this tailing sample has already been described in previous studies.[25,27] For the solvent extraction tests, industrial grade di-(2-ethylhexyl) phosphoric acid (D2EHPA) industrial grade was used, while the diluent was analytical grade hexane (Sigma-Aldrich, USA). $ZnSO_4.7H_2O$ (99.5% purity, Merck) was used in the scrubbing experiments. For pH arrangements, analytical grade sodium hydroxide (NaOH) (Merck, Belgium) and sulfuric acid (H_2SO_4) (Merck, Belgium) were used. When necessary, deionized water was used for dilutions. The main chemical elements present in the PLS and their corresponding concentrations are given in Table I. The conditions applied to obtain this PLS were as follows: leaching duration of 180 min, leaching temperature of 80 °C, citric acid concentration of 1 M and solid-to-liquid ratio of 1/5.

Method

Since lead was one of the principal contaminants in the PLS, lead precipitation tests were performed using a 5 M sulfuric acidic solution before starting the solvent extraction tests. These precipitation experiments were carried out under the following conditions: 200 rpm mixing speed and temperature of 25 °C. The pH of the PLS was monitored by Hach HQ40d with a probe (IntelliCAL PHC 28,101) attached to it. The precipitation tests lasted 30 min; then, measurement and filtration of the solution were carried out. Whatman 1 filter paper was used to filter the solution, after which the solution was sent to atomic absorption spectroscopic analysis (AAS, PinAAcle 900F PerkinElmer and 3300 ThermoScientific) to determine the quantity of lead precipitated as well as other metal ions. The precipitate was also sent to x-ray diffraction (XRD) analysis to identify the mineralogical composition of the precipitate. The XRD analysis was carried out using a Bruke Discover XRD device with alignment $2\theta = 5–85°$ of silicon standard calibration, and radiation was read at 40 mA and 40 kV. Mineral phases were identified using Diffrac Suite EVA software with the ICDD PDF-2/Minerals database. The difference in metal concentration in the solution before and after the precipitation percentages was reported our previous publication.[4]

Solvent extraction tests were carried out after the precipitation tests were completed. First, precipitation tests were done and then solvent extraction experiments were performed. For temperature regulation, a MTOPS heating mantle was used. The aqueous-organic ratio was equal to one throughout the experiments unless mentioned otherwise. pH adjustment here was done using droplets of 5 M NaOH. The immiscible mixture was left to stand for about 10 min after the experiment to improve the phase disengagement and then transferred to a separation funnel. To avoid phase entrainment, a special phase separation filter paper (Whatman 1PS) was used to effectively separate the aqueous and organic phases. Analysis was carried out on the obtained aqueous phase at ALS Minerals, Izmir, Turkey, using inductively coupled plasma mass spectrometry (ICP-MS). The metal ion concentration in the organic phase was determined through mass balance calculation. The metal ion extraction percentage (E) was obtained using the following equation (Eq. 4):

$$E = \frac{[M]_{\text{org}}}{[M]_{\text{aq}}} \times 100 \tag{4}$$

where [M]org and [M]aq are the metal ion concentrations in the organic and aqueous phases (mg/L), respectively. The following formulae were used to determine the distribution coefficient (D) (Eq. 5):

$$\mathrm{D} = \frac{C_{\text{org}}}{C_{\text{aq}}} \tag{5}$$

The equilibrium concentrations of metal ions in the organic and aqueous phases, respectively, are C_{org} and C_{aq}. The separation factor (β) was determined as follows (Eq. 6):

$$\beta_{M2/M1} = \frac{\mathrm{D}_2}{\mathrm{D}_1} \tag{6}$$

D_1 and D_2 are the distribution coefficients of elements 1 and 2 in a given solvent system, respectively.

In an attempt to construct a McCabe–Thiele diagram of the extraction of zinc from a citric acid solution using DEHPA as extractant, solvent extraction experiments were conducted with varying A/O ratio, while other parameters were kept constant.

Table I. Chemical components of pregnant leach solution after citric acid leaching (pH: 2.11)

Elements	Pb	Zn	Fe	Ca	As	Mg
Concentration (mg/L)	1220	12,100	8410	7790	1670	457

RESULTS AND DISCUSSION

Removal of Lead from Zinc via Selective Precipitation

The precipitation of metal ions as a function of pH is shown in Fig. 1. Most of the Pb and a considerable amount of Ca precipitated when 5 M sulfuric acid was added, while the other metal ions remained stable in the aqueous phase. At pH 1, the maximum precipitation of Pb (98.9%) and Ca (73.2%) was achieved within the tested experimental range.

It was possible to separate Pb from Zn by selective precipitation with sulfuric acid because of the low solubility of $PbSO_4$ in aqueous solutions. The reaction product, $PbSO_4$ (anglesite) (Eq. 7), was confirmed by XRD examination of the precipitate as illustrated in Fig. 2. According to Fusi et al. (2015), the dissolved sulfate ions $SO^{2-}{}_4$ seek out accessible Ca^{2+} ions and bond with them to generate calcium sulfate dihydrate $CaSO_4.2H_2O$, as illustrated in Eq. 8. In addition, according to the Ksp values for calcium sulfate dihydrate (3.14×10^{-5}) and lead sulfate (1.6×10^{-8}), lead sulfate is expected to precipitate from the PLS before calcium sulfate dihydrate, and it depends on the concentrations of the metals.[40] In our previous work,[4] where malic acid PLS was precipitated, no $CaSO_4$ $0.2H_2O$ was seen in the precipitate from the XRD results, unlike in this present investigation, where we observed a high concentration of gypsum in the precipitate, which was a concern, as it was considered one of the major impurities. As a result, the overall precipitation reaction can be written as:

$$Pb^{2+}_{(aq)} + H_2SO_4 = PbSO_{4(s)} + 2H^{+}_{(aq)} \quad (7)$$

$$Ca^{2+}_{(aq)} + H_2SO_4 + 2H_2O_{(l)} = CaSO_4.2H_2O_{(s)} + 2H^{+}_{(aq)} \quad (8)$$

Separation of Zinc from Impurities by Solvent Extraction

After the lead precipitation was completed, the PLS was sent to solvent extraction stage to extract Zn from the principal impurities, which included Fe, As, Ca and Mg. Except for Pb, which was almost eliminated from the solution after precipitation, the chemical composition of the PLS remained largely unchanged, which is given in online supplementary material (see supplementary Table S1). The extraction of metal ions with D2EHPA as a function of pH at various extractant concentrations ranging from 10 to 20% is shown in Fig. 3. The pH ranges in the three figures differ because extractions at pH levels greater than those required for a basically quantitative Zn extraction were not performed. Using the three extractant concentrations, Zn extraction typically increases as pH increases. This is a common property of D2EHPA as an acidic extractant, as demonstrated by previous researchers who extracted Zn from various acidic aqueous solutions using D2EHPA.[3,4,29,30,33,41] In all pH ranges examined, Zn is extracted before the other impurities. Ca extraction followed the same pattern as Zn extraction. Fe, on the other hand, exhibited a distinct pattern. When the pH was increased from 1 to 1.9 at a D2EHPA concentration of 10%, Fe extraction decreased at first, but then remained constant when the pH was raised to 3.6. In all of the investigated ranges, the extractions of As were quite modest but for Mg they increased when pH was raised, at 15% and 20% D2EHPA, respectively.

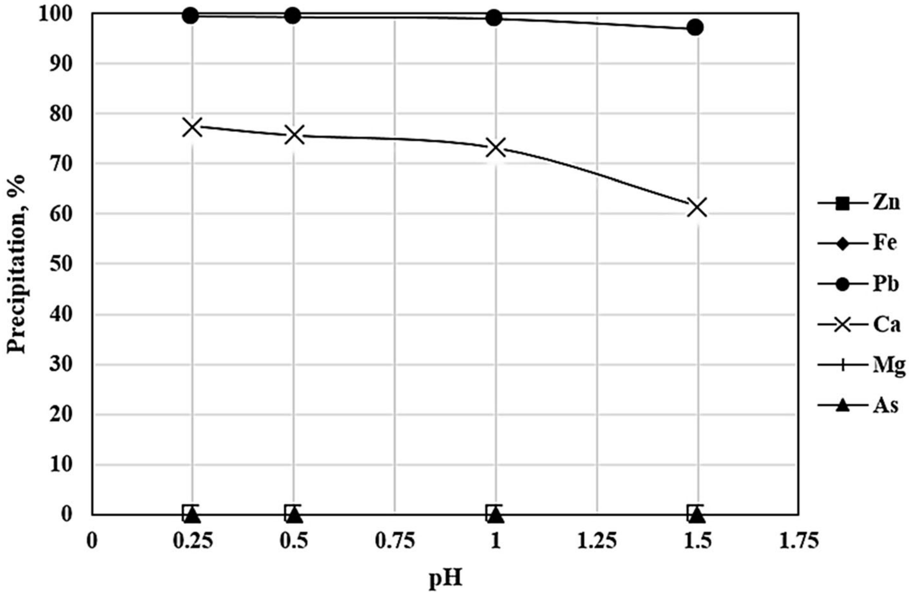

Fig. 1. Precipitation of metal ions from the citric leach solution using 5 M H_2SO_4 as a function of pH (conditions: T: 25 °C, t: 30 min).

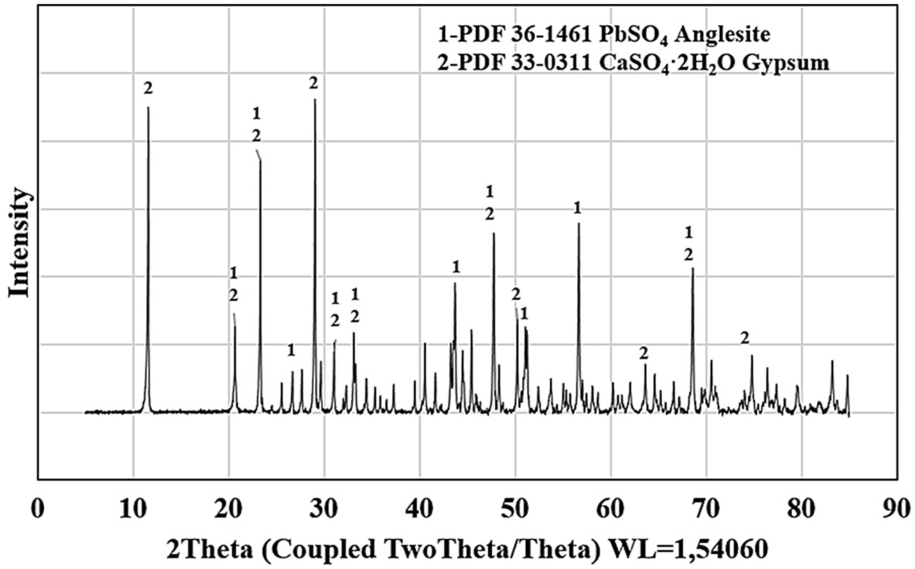

Fig. 2. XRD pattern of the precipitate demonstrating the presence of anglesite and gypsum.

At the same pH, increasing the extractant concentration increased the extraction of Ca, Fe and Zn into the organic phase. This shows that the crowding effect may be to blame for the declines in Fe extraction at pH levels > 2, as Ca and Mg extraction became preferred.[4] While Ca extraction increased significantly as extractant concentrations increased, Fe extraction increased at a slower rate than Zn extraction, resulting in a higher separation factor (β) between Zn and Fe (Table II). At pH 3.6, the maximum separation factor (Zn/Fe = $\sim$ 613) was obtained using a 20% D2EHPA concentration. As extraction percentages (< 1%) remained constant. As a result, it was established that using a 20% extractant concentration and a pH of 3.6 to extract 98.3% Zn together with 79% Ca, 18% Mg and 8.6% Fe in a single contact was optimal for separating Zn from the impurities.

Effect of Contact Time and Temperature on the Solvent Extraction Process

Figure 4 demonstrates the extraction of metal ions as a function of time using 20% D2EHPA at a pH of 3.6 and a temperature of 25 °C. The extractions of metal ions after the first 3 min and 20 min of contact time were nearly identical, indicating that most of the extraction reactions took place in < 3 min; however, less Fe extraction was observed in 10 min than in 3 min. Less impurity, especially less Fe, means less cost during generation of the organic phase after the stripping experiment. The staggered extraction percentages of the metal ions, particularly those of As and Mg, indicate that equilibrium had not yet been achieved after 20 min of contact time.

When the contact duration was adjusted to 10 min, the extractions of As were continuously below 1%, even at different operating temperatures ranging from 25 to 40 °C as seen in Fig. 5. This demonstrates the value of using a 10-min contact duration to reduce impurity extraction. When the temperature was raised to 40 °C, the extractions of magnesium and iron remained constant. The extraction of Ca with D2EHPA from the citric acid solution, on the other hand, decreased as the temperature increased, indicating that higher temperatures were favorable for the limited extraction of Ca, and this tendency portrays an exothermically driven extraction. The extraction of Zn, on the other hand, was rather consistent across all studied ranges. Therefore, there was no discernible benefit from raising the temperature; a temperature of 25 °C with a contact period of 10 min was chosen as optimal.

McCabe–Thiele Diagram for Zinc Extraction

According to the McCabe–Thiele analysis (Fig. 6), Zn was almost entirely loaded into the organic phase using a single theoretical counter-current stage at an operating line unity. A feed solution containing 10,350 mg/L Zn loaded an organic phase containing 10,247 mg/L Zn. Scrubbing experiments were performed on the organic phase, which was loaded with 10,247 mg/L Zn by a single-stage extraction at pH 3.6, 25 °C and an O/A ratio of unity.

Scrubbing of the Loaded Organic Phase with Zinc Salt Solution

All these studies show that a scrubbing step is required after the extraction phases to remove impurities from the organic phase. Scrubbing tests were carried out using the loaded organic solutions generated from the extraction tests at previously determined optimum conditions to remove calcium

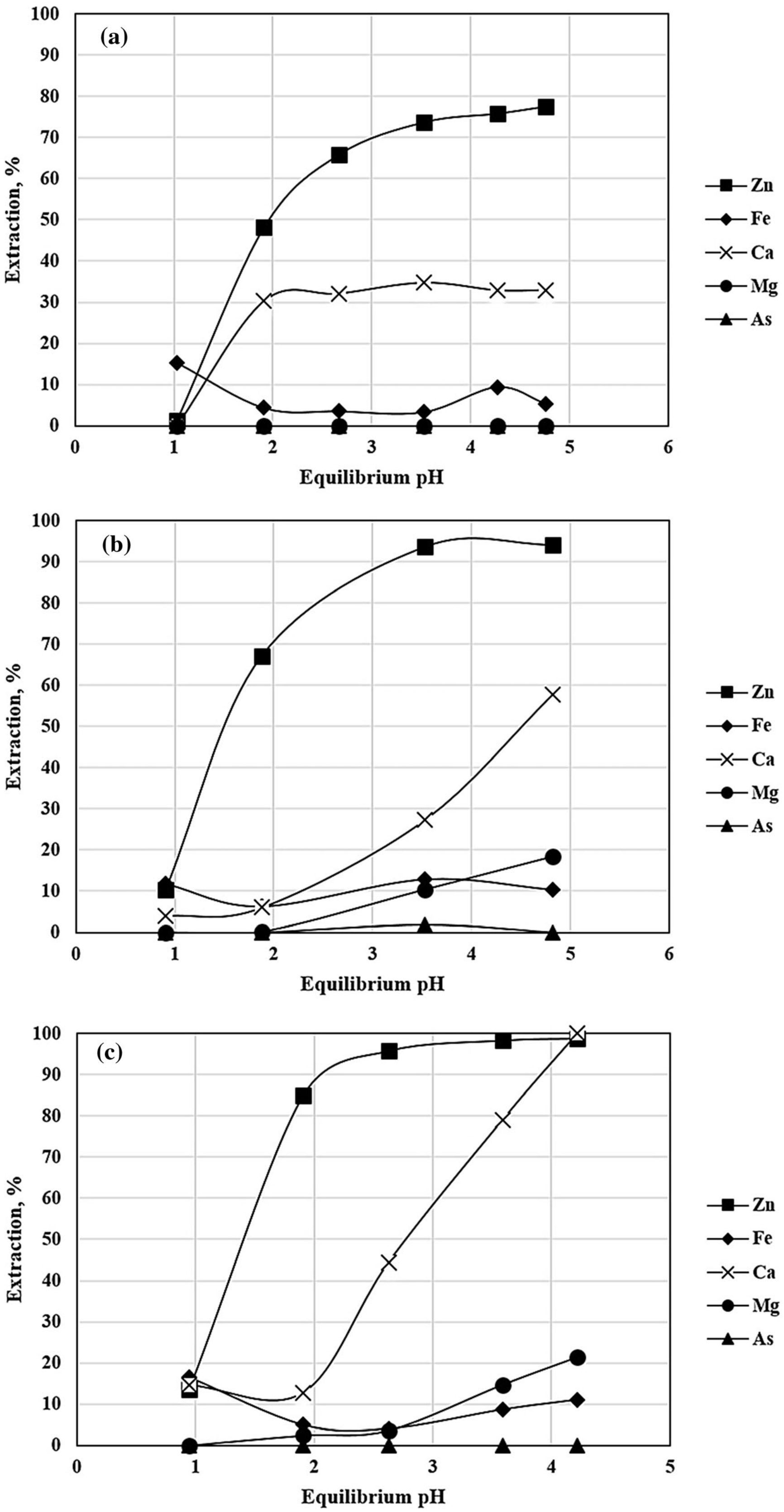

Fig. 3. Extraction of metal ions as a function of pH: (a) 10% D2EHPA, (b) 15% D2EHPA, (c) 20% D2EHPA. (Conditions: T: 25 °C, t:10 min).

Table II. Separation factors of Zn with respect to Fe using D2EHPA in citric acid solution

10% D2EHPA		15% D2EHPA		20% D2EHPA	
pH	βZn/Fe	pH	βZn/Fe	pH	βZn/Fe
1.03	0.1	0.91	0.9	0.95	0.8
1.91	20.6	1.88	30.2	1.91	107.7
2.67	53.4	3.53	99.0	2.63	537.4
4.76	61.7	4.82	138.3	3.6	612.7

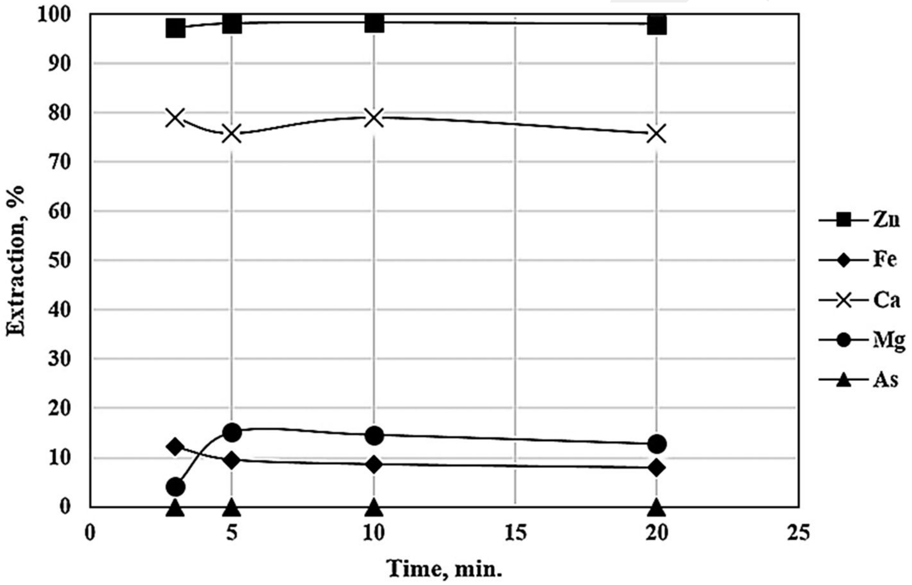

Fig. 4. Extraction of metal ions as a function of time (conditions: 20% D2EHPA, pH: 3.6, T: 25 °C).

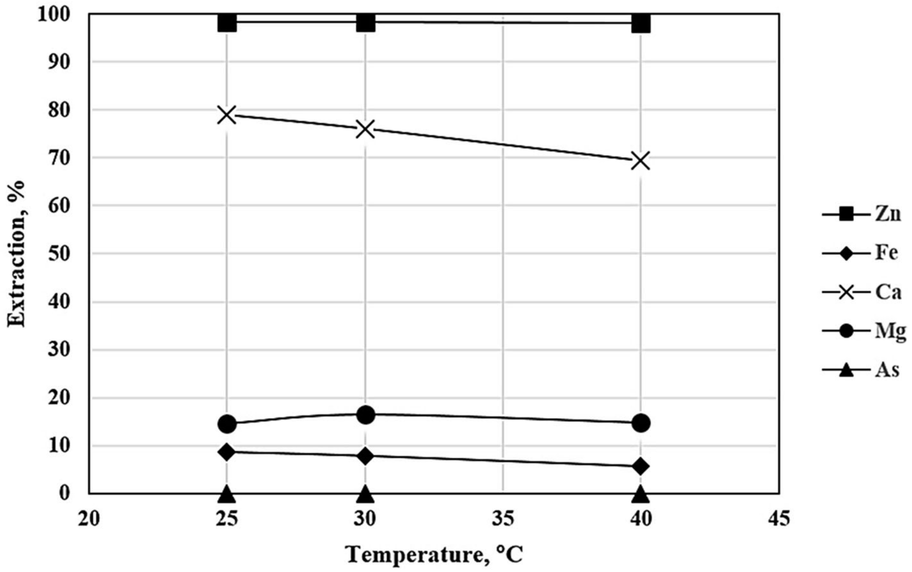

Fig. 5. Extraction of metal ions as a function of temperature (conditions: 20% D2EHPA, pH: 3.6, t: 10 min).

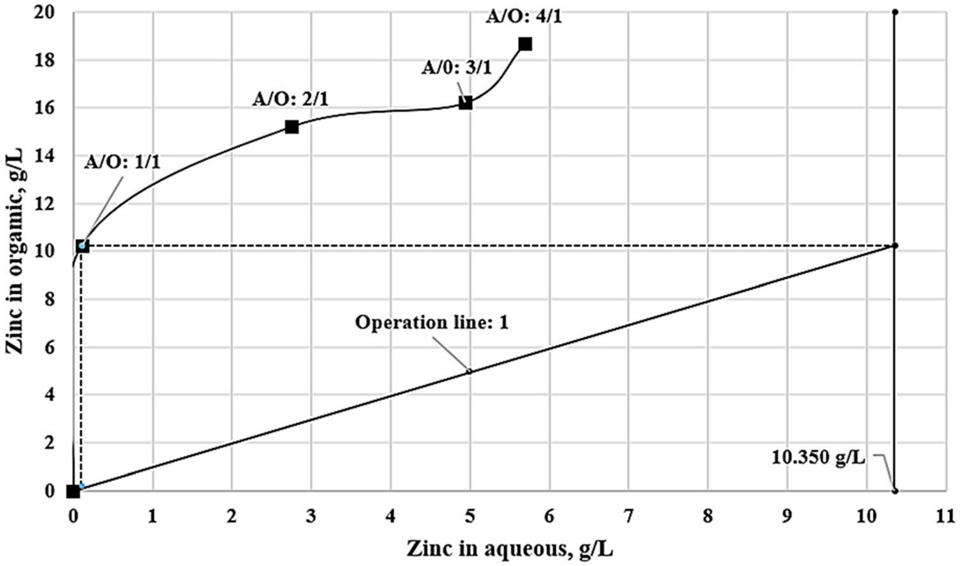

Fig. 6. McCabe–Thiele diagram for extraction of Zn using D2EHPA in citric acid solution (conditions: 20% D2EHPA, T: 25 °C, t: 10 min, pH: 3.6).

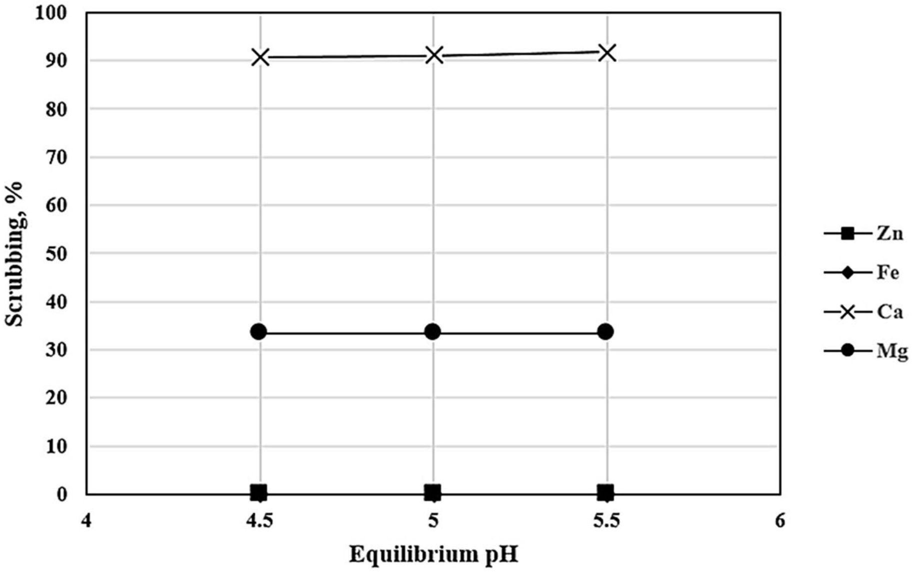

Fig. 7. Scrubbing of the loaded organic solution with 20 g/L $ZnSO_4$ solution at different pHs (conditions: *T*: 25 °C, t: 10 min).

and magnesium from the loaded organic solutions and ensure the high purity of the final zinc product. Scrubbing experiments were performed using an A/O ratio of unity and pH 4.5, 5 and 5.5. A zinc salt solution containing 20 g/L of zinc was interacted with the loaded organic.[42,43] The zinc in the aqueous solution displaced calcium and magnesium from loaded organic. This operation results in a higher zinc loading in the organic phase. Equation 9 demonstrates the displacement mechanism. Almost 90% of calcium was scrubbed out from the loaded organic solution, whereas magnesium scrubbing efficiency was 34% (Fig. 7). Furthermore, the experiments showed that scrubbing had no effect on Fe, but despite this, the scrubbing process was still advantageous because of the higher zinc loading in the organic phase after Ca and Mg were scrubbed out.

$$\begin{aligned}&(C_{16}H_{35}O_4P)(Ca, Mg) + ZnSO_4\\ &\rightleftharpoons (C_{16}H_{35}O_4P)Zn + (Ca, Mg)SO_4 \qquad (9)\end{aligned}$$

Stripping of the Loaded Organic Phase

The Zn was stripped from the loaded organic in a pH range of 0.25 to 1 using sulfuric acid solutions at 25 °C and a 10-min stripping duration. The percentages of metal ions stripped from the loaded organic solution as a function of pH are shown in

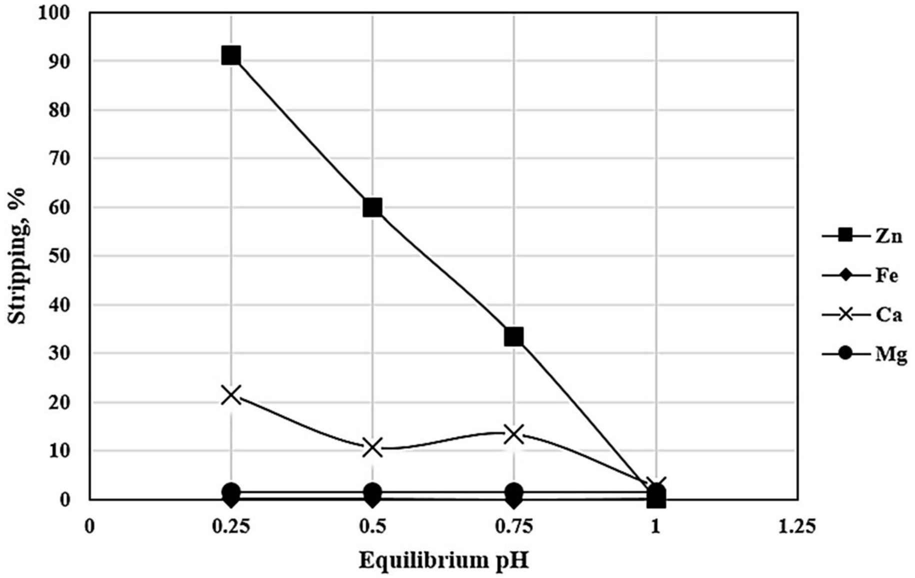

Fig. 8. Stripping of the loaded organic solution at different pHs using H_2SO_4 (conditions: *T*: 25 °C, t: 10 min).

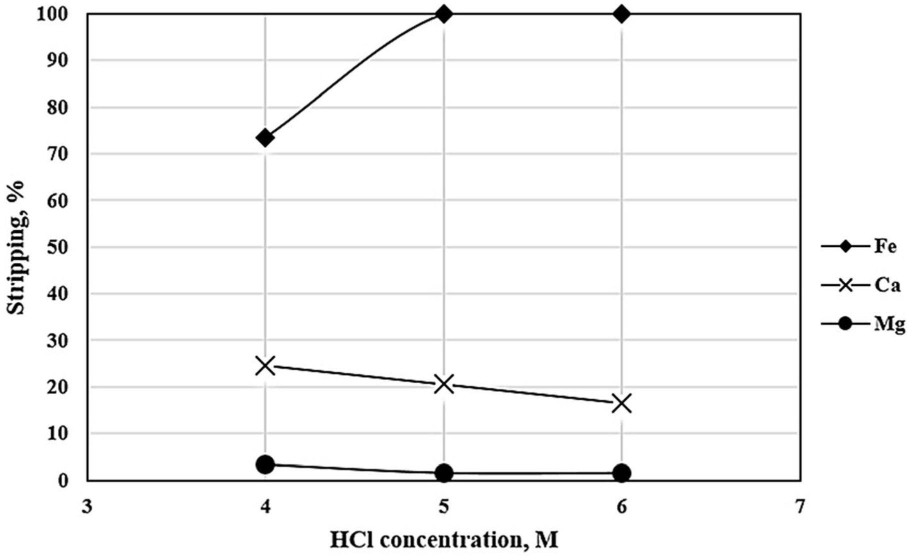

Fig. 9. Stripping of the stripped organic solution at different concentrations using HCl (conditions: *T*: 25 °C, *t*: 10 min).

Fig. 8. D2EHPA forms a 1:2 complex with Zn^{2+} by coordinating through O atoms, which is simple for the stripping of zinc with inorganic acids. At pHs ranging from 0.25 to 1, the stripped Zn from the loaded organic solution increased; 91.3% was achieved at pH 0.25. It means a second stage stripping is needed for transferring zinc completely. Because of that, the second step of stripping was carried out at pH 0.25. Supplementary Table S2 shows the remaining metal concentration in organic phase after two-stage stripping. The stripping percentages of the Fe and Mg were negligible at tested pH ranges but for Ca stripping, the percentage increased with decreasing pH. Fe forms a strong combination with D2EHPA, which is difficult to remove using an inorganic acid. This is because Fe forms octahedral complexes with D2EHPA, and the hydrophobic end of the complex is directed toward the organic phase, but the hydrogen ions and acid anions of inorganic acid are highly hydrated.[4,44] As other investigations reported, the extracted complexes have low concentrations, and the inorganic acids are present at the interface, allowing Fe to be stripped from the organic phase. According to Hu et al. (2014), Fe stripping was slow, and even with 4.0 mol/L sulfuric acid, only around 40% of Fe was removed from Fe-loaded D2EHPA solution. On the other hand, it was demonstrated that reductive stripping with an oxalic acid solution could completely remove Fe from the organic phase, allowing

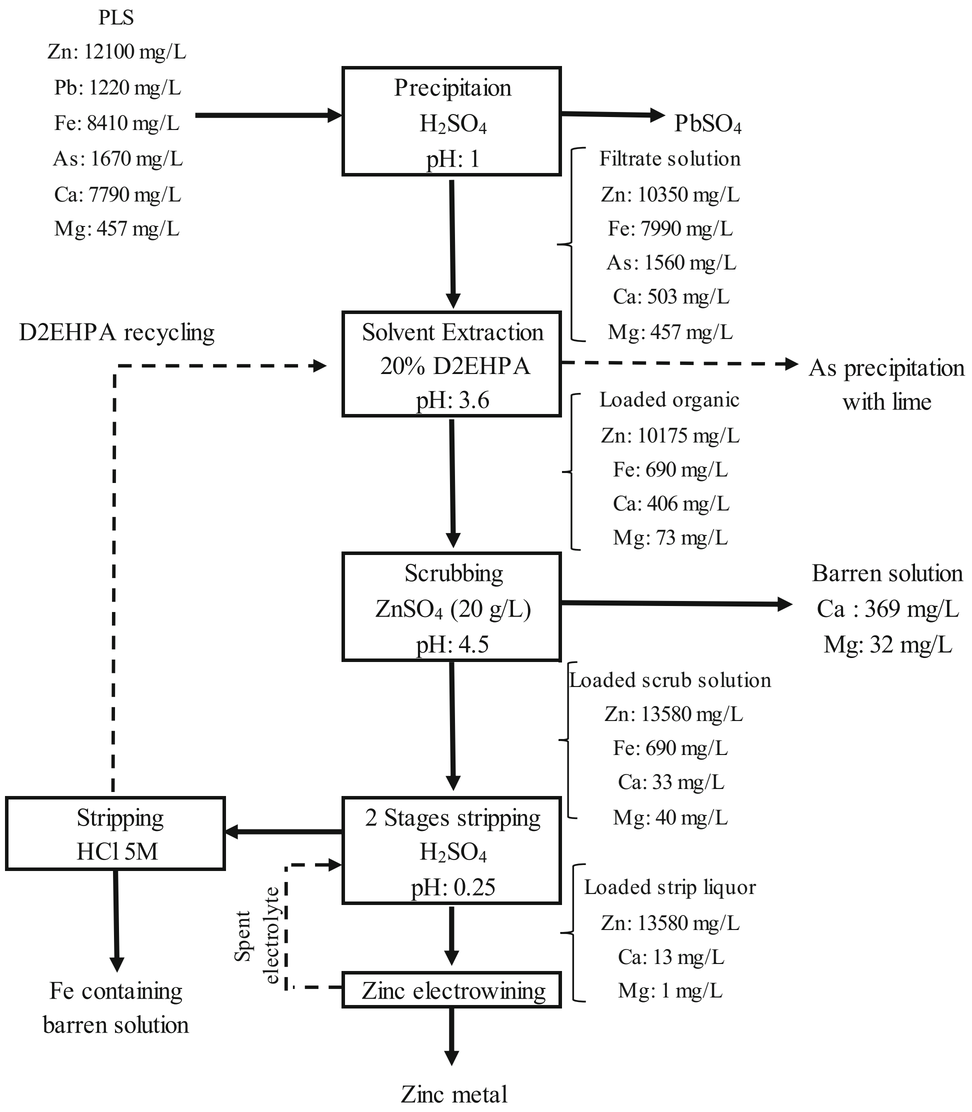

Fig. 10. Proposed flowsheet for the Pb-Zn recovery from a citric leach solution.

the D2EHPA solution to be recycled.[45] As other methods, the reduction of Fe from its trivalent to divalent states, such as so-called galvanic stripping, was shown to be capable of completely stripping Fe from loaded D2EHPA solution.[46,47] Figure 9 shows Fe removal from stripped organic solution with HCl at concentrations of 4-6 M. As the result shows, at concentration of 5 M, Fe was almost completely removed from the organic solution whereas Ca and Mg removal decreased slightly.

Process Development

By precipitation and solvent extraction, a proposed process for recovering lead and zinc from a citric leach solution of a non-sulfide flotation tailing is shown in Fig. 10. The flotation tailing was first leached in 1 M citric acid at 80 °C for 180 min with a solid-to-liquid ratio of 2/10. The slurry was filtered after leaching, and the filtered pregnant leach solution was transferred to a precipitation stage, where it was treated with sulfuric acid to produce a Pb-free solution. At a pH of 1, 98.9% of Pb precipitation was achieved in the current investigation. Solvent extraction, scrubbing and stripping methods were applied to the Pb-free aqueous solution. Using 20% D2EHPA at a pH of 3.6, a temperature of 25 °C and an O/A of 1/1, 98.3% Zn, 79% Ca, 14.7% Mg and 8.6% Fe could be extracted in a single contact. At pH 4.5, the loaded organic solution was transferred to the scrubbing stage, where nearly 91% Ca and 34% Mg were removed from the organic solution using a 20 g/L zinc solution. After the scrubbing stage, the loaded organic was transferred to the stripping stage, where $>$ 99.9% of Zn and 27% of Ca were stripped out of the organic phase in two steps using a dilute sulfuric acid solution with a pH of 0.25. The remaining Fe in the loaded organic phase was completely removed with 5 M HCl solution as the recycled organic could be used in the solvent extraction circuit again.

CONCLUSION

Precipitation and solvent extraction were used to recover Pb and Zn from a citric leach solution of a non-sulfide flotation tailing. The Pb was precipitated from the citric acid leach solution at pH 1. $PbSO_4$ (anglesite) and $CaSO_4$ (gypsum) were identified as the precipitates. Sulfate precipitation was shown to be an effective method for removing Pb with negligible Zn losses; however, it created a gypsum formation in the lead sulfate precipitate. Following that, the filtrate was sent to a solvent extraction stage with D2EHPA. At pH 3.6, 98.3% Zn was taken into the organic phase, along with a significant amount of Ca (79%) and a small amount of Mg (14.7%) and Fe (8.6%), using 20% D2EHPA, and A/O ratio of unity at 25°CS for 10 min. Between Zn and Fe, the largest separation factor (β) was determined to be ~ 613. According to McCabe–Thiele results, 10,247 mg/L of Zn was loaded in organic solution in one counter-current stage at a 1:1 operating line (O/A) under optimal solvent extraction conditions. The loaded organic solution was fed to the scrubbing step at pH 4.5, where a 20 g/L Zn solution was used to remove roughly 91% Ca and 34% Mg from the organic solution. At pH 0.25, with an O/A ratio of 1:1, the loaded organic phase was stripped out about 100% Zn and 27% Ca for 10 min. A new hydrometallurgical process flowsheet for the recovery of Pb and Zn from citric acid leach solution was proposed based on the experimental results acquired from the bench-scale study. After citric acid leaching from Pb-Zn containing tailings and possibly from Pb-Zn ores, separate product streams of Pb and Zn were created.

SUPPLEMENTARY INFORMATION

The online version contains supplementary material available at https://doi.org/10.1007/s11837-022-05691-5.

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CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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